ElectroCat
Electrocatalysis Consortium

WORKSHOP

July 26, 2016
Sponsored by
U.S. Department of Energy
Fuel Cell Technologies Office (FCTO)

Organized by Argonne National Laboratory and
Los Alamos National Laboratory

Energy Materials Network
U.S. Department of Energy

2016 ElectroCat Workshop Summary Report

Workshop held July 26, 2016
Argonne National Laboratory,
9700 South Cass Ave.
Lemont, IL 60439

Sponsored by
U.S. Department of Energy (DOE) - Fuel Cell Technologies Office (FCTO)

Organized by
Argonne National Laboratory and Los Alamos National Laboratory

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NOTICE

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Executive Summary

The Fuel Cell Technologies Office (FCTO) in the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy (DOE-EERE) has established the ElectroCat (ElectroCatalysis) Consortium as part of the Energy Materials Network (EMN). ElectroCat will serve to coordinate platinum group metal-free (PGM-free) catalyst development and gather state-of-the-art tools at the national labs under one umbrella for easy access by stakeholders and the research community, to fulfill its mission to accelerate the development and implementation of PGM-free catalysts. It will do so by streamlining access to unique synthesis and characterization tools across national labs, developing missing strategic capabilities, and curating a public database of information.

A workshop was held at Argonne National Laboratory in Lemont, Illinois, on Tuesday, July 26th, 2016 to introduce stakeholders to the consortium and its capabilities and to solicit feedback on potential ways to effectively utilize the existing capabilities, what new capabilities should be developed, and how to efficiently communicate and share data with the fuel cell community and stakeholders.

The current state-of-the-art for PGM-free catalysts was discussed. Although there has been impressive progress in the past decade, PGM-free catalysts need further advancement to meet the DOE technical and cost targets. The main challenges of the technology are low oxygen reduction reaction (ORR) activity, limited durability, and a heavy reliance on Fe-derived materials, which accelerate membrane degradation. Progress in PGM-free electrocatalysis is hampered by our lack of fundamental knowledge of PGM-free catalysts. Advances will depend on focused catalyst design, guided by multi-scale modeling methods and facilitated by high-throughput methodologies for synthesis and screening.

Participants discussed the capabilities at the National Laboratories that are being utilized to address the challenges in PGM-free electrocatalysis for fuel cells. This suite of capabilities includes high-throughput synthesis and characterization techniques, advanced physical and chemical characterization techniques applied to understand the structure and chemical composition of PGM-free systems, and modeling efforts at the National Laboratories that will guide the synthesis of improved PGM-free electrocatalysts and aid in characterization by linking structure to experimentally observed properties. The effort will utilize automation to increase throughput of the calculations and will generate a publically accessible structure-property library.

At rated power, electrode structure and transport properties play key roles in determining performance. Thus, a hybrid approach utilizing experimental and numerical microstructure characterization, previously used to reconstruct the microstructure of Pt-based polymer electrolyte membrane fuel cell (PEMFC) electrodes, will be applied through ElectroCat to investigate PGM-free electrode microstructural transport and performance.

An important part of ElectroCat will be management of the data generated. Among other data management tools, ElectroCat plans to evaluate and leverage existing capabilities within the Materials Data Facility (MDF), a service through which researchers can share and search for published materials data, for data management, and incrementally develop capabilities

where needed. The MDF plans to interface with multiple national materials efforts over time and include a discovery service that supports full text search across all metadata fields. The goal is for intuitive search (Google-style) with support for more complex range queries and faceting (Amazon-style).

The workshop also discussed the process for partnering with ElectroCat. The consortium plans to provide streamlined access for partners to its capabilities through a suite of pre-negotiated technology transfer agreements specifically designed for ElectroCat. The hope is that this will facilitate rapid, uniform agreement execution amongst participating laboratories, as well as between the ElectroCat Consortium and industrial partners.

Breakout sessions were held in the areas of PGM-free catalysts and electrodes, high-throughput/combinatorial tool development, and advanced computational modeling. Table 1 shows a few selected highlights from the breakout sessions.

Table 1 Select Highlights of Breakout Groups

Breakout Session	Gaps	Potential Approaches
Catalysts and Electrodes		
	Understanding of ORR mechanism for PGM-free catalysts	Develop surface specific characterization techniques and more controlled synthesis or purification techniques to reduce or eliminate spurious species.
	Understanding of PGM-free degradation mechanism	Develop *operando* characterization techniques to follow degradation
	Understanding of catalyst/ionomer interactions	Develop surface specific characterization techniques and techniques to visualize ionomer distribution in the catalyst layer
Tool Development		
	Differences between thin film model systems used in high-throughput experiments and high surface area catalysts in real fuel cell systems	Perform pretreatments on the thin film model systems, such as soaking the system array in 0.5 M H_2SO_4 and/or expose the materials to a perfluorosulfonic acid ionomer.
		In the focus phase of catalyst development, decouple activity and durability screening from the preparative method and utilize test conditions that are as close to real life conditions as possible.
Computational Modeling		
	An accurate microstructure model	Methods need to be developed to extract the catalyst microstructure from experimental measurements

		to be able to develop and validate such a model.
	Lack of capabilities for mesoscale analysis and limited size of the effort in modeling at the atomistic and continuum levels.	Tighter collaboration with other theory groups at the national labs and better use of the academic communities.
	Combinatorial simulation models are needed.	Develop predictive models including descriptors at both the atomistic and microstructural level.

ElectroCat Workshop Agenda

8:30 am **Welcome and introductions**

8:40 am **Energy Materials Network overview** (Eric Miller, DOE-FCTO)

8:50 am **Introduction to ElectroCat: DOE perspective** (Dimitrios Papageorgopoulos, DOE-FCTO)

9:00 am **State of the art of PGM-free catalyst activity and durability** (Piotr Zelenay, LANL)

9:30 am **Overview of high-throughput techniques as applied to fuel cell catalysts and electrodes** (Debbie Myers, ANL)

10:00 am *Break*

10:15 am **Summary of ElectroCat experimental capabilities** (Piotr Zelenay and Debbie Myers)

11:00 am **DFT modeling of PGM-free catalyst activity and durability** (Ted Holby, LANL)

11:30 am **Hybrid approach for PEM fuel cell electrode microstructural analysis** (Firat Cetinbas ANL)

12:00 pm **Lunch, Argonne cafeteria**

1:10 pm **Data management and technology transfer/agreement approaches** (Ian Foster, ANL, and Laura Barber, LANL)

1:40 pm **Description of break-out sessions and goals** (Adria Wilson, DOE-FCTO)

1:45 pm **Break-out session discussions**

- PGM-free catalysts and electrodes
- High-throughput/combinatorial tool development
- Advanced computational modeling

3:15 pm **Reports from break-out sessions** (Break-out session discussion leaders)

4:00 pm **Summary and action items**

4:15 pm **Tour of High-Throughput Research Laboratory** (Ted Krause, Magali Ferrandon, ANL)

5:00 pm **Adjourn**

Workshop Objectives and Organization

The ElectroCat Workshop was held at Argonne National Laboratory on July 26, 2016, and featured 83 participants from industry, government agencies, advocacy groups, universities, and national laboratories with expertise in the relevant fields (catalyst developers, material suppliers, modelers, analysis and characterization experts, and combinatorial experts).

The overarching purpose of these discussions was to investigate ways in which the consortium capability set can be utilized by the fuel cell community and where the capabilities need to be augmented to accomplish the mission of developing PGM-free catalysts, as well as PGM-free electrodes and membrane electrode assemblies (MEAs).

The workshop began with an introductory session on the DOE Energy Materials Network by Eric Miller (FCTO-DOE). Dimitrios Papageorgopoulos (FCTO-DOE) provided DOE's perspective on ElectroCat. The state of the art of PGM-free catalyst activity and durability was presented by Piotr Zelenay (LANL). Debbie Myers (ANL) provided an overview of high-throughput techniques as applied to fuel cell catalysts and electrodes. Piotr Zelenay, Debbie Myers, Huyen Dinh, and Karren More summarized ElectroCat experimental capabilities at LANL, ANL, NREL, and ORNL, respectively. Density functional theory (DFT) modeling of PGM-free catalyst activity and durability was discussed by Ted Holby (LANL). Finally, electrode microstructure and transport modeling was presented by Firat Cetinbas (Rajesh Ahluwalia's group - ANL).

Discussions related to issues with technology transfer and data management were led by Laura Barber (LANL) and Ian Foster (ANL/U Chicago), respectively.

Three breakout sessions were convened. Each of the break-out sessions addressed a different component of the ElectroCat capability toolset. The components discussed were:

1. PGM-free catalysts and electrodes
   Discussion Leader: John Kopasz, Argonne National Laboratory
2. High-throughput/combinatorial tool development
   Discussion Leader: Gene Smotkin, NuVant and Northeastern University
3. Advanced computational modeling
   Discussion Leader: Jeff Greeley, Purdue University

The session ended with a representative from each breakout group summarizing the outcome of the discussions to all of the workshop participants.

Presentations

Energy Materials Network (Eric Miller, DOE-FCTO)

The DOE's Energy Materials Network (EMN) was described. This effort is working to discover, manufacture, and deploy advanced materials twice as fast, at a fraction of the cost. The objective of the EMN is to create and manage a unique, accessible set of capabilities within the DOE National Laboratory system. This is to be accomplished by integrating all phases of research and development (R&D), from discovery through end-use qualification, and facilitating industry access to national laboratories' capabilities, tools, and expertise to accelerate the materials development cycle and enable U.S. manufacturers to deliver innovative, made-in-America products to the world market. This will be accomplished through national laboratory consortia that operate under the following principles:

1. WORLD CLASS MATERIALS CAPABILITY NETWORK: Create and manage a unique, accessible set of capabilities within the DOE National Laboratory system.
2. CLEAR POINT OF ENGAGEMENT: Provide a single point-of-contact and concierge to direct interested users (e.g. industry research teams) to the appropriate laboratory capabilities, and to facilitate efficient access. The EMN Concierge, a one-stop-shop for learning about and accessing the network, is responsible for:
    - match-making industry needs with resources across the network;
    - facilitating rapid intellectual property (IP) agreements, non-disclosure agreements (NDA), and contract agreements;
    - coordinating movement, storage, and analysis of project data; and
    - conducting outreach activities.

3. DATA AND TOOL COLLABORATION FRAMEWORK: Capture data, tools, and expertise developed at each node such that they can be shared and leveraged throughout the EMN and in future programs. Establish data repositories and, where appropriate, distribute data to the scientific community and public. Accelerate learning and development through data analysis using advanced informatics tools.

4. STREAMLINED ACCESS: Facilitate rapid completion of agreements for external partners and aggressively pursue approaches to reduce the non-technical burden on organizations seeking to leverage the EMN for accelerated materials development and deployment. To accomplish this the consortium will:

- simplify the agreement process to the greatest extent possible;
- maintain a catalog of short-form or rapid cooperative research and development agreements (CRADAs), agreements for commercializing technology (ACT), Strategic Partnership Projects (SPP), etc. for use whenever possible;
- develop a single, pre-approved, mutual NDA between all consortium partners; and
- use exploratory licenses whenever possible.

Each consortium will assemble national lab resources, led by a Steering Committee.

Introduction to ElectroCat (Dimitrios Papageorgopoulos DOE-FCTO)

Fuel cell costs must be reduced for fuel cell vehicles to be competitive and to make a significant impact. One of the main contributors to fuel cell costs is the PGM catalyst, which accounts for almost half of the cost of a fuel cell stack when manufactured at high volumes. The goal of ElectroCat is to accelerate the deployment of fuel cell systems by eliminating the use of PGM catalysts, allowing for lower cost fuel cells. PGM-free catalysts lag behind platinum in activity, durability, and ease of integration into MEAs. ElectroCat was launched to coordinate PGM-free catalyst and electrode development and gather state-of-the-art tools at the national labs under one umbrella for easy access by stakeholders and the research community. The mission is to develop and implement PGM-free catalysts by streamlining access to unique synthesis and characterization tools across national labs, developing missing strategic capabilities, and curating a public database of information.

ElectroCat's strategy is to pursue a high-throughput approach to materials discovery, prioritizing discovery and development of catalysts for oxygen reduction in PEMFCs and phosphoric acid fuel cells (PAFCs), catalysts for oxygen reduction and hydrogen oxidation in alkaline membrane fuel cells (AMFCs), and development of electrodes and MEAs that are compatible with PGM-free catalysts. To be successful in this effort, new or improved techniques and tools will be required. Tool development activities will include optimization of atomic-scale and meso-scale models of catalyst activity to predict macro-scale behavior, as well as development of high-throughput techniques for catalyst synthesis and characterization of catalysts, electrodes, and MEAs. These high-throughput activities are expected to generate large amounts of data. Tools will be developed for aggregation of data in an easily searchable, public database to facilitate the development of catalyst materials and MEAs.

ElectroCat brings together expertise in synthesis of PGM-free catalysts and electrodes; high-throughput combinatorial materials discovery, characterization, testing and design; microstructural characterization; and data management from multiple National Laboratories and will make these tools and expertise available to the fuel cell community. The co-directors of ElectroCat are Debbie Myers of Argonne National Laboratory and Piotr Zelenay of Los Alamos National Laboratory; the consortium also includes participation from researchers at Oak Ridge National Laboratory and the National Renewable Energy Laboratory. Further information can be found at http://energy.gov/eere/fuelcells/ElectroCat-ElectroCatalysis-consortium.

Technology Transfer and Agreements (Laura Barber LANL)

One of the EMN principles is streamlined access to the network through standard agreements (NDAs, CRADAs, etc.). The goal of these agreements is to reduce the non-technical burden on organizations seeking to leverage the EMN for accelerated materials development and deployment. ElectroCat plans to reduce this burden by both developing a suite of pre-negotiated technology transfer agreements specifically designed for the ElectroCat Consortium and facilitating rapid, uniform agreement execution amongst participating laboratories, as well as between the ElectroCat Consortium and industrial partners.

The suite of streamlined ElectroCat agreements include:

- NDAs to allow secure information disclosure;
- an IP Management Plan (IPMP) to provide IP protection;
- Sponsored Research Agreements (CRADAs and SPPs) to foster collaboration; and
- Licensing and Material Transfer Agreements (MTAs) to ensure access and freedom to operate.

The ElectroCat Partnership Process begins with contacting the Concierge (aka Coordinator) to discuss capabilities and high-level needs of the external partner, followed by executing a NDA. After the NDA is signed, the problem to be addressed is identified, a statement of work is developed, and expectations are set with Technology Transfer and their business counterparts. The CRADA or SPP is then executed, and work can begin.

When the IP and Data Management Plan is in place, a Market Transition/ Commercial Deployment Strategy is developed. Finally, a License Agreement to provide commercial access to IP is executed.

Technology Transfer Contacts for ElectroCat are:

Laura Barber – Los Alamos National Laboratory ljbb@lanl.gov, (505) 667-9266
Elizabeth Jordan – Argonne National Laboratory ekjordan@anl.gov, (630) 252-7617

Data Management (Ian Foster of ANL/University of Chicago and Ben Blaiszik of ANL)

Two main EMN Principles are to develop and establish a data and tool collaboration framework to capture data, tools, and expertise developed at each node such that they can be shared and leveraged throughout the EMN and in future programs; and to establish data repositories and, where appropriate, distribute data to the scientific community and public.

Data management and analysis will be key to ElectroCat's success, as the high throughput/combinatorial approach is expected to generate extensive amounts of data. A data management system was proposed that leverages existing resources within the Materials Data Facility where applicable, and incrementally develops capabilities where needed. The proposed data system for ElectroCat is composed of the following three components:

1) ElectroCat Portal
2) ElectroCat Data Hub
3) ElectroCat Acceleration Engine

The proposed Data Hub would house data generated through use of ElectroCat facilities to make it publicly available. It would provide centralized data/model storage capability for various ElectroCat generated information, including codes and models; experimental and simulated data; and journal publications and presentations tagged with the appropriate provenance. The Hub would also provide virtual linkages to other relevant materials databases. To facilitate management of the data, the proposed Data Hub would develop protocols that researchers must follow when submitting data to the Hub (data formats and information on test conditions). The Data Hub would also provide keyword-based searching capability and publish curated metadata to commercial search engines.

A tiered approach to data management was proposed, evaluating and leveraging existing resources where applicable, and incrementally developing capabilities where needed. Data would be divided between:

1) Basic consortium collaboration database: Data submission, metadata, basic search, continued metadata development, data sharing within the consortium
2) Consortium materials database: Database of relevant materials properties and data
3) Public access: Release data to public
4) Advanced analysis: organize and structure data for data mining and informatics approaches

The proposed approach would also provide a security system with flexibility to accommodate access and use by different classes of projects and data – from highly sensitive proprietary, to embargoed, to publicly available data. Integration with the community is key and interactions with other facilities, institutional repositories, and publishers will be pursued to maximize the utility and impact of ElectroCat.

State-of-the-Art of PGM-Free Catalyst Activity and Durability (Piotr Zelenay of LANL)

The DOE targets for oxygen reduction reaction (ORR) catalysts for transportation applications are shown in Table 1 below. According to automotive OEMs, PGM-free ORR catalysts will bring value to fuel cell systems for cars only if they meet the performance targets established for PGM catalysts. PGM-free catalysts may provide a cost-equivalent stack at lower performance levels, but such a stack would not meet the automotive size and weight requirements and would not readily fit into the vehicle.

Table 1. Technical Targets: Electrocatalysts for Transportation Applications

Characteristic	Units	2015 Status	2020 Targets
Platinum group metal total content (both electrodes)	g/kW (rated, gross) @ 150 kPa (abs)	0.16	0.125
Platinum group metal (PGM) total loading (both electrodes)	mg_{PGM}/cm^2 (electrode area)	0.13	0.125
Mass activity	A/mg_{PGM} @ 0.9 $V_{iR\text{-}free}$	> 0.5	0.44
Loss in initial catalytic activity*	% mass activity loss	66	< 40
Loss in performance at 0.8 A/cm^{2*}	mV	13	< 30
Electrocatalyst support stability*	% mass activity loss	41	< 40
Loss in performance at 1.5 A/cm^{2*}	mV	65	< 30
PGM-free catalyst activity	**A/cm^2 @ 0.9 $V_{IR\text{-}free}$**	**0.024**	**> 0.044***

*Measured using the appropriate protocols outlined in the DOE MYRD&D plan at http://energy.gov/sites/prod/files/2016/10/f33/fcto_myrdd_fuel_cells.pdf. Target is equivalent to PGM catalyst mass activity target of 0.44 A/mg_{PGM} at 0.1 mg_{PGM}/cm^2.

There has been impressive progress in PGM-free catalysts in the past decade. The best PGM-free catalysts have achieved power densities of > 0.9 W/cm^2 in H_2/O_2, and are approaching the PGM-free activity target of > 0.044 A/cm^2 at 0.9 V (having achieved 0.044 A/cm^2 at 0.87 V in H_2/O_2). However, while showing good potential-cycling stability in N_2 atmosphere, PGM-free catalysts tend to lose performance much faster in air or O_2. Furthermore, performance in air is

limited, with peak power much below that needed for automotive applications. Preliminary analysis of a PGM-free catalyst PEMFC system indicates the specific power density of the PGM-free MEAs needs improvement from the current level of < 500 mW/cm^2 in order for catalyst cost to make significant impact on the stack cost.

Additional improvements are needed to meet the DOE goals above. The main challenges for PGM-free catalyst technology are increasing the ORR activity in the MEA, increasing power densities in operation with air, increasing durability, and moving away from Fe-derived materials (which, if leached, promote membrane degradation).

The acceleration of progress in PGM-free ORR electrocatalysis critically depends on focused catalyst design, guided by multi-scale modeling methods and facilitated by high-throughput methodologies for synthesis and screening, both of which are based on fundamental knowledge of reaction mechanisms and of catalyst design and synthesis.

PGM-free ORR catalysts are also highly attractive for other fuel cell systems, including AMFCs for their high activity and stability, direct methanol fuel cells (DMFCs) for their tolerance to methanol, and in PAFCs and HT-PEMFCs for their tolerance to phosphates. PGM-free catalysts may find use in some of these applications prior to use in automotive applications, due to lower performance requirements.

Summary of ElectroCat Experimental Capabilities

ElectroCat has capabilities in synthesis, processing and manufacturing, characterization and testing, and in computation, modeling and data management. The capabilities are briefly described below. More details on the capabilities can be found on the ElectroCat website at http://www.electrocat.org/capabilities.

Synthesis/Processing/Manufacturing

ElectroCat has multiple capabilities for the synthesis, processing and manufacturing of PGM-free catalysts and electrodes. These include capabilities for high-throughput (HT) fabrication of PGM-free electrodes that enable optimization of electrode inks for new catalysts and for fabrication of catalyst-coated membrane and gas-diffusion electrode-based membrane-electrode assemblies. The decades-long experience and proven results of the ElectroCat technical team also provides important capabilities in PGM-free catalyst synthesis, analytical characterization, and electrochemical and fuel cell testing. Controlled functionalization of model catalysts is possible utilizing energetic neutral atom beam lithography and epitaxy (ENABLE), a controlled method for clean and selective introduction of heteroatom dopants into a variety of substrates, supported by *in situ* characterization and diagnostic capabilities. Sputter deposition of thin films and high surface area PGM-free catalysts is also possible with two sputter deposition chambers available in ElectroCat (these samples can be grown in thin film form or as conformally deposited supported nanoparticles on any vacuum stable support powder). ElectroCat is also capable of implanting heteroatoms onto "flat" substrates or powders and subsequent sputtering onto the substrate surface without breaking vacuum; in this way nitrogen and Freon implantation has been shown to enhance the durability of fuel cell catalysts by affecting the catalyst-support interaction. In terms of membrane-electrode assembly (MEA) fabrication, ElectroCat includes capabilities to control catalyst ink optimization and preparation, catalyst layer deposition onto the polymer electrolyte membrane or gas diffusion layer, and integration of all required components into an MEA. There also exists expertise in manufacturing porous electrodes, including capabilities in materials characterization (particle size, zeta potential, surface energy, rheological property, morphology), materials processing (electrode formulation, slurry preparation), electrode coating (tape casting, slot die coating, UV curing, electron beam curing), electrode calendering, cell assembly, and testing. For thin film samples in particular, ElectroCat has HT thin film fabrication and characterization, including combinatorial synthesis, spatially-resolved characterization, and semi-automated data analysis for thin film samples. Finally, ElectroCat has capabilities for HT synthesis of PGM-free catalysts and electrodes, utilizing robotic platforms with solid and liquid handling, cooling and heating, and dispensing capabilities including inert atmosphere capabilities.

Characterization and Testing

ElectroCat's capabilities in characterization and testing span multiple techniques. Electrochemical characterization capabilities include kinetics and transport studies at NREL done with fully automated differential cell, in-operando testing equipment, and coupled ring-disk

electrode and ICP-MS (inductively coupled plasma – mass spectrometry) techniques to determine structure/composition-function relationships and active sites. ElectroCat also has extensive microscopy capabilities, including analytical electron microscopy capabilities (High-resolution transmission electron microscopy (TEM) and aberration-corrected scanning transmission electron microscopy (STEM)), used to characterize the atomic-scale structure of PGM-free catalysts (typically in powder form) and the material constituents (catalyst and ionomer) comprising MEAs, and in situ electron microscopy, used to study the dynamic behavior of PGM-free catalysts under relevant operating and/or synthesis conditions (e.g., temperature, pressure, potential cycling, and environment) to provide unprecedented nanometer-level insight regarding morphological and compositional changes that contribute to performance degradation. ElectroCat's expertise extends to X-ray techniques as well, where capabilities include X-Ray characterization techniques that encompass a variety of lab-based equipment specifically targeting the development of PGM-free catalysts, electrodes, and MEAs, including fundamental materials characterization techniques providing information about the physical and chemical properties of electrocatalysts, catalyst precursors, and electrodes, and X-Ray Photoelectron Spectroscopy (XPS), a surface sensitive method for obtaining both composition (atomic percentage) and chemical bonding (oxidation state) information. For PGM-free catalysts, XPS is particularly powerful for characterizing the transition metal, carbon, and nitrogen composition and chemical bonding.

Imaging capabilities also are present within the ElectroCat consortium. STEM-based electron tomography is used to provide three-dimensional (3D) reconstructions of the structure (STEM image reconstruction) and composition (chemical map reconstruction) of materials. Electron tomography is analogous to bulk tomography techniques like X-ray tomography, but can provide information at a much higher resolution (sub-nm-scale) and can be used to combine morphological, crystallographic, and compositional data into 3D renderings. ElectroCat also contains Electrode Microstructure Characterization and Simulation capabilities that encompass structural imaging of electrodes, using synchrotron X-rays, combined with characterization via other techniques such as porosimetry and ultra-small angle X-ray scattering (USAXS), and use the data from these multiple techniques to build a structural and transport model of the electrode.

Lastly, ElectroCat has *in situ* and *operando* atomic, nano-, and micro-structure characterization capabilities that utilize a combination of synchrotron X-ray spectroscopy, microscopy, tomography, and scattering and custom-built cells to determine the atomic structure, oxidation state, and nano- and micro-structure of catalysts, catalyst-ionomer inks, and electrodes in various environments**.**

Computation & Modeling

Computation and modeling are an integral part of the ElectroCat Consortium. Modeling **c**apabilities include multi-scale modeling and rational design of PGM-free catalysts to provide structure-to-function relationships of electrocatalysts. These models can provide valuable input for developing syntheses to produce catalysts with improved activity, selectivity, and durability, and aid in the interpretation of experimental data. Modeling capabilities in kinetic and transport

processes in PGM-free electrodes are presently available in ElectroCat, and are detailed below in the section on DFT modeling.

Computational methods and models are available to characterize the kinetic and transport behavior of PGM-free electrodes. These models are useful in designing test matrices and protocols that enable the systematic extraction of relevant model parameters that define hydrogen oxidation reaction and oxygen reduction reaction kinetics; oxygen/water transport in gas channels, diffusion media and electrodes; and ohmic losses in the electrodes and membrane. Lastly, ElectroCat's capabilities include electrode microstructure characterization and simulation. This capability encompasses structural imaging of electrodes, using synchrotron X-rays, combined with characterization via other techniques such as porosimetry and ultra-small angle X-ray scattering (USAXS). Data from these multiple techniques are used to build a structural and transport model of the electrode. To be successful, the modeling teams within ElectroCat will collaborate closely with experimentalists to help guide the synthesis and testing of most promising systems and include a robust feedback loop to refine models as experimental data is generated.

Capabilities are listed by National Laboratory in Appendix A. Further information on capabilities can be found at the ElectroCat website at http://www.electrocat.org/.

Overview of High-Throughput Techniques as Applied to Fuel Cell Catalysts and Electrodes (Debbie Myers of ANL)

ElectroCat's objective is to accelerate the development and implementation of highly active, stable PGM-free cathode catalysts and electrodes primarily for the ORR in polymer electrolyte membrane fuel cells, but also for phosphoric acid and phosphoric acid-based fuel cells, and alkaline membrane fuel cells, as well as for the hydrogen oxidation reaction (HOR) in alkaline membrane fuel cells using high-throughput techniques. Key to realizing the full time-saving benefits of the high-throughput methodology is making every step in the process (synthesis, discovery, physical and chemical characterization, catalytic activity and durability screening, electrode fabrication and implementation in a fuel cell) combinatorial or high-throughput (HT).

The catalyst discovery phase will employ model systems, utilizing deposition of gradients of materials by physical vapor deposition (sputtering, heating), chemical vapor deposition, deposition of metal salts with simultaneous chemical reduction, or electrodeposition. It will also include high-throughput/robotic synthesis of realistic forms of catalysts using scalable methods (Argonne case study). To provide a high-throughput method of measuring activity of these catalysts in a hydrodynamic environment, Argonne has resolved issues related to previous channel flow double electrode (CFDE) apparatus designs. Using the improved design, Argonne has achieved excellent agreement of activity trends, determined using CFDE, for HT small batch samples prepared in this project with trends observed using rotating disk electrodes (RDE) for large batches prepared by LANL. Others active in the HT catalyst activity measurements for ORR are NuVant Systems (segmented array cell) and NREL (spatial performance of electrode defects).

The next steps for high-throughput activities in ElectroCat are for full automation of PGM-free catalyst synthesis steps, including the grinding step, and automation of uniform deposition of ink on glassy carbon electrodes. High throughput pyrolysis will be coupled with *in situ* effluent analysis and X-ray absorption fine structure (XAFS) characterization of species. High-throughput XAFS characterization will also be developed for identifying metal species present in the cathode catalyst layer and for following changes in these species during operation in a fuel cell. Tools to characterize the stability of PGM-free catalysts will be developed, including combinatorial characterization of ORR activity using the CFDE cell with downstream electrochemical and on-line inductively coupled plasma-mass spectrometry (ICP-MS) detection of dissolved catalyst components and *in situ*/*operando* high throughput analysis of species formed, catalyst particle size evolution, and carbon agglomerate structure using XAFS and X-ray scattering.

ElectroCat will also investigate electrodes/MEAs using combinatorial and high-throughput techniques. ElectroCat will develop complete robotic synthesis and characterization of the agglomerate structure of catalyst-ionomer inks (light scattering of dilute inks; X-ray scattering of concentrated inks) as well as complete robotic fabrication of catalyst-ionomer decals; and *ex situ* characterization of ionic and electronic conductivities of ink layers on decals as a function of temperature and relative humidity (RH). "High throughput" tomography with automated image analysis and output of structural parameters to cathode catalyst layer structure-transport-performance models will be developed to optimize MEA structure and attain high performance in the high current density region for PGM-free cathode fuel cells.

Lastly, ElectroCat plans to identify and utilize other high-throughput synthesis and screening techniques developed at other labs (outside ElectroCat), and to apply the high throughput techniques developed to other classes of catalysts studied within ElectroCat.

DFT Modeling of PGM-free Catalyst Activity and Durability (Ted Holby of LANL)

The goal is for the modeling activity to guide the synthesis of improved PGM-free electrocatalysts by identifying the active sites and reaction mechanisms, and to aid in the characterization of synthesized materials by linking atomic scale structure to experimental spectroscopic signatures and observed properties. ElectroCat has access to advanced computing facilities and expertise at Los Alamos National Laboratory for this activity. LANL personnel have experience utilizing multiple codes for materials modeling, including Vienna *ab initio* Simulation Package (VASP), Amsterdam Density Function Suite (ADF), Gaussian09, and Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). The facilities available include large clusters with up to 9856 Intel Xeon cores and speeds of up to 488 Tflops/s (peak). The modeling effort will leverage software developed as part of the Materials Genome Initiative, and utilize automation to speed the throughput of calculations and create a structure-property library for PGM-free electrocatalysts that is accessible via a web portal.

Initial studies have focused on structures guided by previously proposed structures and relative thermodynamic stability determined via Metropolis Monte Carlo search and DFT studies. These studies indicate that N-metal complexes have lower formation energies at edges and that the edge-N-metal complexes thermodynamics drive the formation of small clusters. ORR activity is determined using DFT. The calculated maximum exergonic potential U_i has been found to be a good ORR activity descriptor.

First-principles molecular dynamics is being utilized to model the durability of PGM-free electrocatalysts. The complex degradation phenomenon includes kinetic barriers, defects, adsorbates, etc. It is not yet clear how best to simplify this complex behavior and what computational descriptor of durability is best to use for application of high-throughput modeling to this problem. One model being investigated is a beam damage model, utilizing knock on displacement threshold energy for C neighboring defects and adsorbates as an initial durability descriptor. Further testing and validation is required.

Specific paths to be investigated via computation for improving PGM-free catalysts include replacing Fe, ligand modification, and strain engineering.

Hybrid Approach for PEM Fuel Cell Electrode Microstructural Analysis (Firat Cetinbas of ANL)

At rated power, which determines the size and cost of the fuel cell stack, electrode structure and transport properties play key roles in determining performance. A new approach was presented to characterize the cathode microstructure from nm to μm length scales by combining information from different experimental and numerical techniques. In this context, nano-scale X-ray computed tomography (X-CT) was performed utilizing the Hard X-ray Nanoprobe Beamline at ANL's Advanced Photon Source (APS) to extract the secondary pore space of the electrode. The number of primary pores that can't be resolved by X-CT was approximated using mercury intrusion porosimetry (MIP). An algorithm was developed to regenerate the microstructure from the C, Pt, and ionomer content and information on the primary C particle and Pt particle size distribution determined from Transmission Electron Microscopy (TEM). Brunauer Emmett Teller (BET) porosimetry was used to validate the computed pore structure. The calculated structure provides an estimate of the ionomer structure in the electrode. Direct imaging of the 3D ionomer network in the electrode still remains a challenge, and the ionomer structure is critical in determining transport properties in the electrode. With the calculated structure, transport related characteristics and effective properties for the hybrid microstructure can be calculated and compared to measured properties.

Future work will add electrochemical reactions to the microstructural model to allow comparisons of activity and performance with experimental data. Water transport will be investigated by performing X-CT on waterlogged samples and the microstructural calculations will be expanded from Pt/C to PGM-free electrodes.

Breakout Sessions

PGM-Free Catalysts and Electrodes Break-Out Session

The breakout session focused on discussing gaps and shortcomings in the area of PGM-free catalysis and on ways or means to try to address those gaps and shortcomings. Major issues identified were the low level of understanding of the active sites in current PGM-free catalysts and of the reaction mechanisms and degradation mechanisms for PGM-free catalysts. This comes about partially from the destructive methods used to synthesize active catalysts that result in mixtures of components and phases. A controlled synthesis method, or potentially non-destructive method, with a thorough characterization of the synthesis process would prove helpful for identification of the active site or sites. Development of surface-specific characterization techniques (for example infrared (IR) and/or Raman spectroscopy) of PGM-free materials could also help identify active sites and elucidate reaction and degradation mechanisms. *In situ* and *operando* techniques should be particularly useful for studying degradation of PGM-free catalysts. The Fe used in the most active PGM-free catalysts to date is a concern, as any Fe leached from the catalyst layer that makes it into the membrane will accelerate membrane degradation. Catalysts with less-active Fenton reagents would be preferable.

A second gap identified is in the area of optimizing electrode structure for PGM-free catalysts. PGM-free catalysts are different than traditional PGM catalysts. The catalyst and support are generated together in the PGM-free synthesis and, in some cases, the support and the catalyst are one and the same. The interdependence between the chemical composition and the morphology that results from this process makes it difficult to change one without affecting the other. Another difference is in ionomer-catalyst interactions. In PGM-free catalysts, where the density of active sites is believed to be much lower (~1000 x less than for PGM catalysts), transport to and from these sites becomes much more important and understanding ionomer-catalyst interactions will be crucial to optimizing this transport.

Other gaps discussed include difficulties in measuring performance. Performance in an RDE is often not indicative of fuel cell performance. The breakout session suggested that RDE be limited to determining fundamental kinetic information, not for determining performance values. Alternative electrochemical techniques should be utilized, with careful use of Tafel methodology. High-throughput electrochemical techniques should take care to include reference electrodes. Applying RDE in a high-throughput method is a difficult task. Relevant testing protocols need to be developed. There is a lack of agreed-upon protocols for accelerated stress tests (AST) to assess loss of performance under galvanostatic/potentiostatic conditions. These tests should be performed in air, not N_2. Recording practices should be standardized (i.e. thickness, ionomer loading, etc.). Lastly, a better descriptor for PGM-free activity/performance should be developed. The present descriptor (A/cm^2 at 0.9V) is a crude measure that does not take into account actual active site loading or turnover frequency.

High-Throughput/Combinatorial Tool Development Break-Out Session

The discussion focused on the differences between discovery and focus modes, the usefulness of model systems, and the potential for "false negatives" with model systems.

The discovery mode is typically screening a large library of materials and often utilizes arrays of thin films of a potential catalyst material or may use nanoparticle materials, but almost without exception utilizes synthetic methods that are far from what would be used to make high-surface-area materials which can be incorporated into fuel cells. This raises the concern of studies of model systems ruling out materials which may be active when fabricated by other, realistic and scalable methods.

An example of this false negative is the PtRu system for methanol electro oxidation where a Pt to Ru ratio that showed very low activity in the model system form actually turned out to be the most active when synthesized by Johnson Matthey in a high-surface-area form. Some of the problems with false negatives in the discovery mode also arise from differences in the "catalyst" treatment prior to activity screening.

The break-out group discussed means of mitigating this issue, such as soaking the model system array in 0.5 M H_2SO_4 prior to activity testing or exposing the model system materials to a perfluorosulfonic acid ionomer. It was also suggested that the phase composition of the model system materials be characterized immediately after deposition, after the acid and/or ionomer treatment step, and after the electrochemical activity measurements.

The focus mode involves testing just a sub-set of the materials deemed active during the discovery phase and must utilize catalysts in the form which will ultimately be used in a fuel cell. The activity and durability testing method must also incorporate a state-of-the-art catalyst to validate the method. It was suggested that the ElectroCat Technical Experts devise a set of metrics by which to judge the stability and performance of materials studied in the focus phase of catalyst development. Finally, it was suggested that the activity and durability screening be decoupled from the preparative method and that the screening utilize as realistic as possible conditions.

Two other comments arising from this break-out session are that materials should be designed with the active physical structure of the catalyst and the combinatorial equipment should be designed such that the equipment is versatile and can be used to develop materials for other electrochemical devices, such as electrolyzers.

Theory and Computation Break-Out Session

Summary of approach: The discussion group began by preparing a list of goals and capabilities of the current ElectroCat consortium. By comparing these lists, several general gaps in ElectroCat's current approach and capabilities were identified and some suggestions as to how these gaps could be addressed were made by panel members.

Goals for ElectroCat in theory and modeling were identified in two main areas: methodological developments for computation and modeling, and scientific goals related to PGM-free catalysis. To model PGM-free catalysts, several length scales need to be addressed, from atomistic to mesoscale. To be able to model the catalysts, one needs an accurate microstructure model.

Methods need to be developed to extract the catalyst microstructure from experimental measurements to be able to develop and validate such a model. At the atomistic scale there needs to be continued refinement of atomistic electronic structure approaches through interactions with the algorithm development community. Mesoscale methods such as phase field or related techniques are needed for simulations of transport and degradation processes. Lastly, these approaches should be integrated across these length scales to provide a predictive model. Combinatorial simulation models are also needed. An integration of experimental and computational combinatorial methods is desired to enable faster discovery by narrowing the experimental search space through computation. Predictive models are a goal, including descriptors at both the atomistic and microstructural level.

Scientific goals identified for the computation and modeling efforts include being able to predict PGM-free MEA performance and responses to changing conditions, as well as degradation. This will require determination of thermodynamics and kinetics of PGM-free degradation at all length scales. Scientific goals also include identification of elementary mechanistic pathways of HOR and ORR on PGM-free electrodes in acidic and basic environments and identification of descriptors for PGM-free electrocatalyst activity. Lastly, the goal is to exploit this mechanistic knowledge and design principles from the PGM community to accelerate PGM-free development.

Current capabilities that exist in the consortium were identified. Within the consortium, capabilities are evolving in modeling at the micro/continuum scale for analysis of liquid and gas transport in thick electrodes and for MEA-cell level simulations of transport, kinetics, and performance (polarization curves). Methods are also being developed for reconstruction of microstructure from microscopy images. At the atomistic scale, capabilities for *ab initio* thermodynamic phase diagrams of active site regions are being utilized and descriptor-motivated descriptions of the active site kinetics and durability are being developed.

The breakout group concluded that, while the ElectroCat consortium's modeling and computational capabilities are state-of-the-art, they are not adequate in either scale or scope to address the ambitious scientific goals of ElectroCat. Gaps identified include the lack of capabilities for mesoscale analysis and the limited size of the effort in ElectroCat modeling at the atomistic and continuum levels. Possible solutions identified include tighter collaboration with other theory groups at the national labs and better use of the academic communities. Integration of theory and experiment needs to be enhanced and standardized throughout the consortium.

Conclusions

The ElectroCat (ElectroCatalysis) Consortium's mission is to develop and implement PGM-free catalysts by streamlining access to unique synthesis and characterization tools across National Labs, developing missing strategic capabilities, facilitating IP agreements, and curating a public database of information. World-class facilities and capabilities exist at the national labs. These include capabilities and expertise in synthesis and post-synthesis processing of PGM-free catalysts in high surface area forms or as planar model systems, and in incorporating these catalysts into electrodes and MEAs. Some of the most active PGM-free catalysts reported to date have been synthesized at the National Labs associated with ElectroCat. The ElectroCat consortium also has a wide array of capabilities to characterize the composition, structure, and performance of PGM-free catalysts, electrode layers, and MEAs including world class capabilities to characterize the catalyst and catalyst support distribution, ionomer distribution, and pore size distribution. ElectroCat's experimental capabilities are complemented by computational and modeling capabilities at the catalyst, electrode, and MEA levels, as well as by data management expertise. Modeling capabilities include active catalyst site identification and models to characterize the kinetic and transport behavior of PGM-free electrodes.

The workshop also identified gaps in understanding that should be addressed. There are still gaps in our understanding of the ORR reaction mechanisms and degradation mechanisms for PGM-free catalysts, partly due to the multiple species produced in current PGM-free synthesis techniques. Synthesis techniques that reduce or eliminate spurious species would be beneficial, as well as *operando* characterization techniques that can follow catalyst degradation. There is a gap between thin-film model PGM-free systems utilized for discovery-mode high-throughput experiments and high-surface area PGM-free catalysts in real fuel cell systems. Pretreatment techniques to bring the model systems closer to the real world systems are needed. In the computational modeling area, the community lacks an accurate microstructural model, and methods to extract the catalyst microstructure from experimental measurements needs to be developed.

One key aspect of the ElectroCat Consortium is to discover ongoing capability needs through collaboration with external partners, and to provide these resources to further advance the development of PGM-free catalysts and electrodes, and in the long term, to integrate these into these into high-performing, durable MEAs. Since an upcoming FOA opportunity will be used to bring in partners to collaborate with the consortium, there has not been a great deal of feedback regarding capability needs. Over the course of the coming year, these needs will be investigated and needs will be addressed going forward. However, the workshop already uncovered a need for including mesoscale modeling capabilities in ElectroCat.

Appendix A

Capabilities by National Laboratory

ANL (Debbie Myers)

- High-throughput characterization
- High-throughput synthesis
- Kinetic transport modeling
- Combinatorial hydrodynamic screening
- Model system synthesis and characterization
- Electrode structural modeling
- *In situ* and *operando* and nanostructure characterization

LANL (Piotr Zelenay)

- Advanced fuel cell characterization techniques
- Analytical techniques for PGM-free catalysts
- Electrochemical and fuel cell testing
- Controlled functionalization of model catalysts
- In situ fluoride and carbon dioxide emission measurements
- MEA fabrication
- Multi-scale modeling and rational design of PGM-free catalysts
- PGM-free catalyst synthesis
- X-ray characterization techniques

NREL (Huyen Dinh)

- High-resolution segmented cell
- Differential cell measurement of kinetics and transport
- Experimental and computational materials data infrastructure

- Thin-film high-throughput capability suite
- High-throughput scale-up of PGM-free catalysts to electrodes
- Cube2 sputtering and heteroatom implanting

ORNL (Karren More)

- Sputtering deposition of PGM-free catalysts
- Manufacturing porous electrodes
- *In situ* STEM
- High-resolution analytical STEM
- STEM-based 3D electron tomography
- X-ray photoelectron spectroscopy

Appendix B

List of attendees. The ElectroCat Workshop was an open-invitation meeting.

Name	Organization
Benjamin Blaiszik	Argonne National Laboratory
Thomas Benjamin	Argonne National Laboratory
C. Firat Cetinbas	Argonne National Laboratory
Di-Jia Liu	Argonne National Laboratory
Dongguo Li	Argonne National Laboratory
Debbie Myers	Argonne National Laboratory
Liz Jordan	Argonne National Laboratory
Magali Ferrandon	Argonne National Laboratory
Nancy Kariuki	Argonne National Laboratory
John Kopasz	Argonne National Laboratory
Ted Krause	Argonne National Laboratory
Maria Chan	Argonne National Laboratory
Vojislav Stamenkovic	Argonne National Laboratory
Rajesh Ahluwalia	Argonne National Laboratory
Ian Foster	Argonne and University of Chicago
Massimiliano Cimenti	Automotive Fuel Cell Cooperation, Canada
Dustin Banham	Ballard Power Systems
Alex Harris	Brookhaven National Laboratory
Radoslav Adzic	Brookhaven National Laboratory
Shawn Litster	Carnegie Mellon University
Siddharth Komini Babu	Carnegie Mellon University
Ed Halpin	Chemspeed
Svitlana Pylypenko	Colorado School of Mines
Adria Wilson	Department of Energy
David Peterson	Department of Energy
Dimitrios Papageorgopoulos	Department of Energy
Eric Miller	Department of Energy
Jonathan Jin	Department of Energy
Nancy Garland	Department of Energy
James Waldecker	Ford
Whitney Collela	GAIA Energy Research Institute
Anusorn Kongkanand	General Motors
YuYe Jay Tong	Georgetown University
Hui Xu	Giner
Ting He	Idaho National Laboratory
Jian Xie	Indiana University-Purdue University Indianapolis
Le Xin	Indiana University-Purdue University Indianapolis
Lior Elbaz	Israel Fuel Cells Consortium, Institute of Nanotechnology and Advanced Materials
Jonathan Sharman	Johnson Matthey, U.K.

Andrew Dattelbaum	Los Alamos National Laboratory
Hoon Chung	Los Alamos National Laboratory
Ted Holby	Los Alamos National Laboratory
Laura Barber	Los Alamos National Laboratory
Ulises Martinez	Los Alamos National Laboratory
Piotr Zelenay	Los Alamos National Laboratory
Frances A. Houle	Lawrence Berkeley National Laboratory
Anthony Vanbuuren	Lawrence Livermore National Laboratory
Scott Calbrese Barton	Michigan State University
Jacob LaManna	National Institute of Standards and Technology
Huyen Dinh	National Renewable Energy Laboratory
Kenneth Neyerlin	National Renewable Energy Laboratory
Thomas Gennet	National Renewable Energy Laboratory
Amod Kumar	Nissan, U.S.
Nilesh Dale	Nissan, U.S.
Sanjeev Mukerjee	Northeastern University
Eugene Smotkin	NuVant and Northeastern University
Karren More	Oak Ridge National Laboratory
David Wood	Oak Ridge National Laboratory
Robert Weber	Pacific Northwest National Laboratory
Yuyan Shao	Pacific Northwest National Laboratory
Webb Johnson	Pajarito Powder
Paul Matter	PH Matter
Timothy Lambert	Sandia National Laboratory
Hector Colon-Mercado	Savannah River National Laboratory
Prabhu Ganesan	Savannah River National Laboratory
Pezhman Shirvanian	Tennessee Tech University
Gang Wu	The State University of New York - Buffalo
Steven Chuang	The University of Akron
Hongfei Jia	Toyota Institute of North America
Iryna Zenyuk	Tufts University
Magda Lowisz	UK Trade & Investment, British Consulate-General, Chicago
Paul DiGregorio	Unchained Labs
Hong Yang	University of Illinois, Urbana-Champaign
Yangchuan (Chad) Xing	University of Missouri