# 1. Battery R&D

The Vehicle Technologies Office (VTO) supports research, development, demonstration, and deployment (RDD&D) of new, efficient, and clean mobility options that are affordable for all Americans. The office's investments leverage the unique capabilities and world-class expertise of the national laboratory system to develop new innovations in vehicle technologies, including: advanced battery technologies; advanced materials for lighter-weight vehicle structures and better powertrains; energy-efficient mobility technologies and systems (including automated and connected vehicles as well innovations in connected infrastructure for significant systems-level energy efficiency improvement); innovative powertrains to reduce greenhouse gas (GHG) and criteria emissions from hard to decarbonize off-road, maritime, rail, and aviation sectors; and technology integration that helps demonstrate and deploy new technology at the community level. In coordination with the other offices across the Office of Energy Efficiency and Renewable Energy (EERE) and the U.S. Department of Energy (DOE), VTO advances technologies that assure affordable, reliable mobility solutions for people and goods across all economic and social groups; enable and support competitiveness for industry and the economy/workforce; and address local air quality and use of water, land, and domestic resources.

The Batteries subprogram supports the decarbonization of transportation across all modes, serves to increase American advancement/manufacturing of battery technology, and creates good paying jobs with the free and fair chance to join a union and bargain collectively. The subprogram supports research with partners in academia, national laboratories, and industry covered under the Energy Storage Grand Challenge key priority and four distinct crosscuts including: Critical Materials, Grid Modernization, Advanced Manufacturing, and Energy Sector Cybersecurity.

The subprogram supports early-stage R&D of high-energy and high-power battery materials, cells, and battery development that can enable industry to significantly reduce the cost, weight, volume, and charge time of plug-in electric vehicle (PEV) batteries. This activity is organized into three sub-activities: advanced battery materials research, advanced battery cell R&D, and battery recycling R&D. Advanced battery materials research is coordinated with the Critical Minerals Initiative and includes: early-stage research of new lithium ion (Li-ion) cathode, anode, and electrolyte materials (currently accounting for 50% to 70% of PEV battery cost) and the development of "beyond Li-ion" technologies, such as lithium (Li) metal anodes, solid-state electrolytes (SSEs), and sulfur-based cathodes, that have the potential to significantly reduce weight, volume, and cost reduction of over 80% 2008 baseline, with a target of $60/kWh.

Advanced battery cell R&D includes early-stage R&D of new battery cell technology that contains new materials and electrodes that can reduce the overall battery cost, weight, and volume while improving energy, life, safety, and fast charging. Battery recycling R&D includes the development of innovative battery materials recycling and reuse technologies, and the Lithium-Ion Battery Recycling Prize, both of which aim to assure sustainability and domestic supplies of key battery materials and minerals.

## Project Feedback

In this merit review activity, each reviewer was asked to respond to a series of questions, involving multiple-choice responses, expository responses where text comments were requested, and numeric score responses (on a scale of 1.0 to 4.0). In the pages that follow, the reviewer responses to each question for each project will be summarized: the multiple choice and numeric score questions will be presented in graph form for each project, and the expository text responses will be summarized in paragraph form for each question. A table presenting the average numeric score for each question for each project is presented below.

Table 1-1 – Project Feedback

| Presentation ID | Presentation Title | Principal Investigator (Organization) | Page Number | Approach | Technical Accomplishments | Collaboration | Future Research | Weighted Average |
|---|---|---|---|---|---|---|---|---|
| BAT085 | Interfacial Processes† | Robert Kostecki (Lawrence Berkeley National Laboratory) | 1-8 | 3.50 | 3.33 | 3.17 | 3.50 | 3.38 |
| BAT091 | Characterization and Modeling of Lithium-Metal Batteries First-Principles Modeling and Machine Learning† | Kristin Persson (Lawrence Berkeley National Laboratory) | 1-12 | 3.50 | 3.38 | 3.38 | 3.33 | 3.41 |
| BAT183 | In Situ Spectroscopies of Processing Next-Generation Cathode Materials | Feng Wang (Argonne National Laboratory) | 1-16 | 3.50 | 3.57 | 3.43 | 3.29 | 3.50 |
| BAT287 | Advanced In Situ Diagnostic Techniques for Battery Materials† | Xiao-Qing Yang (Brookhaven National Laboratory) | 1-23 | 3.50 | 3.17 | 3.67 | 3.33 | 3.33 |
| BAT309 | Electrode Materials Design and Failure Prediction† | Venkat Srinivasan (Argonne National Laboratory) | 1-27 | 3.38 | 3.25 | 3.63 | 3.50 | 3.36 |
| BAT360 | Cathodes Beyond Lithium Nickel Manganese Cobalt Oxide (NMC) 811 | Arumugam Manthiram (University of Texas at Austin) | 1-31 | 3.70 | 3.80 | 3.40 | 3.40 | 3.68 |
| BAT361 | Understanding and Improving Lithium Anode Stability | Yi Cui (Stanford University / SLAC National Accelerator Laboratory) | 1-36 | 3.50 | 3.63 | 3.75 | 3.25 | 3.56 |

| Presentation ID | Presentation Title | Principal Investigator (Organization) | Page Number | Approach | Technical Accomplishments | Collaboration | Future Research | Weighted Average |
|---|---|---|---|---|---|---|---|---|
| BAT362 | High Capacity S Cathode Materials | Prashant Kumta (University of Pittsburgh) | 1-41 | 3.50 | 3.50 | 3.38 | 3.38 | 3.47 |
| BAT364 | Synergistic Effects of Electrode and Electrolyte Materials for High Energy Lithium Cells | Jihui Yang (University of Washington) | 1-45 | 3.50 | 3.50 | 3.63 | 3.38 | 3.50 |
| BAT365 | Stabilizing Lithium Metal Anodes by Interfacial Layer and New Electrolytes | Zhenan Bao (Stanford University/ SLAC National Accelerator Laboratory) | 1-49 | 3.60 | 3.70 | 3.90 | 3.40 | 3.66 |
| BAT366 | Manufacturing and Validation of Lithium Pouch Cells | Mei Cai (General Motors) | 1-54 | 3.50 | 3.50 | 3.38 | 3.63 | 3.50 |
| BAT367 | Multiscale Characterization Studies of Lithium Metal Batteries | Peter Khalifah (Brookhaven National Laboratory) | 1-59 | 3.38 | 3.38 | 3.75 | 3.25 | 3.41 |
| BAT368 | Full Cell Diagnostics and Validation to Achieving High Cycle Life | Eric Dufek (Idaho National Laboratory) | 1-65 | 3.40 | 3.30 | 3.50 | 3.40 | 3.36 |
| BAT369 | High Energy Rechargeable Lithium-Metal Cells Design Fabrication and Testing | Jie Xiao (Pacific Northwest National Laboratory) | 1-69 | 3.33 | 3.33 | 3.67 | 3.33 | 3.38 |
| BAT402 | Improving Battery Performance through Structure-Morphology Optimization | Venkat Srinivasan (Argonne National Laboratory) | 1-74 | 3.75 | 3.75 | 3.67 | 3.42 | 3.70 |

| Presentation ID | Presentation Title | Principal Investigator (Organization) | Page Number | Approach | Technical Accomplishments | Collaboration | Future Research | Weighted Average |
|---|---|---|---|---|---|---|---|---|
| BAT496 | Silicon Consortium Project Advanced Characterization of Silicon Electrodes | Robert Kostecki (Lawrence Berkeley National Laboratory) | 1-80 | 3.33 | 3.50 | 4.00 | 3.50 | 3.52 |
| BAT497 | Silicon Consortium Project Electrochemistry of Silicon Electrodes | Christopher Johnson (Argonne National Laboratory) | 1-83 | 3.38 | 3.13 | 3.88 | 3.50 | 3.33 |
| BAT498 | Silicon Consortium Project Next-Gen Materials for Silicon Anodes | Nathan Neale (National Renewable Energy Laboratory) | 1-87 | 3.38 | 3.25 | 3.75 | 3.25 | 3.34 |
| BAT499 | Silicon Consortium Project: Mechanical Properties of Silicon Anodes | Katherine Harrison (National Renewable Energy Laboratory) | 1-91 | 3.00 | 3.00 | 3.75 | 3.25 | 3.13 |
| BAT501 | Integrated Modeling and Machine Learning of Solid-Electrolyte Interface Reactions of the Si Anode | Kristin Persson (Lawrence Berkeley National Laboratory) | 1-95 | 3.50 | 3.38 | 3.63 | 3.50 | 3.45 |
| BAT523 | Development of Long Life Lithium and sulfurized polyacrylonitrile (SPAN) Cells | Ping Liu (University of California-San Diego) | 1-99 | 3.67 | 3.17 | 3.83 | 3.17 | 3.38 |
| BAT524 | Advanced Electrolytes for Lithium Metal Batteries | Chunsheng Wang (University of Maryland, College Park) | 1-103 | 3.50 | 3.50 | 3.67 | 3.50 | 3.52 |
| BAT536 | Polyester-Based Block Copolymer Electrolytes for Lithium Metal Batteries | Nitash Balsara (Lawrence Berkeley National Laboratory) | 1-106 | 3.67 | 3.67 | 3.67 | 3.67 | 3.67 |

| Presentation ID | Presentation Title | Principal Investigator (Organization) | Page Number | Approach | Technical Accomplishments | Collaboration | Future Research | Weighted Average |
|---|---|---|---|---|---|---|---|---|
| BAT538 | Ion conductive high Li+ transference number polymer composites for solid-state batteries | Bryan McCloskey (Lawrence Berkeley National Laboratory) | 1-110 | 3.75 | 3.75 | 3.25 | 3.75 | 3.69 |
| BAT539 | 3D Printing of All-Solid-State Lithium Batteries | Jianchao Ye (Lawrence Livermore National Laboratory) | 1-113 | 3.33 | 3.33 | 3.17 | 3.00 | 3.27 |
| BAT540 | Synthesis of Composite Electrolytes with Integrated Interface Design | Sanja Tepavcevic (Argonne National Laboratory) | 1-116 | 3.50 | 3.67 | 3.83 | 3.50 | 3.63 |
| BAT541 | Substituted Argyrodite Solid Electrolytes and High Capacity Conversion Cathodes for All-Solid-State Batteries | Jagjit Nanda (Stanford University / SLAC National Accelerator Laboratory) | 1-119 | 3.17 | 3.17 | 3.50 | 3.17 | 3.21 |
| BAT542 | Polymer Electrolytes for Stable Low Impedance Solid State Battery Interfaces | Chelsea Chen (Oak Ridge National Laboratory) | 1-123 | 3.50 | 3.50 | 3.67 | 3.17 | 3.48 |
| BAT543 | Integrated Multiscale Model for Design of Robust 3D Solid-state Lithium Batteries | Brandon Wood (Lawrence Livermore National Laboratory) | 1-127 | 3.17 | 3.17 | 3.33 | 3.17 | 3.19 |
| BAT553 | Understanding solid electrolyte interphase (SEI) reactions in Lithium metal and Lithium-Sulfur batteries | Perla Balbuena (Texas A&M University) | 1-130 | 3.50 | 3.63 | 3.63 | 3.63 | 3.59 |
| BAT587 | Earth-abundant Cathode Active Materials for Li-Ion Batteries Theory and Modeling† | Hakim Iddir (Argonne National Laboratory) | 1-134 | 3.17 | 3.33 | 3.17 | 3.00 | 3.23 |

| Presentation ID | Presentation Title | Principal Investigator (Organization) | Page Number | Approach | Technical Accomplishments | Collaboration | Future Research | Weighted Average |
|---|---|---|---|---|---|---|---|---|
| BAT590 | Lithium Halide-Based Superionic Solid Electrolyte and High-Voltage Cathode Interfaces | Robert Sacci (Oak Ridge National Laboratory) | 1-137 | 3.38 | 3.50 | 3.50 | 3.25 | 3.44 |
| BAT591 | High-Conductivity and Electrochemically Stable Thioborate Solid-State Electrolytes for Practical All-Solid-State Batteries | Yi Cui (Stanford University / SLAC National Accelerator Laboratory) | 1-141 | 3.30 | 3.50 | 3.50 | 3.30 | 3.43 |
| BAT599 | Fluorinated Glyme Solvents to Extend Lithium-Sulfur Battery Life | Taylor Xu (Navitas Systems) | 1-146 | 3.20 | 3.10 | 3.10 | 3.10 | 3.13 |
| BAT600 | Liquid Electrolytes for Lithium-Sulfur Batteries with Enhanced Cycle Life and Energy Density Performance | Gaind P. Pandey (Giner Inc) | 1-151 | 3.08 | 3.17 | 3.08 | 3.08 | 3.13 |
| BAT601 | Development of Functional Electrolytes for Lithium Sulfur Battery Cells | Donghai Wang (Penn State University) | 1-157 | 3.75 | 3.75 | 3.50 | 3.50 | 3.69 |
| BAT602 | Extending the Operating Range and Safety of Li-Ion Batteries with New Fluorinated Electrolytes | Suresh Sriramulu (Koura) | 1-161 | 3.40 | 3.30 | 3.40 | 3.30 | 3.34 |
| BAT603 | Fluorinated Ester Local High Concentration Electrolytes for Operation of Li-Ion Batteries under Extreme Conditions | Esther Takeuchi (Stony Brook University) | 1-166 | 3.42 | 3.33 | 3.25 | 3.00 | 3.30 |

| Presentation ID | Presentation Title | Principal Investigator (Organization) | Page Number | Approach | Technical Accomplishments | Collaboration | Future Research | Weighted Average |
|---|---|---|---|---|---|---|---|---|
| BAT604 | Novel Organosulfur-Based Electrolytes for Safe Operation of High Voltage Li-Ion Batteries Over a Wide Operating Temperature | Meinan He (General Motors) | 1-171 | 3.30 | 3.50 | 3.30 | 3.20 | 3.39 |
| BAT605 | Silicon Consortium Project Next Generation Electrolytes for Silicon Anodes | Gabriel Veith (Oak Ridge National Laboratory) | 1-176 | 3.30 | 3.10 | 3.80 | 3.00 | 3.23 |
| Overall Average | | | | 3.43 | 3.41 | 3.54 | 3.33 | 3.42 |

† Denotes a poster presentation.

**Presentation Number:** BAT085
**Presentation Title:** Interfacial Processes
**Principal Investigator:** Robert Kostecki, Lawrence Berkeley National Laboratory

***Presenter***

Robert Kostecki, Lawrence Berkeley National Laboratory

***Reviewer Sample Size***

A total of three reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

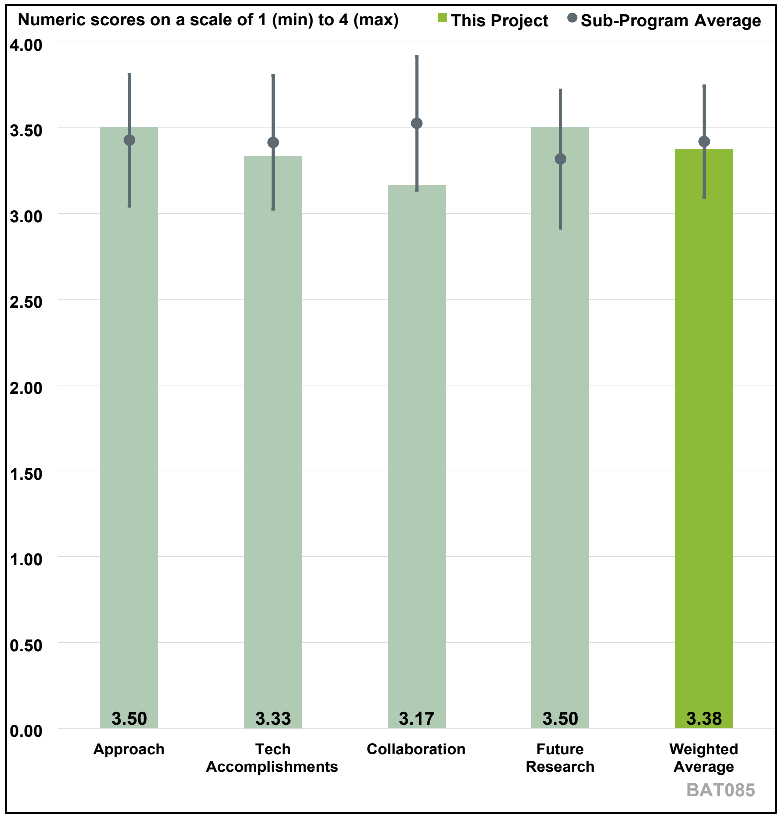


Figure 1-1. Presentation Number: BAT085 Presentation Title: Interfacial Processes Principal Investigator: Robert Kostecki, Lawrence Berkeley National Laboratory

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer remarked the proposed technique, in-situ nano-Fourier transform infrared spectroscopy (FTIR), is a very powerful and less studied technique to study the solid-electrolyte interphase (SEI) formation on a lithium (Li)-metal anode. The project is well designed, and the timeline is reasonably planned.

**Reviewer 2**

The reviewer said this project focuses on addressing the major barriers of the inadequate energy and power density, calendar/cycle lifetimes of Li-metal and Li-ion batteries for plug-in hybrid and electric vehicle (EV) applications. The team explored the origin of the high cell/electrode/interface impedance that limits power and affects the system safety. To find the fundamental cause of these barriers, the reviewer noted the investigators developed near-field nano- FTIR spectroscopy to analyze the spontaneously formed SEI layer on a Li surface in a novel localized high-concentration electrolyte (LHCE). The work is featured by four coherently connected milestones. Accomplishment of these four milestones will provide insights for finding the path to address the barriers. The reviewer said the project is well designed and the timeline of completion of the proposed work is adequate. It appears that a theoretical modeling will be beneficial for the interpretation of the results of the present work.

**Reviewer 3**

The reviewer said the project utilized ex situ spectroscopy (nano-FTIR) to characterize the chemistry fingerprints of SEI on a Li surface. Ex situ spectroscopic data were collected for a baseline Gen2 electrolyte and a LiTFSI/DME/TTE LHCE. The technique is powerful to reveal vibrational signal of SEI component with a very high spatial resolution. The reviewer remarked the proposed technique is somewhat biased towards organic species, and a supplementary characterization tool biased towards inorganic species is crucial for a comprehensive understanding of SEI.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer said great two-dimensional vibrational data were collected using nano-FTIR. It is interesting to see the difference among different LHCEs, as well as the comparison between high concentrations version to low concentration versions.

**Reviewer 2**

The reviewer said the technical progress is well matched with what has been proposed. The reviewer summarized the team first developed a spectro-electrochemical cell for in situ nano-FTIR studies of the SEI. The team used a model material of graphene to study the in-situ formation of SEI layer. Subsequently, the team used ex situ nano-FTIR to study the SEI layer on Li in a Gen2 electrolyte. The researchers reveal that after Li has a short exposure to the Gen2 electrolyte, the Li surface immediately becomes highly inhomogeneous on nanometer scale and rich in Li organic carbonates. The technical progress up to date follows what has been proposed. The reviewer remarked these studies provide insight as how electrolytes react with the Li-metal surface to form SEI layer. Integration of theoretical modeling will be great for enhancing the interpretation of the results.

**Reviewer 3**

The reviewer remarked using FTIR, the project provided important insights in understanding the reaction mechanism for the SEI formation on Li-metal anodes in different liquid electrolytes. Current studies on the Li SEI are primarily ex-situ. The in-situ study of the SEI formation is done on single-layer graphene. The reviewer asked if there is a particular challenge that prevents in-situ study of SEI formation on a Li-metal anode.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer commented the project encompasses wide-board collaborations within the United States and internationally of both experiments and theoretical modeling. In particular, the collaboration team has different experimental techniques, which will provide complementary information across different scales. The reviewer recommended a baseline material should be selected for a cross-scale study.

**Reviewer 2**

The reviewer said the project involves collaborations with multiple national laboratories and encouraged industrial collaboration to validate the results from the project.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer remarked the investigator is very ambitious for the proposed future research, which covers time-resolved methodology, ranging from pico-second to second, under the in-situ and operando condition of the battery cell. The techniques developed in this project will be extended to X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS). The proposed research aligns well with what is going on in this field of research. The reviewer noted that integrating a theoretical component should be beneficial for this project.

**Reviewer 2**

The reviewer commented in situ experiments are proposed to follow the change of SEI during electrochemical processes.

**Reviewer 3**

The reviewer said the project is more than 80% done. The proposed future research to observe the changes in SEI of Li at different states of charge is reasonable. It is unclear to the reviewer whether that would be done in-situ or ex-situ.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer commented developing advanced characterization technique is important to provide insights for interfacial design of Li-metal batteries. The proposed research also support VTO's overall objective of developing high performance batteries for EV applications.

**Reviewer 2**

The reviewer said performance of rechargeable batteries is critically controlled by the interfacial process, which is simultaneously formed upon battery operation. The proposed research of probing into the interfacial process in rechargeable batteries will gain insights for tackling the key technical barriers for enhancing the performance of battery. Therefore, this project is very relevant for the VTO subprogram objective.

**Reviewer 3**

The reviewer said the effort supports VTO's efforts in developing high energy density Li-metal based batteries for transportation applications.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer said the resources that the principal investigator's (PI's) lab possessed are adequate for carrying out the proposed research. In particular, the in-situ technique developed by the PI in Lawrence Berkeley National Laboratory. In terms of both resources and time scale, the resources and instruments can meet the stated milestone of the proposed research. The reviewer pointed out that integrating theoretical modeling will be useful for this project.

**Reviewer 2**

The reviewer said resources of the project look reasonable.

**Presentation Number:** BAT091
**Presentation Title:** Characterization and Modeling of Lithium-Metal Batteries First-Principles Modeling and Machine Learning
**Principal Investigator:** Kristin Persson, Lawrence Berkeley National Laboratory

***Presenter***

Kristin Persson, Lawrence Berkeley National Laboratory

***Reviewer Sample Size***

A total of four reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 75% of reviewers felt that the resources were sufficient, 25% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

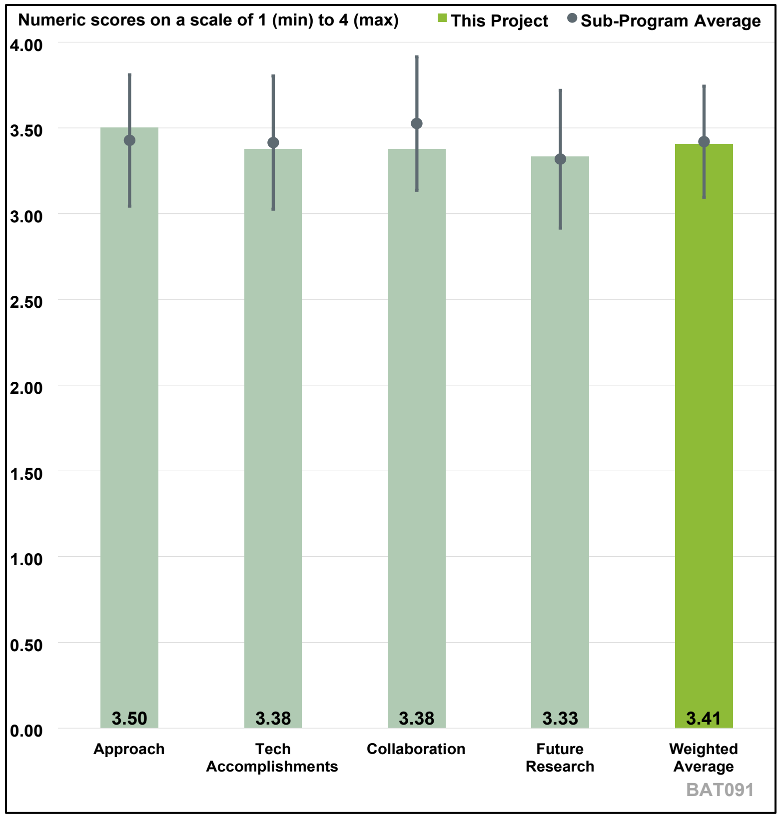


Figure 1-2. Presentation Number: BAT091 Presentation Title: Characterization and Modeling of Lithium-Metal Batteries First-Principles Modeling and Machine Learning Principal Investigator: Kristin Persson, Lawrence Berkeley National Laboratory

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer said this is a very well-designed project that, with modeling, aims to understand and develop quantification metric for solid-liquid (lithium hexafluorophosphate, $LiPF_6$) and solid-solid interfacial reactivity and decomposition at Li-metal anode. The reviewer said the timeline is reasonably planned and proposed milestones were delivered with great depth. Note that amorphous coating milestones cover work from the first and second quarters of 2023.

**Reviewer 2**

The reviewer said the approach appears promising to address individual issues, and a cohesive final goal that unifies the objectives of the 3 approaches would be useful.

**Reviewer 3**

The reviewer remarked the project's goal is to design interphase/coatings in Li-metal batteries for EV applications. It provides fundamental insights to address the technical barrier (Cost, Performance, and Safety). The computational approach is well-designed and leverages multiple data infostructures

(Materials Project, atomate, and Maggma). The reviewer said the project seems to touch many different areas for Li-metal batteries, e.g., coatings on cathodes, SEI on Li-metal in both liquid and solid electrolytes. It could be more focused on solving more specific technical barriers quickly.

**Reviewer 4**

The reviewer said the project is on track to address the proposed technical barriers including cathode coating development, SEI formation in liquid electrolyte, transport and stability of organic electrolyte and interfacial design of solid-state batteries. Computational study on these surfaces are particularly challenges due to the absence of a particular crystal structure and usually a mix of multiple phases. The project provides many important insights with relatively high throughput computations. One technical comment the reviewer provided for the cathode coating development is that many coating materials actually react with the cathode during coating or cycling. However, the chemical stability between the coating material and the cathode is not considered in the computation.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer said this computational work beautifully connects with experimental (in-situ XPS) and thermodynamic predictions on solid-solid interfaces to reveal reaction kinetics and interface morphology.

**Reviewer 2**

The reviewer remarked the theoretical results from the project's previous work tested experimentally by internal and external collaborations is interesting and useful. It would be useful to compare oxygen diffusion in actual coating conditions (thickness; extent of amorphous state) with the predictions for similar lithiation condition. Solid-solid interfaces are very complex and usually kinetically slow. The reviewer said the ab initio molecular dynamics (AIMD)-driven machine learning interatomic potentials (MLPs) are a reasonable attempt for the description of the longer time evolution, but the 10 ns shown seem too short. Generating appropriate interfacial configurations is another bottleneck. It is mentioned but not sufficiently explained. It is unclear how the kinetic data is predicted via MLPs. Are the MLPs trained with experimental or theoretical data? If from AIMD, are the data obtained close to the Li-metal anode, i.e., close to the electron source? Various tools for solvation and transport analysis mentioned but their use not explained, except for the solvent effects on the dielectric constant. Besides fundamental understanding of solvation, what is the practical knowledge expected from this part of the research? In other words, how are solvation structures, speciation, coordination, related to the battery performance under cycling conditions?

**Reviewer 3**

The reviewer stated that the project provided multiple important insights for the interphase design for enabling nickel manganese cobalt oxide (NMC) cathode, Li-metal anode, and solid-state batteries. The computational result on the thickness of the interphase formed between Li-metal and sulfide electrolyte seems to be much thinner compared with the experimental results (4.8 nm versus 200 nm) based on Janek's study. The reviewer suggested more detailed study on the transport property, particularly electronic transport, of the interphase to predict its growth behavior.

**Reviewer 4**

The reviewer remarked simulations did a very nice job of predicting oxide coating predictions that were experimentally validated. This is largely because the design objectives for the coating on the cathode are very clear. In comparison, the SEI design objectives on Li-metal electrodes are not very clear. So far, the simulation tools have been built to show amorphous SEI formation. The reviewer said the desired SEI layer and how to form it are still not clear.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer said there are great internal collaborations within Lawrence Berkeley National Laboratory (LBNL) and University of California-Berkeley, as well as with some external related companies.

**Reviewer 2**

The reviewer remarked this team work together very effectively and complement each other.

**Reviewer 3**

The reviewer noted good collaborations with different experimental groups.

**Reviewer 4**

The reviewer said the project listed a couple of collaborations from CoreShell, Sandia National Laboratories, and LBNL, and that more details of these collaborations should be provided.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer said that with about a quarter remaining at the time of the review, the proposed future research looks reasonable.

**Reviewer 2**

The reviewer said the project will end in September 2024 and the last two milestones are in progress. The reviewer asked if this high-throughput tool for predicting electrolyte transport, solvation and stability can be developed to be used for developing polymers (for example, linear poly(ethylene) oxide [PEO]/bis(trifluoromethysulfonyl)imide [TFSI] or crosslinked PEO/TFSI) and ultimately composite polymer electrolytes.

**Reviewer 3**

The reviewer referenced a prior comment. A unified view that connects the individual goals among themselves and with the actual battery performance and lifetime would be useful.

**Reviewer 4**

The reviewer noted that proposed future research, "Develop quantification metrics for solid-state interfacial reactivity and decomposition product formation for solid-solid interfaces at the Li-metal anode," will address the reviewer's question on the SEI design criteria for Li-metal. It will be highly appreciated by the research community as well. The other future research milestone, "Identify thermodynamically and kinetically favorable mechanisms of ethylene carbonate (EC) oxidation on model cathode materials", can be better aligned with the most advanced electrolytes for Li-metal batteries (e.g., multiple electrolytes projects related to Li-metal electrodes). The reviewer noted it is known that EC is not a good electrolyte for Li-metal. The cathode material and surface states should be well-defined in the research task/milestone.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer remarked the proposed research on computational study of the interfacial processes is relevant and support the overall VTO goal to develop high-performing batteries.

**Reviewer 2**

The reviewer commented the project supports VTO objectives of developing fundamental understanding of battery materials and their interactions that can lead to an improved practical design.

**Reviewer 3**

The reviewer agreed that developing new machine learning potentials to predict and understand solid electrolyte interface reactions is a very important topic to achieve overall VTO objective for solid-state batteries. Similarly, identifying solvation environments, viscosity, and conduction mechanisms in nonaqueous electrolytes, and proposing changes to solvent/salt compositions to improve active ion conductivity, are valuable contributions to Li-ion batteries.

**Reviewer 4**

The reviewer said this project builds computational approaches that can accelerate battery design, achieving the Batteries program objectives.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

For a project with so many different tasks on various cell chemistry, the reviewer thought the resources are not sufficient to reveal all the insights covering cathode coating in liquid electrolyte, liquid electrolyte development, solid-state battery interface, and SEI formation. The proposed research can potentially be divided into a few different projects, in this person’s mind.

**Reviewer 2**

The reviewer said resources are sufficient.

**Reviewer 3**

The reviewer commented the resources are sufficient for the project to achieve milestones in timely fashion.

**Reviewer 4**

The reviewer found that the overall budget is well aligned with the tasks in the projects.

**Presentation Number:** BAT183
**Presentation Title:** In Situ Spectroscopies of Processing Next-Generation Cathode Materials
**Principal Investigator:** Feng Wang, Argonne National Laboratory

***Presenter***

Feng Wang, Argonne National Laboratory

***Reviewer Sample Size***

A total of seven reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

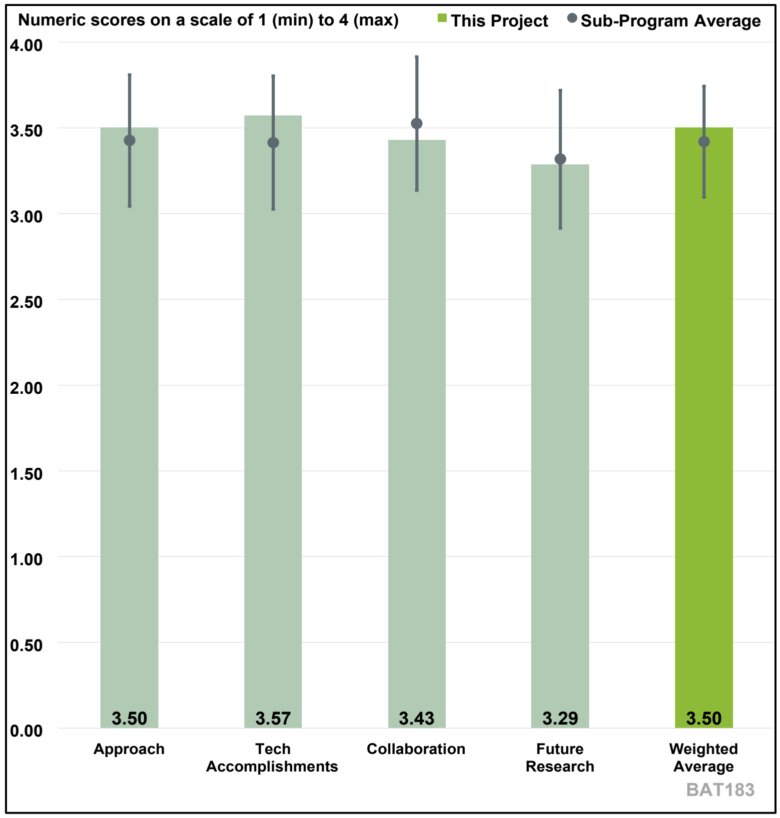


Figure 1-3. Presentation Number: BAT183 Presentation Title: In Situ Spectroscopies of Processing Next-Generation Cathode Materials Principal Investigator: Feng Wang, Argonne National Laboratory

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer said these researchers have demonstrated over several years that their approach to understanding the effect of synthesis conditions on the structure of the final product and its performance is outstanding.

**Reviewer 2**

The reviewer remarked the project focuses heavily on the first and second barriers, cathode materials performance, and corresponding structure change. The project is well designed, and the structure analysis is phenomenal.

**Reviewer 3**

The reviewer said battery precursor and cathode synthesis processes are well established in the battery industry, but there are still fundamentals about the process that are not fully understood. This project is focusing on investigating this area using various in-situ techniques. This will help researchers understand and improve the established process and benefit new chemistry development.

**Reviewer 4**

The reviewer said the approach of this project is excellent. A combination of in situ synchrotron X-ray spectroscopies, such as in situ X-ray diffraction (XRD), pair-distribution function (PDF), and X-ray absorption near edge structure spectroscopy (XANES) were utilized to gain insights into predictive process design and synthesis and provide input for modeling and process development/scale-up for cobalt (Co)-free nickel (Ni)/manganese (Mn)-based cathode active materials (CAMs). Strategies for cathode processing to improve performance and safety were developed through tuning Li-stoichiometry during cathode calcination and through tuning transition metal (TM) stoichiometry in the bulk and locally via coating/doping. The reviewer said this is an innovative approach.

**Reviewer 5**

The reviewer said the project is well designed and the timeline is reasonably planned. Current achievements provide an in-depth understanding of the processes and reaction kinetics/thermodynamics underlying the synthesis and processing of cathode active materials.

**Reviewer 6**

The reviewer remarked the objective of the work is to develop processing science and technologies to enable the scalable production of next-generation industrially relevant cathode materials. The approach to use in situ spectroscopy for real-time tracking of the phase progression and structure evolution was novel and provided insights and strategies for cathode processing to improve performance. But it is not applicable to scaling up as discussed by the researchers.

**Reviewer 7**

The reviewer detailed that the project's overall objective is to use in-situ spectroscopic methods and modeling to analyze synthesis and processing procedures for cathode active materials. The slide deck and presentation were a little difficult to follow, but show that many techniques (differential scanning calorimetry, time resolved in-situ X-ray diffraction, X-ray scattering, microscopy) were utilized to understand the phase/particle evolution of various cathode active materials (Co-free Ni/Mn oxides, cation disordered rocksalts, and $LiNiO_2$ specifically), including those with coatings. Overall, the project is reasonably well-designed, although it does feel like multiple individual projects tied together (multiple materials are studied using various techniques, without a clear scientific objective that ties everything together).

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer said the team has successfully achieved the following accomplishments: First, process design strategies have been developed to address performance, safety and cost/scalability by tuning Li/TM-stoichiometry and controlling local stoichiometry through surface coating/doping. Second, important insights were obtained through correlated experimentation and theoretical modeling on a lithiation-induced kinetic pathway of phase propagation and crystallization; intrinsic roles of Li and TM stoichiometries in controlling the structure and morphology of CAM as well as roles of surface coating on precursor cathode active materials (pCAMs) in tuning the crystal growth of CAMs during calcination, which in turn determine their structure, morphology, and performance. Third, new in situ spectroscopies have been developed for processing CAMs including absorption/scattering spectroscopy for correlating phase progression to lithiation and multimodal X-ray, neutron and electron spectroscopy/microscopy for examining short- and long-range structural ordering and chemical heterogeneity.

The reviewer said these accomplishments are outstanding and have important impact in guiding the synthesis of pCAM and cathode materials for Li-ion batteries.

**Reviewer 2**

The reviewer said the kinetics and thermodynamics during battery calcination of high-Ni low Co were well studied and documented.

**Reviewer 3**

The reviewer said progress is reasonable as compared to the plan.

**Reviewer 4**

The reviewer commented the impact of transitional metals (Co and Mn) in determining the phase propagation and crystallization was elucidated. It might be better to manifest the role of ratio of lithium hydroxide (LiOH), or the ratio of LiOH to the precursor, in the phase propagation and crystallization.

**Reviewer 5**

The reviewer said good progress has been made. Specific conclusions gleaned included $LiNiO_2$ tends to degrade at lower temperatures when delithiated to some extent; $Li_xNiO_2$ and NMC811 calcination temperature controls the Li/Ni stoichiometry in the ultimate material, minor Co incorporation improves low temperature layering of nickel manganese oxides, and niobium (Nb) and Mn coatings can be applied by dry coating methods. These conclusions are all supported by the spectroscopic, imaging and modeling analysis provided.

**Reviewer 6**

The reviewer detailed the project's accomplishments.

Accomplishment 1. Argonne National Laboratory (ANL) shows through differential scanning calorimetry (DSC) that there appears to be a different mechanism from pCAMs to CAM of $NiO_2$ when LiOH is present that is supported by DSC measurements. Brookhaven National Laboratory (BNL) conducted their in situ spectroscopy analysis to show that lithiation and dehydration were occurring at the same time as the temperature was increasing to lead to the final preferred composite structure. This material had good capacity and excellent capacity retention.

Accomplishment 2: Researchers then turned their attention to Co/Mn substitution in Ni-oxides to understand their role and found that the Co and Mn result in early layering of the Ni-based oxides while limited the rate of crystal growth. By investigating the components separately, the team found that Co accelerates layering and crystal growth whereas Mn hinders layering and crystal growth but promotes stability over long calcination times.

Accomplishment 3: The team found that they can play with the Li fraction to change cyclable capacity and stability.

Accomplishment 4: The team helped identify synthesis conditions for deposition of a Nb surface coating on NMC 90 5 5.

Accomplishment 5: The team also helped identify conditions for Mn coating on Ni materials.

**Reviewer 7**

The reviewer remarked technical progress was very good in linking the cathode performance to changes in synthesis approach; for example, on the control of Li/TM stoichiometry control. Suggested processes could lead to making high-performance CAMs, but how scalable it could be was not demonstrated. The reviewer noted several chemistries were investigated: composite $LiNiO_2$ (LNO), NMC811, Mn/Co substitution, composite NM9505, etc., but there was no deep focus on either of these systems to provide a practical system for industrial applications.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer said like most DOE research projects, all work is done by extensive collaboration among various national laboratories and universities.

**Reviewer 2**

The reviewer referenced prior comments. It does feel as though there may be some close collaboration, particularly between the modelling efforts and certain experimental analyses, but for the most part, this feels like many individual projects stitched together. Nevertheless, the team is very strong and are making good progress in understanding the synthesis of many materials.

**Reviewer 3**

The reviewer said collaboration of this project is excellent, involving many research groups funded by VTO, including modeling scientists at ANL, scientists at the Advanced Photon Source (APS) of ANL, National Synchrotron Light Source II at BNL, at LBNL and Oak Ridge National Laboratory (ORNL), as well as scientists at Binghamton University, University of Texas at Austin, and University of Buffalo.

**Reviewer 4**

The reviewer commented these researchers list a number of collaborators and a number of materials they have worked on. The reviewer cannot tell if this was over the past year or over the years the team has developed and applied this technique.

**Reviewer 5**

The reviewer noted there was strong team collaboration with participation from three other national laboratories and four universities. The reviewer noted no participation from industry. There was good coordination among the team members.

**Reviewer 6**

The reviewer noted excellent collaborations among national laboratories and universities. Collaborating with industries might be necessary, especially when the project move to the process design to address safety, cost and scalability.

**Reviewer 7**

The reviewer remarked collaboration is great among team members. However, it would be better to develop the low-cost/scalable processes together with an established materials company to speed up the process.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer said the project has clearly defined a purpose for future work as developing process design by in situ spectroscopy for scalable synthesis and processing of next generation industrially relevant CAMs. It includes developing process design strategies to address performance, safety and cost/scalability; investigating coating processes for improving cycling and thermal stability through correlated experimentation and modeling; investigating the calcination process of Li/Mn-rich, disordered rock salt and other Co/Ni-free CAMs; and designing scalable processes for pCAM fabrication, alternative to the traditional coprecipitation. The reviewer said these planned future works are likely to achieve the targets and objectives of this project.

**Reviewer 2**

The reviewer said the future work has been clearly defined for scalable synthesis to address disparities in materials, process and heat/mass transport. The reviewer suggested collaboration with industry in the future.

**Reviewer 3**

The reviewer said looks like the project plans to continue on many of the projects already listed above. The team is planning to develop a new capability with ORNL to combine information from neutron scattering with X-ray data to look at disparities in high volume production.

**Reviewer 4**

The reviewer remarked future work is to process design by in situ spectroscopy for scalable synthesis and processing of next generation industrially relevant CAMs. The reviewer said the team proposed several future research activities that are part of other projects and the reviewer was not clear what the role of this project is. If the syntheses process needs to be scalable, the presentation did not identify how the scaleup process would work. The reviewer was not clear what problems the new proposed technique/capability development would address and recommended that the project focus on 2-3 chemistries and go deeper to finalize and optimize the synthesis process rather than going from one research area to another.

**Reviewer 5**

The reviewer reiterated the majority of the future work is the low-cost/scalable process development. It is better to develop the processes together with an established materials company.

**Reviewer 6**

The reviewer remarked the future work all appears to be fairly generic, unfocused extensions of the current efforts. It will be interesting to see how correlated X-ray/neutron characterization will be implemented to study the synthesis of various materials.

**Reviewer 7**

The reviewer provided a general comment related to all Co-free projects in VTO. Co-free research ideas were proposed for a few reasons: 1) Cost: Co price jumped almost 300% in 2018. This pushed many original equipment manufacturers (OEMs) to move to high Ni, low Co NMC cathodes. 2) Geopolitical: majority of Co has been mined in Congo and processed in China. 3) Supply shortage: over-optimism about EV sales growth causes concern of Co shortage.

The reviewer noted the situation has changed over the past several years: 1) Supply: there is enough Co resources and reserves for EV demand and there is a market oversupply of Co in the near and medium term. The reviewer referenced https://www.ft.com/content/e6f131c8-4945-45f9-84ad-18eec58df0d9. 2) Cost: due to oversupply of Co, the price of Co is back to normal and only 30% of the highest price in 2018. Besides, Co prices are currently close to or even lower than Ni's price. The reviewer referenced https://www.reuters.com/default/surpluses-low-prices-remain-feature-cobalt-market-2023-08-14/. 3) Geopolitical: by 2030, close to 40% of global Co will come from Indonesia and the Democratic Republic of the Congo will have less dominance in this market. The reviewer referenced https://www.mining.com/indonesia-emerges-as-a-cobalt-powerhouse-amid-surge-in-demand/. Co is critical to maintain NMC structure stability. High-Ni low-Co makes more sense like NMC811 due to high capacity. But, according to the reviewer, the benefit of Co-free cathodes is in question.

Since the concerns on Co price, supply, and geopolitical have changed, the VTO Program Manager could shift the future research focus away from Co-free work.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer commented the achievements obtained from this project will enable next-generation cathode materials for electric batteries, which support the overall VTO objectives.

**Reviewer 2**

The reviewer remarked yes, this work is relevant to Batteries, Mobility, etc., sub-programs.

**Reviewer 3**

The reviewer said yes, the project supports the overall VTO subprogram objectives. It focuses on the novel high energy cathode materials development and synthesis.

**Reviewer 4**

The reviewer noted there are many researchers seeking to make new materials for Li-ion batteries with high capacity and better cycle stability. This research allows one to better understand the material transformation during high temperature synthesis conditions in order to optimize the synthesis conditions and the resulting material. This is an extremely valuable resource.

**Reviewer 5**

The reviewer said this project focuses on CAM synthesis, which is entirely relevant to VTO subprogram objectives.

**Reviewer 6**

The reviewer said this project is relevant to current DOE objectives by providing guidance for pCAM and CAM synthesis to improve the performance of Li-ion batteries.

**Reviewer 7**

The reviewer said this project support the overall VTO Battery objectives by synthesizing better pCAMs and CAMs.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer remarked yes, there is sufficient research staff and lab facilities for this project.

**Reviewer 2**

The reviewer said resources are sufficient.

**Reviewer 3**

The reviewer said resources from ANL, ORNL, BNL, LBNL, Binghamton University, University of Texas at Austin, and University of Buffalo are sufficient to achieve the stated milestones.

**Reviewer 4**

The reviewer commented the researchers appear to be able to collaborate with several PIs using the present resources.

**Reviewer 5**

The reviewer said resources appear sufficient for the scope of the project.

**Reviewer 6**

The reviewer remarked resources are sufficient for the project to achieve the milestones and objectives.

**Reviewer 7**

The reviewer found that the $500,000 provided is sufficient for achieving the objectives of the project.

**Presentation Number:** BAT287
**Presentation Title:** Advanced In Situ Diagnostic Techniques for Battery Materials
**Principal Investigator:** Xiao-Qing Yang, Brookhaven National Laboratory

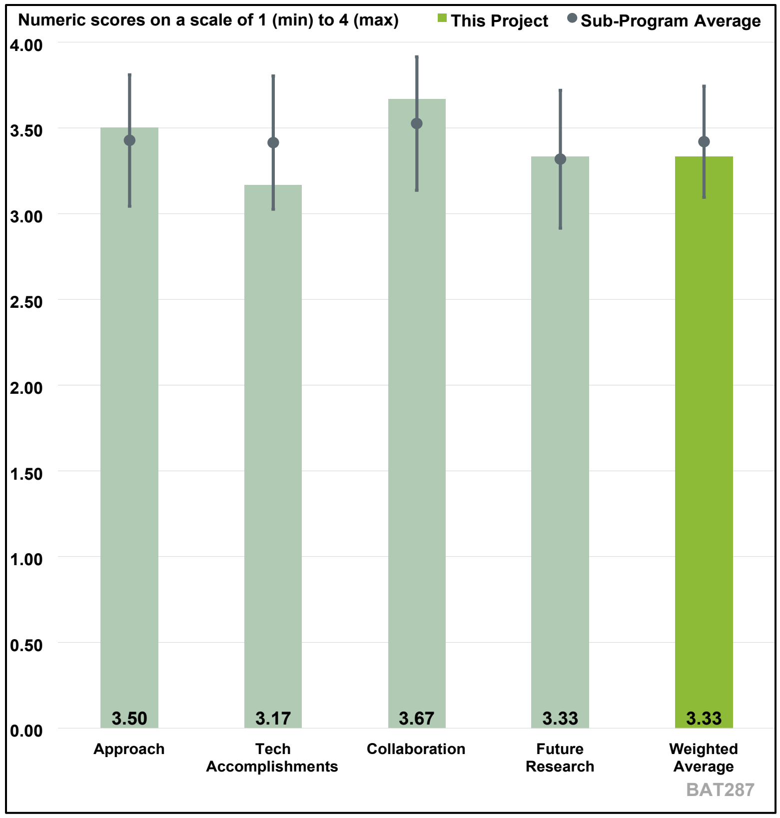


Figure 1-4. Presentation Number: BAT287 Presentation Title: Advanced In Situ Diagnostic Techniques for Battery Materials Principal Investigator: Xiao-Qing Yang, Brookhaven National Laboratory

### *Presenter*

Xiao-Qing Yang, Brookhaven National Laboratory

### *Reviewer Sample Size*

A total of three reviewers evaluated this project.

### *Project Relevance and Resources*

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

### *Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?*

#### Reviewer 1

The reviewer said the project developed synchrotron-based in situ and ex situ X-ray techniques and uses them to perform advanced diagnostic studies on battery materials and cells. The approach is excellent, and it has been demonstrated to be effective in numerous studies. The reviewer noted the team has a long history of productive research in this space.

#### Reviewer 2

The reviewer said the goal of the project is to couple a Li-metal anode with a high-Ni-NMC or sulfur (S) cathode to "achieve a specific energy of up to 500 Wh/kg through cell level design and optimization of materials and architectures." The approach includes "integrating development and discoveries from materials to cell level" and leveraging "state-of-the-art DOE facilities to understand and prevent degradation." The reviewer noted that in this project presentation, use of BNL's synchrotron facilities is used to examine cathode and anode materials used in the B500 cells. The techniques included XRD, PDF, XAS and transmission X-ray microscopy (TXM). The project design and timelines appear to be reasonable and appropriate technical barriers are being addressed.

**Reviewer 3**

This project focuses on addressing the barriers of rechargeable batteries for plug-in hybrid electric vehicle (PHEV) applications, typically such as the calendar and cycle life of rechargeable batteries as well as their abuse tolerance. The team develops and integrates advanced in-situ X-ray techniques, such as synchrotron-based XRD and PDF, to probe into the fundamental cause of the fading of battery performance with the microstructural evolutions. The materials studied include cathode, solid electrolyte, and solid electrolyte interphase. The reviewer said the project is well designed and the timeline for carrying out the proposed research is reasonable. It would be expected that this team's research can be complementary at scale with other experimental techniques.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer said the presentation includes a summary of characterization of interphases in Li-metal cells using various fluorinated ether electrolytes developed at Stanford University. The presentation shows the S fluorescence mapping of the Li-metal anodes and S-edge XAS of the NMC811 cathode showing S in the cathode electrolyte interphase (CEI). For in situ TXM, beam damage was observed in coin cells but not in pouch cells with applied pressure. PDF studies were conducted on a sulfur-iodine (S-I) cathode material developed at the University of California San Diego (UCSD). The reviewer said results show that the S-S bonds are maintained while the iodine (I) exists as $I_2$ and in S-I bonds. The technical progress appears to be in line with the project plan.

**Reviewer 2**

The reviewer said the team made good progress toward reaching their milestones. Using fluorinated ether electrolytes, the team studied the interphases, such as CEI and SEI layer, in the Li-metal cell (Li||NMC811) by synchrotron-based imaging and spectroscopy techniques. These studies provide insights into the interphase formation mechanism and its dependence on the charging voltage. Even though the X-ray based technique is widely used, the beam damage to the sample has never been symmetrically evaluated. This team evaluated the X-ray beam damage effect, which will benefit the development of in-situ X-ray techniques for battery studies. The reviewer said for the novel S-I cathode material for lithium-sulfur (Li-S) solid-state batteries, the team shows that the S-S bond in S8 puckered ring structure is preserved in the new cathode while the iodine in the form of $I_2$ and S-I bonds are formed through sintering. The reviewer said the research progress is in accordance with what the team has proposed, which all align well with their milestones.

**Reviewer 3**

The reviewer found that overall, good progress has been made in a number of areas. The team investigated the interphases in the Li-metal cell (Li||NMC811) using various fluorinated ether electrolytes, evaluated cell configurations for in situ TXM studies, and analyzed S-I cathode materials for Li-S solid-state batteries developed at UCSD. The PIs have produced several publications and delivered invited presentations. The reviewer said that while these results are interesting, their significance is not clear to this reviewer as the background info on the studies were not provided. It would be good to indicate what specific challenges the team is trying to address in each study, why their techniques are unique in doing so, and how their work complements the overall goals. For example, why is the S-I cathode material chosen for investigation, and do they have particular advantages and challenges?

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer said the BNL team has been collaborating with various teams in the Battery500 program.

**Reviewer 2**

The reviewer remarked the team is collaborating with universities and other national laboratories. The benefit of such a broad collaboration is that characterizing team can use the advanced technique to study the most advanced materials, which is apparently verified by the high impact publications of the project. Integration of other experimental techniques and results across the research board will be beneficial for the interpretation of the results captured in this work.

**Reviewer 3**

The reviewer commented there are several effective and productive collaborations with researchers from Stanford University and UCSD. The team uses their diagnostic tools to obtain a deeper understanding of materials provided by their collaborators. The reviewer said it would be helpful to provide more information on each collaboration, particularly as to what was the context for the study, and how the PI’s work helps to tackle the specific challenges etc.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer pointed out the proposed next steps include “the study of polysulfides using PDF techniques” and X-ray fluorescence mapping to study dissolution, deposition and distribution of polysulfides in Li-S batteries. The team also plans to use X-ray techniques to examine the interphases formed during cycling. The reviewer found that in general, the future plans appear to be reasonable and have a defined purpose.

**Reviewer 2**

The reviewer said the future work plan includes further diagnostic studies of Li-metal interphases and the behavior of polysulfides in Li-S batteries. Considering the expertise of the team and the wide array of diagnostic tools at their disposal, this is a reasonable and achievable list for the team.

**Reviewer 3**

The reviewer said the proposed future research aligns well with the overall milestone of the project. What has been accomplished and planned to be done are well conceived for gaining insights on the fading mechanism of rechargeable batteries. The insights gained from these studies can be used to guide the design of novel electrode and electrolyte system toward enhanced performance of the rechargeable batteries. The reviewer noted the team has a good track record of accomplishing what they proposed to do. It would be beneficial to consider integrating experimental observation of other techniques with the same materials system.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer remarked yes, the project supports overall VTO subprogram objectives.

**Reviewer 2**

The reviewer commented microstructural features of the electrode and solid electrolyte as well as their evolution upon battery cycling are critical factors that control the stability of rechargeable battery. This project is primarily focused on investigating the microstructural feature of the active battery materials and their correlation with battery performance. The reviewer said the proposed research is highly correlated with the overall objectives of VTO subprogram.

**Reviewer 3**

The reviewer said research using state-of-the-art diagnostic techniques to obtain fundamental knowledge at both material level and cell level is critical to future development of advanced batteries, which is directly related to DOE goals.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer said the team members of the project possess expertise for using synchrotron-based X-ray techniques for rechargeable battery studies. It is apparent that the team has the privilege for accessing to the light source at BNL for carrying out the proposed research, which will warrant, timewise, what they proposed to be carried out in this project. The reviewer said integration of other experimental techniques across different teams will be complementary and therefore gain insights at different scales.

**Reviewer 2**

The reviewer said the PIs have adequate resources to conduct the proposed research activities.

**Reviewer 3**

The reviewer said the total resources available to the project are sufficient. It is not known whether the resources available for this particular project are sufficient, as no information is provided.

**Presentation Number:** BAT309
**Presentation Title:** Electrode Materials Design and Failure Prediction
**Principal Investigator:** Venkat Srinivasan, Argonne National Laboratory

***Presenter***

Venkat Srinivasan, Argonne National Laboratory

***Reviewer Sample Size***

A total of four reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

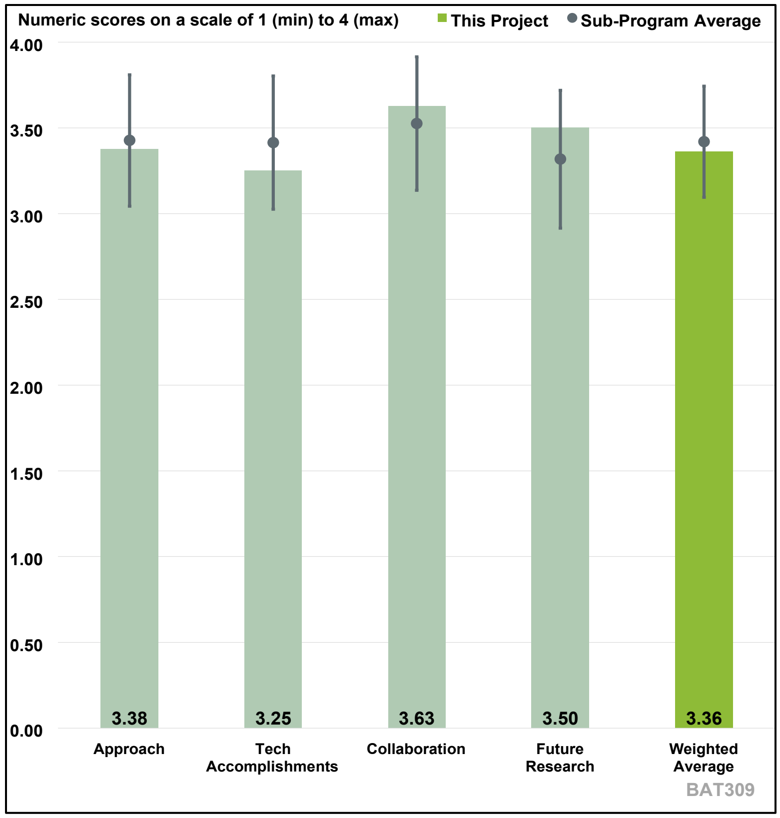


Figure 1-5. Presentation Number: BAT309 Presentation Title: Electrode Materials Design and Failure Prediction Principal Investigator: Venkat Srinivasan, Argonne National Laboratory

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer said the team has correctly identified the key barriers in solid state Li-ion batteries.

**Reviewer 2**

The reviewer said the project is well designed and the listed technical barriers are systematically addressed, especially in the first part of the project as discussed below.

**Reviewer 3**

The reviewer remarked that to achieve a highly reversible Li-metal anode, the team has been addressing the following technical barriers in this fiscal year presentation report: Modeling ionic electronic conducting interphase layers; determining the location of Li deposition; and understanding the diffusion of ions between cathode and solid electrolyte. The project is well designed and the timing is well planned. The reviewer said it would be ideal if the Li deposition position can be in-situ experimentally visualized. It would also be ideal if the electronic and ionic conductivity in the interphase can be quantified through experimental methods.

**Reviewer 4**

The reviewer remarked this project aims to develop a multiscale and multiphysics model to simulate various failure mechanisms related to Li-metal solid electrolyte batteries. It provides fundamental insights for several key design challenges in solid-state Li-ion batteries, e.g., dendrite growth during plating and maintaining contacts during stripping.

The reviewer said it is often seen that the model varies material properties by five orders of magnitude, but without mentioning the matching materials. For example, high ionic and lower electronic conductivity are desired, but how to achieve it? Another example is the adhesion energy. It varied from 0.001 to 10 $J/m^2$. The reviewer said it is rare to see any measured adhesion energy below 0.1 $J/m^2$. The model can further guide the experiments if it can point out what type of materials to be used.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer said technical progress is satisfactory. About 45% of the work is remaining, whereas only 30% time is remaining.

**Reviewer 2**

The reviewer said technical progress well aligned with the project plan.

**Reviewer 3**

The reviewer said the project seems to touch many different areas for Li-metal batteries, e.g., interphase design for Li-plating, plating and stripping, and solid electrolyte/cathode interface. The reviewer said it could be more focused on solving more specific technical barriers quickly.

**Reviewer 4**

The reviewer said overall, the results are interesting and well discussed. However, some aspects need work. The reviewer pointed out Section 1, modeling of interfacial reactions: This section is excellent. It is not clear how the model considers that Li reaches the back side of the interphase. The reviewer said that selection of silver (Ag) as an alloying material for the interphase is not clear and asked does it come only from literature reports, what would be the additional impacts of the presence of Ag in that layer, and how is the allowing proportion decided.

Regarding Section 2, Cathode surface degradation, the reviewer said this section appears not well-advanced; it was unclear what theory has been used in the graph displaying theory/experiments for interdiffusion. Analysis of stress evolution is also very unclear. Experimental results are shown but not commented on. Regarding plating/stripping modeling, the reviewer said the effect of the SSE modulus is included. However, the interphase effect which is discussed in the first section of the modeling is not included here. Same as the previous section, this modeling appears at its initial stage.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer remarked collaboration is excellent. The teams consist of the needed expertise from LBNL, ANL, and the University of Giessen. The computational simulation of plating and stripping of Li is notably strong.

**Reviewer 2**

The reviewer said the project has outstanding collaborations with different experimental groups.

**Reviewer 3**

The reviewer said the team had collaborations with national laboratories (e.g., LBNL), universities (e.g., University of California, Berkely; University of Chicago), and a German institution (i.e., Justus-Liebig-Universität,), which broaden the impact of this work.

**Reviewer 4**

The reviewer said good collaboration, but these could be enhanced so sections 2 and 3 receive the benefits of the knowledge developed in section 1.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer said proposed research is aligned with current results and expectations.

**Reviewer 2**

The reviewer remarked most future work is excellent. One point is unclear on the plan to simulate Li plating in the presence of alloying. The plan did not address the alloying effect.

**Reviewer 3**

The reviewer commented future work is well articulated.

**Reviewer 4**

The reviewer said it would be ideal if some detailed plan on combining research with experimental groups can be listed.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer said yes, the project is very relevant to developing further understanding of battery materials and interfaces.

**Reviewer 2**

The reviewer remarked this project builds simulation capabilities that can accelerate battery design, achieving the Batteries program objectives.

**Reviewer 3**

The reviewer remarked the project will support the VTO program objectives.

**Reviewer 4**

The reviewer commented the proposed work well supports the Batteries program in VTO. This team's work on theoretical modeling part will support experimental progress towards the development of Li-metal batteries.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer commented the overall budget is well aligned with the tasks in the projects.

**Reviewer 2**

The reviewer said resources are sufficient.

**Reviewer 3**

The reviewer said sufficient resources are available for the team to achieve their proposed tasks.

**Reviewer 4**

The reviewer said resources are abundant.

**Presentation Number:** BAT360
**Presentation Title:** Cathodes Beyond Lithium Nickel Manganese Cobalt Oxide (NMC) 811
**Principal Investigator:** Arumugam Manthiram, University of Texas at Austin

***Presenter***

Arumugam Manthiram, University of Texas at Austin

***Reviewer Sample Size***

A total of five reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

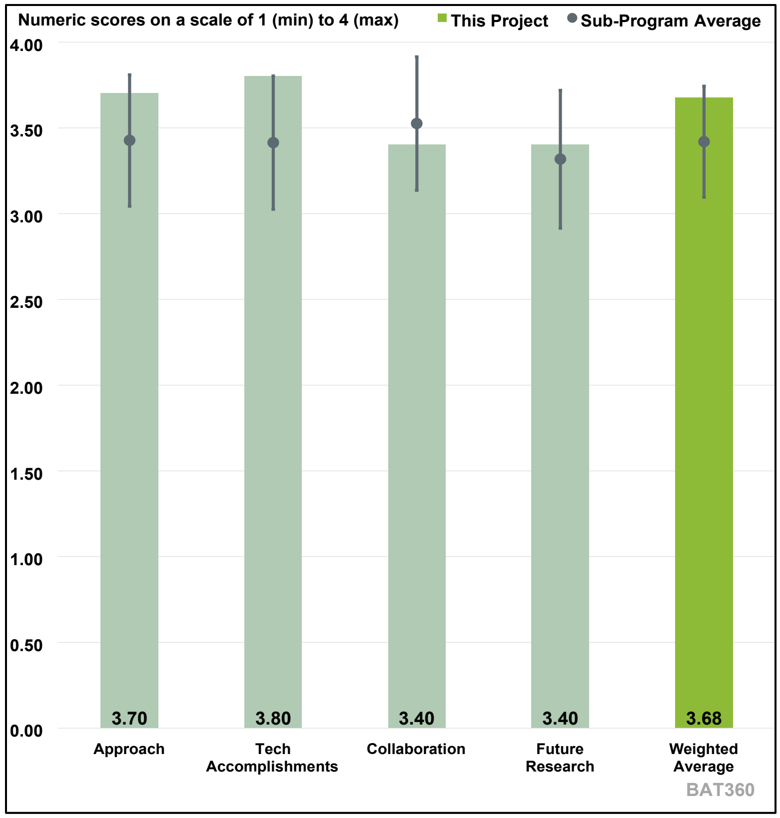


Figure 1-6. Presentation Number: BAT360 Presentation Title: Cathodes Beyond Lithium Nickel Manganese Cobalt Oxide (NMC) 811 Principal Investigator: Arumugam Manthiram, University of Texas at Austin

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer commented Dr. Manthiram's approach to R&D is always insightful and uses well thought-out approaches to investigating fundamental issues with high energy cathodes. The reviewer was very impressed by all of the high Ni and S work, and encouraged the program to shift more and more of its focus to S as industry is heavily invested in improving high-Ni NMC.

**Reviewer 2**

The reviewer said Professor Manthiram's approach to developing high-capacity, stable cathode materials is logical and well-structured. The research team is methodical in identifying the key factors responsible for the cycle, air, and thermal instabilities of high-Ni cathodes. The increased focus on S cathodes is a positive development as it addresses the cost barrier ($80/kWh).

**Reviewer 3**

The reviewer said the project is very well designed, with a clear experimental plan and realistic goals and timeline. The team has expertise in this topic and extensive experience in the techniques they are using. The team executed all proposed milestones and delivered an in-depth study on proposed objectives. The work is very systematic and of high quality.

**Reviewer 4**

The reviewer remarked high Ni content for cathode materials are pursued for maximum specific capacity and energy density at the material level. The project systematically investigated the impact of doping and electrolytes on the cycling performance, storage stability, as well as thermal stability. The reviewer said the safety characterization at cell level can be of value for cell development, module and pack design.

**Reviewer 5**

The reviewer remarked this project aims to develop high-energy-density, long cycle life high-Ni cathodes to support Battery500's cell development. The project is well designed and the timeline looks reasonable.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer said the project is on track with the milestones and has a few world-class accomplishments to address the challenges of utilizing a high Ni cathode with a Li-metal anode, including air, thermal, and surface stabilities and transition metal cross over. The reviewer had two technical comments: first, most of the cathodes developed by University of Texas-Austin experience a capacity increase for the first 20 cycles. This capacity increase is not clearly observed in commercial NMC811 and may have important implication in interfacial stability, particularly cathode/electrolyte interface. A more detailed study is suggested to understand the differences. The reviewer also wondered whether coating development is planned for this project, since most commercial cathodes will have certain coatings. Second, to provide more insights to support Battery500's overall goal, this reviewer suggested studying the transition metal crossover on SEI chemistry using the Battery500's liquid electrolyte, rather than the typical $LiPF_6$ in an EC/ethylmethyl carbonate (EMC)-based liquid electrolyte.

**Reviewer 2**

The reviewer said milestones were well delivered.

**Reviewer 3**

The reviewer remarked the amount of data that Dr. Manthiram generates and presents is incredibly impressive. Outstanding data on a variety of critical subjects, including the impact of air exposure on high Ni gas generation and cycling, impact of dopants on thermal stability and gas generation, impact of Ni oxidation state on gas generation, and influence of electrolyte composition on cycling and gassing, among others.

**Reviewer 4**

The reviewer said the Manthiram Group is successfully meeting its milestone objectives and making significant progress on the high-nickel cobalt effort. They have synthesized several materials delivering over 200 mAh/g and determined the role of common dopants on air, thermal, and surface stabilities. The group has also authored numerous journal articles, significantly enhancing battery knowledge within the community.

**Reviewer 5**

The reviewer noted that high Ni cathodes suffer from cycle, air, and thermal instabilities; cation doping is beneficial, but there is no clear understanding of what dopants do and which dopant does what. This is very important goal and team did great job assessing the role of common dopants (Mn, Co, Al, and magnesium [Mg]) on cycle, air, and thermal stability. Confirm with different characterization techniques (time of flight secondary ion mass spectrometry [TOF SIMS]?) dopants sites and correlate with the electrochemical performance. The reviewer asked if $LiNi_{0.95}Al_{0.05}O_2$ nickel aluminum cathode chemistry is the most promising for overall performance metric investigated. The reviewer said the team did not recommend dopant of choice in regard to cycle, thermal stability, and gas evolution. If Al is the best performing dopant they the team should study if there is an additional effect of Al dissolution and crossover (at 10% dopants?) on Li deposition morphology. The reviewer asked does the spinel phase stabilize nickel manganese (NM) cathode chemistry for O-loss, is there a trade-off with aging degradation and suppression of gas generation?

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer said Professor Manthiram’s work on high-Ni NMC and S cathodes is well coordinated with others in the Battery500 consortium and hopefully his best performing cathodes are used and validated by others in the program soon.

**Reviewer 2**

The reviewer remarked the Manthiram Group has demonstrated outstanding collaboration with the Battery500 Consortium’s national laboratories and universities. High-Ni samples have been evaluated by Pacific Northwest National Laboratory (PNNL), BNL, ANL, and Stanford University. If testing by PNNL and the University of Washington proves promising, the General Motors (GM) group will proceed with cathode evaluation. It is clear that the Manthiram Group is actively seeking support from the community as needed.

**Reviewer 3**

The reviewer said the team clearly listed contributions from various collaborators, both from national laboratories and academia. This is really a very big team, so this reviewer’s only comment is when different teams have some overlap in their investigations (like dopants in this case) they need to communicate results and help each other in interpretation using all available characterization and expertise resources.

**Reviewer 4**

The reviewer said the project greatly leverages the team members in Battery500, and other expertise outside of Battery500. The project is also engaged in collaboration with industrial partners like GM. The reviewer said more industrial engagement on battery/pack design can add more value to the project.

**Reviewer 5**

The reviewer said the project shows a strong record of collaborating with multiple national laboratories on materials characterizations. The reviewer recommended extending the collaboration beyond characterization to facilitate the integration of these cathodes with Li-metal anodes.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer said proposed future efforts are appropriate and built on the current successful initiatives. The proposed future efforts are well-suited and build on the current successful initiatives.

Significant knowledge has been gained about the benefits of dopants, which should lead to the development of a cathode with enhanced thermal stability and cycle life.

**Reviewer 2**

The reviewer remarked Professor Manthiram's future work is well focused, particularly on the need to reduce cathode irreversible capacity loss to improve cell watt-hours per kilogram and the impact of anode to cathode and cathode to anode cross talk.

**Reviewer 3**

The reviewer said good future research was proposed to address the potential barriers at the materials level.

**Reviewer 4**

The reviewer commented future work is clearly defined and justified. The reviewer's suggestion to the team is to systematically look into the roles of bulk and surface dopants (such as Nb?). The team said at the Annual Merit Review (AMR) that they did not investigate Nb as dopant (even though it was displaying great performance) because some Nb stays in the lattice and some goes to the surface. The reviewer asked if bulk and surface dopants can be combined to take advantage of their different roles on electrochemical performance. Regarding the impact of transition-metal crossover on SEI chemistry: the reviewer asked if the team can think creatively about how to strategically design desirable crossover to achieve beneficial SEI, and if reactive/reducible surface dopants can passivate cathode surface and prevent gas release at lower SOC with low Ni-cathodes.

**Reviewer 5**

The reviewer said proposed future work looks reasonable to achieve the project target. The reviewer recommended the PI quantitively study the effects of the catalyst on the kinetics of the S cathode, to hopefully provide more insights to develop high-loading S cathode to achieve 500 Wh/kg cell energy density.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer remarked this very exciting and important work aims to systematically study and design Li cells with high-energy density, long cycle life, and safe operation at an affordable cost that can accelerate vehicle electrification. It fully supports VTO objectives, the team has a high number of high impact publications and invited presentations.

**Reviewer 2**

The reviewer remarked the project is highly relevant, aligning with VTO goals of achieving higher energy density, longer-lasting batteries, and reducing the cost of EV batteries (ultimate goal $80/kWh).

**Reviewer 3**

The reviewer said the effort greatly supports the ultimate goal of Battery500.

**Reviewer 4**

The reviewer said yes, the development of high-energy-density cathodes including Ni-rich oxides and S is critical to achieve 500 Wh/kg.

**Reviewer 5**

The reviewer said highly relevant. The reviewer referenced prior comments; although the high-Ni NMC work is world-class, it might be time for the program to shift more and more of its focus to S as industry is heavily invested in improving high-Ni NMC.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer said excellent value for the R&D investment.

**Reviewer 2**

The reviewer commented the team possesses excellent resources and is well-equipped to successfully complete their milestones in a timely manner.

**Reviewer 3**

The reviewer said resources of the project look reasonable.

**Reviewer 4**

The reviewer remarked the resources were sufficient and effectively utilized (advanced in-situ and ex-situ characterization: XRD, scanning electron microscopy [SEM], transmission electron microscopy [TEM], XPS, TOF-SIMS, DSC, differential electrochemical mass spectrometry) to achieve the proposed milestones in a timely fashion.

**Reviewer 5**

The reviewer remarked this is a subtask of Battery500. No detailed resource on the subtask was disclosed.

**Presentation Number:** BAT361
**Presentation Title:** Understanding and Improving Lithium Anode Stability
**Principal Investigator:** Yi Cui, SLAC National Accelerator Laboratory

### *Presenter*

Yi Cui, Stanford University / SLAC National Accelerator Laboratory

### *Reviewer Sample Size*

A total of four reviewers evaluated this project.

### *Project Relevance and Resources*

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 75% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 25% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

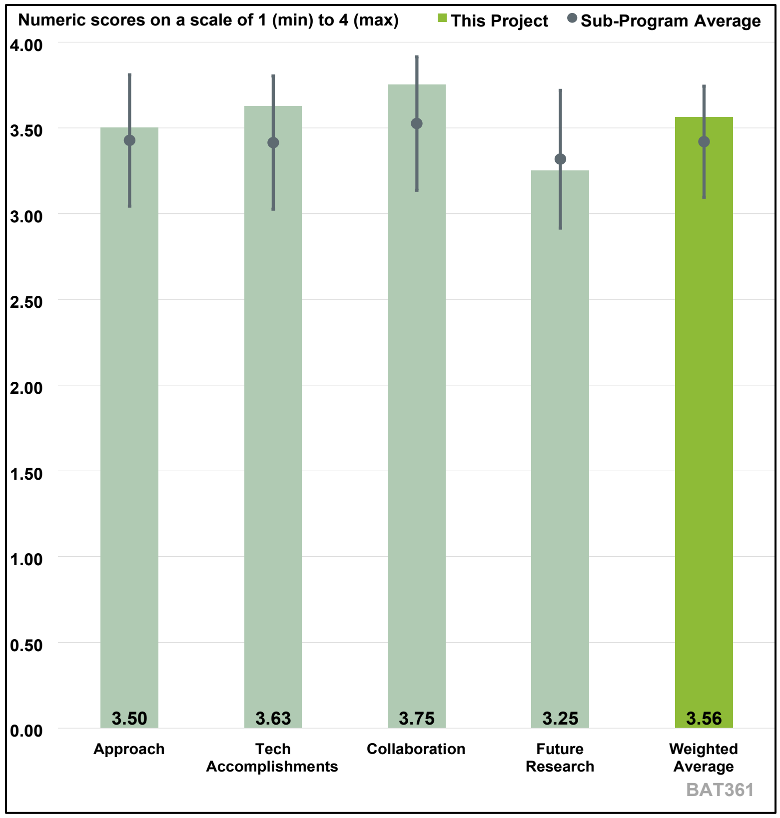


Figure 1-7. Presentation Number: BAT361 Presentation Title: Understanding and Improving Lithium Anode Stability Principal Investigator: Yi Cui, SLAC National Accelerator Laboratory

### *Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?*

**Reviewer 1**

The reviewer said the project approaches to addressing technical barriers in next-generation Li-metal battery technology are both innovative and commendable. By focusing on fundamental breakthroughs in controlling Li-metal electrochemical reactions, the discoveries set a solid foundation for substantial advancements. The integration of materials and cell-level discoveries is particularly noteworthy, as it ensures rapid incorporation and validation of the latest research findings, leading to more realistic and practical applications. Leveraging materials from other DOE programs and utilizing state-of-the-art DOE facilities at SLAC to understand and prevent degradation is a strategic and efficient use of resources. The reviewer said the emphasis on multi-disciplinary approaches and enhancing collaborations between national laboratories, universities, and industry highlights a holistic and synergistic strategy. This comprehensive and well-coordinated effort is likely to yield highly productive results, driving significant progress in the development of high-energy, low-cost Li-metal based batteries. Overall, the approach is excellently designed and executed, promising to overcome technical barriers effectively.

**Reviewer 2**

The reviewer pointed out that one of the major issues related to the metallic Li anode is the formation of the SEI. While SEI protects the Li anode, it also results in the creation of unrechargeable Li (dead Li). The PI utilized advanced analytical and electrochemical diagnostic techniques to investigate SEI formation, dissolution, and potential capacity recovery. These findings represent a significant step towards understanding the complex Li redox reactions and corrosion mechanisms. This research is valuable for future developments in Li anode and electrolyte technology. The project is well planned.

**Reviewer 3**

The reviewer said Dr. Cui's approach is excellent as always and encouraged this team to consider adopting quantitative milestones to demonstrate progress towards improving either Wh/kg, cycle, or calendar life. The existing milestones are good but are all qualitative. The use of Li hosts is a good one but has been under development for several years or more. The reviewer said there may be much more to do in this area but wondered if a go/no go decision is possible in the near future.

**Reviewer 4**

The reviewer said the Approach as outlined on the Approach slide is too generic to understand the specific approach used over the past year to address the problems of making cyclable Li foil. In the future, please complete the slides for this specific project.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer said the technical accomplishments achieved by the team are outstanding, with a sharp focus on addressing the critical barriers associated with Li-metal and electrolyte reactions. Through comprehensive and innovatively designed electrochemical experiments, the team has successfully navigated complex challenges that have long hindered progress in battery technology. The productivity of the team is commendable, as they have demonstrated a high level of expertise and dedication in their approach. Their ability to integrate cutting-edge research with practical applications has resulted in significant advancements, paving the way for the development of next-generation high-energy, low-cost batteries.

**Reviewer 2**

The reviewer commented it is amazing, and somewhat disconcerting, that aging a cell for 24 hours decreases the next cycle coulombic efficiency as shown on Slide 13. Calendar aging is much more important than we first thought, excellent data. Data shown on Slide 15 is an excellent idea, measuring SEI dissolution could be immensely valuable in many other chemistries, specifically silicon-based anodes which are believed to have an unstable or non-passivating SEI. The reviewer said it is also excellent to see the correspondence between SEI dissolution and cycling stability as shown on Slide 17 The idea of letting the SEI dissolve to improve cyclability is fascinating but appears very impractical in any real cell due to the time frames involved.

**Reviewer 3**

The reviewer said the major technical advancements include the proposal of SEI dissolution and the elucidation of the SEI propagation mechanism. The concept of potential capacity recovery is novel. These discoveries can significantly contribute to the development of long-cycle Li anodes.

**Reviewer 4**

Regarding Technical Accomplishment 1, the reviewer believed the team plated Li and used cryo SEM to measure the cross section and then looked at the deposited Li a day later and the deposited Li was thinner and the SEI was thicker. Regarding Technical Accomplishment 2, the team used a quartz crystal microbalance and held a piece of copper foil on the balance at a potential low enough to deposit an SEI but not low enough to deposit Li-metal. The potential was then allowed to float, the SEI dissolved and there was a decrease in weight as measured by the electrochemical quartz crystal microbalance. The time constant for dissolution was around 15 minutes. Regarding Technical Accomplishment 3, the reviewer remarked if you use a LHCE, the majority of components in the SEI are inorganic and this SEI is more stable and does not dissolve as badly as the SEI's formed from other electrolytes. Regarding Technical Accomplishment 4, if you perform plating and stripping in a Li|copper (Cu) cell and go to open circuit when the Cu is bare instead of when the Cu has Li on it, you have a better coulombic efficiency (i.e., you lose less Li from the copper if the Li is not there to begin with.) Regarding Technical Accomplishment 5, if you let the residual SEI dissolve away from the Cu surface, you are better able to access the isolated Li that forms near the Cu during plating and stripping. Regarding Technical Accomplishment 6, the reviewer noted that during discharge, isolated Li will grow on the end that is closest to the anode. The speaker focused on the effect of electrolytes on Li cycling efficiency and the mechanism for formation of isolated Li and how one might reconnect it. It appears that some electrolytes dissolve and result in low coulombic efficiency and others dissolve less and result in higher coulombic efficiency. The reviewer was curious, which electrolyte is better for reconnecting isolated Li, an electrolyte that dissolves easily or the opposite?

The reviewer said these accomplishments point to a better understanding of Li deposition and SEI formation and dissolution, but the reviewer did not see a solution to these problems emerging. We have known about mossy Li for some time now and the co-deposition of Li and SEI during plating. No one has figured out how to stop that phenomena without using hosts.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer remarked excellent collaboration with many other institutions and saw no issues.

**Reviewer 2**

The reviewer said Battery500 has demonstrated a highly creative and successful collaboration among a diverse group of PIs and institutions.

**Reviewer 3**

The reviewer said this project is a key component of the Battery500 team effort, showcasing major collaboration within Stanford/SLAC and extending to many top institutions within the Battery500 network. The collaborative nature of this initiative has facilitated the pooling of diverse expertise and resources, leading to groundbreaking advancements. The project's integration of innovative electrochemical experiments with a strong, productive team has significantly addressed critical barriers in Li-metal and electrolyte reactions, driving substantial progress in battery technology.

**Reviewer 4**

The reviewer said there is a lot of collaboration but that it appears that the team is out of ideas. The team is trying stuff and looking at it to see what happens, and the result is usually the same.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer remarked excellent future research plans based on stabilizing the Li SEI.

**Reviewer 2**

The reviewer said the proposed future research is commendable, with a clear focus on understanding and designing host materials for Li-metal anodes, investigating SEI dynamics across different stages of charge/discharge, and developing innovative solvent molecules and polymer coatings. The commitment to collaboration with other groups will undoubtedly accelerate advancements and deepen understanding in these critical areas.

**Reviewer 3**

The reviewer remarked the proposed research aligns well with the overall goals, though the PI should provide details for the future work.

**Reviewer 4**

The reviewer said proposed future research is to continue to go back to looking at hosts for Li. The reviewer pointed out graphite and silicon are hosts for Li. If the team does this, they will essentially be making a Li-ion battery and lose the energy density benefit of going to pure Li deposition, which is the purpose of the program. The team wants to continue to study the dynamics of SEI formation and dissolution. The reviewer commented that the team will continue to try new solvent molecules and polymers and increase their collaboration; however, none of this really bodes well toward ultimate success.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer said the project is highly relevant. Li-metal is the core issue with Battery500 cells using NCM cathodes.

**Reviewer 2**

The reviewer said enabling Li-metal as an anode for rechargeable batteries is a critical focus for achieving high energy density. This advancement is essential for enhancing battery performance, offering significantly higher capacity and efficiency compared to traditional anodes.

**Reviewer 3**

The reviewer remarked the research toward the high-performing metallic Li anode is very relevant to the overall VTO objectives and Battery500 goals.

**Reviewer 4**

My comments are fairly pessimistic. This is not to reflect on the capabilities of the researchers, who are trying everything they can with liquid electrolytes and not much is working, but that has been true with all of the researchers that preceded them. This is still a very hard problem.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer said good use of appropriate resources.

**Reviewer 2**

The reviewer remarked the PI's institution and his collaboration institutions have more than sufficient resource for the proposed research.

**Reviewer 3**

The reviewer said the overall resources for the Battery500 program appear sufficient, supporting its ambitious goals. However, it is noted that the actual budget allocation for the Stanford/SLAC team has not been reported in the presentation. The team should consider including this information for reviewers, ensuring that all sub-teams have adequate funding to meet their objectives.

**Reviewer 4**

The reviewer did not see a lot of new ideas that suggest the researchers need more resources to investigate those ideas.

**Presentation Number:** BAT362
**Presentation Title:** High Capacity S Cathode Materials
**Principal Investigator:** Prashant Kumta, University of Pittsburgh

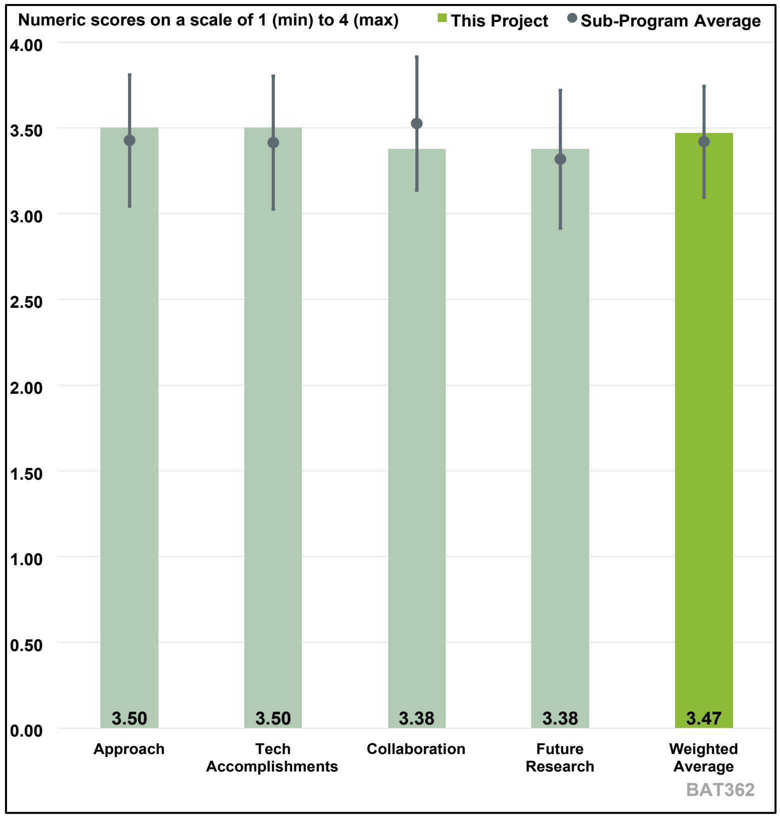


Figure 1-8. Presentation Number: BAT362
Presentation Title: High Capacity S Cathode Materials
Principal Investigator: Prashant Kumta, University of Pittsburgh

***Presenter***

Prashant Kumta, University of Pittsburgh

***Reviewer Sample Size***

A total of four reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 75% of reviewers felt that the resources were sufficient, 25% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer said the project approaches to addressing technical barriers in next-generation Li-S battery technology are both innovative and commendable. By focusing on fundamental breakthroughs in controlling S electrochemical reactions, the development of the functional electrocatalysts as well as the spun polyacrylonitrile (PAN) fiber approach set a solid foundation for substantial advancements. The integration of materials and cell-level discoveries is particularly noteworthy, as it ensures rapid incorporation and validation of the latest research findings, leading to more realistic and practical applications. The reviewer said leveraging materials from other DOE programs and utilizing state-of-the-art DOE facilities, and industry collaborations to understand and prevent S electrode degradation is a strategic and efficient use of resources. The emphasis on multi-disciplinary approaches and enhancing collaborations between national laboratories, universities, and industry highlights a holistic and synergistic strategy. The reviewer said this comprehensive and well-coordinated effort is likely to yield highly productive results, driving significant progress in the development of high-energy, low-cost Li-metal based batteries. Overall, the approach is excellently designed and executed, promising to overcome technical barriers for S electrodes effectively.

**Reviewer 2**

The reviewer said excellent approach to addressing an extremely difficult problem, enabling high-energy S cathodes. Technical milestones are quantitative and excellent. The use of theory to guide experimental investigations into polysulfide trapping agents and catalysts to enable the conversion of $Li_2S_2$ to $Li_2S$ is excellent.

**Reviewer 3**

The reviewer remarked the host design and incorporation of advanced catalysts have shown as good approaches to suppress shuttle effect and improve S utilization. This project focused on processing of integration of catalysts and host to achieve better S cathode performance. However, the demonstrated S utilization is less than 1,000 mAh/g (400-500 mAh/g in most cases) even with a higher electrolyte-to-sulfur (E/S) ratio of 8. The reviewer was not expecting a possibility of 500 Wh/kg (project goal) by using this cathode. The reviewer recommended the PI explore other catalysts or a combination of multiple catalysts.

**Reviewer 4**

The reviewer detailed that to realize long lifetime Li-S batteries, the team addressed two technical barriers: Identify functional electrocatalyst (FEC) using theoretical calculations, and synthesize FEC and integrate it into the S cathode. The project is well designed and the timing is well planned, but the reviewer expressed concerns. The content of FEC in the cathode is more than 5%, which could decrease the energy density a lot; the porosity of cathode is 50%, which could also decrease the volumetric energy density.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer remarked the team developed a series of electrocatalysts to control S to $Li_2S$ transformation. This is a crucial area, and the team made excellent progress this period. The spun PAN fiber approach to confine S and provide a two-dimensional effect are also innovative accomplishment, achieving high capacity and stable cycle life for S electrodes effectively.

**Reviewer 2**

The reviewer said making any progress in S cathodes is extraordinarily difficult. The down-select of several possibly electrocatalysts to one or two that perform best, for further testing, is promising. The improvements in cycling compared to the baseline carbon/sulfur composite (C/S) cathode shown in Slides 14 and 15 is impressive and promising. The reviewer noted it is impressive that Prof. Kumta shows both improvements and lack of improvements with the different functional electrocatalyst carbon framework materials. The reviewer believed industry has already demonstrated the ability to grow/incorporate carbon nanotubes in electrodes and on current collectors. This portion of the work is not bad, but hopefully is not a major effort.

**Reviewer 3**

The reviewer remarked the technical progress is well aligned with the project plan. The team demonstrated the use of FEC can improve the cell performance.

**Reviewer 4**

The reviewer commented the project should look for approaches to significantly improve S utilization at high S loading and lean electrolytes.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer remarked this project is part of Battery500 team effort. The project team has made great efforts to collaborate within the Battery500 team and beyond, as demonstrated by their partnerships with Brookhaven National Laboratory, Malvern Panalytical, PNNL, and GM. These collaborations have significantly advanced the understanding and development of innovative battery technologies, showcasing the team's commitment to leveraging collective expertise and resources.

**Reviewer 2**

The reviewer said excellent collaboration with others on the Battery500 team.

**Reviewer 3**

The reviewer noted the team had collaborations with national laboratories (e.g., PNNL, BNL) and industries (e.g., GM), which further extended the impact of this work.

**Reviewer 4**

The reviewer noted the project is part of the Battery500 consortium, including multiple teams. However, the reviewer did not see the supporting characterization results to understand the reason for low S utilization. The reviewer recommended the PI work with other team members to understand and improve S utilization at the next AMR.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer said very good list of future research, attempting to address a lot of issues though. Just want to make sure the team has enough resources to deal with optimizing carbon framework material (CFM) structures, generating polysulfide trapping agents, stabilizing agents on Li-metal, etc.

**Reviewer 2**

The reviewer said future work focuses on optimizing CFM structures with FEC and lithium-ion conductors, identifying stabilizing agents for the anode, developing low-temperature electrocatalysts, and enhancing cathode composites. Additionally, it aims to incorporate FECs in cathode architectures and optimize binder-free systems for higher capacity, cyclability, and stability in sulfur-based batteries. The reviewer said these are all critical areas need to be address.

**Reviewer 3**

The reviewer suggested focusing on understanding the effect of FEC on cell energy density and how to optimize the FEC content in the future work.

**Reviewer 4**

The reviewer said more understanding on the characterization of the cathode structure and their evolution during charge/discharge should be implemented.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer said it is excellent that so many of the challenges are presented with quantitative metrics, this is an excellent way to ensure that the future research is relevant and impactful.

**Reviewer 2**

The reviewer remarked the project is developing an advanced high-capacity and Earth-abundant S cathode to enable Li-metal batteries beyond what can be achieved in today's Li-ion batteries.

**Reviewer 3**

The reviewer said mediating S material transformation and controlling S dissolution in the electrolyte are crucial research areas. This work effectively addresses these critical issues, providing significant advancements in enhancing battery performance. By tackling these challenges, the research paves the way for more stable and efficient S-based battery technologies.

**Reviewer 4**

The reviewer said the proposed work well supports the Batteries program in VTO by developing long lifetime Li-S batteries.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer said good use of resources.

**Reviewer 2**

The reviewer said overall resources for the Battery500 program appear sufficient, supporting its ambitious goals.

**Reviewer 3**

The reviewer commented sufficient resources are available for the team to achieve their proposed tasks.

**Reviewer 4**

The noted remarked weakness in the characterization of the proposed concept at the material and device level.

**Presentation Number:** BAT364
**Presentation Title:** Synergistic Effects of Electrode and Electrolyte Materials for High Energy Lithium Cells
**Principal Investigator:** Jihui Yang, University of Washington

***Presenter***

Jihui Yang, University of Washington

***Reviewer Sample Size***

A total of four reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

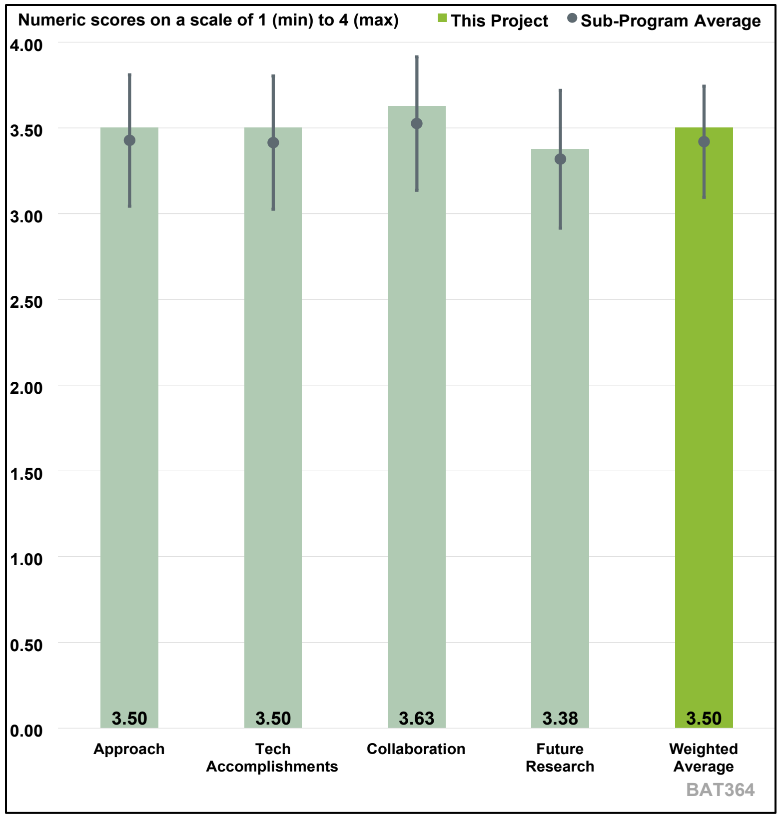


Figure 1-9. Presentation Number: BAT364
Presentation Title: Synergistic Effects of Electrode and Electrolyte Materials for High Energy Lithium Cells
Principal Investigator: Jihui Yang, University of Washington

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer said this project is considering failure modes involved in realistic cells, which have high cathode loading and lean electrolyte. Understanding the function under such conditions is essential to developing practical solutions, which will be relevant to making future high-energy, low-cost batteries. The reviewer said this is an approach less commonly used in the field and is important to the community. It is important to integrate capabilities across different disciplines, which take advantage of complementary strengths within the national laboratory system, universities, and industry. It is valuable that various materials science, chemistry and cell engineering approaches are being deployed within the study.

**Reviewer 2**

The reviewer remarked the team's evaluation of critical current density for thick cathode electrodes and the assessment of the ability of such cathodes to operate with reasonable current rates was well conceived and the approach is valid. The team approach to look at the literature for direction and behavior of thick electrodes is useful, and compare their calculations is an important aspect. The reviewer noted the LATP coating approach on the separator is novel.

**Reviewer 3**

The reviewer commented based on the team's report, they have addressed two technical barriers: determined the relationship between cathode thickness and rate; and used an LATP-coated separator to prevent dendrite formation by homogenizing the Li morphology. The project is well-designed, and the timing is well planned. The reviewer suggested understanding the effect of temperature and cathode chemistry (e.g., Co-free cathode) on the thickness rate dependency in the future work.

**Reviewer 4**

The reviewer said there are two sections to this work. The first is determination of cathode thickness rate dependence. The approach empirically determines the critical thickness to achieve C/3 rates for a series of porosities. The work was well designed for this purpose. The second section designed a functional coating on the separators. The reviewer said using LATP as the functional coating indicates improved Li-metal pulverization; however, the direct reaction with Li-ion (which is expected) was not discussed in depth. In particular, any changes to the Li-metal impedance are not presented.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer noted that progress since last year is good. Direct electrochemical/electrical performance (i.e., impedance rise) of Li-metal anodes in contact with LATP to be completed to demonstrate long cycle life of up to 1,000 deep charge-discharge cycles.

**Reviewer 2**

The reviewer said technical accomplishment in understanding the critical cathode thickness rate dependence is notable. While this has been described previously theoretically as highlighted by the presenter, having a practical study which involves NMC electrodes calendared to different porosity is valuable. The reviewer said it is important to recognize that depending on the material and the electrode characteristics, transport can be limited at different length scales. It would be useful to link the information at the mesoscale electrode level to information at the atomic and particle level in future investigations, i.e., incorporating NMC type (single crystal, polycrystal) and associated particle morphology into the study to determine the effect on critical C-rate. The reviewer said it would be interesting to understand if greater than 250 µm thick without experiencing an electrolyte diffusion limit at C/3 is a universal or a specific limit.

The reviewer said the microscopy evidence of reduced Li pulverization and mitigation of pit formation is clear and impressive, as are the electrochemical cycling results. The plans not to pursue the three dimensional (3D) electrode architecture and to use impedance measurements to better understand the liquid electrolyte/LATP solid state electrolyte interfacial properties are appropriate.

**Reviewer 3**

The reviewer said technical progress well aligned with the project plan. The team completed the first phase study of thickness effects of cathode on charge transport by 03/31/2024.

**Reviewer 4**

The reviewer said the team measured the current rate at C/3 for various cathode thickness of NMC and showed that there is no electrolyte diffusion limitations that could hinder their operation at this rate. The authors did not specify what NMC chemistry was used; the electrical conductivity of the material could make a difference. The reviewer said Slide 7 is noted as Technical Accomplishments but in actuality, this is simply data taken from the literature. As for the LATP coated polypropylene, the team provided SEM of the Li-metal and it is clear that the Li deposits more evenly. The number of cycles is only one, and the reviewer said the team should have done more cycles to look at the Li morphology. Also, the impedance of the LATP coated separator was not measured. Certainly, this could make a big difference in the practicality of the approach. However, the team's full body of work is not sufficient and all-encompassing.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer said that as part of Battery500, this work is in close collaboration with PNNL researchers. The reviewer noted future work to scale to 5-10 Ah pouch cells will require additional collaborations.

**Reviewer 2**

The reviewer said impressive collaboration across the members of Battery500 is noted, and this work is no exception. Highly successful coordination was completed.

**Reviewer 3**

In this project, the University of Washington is collaborating with Stanford/SLAC and the University of Maryland to analyze the mechanisms of coated separator. The reviewer was not sure if any battery separator industry is involved in this project. If not, it might be helpful to involve one (e.g., Celgard).

**Reviewer 4**

The reviewer was well aware of the very interactive collaboration and exciting work happening across the Battery500 consortium. However, this specific presentation, while emphasizing important recent results at PNNL and the University of Wash, did not showcase the collaboration and coordination across the project. In future presentations it would be valuable for the coordination across the project team to be highlighted in more detail.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer said future plans to implement the nano-coated separator in coin-cell and pouch cells applications aligns with the program targets. Future work should be considered to identify and characterize the impedance increase due to the expected reaction products between LATP and Li-ion metal. The reviewer said a comparison of LATP versus another coating material based on this analysis is important before scale up and cell builds.

**Reviewer 2**

The reviewer noted that further understanding the reaction-diffusion dynamics in thick cathodes is a useful goal. Additional specific suggestions relevant to future studies are noted above. The long-term stability of a PE separator with a nano coating in Li-metal batteries merits further investigation. Comparisons employing symmetric and full cells should yield useful information.

**Reviewer 3**

The reviewer said proposed future work is plausible and good. More work is needed, however, on the understanding of LATP functionality, just like what was presented in previous AMR reports.

**Reviewer 4**

The reviewer commented the team clearly defined the purpose for future work, which is to achieve Li-metal batteries with long lifetime and high energy density. In the near future, the team proposes to understand the separator coating mechanisms and integrate the functional separator in their battery demonstration. This will increase their successful rate.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer said yes, this work aligns and supports the goals of the Battery500 consortium.

**Reviewer 2**

The reviewer said this program is highly relevant to EERE VTO subprogram objectives, toward developing next-generation high-energy, low-cost batteries for EVs.

**Reviewer 3**

The reviewer remarked this project is very relevant and important to the Battery500 objectives of using Li-metal and thick high-Ni cathodes.

**Reviewer 4**

The reviewer commented the proposed work well supports the Batteries program in VTO. The proposed Li battery will have long lifetime, and high energy density, which fulfills the objectives of reducing volume, and weight of batteries, while simultaneously improving the vehicle batteries' performance (power, energy, and durability). It is worth considering the safety performance of Li-metal batteries because one of the VTO's objective is to increase the ability to tolerate abuse conditions.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer said resources for this project are sufficient.

**Reviewer 2**

The reviewer remarked the current project resources are sufficient and appropriate.

**Reviewer 3**

The reviewer said sufficient resources are available for the team to achieve their proposed tasks.

**Reviewer 4**

The reviewer said more impedance (for example analysis with electrochemical impedance spectroscopy [EIS]) is needed in this work. Perhaps the team needs additional electrochemical instrumentation to fully measure the LATP properties and the impedance associated with thicker cathodes.

**Presentation Number:** BAT365
**Presentation Title:** Stabilizing Lithium Metal Anodes by Interfacial Layer and New Electrolytes
**Principal Investigator:** Zhenan Bao, SLAC National Accelerator Laboratory

***Presenter***

Zhenan Bao, Stanford University / SLAC National Accelerator Laboratory

***Reviewer Sample Size***

A total of five reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

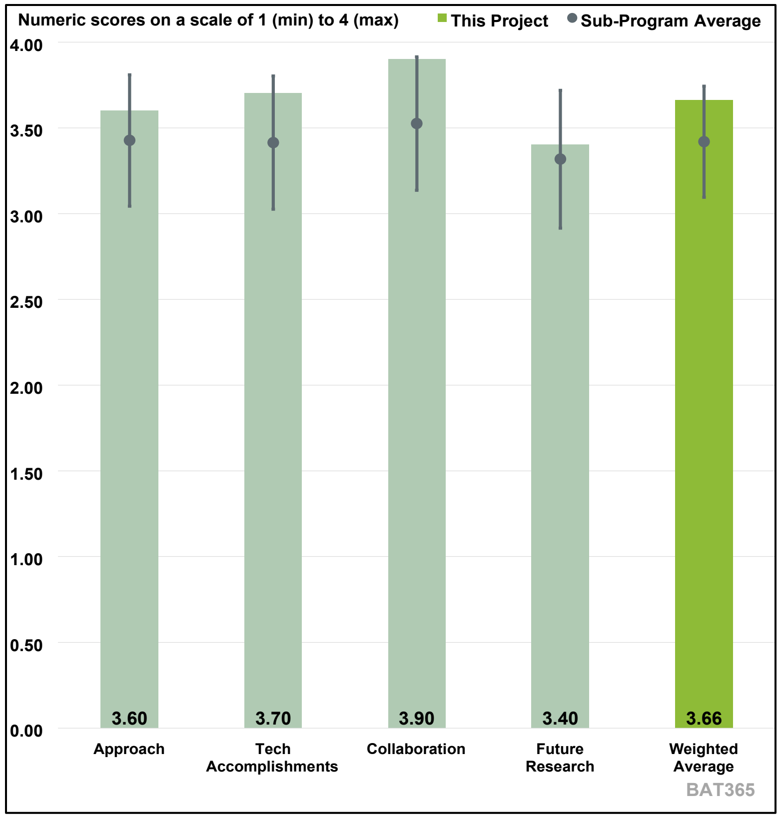


Figure 1-10. Presentation Number: BAT365 Presentation Title: Stabilizing Lithium Metal Anodes by Interfacial Layer and New Electrolytes Principal Investigator: Zhenan Bao, SLAC National Accelerator Laboratory

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer said the proposal is geared toward discovering electrolytes and interfacial layers for stabilizing 500 Wh/kg rechargeable batteries. The team has settled on Li-S and Li-NMC (high Ni content). The team is expansive covering 14 institutions, and the PIs are world leaders. The reviewer said the project is well-designed, and the approach is rigorous and noteworthy.

**Reviewer 2**

The reviewer remarked the approach by Dr. Bao is excellent as always. Improved electrolytes and stable interlayers are critical to enabling Li-metal anodes. The reviewer encouraged this team to consider adopting quantitative milestones to demonstrate progress towards improving either Wh/kg, cycle or calendar life. The existing milestones are good but are all qualitative.

**Reviewer 3**

The reviewer said there is a clear approach to drive fundamental breakthroughs in controlling the electrochemical reactions in high-energy electrode materials and cells for next generation high-energy, low-cost batteries. Incorporating both high CE electrolytes and novel coatings into the study provides two complementary pathways from which to address the challenges.

**Reviewer 4**

The reviewer said Dr. Bao's overarching goal is to design electrolytes and Li-metal coatings for high coulombic efficiencies in Li-metal cycling. In so doing she systematically explored how fluorination of ethers affects the SEI composition on Li. This is a really well thought out study that involved changing the number of fluorine on various carbons within the ether as well as looking at the effect of solvent purification (impurities). She found that the use of such solvents will require proper purification in the scale up stage, which may add cost in the short term before economies at scale catches up. The reviewer said the shift to full pouch cells by working with University of Texas-Austin was good to see pushing the technology further.

**Reviewer 5**

The reviewer commented the presenter listed the general approaches to control the electrochemical reactions in high energy electrode, and to scale up the discovered materials with resources within the DOE programs and industry. They are all encouraging but too general. The critical issues such as the compatibility between the designed electrolyte and high-Ni NMC/S cathode, the problem of cell thickness variation during cycling, material utilization of high loading electrode and the fading mode under lean electrolyte in lithium metal batteries (LMB) were not specified and were not addressed in this annual review. The reviewer said maybe it is more appropriate to state that the project is to limit the dendritic growth of Li-metal anode and achieve high CE cycling with rationale electrolyte and anode coating design.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer said technical progress is excellent. The reviewer appreciated the attention to the relationship between molecular structure, solvation, and electrochemical stability (Slides 8-10, 17). The reviewer thought the inclusion of acetals is interesting. The conductivity of F2DEM is very interesting. The collaboration between Stanford, where solvents are being designed, and ANL where, the solvents are being scaled up, is impressive.

The reviewer also appreciates the attention to purity. Very often, small levels of contaminants can dominate side reactions in electrochemical systems and ensuring that the data reflect the designed molecule is important. Stability of solvent F5DEE to NMC622 is noteworthy. The use of molecular simulations to elucidate degradation mechanisms is complementary to the experimental program. The reviewer also appreciates the honest reporting of instability against the target-NMC811 for high energy. However, it is only with this kind of discrimination that we can hope to achieve the high goal of 500 Wh/kg. Moving on to the design of layers, it is interesting to see that creep (not modulus) has been identified as the important metric for cycling stability (Slide 14). It seems to be consistent with emerging literature. The new material being patented (Slide 20) is innovative and interesting, and the cycling performance of FDMB is very impressive.

**Reviewer 2**

The reviewer pointed out that the importance of electrolyte purity is a critical item to be understood by the entire program. It seems likely that critical impurity levels will vary depending on the specific electrolyte being used, but a minimum purity level for all to adhere to might be a good idea. Cycle data in Slides 12&13 is impressive and encouraging. Would be nice to see cycling data with varying levels of impurity in the electrolytes, but perhaps that is down elsewhere. The reviewer said it is also very promising to see some of these materials tested in cells at PNNL, and noted a very impressive diagnosis of SEI evolution during cycling shown on Slide 15.

**Reviewer 3**

The reviewer said a rational design of weakly solvating electrolyte solvents has shown significant progress through the project. Understanding the steric and electronic effects and the role of solvation in the system is valuable for the community. For the most promising electrolytes, it would be useful to have more information about the conductivity impacts on use of the electrolytes under different use cases (i.e., different rate cycling). Often there is a tradeoff between stability and transport, and it would be useful to understand this in greater detail based on the findings of the team.

**Reviewer 4**

The reviewer remarked the publication record proves the technical progress of this project. The work has brought good understanding of how fluoro-ethers coordinate to Li ions and the team has looked at Li-metal cycling, Li plating, and explored the use of the electrolytes in various full cells with differing cathode materials. The reviewer appreciated the logic of keeping the system binary, one salt with one solvent. This will add in understanding more complex electrolyte formulations.

**Reviewer 5**

The reviewer commented the deliverables partly align with the project plan. The mechanistic properties and the evolution of the SEI was studied in SLAC and BNL, acetal-based solvent was designed to further stabilize the LMB, validation of the electrolyte was done by PNNL and other universities, new study on Li-metal coating was published on Nature Energy. However, it does not seem to have any deliverables related to "understand the good fluorinated electrolytes developed recently."

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer said there are clear handoffs between different team members. Electrolytes designed and synthesized on a small scale are being purified at ANL. Electrochemical stability of the same compounds is being studied in full cells at Binghamton and Idaho National Laboratory (INL), and examined theoretically at Texas A&M.

**Reviewer 2**

The reviewer noted very strong collaboration.

**Reviewer 3**

The reviewer said the project shows engagement across the program taking advantage of complementary expertise in theory, experiment, and characterization within the national laboratories and university partners. The presentation effectively highlighted roles of the teaming partners and their valuable contributions to the program.

**Reviewer 4**

The reviewer said that the PI's group is very much integrated with the Battery500 team, as well as outside.

**Reviewer 5**

The reviewer remarked there are active collaborations within and outside of the project team, and it serves as a good example of how the synergy from the Battery500 team accelerates and deepens understanding of new electrolyte systems. It will be even better to develop capabilities to predict the physiochemical properties of the fluorinated ethers with potentially different structures in the future.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer commented proposed future work follows directly from the accomplishments described and is consistent with the milestones. It follows logically from prior work and is aimed at meeting overall programmatic needs.

**Reviewer 2**

The reviewer said excellent proposed future work is focused on further understanding the Li-metal SEI and its evolution during cycling with different electrolytes and current densities.

**Reviewer 3**

The reviewer said the proposed research is good, and takes the necessary next steps. However, the reviewer suggested that increased stress tests and advanced cycling protocols be incorporated to facilitate low Co cathode degradation (or to show electrolyte’s ability to stabilize).

**Reviewer 4**

The reviewer remarked while the key targets of this project are to develop electrolyte and Li-metal coating to enable high CE cycling of Li-metal anode, it is necessary to consider the compatibility of the new solvent with other components in the cell, their physical properties (vapor pressure, boiling point, density) and the ion transport kinetics at industry relevant conditions to understand the limits of the design and truly enable high-energy Li-metal batteries.

**Reviewer 5**

The reviewer said results reported were very impressive for understanding fundamentals and moderate cycle life behavior (200-500 cycles). The proposed future research emphasizes continuing to elucidate fundamental SEI properties. However, the reviewer encouraged the team to provide more specific plans toward the objective of achieving long cycle life of up to 1,000 deep charge-discharge cycles. Understanding the onset of electrolyte breakdown in terms of cycling condition (depth of (dis)charge, and cycle life) would be valuable for the community. The reviewer asked is there an inherent advantage to the liquid electrolyte approach or the novel coatings approach, or are specific chemistries more beneficial in this regard?

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer pointed out one of the objectives of the VTO program is to enable high specific energy rechargeable batteries and enabling Li-metal is the key to meeting this objective. The work of the team is clearly aimed at this goal.

**Reviewer 2**

The reviewer said understanding and improving Li-metal stability during cycling is critical to enabling Battery500’s success.

**Reviewer 3**

The reviewer said this is a relevant project which supports VTO subprogram objectives.

**Reviewer 4**

The reviewer said this work supports the development of next-generation batteries for vehicular transportation. One of the benefits of this project is the understanding gained in how the SEI forms on Li-metal and evolves from the initial cycle to 100s of cycles. This is important to follow to understand and track the health of Li-metal batteries which is much more than just capacity retention. Li dendrites are still an issue and, for liquid electrolytes, the SEI is the only preventor of this.

**Reviewer 5**

The reviewer commented the project is highly related to the Battery500 target of achieving battery energy density of greater than 500 Wh/kg with the Li-metal battery.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer said that all the institutions have sufficient resources to meet milestones in a timely fashion.

**Reviewer 2**

The reviewer said good use of resources.

**Reviewer 3**

The reviewer remarked project resources are sufficient.

**Reviewer 4**

The reviewer had no information on the funding of this subproject, but the PI clearly has the support she needs to contribute significant understanding to the Battery500 project.

**Reviewer 5**

The reviewer said resources are sufficient to achieve the stated goals.

**Presentation Number:** BAT366
**Presentation Title:** Manufacturing and Validation of Lithium Pouch Cells
**Principal Investigator:** Mei Cai, General Motors

***Presenter***

Mei Cai, General Motors

***Reviewer Sample Size***

A total of four reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

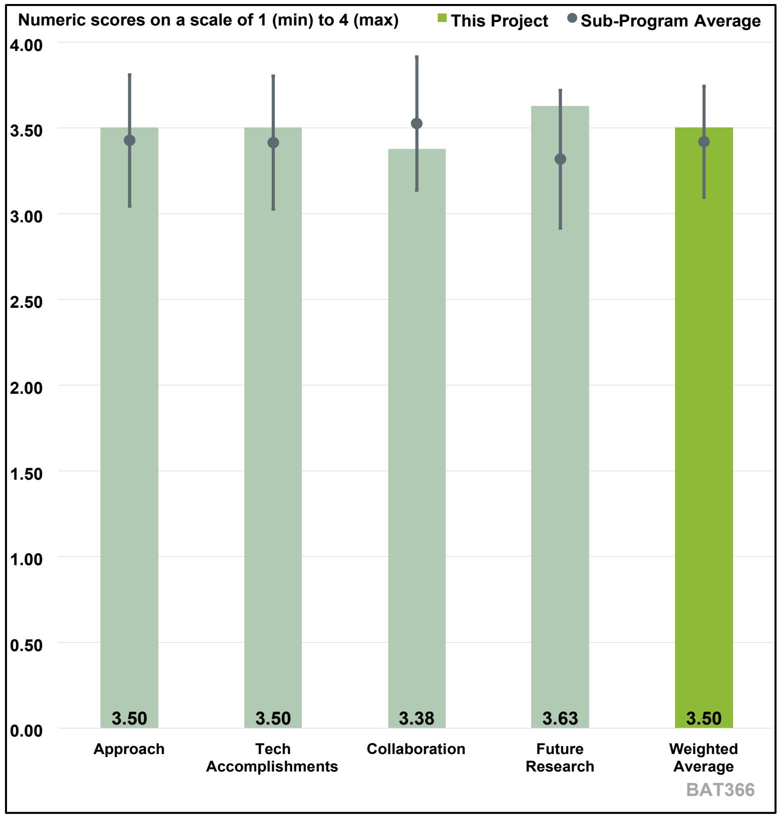


Figure 1-11. Presentation Number: BAT366 Presentation Title: Manufacturing and Validation of Lithium Pouch Cells Principal Investigator: Mei Cai, General Motors

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer said the project's goal is to couple a Li-metal anode with a high-Ni-NMC or S cathode to "achieve a specific energy of up to 500 Wh/kg through cell level design and optimization of materials and architectures." The approach includes "integrating development and discoveries from materials to cell level" and leveraging "state-of-the-art DOE facilities to understand and prevent degradation." In this project presentation, GM has been assigned the task of C/S composite electrode fabrication and Li-S pouch cell development. Multiple C/S active materials, electron conduction additives, binders, and current collectors are being evaluated to optimize electrode fabrication. The reviewer said initial electrochemical tests were conducted with various electrode formulations and reasons for cell performance loss examined with techniques that include ultrasonic testing. In general, the project design and timelines appear to be reasonable, and the appropriate technical barriers are being addressed.

**Reviewer 2**

The reviewer said Dr. Cai's team conducted some optimization baseline measurements to evaluate Li-S and Li- Sulfurized polyacrylonitrile (SPAN) cells. They also developed ultrasonic imaging to correlate cell failure (capacity loss) with electrolyte depletion. The team used a material design sheet to predict the energy density. The team's characterization is focused on understanding why actual cells miss the energy density predictions in pouch cells.

**Reviewer 3**

The reviewer said the project is well designed and focused on resolving the issues currently present in Li-S technology.

**Reviewer 4**

The reviewer remarked the approach as presented in the approach section is fairly generic and does not really get at the unique capabilities that will be applied to this problem. The team indicated that their job is to confirm that the S cells will be manufacturable. This is great.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer noted the presentation includes a summary of electrode optimization tests. Some cathode binders are more suitable than others. For example, carboxymethyl cellulose (CMC)-only binder yields brittle coatings, whereas CMC-styrene butadiene rubber (SBR) improves initial mechanical properties, but the SBR oxidizes and degrades during cycling. Polyacrylic acid (PAA-) type binders have been selected for "fine formulation tuning." Pouch cells containing elemental S cathode (1Ah) and SPAN cathode (1.4 Ah) have been assembled and are being tested. The reviewer said cell parameters (including cathode capacity, electrolyte content, etc.) are first determined to achieve the target energy density. Initial tests conducted on the pouch cells appear promising and the technical progress appears to be in line with project plan.

**Reviewer 2**

The reviewer said the team has systematically down-selected cathode and binder components using coin cells and processability in roll-2-roll methods. The team correlated nonuniform Li plating with gas generation from electrolyte decomposition. The ultrasonic imaging effective in understanding gas distribution after cycling.

**Reviewer 3**

The reviewer said the project has made good technical progress and 1 Ah pouch cells have been designed and fabricated that meet goal of 300 Wh/kg.

**Reviewer 4**

The reviewer detailed technical accomplishments. Technical Accomplishment 1) The team performed a complete design of experiment of 3 carbon additives and 4 binders and found that a blend of MWCNT and PAA with or without Li performed the best. Technical Accomplishment 2) The team performed a root cause and tear down analysis of the pouch cell of the cell with CMC binder and found gassing, that the binder was brittle, non-uniform plating, and a change in color of the separator. This cell performed the worst of the four with a blend of MWCNTs. Technical Accomplishment 3) Gas analysis of CMC-SBR cell showed methane and other hydrocarbons. This cell lost half of its capacity in the first 5 cycles and then maintained capacity for the next 20. Technical Accomplishment 4) A cyclic voltammetry was performed on SBR. It appears it is not stable above 2.5V vs Li/Li+. The team believes vulcanization occurs in the presence of S and conclude they cannot use CMC or CMC/SBR. Technical Accomplishment 5) The team measured the rheological properties of the slurries with different binders and the adhesion and found that the Li-PAA has almost no adhesion. PAA-co polymer had the best adhesion. Technical Accomplishment 6)

Using a spreadsheet the team designed 4 batteries of energy densities of 500, 400, 350, and 300 Wh/kg by varying the electrolyte content, porosity and cathode loading. The specific capacity used in designing batteries of a given energy density is much higher that the practical capacity achieved in actual cells. Technical Accomplishment 7) Increased charge voltage results in improved capacity but significant gassing—pressure increased from 10 psi to 47 psi. Technical Accomplishment 8) Evaluated SPAN in coin cells and pouch cells. The coin cell performance is good. Delivers just under 700 mAh/g for 200 cycles. Pouch cells just started. Technical Accomplishment 9) Still developing a technique for using ultrasonic mapping to map concentration of electrolyte in a pouch cell.

In general, the team is trying to establish a reasonable baseline pouch cell by screening binders and additives. One concern the reviewer expressed is that the cells' CE appears to worsen with cycles and finishes near 80% after around 100 cycles. Seems like the team needs to address the crossover problem. The team is using 2x Li in their cells, so it is mostly an evaluation of the cyclability of the cathodes with different in actives. There have been reports that the excess Li needs to be about 50% to meet energy density goals. The reviewer would like to see more about manufacturing and if the PIs have a plan for removing the non-uniform utilization of the battery.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer said the GM team appears to be well connected to the rest of the Batt500 team.

**Reviewer 2**

The reviewer said the GM team appears to be collaborating with the PNNL team and INL team for the cell engineering development. It is not clear from the presentation where the characterization work (SEM, infrared, XPS) was conducted; it appears to have been conducted at GM. Collaborating with the other team partners for electrode and cell characterization may help accelerate cell development.

**Reviewer 3**

The reviewer noted GM is working with INL testing cells and thinks more correspondence with PNNL and other Battery500 partners on the material design landscape would be benefitable. A lot of work is happening in Battery500 and the imaging tool and pouch cell processing developed here should be used throughout.

**Reviewer 4**

The reviewer said it appears that GM is out on their own testing binders and carbons in their pouch cells as they work on electrode and cell optimization. The reviewer noted the team received SPAN from INL.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer noted proposed next steps include "further optimization of electrode formulation," "processing and integration of optimized components from [Battery500] teams" and testing cell designs which yield more than 300 Wh/kg energy density. In addition, it would be good to understand the effect of other temperatures (both lower and higher than room temperature) on cell cycle and calendar aging.

**Reviewer 2**

The reviewer commented future plans are to continue optimization and to integrate with Battery500 teams' optimized components. The reviewer would like to see the expansion of the ultrasonic mapping to other Battery500 systems.

**Reviewer 3**

The reviewer said the proposed future research focused on further improving energy density and using non-destructive ultrasound to monitor electrolyte consumption/gassing seem like a good plan.

**Reviewer 4**

The reviewer noted the team's next step is they plan to keep doing what they have been doing which is trying different materials until they come across something that works better than previously tried materials. The big problem this reviewer has is the summary does not really relay that the team fully understands why what they have been trying is not working. The reviewer would like to see more work on understanding the nonuniformity that grows in the cells and maybe achieve some basic understanding of this problem.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer said the project is very relevant to VTO's goal of improving energy density and removing dependency on critical materials.

**Reviewer 2**

The reviewer said the PI's team is focused on Li-S system for the high energy density applications for VTO. The development of non-destructive pouch cell level characterization methods is important for quality control and assurance. The reviewer noted work like this is sometimes neglected in favor of route optimization and new materials, which are important, but consumer safety and commercial reliability/predictability are key in economic advancement.

**Reviewer 3**

The reviewer guessed that the end game here is a full, pouch cell that meets a specific energy target and achieves 1000 cycles. Since GM has large cell build capability, the reviewer assumed they will play a large role in meeting this target, so their effort is very relevant.

**Reviewer 4**

The reviewer affirmed yes, the project supports overall VTO subprogram objectives. That said, for commercial viability, cell performance at various temperatures needs to be determined. Furthermore, safety tests (overcharge, overdischarge, etc.) needs to be conducted on these Li anode cells.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer said funding support seems reasonable for this work, the team is hitting their milestones.

**Reviewer 2**

The reviewer said total resources available for the overall project are sufficient. It is not known whether the resources available for this particular project are sufficient, as no information is provided.

**Reviewer 3**

The reviewer noted the Battery500 team goals are very ambitious, and the high budget is in line with what is needed to meet those goals.

**Reviewer 4**

The reviewer said it is hard to give a good answer to this question because, like all of the other Battery500 projects, the PIs report funds spent for the entire program instead of specific to the individual project under review. That said, there was not significant work proposed that was much different than the level of work presented so the reviewer believed the present funds are sufficient.

**Presentation Number:** BAT367
**Presentation Title:** Multiscale Characterization Studies of Lithium Metal Batteries
**Principal Investigator:** Peter Khalifah, Brookhaven National Laboratory

***Presenter***

Peter Khalifah, Brookhaven National Laboratory

***Reviewer Sample Size***

A total of four reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

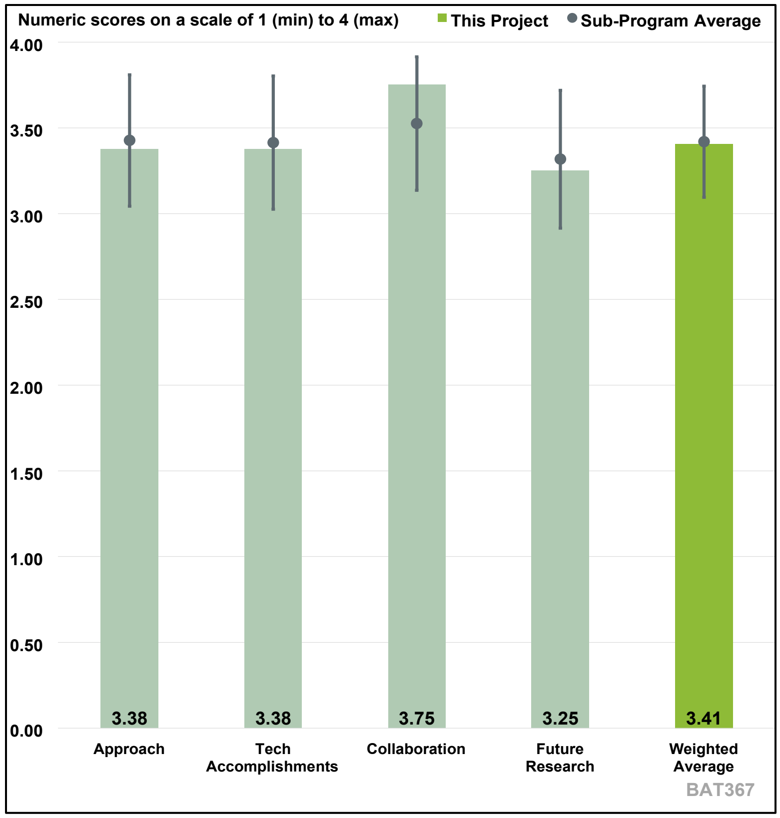


Figure 1-12. Presentation Number: BAT367 Presentation Title: Multiscale Characterization Studies of Lithium Metal Batteries Principal Investigator: Peter Khalifah, Brookhaven National Laboratory

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer said the project team investigates cell aging in NMC cathodes, heterogeneity in Li-S cells, and the SEI using advanced synchrotron X-ray techniques. These techniques include operando X-ray diffraction (XRD) and PDF analysis, spatially resolved 2D XRD mapping, and soft XAS of Li and S. The results deepen our understanding of the electrochemical properties of these systems and provide guidance for new materials synthesis. The reviewer said that with years of experience in applying synchrotron techniques to battery studies, the team is at the forefront of cutting-edge research to advance energy storage technology.

**Reviewer 2**

The reviewer said that most of the first 3 to 4 slides are generic to the program so one does not get a good understanding of how the researchers listed on the first slide approached the problem defined in the title of the first slide. The Milestones let us know that several different advanced characterization techniques will be used on all parts of the system.

**Reviewer 3**

The reviewer remarked as a cross-cutting activity, this effort effectively contributes to addressing technical barriers in many areas within the Battery500 program. The first two examples given—the PDF study helping to explain the extra capacity of the new UCSD SPAN material and the ultrasound/synchrotron mapping to help partner GM explain the heterogeneity in thick S cathodes—support the conclusion that the cross-cutting team is effective in helping other team members surmount challenges. In fact, perhaps due to the nature of the cross-cut effort, this research effort seems much more integrated and less isolated than some of the other Battery500 efforts that were presented throughout the day, where it often appears that a small team was tackling a challenge by themselves. The reviewer said this would argue for more resources being devoted to the cross-cut efforts when appropriate opportunities appear.

In general, an area for improvement in the overall approach might be to not stop when an explanation that is consistent with the data is generated, but to continue on to rule out other explanations that might also be consistent with the data. The reviewer cited as an example, in the new SPAN material study, it was not clear that the offered explanation was the only possible mechanism or that the PDF and modeling uniquely pinpointed the reason for the higher capacity. It would be nice to see a project designed to pursue experimental and computational data that definitely rule out competing explanations. Also, data is often not shown with error bars, so the uncertainty in the conclusions is not evident. The reviewer said it is hard to believe claims of super sensitivity of 1% SOC and 1% loading uniformity without seeing some error bars and uncertainty analysis now and again. Similarly, for the SEI work on F5DEE, it would have been nice to see error bars and how repeatable the non-linear speciation really is. The reviewer said that despite this, the cross-cutting effort is generally designed well and is overall making important and substantial contributions to Battery500 by providing key data to unravel mechanisms, performance changes, etc., throughout the larger program.

**Reviewer 4**

The reviewer said the approach using state-of-the-art characterization techniques for investigating the different systems being studied by the Battery500 consortium is very good. However, it seems to be a collection of results, without a clear statement of how they are helping Battery500 to meet its goals.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer detailed accomplishments. Accomplishment 1) Position-dependent speciation in Li-S ouch cells. The team conducted two-dimensional mappings of $Li_2S$ distribution in a Li-S pouch cell using XRD measurements. The team observed that the spatial heterogeneity in speciation changes with the state of charge and is not fully irreversible—the $Li_2S$ distribution differs significantly between the 1st and 2nd charge cycles. The team infers that this heterogeneity depends on the electrolyte distribution. Investigating the cause of this irreversibility could provide valuable insights for improving cycle stability.

Accomplishment 2) Synchrotron diffraction mapping of aged NMC: The team conducted Li cell SOC mapping using XRD on four Li/NMC cells aged 11 months under different pressures, SOCs, and temperature operating modes, with a cell aged under open circuit voltage (OCV) at 10 psi, 25°C, and 100% SOC as the reference. The spatially resolved SOC provides new insights into the effects of aging. The mapping was performed at the discharged state. The reviewer noted that although technically challenging, in situ mapping during a full discharge process would yield more informative results.

Accomplishment 3) SEI evolution when using new F5DEE electrolyte: Using synchrotron XRD, the team measured the detectable crystalline amounts of $Li_2O$ and LiF in the SEI of a Li-metal cell with F5DEE electrolyte. Both $Li_2O$ and LiF increase with cycle numbers, but their ratio exhibits a non-monotonic trend.

The reviewer said it would be helpful to combine the in situ and operando characterization with thermodynamic modeling to predict long term performance of battery systems. The reviewer found that in general, the project is making steadfast progresses, as evidenced by the high-quality research outcomes.

**Reviewer 2**

The reviewer said that the technical progress in the various areas is very good. The SEI studies are providing insight into mechanisms for formation. The reviewer was not clear how crystalline $Li_2O$ contributes to SEI effectiveness since it is not a good Li ion conductor. The reviewer said that overall, it would be good to show better how the characterization and understanding is contributing to the overall goal of the Battery500 program.

**Reviewer 3**

The reviewer said this research effort is continually meeting its objectives and timelines, and the results are translating in a timely fashion to many efforts across Battery500, contributing to the overall success of the larger program. The reviewer said it is notable that the cross-cut milestones are being met with regularity because many of the experiments and computations are difficult to do or otherwise require some level of invention to apply a particular characterization or modeling technique to the present problem. The reviewer said that having to unravel coupled processes across length scales (1 Å –10 cm) and time scales (1 s –1 yr) is not easy. Given that national laboratory user facilities—both experimental and computational—are necessary for much of this work, it is impressive that the progress has been steady and that milestones are being met.

**Reviewer 4**

Regarding Technical Accomplishment 1, the reviewer noted the team completed a PDF study of a new span from UCSD and discovered that mechanism for the 25% enhancement capacity. Regarding Technical Accomplishment 2, the team used modeling to support understanding of SPAN lithiation mechanism and developed a method for casting a thin layer of SPAN that did not require an additive. Regarding Technical Accomplishment 3, the team used ultrasound to follow uneven electrolyte consumption during cycling and correlated that with synchrotron data that tracked $Li_2S$ non-uniform generation and consumption. Regarding Technical Accomplishment 4, using XRD data, the team was able to chart the ratio of $Li_2O$/LiF with cycle life and show that this ratio first increases and then decreases. Regarding Technical Accomplishment 5, the team used AFM to show that CE correlated well with the creep of the SEI, which was dependent on electrolyte components. Regarding Technical Accomplishment 6, the team used TOF-mass spectrometry to map the CEI on the surface of cathode material at full charge and full discharge.

The reviewer noted the emphasis of the presentation was work at BNL, and asked why is the electrolyte not uniformly distributed, and why so much non-uniformity in the cell? The Li is reacting non-uniformly which is leading to non-uniform use of the cathode. The reviewer found that overall, this was a presentation of many efforts at characterizing different aspects of Li/NMC cell performance. The team is starting to understand the system a little better with each experiment. It is not yet clear how this is translating to solutions.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer said the team has established extensive and productive collaborations within the Battery500 Consortium. The collaboration model of the Battery500 Consortium, which combines the strengths of national laboratories, universities, and the R&D sections of industrial companies, is exemplary and highly effective.

**Reviewer 2**

The reviewer said the team has excellent collaborations across the different institutions. An example of this is the studies of the F5DEE electrolyte by different institutions to understand its SEI formation mechanism.

**Reviewer 3**

The reviewer said as implied in response to a prior question, the collaboration and coordination in this effort is very impressive. There obviously has to be coordination between cross-cut team members (e.g., experimental and computational efforts have to be aligned), but the coordination with most of the rest of the Battery500 team is outstanding based on the results presented at the review. Most of the work presented had many moving parts, and the coordination of the efforts was the key to making progress.

**Reviewer 4**

The reviewer noted there are several different institutions using their specific techniques to study the myriad of problems of trying to a get a Li-based battery to cycle a thousand times. The teams are doing good research but as mentioned above, it is not clear how this information is being used to design better electrolytes that allow for high CE and uniform plating characteristics.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer believed that the “Remaining Challenges and Barriers” section should outline the problems to be resolved in the next stage of research. Therefore, ‘N/A’ is not a proper answer. Nevertheless, the team has proposed future research with concrete plans. These plans remain centered on synchrotron and neutron techniques and focus on Li-S and Li-metal battery systems. The primary objective of the research is to develop an atomic-scale understanding of the electrochemical processes in these battery systems to improve their performance.

**Reviewer 2**

The reviewer said the PIs talk about continuing to study the NMC surface but is not sure why when there are several cathode programs already doing this. The proposed future work also includes a mapping study of Li-S when varying the cell formulation, pressure and with aging. To better understand the mechanisms of SPAN lithiation to develop new materials, and to study the SEI formed from alternative electrolytes. It would be nice if the team had some hypotheses on some of these problems that they were testing but it looks like a lot of the work is still mapping.

**Reviewer 3**

The reviewer commented future plans are okay, but they are a bit generic and were only very briefly presented. Objectives such as “continue to understand and enhance capacity of SPAN systems” translate to a vague promise to do more good work in the future. It would have been nice to see a little more prioritization and specificity in the future plan. The reviewer asked what is the biggest challenge for the cross-cut team, and where can they have the most effect and contribute the most?

**Reviewer 4**

The reviewer remarked the proposed work is clearly defined, but its contribution to meeting the consortium goals is not so well defined.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer said the cross-cut effort clearly supports the overall VTO objectives by making substantial contributions to the progress of the Battery500 effort, which itself is a flagship effort within the VTO portfolio of energy storage research. It is fairly easy to look at the overall progress of Battery500 towards its objectives each year and be able to attribute some of that progress to the key efforts coming from the cross-cut team. These contributions are most obvious in two Battery500 objectives: demonstrate long cycle life of up to 1,000 deep charge-discharge cycles; and achieve total control of battery chemistries for robust, scalable and commercially viable technologies. It is really hard to reach those kinds of performance objectives when designing, building, testing, and optimizing battery systems with blinders. The cross-cut team continually provides the relevant information to Battery500 colleagues so that they can see what is actually happening and then control it to achieve long life and safe performance.

**Reviewer 2**

The reviewer noted the project is a part of the Battery500 consortium, which aims on developing next generation high-energy low-cost batteries for EVs.

**Reviewer 3**

The reviewer said the program supports the VTO objectives in achieving a higher energy density battery through use if Li anodes and NMC as well as Li-S batteries. It contributes to the crosscutting effort of the consortium.

**Reviewer 4**

The reviewer said the work is relevant to VTO’s mission as a Li-metal based system is considered one of the best approaches to getting to 500 Wh/kg. All of this work goes to understanding the present limitations in such a system.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer commented resources are clearly sufficient. However, new opportunities may arise as experimental and computational capabilities increase and researchers “learn by doing.” So, if appropriate, funding could be increased if the proper opportunity appeared.

**Reviewer 2**

The reviewer said funding is sufficient for the project to successfully achieve its adjectives.

**Reviewer 3**

The reviewer remarked resources for the characterization is excellent and contribute to the objectives of the program.

**Reviewer 4**

The reviewer said there is no indication of the resources dedicated to this effort in the presentation. That said, there does not appear to be a lot of work proposed that would require more resources than the work performed this year.

**Presentation Number:** BAT368
**Presentation Title:** Full Cell Diagnostics and Validation to Achieving High Cycle Life
**Principal Investigator:** Eric Dufek, Idaho National Laboratory

***Presenter***

Eric Dufek, Idaho National Laboratory

***Reviewer Sample Size***

A total of five reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 80% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 20% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

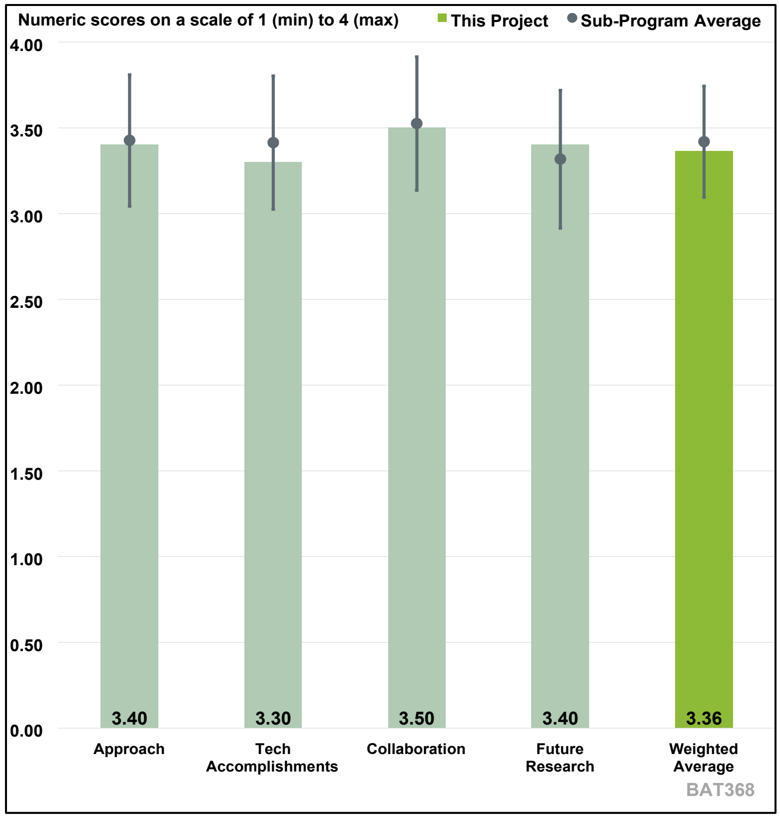


Figure 1-13. Presentation Number: BAT368 Presentation Title: Full Cell Diagnostics and Validation to Achieving High Cycle Life Principal Investigator: Eric Dufek, Idaho National Laboratory

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer remarked this project's focus is to explore failure modes in real cells involving SPAN cathodes. It seems like calendar life and aging was the focus of this year. Timeline is appropriate and shows steady process in understanding cycle and calendar life with the development of accelerated aging.

**Reviewer 2**

The reviewer said standard testing protocols were developed and applied to evaluate the electrochemical performance of Li/MNC cells.

**Reviewer 3**

The reviewer remarked the project focuses on the needed full cell testing for long term, which help reveal technical barriers faced at more practical conditions.

**Reviewer 4**

The reviewer said the goal of the project is to couple a Li-metal anode with a high-Ni-NMC or S cathode to "achieve a specific energy of up to 500 Wh/kg through cell level design and optimization of materials and architectures." The approach includes "integrating development and discoveries from materials to cell level' and leveraging "state-of-the-art DOE facilities to understand and prevent degradation." In this project resources at INL and BNL are used to examine calendar life of NMC/Li cells. The reviewer said the approach is reasonable, though it is unclear why 4.4V was chosen as 100% SOC for the tests, as NMC811 electrodes yield little capacity when cycled past 4.3V versus Li. The calendar aging tests at 25 and 45° Celsius (C) are reasonable—though tests at higher temperatures (such as 55°C) and lower temperatures (such as -10°C) would be needed for the cells to be considered in vehicular applications.

**Reviewer 5**

The reviewer remarked in this FY, the team has been mainly working on the two technical barriers: Understanding the calendar lifetime decay; and extending cell lifetime under lean electrolyte condition. While some progress has been made, some details could be further explored. For example, how did the team understand the cathode capacity decay and anode capacity decay during OCV storage? If this is studied by ex-situ method, is this real for storage process? It is not clear about the temperature condition during the calendar lifetime testing.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer said the NMC/Li calendar aging studies reported in this project are for up to a 18-month period. The data show that cells held at the higher SOC (100% or 4.4V) fail faster than cells held at the lower SOC (70%). Cells held at the higher temperature (45°C) degrade faster than cells held at the lower temperature (25°C). And cells tested at lower pressure (10 psi) degrade faster than cells tested at the higher pressure (50 psi). The reviewer said the effect of lean and "non-lean" electrolytes are also studied with the latter performing better than the former. In addition to electrochemistry tests, microscopy on the Li anode and X-ray diffraction of the NMC811 cathode were also performed to determine reasons for the performance loss. All in all, the electrochemical and physicochemical tests conducted are reasonable and important to support the overall project plan.

**Reviewer 2**

The reviewer remarked a good effort was utilized to characterize the long term electrochemical behavior of cells under different operation/storage conditions.

**Reviewer 3**

The reviewer said the project is making good progress towards technical accomplishment.

**Reviewer 4**

The reviewer said technical progress is aligned with the project plan.

**Reviewer 5**

For the Calendar life work, it was difficult for this reviewer to have a feel for the confidence of the data, as in, having multiple cells or at least a small discussion to the effect of "2 out of 3 these cells fail by 5 months." This is important as nonlinear processes (such as reactions, corrosions, etc.) are stochastic prior to the runaway/takeoff event. The differential analysis was important to understand how cycling may be contributing to gas evolution (electrolyte degradation). The reviewer was interested in the accelerated stress tests. More work should be done here.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer remarked work is well supported by the partners.

**Reviewer 2**

The reviewer said the project presented work conducted at INL, BNL, and SUNY Stony Brook. The NMC811 electrolyte was obtained from PNNL and the LHCE electrolyte was also likely designed at PNNL. That is, the project shows good collaboration across the multiple national laboratories and universities.

**Reviewer 3**

The reviewer remarked collaboration was limited to Battery500 team.

**Reviewer 4**

This reviewer wanted to see these accelerated stress tests on other systems to understand exactly what is being stressed and how different chemistries and formulations response to them.

**Reviewer 5**

The reviewer remarked in addition to Battery500 consortium partners, Brown University and University of Connecticut were involved for Li-S work. The reviewer was not sure if any industry partners are involved in the project or not.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer remarked good future research was proposed to support Battery500.

**Reviewer 2**

The reviewer noted a good focus on cycling impact and Li electrode performance, SPAN/Li-S cells, and wetting.

**Reviewer 3**

The reviewer said the team proposed to understand “how variation in initial Li state impacts life and performance.” It is not clear where the difference of initial Li state is from. Is this from air-exposure or somewhere else? It could be further elaborated.

**Reviewer 4**

The reviewer commented that future plans include studying “how variations in cycling impact life and Li electrode performance” and “understanding how variation in initial Li state impacts life and performance.” In addition, it would be good to understand the effect of lower temperatures (0°C and below) on cell cycle and calendar aging. In addition, the effect of other promising electrolytes should be examined.

**Reviewer 5**

The reviewer said there were a lot of confounds in this report. The future plans actually focus on deconvoluting these confounds (such as electrolyte formulation versus using excessive electrolyte) to aid in moving from correlative understanding to causal. This is important for others to make reasonable predictions for optimizing these Li-S/SPAN systems.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer said the team goal is to develop high-energy (500 Wh/kg), low-cost batteries for EVs. This project examines electrochemical performance of 100 mAh cells, with various chemistries, designed to meet the project goal. Hence, the project is relevant to overall VTO subprogram objectives.

**Reviewer 2**

The reviewer remarked good alignment with Battery500.

**Reviewer 3**

The reviewer said calendar life tests and accelerated tests are invaluable to the development and commercialization of next generation energy storage devices.

**Reviewer 4**

The reviewer affirmed yes, the project supports overall VTO subprogram objectives.

**Reviewer 5**

The reviewer said the proposed work well supports the Batteries program in VTO by developing high energy density Li-metal batteries. It is worth considering the safety performance of Li-metal batteries because one of the VTO's objective is to increase the ability to tolerate abuse conditions.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer said the total resources available to the project are sufficient. It is not known whether the resources available for this particular project are sufficient, as no subproject financial information is provided.

**Reviewer 2**

The reviewer said this project is slightly ahead of schedule and is making great progress. Funding seems appropriate.

**Reviewer 3**

The reviewer said there are sufficient resources.

**Reviewer 4**

The reviewer said sufficient resources are available to achieve the proposed tasks.

**Presentation Number:** BAT369
**Presentation Title:** High Energy Rechargeable Lithium-Metal Cells Design Fabrication and Testing
**Principal Investigator:** Jie Xiao, Pacific Northwest National Laboratory

***Presenter***

Jie Xiao, Pacific Northwest National Laboratory

***Reviewer Sample Size***

A total of three reviewers evaluated this project.

***Project Relevance and Resources***

67% of reviewers felt that the project was relevant to current DOE objectives, 33% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

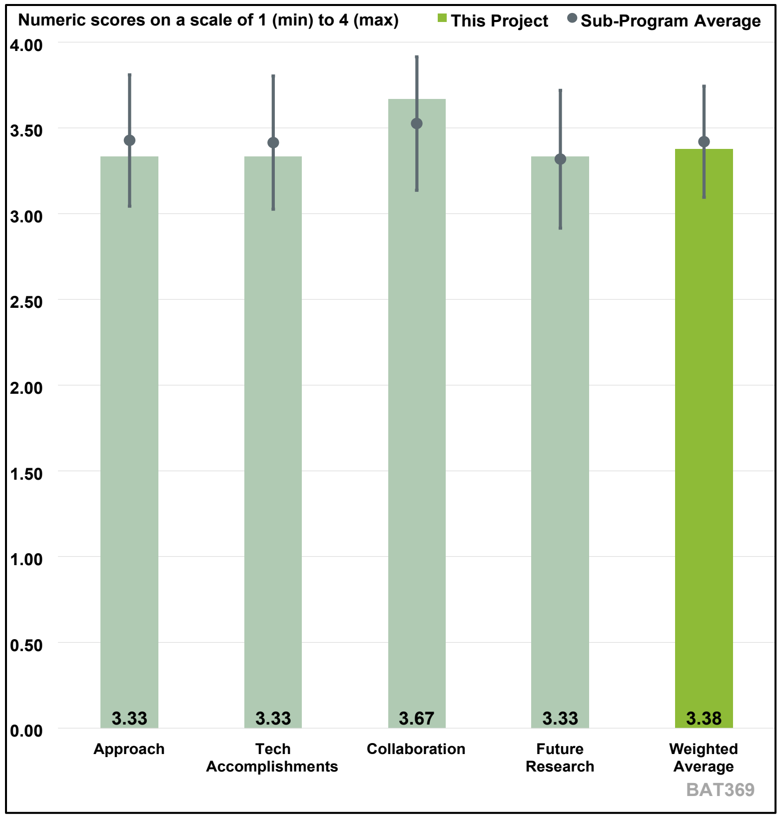


Figure 1-14. Presentation Number: BAT369 Presentation Title: High Energy Rechargeable Lithium-Metal Cells Design Fabrication and Testing Principal Investigator: Jie Xiao, Pacific Northwest National Laboratory

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer said BAT369 is one of the three keystone projects in the Battery500 Consortium, aiming for pouch cell fabrication, testing, and diagnosis. The team's approach involves developing scientific insights and a research roadmap to enable high-energy, long-lasting Li-metal batteries by testing Li-metal pouch cells under different designs and conditions, using new cell components (electrodes and electrolytes) developed by other Battery500 teams. The approach has been effective so far, and the milestones are well defined with a reasonably planned timeline.

**Reviewer 2**

The reviewer remarked very good progress is being made in addressing technical barriers including demonstration of a 500Wh/kg pouch cell and understanding of pressure effects. The Li anode work is well defined and systematic. The charge rate is still low and has to be overcome. It is not clear how this will be overcome.

**Reviewer 3**

The reviewer remarked the team says in the Approach slide that part of their approach is to develop a research roadmap to enable rechargeable high energy Li-metal pouch cells. Which essentially means they will start from a 350 Wh/kg battery and work their way up to a 500 Wh/kg battery and try to understand the engineering and cycling limits along the way. The team also plans to benchmark new material in coin cells and advance pouch cell development, which means trying to get good cycling in pouch cells. It is an Edisonian approach where they will try things and take note of the results.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer remarked the team has made good progress on the overall goals of getting to 500 Wh/kg battery according to the project plan. The team exceeded this year's goal for 450 Wh/kg cycling. Much remains to be accomplished including longer cycle life and charge rates. Very good progress has been made on the pressure effects.

**Reviewer 2**

The reviewer said the team conducted a systematic investigation on Li-metal coin cells and found that high areal capacity increases cell capacity but shortens cycle life, while higher electrolyte loading effectively prolongs cycle life (though it obviously lowers energy density) for thicker Li anodes. For thin Li-metal, the effect is much weaker. The conclusion is that these parameters can be used to tune the Li-metal coin cell as a model system.

For the 350 Wh/kg pouch cell, the team found that the electrolyte amount is still a deciding factor for cycle life, and thinner Li anodes work better than thicker ones. The 600-cycle capacity retention for the 350 Wh/kg cell is impressive. The reviewer noted the team also demonstrated 80% capacity retention at 215 cycles for a 450 Wh/kg pouch cell. The reviewer noted the Pressure Study: The team reported their research efforts on the interplay between uneven pressure distribution and Li deposition, concluding that the origin of the uneven distribution is the "'Li+ detour phenomenon." The team suggested that utilizing external pressure (using a hybrid device) to facilitate preferred deposition in specific anode regions can solve the problem of uneven Li plating during charging. The reviewer was not fully convinced that the electric field (EF) distribution calculated in Figure 5 of the team's Nature Energy paper can explain the origin of the uneven Li plating and does not believe that using the hybrid pressure device will solve the problem. In general, the reviewer believed that the team is making solid progress following the project plan.

**Reviewer 3**

The reviewer detailed accomplishments. Technical Accomplishment 1: The team first evaluated coin cell performance of Li/NMC cells varying the amount of electrolyte with thick Li foil (250 micron) and thin Li foil (50 micron), varied the loading of the cathode with thin Li foil, and used a low loading cathode, lots of electrolyte, and a thick Li foil to optimize cycle life. From this the researchers learned that for thick Li foil, the more the electrolyte the better, but the effect goes away for thin Li foil. The team also found that the cycle life goes down proportionately to the loading of the cathode going up. So the best cycle performance they could get is thick Li foil, at low loading and high electrolyte concentration.

Regarding Technical Accomplishment 2: The team then switched to pouch cell cycling, tried two different electrolyte levels, and found a 15% increase in electrolyte lead to a 66% increase in cycle life. The team also found that the cycle life improved with reduced Li thickness. The researchers say thicker Li may lead to more dry layers of SEI—this reviewer did not understand what this means.

Regarding Technical Accomplishment 3: The team now applied pressure to a cell with a loading around 3.5 $mAh/cm^2$ and found that the pressure in the cell cycles with cycling and that the peak in pressure is inversely related to the external applied pressure, i.e., low applied pressures result in very high internal pressures at top of charge (high level of plating). The researchers claim the pressure results in less fluffiness of Li from cycling, less exposed surface area. This also slightly extends cycle life. Eventually the cells dry out.

Regarding Technical Accomplishment 4: The team shows that the cells cycling under pressure only swell 6% to 8 %, which the reviewer assumed that is all the room there is for swelling. Not sure what the accomplishment is here. The team also took some SEMs of the edges of the cells and found Li to be very non-uniform with large columns everywhere. Regarding Technical Accomplishment 5: The team cycled multi-layered pouch cells (16 layers of Li) and found after 335 cycles that the Li in the center of the electrode is still shiny and that around the edges is dark.

Regarding Technical Accomplishment 6: The team found that for a cycled discharge anode where the Li is now in the cathode, that the Li in the center of the cell seems less used that that on the edges. Regarding Technical Accomplishment 7: The team cycled pouch cells under pressure and opened them up after discharge and claimed that the Li from the cathode seems to like to cycle in the middle of the cell. The researchers believe the pressure in the cell is uneven. The researchers gave no explanation for either hypothesis.

Regarding Technical Accomplishment 8: The team open cycled cells after charge and again claim that the Li that is originally from the NMC is cycling in the center. The reviewer did not know how the researchers deduced this. Regarding Technical Accomplishment 9: The team provided a schematic of what they think is happening and say that Li from the NMC in the early cycles preferentially plates on the Li in the center of the electrode. So, after long-term cycling, there is more pressure in the center and Li cycling at the edges goes deeper and deeper, which may be driven by lack of pressure on the edges where side reactions are greater, while the Li foil in the center is under higher pressure and plates more uniformly. The reviewer noted it helps to understand why the Li from the cathode wants to go to the center of the Li anode.

Regarding Technical Accomplishment 10: Cells were made at PNNL in 2023 at 450Wh/kg and cycled about 130 times. Similar cells were sent to GM for testing and achieved about 180 cycles. More cells built at PNNL in 2024 and they now achieve more than 200 cycles, with no explanation as to why the improvement–was this due to experience?

Regarding Technical Accomplishment 11: The last achievement reported was that the team made a cell of 500 Wh/kg specific energy and just started cycling it. The researchers basically have mapped out the space for cell construction and are learning about the effects of thin Li, high loadings, pressure, and electrolyte volumes, and are fine tuning their formulation. Not sure we are learning anything very fundamental that will lead to a specific change in one of the components that will result in a step change in cyclability.

The researchers say they say need 3.5 to 4 $mAh/cm^2$ to meet Battery500 energy goals. 20 micron thick Li-metal films work better because there is less Li for the electrolyte to react with. If the applied pressure is higher, the rise in pressure in the cell is less. The cycle life only partly improves because of electrolyte dry out. The researchers show pressure increase and decrease in cell from gas generation and then show a distribution of gas pressure in the cell with cycling—the reviewer asked how can a gas not be at uniform pressure in the cell. The reviewer asked why the non-uniformly plated Li does not reverse, and asked for any explanation of why the cell cyclability is improving by 40 cycles a year.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer said the team has established extensive and productive collaborations within the Battery500 Consortium. The collaboration model of the Battery500 Consortium, which combines the strengths of national laboratories, universities, and the R&D sections of industrial companies, is exemplary and highly effective.

**Reviewer 2**

The reviewer observed excellent collaboration among many industrial partners, university, and national laboratories that make use of expertise on materials, design, and characterization. For example, the new results on the 450 Wh/kg cell cycling over 200 cycles.

**Reviewer 3**

The reviewer said the team lists tons of collaborators on the collaboration page and on the second slide but really do not point to much collaboration on the Technical Accomplishments slides other than trading cells with GM.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer remarked the research plan addresses the targets of the Battery500 program including redesigning cells for pressure effects, new electrolyte development, and other challenges.

**Reviewer 2**

The reviewer said the team has a very clear awareness of the remaining challenges. The reviewer agreed that more innovations are needed in electrolyte design and SEI control and also suggests keeping abreast of the latest developments in high-Ni or Co-free cathodes, especially those with better compatibility with high-pressure electrolytes. The proposed future research is clearly defined and heading in the right direction.

**Reviewer 3**

The reviewer said for future research the researchers said they have found that pressure has an effect on cyclability so the team will redesign the pouch cell structure to enhance homogenous Li plating. The reviewer was not sure how exactly what the researchers are going to do here. The PI said the team will develop a new electrolyte compatible with Li-metal and NMC—not sure how any of the work presented will lead to a better electrolyte formulation. And the researchers will continue to make cells and try to figure out what leads to better cyclability. It would be nice if there was a list of things the team learned that will guide the cell changes.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer noted the project is a part of the Battery500 consortium which aims to develop next generation high-energy low-cost batteries for EVs.

**Reviewer 2**

The reviewer affirmed this project is relevant to the VTO goals of achieving a high energy density battery based on use of Li in combination with NMC.

**Reviewer 3**

The reviewer said the goal of the program is to make batteries with 500 Wh/kg specific energy that cycle 1000 times without a lot of chemistry development. The researchers are making some progress.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer said resources are sufficient for the project to achieve the goals as planned.

**Reviewer 2**

The reviewer commented the project has sufficient resources.

**Reviewer 3**

The reviewer said the team did not provide an amount on the second slide as to how much was spent on the effort presented and the proposed work is not outside the limits of the conducted work, thus the reviewer would have to say that funds are sufficient.

**Presentation Number:** BAT402
**Presentation Title:** Improving Battery Performance through Structure-Morphology Optimization
**Principal Investigator:** Venkat Srinivasan, Argonne National Laboratory

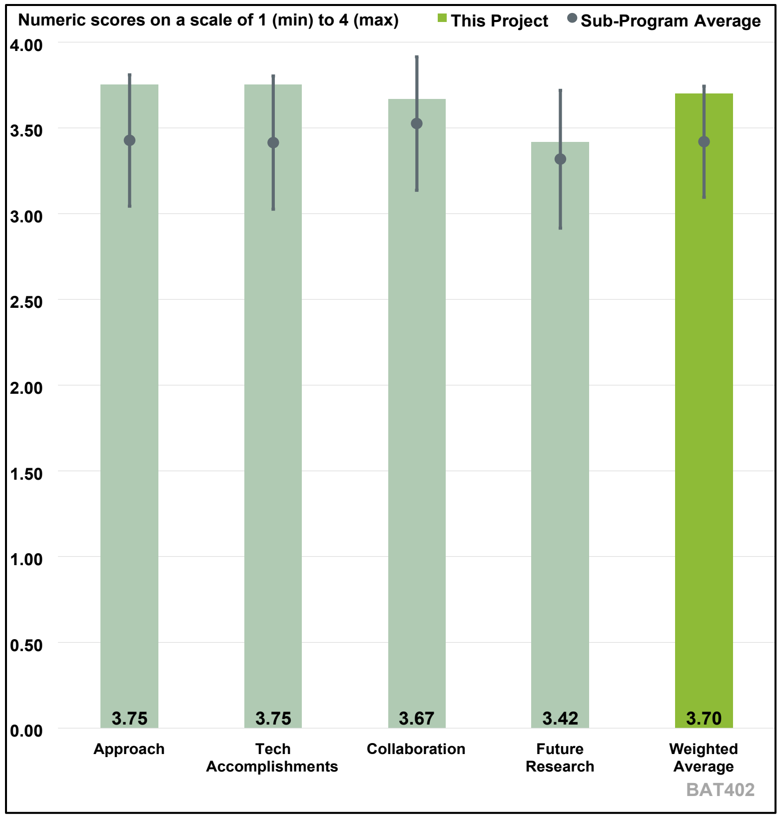


Figure 1-15. Presentation Number: BAT402 Presentation Title: Improving Battery Performance through Structure-Morphology Optimization Principal Investigator: Venkat Srinivasan, Argonne National Laboratory

***Presenter***

Venkat Srinivasan, Argonne National Laboratory

***Reviewer Sample Size***

A total of six reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer stated that understanding the intricate relationship of cathode materials among synthesis, morphology/structure, and electrochemical performance is critical for developing new lithium-ion battery (LIB) chemistry, e.g., Li-rich NMC and single crystal NMC. The reviewer believed this project is aiming to achieve that by studying the key control factors during the pCAM and calcination process that can affect the morphology/structure/chemistry and thus the performance of the final products. The project is well-designed to focus on lithium manganese-rich (LMR)-NMC and single-crystal NMC cathodes.

**Reviewer 2**

The reviewer stated the project represents an excellent combination of the use of experiments and modeling to predict particle morphology and material performance.

**Reviewer 3**

The reviewer stated that the objective of this project is to understand how synthesis conditions and precursors impact LMR and nickel-rich NMC morphology and performance. The approach uses a feedback loop between experiments and DFT/continuum scale modeling to fully understand the synthesis condition/morphology relationship. Coprecipitation and hydrothermal methods have been studied, as have been various precursors and final sintering temperatures and protocols. The approach leads to an impressive understanding of how to control NMC morphology.

**Reviewer 4**

The reviewer stated that the approach for this project is excellent. It forms a combination of expertise in synthesis, in situ characterization and multiscale modeling to decipher the relationship between the synthesis process and the morphology of pCAM and the CAM of Li-rich NMC, as well as high nickel NMC811. This relationship is also extended to performance of the CAM materials. The reviewer stated this is an innovative approach.

**Reviewer 5**

The reviewer stated that the objective of this effort is to understand the relation between synthesis condition, morphology, and performance. The reviewer believed the researchers used a novel combination of in-situ analysis and fundamental density functional theory molecular dynamics (DFT-MD) modeling. The researchers studied the synthesis process of making cathodes from precursors at various conditions and built cells to evaluate performance. The reviewer stated this approach was appropriate and novel to address technical barriers in a scientific way. The reviewer believed the project was well-designed, and the timeline was well-planned.

**Reviewer 6**

The reviewer stated that the project combines experimental results with computational modeling and it has made significant progress in the understanding of pCAM particle formation and growth. Several research topic areas were explored, including single crystal NCM synthesis, LMR-NMC and calcination processes. It is appropriate to look into diverse areas of development in the early stage of the project, but in future, resources might get spread too thin if the project team dives deeper into all these topics. The reviewer would recommend some prioritization for the next phase of work to focus on the most valuable research topics and on addressing them.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer stated the project has made great achievements: it completed LMR-NMC cathode calcination process study and modeling, it studied pCAM synthesis with co-precipitation and hydrothermal methods, it looked into the composition gradients in pCAM particles with both co-precipitation and hydrothermal methods, and it studied the NMC811 calcination process and the effect of temperature on product morphology.

**Reviewer 2**

The reviewer stated the project team has applied its modeling approach to the synthesis of several materials and material types and is able to predict critical lengths for transport. The reviewer believed that since this is such a model-heavy project, the researcher should probably be able to provide more dimensionless parameters of properties that are easily measured and that will allow anyone starting a synthesis optimization some guidelines on what measurements should be made in order to fine tune synthesis.

**Reviewer 3**

The reviewer stated that the project progress has been excellent, leading to many insights. New established observations include the relationship between precursor and particle growth, the role of supersaturation on transition metal ™ gradients within a single particle, and the role that sintering plays on particle agglomeration and porosity. Five publications have resulted from this work, the reviewer believed that is a very solid number at the given funding rate.

**Reviewer 4**

The reviewer believed the project team has successfully connected synthesis conditions to composition and morphology and their impact on performance by developing: 1) models for pCAM synthesis using coprecipitation and hydrothermal synthesis; 2) models providing insights into single crystal formation as well as formation of compositional gradients; 3) models for calcination capture of the chemical reactions along with particle sintering effects, and 4) performance models showing the balance between transport in electrolyte pores, primary particle, agglomerates, and grain boundaries. The reviewer believed these are outstanding accomplishments with important impact in guiding the synthesis of pCAM and cathode materials for Li-ion batteries.

**Reviewer 5**

The reviewer stated that the technical progress was in line with the proposed project plan. The reviewer believed the researchers examined different pCAM synthesis processes such as co-precipitation and hydrothermal to provide an interesting hypothesis that surface energy minimization dictates growth morphology, and they support it by showing the evolution of surface energy with time due to increasing particle size. The time scale of the synthesis process the researchers studied for various cathodes was of the order of hours, in industrial processes they are of the order of seconds; so the reviewer suggested that future studies focus on finding a correlation between laboratory- and industry-scale processes.

**Reviewer 6**

The reviewer believed that great progress has been made in this project in multiple fronts of CAM synthesis.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer observed that the project accomplished a collaborative effort among ANL, BNL, University of Chicago, and a few DOE facilities. This observation is supported by the fact that most journal publications and presentations resulting from this project were done by authors from multiple organizations.

**Reviewer 2**

The reviewer observed that the project involved working with several principal investigators (PIs) across the VTO-supported program. The reviewer found that very impressive.

**Reviewer 3**

The reviewer observed that the project represents a collaboration between ANL PIs primarily, all of whom appear to contribute different expertise. The reviewer stated that the project appears well-coordinated.

**Reviewer 4**

The reviewer observed that the project is highly collaborative across multiple research groups funded by VTO, including the synthesis groups at the Materials Engineering Research Facility

(MERF) at ANL, the APS at ANL, the national synchrotron light source II (NSLSII) at BNL, and the University of Chicago.

**Reviewer 5**

The reviewer considered the collaboration between the team members, including that between the national laboratories and university partners, as excellent. The reviewer observed that it could be even more improved by including an industry partner to provide insight on usability of the results from laboratory scale to industrial scale.

**Reviewer 6**

The reviewer stated that more collaboration with industry will be helpful. The reviewer has the understanding that since there are currently no US-based NCM CAM producers, obtaining commercial single crystal NCM and testing it as a benchmark material will be helpful in comparing the materials under this project with what is in the market. The reviewer also believes that more collaboration on the calcination process of pCAM (to better understand it) will be helpful.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer believed this project helps gain a better understanding of the synthesis-performance relationship of LMR-NMC and single crystal NMC. It is desirable that with all these new findings, at the end of this project, the project team can recommend optimal synthesis conditions, to help solve the LMR-NMC, single crystal NMC performance issues. Commercial single crystal NMC cathodes have been available in the Chinese market for at least 5 years. So far, they do not seem of much interest to EV OEMs, possibly because of low rate performance and higher cost. The reviewer suggested that future work could focus more on lithium iron phosphate (LFP) chemistry for battery energy storage system (BESS) applications that require a longer cycle life and have lower rate requirements.

**Reviewer 2**

The reviewer believed the project team is planning to move to other materials and other processes. The reviewer commended the expansion of work.

**Reviewer 3**

The reviewer stated that future work will focus on further answering open questions related to unexplained experimental observations, including particle morphology differences between various precursors. Also, phosphate morphologies and the formation of coatings via solution/hydrothermal methods are being proposed. The reviewer believed these are reasonable directions to pursue.

**Reviewer 4**

The reviewer believed the PI and the project team has clearly identified a set of questions to be answered in future research, including: why do NMC-hydroxide pCAMs form a plate-like morphology while NMC-carbonates form spherical primary particles; what are the underlying processes driving supercritical hydrothermal reactions and can they be modeled; can the understanding gained on NMC be utilized towards phosphate cathodes; can the synthesis of coatings and their impact on particle morphology be understood; and can a mathematical model be used to optimize the synthesis conditions of LMR-NMC to obtain particles that can maximize energy density and rate capability? The reviewer believed answering these questions could help develop a good research plan in future.

**Reviewer 5**

The reviewer drew attention to the proposed future work plan which lists the ‘questions’ for the remaining challenges and barriers. The reviewer emphasized that it is to be assumed that the future plan would propose an approach and specific plan on addressing those questions; but those are missing.

**Reviewer 6**

The reviewer stated that many commercial high nickel NCMs contain either alumina coating or doping to enhance cycling stability. Also, those coatings are typically applied on pCAM before calcination. The reviewer recommended a study of how such a coating will impact the calcination process and CAM structure/performance – both experimentally and through computational simulation in future work.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer believed a good understanding of fundamentals of the cathode synthesis process is critical to improve the performance of Li-ion battery with new chemistry. Therefore, the reviewer considered this work relevant to VTO subprograms like Batteries and Electrification.

**Reviewer 2**

The reviewer believed this work is very relevant to the battery industry as new materials are critical to reducing the nickel and cobalt contents of the cathode, or even the replacement of Li altogether. This work helps the synthesis researchers on how to tune reactors to achieve material properties needed for high rate, high density, and good stability.

**Reviewer 3**

The reviewer believed this project is highly relevant to the overall VTO subprogram objectives.

**Reviewer 4**

The reviewer believed this project is relevant to current DOE objectives because it provides guidance for pCAM and CAM synthesis to help improve the performance of Li-ion batteries.

**Reviewer 5**

The reviewer believed this project is very relevant to VTO Battery R&D activity because finding the relationship between synthesis impacts, composition, and morphology (and in turn, the performance) is crucial.

**Reviewer 6**

The reviewer believed this project is highly relevant to the battery R&D objectives.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer believed the resources (including research staff and laboratory facilities) are enough for this project.

**Reviewer 2**

The reviewer believed this research group has been very productive with current resources and has not proposed a significant increase.

**Reviewer 3**

The reviewer believed the funding level appears reasonable for the effort involved.

**Reviewer 4**

The reviewer believed the resources are sufficient for the project to achieve the milestones and objectives.

**Reviewer 5**

The reviewer believed the current resources ($500,000 per year) are sufficient for this project. The reviewer also believes it could utilize information available from several other related projects.

**Reviewer 6**

The reviewer believed the resources are sufficient.

**Presentation Number:** BAT496
**Presentation Title:** Silicon Consortium Project Advanced Characterization of Silicon Electrodes
**Principal Investigator:** Robert Kostecki, Lawrence Berkeley National Laboratory

***Presenter***

Robert Kostecki, Lawrence Berkeley National Laboratory

***Reviewer Sample Size***

A total of three reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

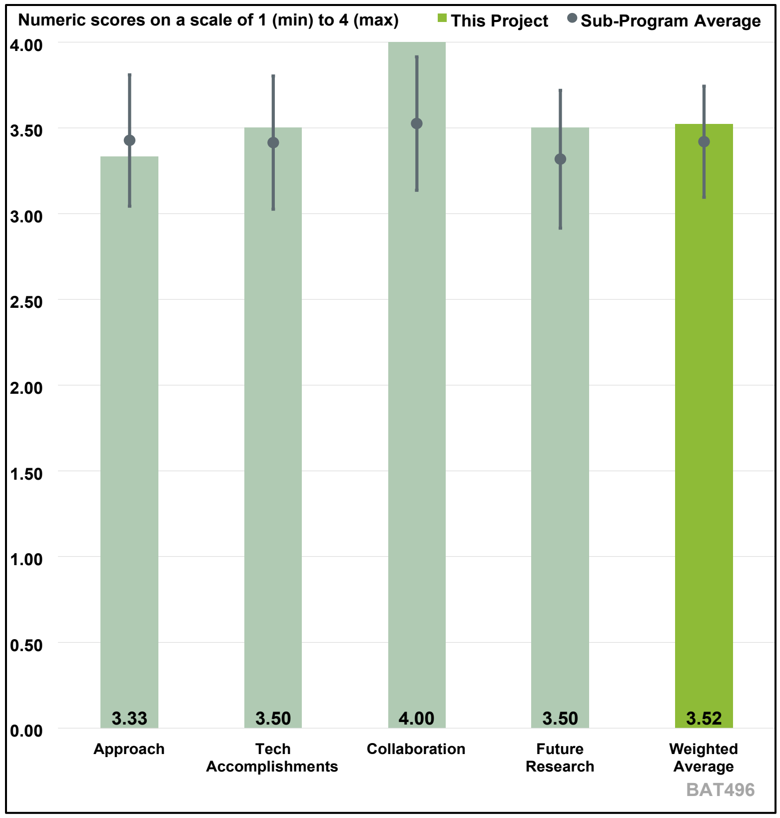


Figure 1-16. Presentation Number: BAT496 Presentation Title: Silicon Consortium Project Advanced Characterization of Silicon Electrodes Principal Investigator: Robert Kostecki, Lawrence Berkeley National Laboratory

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer believed the program is broad and comprehensive in scope and fundamental progress and understanding is taking place. The reviewer also believes that the Si-PEO system is arguably not representative of the best-in-class silicon materials. The reviewer suggested that if possible, some incorporation of commercial Si-C composites should be added to the program. The reviewer stated that even inclusion of some commercial Si manufacturers or cell manufacturers would add insight and make the project more relevant to industry.

**Reviewer 2**

The reviewer stated that the project's approach is to study the fundamental reason for Li loss in Si based cells. The reviewer believed the study focuses on studying this problem using ideal samples and better-focused characterization techniques to deep-dive Si solid-electrolyte interphase (SEI).

**Reviewer 3**

The reviewer believed that the approach has been well thought-out and the project team has shown great depth in developing analytical tools necessary to study the SEI phenomenon within silicon-containing anodes. However, the reviewer also stated that the third design approach of ‘rational Si electrode design principles to address performance challenges’ was not sufficiently addressed in the presentation – it was somewhat talked about with the role of electrolyte and carbon in the anode system, but further explanation/discussion in future presentations would be appreciated.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer believed that understanding the SEI layer formation, structure and stability is key to improving Si anodes. The reviewer stated that this project is making important strides toward obtaining that understanding.

**Reviewer 2**

The reviewer believed the project is very systematically studying the dissolving of SEI. The project has developed new focused characterizations to study this phenomenon. The project observed SEI to be inhomogeneous which can create more failure paths.

**Reviewer 3**

The reviewer believed that the project has made significant technical progress, and its results have been of assistance to other groups/projects within the consortium.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer believed that the overall Si program is well-connected across many organizations.

**Reviewer 2**

The reviewer believed that the project facilitates collaboration with seven national laboratories and multiple universities. The reviewer emphasized that silicon is very surface-sensitive, and it would be ambitious for the teams to be studying and understanding its mechanism.

**Reviewer 3**

The reviewer stated that it is evident from this presentation and from other silicon-anode consortium presentations, that the project team is highly integrated and is collaborating well. The reviewer would like more participation/transition from/to industry partners as the consortium winds down.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer stated that future work is well laid out and relevant.

**Reviewer 2**

The reviewer remarked that exploring NMR to study dissolving SEI should give more details on its mechanism and on how to mitigate it.

**Reviewer 3**

The reviewer stated that proposed future research is clearly defined and appropriate for the outlined project. The reviewer did have concerns concerning the large scope of the proposed future research (‘develop new, expand existing and combine in situ and ex situ diagnostic approaches’ can involve five distinct techniques). As such, the reviewer believed it may be necessary for the PI to scrutinize the project to reduce the scope of future research if the work timeline increases.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer referenced earlier comments (for question 1).

**Reviewer 2**

The reviewer believed that the Si anode has a lot of potential in electrification and studying its failure modes is necessary for its commercialization.

**Reviewer 3**

The reviewer believed that the project actively addresses analysis and battery subprogram objectives, as set by VTO. The reviewer also believes that numerous analytical techniques were developed and utilized to address the long withstanding issues concerning silicon-containing anodes for battery applications. The reviewer stated that over the long term, manufactured cells/batteries are not just for EV markets but for all high-energy-density applications.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer stated that the research teams appear well-staffed, and their resources seem adequate.

**Reviewer 2**

The reviewer stated that the resources provided are sufficient for the program.

**Reviewer 3**

The reviewer believed that the resources for this project and the rest of the silicon anode consortium, are sufficient to achieve its stated milestones in a timely fashion.

**Presentation Number:** BAT497
**Presentation Title:** Silicon Consortium Project Electrochemistry of Silicon Electrodes
**Principal Investigator:** Christopher Johnson, Argonne National Laboratory

***Presenter***

Christopher Johnson, Argonne National Laboratory

***Reviewer Sample Size***

A total of four reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

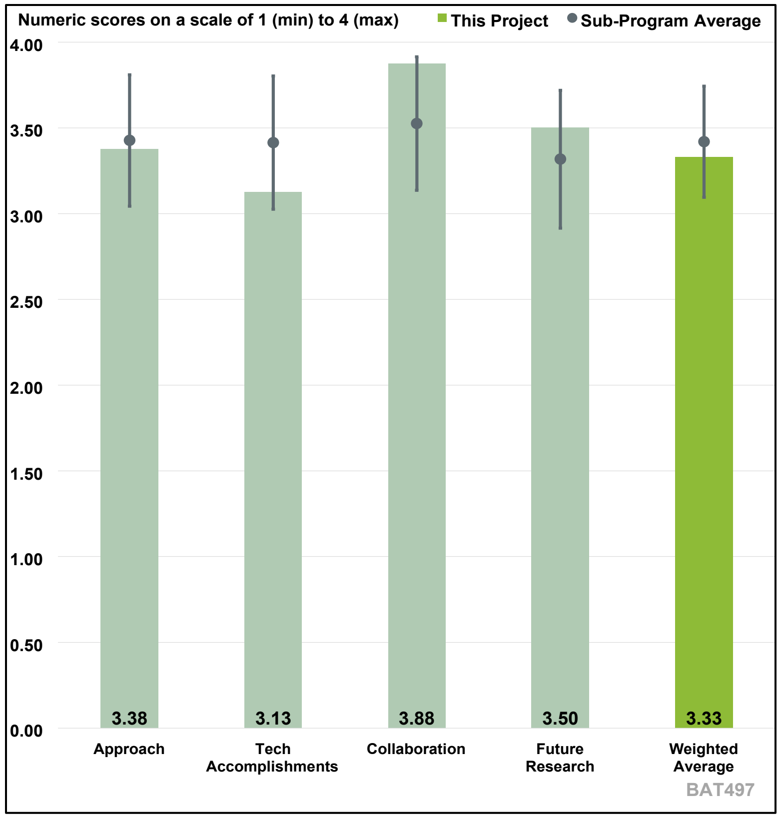


Figure 1-17. Presentation Number: BAT497 Presentation Title: Silicon Consortium Project Electrochemistry of Silicon Electrodes Principal Investigator: Christopher Johnson, Argonne National Laboratory

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer stated that the project is more academic oriented and focusing on fundamental studies.

**Reviewer 2**

The reviewer stated that silicon anodes remain an important focus for EV development. The reviewer believed this project is doing a good job of expanding analysis tools to better understand the degradation mechanisms of Si anodes. The reviewer thinks the robustness of the voltage hold method is unverified, which was pointed out in the prior year. The reviewer would like verification of the variables Qhold, Qrev, and Qirrev by recharging the cell and directly measuring Qirrev and Qrev. The reviewer would like to know if that has was done. The reviewer also would like to know how accurate the studies of electrolyte additives are in this setup, whether the cell flooded such that there is always massive excess electrolyte and additives, and ow this corresponds to larger, more EV-relevant cells.

**Reviewer 3**

The reviewer believed the calendar life is a complex parameter to study. The reviewer also believes that using three electrode cells opens up a new level of evaluating Vhold and developing the protocols to screen material is a useful process.

**Reviewer 4**

The reviewer commended the use of a three-tier approach for addressing the objective of identifying calendar life within a 15-month window. However, the reviewer felt that most of the discussion focused on the Tier 1 approach of a voltage hold and it was unclear how much evaluation was done using Tier 2 and Tier 3 methodologies. The reviewer understood that Tier 3 methodologies, which involve a 12-month test, may not have been available at the time, but the reviewer would appreciate knowing how the Tier 2 approach fared or whether it provided additional information over the Tier 1 approach. At minimum, it would be nice to know which tier was used in each test (i.e., machine learning used Tier X approach).

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer stated that many tests are being conducted in coin cells. Such cells are good for early-stage materials screening, but their performance is very different from large format cells, including in the area of gas generation and calendar life. The reviewer believed that with only 1 year left in the program, it is time to study those parameters in large format cells (i.e., 2-5Ah cells).

**Reviewer 2**

The reviewer believed that the project utilizes a wide range of electrochemical methods to characterize the cells. This work helps the research community in both developing the methods as well as in understanding them better.

**Reviewer 3**

The reviewer believed that screening protocols need to be continuously evaluated for robustness. They represent a useful tool but the tool should be consciously checked periodically to ensure it continues to apply. The evaluated materials continuously change with program evolution. Identifying that the SEI dissolves and reforms based on voltage, the reviewer would like to know if there have been any changes to the screen protocols based on that finding.

**Reviewer 4**

The reviewer believed the project team has developed some good insights into silicon-containing anodes by using mechanistic and electrochemical techniques. However, the true technical ‘achievements’ are unclear for the project and it is also unclear how those are tied to determining the final calendar cell life.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer believed the collaboration among team members is excellent.

**Reviewer 2**

The reviewer believed the work is well coordinated across the teams.

**Reviewer 3**

The reviewer believed that the collaboration with other national laboratories has been outstanding (including in having regular meetings and data sharing).

**Reviewer 4**

The reviewer believed that as for all of the silicon-anode consortium, the project maintains extensive collaboration between all the group members.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer was pleased to see pouch cells proposed for Si SEI study. The reviewer recommended ensuring that its capacity remains at Ampere-hour (Ah) level in order to represent real applications.

**Reviewer 2**

The reviewer stated that the planned future work appears interesting and useful.

**Reviewer 3**

The reviewer stated that predicting and validating SEI represents an excellent approach. The reviewer also stated that continued material evolution from different methods is technically sound.

**Reviewer 4**

This reviewer agrees with prior suggestions that future work needs to focus on the relationship between short-term and long-term testing needs. The reviewer believed that those tests are ongoing at this time, but it is unclear if the long-term tests will ultimately achieve the program targets.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer believed the project supports the overall VTO subprogram objectives. The reviewer stated that Si anode is a very promising candidate for high-energy EV batteries.

**Reviewer 2**

The reviewer stated that the work in the project strongly contributes to the development of Si anodes for EVs.

**Reviewer 3**

The reviewer stated that the program is very relevant to Batteries, Electrification and Energy Efficient Mobility Systems. The reviewer stated that this research is highly needed for progress in automotive industry.

**Reviewer 4**

The reviewer believed the project is highly relevant to the overall VTO subprogram objectives for analysis and battery areas.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer believed the resources are sufficient.

**Reviewer 2**

The reviewer believed the project seems appropriately resourced.

**Reviewer 3**

The reviewer believed that the funding for the project is sufficient.

**Reviewer 4**

The reviewer believed that the resources for this project appear sufficient to achieve the stated milestones.

**Presentation Number:** BAT498
**Presentation Title:** Silicon Consortium Project Next-Gen Materials for Silicon Anodes
**Principal Investigator:** Nathan Neale, National Renewable Energy Laboratory

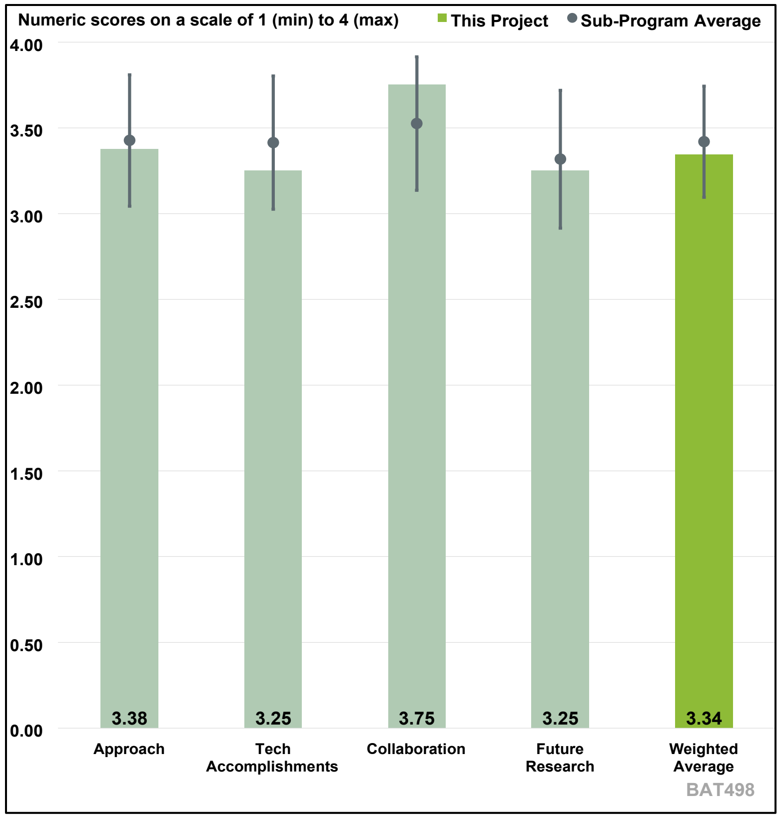


Figure 1-18. Presentation Number: BAT498 Presentation Title: Silicon Consortium Project Next-Gen Materials for Silicon Anodes Principal Investigator: Nathan Neale, National Renewable Energy Laboratory

***Presenter***

Nathan Neale, National Renewable Energy Laboratory

***Reviewer Sample Size***

A total of four reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer stated that the project is more academic oriented and is focusing on fundamental studies at small scales.

**Reviewer 2**

The reviewer believed that the structure of the silicon particles and the electrode design is crucial to create silicon anodes that will impact the next generation of EV. The reviewer also praised the project for investigating those areas.

**Reviewer 3**

The reviewer stated that the approach to systematically study the various combinations of Si particle structure, coatings, conductive materials while keeping the scalability of these methods is excellent.

**Reviewer 4**

The reviewer stated that this project addressed some key parameters that could affect battery performance of composite electrode. The reviewer believed the current work clearly demonstrated how different type of conductive carbon affects electrical and ionic conductivity of the resulting electrode as well as the Si utilization. However, no full cell testing results are provided at this time. Unlike the effect on conductive carbon effect, the effect on Si particle size was demonstrated with full cell testing results. The reviewer considered this work as well-designed. Lithium iron phosphate (LFP) was selected as the counter electrode to understand the Si particle size effect on cycle life and calendar life. The reviewer was optimistic that the optimal particle size in LFP//Si full cell can be translated to NMC//Si.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer stated that many tests are being conducted in coin cells. The reviewer opined that coin cells are good for early-stage materials screening, but their performance is very different from large format cells. Therefore, coin cells are not good tools to evaluate the effects of particle size, conductive additive (CA) and binders. For example, industrial CA is about 1%, and variations is at 0.1% level. The difference is hard to see based on laboratory-scale experiment.

**Reviewer 2**

The reviewer believed the project has provided useful and interesting results on carbon additives, binders, and Si particle size. All of this is essential to further improve the performance of Si anodes. The reviewer questioned the relevancy of conclusions due to the specific Si anode material used. If possible, the reviewer recommended that this should be benchmarked against commercial materials which have improved dramatically in the last few years.

**Reviewer 3**

The reviewer opined that deep dives into the mechanism by which improvements are observed is very insightful. The reviewer found it interesting that the project identified that smaller particles and RT14 works best.

**Reviewer 4**

The reviewer believed that there has been good progress in scaling up the composite electrode and enough amount of electrode film has been prepared and shared with collaborators. The reviewer would like to see more work around binder optimization in the future. The reviewer mentioned that PI's binder has some negative effect on cell performance compared to either polyacrylic acid (PAA) or polyvinylidene fluoride (PVDF). However, future plans on how to integrate different types of binder into this composite electrode are not clear.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer believed that the collaboration among team members is excellent.

**Reviewer 2**

The reviewer believed that the project teams are well connected and coordinated.

**Reviewer 3**

The reviewer believed that Si consortium maintains outstanding collaboration within the national laboratories.

**Reviewer 4**

The reviewer believed that this work greatly benefitted from collaboration within the project team across seven different national laboratories as well as the University of Maryland. It would be nice to have some collaboration with industry to gain some knowledge on what is needed to commercialize this material.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer was pleased at proposals of larger scale experiments critical to real applications. First-cycle efficiency needed to be greatly increased from 80% to 90% for real applications.

**Reviewer 2**

The reviewer believed that the future work is well detailed and relevant.

**Reviewer 3**

The reviewer believed that the observation of SEI dissolution and reformation based on voltage is an interesting finding in the Si consortium. How this finding impacts this program is unclear.

**Reviewer 4**

The reviewer believed that the project clearly defined the purpose for future work, such as, the continuous improvement on scaling up plasma enhanced chemical vapor deposition (PECVD) Si nano particle production and optimization of electrode composition to enable high loading and enhance Si utilization. However, it is unclear if the proposed solution will likely achieve the targets. The high surface area of conductive carbon indeed showed improved electrical and ionic conductivity, but also increased parasitic reaction which likely will have negative impact on cycle life and calendar life. The reviewer was not sure if the calendar life target can be achieved by optimizing the wt% of single-wall carbon nanotubes (SWNT). The reviewer stated that the binder plays an important role in Si anode due to its high-volume expansion during charging and discharging, more binder optimization seems to be needed to further work.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer believed the project supports the overall VTO subprogram objectives. The Si anode is a very promising approach for high-energy EV batteries.

**Reviewer 2**

The reviewer believed the project contributes toward better understanding of Si anode designs.

**Reviewer 3**

The reviewer believed the program is very interesting and relevant for electrification.

**Reviewer 4**

The reviewer agreed that this program clearly supports the overall VTO objectives, especially for batteries and materials subprogram.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer believed the resources are sufficient.

**Reviewer 2**

The reviewer believed the resources are in balance.

**Reviewer 3**

The reviewer believed the funding is sufficient for the program.

**Reviewer 4**

The reviewer believed that the resources are sufficient for the project to achieve the state milestone on time so far.

**Presentation Number:** BAT499
**Presentation Title:** Silicon Consortium Project: Mechanical Properties of Silicon Anodes
**Principal Investigator:** Katherine Harrison, National Renewable Energy Laboratory

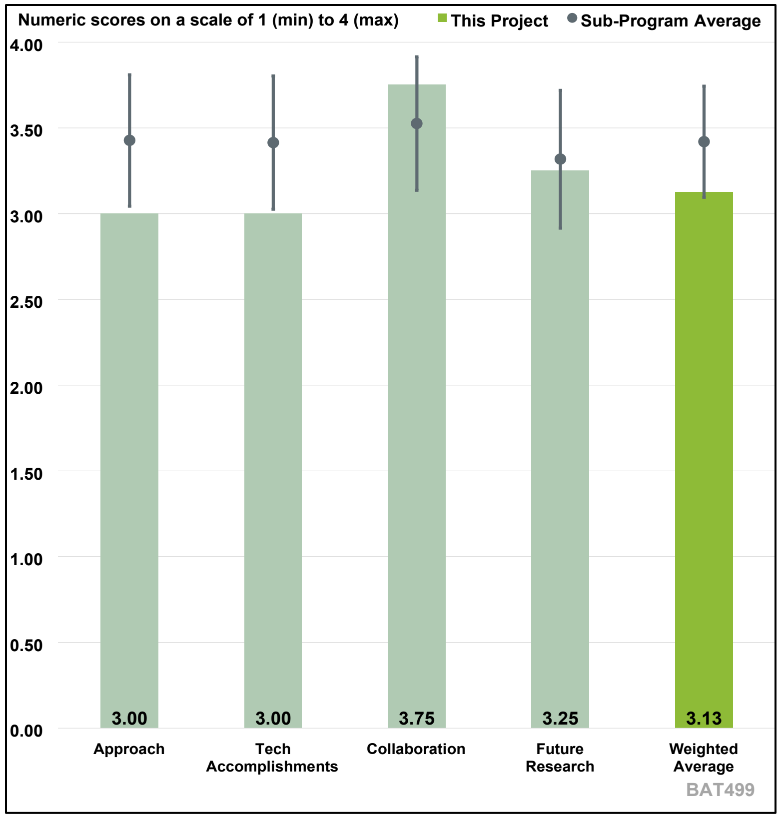


Figure 1-19. Presentation Number: BAT499 Presentation Title: Silicon Consortium Project: Mechanical Properties of Silicon Anodes Principal Investigator: Katherine Harrison, National Renewable Energy Laboratory

***Presenter***

Katharine Harrison, National Renewable Energy Laboratory

***Reviewer Sample Size***

A total of four reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer observed that the structure of the Si is key to improving its performance. This project made and characterized unique Si structures to help guide future development. It is not clear to the reviewer how applicable that is to commercial EVs because the methods are not easily scaled. The reviewer stated that the work on wrinkling and processing is useful for cell manufacturers.

**Reviewer 2**

The reviewer stated that the overall approach of the silicon consortium project (SCP) is quite specific and appears well-focused on the issue of calendar life for cells that achieve high specific energy and cycle life. The approach of the architectures thrust sub-project appears to be good, addressing most barriers. The approach is to identify different architecture routes to achieve the goals, and to try to evaluate whether architecture affects calendar life. However, it seems to the reviewer that the work is mostly focused on low-loading electrodes that will not lead to 375 Wh/kg cells. Also, there are several companies (Sila, Enovix, etc.) specializing in high-loading Si anodes, and the present work could be informed by their efforts. The reviewer was not convinced that the ‘architecture’ needs to be addressed on a priority basis, compared to alternate approaches like having a stronger current collector, changing stack pressure, etc.

**Reviewer 3**

The reviewer observed that this project took various approaches to resolve challenges presented by Si anode, including micro-patterning, deposition techniques, electrolyte formulation, and binder materials.

**Reviewer 4**

The reviewer stated that in this thrust, the project goal is to develop electrode architectures to enable high loading Si electrode and to understand how electrode architecture impacts calendar life. Several approaches had been proposed and tested, including: 1) increasing electrode porosity; 2) introduction of micropattern into the electrode to help electrolyte wettability and transport as well as stress relief of electrode; 3) using alternative anode current collector to reduce the stress etc. The reviewer noted that although many of those approaches showed impact on reducing the mechanical stress (e.g., less wrinkle of the electrode or less pulverization of electrode), none of them seems to be able to improve cycle life so far. The reviewer stated that other approaches focused on understanding at the material level should be also considered in the future study.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer noted that the project is testing some interesting architectures which would be leading to a better understanding of Si structures that can be commercially viable.

**Reviewer 2**

The reviewer stated that the results of the architecture thrust appear to be good. There are specific ideas that are being explored to deal with the volume change, such as porosity engineering at different length scales. It seems to the reviewer that most results are on low-loading electrodes, and the performance even at low loading is not that good. Hence, while some lessons are being learned, it’s unclear to the reviewer how well they will apply to the best high-loading electrodes. Also, on the key point of how architecture affects calendar life, some work has been reported, but it does not appear definitive. The reviewer observed that most battery experts would consider architecture alone as less important to calendar life than numerous other factors (e.g., active material design, electrode formulation, etc.) so it is important to have a well-defined case to assess whether architecture affects calendar life.

**Reviewer 3**

The reviewer noted that the project achieved some advances in understanding about Si electrode fabrication. But when compared with the commercialized Si-based LIBs, this project is not at the forefront of the technology. The reviewer noted that the performances are still below the DOE goal. The reviewer suggested rethinking approaches, especially the electrolyte design philosophy.

**Reviewer 4**

The reviewer stated that the current project figured out how to manipulate electrode porosity by either from Si particle size control and composition of the resulting slurry or from controlling electrode architecture via laser ablation. Those approaches are pretty novel. It is valuable to accumulate the knowledge and understand their impact on battery performance from an electrode engineering perspective. However, the reviewer has not seen any calendar life data generated by those electrodes from this work although those approaches do not seem to improve the cycle life. The reviewer would recommend starting calendar aging test as soon as possible.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer observed that the project is well-coordinated.

**Reviewer 2**

The reviewer observed that it appears the team is well-integrated within the large SCP.

**Reviewer 3**

The reviewer stated that the collaborations are outstanding.

**Reviewer 4**

The reviewer observed that this project involves multiple national laboratories with different cross functional teams. All teams work on the same coherent goal from different perspectives, which the reviewer praised. However, it seems to the reviewer that the project lacks input from industry. The reviewer recommended evaluating this novel approach from operation cost perspective.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer stated that the proposed research is relevant. The reviewer would like to understand how commercially scalable the structures are.

**Reviewer 2**

The reviewer observed that overall, the future research on the project is to continue along the current directions. The reviewer considered it important to move as quickly as possible to a high-loading electrode to evaluate concepts in that format. Evaluating concepts with low-loading electrodes may have little relevance to solving problems with higher loadings. The reviewer also considers it important to receive more specifics on future architecture work and on how it will help address the calendar life.

**Reviewer 3**

The reviewer stated that the proposed future direction seems reasonable.

**Reviewer 4**

The reviewer understood that the next step is to integrate the successful mitigation into pouch cells. Hopefully, the combination of those mitigations could result in a better outcome. The reviewer remarked that is a certainly good approach and the reviewer thinks that it will definitely mitigate the mechanical stress of the cell when using high Si percentage with high electrode loadings. However, the reviewer would like to see new approaches to be proposed as well. For example, porosity, micropatterning and current collector architecture could mitigate the wrinkling effect, those solutions often reduce cell energy density. The reviewer asked if there is any other way to mitigate the adverse effect from volume expansion of Si anode without sacrificing the overall energy density.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer stated that the work is contributing toward fundamental understanding of Si anodes.

**Reviewer 2**

The reviewer stated that the present work is relevant to the Batteries program.

**Reviewer 3**

The reviewer stated that the project is highly relevant.

**Reviewer 4**

The reviewer stated that this project directly supports the overall VTO subprogram objectives, especially for Materials, Batteries and Energy Efficient Mobility Systems.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer stated that the resources are appropriate.

**Reviewer 2**

The reviewer stated that the resources appear sufficient.

**Reviewer 3**

The reviewer stated that the resources allocated are sufficient.

**Reviewer 4**

The reviewer remarked that this project seems to have enough resources. The project received enough materials for evaluation not only at material level but also at pouch cell level. The team possesses adequate analytical tools to understand the mechanical aspect of the electrode. The researchers also have access to the modeling team to provide explanation on the high stress phenomena observed for high-loading Si anode electrodes.

**Presentation Number:** BAT501
**Presentation Title:** Integrated Modeling and Machine Learning of Solid-Electrolyte Interface Reactions of the Si Anode
**Principal Investigator:** Kristin Persson, Lawrence Berkeley National Laboratory

***Presenter***

Kristin Persson, Lawrence Berkeley National Laboratory

***Reviewer Sample Size***

A total of four reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 75% of reviewers felt that the resources were sufficient, 25% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

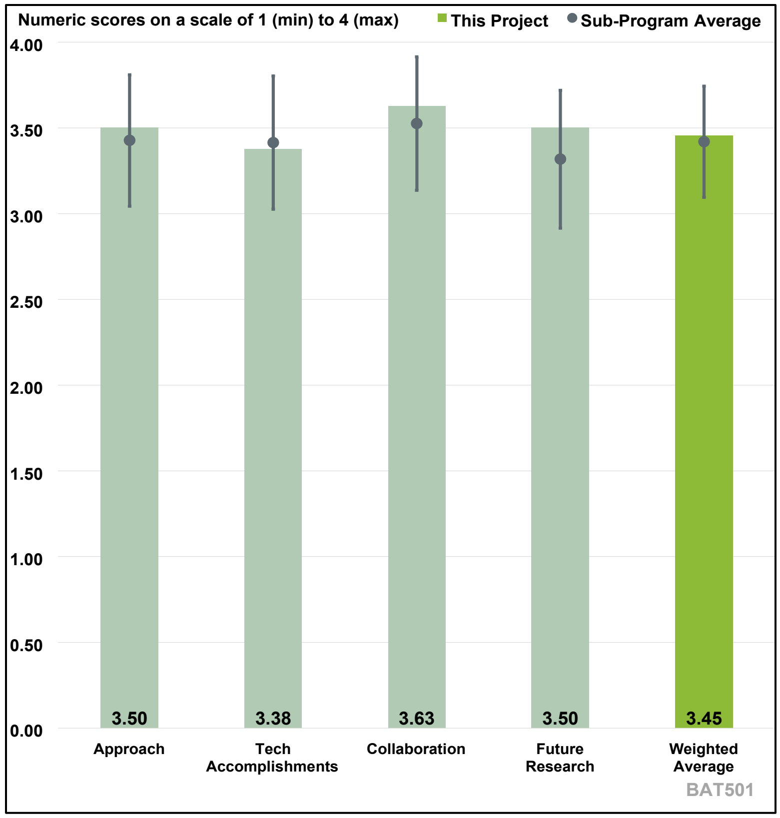


Figure 1-20. Presentation Number: BAT501 Presentation Title: Integrated Modeling and Machine Learning of Solid-Electrolyte Interface Reactions of the Si Anode Principal Investigator: Kristin Persson, Lawrence Berkeley National Laboratory

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer stated that the interaction between electrolyte and Si anodes is key to making them commercially viable. The reviewer added that this project explores such interaction with well-designed experiments. The reviewer inquired if the cells are flooded and if so, if the study of additives in commercial, non-flooded cells can still be considered accurate.

**Reviewer 2**

The reviewer stated that the project uses an ambitious and impressive approach to improve understanding of the fundamental mechanisms of SEI formation on anode materials. The reviewer found the chemical complexity and number of pathways as truly impressive. The reviewer also sees a connection to experiments through the voltage hold experiments.

**Reviewer 3**

The reviewer stated that the overall approach to 'characterize the paths and mechanisms that form key SEI species' using atomistic simulations/machine learning, continuum modeling, and experimental modeling is comprehensive and addresses the project goal of assisting team members with understanding on SEI evolution affects silicon-anode calendar life.

**Reviewer 4**

The reviewer stated that it is extremely challenging to develop atomistic simulations to monitor/modeling SEI growth. The reviewer considered the approach took in this project as quite novel.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer stated that the salt/solvent/Si interactions are fundamentally important to make Si anodes a success. The reviewer added that this program is contributing valuable information toward understanding them.

**Reviewer 2**

The reviewer considered the technical accomplishments to be impressive. To the reviewer, it appears to be first-of-a-kind work that heavily invests in new methods development, which is a valuable part of the Batteries program, and highly relevant to the chemical complexity of SEI formation. The reviewer stated that the work provides fundamental insights on how SEI formation on Si can differ from that on graphite (i.e., differences in inner vs. outer SEI properties as a result of the voltage at which the electrode operates), which in turn can help with insight on calendar life. The reviewer saw some limitations due to the complexity of the chemical mechanisms and time scales for the atomistic reaction network which puts a limit on the number of electrolyte formulations that can be studied. There also could be limits on how much detailed chemistry of the Si surface can be included in the reaction network.

**Reviewer 3**

The reviewer praised the team on its great technical work in identifying an elementary mechanism for $PF_5$ decomposition and prediction tools for SEI growth and trends in its continuum modeling.

**Reviewer 4**

The reviewer stated that so far, the model developed in this project is able to reproduce the Peled model without any fitted parameters. More importantly, it can also predict SEI evolution at both large time and length scale which could be really valuable. Currently, SEI evolution was done at an electrochemical potential similar to a constant current discharging. The reviewer would find it interesting if it were investigated how SEI evolution could be altered at a certain constant potential. It could be really valuable to understand how to design and optimize formation protocol when electrolyte formulation contains several SEI forming additives.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer stated that the project is well coordinated.

**Reviewer 2**

The reviewer stated that the work with NREL in particular is impressive. The reviewer stated that it must have been a major effort to bring the atomistic reaction network results into a continuum model.

**Reviewer 3**

The reviewer stated that the collaboration for the project is outstanding—the team is taking research results from all consortium members and integrating into the machine learning algorithms.

**Reviewer 4**

The reviewer stated that the model developed in this project has been used to understand promising electrolyte candidates developed by other projects, this received praise from the reviewer.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer stated that the proposed future work is well documented and relevant.

**Reviewer 2**

The reviewer stated that the future work looks excellent. The reviewer remarked that some additional focus on calendar life prediction and improvement could be added.

**Reviewer 3**

The reviewer stated that the team's proposed future research is extensive and addresses the consortium's needs. The reviewer advised the PI to ensure the project team focus on necessary and relevant tasks, especially referencing the proposed task entitled 'create chemically complex SEI model framework bridging length-/time-scales'.

**Reviewer 4**

The reviewer stated that all of the proposed future directions seem to be very relevant. In particular, the reviewer was very interested in the future work to predict degradation mechanism in novel chemistries where there is not much reported literature available.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer restated that the project is highly relevant.

**Reviewer 2**

The reviewer stated that the work is relevant to Batteries.

**Reviewer 3**

The reviewer stated that the project supports VTO subprogram objectives of Analysis and Batteries.

**Reviewer 4**

The reviewer stated that this work is relevant in support of the overall VTO subprogram. The reviewer remarked that if the model can be successfully developed, it can significantly accelerate the battery material development process, and directly benefit Batteries, Electrification, and Materials subprograms.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer stated that the resources are sufficient.

**Reviewer 2**

The reviewer commented that the project budget was cut for the past year. The context on this decision was not clear. The reviewer stated that the funds are probably insufficient to support a heavy workload from LBNL and NREL but may be sufficient in case of a reduced scope of work.

**Reviewer 3**

The reviewer commented that the resources of the project are sufficient for achieving the stated milestones in a timely fashion.

**Reviewer 4**

The reviewer stated that the project seems to have access to the high-performance computing power as well as the electrolyte expert with deep mechanistic understanding of electrolyte degradation and it appears to have sufficient resources to achieve the milestone on time.

**Presentation Number:** BAT523
**Presentation Title:** Development of Long Life Lithium and sulfurized polyacrylonitrile (SPAN) Cells
**Principal Investigator:** Ping Liu, University of California-San Diego

***Presenter***

Ping Liu, University of California-San Diego

***Reviewer Sample Size***

A total of three reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 67% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 33% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

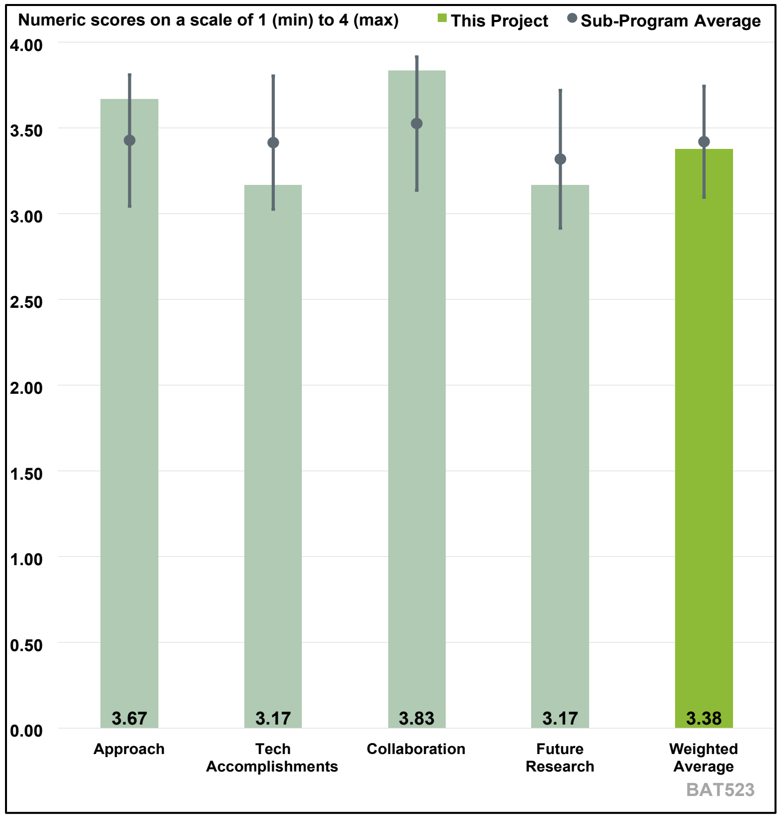


Figure 1-21. Presentation Number: BAT523 Presentation Title: Development of Long Life Lithium and sulfurized polyacrylonitrile (SPAN) Cells Principal Investigator: Ping Liu, University of California-San Diego

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer stated that the PI has concentrated on addressing the primary technical barrier of the sulfur—sulfurized polyacrylonitrile (S-SPAN) cathode material—its capacity limitation to around 600 mAh/g. The reviewer observed that they aimed to understand the reaction mechanism of S-SPAN and proposed a material structure and potential approach to enhance its specific capacity. The resulting CS-SPAN, based on a saturated short-chain sulfur environment, demonstrated promising performance, marking significant progress. The reviewer remarked that further detailed investigation into the reaction mechanism is needed.

**Reviewer 2**

The reviewer stated that the project utilized multiscale characterization tools to understand the structure of SPAN and to further develop high-capacity SPAN cathode to increase the capacity and stability. The developed new cathode shows the promise to achieve 300-350 Wh/kg Li-S batteries. The reviewer remarked that the role of electrolyte needs more understanding.

**Reviewer 3**

The reviewer stated that the project's approach for addressing technical barriers in next-generation LiS battery technology is both innovative and commendable. By focusing on fundamental breakthroughs in controlling sulfur electrochemical reactions, the discoveries set a solid foundation for substantial advancements. The integration of materials and cell-level discoveries is particularly noteworthy, as it ensures rapid incorporation and validation of the latest research findings, leading to more realistic and practical applications. The reviewer remarked that leveraging materials from other DOE programs and utilizing state-of-the-art DOE facilities and industry to understand and prevent degradation is a strategic and efficient use of resources. The emphasis on multi-disciplinary approaches and enhancing collaborations between national laboratories, universities, and industry highlights a holistic and synergistic strategy. This comprehensive and well-coordinated effort is likely to yield highly productive results, driving significant progress in the development of high-energy, low-cost LiS based batteries. The reviewer stated that the project particularly focuses on understanding the fundamentals of SPAN chemical transformation. SPAN is one of the few sulfur composites demonstrating excellent cycling performance in Li-S batteries. This approach and understanding can significantly contribute to designing better sulfur composites, enhancing battery performance and stability.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer stated that the PI demonstrated an increase in the specific capacity of S-SPAN, a successful accomplishment for the budget year. In addition to enhancing the material's performance, the PI conducted thorough analyses using Mass Spectroscopy and XPS to identify the reaction products and the chemical environment in the active material. A hypothesis was proposed regarding the formation of N-S bonds. The reviewer recommended further electrochemical analysis.

**Reviewer 2**

The reviewer commented that multiscale characterization tools and modeling were used to clearly understand the structure of the SPAN and the extra capacity beyond the theoretical value. The reviewer observed that loading needs improvement, as may the E/S ratio, which is not provided.

**Reviewer 3**

The reviewer commented that during this period, two major accomplishments stand out. First, the team has provided a detailed characterization of SPAN materials' performance as a Li-S cell cathode. This involved extensive testing and analysis, demonstrating SPAN's exceptional cycling stability, capacity retention, and overall efficiency in Li-S batteries. Second, the team has gained a fundamental understanding of SPAN chemistry transformation. Through advanced electrochemical and spectroscopic techniques, the team has elucidated the underlying mechanisms of SPAN's chemical changes during battery operation. The reviewer stated that this insight is crucial for optimizing SPAN's structure and composition, paving the way for the development of superior sulfur composites for high-performance batteries.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer commented that the collaboration among Battery500 team members has been proven very productive and effective.

**Reviewer 2**

The reviewer commented that the collaboration with other teams at the Battery500 Consortium on modeling and characterization as well as cell integration are well demonstrated to resolve the technical barriers.

**Reviewer 3**

The reviewer commented that the project team demonstrates excellent collaboration within the Battery500 team, addressing critical issues in battery technology through a diverse network of partners. Idaho National Laboratory is scaling up SPAN synthesis, while multiple universities, including the University of Maryland, Pennsylvania State University, and the University of Pittsburgh, supply standard SPAN electrodes. Pacific Northwest National Laboratory focuses on electrolyte studies, and Stanford University evaluates these electrolytes. Brookhaven National Laboratory provides insights into mechanisms using in-situ X-ray diffraction (XRD) and atomic PDF, Texas A&M University conducts computational studies, and GM contributes to pouch cell fabrication, showcasing a well-coordinated, multidisciplinary effort.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer stated that the proposed future works were good. But the reviewer suggested that the PI spend effort to better understand the mechanism, particularly the S-S- bond formation during the charging process.

**Reviewer 2**

The reviewer stated that the increase of sulfur loading, the reduction in electrolyte/sulfur ratio and a demonstration of pouch cell are planned for the next year.

**Reviewer 3**

The reviewer stated that the proposed future work effectively addresses the immediate challenges facing SPAN materials. By focusing on optimizing electrode compositions, enhancing binder interactions, and developing suitable electrolytes, the research aims to improve SPAN stability and performance. Additionally, fabricating SPAN pouch cells will translate laboratory-scale findings into practical applications.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer stated that the research on S-SPAN was very relevant to the VTO goal of developing high-energy-density battery systems.

**Reviewer 2**

The reviewer stated that the project is developing a high-capacity SPAN cathode alternative to element sulfur cathode to demonstrate 300-350 Wh/kg Li-S batteries, offering improved energy density, lower cost and better sustainability than today’s Li-ion batteries.

**Reviewer 3**

The reviewer stated that the SPAN is one of the few sulfur composites that offer excellent cycling stability in batteries. Understanding the fundamental properties and chemical transformations of SPAN is crucial to advancing Li-S battery technology, as it provides insights necessary for optimizing performance, enhancing durability, and achieving higher capacity in practical applications.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer stated that the PI and collaborators can access more than sufficient resources to conduct the proposed research.

**Reviewer 2**

The reviewer stated that the project has sufficient resources on the synthesis of SPAN cathode, characterization and modeling from Battery500 Consortium team.

**Reviewer 3**

The reviewer stated that the overall resources for the Battery500 program appear sufficient, supporting its ambitious goals.

**Presentation Number:** BAT524
**Presentation Title:** Advanced Electrolytes for Lithium Metal Batteries
**Principal Investigator:** Chunsheng Wang, University of Maryland

***Presenter***

Chunsheng Wang, University of Maryland

***Reviewer Sample Size***

A total of three reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

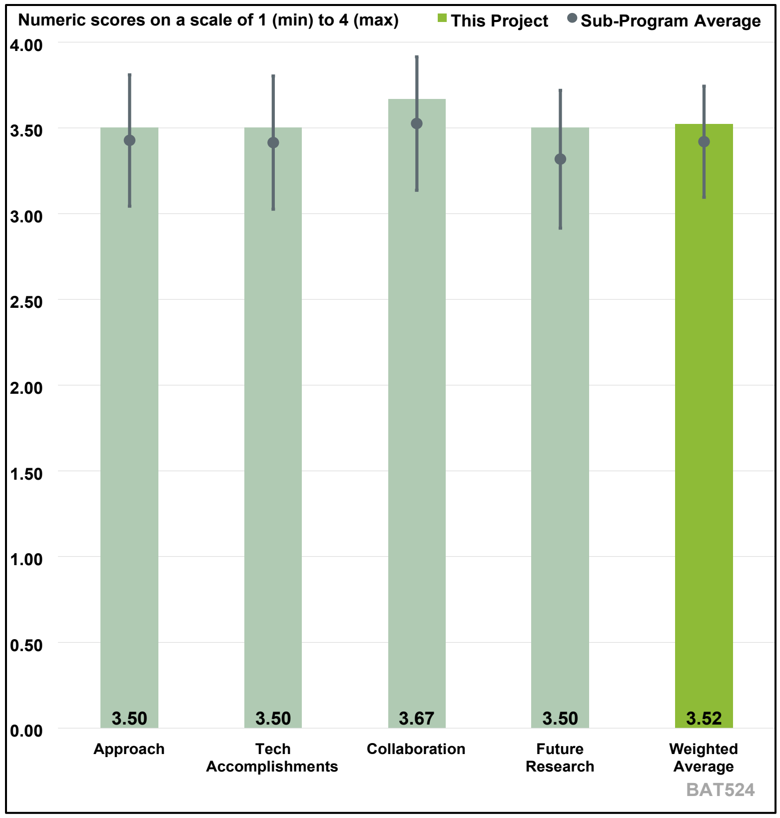


Figure 1-22. Presentation Number: BAT524 Presentation Title: Advanced Electrolytes for Lithium Metal Batteries Principal Investigator: Chunsheng Wang, University of Maryland

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer stated that this project on all-anion electrolyte and weak solvation electrolyte has provided preliminary evidence demonstrating that LiF-rich SEI and CEI, through promoting anion/additives decomposition and suppressing solvent degradation, could stabilize Li anodes and NMC811/SPAN cathodes. Studies on two types of all-anion electrolytes for Li||SPAN cells were conducted, using 0.5C and 1C rates respectively for the two cells with different loading (Slides 16 & 17). The reviewer remarked that it might be helpful to provide data with the same current rate for the cells with the different loading and/or different current rates for the cells with the same loading.

**Reviewer 2**

The reviewer commented that this project was difficult to review because of insufficient information on developments. It appears that the goal is to improve cell life and coulombic efficiency with electrolyte additives and design. The reviewer was unable to ascertain the systematic development and its understanding. The ionic liquid was not specified, and because (except for some Li carboborates) there are no ionic liquids so this must be Li+ ionic liquid mixture. There was no discussion on costs with Li. Since the research direction and the reason for the choices are unclear, the reviewer believed that cost is a fair question.

**Reviewer 3**

The reviewer stated that the research team addresses the challenge of developing high-energy-density Li-metal batteries through innovative electrolyte design. The testing conditions are highly relevant to practical applications, including high cathode loading, low N/P ratio, and lean electrolyte. The reviewer commented that the team tackles the challenge from a fundamental perspective, incorporating molecular design, leveraging experience from other DOE-supported programs, and closely collaborating with other U.S. institutions using multidisciplinary approaches. In its electrolyte design, the team employs two primary technical approaches: using a TFSI-derived solvent and a weak solvating solvent, dibutyl ether. Both strategies facilitate the decomposition of anions or anion-like molecular motifs at the interface, forming robust and stable interphases on the Li-metal anode. The reviewer remarked that based on the set milestones and current achievements, the project is well designed, and the timeline is reasonably planned.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer stated that the coulombic efficiency appears higher for higher capacity, but there seems to be no discussion on the reasons for this (Slide 11).

**Reviewer 2**

The reviewer remarked that there were a lot of good results shown. Coulombic efficiencies were improved through electrolyte design. However, the reviewer was unable to develop an understanding of what actually happened and what was learnt from it. The reviewer observed that the total pouch cell capacitance is good, and the 5C cycle rate result was astounding. The improvement of the Li transference number correlates to high cycle rate performance improvement. However, the reviewer was unable to see what was learned – only how well the best cell performed.

**Reviewer 3**

The reviewer remarked that the research team's novel electrolyte systems have enabled significant technical progress. Various coin cells and pouch cells, including those at the hundreds of mAh level, using different high-energy battery chemistries such as NMC||Li and SPAN||Li, have been tested and show performance at or above the state-of-the-art. The testing conditions consistently feature high cathode loading and a low N/P ratio, with some tests even utilizing zero N/P (anode-less) configurations. Lean electrolyte is implemented in some pouch cell tests, though it is likely not used for coin cell tests due to reproducibility issues. The reviewer stated that overall, technical progress is in line with, or even ahead of, the project plan.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer remarked that the research group is gaining a lot of understanding of the electrolyte physics and chemistry from Brookhaven and ARL, and clearly utilizes SAFT for high quality electrode and pouch cells.

**Reviewer 2**

The reviewer remarked that the research team collaborates with national laboratories (BNL and Army Research Laboratory), universities (UC San Diego), and industry (SAFT). The reviewer stated that the collaboration is comprehensive and synergistic.

**Reviewer 3**

There were no collaborations noted.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer stated that one of the targets for the proposed future research is to achieve Li CE: greater than 99.7% and high-loading NMC811 CE: greater than 99.9%. The reviewer suggested analyzing which of the two CE’s is more important for cell life to address key challenges, although improving both the CE’s is beneficial.

**Reviewer 2**

The reviewer was favorably impressed to see the electrolyte formulations on high NMC loaded pouch cells and Li-SPAN batteries for high-energy-density cells. The reviewer considered this a logical progression.

**Reviewer 3**

The reviewer stated that the research team has proposed to further address the challenges in Li||NMC811 and Li||SPAN cell chemistries with a target of more harsh testing conditions.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer commented that while cost may be an issue in the future, the knowledge gained here will be valuable in developing high charge and discharge rate batteries for high power applications.

**Reviewer 2**

The reviewer commented that the project addresses the high-energy-density objective of VTO. It also pays some attention to the low-cost aspect.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer commented that current level of funding seems to support this work well.

**Reviewer 2**

The reviewer commented that the resources are sufficient to achieve the stated milestones in a timely fashion.

**Presentation Number:** BAT536
**Presentation Title:** Polyester-Based Block Copolymer Electrolytes for Lithium Metal Batteries
**Principal Investigator:** Nitash Balsara, Lawrence Berkeley National Laboratory

***Presenter***

Nitash Balsara, Lawrence Berkeley National Laboratory

***Reviewer Sample Size***

A total of three reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

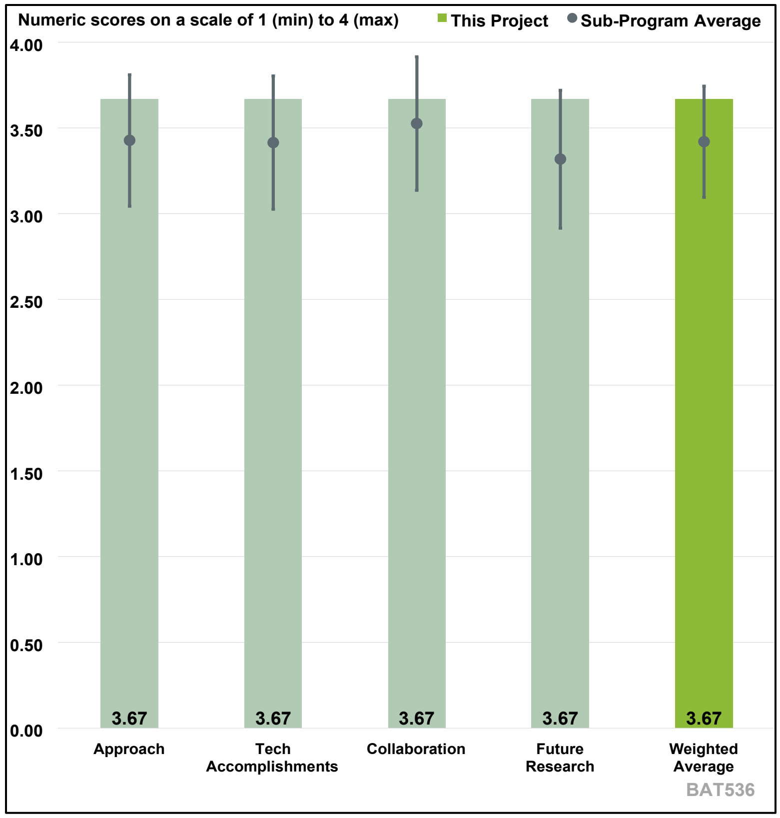


Figure 1-23. Presentation Number: BAT536 Presentation Title: Polyester-Based Block Copolymer Electrolytes for Lithium Metal Batteries Principal Investigator: Nitash Balsara, Lawrence Berkeley National Laboratory

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer agreed with the argument that polymers may be advantageous due to their deformability, which seems critical given the huge volume change of Li during cycling and the need to deform when non-uniform plating occurs. The reviewer remarked that the approach by Dr. Balsara is excellent as always. The reviewer would encourage this team to consider adopting quantitative milestones to demonstrate progress towards developing an optimal block copolymer electrolyte. The reviewer stated that the existing milestones are good but are all qualitative.

**Reviewer 2**

The reviewer stated that the project uses an excellent fundamental approach to understanding transport in polymer electrolytes. A new polymer poly(pentyl malonate) (PPM) electrolyte is also identified, but the most important part of the approach is that it is well-grounded in fundamental understanding and connected with several methods (modeling, tomography). The reviewer remarked that this type of foundational knowledge can help eventually overcome barriers and is an important part of the Batteries program.

**Reviewer 3**

The reviewer stated that this project employs fundamental electrochemical techniques and X-ray characterizations to address performance bottlenecks in solid-state cells. The research team has designed experiments to identify the factors limiting the current of polymer electrolytes and have improved these experiments by transitioning from Li||Li symmetric cells to LiIn||LiIn cells. The mechanism is analyzed by fitting experimental data to the Newman model. X-ray tomography has been used to characterize the solid-state cells, revealing void formation at the interface between Li and polymer. This information has been utilized to analyze impedance data, leading to the conclusion that the increase in interfacial impedance is due to the polymer moving away from the Li metal. To enhance the stability between the polymer electrolyte and Li-metal anode, a new polymer, poly(pentyl malonate) (PPM), has been synthesized and characterized. Based on the milestones and achievements, the project is well-designed with a reasonably planned timeline.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer agreed with the argument that polymers may be advantageous due to their deformability, which seems critical given the huge volume change of Li during cycling and the need to deform when non-uniform plating occurs. However, as expected and demonstrated here, the polymer must be designed to maintain contact with the highly mobile Li-metal surface or external pressure (sometimes significant external pressure) must be applied. The rapid growth in impedance in solid-state cells is a long-standing problem, since the earliest years of solid-state cell research. The reviewer wondered if a radically novel approach will be needed to address it.

**Reviewer 2**

The reviewer stated that the technical accomplishments are outstanding. The measurements of the limiting current are very valuable and capture much more of what is important about an electrolyte than simpler measures often used (e.g., ionic conductivity at an equilibrium concentration). A wider use of limiting current measurements, and methods for getting reliable results, is a major accomplishment for the project. Connecting these measurements with both transport theory / modeling and tomography enhances the fundamental understanding of limits in these systems. The reviewer suggested that information about the temperature at which each test was conducted could be added. The reviewer would also like to know if PPM have a higher limiting current than PEO polymer electrolyte at the same temperature. The reviewer noted that some information on temperature dependence of the transport properties would help understand whether the materials would only work in heated cells.

**Reviewer 3**

The reviewer stated that several technical accomplishments have been made: the team has identified the LiIn||LiIn symmetric cell as a reliable platform to measure the limiting current for polymer electrolytes. The excellent fitting results between the measured data and the predictions by the Newman model confirm the reliability of this method. The synthesized PPM polymer electrolyte has shown a higher limiting current than the conventional PEO polymer electrolyte, indicating better ion transport properties and/or better stability with Li. X-ray tomography characterization has revealed that the rise in impedance is mainly due to the polymer moving away from the Li metal, a new and inspirational finding. These accomplishments are crucial to understanding the bottlenecks in solid-state batteries and may provide opportunities to solve the problem, such as with the synthesized PPM polymer electrolyte. Overall, the technical progress is following or even surpassing the project plan.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer stated there was good collaboration with modelers at ANL and diagnosticians at SSRL.

**Reviewer 2**

The reviewer stated that results from collaborators are mentioned and considered valuable.

**Reviewer 3**

The reviewer stated that the PI collaborates with scientists from SSRL and ANL on both experiments and theories.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer stated that the research team has a very reasonable approach to future work, without any major issues.

**Reviewer 2**

The reviewer stated that the proposed future work builds on previous accomplishments and will extend it in important ways.

**Reviewer 3**

The reviewer stated that detailed future research plan is provided, both from experimental and theoretical aspects.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer stated that the project is highly relevant. Polymer electrolytes, however, need to be engineered to work at room temperature for automotive applications, which entails a very high degree of difficulty.

**Reviewer 2**

The reviewer stated that the work is relevant to the Batteries program.

**Reviewer 3**

The reviewer stated that the project is highly relevant to the VTO solid-state batteries subprogram. Solid-state batteries provide possible solutions to the high-energy safe batteries goals of DOE.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer stated that the project has made good use of resources.

**Reviewer 2**

The reviewer stated that the resources appear sufficient for the work.

**Reviewer 3**

The resources are sufficient for the project to achieve the stated milestones in a timely fashion.

**Presentation Number:** BAT538
**Presentation Title:** Ion conductive high Li+ transference number polymer composites for solid-state batteries
**Principal Investigator:** Bryan McCloskey, Lawrence Berkeley National Laboratory

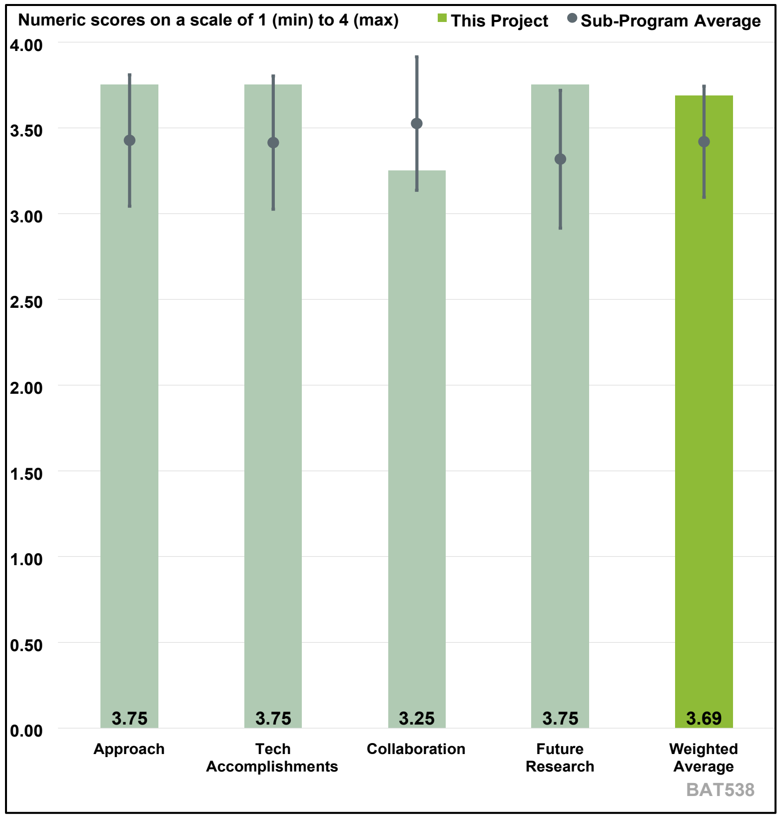


Figure 1-24. Presentation Number: BAT538 Presentation Title: Ion conductive high Li+ transference number polymer composites for solid-state batteries Principal Investigator: Bryan McCloskey, Lawrence Berkeley National Laboratory

### *Presenter*

Bryan McCloskey, Lawrence Berkeley National Laboratory

### *Reviewer Sample Size*

A total of two reviewers evaluated this project.

### *Project Relevance and Resources*

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

### *Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?*

**Reviewer 1**

The reviewer stated that the approach is novel, in that the initial work uses a viscous liquid electrolyte instead of a polymer. This simplifies processing, and it allows the investigators to focus on varying the type and size of the conductive particles. Extending this to polymer electrolytes in the second half of the project is critical. The reviewer remarked that it would be useful to include more modeling work. In light of the complexity of these systems, it might be difficult to define relevant atomic scale modeling at this point. However, some initial continuum modeling could allow the investigators to better interpret their experimental results.

**Reviewer 2**

The reviewer attended the talk, analyzed the talk slides in detail, asked questions, and then viewed a few of the quarterly reports on this project. Based on these review activities, the PI appears to understand the technical barriers very well and has designed the project and timeline well. The design of the polymer-inorganic composite systems is careful and grounded in sound fundamental principles, and the characterization techniques and choice of system materials and the specific range of compositions excellent. Based on the approach stated in the presentation and reports, it appears that the timeline makes sense and the PI's team is learning new aspects of polymer-inorganic composite design. The PI presented specific barriers to the approach such as the high interfacial impedance arising from the slow transport of Li+ from polymer to inorganic particle and back. The team wisely proceeded to vary the particle diameter and type and is starting to explore surface treatments to understand and then control this interface issue.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer stated that the milestones have been met, and future work appears to be on track.

**Reviewer 2**

The reviewer stated that the PI's group wisely chose to start with suspensions of liquid electrolytes (with chemical similarity to polymer electrolytes) and a wide range of inorganic particle chemistries and sizes. This, as stated, helps eliminate polymer processing variations in order to focus on the soft-hard electrolyte interfacial aspects. The PI's group has subsequently built an experimentally validated model that shows the importance of the soft-hard interface, and quantitatively shows the effects of particle size on overall composite electrolyte performance. The reviewer remarked that this has not been achieved before, and the quality of this work should help the entire community more predictively design and understand the composite electrolytes. This satisfies many of the key project goals and plan. The reviewer commented that the next step is to use this model and knowledge to build polymer-inorganic particle composites, and to investigate and employ surface treatments to improve soft-hard interfacial transport.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer commented that primary collaborations are relevant during the second half of this project (which was just starting at the time of this review). This makes sense, based on the proposed work. However, it is not possible to evaluate these efforts at this time.

**Reviewer 2**

The reviewer stated that the PI's team appears to be handling nearly all aspects of this project in-house, and calling on collaborators at LBNL to assist with specific knowledge and handling of inorganic conductor particles. The PI's group has deep experience in appropriate electrochemical methods and other transport characterization methods and is employing these across the group to great effect. The reviewer wondered if collaboration with surface science experts outside the group, in order to go to the next stage of the project, might be prudent to best improve the interfacial chemistry and effective contact between particles and polymeric electrolyte.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer commented that the overall success of the project hinges on extending this work to polymer matrices. This is ongoing, and it is likely that the results will be interesting and relevant. The results to date indicate that modeled circuit resistor 2 (R2) must be reduced to improve the conductivity of organic-inorganic composite electrolytes. A better mechanistic understanding of R2 is needed here. The reviewer hoped that the second half of this project will begin to explore some approaches for reducing R2.

**Reviewer 2**

The reviewer commented that the PI has chosen and described relevant goals and objectives to the VTO Battery subprogram. The goals of developing and understanding polymer-ceramic composite electrolytes and studying them by systematic electrochemical and other transport/property measurements are very relevant to advancing solid-state batteries, Li-metal batteries, and other subprogram goals. It is very likely that the results to date and the proposed future work (creating reproducible polymer-inorganic composites and understanding/improving interfacial properties and transport) will achieve the stated targets and help advance composite electrolytes on a sound and reliable foundation. This reviewer asked several questions of the PI during and after the AMR presentation, including: 1) what are the plans for the PI to do controlled surface treatment of ceramic particles and characterize these effects? (The PI answered that it is being done now following different chemical and physical procedures; 2) you are using large cells with low voltage, which is wise for avoiding nonlinear effects. However, 0.05V over 0.02 electrode distance means that the movement of ions are undergoing average oscillatory motions over angstrom distances (assuming mobility of 10^-7 $m^2$/V-s and 1kHz frequencies). How does this effect the quantitative values of impedances and what structures are averaged in the electrolytes? (The PI answered that this needs to be looked into); and 3) can you make particles intentionally with negative surface charge to ty to help Li+ interfacial transport? (The PI answered this is not known yet but will be tried.)

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer stated that organic-inorganic composite electrolytes have several practical advantages, and the successful development of these types of materials has the potential to be transformational. This project addresses high interfacial impedance between the two phases, which is one of the key problems that has been identified with these types of materials.

**Reviewer 2**

The reviewer remarked that the PIs have chosen and described relevant goals and objectives to the Battery subprogram of VTO. The goals of developing and understanding new polymer-ceramic composite electrolytes are highly relevant to advancing solid-state batteries, Li-metal batteries, and other subprogram goals. The reviewer referenced prior comments.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer stated that the resources needed for this project are well-defined. For the work date, this project focuses on electrochemical characterization. Processing capabilities are important for the future work, and the collaborators bring important expertise in that area.

**Reviewer 2**

The reviewer stated that the PI has sufficient resources (both in terms of funding and laboratory manpower infrastructure) to conduct this work and achieve the stated milestones. The synthetic and materials formulation abilities/expertise/experience and the materials analysis capabilities/expertise are very well-matched to this project and sufficient to achieve the project objectives.

**Presentation Number:** BAT539
**Presentation Title:** 3D Printing of All-Solid-State Lithium Batteries
**Principal Investigator:** Jianchao Ye, Lawrence Livermore National Laboratory

***Presenter***

Jianchao Ye, Lawrence Livermore National Laboratory

***Reviewer Sample Size***

A total of three reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

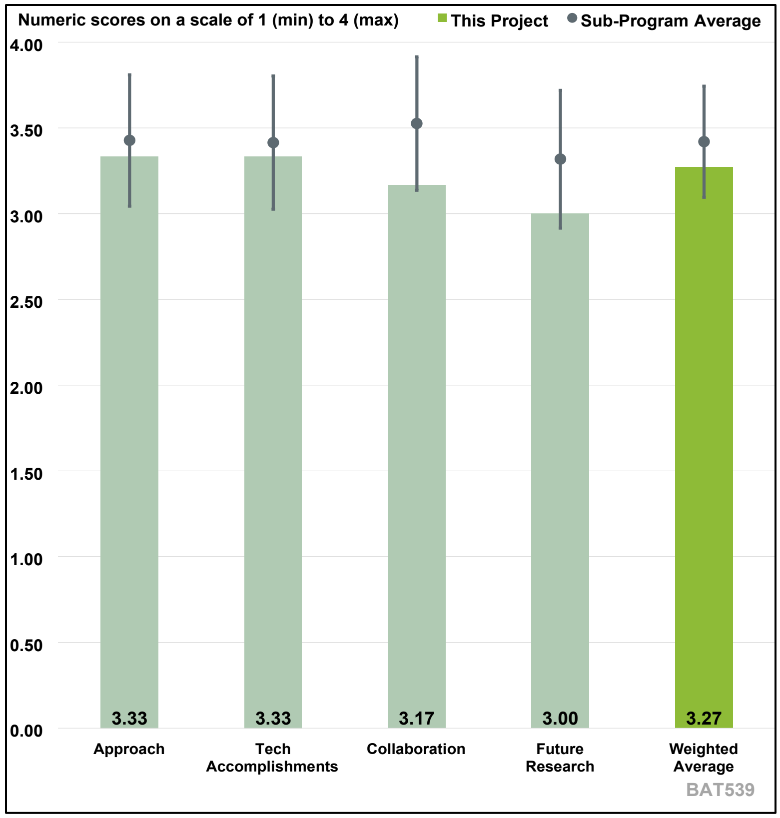


Figure 1-25. Presentation Number: BAT539 Presentation Title: 3D Printing of All-Solid-State Lithium Batteries Principal Investigator: Jianchao Ye, Lawrence Livermore National Laboratory

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer stated that after a two-year study, the team thinks that composite polymer electrolyte (CPE) approach is suitable for 3D printing solid-state batteries (SSBs) due to issues of co-sintering between the solid electrolyte and the cathode. Therefore, the team demonstrated the cell performances via CPE approach. The reviewer was pleased to see the variation and the optimization of 3D printing geometries can help improve the battery performances especially for high-mass loading cells. However, in Slide 14, the labeling is not clear to the reviewer (e.g., it is unclear what the label 200N1L1X stands for). In addition, in Slide 16 and 17, the same labeling exists in the right figures. The reviewer remarked that the presenter should highlight the direction or principles of designing geometries.

**Reviewer 2**

The reviewer stated that 3D printing can enhance the reaction kinetics, but cannot solve the intrinsic challenges of solid-state batteries, such as Li dendrite growth, $LiCoO_2$/LLZO (lithium lanthanum zirconium oxide) reaction during sintering.

**Reviewer 3**

The reviewer remarked that the PI and team have made substantial progress addressing and mitigating several technical challenges associated with 3D printing method to develop solid-state polymer composite batteries. The main highlights and comments are: 1) Co-sintering of lithium lanthanum tantalum zirconate (LLZTO) with $LiCoO_2$ cathodes was clearly a no-go. The reviewer thinks this approach should never have been followed given so many earlier reports that cobalt diffusion is one of the issues. Sintering free approach for CPE seemed the right one. 2) The polymer composite electrolyte design, although complex, seems to be working with 3D printing approach. (The reviewer will highlight the complexities in the next section.) 3) 3D printing approach allows higher mass loading. The reviewer commended the PI and team for 3D printed device results with planar 2D for the same CPE and cathode [LFP]).

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer noted that the team completed the work as planned although the results are not as good as expected. 3D printing SSBs are still at early stage and needs more efforts in the future.

**Reviewer 2**

The reviewer inquired why cobalt-doped LLZTO has a low electronic conductivity than pristine LLZTO. (The reviewer expected it should have a high electronic conductivity.) The reviewer also inquired about the particle size of LLZTO filled into SPE and whether LLZTO particles are uniformed distributed into the SPE matrix. The reviewer also inquired why the mechanical property of SPE increased with content of FEC in SPE and what the stability window of SPE is. The reviewer asked if SPE can support NMC811 cathode.

**Reviewer 3**

The reviewer remarked that the CPE design includes three different kinds of polymers based on the functionality and properties necessary for a solid electrolyte. In addition, as for Li-ion salt the CPE has LiTFSI and 7 wt% LLZTO plus 1-5 wt% FEC added for enhancing interfacial stability and to facilitate polymerization (Slide 11) 1). The two added salts have different ion-transport properties. LiTFSI is solvated in the polymer matrix and LLZTO is a single ion conductor. It would be worth investigating their contribution to the total conductivity and the mechanism of ion transport behavior in such a complex matrix. 2). Long term stability of FEC: In-depth studies need to be done to further quantify the role of FEC towards performance improvements.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer stated that the team needs more collaboration with other teams/organizations (e.g., in the selection of composite polymer electrolytes).

**Reviewer 2**

The reviewer stated that no simulation work from collaborators was presented.

**Reviewer 3**

The reviewer remarked that there was good internal collaboration. The reviewer would encourage collaboration with external institutions. This can be done at the unfunded level, since many groups would like to leverage the capabilities developed at the PI laboratory. Collaboration with partners having advanced characterization capability, X-ray synchrotron for operando studies among other things would be valuable.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer stated that the team needs to collaborate with other laboratories. The battery materials optimization should not be the focus in this project, which can be collected from other laboratories. More efforts should be put on the materials development for 3D printing, such as the ink recipes as the presenter proposed and the patterns/structure design. In particular, the structure design should be guided by modeling.

**Reviewer 2**

The reviewer remarked that the PI has identified the future work.

**Reviewer 3**

The reviewer would like to know if the PI and team have plans to integrate other cathode chemistries beyond LFP in their 3D printing approach.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer remarked that the project supports VTO Batteries subprogram.

**Reviewer 2**

The reviewer remarked that the project supports the VTO objective.

**Reviewer 3**

The reviewer remarked that the project supports the VTO battery development goal of attaining 500 Wh/Kg and 750 Wh/L. This project advances scalable approach for fabricating solid-state batteries by demonstrating 3D printing method.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer stated that the resources are enough to perform the work in this project well and in a timely manner.

**Reviewer 2**

The reviewer stated that the resources are sufficient for the project to achieve the stated milestones in a timely fashion.

**Reviewer 3**

The reviewer stated that the resources are adequate. The PI and team are successfully leveraging the outstanding modeling capabilities in the sister group.

**Presentation Number:** BAT540
**Presentation Title:** Synthesis of Composite Electrolytes with Integrated Interface Design
**Principal Investigator:** Sanja Tepavcevic, Argonne National Laboratory

***Presenter***

Sanja Tepavcevic, Argonne National Laboratory

***Reviewer Sample Size***

A total of three reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

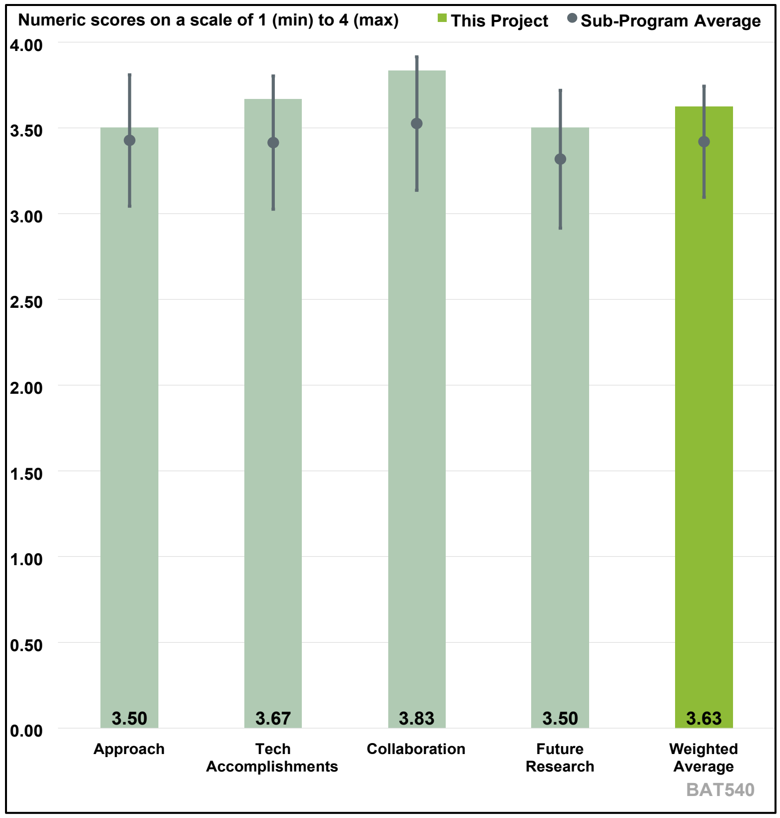


Figure 1-26. Presentation Number: BAT540 Presentation Title: Synthesis of Composite Electrolytes with Integrated Interface Design Principal Investigator: Sanja Tepavcevic, Argonne National Laboratory

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer stated that recent progress in this project is focused on understanding and improving interfacial properties. This is a critical issue that must be solved to implement these types of materials. The nanofiber architectures being explored in this project are a promising direction. These are complex structures, with a variety of technical barriers. Since a number of problems need to be solved, the reviewer recommended making sure that significant attention is focused on specific issues related to the nanofiber architectures.

**Reviewer 2**

The reviewer stated that the project approach is a viable method to achieve processable electrolytes that show promise in achieving the ion transport kinetics necessary for practical applications. An outstanding challenge is how these composites will interface with desirable cathode chemistries and Li-metal anodes.

**Reviewer 3**

The reviewer stated that there are fundamental barriers to Li+ exchange between LLZO and PEO that produce high interphase resistances. The goal of this project is to develop well-controlled, scalable LLZO nanofiber and CPE synthesis processes and demonstrate the fabrication of large-area, thin CPE membranes with outstanding electro-chemo-mechanical properties. The reviewer remarked that the team correctly identified the technical barriers in CPE and designed three approaches to address the challenges. The timeline is reasonably planned.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer stated that the milestones have been met, and future work appears to be on track.

**Reviewer 2**

The reviewer stated that the team has made strides in materials engineering and processing of LLZO-PEO and lithium lanthanum titanate oxide (LLTO)-PEO composite electrolytes to meet their listed milestones. In particular, the team has achieved ionic conductivities of 0.1 mS/cm for these composites. The team also demonstrates that these composites can be fabricated into free-standing films. The project is on track according to the presented milestones. There are outstanding questions regarding the electrochemical stability of these composites with Li-metal anodes.

**Reviewer 3**

The reviewer stated that the project team demonstrated improved ionic conductivity of CPE to 5 * 10^-4 S/cm by improving percolation of LLZO nanofibers, which is the highest value ever reported for CPE. The team also explored the other approaches such as surface modification of LLZO particles, in situ polymerization and crosslinking PEO.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer stated that the collaborations outside of Argonne are well integrated into the project and are providing relevant and important information. Clearer explanations of the contributions of the individual team members at Argonne would be helpful.

**Reviewer 2**

The reviewer stated that the work appears to be highly collaborative among the participating team members. The team is collaborating externally with experts in solid-state nuclear magnetic resonance spectroscopy, TOF-SIMs, ionic conductivity measurements, and interfacial transport. These collaborations have been successful in understanding how PEO-LLZO and PEO-LLTO composites can be engineered to improve ion transport and scalability of processing.

**Reviewer 3**

The reviewer stated that the PI collaborated with Prof. Chibueze Amanchukwu, University of Chicago in solid-state NMR to identify Li+ transport pathway. The team also collaborated with Luke Hanley at the University of Illinois, Chicago to image 6Li transport in cycled composite electrolytes with ToF-SIMS; conductivity measurements of cold and hot-pressed pellets of LLZO nanofibers with LBNL, and measuring interface resistances in planar trilayer cells, dense LLZO pellets (Chih-Long Tsai, IEK-9, FZ Jülich).

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer stated that the current work (Fiscal Year 2024) is moving towards additional improvements in interfacial properties, and towards optimizing the microstructure, which are good directions. A significant focus for the Fiscal Year 2025 work is the demonstration of full cells. This may be premature, since a number of improvements are needed to make these complex materials practically viable.

**Reviewer 2**

The reviewer stated that the future research is well-aligned with the project goals and will address additional barriers that are still outstanding challenges (e.g., Li-metal anode stability).

**Reviewer 3**

The reviewer stated that the project has clearly defined the future work in two areas: improving ion transport and fabricating full cells. Plans are proposed.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer stated that the organic-inorganic composite electrolytes have several practical advantages, and the successful development of these types of materials has the potential to be transformational.

**Reviewer 2**

The reviewer stated that the work is focused on new composite solid-state electrolytes for all-solid-state batteries and is well-aligned with the VTO Batteries subprogram.

**Reviewer 3**

The reviewer stated that developing polymer-based composite electrolyte with improved ionic conductivity is directly related to VTO program to enable batteries with higher energy density.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer stated that the project makes good use of a variety of important resources, both within the core team and via outside collaborators.

**Reviewer 2**

The reviewer stated that the resources are sufficient to complete the project objectives.

**Reviewer 3**

The reviewer stated that the project team has suitable and sufficient resources to carry out the proposed work.

**Presentation Number:** BAT541
**Presentation Title:** Substituted Argyrodite Solid Electrolytes and High Capacity Conversion Cathodes for All-Solid-State Batteries
**Principal Investigator:** Jagjit Nanda, SLAC National Accelerator Laboratory

***Presenter***

Jagjit Nanda, SLAC National Accelerator Laboratory

***Reviewer Sample Size***

A total of three reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 67% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 33% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

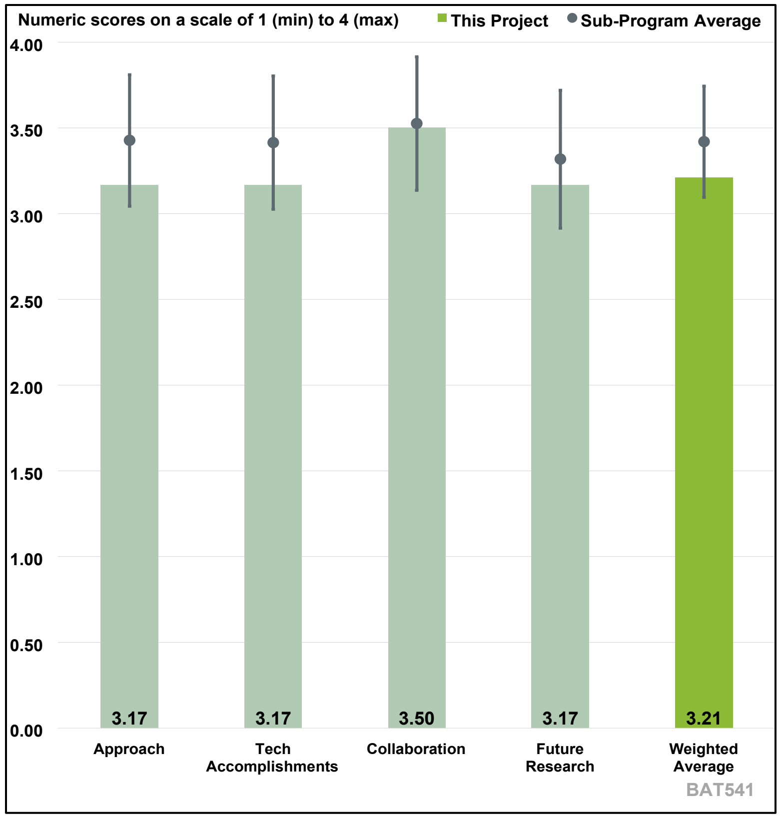


Figure 1-27. Presentation Number: BAT541 Presentation Title: Substituted Argyrodite Solid Electrolytes and High Capacity Conversion Cathodes for All-Solid-State Batteries Principal Investigator: Jagjit Nanda, SLAC National Accelerator Laboratory

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer stated that the major barriers that need to be addressed include performance, interfacial stability, areal specific resistance, and current density, all of which are related to the conductivity and thickness of the SSE. The PIs attempted to fabricate thin SSE films using slurry casting methods, successfully producing thin, free-standing SSE films with decent conductivity. The researchers also investigated the impacts of binders. The project was well-designed to address these technical barriers, particularly in creating thin SSE films. The PIs reported that the thickness of the SSE can be as low as 30 µm. The reviewer stated that they should also mention the durability of the cells and the success rate during cell production.

**Reviewer 2**

The reviewer stated that thin and free-standing SSE is required for practical SSBs. The team is developing LPSC-based SSE films by screening different binders. It is found that the binder with high molecular weight benefits the formation of crack-free films but significantly lowers the conductivity of the films. Although the mechanisms on the selection of binders are unclear and needs to be further investigated for pursuing more appropriate binders, the results look promising. In addition, the pressure effect on the free-standing SSE films needs to be studied. New discoveries are expected through advanced characterizations from SLAC, which would be helpful to speed up the study on the failure mechanisms of SSBs.

**Reviewer 3**

The reviewer stated that the project focuses on development of thin sulfide solid electrolyte for all-solid-state batteries, which is one of the keys to achieve 500 Wh/kg at the cell level. The group investigated the effect of binder on the mechanical properties, thickness and electrochemical properties of the fabricated thin film separator. Improvement has been achieved. The project also utilized advanced characterization tools including Raman imaging and synchrotron TXM to probe the degradation mechanism of NMC cathode for further improvement. However, the project title is high-capacity conversion cathodes. The reviewer stated that the group should specify their plan on the conversion cathodes in their system.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer stated that the PIs successfully demonstrated the fabrication of a thin SSE with a thickness of less than 30 µm. In addition to this achievement, the research team also investigated the use of binders for making thin SSE films, as well as the performance of high-nickel cathode electrodes in combination with these thin films. The PIs made significant progress in accordance with the project plan, and their results were comprehensively reported, providing strong support for their conclusions. The reviewer suggested that the PIs conduct more extensive full cell testing on the thin SSE to further demonstrate the durability and long-term reliability of their design. This additional testing would provide valuable data to ensure that the thin SSE can maintain its performance under practical operating conditions.

**Reviewer 2**

The reviewer stated that the team has achieved the goals set in the project plan.

**Reviewer 3**

The reviewer stated that the project has demonstrated the capability to fabricate 30-80 um thick LPSCl thin film separator and indicated possibility for further improvement. Advanced characterization to reveal the failure mechanism of NMC cathode is on-going.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer stated that the PI and co-PI demonstrated extensive and highly successful collaboration within the project team. Their coordinated efforts and effective communication significantly contributed to the project’s overall success. The level of collaboration among the team members was sufficient to achieve the project’s goals and milestones. However, to further enhance the project’s impact and ensure its practical application, it would be beneficial for the PI to consult with industry experts regarding the feasibility of the thin SSE. Specifically, discussions with industry professionals could provide valuable insights into the processability and scalability of the thin SSE, addressing any potential challenges that may arise during mass production. Engaging with industry stakeholders could also facilitate the transition from laboratory research to commercial application, ensuring that the thin SSE can be effectively manufactured and implemented on a larger scale.

**Reviewer 2**

The reviewer stated that the team is well coordinated and performs the proposed work well and in a timely manner.

**Reviewer 3**

The reviewer stated that the Collaboration within SLAC, ORNL, University of Houston, Virginia Commonwealth University, UT-Austin, FSU on thin film fabrication, advanced synchrotron X-ray characterization, cell integration, modeling and interface characterization have been well demonstrated. Suggest collaboration with conversion cathode.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer stated that the PIs have proposed further investigation into binder loading to minimize the thickness of the SSE and optimize the properties of the cathode. Additionally, they plan to explore the potential of other Li alloy anodes. These future research directions are aligned with the overall project plan and objectives, aiming to increase the energy density of the Li-S solid electrolyte full cell. Success in these areas will provide the PIs with a deeper understanding of the existing barriers and opportunities for improvement. To enhance the impact of their research, it is recommended that the PIs allocate more time to studying metallic Li rather than Li alloys.

**Reviewer 2**

The reviewer stated that the proposed future work makes sense. The reviewer suggested that more efforts should be focused on the binder study.

**Reviewer 3**

The reviewer stated that the project will further optimize binder to reduce the thickness of solid electrolyte membrane, enabling better performance with NMC cathodes. The project will also develop new substituted argyrodite solid electrolyte to achieve higher conductivity and better electrochemical properties.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer stated that the project is related to the solid-state Li batteries. It is very relevant to the VTO objectives for 500 Wh/kg and 1000 cycles batteries for EV applications.

**Reviewer 2**

The reviewer stated that the project supports the VTO Battery programs.

**Reviewer 3**

The reviewer stated that the development of thin solid electrolyte membrane is one of the keys to enable high-energy all-solid-state batteries.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer stated that the team has sufficient characterization and cell fabrication tools to accomplish the proposed task.

**Reviewer 2**

The reviewer stated that the resources are sufficient for the team to timely support the proposed work in this project.

**Presentation Number:** BAT542
**Presentation Title:** Polymer Electrolytes for Stable Low Impedance Solid State Battery Interfaces
**Principal Investigator:** Chelsea Chen, Oak Ridge National Laboratory

***Presenter***

Chelsea Chen, Oak Ridge National Laboratory

***Reviewer Sample Size***

A total of three reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

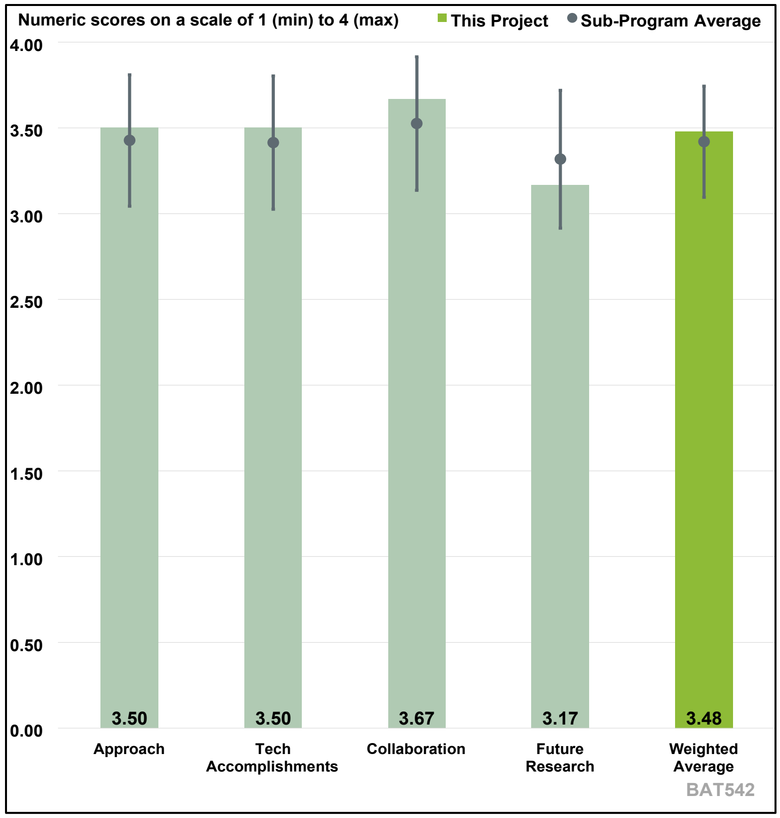


Figure 1-28. Presentation Number: BAT542 Presentation Title: Polymer Electrolytes for Stable Low Impedance Solid State Battery Interfaces Principal Investigator: Chelsea Chen, Oak Ridge National Laboratory

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer stated that the integrated efforts in this project address a range of important challenges in a logical fashion. However, the low conductivity of the polymer being studied is a significant impediment.

**Reviewer 2**

The reviewer stated that the project is well-designed and has a reasonable timeline planned. The reviewer commented that this project would benefit greatly by demonstrating the performance of the 3D composite structure in industry-relevant pouch cells.

**Reviewer 3**

This reviewer affirmed attending the talk, analyzing the talk slides in detail, asking questions, and then viewing a few of the quarterly reports on this project. The reviewer commented that based on these review activities, the PI and the team appear to understand very well the technical barriers and have designed the project and timeline sensibly. The reviewer praised how the team has designed this project, from the choice of ceramic electrolyte to the choice of in-situ polymerized single-ion-conducting polymer electrolyte. The overall approach is to vary the ceramic interpenetrating network porosity and void/particle size and vary the polymer parameters, including comparison to benchmark salt-in-PEO polymer systems, and then systematically study the interfacial aspects, and overall battery performance including limiting current. The reviewer said that given the complexity of this project, the timeline is reasonable, although a bit ambitious. The technical barriers are many and significant and include the brittle nature and low interfacial contact of ceramics and the inherently low conductivity of single-ion-conducting polymers. The team is operating near the cutting edge of what is possible and is wisely choosing to carefully understand the limiting factors in a polymer-ceramic composite system. The team is building key knowledge to understand and improve these systems both experimentally and computationally/theoretically.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer stated that the milestones have been met, and future work appears to be on track.

**Reviewer 2**

The reviewer stated that the team has made excellent technical progress in a short time frame.

**Reviewer 3**

The reviewer stated that the PI's group wisely chose to start with LLZO ceramic networks with known and controllable porosity and pore size. The single-ion-conducting (SIC) polymer can then be filled into this network as a monomer and then in-situ polymerized to go for uniform and conformal interfaces within the composite and with anode and cathode. The team has shown that LLZO ceramic + polymer has higher conductivity than the component parts and that this composite exceeds PEO-salt-ceramic systems in terms of the limiting current and ASR. The team has found an optimum porosity of 35%. It appears also that the polymer part of the composite reduces/eliminates the need for high stack pressure. These results all address technical goals of the project and demonstrate clear progress. One criticism from the reviewer was that the performance parameters are still somewhat modest and further improvement should be expected. Also, some of the polymer parameters are not measured or well defined. The reviewer addressed this in more detail later.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer stated that the current collaborations are integrated and well defined. Additional work characterizing the porous structure of the ceramic scaffolds would be a valuable addition.

**Reviewer 2**

The reviewer stated that the project has an excellent research team comprising ORNL as the lead with collaborators at LBNL and MERF. However, the project would benefit greatly with an industry partner to evaluate the technology in industry relevant pouch cells.

**Reviewer 3**

The reviewer stated that the project has experimental and theoretical participants and collaborators across many national laboratories (ORNL, ANL, SLAC, LBNL, PNNL, and NREL). This represents a very impressive integration of researchers with diverse skillsets, and it appears to the reviewer that all of these members are collaborating very effectively to achieve the project goals. It also appears to the reviewer that these members can address any future issues of fabrication, characterization, or conceptual/theoretical understanding.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer stated that the future work is directed at goals that make sense. However, it is not clear what the team is doing to pursue improved resistance to dendrites. Also, it looks like the performance target of 1 mA/cm$^2$ requires operation at elevated temperatures (due primarily to the relatively low conductivity of the polymer).

**Reviewer 2**

The reviewer stated that the proposed future research plan is sufficiently defined. It is great to see that the project team is continuing to search for new materials to form composites in order to reach the DOE goal of $10^{-3}$ S/cm. But there does not appear to be a proposed plan on demonstrating the performance of the 3D composite structure in a real pouch cell.

**Reviewer 3**

The reviewer stated that the future research goals and plans are well-described in the presentation and in reports. It is very likely that the future targets will be achieved, at least in terms of basic understanding and development of a working and well characterized composite systems. It is possible that battery performance goals will be achieved but is not certain in any study like this. The reviewer asked several questions of the PI during and after the AMR presentation:1) What is the molecular weight of the SIC polymer and is it possible there are oligomers left in the material giving a liquid-like internal environment? The PI answered that they need to check into that. 2) Assuming you can determine what is the actual polymer composition inside the composite, what are its mechanical properties (e.g., moduli) and fragility (e.g., compressive/tensile strength)? The PI is planning to study this. 3) The reviewer asked if the PIs checked for or removed residual salt (e.g., charged monomers + Li+)? The Bruce-Vincent method says $t^+ = 0.86$-$0.9$. PI: We did pulsed field gradient NMR on the polymer only (not in composite) and get 100x slower D for the anion species. Thus, the transference is 0.99 by nuclear magnetic resonance (NMR) in the neat polymer. This reviewer recommended trying pulse Fourier transformation (PFT) NMR in the 6um pores in the composite, which may be possible. The reviewer also recommended checking for diffusion of residual monomers or mobile oligomers. 4) How will you improve the interface between polymer and ceramic? PI: (Preliminary Answer) The team needs better polymer with better transport and mechanical properties.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer stated that the organic-inorganic composite electrolytes have several practical advantages. However, to make this project more relevant, more effort should be directed towards a polymer with improved conductivity.

**Reviewer 2**

The reviewer stated that the project does support the overall VTO subprogram objectives.

**Reviewer 3**

The reviewer stated that the PIs have chosen and described relevant goals and objectives to the VTO Battery subprogram. The goals of developing and understanding new polymer-ceramic composite electrolytes and integrating them into practical battery cells are highly relevant to advancing solid-state batteries, Li-metal batteries, and other subprogram goals. This project is doing that well. The reviewer also referred to earlier comments.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer stated that this project makes good use of a variety of important resources, both within the core team and via outside collaborators.

**Reviewer 2**

The reviewer stated that the resources are sufficient for the project to achieve the stated milestones in a timely fashion. However, the resources may not be sufficient to achieve performance in pouch cells, as suggested.

**Reviewer 3**

The reviewer stated that the PI and the team members and institutions have impressive and sufficient resources (both funding and laboratory and human infrastructure) to conduct this work and achieve the stated goals and milestones. The synthetic and materials formulation abilities/expertise/experience, the materials analysis capabilities/expertise, the battery cell development skills, and the computational/theoretical experience are very well-matched to this project.

**Presentation Number:** BAT543
**Presentation Title:** Integrated Multiscale Model for Design of Robust 3D Solid-state Lithium Batteries
**Principal Investigator:** Brandon Wood, Lawrence Livermore National Laboratory

***Presenter***

Brandon Wood, Lawrence Livermore National Laboratory

***Reviewer Sample Size***

A total of three reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

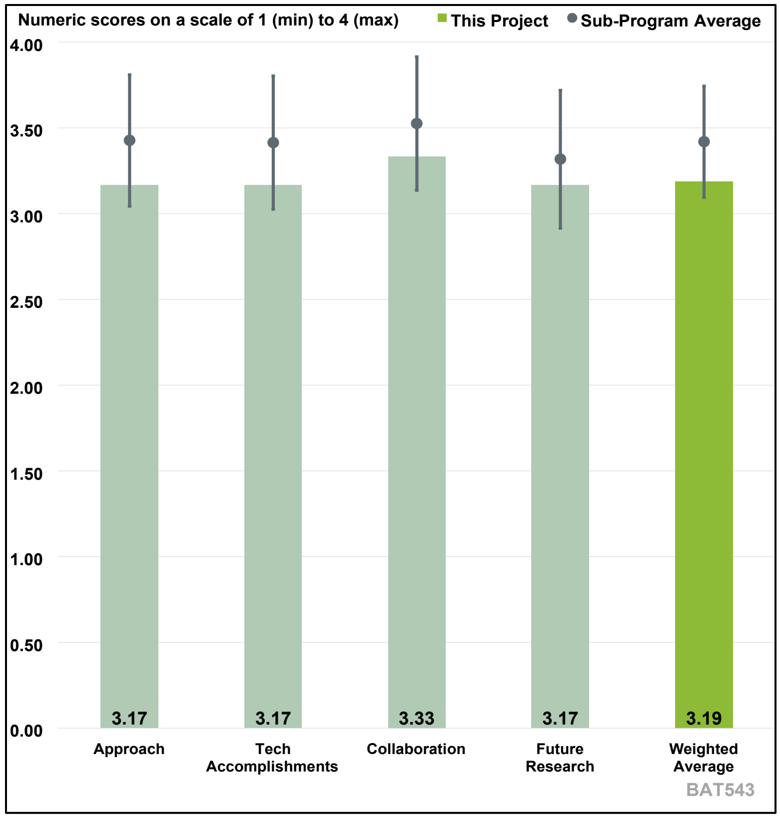


Figure 1-29. Presentation Number: BAT543 Presentation Title: Integrated Multiscale Model for Design of Robust 3D Solid-state Lithium Batteries Principal Investigator: Brandon Wood, Lawrence Livermore National Laboratory

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer stated that the project is focusing on the poor battery cyclability due to interfacial chemical reactions, which is critical for solid-state batteries. The project is well-designed and reasonably planned. However, the work is based on the materials made by the chemomechanics method, with limited applications in industry.

**Reviewer 2**

The reviewer stated that this project aims to develop and apply multiscale, multiphysics models to connect composition, microstructure, and architecture to chemomechanical integrity and transport performance of 3D solid-state battery materials. The project is well-designed and has a reasonably planned timeline.

**Reviewer 3**

The reviewer stated that the project is well-designed, and the timeline is reasonably planned.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer stated that the progress is reasonable compared to the plan.

**Reviewer 2**

The reviewer stated that significant technical progress has been made in the project.

**Reviewer 3**

The reviewer stated that the project does not include any experimental validation, which needs to be addressed.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer stated that the collaboration and coordination across the project team is excellent. It would be better to obtain industrial inputs and to work on more representative materials in industry, such as sulfide-based electrolytes.

**Reviewer 2**

The reviewer stated that this project is well-rounded in collaboration with an excellent lead and partners from the national laboratories, academia, and “industry”. Note that while there is no specific industry entity listed, certain researchers do bring that to the table.

**Reviewer 3**

The reviewer stated that the project really needs to collaborate with experimentalists.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer stated that the proposed work is limited to evaluating the materials made by the chemomechanics method. It may be more effective if investigating widely used materials and its combinations, such as NMC/sulfide/Li-metal. It is critical to include the effect of time in the modeling since the interfacial reactions do not stop. And the ratio of electrolyte/electrode active materials is also critical for high energy.

**Reviewer 2**

The reviewer stated that the project has clearly defined a purpose for future work is likely to achieve its targets.

**Reviewer 3**

The reviewer stated that the project clearly defined a purpose for future work.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer stated that the project supports the overall VTO subprogram objectives since solid-state batteries represent a promising approach for potential high energy and long-life EV batteries.

**Reviewer 2**

The reviewer stated that the project does support the overall VTO subprogram objectives.

**Reviewer 3**

The reviewer stated that the project supports the overall VTO subprogram objectives.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer stated that the resources are sufficient.

**Reviewer 2**

The reviewer stated that the resources are sufficient to achieve the stated milestones in a timely fashion.

**Reviewer 3**

The reviewer stated that the resources are sufficient for the project to achieve the stated milestones.

**Presentation Number:** BAT553
**Presentation Title:** Understanding solid electrolyte interphase (SEI) reactions in Lithium metal and Lithium-Sulfur batteries
**Principal Investigator:** Perla Balbuena, Texas A&M University

***Presenter***

Perla Balbuena, Texas A&M University

***Reviewer Sample Size***

A total of four reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

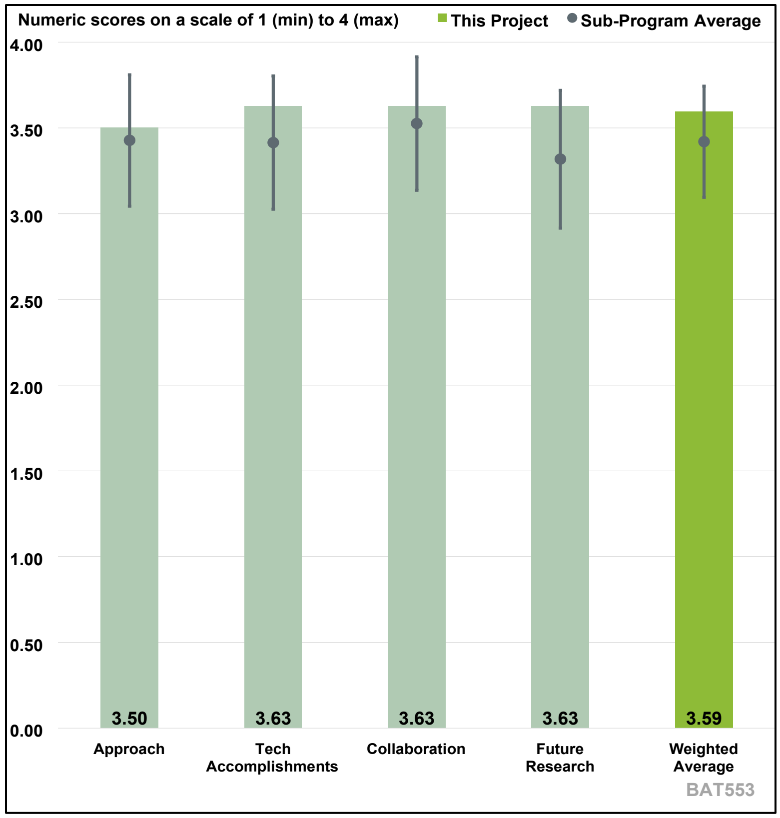


Figure 1-30. Presentation Number: BAT553 Presentation Title: Understanding solid electrolyte interphase (SEI) reactions in Lithium metal and Lithium-Sulfur batteries Principal Investigator: Perla Balbuena, Texas A&M University

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer stated that the project aims to address the challenges in developing safe, high-energy-density Li-metal rechargeable batteries. This modeling effort is meticulously designed to integrate seamlessly with other ongoing Battery500 material synthesis and diagnostic experimental endeavors. The Balbuena group provides a fundamental understanding of the charge-transfer and electrochemical/chemical reactions, enabling laboratory scientists to better select the materials that are to be explored. Several promising areas of exploration are being pursued, including SPAN reactions, electrical conductance properties of Li, transition metal dissolution mechanisms, and pressure effects. The reviewer stated that the proposed timeline is both realistic and appropriate for the scope of the work.

**Reviewer 2**

The reviewer stated that the Ab initio calculations and kinetic Monte Carlo method were utilized to investigate the interactions between electrolytes and electrode materials. This provides important chemical information on solid electrolyte interphase/cathode electrolyte interphase (SEI/CEI) that is difficult to get from experimental approaches alone.

**Reviewer 3**

The reviewer stated that this project aims to provide theoretical understanding of the Battery500 cell chemistry using multi-scale computation and simulation approaches. The approach is well-designed and is critical for the success of the Battery500 project. Since pressure control has an important effect on the cycle life of the high energy density battery, the reviewer was not clear how the pressure effect, proposed in the project, will be studied computationally.

**Reviewer 4**

The reviewer stated that to achieve a highly reversible Li-metal anode, the team addressed three technical barriers in this fiscal year (FY) presentation report: 1) Characterize the relationship between SEI and Li anode reversibility using first principle calculations; 2) Understand the degradation reactions of transition metal oxide cathode; 3) Understand the role of electrolyte in S cathode conversion reactions. The project is well designed, and the timing is well planned.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer stated that the team was highly productive and has made significant contributions useful to the battery research community. The team helped develop a deep understanding of the effect of Li SEI structure/morphology and electrical conductance properties. New insights were also obtained on the pressure effects of NMC cells and alternative SPAN chemistries. Several journal articles were published.

**Reviewer 2**

The reviewer stated that chemical/electrochemical events were used as an indicator of interfacial reactivities. This indicator works well for guiding the design of stable interface. However, the importance of the events is not functionally equivalent to the SEI/CEI. For instance, the formation of ‘good’ or ‘bad’ can be equally counted as ‘event’ at the interface. Statistical analysis of these events can play a more important role in guiding interfacial design.

**Reviewer 3**

The reviewer stated that the project has provided fundamental understanding on multiple topics of Battery500 cell components, including NMC, Li-metal and sulfur cathodes. The proposed pathway for the SEI formation is particularly impressive and will be important in designing better electrolytes. The PI shows sharply different solubilities of NMC in liquid electrolyte for the pristine and protonated surfaces, the results are inspiring and the reviewer wonders if there is a plan to collaborate with experimentalist to validate this results.

**Reviewer 4**

The reviewer stated that the technical progress is well aligned with the project plan. The team’s calculation capability well supports the experimental teams.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer stated that the PI has demonstrated outstanding collaboration within the Battery500 Team. That group’s efforts dovetail the research of several material scientists and battery engineers (PNNL, BNL, Stanford, UCSD) in the Battery500 Consortium. The team provides fundamental chemical and electrochemical insights to address challenges associated with the Li anode and SPAN cathode/electrolytes. These efforts have resulted in several significant publications.

**Reviewer 2**

The reviewer commended good collaboration within Battery500. The reviewer observed that stronger benchmarking with experimental data will add more value to the effort.

**Reviewer 3**

The reviewer stated that the PI has established strong collaborations with multiple PIs within the Battery500 team.

**Reviewer 4**

The reviewer stated that the research team had collaborations with national laboratories (e.g. PNNL, BNL) and universities (e.g., UCSD, Stanford), which shows the considerable impact of this work. The reviewer remarked that it has been reported that Germany is also involved in the collaboration. The reviewer was uncertain regarding specific contributions from Germany.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer stated that the proposed future research is well-conceived. Building on this year's achievements, the project is poised to continue delivering excellent results.

**Reviewer 2**

The reviewer stated that the proposed future research is reasonable. The SPAN chemistry is really complex, and the reviewer recommended more computational focus on that particular chemistry.

**Reviewer 3**

The reviewer stated that thermal runaway reaction studies are proposed in the future work. This will be important for addressing Li-metal battery safety issues.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer stated that this is a valuable project in the VTO portfolio. The solid–electrolyte interphase critically governs the performance of rechargeable batteries. Developing a fundamental understanding of the SEI will enable investigators find methods to better control electrode-electrolyte reactions resulting in prolonging the battery cycle life and improving performance.

**Reviewer 2**

The reviewer stated that the project supports the ultimate goal of Battery500.

**Reviewer 3**

The reviewer stated that theoretical studies using multi-scale computations and modeling are important and the project supports the Battery500's goal of developing high-energy-density batteries.

**Reviewer 4**

The reviewer stated that the proposed work well supports the Batteries program in VTO. This team's contribution from the theoretical modeling part will support experimental results and accelerate the development of Li-metal batteries.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer stated that the project has the necessary resources to complete the tasks on time.

**Reviewer 2**

The reviewer stated that the resources of for proposed research are reasonable.

**Reviewer 3**

The reviewer stated that sufficient resources are available for the team to achieve their proposed tasks.

**Presentation Number:** BAT587
**Presentation Title:** Earth-abundant Cathode Active Materials for Li-Ion Batteries Theory and Modeling
**Principal Investigator:** Hakim Iddir, Argonne National Laboratory

***Presenter***

Hakim Iddir, Argonne National Laboratory

***Reviewer Sample Size***

A total of three reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

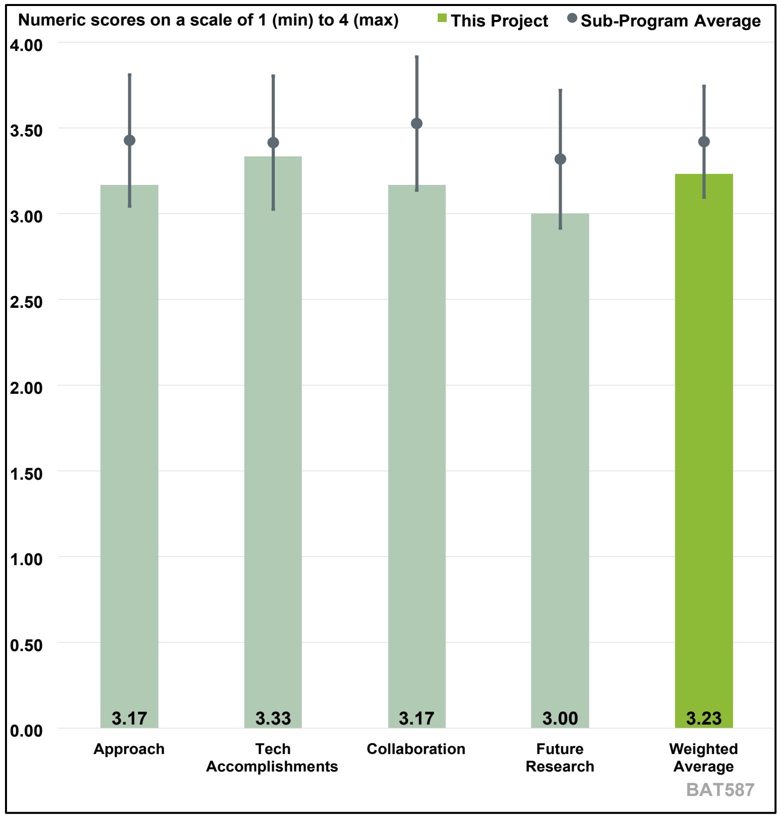


Figure 1-31. Presentation Number: BAT587 Presentation Title: Earth-abundant Cathode Active Materials for Li-Ion Batteries Theory and Modeling Principal Investigator: Hakim Iddir, Argonne National Laboratory

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer stated that this project is part of the consortium led by Argonne National Laboratory, which addresses the major barriers of cost, performance, safety, and supply chain for rechargeable batteries. The overall strategy is to develop electrode materials to eliminate expensive and limited availability elements, typically cobalt and nickel in the cathode. Toward this end, the objective of the proposed research focuses on developing cathodes based on earth-abundant materials, such as manganese-based materials. Specifically, this project is oriented toward theoretical understanding of such cathode materials. The team uses a combined theoretical approach and model system to gain fundamental insights for correlating design, synthesis, and structure-property relations of the cathode based on earth-abundant materials. Overall, the project is well-designed and streamlined in time scale for carrying out the proposed research. The reviewer stated that the theoretical result appears to be standalone, it would be beneficial if the theoretical result can be directly integrated with the experimental observations.

**Reviewer 2**

The reviewer stated that density function theory was applied to investigate the transport properties of Li ions in cathode materials containing earth-abundant elements like manganese. Particularly, lithium-manganese-rich cathodes were the primary focus. It was claimed that the extremely low Li-ion diffusivity at low state of charge (SOC) can be problematic for adopting this class of materials. However, it is not clear that transport properties are taking priority over the structural stability.

**Reviewer 3**

The reviewer stated that project focuses on key barriers in non-cobalt, lithium-nickel-manganese batteries.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer stated that to accomplish the proposed research and meet the technical milestones, the team has carried out Ab-Initio Molecular Dynamics (AIMD) at 900K for $0.4Li_2MnO_3$•$0.6LiMn_{0.5}0Ni_{0.5}0O_2$, revealing the domain distribution in the Li-rich and manganese-rich cathode (LMR). Further, the team calculated the Li diffusivity in each of the domains of the LMR cathode, revealing that diffusivity in the half-lithiated $Mn_{0.50}Ni_{0.50}$ domains is almost 3 times the diffusivity in staggered domains at an equivalent SOC during activation. The team also revealed the anionic redox process in the LMR cathode, demonstrating the oxygen formation. All these insights represent great progress in developing the LMR-based cathode for the next generation high-capacity battery. The reviewer stated that the modeling results should be compared with experimental observations in the same materials system.

**Reviewer 2**

The reviewer stated that effort was made to calculate the Li ion diffusivity and technical difficulty at low SOC was identified.

**Reviewer 3**

The reviewer stated that excellent progress was made in all three components of the project: lithium- and manganese-rich (LMR) cathodes: structure-property-performance; first principles phase diagram of the $LiMnO_2$-$Li_2MnO_3$ space; and single-crystal models: particle size effects.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer stated that the team is outreaching well and collaborating with other institutions, in particles including universities and national laboratories. It would be expected that the team's expertise in theoretical modeling will be integrated with experimental tools, in order to warrant the success of the proposed research.

**Reviewer 2**

The reviewer stated that there is good collaboration within and across the consortium teams.

**Reviewer 3**

The reviewer stated that the collaboration among the team members consisting of ANL, NREL, ORNL, LBNL, PNNL, SLAC is satisfactory.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer stated that for future research, the team proposed to evaluate the effect of dopant concentrations on manganese stability and irreversible oxygen redox, which is critical to the performance of the LMR cathode. Further, the team will assess the impact of spinel-layered, integrated domains on stability of LMR cathode, which is another emerging domain with a lot yet unknown for LMR cathode. The team also plans to develop techniques for improving and increasing the use of machine-learning potentials in molecular dynamics simulations to extend the time scale and system sizes. All the proposed future research steps are well-conceived and carrying out the proposed tasks will lead to insights for the optimization of LMR cathode. A close integration with experimental observation will be complementary to the proposed theoretical modeling results.

**Reviewer 2**

The reviewer stated that the effort can be better utilized to tackle more important barrier—structural stability.

**Reviewer 3**

The reviewer stated that the extension of the current approach is well-proposed. However, a comparison with some experimental data is important to ensure that the modeling is accurate.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer stated that developing cathode with earth-abundant elements is a critical step for energy sustainability. This project focuses on gaining insight on the fading mechanism of LMR cathode, which is very important and relevant to the objective of VTO subprogram on developing high-capacity battery with sustainable element and affordability.

**Reviewer 2**

The reviewer stated that developing cathode materials using earth-abundant element supports DOE’s mission to maximize the sustainability of low-carbon transportation.

**Reviewer 3**

The reviewer affirmed that the project supports overall VTO subprogram objectives.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer stated that the PI and team of this sub-project of the consortium possess the theoretical expertise for carrying out the proposed research. The computational power and resources are adequate for the proposed research to reach the laid-out milestones in a timely fashion. The reviewer articulated the desirability of the team closely integrating theoretical results with experimental observations.

**Reviewer 2**

The reviewer stated that there are sufficient resources available.

**Presentation Number:** BAT590
**Presentation Title:** Lithium Halide-Based Superionic Solid Electrolyte and High-Voltage Cathode Interfaces
**Principal Investigator:** Robert Sacci, Oak Ridge National Laboratory

***Presenter***

Robert Sacci, Oak Ridge National Laboratory

***Reviewer Sample Size***

A total of four reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

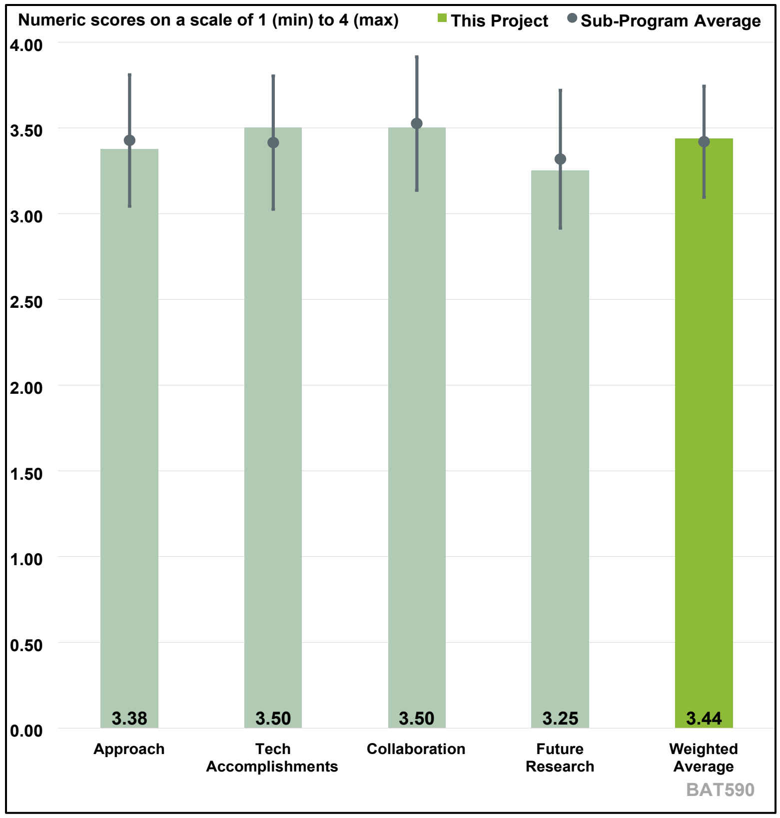


Figure 1-32. Presentation Number: BAT590 Presentation Title: Lithium Halide-Based Superionic Solid Electrolyte and High-Voltage Cathode Interfaces Principal Investigator: Robert Sacci, Oak Ridge National Laboratory

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer stated that the need for a solid catholyte, which can be integrated throughout the cathode porous structure, is often neglected in solid-state battery R&D. The reviewer commended the focus on that issue. The reviewer commended the excellence of the milestones to measure progress towards a functional solid catholyte. As with much solid-state research, there are non-ideal material choices made that may impact the interpretation of results. For example, 1 mm thick SSE as mentioned on Slide 6. Slide 7 mentions the recent manufacture of thin (possibly about 20 microns) LIC layers which represents a huge improvement.

**Reviewer 2**

The reviewer stated that the basic concept of the project and the approach are good. Methods to make a cathode with a solid electrolyte are important, and solution processing is a reasonable approach for doing so. The methods used, including evaluation in full cells, are reasonable. The reviewer pointed out that the limitation that several of the elements may apparently be too expensive for any commercial cell—for example, Indium. Another limitation is the full cells have multiple layers.

**Reviewer 3**

The reviewer stated that the primary approach in this project is the solution-based synthesis of halide SSEs. This method has several advantages over the mechano-synthesis method. Solution-based synthesis allows for better control over the parameters of the final products, making it easier to achieve the desired specifications. It is also more cost-effective and scalable, therefore suitable for larger production runs. The reviewer recommended that the PI explore a wider range of options for full cell fabrication beyond the bi-electrolyte approach. By investigating and experimenting with various methodologies, the PI can potentially identify more efficient or effective techniques for constructing full cells, thereby improving the overall outcome.

**Reviewer 4**

The reviewer stated that the project sets very specific objectives: developing inexpensive, solution-based methods that allow for growing halide-based solid electrolyte within the porous high-voltage cathode matrix, leading to a drastic increase in the mechanical robustness and high-rate performance. However, the approach being taken is not very clear to the reviewer. On the other hand, research presented by the team deals with the practical issues in developing halide SSEs, including scalable synthesis using solution-based methods, making thin membranes, and lowering applied pressure during cycling. These are valuable contributions towards accomplishing better processing and engineering of solid-state batteries, and they are important to achieving overall VTO goals.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer praised the researchers on their practical (cycling) and diagnostics accomplishments. The reviewer encouraged this project team, and others, to report mAh/g quantity of the electrode, not of the active material. For example, the results shown on Slide 10 must be active material as 200mAh/g is not possible at the electrode level with just 50% NMC in the cathode. This is critical to understand the likely attainable cell energy. The reviewer praised the researchers on their pressure study. The reviewer remarked that external pressure requirements are a large concern for automotive OEMs, so the reviewer was pleased to see it explicitly addressed here. The reviewer also remarked that the high voltage stability of the halide SSEs is critical and impressive.

**Reviewer 2**

The reviewer stated that overall, the technical accomplishments are strong and clearly presented. The demonstration of the solid electrolytes in the full cells is really the best way to evaluate their performance, and this was done in a systematic and reasonable way. The work on solid electrolyte films and consideration of the mechanical properties and applied pressure are also valuable accomplishments. The reviewer was quite impressed with the cycling with single crystal NMC.

**Reviewer 3**

The reviewer stated that the most significant accomplishment and contribution from this project is the successful synthesis of halide SSEs using a solution-based method. This achievement is particularly noteworthy because it includes the development of an effective technique for drying and removing the attached solvent molecules, specifically water. This aspect of the synthesis process has posed a considerable challenge to researchers for many years, making this breakthrough especially impactful. By overcoming this long-standing obstacle, the project has made a substantial contribution to the field. The ability to efficiently dry and purify the synthesized halides is a crucial step towards the scale-up of halide production. This advancement not only improves the quality and consistency of the final products but also makes the production process more viable for larger-scale applications.

**Reviewer 4**

The reviewer stated that overall, good progress has been made on this project. The team evaluated solution synthesis of $Li_3InCl_6$ (LIC) and LYC, fabricated thin membranes of LIC, and evaluated pressure effect on cell cycling performance. Particle size appears to play an important role. The reviewer asked one question relating to particle size and morphology control in solution synthesis. What are the parameters for optimization and how can they be controlled during the synthesis?

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer praised the collaboration as excellent.

**Reviewer 2**

The reviewer stated that the collaboration across team members appears to be strong.

**Reviewer 3**

The reviewer stated that the PI collaborated with another national laboratory and two universities for testing and diagnostic purposes. This collaboration proved to be generally effective, with clearly defined roles for each partner. However, the reviewer commented that as part of a larger program, efforts should be made to minimize redundancy. For example, the same bi-layer SSE has been reported by multiple groups, highlighting the need for better coordination to avoid duplicate work.

**Reviewer 4**

The reviewer stated that the collaborations across the teams of ORNL, SLAC and the University of Houston are excellent. There appears to be clear integration of expertise in different areas.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer commended the excellence of the future research described. The reviewer posed the question whether it is reasonable to target a significant reduction in the non-active weight percent in the cathode. The reviewer expressed that a value of 50% active material will make any solid-state cell significantly less competitive in comparison to a graphite/NMC Li-ion liquid cell.

**Reviewer 2**

The reviewer stated that the future research is clear and specific, and well prioritized based on work to date.

**Reviewer 3**

The reviewer stated that the PI proposes to further investigate the stability of halide SSEs, modify the SSE through transition metal doping, enhance the cathode, and develop thin SSE separators. The reviewer remarked that the proposed research activities are well-aligned with the overall project objectives. The reviewer encouraged the PI to consult with industry experts regarding the scale-up processes for halide production. This collaboration could provide valuable insights and help ensure that the project’s advancements are practical and scalable for commercial applications.

**Reviewer 4**

The reviewer stated that the list of future work items seems to cover various directions and a bit scattered. The reviewer suggested narrowing down the scope and focusing on developing a more in-depth understanding, maybe in just one or two areas. For example, it would be helpful to have more knowledge on halide processing and membrane fabrication, and outline where the potential barriers might be in this area.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer stated that as mentioned earlier, the project is highly relevant. The reviewer clarified that a major issue with consideration of different solid anolyte and catholyte usage is the need to keep the total thickness of those layers (combined) to 30 microns, which is exceedingly difficult to accomplish with a solid electrolyte.

**Reviewer 2**

The reviewer stated that the work is relevant to the Batteries program.

**Reviewer 3**

The reviewer stated that solid-state batteries and scale-up material manufacture are relevant to VTO’s goal of making 500Wh/Kg, 1000 cycle batteries for EV applications.

**Reviewer 4**

The reviewer stated that addressing the practical issues in solid electrolyte synthesis, processing, manufacturing, and cell integration is critical to the future development of solid-state batteries. The project is relevant to the overall DOE objectives.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer commended the excellent value received for the $250,000/year investment in the project. The reviewer would also consider slightly more resources to accelerate this work.

**Reviewer 2**

The reviewer commended the budget was only $250,000/year—yet a significant amount of results were achieved. The reviewer would consider increasing the budget.

**Reviewer 3**

The reviewer commended the PI, and the team can access adequate resources to conduct the proposed research.

**Reviewer 4**

The reviewer commended the project has sufficient resources.

**Presentation Number:** BAT591
**Presentation Title:** High-Conductivity and Electrochemically Stable Thioborate Solid-State Electrolytes for Practical All-Solid-State Batteries
**Principal Investigator:** Yi Cui, SLAC National Accelerator Laboratory

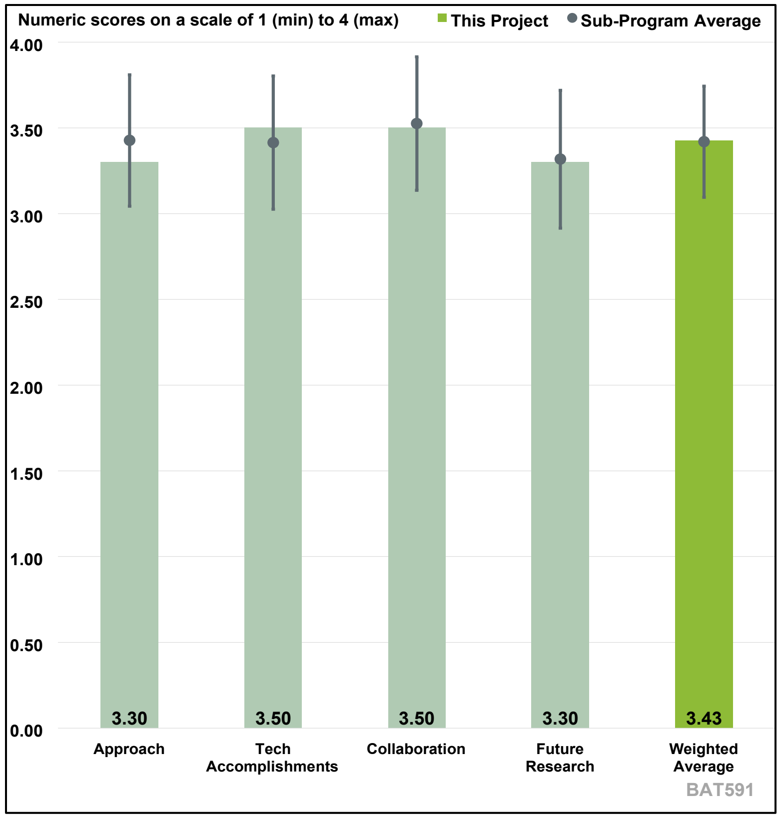


Figure 1-33. Presentation Number: BAT591 Presentation Title: High-Conductivity and Electrochemically Stable Thioborate Solid-State Electrolytes for Practical All-Solid-State Batteries Principal Investigator: Yi Cui, SLAC National Accelerator Laboratory

### *Presenter*

Yi Cui, SLAC National Accelerator Laboratory

### *Reviewer Sample Size*

A total of five reviewers evaluated this project.

### *Project Relevance and Resources*

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 80% of reviewers felt that the resources were sufficient, 20% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

### *Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?*

#### Reviewer 1

The reviewer stated that the project focuses on the development of a new electrolyte Li-B-S. But it seems having a compatibility issue with Li-metal and cathode materials, and buffer layers have to be used to make it cycle.

#### Reviewer 2

The reviewer stated that the materials closely related to thioborates which have been studied as solid-state electrolytes for over 30 years. Perhaps this specific class of material is new, but materials like $B_2S_3$-$Li_2S$ were known to provide 10-100x the conductivity of their oxide counterparts long ago. These are attractive low-cost materials and there may be a path forward with them. It's interesting that the ratio of B/S/Li of the highest conductivity material here, $Li_{10}B_{10}S_{20}$ is the same as that of $Li_2S$-$B_2S_3$. The relatively low voltage stability of any sulfide electrolyte will require either a catholyte or a low voltage cathode, and of course the latter will limit cell energy.

**Reviewer 3**

The reviewer stated that the project has a unique approach using machine learning to identify high ionically conductive thioborate-based solid electrolytes—theoretically $Li_5B_7S_{13}$ has the highest ionic conductivity at 74 mS/cm. However, experimentally $Li_{10}B_{10}S_{20}$ had the highest ionic conductivity at 0.1 mS/cm (experimentally, $Li_5B_7S_{13}$ was several orders of magnitude lower). Ionic conductivity increases to over 1 mS/cm with the addition of LiI. The reviewer remarked that the advantages of Li thioborate electrolytes over other solid electrolytes are unclear. Moreover, the unique annealing process needs to be better understood—its unusual that the formulation requires a 12 hour anneal at 550°C work after a 2 hour anneal at 750°C.

**Reviewer 4**

The reviewer stated that the researcher plans to understand the structure and transport mechanism of thioborate solid electrolytes. The researcher also plans to figure out its integration into a full cell design.

**Reviewer 5**

The reviewer stated that exploring new and high-performance solid-state electrolyte is critical to the development and improvement of solid-state battery technology. The reviewer remarked that the project is well designed, planned and executed at the given budget level and timeframe.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer stated that reasonable progress has been made towards the project plan.

**Reviewer 2**

The reviewer stated that as with many solid-state research projects, it’s difficult to understand how some of these measurements, like EIS as 350MPa and 500 microns thick, will relate to materials used in actual cells. The addition of LiI to increase the conductivity is interesting and valuable. Similar additives were used to increase the conductivity of B2S3, The reviewer also found it very interesting that ball milling decreases the conductivity, and that the crystallinity is helpful.

**Reviewer 3**

The reviewer stated that there has been significant technical progress made in the project thus far. The addition of LiI demonstrated enhanced performance which increases the ionic conductivity by an order of magnitude.

**Reviewer 4**

The reviewer identified the technical accomplishment for the project. The first technical accomplishment the research team found is that Li-S battery 10-10-20 had the best ionic conductivity of the materials synthesized. The researchers wanted to improve it even more and also improve the electrochemical stability by doping with different halides. The addition of 24% LiI further improved the conductivity to approximately 1 mS/cm. Using SEM EDS and TEM with EELS, the researchers demonstrated that the LiI was not integrated into the electrolyte. Using EIS the research team determined that there are no grain boundaries in the mixture of Li and thioborate. Ball milling reduced the crystallinity of the mixture and decreased the conductivity. The team showed through EIS and cycling that the addition of LiI also improved the interface stability. XPS of the interface revealed LiI, $Li_2S$, and Li metal. Little LBS remained. The team then investigated different solid electrolytes that should be compatible with the cathode and found the $Li_2ZrCl_6$ was the most stable and it resulted in the highest capacity when mixed with NMC in a composite cathode. Lastly, the team put together a full cell of In-LBS-LiZCl-NMC. The reviewer would like to see how this cell performed without the use of Indium. Apparently, the electrolyte does not cycle large amounts of Li very well. The reviewer remarked that it appears additional work on stabilizing the interface through dopants is needed. The project team made a lot of progress in creating a cell with high initial capacity that could cycle fairly well and also in optimizing the thioborate and understanding the mechanism of how it works.

**Reviewer 5**

The reviewer stated that the synthesized materials demonstrate decent ionic conductivity at room temperature. The research team studied and decoupled conductivity contributions of grain and grain boundaries of the materials, which is helpful in understanding and designing other solid electrolyte materials.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer stated that the collaboration within the project team is excellent, but the reviewer did not see contributions from industry. It is better to have industrial inputs regarding the buffer layers in real applications.

**Reviewer 2**

The reviewer stated that the collaboration was good.

**Reviewer 3**

The reviewer stated that the project has a strong leading team at Stanford University that is well experienced in next-generation Li batteries. The work is also supported by SLAC and ORNL via beamtime. The project would benefit greatly by having an industry partner that can demonstrate the scale up manufacturing capability of the Li thioborate solid electrolyte and the performance in industry relevant pouch cells.

**Reviewer 4**

The reviewer stated that it seems like a small amount of money, and they accomplished quite a bit which would require a team.

**Reviewer 5**

The reviewer stated that there was good collaboration with domestic and international partners.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer stated that the future research plan is clearly defined. It is better to work with industrial partners to figure out if the buffer layers acceptable/applicable or should be removed by improving chemical compatibility between LBS and other active electrode materials.

**Reviewer 2**

The reviewer was uncertain if a 50% capacity retention over 50 cycles is competitive with what industry can currently achieve. Making thin and conformal electrolytes is critical. If they are to be used on the cathode side as well, they must be used in relatively small weight percentages.

**Reviewer 3**

The reviewer stated that the proposed future work is clearly defined and is likely to achieve project targets. However, the proposed future work plan should also include collaboration with an industry partner to demonstrate relevance, manufacturing and performance capabilities. There are already quite a few solid-state electrolyte materials that are much further along development wise in industry (sulfides, oxides, halides). In fact, solid-state batteries comprising sulfides, in particular argyrodites, are near commercialization. Any new class/group of solid electrolytes needs to quickly get into the hands of an industry partner to accelerate development.

**Reviewer 4**

The reviewer stated that for future work, the team hopes to investigate bromine and chlorine substitution in LBS and investigate Yttrium (Y), Indium (In), and Erbium (Er) substitution in LiZCl and investigate the possibility of using doped LBS as the catholyte. The reviewer commended the researcher on working through the development of LBS as an anolyte and the reviewer is looking forward to his work on the catholyte.

**Reviewer 5**

The reviewer praised the plan for future work. Given the target and scale of the project, more efforts would be focused to advance the solid electrolyte development and improvement. Particularly, further enhancement of ionic conductivity and electrochemical window would be interesting direction.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer stated that the project supports the overall VTO subprogram objectives since solid-state batteries are a promising approach for potential high energy and long-life EV batteries.

**Reviewer 2**

The reviewer stated that the project has very high relevance. These are high conductivity and earth-abundant materials. The reviewer would encourage this team to differentiate between this work and that on the $B_2S_3$ class of electrolytes described in the early 1980s.

**Reviewer 3**

The reviewer stated that the project supports the overall VTO subprogram objectives.

**Reviewer 4**

The reviewer remarked that DOE VTO would like see progress in solid-state batteries as the possibility of improved energy density and low flammability is very appealing. This research moves the world closer to that reality.

**Reviewer 5**

The project is relevant to DOE/VTO's mission of vehicle electrification and supports the VTO's solid battery programs.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer stated that the resources are sufficient.

**Reviewer 2**
The reviewer stated that the project showed very good progress for only an investment of $200,000/year.

**Reviewer 3**
The reviewer stated that the project resources are sufficient to achieve the ‘stated’ milestones in a timely fashion. However, the resources may need to be increased in the future to include an industry partner.

**Reviewer 4**
The reviewer stated that the group is making good progress with the present funding. It could probably make faster progress with an increase in funding.

**Reviewer 5**
The reviewer stated that the resources are sufficient to achieve the proposed research goals.

**Presentation Number:** BAT599
**Presentation Title:** Fluorinated Glyme Solvents to Extend Lithium-Sulfur Battery Life
**Principal Investigator:** Taylor Xu, Navitas Systems

***Presenter***

Taylor Xu, Navitas Systems

***Reviewer Sample Size***

A total of five reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

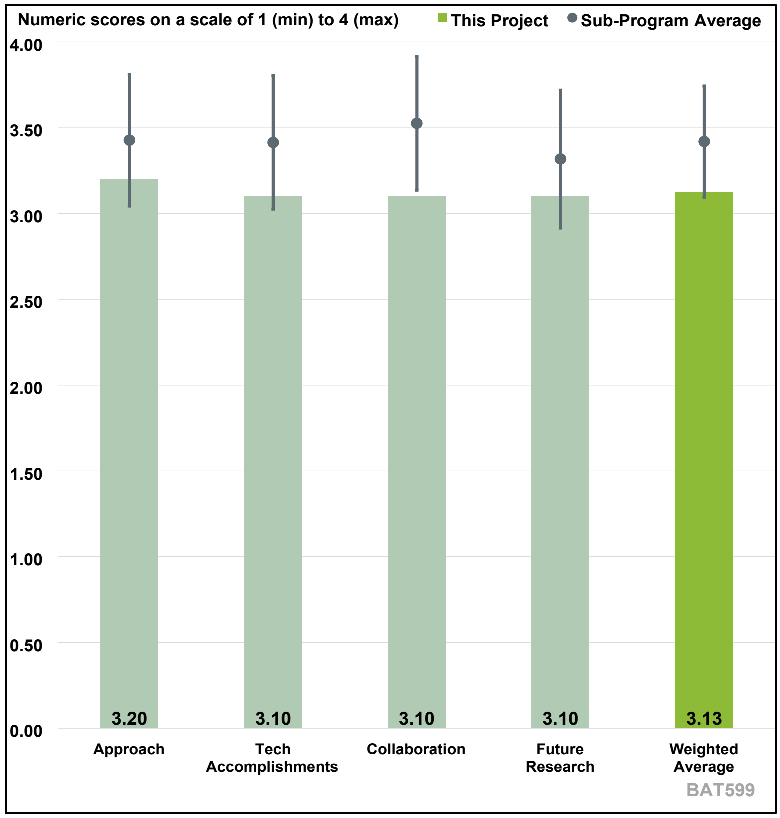


Figure 1-34. Presentation Number: BAT599 Presentation Title: Fluorinated Glyme Solvents to Extend Lithium-Sulfur Battery Life Principal Investigator: Taylor Xu, Navitas Systems

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer stated that even though the project is titled ‘Fluorinated Glyme Solvents to Extend Lithium-Sulfur Battery Life’, it explores a multifaceted approach to enhance the performance and longevity of Li-S batteries. In addition to developing electrolytes based on partially-fluorinated glymes (PFGs), the project incorporates Navitas’ ceramic host cathode and a coated separator. These measures collectively aim to suppress polysulfide shuttling, a critical factor in improving the cycle stability of L-S batteries.

**Reviewer 2**

The reviewer stated that in this project, the team developed ceramic host materials for sulfur with strong polysulfide absorption capability and scaled up the high-mass-loading (more than 3.6 $mgS/cm^2$) sulfur electrode based on the ceramic host. In addition, new solvents (e.g., PFGs) were explored to address the shuttling issues in Li-S batteries. The project is reasonably designed. However, the reviewer stated there is some room to be further improved. For example, the team prefer to choose DOL/PFG solvent in Li-S batteries for shuttling. The reviewer asked why the anode stability testing uses DME/PFG rather DOL/PFG. In addition, >200 mAh pouch cells with 400 cycles need to be set up and tested according to milestones. So far, 70 cycles have been run with obvious capacity decay. The reviewer remarked that the team needs better solutions to achieve the milestone.

**Reviewer 3**

The reviewer stated that a C/ceramic host is used as an host for S, taking advantage of high absorption capability to Li polysulfides and good electronic conductivity. At the same time, fluorinated glyme solvents are used to further suppress the dissolution of Li polysulfide.

**Reviewer 4**

The reviewer praised the approach to performing the work of this project. Three approaches were used: 1) Use ceramic host with high conductivity, strong polysulfide absorption, and catalytic conversion effects on high/low order polysulfides. 2) Use PFGs as multifunctional solvents with high ionic conductivity to increase coulombic efficiency, to improve safety, to suppress polysulfide dissolution in electrolyte, and to promote SEI formation on Li anode surface. 3) Use innovative separators to block polysulfide shuttling and to reduce resistance of assembled cells. The reviewer remarked that these approaches are well designed to address technical barriers, and the timeline is reasonably planned.

**Reviewer 5**

The reviewer stated that the milestones should be better identified with measurable targets. Given the budget level, the research effort and planning need improvement.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer suggested including specific dates in the milestone list, as it is hard to follow the timeline without them. The Navitas team designs and selects PFGs based on their chemical properties (polarity, oxygen number) and their effects in the L-S cell, rather than merely searching among commercial products. The team has demonstrated that the PFG1 (understandably, the molecular formula is not revealed) improves the interfacial stability of the Li anode, reduces lithium polysulfide dissolution, and is non-flammable, thereby enhancing electrolyte safety. The team understands the tradeoff between initial capacity, coulombic efficiency, and capacity retention, which is controlled by the amount of PFG1 added to the electrolyte. Although their double-layer pouch cell has not yet achieved the targeted performance, they have demonstrated the advantages of PFG1 over the baseline electrolyte, indicating that the project is moving in the right direction.

**Reviewer 2**

The reviewer stated that the team is on the right track to improve the cycling performances of Li-S batteries through improvement of electrolytes. Just the experimental design should be further optimized, for example, by improving anode stability with DOL/PFG electrolyte.

**Reviewer 3**

The reviewer stated that good progress was made to improve the cycling performance and coulombic efficiency. Safety study is currently limited to flammability test. With the help of C/ceramic host and FGS, the highest coulombic efficiency achieved was about 90%, which is below expectation for the strong absorption capability of C/ceramic host.

**Reviewer 4**

The reviewer stated that a set of accomplishments took place: 1) Ceramic sulfur host with strong polysulfide absorption capability was used to make sulfur composite cathodes successfully containing 76wt.% sulfur with uniform sulfur distribution. 2) Rolls of high sulfur loading electrode (≥ 3.6 mg of S/cm$^2$) have been made in pilot scale. 3) Low polarity solvents (aliphatic and aromatic group) using PFGs have been designed and synthesized to prevent $Li_2S_x$ dissolution and shuttling, to improve electrode and separator wetting. The cell using DME/PFG1 electrolyte shows less overpotential growth and stable Li stripping and plating indicating improved interphase stability on Li anode. These accomplishments are very good compared to the project plan. The reviewer suggested the project PI may want to present results on why aliphatic PFGs work better than the aromatic ones and discuss the effects of chain length and sites of fluorinations.

**Reviewer 5**

The reviewer stated that although electrode coating quality is visually good, the performance improvement of the C/ceramic cathode is not clear in terms of sulfur utilization, rate capability and polysulfide trapping. The reviewer was unable to see clear improvement of electrolyte or insightful understanding; the research is more like routine test of electrolytes with their electrodes. For practical use, the cell test should be under practical conditions of both high sulfur loading and lean electrolyte conditions. Given the scalable electrode coating by the company, the reviewer suggested to the team to use realistic pouch cells for all the materials/electrolyte test, better identifying real challenges of the technology.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer stated that the project is a good example of synergic collaboration between industry company and national laboratory.

**Reviewer 2**

The reviewer stated that ANL is developing PFG solvents in this project. More characterizations after cell decay from ANL is expected to study the failure mechanisms, which would help further improve cell performance.

**Reviewer 3**

The reviewer stated that there is good collaboration with ANL.

**Reviewer 4**

The reviewer stated that this project includes collaborative research carried out with a VTO-funded project at ANL. Collaborative research with more VTO-funded projects is encouraged for Fiscal Year 2025.

**Reviewer 5**

The reviewer stated that one can see cross-side materials exchange and test, but it would be better to see more on how to further improve the materials or electrolytes based on the collaborations.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer stated that the team has clearly listed the remaining challenges in further developing the Li-S battery. The milestones for the third year are well-defined. Overcoming the barriers in Li-S battery development requires more than just improving a single component. Navitas plans to address these challenges through three main approaches: optimizing the cathode formulation, developing a multi-coating separator, and evaluating new PFGs. The reviewer stated that emphasis should be placed on the compatibility and synergy between components with different features.

**Reviewer 2**

The reviewer has some concerns on achieve BP 3 milestone regarding 2Ah pouch cells with more than 600 cycles. More efforts need to be put on developing electrolytes.

**Reviewer 3**

The reviewer stated that a good plan was proposed to further improve safety, coulombic efficiency and cycle life.

**Reviewer 4**

The reviewer stated that the following future research works are planned: 1) Design and synthesis of new PFG electrolytes to further improve cycle life. 2) New electrolyte additives to stabilize Li anode. 3) Reduce E/S ratio to demonstrate cell level 400 Wh/kg specific energy density. 4) Pass safety and abuse testing with large format 2 Ah pouch cells. 5) Validate and evaluate 2 Ah prototype pouch cells with new electrolytes (more than 600 cycles). These future works are well planned to achieve the targets of this project.

**Reviewer 5**

The reviewer stated that future research and cell test should be under practical conditions such as high mass loading, lean electrolyte and pouch cells. This would be required for industry-lead projects.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer stated that the Li-S batteries are a potential solution to address the shortage of high energy density batteries that meet the DOE-VTO targets, thereby advancing vehicle electrification.

**Reviewer 2**

The reviewer stated that the project supported the VTO Batteries programs.

**Reviewer 3**

The reviewer stated that the project supports DOE’s goal to develop high energy density safe battery for transportation applications.

**Reviewer 4**

The reviewer stated that the project is relevant to current DOE objectives by providing approaches to improve Li-S battery cycle life and performance using innovative electrolytes based on PFGs.

**Reviewer 5**

The reviewer stated that the Li-S battery has great potential as a low-cost and high-energy battery, which is relevant to DOE’s mission of vehicle electrification.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer stated that $748,000 for the 3rd year operation of the project is adequate and sufficient.

**Reviewer 2**
The reviewer stated that the resources in the project are sufficient to perform the proposed work timely.

**Reviewer 3**
The reviewer stated that the resource is reasonable to execute the plan. Given the major challenges to be addressed, the duration of the project is relatively short.

**Reviewer 4**
The reviewer stated that the resources are sufficient for the project to achieve the milestones and objectives.

**Reviewer 5**
The reviewer stated that the resources are sufficient for the project to achieve the goals/milestones.

**Presentation Number:** BAT600
**Presentation Title:** Liquid Electrolytes for Lithium-Sulfur Batteries with Enhanced Cycle Life and Energy Density Performance
**Principal Investigator:** Gaind Pandey, Giner Inc

***Presenter***

Gaind P. Pandey, Giner Inc

***Reviewer Sample Size***

A total of six reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

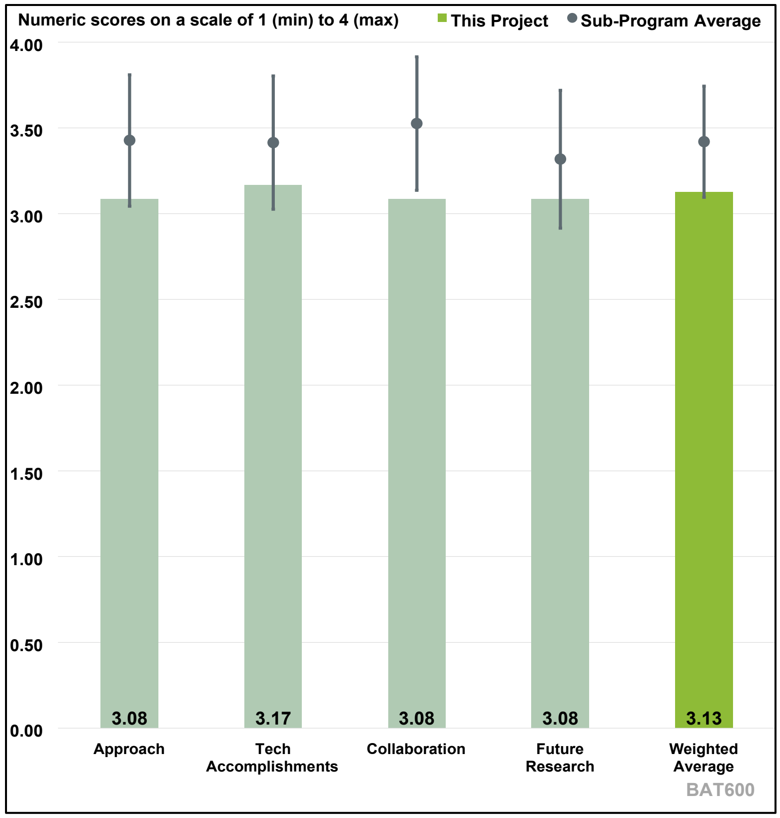


Figure 1-35. Presentation Number: BAT600 Presentation Title: Liquid Electrolytes for Lithium-Sulfur Batteries with Enhanced Cycle Life and Energy Density Performance Principal Investigator: Gaind Pandey, Giner Inc

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer stated the project was designed well to screen nine fluorinated ether cosolvents resulting in a down-selection to two. Spectroscopy was effectively used to identify a reduction in shuttle effects and formation of long-chain polysulfides.

**Reviewer 2**

The reviewer stated the objective of this project is to demonstrate 80% capacity retention with over 500 cycles at an energy density of more than 400 Wh/kg by developing novel electrolytes. The approach involves developing innovative electrolytes with fluorinated co-solvents and strongly bound Li salts to suppress polysulfide dissolution and prevent Li dendrite formation. The effects of fluorinated electrolytes on suppressing Li polysulfide dissolution and Li dendrite formation have been reported as early as 2015 (Journal of The Electrochemical Society, 162 (1) A64-A68). Therefore, the novelty and efficacy of the proposed approach are questionable. Regarding the timeline, the project began in 2021 and is scheduled to finish in 2025, but to date, only 35% of the work has been completed. The primary method to 'develop' novel electrolytes involves screening nine fluorinated co-solvents with four Li salts using coin cell tests. These tests employ relatively low sulfur loading (3.6 to 3.8 mg/cm$^2$) and a high electrolyte-to-sulfur (E/S) ratio (8 μL/mg-S). Many of the co-solvents and Li salts tested, such as TTE, ETFE, TFTFE, LiTFSI, and LiFSI, have been extensively studied in the literature. To achieve the target energy density of 400 Wh/kg in pouch cells, the E/S ratio should be less than 3 μL/mg-S. Potential co-solvents and Li salts for high-energy-density pouch cells should be screened under lean electrolyte conditions.

**Reviewer 3**

The reviewer stated that the PI seems to have a good grasp of the challenges in this very difficult problem for both the Li and the sulfur electrodes. In general, it is hard to believe that all the issues can be addressed with a change of electrolyte, but clearly it is a critical component and the focus of this effort. The reviewer praised the PI's approach of a mixture of electrochemical and analytical analysis. The reviewer remarked the PI also seems to have a good plan for electrolyte development. The reviewer was not sure how the discussed electrode modifications work into the approach. The reviewer stated that the use of pre-dissolved polysulfides was a surprise but seemed to improve performance.

**Reviewer 4**

The reviewer stated that the goal of this project is to develop an electrolyte system for high energy density Li-S batteries under high sulfur loading, low N/P ratio, and lean electrolyte conditions. The PI has proposed using fluorinated co-solvents, strongly-bound Li salts, and additives to suppress polysulfide dissolution and prevent Li dendrite formation. Current review only presents results for fluorinated co-solvents. The reviewer stated the PI also collaborates with others to characterize the new electrolyte system using Raman, NMR, and XAS techniques to gain a mechanistic understanding of the developed system. Using fluorinated co-solvents (ethers) is expected to decrease the overall solvating power of the electrolyte solvents and suppress polysulfide dissolution. However, it is essential to maintain polysulfide dissolution at an optimal level to benefit from the fast kinetics of polysulfide conversion while avoiding reactions with Li metal and the resulting shuttling effect. The reviewer stated that the chosen characterization tools are appropriate for this analysis.

**Reviewer 5**

The reviewer stated that the approach focuses on developing new electrolytes and sulfur composites to significantly enhance Li-S battery performance. By formulating electrolytes with fluorinated co-solvents, strongly-bound salts, and innovative additives, the research aims to suppress polysulfide dissolution and prevent Li dendrite formation. Utilizing advanced characterization techniques and scaling up to high-energy pouch cells, this comprehensive strategy addresses key challenges and promises to deliver batteries with superior stability, capacity, and cycle life. The approach to address both electrolyte and sulfur composite is poised to make meaningful advancements in Li-S battery technology.

**Reviewer 6**

The reviewer stated that from the project objectives, key focus of the project is development of optimal electrolytes. However, too much research efforts rely on co-PIs' fundamental understanding and characterization. Efforts on electrolyte development should be enhanced.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer stated there has been significant progress to meet goals of this project. Namely, screening and evaluating a subset of fluorinated ethers. Empirical investigation of shuttling effects are established for two of the cosolvents. The reviewer inquired that to fully meet the goals if there were other (beyond the original nine) cosolvents considered. The reviewer inquired what knowledge can be gained in the role of the cosolvent to identify alternative (i.e., improved) cosolvents for suppressing S shuttling? The MXenes are shown to be good at adsorbing polysulfides. The reviewer also inquired what the S capacity for MXene is to remove polysulfides. The reviewer inquired what effect extracting generated polysulfides will have on cell capacity fade, if any.

**Reviewer 2**

The reviewer stated that the milestones for March and June 2024 are essentially the same. Achieving 1000 mAh/g is a conservative goal, especially with no E/S ratio specified, as there are already numerous reports in the literature with capacities greater than 1000 mAh/g. Additionally, stating a ‘ >50% improvement’ without context is unclear. The reviewer inquired what the baseline for this improvement is. One of the technical accomplishments mentioned is ‘demonstrated improved cycling stability using fluorinated ether co-solvent-based electrolytes’ in coin cells. However, the figures show no improvements with the 1,1,1,3,3,3-hexafluoro-2-methoxypropane (HFMP)-added electrolytes over the baseline (0% HFMP) in either capacity or coulombic efficiency. No data has been presented for the down-selected TFEM co-solvent and LiTFA salt. The pouch cell development, which is a milestone for June 2024, is far from complete. Not only is the discharge capacity of the 10% TFEM battery lower than 1000 mAh/g, but the cycling test also only runs to 40 cycles with low retention. The high E/S ratio (8 µL/mg) makes the full cell energy density much lower than the targeted 400 Wh/kg.

**Reviewer 3**

The reviewer stated that the PI showed excellent progress with both electrochemical and analytical studies. The reviewer stated had always wanted to see more electrolyte options, but quality over quantity. The reviewer remarked that a better understanding of the pre-dissolved polysulfide additive would be useful.

**Reviewer 4**

The reviewer stated that two fluorinated co-solvents are evaluated in this year’s project review: HFMP and TFEM (bis(2,2,2-trifluoroethoxy)methane). HFMP shows some improvements over the baseline electrolyte, but there is concern that the specific capacity is only around 600 mAh/g during cycling. The state-of-the-art Li-S cell typically achieves capacities above 800 mAh/g during cycling, even under high sulfur loading and low N/P ratio conditions. Similar performance is observed for TFEM, which slightly outperforms the baseline but still exhibits limited capacity. The reviewer remarked that this low-capacity behavior may be related to the PI’s approach. As noted previously, excessive fluorination in the electrolyte can significantly weaken the solvating power and overly suppress polysulfide solubility. This can compromise polysulfide conversion kinetics, leading to limited capacity. Overall, the project has made some technical progress that aligns with the project plan.

**Reviewer 5**

The reviewer stated that the team has made very good progress during this period, particularly in evaluating the effects of various factors on Li-S battery performance. The team has thoroughly investigated the impact of fluoro solvent content and salt concentration on the electrolyte’s stability and effectiveness. Additionally, the incorporation of sulfur composite with MXene materials has been explored, showing promising results. Detailed materials characterization, including structural and compositional analyses, has been performed to understand the interactions and transformations occurring within the battery. Comprehensive electrochemical characterization has also been conducted, assessing parameters such as capacity, cycle life, and efficiency. These efforts have provided valuable insights and advanced the development of high-performance Li-S batteries.

**Reviewer 6**

The reviewer stated that it is not clear which electrolyte (cosolvents and/or salts) comprehensively performs better compared to baseline electrolyte. So far, no electrolyte can really deliver high specific capacity of more than 1000 mAh/g at flooded conditions, not mentioning lean electrolyte conditions. It seems LiFSI shows better cycling when combined with 3% HFMP, but this electrolyte was not used for the following cell test or characterization. The reviewer found that confusing and it seems the research was not well organized across teams with a clear path or focus. The reviewer suggested to be cautious when using Raman or XAS to interpret reactions of Li polysulfides, especially correlating these spectra results to polysulfide conversion kinetics and shuttling suppression.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer stated that clear roles and responsibilities are defined for this project.

**Reviewer 2**

The reviewer stated that the project currently has collaborators only from two universities. The project team needs to broaden its collaborations, particularly with the national laboratories, to access advanced user facilities for in situ/operando studies on Li-S batteries.

**Reviewer 3**

The reviewer stated that the PI's collaborations were clearly helpful to the project.

**Reviewer 4**

The reviewer stated that the PI has established extensive collaboration with Northeastern University and Drexel University on Raman, NMR, XAS measurements. The reviewer suggested the PI may consider working with the national laboratories in the future.

**Reviewer 5**

The reviewer stated that the national laboratories collaboration with Dr. Sanjeev Mukerjee and Dr. Yury Gogotsi has been highly productive, leveraging their expertise in operando studies and MXene synthesis. Their contributions in advanced characterization techniques have provided critical insights and significantly advanced the understanding and development of the Li-S batteries.

**Reviewer 6**

The reviewer stated there was good team structure although inter-team collaboration needs improvement. It appeared to the reviewer that each team worked independently and put the slides together for a report.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer stated that the need to reduce the E/S ratio is identified, however, the strategy to achieve less than 5 µL/mg is not articulated. Also, the role to be played by MXenes future work is not identified.

**Reviewer 2**

The reviewer stated that the team has correctly pointed out the major remaining challenges. The team needs to lower the E/S ratio (less than 3) and increase the areal sulfur loading (more than 5 $mg/cm^2$) to achieve the goal of creating a high energy density Li-S battery (more than 400 Wh/kg). For the proposed future research, there is no clear road map to reach the 400 Wh/kg /500 cycle goal, which is the objective of the project. One of the reported technical progresses is that the MXene composition shows good polysulfide adsorption capability, as evidenced by multi-modal characterizations. The reviewer suggested the team conduct more coin-cell and pouch cell tests to see the effects of the MXene-engineered cathode and separators on improving the Li-S battery performance.

**Reviewer 3**

The reviewer stated that the PI's is plan is good. The reviewer's only criticism is that the latter part of the program is heavy with scale-up and reducing electrolyte amounts.

**Reviewer 4**

The reviewer stated that the PI has proposed future research in many aspects which are needed to make progress in this project.

**Reviewer 5**

The reviewer stated that the proposed future work aims to address key issues and enhance the understanding and development of Li-S cells. By demonstrating high-performance SLP cells, optimizing electrolytes for extreme temperatures, improving cycle performance, and fabricating advanced prototype pouch cells, the research will lead to better stability, capacity, and overall reliability of Li-S batteries.

**Reviewer 6**

The reviewer stated that based on the current progress, the proposed future research would need a big push to achieve the proposed goals. For example, at E/S 8-10 uL/mg, the cells hardly reach 1000 mAh/g, it may not be practical to reach both 1000 mAh/g and 50% improvement in cycling at E/S 5 uL/mg. It is hard to see a clear technology route to reach 50% capacity retention at -40°C, and whether this would come from improved electrolyte, electrode or coating.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer stated that this project supports the overall VTO objectives for beyond Li-ion energy storage.

**Reviewer 2**

The reviewer stated that the L-S battery, with its potential high energy density, if successfully developed will provide reliable portable power for electric vehicles.

**Reviewer 3**

The reviewer stated that the PI is tackling critical problems in battery technology.

**Reviewer 4**

The reviewer stated that this project is highly relevant to VTO's goal of high energy density, beyond Li-ion batteries. Li-S battery is also in line with the supply chain and resource strategy.

**Reviewer 5**

The reviewer stated that the development of Li-S batteries is highly relevant to DOE's battery research goals. By addressing critical issues and advancing the understanding of Li-S cell performance, this research aligns with the DOE's objectives to create high-energy, low-cost, and long-lasting battery technologies. This work contributes significantly to the broader goals of enhancing energy storage solutions and promoting sustainable energy innovations.

**Reviewer 6**

The reviewer stated that the Li-S battery is a promising next-generation battery technology for electric vehicles, so the project is closely relevant to VTO's mission.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer stated that the resources for this project are sufficient.

**Reviewer 2**

The reviewer stated that the project was delayed, perhaps due to the pandemic, with no activity in 2022. It is unclear what the funding level was in Fiscal Year 2022, making it difficult for the reviewer to judge the funding level for the project in 2025. In the past, the funding level has been sufficient.

**Reviewer 3**

The reviewer stated that there seems to be a good amount of work being done on a very difficult problem.

**Reviewer 4**

The reviewer stated that the resources are sufficient for the project to achieve the stated milestones in a timely fashion.

**Reviewer 5**

The reviewer stated that the funding provided is sufficient to support the team's ongoing and proposed research efforts.

**Reviewer 6**

The reviewer stated that the resources would be sufficient, and the lead team need focus more on electrolyte development and evaluation, particularly for new solvents, salts, additives and their compatibility with cathode and Li anode.

**Presentation Number:** BAT601
**Presentation Title:** Development of Functional Electrolytes for Lithium Sulfur Battery Cells
**Principal Investigator:** Donghai Wang, Penn State University

***Presenter***

Donghai Wang, Pennsylvania State University

***Reviewer Sample Size***

A total of four reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

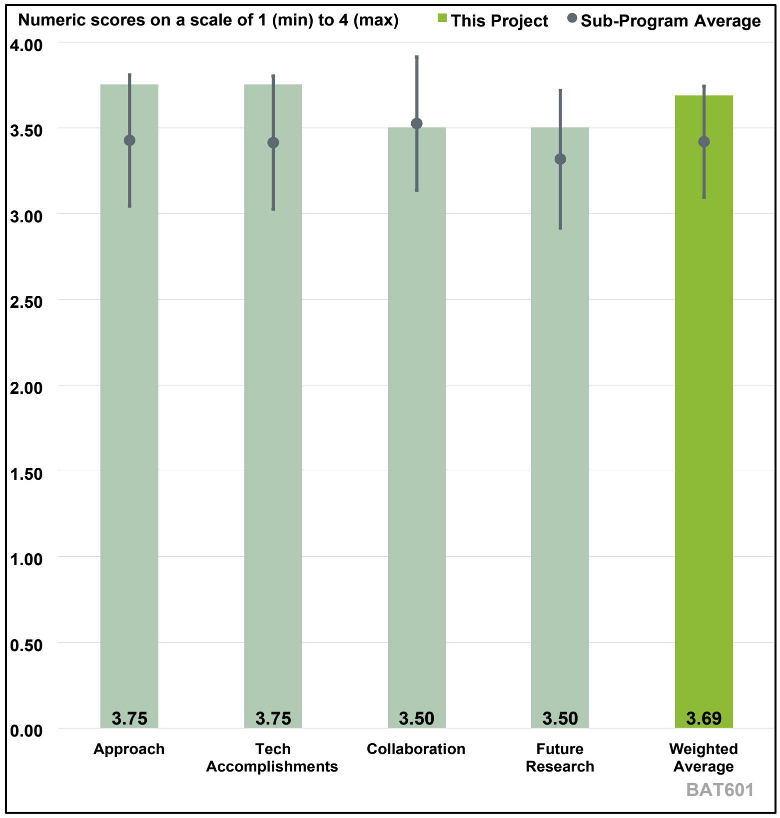


Figure 1-36. Presentation Number: BAT601 Presentation Title: Development of Functional Electrolytes for Li-S Battery Cells Principal Investigator: Donghai Wang, Pennsylvania State University

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer stated that this project aims to address the challenges of polysulfide shuttling and Li-metal instability in Li-S batteries. The approaches include introducing dual additives to the electrolyte system to form stable interphases, coating the Li-metal anode and sulfur cathode with a gel polymer to stabilize the interfaces on both sides, and using an additive that enhances Li2S solubility while suppressing Li polysulfide solubility to improve kinetics. The PI’s team combines experimental and theoretical studies to gain a fundamental understanding of the working mechanisms. Overall, the approaches effectively address the technical barriers, and the project is well designed with a reasonably planned timeline.

**Reviewer 2**

The reviewer stated that the team adopts a novel approach to overcome Li-S battery challenges by focusing on several key strategies. The team is developing innovative electrolyte systems with new solvents, diluents, and additives to suppress polysulfide dissolution and enhance polysulfide conversion kinetics. Additionally, it is optimizing dual-phase gel electrolyte coatings for both Li anodes and S cathodes to stabilize the Li-metal anode and prevent S cathode loss. Advanced characterization techniques, such as Raman spectroscopy and XAS, alongside simulations, are being utilized to gain fundamental insights and optimize Li-S electrolytes. This comprehensive strategy aims to significantly improve battery performance and longevity.

**Reviewer 3**

The reviewer stated that this project targets real challenges of the liquid Li-S battery technology with clear technology solutions. The reviewer stated that the project was well designed, planned, and executed through close collaborations across teams.

**Reviewer 4**

The reviewer stated that the authors focus on one of the most critical challenges in Li-S batteries, i.e., polysulfide shuttling problem. They designed several approaches to overcome this problem, including use of alternative co-solvent DEE to replace conventional DME, use of new additives (AD, MA, as well as ANL-1) to replace typical $LiNO_3$ additive, use of stabilizing gel-electrolyte on both anode and cathode, etc. Most works have been completed on time. The reviewer inquired what the performance of the single additive AD or MA is.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer stated that the dual additive electrolyte maintains the sulfur inventory better than the baseline electrolyte with $LiNO_3$, which consumes sulfur and leads to irreversible sulfur loss. The gel polymer coating strategy enables stable cycling of Li-S cells, achieving over 800 mAh/g specific capacity. The ANL-1 additive significantly improves polysulfide conversion kinetics and enhances the cyclability of high-loading Li-S pouch cells (60 mAh). In all testing conditions, sulfur loading is greater than 4 mg/cm², which is relevant to practical applications. Lean electrolyte is used when possible, and a low N/P ratio is consistently maintained. Based on these results, the reviewer stated the project has made significant technical progress, which is in line with or ahead of the project plan.

**Reviewer 2**

The reviewer stated that the team has developed superb electrolyte additives for Li-S batteries, optimizing a dual-additive electrolyte that significantly improves cycling stability and delivers a high specific capacity of 800 mAh $g^{-1}$ at a 0.1C discharge rate. This innovation greatly reduces SEI waste accumulation and dead Li formation on the Li-metal anode surface. Comprehensive analysis of the dual-additive electrolyte reveals its positive impact on both sulfur and Li electrodes. Additionally, the team has created a dual-phase interface-stabilizing gel electrolyte for Li-S batteries and invented a novel additive to enhance polysulfide kinetics and mitigate the polysulfide shuttling effect. This additive also improves Li deposition morphologies, coulombic efficiency, and cycle life, showcasing a significant advancement in battery technology.

**Reviewer 3**

The reviewer stated that the dual-additive electrolyte fully eliminated the use of $LiNO_3$, which is a very effective approach to solve the cycle life and safety issues. The Li and S cathode coating approaches are also good ways to enhance capacity retention and Li cycling stability. The combined approaches significantly improved cell performance at practical high mass loading and lean electrolyte conditions. The kinetics-enhancing electrolyte also looks promising.

**Reviewer 4**

The reviewer stated that the new additive AD and MA can significantly improve the CE of the Li-S batteries when DEE solvent is used. Cycling stability of the cell has been improved even at lean electrolyte condition for 100 cycles. The effectiveness of additives and long term stability of Li-S cells with these additives still needs to be further investigated. Anode coating is 500 nm thick. The reviewer inquired what the thickness of cathode coating is.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer stated that extensive collaborations have been established with national laboratories (ANL and PNNL) and the University of Illinois Chicago. The expertise from these different institutions is complementary and makes unique contributions to the project.

**Reviewer 2**

The reviewer stated that the project described mostly independent work, with collaboration with ANL for high loading Sulfur electrode.

**Reviewer 3**

The reviewer stated that the project demonstrated clear and close collaborations of multi-teams, which leads to improved cell performance and understanding.

**Reviewer 4**

The reviewer stated that the team used different approaches to address the key challenges in Li-S batteries. The reviewer stated it will be beneficial in future research to combine all these approaches together to test their combined effect.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer stated that the team has proposed to further optimize the electrolyte composition and have more in-depth mechanistic studies.

**Reviewer 2**

The reviewer stated that the proposed future research is crucial for Li-S battery advancements, focusing on optimizing electrolyte additives and gel electrolytes, investigating their protective mechanisms, and demonstrating advanced Li-S pouch cells. These efforts aim to achieve high specific capacity, low E/S ratio, and superior cycle life, addressing key performance challenges.

**Reviewer 3**

The reviewer stated that the team should seek collaboration with Battery500 Consortium to validate their materials/approaches in practical pouch cells under realistic conditions.

**Reviewer 4**

The reviewer stated that the proposed future research is excellent. To have a better understanding of the mechanism behind improved performance will lead to a more clear direction in future work.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer stated that the project is high relevant to the VTO’s goal of high energy density, beyond Li-ion battery systems. Use of sulfur as cathode is also in line with the strategy on supply chain and resources.

**Reviewer 2**

The reviewer stated that the development of Li-S batteries is highly relevant to the DOE's goals of achieving high energy density and low-cost energy storage solutions. By focusing on advanced materials and innovative electrolytes, Li-S technology promises to significantly enhance battery performance, align with DOE's objectives, and contribute to sustainable and efficient energy storage advancements.

**Reviewer 3**

The reviewer stated that the focused Li-S battery is a very promising next generation low-cost but high-energy battery technology for electric vehicles. The project is very relevant to DOE's mission of vehicle electrification and supports VTO's subprograms.

**Reviewer 4**

The reviewer stated that the project is highly relevant to overall VTO subprogram objectives on long term cycle life of Li-S batteries. It addressed one of the most critical challenges in this field.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer stated that the resources are sufficient for the project to achieve the stated milestones in a timely fashion.

**Reviewer 2**

The reviewer stated that the funding provided is sufficient to support the comprehensive R&D efforts. It ensures the team can effectively optimize electrolyte additives, refine gel electrolytes, investigate protective mechanisms, and demonstrate advanced Li-S pouch cells, all aimed at achieving high energy density and low-cost battery solutions in line with DOE goals.

**Reviewer 3**

The reviewer stated that the resources are sufficient for project; and collaborations with Battery500 would be helpful to access more resources or support.

**Reviewer 4**

The reviewer stated that the resources for the project are sufficient.

**Presentation Number:** BAT602
**Presentation Title:** Extending the Operating Range and Safety of Li-Ion Batteries with New Fluorinated Electrolytes
**Principal Investigator:** Suresh Sriramulu, Koura Global

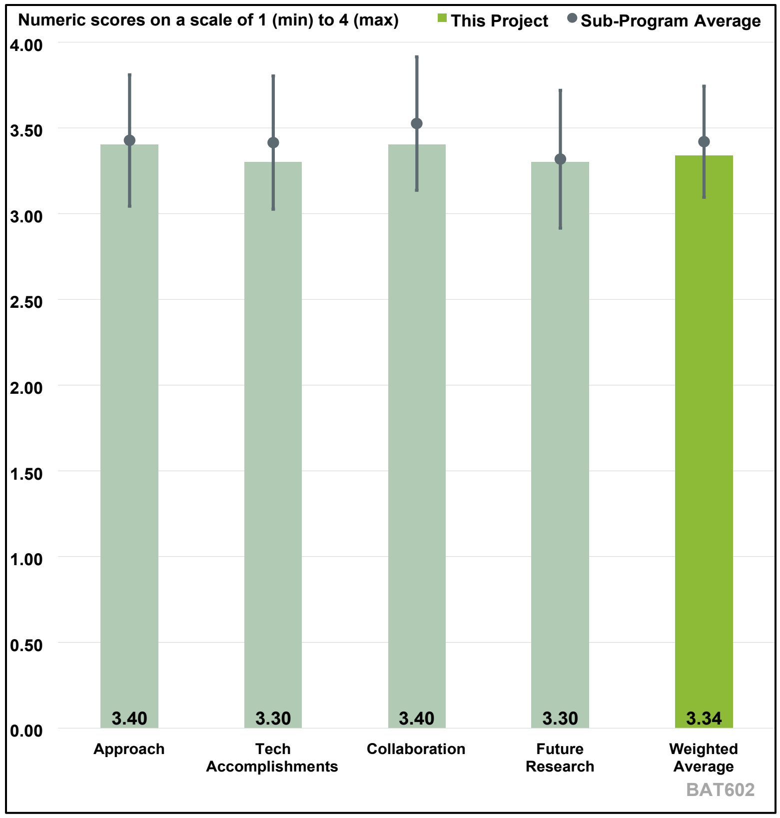


Figure 1-37. Presentation Number: BAT602 Presentation Title: Extending the Operating Range and Safety of Li-Ion Batteries with New Fluorinated Electrolytes Principal Investigator: Suresh Sriramulu, Koura Global

***Presenter***

Sarah Guillot, Orbia

***Reviewer Sample Size***

A total of five reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer stated that the investigators used a platinum working electrode to screen the electrochemical window stability for the various electrolyte solutions. This unfortunately can lead to an overestimation of oxidative stability. Differences in surface properties such as area and porosity of the working electrode are important factors. Electrolyte conductivity measurements at low and room temperature were not reported.

**Reviewer 2**

The reviewer stated that this work screened more than 10 solvents as major electrolyte components to solve the high-rate/low-T performance of LIBs. The identified solvent 403 demonstrated varying improvements in these performance matrices. The timeline is well kept. The progress has been made when compared with the commercial electrolytes, but not with the best electrolytes reported in the literature. The reviewer stated a suggestion: the PIs used Pt electrode as WE and LSV to assess the oxidation stability window. While this is a popular technique, it is also terribly inaccurate. The reviewer recommended the use of real cathode or anode materials as WE for more meaningful results.

**Reviewer 3**

The reviewer stated that fluorinated solvents encounter environmental issues. The reduction of fluorinated solvents to form both LiF SEI and organic SEI. Enhancing F-anion reduction but suppressing non-F solvent reduction is highly recommended.

**Reviewer 4**

The reviewer stated that the objective of this project is to identify fluorinated electrolyte components (additives or solvents) to improve the stability and fast charging/low temperature performance of graphite/NMC811 cells. To do so, multiple fluorinated compounds synthesized by the lead company (Koura) were screened for various properties (high voltage stability, viscosity, conductivity, impedance, etc.), then the best few candidates were further evaluated using a suite of (electro)analytical techniques. Overall, the approach is primarily empirical, but very exhaustive, resulting in a solid understanding of the best performing candidates on battery performance.

**Reviewer 5**

The reviewer stated that the process of down-selecting materials was well described but light on details in the presentation. However, it did achieve the proper results of down-selecting fluorinating materials. The screening of materials using linear sweep voltammetry is a decent first step to determine voltage stability but, as brought up during the presentation, may not convey voltage stability when in contact with different electrode materials. It is not described how electrolyte flammability and how it relates to safety will be addressed in either this phase or the next. In the talk, it was mentioned the work was performed using single crystalline materials. The reviewer inquired if the surface area or if the cathode was poly crystalline could play a role in how well the selected electrolyte performs.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer stated that the investigators have made good progress, keeping the project on schedule. Ten chemicals have undergone a comprehensive electrochemical evaluation for fast charging and wide temperature extremes. Performance feasibility tests using pouch cells were conducted at 0°C, and the initial results are promising.

**Reviewer 2**

The reviewer stated that the improvement achieved in high rate and low T performances appears to be valid, but verification in larger format pouch cells is recommended. The degree of these improvements need to be compared with the best results reported in the literature. The reviewer suggested that in future reports, all PIs should adopt this standard of contrasting their best results against the most updated literature results for the audience to better estimate the progress.

**Reviewer 3**

The reviewer stated that the linear potential scan is useful method to measure the anodic stability of electrolytes. However, the passivation capability of the electrolyte should also be considered by evaluating the currents in the second and third scans. The reviewer inquired what SEI is required to achieved targeted performance.

**Reviewer 4**

The reviewer stated that the progress has been excellent. The project has identified the ‘403’ dioxolane as a top candidate given its various performance-enhancing capabilities. ‘403’ has been extensively characterized in pouch cells, and interfacial and bulk analysis also being performed. Overall, ‘403’ improves the fast charging/low temp rate capability, as well as high temp stability.

**Reviewer 5**

The reviewer stated that the team is meeting their defined technical milestones for their down-select, post analysis testing, and feasibility of pouch cell performance. The biggest factor still remaining that will be the most challenging to predict will be to show the improvement of safety. It is not within the planned work listed in the presentation.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer stated that there has been good collaboration with a national laboratory to fabricate electrodes and test 2Ah pouch cells, and with the University of Wisconsin-Madison for XPS and NMR analysis.

**Reviewer 2**

The reviewer stated that the project has been in good collaboration and coordination with ANL. The electrolytes were provided and tested in the standard pouch made at ANL.

**Reviewer 3**

The reviewer stated that the contribution from ANL were reported.

**Reviewer 4**

The reviewer stated that the team is led by Koura, who also collaborate with ANL. University of Wisconsin-Madison analytical facilities were also utilized in this project. ANL has helped with pouch cell production. The collaborations appear to have been productive, although most of the work appears to occur at Koura.

**Reviewer 5**

The reviewer stated that for the work performed, electrolyte screening and pouch cell cycling, the collaboration is as expected. Argonne validated electrodes for large scale pouch cells in the next phase. Being able to replicate the performance on larger batches of materials will be crucial over the next phase for scale up into the 2 Amp-hour cells.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer stated that the project is expected to end this year. The proposed plans for the remaining few months look reasonable.

**Reviewer 2**

The reviewer stated that the proposed research direction appears to be reasonable.

**Reviewer 3**

The reviewer stated that the future work project is clearly defined.

**Reviewer 4**

The reviewer stated that the project is ending in 2024, so modest future work/milestones are reasonable and primarily focus on further optimization and the construction of larger format pouch cells (2Ah).

**Reviewer 5**

The reviewer stated that the proposed future work with tuning the electrolyte for fast charge and wide operating temperature range will assist in designing the 2 Amp Hour cell. Additionally, investigating manganese dissolution will assist in reaching the required cycling needed in the project goals. However, in the remaining challenges, safety is not listed. There was no flammability test and no safety test listed in the proposed future research. Also, the challenges listed optimizing electrolyte composition for different cell chemistries. The reviewer inquired if this was planned. There is a lot of work to be performed by the end of Fiscal Year 2024. The reviewer recommended not focusing on different cell chemistries but rather on demonstrating the performance in pouch cells.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer stated that the goals for this project are based on the U.S. DRIVE Electrochemical Energy Storage Technical Team Roadmap (2017). It supports VTO objectives.

**Reviewer 2**

The reviewer stated that the project goal is directly relevant to VTO objectives of improving LIB performances in fast charge and low T applications.

**Reviewer 3**

The reviewer stated that the project supports the overall VTO subprogram objectives.

**Reviewer 4**

The reviewer stated that the project is directly relevant to VTO subprogram objectives (better high energy battery performance).

**Reviewer 5**

The reviewer stated that the work looks to research new electrolyte formulations to ease the transition to electric vehicles which would reduce oil consumption and harmful emissions. The work supports a robust US supply chain if the materials cannot be manufactured with.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer stated that the goals for this project are based on the U.S. DRIVE Electrochemical Energy Storage Technical Team Roadmap (2017). It supports VTO objectives.

**Reviewer 2**

The reviewer stated that the resources are sufficient for the project.

**Reviewer 3**

The reviewer stated that the resources are sufficient for the project to achieve the stated milestones.

**Reviewer 4**

The reviewer stated that the project resources/funding appear sufficient.

**Reviewer 5**

The reviewer stated that the resources are sufficient for the work performed. Screening electrolytes, DPA, and making cells takes time and resources. Over the next phase, scaling up to 2 Ahr cells is within line for the requested resources.

**Presentation Number:** BAT603
**Presentation Title:** Fluorinated Ester Local High Concentration Electrolytes for Operation of Li-Ion Batteries under Extreme Conditions
**Principal Investigator:** Esther Takeuchi, Stony Brook University

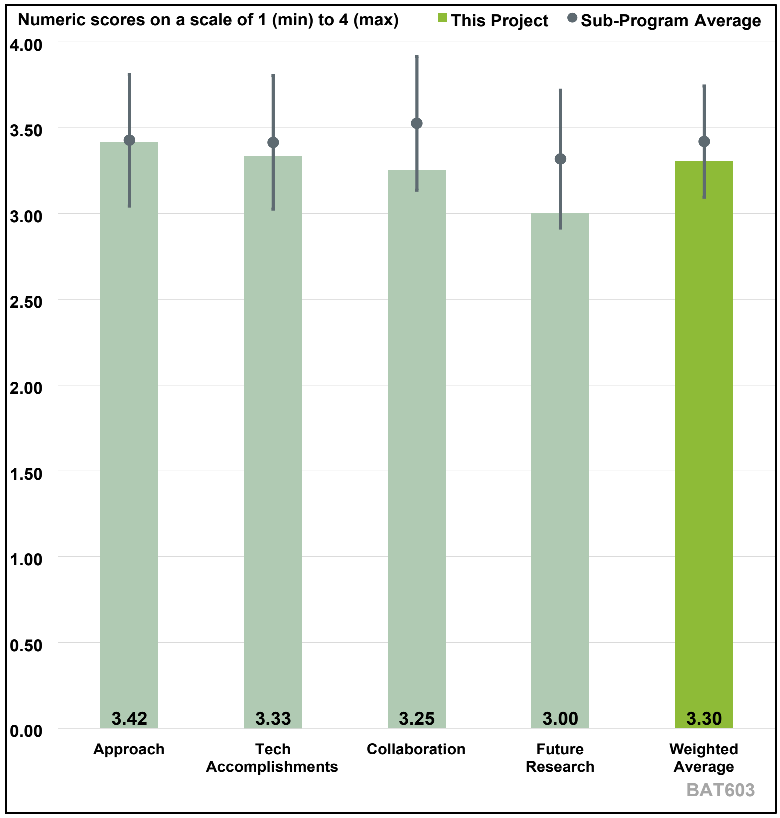


Figure 1-38. Presentation Number: BAT603 Presentation Title: Fluorinated Ester Local High Concentration Electrolytes for Operation of Li-Ion Batteries under Extreme Conditions Principal Investigator: Esther Takeuchi, Stony Brook University

### *Presenter*

Esther Takeuchi, Stony Brook University

### *Reviewer Sample Size*

A total of six reviewers evaluated this project.

### *Project Relevance and Resources*

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer stated that the technical barriers are being effectively addressed, and the approach is very good. Incorporating fluorinated ester solvents into a localized high-concentration electrolyte offers an opportunity to fine-tune the electrolyte's functional properties, enhancing cell performance at low temperatures, fast-charge capability, and safety. However, concerns about the higher cost of these solvents remain.

**Reviewer 2**

The reviewer stated that the LHCE electrolytes are being proposed to solve a range of problems for Li-ion and other advanced batteries. The PI's approach is excellent. Although the reviewer would have liked to see more electrolytes studied, the initial screening was good and produced viable electrolytes. Ultimately, quality takes precedence over quantity. The reviewer remarked that characterization studies should identify the best electrolytes. It will be important to do the larger pouch cell tests with electrodes made on a roll-to-roll coater.

**Reviewer 3**

The reviewer stated that this project screened around 10 electrolytes and tested their fast charge, low temperature and flammability. The localized high concentration electrolytes were adopted from the most recent literature results and modified with proprietary solvents undisclosed. The performance improvements are apparent. For 200 cycles the performances at 4.5V, -20°C or 15 min charge all demonstrated superiority over conventional electrolytes. The simulation of SEI chemistry is of high value, because it is so far the most important missing link in predicting SEI chemistry. With it the entire chain of in silico chemistry will be complete.

**Reviewer 4**

The reviewer stated that the ether LHCE is suitable for Li-metal batteries, but faced challenges of limited anodic stability. Replacing ether solvent and diluent can enhance anodic stability of the LHCE, and also suitable for graphite anode (although it may reduce the Li-metal CE).

**Reviewer 5**

The reviewer stated that the localized high concentration electrolyte (LHCE) concept employed for this project h is not new. The conventional carbonate-based electrolyte (1.2 M $LipF_6$ EC/DEC) is a typical LHCE—EC is the solvating solvent, and linear carbonate DEC was added to EC/$LiPF_6$ solvation structure as diluent to reduce viscosity and conductivity. Solvation could improve the property of electrolyte, however the key technology still lies in the solvent, salt and additive used.

**Reviewer 6**

The reviewer stated that the technical goal of fast charge and low temperature performance was achieved, which is a very aggressive rate at a very low temperature. The data showed progress towards two goals set forth in the project. The electrolyte was studied using flammability tests showing some progress towards improving safety. All cell cycling work was performed at 4.5V as the charging voltage.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer stated that the project has made excellent progress, successfully meeting all milestones. Two electrolytes, MOF and MTF, demonstrated improved capacity retention compared to conventional electrolytes after 200 cycles under extreme test conditions, including high voltage, fast charging, and low temperatures. Additionally, these electrolytes exhibited reduced flammability. The research efforts were documented in two open literature papers and presented during a detailed presentation.

**Reviewer 2**

The reviewer stated that the PI's mix of electrochemical, analytical, and modeling studies are extremely good with a lot of interesting results. Most importantly, improved electrolytes were identified. The reviewer would see value in this project adding to the fundamental understanding of the SEI layer.

**Reviewer 3**

The reviewer stated two suggestions: 1) the PI used Pt electrode as WE and LSV to assess the oxidation stability window. While this is a popular technique, it is also terribly inaccurate. The reviewer recommended the use of real cathode or anode materials as WE for more meaningful results. 2) The safety of the electrolytes cannot be accurately evaluated by ignition only. The reviewer suggested testing electrolyte/electrode combination in DSC or ARC setups.

**Reviewer 4**

The reviewer stated that the coulombic efficiencies of graphite anode and NMC811 cathode in the MTF should be measured.

**Reviewer 5**

The reviewer stated that the electrolyte using fluorinated esters did show some improved performance over the baseline electrolyte (carbonate based), however the research and the discussion are pretty much focused on the additive effect (FEC, LiDFOB) on the LHCE. There is no data to support why fluorinated LHCE is better than the non-fluorinated counterpart. Furthermore, it is fair to compare with non-fluorinated counterpart instead of carbonate baseline electrolyte. Only improved cycling data were shown without any discussions of the mechanism.

**Reviewer 6**

The reviewer stated that the technical accomplishments related to the science of the electrochemistry, finding solvents that work at high rates and wide temperatures, and finding the correct mix of electrodes and electrolytes to meet fast charge is well on its way. However, there was not enough information given on scaling up to meeting the 2 Ah deliverable at end of the year. While that is at the end of the year and not planned yet, scaling up is no trivial task.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer stated that the project is well-coordinated. While the presenter’s slides do not explicitly highlight this, a review of the PI’s journal articles and discussions with team members reveal the collaborative efforts of the team. Adding a small footnote to the relevant tables and plots could be beneficial to avoid confusion in future presentations.

**Reviewer 2**

The reviewer stated that the PI is collaborating with researchers on several of the studies.

**Reviewer 3**

The reviewer stated that the collaboration between the PIs and co-PIs are well managed.

**Reviewer 4**

The reviewer stated that the contributions from collaborators are presented and supported the proposed mechanism.

**Reviewer 5**

The reviewer stated that the collaboration with other organizations looks good.

**Reviewer 6**

The reviewer stated that it is not clear who did what in the presentation but all the work is being accomplished.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer stated that the project is expected to wrap up by the end of the year. The future efforts of full-cell evaluations with optimized electrolyte is appropriate.

**Reviewer 2**

The reviewer stated that there is not a lot of detail on the proposed future work, but continuing the current studies should lead to important insights and advances. The rate of project advancement is good, but puts a lot of challenges on the final year.

**Reviewer 3**

The reviewer stated that the proposed future direction is great.

**Reviewer 4**

The reviewer stated that the future work was clearly defined.

**Reviewer 5**

The reviewer stated that the future study should focus on understanding why LHCE is better than non-fluorinated counterpart and the baseline electrolyte. Also, the correlation of fluorinated ester with cell performance needs to be studied.

**Reviewer 6**

The reviewer stated that the barrier remaining are critical to once in pouch cell. For instance, gas generation at extreme conditions on the electrodes may severely hinder the cycle life. Exploring through SEI measurements in modeling and simulation will provide insight into this as well. The reviewer inquired what the size of the pouch cells used was. The reviewer also asked if there is a concern with LHCEs not forming the proper interface when injected into a multi-layer pouch cell rather than a single layer. Assuming they are not large pouch cells, the reviewer wondered the safety implications once in a pouch cell.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer stated that the project is relevant to the VTO program as it is aimed at fast charge.

**Reviewer 2**

The reviewer stated that the new electrolytes are key to improving the Li-ion battery technology.

**Reviewer 3**

The reviewer stated that the project is highly relevant to VTO objectives in advancing battery chemistries.

**Reviewer 4**

The reviewer stated that the project supports the overall VTO subprogram objectives.

**Reviewer 5**

The project supports the overall VTO subprogram objectives.

**Reviewer 6**

The reviewer stated that the project is exploring using LHCE for fast charge applications, looking to expand the operational temperature range, and be a safe electrolyte.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer stated that the project has the necessary resources to complete the tasks on time.

**Reviewer 2**

The reviewer stated that while not a lot of electrolytes, the depth of studies is impressive.

**Reviewer 3**

The reviewer stated that the project has sufficient resources.

**Reviewer 4**

The reviewer stated that the resources are sufficient for the project to achieve the stated milestones.

**Reviewer 5**

The reviewer stated that the interface analysis and deep understanding of the performance improvement needs to be studied.

**Reviewer 6**

The reviewer stated that the resources are sufficient. 75% of the budget has been spent with less than one year left on the effort.

**Presentation Number:** BAT604
**Presentation Title:** Novel Organosulfur-Based Electrolytes for Safe Operation of High Voltage Li-Ion Batteries Over a Wide Operating Temperature
**Principal Investigator:** Meinan He, General Motors

***Presenter***

Meinan He, General Motors

***Reviewer Sample Size***

A total of five reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

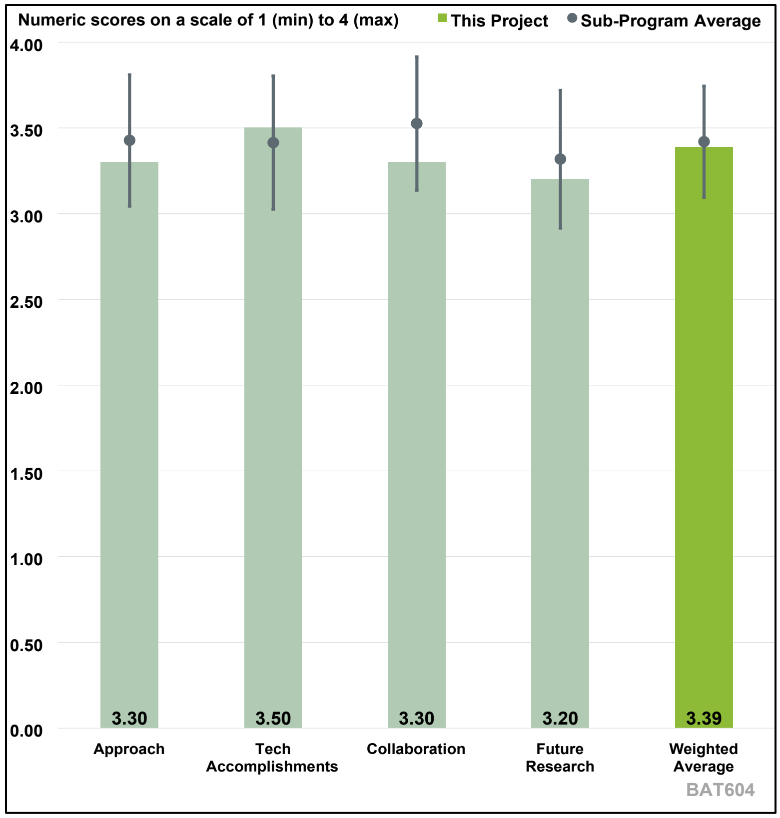


Figure 1-39. Presentation Number: BAT604 Presentation Title: Novel Organosulfur-Based Electrolytes for Safe Operation of High Voltage Li-Ion Batteries Over a Wide Operating Temperature Principal Investigator: Meinan He, General Motors

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer stated that the objective of the project was not clearly identified in the presentation. The only statement was a vague desire to develop a new electrolyte based on organosulfur compounds, with no mention of the desired voltage limits, temperature range, or rate capability. The reviewer suggested that future presentations include specific goals on the slides. Despite this, the reviewer remarked that the approach to developing a high-performance electrolyte is based on sound principles, and the tasks are logical.

**Reviewer 2**

The reviewer stated that this project explores sulfone-based electrolytes, and develops a series of new solvent structures. Considering that the battery community has been playing in the tiny chemical classes of ether and ester for the last 30 years, such highly risky and highly exploratory effort should be encouraged.

**Reviewer 3**

The reviewer stated that the barriers of high voltage stability appear to have been addressed with the organosulfur electrolytes with additives, although optimizations and new improvements to formulations are ongoing. Temperature studies on cell performance have not yet been presented. A lot of the presentation focused on baseline cells. This does help to demonstrate when new formulations/additives do make an improvement. The project has centered on an organosulfur containing electrolyte with better performance than Gen 2 electrolyte baseline. The time remaining in the project is 1 year- there appears enough time remaining to meet the remaining goals of pouch cell abuse testing. Fully completing the remaining studies on SEI formation, thermal stability, and an expanded solvent study may be challenging. The project is well thought out- the strategy of picking a single set of anode/cathode and modifying the electrolyte is a good approach. More projects should focus on electrolyte optimization such as this- each anode/cathode combination potentially benefits from a matched electrolyte. Based on the title, more work on organosulfur materials was expected. The reviewer inquired if there are any additional organosulfur targets competitive with the EMS data shown? The reviewer inquired if there are plans for designer materials.

**Reviewer 4**

The reviewer stated that work studying different cosolvents is very thorough but it is unclear what technical barriers are being addressed as the reviewer could not find them in the presentation. Assuming it is studying 4.5V operation and studying the effect in a pouch cell, the work from coin cells to 2 Ahr cells covers mixtures, most notably FEC, EMS, and additions of non-solvating fluoroaromatic co-solvents to improve cycling performance.

**Reviewer 5**

The reviewer remarked that the objective of this project is to develop a new electrolyte system based onorganosulfur compounds for high voltage LIBs, which is an important topic. The approach was very good to fabricate coin and pouch cells to establish a baseline with standard electrolyte and then test new electrolyte to compare with for any improvement.

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer stated that good progress has been made, with the team synthesizing new solvents and demonstrating a prototype organosulfur-based electrolyte with enhanced performance. However, not all accomplishments were clearly conveyed during the presentation. To fully appreciate the body of work, one had to consult the published journal articles. Perhaps more detail can be provided in any future presentations.

**Reviewer 2**

The reviewer stated that a series of sulfone solvents were thoroughly investigated in rigorous manner. The performances showed varying degree of improvements. The few top picks delivered impressive results in pouch cells. More complete verification especially on the gassing issue will further confirm the usefulness of these electrolytes.

**Reviewer 3**

The reviewer stated that the project has identified an organosulfur containing electrolyte that successfully cycles in 2 Ah pouch cells at high voltage for 100 cycles, much better than Gen2 baseline. Most of the work presented showed baseline data and comparisons of a single organosulfur containing electrolyte. It appeared that the remaining organosulfur targets shown were eliminated on the basis of calculations or modeling? The current pouch cells with the Gen A electrolyte appear to meet the target goals but show a modest improvement over standard Gen2 electrolyte (without additives). The reviewer inquired if this formulation can be cost-competitive with

Gen 2. Identification of fluorobenzene as a new co-solvent to replace fluoroethers showed better ionic conductivity and reduced viscosity. The fluorobenzene co-solvent seems to be a discontinuity in the program- it was not clear if this new formulation with fluorobenzene will be incorporated into the final pouch cell testing. The reviewer inquired if the team plans to explore other fluoroaromatics as co-solvents. The reviewer also inquired if fluorobenzene act similarly to local high concentration electrolytes (LHCE's). It seems counterintuitive that fluorobenzene shows the best conductivity but doesn't affect the solvation of the electrolyte. The review inquired if did the modelling studies on activation energies of the co-solvents towards singlet oxygen reactivity examine the para-hydrogen position of fluorobenzene as well as the ortho-position?

**Reviewer 4**

The reviewer stated that it was difficult to judge based on the presentation. They are using a feedback loop of coin cell results to feed into 2 Ah cell results and back again, while designing different electrochemical mass spectrometry to study off gassing of the 2 Ah cells.

**Reviewer 5**

The reviewer stated that good progress was made by identifying EMS as a good potential organosulfur compound. The results of showed improvement of EMS over the baseline. replacing $LiPF_6$ with LiFSI presents a promising and innovative approach to stabilize the organosulfur electrolyte. However, considering the potential corrosion of LiFSI with the Al current collector needs to be addressed. Impact of Co-solvent was investigated and showed that performance could be improved. The project was about safe operation over a wide range of temperatures. The presentation results seem to be at room temperature and did not provide any information on how the cells perform at higher or lower temperatures. No safety testing was presented.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer stated that the team is highly qualified; however, it is difficult to discern the specific efforts of each collaborator. Providing footnotes for individual contributions in future reporting would be helpful.

**Reviewer 2**

The reviewer stated that the collaboration and coordination are excellent.

**Reviewer 3**

The reviewer stated that each team partner contributed to the presentation, and each section showed interesting data. However, the initial impression was that each team focused on their own area, and it was not merged until recently, with the more collaborative work with the fluorobenzene cosolvent. The presentation would have benefited from a more clear assignment of work activities from each group.

**Reviewer 4**

The reviewer stated that a mention in the presentation on who was participating in which aspects of the project but the group appears to be making progress towards their goals.

**Reviewer 5**

The reviewer stated that the team collaboration with participation from Industry (GM), a national laboratory, and two universities is good. Coordination between team member were acceptable.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer stated that the proposed future plans are satisfactory, but no specific details were provided.

**Reviewer 2**

The reviewer stated that the proposed future research is promising and worth looking into. The new solvents as well as new formulations will be interesting not only for LIBs but also for other battery chemistries.

**Reviewer 3**

The reviewer stated that the remaining project objectives (wide temperature studies, different organosulfur solvents) do not fully agree with the final slide next steps to study SEI formation and other SEI formers. It is not clear what new solvents are targets- commercial materials or newly designed and synthesized organosulfur solvents- that should be clarified. Several times the PI presented sulfates as a potential class of materials- has the toxicity and reactivity been examined? Has any data on flammability been established for the fully formulated electrolyte?

**Reviewer 4**

The reviewer stated that the part of what the issue was mentioned during the presentation was SEI formation during 4.5V operation, which is not surprising, and the team has proposed exploring other SEI forming co-solvents to combat this issue.

**Reviewer 5**

The reviewer stated that the future work was only three bullets and did not address how to prevent gas generation at higher temperature. The plan to looks at thermal stability of the electrolyte, but they also need to do some abuse/safety testing to show the cell with this electrolyte is safe.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer stated that the project supports the VTO battery objectives; however, these objectives were not clearly identified in the presentation due to the vagueness of the stated goals.

**Reviewer 2**

The reviewer stated that the project is highly relevant to VTO objectives of advancing battery technologies.

**Reviewer 3**

The reviewer stated that the organosulfur electrolytes have a potential to operate at higher voltages, thereby avoiding some of the voltage instability issues with current electrolyte formulations. The PI presented interesting additive- fluorobenzene- which may prove useful for other projects as well. The development of high voltage electrolytes clearly is of interest to the overall subprogram goals to improve LIB technology through stable high voltage cells. Although clearly the best cells, it was not entirely clear if this was a purely physical effect on viscosity, conductivity, etc., or there was also an effect on the SEI. PI's have demonstrated better high voltage cycling than baseline by using organosulfur electrolytes with additives. The reviewer inquired how the baseline electrolyte plus additives compare to the organosulfur cells, and how do these cells perform at high/low temperature?

**Reviewer 4**

The reviewer stated that the goal of the project is to explore high voltage electrolytes that are safe, while performing more in-depth characterization at the pouch cell level. The team is performing all of those but more safety data would be interesting, especially at the pouch cell level.

**Reviewer 5**

The reviewer stated that the projects support the overall VTO Battery objective of producing high voltage and safe electrolytes for Li-ion batteries.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer stated that the available resources seem adequate to achieve the stated milestones, indicating that there are no concerns about resource sufficiency.

**Reviewer 2**

The reviewer stated that the resources are sufficient.

**Reviewer 3**

The reviewer stated that the resources appear sufficient for the project.

**Reviewer 4**

The reviewer stated that it is unclear if it is sufficient. The original budget was sufficient for the work being performed during the time line proposed.

**Reviewer 5**

The total budget of $3.2 million is sufficient for achieving the objectives of the project.

**Presentation Number:** BAT605
**Presentation Title:** Silicon Consortium Project Next Generation Electrolytes for Silicon Anodes
**Principal Investigator:** Gabriel Veith, Oak Ridge National Laboratory

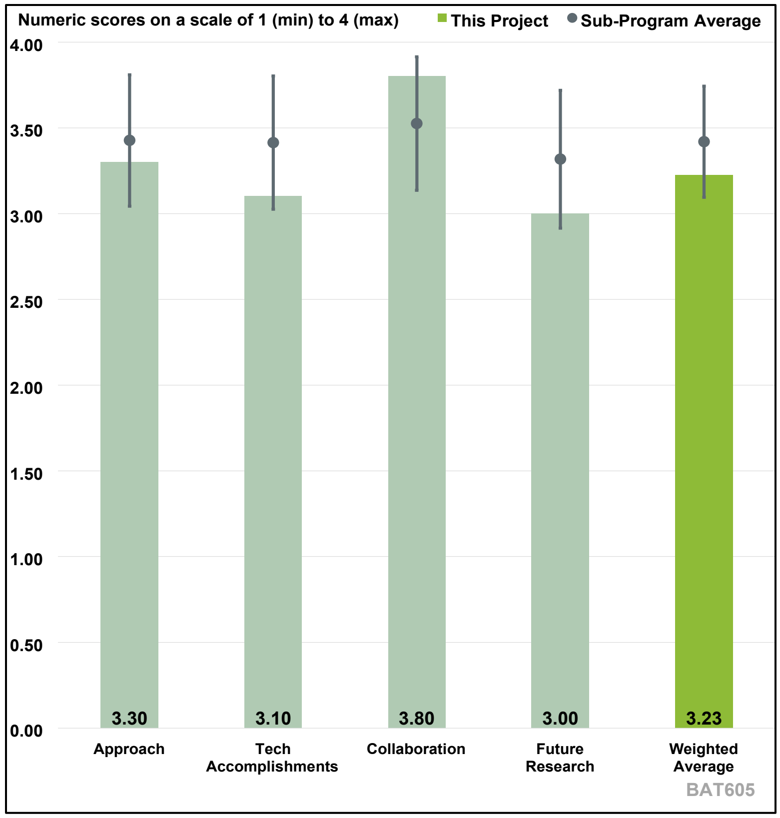


Figure 1-40. Presentation Number: BAT605 Presentation Title: Silicon Consortium Project Next Generation Electrolytes for Silicon Anodes Principal Investigator: Gabriel Veith, Oak Ridge National Laboratory

***Presenter***

Gabriel Veith, Oak Ridge National Laboratory

***Reviewer Sample Size***

A total of five reviewers evaluated this project.

***Project Relevance and Resources***

100% of reviewers felt that the project was relevant to current DOE objectives, 0% of reviewers felt that the project was not relevant, and 0% of reviewers did not indicate an answer. 100% of reviewers felt that the resources were sufficient, 0% of reviewers felt that the resources were insufficient, 0% of reviewers felt that the resources were excessive, and 0% of reviewers did not indicate an answer.

***Question 1: Please comment on the degree to which technical barriers are addressed. Is the project well designed, and is the timeline reasonably planned?***

**Reviewer 1**

The reviewer stated that understanding and stabilizing the SEI is key to commercial success of Si anodes. This work is fundamental in nature and is contributing significantly to this goal.

**Reviewer 2**

The reviewer stated that the approach is very focused on the key challenge for the SCP, with a clear hypothesis and a work plan that pursues that hypothesis. Significant progress on evaluating this hypothesis is being made using the current approach.

**Reviewer 3**

The reviewer stated that the PIs proposed mechanism how Si-based batteries lose performance and believed that forming long chain SEI components is the key. The researchers adjusted electrolyte composition to execute such a strategy. The performance of the new electrolyte seems to provide certain improvements. But the performance are still under the targets.

**Reviewer 4**

The reviewer stated that the approach is satisfactory as a hypothesis is stated that can lead to an unstable SEI in silicon-containing anodes. However, while the team details how changing the solvation structure will decrease the SEI dissolution and promote larger polymerization products, there is no discussion how this change will address the consortium's overall goal of a 10 year calendar life silicon-anode containing cell.

**Reviewer 5**

The reviewer stated that the project focused on one leading hypothesis on might be the difference between Graphite SEI and Silicon SEI. The work focused on developing understanding of solvation structure/solvation energy effect on the resulting SEI on Si anode surface, which is believed to be the key to achieve superior cycle life and calendar life. Several different tests have been conducted with different electrolyte formulations with various solvent ratios and Li salts. This work clearly demonstrates that solvent ratio and Li salt type and combinations of them will significantly affect solvent structure/solvation energy. However, the reviewer commented that it would be beneficial if the correlation between the solvation energy and SEI stability (cycle life or calendar life) can be established in a clearer fashion. (For example, there is no cell test results for the electrolyte formulations showed different solvation energy on Slide 11. There is no solvation energy data of the different new electrolyte formulations on Slide 13 where the electrolyte formulations showed different calendar life.)

***Question 2: Please comment on the technical progress that has been made compared to the project plan.***

**Reviewer 1**

The reviewer stated that the work is innovative and broad in scope. The results are interesting and relevant to further silicon anode electrolyte design and SEI understanding.

**Reviewer 2**

The reviewer praised the technical accomplishments to date. An electrolyte with improved performance has been identified. Methods to assess solvation—the key part of the idea—are being used to quantify the properties of candidate electrolytes. Full cell work is underway. One limitation is that in the focus on calendar life, other required electrolyte properties may be getting overlooked, in particular transport properties (e.g., ionic conductivity) and rate capability. If the new electrolyte improves calendar life but significantly impacts rate capability or other key properties, that is an issue. The impact of the electrolyte on the cathode is being pursued, which the reviewer approved, but other impacts should also be considered.

**Reviewer 3**

The reviewer stated that the electrolyte strategy may not be working as the PI suggested. According to the structures of the proposed SEI components, the solubility of these SEI ingredient should not be as pronounced as the PI expects. The reviewer commented that maybe an inorganic-rich, polymer-free SEI should be considered instead.

**Reviewer 4**

The reviewer praised the project's accomplishment of achieving 500+ cycles with its new electrolyte combinations, however this result is still far below the 1000 cycle threshold dictated by the consortium milestones (which was already achieved in previous programs). Also, while the project presentation details a four-times improvement in calendar life, the results are still significantly behind the ten-year goal of the consortium.

**Reviewer 5**

The reviewer stated that the EC-free electrolyte formulation was proposed and tested using NMC811//$SiO_x$/Gr composite anode. It is interesting to see that EC-free formulation showed superior cycle life than EC containing electrolytes. A systematic study on EC/EMC/$LiPF_6$ molar ratio suggests that $PF_6$- : EC concentration is strongly correlated with poorer cycle life and stability. However, those EC-free electrolyte formulations have not been demonstrated in PECVD Si/C composite anode yet, the reviewer was wondering if the positive impact can be translated to a different Si anode. FEC has been reported in several literatures as a beneficial additive for Si containing anode. However, in this work, the addition of FEC as an additive showed poorer cyclability in the NMC811/$SiO_x$/Gr pouch cell. The reviewer wondered if an explanation can be provided. The reviewer suggested this could possibly be due to the difference on the Si anode. If that is the case, the reviewer inquired if the optimal electrolyte formulations identified in $SiO_x$/Gr composite be able to show positive impact on PECVD Si/C anode.

***Question 3: Please comment on the collaboration within the project team. Are there specific contributions made by industry, national laboratories, or other external entities? Are there areas where more collaboration is needed?***

**Reviewer 1**

The reviewer stated that the coordination is excellent across the different groups.

**Reviewer 2**

The reviewer stated that the it appears there are valuable contributions from many team members.

**Reviewer 3**

The reviewer stated that the collaboration is tight and well managed.

**Reviewer 4**

The reviewer stated that as with the other consortium projects, the team has outstanding and extensive collaboration with the partner national laboratories.

**Reviewer 5**

The reviewer stated that this work has involved multiple national laboratories. The team is composed of modeling experts, organic chemists, characterization experts and electrochemists, all of which are critical to developing a new electrolyte formulation for such a challenging system. However, the reviewer believed it would be beneficial to have more interaction with silicon anode development team, which will help understand the surface reactivity between electrolyte and silicon anode better.

***Question 4: Please comment on the proposed future research. Has the project clearly defined a purpose for future work? To what extent will future work likely achieve its targets?***

**Reviewer 1**

The reviewer stated that further experimental verification of the model results are planned and should be the focus of work.

**Reviewer 2**

The reviewer stated that future research is specific and looks excellent. The reviewer reiterated the suggestion on looking at key transport properties as a function of temperature and salt concentration to make sure the rate capability remains high enough.

**Reviewer 3**

The reviewer stated that the proposed future activity of looking into electrolyte composition is reasonable.

**Reviewer 4**

The reviewer stated that the future proposed research, while analytically sound, does little to exude confidence that an electrolyte solution can or will be developed to help create a silicon-containing anode that will have a calendar life of 10 years.

**Reviewer 5**

The reviewer stated that at this stage of project, several promising candidates have been identified, such as EC-free solvent system, Li salt with low solvation energy with certain solvents and promising additives that extended cycle life. However, no clear plan has been revealed on how to incorporate those promising findings into electrolyte formulation development. Additionally, it is not clear to the reviewer if those promising candidates will be validated in PECVD silicon based anode prior to combining them together to seek further improvement. More importantly, calendar life tests should be used as the primary test protocol in the future along with cycle life test. So far, the reviewer has seen more cycle life tests even though the project goal is to solve the calendar life issue of this chemistry.

***Question 5: Please comment on the relevance of the project. Does the project support the overall VTO subprogram objectives?***

**Reviewer 1**

The reviewer stated that the project is highly relevant for fundamental understanding of SEI, solvent and salt interactions.

**Reviewer 2**

The reviewer stated that the project is relevant to batteries.

**Reviewer 3**

The reviewer stated that the project is highly relevant.

**Reviewer 4**

The reviewer stated that the project supports the overall VTO subprogram objective of analysis, batteries, and materials.

**Reviewer 5**

The reviewer stated that this project is critical to address the calendar life issue of high energy density batteries. It supports the overall VTO subprogram objectives, especially for Batteries, Materials and Electrification.

***Question 6: Please provide comments on the resources of the project. Are the resources sufficient for the project to achieve the stated milestones in a timely fashion?***

**Reviewer 1**

The reviewer stated that the resources are sufficient.

**Reviewer 2**

The reviewer stated that the resources appear sufficient.

**Reviewer 3**

The reviewer stated that there are sufficient resources available.

**Reviewer 4**

The reviewer stated that the resources are sufficient for this program to achieve the stated milestones in a timely fashion.

**Reviewer 5**

The reviewer stated that this project is composed by a team of experts from different areas including modeling, organic synthesis, characterization and pouch cell testing, which seems to be sufficient for its needs. The reviewer made the recommendation, that it would be beneficial to plan enough resources to supply PECVD Si anode for initial electrolyte study to validate the positive impact observed in $SiO_x$ based anodes.

## Acronyms and Abbreviations – BAT

| Abbreviation | Definition |
|---|---|
| **µL/mg-S** | Microliter per milligrams sulfide |
| **0D** | Zero-dimensional |
| **1 Å –10 cm** | Angstroms to centimeters scale |
| **1 s – 1 yr** | Seconds to year scale |
| **1D** | One-dimensional |
| **2D** | Two-dimensional |
| **3D** | Three-dimensional |
| **AD** | Additives type |
| **AFM** | Atomic force microscopy |
| **Ag** | Silver |
| **Ah** | Ampere-hour |
| **AIMD** | Ab initio molecular dynamics |
| **Al** | Aluminum |
| **AMR** | Annual Merit Review |
| **ANL** | Argonne National Laboratory |
| **APS** | Advanced Photon Source |
| **ARC** | Accelerating rate calorimetry |
| **ARL** | Army Research Laboratory |
| **ASR** | Double-loop DC drive system, speed loop (ASR) |
| **$B_2S_3$** | Boron Sulfide |
| **$B_2S_3$-$Li_2S$** | Boron Sulfide and Lithium Sulfide |
| **B500** | Battery 500 Consortium |
| **BESS** | Battery energy storage system |
| **BNL** | Brookhaven National Laboratory |
| **BP** | Budget Period |
| **C/S** | Carbon/sulfur |
| **CA** | Conductive additive |
| **CAM** | Cathode active materials |

| Abbreviation | Definition |
|---|---|
| **CE** | Coulombic efficiency |
| **CEI** | Cathode electrolyte interphase |
| **CFM** | Carbon framework material |
| **CMC-SBR** | Sodium carboxymethyl cellulose (CMC) and Styrene butadiene rubber (SBR) |
| **Co** | Cobalt |
| **CPE** | Composite polymer electrolyte |
| **CS-SPAN** | Carbon Supported Sulfurized polyacrylonitrile |
| **Cu** | Copper |
| **CV** | Cyclic voltammetry |
| **DEC** | Diethyl carbonate |
| **DEE** | 1,2-diethoxyethane |
| **DEMS** | Differential electrochemical mass spectrometry |
| **DFT** | Density functional theory |
| **DFT-MD** | Density functional theory molecular dynamics |
| **DME** | 1,2-Dimethoxyethane |
| **DOE** | U.S. Department of Energy |
| **DOL** | Electrolyte solvent 1,3-dioxolane |
| **DPA** | Diphenylamine |
| **DRX** | Disordered rock salt |
| **DSC** | Differential scanning calorimetry |
| **E/S ratio** | Electrolyte/Sulfur ratio |
| **EC** | Ethylene Carbonate |
| **EDS** | Energy-dispersive X-ray spectroscopy |
| **EELS** | In situ Electron Energy Loss Spectroscopy |
| **EERE** | Office of Energy Efficiency and Renewable Energy |
| **EF** | Electric field |
| **EIS** | Electrochemical impedance spectroscopy |
| **EMC** | Ethyl methyl carbonate |
| **EMS** | Ethyl methyl sulfone-based electrolytes |

| Abbreviation | Definition |
|---|---|
| **EQCM** | Electrochemical quartz crystal microbalance |
| **Er** | Erbium |
| **ETFE** | Ethylene tetrafluoroethylene |
| **EV** | Electric vehicle |
| **F2DEM** | bis(2-fluoroethoxy)methane |
| **F5DEE** | 2-[2-(2,2-Difluoroethoxy)ethoxy]-1,1,1-Trifluoroethane |
| **FDMB** | Fluoro-dimethoxylbutane |
| **FEC** | Fluoroethylene carbonate |
| **FGS** | Functionally graded scaffold |
| **FSU** | Florida State University |
| **FTIR** | Fourier transform infrared spectroscopy |
| **FY** | Fiscal year |
| **FZ** | FZ Jülich-Company Name |
| **Gen** | Generation |
| **GHG** | Greenhouse gas |
| **GM** | General Motors |
| **HFMP** | 1,1,1,3,3,3-hexafluoro-2-methoxypropane |
| **$I_2$** | Iodine |
| **ID** | Identification |
| **IEK** | IEK-9 - Company Name |
| **In** | Indium |
| **INL** | Idaho National Laboratory |
| **J/m2** | Joules per meters squared |
| **Koura** | Koura - Company name |
| **kWh** | Kilowatt-hour |
| **LATP** | $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$, a potential solid-state electrolyte |
| **LBNL** | Lawrence Berkeley National Laboratory |
| **LBS** | Lithium thioborates |
| **LFP** | Lithium iron phosphate |

| Abbreviation | Definition |
|---|---|
| **LHCE** | localized high-concentration electrolyte |
| **Li** | Lithium |
| **Li CE** | Lithium coulombic efficiency |
| **Li nm** | Lithium and nanometers |
| **Li NMC** | Lithium nickel manganese cobalt oxides |
| **Li SPAN** | Lithium sulfurized polyacrylonitrile |
| **Li/Ni** | Lithium/nickel |
| **$Li_2O$** | Lithium oxide |
| **$Li_2O/LiF$** | Lithium oxide per lithium fluoride |
| **$Li_2S$** | Lithium Sulfide |
| **$Li_2S_2$** | Lithium disulfide |
| **$Li_2S-B_2S_3$** | Lithium Sulfide and Boron Sulfide |
| **$Li_2S_x$** | Lithium Sulfide type |
| **$Li_2ZrCl_6$** | Lithium zirconium chloride |
| **$Li_5B_7S_{13}$** | Lithium boron sulfide |
| **LIBs** | Lithium-ion battery(ies) |
| **LIC** | $Li_3InCl_6$ |
| **LiCoO2** | Lithium cobalt oxide |
| **LiF** | Lithium fluoride |
| **LiFSI** | Lithium bis(fluorosulfonyl)imide |
| **Li-ion** | Lithium-ion |
| **$LiNiO_2$** | Li−Ni−O compound |
| **$LiNO_3$** | Lithium nitrate |
| **LiOH** | Lithium Hydroxide |
| **$LiPF_6$** | Lithium hexafluorophosphate |
| **LiPS** | Lithium polysulfide |
| **Li-S** | Lithium-sulfur |
| **LiTFSI** | Lithium bis(trifluoromethanesulfonyl)imide |
| **$Li_xNiO_2$** | Lithium nickel oxide cathode with variable lithium content |

| Abbreviation | Definition |
|---|---|
| **LLTO** | Lithium lanthanum titanate |
| **LLZO** | Lithium lanthanum zirconate |
| **LLZTO** | Garnet-type fast lithium-ion conductor $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ |
| **LMB** | Lithium metal batteries |
| **LMR** | Lithium manganese-rich |
| **LNO** | $LiNiO_2$ |
| **LPSC** | $Li_6PS_5Cl$ |
| **LPSCl** | Lithium phosphorus sulfide chloride |
| **LSV** | Linear sweep voltammetry |
| **LYC** | Li3YCl6 (LYC) |
| **m2/V-s** | meters squared per volt seconds |
| **MA** | An (undefined) electrolyte additive |
| **mAh** | Milliampere-hour |
| **mAh/g or mAh $g^{-1}$** | Specific capacity [mAh/g] refers to the amount of electric charge [mAh] a material can deliver per gram of that material. |
| **mAh/g** | milliampere-hours per gram |
| **MERF** | Materials Engineering Research Facility |
| **mg/cm²** | milligrams per square centimeter |
| **MLPs** | Machine learning interatomic potentials |
| **Mn** | Manganese |
| **MNC** | $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ a lithium manganese compound |
| **MOF** | Type of electrolyte |
| **MPa** | Megapascal |
| **mS/cm** | Millisiemens per centimeter |
| **MTF** | Type of electrolyte |
| **MWCNT** | Multi-walled carbon nanotubes |
| **N/P ratio** | Negative-to-positive electrode capacity ratio |
| **Nb** | Niobium |
| **NCM** | Lithium nickel manganese cobalt oxides (abbreviated NMC, Li-NMC) |
| **Ni** | Nickel |

| Abbreviation | Definition |
| --- | --- |
| **$NiO_2$** | Nickel (II) oxide |
| **NM** | Nickel manganese oxides |
| **nm** | Nanometers |
| **NM9505** | $LiNi_{0.95}Mn_{0.05}O_2$ |
| **NMC** | Nickel manganese cobalt oxide |
| **NMC/Li** | Battery system with a nickel manganese cobalt oxide cathode and a lithium metal anode |
| **NMC622** | cathode type with 60% nickel, 20% manganese, and 20% cobalt |
| **NMC811** | cathode type with 80% nickel, 10% manganese, and 10% cobalt |
| **NMR** | Nuclear magnetic resonance spectroscopy |
| **NREL** | National Renewable Energy Laboratory |
| **NSLSII** | National Synchrotron Light Source II |
| **OCV** | Open circuit voltage |
| **ORNL** | Oak Ridge National Laboratory |
| **PAA** | Polyacrylic acid |
| **PAN** | Polyacrylonitrile |
| **pCAM** | Precursor cathode active material |
| **PDF** | Pair distribution function |
| **PE** | Polyethylene separator |
| **PECVD** | Plasma-enhanced chemical vapor deposition |
| **PEO** | Poly(ethylene) oxide |
| **PEV** | Plug-in electric vehicle |
| **PF5** | Phosphorus pentafluoride anion |
| **PF6** | Hexafluorophosphate anion |
| **PFG1** | Partially-fluorinated glymes type |
| **PFGs** | Partially-fluorinated glymes |
| **PFT** | Pulse Fourier transformation |
| **PHEV** | Plug-in hybrid electric vehicle |
| **PI** | Principal investigator |
| **PNNL** | Pacific Northwest National Laboratory |

| Abbreviation | Definition |
|---|---|
| **PP** | Polypropylene |
| **PPM** | Polymer poly(pentyl malonate) |
| **PS** | Polysulfide |
| **psi** | Pound per square inch |
| **PVDF** | Polyvinylidene fluoride |
| **Q1** | Quarter 1/Quarter 2 |
| **R2** | Modeled circuit resistor 2 |
| **ratio of B/S/Li** | ratio of Boron per Sulfur per Lithium |
| **RDD&D** | Research, development, demonstration, and deployment |
| **RT14** | Particle Type |
| **S** | Sulfur |
| **S/cm** | Siemens per centimeter |
| **S8** | Octasulfur |
| **SBR** | Styrene–butadiene rubber |
| **SCP** | Silicon consortium project |
| **SE** | Solid electrolyte |
| **SEI** | Solid-electrolyte interphase |
| **SEM** | Scanning electron microscopy |
| **SEMs** | Scanning electron microscopies |
| **SIC** | Single-ion-conducting |
| **$SiO_x$** | Silicon Oxide Type |
| **SLAC** | SLAC National Accelerator Laboratory |
| **SLP** | Single-layer pouch |
| **SOC** | State of charge |
| **SPAN** | Sulfurized polyacrylonitrile |
| **SPE** | Solid polymer electrolyte |
| **SSE** | Solid-state electrolyte |
| **S-SPAN** | Sulfur – sulfurized polyacrylonitrile |
| **SSRL** | Stanford Synchrotron Radiation Light Source (SSRL) is a general user facility supported by the DOE Office of Science |

| Abbreviation | Definition |
|---|---|
| **SUNY** | State University of New York |
| **SWNT** | Single-wall carbon nanotubes |
| **TEM** | Transmission electron microscopy |
| **TFEM** | Time-frequency electromagnetic method |
| **TFSI** | Bis(trifluoromethanesulfonyl)imide (TFSI), [(CF3SO2)2N]− |
| **TFTFE** | 1,1,2,2-Tetrafluoroethyl 2,2,2-trifluoroethyl ether |
| **TM** | Transition metal |
| **TOF** | SIMS Time-of-flight secondary ion mass spectrometry |
| **TofF SIMS** | Time-of flight secondary ion mass spectrometry |
| **TTE** | 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether |
| **TXM** | Transmission X-ray microscopy |
| **UC** | University of California |
| **UCB** | University of California, Berkeley |
| **UCSD** | University of California-San Diego |
| **uL/mg** | micro liters per milligram |
| **US** | United States |
| **UT** | University of Texas |
| **UW** | University of Washington |
| **V** | Volts |
| **VTO** | Vehicle Technologies Office |
| **WE** | Working Electrode |
| **Wh/kg** | Watt hours per kilogram |
| **Wh/L** | Watt hours per liter |
| **XANES** | X-ray absorption near edge structure spectroscopy |
| **XAS** | X-ray absorption spectroscopy |
| **XPS** | X-ray photoelectron spectroscopy |
| **XRD** | X-ray diffraction |
| **XRF** | X-ray fluorescence |