V.I.3 Characterization of Fuel Cell Materials

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Project End Date: Project continuation and direction
determined annually by DOE

Overall Objectives

- Identify, develop, and optimize novel high-resolution imaging and compositional/chemical analysis techniques, and unique specimen preparation methodologies, for the μm- to sub-Å-scale characterization of material constituents comprising fuel cells (electrocatalysts, supports, ionomer films).

- Understand fundamental relationships between the material constituents within fuel cell membrane electrode assemblies (MEAs) and correlate these data with stability and performance as per guidance/input from the fuel cell community.

- Integrate microstructural characterization within other DOE fuel cell projects.

- Apply advanced analytical and imaging techniques for the evaluation of microstructural and microchemical changes to elucidate microstructure-related degradation mechanisms contributing to fuel cell performance loss.

- Make capabilities and expertise available to broad fuel cell research community.

Fiscal Year (FY) 2014 Objectives

- Establish several new collaborations with fuel cell manufacturers and researchers to identify and quantify fuel cell materials degradation mechanisms and to characterize new fuel cell materials.

- Follow-on to studies conducted in FY 2013 to image (map) and quantify the through-thickness distribution of ionomer thin films within catalyst layers.

- Study microstructural origin of compression/compaction observed in cathode catalyst layers during carbon corrosion accelerated stress tests (ASTs).

- Continue development of in situ electrochemical transmission electron microscopy methods to study degradation of catalyst and support materials.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(A) Durability

(C) Performance

Technical Targets

This project is focused on conducting fundamental characterization studies on the stability of individual material constituents comprising fuel cell MEAs. Of primary importance is relating electrode microstructural/material changes occurring during electrochemical aging with measured fuel cell durability and performance. Insights gained through extensive microstructural studies will be applied toward the design and manufacture of catalysts and catalyst supports that meet the DOE 2017 and 2020 targets for integrated proton exchange membrane (PEM) fuel cell power systems and fuel cell stacks operating on direct hydrogen for transportation applications (listed in Table 1).

TABLE 1. Technical Targets: Electrocatalysts for Transportation Applications

Characteristic	Unit	2011 Status	2017 Target	2020 Target
PGM Total Content (both electrodes)	g/kW (rated)	0.19	0.125	0.125
PGM Total Loading	mg PGM/cm^2 electrode area	0.15	0.125	0.125
Loss in Initial Catalytic Activity	% mass activity loss	48	<40	<40
Electrocatalyst Support Stability	% mass activity loss	<10	<10	<10
Mass Activity	A/mg Pt @ 900 mV	0.24	0.44	0.44
Non-PGM Catalyst Activity per Volume of Supported Catalyst	A/cm^2 @ 800 mV	60 (at 0.8 V) 165 (extrapolated from >0.85V)	300	300

PGM – Pt group metal

FY 2014 Accomplishments

- Completed parametric study with General Motors (GM) to identify the proper electron microscopy imaging and analysis conditions to compositionally map and quantify ionomer distributions at multiple length scales within MEAs, e.g., through-thickness distributions within catalyst layers (100-nm level) and surrounding individual pores within catalyst layers (<10-nm level). Results from this study have recently been accepted for publication in the *Journal of The Electrochemical Society* and represents a successful collaboration between ORNL, GM, and Clarkson University.

- Established a new collaboration with Ford to study catalyst dispersions on various catalyst support structures using X-ray photoelectron spectroscopy, high-resolution scanning transmission electron microscopy (STEM), and electron energy loss spectroscopy (EELS).

- Correlated initial Pt dispersions with localized regions of accelerated carbon corrosion in cathode catalyst layers subjected to ASTs, the results of which were used to further quantify observed differences in MEA performance based on the type of carbon support used and provided additional insight regarding cathode thinning mechanisms.

- Collaborated with FuelCell Energy to characterize novel PEM fuel cell membranes and identify degradation mechanisms as a function of aging protocols.

- Initiated collaboration with the University of Tennessee and 3M to characterize the effect of Pt loading on the stability and performance of MEAs prepared with low-surface-area carbon (LSAC) supports. Two students from Tom Zawodzinski's University of Tennessee group work at ORNL to conduct the microscopy studies to identify ionomer distrubutions, Pt dispersions, and degradation mechanisms as a function of Pt loading on LSAC.

- Demonstrated initial in situ electrochemical microscopy results for Pt/C in a dilute H_2SO_4 electrolyte (Pt supported on pyrolyzed carbon nanofibers prepared from polypyrrole supplied by Los Alamos National Laboratory); further optimization of the liquid cell is required to quantify electrochemical behavior.

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INTRODUCTION

PEM fuel cells are being developed for future use as efficient, zero-emission power sources. However, the performance of PEM fuel cells degrades with time at elevated temperature and relative humidity during electrochemical aging in automotive and stationary applications. Performance degradation can be directly attributed to the durability of individual material constituents comprising the MEA, including the electrocatalyst, catalyst support, recast ionomer, polymer membrane, and gas diffusion layer/microporous layer. The structural and chemical degradation mechanisms contributing to performance loss have not been fully quantified. The Microstructural Characterization Project at ORNL has been focused on forming collaborative relationships with numerous industrial PEM fuel cell developers/manufacturers, universities, and national laboratories, to apply ORNL's advanced electron microscopy techniques and expertise to characterize as-fabricated (fresh) fuel cell materials (individual constituents and/or materials incorporated in fresh MEAs), MEAs subjected to ASTs designed to degrade specific MEA components, and field-aged MEAs, with the ultimate goal of establishing critical processing-microstructure-performance correlations to elucidate the individual materials changes contributing to measured MEA degradation, performance loss, and failure. Understanding the structural and compositional changes of the materials comprising MEAs during electrochemical aging will allow for the implementation of materials-based mitigation strategies required for optimizing PEM fuel cell durability and performance.

APPROACH

The microstructural characterization task utilizes advanced electron microscopy analysis techniques to characterize the individual material components comprising PEM fuel cells, before and after incorporation into an MEA, and after electrochemical aging. Our approach is focused on identifying and optimizing novel high-resolution imaging and compositional/chemical analysis techniques, and developing unique specimen preparation methodologies, for the μm-to-Å-scale characterization of the material constituents of fuel cell MEAs (electrocatalysts, catalyst supports, recast ionomer films, membranes, etc.) ORNL applies these advanced analytical and imaging techniques for the evaluation of the microstructural and microchemical characteristics of each material constituent and correlates these observations with fuel cell performance (aging studies are conducted at the collaborator's laboratories). These studies are designed to elucidate the materials-based microstructure-related degradation mechanisms contributing to fuel cell performance loss. Most importantly, ORNL is making the techniques and expertise available to fuel cell researchers outside of ORNL via several mechanisms (1) work for others (proprietary) research, (2) ORNL User Facilities (e.g., Center for Nanophase Materials Sciences), and (3) collaborative non-proprietary research projects via the Microstructural Characterization Project that are consistent with ORNL's research activities.

RESULTS

The primary focus of research conducted in FY 2014 has been on identifying the proper microscopy conditions to characterize ionomer distributions at multiple length scales (on the 100-nm scale and the ~5-nm scale) within catalyst layers through collaborations with GM and Ballard. This research was initiated in FY 2013 by studying model systems (Nafion® thin films supported on nanostructured thin film catalysts and silicon substrates) and continued through FY 2014 with studies focused on quantifying the distribution of ionomer layers within MEAs.

Model substrates were initially prepared to identify the proper microscopy imaging and analysis conditions that were required to minimize electron beam damage (primarily radiolysis) during evaluation of the ionomer. The primary microscope variables assessed were the effect of accelerating voltage, electron dose, and specimen temperature on F-loss. Figure 1 summarizes the results of this parametric study for thin Nafion® films (ranging from 5-25 nm thick) and clearly shows that analysis of ionomer films to minimize F-loss should be conducted at higher voltages (200 kV), low electron doses, and with cryogenic cooling (temperatures less than
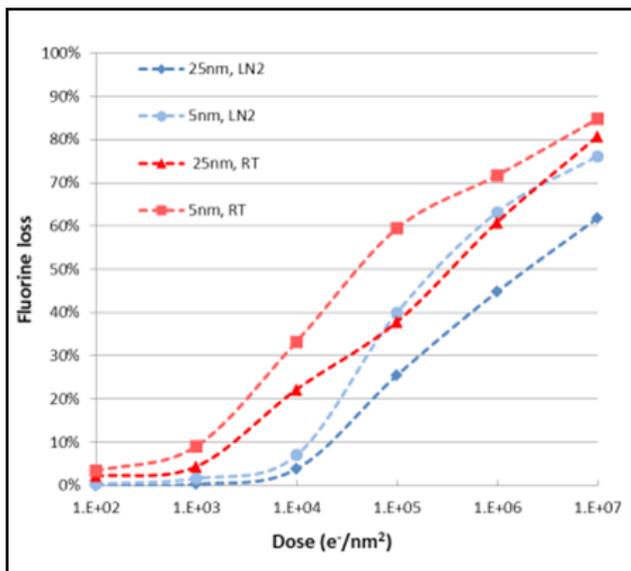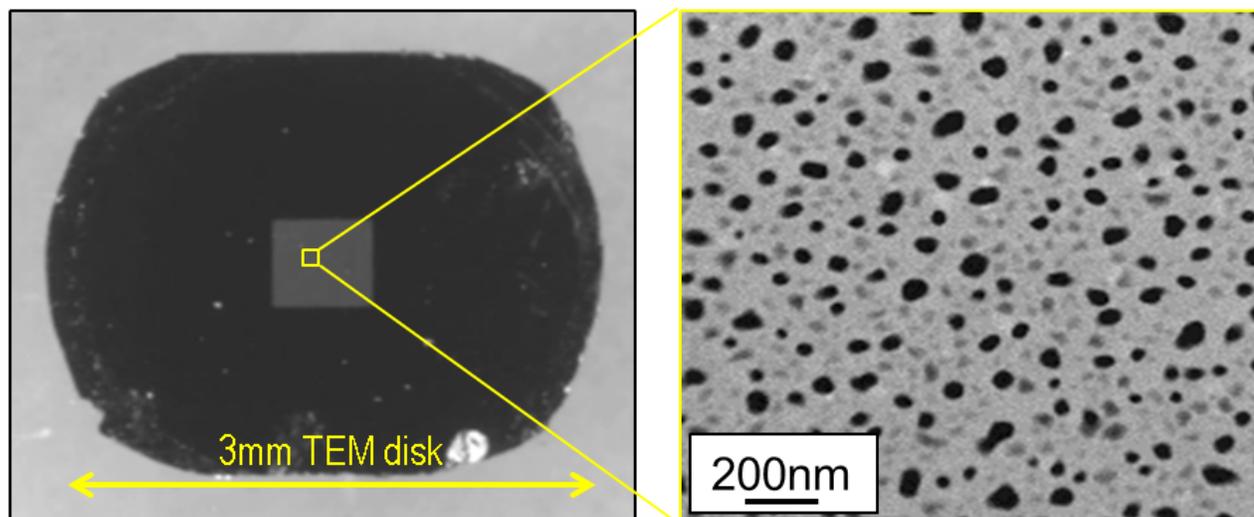
Flourine loss as a function of electron dose @ 60kV during STEM-EELS
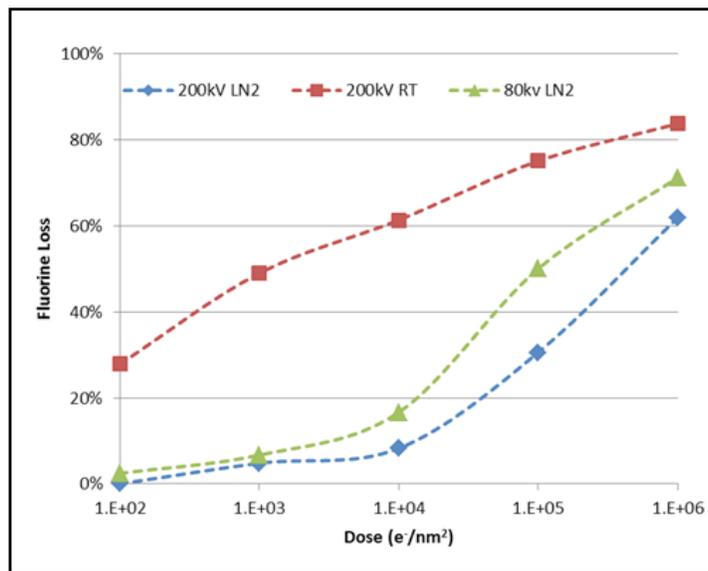
Flourine loss as a function of voltage and specimen cooling during STEM-EDS

TEM - transmission electron microscope

FIGURE 1. STEM-EELS and STEM-EDS data acquired from Nafion® thin films suspended across nanoporour silicon—microscope parameters (accelerating voltage, electron dose, and specimen temperature) were varied to identify conditions to minimize fluorine loss.

-100°C). When combined, a 2-3X decrease in beam damage can be achieved.

As part of an ongoing collaboration with GM and using the "lessons learned" from the initial Nafion® thin film characterization study using model substrates, the through-electrode-loading variation of the ionomer distributions were studied for two different electrode geometries to understand the effect of underlying microporous layers on the ionomer distribution. The Pt/C electrode layers were coated either on a sacrificial ethylene-tetrafluoroethylene co-polymer decal (catalyst coating on decal or CCD) or directly on the diffusion media (catalyst coating on diffusion media or CCDM). The ionomer/carbon (I/C=1) ratio and the Pt loading were kept constant for both the CCD and CCDM electrodes (same ink formulation was used to prepare both electrodes). Thin cross-sections were prepared by ultramicrotomy, then cryogenically cooled to -105°C in the electron microscope to limit the rate of F-loss under the electron beam. Energy dispersive X-ray spectroscopy (EDS) spectrum images were recorded of each electrode, then quantified to determine the Pt:F ratio through the electrode layer thickness. As shown in Figure 2, two different I/C profiles were observed for the CCD and CCDM samples. The I/C profile for the CCD electrode (green) exhibits a bowed profile, with a higher ionomer loading at both the top and bottom surfaces of the electrode and a slightly lower ionomer content in the center. The CCDM electrode exhibits an overall lower ionomer content (I/C=0.6) as well as a lower local ionomer content at the diffusion media interface, indicating the ionomer is able to easily leach out the back of the electrode and move tens of microns deep into the diffusion media. This case study clearly demonstrates that quantitative ionomer measurements can be performed in STEM by mitigating electron beam damage through controlled electron beam dose, sample cooling, and using high accelerating voltages. This result is comparable to scanning transmission X-ray microscopy performed using a synchrotron source. We are currently working with Adam Hitchcock at McMaster University to directly compare STEM-based analyses with scanning transmission X-ray microscopy acquired on the exact same areas of microtomed samples.

Two spectroscopic techniques, STEM-based EELS and EDS, were used to map and quantify the ionomer distribution within fuel cell electrodes with high spatial resolution such that much finer scale features can be resolved. In collaboration with CEA-Grenoble, France, a large-solid-angle EDS system was used to map C, Pt, and F within a partially embedded CCD electrode with an I/C of 1.5 (Figure 3). Multivariate statistical analysis combined with principal component analysis (PCA) methods were applied to the EDS data to improve the ability to identify small-signal features and identify the chemically relevant components in the spectrum image. The score image or "PCA map" in Figure 3 shows clear resolution of the ionomer strands (less than 10 nm thick and shown for component #2 corresponding to fluorine in green) and larger regions of "clumped" ionomer
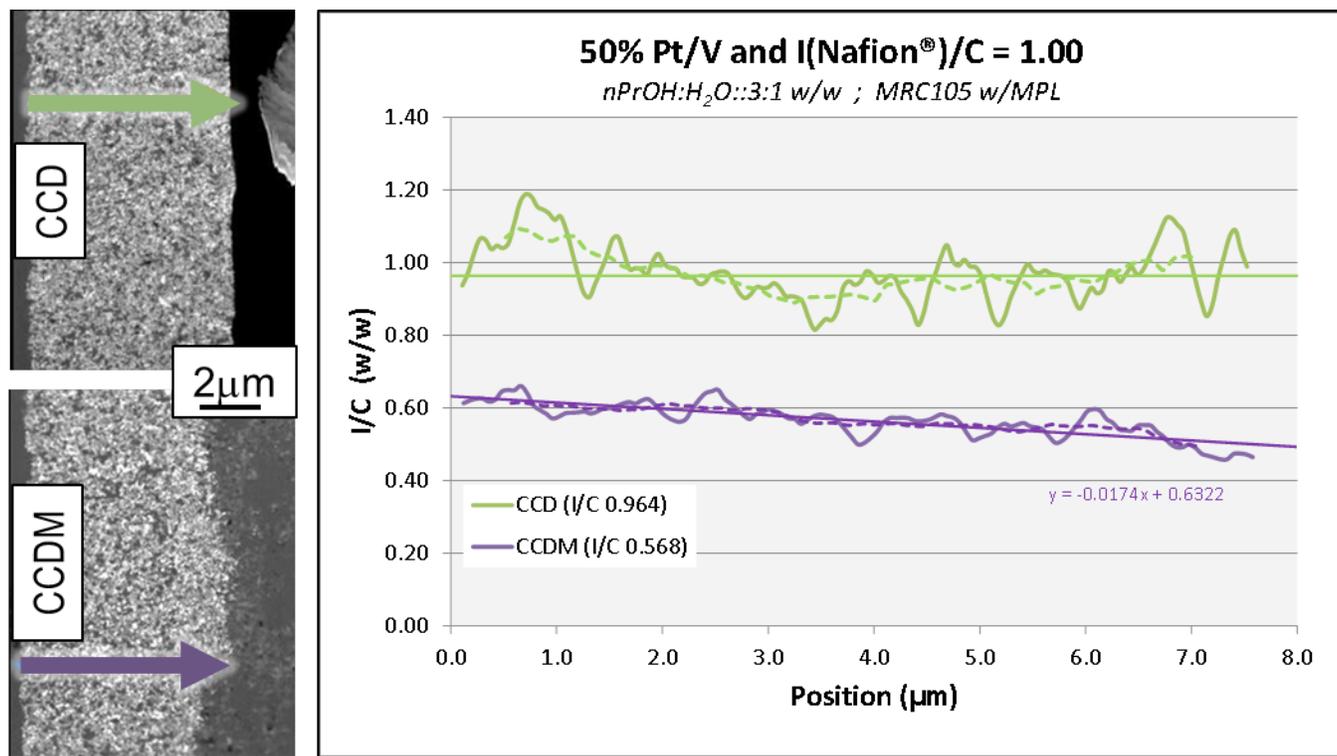

FIGURE 2. I/C profiles (STEM-EDS) acquired across the entire electrode thickness, comparing CCD and CCDM electrode profiles.
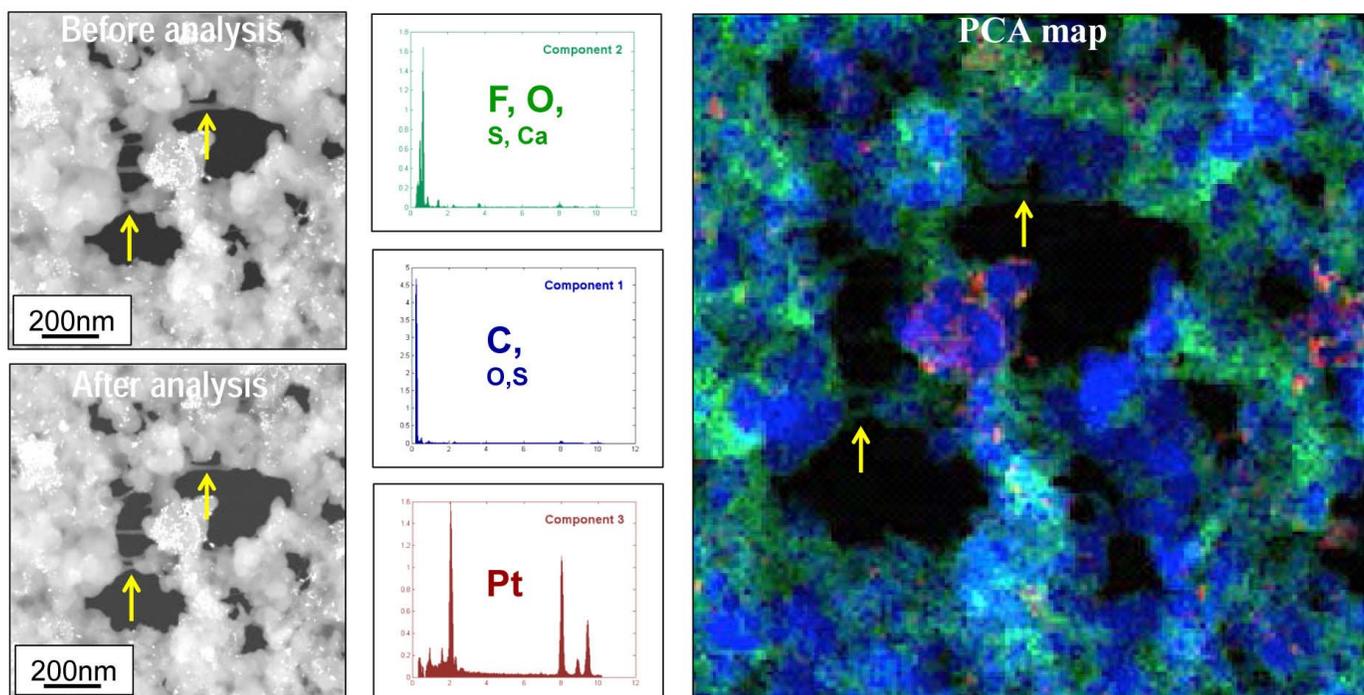
FIGURE 3. EDS Maps Acquired from a Region of a Partially Embedded CCD Electrode (Data acquired in an FEI Osirus TEM/STEM equipped with large solid-angle SDD with pixel size of 5 nm, 200-kV operating voltage, liquid nitrogen cooling, and electron dose of 4×10^6 e$^-$/nm^2. Multivariate statistical analysis-PCA methods applied to "denoise" spectra).

and thicker ionomer films on the carbon support (also shown in green).

By utilizing a cryogenic specimen holder, the loss of F due to electron beam interactions was greatly reduced, such that thin strands (<10-nm) of ionomer could be detected and analyzed. By utilizing in-house expertise with PCA, very weak F signals could be amplified, leading to a much clearer view of the thin ionomer films within the electrode. These results show a significant step forward in mapping the ionomer distributions within the electrodes of MEAs with high spatial resolution (<10-nm) in the TEM/STEM.

CONCLUSIONS AND FUTURE DIRECTIONS

ORNL's microstructural studies continue to provide insight regarding the structural and compositional factors of MEA material components that ultimately contribute to the stability and durability of fuel cells. We have focused primarily on characterizing ionomer distributions within catalyst layers, further understanding carbon corrosion mechanisms, and electrocatalyst evaluation during FY 2014, and will continue to support these studies in FY 2015 through collaborations with industrial and academic partners while emphasizing new studies focused on optimizing electrocatalyst interactions and dispersion on novel carbon supports (e.g., LSAC):

- Continue to establish new collaborations with fuel cell manufacturers and researchers to identify and quantify fuel cell materials degradation mechanisms and to characterize new fuel cell materials. Input from the Fuel Cell Tech Team, reviewer comments from the Annual Merit Review, and collaborations are key to the success of this Microstructural Characterization Project and to identify critical research directions.

- Through a systematic study using model systems, the proper imaging and analysis conditions were established for studying ionomer layers and through-thickness ionomer distributions. This work will be expanded in FY 2015 to specifically focus on aging effects within cathode catalyst layers as well as electrode/membrane interfaces.

- Combine ionomer imaging and microanalysis with modeling efforts to identify ionomer interactions with different carbon surfaces (this task has already been initiated). Further characterize ionomer distributions through the use of high-resolution three-dimensional electron tomography studies (both structure and compositional tomography).

- Perform dispersion optimization studies for ionomer and Pt on LSAC.

- Continue the development, optimization, and application of in situ electrochemical TEM/STEM—correlate with bench-scale (rotating disk electrode) catalyst testing and

apply to other fuel cell material components (e.g., Pt on other supports, catalyst nucleation and growth studies, with/without ionomer, etc.).

FY 2014 PUBLICATIONS/PRESENTATIONS

1. G. Wu, K.L. More, P. Xu, H.L. Wang, M. Ferrandon, A.J. Kropf, D.J. Myers, S.G. Ma, C.M. Johnston, and P. Zelenay," *Chemical Communications* 49[32] 3291-3293 (2013).

2. Y. Garsany, A. Epshteyn, K.L. More, and K.E. Swider-Lyons, "Oxygen Electroreduction on a Nanoscale Pt/[TaOPO$_4$/VC] and Pt/[Ta$_2$O$_5$/VC] in Alkaline Electrolyte," *ECS Electrochemistry Letters* 2[10] H46-H50 (2013).

3. C.-N. Sun, K.L. More, G.M. Veith, and T.A. Zawodzinski, "Composition Dependence of the Pore Structure and Water Transport of Composite Catalyst Layers," *Journal of the Electrochemical Society* 160[9] F1000-F1005 (2013).

4. M. Li, D.A. Cullen, K. Sasaki, N.S. Marinkovic, K.L. More, and R.R. Adzic, "Ternary Electrocatalysts for Oxidizing Ethanol to Carbon Dioxide: Making Ir Capable of Splitting C-C," *Journal of The American Chemical Society* 135[1] 132-141 (2013).

5. S. Pylypenko, A. Borisevich, K.L. More, A.R. Corpuz, T. Holme, A.A. Dameron, T.S. Olson, H.N. Dihn, T. Gennett, and R. O'Hayre, "Nitrogen: Unraveling the Secret to Stable Carbon-supported Pt-alloy Electrocatalysts," *Energy & Environmental Science* 6[10] 2957-2964 (2013).

6. K.A. Perry, K.L. More, E.A. Payzant, R.A. Meisner, B.G. Sumpter, and B.C. Benicewicz, "A Comparative Study of Phosphoric Acid-doped m-PBI Membranes," *Journal of Polymer Science B* 52[1] 26-35 (2014).

7. C. Chen, Y.J. Kang, Z.Y. Huo, Z.W. Zhu, W.Y. Huang, H.L.L. Xin, J.D. Snyder, D.G. Li, J.A. Herron, M. Mavrikakis, M. Chi, K.L. More, Y.D. Li, N.M. Markovic, G.A. Somorjai, P.D. Yang, and V.R. Stamenkovic, "Highly Crystalline Multimetallic Nanoframes with 3D Electrocatalytic Surfaces," *Science* 343[6177] 1339-1343 (2014).

8. W. Gao, G. Wu, M.T. Janicke, D.A. Cullen, R. Mukundan, J.K. Baldwin, E.L. Brosha, C. Galande, P.M. Ajayan, K.L. More, A.M. Dattelbaum, and P. Zelenay, "Ozonated Graphene Oxide Film as a Proton Exchange Membrane," *Angewandte Chemie International Edition* 53[14] 3588-3593 (2014).

9. Invited Presentation: K.L. More, D.A. Cullen, and K.S. Reeves, "Application of Advanced Microscopy to Elucidate Materials Degradation Mechanisms in PEM Fuel Cells," TMS Pacific Rim Conference on Advanced Materials, Waikaloa, HI - August 4–8, 2013.

10. Invited Presentation: D.A. Cullen, H.M. Meyer, K.S. Reeves, D. Coffey, and K.L. More, "Developing Fuel Cell Technologies Through Electron Microscopy," Microscopy & Microanalysis 2013, Indianapolis, IN - August 4–8, 2013.

11. Invited Presentation: K.L. More, D.A. Cullen, and K.S. Reeves, "Characterization and Optimization of Cathode Materials for PEM Fuel Cells," 246th American Chemical Society National Meeting, Indianapolis, IN – September 8, 2013.

12. Contributed Presentation: D.A. Cullen, H. Meyer, K.L. More, R. Koestner, R. Kukreja, S. Minko, O. Trotsenko, A. Tokarev, and L. Guetaz, "Characterization of Thin Ionomer Films," 224th ECS Meeting, San Francisco, CA – October 27 – November 1, 2013.

13. Invited Presentation: K.L. More, D.A. Cullen, and K.S. Reeves, "Correlating Catalyst Stability and Degradation with Cathode Materials Interactions in PEM Fuel Cells," 2013 MRS Fall Meeting, Boston, MA – December 1–5, 2013.

14. Invited Presentation: K.L. More, D.A. Cullen, and K.S. Reeves, "Advanced Microscopy Methods to Understand Materials Degradation in PEM Fuel Cell MEAs," 556th WE-Herraeus Seminar Analytical Tools for Fuel Cells and Batteries, Bad Honnef, Germany – March 23–26, 2014.

15. Invited Presentation: K.L. More, D.A. Cullen, and K.S. Reeves, "Microscopy of Fuel Cell Catalyst and Catalyst Support Degradation," Spring Meeting of the Materials Research Society, San Francisco, CA - April 20–24, 2014.

16. Contributed Presentation: K.L. More, R.R. Unocic, and D.A. Cullen, "In Situ Electrochemical Microscopy of PEM Fuel Cell Materials," 225th Meeting of The Electrochemical Society, Orlando, FL – May 11–15, 2014.

17. Invited Presentation: K.L. More, D.A. Cullen, and K.S. Reeves, "Correlating Catalyst Stability with Improved Cathode Materials for PEM Fuel Cells," Fuel Cells Gordon Research Conference, Bryant University, Smithfield, RI – August 3–8, 2014.

18. Contributed Presentation: D.A. Cullen, K.L. More, M. Lopez-Haro, P. Bayle-Guillemaud, L. Guetaz, M.K. Debe, D.F. van der Vliet, and A.J Steinbach, "Fine Tuning Highly Active Pt$_3$Ni$_7$ Nanostructured Thin Films for Fuel Cell Cathodes," Microscopy & Microanalysis 2014 Annual Meeting, Hartford, CT – August 3–8, 2014.