

Applied Science for Electrode Cost, Performance, and Durability

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Timeline

Start: FY2005

Status: Ongoing

Budget

Funding in FY08: \$600K

Funding in FY09
(estimated): \$600K

Not cost-shared

Barriers Addressed

- A. Durability
- B. Cost
- C. Electrode Performance

Partners

Oak Ridge National Laboratory
NIST Center for Neutron Research
Los Alamos Neutron Science Center

Relevance: Objectives and Barriers Addressed

Overall Project Objective

To assist the DOE Hydrogen, Fuel Cells & Infrastructure Technologies (HFCIT) Program in meeting cost, durability and performance targets by addressing issues directly associated with electrodes (electrode science not specifically addressed by FY '06 call).

Table 3.4.12 Technical Targets: Electrocatalysts for Transportation Applications

Characteristic	Units	2005 Status ^a		Stack Targets	
		Cell	Stack	2010	2015
Platinum group metal (pgm) total loading ^b	mg PGM / cm ² electrode area	0.45	0.8	0.8	0.2
Cost	\$ / kW	9	55 ^c	5 ^d	3 ^d
Durability with cycling					
Operating temp ≤80°C	hours	>2,000	~2,000 ^e	5,000 ^f	5,000 ^f
Operating temp >80°C	hours	N/A ^g	N/A ^g	2,000	5,000 ^f
Electrochemical area loss ^h	%	90	90	<40	<40
Mass activity ⁱ	A / mg Pt @ 900 mV _{IR-free}	0.28	0.11	0.44	0.44
Specific activity ^j	μA / cm ² @ 900 mV _{IR-free}	550	180	720	720

FY09 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

Barriers Addressed

Electrode composition and structure must be understood and controlled to achieve the highest platinum utilization and durability

- Durability**: Assessing effect of electrode composition and processing on durability
- Cost**: Measuring catalyst utilization after altering electrode composition and processing
- Electrode Performance**: Evaluating effect of varying electrode inks and processing on the performance of fuel cells

Approach: Targets and Milestones

- Explore effect of catalyst ink composition and processing on utilization and performance

- FY09**
- Wide range of solvents explored in catalyst inks; marked effect on performance observed
 - Bilayer/gradient electrode work initiated

- Use microscopy and other tools to better understand electrode structure and impact on performance

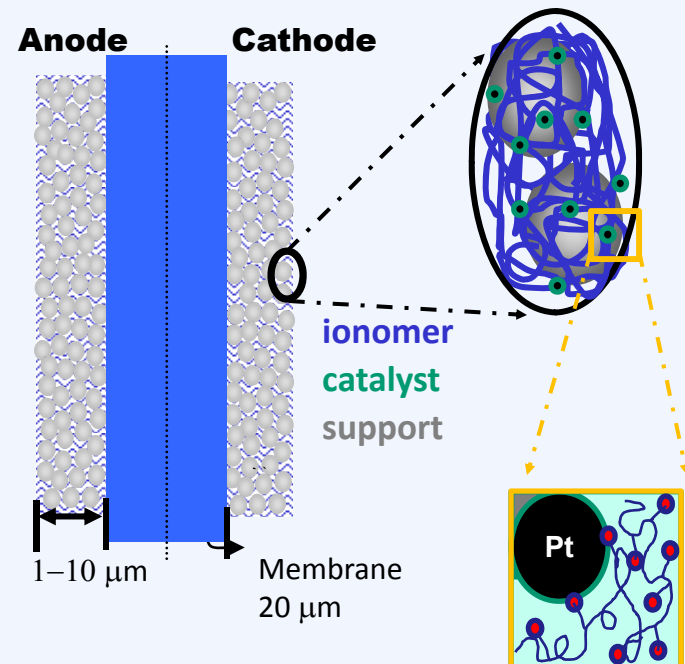
- FY09**
- Structure and local chemical environment of Nafion[®] dispersed in different solvents examined by neutron scattering and NMR
 - TEM and HR-TEM used to examine the inks and electrode structures from different solvents

Month/Year	Milestone
Mar 08	Perform gravimetry experiments of H ₂ S adsorption and CO adsorption to compare with heterogeneous surface area measurements obtained by ion selective electrodes (completed)
Jul 08	Modify MEAs processing to obtain electrochemical surface areas that vary by a factor of 3, and correlate these differences in surface area with fuel cell performance (completed)
June 09	Measure the total platinum surface area and ESA of MEAs prepared with two previously unstudied carbon supports, and rationalize the results compared to FY2008 data using structural and chemical information obtained through TEM and spectroscopy (ongoing)
Sept 09	Fabricate an MEA with a layered structure and evaluate the approach in terms of ESA versus performance (ongoing)

Approach: Main Ideas and Overall Goals

Main Ideas

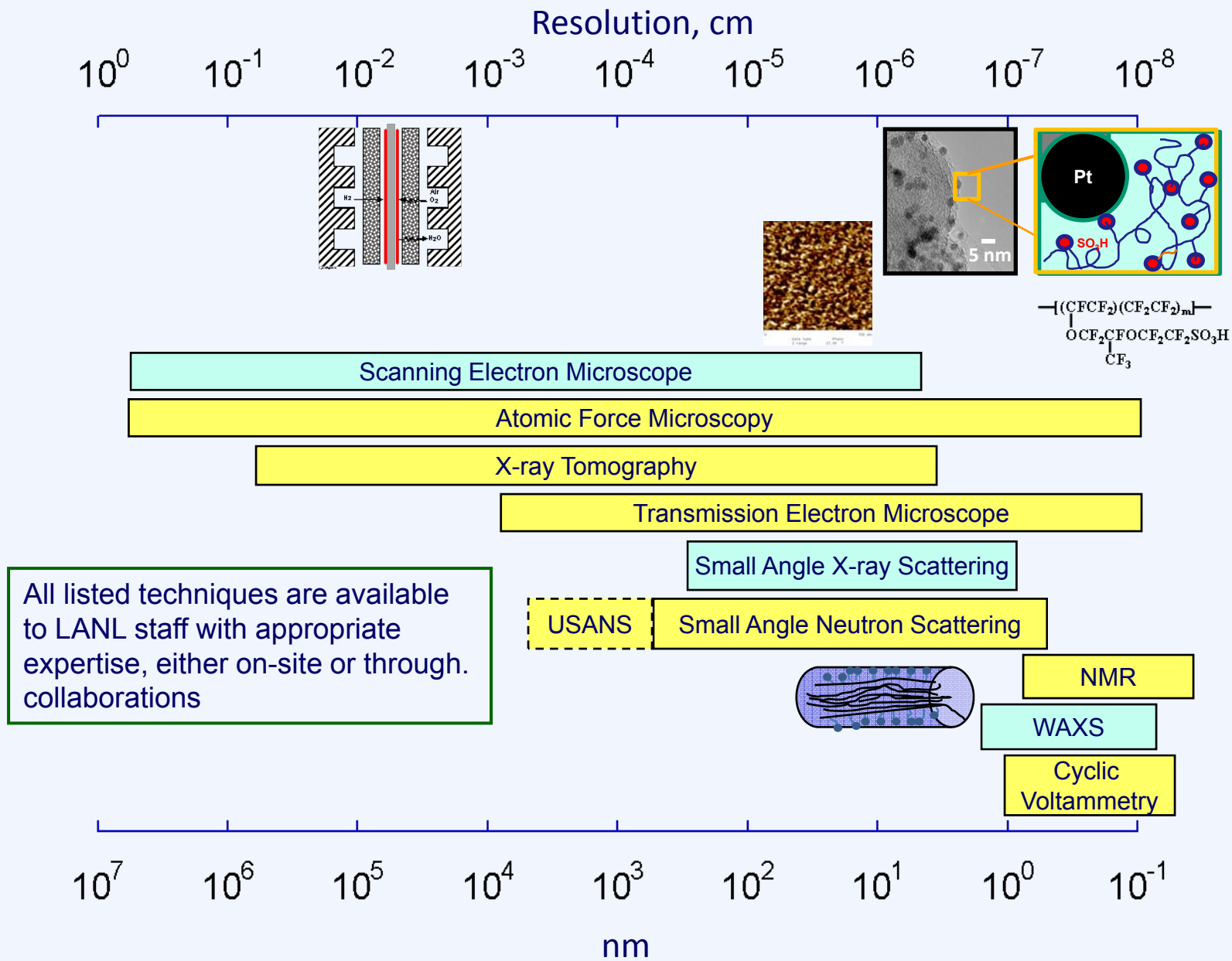
- Well-designed electrode structures could lead to a reduction in catalyst loading, as well as improved performance and durability
- Novel materials may require novel electrode structures; understanding a “typical” Pt/C electrode structure is a good starting point



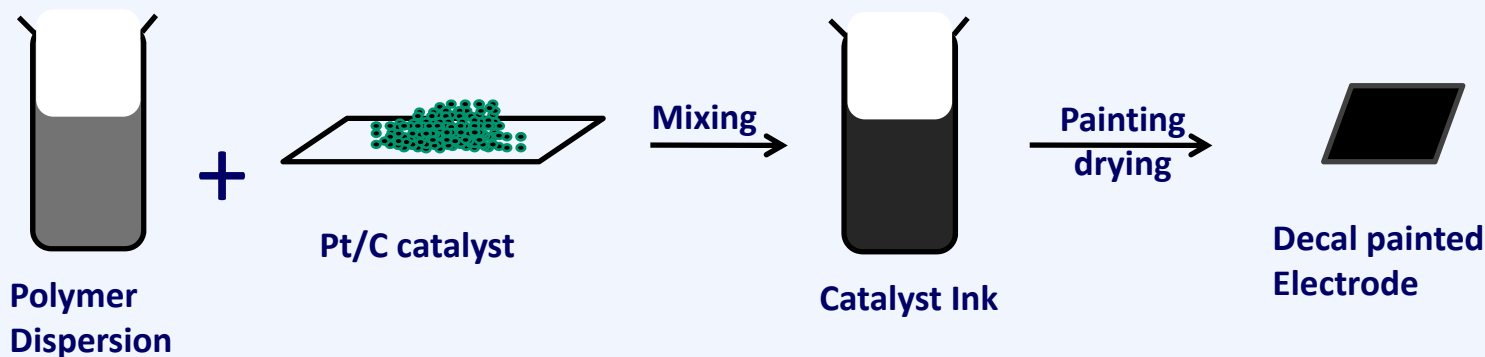
Overall Goals of This Work

- Study structure and chemical properties of fuel cell catalyst ink components as they interact—solvent (FY09), ionomer (FY09), carbon, platinum (future work), and relate to final electrode performance
- Evaluate ink and electrode processing procedures (e.g., drying temperature) with focus on correlating structure to performance (ongoing)
- Vary the components and processing conditions, based on this understanding, to improve fuel cell performance (ongoing)
- Combine microscopy, neutron scattering, other analysis methods, and modeling to develop structure/performance relationships (ongoing)

Approach: Probe Fuel Cell Component Interactions at Various Length Scales



MEA Preparation: Factors that Impact Electrode Morphology Development

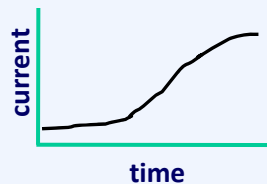


Polymer Morphology in Dispersion

Catalyst adding
Mech. Stirring

Drying

Initial Electrode Morphology



Cell break-in

Drying

Acidification

Hot pressing

Final Electrode Morphology

Electrochemical treatment

Drying

Hydrothermal effect

Thermal effect

Approach for Evaluating Solvent Effect on Fuel Cell Electrodes

Preparation of Polymer Dispersion*

Characterization of Polymer/Pt/Carbon Dispersion

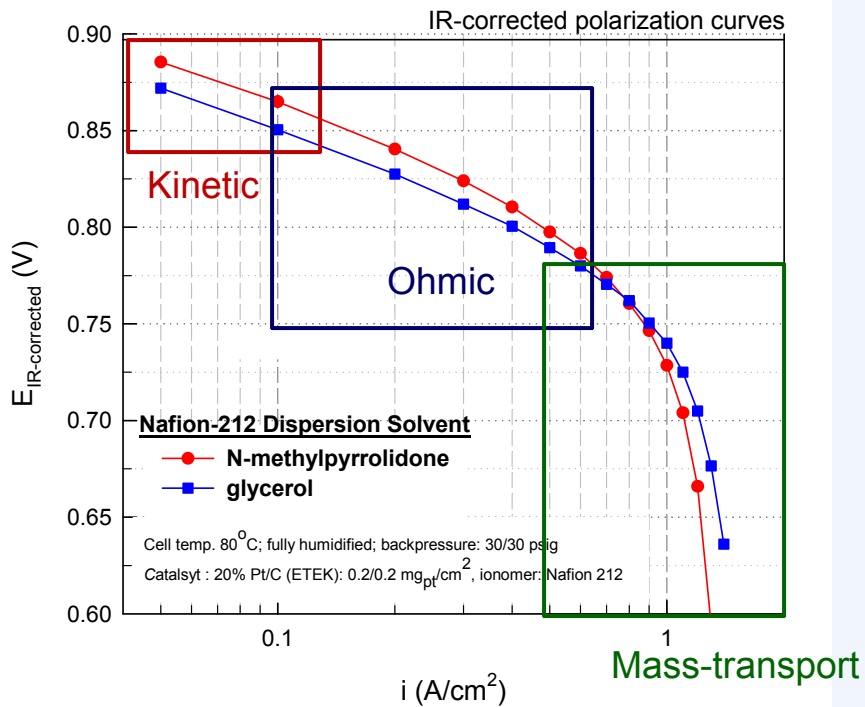
Polymer/Solvent Interaction (^{19}F NMR)
Polymer Morphology in Dispersion (SANS) and in Solid Electrode (AFM)
Electrode Morphology (SANS, AFM and TEM)

Fuel Cell Performance

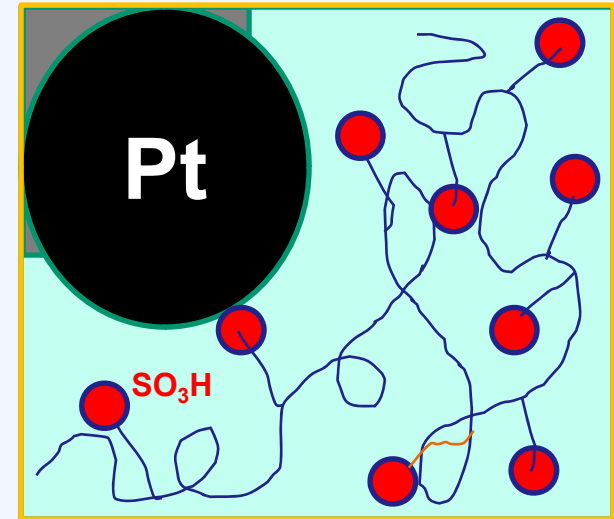
Initial Fuel Cell Performance (Pt ORR kinetic and mass transfer region)
Electrode Durability Test (Potential cycling test)

*Y.S. Kim et al. LANL US Patent Application "Non-Aqueous Liquid Comprising Ion Exchange Polymers" (2009)

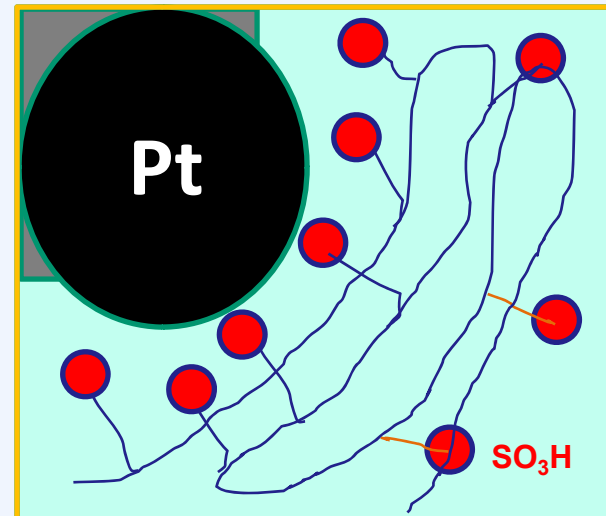
Motivation for FY09 Work



Less phase-separated



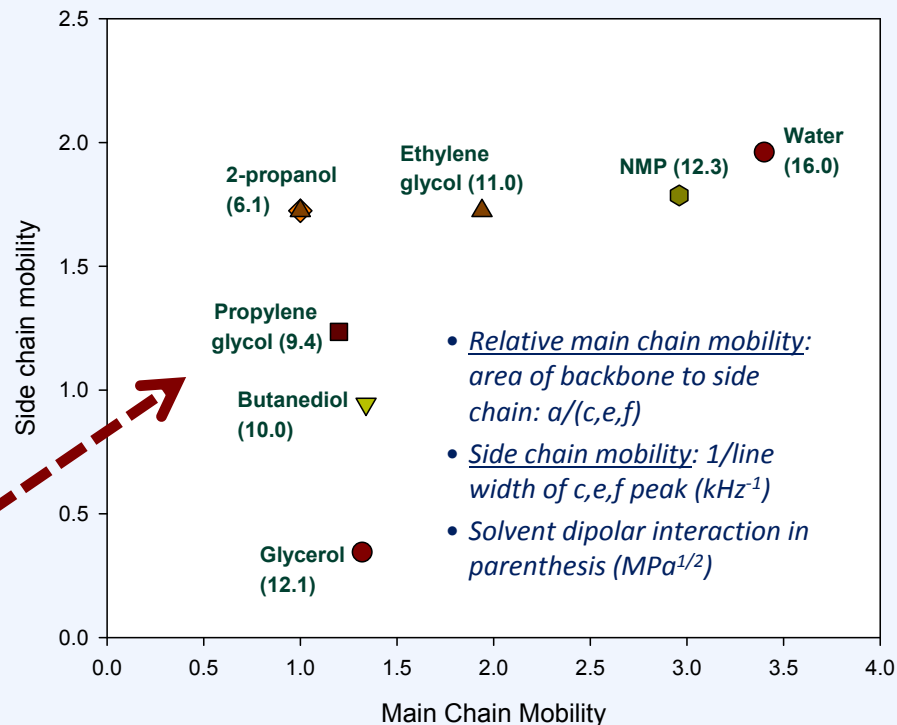
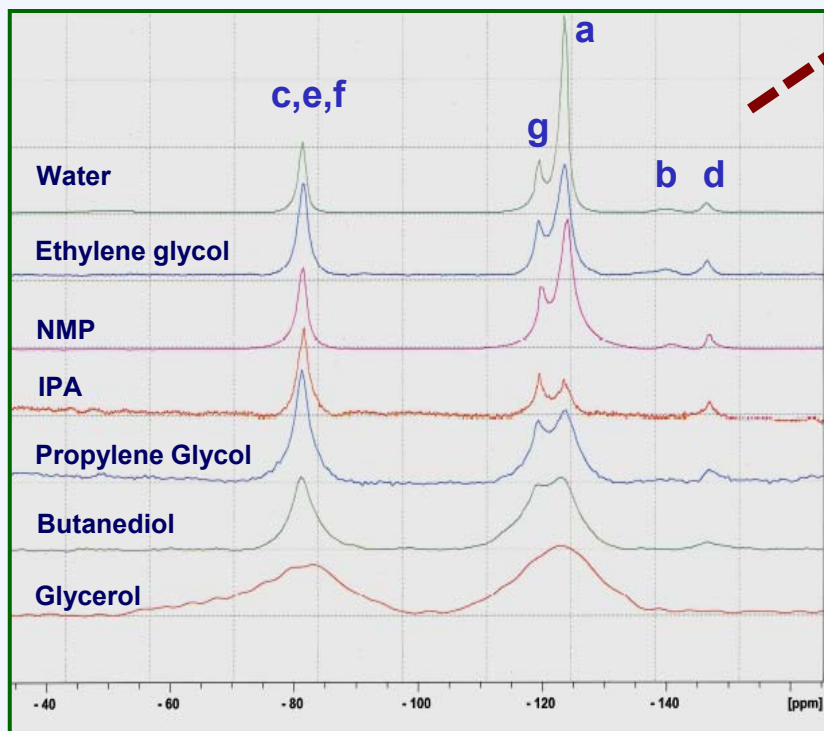
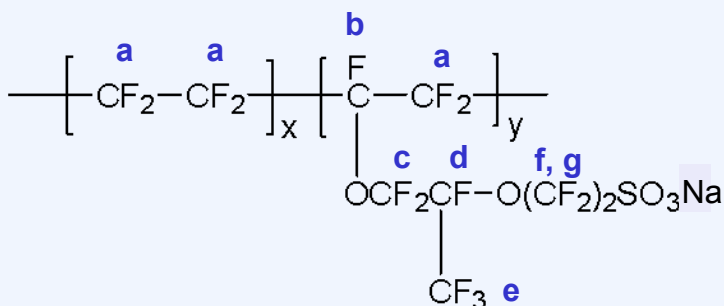
More phase-separated



*Structures are visual aids reflecting current understanding, and may be later updated

- Solvent choice in ink studied first
- Various dispersions of Nafion[®]-212 made in-house through novel method (subject of patent disclosure)
- Marked differences in fuel cell performance noted
- Kinetic and mass transport region impacted differently by solvent choice
- Questions raised about effect of nanoscale structure and interactions of electrode components

¹⁹F NMR of Nafion®-212 Dispersions

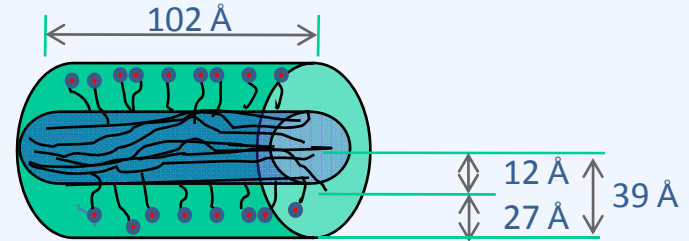
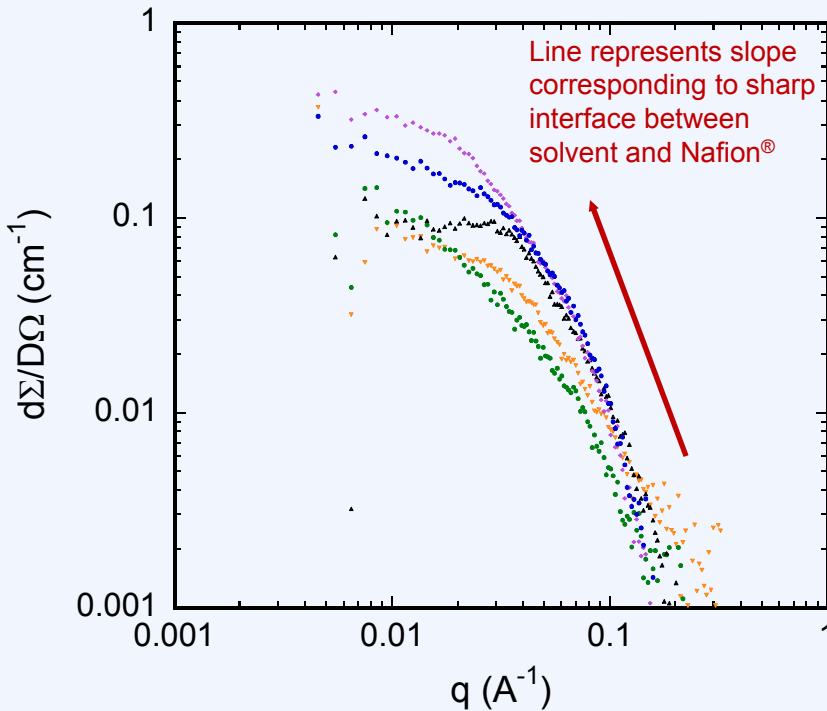


- **Mobility of Nafion® backbone and sidechains greatly differs from solvent to solvent**
- **Glycerol:** fuel cell mass-transport enhanced; Nafion® has low overall mobility in solvent
- **NMP:** fuel cell kinetics enhanced; Nafion® has high overall mobility
- **Propylene glycol:** Intermediate behavior, but more similar to glycerol

Small-Angle Neutron Scattering of Nafion®-212 Dispersion

NMP dispersion: Core-Shell Cylinder

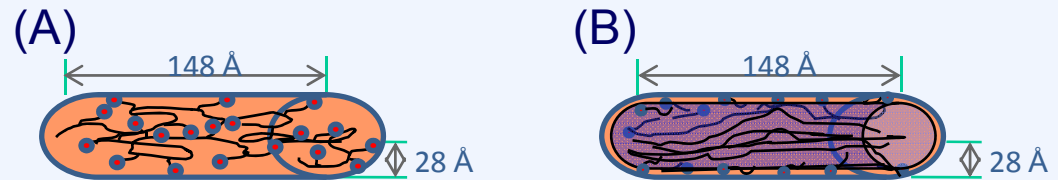
*Structures are visual aids reflecting current understanding, and may be later updated



- Sharp interface between core and shell
- SLD* of core = ~calculated Nafion® backbone
- SLD of shell = ~solvent
- No solvent penetration into the core
- Solvent penetrates side chains (low slope)

Solvent	Slope
NMP	-1.7
Ethylene glycol	-2.0
Water/IPA (2:3)	-2.0
Butanediol	-3.3
Glycerol	-3.5

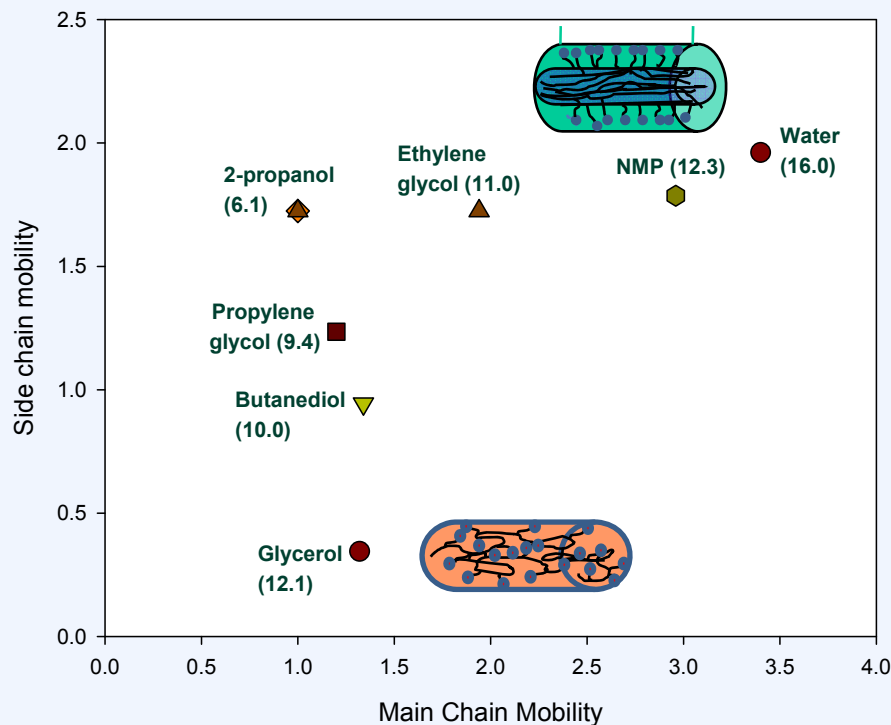
Glycerol dispersion: Cylinder Model



- Less phase separation between Nafion® backbone and side chains
- Glycerol appears to penetrate Nafion® less than NMP (high slope), but some penetration may occur

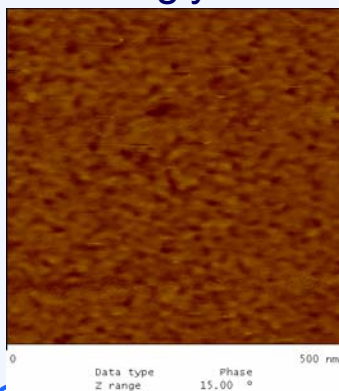
* SLD = scattering length density

Atomic Force Microscopy of Nafion®-212 Films Cast from Different Solvents

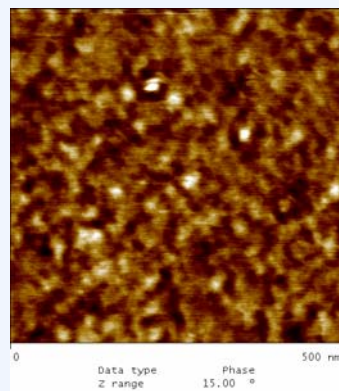


- Demonstrates impact of solvent on final ionomer structure, rather than just while in dispersion
- Correlation observed between phase separation (from SANS) and mobility (from NMR) in dispersions with final film morphology (from AFM)
- Ongoing studies: adding Pt/C incrementally to dispersions to see effect on resulting film structure, and effect of temperature of casting

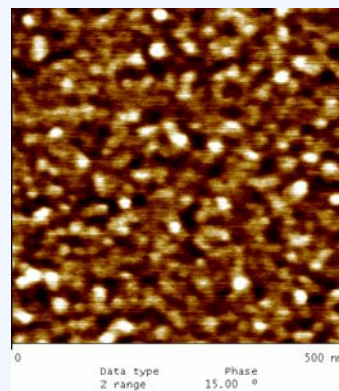
From glycerol



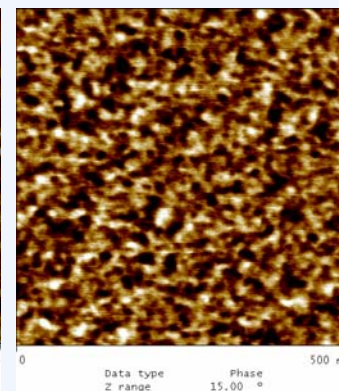
From butanediol



From water



From NMP

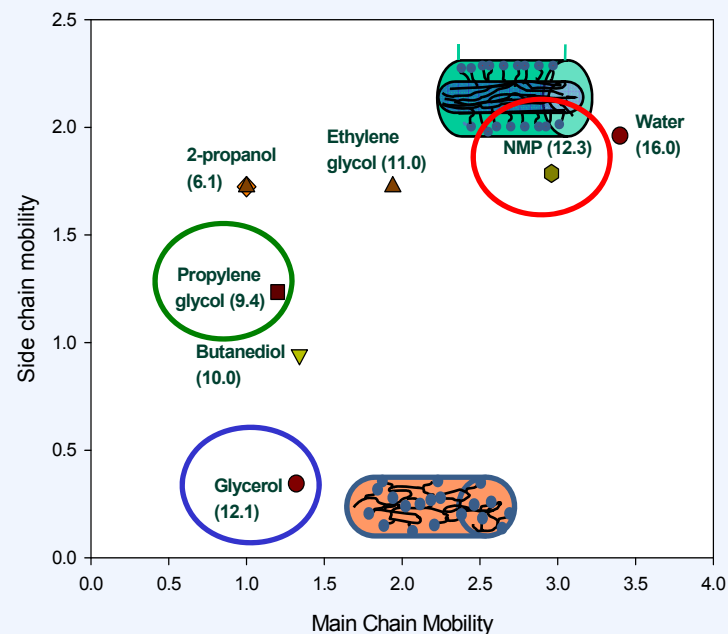
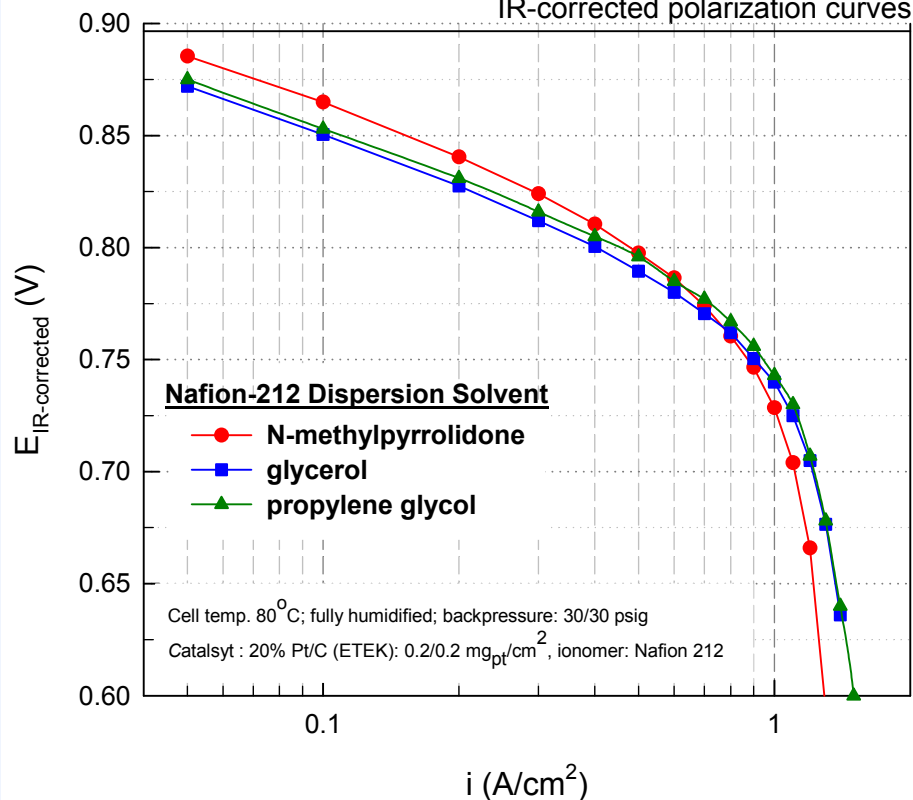


Nafion® 212 dispersions after drying at temperatures well below respective boiling points

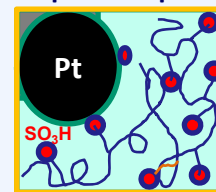
Comparison of Fuel Cell Tests to Model based on NMR, SANS, and AFM Results

H₂/air Fuel Cell Tests

IR-corrected polarization curves

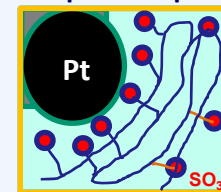


Less phase-separated



Model for glycerol

More phase-separated



Model for NMP

- **From NMP dispersion:** Good performance at kinetically-controlled voltages, but poor performance at mass-transport controlled voltages
- **From glycerol dispersion:** Opposite pattern
- **From propylene glycol dispersion:** Intermediate behavior, but closer to glycerol (agrees with NMR)

Extension of Study to Solvent Mixtures: Water/Isopropanol Dispersions of Nafion[®]-212

Decreasing water content

Increasing performance

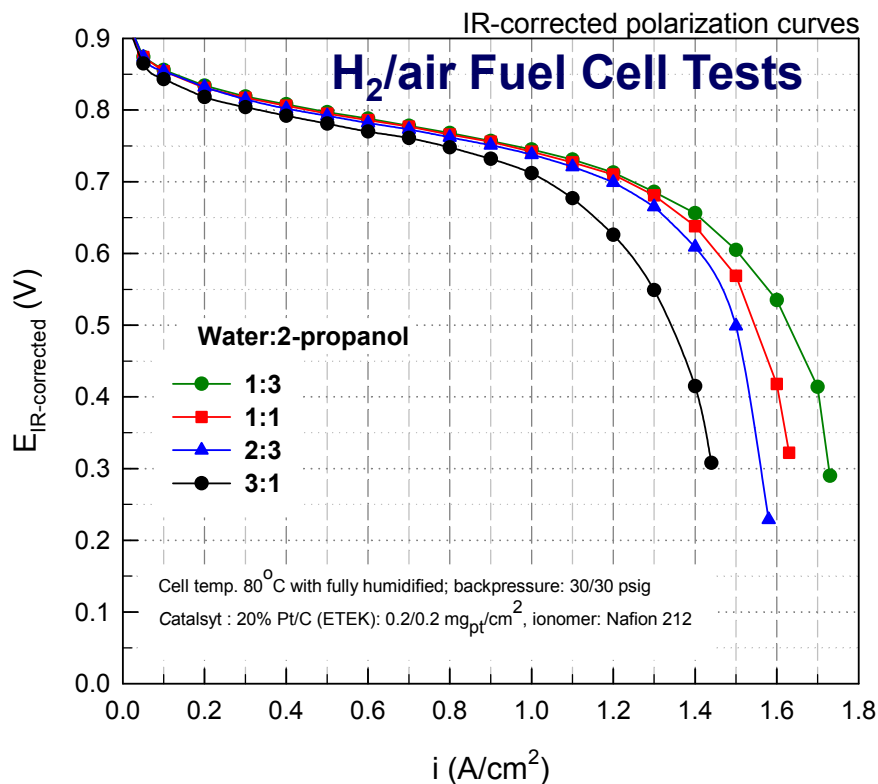


Water: IPA 1:3

Water: IPA 1:1

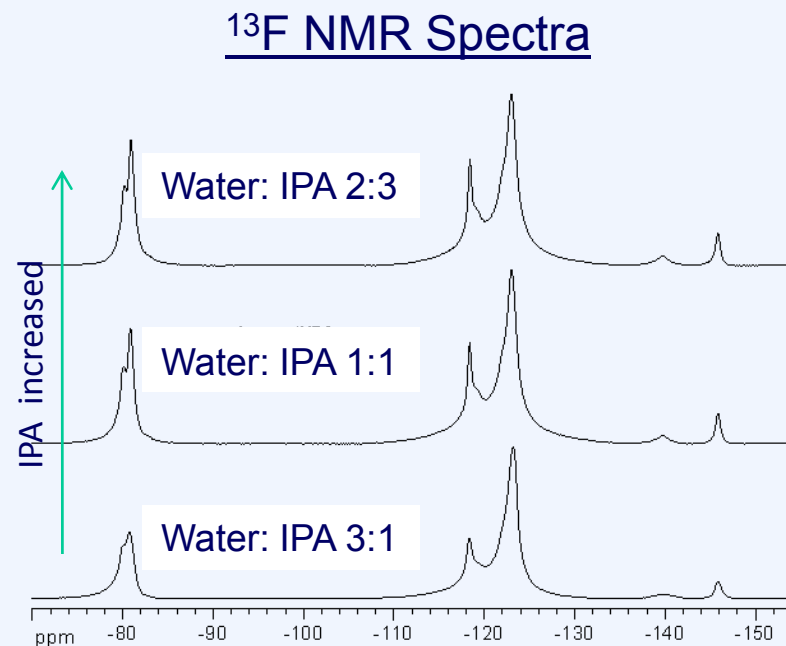
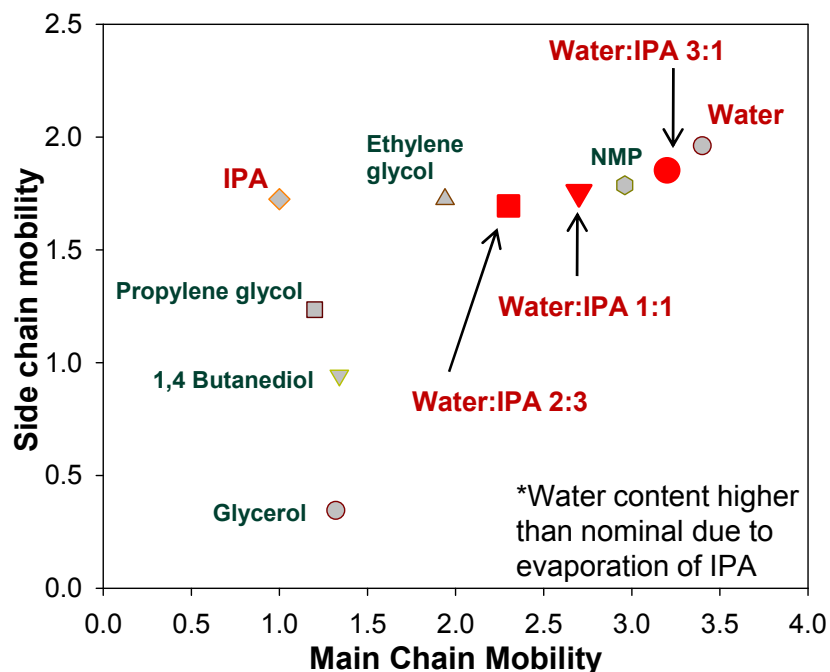
Water: IPA 2:3

Water: IPA 3:1



- Performance improved in both kinetic and mass-transport regions with decreased ratio of water to IPA
- Formation of continuous electrode film challenging with highest water content (Water: IPA 3:1), which could have reduced performance

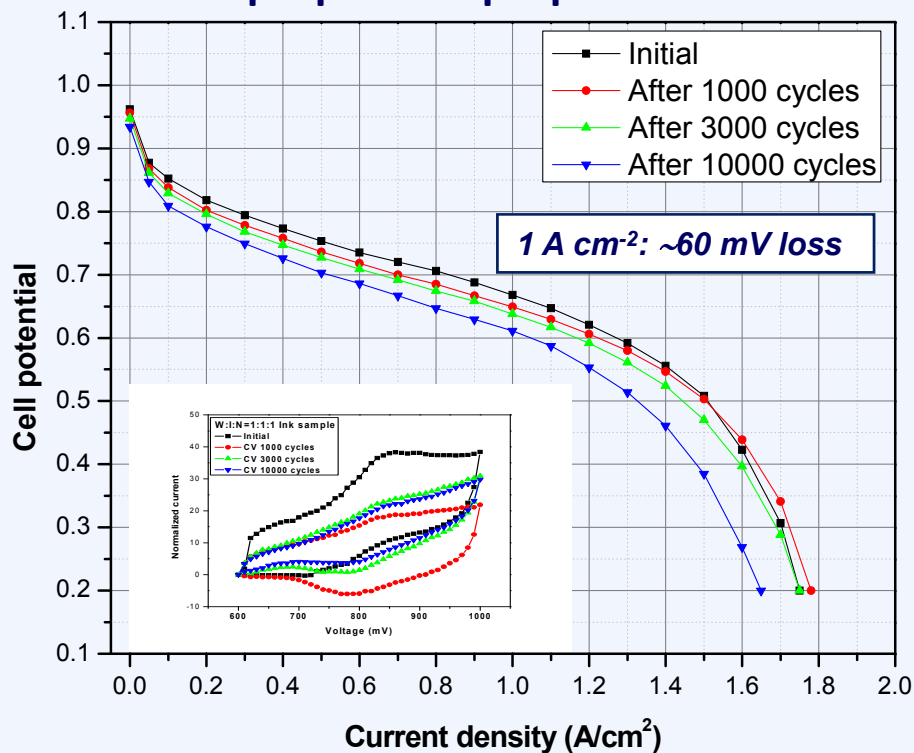
Nafion[®]/Solvent Interaction in Water: IPA Solvent Mixture (2.5 wt%)



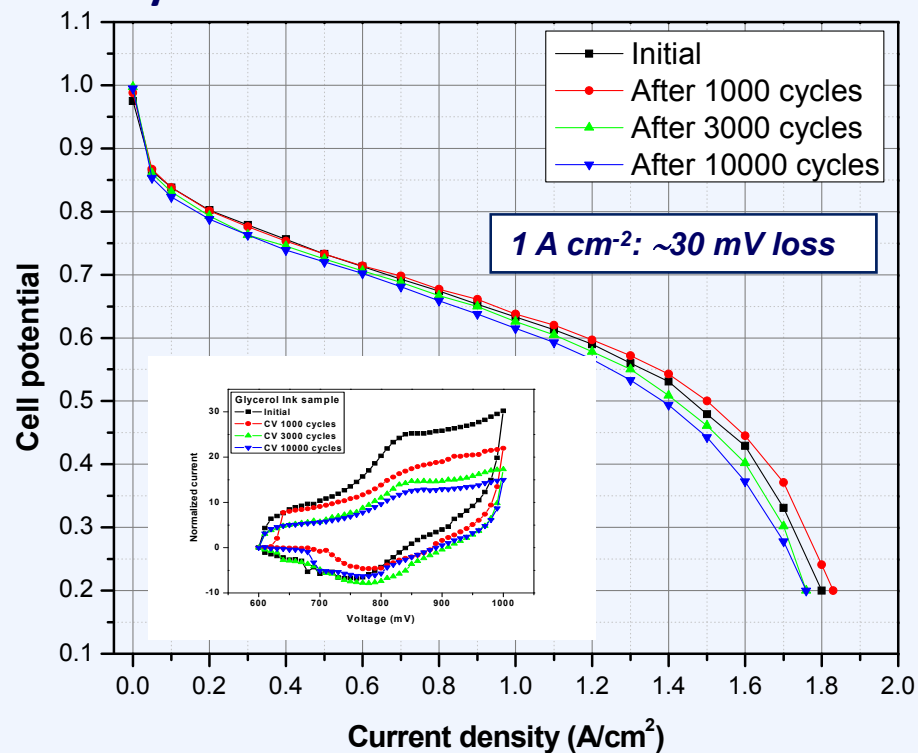
- NMR shows that side-chain and main-chain mobility are intermediate those of water and IPA for water:IPA mixtures, as expected
- Kinetic performance of Water: IPA 1:1 and 2:3 electrodes similar to NMP (tending lower), but mass-transport better
- Mass transport performance of Water: IPA 1:1 and 2:3 electrodes similar to glycerol (tending higher); kinetic performance superior
- SANS data collected for 2:3 Water:IPA dispersion, but not fully analyzed; sphere-like structure of Nafion[®] observed—different than for NMP and glycerol; may help explain mass-transport difference

Effect of Dispersion Solvent on Catalyst Durability

Water-Isopropanol-n-propanol

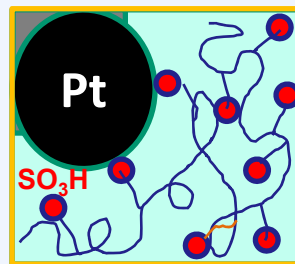


Glycerol



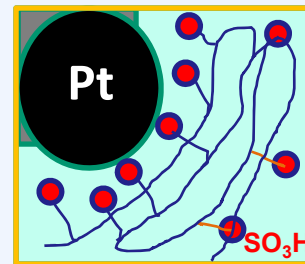
- Better performance in kinetic region observed at the beginning of test from electrode made from water/isopropanol dispersion, but much higher performance degradation during potential cycling
- Question raised about impact of nanostructure resulting from different solvents on durability

Less phase-separated



Model for glycerol

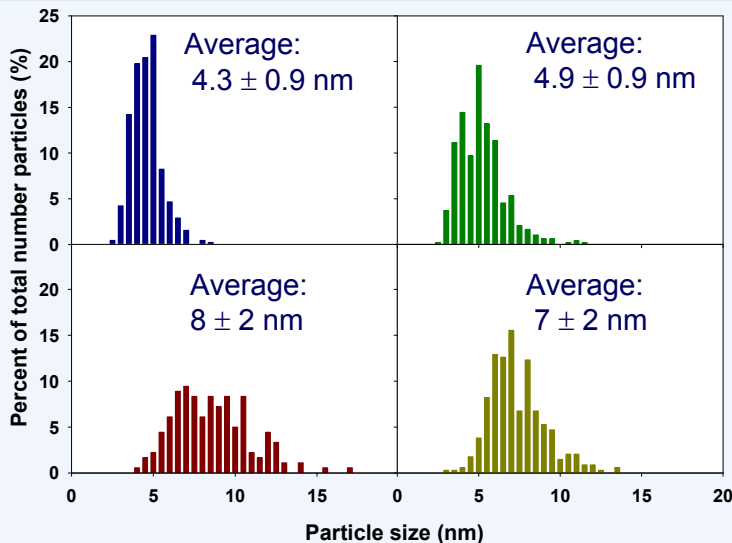
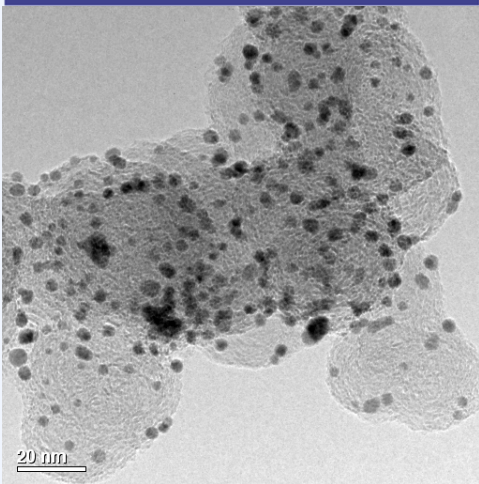
More phase-separated



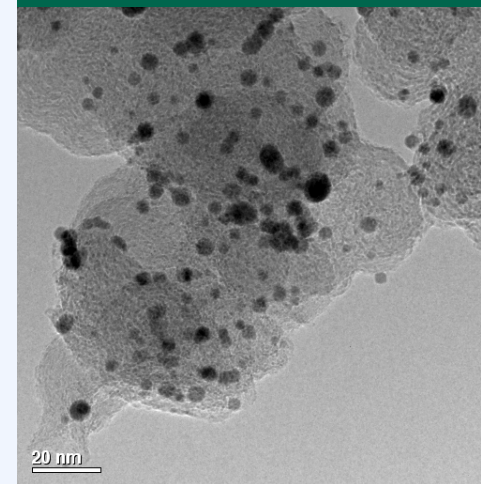
Model for NMP

TEM Micrographs of Catalyst Before and After Potential Cycling Test

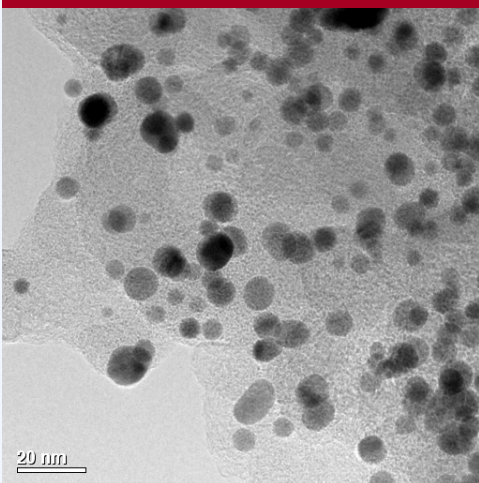
From 1:1:1 water:IPA:n-prop:
Before potential cycling



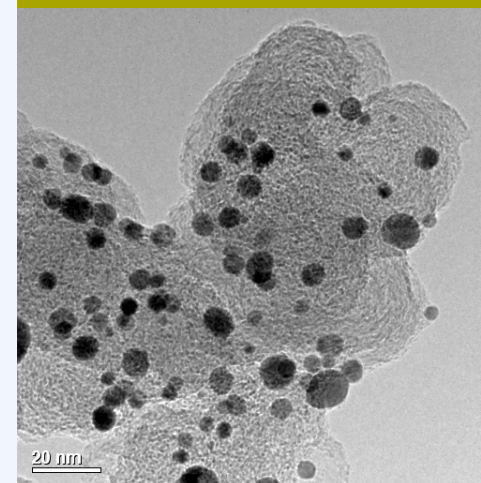
From glycerol:
Before potential cycling



From 1:1:1 water:IPA:n-prop:
After 10,000 potential cycles

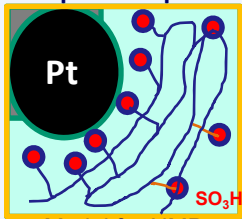


From glycerol: After 10,000
potential cycles



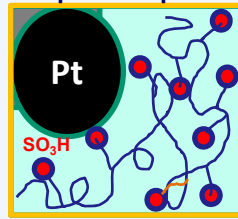
- Initial particle size distributions are similar for 1:1:1 water:IPA:n-prop mixture and glycerol
- Particle growth with cycling tends to be greater for electrode from glycerol dispersion; more statistics needed
- Details of Nafion®-Pt interface may be different when formed from different solvents; lateral connectivity of Pt?

More phase-separated



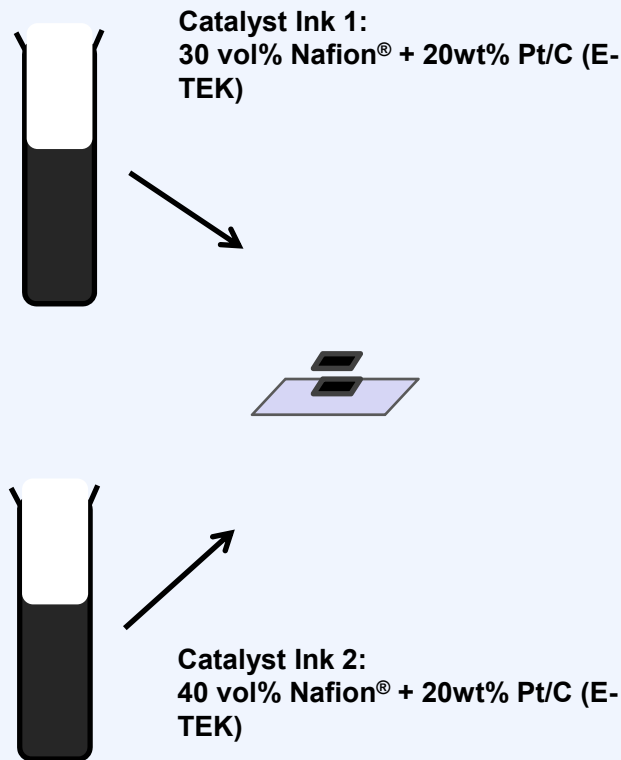
Model for NMP

Less phase-separated



Model for glycerol

Bilayer/Gradient Electrode Structures



MEA type 1: Ink 1 only (standard)

MEA type 2: Ink 2 (↑ Nafion® content) near GDL; Ink 1 near membrane

MEA type 3: Ink 1 (↓ Nafion® content) near GDL; Ink 2 near membrane



MEA type 1 (standard ink)



MEA type 2

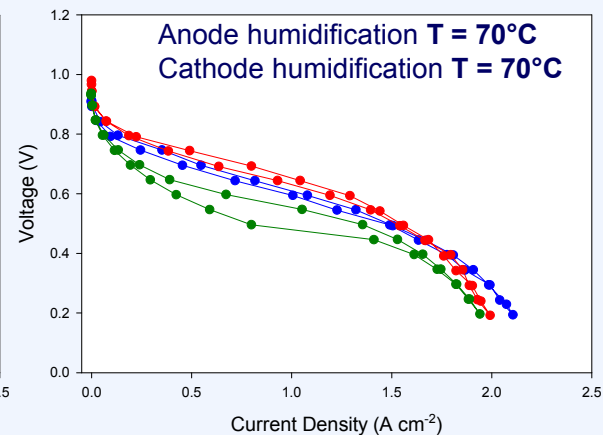
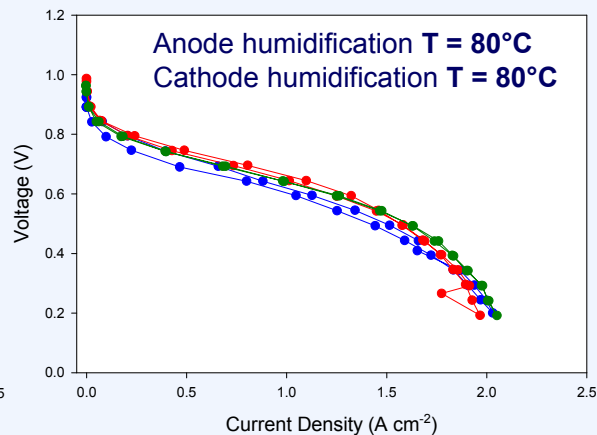
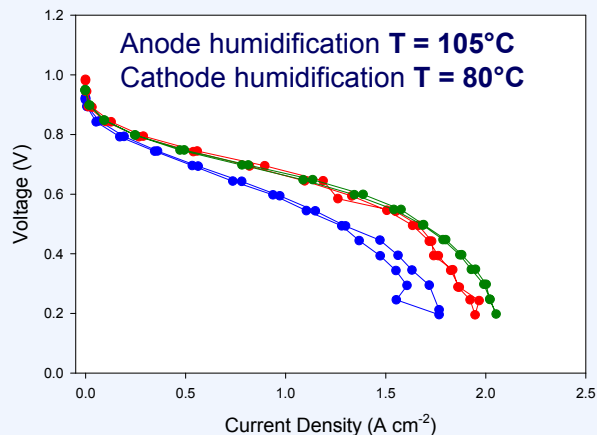


MEA type 3

“The DNS calculations predict that a higher electrolyte phase volume fraction near the membrane-CL interface provides an extended active reaction zone and exhibits enhanced performance. A higher void phase fraction near the gas diffusion layer aids in better oxygen transport.”

Direct numerical simulation modeling of bilayer cathode catalyst layers in polymer electrolyte fuel cells. [Mukherjee, PP ; Wang, CY. J. Electrochem. Soc \(2007\) Vol.154, iss.11, p.B1121-B1131](#)

Bilayer/Gradient Electrode Structures



MEA type 1: Performance only slightly decreased with decreased humidification

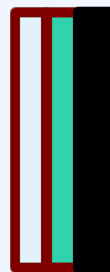
MEA type 2: Performance increased with decreased humidification

MEA type 3: Performance decreased with decreased humidification

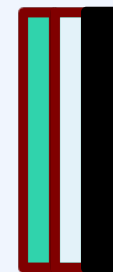
- Changing Nafion[®] content in layer greatly impacts the performance pattern with humidity levels
- Coupled with maximizing catalyst utilization with solvents, could lead to better design of electrode at different length scales



MEA type 1
(standard ink)



MEA type 2



MEA type 3

Summary

- To date, the formation and optimization of the PEFC electrode structure is poorly understood and controlled
- Work has begun to understand how materials properties and interactions govern electrode structure with the variation of solvent in catalyst inks
- Fuel cell performance depends on the solvent(s) used to fabricate electrodes (cathodes in this study)
- Data from NMR demonstrate that Nafion[®] side-chains and main-chain have different mobilities in different solvents
- Ionomer mobility could affect final ionomer structure, as indicated by AFM results
- SANS data show that dispersed ionomer size and structure vary with solvent
- Side-chain arrangement in NMP may be better oriented for interaction with Pt than glycerol (higher ECSA, higher kinetic performance)
- Glycerol, however, creates beneficial structures for mass-transport and durability—smaller Nafion[®] profile (SANS); less lateral Pt ion migration?
- Use of multiple inks to create bilayer/gradient structures could lead to improved performance

Shorter term (FY09 and early FY10)

- Use NMR, SANS, and dynamic light scattering to understand the effect of solvent on Nafion® dispersions
 - Focus: influence of **co-solvent mixtures (water:IPA)** on Nafion® morphology
 - NMR: molecular interactions of Nafion® with co-solvent mixtures
 - SANS: effect of water content on Nafion® morphology for co-solvent mixtures
- AFM study of impact of **catalyst** and **temperature** on ionomer film formation
- Continued fabrication and study of **multilayer/gradient** electrode structures
 - Add AC impedance and modeling to guide/validate optimization of electrode layers

Longer term (FY10)

- Nafion® interactions with the **catalyst** in solution (dispersions) and **solid** (film) states:
 - Analyze SANS data (NIST) of Nafion®/catalyst dispersion in glycerol
 - NMR and SANS (NIST) will focus on Nafion®/ink interactions (in solvent)
 - NMR and SANS (LANSCE) will focus on determining Nafion® in films
- Study impact of **Pt interparticle distance** on Nafion® organization (patterned electrodes, neutron scattering)
- Use different **carbon dimensions** to determine impact of size and shape in performance of electrode layers (important for **novel catalyst integration** into MEAs)
- Model evolution of electrode structure with inputs gained from experiments