

Energy Storage

VEHICLE TECHNOLOGIES OFFICE

2012

annual progress report

FISCAL YEAR 2012
ANNUAL PROGRESS REPORT FOR
ENERGY STORAGE R&D

January 2013

Approved by
David Howell, Hybrid Electric Systems Team Lead
Vehicle Technologies Program, Energy Efficiency and Renewable Energy

Table of Contents

I. INTRODUCTION.....	1
I.A Vehicle Technologies Program Overview.....	1
I.B Vehicle Technologies Battery R&D Overview.....	1
I.B.1 DOE Battery R&D Goals and Technical Targets.....	1
I.B.2 DOE Battery R&D Plans.....	2
I.B.3 Energy Storage R&D Programmatic Structure.....	3
I.B.4 Recent Energy Storage Highlights.....	4
I.B.5 Organization of this Report.....	8
II. American Recovery & Reinvestment Act (ARRA) of 2009.....	11
II.A Integrated Battery Materials Production, Cell Manufacturing, and Battery Assembly Facilities.....	13
II.A.1 ARRA-supported Production Facility Project (JCI).....	13
II.A.2 Vertically Integrated Mass Production of Automotive Class Lithium-ion Batteries (A123 Systems).....	17
II.A.3 ARRA-supported Production Facility Project (Exide).....	18
II.A.4 ARRA-supported Production Facility Project (East Penn).....	21
II.B Battery Cell and Pack Assembly Facilities.....	24
II.B.1 ARRA-supported Production Facility Project (Dow Kokam, MI).....	24
II.B.2 ARRA-supported Production Facility Project - Li-Ion Battery Manufacturing (LG Chem, MI).....	26
II.B.3 ARRA-supported Lithium-ion Cell Production and Battery Pack Assembly (EnerDel).....	30
II.B.4 Li-Ion Battery Pack Manufacturing (GM).....	33
II.B.5 Lithium-ion Cell Production and Battery Pack Assembly (Saft America).....	36
II.C Battery Materials Production Facilities.....	38
II.C.1 ARRA-supported Production Facilities (Celgard).....	38
II.C.2 Advanced Cathode Materials Production Facility (Toda America).....	41
II.C.3 ARRA-supported Production Facility Project (Chemetall Foote Corp).....	42
II.C.4 High-Volume Manufacturing of LiPF ₆ - A Critical Lithium-ion Battery Material (Honeywell).....	44
II.C.5 Construction of a Li-ion Battery Cathode Production Plant (BASF).....	46
II.C.6 ARRA-supported Nanoengineered Ultracapacitor Material Production Facility Project (EnerG2).....	47
II.C.7 ARRA-supported Production Facility Project (Novolyte).....	49
II.C.8 ARRA-supported Production Facility Project (FutureFuel Chemical Co.).....	51
II.C.9 ARRA-supported Production Facility Project (Pyrotek).....	53
II.C.10 Manufacture of Advanced Battery Components (HTTM LLC, H&T, Trans-Matic).....	56
II.D Battery Recycling Facilities.....	59
II.D.1 ARRA-supported Production Facility Project (Toxco).....	59
II.E Battery Research Facilities.....	61
II.E.1 ARRA-supported Prototype Cell Fabrication Facility (ANL).....	61
II.E.2 ARRA-supported Material Scale-Up Facility (ANL).....	63
II.E.3 Post-test Laboratory Facility (ANL).....	66
II.E.4 High-Energy Battery Testing Facility (INL).....	69
II.E.5 Battery Thermal Test Laboratory (NREL).....	72

II.E.6 Battery Abuse Test Facility (SNL).....	76
III Advanced Battery Development, Systems Analysis, and Testing.....	81
III.A Advanced Battery Development	82
III.A.1 High Energy/EV Systems	84
III.A.1.1 EV Battery Development (Envia Systems).....	84
III.A.1.2 EV Battery Development (Cobasys)	87
III.A.1.3 Development of High Performance Advanced Batteries for Electric Vehicle Applications (Quallion)	92
III.A.1.4 Solid Polymer Batteries for Electric Drive Vehicles (Seeo).....	96
III.A.1.5 Development of High-Energy Lithium Sulfur Cells (PSU).....	98
III.A.1.6 Stand Alone Battery Thermal Management System (Denso).....	102
III.A.1.7 EV Technology Assessment Program (K2 Energy).....	104
III.A.1.8 EV Technology Assessment Program (Leyden Energy)	105
III.A.1.9 EV Battery Technology Assessment Program (Farasis).....	106
III.A.2 High Energy/PHEV Systems	108
III.A.2.1 Advanced High-Performance Batteries for Plug-In Hybrid Electric Vehicle Applications (JCI).....	108
III.A.2.2 Development of a High-Performance PHEV Battery Pack (LG Chem MI).....	114
III.A.3 High Power/HEV and LEESS Systems.....	118
III.A.3.1 Energy Storage System for High Power LEESS PAHEV Applications (Maxwell Technologies).....	118
III.A.3.2 Capacitor Development (NSWC).....	122
III.A.3.3 LEESS Technology Assessment Program (Actacell)	125
III.A.4 Development of Advanced Lithium-ion Battery Cell Materials.....	126
III.A.4.1 Silicon-nanowire Based Lithium Ion Batteries for Vehicles with Double the Energy Density (Amprius)	126
III.A.4.2 Development of Large Format Lithium-Ion Cells with Higher Energy Density (Dow Kokam)	129
III.A.4.3 Innovative Cell Materials and Designs for 300 Mile Range EVs (Nanosys).....	132
III.A.4.4 High Energy Novel Cathode/Alloy Automotive Cell (3M).....	137
III.A.5 Low-cost Processing	141
III.A.5.1 Low Cost Manufacturing Project (JCI).....	141
III.A.5.2 Ultraviolet and Electron Beam Curing Technology to Reduce Electrode Manufacturing Cost (Miltec UV International)	144
III.A.5.3 Dry Process Electrode Fabrication (A123 Systems).....	146
III.A.5.4 Modular Process Equipment for Low Cost Manufacturing of High Capacity Prismatic Li-Ion Cell Alloy Anodes (Applied Materials)	150
III.A.5.5 Innovative Manufacturing and Materials for Low Cost Lithium Ion Batteries (Optodot Corporation).....	154
III.B Advanced Materials and Processing (from FY 2008 DOE FOA)	156
III.B.1 Multifunctional, Inorganic-Filled Separator Development for Large Format Li-ion Batteries (ENTEK Membranes)	156
III.B.2 Stabilized Lithium Metal Powder (SLMP®), Enabling Material and Technology for High Energy Li-ion Batteries (FMC).....	160
III.B.3 Protection of Lithium (Li) Anodes Using Dual Phase Electrolytes (Sion Power).....	164

III.B.4 Process for Low-cost Domestic Production of LIB Cathode Materials (BASF Corporation).....	170
III.B.5 Hybrid Nano Carbon Fiber/Graphene Platelet-Based High-Capacity Anodes for Lithium-Ion Batteries (Angstrom).....	173
III.B.6 New High-Energy Nanofiber Anode Materials (NCSSU).....	177
III.B.7 Perfluoro Aryl Boronic Esters as Chemical Shuttle Additives in Lithium-Ion Batteries (EnerDel).....	182
III.B.8 Internal Short Circuits in Lithium-Ion Cells for PHEVs (TIAX, LLC)	184
III.B.9 High Throughput Fabrication of 10 Year PHEV Battery Electrodes (A123 Systems).....	188
III.C Systems Analysis.....	191
III.C.1 Cost Assessments.....	191
III.C.1.1 PHEV Battery Cost Assessments (TIAX).....	191
III.C.1.2 Battery Ownership Model: A Tool for Evaluating the Economics of Electrified Vehicles and Related Infrastructure (NREL).....	195
III.C.1.3 PEV Battery Second Use (NREL)	198
III.C.1.4 PHEV Battery Cost Assessment (ANL).....	203
III.C.2 Requirements Analysis	207
III.C.2.1 Battery Pack Requirements and Targets Validation (ANL).....	207
III.C.2.2 Battery Life Trade-Off Studies (NREL)	213
III.C.2.3 Lithium Battery Recycling Issues (ANL)	216
III.C.2.4 Low Energy HEV Requirements Analysis (NREL).....	221
III.C.2.5 Updating USABC Battery Technology Targets for Battery Electric Vehicles (NREL).....	225
III.D Battery Testing Activities.....	227
III.D.1 Battery Performance and Life Testing (ANL)	227
III.D.2 Advanced Energy Storage Life and Health Prognostics (INL)	230
III.D.3 Battery Performance and Life Testing (INL).....	235
III.D.4 Battery Abuse Testing (SNL)	240
III.D.5 Developmental & Applied Diagnostic Testing (INL).....	245
III.D.6 Battery Thermal Analysis and Characterization Activities (NREL)	250
III.D.7 Development of an On-Demand Internal Short Circuit (NREL)	254
III.E Computer Aided Engineering of Batteries.....	258
III.E.1 Computer Aided Engineering of Batteries – CAEBAT (NREL).....	258
III.E.2 Computer Aided Engineering of Batteries Effort (ORNL).....	262
III.E.3 Development of Computer Aided Design Tools for Automotive Batteries - (CAEBAT GM Contract).....	267
III.E.4 Development of Computer Aided Design Tools for Automotive Batteries (CD-Adapco).....	272
III.E.5 Development of Computer Aided Design Tools for Automotive Batteries (EC Power).....	277
III.E.6 Battery Multiscale Multidomain Framework & Modeling (NREL).....	280
III.E.7 Lithium-Ion Abuse Model Development (NREL).....	284
III.F Small Business Innovative Research Projects (SBIR)	288
III.G Energy Storage R&D Collaborative Activities with the International Energy Agency and China (NW Tech)	290
IV Applied Battery Research for Transportation	295
IV.A Introduction.....	295
IV.B Materials Research	297

IV.B.1 ABR Project: Mitigation of Voltage Fade in Lithium-Manganese-rich Oxide Cathode Materials (ANL)	297
IV.B.2 Electrode Composition and Processing.....	319
IV.B.2.1 Scale-up and Testing of Advanced Materials from the BATT Program (LBNL)	319
IV.B.2.2 Cathode Processing Comparison (ANL).....	323
IV.B.2.3 Optimization of Li-ion Battery Electrodes (ANL).....	329
IV.B.2.4 Development of Industrially Viable Battery Electrode Coatings (NREL).....	334
IV.B.2.5 Evaluate the Impact of ALD Coating on Li/Mn-rich Cathodes (NREL)	339
IV.B.2.6 Overcoming Processing Cost Barriers of High-Performance Lithium-Ion Battery Electrodes (ORNL).....	342
IV.B.2.7 Roll-to-Roll Electrode Processing and Materials NDE for Advanced Lithium Secondary Batteries (ORNL).....	348
IV.B.3 Applied Battery Research on Anodes	356
IV.B.3.1 Developing a New High Capacity Anode with Long Life (ANL)	356
IV.B.3.2 Spherical Carbon Anodes Fabricated by Autogenic Reactions (ANL).....	359
IV.B.3.3 Functionalized Surface Modification Agents to Suppress Gassing Issue of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - Based Lithium-Ion Chemistry (ANL).....	363
IV.B.4 Applied Battery Research on Cathodes.....	367
IV.B.4.1 Engineering of High Energy Cathode Material (ANL).....	367
IV.B.4.2 Developing New High Energy Gradient Concentration Cathode Material (ANL).....	372
IV.B.4.3 Novel Composite Cathode Structures (ANL).....	377
IV.B.4.4 Development of High-Capacity Cathodes with Integrated Structures (ANL).....	382
IV.B.5 Applied Battery Research on Electrolytes	386
IV.B.5.1 Develop Electrolyte Additives (ANL)	386
IV.B.5.2 High Voltage Electrolyte for Lithium-ion Battery (ANL).....	391
IV.B.5.3 High Voltage Electrolytes for Li-ion Batteries (ARL).....	397
IV.B.5.4 Development of Novel Electrolytes for Use in High Energy Lithium-Ion Batteries with Wide Operating Temperature Range (JPL).....	404
IV.B.5.5 Novel Phosphazene-based Compounds to Enhance Safety and Stability of Cell Chemistries for High Voltage Applications (INL).....	413
IV.C Modeling, Diagnostics, and Performance Studies.....	418
IV.C.1 Electrochemistry Cell Model (ANL)	418
IV.C.2 Battery Design Modeling (ANL).....	422
IV.C.3 Electrochemical and Physicochemical Diagnostics of High-Energy Lithium-ion Cell Couples (ANL)	426
IV.C.4 Electrochemistry Diagnostics of Baseline and New Materials (LBNL)	433
IV.C.5 Mechanistic, Molecular, and Thermodynamic Modeling/Diagnostics in Support of ABR Cell Performance and Aging Studies (INL)	437
IV.D Abuse Diagnostics & Mitigation.....	442
IV.D.1 Diagnostic Studies Supporting Improved Abuse Tolerance (BNL).....	442
IV.D.2 Develop & Evaluate Materials & Additives that Enhance Thermal & Overcharge Abuse (ANL).....	449
IV.D.3 Impact of Materials on Abuse Response (SNL)	455
IV.D.4 Overcharge Protection for PHEV Cells (LBNL)	460
IV.E Applied Research Facilities.....	465

IV.E.1 Battery Materials Pilot Production Facility	465
IV.E.1.1 Process Development and Scale up of Advanced Cathode Materials (ANL).....	465
IV.E.1.2 Process Development and Scale-up of Advanced Electrolyte Materials (ANL).....	469
IV.E.2 Post-Test Diagnostics Facility.....	472
IV.E.2.1 Post-Test Diagnostic Activities (ANL)	472
IV.E.3 Battery Electrode and Cell Fabrication Facility.....	475
IV.E.3.1 Screening of Electrode Compositions and Cell Chemistries (ANL)	475
IV.E.3.2 Cell and Cell Component Activities (ANL).....	479
V. Focused Fundamental Research	489
V.A Introduction.....	489
V.B. Cathode Development	492
V.B.1 First Principles Calculations and NMR Spectroscopy of Electrode Materials (MIT/U. Cambridge).....	492
V.B.2 Cell Analysis, High-energy Density Cathodes and Anodes (LBNL)	496
V.B.3 Olivines and Substituted Layered Materials (LBNL).....	500
V.B.4 Cell Analysis-Interfacial Processes: SEI Formation and Stability on Cycling (HQ).....	504
V.B.5 The Role of Surface Chemistry on the Cycling and Rate Capability of Lithium Positive Electrode Materials (MIT)	508
V.B.6 Diagnostics – Battery Materials: Structure and Characterization (Yang, Nam, BNL).....	512
V.B.7 Development of High Energy Cathode (PNNL)	516
V.B.8 Crystal Studies on High-energy Density Cathodes (LBNL)	520
V.B.9 Developing Materials for Lithium-Sulfur Batteries (ORNL).....	524
V.B.10 Studies on High Energy Density Lithium-ion Electrodes (ORNL).....	529
V.B.11 High -capacity Composite Cathode Materials: New Synthesis Routes and Structures (ANL).....	533
V.B.12 <i>In Situ</i> Solvothermal Synthesis of Novel High Capacity Cathodes (BNL)	537
V.B.13 Lithium-bearing Mixed Polyanion (LBMP) Glasses as Cathode Materials (ORNL).....	541
V.B.14 High-capacity, High-voltage Cathode Materials for Lithium-ion Batteries (U. Texas)	544
V.B.15 Novel and Optimized Phases for High-energy Density Batteries (LBNL).....	548
V.C Anode Development.....	552
V.C.1 Nanoscale Composite Hetero-structures and Thermoplastic Resin Binders (U. Pittsburgh).....	552
V.C.2 Interfacial Processes - Diagnostics (LBNL).....	557
V.C.3 Development of High Capacity Anodes (PNNL).....	560
V.C.4 Advanced Binder for Electrode Materials (LBNL).....	564
V.C.5 Three Dimensional Anode Architecture and Materials (ANL)	568
V.C.6 Metal-Based High Capacity Li-Ion Anodes (Binghamton U.)	572
V.C.7 New Layered Nanolaminates for Use in Lithium Battery Anodes (Drexel U.).....	575
V.C.8 Atomic Layer Deposition for Stabilization of Amorphous Silicon Anodes (NREL, U. Col).....	579
V.C.9 Synthesis and Characterization of Si/SiO _x -Graphene Nanocomposite Anodes and Polymer Binders (Penn State U).....	583
V.C.10 Synthesis and Characterization of Silicon Clathrates for Anode Applications in Lithium-ion Batteries (SwRI).....	587
V.C.11 Wiring up Silicon Nanoparticles for High Performance Lithium Ion Battery Anodes (Stanford U)	591
V.D Electrolyte Development.....	595
V.D.1 Polymer Electrolytes for Advanced Lithium Batteries (UC, Berkeley).....	595

V.D.2 Interfacial Behavior of Electrodes (LBNL).....	599
V.D.3 Molecular Dynamics Stimulation Studies of Electrolytes and Electrolyte/Electrode Interfaces (Univ. Utah, ARL).....	603
V.D.4 Bifunctional Electrolytes for Lithium-ion Batteries (CWRU).....	607
V.D.5 Advanced Electrolyte and Electrolyte Additives (ANL).....	611
V.D.6 Inexpensive, Nonfluorinated (or Partially Fluorinated) Anions for Lithium Salts and Ionic Liquids for Lithium Battery Electrolytes (NCSU).....	614
V.D.7 Development of Electrolytes for Lithium-ion Batteries (URI).....	618
V.D.8 Sulfones with Additives as Electrolyte (ASU).....	622
V.D.9 Lithium Batteries of Higher Capacities and Voltage (U. Texas).....	626
V.E Cell Analysis, Modeling, and Fabrication	629
V.E.1 Electrode Fabrication and Failure Analysis (LBNL).....	629
V.E.2 Modeling - Thermo-electrochemistry, Capacity Degradation, and Mechanics with SEI Layer (U. Michigan).....	633
V.E.3 Mathematical Modeling of Next-generation Li-ion Chemistries (LBNL).....	637
V.E.4 Analysis and Simulation of Electrochemical Energy Systems (LBNL).....	641
V.E.5 Modeling - Predicting and Understanding New Li-ion Materials Using <i>Ab Initio</i> Atomistic Computational Methods (LBNL).....	644
V.E.6 New Electrode Designs for Ultra-high Energy Density (MIT).....	648
V.E.7 <i>In Situ</i> Electron Microscopy of Electrical Energy Storage Materials (ORNL).....	652
V.F Energy Frontier Research Centers	655
V.F.1 Energy Frontier Research Center at ANL.....	655
V.G. Integrated Lab-Industry Research Program.....	660
V.G.1 Integrated Lab-Industry Research Project (LBNL, ANL).....	660
V.G.2 Integrated Lab Research Project II (LBNL, ANL, FMC, Saft).....	666
V.G.3 Composite Electrolyte to Stabilize Metallic Lithium Anodes (ORNL).....	673
Appendix A: List of Contributors and Research Collaborators.....	A - 1
Appendix B: Acronyms	B - 1

List of Figures

Figure I - 1: Battery advancements needed to enable a large market penetration of PEVs.....	2
Figure I - 2: New PEV sales compared to hybrid electric vehicle (HEV) sales over their respective 24 month introductory periods.....	5
Figure II - 1: American Recovery and Reinvestment Act (ARRA) 2009 grants distribution for battery and electric drive manufacturing.....	11
Figure II - 2: Michigan Li-ion battery plant during construction – 1000 construction workers were employed in the construction of our Michigan plant.....	14
Figure II - 3: Construction included the upfit of an existing building for Li-ion battery production, including the construction of new outbuildings to house equipment and materials.....	15
Figure II - 4: This project helped fund the material characterization and test facilities critical to support advanced energy production programs.....	15
Figure II - 5: Johnson Controls' facilities include the equipment necessary to perform all relevant battery and cell tests, including cycle testing in controlled temperature environments.....	15
Figure II - 6: Pilot scale equipment installed in controlled environments support the mass production programs.....	15
Figure II - 7: Equipment – Pack assembly was up and running within 10 months of receiving the award from the Department of Energy.....	15
Figure II - 8: Equipment – Cell assembly equipment is installed and production has begun.....	15
Figure II - 9: Complete battery packs and systems are assembled domestically prior to being sent to the customer.....	16
Figure II - 10: Livonia Cell Assembly Line.....	17
Figure II - 11: Photograph showing the Entrance to the Exide Technologies Battery Manufacturing Site that is Located in Columbus, Georgia.....	18
Figure II - 12: Exide's new advanced AGM battery, the Exide Edge™ with SureLife™ Graphite Technology.....	19
Figure II - 13: Exide Technologies' New Expanded Facility for Production of Advanced Spiral Wound AGM Batteries Located in Bristol, Tennessee.....	19
Figure II - 14: Exide's new advanced Spiral Wound AGM battery, the Vortex™ with SureLife™ Graphite Technology.....	20
Figure II - 15: Overall View of new State of the Art Spiral Wound AGM Battery Production area in Bristol, Tennessee Exide Battery Plant.....	20
Figure II - 16: Facility 1 – Automotive Battery Plant A4 Equipment (View 1).....	21
Figure II - 17: Facility 1 – Automotive Battery Plant A4 Equipment (View 2).....	22
Figure II - 18: Facility 1 – Automotive Battery Plant A4 Equipment (View 3).....	22
Figure II - 19: Facility 1 – Automotive Battery Plant A4 Equipment (View 4).....	22
Figure II - 20: Facility 2 – Injection Molding Plants IM1/IM2 Equipment (View 1).....	22
Figure II - 21: Facility 2 – Injection Molding Plants IM1/IM2 Equipment (View 2).....	22
Figure II - 22: Facility 2 – Injection Molding Plants IM1/IM2 Equipment (View 3).....	22
Figure II - 23: UltraBattery Test Vehicle on site at East Penn Mfg.....	23
Figure II - 24: Photograph(s) of the Dow Kokam, Midland Battery Park Facility.....	25
Figure II - 25: An overhead view of the LG Chem Michigan Inc. facilities.....	28
Figure II - 26: A street view of LG Chem Michigan Inc. facilities.....	28
Figure II - 27: The Regenerative Thermal Oxidizer (RTO) by the separator facility.....	28
Figure II - 28: The SRP outdoor facility in front of the separator facility.....	28
Figure II - 29: The bag filters on the 4 th floor of the mixing tower of the electrode process.....	28
Figure II - 30: The roll press equipment for the electrode process.....	28
Figure II - 31: The folding equipment for the assembly process.....	29
Figure II - 32: The end of line inspection equipment for the formation process.....	29
Figure II - 33: LGCM employees at the main lobby in February, 2012.....	29
Figure II - 34: The Li-ion battery cell produced during the equipment validation process.....	29
Figure II - 35: EnerDel Hague Rd. Facility.....	30
Figure II - 36: EnerDel Mt. Comfort Facility.....	30
Figure II - 37: Dry-room Construction – Hague Rd.....	31
Figure II - 38: Cell Formation Equipment – Mt. Comfort.....	31
Figure II - 39: Facility Preparation – Mt. Comfort.....	31
Figure II - 40: Completed Dry-room – Hague Rd.....	31
Figure II - 41: Cell Assembly Equipment – Hague Rd.....	31

Figure II - 42: Unwinder Anode Coater – Hague Rd.....	31
Figure II - 43: Battery Module Assembly Line – Mt. Comfort.....	32
Figure II - 44: EnerDel Li-Ion Cell.....	32
Figure II - 45: EnerDel Battery Modules.....	32
Figure II - 46: Facility location in Brownstown Township, MI.....	34
Figure II - 47: GM Brownstown Battery Assembly Plant, Brownstown Township, MI.....	34
Figure II - 48: Battery Pack Lift Assist.....	34
Figure II - 49: Battery Pack Assembly on Automated Guided Carts.....	34
Figure II - 50: Chevrolet Volt Battery in the GM Battery Systems Lab in Warren, MI.....	34
Figure II - 51: 2013 Chevrolet Volt Battery & Specifications.....	34
Figure II - 52: Saft Factory of the Future – completed.....	36
Figure II - 53: Celgard completed warehouse in Charlotte, NC.....	39
Figure II - 54: Celgard facility in Charlotte, NC.....	39
Figure II - 55: Celgard Fully-formed flat sheet membrane from new equipment.....	39
Figure II - 56: Celgard Quality testing on the manufacturing floor.....	39
Figure II - 57: Celgard Concord building.....	39
Figure II - 58: Celgard Concord Grand Opening event.....	39
Figure II - 59: Celgard Concord Equipment installation activity.....	40
Figure II - 60: Celgard Concord Operations' install and startup team.....	40
Figure II - 61: Celgard Concord Completed internal qualification of Slitters.....	40
Figure II - 62: Celgard Concord Oven line startup.....	40
Figure II - 63: Toda America Inc. Battle Creek Facility, Phase 1.....	41
Figure II - 64: Photographs of the Chemetall Foote Corp. Facilities.....	43
Figure II - 65: LiPF ₆ is Required in all Li-ion Batteries.....	44
Figure II - 66: Honeywell Produces Key Raw Materials.....	44
Figure II - 67: Aerial view of Honeywell's Buffalo, NY facility.....	45
Figure II - 68: Buffalo NY LiPF ₆ plant.....	45
Figure II - 69: Special container for shipping finished product.....	45
Figure II - 70: Current Picture of BASF Cathode Facility.....	46
Figure II - 71: EnerG2 Ribbon Cutting Ceremony in Albany, Oregon (February 2012).....	47
Figure II - 72: EnerG2 Freeze Drying in Process.....	47
Figure II - 73: EnerG2 Pyrolysis Kilns.....	48
Figure II - 74: Several examples of the 400 215-L Electrolytes shipping vessels purchased in 2010 (Novolyte).....	50
Figure II - 75: Ion Chromatograph (Novolyte).....	50
Figure II - 76: Two examples of the small Electrolytes shipping vessels purchased in 2011 (Novolyte).....	50
Figure II - 77: Xylene Tanks (FutureFuel Chemical Company).....	51
Figure II - 78: Pitch Loading Hopper (FutureFuel Chemical Company).....	51
Figure II - 79: Coke Loading Hopper (FutureFuel Chemical Company).....	52
Figure II - 80: Anode Material Bag Out (FutureFuel Chemical Company).....	52
Figure II - 81: Anode Material (FutureFuel Chemical Company).....	52
Figure II - 82: Construction at Pyrotech Incorporated.....	54
Figure II - 83: Facilities at Pyrotech Incorporated.....	54
Figure II - 84: Equipment at Pyrotech Incorporated.....	55
Figure II - 85: Trans-Matic/HTTM Manufacturing Facility.....	57
Figure II - 86: Equipment – Battery Can Stamping Press (HTTM LLC, H&T, Trans-Matic).....	57
Figure II - 87: Equipment – Battery Cover Assembly Equipment (HTTM LLC, H&T, Trans-Matic).....	57
Figure II - 88: Component Pre-Cleaner (HTTM LLC, H&T, Trans-Matic).....	57
Figure II - 89: HTTM Website www.htmllc.com (HTTM LLC, H&T, Trans-Matic).....	58
Figure II - 90: Toxco Processing Facility completed Exterior.....	59
Figure II - 91: Toxco Building Exterior.....	59
Figure II - 92: Toxco Interior Offices.....	59
Figure II - 93: Process Area.....	60
Figure II - 94: Maccor Series 4000 Automated Test System for testing and formation of prototype cells with environmental chambers and ovens.....	61
Figure II - 95: Bruker D8 advanced powder diffraction system.....	62
Figure II - 96: ARC-254 from NETZSCH.....	62
Figure II - 97: Solartron (Ametek) eight channel electrochemical test station and impedance analyzer.....	62

Figure II - 98: MERF Construction Completed (ANL).....	64
Figure II - 99: Electrolyte Materials Process R&D Lab (ANL).....	64
Figure II - 100: Electrolyte Materials Scale-up Lab (ANL).....	64
Figure II - 101: Cathode Analytical Lab (ANL).....	64
Figure II - 102: Highbay for Cathode Scale-up Lab (ANL).....	64
Figure II - 103: 20L Reactor and Rotavap (ANL).....	64
Figure II - 104: Reaction Calorimeter (ANL).....	65
Figure II - 105: Filter-Washer-Dryer Unit (ANL).....	65
Figure II - 106: Glovebox for Coin Cell Fabrication (ANL).....	65
Figure II - 107: Overall design of the post-test facility. The large, open area at the top of the figure is not part of the post-test facility. The VersaProbe X-ray photoelectron spectrometer (XPS) was purchased with funds from the US Department of Defense.....	67
Figure II - 109: Argonne scientist Nancy Dietz Rago analyzes results in the Post-Test Facility. After a battery sample is characterized in the large glove box, it is transferred without exposure to air to the scanning-electron microscope for detailed, microstructural characterization.....	68
Figure II - 110: Street view of completed 10,000 sq. ft. High Energy Battery Test laboratory building. Part of New INL Energy Systems Laboratory complex.....	70
Figure II - 111: View of completed battery test bay laboratory control room.....	70
Figure II - 112: View of the 10,000 sq. ft high bay testing facility, initial test station installations.....	70
Figure II - 113: Additional view of initial test station installations with temperature chambers.....	70
Figure II - 114: View of mid-size thermal temperature chambers delivered in FY12.....	70
Figure II - 115: Energy Storage Thermal Test Facility occupying 2000 ft ² in NREL's Thermal Test Facility.....	72
Figure II - 116: New Battery Space at TTF Laboratory before Construction.....	74
Figure II - 117: TTF Laboratory after Construction and Equipment Installation.....	74
Figure II - 118: High and Medium Power Battery Cyclers.....	74
Figure II - 119: NREL Designed and Fabricated Cell Calorimeter in Fluke Isothermal Bath.....	74
Figure II - 120: Liquid Handling Thermal Management In-the-Loop.....	74
Figure II - 121: Isothermal Bath with battery under test.....	75
Figure II - 122: Laser Flash Thermal Conductivity Meter for thin battery electrodes.....	75
Figure II - 123: Environmental chambers and isothermal bath for battery cell and pack testing.....	75
Figure II - 124: Life cycle testing of batteries for secondary use applications.....	75
Figure II - 125: (right) before and (left) after photographs of a typical test cell in the Battery Abuse Laboratory.....	76
Figure II - 126: CT image of an 18650 lithium-ion showing the mechanical abuse failure point in the electrode roll.....	77
Figure III - 1: Cycle life of 22 Ah pouch cells from current cell build.....	86
Figure III - 2: Cycle life performance of ex-NCM and mo-NCM materials using 18650 cells.....	88
Figure III - 3: USABC HVBS.....	89
Figure III - 4: State Machine.....	90
Figure III - 5: Module mounting within pack.....	90
Figure III - 6: Housing assembly.....	90
Figure III - 7: Cross section of structural foam part.....	91
Figure III - 8: Thermal Plates Positioned in Battery Pack Housing Bottom.....	91
Figure III - 9: Ambient Liquid Thermal System.....	91
Figure III - 10: Carbon Nanofiber Impregnated Soft Carbon (CN-SC) Schematic (top) and SEM of Actual Combination.....	93
Figure III - 11: Battery shown with COTS HP (top) and COTS HC (bottom).....	93
Figure III - 12: Quallion HP Module, 9.7 kW and 207 A Max Discharge Current.....	94
Figure III - 13: Quallion HP Pouch Cell, 2300 mAh.....	94
Figure III - 14: Cycling performance of 3 Ah baseline cells.....	99
Figure III - 15: Cycling performance of PSU-3 cathode with different sulfur loadings, as given in mg of sulfur per cm ² of electrode face area. Cell was tested using the baseline electrolyte, at C/20 rate for the first 2 cycles and C/10 rate thereafter.....	99
Figure III - 16: (top) Capacity retention of Si-C composite cathode in different electrolyte systems. (bottom) Cycling performance of Li foil, Li powder, and Li powder-graphite composite anodes in baseline electrolyte.....	100
Figure III - 17: Performance of new 2 nd -generation electrolyte A with PSU-1 cathodes: (a) charge-discharge curves, (b) cycling, and (c) coulombic efficiency.....	100
Figure III - 18: Performance of new 2 nd -generation electrolyte B: (top) charge-discharge curves and (bottom) cycling and coulombic efficiency.....	101

Figure III - 19: DSC curves of PSU-1 cathode with electrolyte, (top) unliithiated and (bottom) lithiated.	101
Figure III - 20: Battery Model using AMESim.	103
Figure III - 21: Example K2 Batteries under Test – LFP165HES module (top), and LFP45 cell (bottom).	104
Figure III - 22: Resistance and OCV comparison for K2 Batteries under Test, as a function of Depth of Discharge.	104
Figure III - 23: Leyden 10 Ah Pouch Cell.	105
Figure III - 24: Commercial 25 Ah Li-ion pouch cell.	106
Figure III - 25: Rate Capability of 25 Ah Li-ion Pouch Cell.	107
Figure III - 26: Cell cycling data of processed HENCM Cathode material to be used to construct deliverable cells for USABC.	107
Figure III - 27: Energy Density Roadmap.	109
Figure III - 28: NMP Solvent Use Continuum.	110
Figure III - 29: Dry Compounding SEM.	110
Figure III - 30: Prismatic Cell 60 °C Calendar Life.	111
Figure III - 31: High Temperature (70°C) Stability of Baseline Chemistry.	111
Figure III - 32: Dry Compounding and Paste Mixing Results.	112
Figure III - 33: Degrees of Anode Densification.	112
Figure III - 34: Fill Hole Seal Concepts.	112
Figure III - 35: Can with clamping feature.	113
Figure III - 36: Example of the beneficial effect of electrolyte additive stable at high voltage on prolonging cycle-life.	115
Figure III - 37: Data showing the strong dependency of cell life on the charge voltage of the Mn-rich cathode cells.	115
Figure III - 38: Effect of surface coatings on cyclability.	115
Figure III - 39: (Top) Schematic of the PHEV-40 Mile pack LG-Chem, MI developed. The thermal chamber containing elements such as the compressor, the cold-plate and the evaporator is on the right while the electrical chamber is on the left; (Bottom) picture of a prototype pack under test.	116
Figure III - 40: Sample thermal performance of the pack using the cooling system developed by LG-Chem, MI.	117
Figure III - 41: Gen 2 0.54 Wh cells delivered to INL for testing.	120
Figure III - 42: Gen 2 0.54 Wh HPPC BOL pulse power capability.	120
Figure III - 43: Proposed system design (Maxwell Technologies).	120
Figure III - 44: Color plot showing the effect of temperature and discharge current on the capacitance of experimental 1,000F LIC cells. Top graph shows cells that contain Gen-1 electrolyte. Bottom graph shows cells that contain Gen-2 electrolyte.	123
Figure III - 45: Self discharge comparison of LIC, EDLC, and LIB cells. Cells were charged, allowed to stand at open circuit for 3 days, and then immediately discharged.	123
Figure III - 46: Results of ARC experiment conducted on a 2,000F EDLC. Graph shows calorimeter/EDLC temperature profile.	124
Figure III - 47: Results of ARC experiment conducted on a 2.4 Ah lithium-ion battery, (a) calorimeter/LIB temperature profile, (b) LIB self-heating rate profile.	124
Figure III - 48: Actacell 8 Ah pouch cell.	125
Figure III - 49: Silicon swelling causes capacity fade and mechanical failure. Amprius' nanowires address swelling by allowing silicon to swell successfully.	127
Figure III - 50: Amprius improved the cycle life of laboratory cells matching silicon anodes and NCA cathodes.	127
Figure III - 51: Amprius identified additives that extended the cycle life of early-stage, silicon-based lab cells.	128
Figure III - 52: Amprius delivered to the DOE 18 baseline cells matching graphite anodes and NCM cathodes.	128
Figure III - 53: (a) Discharge performance and (b) HPPC Power of the sample cells.	130
Figure III - 54: Charge – Discharge curves of CM1+EM1 / Graphite sample cell.	131
Figure III - 55: Comparison of the two HCC materials developed at WDT.	131
Figure III - 56: Baseline SiNANOde/LCO full cell.	133
Figure III - 57: Voltage hysteresis of two SiNANOde full cells.	133
Figure III - 58: SiNANOde half cell with 700~1000mAh/g.	134
Figure III - 59: >1600mAh/g SiNANOde's voltage profile.	134
Figure III - 60: Uniform Si Nanowire distribution on graphite powders for 700mAh/g (Left) and >1600mAh/g (Right).	134
Figure III - 61: Rate capabilities of cathode candidates.	134
Figure III - 62: Cathode cyclability vs. different electrolyte.	135
Figure III - 63: Cycle life at 0.3C rate (DOD 80).	135
Figure III - 64: Cycle life of 250 Wh/kg pouch cell using 550 mAh/g SiNANOde at 0.5C rate (DOD 100).	136
Figure III - 65: Comparative voltage curves for 3M cathode materials A and B.	138
Figure III - 66: Cycling of 18650 cells with NMC cathode and L-19725, and L-20772 alloy anodes.	139

Figure III - 67: Core shell cathode cycling in full cells w/L-19869.....	139
Figure III - 68: Core shell cathode, L-20772 and L-19725 Alloy anodes, cycling at 9Wh.....	140
Figure III - 69: 3Ah Test Cell.....	142
Figure III - 70: 3Ah Test Cell HPPC Test Result.....	142
Figure III - 71: 3Ah Test Cell Full Cycle Life Test.....	142
Figure III - 72: Dry Processed Anode Cycling Performance.....	142
Figure III - 73: Rate capability of separator technologies.....	143
Figure III - 74: Reference Cell.....	145
Figure III - 75: Initial Charge/Discharge.....	145
Figure III - 76: 50 Cycle Performance.....	145
Figure III - 77: Charge and discharge curve for dry process nFP cathode. 1 wt% of each A123 additives were introduced (red) to the electrode to reduce over-potential.....	147
Figure III - 78: The electronic conductivity of dry process cathodes is in line with commercially produced slurry cast electrodes.....	148
Figure III - 79: Flexible free-standing dry process anodes have been fabricated and laminated to copper current collectors.....	148
Figure III - 80: The anode binder forms the desired fibril network to provide cohesive strength.....	149
Figure III - 81: Industry customers and partners for technology validation.....	150
Figure III - 82: Schematic diagram of process flows for manufacturing baseline cells, interim cells and final cells with 3D current collector and alloy anodes.....	151
Figure III - 83: Modeling results showing effect of first cycle irreversible capacity loss (ICL) on cell level energy density.....	151
Figure III - 84: Cycling test results for baseline cell: 3DCu/Graphite vs. NMC. Projection for capacity retention over 80% is ~1150 cycles.....	152
Figure III - 85: Cycling test results for interim cell: 3DCuSnFe/Graphite vs. NMC. Projection for capacity retention over 80% is ~650 cycles.....	152
Figure III - 86: SEM image of anode overcoated onto the separator layer to form the separator/electrode composite.....	154
Figure III - 87: Pore size distribution of the separator layer.....	154
Figure III - 88: 18650 cells with silica-filled separators.....	157
Figure III - 89: 18650 cells with unfilled polyolefin separators.....	157
Figure III - 90: Standard Capacity at -20°C for Cells Stored at 60°C.....	158
Figure III - 91: 27 Ah Prismatic Cells Stored at 60°C.....	158
Figure III - 92: Pouch Cell Shout Circuit, Silica Filled Separator.....	158
Figure III - 93: Pouch Cell Shout Circuit, Unfilled Polyolefin Separator.....	158
Figure III - 94: Pilot-scale unit in operating mode.....	161
Figure III - 95: First cycle efficiency for nano-Si composite/LiCoO ₂ full cell.....	162
Figure III - 96: Hard carbon (E) half cell test.....	162
Figure III - 97: (E) hard carbon / LiMn ₂ O ₄ full cell test.....	162
Figure III - 98: Anode specific capacity vs cycle.....	165
Figure III - 99: Lithium surface after cycling.....	165
Figure III - 100: Cells discharge profiles at 50 th cycle at C/5 discharge rate with dual phase and single phase electrolytes.....	165
Figure III - 101: Thermal ramp test of fully charged 0.25 Ah cell after 10 th cycle.....	166
Figure III - 102: Structural and electrical schemes for modeling of Dual-Phase electrolyte cell.....	166
Figure III - 103: Current distribution over electrode area with terminal along the entire electrode (a) and with one point terminal connection (b).....	166
Figure III - 104: Simulated Li anode thickness profiles after discharge at various electrodes length.....	166
Figure III - 105: Simulated Li thickness non-uniformity after discharge as function of cathode substrate thickness.....	167
Figure III - 106: Simulated Li anode thickness profiles at high depths of discharge and subsequent charge.....	167
Figure III - 107: Simulated cell Area Specific Resistance vs Li Depths of Discharge.....	167
Figure III - 108: a) Anode and cathode with terminals; b) 2.5 Ah cell.....	168
Figure III - 109: Dual-Phase electrolyte anode structure.....	168
Figure III - 110: a) 2.5 Ah format Dual-Phase Electrolyte cell discharge capacity vs cycle; b) 2.5 Ah format Dual-Phase Electrolyte cell 5 th cycle discharge profile.....	168
Figure III - 111: Thermal ramp test of fully charged 2.5 Ah cells with and w/o Dual-Phase Electrolyte.....	169
Figure III - 112: NCM 111 C-Rate Data of Pilot Plant vs Production Plant.....	171
Figure III - 113: NCM 111 Cycling Data of Pilot Plant vs. Production Plant.....	171
Figure III - 114: NCM 424/LMO Power Capability.....	172
Figure III - 115: NCM 111/LMO Power Capability.....	172
Figure III - 116: EV/PHEV Application Qualification.....	172

Figure III - 117: Power Retention of Cells	172
Figure III - 118: SEM image of SiNP/CNF-30-2.....	174
Figure III - 119: Cycling performance of SiNP/CNF-30-2 at 0.2 C (half-cell).....	175
Figure III - 120: Cycling performance of SiNP/CNF-30-2 with a new binder at 0.2 C (half-cell). Please note that the first two cycles were charged/discharged at 0.05 C.....	175
Figure III - 121: Rate performance of SiNP/CNF-30-2 at various charge/discharge currents (half-cell).....	175
Figure III - 122: (a) Cycling performance and (b) charge/discharge curves of a full cell consisting of SiNP/CNF-30-2 anode and LiCoO ₂ cathode.....	176
Figure III - 123: Schematic of composite nanofiber anode.....	178
Figure III - 124: Chemical structure of surfactant NaD.....	178
Figure III - 125: Cycling performance of Si/C nanofiber anodes prepared from 10 wt % Si/PAN with different concentrations of surfactant NaD. Electrolyte: 1 M LiPF ₆ in EC/EMC; and current density: 100 mA g ⁻¹	178
Figure III - 126: Cycling performance of Si/C nanofiber anodes prepared from Si/PAN with different Si contents. Electrolyte: 1 M LiPF ₆ in EC/EMC; and current density: 100 mA g ⁻¹	179
Figure III - 127: Cycling performance of Si/C nanofiber anodes prepared from 25 wt% Si/PAN with different Si particle sizes. Electrolyte: 1 M LiPF ₆ in EC/EMC; and current density: 100 mA g ⁻¹	179
Figure III - 128: Cycling performance of Si/C, Ge/C and Sn/C nanofiber anodes prepared from their 25 wt% precursors. Electrolyte: 1 M LiPF ₆ in EC/EMC; and current density: 100 mA g ⁻¹	179
Figure III - 129: Cycling performance of Si/C nanofiber anodes prepared using different carboinization temperatures. Electrolyte: 1 M LiPF ₆ in EC/EMC; and current density: 100 mA g ⁻¹	179
Figure III - 130: Yflow's eSpinning unit and its fiber formation process.....	180
Figure III - 131: Cycling performance of Si/C nanofiber anodes prepared from lab-scale electrospinning device and Yflow's eSpinning unit. Electrolyte: 1 M LiPF ₆ in EC/EMC; and current density: 100 mA g ⁻¹	180
Figure III - 132: Cycling performance of Si/C nanofiber anodes prepared from 25 wt % Si/PAN precursor. First two cycles: full charge/discharge (cut-off voltages: 0.05 – 2.5 V). Following cycles: 70% state-of-charge swing, <i>i.e.</i> , changing the current polarity if: 1) capacity reaches 70% of first-cycle capacity, or 2) voltage reaches cut-off values: 0.05 – 2.5 V. Electrolyte: 1 M LiPF ₆ in EC/EMC; and current density: 100 mA g ⁻¹	181
Figure III - 133: N/P ratio for LFP-graphite and LFP-LTO cells after formation, 10 overcharge cycles, and failure (40 overcharge cycles for the LFP-LTO cells).....	183
Figure III - 134: Porosity for graphite and LTO electrodes from LFP-graphite and LFP-LTO cells after formation, 10 overcharge cycles, and failure (40 overcharge cycles for the LFP-LTO cells).....	183
Figure III - 135: Discharge voltage curves for a 1.0 Ah stacked prismatic cell constructed with electrodes fabricated on the coater in our prototyping facility.....	185
Figure III - 136: Cycle life of 2.2 Ah and 2.3 Ah cells fabricated at TIAX. The plot shows discharge capacity for 1 C CCCV charge to 4.2 V and 1 C discharge to 2.75 V. The electrode capacities in these cells — 3.0 to 3.2 mAh/cm ² — correspond to the electrode designs typically employed for PHEV cells.....	186
Figure III - 137: A photograph of the test chamber for controlled heat transfer studies. The photograph shows a close up of the see-through chamber that houses instrumented test and reference cells.....	186
Figure III - 138: Summary of the measured film heat transfer coefficient at the surface of an 18650 cell as a function of the air flow rate in the heat transfer chamber.....	187
Figure III - 139: Comparison of experimental data and model simulations to further validate model parameters. In this experiment, heat dissipation within the cell was fixed at 10 W for a period of 885 s. The surface heat transfer coefficient was set at 13 W/m ² -K at the beginning of the experiment. The heat transfer coefficient was raised to 26 W/m ² -K after ~360 s when the cell temperature reached 80°C. The power dissipation was turned off after 885 s. As can be seen, without adjustable parameters the model not only predicts the rate of initial surface temperature increase, but also the decreased rate of temperature increase when the heat transfer coefficient is increased after 360 s.....	187
Figure III - 140: Experimental data for thermal runaway of an 18650 cell. In this experiment, performed in the heat transfer chamber, thermal runaway was induced in an 18650 cell fabricated at TIAX using the heater method. This data set is being used to further calibrate model parameters.....	187
Figure III - 141: In-Line Shear Mixing Trial.....	189
Figure III - 142: Tensile Strength.....	189
Figure III - 143: Additive Material Handling system.....	189
Figure III - 144: Percent Additive viscosity vs time.....	189
Figure III - 145: IR Impact on Drying Time.....	190
Figure III - 146: PHEV battery manufacturing costs are likely to fall between \$220 to \$470/kWh usable energy depending on cell chemistry, design, and life.....	192

Figure III - 147: HEV Li-ion battery costs are likely to range between \$460 and \$1200/pack, depending on the cell chemistry, cell design, and the degree to which energy of the cell is oversized to meet the power requirements.....	193
Figure III - 148: Probability distribution function of daily vehicle miles travelled.....	196
Figure III - 149: Distribution of BEV to CV cost ratios for various vehicle range, cost of unachievable VMT, and drive patterns.....	196
Figure III - 150: Projected second use battery sale price.....	199
Figure III - 151: Projected second use battery repurposing cost for a repurposed battery selling price of \$132/kWh.....	200
Figure III - 152: Preliminary Application Analysis Results.....	200
Figure III - 153: Measured battery response to regulation testing.....	201
Figure III - 154: Relationship between price and energy density to average open-circuit voltage for a number of common Li-ion chemistries. The calculations are completed for a 17 kWh, 60 kW PHEV40 with a nominal pack voltage of 360 V.....	204
Figure III - 155: PHEV40 17 kWh and 60 kW based contour plot for a sloping discharge curve with OCV of 3.6 V at 50% SOC and a positive active material cost of \$30 kg ⁻¹ and negative active material cost of \$20 kg ⁻¹ . Gravimetric capacities here are scaled assuming the physical properties of graphite for the negative (2.2 g cm ⁻³) and a lithium transition-metal oxide for the positive (4.6 g cm ⁻³) both near 33% porosity for electrolyte transport.....	205
Figure III - 156: Predicted price to OEM for a 17 kWh, 60 kW 360 V PHEV battery based on advanced Li-ion chemistries.....	206
Figure III - 157: Performance and cost for advanced Li-ion cell chemistries for a 17 kWh, 60 kW 360 V PHEV battery with a 50 micron maximum electrode thickness limitation.....	206
Figure III - 158: Capacity fade under storage at 90% SOC for two geographic locations with and without impact of solar loading on the parked vehicle. Blue and green curves consider various simplifications of the full hour-by-hour temperature data and should be compared to the ambient + solar case.....	214
Figure III - 159: Typical meteorological year temperature data for Phoenix, AZ. For a resource-constrained test environment, the seasonal average 24 hour temperature variation, case "F", best approximates the impact of daily and seasonal peak temperatures on vehicle battery life.....	215
Figure III - 160: Energy Consumption for Li ₂ CO ₃ Production.....	217
Figure III - 161: Schematic of Processes Avoided by Recycling.....	218
Figure III - 162: Energy Required to Produce Cathode Material.....	219
Figure III - 163: Energy Required to Produce Battery.....	219
Figure III - 164: Ford Fusion Hybrid Test Platform at NREL.....	222
Figure III - 165: Schematic and Photo of the Fusion Hybrid's High-Voltage Traction Battery (HVTB).....	222
Figure III - 166: Replacement Interface Components for Use with the Alternate LEESS.....	223
Figure III - 167: Schematic of Connections between Replacement Components and the Vehicle.....	223
Figure III - 168: Photo of the JSR Micro LIC Modules.....	223
Figure III - 169: CD energy vs. time from a cell undergoing a life-cycle test. From these data, two energy fade processes may be occurring.....	228
Figure III - 170: Average, relative resistance at 80% DOD vs. cycle count.....	228
Figure III - 171: Average power fade for BLE Sanyo cells.....	232
Figure III - 172: Generalized rate-based model fit of relative resistance using INL cell groups.....	232
Figure III - 173: Hourly temperature profile for Phoenix, AZ (2010).....	232
Figure III - 174: HCSD vs. DOD at RPT0.....	233
Figure III - 175: HCSD vs. RPT at 40% DOD.....	234
Figure III - 176: Typical effect of temperature on lithium ion battery resistance rise (built in 2008).....	236
Figure III - 177: Quallion Li-Ion Module.....	236
Figure III - 178: Capacity fade during calendar life testing.....	236
Figure III - 179: Capacity fade during charge depleting cycle life testing at four temperatures.....	237
Figure III - 180: Resistance rise during calendar life testing at four temperatures.....	237
Figure III - 181: Capacity fade during calendar life testing as function of state of charge.....	237
Figure III - 182: Reference electrode work shows the resistance rise on the cathode.....	238
Figure III - 183: Typical effect of temperature for EV batteries.....	238
Figure III - 184: Typical effect of temperature on resistance for HEV batteries.....	238
Figure III - 185: Typical effect of temperature for HEV batteries.....	238
Figure III - 186: Schematic of sacrificial electrode placement and dendrite growth within a cell.....	241
Figure III - 187: Cell voltage (blue) and temperature (red) during a 2C overcharge test of a COTS 10 Ah cell (20 amp applied current).....	241

Figure III - 188: Venting and ignition of COTS Li-ion cell contents during overcharge abuse test.	242
Figure III - 189: Propagation of cell failure in a 5-cell series configured battery. After initiation of failure in the center cell sufficient heat is produced to induce thermal runaway starting with the adjacent cells and proceeding to the outermost cells in the pack.	242
Figure III - 190: Sacrificial anode dissolution current and voltage as a function of time during a dissolution and plating step in a lithium ion cell.	243
Figure III - 191: Current and voltage as a function of time during a dissolution and plating step in a lithium ion cell.	243
Figure III - 192: Frequency of duty cycles – temperature profiles.	247
Figure III - 193: Capacity loss mechanisms for Sanyo Y chemistry.	247
Figure III - 194: Capacity loss data for cells under calendar-life conditions with daily thermal cycling. In general terms, early capacity degradation involves loss of lithium inventory (LLI), followed by loss of active material (LAM), kinetic limitations, cell polarization effects, and complex combinations of such. The relative contribution of these to overall capacity is path dependent, and is likely to shift under conditions of significant daily thermal cycles.	248
Figure III - 195: String Testing Results.	248
Figure III - 196: String Testing Results (cont'd).	248
Figure III - 197: NREL's Energy Storage Laboratory.	251
Figure III - 198: Efficiency of cells tested at 30°C in NREL's calorimeter during FY12.	251
Figure III - 199: Efficiency of selected cells tested in FY12 at 0°C and 30°C in NREL's calorimeters.	251
Figure III - 200: Normalized heat rate of cells tested at 30°C in NREL's calorimeter during FY12.	252
Figure III - 201: Normalized heat rate at 30°C for cells discharged from 100% to 0% SOC in FY12.	252
Figure III - 202: Infrared image of cells under constant current discharge.	252
Figure III - 203: Thermal management system performance during US06 cycling.	253
Figure III - 204: ISC schematic (top picture) and ISC placed in a cell (bottom picture) – not to scale.	255
Figure III - 205: ISC in E-One Moli 18650 cell (top picture) and ISC placed in a Dow Kokam 8 Ah cell (bottom picture). Note that the actual size of the short (Cu puck) is 0.125" in diameter.	256
Figure III - 206: Voltage response to various ISC activations in E-One Moli 18650 cell at 0% SOC.	256
Figure III - 207: Voltage response to a collector to collector ISC activation in the E-One Moli 18650 cell at 100% SOC.	256
Figure III - 208: E-One Moli 18650 cathode and anode assemblies unrolled after ISC activation.	257
Figure III - 209: Four Elements of the Computer Aided Engineering for Batteries (CAEBAT) Activity.	259
Figure III - 210: A typical result from CD-adapco coupled flow, thermal & electrochemical model of a pack with cylindrical cells.	260
Figure III - 211: A typical result from EC Power thermal and electrochemical model of a pack with prismatic cells.	260
Figure III - 212: Pack level simulation vision by GM/ANSYS/ESim team.	261
Figure III - 213: Schematic of the OAS modeling framework and interactions with other tasks within the CAEBAT program and external activities.	263
Figure III - 214: Coupling scenarios in battery modeling. We started with one-way and two-way loose coupling. In later years, as needed, we will move towards two-way tight coupling with Picard and Full-implicit methodologies.	263
Figure III - 215: Schematic of the OAS modeling framework encapsulating the various components through component adapters and link to the battery state through the state adapters. The collection of the different tools, adapters, and OAS framework will give one realization of VIBE (Virtual Integrated Battery Environment).	264
Figure III - 216: Overall Structure of the Battery ML.	264
Figure III - 217: Battery state file – the core for passing data between components.	265
Figure III - 218: Geometry and mesh of the simulated cylindrical cell.	265
Figure III - 219: Sample results for cylindrical cell (electrical potential on the left and the temperature on the right).	265
Figure III - 220: Battery design tool user requirements.	267
Figure III - 221: Comparison of the discharge voltages for various simplifications compared to the full P2D model.	269
Figure III - 222: Comparison of the cell temperatures for various simplifications compared to the full P2D model.	269
Figure III - 223: MSMD approach for the cell level.	269
Figure III - 224: First version of cell level tool from ANSYS.	269
Figure III - 225: Cell level validation test setup and test data.	270
Figure III - 226: System level modeling for pack level simulations.	270
Figure III - 227: Previous work using flow, thermal & electrochemistry models, courtesy of Automotive Simulation Centre Stuttgart (ASCS) project, Germany (Daimler, GM Opel, Porsche).	273
Figure III - 228: Schematic of the underlying modeling abstraction.	274
Figure III - 229: Parameters used to describe the positive and negative electrodes in the host BDS code.	274

Figure III - 230: Voltage against time, Simulation (Green) plotted against test data (Red) for a given set of discharge pulses. Note, this is example data not related to the clients confidential results.	275
Figure III - 231: Screen shots of spiral cell examples within STAR-CCM+ showing the resolved current carrying tabs.	275
Figure III - 232: Prediction of temperature on the jelly roll of 3 cells in series.	275
Figure III - 233: Generic battery module using the generated wound cell models.	275
Figure III - 234: Maximum and minimum temperatures occurring within the Jellyrolls.	275
Figure III - 235: Electrode current density for positive and negative electrodes from a generic cell.	276
Figure III - 236: Plots generated by PSU during materials database development.	278
Figure III - 237: Plots generated by PSU during materials database development (cont'd).	278
Figure III - 238: 1C discharge of a 2P-12S configured 2.8kWh pack with a parallel air cooling system.	279
Figure III - 239: Electrochemical output of the selected cell.	279
Figure III - 240: Temperature distributions resulting from a partially penetrated nail in a prismatic cell.	279
Figure III - 241: Temperature distributions resulting from a partially penetrated nail in a prismatic cell (cont'd).	279
Figure III - 242: Schematics of a typical jelly-roll wound structure.	281
Figure III - 243: Schematics of a typical jelly-roll wound structure.	281
Figure III - 244: MSMD submodel choice of present work.	281
Figure III - 245: Schematic description for nominal cell design and electrical tab configuration of the 50Ah wound prismatic cell.	282
Figure III - 246: Form factor case description investigated in the present work.	282
Figure III - 247: Comparison of voltage outputs from the compared cases for constant current discharge at 100A.	282
Figure III - 248: Thermal behavior of the investigated cell designs.	282
Figure III - 249: Non-uniform kinetics during discharge of the investigated cell designs.	283
Figure III - 250: Potential drop across the electrode/electrolyte interface due to the formation of a gas bubble on the electrode surface during overcharge: the ordinate $y=0$ represents the electrode surface.	285
Figure III - 251: Scaling up results from the component models to cell level abuse simulations: this figure indicates the unequal pressure build-up across the interior of the cell during the swelling of a pouch cell. Notably, the region close to the tabs is highly constrained and is likely to suffer much more stress than the region far from it.	285
Figure III - 252: Experimental results of fault signals (FS) at positive and negative module terminals (a) for a 0.1- Ω ISC, (b) for a 0.5- Ω ISC, and (c) for a 1- Ω ISC induced in cell(1,1) in a module with conditions, $C_{mdl} = 16$ Ah (8 Ah + 8 Ah), $I_{mdl} = 0A$, $N_s = 3$, $R_b = 0.2 \Omega$; same with (d), (e), (f) for ISCs induced in cell(1,2); same with (g), (h), (i) for ISCs induced in cell(1,3); same with (j), (k), (l) ISCs induced in cell(1,3) and $R_b = 0.1\Omega$	286
Figure IV - 1: Charge and discharge voltage profiles of the LMR-NMC $0.5Li_2MnO_3 \cdot 0.5LiMn_{0.375}Ni_{0.375}Co_{0.25}O_2$ cycled against metallic Li for 20 cycles. Various mechanisms have been identified to cause the apparent capacity fade.	299
Figure IV - 2: LMR-NMC voltage profiles during charge and discharge versus normalized capacity. Voltage fade is clearly evident.	300
Figure IV - 3: Resistance-corrected average cell potentials plotted versus cycle number. A continuous drop in average potential exceeding 0.1V is apparent during charging and discharging. The drop in average charge potential is larger than the drop in the average discharge potential. The average potential is calculated by dividing the measured total energy (current x time x voltage) by the measured cell capacity (current x time).	300
Figure IV - 4: Capacity-normalized voltage profiles for NCA. Some minor voltage fade is apparent at the end of charge and beginning of discharge.	301
Figure IV - 5: Capacity-normalized voltage profiles for NCM333. Some voltage fade is apparent over all charge states and discharge depths.	301
Figure IV - 6: Resistance corrected average charge and discharge voltages for the LMR-NMC, NCA and the NCM333 oxides. All three materials show voltage fade, however fade is strongest for the baseline material.	302
Figure IV - 7: Gravimetric energy densities during discharge plotted versus cycle number for LMR-NMC, NCA, and NCM. Voltage fade, along with capacity loss and cell resistance increase, lead to an overall loss in deliverable energy for a given amount of active oxide.	303
Figure IV - 8: Battery Price to OEM for an advanced Li-ion anode with LMR-NMC cathodes with varying capacities as a function of cathode OCV for (left) an EV150 compared against the next best Li-ion cathode option and (right) a PHEV40 compared against DOE goals.	303
Figure IV - 9: Discharge capacity after 1st and 6th cycles under various testing conditions.	304
Figure IV - 10: Voltage fade observed after a 4.7V formation with various cycling voltages.	305
Figure IV - 11: Data base established for all voltage fade materials.	305

Figure IV - 12: Example Li_2MnO_3 Domain within LiCoO_2 Matrix.....	306
Figure IV - 13: DFT results for relative energies of thirty configurations of $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$. The lowest energy configuration is the ordered arrangement C1. The partially segregated arrangement of C30, with NiMn zigzags interrupted by lines of Co, is still low enough in energy to be present at elevated temperatures.....	306
Figure IV - 14: Voltage and heat profile of HE5050 during charge and discharge.....	307
Figure IV - 15: Measured Open Circuit Voltages (a) and (b), and the corresponding dQ/dV (c) and (d) for $\text{Li}_{1.25}\text{Ni}_{0.33}\text{Mg}_{0.02}\text{Mn}_{0.65}\text{O}_y$	307
Figure IV - 16: Measured open circuit voltages at 3.7V on charge (red) and discharge (blue) after a 7 day potentiostatic hold for $\text{Li}_{1.25}\text{Ni}_{0.33}\text{Mg}_{0.02}\text{Mn}_{0.65}\text{O}_y$	308
Figure IV - 17: (a) Voltage profile of cycle #10 during <i>in situ</i> XRD measurements and (b) the corresponding dQ/dV plot. (c) Raw XRD data during the charge/discharge process.....	308
Figure IV - 18: Refined lattice parameters as a function of charge and discharge for $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ (a) and the Toda HE5050 (b).....	308
Figure IV - 19: Ni K XANES data for the Toda HE5050 comparing edge energies at different SOC's on charge and discharge.....	309
Figure IV - 20: (left) HR-SXRD pattern of HE5050 shows the super-reflections (020), (110), (11-1), (021), etc. due to the presence of Li/M ordering and associated monoclinic phase (C2/m). (right) HR-SXRD patterns of HE5050. HE5050_4.3V-2V_1 cycle, and HE5050_4.7V-2V_1cycle. The inset drawing shows a possible interconnected layered structure for the heterogeneous structure after the activation.	309
Figure IV - 21: Crystal structure models for Li_xTMO_2 phases; (a) Li_2TMO_3 (110 plane), (b) layered (1-100), (c) spinel (112) and (d) simple rock-salt (112). Oxygen is drawn as red, TM as purple, and Li as blue. The atom columns with circles represent randomly mixed Li/TM columns. The corresponding experimental selctron diffraction patterns, high resolution images, and Fourier Transform patterns from the high resolution images are shown under each crystal model (e-h).....	310
Figure IV - 22: Electron diffraction patterns from (a) fresh and (b) 1500 times cycled $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{CO}_{0.1}\text{O}_2$ showing the transformation from layered to spinel-like structure. Corresponding high resolution images are presented in (c) and (d).	310
Figure IV - 23: High resolution image of $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{CO}_{0.1}\text{O}_2$ after cycling (1500x) showing the uniform transformation to spinel-like phase.....	311
Figure IV - 24: Scanning electron microscope image of our microscale battery set up. A single $\text{Li}_{1+x}(\text{Mn},\text{TM})\text{O}_2$ particle is attached to a probe tip which serves as one electrode and is used to place the particle in the electrolyte covering the anode (Li metal in this case). In this image, the particle is just above the electrolyte.	311
Figure IV - 25: Electrochemistry cycling data from a single $\text{Li}_{1+x}(\text{Mn},\text{TM})\text{O}_2$ particle collected using the setup shown in the previous figure.	311
Figure IV - 26: Scanning electron micrographs of the $\text{Li}_{1+x}(\text{Mn},\text{TM})\text{O}_2$ particle from the previous figure (a) in the pristine condition before cycling and (b) after 26 complete charge/discharge cycles.	312
Figure IV - 27: ^6Li MAS NMR of pristine TODA HE5050 material at a spinning speed of 35 kHz at 11.7 Tesla magnetic field. * indicates spinning side bands.....	313
Figure IV - 28: ^6Li MAS NMR of cycled Li_2MnO_3 material at a spinning speed of 35 kHz at 11.7 Tesla magnetic field. * indicates spinning side bands.....	313
Figure IV - 29: ^2H MAS NMR of cycled TODA HE5050 material at a spinning speed of 20 kHz at 11.7 Tesla magnetic field. * indicates spinning side bands.....	314
Figure IV - 30: A compositional phase diagram of a 'layered-layered-spinel' system with $\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ('layered-layered') and $\text{LiM}'_2\text{O}_4$ (spinel) components.	314
Figure IV - 31: Variation in capacity (mAh/g) and first-cycle efficiency (%) as a function of x in $\text{Li}_x\text{Mn}_{0.65}\text{Ni}_{0.35}\text{O}_y$ electrodes.....	315
Figure IV - 32: XRD patterns of various materials derived from the 'layered-layered-spinel' $\text{Li}_x\text{Mn}_{0.65}\text{Ni}_{0.35}\text{O}_y$ system.....	315
Figure IV - 33: Effect of activation voltage on the performance of 'layered-layered-spinel' $\text{Li}_{1.25}\text{Mn}_{0.65}\text{Ni}_{0.33}\text{Mg}_{0.02}\text{O}_{2.28}$ and AlF_3 -treated electrodes: a) typical voltage profile of an uncoated electrode; b) and c) dQ/dV plots of lithium cells with uncoated and AlF_3 -coated electrodes, respectively. The cells in a) and c) were subjected to two activation cycles between 4.95 and 2.5 V, before being cycled between 4.6 and 2.5 V, whereas the cell in b) was cycled only between 4.6 and 2.0 V followed by an additional 49 cycles between 4.6 and 2.5 V (c). These data indicate that the untreated $\text{Li}_{1.25}\text{Mn}_{0.65}\text{Ni}_{0.33}\text{Mg}_{0.02}\text{O}_{2.28}$ cathode suffers from continuous voltage fade, which is apparent in two dominant reduction peaks (indicated by arrows in Fig. 32b), when cycled over a 4.6 to 2.5 V range. The chemistry of the AlF_3 electrode has changed significantly from the untreated version and further work is needed to determine the cause of this change.....	316

Figure IV - 34: a) XRD patterns and b) PDF spectra of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiCoO}_2$, for $x=0.1, 0.3, 0.7, \text{ and } 0.9$ annealed at 850°C	316
Figure IV - 35: Average particle size evolution of $\text{Ni}_{0.25}\text{Mn}_{0.75}(\text{OH})_2$ precursors as a function of reaction time.....	317
Figure IV - 36: SEM images of $\text{Ni}_{0.25}\text{Mn}_{0.75}(\text{OH})_2$ secondary particles synthesized with different M_S/M_A in the base solutions (a) 0.667, (b) 1.5, (c) 1.8, (d) 2, (e) 2.5, (f) 4.....	317
Figure IV - 37: SEM images of $\text{Ni}_{0.25}\text{Mn}_{0.75}(\text{OH})_2$ primary particles synthesized with different M_S/M_A in the base solutions (a) 0.667, (b) 1.5, (c) 1.8, (d) 2, (e) 2.5, (f) 4.....	317
Figure IV - 38: First 5 cycles of a half cell of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{Mn}_4$ with 1 M LiPF_6 in EC:DEC 1:2.....	320
Figure IV - 39: First 5 cycles of a half cell of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{Mn}_4$ with 1 M LiPF_6 in EC:DEC 1:2 with 1% HFIP.....	320
Figure IV - 40: Rate performance of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ materials.....	320
Figure IV - 41: The effect of electrolyte additives on full-cell rate performance.....	321
Figure IV - 42: a.) Graphite/NCM without additive, b.) Graphite/NCM with VC and FRION.....	321
Figure IV - 43: X-ray diffraction pattern of the synthesized carbonate precursor.....	324
Figure IV - 44: Particle size distribution superimposed on SEM image of synthesized carbonate precursor.....	325
Figure IV - 45: Cathode morphologies and particle size distributions before and after sieving.....	325
Figure IV - 46: EDXS curves superimposed on SEM images of bisected precursors with particle sizes of (a) $<20 \mu\text{m}$ (b) 20-38 μm , and (c) 38-75 μm and cathode materials with particle sizes of (d) $<20 \mu\text{m}$ (e) 20-38 μm , and (f) 38-75 μm	325
Figure IV - 47: SEM images of cathode materials with core-shell like features: (a) low magnification image and (b) higher magnification image of local area.....	326
Figure IV - 48: High-energy XRD patterns for cathodes with different particle sizes.....	326
Figure IV - 49: Electrochemical performance of cells prepared with cathodes with different particle sizes: left, voltage-capacity profile; right, cycling performance.....	326
Figure IV - 50: Rate performance of half cells prepared with cathodes of different secondary particle sizes.....	327
Figure IV - 51: Schematic diagram of streamlining the optimization of electrode.....	330
Figure IV - 52: Conductivity measurement using nano probe SEM.....	330
Figure IV - 53: Carbon Additive Effect on Conductivity of $\text{LiFePO}_4/\text{Carbon Blend}$	331
Figure IV - 54: SEM images of electrode with no carbon coating (left) and with 3% carbon coating on the particles.....	331
Figure IV - 55: Four point probe electrode conductivity geometry.....	331
Figure IV - 56: Electrode conductivity of coating using polyester as substrate.....	332
Figure IV - 57: ASI of NCM electrode with and without carbon coating.....	332
Figure IV - 58: ASI of NCM electrode with and without carbon coating.....	332
Figure IV - 59: Cycling performance for ALD alumina coated samples of LiCoO_2 cycled between 3.3V and 4.5V.....	334
Figure IV - 60: A typical ALD chamber with sequentially separated precursor exposure which draws out overall processing time.....	335
Figure IV - 61: A simplified schematic demonstrating the in-line spatial ALD concept.....	335
Figure IV - 62: A preliminary design from the George Group for demonstration of in-line AP-ALD.....	336
Figure IV - 63: Demonstration of in-line deposition of aluminum oxide onto a silicon wafer at atmospheric pressure.....	336
Figure IV - 64: Initial design of an in-line ALD reactor for deposition on porous substrates.....	336
Figure IV - 65: A 6" by 6" foil of TodaHE5050 following coating with 5 cycles of ALD alumina.....	336
Figure IV - 66: (A) Samples of NMC 111 and A10 Graphite provided by Sandia NL and coated with ALD alumina by NREL/CU (B) 18650 cells fabricated from coated ALD foils for testing at Sandia.....	337
Figure IV - 67: Accelerated Rate Calorimetry Data for Cells with and without an ALD alumina coated anode.....	337
Figure IV - 68: Cycling capacity performance for a variety of HE5050 samples with and without ALD coatings. Condition details are given in the text.....	338
Figure IV - 69: Fluidized Bed Reactor to coat powders with ALD cycles: the existing reactor at ALD Nanosolutions can process up to 8L of powder per batch.....	340
Figure IV - 70: SEM images of two different batches of Mn-rich cathode powders coated with alumina: the coatings are uniform and conformal over a range of baseline particle sizes.....	340
Figure IV - 71: Initial evaluation of Sample 2 coated with Al_2O_3 in Run 1 using coin cells at NREL: Charge and Discharge at C/5 (25°C) with 1C-discharge pulses for 20s after every 10% discharge.....	341
Figure IV - 72: Cycling performance of pouch cells at 25°C subjected to 100% DOD cycles at the C/2-rate.....	341
Figure IV - 73: EIS measurements on Mn-rich cathode material coated with different ALD layers of Al_2O_3 : the powders coated in Run 2 show larger impedance build up compared to the baseline.....	341
Figure IV - 74: Surface energy of treated and untreated Al foils and LiFePO_4 aqueous dispersion; the surface energy and polarity of Al foils increased with increasing corona treatment energy density.....	343

Figure IV - 75: Cycling of LiFePO ₄ cathodes at 0.5C/-0.5C (0.34 mA/cm ²) confirming 0.4 J/cm ² as the best corona treatment energy density for long term performance.....	344
Figure IV - 76: A roll of NCM523 cathode and A12 graphite anode from baseline coating.....	344
Figure IV - 77: Initial performance of NCM 523 cathodes; a) 25 cycles discharged at C/5 and b) rate performance.....	345
Figure IV - 78: Zeta potential of A12 graphite with and without CMC; the addition of 1 wt% CMC resulted in a more negative charge on the A12 surface.....	345
Figure IV - 79: Zeta potential of NCM 523 with and without CMC; the addition of 1 wt% CMC resulted in a more negative charge on the NCM 523 surface.....	345
Figure IV - 80: Rheologic properties of aqueous NCM 523 suspensions with various CMC concentrations a) viscosity vs shear rate and b) shear stress vs shear rate.....	346
Figure IV - 81: Agglomerate size of aqueous NCM523 suspension with various CMC concentrations.....	347
Figure IV - 82: In-line laser caliper set-up inside slot-die coater for wet thickness measurement.....	350
Figure IV - 83: Baseline noise determination from using calibration shim.....	350
Figure IV - 84: Thickness measurement of LiFePO ₄ electrode on Al foil.....	350
Figure IV - 85: In line thickness measurement of LiNi _{0.5} Co _{0.2} Mn _{0.3} O ₂ (NCM 523) electrode at different regions; the y-axis represents the temperature at which data were collected.....	351
Figure IV - 86: Homogeneity and defect analysis of LiFePO ₄ electrode coating: visual digital image (a), IR image (b), temperature profile (c), and image taken when quartz lamp is viewed through the electrode (d).....	351
Figure IV - 87: In line IR imaging set-up on a slot-die coater.....	351
Figure IV - 88: Processed in-line IR imaging data at different regions of a LiNi _{0.5} Co _{0.2} Mn _{0.3} O ₂ (NCM 523) cathode coating.....	351
Figure IV - 89: Stoichiometry and thickness uniformity of Ni, Co, and Mn at different locations of a NCM 523 electrode coating.....	352
Figure IV - 90: Galvanostatic charge/discharge profiles of Toda HE5050 cathode showing voltage fade after subsequent cycling.....	352
Figure IV - 91: Change in lattice parameter (with error bars) in Toda HE5050 cathode material at different points in the electrochemical charge/discharge profile; these plots were collected from the freshly prepared cell (first 1.5 cycles) and after 36 cycles.....	352
Figure IV - 92: (108), (110), (13) reflection during first 1.5 cycles, after 16 cycles, and after 36 cycles. The R and M subscripts designate the rhombohedral (trigonal) phase and monoclinic phase, respectively. The color stacks represents the different charge/discharge voltages. The appearance of new peaks is highlighted in the dotted regions.....	353
Figure IV - 93: Electrochemical voltage profile showing the desired point of interest for analysis (before hold and after holding for 60h, 70h, and 90h).....	353
Figure IV - 94: Magnetic susceptibility data for pristine Toda HE5050 after charging to 4.5 V and after holding for 90h.....	354
Figure IV - 95: High-resolution TEM showing both the O3 and spinel type lattice fringe in agreement with the corresponding FFT; the particle was analysed from AH70 sample.....	354
Figure IV - 96: Magnetic model showing the different exchange interaction (a) and the M(H) curves at 5K (b); the linear extrapolation was done to calculate the magnetic saturation values.....	355
Figure IV - 97: High-resolution TEM image from the AH90 particle showing spinel like lattice fringes (see the simulated image of cubic spinel phase along [100] direction; the FFT and SAED shows spinel phase reflections).....	355
Figure IV - 98: Cycle performance and rate capability of 50wt.%SiO-50wt.%Sn ₃₀ Fe ₃₀ C ₄₀ prepared by spex-milling.....	357
Figure IV - 99: Cycle performance of different compositions.....	358
Figure IV - 100: XRD pattern of SiO-Sn ₃₀ Fe ₃₀ C ₄₀	358
Figure IV - 101: a) First and second charge-discharge profiles, and b) cathode capacity vs. cycle number plot of a lithium-ion cell with a heat-treated (2800 °C) carbon sphere anode and a lithium manganese rich cathode between 4.6 and 2.0 V at a C/3 rate. (Note: the capacity refers to the cathode only).....	360
Figure IV - 102: a) SEM and TEM (inset) of Sn-coated carbon spheres and b) First and second discharge-charge- profiles (inset) and capacity vs. cycle number plot of a lithium half-cell with Sn-carbon sphere electrodes between 1.5 V and 0.01 V at a C/2.7 rate.....	361
Figure IV - 103: (a) SEM and TEM (inset) images of SnO ₂ /Sb-coated carbon spheres, (b) First and second discharge-charge-profiles (inset) and capacity vs. cycle number plot of a lithium half-cell with a SnO ₂ /Sb-carbon sphere electrode cycled between 1.5 and 0.01 V at a C/5.5 rate.....	361
Figure IV - 104: (a) First and second discharge-charge-profiles of a lithium cell with a G8 graphite/25wt.% SnO ₂ electrode, and (b) capacity vs. cycle number plot of a lithium half-cell with a SnO ₂ -graphite electrode, cycled between 1.5 and 0.01 V at a C/4 rate (top), relative to a cell with a standard G8 graphite electrode (bottom).....	362

Figure IV - 105: Hydrogen concentration change with reaction time measured by <i>in situ</i> GC. The supporting Ar flow rate is 14 mL/min. Black squares represent condition with LiPF ₆ in the electrolyte; red circles, no LiPF ₆ in the electrolyte.....	364
Figure IV - 106: Evolution of XANES spectra of Ti K-edge during aging at 60°C. The spectra were taken every 5 minutes.....	364
Figure IV - 107: Contour plots of the derivatives of the normalized energy for three temperature settings, (a) 50°C, (b) 60°C and (c) 70°C.....	365
Figure IV - 108: Gas evolution in pouch cells LTO/LMO with /without 1% SL2 as the additive in the electrolyte of 1.2M LiPF ₆ in EC/EMC in 3:7 in weight.....	365
Figure IV - 109: Gas volume change for the LTO/LMO pouch cells with and without ALD coating on the LTO particle surface. The pouch cells have capacity of 100 mAh which is different from the ones used in the previous figure.....	366
Figure IV - 110: SEM images of Li _{1.2} Ni _{0.3} Mn _{0.6} O _{2.1} showing spherical secondary particle and dense nano-primary particles.....	368
Figure IV - 111: TEM images of high energy cathode coated and uncoated with AlF ₃	368
Figure IV - 112: Cycling performance of AlF ₃ coated and uncoated (bare) high energy cathode at 55°C.....	368
Figure IV - 113: AC Impedance of cells based on coated and uncoated high energy cathode material.....	369
Figure IV - 114: Rate capability of cells based on coated and uncoated high energy cathode material.....	369
Figure IV - 115: SEM images of high energy electrode made by the carbonate process.....	369
Figure IV - 116: Cross section of high energy cathode particles made by the carbonate process.....	369
Figure IV - 117: SEM images of high energy electrode made by carbonate process.....	369
Figure IV - 118: First charge and discharge cycle and capacity vs cycling of cells based on cathodes made by the hydroxide and the carbonate process.....	370
Figure IV - 119: Rate performance of cells based on cathodes made by hydroxide and carbonate process.....	370
Figure IV - 120: Schematic diagram of the full concentration gradient lithium transition metal oxide particle with the nickel concentration decreasing from the center toward outer layer and the concentration of manganese increasing accordingly.....	373
Figure IV - 121: Scanning electron microscopy images and electron-probe X-ray micro-analyzer mapping of (a) a precursor particle and (b) a lithiated particle; and integrated atomic ratio of transition metals as a function of the distance from the center of the particle for (c) the precursor and (d) the lithiated material.....	373
Figure IV - 122: (a) 3D presentation of nickel distribution in a single lithiated full concentration gradient lithium transition metal oxide particle; (b) 2D distribution of nickel on a plane going through the center of the particle; (c) transmission electron microscopy image of local structural feature near the edge of the particle; and (d) transmission electron microscopy image of local structural feature at the center of the particle.....	374
Figure IV - 123: Charge–discharge characteristics of LiNi _{0.86} Co _{0.10} Mn _{0.04} O ₂ , LiNi _{0.70} Co _{0.10} Mn _{0.20} O ₂ , and full concentration gradient LiNi _{0.75} Co _{0.10} Mn _{0.15} O ₂ . a, Rate capabilities of the full concentration gradient material against the inner composition [LiNi _{0.86} Co _{0.10} Mn _{0.04} O ₂] and outer composition [LiNi _{0.70} Co _{0.10} Mn _{0.20} O ₂] materials (upper cutoff voltage of 4.3 V vs. Li ⁺ /Li); b, initial charge-discharge curves and c, cycling performance of half cells using the full concentration gradient material, inner composition [LiNi _{0.86} Co _{0.10} Mn _{0.04} O ₂] and the outer composition [LiNi _{0.70} Co _{0.10} Mn _{0.20} O ₂] materials cycled between 2.7 V and 4.5 V vs. Li ⁺ /Li; and d, discharge capacity of MCMB/full concentration gradient cathode full cells at room and high temperature. The electrolyte used was 1.2 LiPF ₆ in EC/EMC (3:7 by volume) with 1 wt% vinylene carbonate as electrolyte additive.....	374
Figure IV - 124: a) Contour plots of <i>in situ</i> high energy X-ray diffraction profile. a, delithiated inner composition material [Li _{1-x} Ni _{0.86} Co _{0.10} Mn _{0.04} O ₂] and b), delithiated full concentration gradient material during thermal ramping from room temperature to 375 °C with a scanning rate of 10 °C min ⁻¹ . c), differential scanning calorimetry profiles of the delithiated full concentration gradient material, the delithiated inner composition [Li _{1-x} Ni _{0.86} Co _{0.10} Mn _{0.04} O ₂], and the delithiated outer composition [Li _{1-x} Ni _{0.70} Co _{0.10} Mn _{0.20} O ₂] with a scanning rate of 1 °C min ⁻¹ . The cells were constant-voltage charged to 4.3 V vs. Li ⁺ /Li before disassembling.....	375
Figure IV - 125: X-ray powder diffraction patterns of Na _a Li _b Ni _{0.25} Mn _{0.75} O ₆ precursor. The asterisk indicates a superlattice peak, and the additional peaks in the top pattern indicate the formation of LiM ₆ sites within the Na(Li,M)O ₂ structure.....	378
Figure IV - 126: X-ray powder diffraction patterns magnified between 18 and 24 degrees CuKα 2-theta of Na _a Li _b Ni _{0.25} Mn _{0.75} O ₆ precursor.....	378
Figure IV - 127: X-ray powder diffraction patterns measured using a synchrotron source. Bottom pattern is Na _{1.0} Li _{0.2} Ni _{0.25} Mn _{0.75} O _y and the top is synthesized Na _{0.7} Ni _{0.25} Mn _{0.75} O _y to show the clean pattern for non-Li P2 precursor.....	378
Figure IV - 128: XRD pattern of IE product, made by refluxing Na _{1.0} Li _{0.2} Ni _{0.25} Mn _{0.75} O _y in hexanol with 2 fold LiCl for 4 hours, followed by washing with methanol, and vacuum drying.....	379

Figure IV - 129: P2 to O4 transition showing the DIFFAX results which models the XRD patterns. Note the middle area is the transition whereby stacking faults are present, and the likelihood of mixed O2, O4 and O6 is possible.....	379
Figure IV - 130: This is a schematic model showing the layer gliding process of P2 to O2, O4 or O6 stacking. O stacking occurs when Li enters the alkali metal layer for Na. Li prefers octahedral coordination instead of prismatic coordination so a shear occurs leaving the stacking faults in the material.	379
Figure IV - 131: Electrochemical performance of a number of IE samples.....	379
Figure IV - 132: Charge-discharge voltage profiles of 550 °C HT-Li _{1.05} Na _{0.02} Ni _{0.21} Mn _{0.63} O ₂ IE cathode materials.....	380
Figure IV - 133: Discharge voltage profiles of various IE cathode materials.....	380
Figure IV - 134: Cycling of IE cathode material over 50 cycles at a C/15 rate.....	380
Figure IV - 135: XRD pattern of IE material electrode laminate before (top) and after (bottom) 50 cycles.....	380
Figure IV - 136: Voltage profiles of direct synthesized Li _{1.2} Ni _{0.25} Mn _{0.75} O _y (SS-LNMO) and ion-exchange sample Li _{1.26} Na _{0.02} Ni _{0.25} Mn _{0.75} O ₂ (IE-LNMO). Current rate for both is 15 mA g ⁻¹	381
Figure IV - 137: TEM of IE-LNMO showing the spinel regions in the marked circle.....	381
Figure IV - 138: A compositional phase diagram of a 'layered-layered-spinel' system with Li ₂ MnO ₃ •(1-x)LiMO ₂ ('layered-layered') and LiM ₂ O ₄ (spinel) components.....	383
Figure IV - 139: Variation in capacity (mAh/g) and first-cycle efficiency (%) as a function of x in Li _x Mn _{0.65} Ni _{0.35} O _y electrodes.....	383
Figure IV - 140: XRD patterns of various materials derived from the 'layered-layered-spinel' Li _x Mn _{0.65} Ni _{0.35} O _y system.....	384
Figure IV - 141: Effect of activation voltage on the performance of 'layered-layered-spinel' Li _{1.25} Mn _{0.65} Ni _{0.33} Mg _{0.02} O _{2.28} and AlF ₃ -treated electrodes: a) typical voltage profile of an uncoated electrode; b) and c) dQ/dV plots of lithium cells with uncoated and AlF ₃ -coated electrodes, respectively. The cells in a) and c) were subjected to two activation cycles between 4.95 and 2.5 V, before being cycled between 4.6 and 2.5 V, whereas the cell in b) was cycled only between 4.6 and 2.0 V.....	384
Figure IV - 142: a) XRD patterns and b) PDF spectra of xLi ₂ MnO ₃ •(1-x)LiCoO ₂ , for x=0.1, 0.3, 0.7, and 0.9 annealed at 850°C.....	385
Figure IV - 143: Representative examples of screening list.....	387
Figure IV - 144: FTIR spectra of MCMB electrodes obtained from MCMB/NCM coin cells containing different amounts of OHD in electrolyte of 1.2M LiPF ₆ with EC/DEC (3:7 weight ratio) after formation cycles.....	388
Figure IV - 145: SEM images of electrodes harvested after formation cycles. (a) MCMB electrode from Gen 2 electrolyte; (b) MCMB electrode from Gen2 electrolyte with 0.2 w% OHD; (c) MCMB electrode from Gen2 electrolyte with 1.0w% OHD; (d) NCM electrode from Gen2 electrolyte; (d) NCM electrode from Gem 2 electrolyte with 0.2 w% OHD.....	388
Figure IV - 146: Diff. Capacity vs voltage MCMB/NCM coin cells in 3E7EMC/PF12 with none or various amount of TPP (A-47). The cells were cycled at 55 °C. The charge rate was C/10. The cut-off voltages were 3 ~ 4V.....	388
Figure IV - 147: Capacity retention of MCMB/NCM coin cells in 3E7EMC/PF12 with none or various amount of TPP (A-47). The cells were cycled at 55 °C. The charge rate was 1C. The cut-off voltages were 3~4 V.....	388
Figure IV - 148: AC impedance profiles of MCMB/NCM coin cells in 3E7EMC/PF12 with none or various amount of TPP (A-47) before (left) and after (right) 200 cycles under 55 °C at 1C rate. The cells were charged to 3.8 V. The charge rate was 1C.....	389
Figure IV - 149: Cyclic voltammetry profile 10mM TPP in Gen 2 electrolyte using Pt/Li/Li three electrode system. Scan rate is 100 mV/s.....	389
Figure IV - 150: Cyclic voltammetry profile 10mM PDP in Gen 2 electrolyte using Pt/Li/Li three electrode system. Scan rate is 100 mV/s.....	389
Figure IV - 151: Capacity retention of Li/LNMO coin cells in 3E7EMC/PF12 with none or 1 wt % additives. The cells were cycled at room temperature. The charge rate was C/5 (1mA). The cut-off voltages were 3.5 ~ 4.95 V.....	390
Figure IV - 152: Gen2 electrolyte and fluorinated electrolyte leakage currents at various potentials with Pt/Li/Li cell.....	393
Figure IV - 153: Gen2 electrolyte and fluorinated electrolyte leakage currents at various potentials with LNMO/Li cell.....	393
Figure IV - 154: Cyclic voltammetry profiles of LNMO/graphite cells using fluorinated electrolytes.....	394
Figure IV - 155: LNMO/Graphite cell cycling profiles at room temperature (a) and the cycling performance using fluorinated electrolytes (b) Normalized capacity retention of fluorinated electrolyte and Gen2. Cycling rate is C/10, cutoff voltage is 3.5-4.9 V.....	394
Figure IV - 156: LNMO/Graphite cell cycling profiles at 55°C(a) and the cycling performance using fluorinated electrolytes (b) Normalized capacity retention of fluorinated electrolyte and Gen2. Cycling rate is C/10, cutoff voltage is 3.5-4.9 V.....	395
Figure IV - 157: dQ/dV plots of Gen2 electrolyte compared with fluorinated electrolytes.....	395
Figure IV - 158: Capacity as a function of cycle number plots at room temperature LMNO half cells in 1 m LiPF ₆ /EC:EMC (30:70) with HFIP. Baseline electrolyte was also used as benchmark.....	398

Figure IV - 159: Capacity as a function of cycle number plots at room temperature LMNO/A12 full Li ion cells in 1 m LiPF ₆ /EC:EMC (30:70) with 5 mM HFIP. Baseline electrolyte was also used as benchmark.	398
Figure IV - 160: Sub-structures of HFIP (a), and HR-XPS of cycled anode (b) and cathode (c) surfaces in baseline and HFIP-based electrolytes.	398
Figure IV - 161: DSC traces of Al(HFIP) (a); FTIR (b) and MS (c) of B(PFB) ₃	400
Figure IV - 162: Preliminary cycling results of electrolytes based on new additives in ANL LMNO/A12 full Li ion cells.	401
Figure IV - 163: Optimized geometry of HFIB/BF ₄ complex before (a) and after (b) oxidation. From M05-2X/6-31+G** calculations with PCM($\epsilon=23$).	401
Figure IV - 164: Cycle life performance of LiFePO ₄ -based A123 cells containing various electrolytes at +23°C.	406
Figure IV - 165: Cycle life performance of LiFePO ₄ -based A123 cells containing various electrolytes subjected to variable temperature cycling between +50°C and -20°C.	406
Figure IV - 166: Discharge rate capability of 12 Ah MCMB-LiNiCoAlO ₂ cells (Quallion, LCC) containing various electrolytes at +20°C and -50°C (See first figure, A).	407
Figure IV - 167: Discharge rate capability of 12 Ah MCMB-LiNiCoAlO ₂ cells (Quallion, LCC) containing various electrolytes at +20°C and -50°C (See first figure, A).	407
Figure IV - 168: Discharge performance of 0.25Ah MCMB-LiNiCoAlO ₂ cells (Quallion, LCC) containing various electrolytes -50°C using a C-rate discharge.	408
Figure IV - 169: Discharge performance of a 0.25Ah MCMB-LiNiCoAlO ₂ cell containing a methyl propionate-based electrolyte with LiBOB at -40°C.	409
Figure IV - 170: Discharge performance of a 0.25Ah MCMB-LiNiCoAlO ₂ cell containing a methyl propionate-based electrolyte with LiBOB at -20°C.	409
Figure IV - 171: Cycle life performance of 0.25Ah MCMB-LiNiCoAlO ₂ cells (Quallion, LCC) containing various electrolytes at 20°C, using C rate charge and discharge over a voltage range of 2.50V to 4.10V.	410
Figure IV - 172: Cycle life performance of Cononco A12 graphite/Toda HE 5050 LiNiCoMnO ₂ cells containing containing various electrolytes (Fig. 2B).	411
Figure IV - 173: Tafel polarization measurements at 0°C of three electrode cells consisting of Cononco A12 graphite/Toda HE 5050 LiNiCoMnO ₂ or LiNiCoAlO ₂ and containing various MB-based electrolytes.	411
Figure IV - 174: General heterocyclic phosphazene structure.	414
Figure IV - 175: Coin cell capacity data for the first generation INL alternative anode formulations based on phosphazene polymer host.	415
Figure IV - 176: The effect of INL FM-series phosphazene additives on the electrochemical window of the baseline electrolyte.	415
Figure IV - 177: Early life capacity performance of coin cells having SM4, SM6, FM2, and PhIL-1 at 1 and/or 3 wt% in the baseline.	416
Figure IV - 178: Early life capacity performance of coin cells having SM4, SM6, FM2, and PhIL-1 at 1 and/or 3 wt% in the baseline (cont'd).	416
Figure IV - 179: Early results from SNL abuse testing of the INL electrolyte systems.	417
Figure IV - 180: Early results from SNL abuse testing of the INL electrolyte systems (cont'd).	417
Figure IV - 181: EIS model simulation of LMR-NMC positive electrode impedance data (100 kHz-10 mHz) taken at a cell voltage of 3.75 volts and 30°C.	419
Figure IV - 182: Mass specific particle contact resistance determined by electrochemical model for NCA, NMC333 and LMR-NMC electrodes compared to the dry powder's particle conductivity.	420
Figure IV - 183: (top) Experimental EIS measurements on Toda HE5050 LMR-NMC material before and after aging taken at an electrode voltage of 3.75 V and 30 °C (100 kHz-10 mHz). (middle) model parameter sensitivity analysis showing sensitivity to contact resistance and SEI film conductivity (bottom) model parameter sensitivity analysis for mid-frequency arc.	420
Figure IV - 184: OCV curves from GITT measurements to examine hysteresis in LMR-NMC cathode materials. An approximately 1 V hysteresis in site energy is observed between lithium removed at 4.3 V and that re-entered at 3.3 V.	421
Figure IV - 185: Initial simulation of hysteresis in LMR-NMC OCV curves.	421
Figure IV - 186: Breakdown of the more than 450 independent downloads of BatPaC during FY2012.	423
Figure IV - 187: New module (top) and pack (bottom) design for batteries utilizing air thermal management in BatPaC.	424
Figure IV - 188: Effects of electric-vehicle range on price and error bars for battery pack with NMC441-Gr cell chemistry, 120-kW 360 V.	424
Figure IV - 189: a) Cost breakdown for a PHEV40, b) overhead distributed to processes, and c) summarized in basic cost factors.	425
Figure IV - 190: Capacity-voltage plot, at a ~C/35 rate and 30°C, from a Li _{1.2} Ni _{0.15} Mn _{0.55} Co _{0.1} O ₂ /Li cell.	427

Figure IV - 191: AC impedance data from (a) the full cell, and from the (b), (c) positive and negative electrodes showing changes that result from cell cycling. The data were obtained at 30 °C, at a full cell voltage of 3.75V, in the 100kHz to 0.01 Hz frequency range.	428
Figure IV - 192: dQ/dV plots from SFG-6 graphite- and SuperP- based electrodes. Inset is an expanded view along the Y-axis.	428
Figure IV - 193: X-ray diffraction patterns from fresh (as-prepared) and positive electrodes harvested from full cells after characterization cycles, 300 cycles, and 1500 cycles.	429
Figure IV - 194: XAS data at the Ni K-edge and Mn K-edge for a fresh positive electrode and for electrodes harvested from cells after initial cycles and after 1500 cycles. The 1500_L data is from a "relithiated" 1500_cycle electrode.	429
Figure IV - 195: SEM images of the fresh and aged (1500 cycles) negative electrodes.	430
Figure IV - 196: SIMS sputter depth profiles from negative electrodes after (a) characterization cycles, and (b) 1500 cycles. Data for carbon, manganese, nickel, cobalt and lithium are shown. The Y-axis scales are the same for (a) and (b), but the X-axis scales are different.	430
Figure IV - 197: EIS data from a $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ //Graphite cells containing the LiDFOB electrolyte additive.	431
Figure IV - 198: Impedance spectra of a symmetric graphite-graphite cell obtained every ten cycles between 1 and 450 cycles.	434
Figure IV - 199: TGA analysis (a) and Raman spectra (b) of pyrolyzed polyimide sample with and without heat treatments. (Arrows in the TGA curve mark with corresponding colors the points where Raman spectra were obtained).	435
Figure IV - 200: Specific charge of potentiostatic step investigation of pristine and heat-treated Super-P samples.	435
Figure IV - 201: Charge/Discharge capacity vs. cycle number of coin cells utilizing Toda He5050 and pristine (red) or heat treated (blue) carbon black.	436
Figure IV - 202: Modeling Aging Cells as batch reactors.	438
Figure IV - 203: C1/1 Capacity Loss, Sanyo Y.	439
Figure IV - 204: Extent of Reaction versus Relative Rate Constant for various Particle Stability Parameters.	439
Figure IV - 205: Annual Temperature Profiles for Chosen Cities.	440
Figure IV - 206: Results for Cellstage Simulations.	440
Figure IV - 207: Results for Cellstage Simulations (cont'd).	440
Figure IV - 208: Reductions in Capacity Loss with more aggressive thermal management.	440
Figure IV - 209: Reductions in Capacity Loss with more aggressive thermal management (cont'd).	441
Figure IV - 210: (a) Time-resolved (TR) XRD patterns, and, (b) results from simultaneously measured mass spectroscopy (MS) that trace oxygen gas released from the overcharged $\text{Li}_{0.33}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ during heating up to 500 °C. The cathode sample in a glass tube was heated from 25- to 500-°C for 4 h during the TR-XRD and MS measurements (heating rate = 2.0 °C min ⁻¹). Left panel shows the ideal crystal-structure models for rhombohedral-, spinel-, and rock-salt-structures.	443
Figure IV - 211: TR-XRD of $\text{Li}_{0.1}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (G3) with released oxygen MS during heating.	444
Figure IV - 212: TR-XRD of $\text{Li}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (G2) with released oxygen MS during heating.	445
Figure IV - 213: Crystal structure changes of fully charged cathode material $\text{Li}_{1.2}\text{Ni}_{0.17}\text{Co}_{0.07}\text{Mn}_{0.56}\text{O}_2$ with (B) and without (A) Al_2O_3 ALD coating studied by TR-XRD during heating from 25 °C to 600 °C.	445
Figure IV - 214: Crystal structure changes of Li-rich cathode material $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ during first one and half charge-discharge cycle.	446
Figure IV - 215: Crystal structure changes of Li-rich cathode material $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ during 46th charge-discharge cycle.	446
Figure IV - 216: Picture of <i>in situ</i> XRD set up at APS.	450
Figure IV - 217: Image of the sample holder used for <i>in situ</i> high energy X-ray diffraction, and an exemplary high energy X-ray diffraction pattern that was fully indexed with sample holder and layer lithium transition metal oxide.	450
Figure IV - 218: Contour plot of <i>in situ</i> HEXRD data during thermal decomposition of lithiated graphite.	451
Figure IV - 219: Contour plot of <i>in situ</i> HEXRD data during thermal decomposition of delithiated NMC with the presence of (a) 1.2 M LiPF_6 in EC/EMC (3:7, by weight), (b) EC/EMC (3:7, by weight), and (c) 1.0 M LiTFSI in EC/EMC (3:7, by weight).	451
Figure IV - 220: (a) Comparison of HEXDRD patterns of abused delithiated HE5050 (charged to 4.6 V vs. Li^+/Li) showing that the decomposition pathway strongly depended on the chemical environmental it was exposed to, (b) <i>in situ</i> HEXRD pattern of delithiated HE5050 with the presence of electrolyte, and (c) proposed decomposition pathway for delithiated HE5050 with the presence of electrolyte.	452
Figure IV - 221: Contour plot of <i>in situ</i> HEXRD data during thermal decomposition of delithiated HE5050 charged to (a) 4.4 V, (b) 4.5 V, (c) 4.6 V, and (d) 4.8 V with the presence of 1.2 M LiPF_6 in EC/EMC (3:7, by weight).	452

Figure IV - 222: (a) Schematic energy diagram illustrating the potential heat generation at the anode side. <i>In situ</i> HEXRD profiles of a $\text{Li}_4\text{Ti}_5\text{O}_4/\text{LiMn}_2\text{O}_4$ cell during overcharge test showing the lattice variation of (b) Al and (c) Cu. The electrolyte was 0.4 M $\text{Li}_2\text{B}_{12}\text{F}_9\text{H}_3$ in EC/EMC (3:7, by weight). The current was 0.2 A (~1C).....	453
Figure IV - 223: Round robin NMC 523 cathode performance during formation cycling.....	456
Figure IV - 224: Cell response to sharp nail penetration of 300 mAh prismatic pouch cell.....	456
Figure IV - 225: ARC performance of INL synthesized phosphazene electrolytes.....	457
Figure IV - 226: Full cell performance comparison for 18650 cells using phosphazene electrolytes.....	457
Figure IV - 227: Overcharge abuse behavior of control cells (18650, nom. 1 Ah) as well as cells containing 0.2 M RS2 overcharge shuttle additive.....	457
Figure IV - 228: Imbalance charging of a 2-cell series string at 200 mA. Cell 1 was initially at 100% SOC while Cell 2 was initially at 90% SOC.....	458
Figure IV - 229: Differential scanning calorimetry results for a variety of cathode materials with 1M ABA: 1M LiF electrolyte in EC:EMC solvent. For comparison, the DSC result for the same electrode material using 1.2 M LiPF_6 is also shown (dark blue).....	458
Figure IV - 230: Discharge curve comparison of full cells tested using standard LiPF_6 electrolyte and a blended ionic liquid / carbonate electrolyte.....	459
Figure IV - 231: SEM images of the membrane substrates: (a) Celgard 2500, b) GF/D-type, (c) GF/A-type, and (d) GF/C-type glass-fiber membranes.....	461
Figure IV - 232: (a) Voltage profile of the P3BT-GF/C composite at the indicated current densities and (b) comparison of the sustainable current densities achieved by the P3BT composites on various substrates.....	461
Figure IV - 233: (a) Voltage profile and b) cycling capacities of the polymer-protected cell with a LiFePO_4 cathode.....	462
Figure IV - 234: (a) Voltage profile and b) cycling capacities of the polymer-protected cell with a spinel $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ cathode.....	462
Figure IV - 235: (a) Voltage profile and b) cycling capacities of the polymer-protected cell with a $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ (Gen3) cathode.....	462
Figure IV - 236: SEM image a) and EDS maps of oxygen b) and sulfur c) of a P3BT and PEO composite prepared by electrospinning.....	463
Figure IV - 237: a) SEM and digital (inset) images of the PFO and PEO composite separator and b) cycling voltage profiles of a protected $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ half-cell.....	463
Figure IV - 238: Particle size distribution without growth control technology.....	466
Figure IV - 239: Particle size distribution with growth control technology.....	466
Figure IV - 240: Fractured cathode particles from calendaring from lot#2012-02-22.....	466
Figure IV - 241: Coin cell results from lot#2012-07-09&11.....	467
Figure IV - 242: 1kg lot #2012-07-09&11 delivered to Material Screening.....	467
Figure IV - 243: Fractured cathode particles from calendaring from lot#2012-07-09&11.....	467
Figure IV - 244: Tap density optimization.....	467
Figure IV - 245: Coin cell results after tap density optimization.....	467
Figure IV - 246: Synthesized MnCO_3 precursors.....	468
Figure IV - 247: MERF Cathode Analytical Lab.....	468
Figure IV - 248: MERF High bay, soon home to the Cathode Materials Scale-up Lab.....	468
Figure IV - 249: Electrolyte Materials Process R&D Flowchart.....	470
Figure IV - 250: Electrolyte Materials Process R&D Laboratory.....	470
Figure IV - 251: Electrolyte Materials Scale-up Laboratory.....	471
Figure IV - 252: A pouch cell being taken apart in the PTF.....	473
Figure IV - 253: SEM micrograph of a section of a pristine anode.....	473
Figure IV - 254: SEM micrograph of a section of a cycled anode.....	473
Figure IV - 255: SEM micrograph of Celgard separator before cycling.....	473
Figure IV - 256: SEM micrograph of the cathode side of the separator.....	474
Figure IV - 257: SEM micrograph of the anode side of the separator.....	474
Figure IV - 258: XPS results from the anodes of ABR cells. With increased sputtering time, the F(1s) and O(1s) peaks decrease in intensity, indicating that these peaks are from surface layers, such as an SEI.....	474
Figure IV - 259: Cycle performance of HE5050 full cell.....	476
Figure IV - 260: Formation of LNMO half cell.....	477
Figure IV - 261: Cycle performance of graphite/LNMO cell.....	477
Figure IV - 262: Cycle performance of graphite/HE5050 cell with and without additives.....	477
Figure IV - 263: EIS of Silicon half cell with and without additives.....	478
Figure IV - 264: Cycle performance of Silicon half cell with and without additives.....	478

Figure IV - 265: High energy/shear planetary mixer from Ross with a 2 liter chamber capacity.	480
Figure IV - 266: SEM photos of electrodes based on Toda HE5050 high energy cathode materials made with 1) Thinky mixer, and 2) Ross mixer.	481
Figure IV - 267: SEM photos of electrode based on MERF-1B high energy cathode material. Note particle cracking from calendaring process.	481
Figure IV - 268: Rate performance of MERF-1B high energy cathode material.	482
Figure IV - 269: Cycling data of cell from first 18650 cell build in Cell Fabrication Facility, ConocoPhillips A12 Graphite vs. Toda NCM523 cathode.	482
Figure IV - 270: Summary of the cycling data of prominent cell builds conducted in the CFF since February 2011.	482
Figure IV - 271: HPPC impedance summary of cell builds based on Toda HE5050 high energy cathode materials vs. ConocoPhillips A12 graphite.	483
Figure IV - 272: Voltage profile change of ConocoPhillips A12 Graphite vs. Toda HE5050 (4 th Cell Build).	484
Figure V - 1: BATT Overview.	489
Figure V - 2: BATT Focus Areas.	490
Figure V - 3: ⁶ Li MAS NMR spectra of "LiNi _{0.5} Mn _{1.5} O ₄ " samples as a function of calcination temperature.	493
Figure V - 4: ²⁷ Al NMR of (a) 1% Al/F-coated Li[L ₁ /9Ni ₁ /3Mn ₅ /9]O ₂ after heating at 120°C and (b) 400°C (in N ₂), (c) 5% reference AlF ₃ -coated Li[L ₁ /9Ni ₁ /3Mn ₅ /9]O ₂ after heating at 400°C in N ₂ , and (d) 5% Al/F-coated Li[L ₁ /9Ni ₁ /3Mn ₅ /9]O ₂ after heating at 400°C in N ₂	493
Figure V - 5: <i>In situ</i> X-ray fluorescence imaging maps at the Cu+ energy (8981 eV) for Cu K α and Mn K α of an <i>in situ</i> Sr ₂ MnO ₂ Cu _{3.5} S ₃ Li cell at different stages of discharge, (from up to down): Li0, Li1.4-1.6 and Li4.0 (fully discharged) maps. The Li contents, denoted by x in Li _x , indicate the amount of Li inserted in the Sr ₂ MnO ₂ Cu _{3.5-x} Li _x S ₃ structure. The maps were collected at a same region on the electrode film of an area (120/ 130 μ m x 140 μ m) at 5 μ m/step with dwell time of 2s/pixel.1	494
Figure V - 6: Average computed voltage for redox couples in phosphates	494
Figure V - 7: The voltage profile of Li ₃ FePO ₄ CO ₃ at C/5 at room temperature. (b) The voltage profile of non-ball-milled Li ₃ FePO ₄ CO ₃ at 60 \square and C/10. (c) The capacity retention of condition (a). (d) The voltage profile of Li _{2.67} Na _{0.63} Mn _{0.96} PO ₄ CO ₃ , both ball-milled and non-ball-milled samples, cycled at C/100 rate.	495
Figure V - 8: Charge mapping by XRD.	497
Figure V - 9: Top: A123 Nanophosphate cathode cross section (inset 30,000X).	497
Figure V - 10: Cell voltage during fast discharge.	497
Figure V - 11: FTIR spectra of electrode samples and reference mixtures.	497
Figure V - 12: Measured SOC vs. distance from the tab.	497
Figure V - 13: LIBS technique.	498
Figure V - 14: Li/Fe ratio vs. laser pulse number.	498
Figure V - 15: Comparison of XRD and LIBS results.	498
Figure V - 16: LiOH•H ₂ O cluster in PC, a) before, b) after polarization at 5.0 V.	498
Figure V - 17: Scanning electron micrograph of a broken composite LiFePO ₄ @LiNi _{0.5} Mn _{1.5} O ₄ particle prepared by spray pyrolysis and infiltration.	501
Figure V - 18: EDS mapping of a core-shell particle similar to the one pictured in Figure V - 17, showing distribution of P, Fe, Mn, and Ni.	501
Figure V - 19: Scanning electron images of cross-sectioned particles showing that many core-shell particles contain large void spaces.	501
Figure V - 20: Discharge capacity as a function of cycle number for baseline and Ti-substituted NMC-333 (top) and NMC-442 (bottom) compounds in lithium half-cells, cycled between 4.7 and 2.0V. Legend indicates the amount of Ti-substitution (x in Li[Ni _{1/3} Mn _{1/3} Co _{1/3-x} Ti _x]O ₂ or Li[Ni _{0.4} Mn _{0.4} Co _{0.2-x} Ti _x]O ₂) and the synthesis method (GNC=glycine-nitrate combustion, nanoTi=combustion synthesis using a nano TiO ₂ precursor, and COH=co-precipitation).	502
Figure V - 21: Lattice parameters (top and middle) and unit cell volume changes as a function of state-of-charge for the baseline NMC-333 (unsubstituted, labeled Ti-00) and an NMC-333 containing 3% Ti (labeled, Ti-03).	502
Figure V - 22: Li/C-SiOx that is fully discharged at 5mV and 50mV cut-off voltages in EC-DEC-1M LiPF ₆	505
Figure V - 23: Li/EC-DEC-1M LiPF ₆ /C-SiOx:Gr cells cycled at C/6 at 50 mV cut-off voltages with floating.	505
Figure V - 24: SEM photo for SiOx:Gr anode after discharged to 5 mV.	506
Figure V - 25: First few cycles of LiMn _{1.5} Ni _{0.5} O ₄ /Graphite in EC-DEC-LiPF ₆ with VC and without VC.	506
Figure V - 26: Cycling of HQ-LiMn _{1.45} Cr _{0.1} Ni _{0.45} O ₄ compared to commercial materials vs. Li in EC-DEC-LiPF ₆	506
Figure V - 27: Cycling and rate capability of LiMn _{1.45} Cr _{0.1} Ni _{0.45} O ₄ /Li in EC-DEC-LiPF ₆	506

Figure V - 28: XPS of the O 1s region of (a) pristine LNMO, (b) LNMO after 5 cycles, and (c) LNMO after 10 cycles. Increasing incident energy corresponds to increasing penetration depth	509
Figure V - 29: (a) <i>In situ</i> XPS data of Li 1s, O 1s, V 2p collected during discharge in UHV, (b) schematic representation of the solid-state cell cycling in UHV: lithium intercalation/deintercalation into the vanadium oxide, (c) <i>in situ</i> APXPS data of Li 1s, O 1s and V 2p collected during discharge in $p(O_2) = 500$ mtorr, (d) schematic representation of the solid-state cell cycling in $p(O_2) = 500$ mtorr: formation/oxidation of lithium peroxide on the vanadium oxide.	510
Figure V - 30: Oxidative activity of Pt/C+, Ru/C+, Au/C+, and VC+Li ₂ O ₂ cells. Pt/C+ and Ru/C+Li ₂ O ₂ are more than two orders of magnitude more active than VC+ and Au/C+Li ₂ O ₂	510
Figure V - 31: Quick XAS spectra at Ni, Co, and Mn K-edges of the Li-rich layered Li _{1.2} Ni _{0.15} Co _{0.1} Mn _{0.55} O ₂ cathode material during constant voltage charge at 5V.	513
Figure V - 32: <i>In situ</i> XRD patterns of the NiO-Li ₂ CO ₃ composite powder electrode during electrochemical decomposition.	513
Figure V - 33: (a) charge-discharge profile of the disordered LiNi _{0.5} Mn _{1.5} O ₄ cathode material during <i>in situ</i> XAS, and corresponding <i>in situ</i> XAS spectra at Mn K-edge (b) and (d) and Ni K-edge (c) and (e) during the 1st charge.	514
Figure V - 34: (a) 1 st discharge profile of the ordered LiNi _{0.5} Mn _{1.5} O ₄ cathode during <i>in situ</i> XAS, and corresponding <i>in situ</i> (b) Mn and (c) Ni K-edges XANES spectra.	514
Figure V - 35: SEM images (a1 to e1) and electron diffraction patterns in the [100] (a2 to e2) and [110] (a3 to e3) zones of LiNi _{0.5} Mn _{1.5} O ₄ prepared with different cooling rates. (a) Quenched; (b) 5°C/min; (c) 3°C/min; (d) 1°C/min; (e) 0.5°C/min.	517
Figure V - 36: <i>In situ</i> XRD patterns of spinels at different SOC's and corresponding lattice parameter changes during Li ⁺ extraction process for LiNi _{0.5} Mn _{1.5} O ₄ prepared with cooling rates of (a, b) 0.5°C/min and (c, d) 5°C/min.	517
Figure V - 37: (a) Initial charge-discharge profiles at 0.1 C for LiNi _{0.5} Mn _{1.5} O ₄ prepared with different cooling rates. (b) Discharge capacity vs. cycle number at various C rates; (c) cycling performance; (d) rate capabilities for different LiNi _{0.5} Mn _{1.5} O ₄ at various C rates (1C =140 mA/g).	518
Figure V - 38: a) XRD patterns and b) cycling of Li ₂ MnO ₃ prepared at different temperatures; c) long-term cycling stability and d) voltage profiles of 700°C-prepared Li ₂ MnO ₃ at different cycles. The cells were cycled between 2.0 and 4.8 V at C/20 rate. (1C = 250 mA/g).	518
Figure V - 39: a) TGA and b) DSC profiles of the LiNi _x Mn _{2-x} O ₄ crystals.	521
Figure V - 40: a) Integrated capacity and voltage profiles obtained at C/22 and b) rate capability comparison of LiNi _x Mn _{2-x} O ₄ crystals.	521
Figure V - 41: a) Chemical diffusivity comparison between the plate and octahedral shaped LiMn _{1.5} Ni _{0.5} O ₄ crystals, and incremental capacities and chemical diffusion coefficients in b) Plates and c) Octahedrons.	522
Figure V - 42: a) SEM images of Li _{1.2} Ni _{0.13} Mn _{0.54} Co _{0.13} O ₂ single crystals synthesized from nitrate precursors in a) CsCl flux and b) KCl flux and oxide precursors in c) CsCl flux and d) NaCl flux.	523
Figure V - 43: Top: First-cycle charge and discharge voltage profiles and Bottom: rate capability comparison of the Li _{1.2} Ni _{0.13} Mn _{0.54} Co _{0.13} O ₂ crystals.	523
Figure V - 44: (A) Cycling performance of Li-S batteries with and without P ₂ S ₅ ; (B) Photos showing the promoted solubility of Li ₂ S in liquid electrolyte by P ₂ S ₅ ; (C) A micrograph of the passivation layer on lithium anode surface.	526
Figure V - 45: (A) A cyclic voltammogram of Li on nanoporous β-Li ₃ PS ₄ with a gold counter electrode. (B) Durability test of the solid electrolyte pellet in a symmetric cell configuration with both electrodes of metallic lithium. The thickness of solid electrolyte pellet is 500 μm.	526
Figure V - 46: (A) Ionic conductivity of sulfur-rich compounds as a function of sulfur numbers. (B) Arrhenius plot of Li ₃ PS ₄₊₅	527
Figure V - 47: (A) Cycling performance of Li ₃ PS ₄₊₅ at room temperature and 60°C. (B) Rate performance at 60°C.	527
Figure V - 48: Raman spectra of Li ₃ PS ₄₊₅ (A) before cycling (black), (B) after discharge (red), and (C) after charge (blue). The signs of “◇, ▽, and ☆” indicate the peaks of the S-S bond in Li ₃ PS ₄₊₅ , the P-S bond in Li ₃ PS ₄ , and Li ₂ S, respectively.	527
Figure V - 49: (a) A secondary Li-rich NMC composite cathode particle of spherical morphology (b) Faced structures of primary Li-rich NMC particles having sizes in the range of 80-100 nm (c) Focused ion beam section of a secondary particle showing hollow interior core (d) A single Li-rich high voltage NMC primary particle with faceted surface.	530
Figure V - 50: Capacity vs. Cycle number for (a) 1h-LiPON coated Li-rich NMC, (b) uncoated Li-rich NMC, (c) 3h LiPON coated Li-rich NMC, and (d) LiPON coated on the electrode surface.	530
Figure V - 51: Comparison of rate performance between conventional and LiPON coated high voltage Li-rich NMC composite cathode.	530
Figure V - 52: Voltage fade observed in Li-rich NMC composite cathodes as result of continuous high V cycling. The cells were cycled at room temperature between 4.9-2.5 volts using LiPF ₆ in EC: DMC mixture.	531

Figure V - 53: HRTEM images of pristine Li-rich NMC composite cathodes showing the majority of particles belonging to a hexagonal R3m structure.	531
Figure V - 54: HRTEM and EELS study of cycled Li-rich NMC composite cathodes	531
Figure V - 55: (a) Cycling of $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_0.5\text{Mn}_0.5\text{O}_2$ synthesized with a Li_2MnO_3 template and annealed at 450°C ; (b) <i>In situ</i> XRD of a Li_2MnO_3 -based composite showing the incorporation of a NiO component on heating.	534
Figure V - 56: (a) Rate data of a Li_2MnO_3 -based $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_0.5\text{Ni}_0.5\text{O}_2$ cathode; (b) Ni K-edge EXAFS of fresh and cycled cathodes revealing the stability of the local nickel environment.	534
Figure V - 57: (a) HRTEM images of ZrO_2 -coated LMR-NMC. Rate data of Li cells with (b) uncoated and (c) coated electrodes.	535
Figure V - 58: (a) Rate data of Al_2O_3 -coated $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_0.5\text{Ni}_0.5\text{O}_2$; (b) Voltage profiles of the sample in (a) showing $\sim 230\text{ mAh/g}$ above $\sim 3.0\text{ V}$ after 12 cycles to 4.6 V	535
Figure V - 59: (a) Capillary reactor for investigating hydrothermal synthesis reactions by <i>in situ</i> x-ray diffraction. (b) <i>Time-resolved</i> XRD patterns acquired during the hydrothermal synthesis of $\text{LiFe}_{0.4}\text{Mn}_{0.6}\text{PO}_4$ ($25 - 240^\circ\text{C}$).	538
Figure V - 60: (a) SEM image of as-synthesized CVO nanorods prepared at 200°C for 10 h, (b) corresponding synchrotron XRD and profile fit from $\text{Cu}_{0.95}\text{V}_2\text{O}_5$	538
Figure V - 61: (a) SEM image of the as-synthesized CVO prepared via reaction 3 (180°C , 48 hours), (b) XRD patterns acquired during the synthesis of CVO (200°C).	539
Figure V - 62: Resolved X-ray diffraction patterns from hydrothermal synthesis of CVO showing a direct transformation from the precursor (V_2O_5) to CVO (no intermediate phase).	540
Figure V - 63: (a) Charge-discharge profiles for the first cycle, (b) cyclability and (c) STEM-EDS images of the pristine, lithiated and cycled electrodes showing the extruded Cu identified by EDS mapping (red).	540
Figure V - 64: DTA - TGA analysis has provided insights into precursor behavior to aid glass processing development. DTA - TGA analysis of a mixture of iron (III) oxide and ammonium dihydrogen phosphate (red) showed volatile P_2O_5 loss between 500°C and 605°C . (Blue curve is a sum of DTA - TGA analyses for iron (III) oxide and ammonium dihydrogen phosphate to show the expected weight loss assuming no reaction between the precursors.)	542
Figure V - 65: The first baseline glass cathode composition ($\text{Fe}_4(\text{P}_2\text{O}_7)_3$) has been made. This glass was produced by quenching the melt in a graphite mold.	543
Figure V - 66: Morphologies of the (a) MW-HT and (b) MW-ST $\text{Li}_2\text{FeSiO}_4$ samples, and (c) electrochemical performances of the MW-HT, MW-ST, and MW-ST-Graphene samples.	545
Figure V - 67: Surface-to-bulk ratio of iron in $\text{LiCo}_{1-x}\text{Fe}_x\text{PO}_4$ as a function of sputtering time.	546
Figure V - 68: XRD patterns of the $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ and $\text{LiMn}_{1.5}\text{Ni}_{0.42}\text{M}_{0.08}\text{O}_4$ ($\text{M} = \text{Cr, Fe, and Ga}$) samples after post-annealing at 700°C . The rectangular points indicate the superstructure reflections for the ordered $P4_332$ space group.	546
Figure V - 69: dQ/dV plots of the (a) $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel post-annealed at 700°C , (b) $\text{LiMn}_{1.5}\text{Ni}_{0.42}\text{Fe}_{0.08}\text{O}_4$ spinel synthesized at 900°C , and (c) EIS spectra before and after cycling of both the spinels.	547
Figure V - 70: (a) Morphology and crystal planes of undoped $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel cathodes prepared by two different methods and (b) electrochemical performances of the samples fired at 900°C and annealed at 700°C	547
Figure V - 71: Representative SEM image of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles.	549
Figure V - 72: (Left) Electrochemical performance-crystal chemistry correlations in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles. (Right) Cycling of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at different rates, within different voltage windows.	549
Figure V - 73: XAS for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at different cycling states, as indicated, at the a) Mn, b) Ni $L_{II, III}$, c) O K edges.	550
Figure V - 74: SEM image of inorganic oxide nanowires generated by hydrothermal synthesis techniques.	553
Figure V - 75: Schematic of the LbL assembly of polyelectrolyte layers consisting of Si and Super-P dispersions.	554
Figure V - 76: Cycling of Si/VACNTs by CVD/PLD approach.	554
Figure V - 77: Charge-discharge plot of Si/ICA/VACNTs cycled at 300 mA/g between $0.02-1.2\text{ V}$ vs. Li/Li.	554
Figure V - 78: Variation of specific capacity vs. cycle number of SiNT cycled at different current densities.	554
Figure V - 79: Specific capacity vs. cycle number of the a-Si film cycled at 0.25C , 0.5C , 1C , 2C and 4C	555
Figure V - 80: Current response (upper panel) and fluorescence intensity (lower panel) vs. time during a CV between 3.5 and 5.0 V at 0.1 mV/s for $1\text{M LiPF}_6\text{ EC}$ (red curve) and $1\text{M LiPF}_6\text{ DEC}$ (black curve).	558
Figure V - 81: Current response (blue) and fluorescence intensity (black) vs. time during a CV of Super-P Li/PVdF (90/10) electrode between 3.5 and 5.0 V vs Li/Li ⁺ at 0.1 mV/s , electrolyte EC:DEC 1:2 1M LiPF_6	558
Figure V - 82: <i>Ex situ</i> near-field IR images at different wavelengths of the SEI layer on a polycrystalline Sn electrode after 5 cycles.	559
Figure V - 83: Schematic diagram of the synthesis process of conductive-rigid-skeleton-supported Si with TEM images for the intermediate product of Si/B ₄ C and the final SBG product. a) Starting materials of micron-sized B ₄ C	

and Si. b) Schematic diagram of the Si/B ₄ C core-shell structure and TEM image. c) Schematic diagram of the SBG structure and TEM image.	561
Figure V - 84: Effect of SBG composition and the synthesis condition on the cycling stability at a current density of 0.63 A/g based on the silicon weight. (a) Comparison of the long-term cycling stability for SBG composites with different compositions; (b) Cycling stability of SBG433 with different high-energy ball milling (HEBM) times; (c) Cycling stability of SBG433 with different PBM times.	561
Figure V - 85: Electrochemical performance of SBG with optimized composition and ball-milling conditions. (a) Long-term cycling stability of SBG433 at a current density of 0.63 A/g. (b) Rate performance for SBG433 prepared by 8 h HEBM and 8 h PBM time.	562
Figure V - 86: (a) Schematic structure and (b) TEM image of the hollow core-shell structured porous Si-C nano-composite.	562
Figure V - 87: Electrochemical performance of the core-shell structured porous Si-C nanocomposite. (a) Long-term cycling stability of the composite. (b) Rate performance of the composite.	562
Figure V - 88: Molecular structure of conductive polymer binder.	565
Figure V - 89: Carbon- 1s XAS spectra collected on a series of polymers.	565
Figure V - 90: (a) Cycling performance of Sn electrode with different PFFOMB binder content. Cycling at 0. 1 C rate in the range of 20 mV-1.5 V with electrolyte 1M LiPF ₆ in EC/FEC 3/7. (b) Adhesion force of electrode laminates.	566
Figure V - 91: SEM images of the new PFFOMB/Sn electrode surface, PFFOMB content varies by weight in the pristine electrodes (a) 2%; (b) 5%; (c) 10%, and cycled electrode at 5% PFFOMB content electrode (d) after 1 cycle; (e) after 10 cycles.	566
Figure V - 92: TEM image of the Sn particles in the electrode. (a) New electrode; (b) After 10 cycles.	566
Figure V - 93: Si/PFFOMB conductive polymer electrode over 3.5 mAh/cm ² area specific capacity. The in-set SEM image is the composite Si/PFFOMB particles (scale bar is 10 μm).	566
Figure V - 94: Cycling stability and coulombic efficiency of the Si/PFFOMB electrode at (a) 2% VC and (b) 10% VC in the electrolyte.	567
Figure V - 95: Evolution of new Si environments as a function of annealing temperature.	569
Figure V - 96: Reduction of Si (IV) is seen at -3.5 V (vs Pt) in a PC supporting electrolyte. The -4.2 V peak (vs Pt) is electrolyte decomposition.	569
Figure V - 97: Post 1 st cycle SEM of two films deposited over a 2-hr period and cycled vs Li in the range of 0.1-2 V in Gen2 electrolyte. Film (A) was made under constant potential (-3.3V), and Film (B) was done under constant current (-50 mA).	570
Figure V - 98: First cycle of silicon film (A) made via constant potential deposition.	570
Figure V - 99: Optical image and schematic of <i>in situ</i> tomography cell.	570
Figure V - 100: 3D reconstruction of Sn on Cu electrode during the 1 st and 3 rd discharge and charge cycles.	571
Figure V - 101: (top) Rate capability of lithium removal from the nano-tin anode, and (bottom) rate capability of lithium insertion into the nano-tin anode relative to the SONY SnCoC anode.	573
Figure V - 102: (top) XRD patterns of (A) Solvothermally formed Fe-Sn; (B) Planetary ball-milled (pBM) Sn-Fe-C composite; (C) High-energy ball-milled (HEBM) Sn-Fe-C composite. There is some Sn metal phase in the solvothermally formed material, but it is removed after high-energy milling with graphite. (bottom) Electrochemical cycling of this Sn-Fe alloy in two different voltage windows. The current was 0.3 mA/cm ² in the 1 st cycle and 0.5 mA/cm ² thereafter.	573
Figure V - 103: (top) SEM of (a) initial Al-Si, and of (b) and (c) porous Si spheres; (d) TEM of the Si spheres; (bottom) Electrochemical cycling of the porous Si spheres material at 0.5 mA/cm ² between 0.01 V ~1.5 V. First cycle current density was 0.3 mA/cm ² . The electrodes were made of Si, carbon black additive and binder in a weight ratio of 70:20:10. Capacities were calculated based on the weight of Si (2 ~ 3 mg/cm ²).	574
Figure V - 104: (a) Cyclic voltammetry curves of exfoliated Ti ₂ C at a constant scan rate of 0.2 mV·s ⁻¹ . The solid arrows refer to main peaks positions during lithiation and delithiation cycles. (b) The galvanostatic charge/discharge curves at a C/10 rate. (c) Specific lithiation (circles in the figure) and delithiation (squares in the figure) capacities (per mass of active material) vs. cycle number at different rates. The inset in Fig. 1c is a zoom of the first 20 cycles.	576
Figure V - 105: (a) Cyclic voltammetry curves for Ti ₃ CN, and (b) Ta ₄ C ₃	577
Figure V - 106: Specific capacities (per mass of active material) vs. cycle #, for Ti ₃ C ₂ with different binders and different carbon additives.	577
Figure V - 107: Specific capacities for delaminated Ti ₃ C ₂ . Inset shows SEM image of <i>additive-free</i> Ti ₃ C ₂ film used as anode.	578
Figure V - 108: Hardness and Elastic Modulus of PAN with increasing annealing temperature.	580
Figure V - 109: Raman spectrum of pristine PAN and cyclized PAN.	580

Figure V - 110: Differential capacity vs voltage curves represent the highly reversible cycling of Si-cyclized PAN electrodes, the inset shows EELS mapping image of the core-shell nanostructure.	581
Figure V - 111: Sustainable cycling performance of Si-cyclized PAN electrodes at the higher cycling rates.	581
Figure V - 112: XPS spectra of NG and LCO electrodes before and after the charge-discharge cycles.	582
Figure V - 113: Time-of-flight secondary ion mass spectrometry (SIMS) analyses of cycled NG and LCO electrodes from b-LCO/b-NG and b-LCO/c-NG full cells.	582
Figure V - 114: TEM images of the Si@HC nanocomposite (A) Void/Si = 1.5:1 (B) Void/Si = 3:1 (C) Void/Si = 6:1 and (D) Capacity comparison of three Void/Si ratios.	584
Figure V - 115: (A) (B) HRTEM images of the SiO _x nanocomposite (C) Discharge-charge profiles obtained after 1st, 2nd, 100th and 350th cycles. (D) Discharge capacity and coulombic efficiency of 350 cycles between 0.01 and 1.5V.	585
Figure V - 116: (A) Charge and discharge capacities of all three porous Si/C materials in 100 cycles between 0.01-1.5V. (B) Rate performances of the PSiC-2 materials.	585
Figure V - 117: Swelling of various binders including PVDF and CMC-SBR in EC:DMC electrolyte. Binders that swell quickly and stabilize their electrolyte uptake tend to cycle better.	585
Figure V - 118: Cycling of Na-CMC and S-Radel binders with commercial Si-nanoparticles showing significant capacity fade and low performance in the case of S-Radel samples.	586
Figure V - 119: Chemical structure of sulfonated poly(ether etherketone) and its cycling performance with commercial Si nanoparticles compared to NaCMC.	586
Figure V - 120: PXRD spectra of unpurified synthesis product compared with that of other compounds.	588
Figure V - 121: Powder XRD patterns for Type I clathrate alloys as formed from a revised (200 g) and old vacuum arc-melting process.	588
Figure V - 122: Computed energies of formation for various Type I clathrate compositions.	589
Figure V - 123: Comparisons of computed lattice constant and energy change as a function of Li insertion in Ba ₆ Li _x Al ₈ Si ₃₈ , Ba ₆ Li _x Al ₁₆ Si ₃₀ , Li _x Si ₄₆ , and Li _x Si ₄ : (a) lattice constant, and (b) energy change/Si atom.	589
Figure V - 124: Computed energy change of Na _x Li _y Si ₄₆ as a function of lattice constant.	589
Figure V - 125: Half-cell voltage profiles for the first few delithiation-lithiation cycles of clathrate anode.	590
Figure V - 126: Electrochemical intercalation of Li ⁺ into thin-film Ba ₈ Al ₈ Si ₃₈ anode composition using FEC-based electrolyte.	590
Figure V - 127: A, Image of SEI on Si nanotubes without oxide after 200 cycles. B, Similar image of SEI on nanotubes with an oxide constraining layer. C, Cycling capacity of Si nanotube battery anode showing superior performance.	592
Figure V - 128: Yolk-shell structure.	592
Figure V - 129: Capacity with cycling of yolk-shell anodes.	593
Figure V - 130: <i>In situ</i> TEM of Si nanoparticle lithiation.	593
Figure V - 131: Diameter during lithiation of a single Si particle.	593
Figure V - 132: Galvanostatic voltage profiles during cycling of PEDOT-coated SiNW anodes.	594
Figure V - 133: Battery (blue) and symmetric cell (red) lifetime, C _D , as a function of electrolyte thickness. Filled symbols: SEO diblock copolymers. Open symbols: SEOS tri-block copolymer. Lines are linear regressions. [details in ref. 1].	596
Figure V - 134: Ionic conductivity, σ , of SES separators soaked in 1M LiPF ₆ in EC/DEC 1:1 v/v as a function of the normalized chain length of the sacrificial homopolymer, α . The dashed line represents the conductivity of Celgard® 2400 soaked in the same electrolyte [details in ref. 2].	597
Figure V - 135: TEM of a symmetric P3HT-PEO copolymer showing a lamellar phase.	597
Figure V - 136: Electronic conductivity of P3HT homopolymer and P3HT-PEO block copolymers as a function of the P3HT volume fraction, ϕ (0.085) and without (r ₀ =1) added made with (r salt; r ₀ is the molar ratio of LiTFSI to ethylene oxide monomers. All samples are ionic insulators without salt.	597
Figure V - 137: Methods of immobilizing electrolyte anions in lithium ion batteries. (a) Polyelectrolyte ionomers for use as separators and binders; (b) surface modified carbons for incorporation into composite electrodes to control lithium ion concentration.	600
Figure V - 138: Preparation of functionalized Carbon surfaces. a) Preparation of carbon nanocables on MWCNT templates. b) functionalization of carbon surfaces with imides (Harmer et al, JCS Chem. Commun., 1997 1803)	601
Figure V - 139: Discharge performance of Li-LiFePO ₄ cells (EC, EMC-LiPF ₆ electrolyte) at RT (a) and EIS Nyquist plot before and after cycling (b).	601
Figure V - 140: SEM images of LiFePO ₄ composite cathode. (a) PSSLi-MWCNT, (b) pristine MWCNT.	601

Figure V - 141: Density profiles of oxygen atoms in TMS or EC (solid black line) and DMC (red line) in TMS:DMC(1:2)/LiPF ₆ (left panel) and in EC:DMC(3:7)/LiPF ₆ (right panel) electrolytes at 2.4 V electrode potential. Zero on x-axis is the position of the electrode surface.	605
Figure V - 142: Scheme 1–Improved synthesis of LiC _{Et} BPh.	608
Figure V - 143: TGA of LiCTB Salts.	608
Figure V - 144: Electrostatic potential map of the C _{Et} BPh anion performed at BLY3P/6-31G*.	608
Figure V - 145: Lithium cyclic triol borate salts.	608
Figure V - 146: Scheme 2–Synthesis of FRION salts.	609
Figure V - 147: New DPC FRIONS	609
Figure V - 148: Single Crystal X-Ray Structure of 2 in Figure 4.	609
Figure V - 149: Comparison between the charge discharge curves for the base electrolyte before and after addition of Case Y salt at the 1 and 2% levels.	610
Figure V - 150: Decomposition of TPYT additive upon reduction	612
Figure V - 151: Structures of the of the anhydride derivatives investigated as SEI additives	612
Figure V - 152: Structure of 3-oxabicyclohexane-2,4-dione	612
Figure V - 153: Illustration of possible substituent sites on p-quaterphenyl.	613
Figure V - 154: Anions synthesized as part of the present study.	614
Figure V - 155: Phase diagrams for (PC) _n -LiPF ₆ and (GBL) _n -LiPF ₆ mixtures and ion coordination in the crystal structure of the (GBL) ₄ :LiPF ₆ solvate (Li-purple, O-red, P-orange, F-green)—x and triangle symbols indicate a T _g for fully amorphous and partially crystalline mixtures, respectively.	615
Figure V - 156: Ion coordination in the crystal structure of the (G1) ₂ :LiDFOB solvate (Li-purple, O-red, B-tan, F-green).	615
Figure V - 157: Isothermal ionic conductivity of (AN) _n -LiX solutions at 60°C.	615
Figure V - 158: Ionic conductivity of (PC) _n -LiX solutions.	616
Figure V - 159: Isothermal ionic conductivity of (GBL) _n -LiX solutions at 60°C.	616
Figure V - 160: Ion coordination in the crystal structure of the (G2) ₂ :LiTDI solvate (Li-purple, O-red, N-blue, F-green).	616
Figure V - 161: Ion coordination in the crystal structure of the (AN) ₂ :LiTDI solvate (Li-purple, O-red, N-blue, F-green).	616
Figure V - 162: Ion coordination in the crystal structure of the (G4) ₁ :LiFSI solvate (Li-purple, O-red, N-blue, S-yellow, F-green) (one of the FSI ⁻ anions is disordered).	616
Figure V - 163: CVs of (EC) _n -LiTFSI electrolytes with n = 6 or 2 (i.e., 6/1 or 2/1) on Al and Pt working electrodes	617
Figure V - 164: LiNi _{0.5} Mn _{1.5} O ₄ before storage in the SOA electrolyte (top) and after storage in SOA electrolyte for 2 weeks at 55 °C.	619
Figure V - 165: Cycling capacity and efficiency of Li/LiNi _{0.5} Mn _{1.5} O ₄ cells with and without DMMP.	619
Figure V - 166: Cycling performance of different electrolytes with graphite/LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂ .	620
Figure V - 167: FT-IR spectra of natural graphite anode cycled with LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂ cathode, fresh and after accelerated aging.	620
Figure V - 168: Initial results for the new lithium ion conducting electrolyte compared with some rival materials.	623
Figure V - 169: Comparison of Li4 Li2 and Li3 solid electrolytes preparations with other state of the art lithium cell electrolytes (carbonate liquid electrolyte, EMImidazolium TFSI ionic liquid gel electrolyte, and germaniumthiophosphate crystal electrolyte.)	624
Figure V - 170: X-ray powder pattern of preparation Li3 immediately after preparation, and after 7 days.	624
Figure V - 171: Time dependence of conductivity at different temperatures for Li3 alone (solid lines) and after mixing with Li2 (by ball milling) at mass fraction 1:1(dashed lines, same colors and symbols)	624
Figure V - 172: Comparison of powder and corresponding monolithic film nanopore distributions	624
Figure V - 173: Composition relations between inorganic covalent glasses and present nanoporous glass compositions.	625
Figure V - 174: Powder Xray pattern, showing the large low angle peak due to the pore-pore correlation function and its real space representation, showing the presence of a share distribution of pore sizes around an 18Å mean size for the mixed metal net, and very large average pore size for the Al ₂ (BPP) ₃ net.	625
Figure V - 175: SEM image of the cross section of garnet membrane deposited on a porous substrate.	627
Figure V - 176: Voltage profiles of a Li-Br ₂ cell.	627
Figure V - 177: Capacity retention of a Li-Br ₂ cell. The cell was charged and discharged for 1 h with a current of 0.3 mA. (30% of the theoretical capacity).	627
Figure V - 178: Cyclic voltamogram of a fresh cell at 0.1 mV/s of a Ni-spinel cathode in two different electrolytes.	630
Figure V - 179: Cyclic voltamogram after 4 cycles at 0.01 mV/s of a Ni-spinel cathode in two different electrolytes.	630
Figure V - 180: Cycling data for cathodes of NCM, carbon, and binder mixed for different durations.	631
Figure V - 181: Rate of side reaction of an electrolyte of 1 M LiPF ₆ in EC:DEC 1:2 with and without VC.	631
Figure V - 182: (a) stress intensity factor (b) channeling criteria	634
Figure V - 183: (a) misorientation distribution (b) relative max. principal stress	634

Figure V - 184: (a) probability, (b) relative max. principal stress	635
Figure V - 185: Voltage profiles from a single-grain particle (blue) and a multi-grain particle (red)	635
Figure V - 186: FE mesh for VMS and DNS	635
Figure V - 187: (a) Cell potential, (b) Li-ion concentration (mol/m ³)	635
Figure V - 188: 1C discharge curves predicted by multi-scale and pseudo 2D model	635
Figure V - 189: Quantity of Mn dissolution as a function of storage time at (a) 25°C and (b) 50°C	636
Figure V - 190: Discharge capacity retention at 25°C (a) and 50°C (b)	636
Figure V - 191: Model-experiment comparisons at various discharge rates. The experimental data (dots) was obtained on a NMC electrode with a thickness 159 μm and porosity of 0.62. The calculated potentials (lines) were obtained using the Bruggeman coefficient of 3.0.	638
Figure V - 192: Experimental capacity of NMC electrode as a function of discharge current density based on the interfacial area of active material.	638
Figure V - 193: Calculated Li ⁺ concentration at the Li-metal counter/reference electrode at different discharge rates. The initial Li ⁺ concentration (C _{Li⁺,0}) is 1 M.	639
Figure V - 194: Experimental capacity of NMC electrode as a function of discharge current density based on the cross-sectional area of the porous electrode.	639
Figure V - 195: Thermodynamic factor (1+dlnf/dlnc) as a function of concentration for LiPF ₆ in EC:DEC (1:1), EC:EMC (1:1) and PC:EC:DMC.	639
Figure V - 196: Calculated porosity of 0.45 V formation	642
Figure V - 197: Instability of SEI formed at 0.1 V	642
Figure V - 198: Adding ferrocenium hexafluorophosphate to an electrode passivated in LiClO ₄ causes the SEI to dissolve.	643
Figure V - 199: Li/Vacancy phase diagram for the ordered high-voltage spinel and voltage profile at RT (see inset).	645
Figure V - 200: The calculated LiMn ₂ O ₄ particle equilibrium cubo-octahedral shape with majority (111) facets (aqua) and minority (100) facets (purple) from the calculated (GGA+U) surface energies.	646
Figure V - 201: The Materials Project front page (www.materialsproject.org).	646
Figure V - 202: Model for porous electrode with aligned linear pores of unit tortuosity where available porosity may be distributed between the pore channels and porous matrix.	649
Figure V - 203: Results from model showing effective tortuosity as a function of the pore channel spacing relative to thickness, for an electrode of fixed total porosity (36%) and in which 40% of the available porosity resides in the channels.	649
Figure V - 204: Maximum C-rate vs. areal capacity of sintered LiCoO ₂ electrodes with oriented mesoscale porosity prepared by two methods, compared to conventional calendared Li-ion electrodes.	650
Figure V - 205: Sintered additive-free LMNO samples were measured using ion-blocking Ag electrodes in order to measure electronic conductivity, and electron-blocking/ion-conducting PEO+Li electrodes to measure ionic conductivity.	650
Figure V - 206: Electronic conductivity measurements of disordered and ordered LMNO at 30°C.	651
Figure V - 207: (a) Bright-field TEM image of the natural graphite anode materials within the electron transparent SiNx membrane region of the electrochemical cell (imaged without liquid electrolyte). (b-c), time-lapse images extracted from <i>in situ</i> TEM video showing SEI growth dynamics. Scale bar is 1 micron.	653
Figure V - 208: RF magnetron sputtered LiMn ₂ O ₄ thin films on SiNx membrane. Inset SAED reveals the spinel structure and the nanocrystalline nature of the thin film electrode material. Scale bar is 100 nm.	653
Figure V - 209: Fourier-log deconvoluted EEL spectra of LiMn ₂ O ₄ thin film electrodes deposited on MEMS based <i>in situ</i> microchip platform: (a) dry and (b) with DMC present within the cell.	654
Figure V - 210: (a) Mn and (b) Co K-edge XANES of fresh (black) and cycled (red) 0.5Li ₂ MnO ₃ •0.5LiCoO ₂ treated with Li-Ni-PO ₄ . (c) Magnitude of Fourier transformed Co K-edge data; the arrow indicates tetrahedral Co.	657
Figure V - 211: Magnitude of Fourier transformed Mn (a) and Ni (b) K-edge EXAFS data of composite 0.5Li ₂ MnO ₃ •0.5LiMn _{0.5} Ni _{0.5} O ₂ synthesized via an acid/nickel-treated Li ₂ MnO ₃ precursor followed by annealing at various temperatures. (c) EXAFS determined coordination numbers as a function of temperature. Arrows denote direction of change with T.	657
Figure V - 212: Magnitude of Fourier transformed Mn K-edge EXAFS data of layered LiMn _{0.5} Ni _{0.5} O ₂ (black), an acid/Li-treated (AT) analogue (red), and a Li ₂ MnO ₃ standard (blue).	658
Figure V - 213: Synthesis of LLZ as a function of Al(III) content for a series of samples synthesized using a sol-gel method. The material undergoes a tetragonal to cubic transition around 0.5% Al (III).	661
Figure V - 214: EIS ionic conductivity measurements on Al-substituted tetragonal LLZ (orange) and Al-substituted cubic LLZ (green) are shown. No significant conductivity differences were noted for samples that did not use Au (or Li _x Au) protective coating.	662
Figure V - 215: Cross-sectional SEM micrograph of a cubic- LLZ pellet.	662

Figure V - 216: Modeling energy density requirements for a series of materials at various solid state conductivities and sintered plate thickness.....	662
Figure V - 217: (Left) SEM cross-section image of 200nm thick Li-La-Zr-O films. (Right) Arrhenius plot of the thin films grown on MgO, measured by AC impedance spectroscopy.....	663
Figure V - 218: SEM micrograph of an LLZ sputtered film.....	663
Figure V - 219: SEM of a TiO ₂ /SEO Composite.....	663
Figure V - 220: Cycle life (to 80% of initial capacity) for a series of organosilane coated lithium anodes versus volume of organosilane component.....	664
Figure V - 221: Cycling data on native lithium, chlorotrimethylsilane-coated lithium, and tetraethyl orthosilicate coated lithium anodes.....	664
Figure V - 222: Four probe cole-cole plots for hybrid solid (LATP) and liquid 1M LiPF ₆ /Tetraglyme (I), 1M LiClO ₄ in PC (II) & EC: DEC (III) cells at 323K. All electrodes were lithium.....	664
Figure V - 223: Develop an industrial compatible process to incorporate SLMP into the lithium-ion electrode. a. Optical image of SLMP; b. SEM image of SLMP; c. regular graphite electrode; d graphite with SLMP electrode.....	667
Figure V - 224: SLMP particle characterization by SEM technique.....	668
Figure V - 225: ⁷ Li-NMR spectra of surface-coated SLMP (lower spectrum, the major peak is from the bulk Li at 265.5ppm; the small peak at 1.37ppm indicates Li ₂ CO ₃ species; samples were measured in p-xylene solvent).....	668
Figure V - 226: <i>In situ</i> TEM demonstrate the compression force required to break the SLMP particles and the electric conductivity of the carbonate coating layer. a. Schematic of compression in TEM chamber; b,c. SLMP particle before and after compression; d. load and conduction change during compression; e. Schematic of penetration; f,g. SLMP particle before and after penetration. h. load and conduction change during penetration.....	669
Figure V - 227: Solvent-SLMP reactivity and compatibility test summary.....	669
Figure V - 228: PVDF coated graphite enables SBR/toluene as binder solvent system for graphite and SLMP anode. a. Schematic of PVDF coated graphite particle; b. SEM of graphite; c. 2% PVDF coated graphite; d. electrode made with PVDF coated graphite and SBR/toluene binder system, inset is the schematic of the electrode.....	669
Figure V - 229: Both rate and cycling performance are not compromised at initial testing using SBR/toluene process when the graphite is coated with 2% of PVDF. a. rate performance; b. cycling performance.....	669
Figure V - 230: SEM image of the surface of graphite electrode doped with 2% by weight of SLMP in the laminate. a. As made electrode after drying before compression; b. After compression/calendaring activation, inset is the anode potential after compression.....	669
Figure V - 231: Schematic activation mechanism of SLMP.....	670
Figure V - 232: Cycling stability of the 2% SLMP doped graphite electrode after different duration of storage times. The blue diamond was no storage time.....	670
Figure V - 233: a First cycle voltage profiles and efficiency of MCMB anode with SLMP; b. first cycle voltage profiles and efficiency of MCMB-SLMP/LNMO full cell; c. Initial cycling data of MCMB-SLMP anode; d. Initial cycling data of MCMB-SLMP/LNMO full cell.....	671
Figure V - 234: Impedance spectroscopy of laminated LLZO-PEO ₁₀ :LiTFSI bilayers prepared by two different routes. The modeled response assumes a negligible interfacial resistance.....	674
Figure V - 235: Interfacial resistances between a ceramic plate and two polymer electrolytes: PEO ₁₆ :LiCF ₃ SO ₃ (top) and PEO ₁₀ :LiTFSI (bottom). Values are normalized to the bulk resistance of the two layers. Melting temperatures are 60°C and 35°C, respectively.....	675
Figure V - 236: Simulated conductivity of a composite with 20 vol.% conductive ceramic particles assuming a range of interface conductivities.....	675
Figure V - 237: Fracture edge of composite with 60 vol.% ceramic particles. Arrows indicate polymer rich regions.....	675

List of Tables

Table I - 1: Major Li-ion technology technical challenges and potential pathways to address them.....	3
Table I - 2: Current Production Status for Some Battery Facilities Funded by ARRA Grants.....	6
Table II - 1: Recovery Act Awards for Electric Drive Vehicle Battery and Component Manufacturing Initiative.....	12
Table II - 2: Table of Post-test Lab Facility Milestones.....	66
Table II - 3: Status of equipment purchases.....	67
Table II - 4: Low, Medium, and High Power Battery Channels Purchased with the ARRA Funds.....	73
Table II - 5: Environmental Chambers and Isothermal Baths Acquired with ARRA Funds.....	73
Table II - 6: Equipment for Battery Abuse Test Facility Upgrade.....	77
Table III - 1: Summary of USABC Performance Targets for EV Batteries.....	82
Table III - 2: Summary of USABC Performance Targets for PHEV Batteries.....	83
Table III - 3: Summary of USABC Performance Targets for Power Assist Hybrid Electric Vehicles.....	83
Table III - 4: Energy density comparison between ex-NCM and mo-NCM.....	88
Table III - 5: Decision matrix for cathode material of 180Wh/kg EV cell.....	89
Table III - 6: Specific Power of Modules for Discharge EVPC Test.....	93
Table III - 7: Performance Targets for Deliverables.....	95
Table III - 8: Version Parameters and Base Performance.....	111
Table III - 9: HEV LEESS Gap Analysis as of Q3 2012.....	121
Table III - 10: Cell design for high energy cell.....	135
Table III - 11: Cell design study for high energy cell in consideration of processable loading in plant.....	135
Table III - 12: CEF's for various cathode materials.....	138
Table III - 13: Nail Penetration Test, Pouch Cells.....	159
Table III - 14: First cycle efficiency results for the SLMP-incorporated cells with SLMP produced in the alternative unit.....	161
Table III - 15: Effect of cell loading on 1 st cycle efficiency and cycling performance.....	162
Table III - 16: Theoretical Cost Analysis for NCM Compositions.....	171
Table III - 17: Molecular ion mass-to-charge ratio (m/z) and relative amounts (based on integrated peak area) of ANL-RS2 its oxidation products for formed, 10 overcharge cycles, and overcycled to failure LFP-graphite cells according to GC-MS electrolyte analysis.....	183
Table III - 18: Summary of electrode and cell design parameters employed for initial validation of the coater from the prototyping facility.....	185
Table III - 19: Comparison of Element Values to Cathode Price.....	218
Table III - 20: Comparison of Recycling Processes.....	219
Table III - 21: Sanyo SA cell test matrix for memory study.....	231
Table III - 22: Sanyo SA cell test matrix for memory study.....	232
Table III - 23: Sanyo SA cell performance for HCSD study.....	233
Table III - 24: Cell level simulation time for various simplifications compared to the full P2D model.....	269
Table III - 25: Automotive Li-ion cell formats used for validation of electrochemical thermal models.....	274
Table III - 26: NREL-developed cell domain model options.....	281
Table IV - 1: Chemistry and Formulation of Positive Electrodes Tested for Voltage Fade.....	299
Table IV - 2: Cell parameters after GSAS refinement.....	326
Table IV - 3: ICP result of cathode materials with different particle sizes.....	326
Table IV - 4: ABR Electrode Materials Received for Coating with ALD Alumina.....	337
Table IV - 5: Composition of Alumina on different batches of Mn-rich cathode material coated with Al ₂ O ₃ using ALD.....	340
Table IV - 6: Properties of ABR baseline electrode coatings.....	344
Table IV - 7: Parameters from H-B model for the NCM523 suspensions.....	346
Table IV - 8: Experimental and theoretical effective magnetic moment and magnetic saturation values for pristine, before (BH), and after (AH60, AH70, and AH90) high-voltage hold at 4.5 V. The oxidation states of TM ions which are in agreement with experimental and theoretical effective magnetic moments are also shown.....	354
Table IV - 9: Theoretical Oxidation and Reduction Potential of Some Fluorinated Carbonate Solvents.....	392
Table IV - 10: Additives and Physical Properties.....	399
Table IV - 11: Oxidation ΔG^{ox} and reduction ΔG^{red} potential vs. Li ⁺ /Li calculated with PCM($\epsilon=23$).....	401
Table IV - 12: Discharge capacity (Ah) as a function of temperature and discharge rate.....	412

Table IV - 13: Electrode composition and cell chemistry.	427
Table IV - 14: Decomposition products of delithiated HE5050 (charged to 4.6 V vs. Li ⁺ /Li) after thermal abuse.....	452
Table IV - 15: List of Milestones – Process Development and Scale-Up of Advanced Electrolyte Materials.....	471
Table IV - 16: Summary of cells and materials examined in the Post-Test Facility.....	473
Table IV - 17: Summary of electrode composition for cell builds based on Toda HE5050 high energy cathode materials.	483
Table IV - 18: Summary of rate capability of cell builds based on Toda HE5050 high energy cathode materials.	483
Table V - 1: Products obtained from reaction 3 as a function of time as determined by <i>ex situ</i> XRD (Figure V - 61).	539
Table V - 2: Summary of length scales, d_i , as a function of the normalized chain length of the sacrificial homopolymer, α [details in ref. 2].	597
Table V - 3: Oxidative stability of the solvent/anion complexes from M05-2X/cc-pvTz DFT calculations.....	604
Table V - 4: Char yields of DPC salts as determined by pyrolysis combustion flow calorimetry.	609
Table V - 5: Effective material properties obtained from a 3D micro model.	635

