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 Kostecki, 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)

Relevance - Objectives

DOE Technical Targets

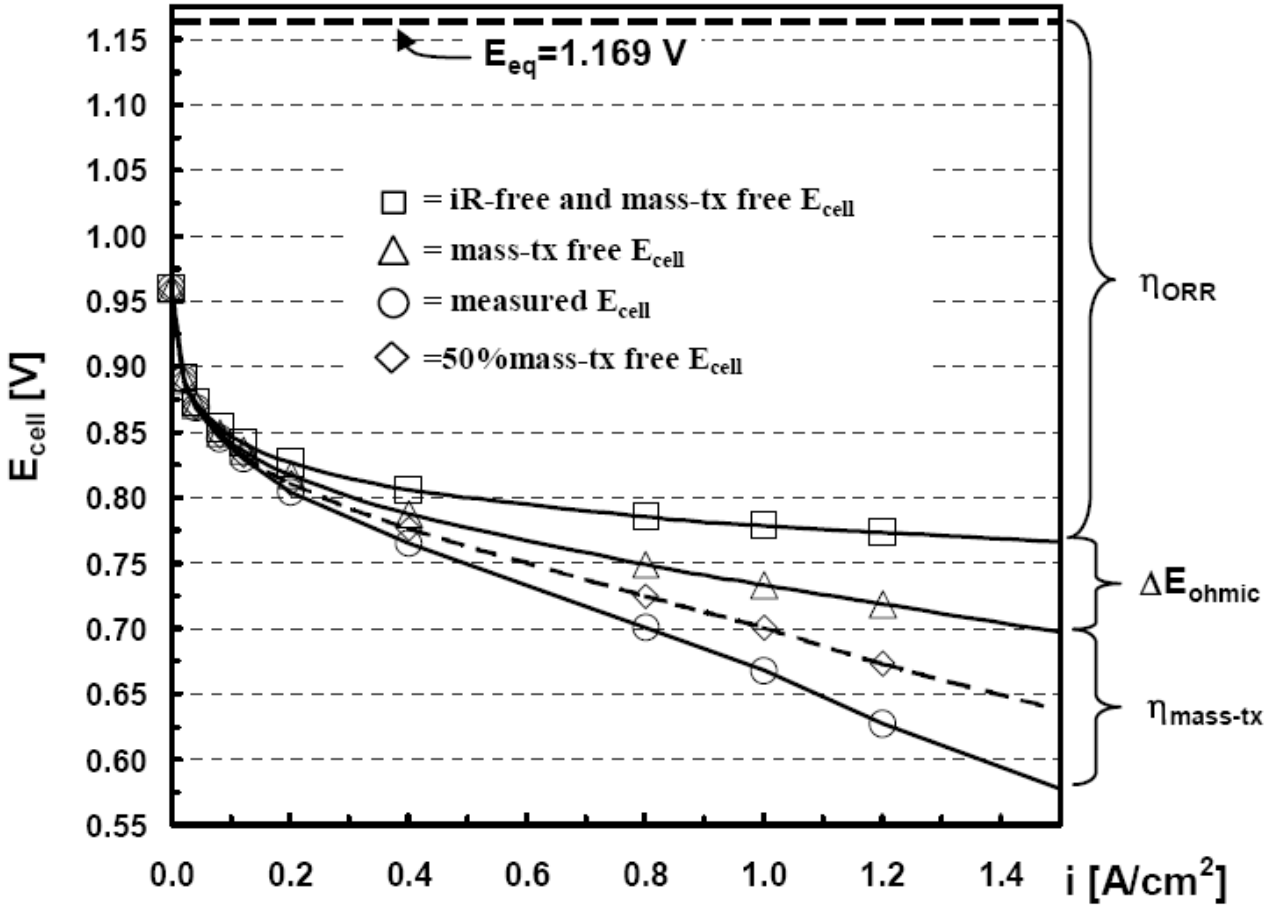
- Non-Pt catalyst activity per volume of supported catalyst – 300A/cm^3
- Cost < $3/kW
- Durability > 5000 hours (> 120^{o}C)
  - Electrochemical area loss <40%
  - Electrochemical support loss < 30mV after 100hrs @ 1.2V

Project Objectives

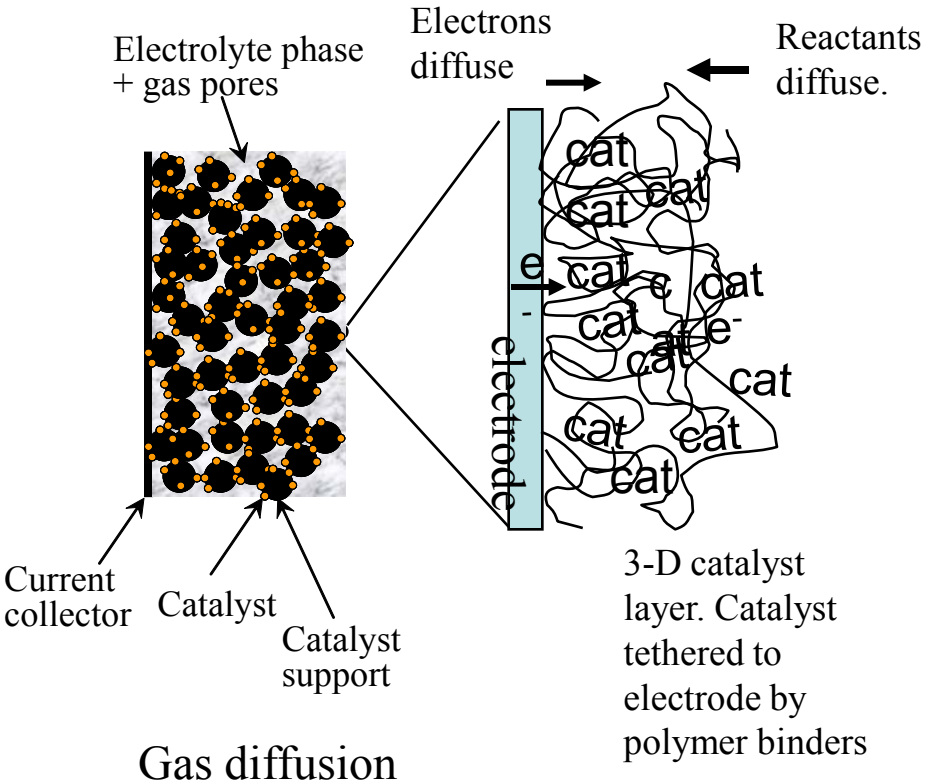
1) Demonstrate that non-platinum group metal catalysts can be used for oxygen reduction in polymer-coated electrode structures based on polyelectrolyte membranes. (Year 1).
2) Incorporate catalysts into polymer binders of composite electrodes for the construction of MEAs to demonstrate that this is an 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



Gas diffusion electrode structure

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

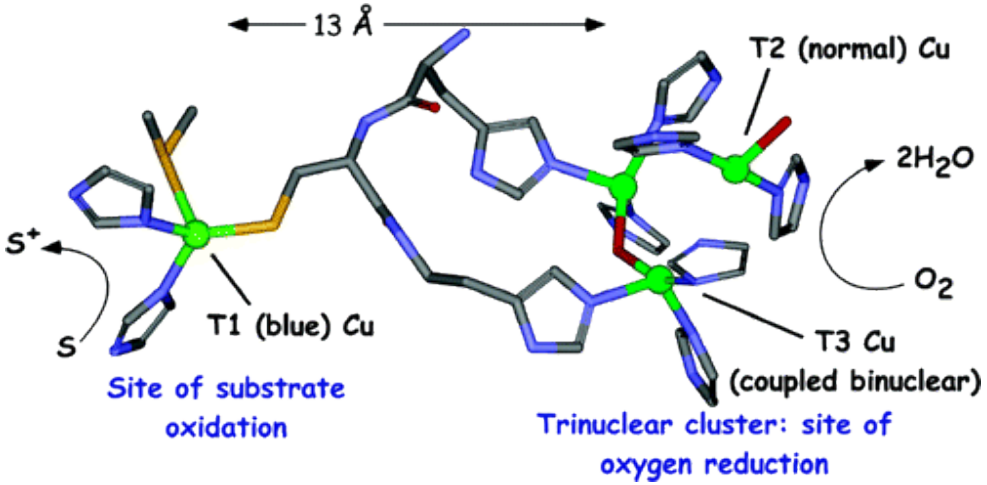
cat = e.g. Fe phenanthroline, heme structures, cobalt co-ordination complexes, copper complexes, biomimetic homogeneous catalysts.

Approach

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

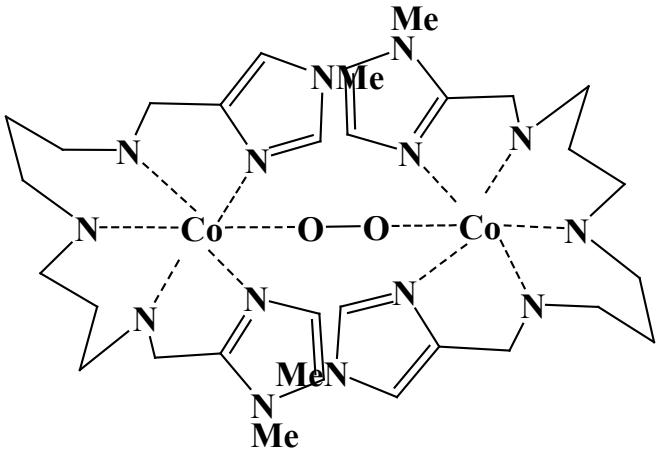
Enzyme ORR catalysts.

Copper catalyst centers are held in place by IMIDAZOLE



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

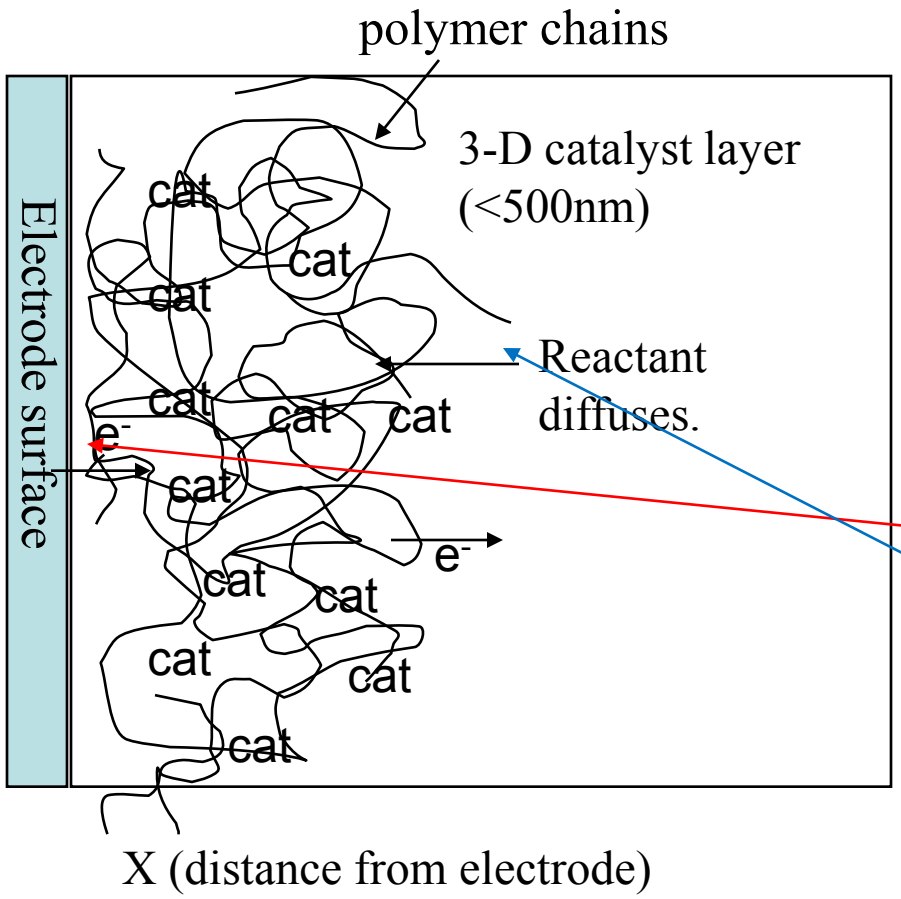
Oxygen separation systems



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

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

$$P + e^- \rightarrow Q$$

$$Q + A \rightarrow QA$$

$$QA + e^- \rightarrow P + B$$

$$B \rightarrow \text{Products}$$

Rate controlled by bridge formation/breaking.

Favored by metal complexes, Adsorbed species/Surfaces

- Outer Sphere

$$P + e^- \rightarrow Q$$

$$Q + A \leftrightarrow P + B$$

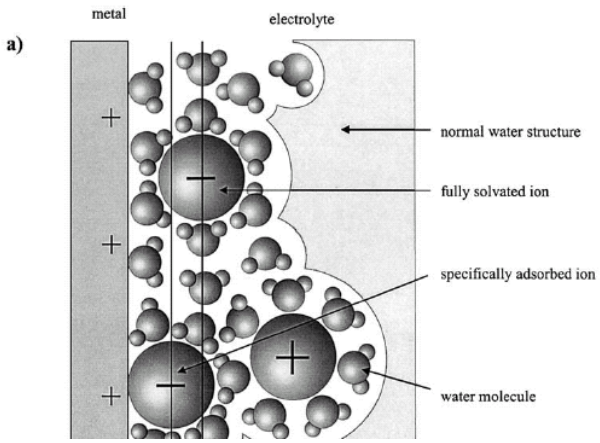
$$B \rightarrow \text{Products}$$

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

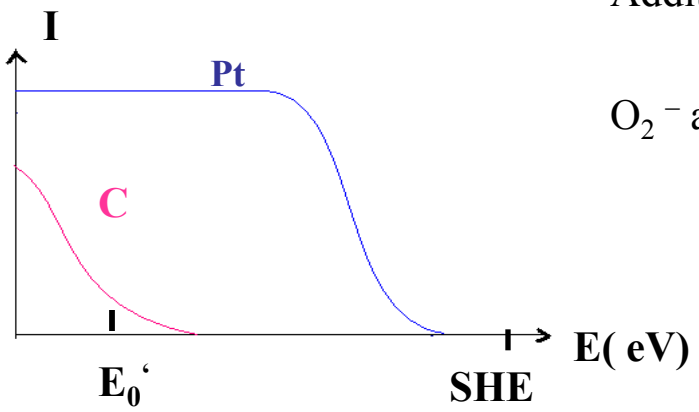


Rate limiting step in electrochemical reduction of O_2 is 1st electron transfer

$O_2 + 1\ e^- \rightarrow (O_2^-)_{sol}$ Outer Sphere ($\mathbf{E_0' = -0.3\ V}$)

$O_2 + 1\ e^- \rightarrow (O_2^-)_{ads}$ Inner Sphere ($\mathbf{E_0' + \Delta G_{ad}/F}$)

Addition of first electron needed to break O-O bond

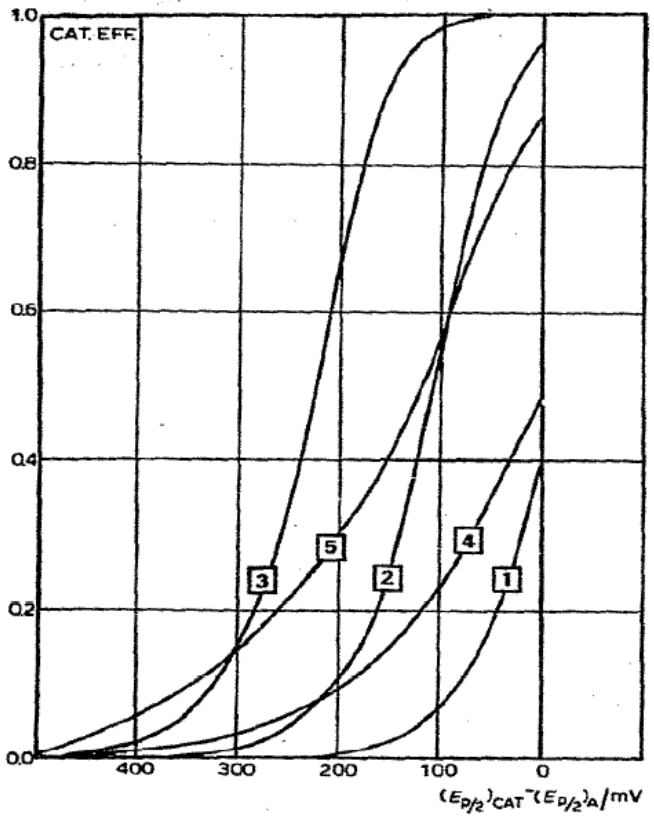


O_2^- adsorption strength related to the electronic properties of the electrode material

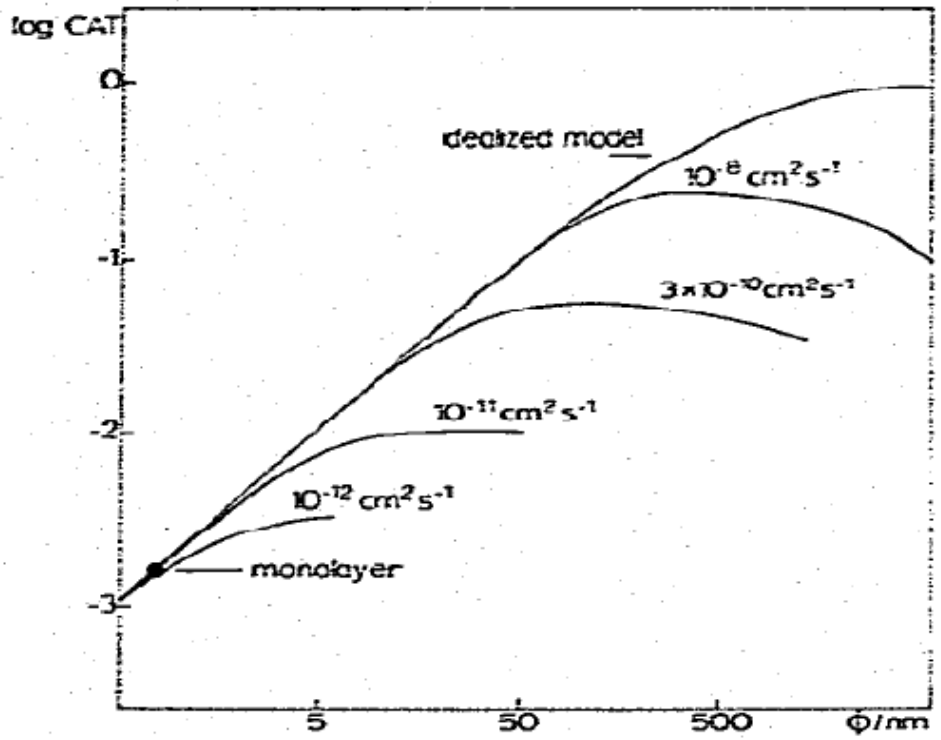
DFT calculations rationalize "Volcano Plot" that indicates Pt is best pure metal.

Catalysis Modeling

(Saveant 1979-80)

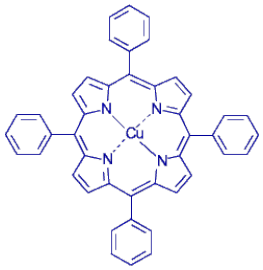


Redox catalysis at a derivatized electrode(1) polymer electrode with two equivalent monolayers(2); 100 equivalent monolayers(3);
in homogeneous systems, c_A = 1mM; c_p = 0.1M (4), 0.01M (5).

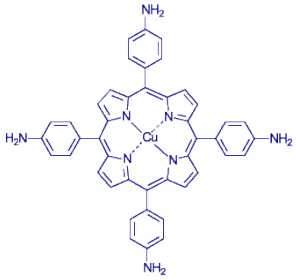


Catalytic efficiency, CAT, at a redox polymer electrode as a function of the film thickness, φ, for various values of the diffusion coefficient of the substrate through the film (indicated on each curve)

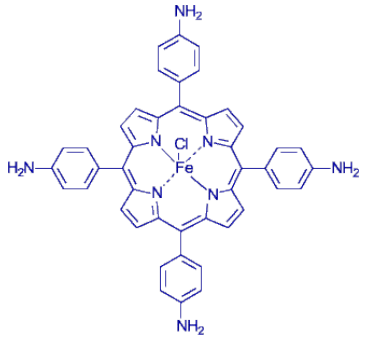
Catalyst screening
(commercial catalysts)
Lior Elbaz, Piotr Zelenay



Cu(II)TPP

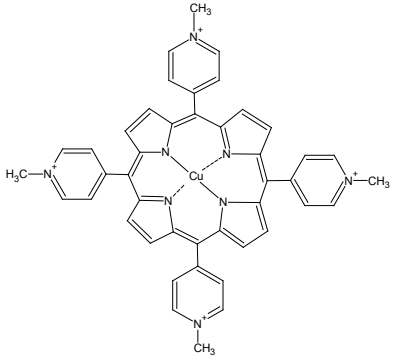


Cu(II)TAPP

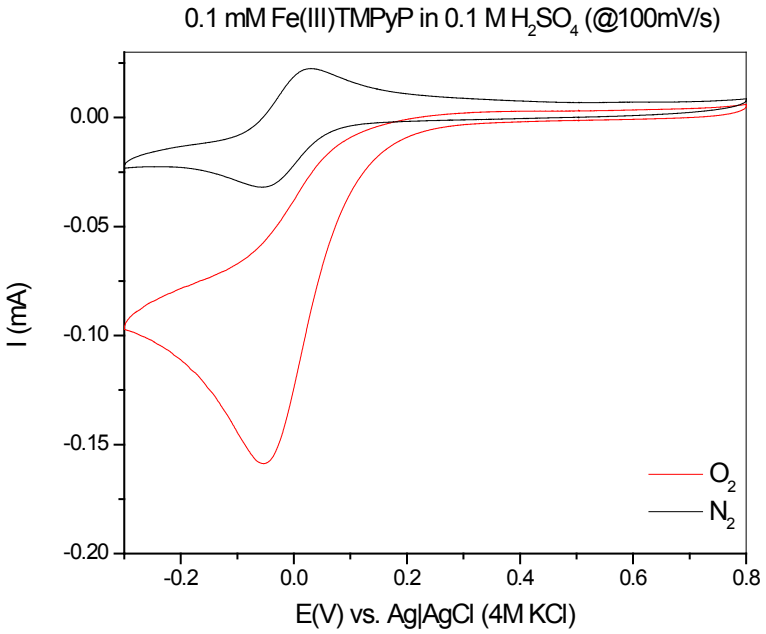


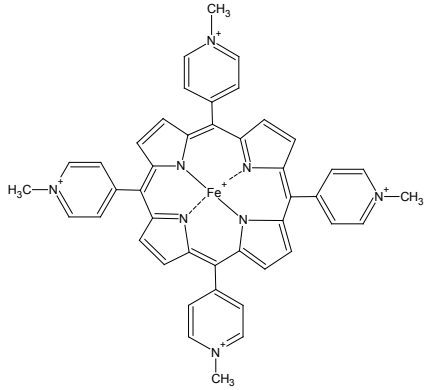
Fe(III)TAPP

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



Cu(II)TMPyP



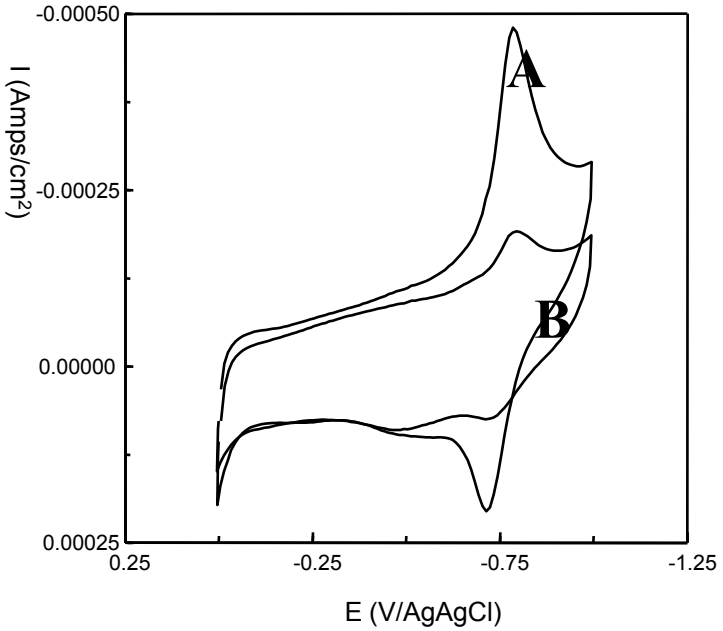


Fe(III)TMPyP

Example of a polymer-tethered metal ion catalyst

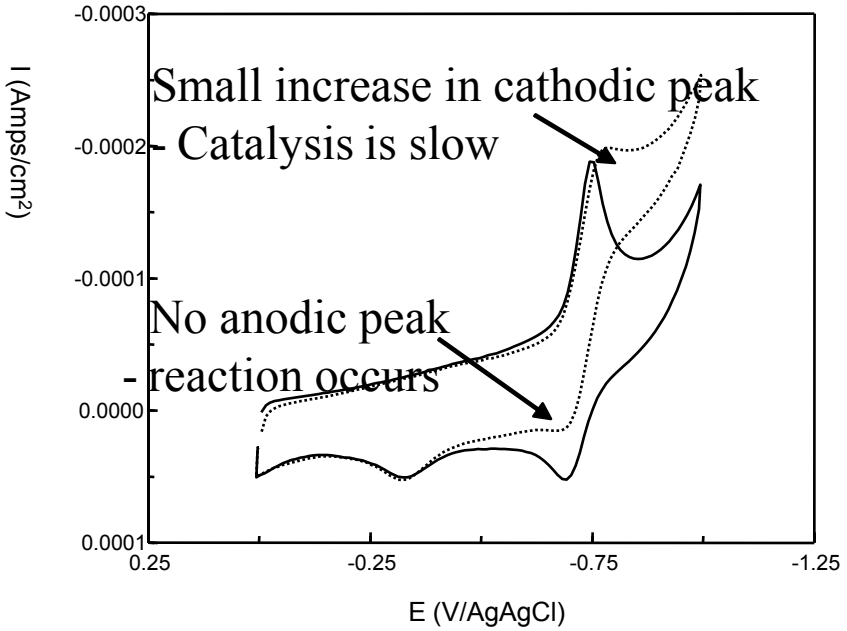
(John Kerr)

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.

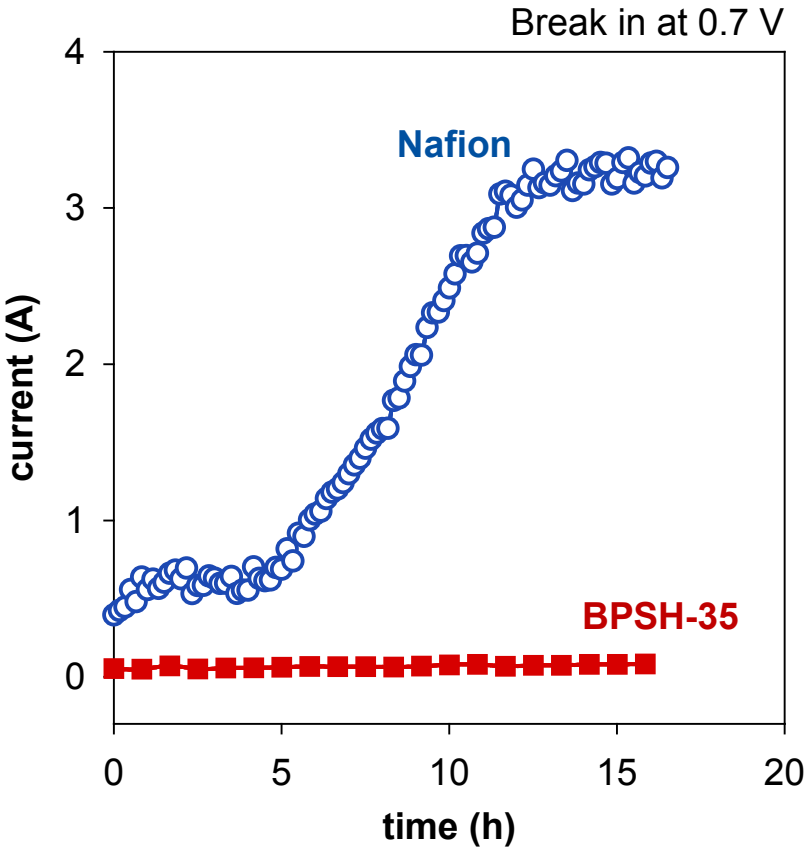


Coated gold electrode with a "Rh" polymer Before (solid line) and after addition of substrate (dotted line).

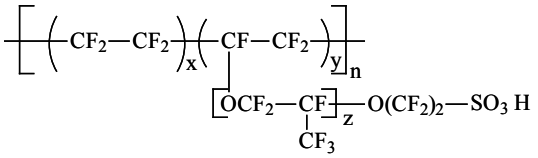
Catalyst activity found to be affected by presence of polymer matrix or organic solvents. Need to provide adequate buffering in the polymer so that proton transport is adequate.

Polymer Properties in MEA electrode

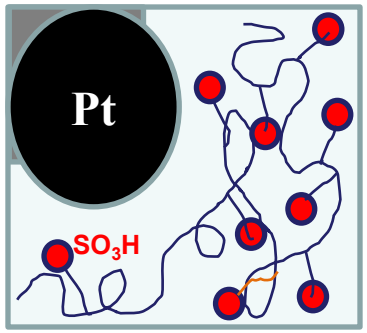
Effect of Chain Mobility on Break-in Process (Yu Seung Kim)



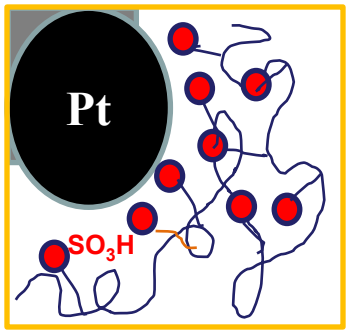
Nafion®



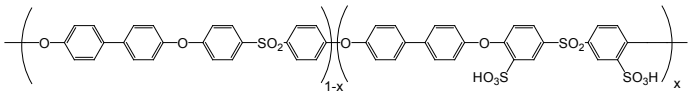
Before break-in



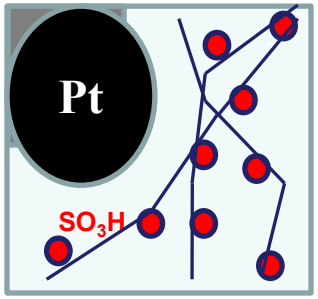
After break-in



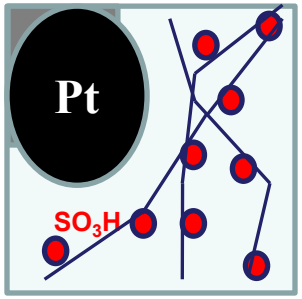
BPSH-35



Before break-in



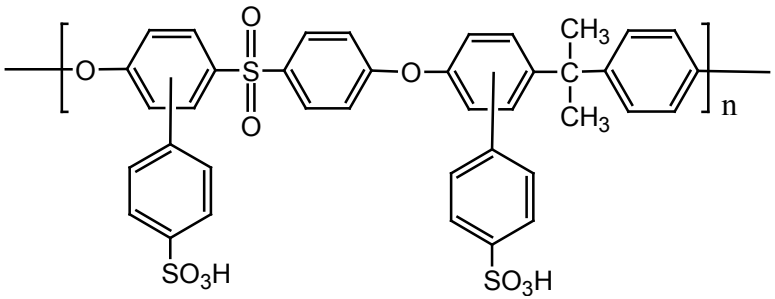
After break-in



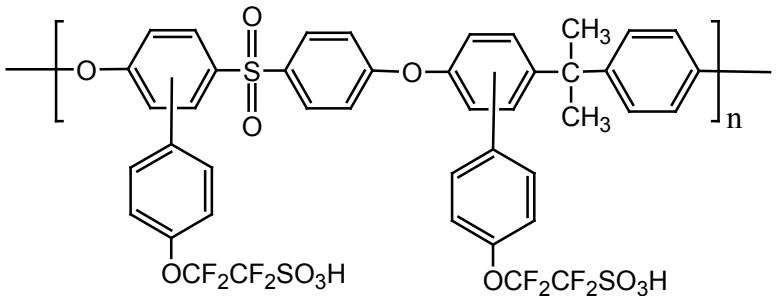
Los Alamos NATIONAL LABORATORY

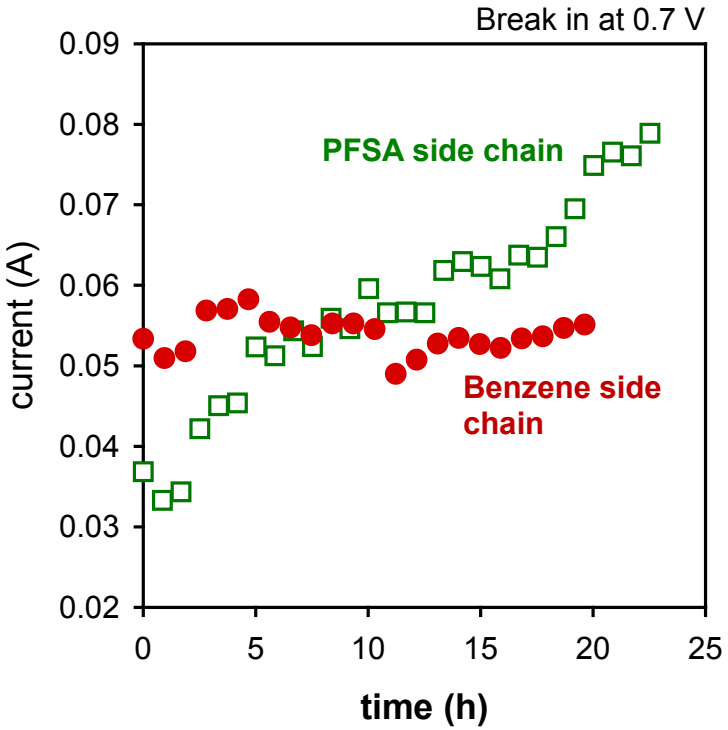
Effect of side chain mobility on electrode performance (Yu Seung Kim)

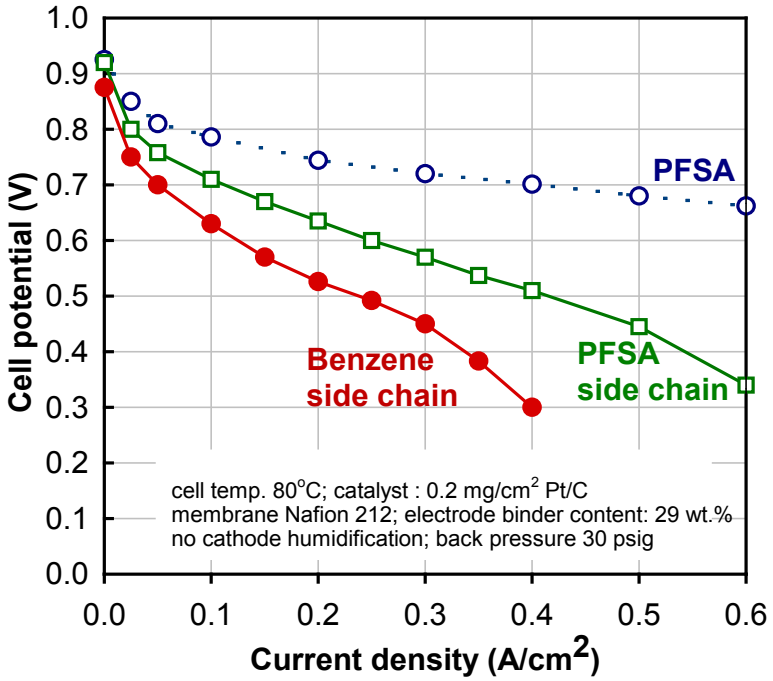
Sulfonated polyaromatic (IEC=2.3 meq/g)*



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







*Courtesy: Prof. Bae (UNLV)

Los Alamos NATIONAL LABORATORY

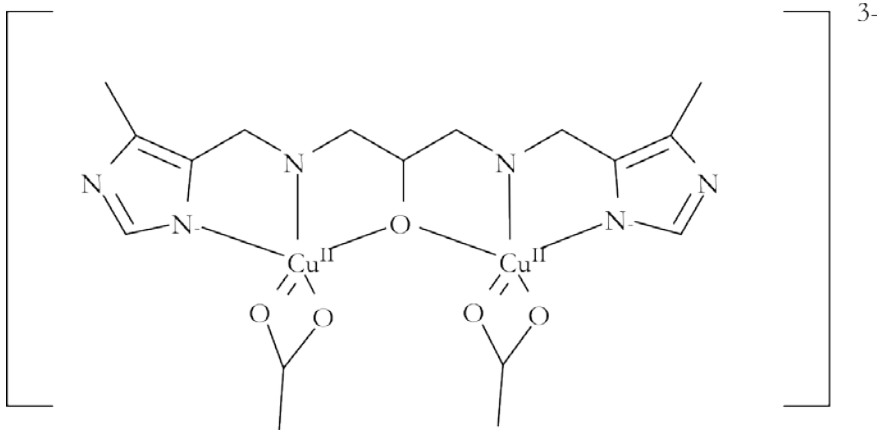
Computational Studies of Di-Copper Complexes as ORR Catalysts

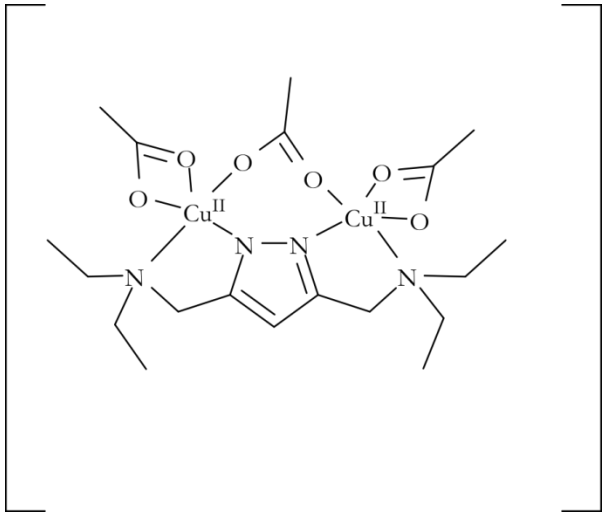
Neil Henson (LANL) and M. Head-Gordon (LBNL)

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

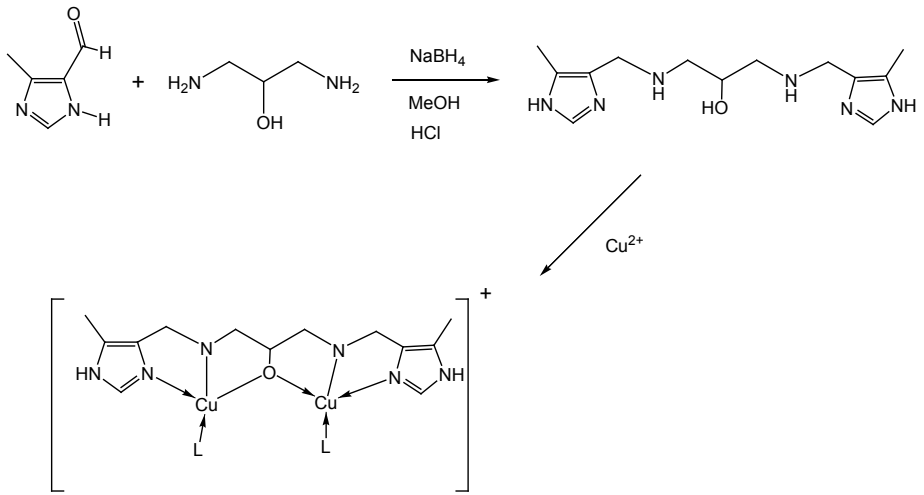


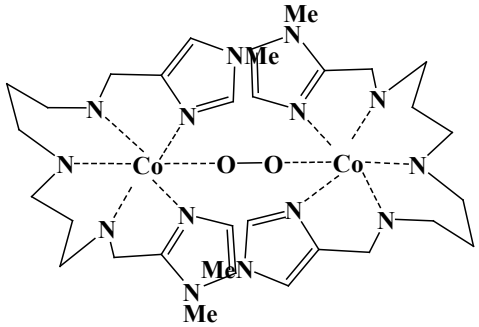


1. **Crucial feature of structure is to allow Cu-Cu distance to be sufficient to allow bridging dioxygen coordination**
2. **Co-planer coppers may be advantageous**
3. **Solvent ligands are the counter-ions: acetate, sulfate or triflate**

Synthetic Routes to Bimetallic Catalysts

Boncella (LANL), Arnold(LBNL)



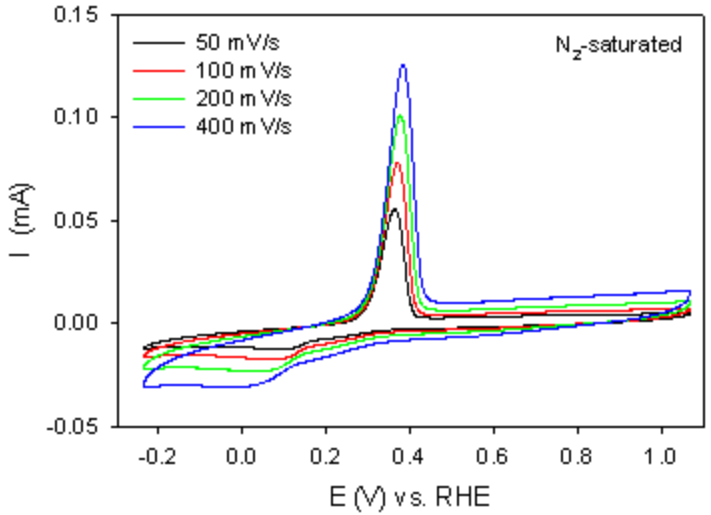


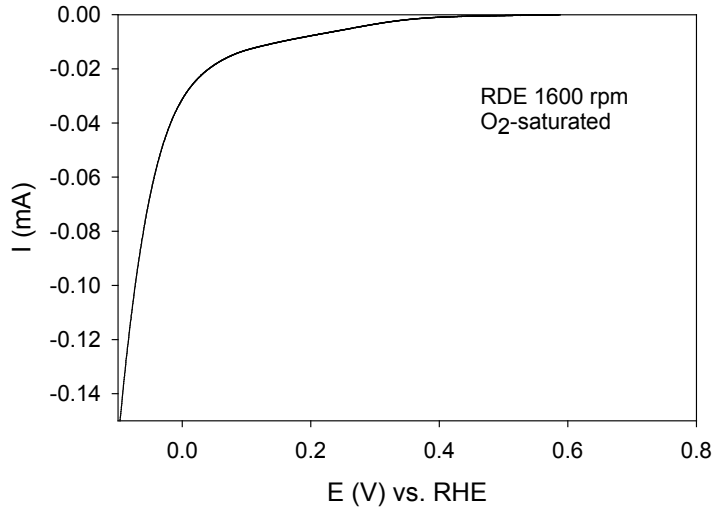
E. De Castro, B. D. Zenner, J. P. Ciccone, L. A. Deardurff, and J. B. Kerr, USP 4,959,135 (1990).

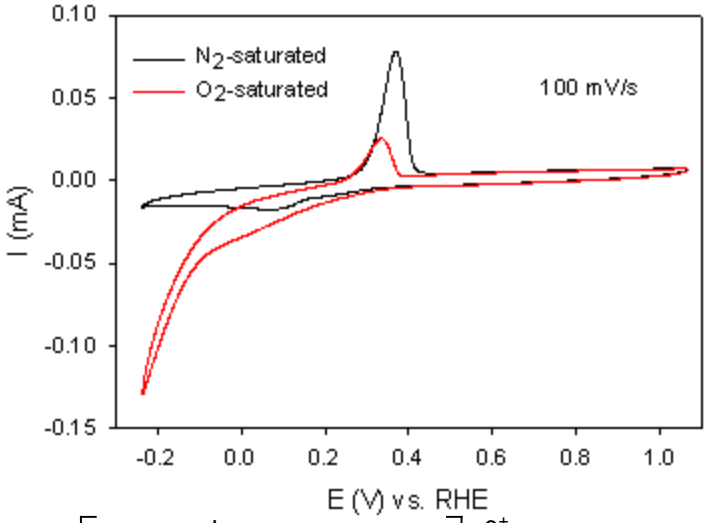
Collaborate with other groups
– e.g. Andy Gewirth, U. of Illinois at Urbana-Champaign(DOE-BES funding),
S. Mukerjee (Northeastern (EERE-funded)
Saveant (Europe)

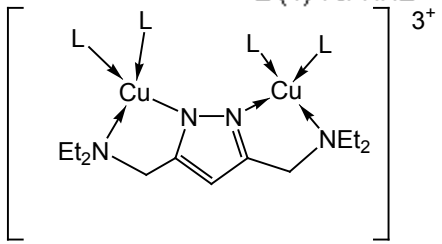
Electrochemical Characterization.

Di-nuclear copper complex dissolved in 0.1 M $HClO_4$







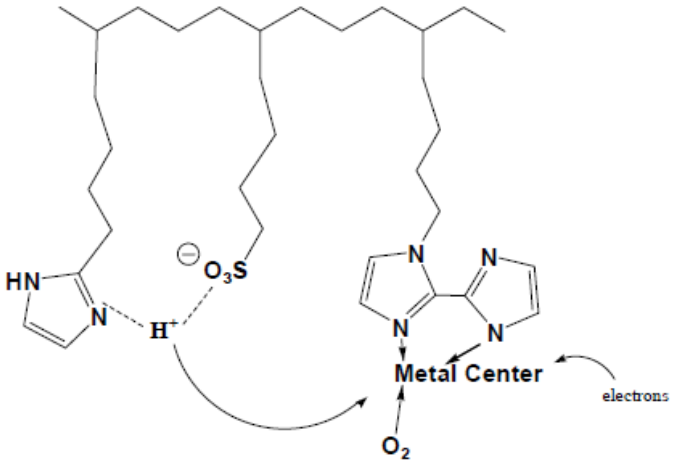


RS034b

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

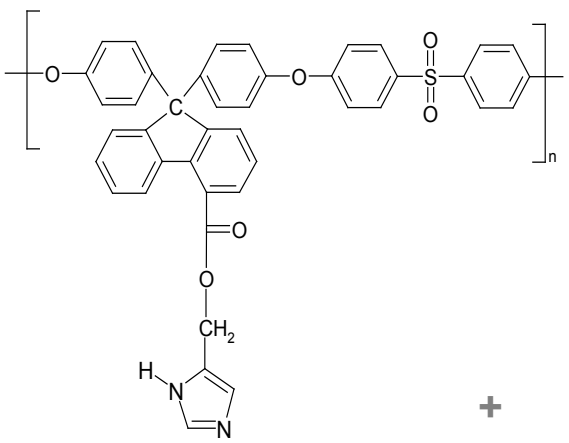
Examples of Catalyst Attachment

Coordination of transition metals in imidazole-containing polymers

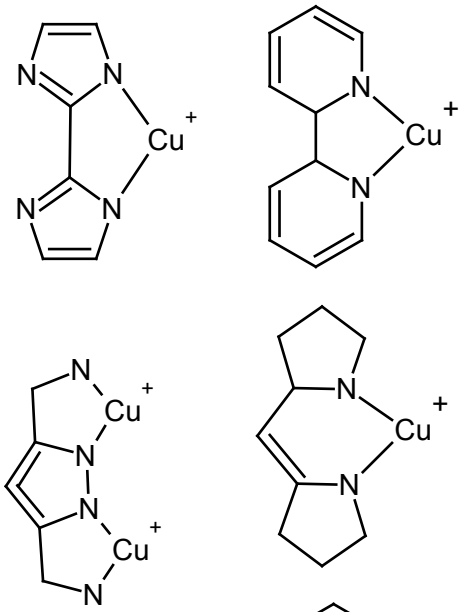


Tethering Cu(I) complexes to imidazole containing polymers

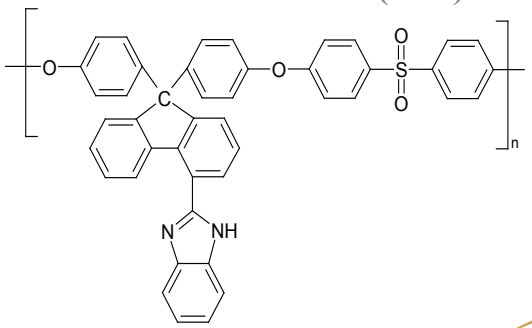
PAES-COOH-Im (Im1)

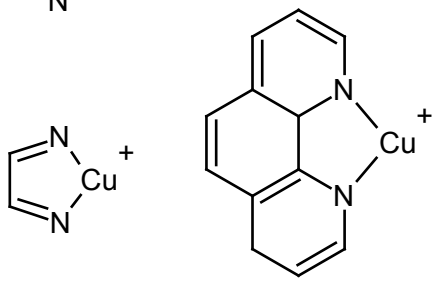


+



PAES-COOH-Bim (Im2)



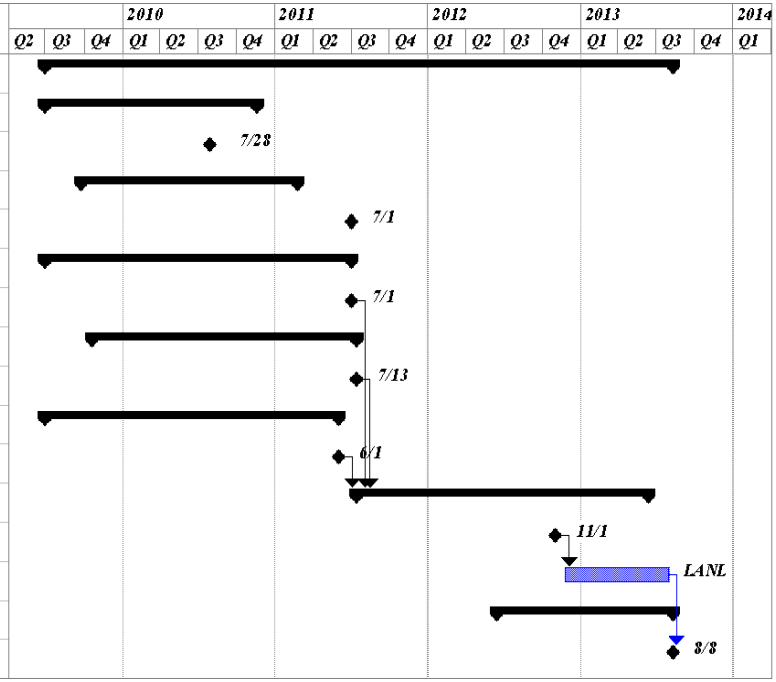


Future Work

- Use Polymer binder/ink to bind homogeneous oxygen catalysts
  - Catalyst structures based on classical Heme, macrocylic 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.

ID	Task Name
1	**Non-PGM Electrodes for Catalysis of Fuel Cell Reactions**
2	**Development of synthesis, and electrochemical screening methods**
8	***Oxygen reduction catalysis demonstrated with polymer coated electrodes***
9	**MEA fabrication and testing methods development**
13	***Go/No-Go Decision(do tethered complexes work in MEAs?)***
14	**Develop optimization Methods for electrode structures**
17	***Methods of optimization of tethered catalysts demonstrated in MEAs***
18	**Develop durability testing**
22	***Durability and degradation testing developed***
23	**New Catalyst development**
27	***New Catalyst development methods demonstrated***
28	**MEA fabrication and testing with new ORR catalysts**
34	***Satisfactory performance from single cell MEA***
35	Short stack Build and test
36	**Hydrogen Oxidation Catalysts**
39	***Project completion -Final Report and Proposal for Further Work.***



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

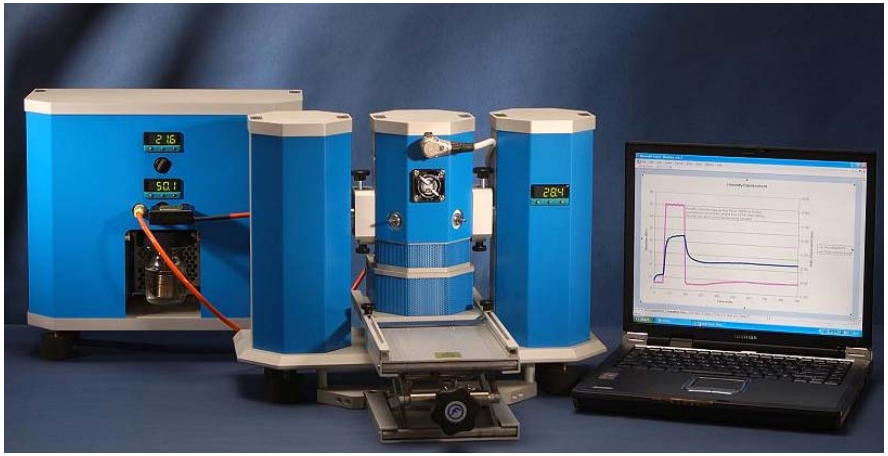
Budget & Tasks.

- 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.

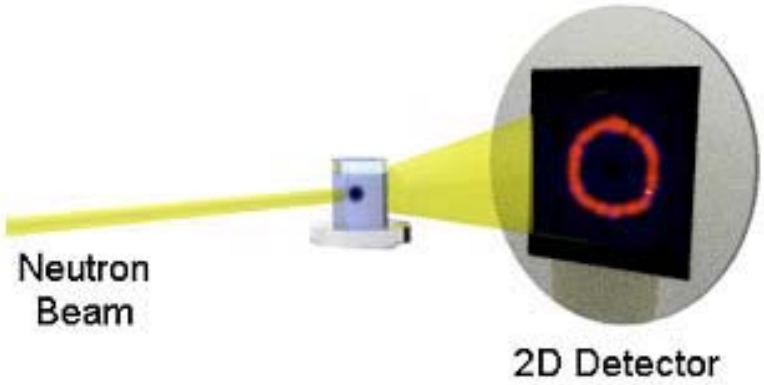
Some available methods to probe polymer dynamics



Dynamic Mechanical Analyzer (& Dielectric Thermal Analysis) with humidification

Scribner High Temperature Fuel Cell Station

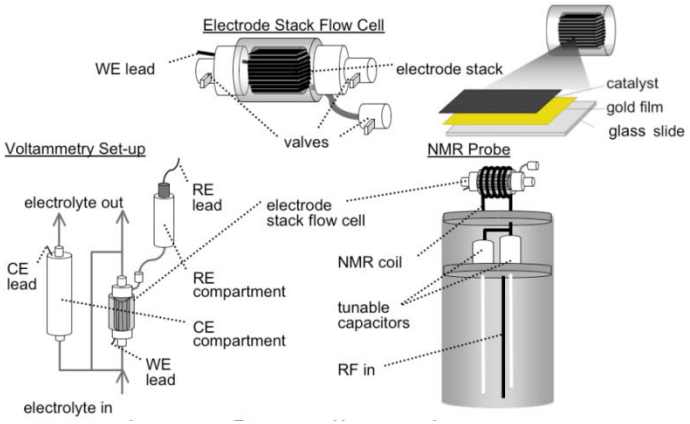
Dynamic Vapor Sorption



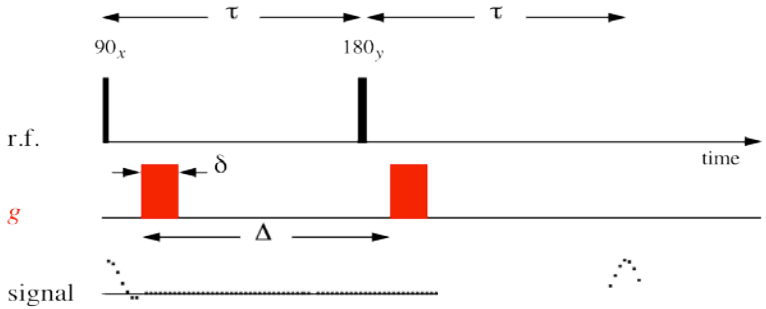
Neutron Scattering (SANS, QENS) with humidity control

Pulsed Field Gradient Spin Echo NMR

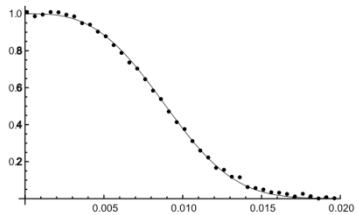
NMR methods for characterization of catalysts and electrodes



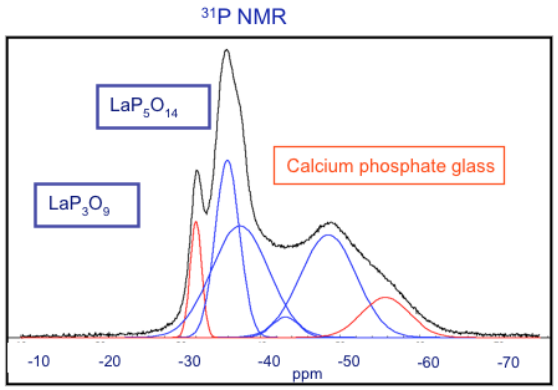
e-chem NMR

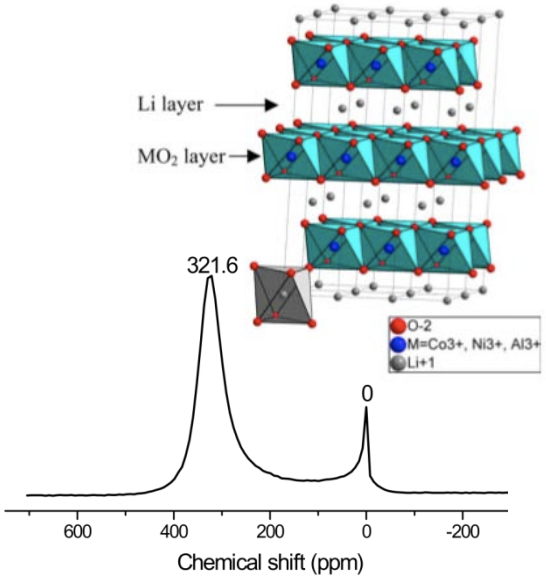


transport properties



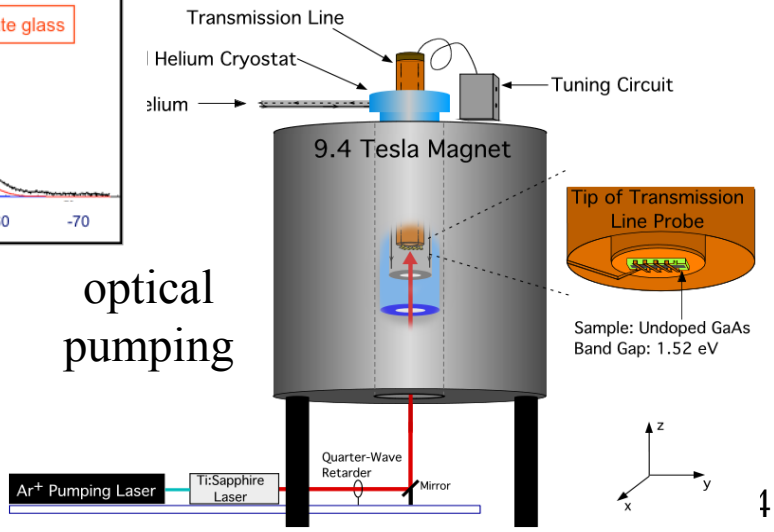
routine solids NMR





paramagnetic systems

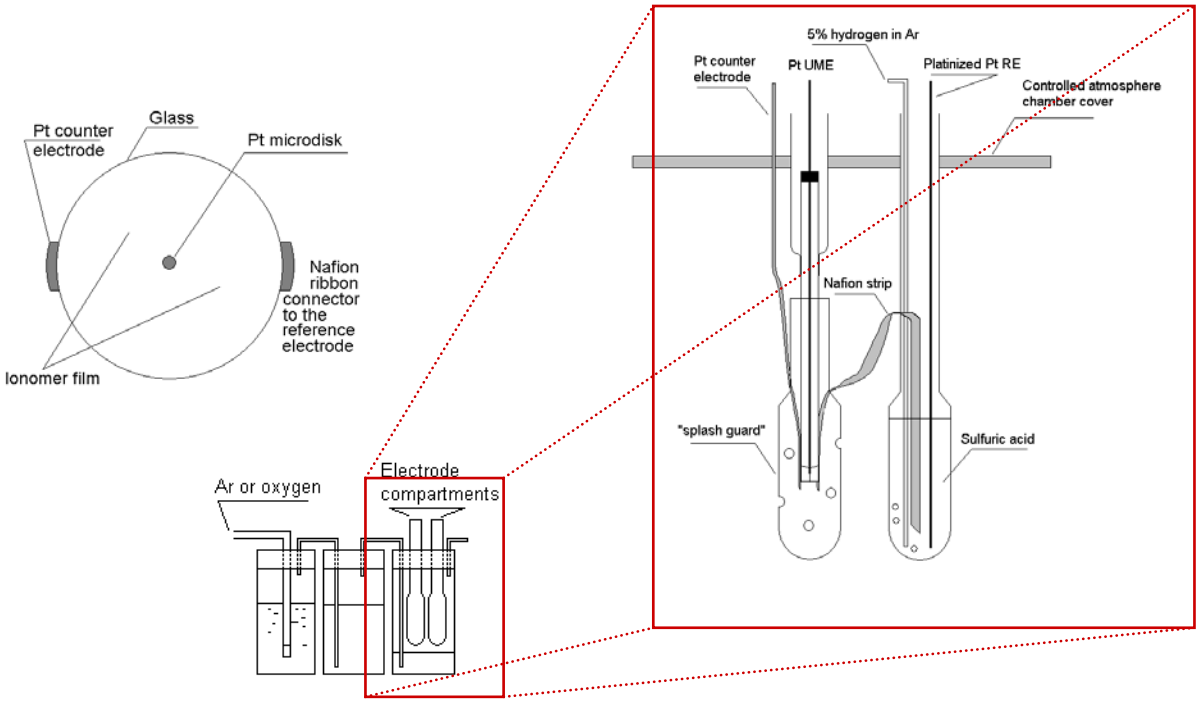
optical pumping



Ionomer Characterization

Available/selected ionomers will be tested for:

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

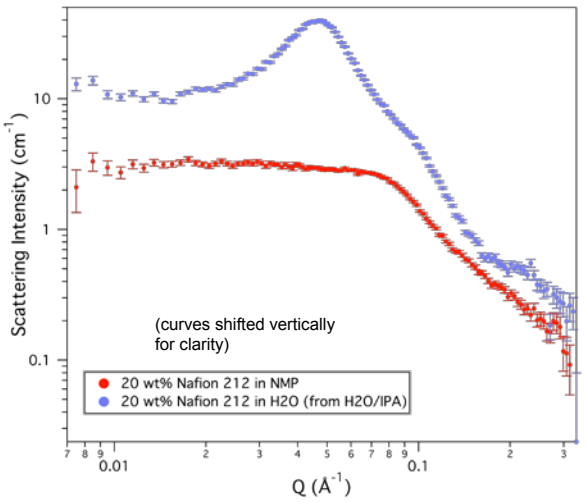


Uribe *et al*, *J. Electrochem. Soc.*, 139 (1992) 765

Los Alamos NATIONAL LABORATORY

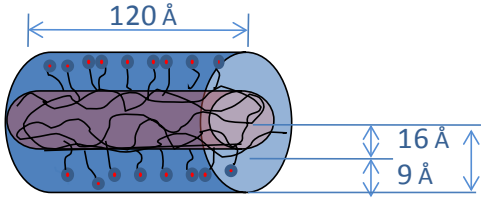
Polymer ink characterization for electrode fabrication (LANL Applied Science Program)

SANS: NMP- vs. H2O-Based Gels



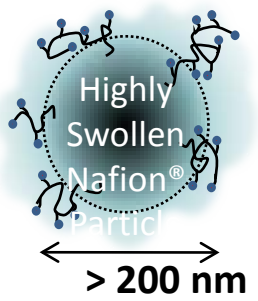
NMP dispersion: Core-Shell Cylinder

- 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)



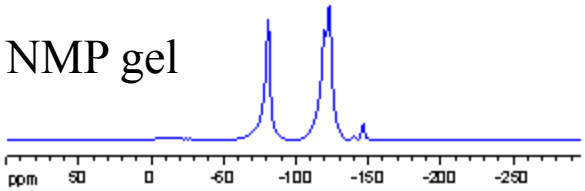
Aqueous mixture: Highly swollen particles

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

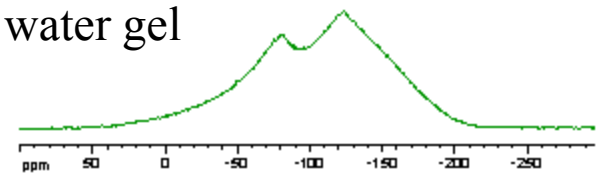


^{19}F NMR

NMP gel

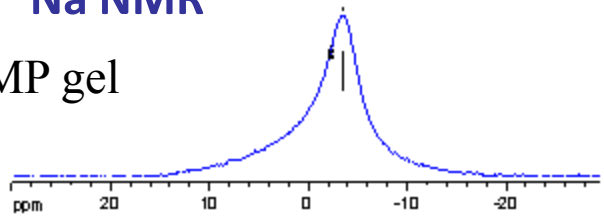


water gel

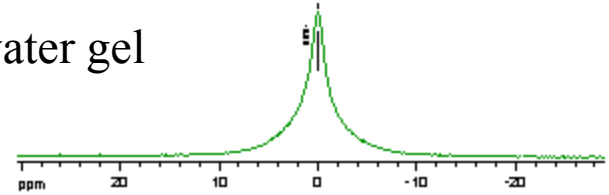


^{23}Na NMR

NMP gel



water gel



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

Los Alamos NATIONAL LABORATORY

Full Project Schedule.

ID	Task Name
1	**Non-PGM Electrodes for Catalysis of Fuel Cell Reactions**
2	**Development of synthesis, and electrochemical screening methods**
3	Synthesis of basic polyelectrolyte polymers with functionalizable side chains
4	Polyarylenesulfone & Polystyrene backbones
5	Perfluorinated polymers
6	Develop catalyst characterization in solutions - water and protic ionic liquids
7	Characterize activity on polymer coated electrodes -simple tethered catalysts
8	***Oxygen reduction catalysis demonstrated with polymer coated electrodes***
9	**MEA fabrication and testing methods development**
10	Characterize mechanical and morphological properties of polymers
11	Characterize polymer with bound catalysts and with electrode support materials
12	Prepare and test MEAs with base polymers with bound non-platinum catalysts.
13	***Go/No-Go Decision(do tethered complexes work in MEAs?)***
14	**Develop optimization Methods for electrode structures**
15	Develop macroscopic property model for MEA operation
16	Use model to optimize catalyst loading, polymer morphology, charge transport
17	***Methods of optimization of tethered catalysts demonstrated in MEAs***
18	**Develop durability testing**
19	Catalyst degradation mechanisms
20	Polymer matrix degradation - chemical and physical modes
21	Degradation and durability testing of MEAs
22	***Durability and degradation testing developed***
23	**New Catalyst development**
24	Fundamental modeling of catalyst chemistry for ORR
25	Synthesis and screening of new catalyst structures for ORR
26	test new catalysts in polymer matrices
27	***New Catalyst development methods demonstrated***
28	**MEA fabrication and testing with new ORR catalysts**
29	New polymer synthesis for better performance
30	New catalyst design, synthesis and screening
31	Transport measurement and modeling
32	Optimization of MEA structures
33	Durability Testing/Lifetime extension
34	***Satisfactory performance from single cell MEA***
35	Short stack Build and test
36	**Hydrogen Oxidation Catalysts**
37	Design, synthesize and screen
38	Fabricate and test MEAs witn non-PGM anode catalysts
39	***Project completion -Final Report and Proposal for Further Work.***