

V.A.6 Applied Science for Electrode Cost, Performance, and Durability

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direction determined annually by DOE

Objectives

- Explore impact of solvent choice in catalyst ink on fuel cell performance.
- Relate the structural and chemical properties of the ionomer in different inks to electrode performance and structure.
- Initiate use of bilayer/gradient structures in electrodes.

Technical Barriers

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

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

Technical Targets

This project engages in studies that enable cost, performance and durability improvements for electrodes, by addressing electrode processes and design criteria that are poorly defined. In Fiscal Year 2009, the structure

and chemical properties of fuel cell ink components were related to performance and durability of the final electrode structure. Insights gained from these studies will be applied toward the design and synthesis of fuel cell materials that meet the following DOE 2010 targets (Tables 3.4.4 and 3.4.12):

- Precious metal loading: 0.3 g/kW
- Cost: \$25/kWe
- Durability with cycling: 5,000 hours

Accomplishments

- Explored wide range of solvents in catalyst inks used to fabricate electrodes; observed marked effect on fuel cell performance.
- Examined structure and local chemical environment of Nafion[®] dispersed in different solvents by neutron scattering and nuclear magnetic resonance (NMR), and related the results to fuel cell performance.
- Demonstrated that solvent choice in catalyst inks has an impact on durability.
- Used transmission electron microscopy (TEM) to examine dried inks and electrode structures from different solvents; determined that all solvents used in study do not cause notable Pt displacement on carbon under our conditions, but solvent choice may have an effect on Pt particle growth during potential cycling.
- Initiated bilayer/gradient electrode work; demonstrated that Nafion[®] content changes response of electrode to humidity conditions.



Introduction

With improved electrode structures, less platinum catalyst could be used in polymer electrolyte fuel cells, reducing the cost and increasing the chances of widespread commercialization. Optimized electrode structures are also necessary to maximize durability and performance under varied conditions, such as with voltage, temperature, and humidity changes. As new catalyst materials and structures emerge, a better understanding of how to incorporate such materials into well-performing electrodes is also required.

Fuel cell electrodes are prepared by combining a dispersed, ionically-conducting polymer (ionomer) with carbon-supported Pt particles in a solvent medium. After further additions (solvents, ionic compounds, etc.), the mixture, called an ink, is painted or sprayed onto the desired surface and dried at elevated temperature.

These many steps have only been partially optimized empirically. At the end, the electrode structure must carry out three types of transport effectively: (1) electronic; (2) ionic; and (3) mass (gases and water). This is accomplished through interpenetrating networks of catalyst, ionomer, and pores, and the organization of the materials at many length scales may be important.

The purpose of this study is to examine the details of the Pt-ionomer interface, how the electrode structure evolves, and to determine how processing conditions affect the final electrode structure. Using a variety of characterization techniques that span multiple length scales, we seek to provide a more complete picture of the formation and function of electrode structure than is currently available.

Approach

The analytical capabilities of LANL have been leveraged to examine the formation of electrode structure across many length scales, including neutron scattering methods, NMR, atomic force microscopy (AFM), and TEM. These techniques allow for the correlation of data from the inks used to prepare fuel cell electrodes to the observed final electrode structure and performance. Ionomer mobility (NMR), particle size and internal structure (neutron scattering), tendency to phase-segregate (AFM), and Pt-carbon size and spatial distributions (TEM) are examples of the information that we have collected in relation to our optimization efforts.

Results

As mentioned above, fuel cell electrodes are prepared using ionomer dispersions in solvent that are combined with the catalyst. In FY 2009, we focused on understanding how the solvent choice (1) affected the structural and chemical properties of the ionomer in the dispersed and dried states, and (2) how those properties related to the observed fuel cell performance of electrodes prepared from the different ionomer dispersions. To carry out this study, a method to prepare ionomer dispersions from Nafion® 212 in a variety of solvents was developed and submitted for a patent [1]. Some additional work using bilayer electrodes was also initiated, to address a larger length scale of electrode design.

As shown in Figure 1, the performance of membrane electrode assemblies (MEAs) with cathodes prepared from inks containing different solvents varied greatly. The MEA with a cathode prepared from n-methylpyrrolidone (NMP-cathode) performed better in the kinetically-controlled region of the plot, whereas the MEA with a cathode prepared from a glycerol ink (glycerol-cathode) performed better at mass-transport controlled current densities above 0.70 V. The propylene-glycol cathode gave an intermediate

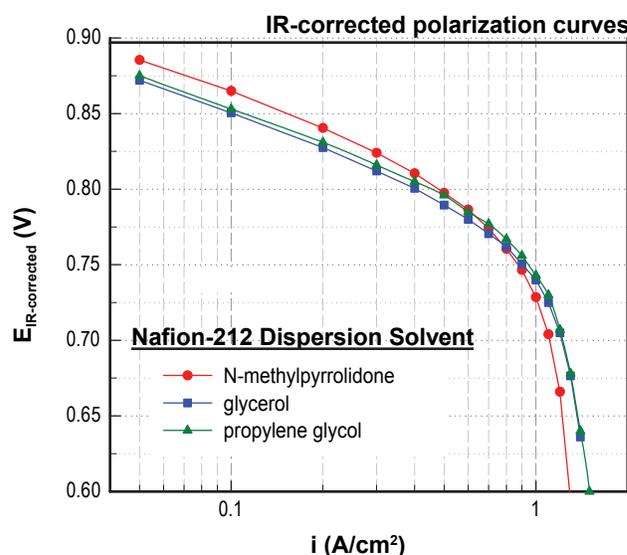


FIGURE 1. Polarization curves of fuel cell MEAs prepared with cathodes cast from ionomer dispersions containing either n-methylpyrrolidone or glycerol solvent. Cell temp. 80°C; fully humidified; backpressure: 30/30 psig; Catalyst: 20% Pt/C (E-TEK): 0.2/0.2 mgpt/cm², ionomer: Nafion® 212.

performance, but was more similar overall to glycerol. These observations raised questions about effect of solvent on the structure of the ionomer, as well as on the interactions of the catalyst and ionomer. A variety of techniques available to LANL staff were thus selected to begin to provide the required answers.

¹⁹Fluorine NMR was used to address the effect of solvent on the chemical environment of Nafion®. As shown in Figure 2, the mobilities of fluorines associated with the polymer backbone or, alternately, with the polymer sidechains are affected greatly the choice of solvent. The relative mobility of ionomer backbone and side-chain fluorines was calculated as indicated within the Figure 2 caption. In glycerol dispersion, the peaks corresponding to Nafion® backbone and sidechain fluorines are very broad, indicating decreased mobility. In contrast, in NMP or water solvent, the peaks corresponding to Nafion® fluorines are very sharp, demonstrating a higher mobility. The mobilities of the fluorines in propylene glycol were intermediate those in glycerol and NMP, but closer to glycerol, following a similar pattern to the fuel cell data.

Our working hypothesis developed from these observations is that the mobility of the polymer backbone and sidechains affects their ability to separate into phases, and that these differences may affect the final electrode structure. Indeed, our recent AFM studies of thick Nafion® films cast from glycerol-based and water-based dispersions show very different degrees of phase-separation of the hydrophobic and hydrophilic portions of the Nafion® chain [2]. Glycerol-cast films

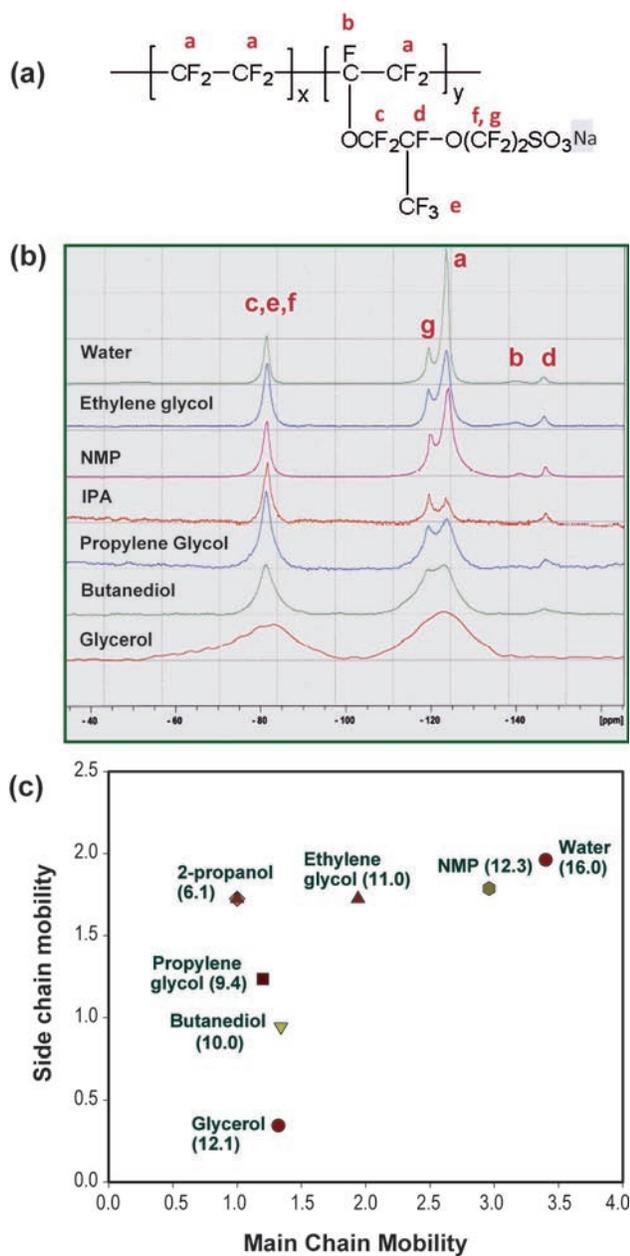
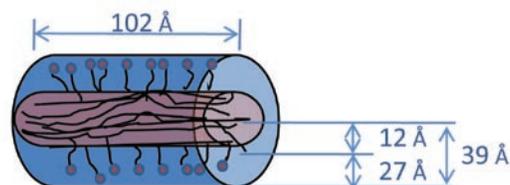


FIGURE 2. (a) Depiction of Nafion[®] chemical structure with each type of fluorine labeled a-g; (b) assignment of NMR peaks using these labels; (c) plot of the relative mobilities of side-chain fluorines and backbone fluorines. Calculation of relative main-chain mobility: peak area (a) / peak area (c,e,f). Calculation of side chain mobility: 1 / line width of (c,e,f) peak (kHz⁻¹).

showed very little phase separation, whereas the water-cast film showed a high degree of phase separation. Thus, the lowered fuel cell performance may be due to the specific arrangement of side-chains containing sulfonic acids groups near the platinum catalyst particles. Of course, the behavior of thick Nafion[®] films cannot be directly related to fuel cell electrodes, and we continue to design experiments closer to the real case.

(a) Nafion[®] dispersion in NMP



(b) Nafion[®] dispersion in glycerol

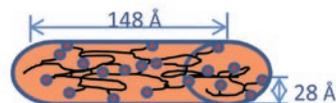


FIGURE 3. Models of the structure of Nafion[®] dispersed in (a) NMP or (b) glycerol solvent as derived from neutron scattering data. Please see ref [2] for further details.

Neutron scattering experiments further support that the ionomer structure differs greatly depending on the solvent. The models of the Nafion[®] structure in glycerol and NMP as derived from small-angle neutron scattering data are shown in Figure 3. The data for Nafion[®] in glycerol can be fit well with a cylindrical model (less phase-separation) with little solvent penetration, whereas the NMP dispersion data require a core-shell model (more phase-separation) and solvent penetration to fit the data properly. These depictions are consistent with the lack of mobility observed by NMR and lack of phase-separation observed by AFM for Nafion[®] dispersed in glycerol, and vice versa for NMP dispersions. It is plausible, though not yet proved, that the final structures of the Pt-ionomer interfaces formed from such dispersions may also differ.

We have begun to examine water-isopropanol mixtures as solvents for ionomer dispersions, and the correspondences between the NMR mobilities and the fuel cell performances were consistent with those discussed above with respect to performance in the kinetically-controlled voltage range. The performance in the mass-transport controlled range was similar to glycerol-derived cathodes, however. This may reflect the importance of larger length scales than shown by NMR. Ongoing neutron scattering experiments and TEM imaging will show the structure at larger scales. Please see ref [2] for further details.

Besides the performance, the durability of cathodes cast from Nafion[®] dispersed in glycerol (glycerol cathode) and, water-propanol-isopropanol (W-P cathode) were compared, as shown in Figure 4. The performance of the W-P cathode was initially much

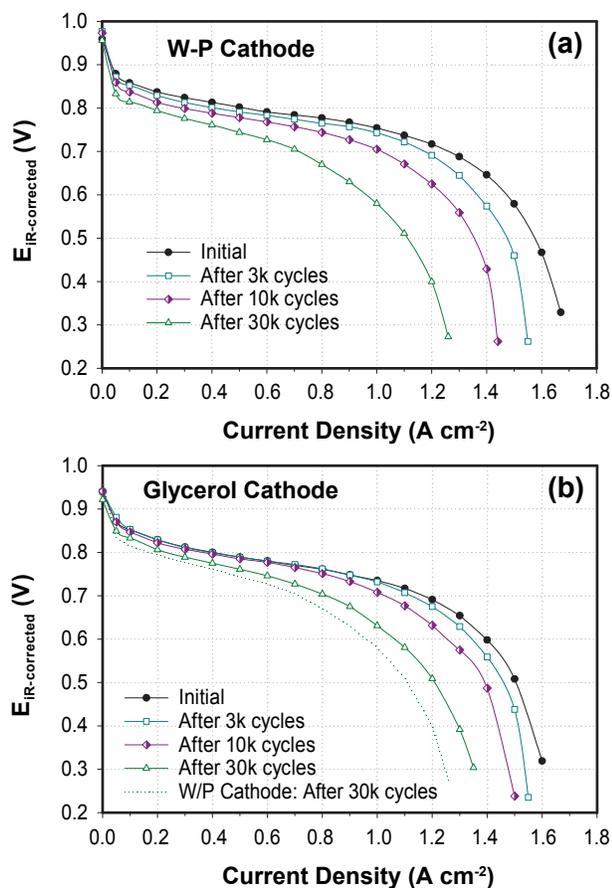


FIGURE 4. H_2 /air polarization curves of MEAs prepared from (a) W-P cathode and (b) Glycerol cathode before (initial) and after potential cycling (3k–30k cyclic voltammetry cycles). H_2/N_2 potential cycling condition [3]: 0.6–1.0 V, 50 mV/sec, 80°C, fully humidified. H_2 /air fuel cell test condition: 80°C, fully humidified, anode/cathode pressure = 30 psig; H_2 : 160 sccm; air: 550 sccm.

higher, but the cathode was affected more seriously by potential cycling. After 30k cycles, the glycerol cathode performed significantly better than the W-P cathode, suggesting a more durable electrode structure. The durability seems to be related in part to less Pt particle growth in the glycerol cathode with potential cycling, as shown by TEM [2]. This difference can result from the tendency of Nafion[®] to phase-separate more in water-propanol dispersions than in glycerol dispersions, as suggested by NMR and AFM studies. Verification of the increased tendency of Nafion[®] to phase separate in W-P solvent even after the addition of Pt/C is required, and this lack of information will be addressed with neutron scattering experiments of catalyst inks.

Initial studies involving bi-layer electrodes with different Nafion[®] content near the membrane versus the gas diffusion layer were also conducted. The electrodes responded differently to relative humidity, but no major performance enhancements were observed in these initial experiments.

Conclusions and Future Directions

We have begun a series of experiments that promises to follow the evolution of electrode structure in detail at multiple length scales. Already, correlations have been identified between the local mobility and structure of Nafion[®] dispersed in various solvents as determined by NMR and neutron scattering, and the performance and durability of fuel cell cathodes prepared from those dispersions. Solvents that increase Nafion[®] mobility and phase-separation enhance the performance in the kinetically-controlled voltage region, whereas pure solvents that hinder the mobility tend to show better performance in the mass-transport controlled voltage range. The solvent also has a marked effect on durability of the generated electrodes to potential cycling.

Overall, we intend to continue to move our experiments towards more accurately reflecting the true conditions used to form electrode structures. Specifically, we plan to (1) further explore solvent mixtures rather than pure solvents, (2) add Pt/carbon to the measurements, and (3) more thoroughly characterize the MEAs with alternating current impedance, oxygen experiments, etc.

Special Recognitions & Awards/Patents Issued

1. Y.S. Kim, T. Rockward and K.-S. Lee, US Patent Application (2009).

FY 2009 Publications/Presentations

- 214th Meeting of the Electrochemical Society, Honolulu, HI, October 12–17, 2008. Title: “Measurement and Understanding of Catalyst Utilization in Fuel Cells.” C.M. Johnston, H. Xu, E.L. Brosha, J. Chlistunoff, K. More, E. Orlor, M. Hawley, and B. Pivovar.
- Canada to USA Fuel Cell and Hydrogen Cluster Connection Workshop, Vancouver, BC, Canada, February 16–17, 2009. Title: “Studies Towards Optimizing Fuel Cell Electrode Structure and Composition.” E. Brosha, F. Garzon, C. Johnston, A. Labourieau, Y.S. Kim, K.-S. Lee, B. Orlor, B. Pivovar, D. Torracco, C. Welch, H. Xu.
- “The Effect of Ink Processing and Composition on Pt Utilization in Polymer Electrolyte Fuel Cells”, H. Xu, E. Brosha, K. More, F. Uribe, F. Garzon, B. Pivovar, J. Power Sources, in preparation.

References

- Y.S. Kim, T. Rockward and K.-S. Lee, US Patent Application (2009).
- C.M. Johnston, Applied Science for Electrode Cost, Performance, and Durability, in *DOE Hydrogen Program Annual Merit Review and Peer Evaluation* (2009).
- U.S. DOE Cell Component Accelerated Stress Test Protocols for PEM Fuel Cells (2008).