V.A.4 Characterization of Fuel Cell Materials

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

FY 2011 Objectives

- Develop new, innovative microanalysis and imaging techniques to characterize fuel cell material constituents before, during, and after electrochemical aging.
- Elucidate membrane electrode assembly (MEA) degradation and/or failure mechanisms by conducting extensive microstructural characterization using advanced electron microscopy techniques. In particular, distinguish individual materials degradation phenomena as a function of aging protocol, including catalysts, supports, ionomer, membrane, microporous layer (MPL), and gas diffusion layer (GDL).
- Develop the critical correlations between MEA microstructure, composition, and architecture, and MEA durability.
- Compare microstructural changes resulting from accelerated stress testing (AST) with microstructures observed after field aging to determine efficacy of ASTs.
- Collaborate with fuel cell component developers and manufacturers, university researchers, and other national laboratories, to evaluate fuel cell material components using electron microscopy and complimentary microstructural and compositional microanalysis techniques.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Fuel Cell Technologies Program Multi-Year Research, Development, and Demonstration Plan:

(A) Durability
(B) Cost
(C) Performance

Technical Targets

Insights gained through extensive microstructure characterization of MEA constituents will be applied toward the design and manufacture of fuel cell materials that meet the following DOE 2015 MEA targets:

- Cost: <$5/kW
- Durability with cycling: 5,000 hours
- Operating temperatures: <120°C
- Total catalyst loading (for both electrodes): 0.2 g/kW (rated)
- Extent of performance degradation over lifetime: 5%

FY 2011 Accomplishments

- Used a combination of analysis techniques and MEA samples to characterize the nature of the recast ionomer (films, pockets, etc.) within electrode structures and to understand the nm-scale phase-separated morphology consistently observed in Nafion® membranes.
- Directly compared degradation phenomena observed in "real world" field-aged proton exchange membrane fuel cell (PEMFC) MEAs with MEAs aged via AST protocols designed to enhance specific degradation mechanisms (e.g., carbon corrosion, catalyst coarsening, etc.).
- Established collaboration with Nissan to evaluate catalysts (in terms of structure, size, and morphology) deposited on a series of carbon supports exhibiting varying degrees of graphitization.
- Initiated fundamental study of Pt deposition on model carbon substrates (graphene) to understand Pt nucleation and growth mechanisms on extended graphitic surfaces.
- Established a new collaboration with General Motors to characterize a complete series of PEM fuel cell MEAs aged to accelerate membrane degradation.
- Optimized analysis parameters for the compositional analysis of catalyst nanoparticles via aberration-corrected scanning transmission electron microscopy (STEM), including elemental mapping.
- Host an international collaborator from Fuel Cell Cubic (FCC), Tokyo, Japan, to characterize new materials for PEM fuel cells. The FCC researcher will work at ORNL for the next year.

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Introduction

PEMFCs are being developed for future use as efficient, zero-emission power sources. The performance of PEMFCs degrades during electrochemical aging, and this performance

degradation can be correlated directly with the durability of individual components comprising the MEA, e.g., the electrocatalyst, catalyst support, ionomer, and/or the proton-conducting polymer membrane. Many of the material's microstructural and compositional attributes that contribute to decreased stability of the MEA during long-term electrochemical aging are not yet fully understood and have not directly been correlated with performance as a function of aging protocols. In order to reach DOE's technical targets for MEAs, correlating the individual component materials structure, composition, and interrelationships within the MEA layers with the measured performance as a function of different aging conditions, is critical for applying materials optimization practices to increase fuel cell materials durability for specific applications.

During the course of this project, the Microstructural Characterization Program at ORNL has been focused on forming collaborative relationships with a wide range of industrial PEMFC developers/manufacturers, university researchers, and national laboratories, to utilize advanced microscopy techniques as a means to evaluate as-fabricated and electrochemically aged PEMFC MEAs and, most importantly, to characterize individual PEMFC material components and relate structural and chemical changes of these materials to the performance degradation resulting from particular aging conditions. These studies are used to establish the critical processing-microstructure-performance relationships that can then be reported to the MEA producers (and in many circumstances, the fuel cell community as a whole), which can result in improved stability of the MEA materials, thereby enhancing MEA performance and lifetimes. Understanding the structural and compositional changes to the materials comprising the MEA during electrochemical aging will allow for the implementation of processing changes and critical materials development that are required for optimized PEMFC durability and performance. The techniques developed as part of this "baseline" research project are being applied to other fuel cell systems.

Approach

The microstructural characterization task utilizes advanced electron microscopy analysis techniques to characterize the individual material components comprising PEMFCs, 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-Å-scale characterization of the material constituents of fuel cells (electrocatalyst, catalyst support, ionomer, membrane, etc.). ORNL applies these advanced analytical and imaging techniques for the evaluation of the microstructural and microchemical changes of each material constituent and correlating these observations with fuel cell performance (aging studies are conducted

at the collaborator's laboratories). These studies are designed to elucidate the 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., Shared Research Equipment User Facility, Center for Nanophase Materials Science), and (3) collaborative non-proprietary research projects via the Microstructural Characterization Project that are in line with ORNL's "baseline" research activities.

Results

Ionomer Characterization

High-resolution microscopy characterization of the recast ionomer "film" distributed within the electrodes of a PEMFC poses numerous challenges, the most critical being the inhomogeneous and non-continuous nature of the ionomer. Typically, the ionomer film is not a uniform-thickness film surrounding the Pt catalysts on carbon black (Pt/CB) supports, but tends to exist in pockets/clumps in localized regions between Pt/CB particles or agglomerates, which have a high number density of Pt nanoparticles. Isolating ionomer regions for high spatial resolution chemical/compositional analysis or imaging is extremely difficult. To study the ionomer phase within an electrode, it was necessary to prepare electrodes with greater amounts of ionomer to create isolated "ionomer-only" regions. Thus, rather than characterizing electrodes with 28-30 wt% ionomer, the samples used for this work contained ~61 wt% ionomer, which resulted in dense electrodes having filled porosity, as shown in Figure 1 where a large pore between Pt/CB regions is completely filled with ionomer. The large ionomer-filled-pore regions (generally >50 μm) were sufficiently large for microanalysis via electron energy loss spectroscopy (EELS) in the transmission electron microscope (TEM)/STEM, and a bulk electrode content high enough for comparing with X-ray photoelectron spectroscopy (XPS) characterization. In addition, these dense electrodes were prepared for TEM/STEM by cryo-microtomy using no epoxy embedding (ensuring that the only polymer present in the sample was the ionomer).

The XPS results acquired from the electrode containing ~61 wt% were also compared with XPS data for a Nafion® 212 membrane. It is important to note that the XPS data were acquired from an electrode that was "chopped up" such that the ionomer inside the electrode (filling pores) was analyzed rather than any ionomer skins present on the bulk electrode surfaces. The primary conclusions from the bulk XPS analyses were (1) the Nafion® 212 membrane exhibited more CF_2-type (PTFE) bonding (the ionomer was depleted in fluorine (CF_2/CF_3=3.8) compared to the membrane (CF_2/CF_3=5.0)) and (2) the $-SO_3$ (sulfonate) peak shifts to a lower binding energy for the 61 wt% ionomer sample, which is consistent with the sulfonate groups no longer being
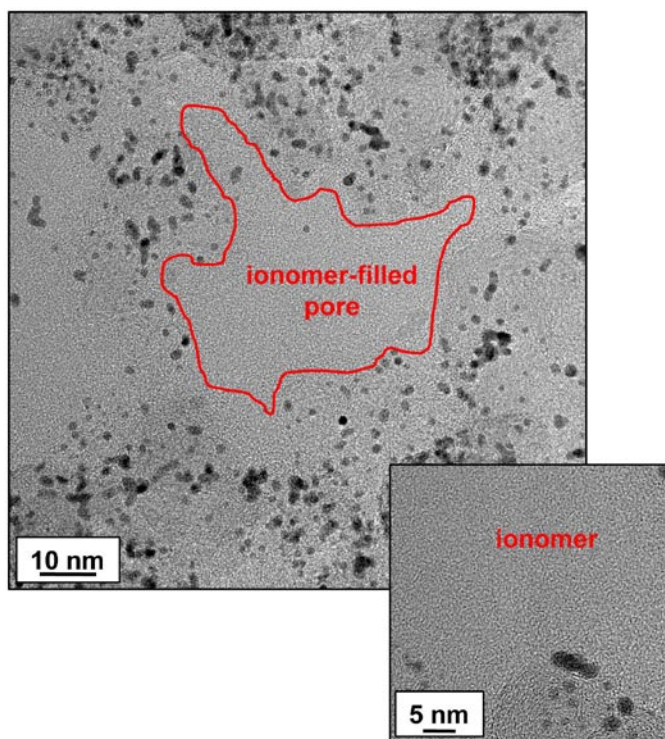
FIGURE 1. To isolate ionomer regions for TEM/STEM/EELS analysis, electrodes were prepared such that the pores were filled with ionomer (61 wt% ionomer mixed with Pt/C decal-electrodes).

influenced by or associated with the $-CF_2$ backbone, i.e., these groups have been removed from the $-CF_2$ backbone or the sulfonate groups are located in a sub-surface position. EELS spectrum images (SI) were acquired in the STEM within the individual ionomer-filled pores surrounded by Pt/CB particles. A typical ionomer pocket used for EELS-SI is shown in the STEM image in Figure 2 together with the derived carbon and sulfur EELS maps. Phase

separation within the ionomer is clear – the sulfur (and oxygen – not shown) is associated with the Pt/CB region, whereas the carbon (and fluorine, not shown) is uniformly present within the ionomer filling the pore. Additionally, energy dispersive spectroscopy (EDS) analysis of an MEA (prepared with a "standard" ionomer content of 28 wt%) consistently shows higher sulfur associated with Pt/CB regions. These data are consistent with the XPS data from the ionomer that shows clear "localization or separation" of the sulfonate groups away from the Teflon®-backbone of the Nafion® and the existence of the sulfonates in a sub-surface position. Separation of the hydrophilic sulfonate groups will have the greatest impact on the confinement of water and water uptake within the electrode. In a recent article by Kim and Pivovar [1], PFSA membranes are described as "highly phase-contrasted polymers" due to the extreme hydrophobicity of the CF_2-backbone and mobility of the SO_3-group – phase contrast refers to the extent of separation between the hydrophilic and hydrophobic regions. The ionomer within the electrodes appears to be more phase-contrasted than the membrane and according to [1], this should have the greatest impact on water uptake.

Initiation of Pt Nucleation and Growth Studies Using "Model" Carbon Surfaces

For fuel cell applications, electrocatalysts are currently supported on a variety of carbon black (CB) supports, each exhibiting different degrees of graphitization. These include Ketjen black and Vulcan (high surface area supports) and their heat-treated counterparts, where heat treatments are employed to enhance the graphitic nature of the CB. The high surface area CB support structures are typically textured turbostratic carbon with a particle (domain) size of ~4-5 nm, where the rounded surfaces of the supports are comprised of highly aligned domains that each terminate predominantly with hexagonal carbon (002) planes on the surface. This "mosaic structure" is shown in Figure 3a,
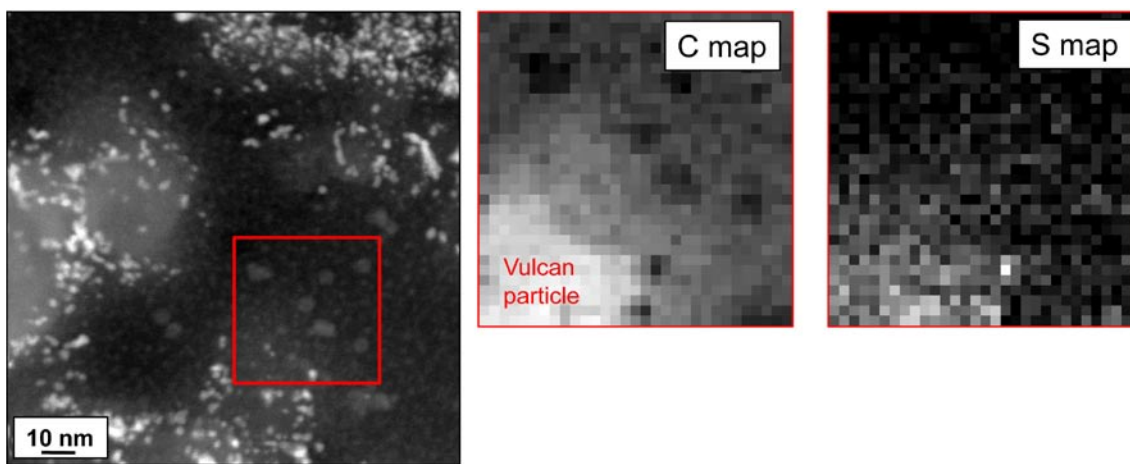

FIGURE 2. EELS spectrum imaging data from 61 wt% ionomer sample. Sulfur was consistently associated with Vulcan Pt/CB regions within the electrode structure.
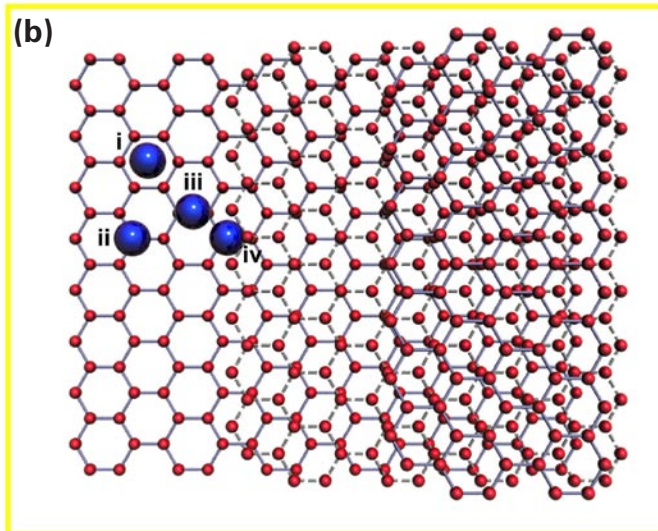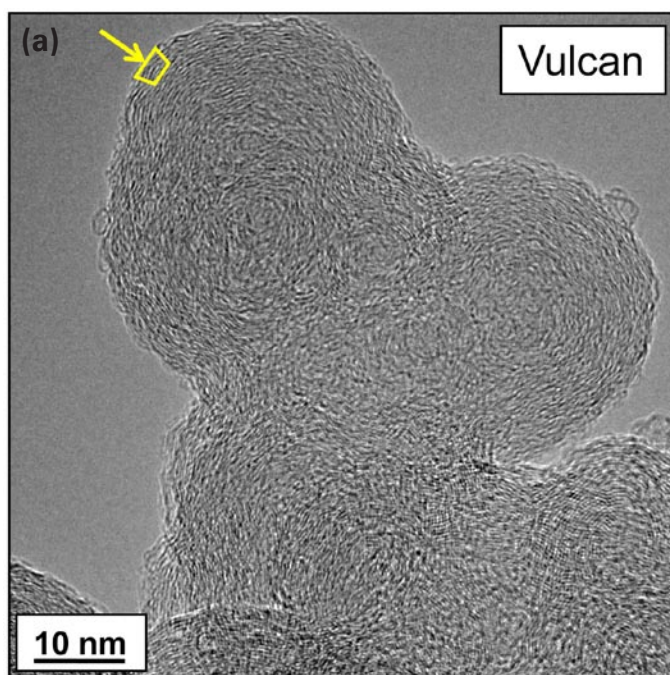
FIGURE 4. Z-contrast STEM image showing the different layers of graphene and individual Pt adatoms (brightly imaging) deposited on surface. Note that all Pt atoms deposit at edge sites and not on sites associated with the sp^2-bonded (002) surfaces.

FIGURE 3. (a) Vulcan particle with overlay of typical carbon crystalline domain (yellow). (b) Schematic of (002) graphene surface showing possible Pt atom deposition sites (i) center of 6-atom carbon ring, (ii) top of single carbon atom, (iii) "bridge" site between two carbon atoms, and (iv) step/edge between graphene layers.

where a typical domain is shown by the yellow outline on the TEM image of a Vulcan CB particle. The (002) domain surfaces can be modeled using graphene films, since all nanostructured carbons have "graphene-based" structures, i.e., layered sheets of graphene comprise highly ordered graphite. In this way, sp^2-bonded graphene sheets/films (single- or multi-layered) are being used (in place of CB spheres that are difficult to characterize by TEM/STEM) to identify preferred Pt deposition sites on CB surfaces and to study Pt nucleation and growth mechanisms. These
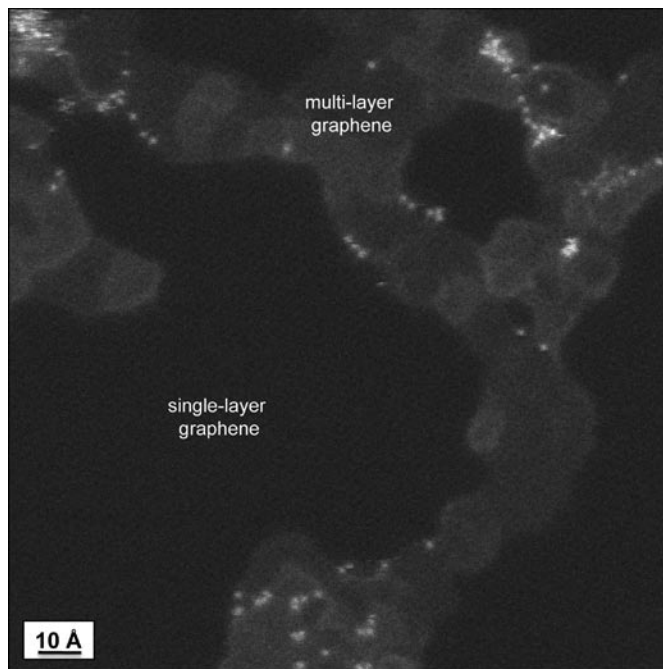
studies will also be used to identify more stable sites for Pt deposition that can enhance catalyst stability.

Several critical steps have been taken to initiate this fundamental Pt nucleation and growth study in FY 2011. We have identified a source of continuous, multi-layered graphene films supported on the 3 mm Cu grids necessary for the TEM/STEM experiments (source - the Graphene Supermarket). These films are relatively pure/clean and exhibit large areas of single-layer graphene as well as defects – steps/edges, vacancies, etc. – at the regions where graphene sheets overlap. We have also successfully deposited very low levels of Pt (<3 wt%) directly on the 3 mm graphene-coated Cu grids using a $[Pt(NO_3)_2 \cdot (NH_3)_4]$ Pt precursor, such that individual Pt atoms as well as small Pt clusters are deposited, which is the desired loading and dispersion. In this way, we can identify the preferred site for Pt deposition and in the future, the most stable site. Possible sites available on the graphene films for Pt deposition are illustrated in Figure 3b and include (i) the center of the 6-atom carbon ring, (ii) on top of a carbon atom, (iii) the "bridge" site between two carbon atoms, and (iv) the step/edge at the sheets layers. Figure 4 shows a preliminary Z-contrast STEM image of individual Pt atoms (bright spots) distributed on graphene sheets. This preliminary data indicates that Pt atoms prefer to deposit at the edge sites where layers of graphene overlap (from single-layer to double-layer, or double-layer to triple-layer, etc.), and in fact, these are the only sites where Pt atoms were identified on the film surface. This is initial experimental

evidence showing that Pt atoms do not deposit on, nor do clusters nucleate on, the sp^2-bonded surfaces of graphite, but preferentially locate on defects. Additional research is planned to fully explore the adsorption, nucleation, and growth of Pt on carbon (002) surfaces such that carbon structures can be optimized to stabilize Pt electrocatalysts for use in fuel cells, including theoretical modeling (density functional theory calculations), Pt loading studies, introduction of defects in the carbon structure, and heating experiments.

Conclusions and Future Directions

- Complete Pt nucleation and growth study using "model" graphene surfaces, including density functional theory calculations for comparison with experimental results, and in situ heating experiments.

- Correlate microstructural/compositional observations with AST protocols (automotive and stationary), especially related to catalyst coarsening and migration, carbon corrosion, membrane degradation – this is a continuing priority of this research project and has been part of ongoing and proposed "future" research each year.

- Acquire the proper series of durability-tested MEAs to further understand the degradation of polymer electrolytes (membrane and ionomer in electrode) using a combination of characterization techniques – continue ionomer studies initiated in FY 2011.

- Correlate observations of Pt nucleation and growth to long-term stability via in situ liquid electrochemistry experiments.

- Continue to establish collaborations with industries, universities, and national laboratories (including access via ORNL User Facilities) to facilitate "transfer" of unique capabilities.

- Support new DOE projects with microstructural characterization and advanced characterization techniques, which remains the primary focus of this project.

FY 2011 Publications/Presentations

1. K.L. More, K.A. Perry, M. Chi, and K.S. Reeves, "Carbon Support Structural Degradation Observed in PEM Fuel Cell Cathodes," *invited* presentation at 218th Meeting of The Electrochemical Society, Las Vegas, NV, October 12, 2010.

2. K.L. More, R.R. Unocic, K.A. Perry,, and K.S. Reeves, "In-Situ Microscopy of Fuel Cell Nanoparticle Catalyst and Catalyst-Support Degradation," presentation at the 2011 MRS Spring Meeting, San Francisco, CA, April 25–29, 2011.

3. V. Mazumder, M. Chi, K.L. More, and S. Sun, "Synthesis and Characterization of Multimetallic Pd/Au and Pd/Au/FePt Core/Shell Nanoparticles," *Angewandte Chemie International Edition* 49[49] 9368–9372 (2010).

4. V. Mazumder, M.F. Chi, K.L. More, and S.H. Sun, "Core/Shell Pd/FePt Nanoparticles as an Active and Durable Catalyst for the Oxygen Reduction Reaction," *Journal of the American Chemical Society* 132[23] 7848-7849 (2010).

5. L.F Xiong, K.L. More, and T. He, "Syntheses, Characterization, and Catalytic Oxygen Electroreduction Activities of Carbon-Supported PtW Nanoparticle Catalysts," *Journal of Power Sources* 195[9] 2570-2578 (2010).

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8. Y. Garsany, A. Epshteyn, A.P. Purdy, K.L. More, and K.E. Swider-Lyons, "High-Activity, Durable Oxygen Reduction Electrocatalyst: Nanoscale Composite of Platinum-Tantalum Oxyphosphate on Vulcan Carbon," *Journal of Physical Chemistry Letters* 1[13] 1977-1981 (2010).

9. K. Sasaki, J.X. Wang, H. Naohara, N. Marinkovic, K.L. More, H. Inada, and R.R. Adzic, "Recent Advances in Platinum Monolayer Electrocatalysts for Oxygen Reduction Reaction: Scale-up Synthesis, Structure and Activity of Pt Shells on Pd Cores," *Electrochimica Acta* 55[8] 2645-2652 (2010).

10. C. Wang, D. van der Vliet, K.L. More, N.J. Zaluzec, S. Peng, S. Sun, H. Daimon, G. Wang, J. Greeley, J. Pearson, A.P. Paulikas, G. Karapetrov, D. Strmcnik, N.M. Markovic, and V.R. Stamenkovic, "Multimetallic Au/FePt$_3$ Nanoparticles as Highly Durable Electrocatalysts," *Nano Letters* 11[3] 919-926 (2011).

11. C. Wang, M.F. Chi, G.F. Wang, D. van der Vliet, D.G. Li, K.L. More, H.H. Wang, J.A. Schlueter, N.M. Markovic, V.R. Stamenkovic, "Correlation Between Surface Chemistry and Electrocatalytic Properties of Monodisperse Pt$_x$Ni$_{1-x}$ Nanoparticles," *Advanced Functional Materials* 21[1] 147-152 (2011).

12. G. Wu, K.L. More, and P. Zelenay, "High-Performance Electrocatalysts for Oxygen Reduction Derived from Polyaniline, Iron, and Cobalt," *Science* 332 443-447 (2011).

References

1. Y.S. Kim and B.S. Pivovar, "Moving Beyond Mass-Based Parameters for Conductivity Analysis of Sulfonated Polymers," Annual Review of Chemical and Biomolecular Engineering Vol: 1 J.M. Prausnitz, M.F. Doherty, and M.A. Segalman, eds., pp. 123-148 (2010).