



Molecular-scale, Three-dimensional Non-Platinum Group Metal Electrodes for Catalysis of Fuel Cell Reactions

John B. Kerr

Lawrence Berkeley National Laboratory (LBNL)

Collaborators:

UC Berkeley (UCB)

Los Alamos National Laboratory (LANL).

3M Company

June 8, 2010

Project ID #

FC 011

Overview

Timeline

- Project start –August 2009
- Project end –August 2013
- Percent complete – 10%

Budget

Total project funding

- DOE share \$9,580k
- Contractor share - in-kind (up to \$1,000k) plus NSF studentships (UCB)

Funding received in FY 10

- \$2,380k

Barriers

- C. Electrode Performance – better efficiency.
- B. Stack Material and Manufacturing Cost.
- E. System Thermal and Water Management.
- A. Durability

Team/Partners

- Adam Weber, Rachel Segalman, Robert Kosteki, Jeff Reimer, John Arnold, Martin Head-Gordon (LBNL)
- Piotr Zelenay, James Boncella, Yu Seung Kim, Neil Henson, Jerzy Chlistunoff (LANL).
- Steve Hamrock, Radoslav Atanasoski (3M)₂

Relevance - Objectives

DOE Technical Targets

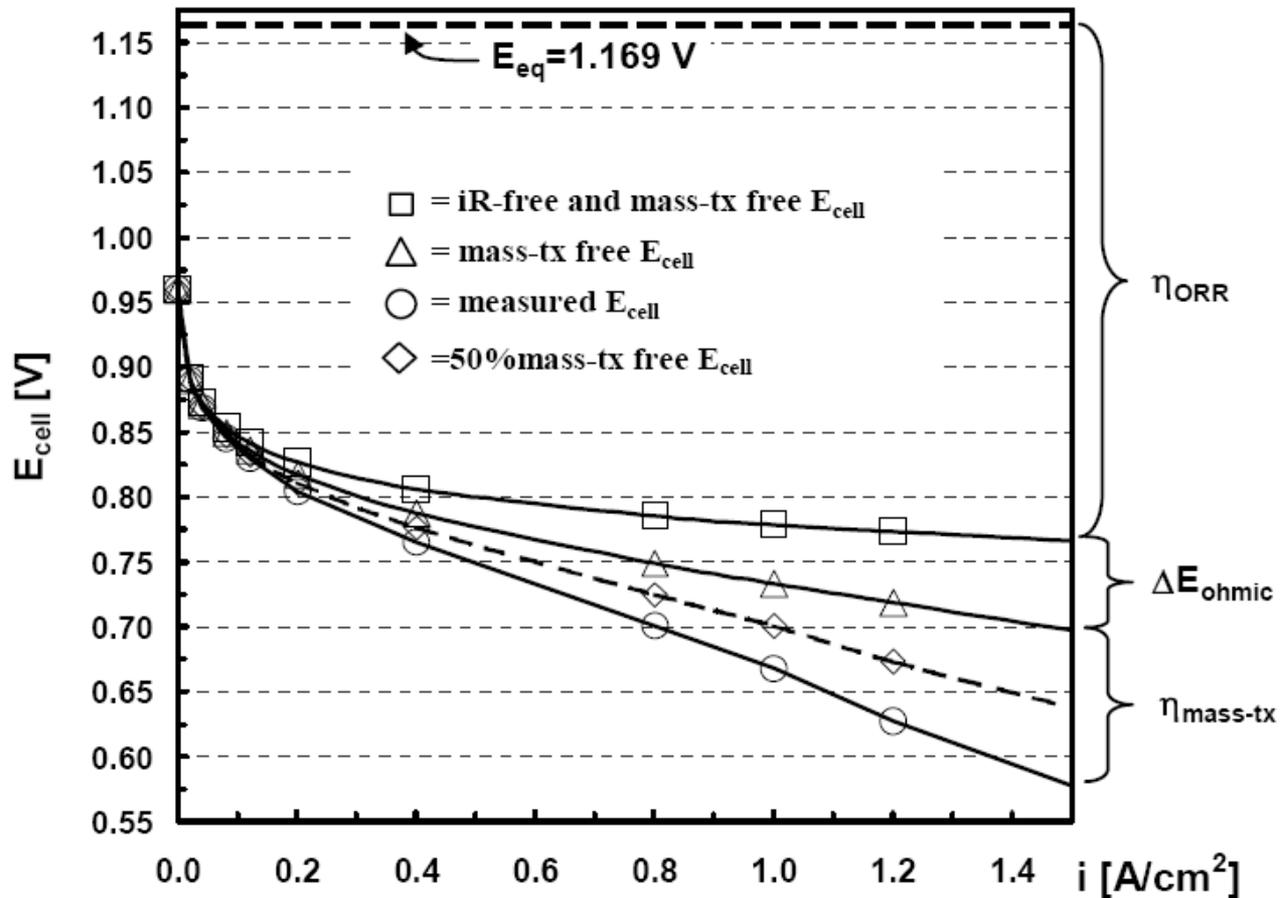
- Non-Pt catalyst activity per volume of supported catalyst – $300\text{A}/\text{cm}^3$
- Cost $< \$3/\text{kW}$
- Durability > 5000 hours ($> 120^\circ\text{C}$)
 - Electrochemical area loss $< 40\%$
 - Electrochemical support loss $< 30\text{mV}$ after 100hrs @ 1.2V

Project Objectives

- 1) Demonstrate that non-platinum group metal catalysts can be used for oxygen reduction in polymer-coated electrode structures based on polyelectrolyte membranes. (Year 1).
- 2) Incorporate catalysts into polymer binders of composite electrodes for the construction of MEAs to demonstrate that this is an effective matrix for testing of new catalysts. (Year 2).
- 3) Demonstrate that the three dimensional structure of polymer-coated electrocatalyst layers can offset slower kinetics of the catalyst centers when compared with two-dimensional platinum or non-platinum catalysts.(Year 3)
- 4) Demonstrate that significant stability of the matrix is possible.(Year 3)
- 5) Demonstrate the design, synthesis and scale up of new catalysts capable of performance that is superior to platinum group metals (Year 4).

Relevance.

We Need New Catalysts for Fuel Cells

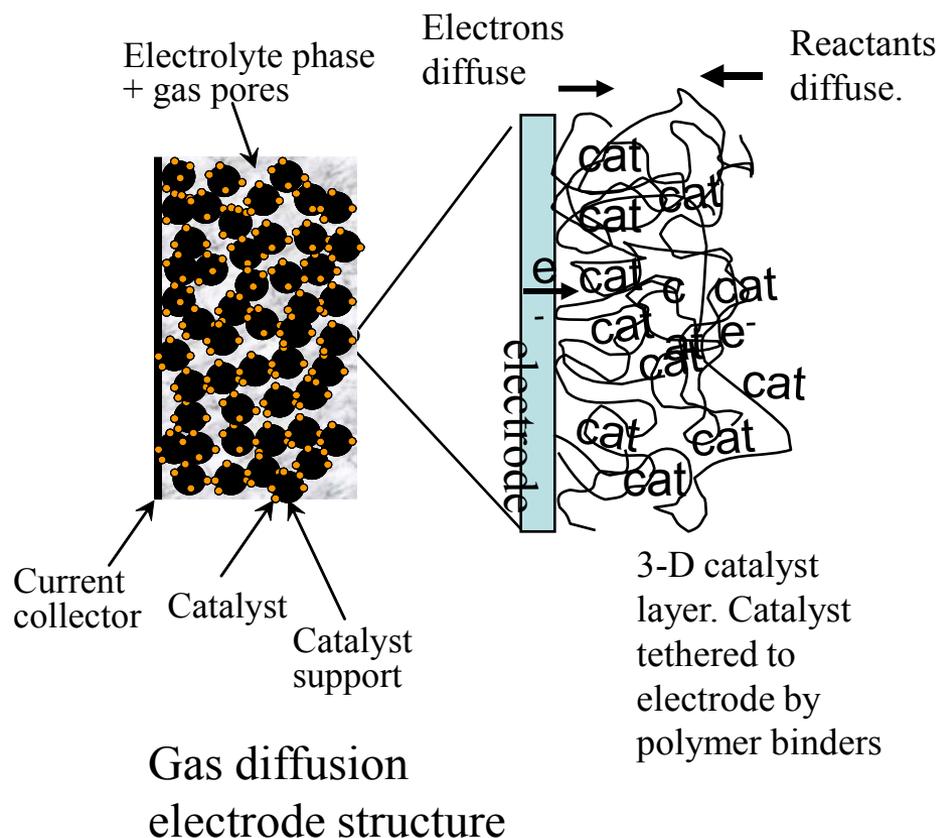


Approach

Objectives

- Develop polymer coated electrodes that can provide viable matrices in MEA's for use of homogeneous catalysts.
- Demonstrate how 3D molecular catalyst electrodes can replace Pt.
- Incorporate catalysts into MEA's and demonstrate viability
- Develop non-PGM Catalysts with better overpotential than Pt – e.g. copper accase

cat = e.g. Fe phenanthroline, heme structures, cobalt co-ordination complexes, copper complexes, biomimetic homogeneous catalysts.

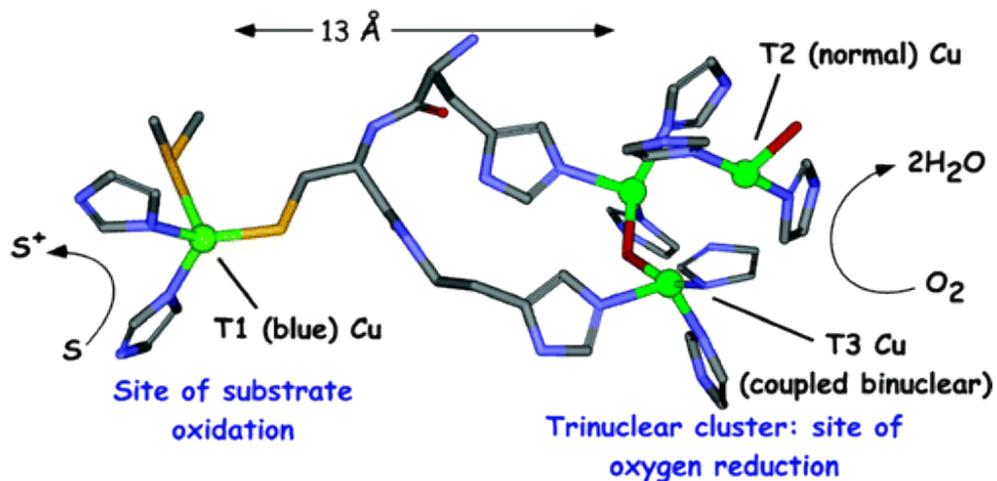


Approach

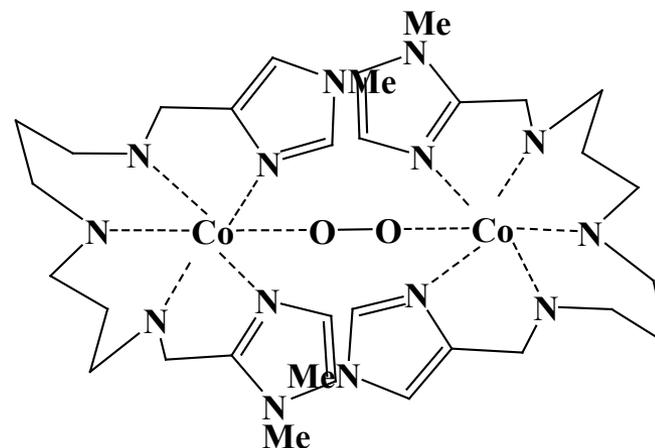
Multi-center Catalysts for better Oxygen Reduction Efficiency? Modeling and Experiment.

Enzyme ORR catalysts.

Copper catalyst centers are held in place
by IMIDAZOLE



Oxygen separation systems

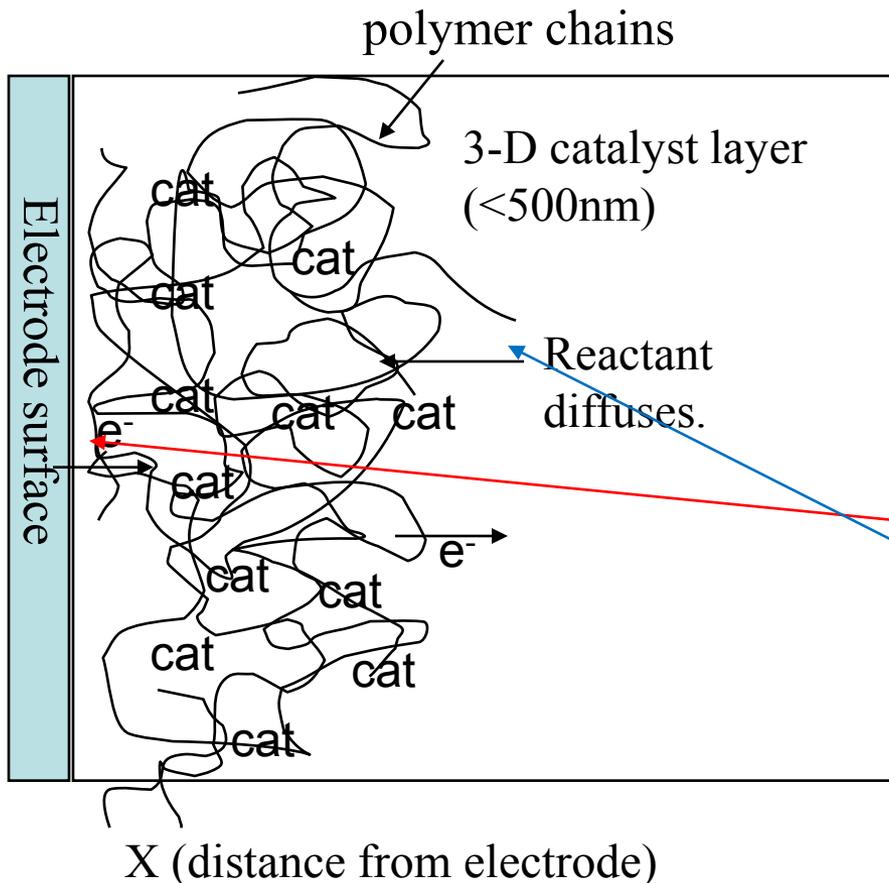


E. De Castro, B. D. Zenner, J. P. Ciccone,
L. A. Deardurff, and J. B. Kerr,
USP 4,959,135 (1990).

Nature chooses imidazole
as a base in the presence of oxygen.
Copper catalysts better than platinum?

Two vs. Three Dimensional Catalysts

3D catalyst layers allow use of homogeneous catalysts and biomimetic catalysts.

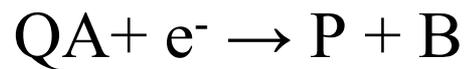


- Polymer-coated electrode provides dynamic 3-D catalyst layer that makes up for slow kinetics of the catalyst by 3-D supply of substrate to catalytic centers- geometric effect.
- Reaction rate limited by rate of charge transport from electrode to catalyst and/or rate of diffusion of reactants into polymer layer
- Catalyst site density increases.
- Overall electrode thickness remains unchanged.

Inner vs. Outer Sphere Redox Catalysis

Jean-Michel Savéant; *Chem. Rev.* **2008**, 108, 2348-2378

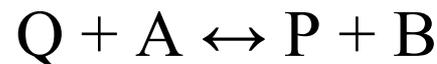
- Inner Sphere



Rate controlled by bridge formation/breaking.

Favored by metal complexes,
Adsorbed species/Surfaces

- Outer Sphere

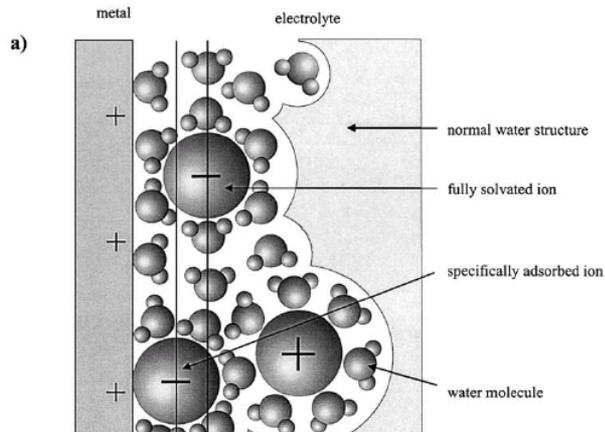


Rate controlled by equilibration rates and final reaction rate. Marcus-Hush electron transfer.

Favored by odd electron species – radical ions, radicals

Mechanism of the ORR at metal electrodes

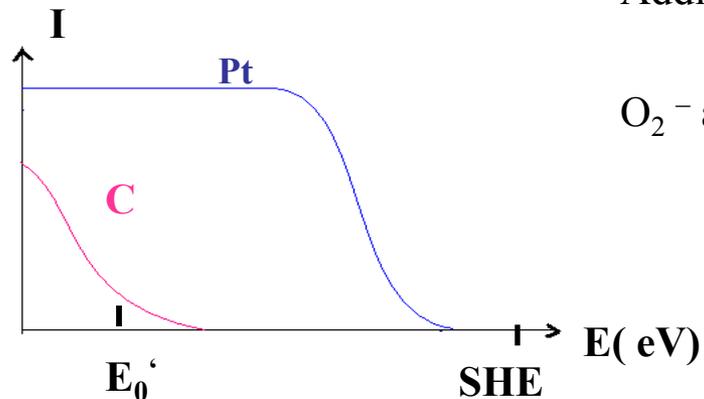
P.N. Ross & M. Head-Gordon



Rate limiting step in electrochemical reduction of O_2 is
1st electron transfer



Addition of first electron needed to break O-O bond

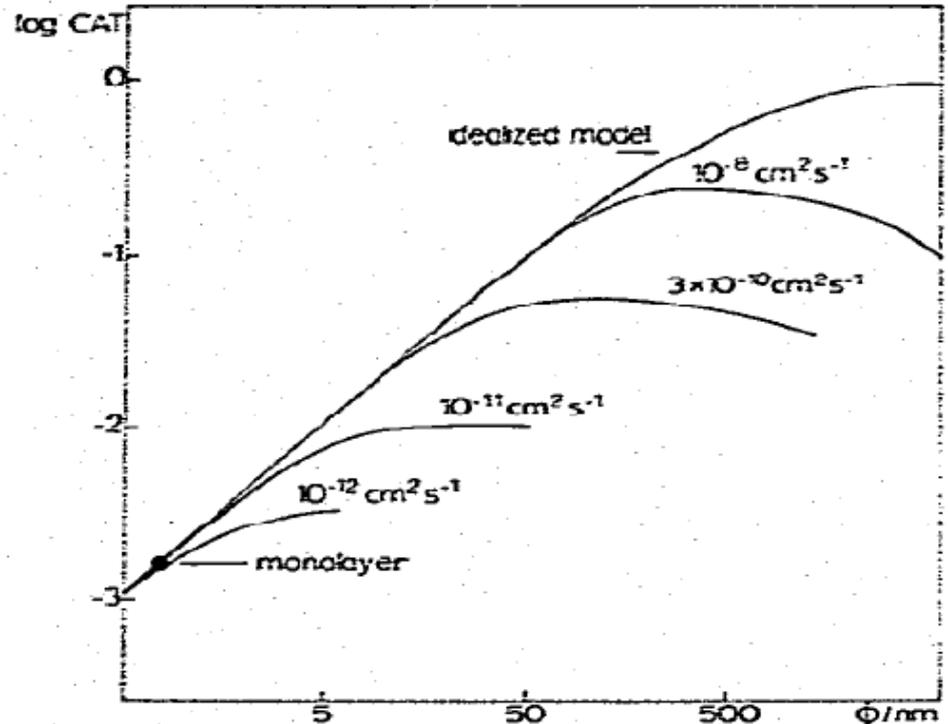
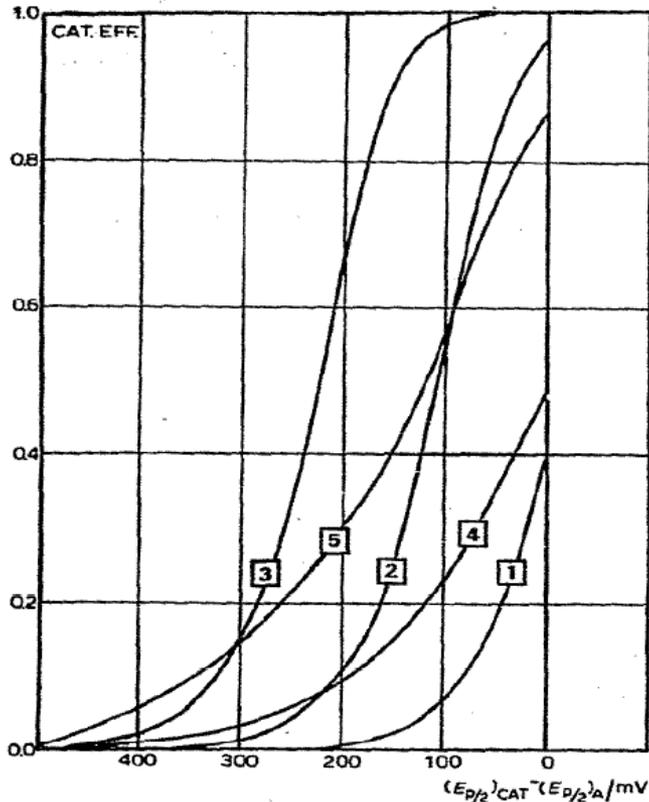


O_2^- adsorption strength related to the electronic properties of the electrode material

DFT calculations rationalize “Volcano Plot” that indicates Pt is best pure metal.

Catalysis Modeling

(Saveant 1979-80)

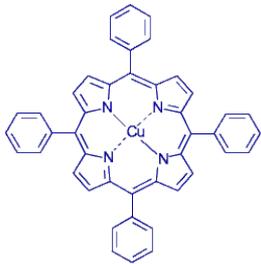


Redox catalysis at a derivatized electrode(1)
 polymer electrode with two equivalent
 monolayers(2); 100 equivalent
 monolayers(3);
 in homogeneous systems, $c_A = 1 \text{ mM}$; $c_p =$
 0.1 M (4), 0.01 M (5).

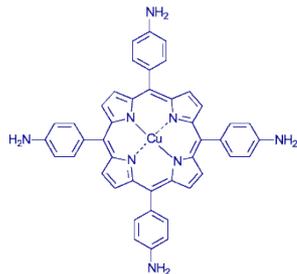
Catalytic efficiency, CAT, at a redox
 polymer electrode as a function of the film
 thickness, ϕ , for various values of the
 diffusion coefficient of the substrate
 through the film (indicated on each curve)

Catalyst screening (commercial catalysts)

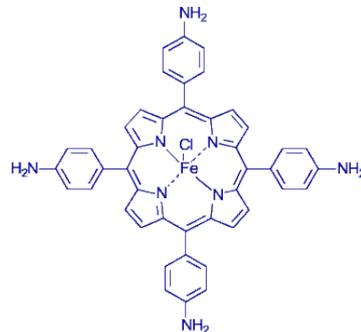
Lior Elbaz, Piotr Zelenay



Cu(II)TPP

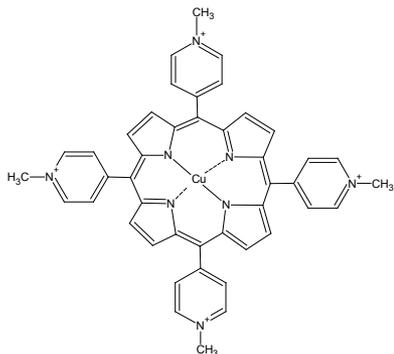
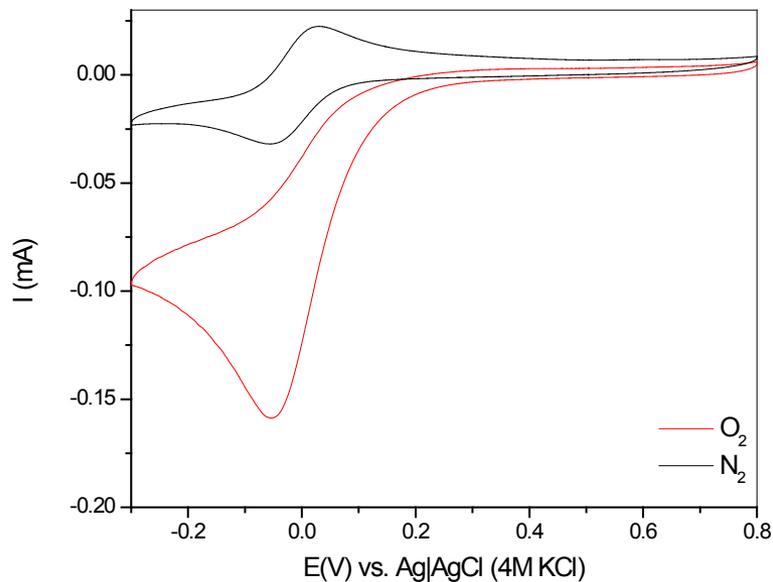


Cu(II)TAPP

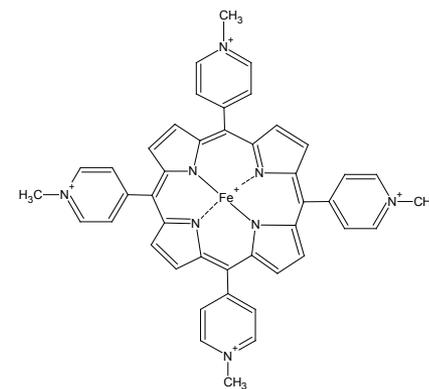


Fe(III)TAPP

0.1 mM Fe(III)TMPyP in 0.1 M H₂SO₄ (@100mV/s)



Cu(II)TMPyP

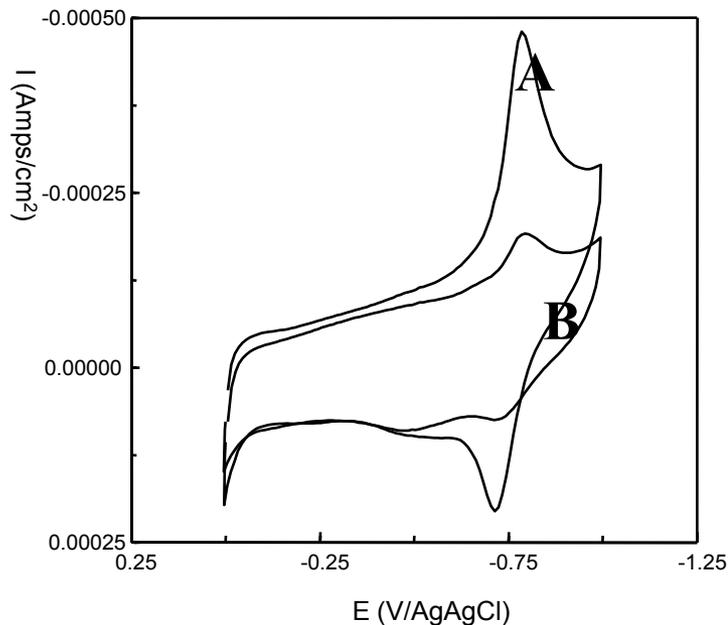


Fe(III)TMPyP

Catalyst	ORR activity
Cu(II)TPP	X
Cu(II)TMPyP	✓
Cu(II)TAPP	X
Fe(III)TMPyP	✓
Fe(III)TAPP	✓

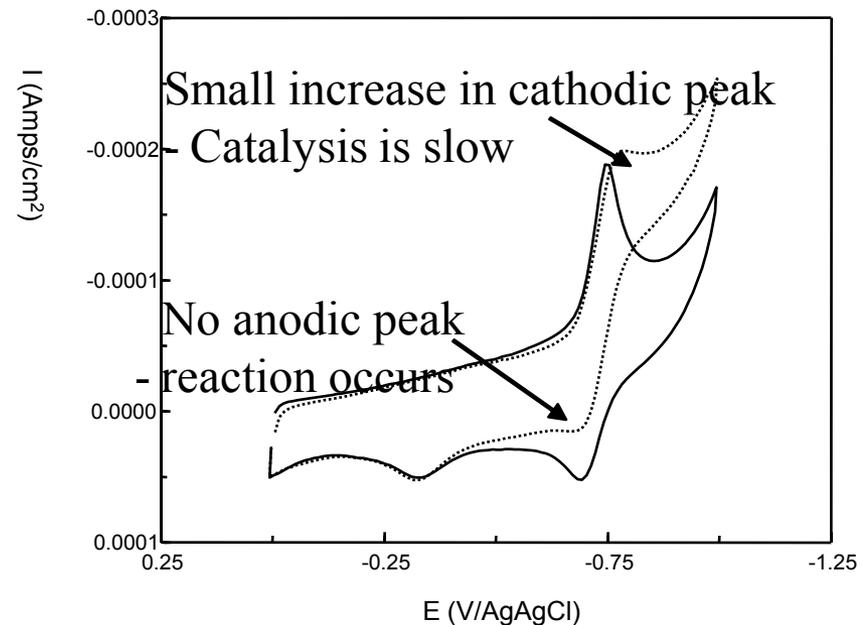
Example of a polymer-tethered metal ion catalyst (John Kerr)

50mV/s in tris/HCl buffer of pH=9



Polymer containing “Rh” monomer
Polymerization at a gold electrode
for 3 hours (B) and overnight (A).

10mV/s in tris/HCl buffer of pH=7.5.

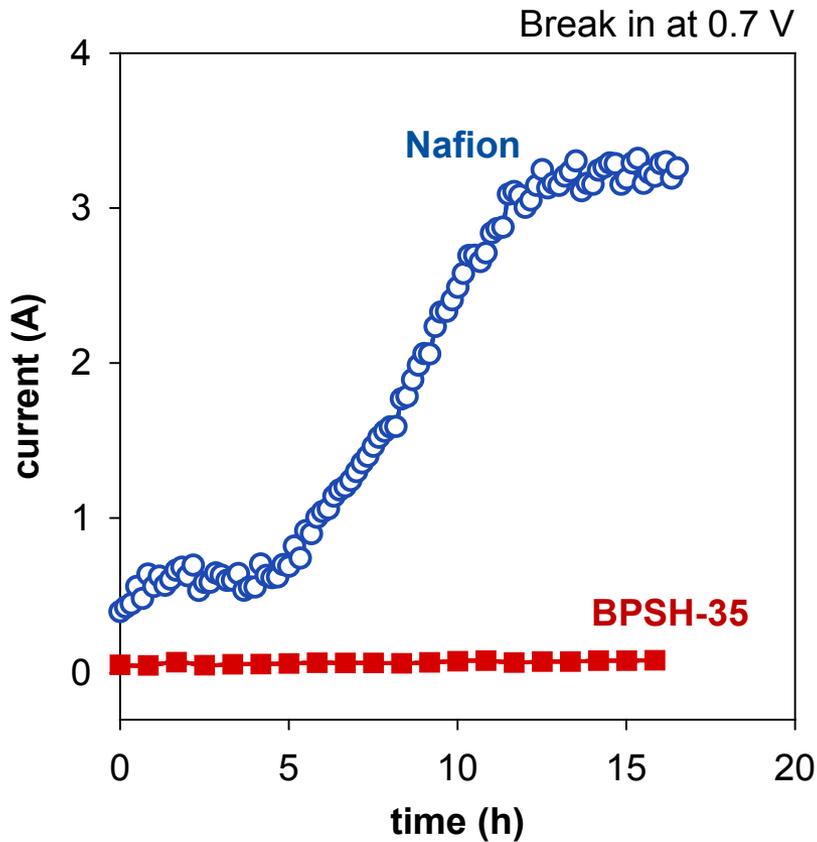


Coated gold electrode with a “Rh” polymer
Before (solid line) and after addition of
substrate (dotted line).

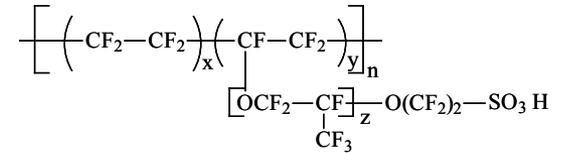
Catalyst activity found to be affected by presence of polymer matrix or organic solvents. Need to provide adequate buffering in the polymer so that proton transport is adequate.

Polymer Properties in MEA electrode

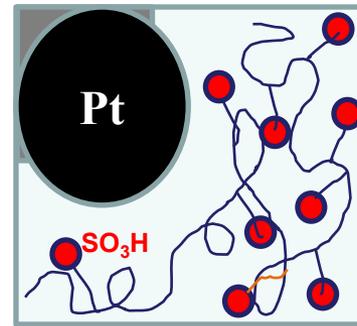
Effect of Chain Mobility on Break-in Process (Yu Seung Kim)



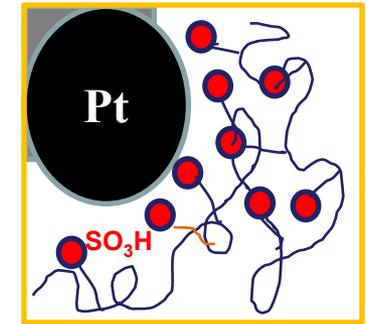
Nafion®



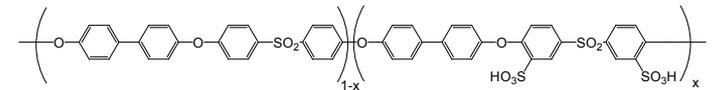
Before break-in



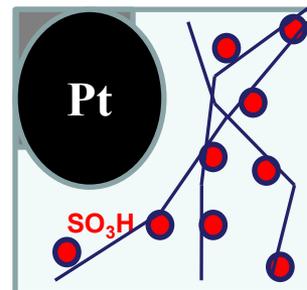
After break-in



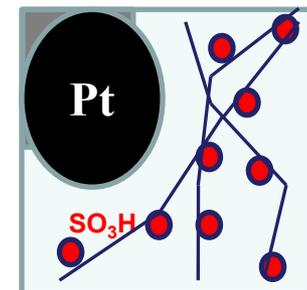
BPSH-35



Before break-in



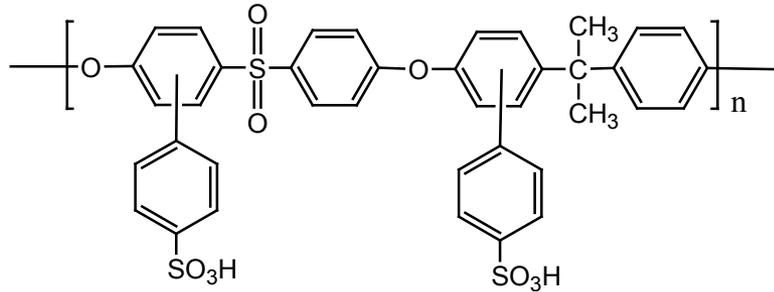
After break-in



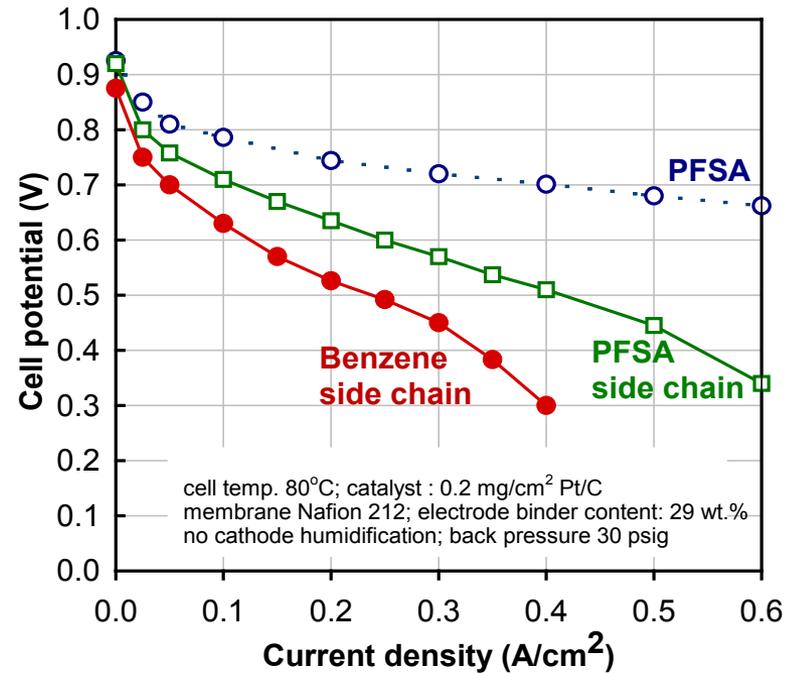
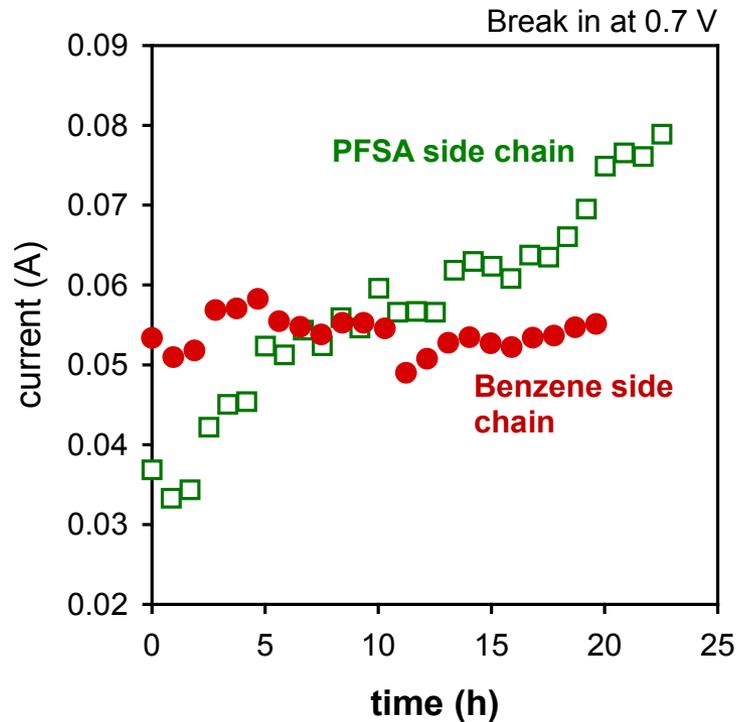
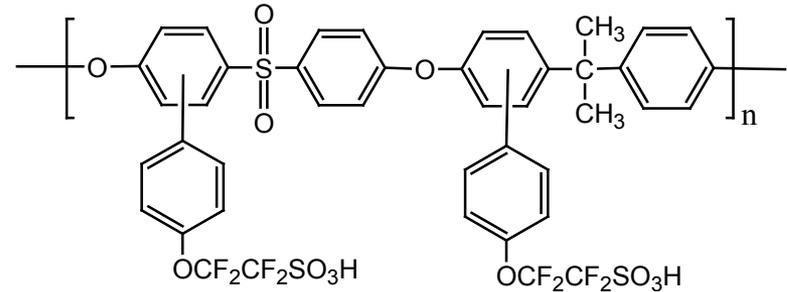
Effect of side chain mobility on electrode performance

(Yu Seung Kim)

Sulfonated polyaromatic (IEC=2.3 meq/g)*



Polyaromatic-PFSA side chain (IEC=2.1 meq/g)*



*Courtesy: Prof. Bae (UNLV)

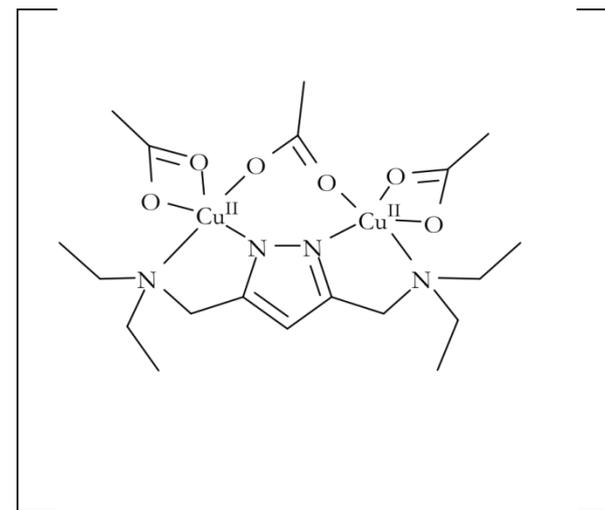
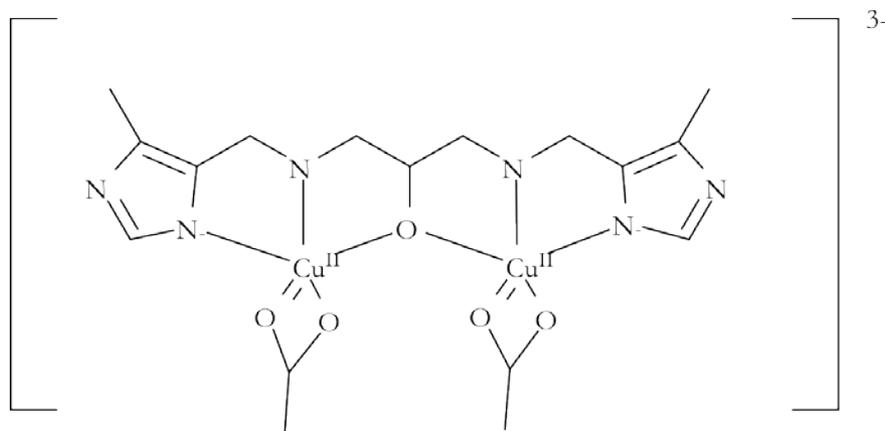
Computational Studies of Di-Copper Complexes as ORR Catalysts

Neil Henson (LANL) and M. Head-Gordon (LBNL)

Approach :

1. Quantum chemical calculations using *Gaussian09* and *QChem* software
2. Screen di-copper complexes based on imidazole and pyrazole heterocycles inspired by copper laccase chemistry

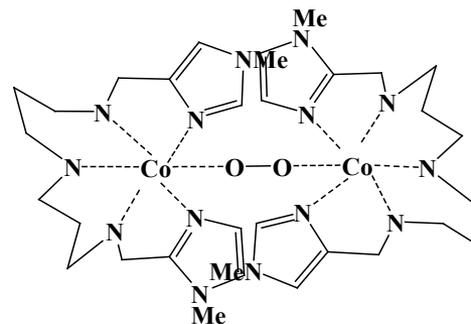
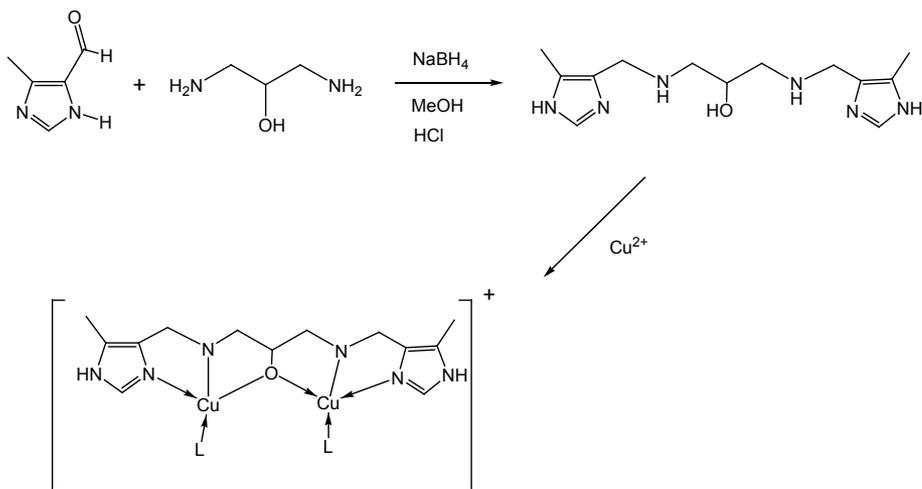
Candidate Coordination Complexes Based on Nitrogen Heterocycles



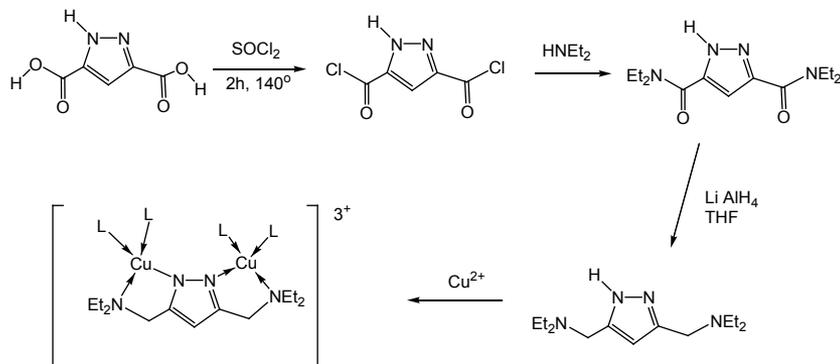
1. Crucial feature of structure is to allow Cu-Cu distance to be sufficient to allow bridging dioxygen coordination
2. Co-planer coppers may be advantageous
3. Solvent ligands are the counter-ions: acetate, sulfate or triflate

Synthetic Routes to Bimetallic Catalysts

Boncella (LANL), Arnold(LBNL)



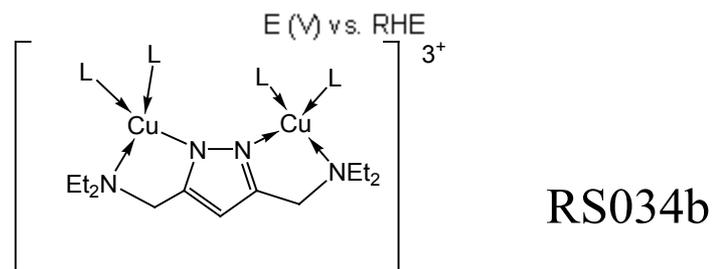
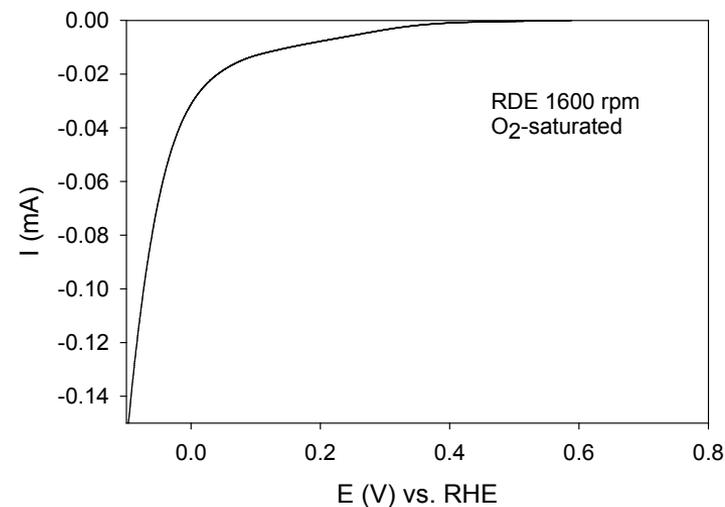
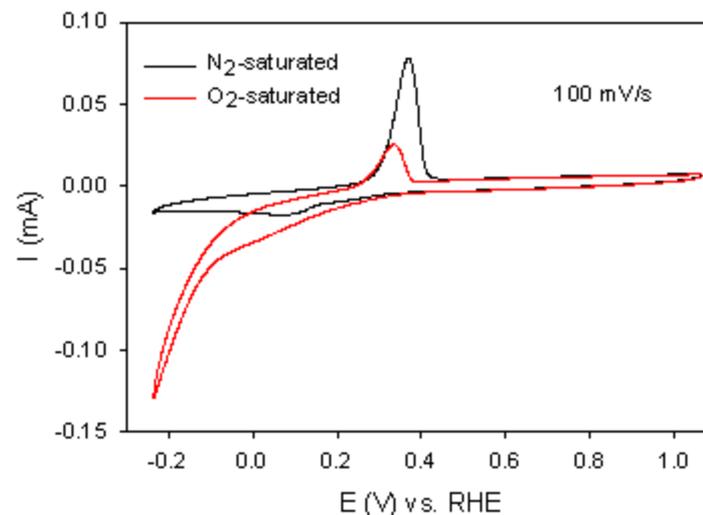
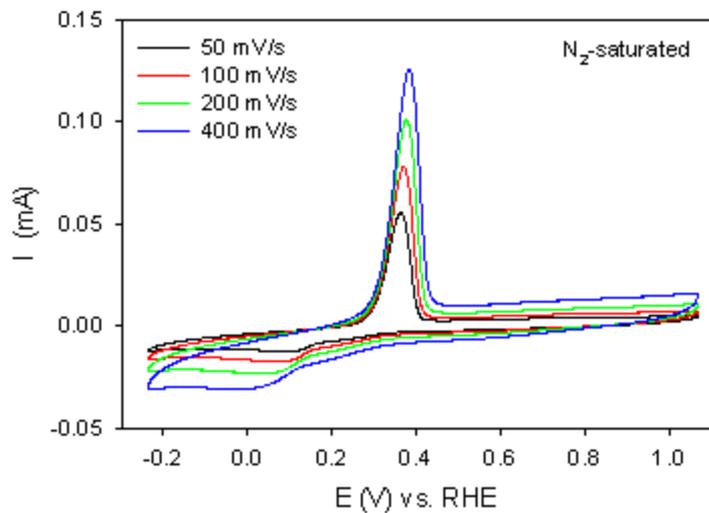
E. De Castro, B. D. Zenner, J. P. Ciccone, L. A. Deardurff, and J. B. Kerr, USP 4,959,135 (1990).



Collaborate with other groups
 – e.g. Andy Gewirth, U. of Illinois at Urbana-Champaign(DOE-BES funding), S. Mukerjee (Northeastern (EERE-funded) Saveant (Europe)

Electrochemical Characterization.

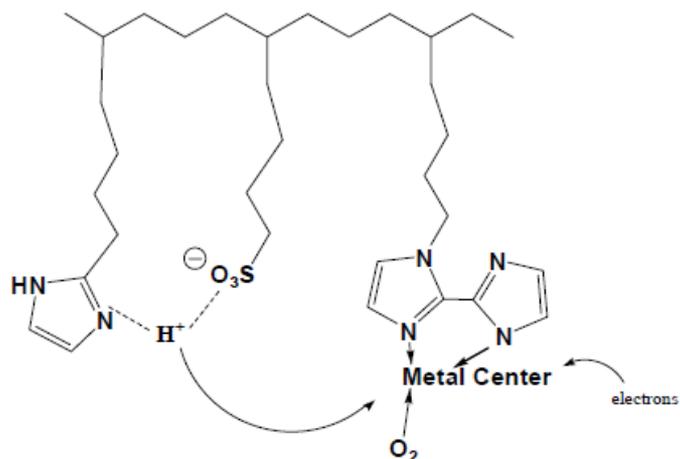
Di-nuclear copper complex dissolved in 0.1 M HClO₄



- Electrochemical-chemical mechanism is likely for ORR catalysis at $E_{1/2}=0.25\text{V}$
- Increase in current observed at high overpotential attributed to ORR on carbon

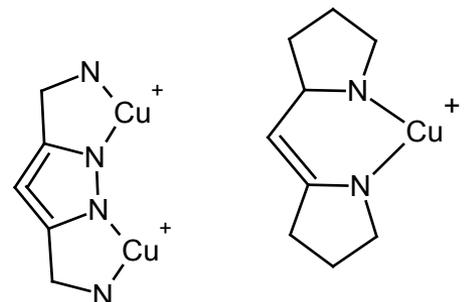
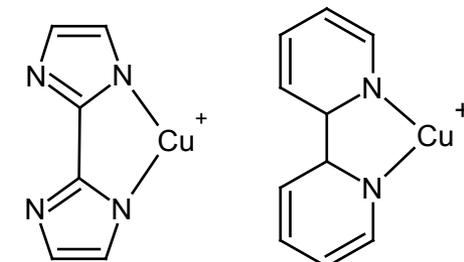
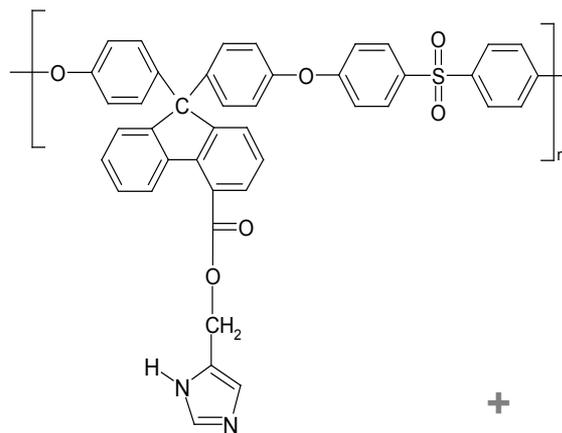
Examples of Catalyst Attachment

Coordination of transition metals in imidazole-containing polymers

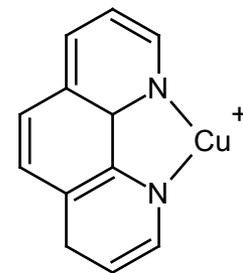
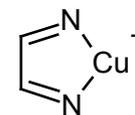
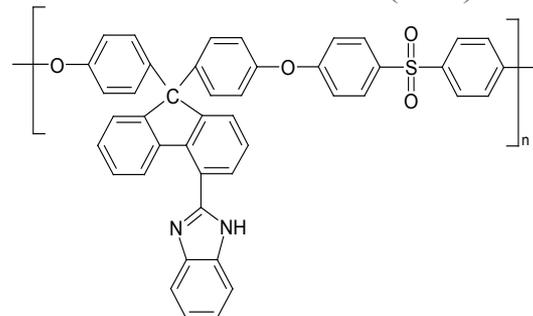


Tethering Cu(I) complexes to imidazole containing polymers

PAES-COOH-Im (Im1)



PAES-COOH-Bim (Im2)

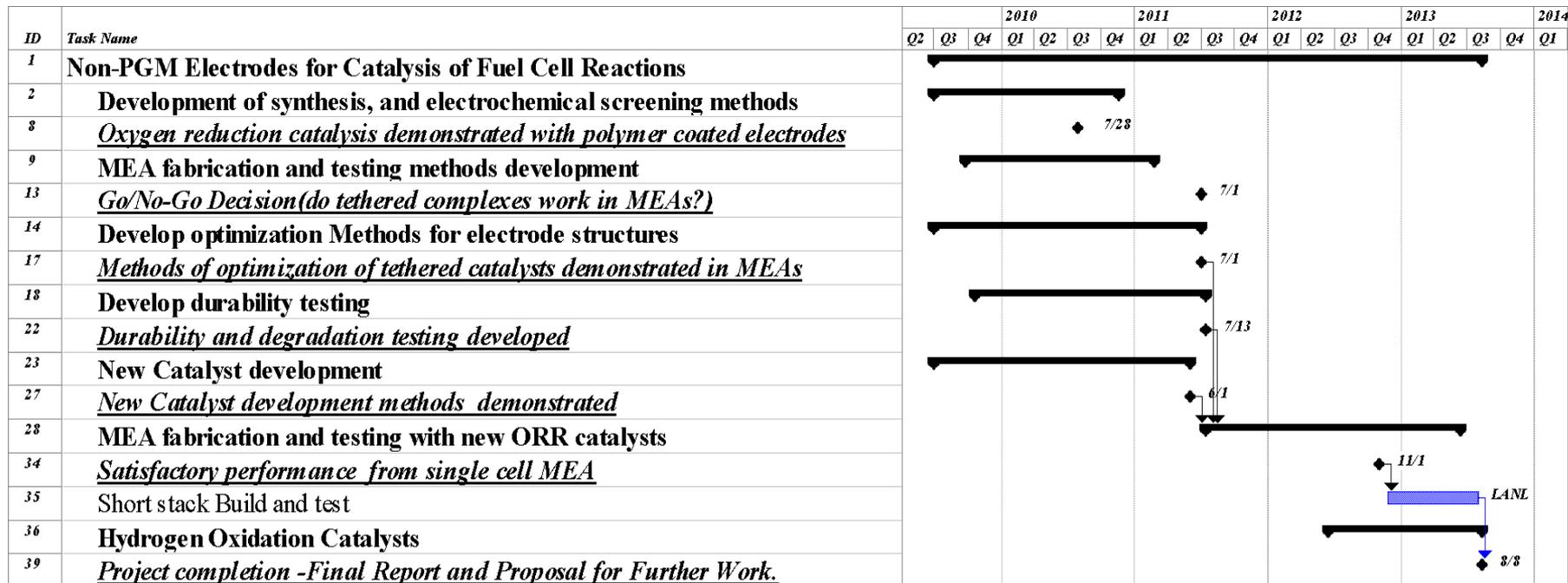


Future Work

- Use Polymer binder/ink to bind homogeneous oxygen catalysts
 - Catalyst structures based on classical Heme, macrocyclic and Salen complexes
 - Catalysts similar to those used by LANL and 3M
 - Catalyst structures mimicked after Copper Laccase- co-operativity.
- Use polymer materials from current Membrane Project (FC033)
 - Modify polymers to accommodate MEA needs.
- Compare catalytic activity to platinum
 - Intrinsic activity -overpotential, Turn-over Frequency (TOF)
- Model behavior to predict required performance.
 - Proton and electron transport rates; substrate diffusion and product removal. Model intrinsic reaction rates.
- Carry out stability/degradation tests
 - Turn-over Number (TON); possible preventive/repair mechanisms
- Build and test MEAs with new electrode structures.
 - Build, test and deliver cell stack.

Project Schedule

Milestones & Go/No-Go Decisions.



Milestone 1. Oxygen reduction catalysis demonstrated with polymer coated electrodes(12mo).

Milestone 2. Go/No-Go Decision. Oxygen reduction catalysis demonstrated with polymer-bound catalyst layers in MEAs (24mo).

Milestone 3. Methods of optimization of catalysts demonstrated in MEAs (24mo).

Milestone 4. Durability and degradation testing developed (24mo).

Milestone 5. New catalyst development methods demonstrated (24mo).

Milestone 6. Satisfactory performance from single cell MEAs (39mo). Go/No-Go decision to build stack and test.

Summary

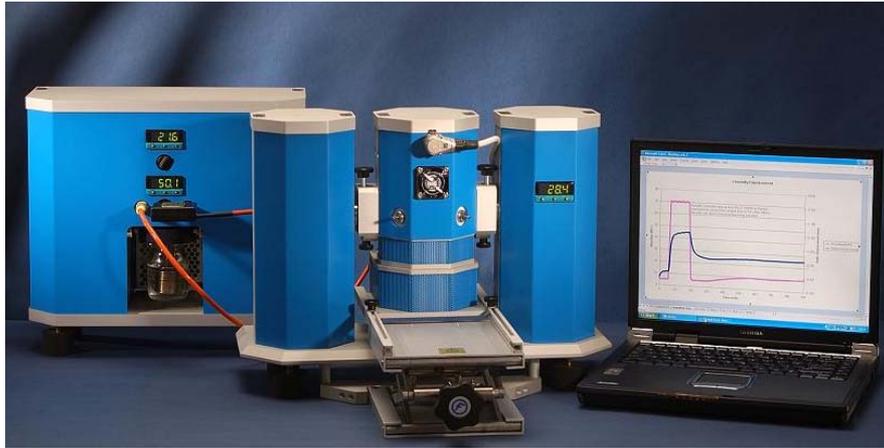
Budget & Tasks.

- Years 1-4. LBNL \$1415k; LANL \$965k; 3M in kind
- Polymer synthesis – LBNL and LANL
- Perfluorinated polymer synthesis – 3M
- Catalyst preparation and testing – LBNL/LANL
- Catalyst modeling – LBNL/LANL
- Catalyst attachment to polymers – all
 - Electrochemical testing - LBNL/LANL/3M
 - Morphological testing – LBNL/LANL
 - Chemical degradation testing- 3M/LBNL
- Macroscopic modeling of transport properties - LBNL
- LANL and 3M make and test MEA's.
- Stack construction and testing – LANL (Giner subcontract)

Supplemental Slides

No responses to Reviewer
Comments. New project.

Some available methods to probe polymer dynamics



Dynamic Mechanical Analyzer (& Dielectric Thermal Analysis) with humidification



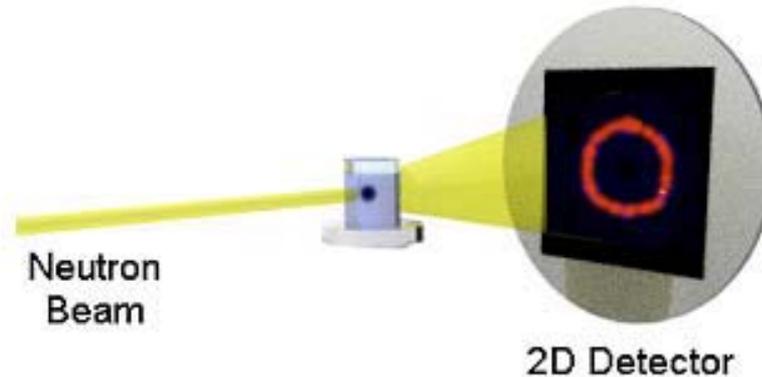
Scribner High Temperature Fuel Cell Station



Pulsed Field Gradient Spin Echo NMR



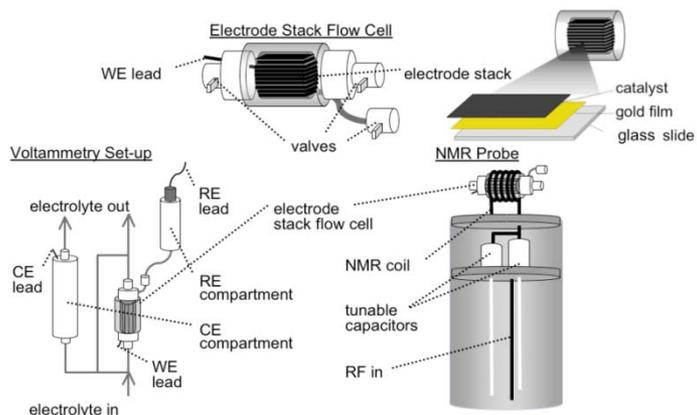
Dynamic Vapor Sorption



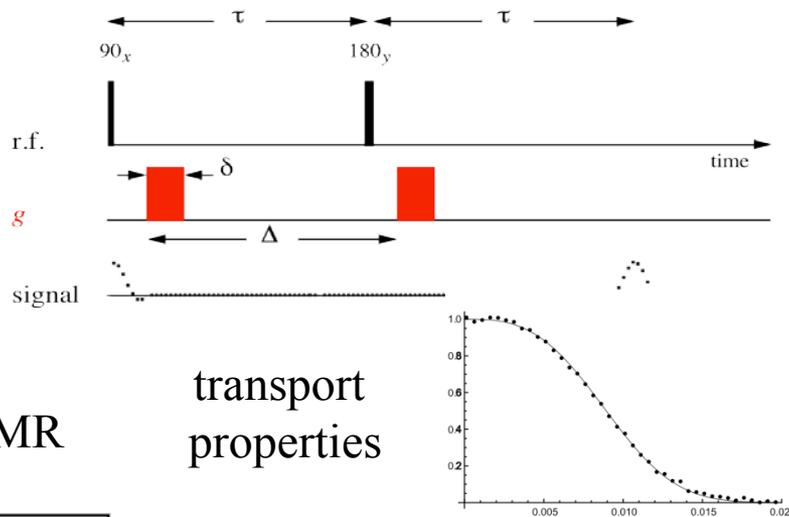
Neutron Scattering (SANS, QENS) with humidity control



NMR methods for characterization of catalysts and electrodes

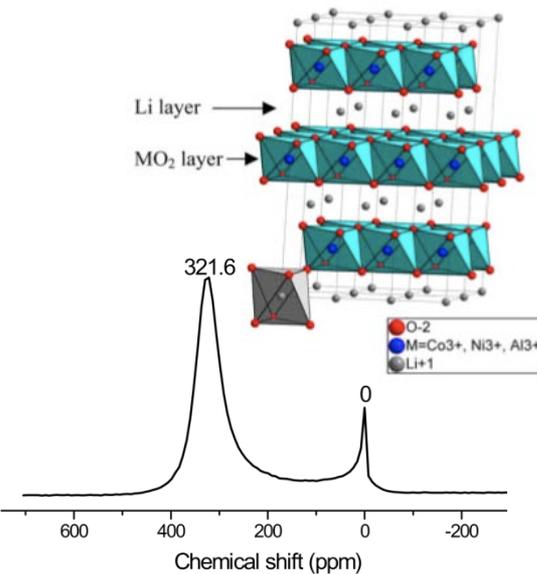
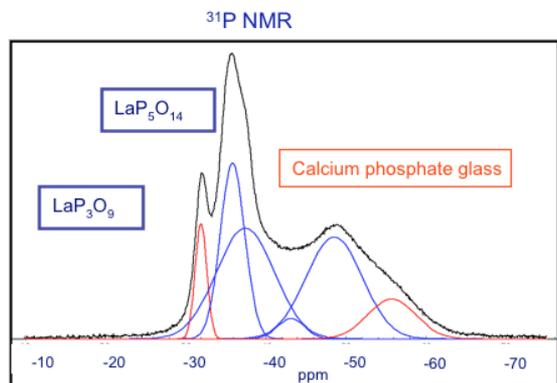


e-chem NMR



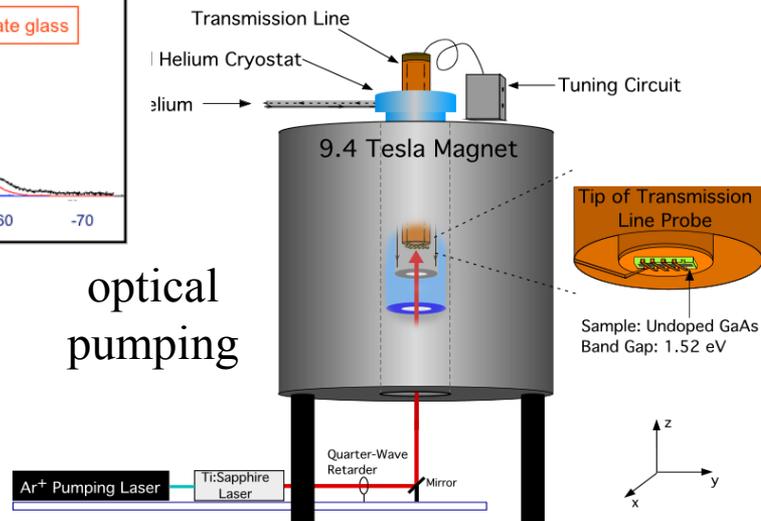
transport properties

routine solids NMR



paramagnetic systems

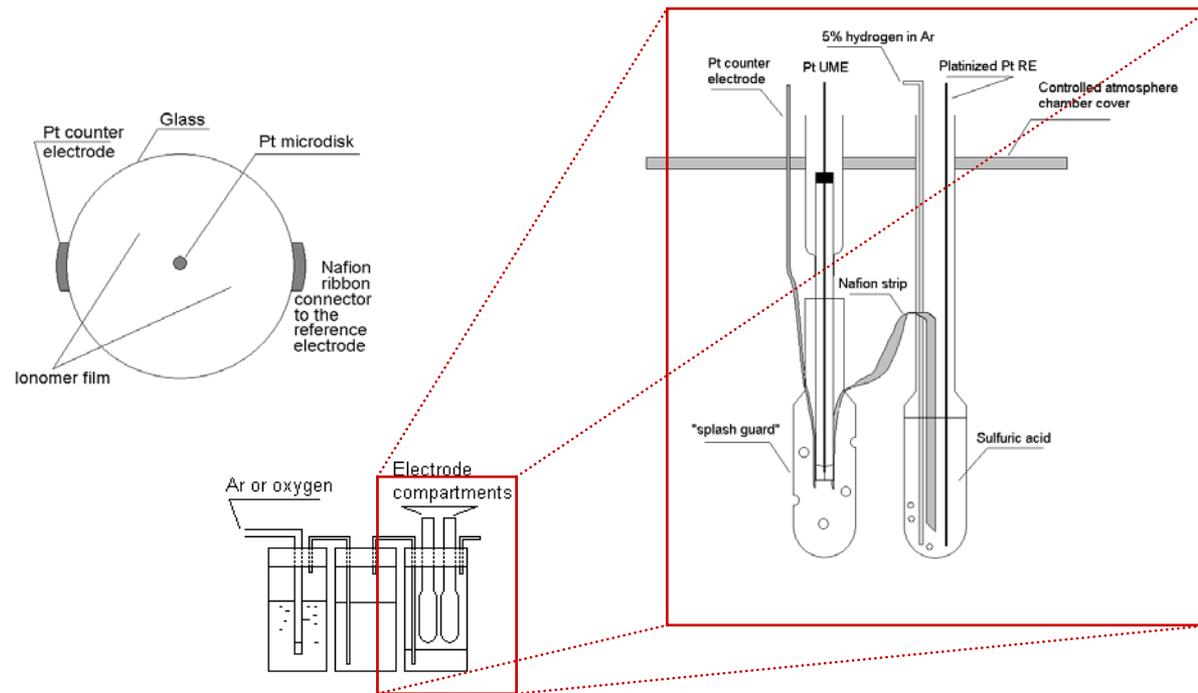
optical pumping



Ionomer Characterization

Available/selected ionomers will be tested for:

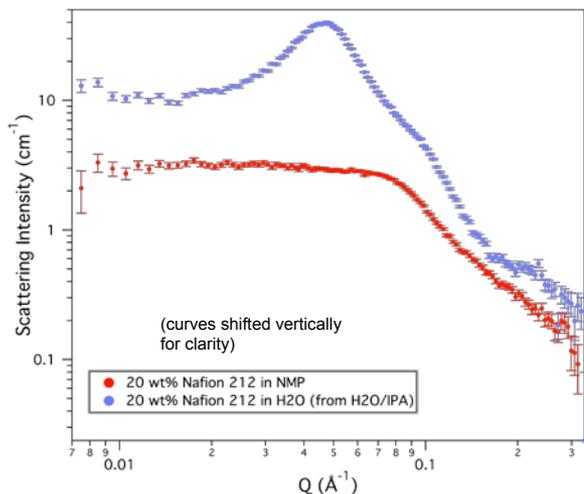
- Oxygen permeability
- Restructuring
- Temperature/humidity effects on the electrochemical behavior



Uribe et al, *J. Electrochem. Soc.*, 139 (1992) 765

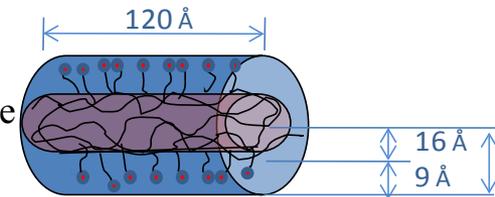
Polymer ink characterization for electrode fabrication (LANL Applied Science Program)

SANS: NMP- vs. H₂O-Based Gels



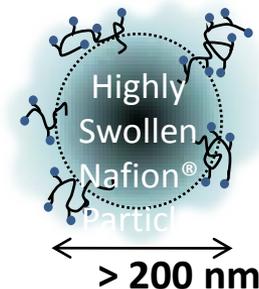
NMP dispersion: Core-Shell Cylinder

- 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)



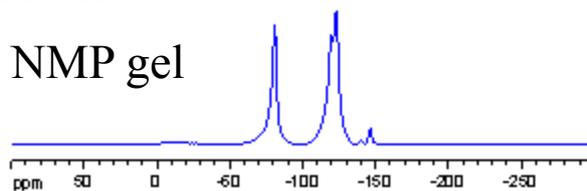
Aqueous mixture: Highly swollen particles

- SANS data cannot be fit to any particle shape form factor
- Data fits well to clustering / solvation model

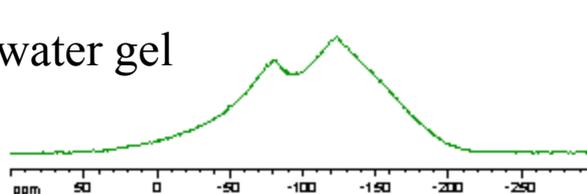


¹⁹F NMR

NMP gel

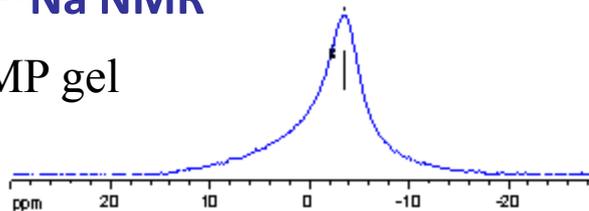


water gel

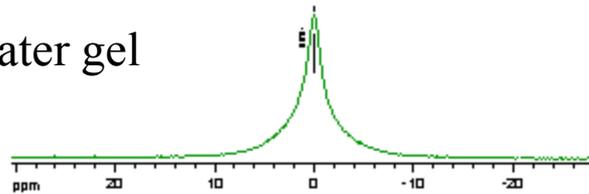


²³Na NMR

NMP gel



water gel



NMP solvates backbone and side chains while Na⁺ clusters. Water solvates Na⁺ with little backbone or side chain solvation

Full Project Schedule.

