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

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Collaborators:
UC Berkeley (UCB)
Los Alamos National Laboratory (LANL)
3M Company

May 10, 2011

Project ID #
FC 011

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Overview

Timeline

- Project start –September 2009
- Project end –August 2013
- Percent complete – 33%

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

- $3520k

Funding received in FY11

-$1140k

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

1) Demonstrate in electroanalytical measurements that non-platinum group metal catalysts supported in three-dimensional polyelectrolyte arrays coated on electrode supports can be used for oxygen reduction reactions (ORR) (Year 1).
   - Voltammetry, RRDE, spectroelectrochemistry of known and new transition metal complexes in homogeneous solution and bound in polymer layers on electrodes.
2) Incorporate catalysts into polymer binders of MEA electrodes to demonstrate that this is an effective matrix for use of new catalysts. (Year 2).
   - Metal complex catalysts bound to polymer binders used in preparation of electrode inks for MEA fabrication. Use common electrode supports with no precious metal catalysts.
3) Demonstrate that the three dimensional structure of polymer-coated electrocatalyst layers can provide sufficient catalyst density and turnover frequency to support the desired DOE targets (Year 3).
   - Combine electroanalytical and polymer property measurements with MEA testing and electrode transport modeling to verify the viability of the concept.
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).

DOE Technical Targets

- Non-Pt catalyst activity per volume of supported catalyst – 300A/cm^3
- Cost < \$3/kW and Durability > 5000 hours (up to 120°C)

Milestones & Go/No-Go Decisions.

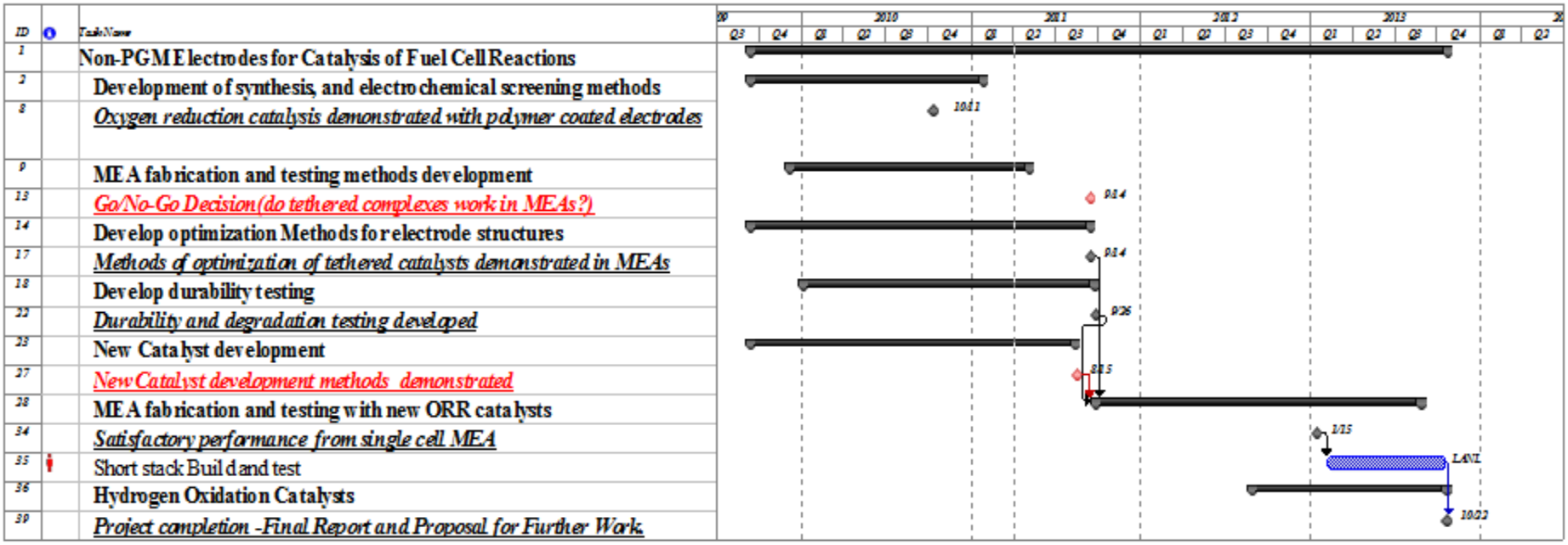
Milestone 1. Oxygen reduction catalysis demonstrated with polymer coated electrodes(12 mo).

Milestone 2. Go/No-Go Decision. Oxygen reduction catalysis demonstrated with polymer-bound catalyst layers in MEAs (24 mo). Interim goal is 100 A/cm^3 of supported catalyst at 800 mV$_{ir\text{-}free}$ with at least 10 hours operational lifetime.

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

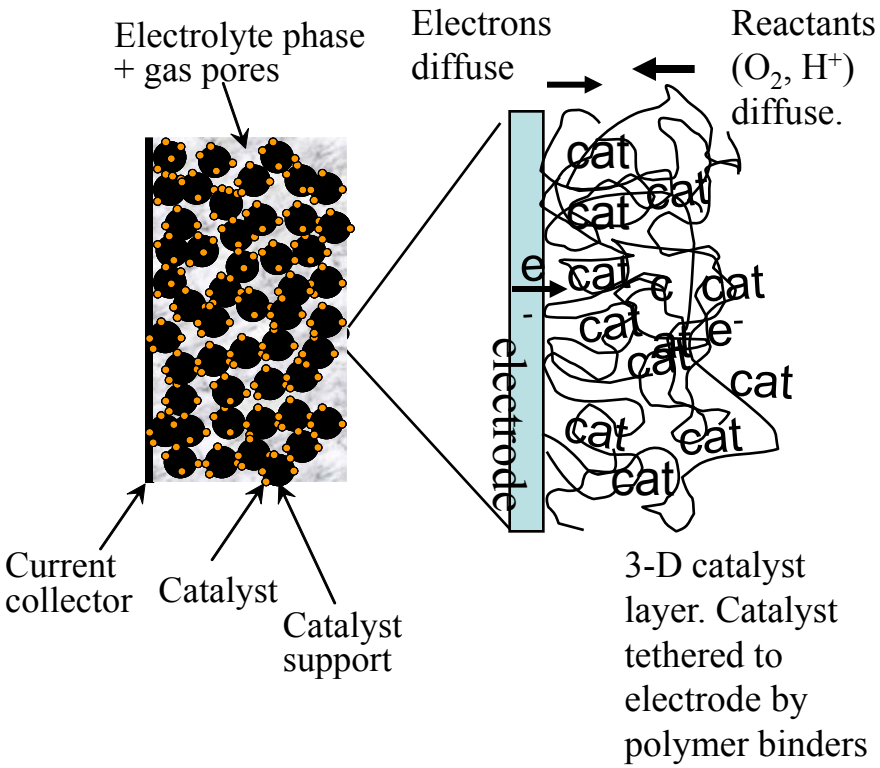
Milestone 4. Durability and degradation testing developed (24 mo).

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



Approach

Traditional fuel-cell electrode structure with increased ionomer film containing catalyst



cat = e.g. Fe, Co, Mn, Cu, Ni
Porphyrins, corroles, salens, biomimetic metal complexes.

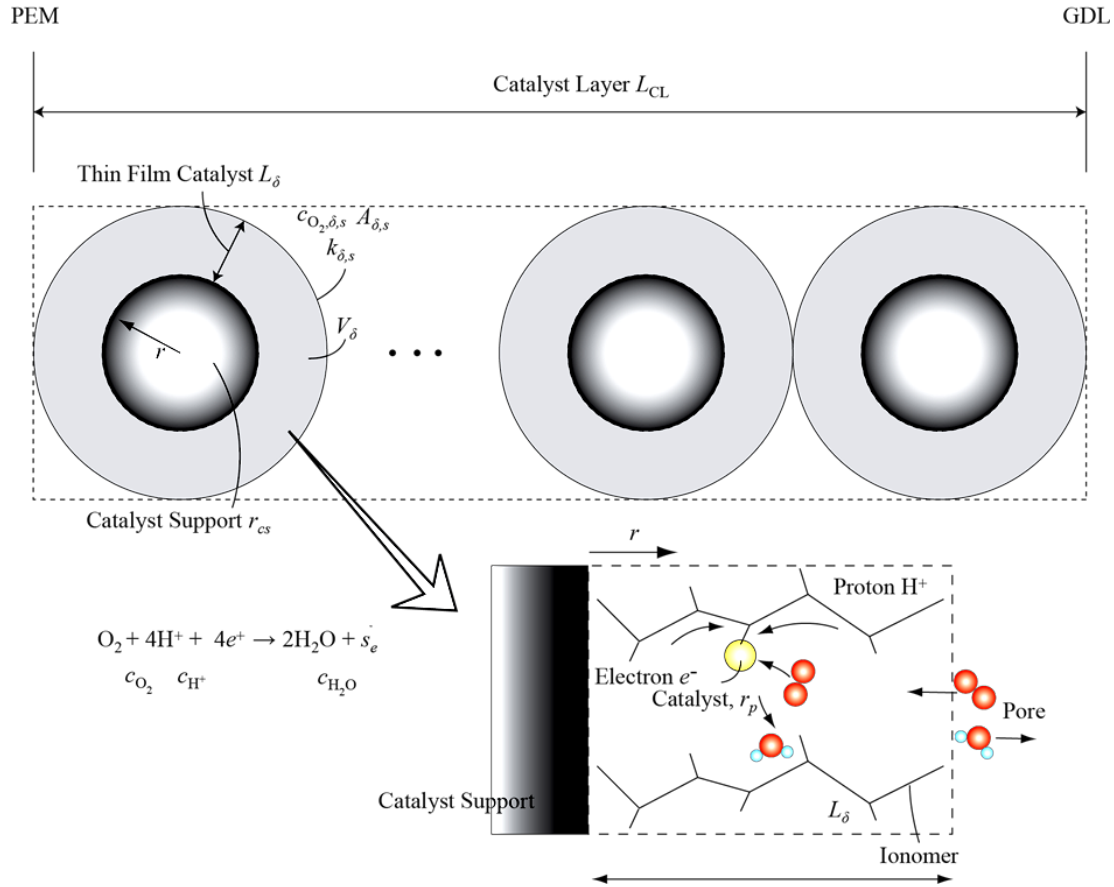
Rationale

- Numbers if monolayer
  Metal porphyrin molecular area ~ 2.5 nm^2
  Monolayer coverage ~ 5 x 10^{13} molecules/cm^2, 10^{-10} moles/cm^2
  To support 1 A/cm^2, need 10^{-5} moles.cm^2/s
  Need TOF = 10^5/s compared to 20/s for Pt
- Homogeneous catalysts can have an increase in rate of nearly 20 times due the geometric, pre-exponential factor.
- A 500 nm polymer layer accommodates 100 equivalent layers of catalyst sites.
- **Geometric effects compensate for catalyst size**

Technical Accomplishments
Modeling of Catalyst Layer

Gi Suk Hwang
Adam Weber

- Structure
  - Composite electrode with polymer reaction layer coated on carbon
  - Particles uniformly distributed over the catalyst layer
- Model
  - Use porous electrode model for layer combined with local diffusion and reaction model for polymer layer containing catalyst
- Goal is to evaluate and optimize parameter set
  - Polymer layer thickness
  - Turnover frequency
  - Transport coefficients (oxygen, proton, and electron)

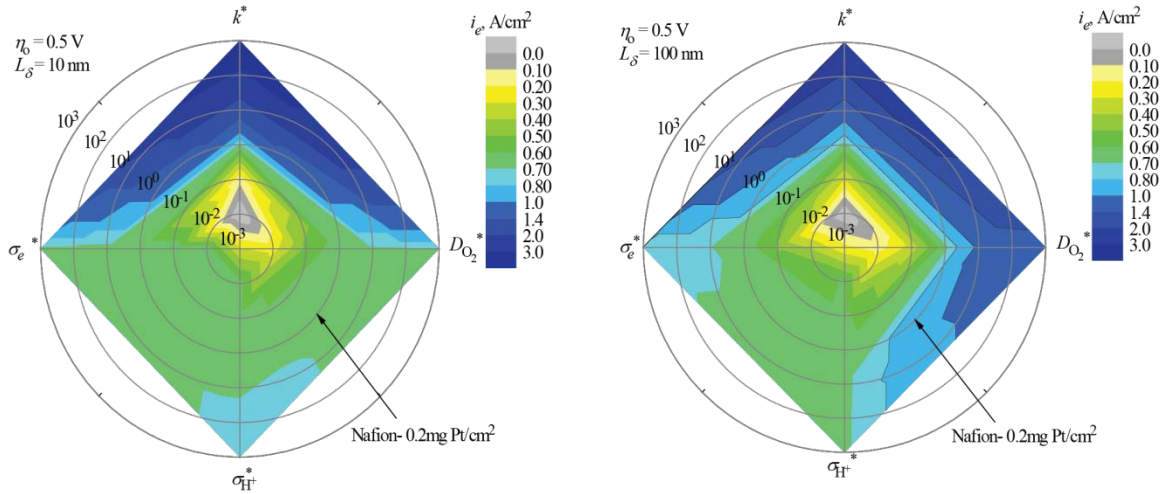


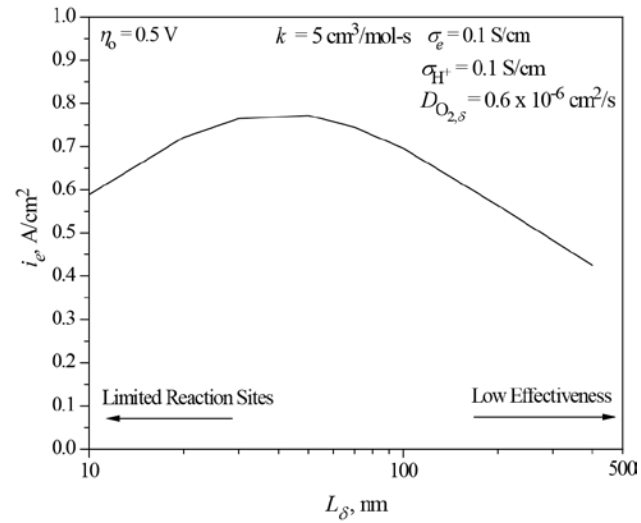
Schematic drawing of oxygen, proton, electron, and water transport though the thin metal catalyst layer through a catalyst layer.

Technical Accomplishments

Gi Suk Hwang
Adam Weber

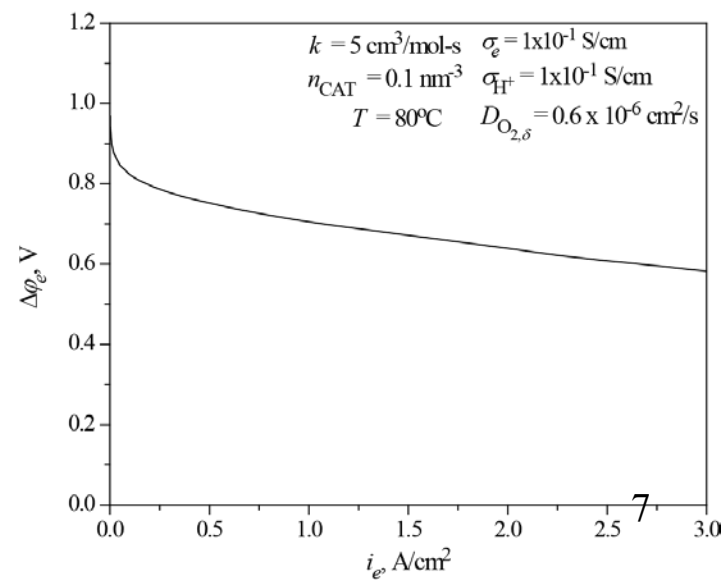
Model Current Density as function of Transport Properties, Geometry & Catalyst Activity – Polarization curve and optimization maps





- Current density significantly increases with increasing oxygen diffusivity/reaction rate, but thick film reduces performance due to the limited O_2 transport
  - Can get limitations due to proton and electron transport as well (not shown)

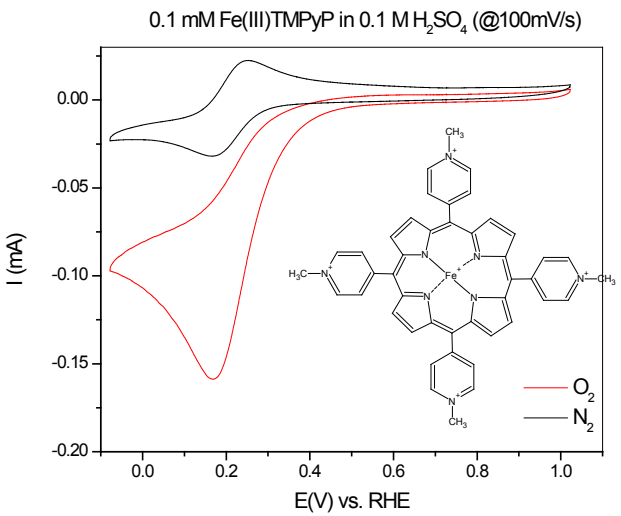
- **Comparable performance to existing Pt/Nafion® structure is achievable with realistic parameters**

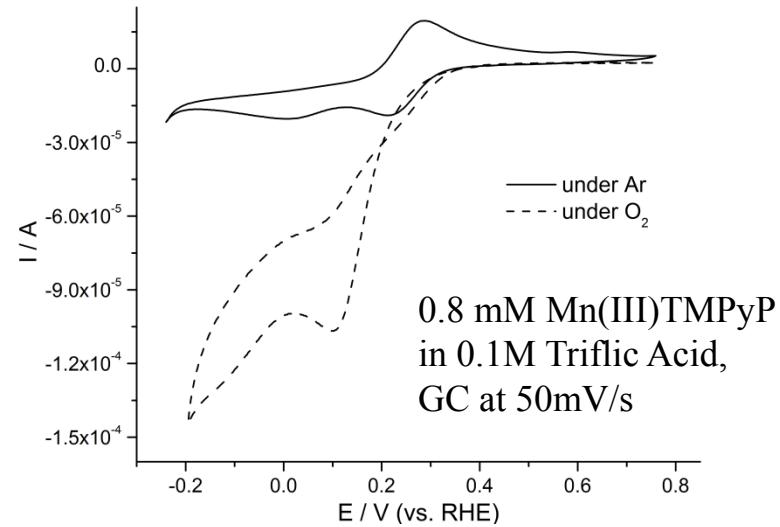


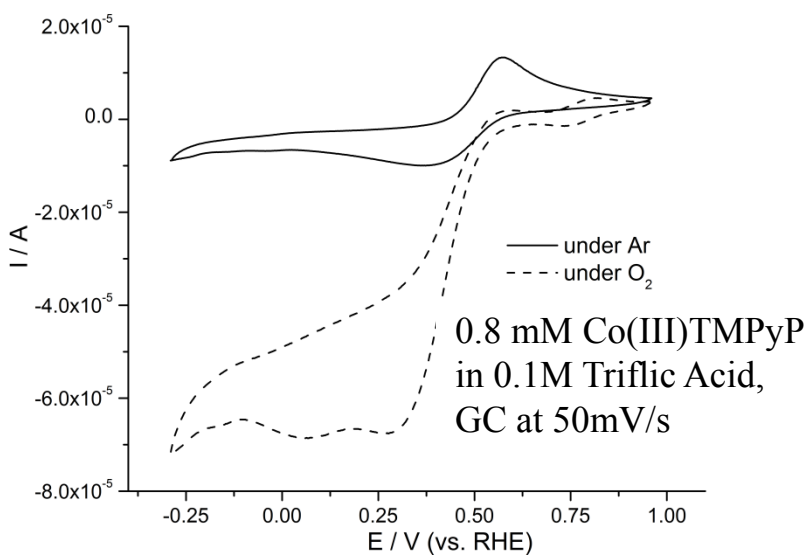
Technical Accomplishments
Catalyst screening

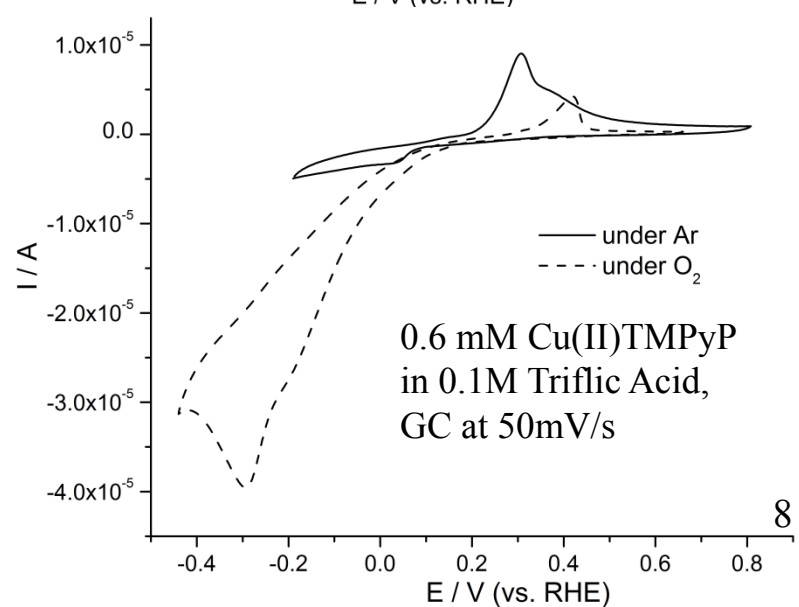
Lior Elbaz, Piotr Zelenay

Qinggang He,
Robert Kostecki





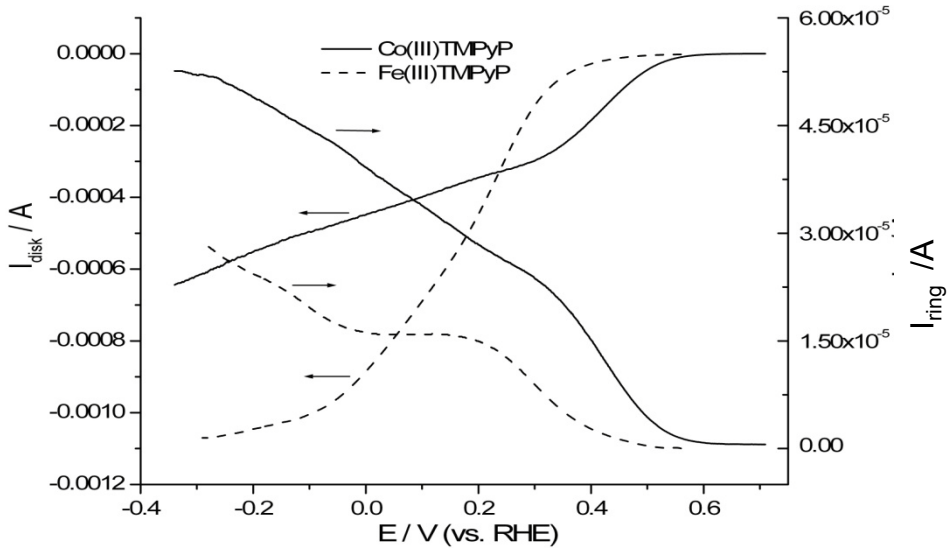




Technical Accomplishments
Catalyst screening

Qinggang He,
Robert Kostecki

Fe catalysts - 4 electron reduction at high concentrations, 2 electrons at low concentrations.
Co catalysts tend to give 2 electron reductions.

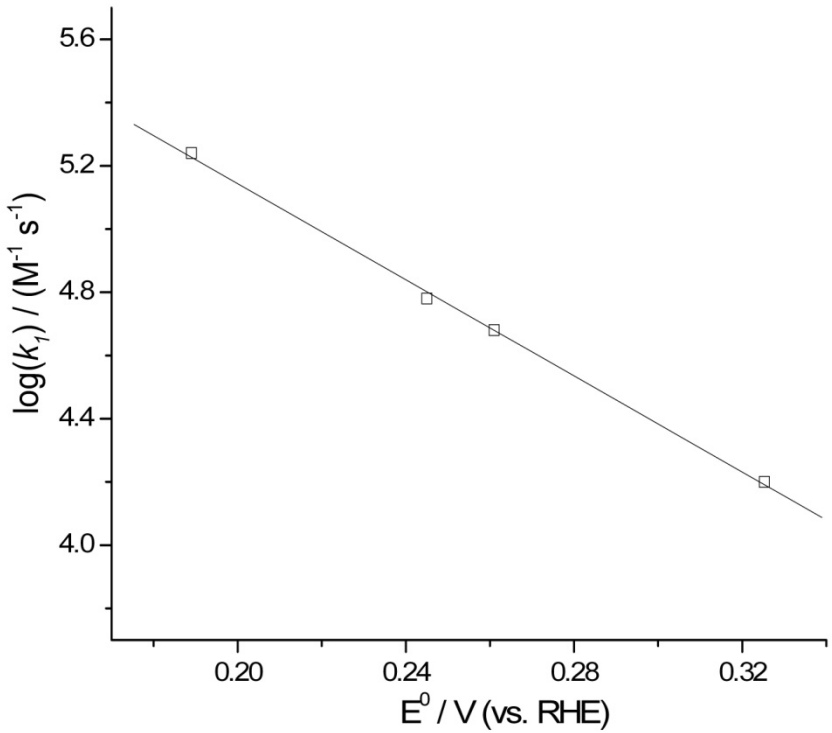


Polarization curves for GC disk and Pt ring electrodes and peroxide yield for O_2 saturated 0.1M TFMSA + 0.8 mM Fe(III)TMPyP and 0.1M TFMSA + 0.8 mM Co(III)TMPyP, rotation speed: 400 rpm, scan rate: 20mV/s.

Complex	E^0/V vs. RHE	D_o ($cm^2 s^{-1}$)	Number of electrons transferred (n)	Tafel slopes / $mV.dec^{-1}$
Co	0.41	1.4 E-6	2.2	64/135
Fe	0.19	1.7 E-6	4.0	70/130
Cu	0.13	1.1 E-6	2.6	112

Technical Accomplishments
Catalysis Mechanism Diagnosis

Qinggang He,
Robert Kostecki



Rate constants, k_1, calculated assuming outer sphere redox mechanism plotted against catalyst E^o. Rates are too high to be consistent with Marcus-Hush theory. Consistent with inner-sphere mechanism.

Outer-sphere Redox catalysis mechanism (Marcus-Hush)

$$\text{TPyPFe(III)} + e^{\ominus} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \text{TPyPFe(II)}$$

$$\text{TPyPFe(II)} + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{TPyPFe(III)} + \dot{O}_2^{-}$$

$$\dot{O}_2^{-} + H^+ \rightleftharpoons O_2\dot{H}$$

$$\text{TPyPFe(II)} + O_2\dot{H} \longrightarrow \text{TPyPFe(III)} + O_2H^-$$

Quasi-redox inner-sphere mechanism.

$$2\text{TPyPFe(II)} + O_2 \rightleftharpoons \text{TPyPFe(III)-}O_2^{2-}\text{-Fe(III)TPyP}$$

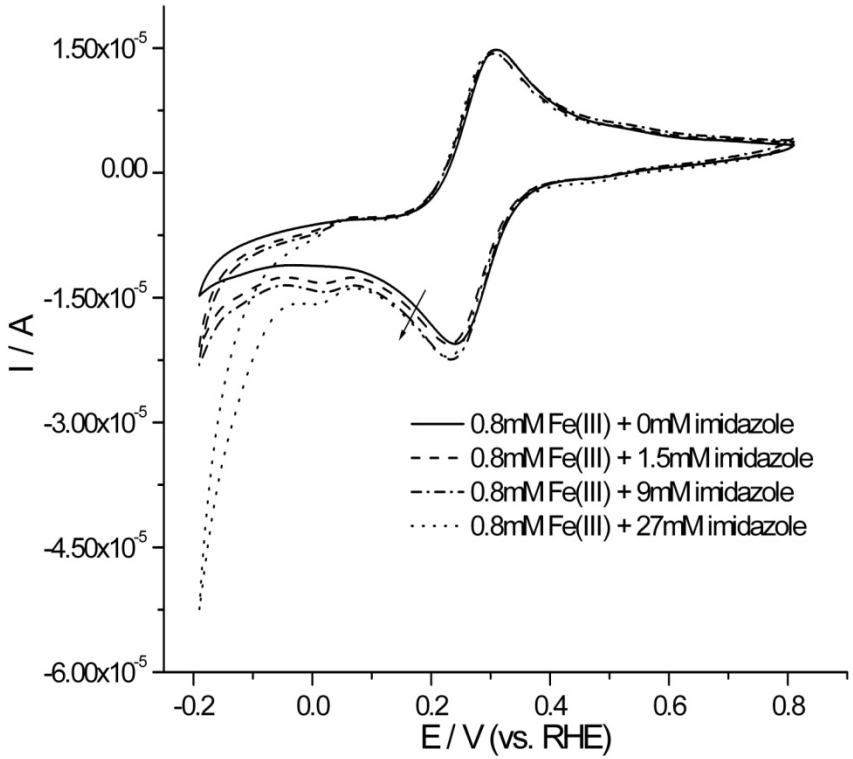
$$\text{TPyPFe(III)-}O_2^{2-}\text{-Fe(III)TPyP} + H^+ \rightleftharpoons \text{TPyPFe(III)-}O_2H^- + \text{TPyPFe(III)}$$

$$\text{TPyPFe(III)-}O_2H^- + 2\text{TPyPFe(II)} + H^+ \longrightarrow 3\ \text{TPyPFe(III)} + 2OH^-$$

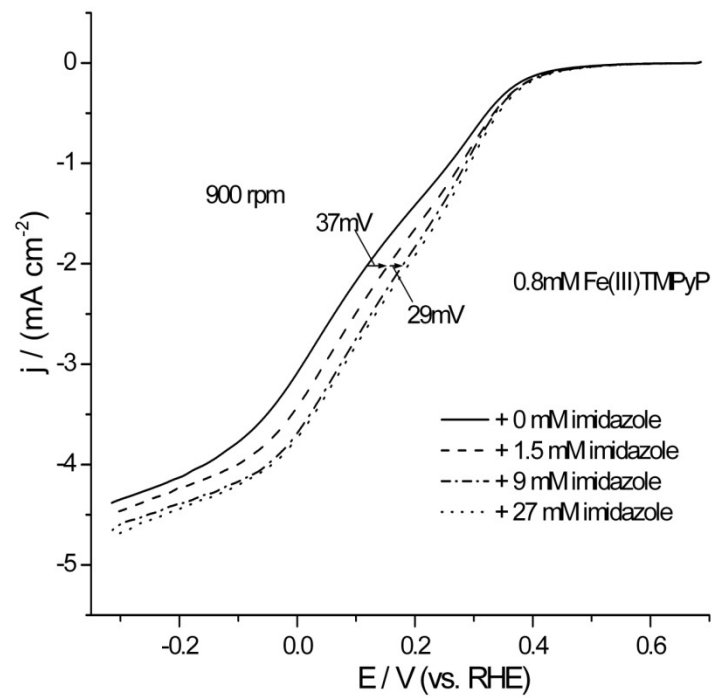
Technical Accomplishments
Catalysis Mechanism Diagnosis

Qinggang He,
Robert Kostecki

glassy carbon in Ar purged 0.1M TFMSA containing 0.8mM Fe(III)TMPyP, scan rate = 50mV/s



RDE GC Disk current density in 0.1M TFMSA , 0.8mM Fe(III)TMPyP, scan rate = 20mV/s

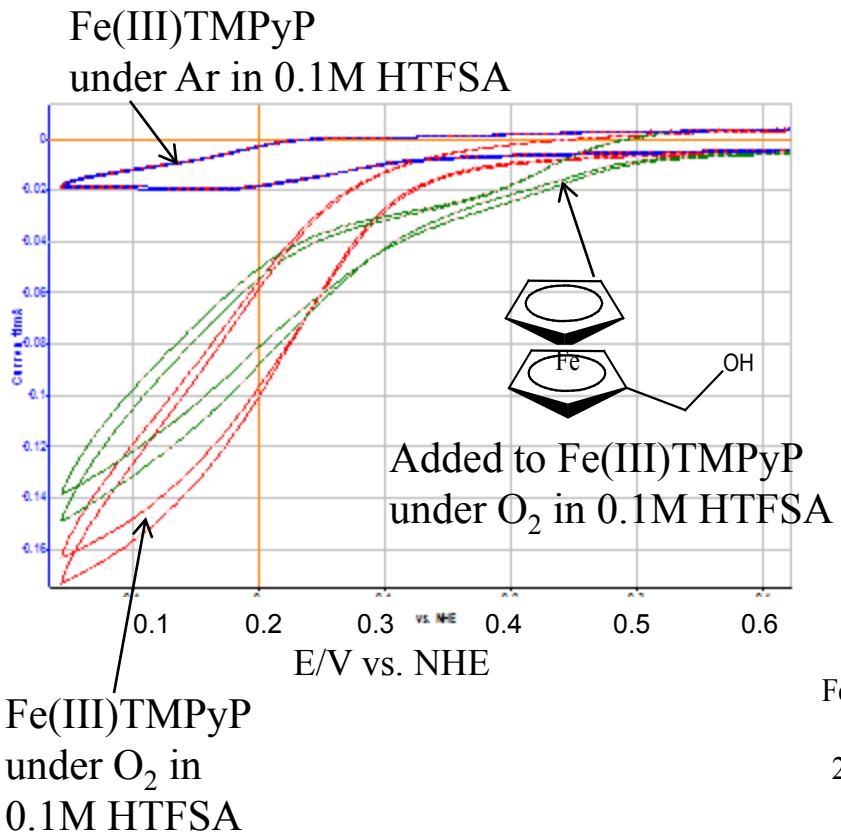


Addition of imidazole base to solution does not change Redox potential of catalyst. Base is protonated and does not bind to the metal center.

Addition of base does not change onset potential but apparently increases rate of catalyst regeneration and catalyst turnover frequency (TOF).

Technical Accomplishments

Redox mediators for overpotential reduction for ORR and for electron transfer in catalyst layers



Addition of ferrocene derivative (Fc) facilitates ORR at 200 mV potentials more positive than potential of FeTMPyP catalyst

-"Molecular Wiring" of catalyst layer.

- Driven by rapid kinetics (k_1) of reaction of Fe(II)TPyP with O_2

$$Fc^{+\cdot} + e^{-\cdot} \rightleftharpoons Fc$$

$$Fc + TMPyPFe(III) \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Fc^{+\cdot} + TMPyPFe(II)$$

$$2TMPyPFe(II) + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} TMPyPFe(III)\text{-}O_2^{2-}\text{-}Fe(III)TMPyP$$

$$TMPyPFe(III)\text{-}O_2^{2-}\text{-}Fe(III)TMPyP + H^+ \rightleftharpoons TMPyPFe(III)\text{-}O_2H^- + TMPyPFe(III)$$

$$TMPyPFe(III)\text{-}O_2H^- + 2TMPyPFe(II) + H^+ \longrightarrow 3\ TMPyPFe(III) + 2OH^-$$

Technical Accomplishments

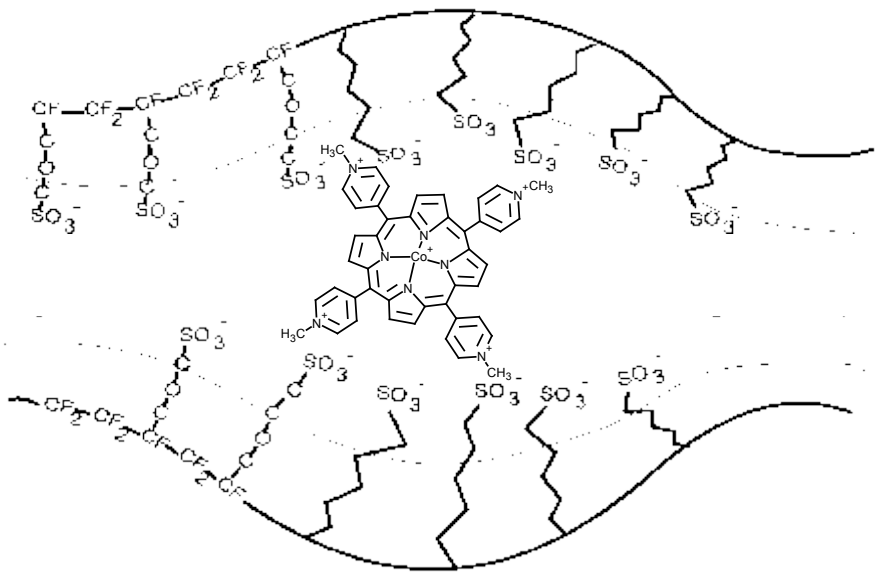
Tethering porphyrins to polyelectrolytes

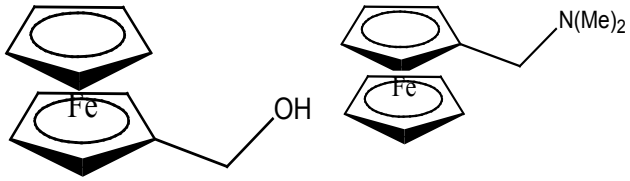
- Different metalloporphyrins :

  1) Fe(III) tetrakis(N-methyl-4-pyridyl)porphyrin (FeTMPyP)

  2) Co(III) tetrakis(N-methyl-4-pyridyl)porphyrin (CoTMPyP)

Porphyrins dissolved in a 5% $_{wt}$ Nafion® dispersion and incorporated in Nafion® 212 membrane and were attached to the polymer by electrostatic interaction between their positively charged substituents and the negatively charged sulfonic groups on the polymer.



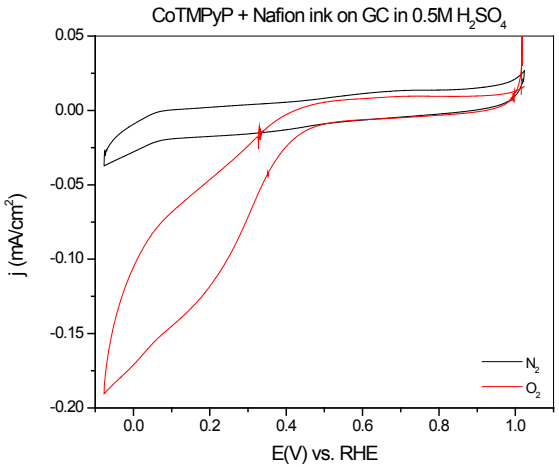


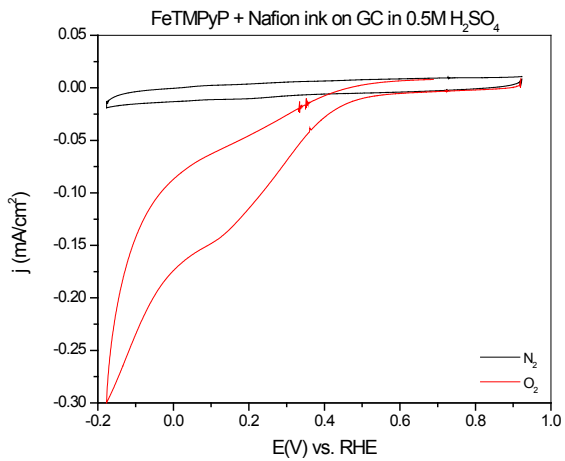
Ferrocenes added as electron carriers
-More mobile in polymer catalyst layer due to lower charge and smaller volume.

Technical Accomplishments

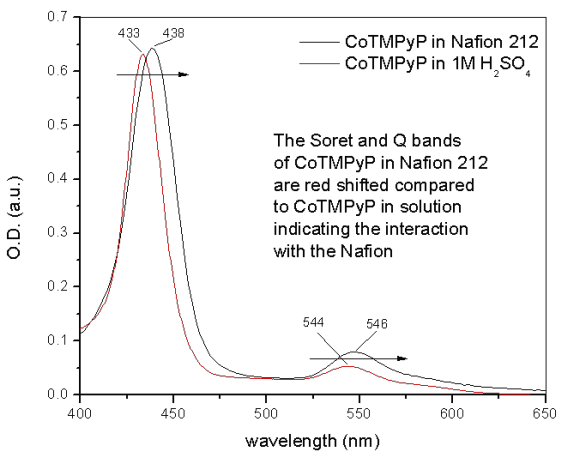
Co and Fe TMPyP complexes tethered in Nafion®

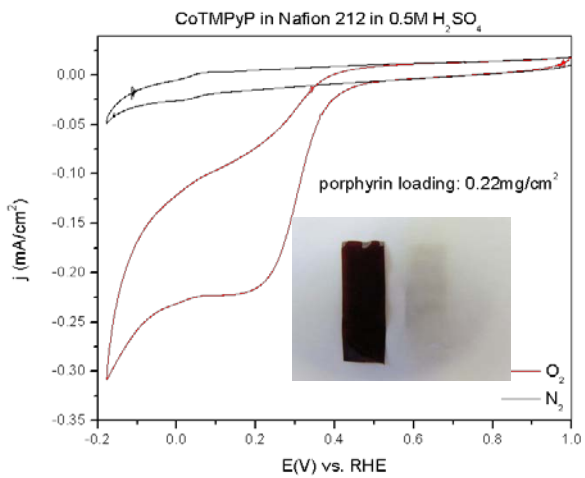
Lior Elbaz, Piotr Zelenay





Nafion® ink cast on glassy carbon electrodes



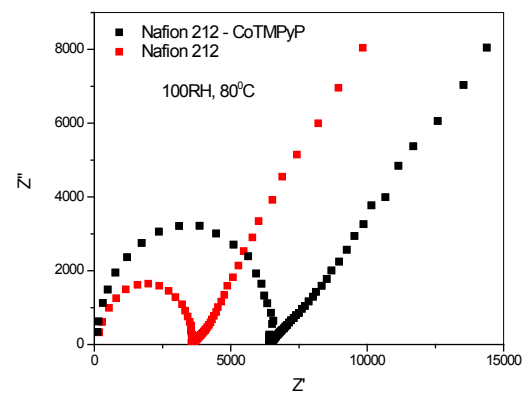


<u>Proton conductivity:</u>

Nafion® -CoP – 58 mS/cm

Nafion® – 115 mS/cm

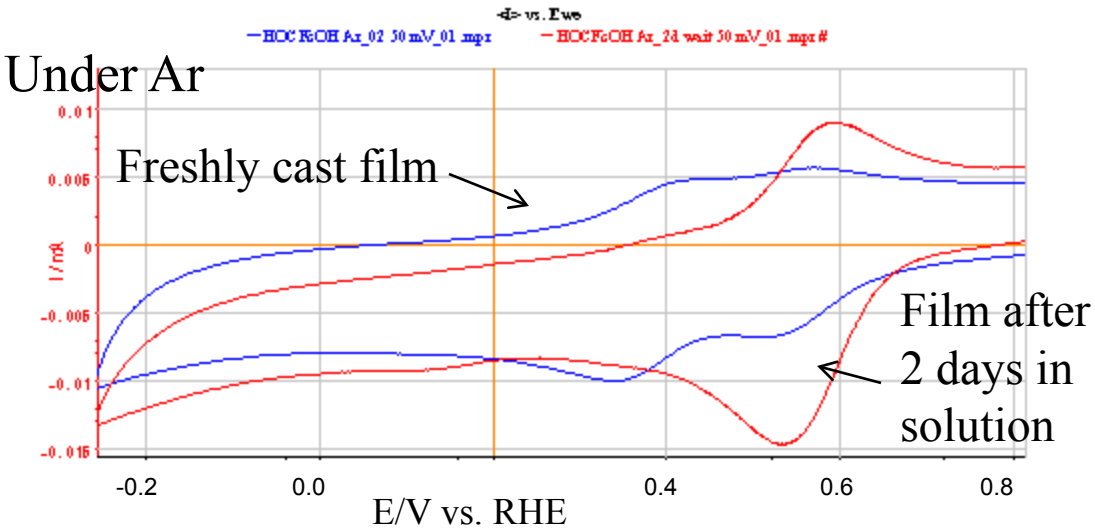
Lower H_2O uptake with CoP

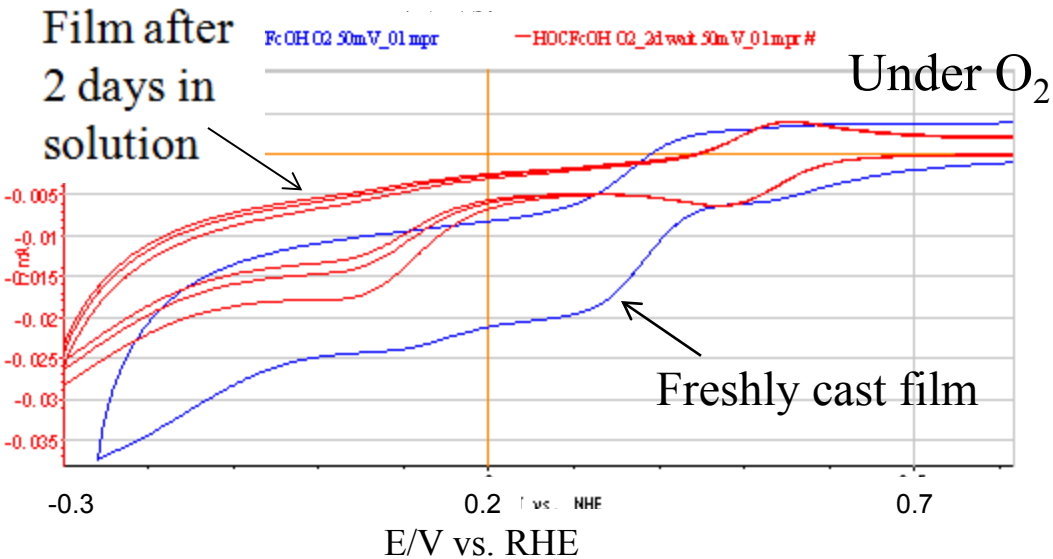


Nafion® 212 membrane with CoTMpyP.

Technical Accomplishments

Tethering porphyrin catalysts and electron "Molecular Wires" to polyelectrolytes



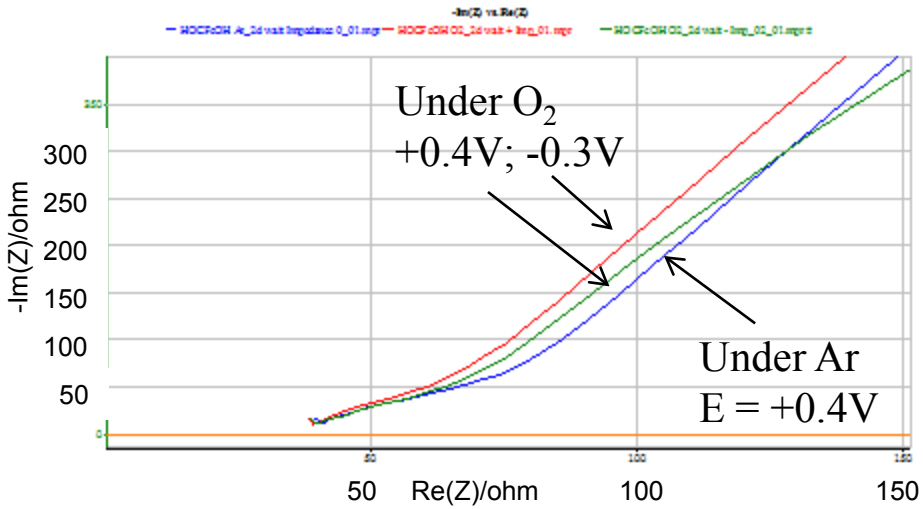


- Initial CV shows two peaks for $FcCH_2OH$, one peak after two days. Reacts with sulfonic acid of Nafion® to form ester and potential shifts positively.
- Freshly cast film shows strong catalysis of ORR.
- Bound ester shows little or weak catalysis.
- FeTMPyP and $FcCH_2OH$ stay in film.

Nafion® ink containing FeTMPyP and hydroxymethylferrocene ($FcCH_2OH$) cast on GC electrodes - ~ 1 micron dry film. CV recorded in 0.1 M TFMSA.

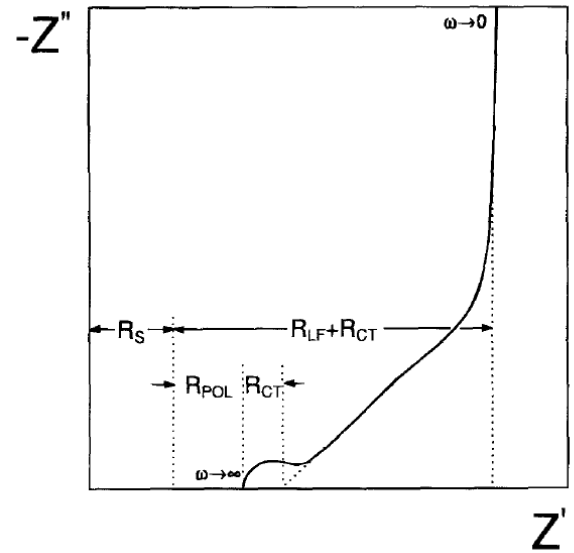
Technical Accomplishments

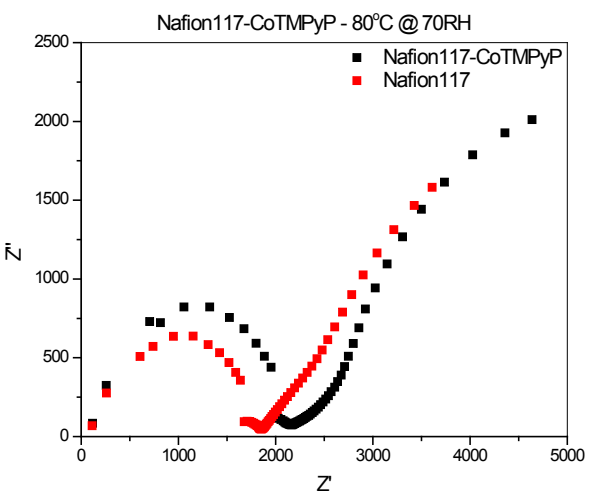
Tethering porphyrin catalysts and "Molecular Wires" to polyelectrolytes



Impedance measurements of coated GC electrode vs. Ag/AgCl

M. F. Mathias, J. Electrochem Soc., 141, 1994, 2722.





Two electrode impedance of Nafion® 117 impregnated with CoTMPyP, cf. catalyst layer impedance measurements.

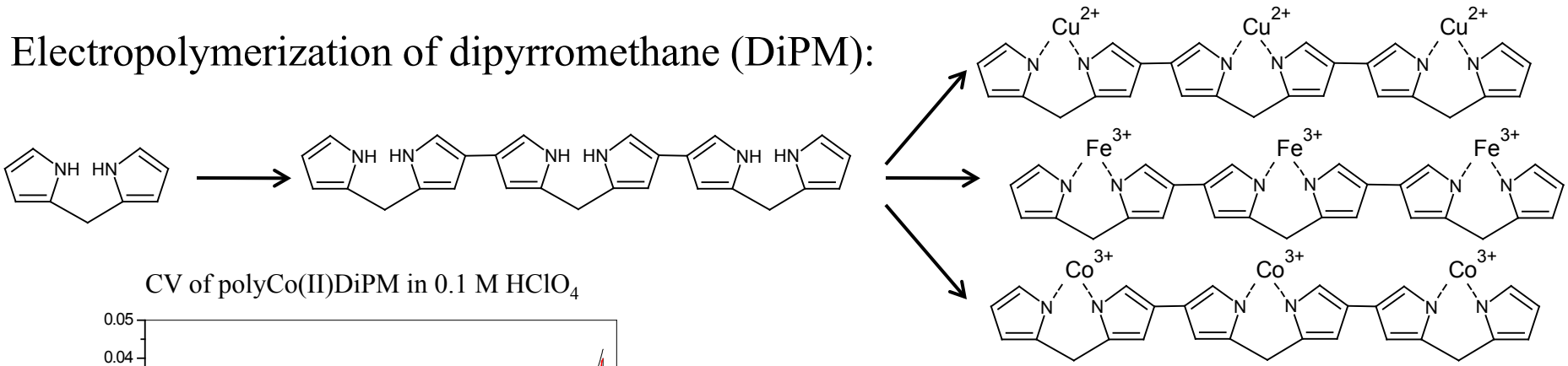
e.g. R. Makharia, M. F. Mathias & D. R. Baker, J. Electrochem Soc. 152 A970 (2005)

R_s = solution (HTFMSA) resistance
R_{POL} = polymer-phase resistance
R_{CT} = charge-transfer resistance
R_{LF} = low frequency resistance from ac impedance.

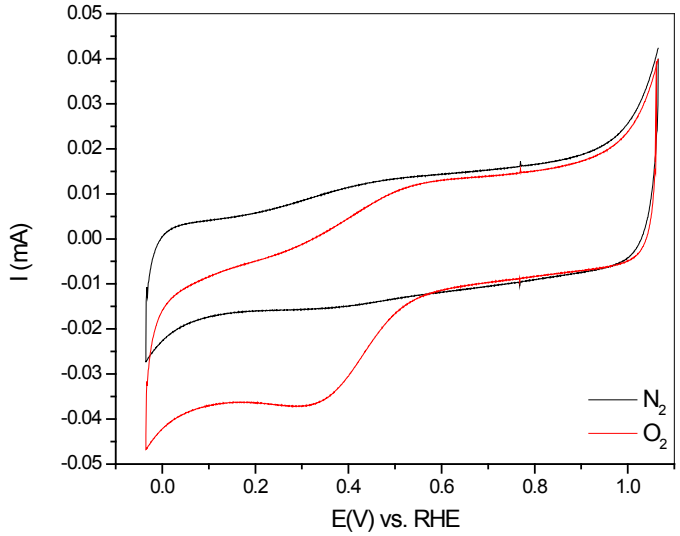
Technical Accomplishments

New Catalysts

Electropolymerization of dipyrromethane (DiPM):

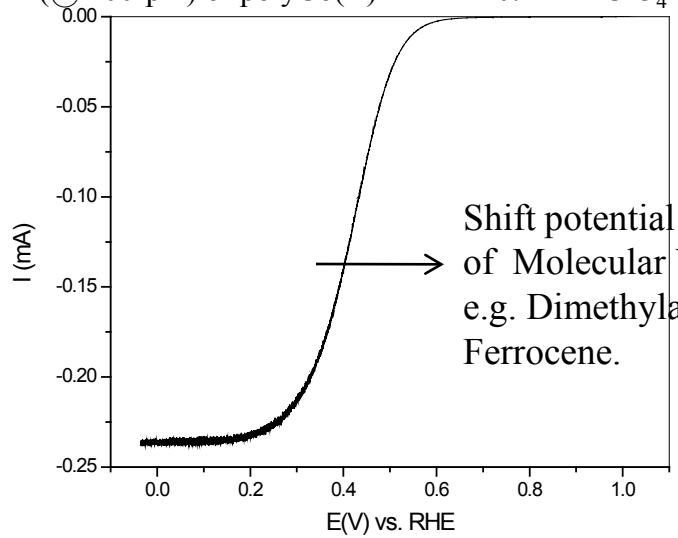


CV of polyCo(II)DiPM in 0.1 M $HClO_4$



- Electropolymerization of DiPM + Co(II) appearing different from that of DiPM alone.

RDE (@ 400rpm) of polyCo(II)DiPM in 0.1 M $HClO_4$

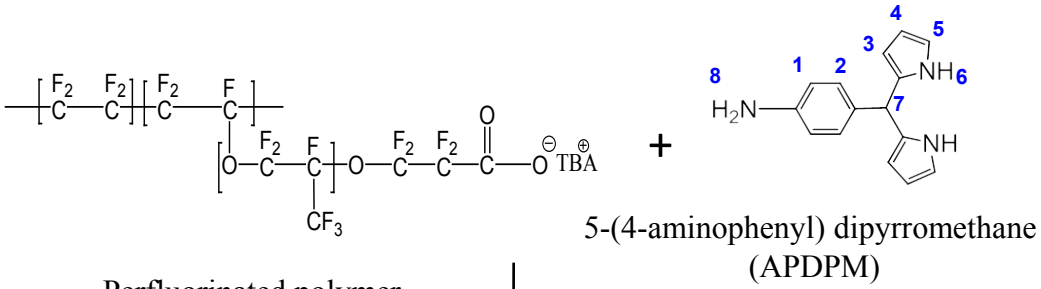


Shift potential by use of Molecular Wire, e.g. Dimethylamino-Ferrocene.

Co-catalyzed polymer showing ORR activity (E_{onset} ~ 0.68 V, $E_{½}$ ~ 0.45 V)

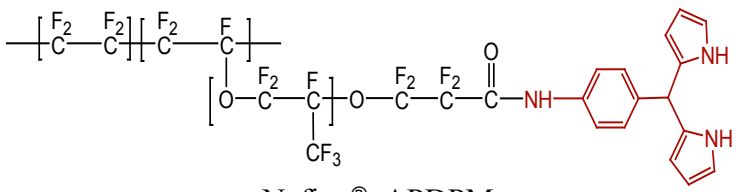
Technical Accomplishments

Synthesis of perfluorinated polymers with tethered Co catalyst



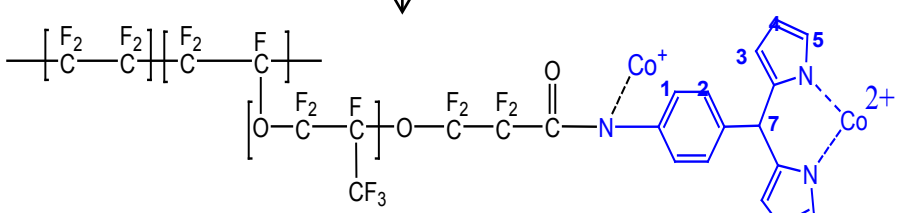
Perfluorinated polymer
(Nafion® -COO TBA)
(IEC = 0.94 meq.g)

DMF 130°C

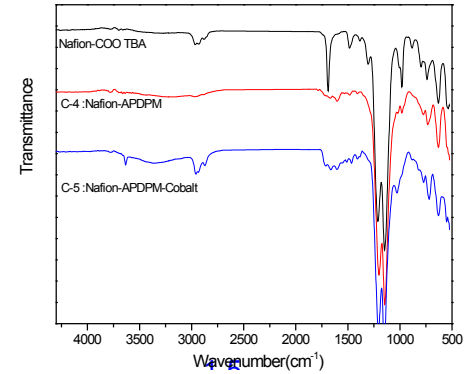


Nafion® -APDPM

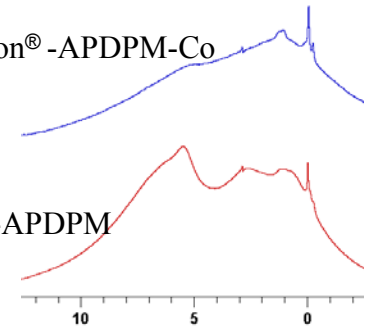
n-BuLi, $Co(NO_3)_2$
DMF, Room Temp.



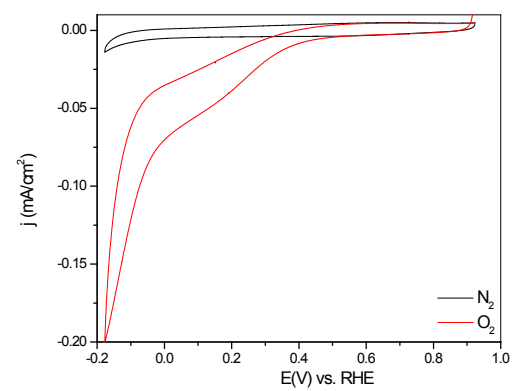
Nafion® -APDPM-Co



^{1}H NMR of APDPM
in $CDCl_3$



^{1}H NMR (Solid)

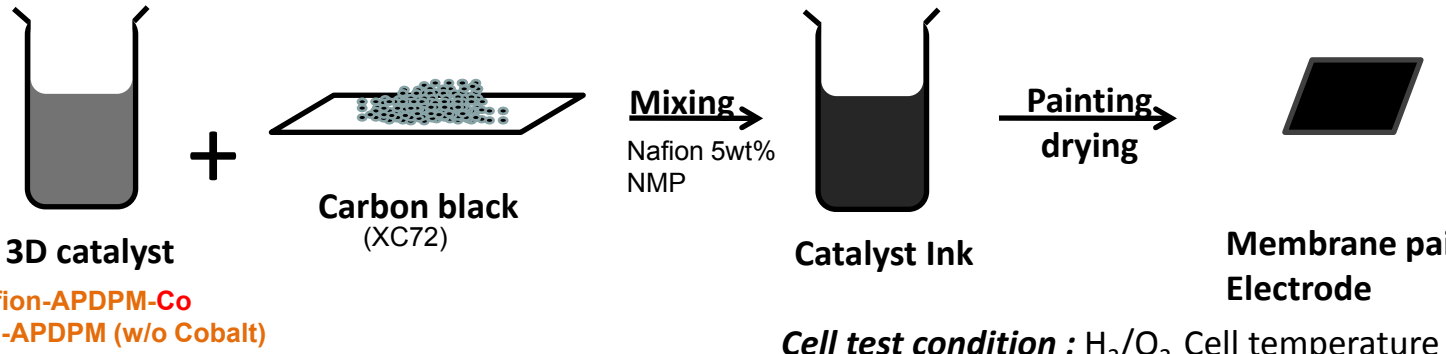


Los Alamos NATIONAL LABORATORY

Yu Seung Kim

Technical Accomplishments

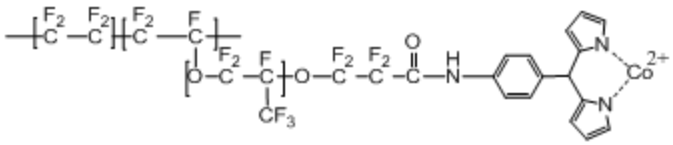
MEA Preparation



MEA 1

-Cathode : 26 μg Co^{2+}/cm^2 and 0.6mg XC72/cm^2

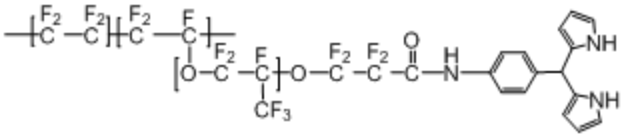
Nafion-APDPM-Co : XC72 = 1:1wt%



MEA 2

-Cathode : 0.6 mg XC72/cm^2

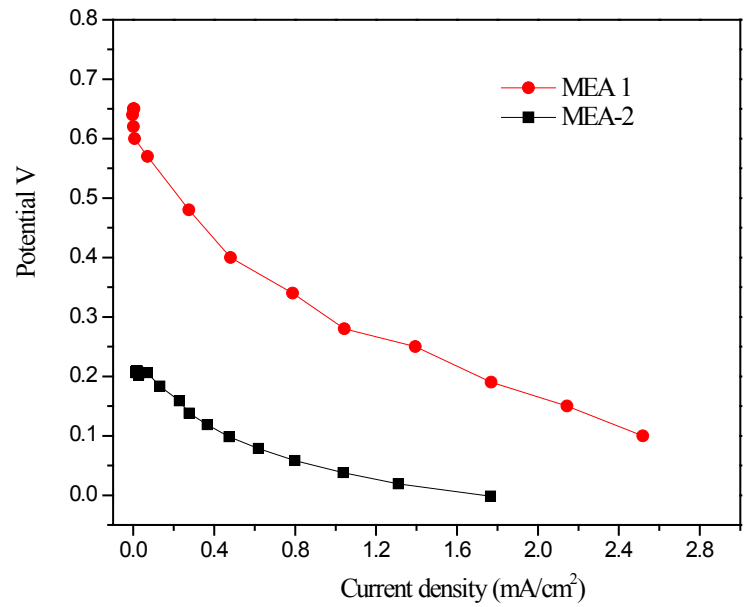
Nafion-APDPM : XC72 = 1:1wt% (W/O Cobalt)



Cell test condition : H_2/O_2, Cell temperature : 80°C

Membrane: Nafion® 212 (H^+ form)

Anode catalyst layer: LANL Standard (0.2 mg Pt/cm^2)



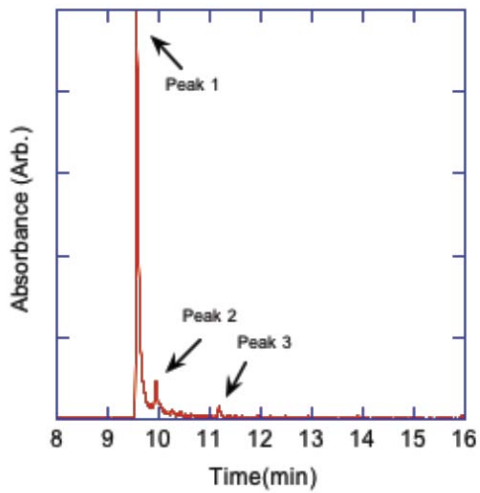
A long way to go! Packing density low

Technical Accomplishments

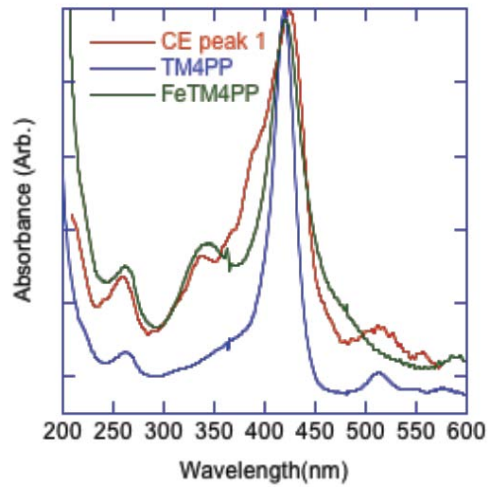
John Chmiola

Stability and Degradation Studies

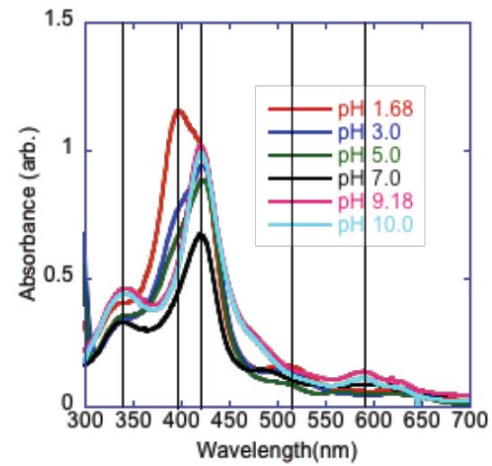
- FeTMPyP measured to be stable to ORR conditions by UV/vis test.
  - Kuwana, Inorg. Chem., 22 (1983), 699.



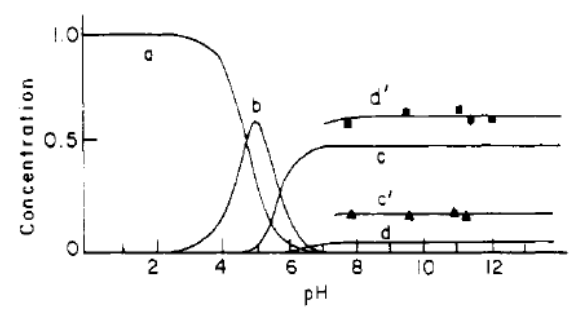
Capillary Electrophoresis(CE) Analysis of FeTMPyP using UV/vis detector



UV/vis Spectra of FeTMPyP, TMPyP and the CE peak



UV/vis Spectra of FeTMPyP as fn. of pH



Speciation of FeTMPyP with pH
a, [Fe'''TMPyP(H,O)]; b, [Fe'TMPyP-(H,O)(OH)]; c = c', [[Fe'''TMPyP(H2O)1,O]; d = d', [Fe'''TMPyP(OH),].

CE analysis shows impurities and degradation products. UV/vis provides spectral confirmation. In progress is CE/Ion Trap Mass Spectroscopy to identify products from O_2 attack.

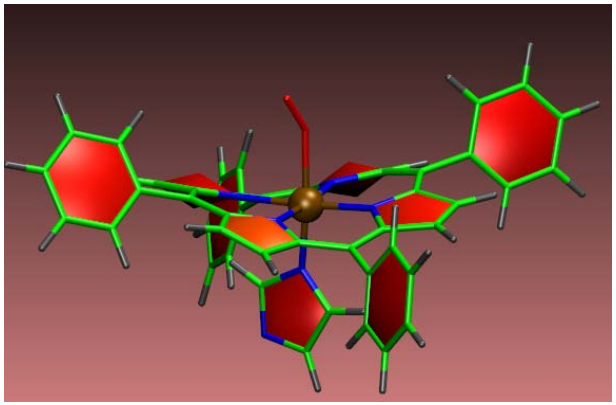
Neil Henson

Technical Accomplishments

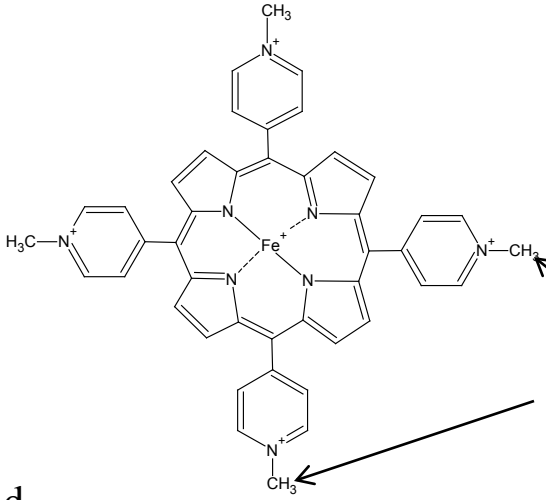
Molecular Modeling and Synthesis of Catalysts.

Martin Head-Gordon, Tom Baker

- Calculate stabilities of complexes with pH and binding to ligands.
- Calculate energy barriers to oxygen reduction.



Fe(II)TMPyP bound with imidazole and oxygen. Geometry changes with ligands.



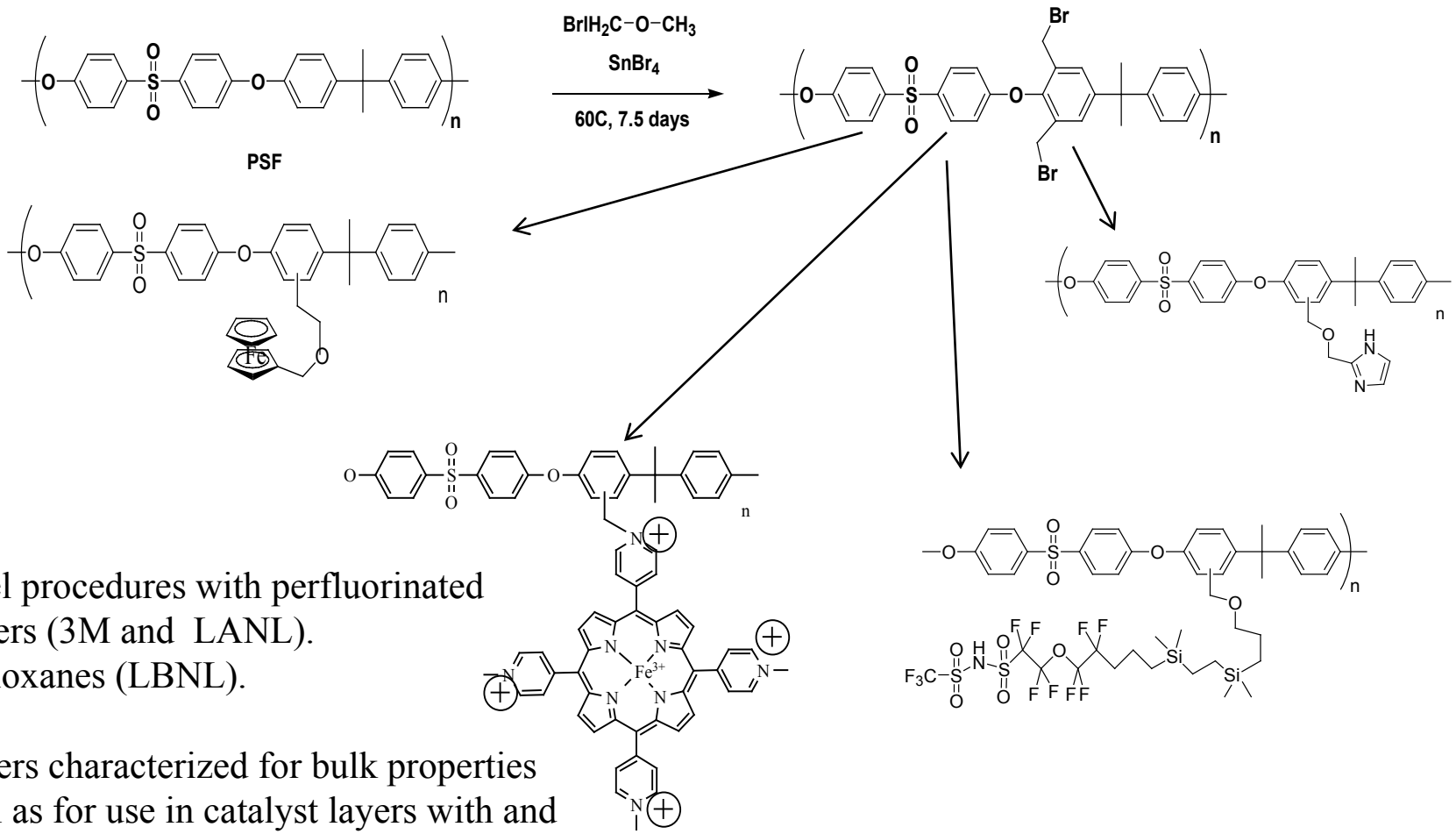
E^o of catalysts change with ligands binding to metal center. Rates of ORR change with substituents on pyridines

Replacement of Me groups with H^+ on the nitrogen results in slower rates.

Model effects of changing substituents on pyridine rings, replace pyridine with imidazoles and model effects of base ligands binding to metal. Synthesize and characterize catalysts and compare results with theoretical predictions.

Technical Accomplishments

Functionalization of polymers with catalysts, mediators, acids and bases



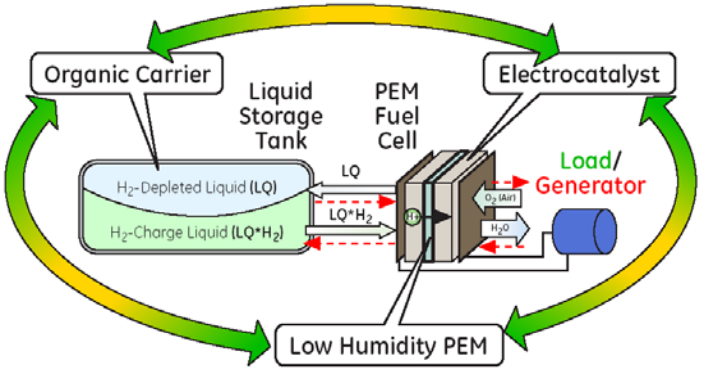
Parallel procedures with perfluorinated polymers (3M and LANL).
Polysiloxanes (LBNL).

Polymers characterized for bulk properties as well as for use in catalyst layers with and without incorporated catalysts.

Collaborations

Project Participants. LBNL/UCB, LANL and 3M. Coordination achieved by weekly web/phone conference calls and instant web meetings to share data, quarterly meetings and personnel exchanges. Project monitored using Project Management tools (see Supplementary slides).
LANL Applied Science Program. DOE funded program to study fundamental science underpinning preparation of MEA electrodes.
Catalyst Sources. Multiple sources of new catalysts from US and European Research Labs/Universities.

DOE Energy Frontier Research Center with GE, Yale Stanford and LBNL. Center for Electrocatalysis, Transport Phenomena, and Materials (CETM) for Innovative Energy Storage. LBNL/UCB P.I.'s are active participants.



Future Work

- Use presently available catalysts – Fe, Mn, Co and Cu TMPyP complexes - and electron mediators – Ferrocenes – to prepare and test MEA's.
  - Use known polymer binders – Nafion®, 3M, polysulfones, polysiloxanes.
  - Optimize loading of catalyst and mediator in catalyst layer.
  - Test MEA's and measure pertinent parameters in screening experiments.
  - Compare MEA results with model predictions using parameters obtained from screening experiments and polymer characterization.
  - Extend impedance models for use with MEA electrodes.
- Complete Go/No Milestone (September 2011).
  - Oxygen reduction catalysis demonstrated with polymer-bound catalyst layers in MEAs. An operational lifetime of at least ten hours is required.
- Degradation Analysis and Lifetime Testing Development.
  - Both Catalyst and polymer matrix analyses – CE, HPLC-Mass Spec, NMR, AFM, SEM, TEM, SAXS, Neutron scattering.
  - Catalyst layer impedance methods development for screening methods to correlate with MEA impedance measurements. MEA testing.
- Synthesis, procurement and screening of new catalysts guided by molecular modeling/computation.

Summary

- Non-PGM transition metal ORR catalysts have been identified with rate constants compatible with DOE target current densities in the proposed 3D catalyst matrix for MEA's. 4 electron reduction to water is favored by high local concentrations of catalysts as is found in the 3D catalyst matrix. Solvent modifies regeneration rates.
- Catalysts have been incorporated into polymer layers on electroanalytical electrodes and display satisfactory activity as well as stability in strong acid and towards active oxygen species. Catalyst and mediators remain in the layers.
- ORR overpotentials are high but may be reduced by use of redox mediators which also function as "Molecular Wires" in the polymer layers containing catalysts. Molecular modeling/computation combined with electrochemical screening will be used to help identify structural factors that favor lower overpotentials and rapid electron mediation to guide synthesis of new catalysts.
- Non-PGM transition metal ORR catalysts and Molecular Wires are being incorporated into MEA structures. Initial performance is poor but rapidly improving with optimization.
- Chemical, physical and microscopy analytical methods are under development to measure catalyst and polymer matrix degradation pathways.
- New catalysts are being synthesized or procured. The protocols for screening, MEA fabrication and testing are almost complete.

Technical Back-Up Slides

Collaborations
Project Participants and Roles

LBNL John Kerr – polymer synthesis/characterization, electrochemical screening, MEA fabrication/testing, degradation analysis.
Robert Kostecki – Catalyst screening, degradation analysis.
Adam Weber – Macroscopic modeling.

UCB John Arnold group – catalyst synthesis/characterization.
Martin Head-Gordon Group – Molecular modeling/computation.
Jeff Reimer/Rachel Segalman – polymer/catalyst layer characterization.

LANL Piotr Zelenay – Electrochemical screening, MEA testing
Yu Seung Kim – Polymer synthesis, characterization; MEA fabrication and testing.
James Boncella - catalyst synthesis/characterization.
Jerzy Chlistunoff- catalyst layer screening/testing
Neil Henson- Molecular modeling/computation

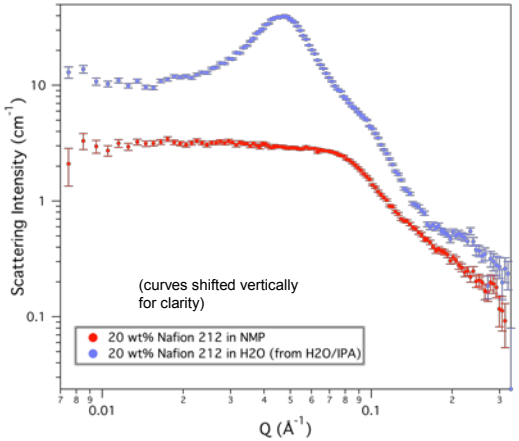
3M Steve Hamrock, Radoslav Atanasoski – Perfluorinated polymers, MEA characterization.

Coordination achieved by weekly web/phone conference calls and instant web meetings to share data, quarterly meetings and personnel exchanges. Project monitored using Project Management tools (see Supplementary slides).

Collaboration

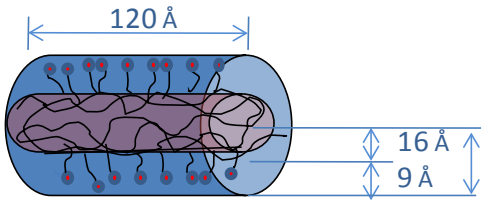
Polymer ink characterization for electrode fabrication (LANL Applied Science Program)

SANS: NMP- vs. H2O-Based Gels



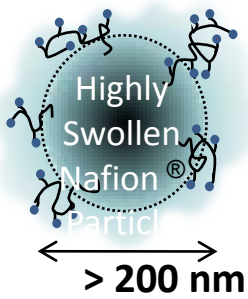
NMP dispersion: Core-Shell Cylinder

- 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)



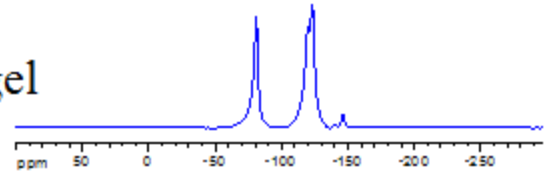
Aqueous mixture: Highly swollen particles

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

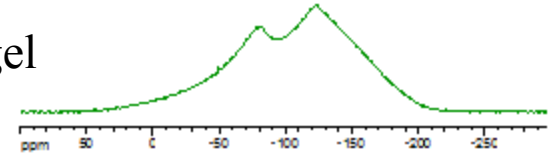


^{19}F NMR

NMP gel

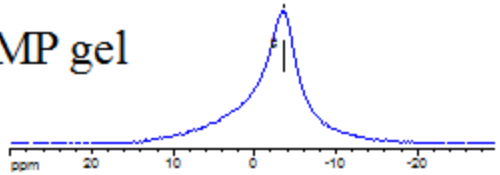


water gel

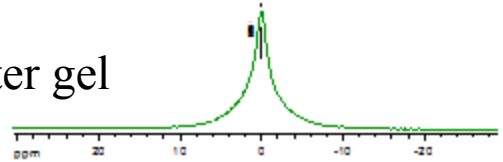


^{23}Na NMR

NMP gel



water gel



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

Technical Accomplishments

Model Parameters (Thin Film) for Catalyst Layers

Table 1. Geometrical/transport properties used for a prototype thin film.

Parameters	Magnitude	Parameters	Magnitude
Oxygen Diffusivity in Film, D_{O2}, cm^2/s	0.6 x 10^{-6} [1]	Proton concentration, c_{H+}, mol/cm^3	1/550
Reaction rate, k, cm^3/mol-s	5 (Nafion®-0.2 mg Pt/cm^2)	Transfer coefficient, α_c, α_a	1, 0.5
Proton conductivity, σ_{H+}, S/cm	0.1	Temperature, T, K	353
Electron conductivity, σ_e, S/cm	0.1	Catalyst particle radius, r_p, nm	0.5
Catalyst Concentration, nm^{-3}	0.1	Catalyst support radius, r_s, nm	50
Polymer film thickness, L_δ nm	50, 100, 500		

Table 2. Geometrical/transport properties used for a catalyst layer and GDL.

Parameters	Magnitude	Parameters	Magnitude
Oxygen Concentration (GDL/Ch at RH = 100%), $c_{O2,o}$, mol/cm^3	4.31 x 10^{-6}	Water Diffusivity in GDL, D_{H2O}, cm^2/s	0.345
Overpotential, η, V	0.5	CL Thickness, L_{CL}, um	10
Oxygen Diffusivity in GDL, D_{O2}, cm^2/s	0.303	GDL Porosity, ε_{GDL}	0.8

[1] A.T. Haug and R.E. White, J. Electrochem. Soc., 147, 980-983, 2000
[2] J.J. Fontanella, C.A. Edmondson, and M.C. Wintersgill, Y. Wu, and S.G. Greenbaum, Macromolecules, 29, 4944-4951, 1996