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

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

May 10, 2011

Project ID #
FC 011

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)

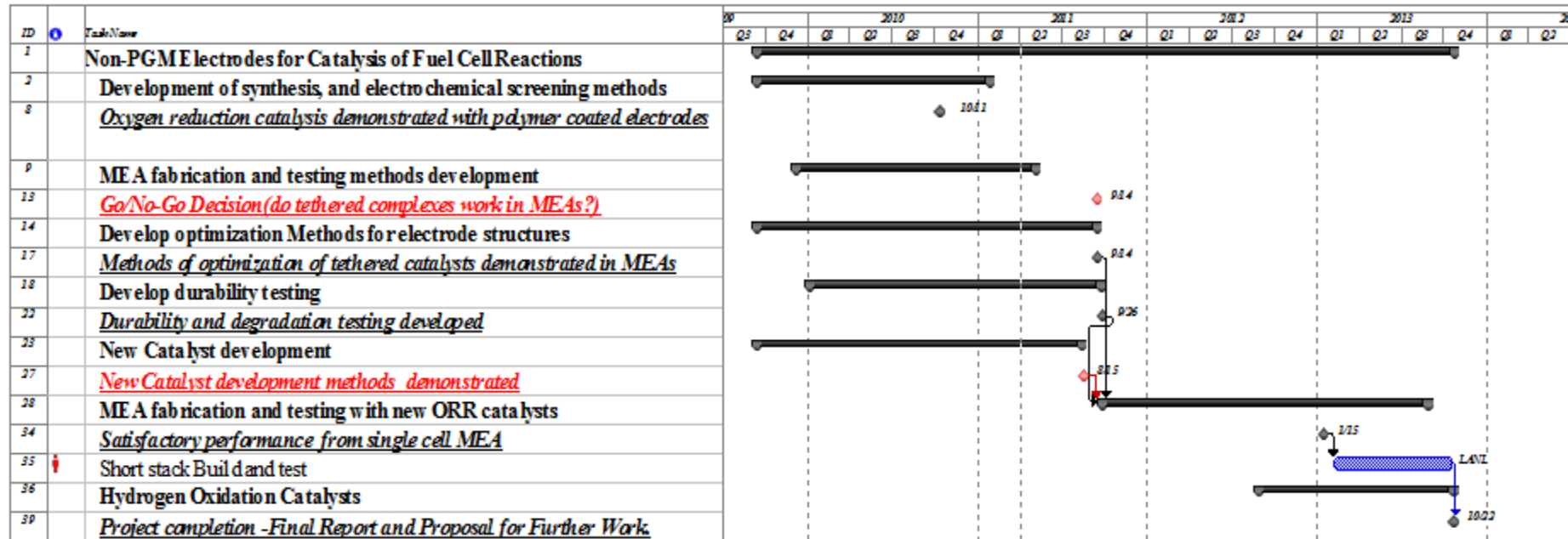# Milestones & Go/No-Go Decisions.

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$_{ir-free}$ with at least 10 hours operational lifetime.
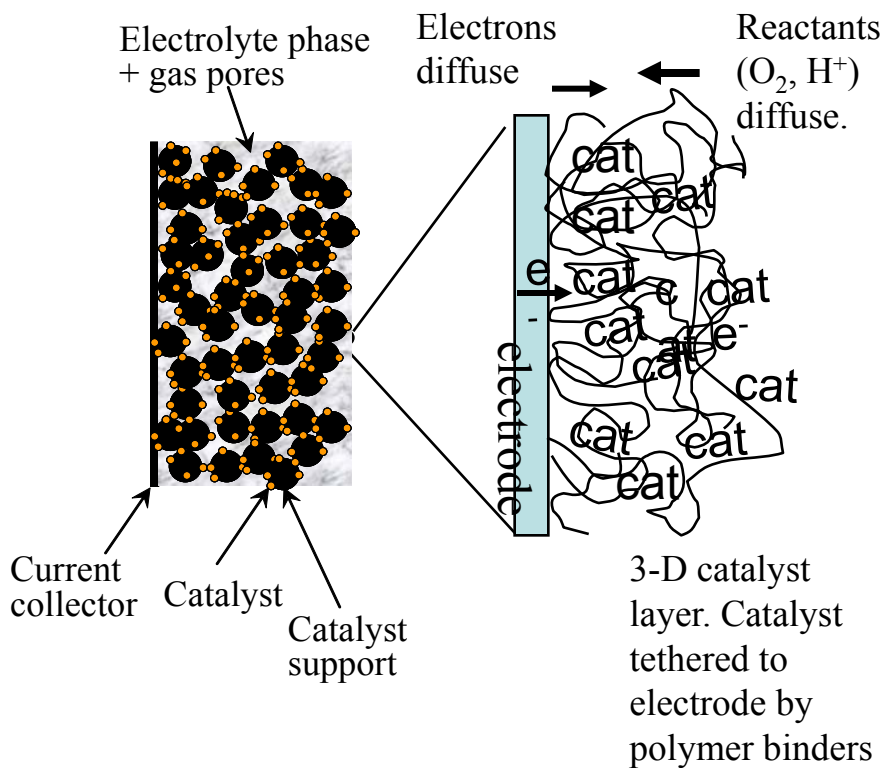Milestone 3. Methods of optimization of catalysts demonstrated in MEAs (24 mo).
Milestone 4. Durability and degradation testing developed (24 mo).
Milestone 5. New catalyst development methods demonstrated (24 mo).

ID	O	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	i	Short stack Build and test
36		Hydrogen Oxidation Catalysts
39		*Project completion –Final Report and Proposal for Further Work.*

Approach

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

Electrolyte phase + gas pores

Electrons diffuse

Reactants (O_2, H^+) diffuse.

e⁻ electrode

Current collector

Catalyst

Catalyst support

3-D catalyst layer. Catalyst tethered to electrode by polymer binders

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**

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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)

$$O_2 + 4H^+ + 4e^+ \rightarrow 2H_2O + \dot{s_e}$$

c_{O_2} c_{H^+} c_{H_2O}
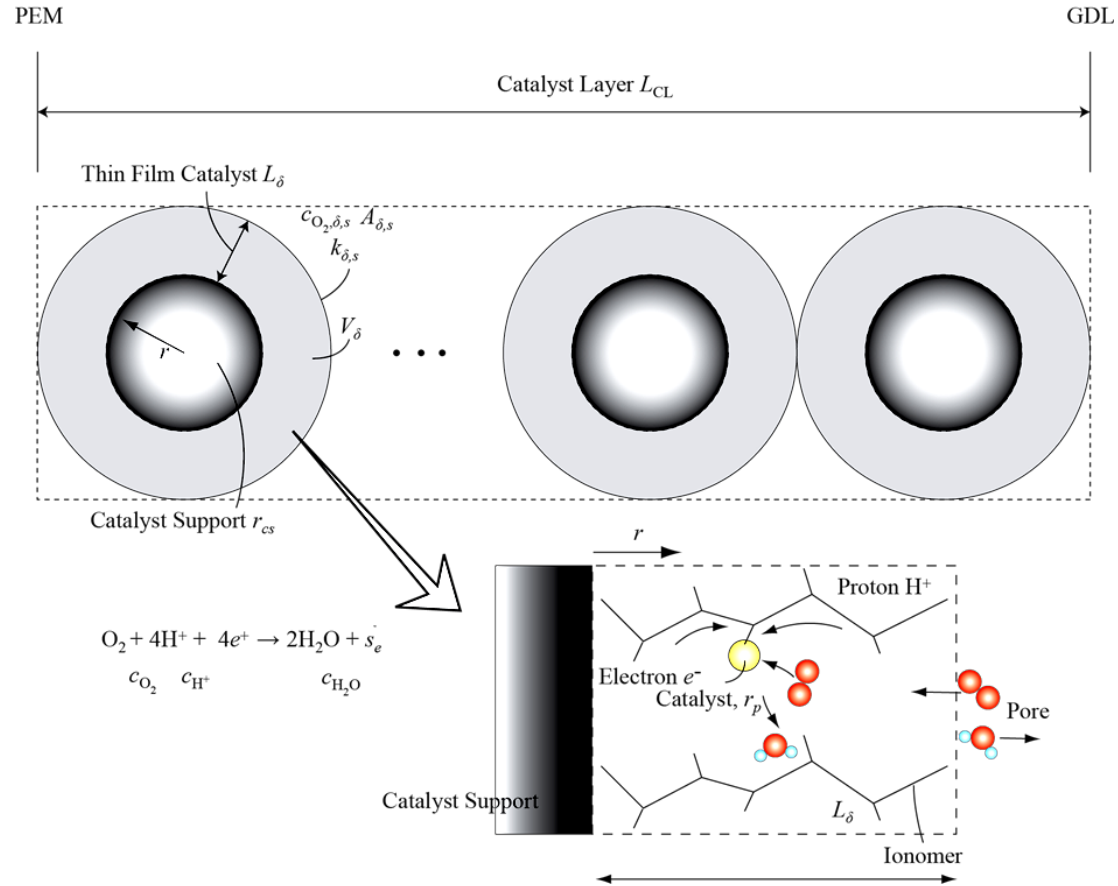
Schematic drawing of oxygen, proton, electron, and water transport though the thin metal catalyst layer through a catalyst layer.

Model Current Density as function of Transport Properties, Geometry & Catalyst Activity – Polarization curve and optimization maps
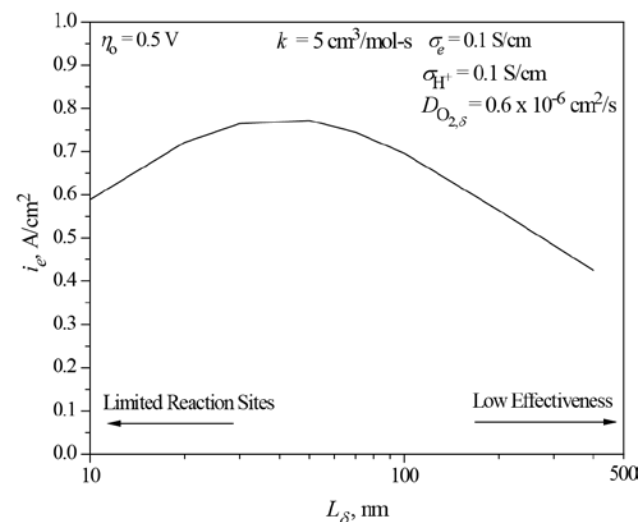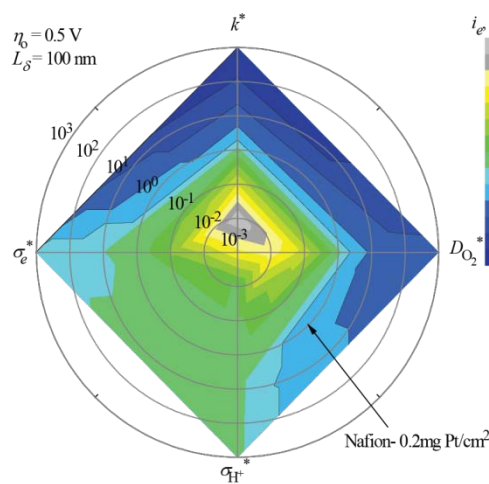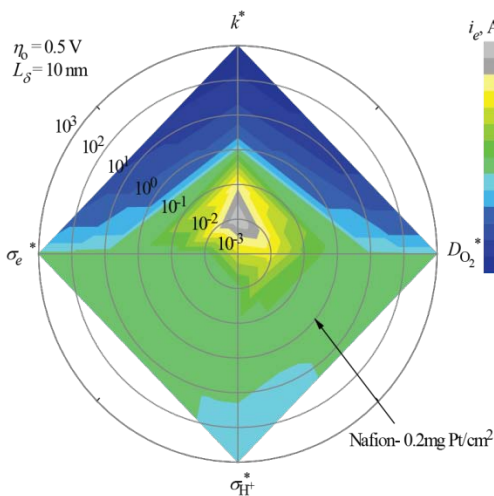
- Current density significantly increases with increasing oxygen diffusivity/reaction rate, but thick film reduces performance due to the limited O_2 transport
  - Can get limitations due to proton and electron transport as well (not shown)

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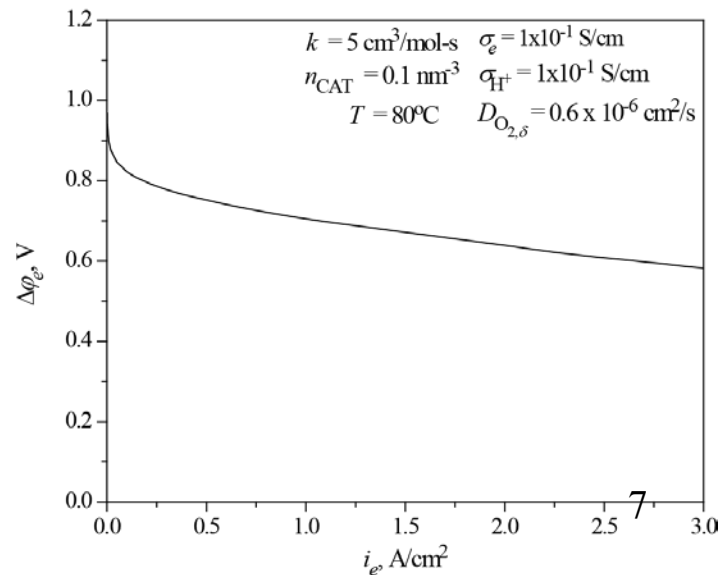
Technical Accomplishments
Catalyst screening

Lior Elbaz, Piotr Zelenay

Qinggang He,
Robert Kostecki

0.1 mM Fe(III)TMPyP in 0.1 M H_2SO_4 (@100mV/s)

0.8 mM Mn(III)TMPyP in 0.1M Triflic Acid, GC at 50mV/s

0.8 mM Co(III)TMPyP in 0.1M Triflic Acid, GC at 50mV/s

0.6 mM Cu(II)TMPyP in 0.1M Triflic Acid, GC at 50mV/s
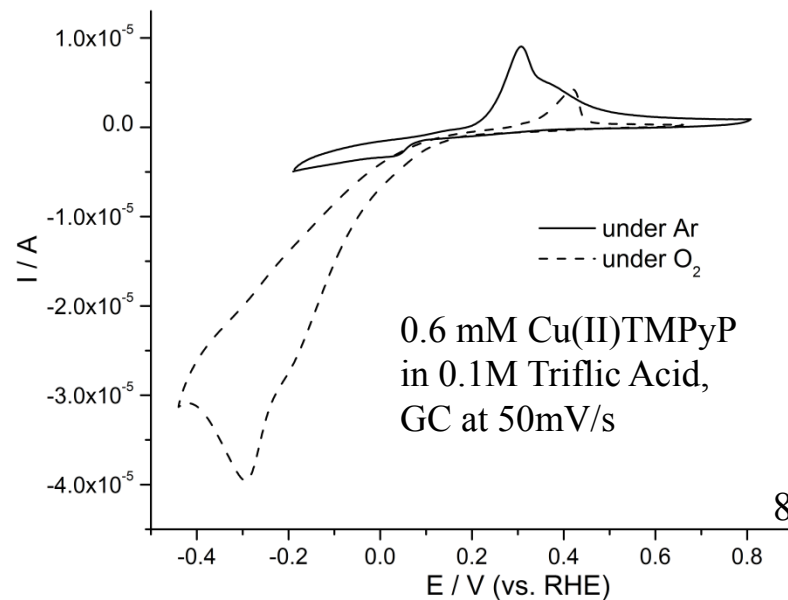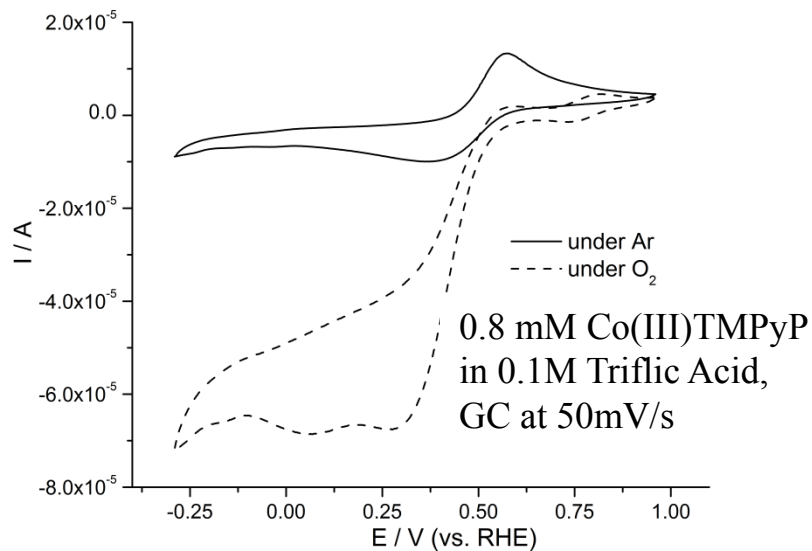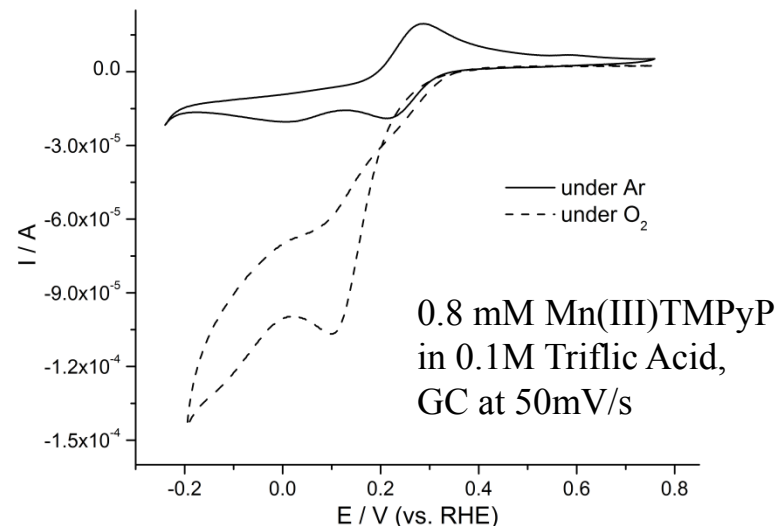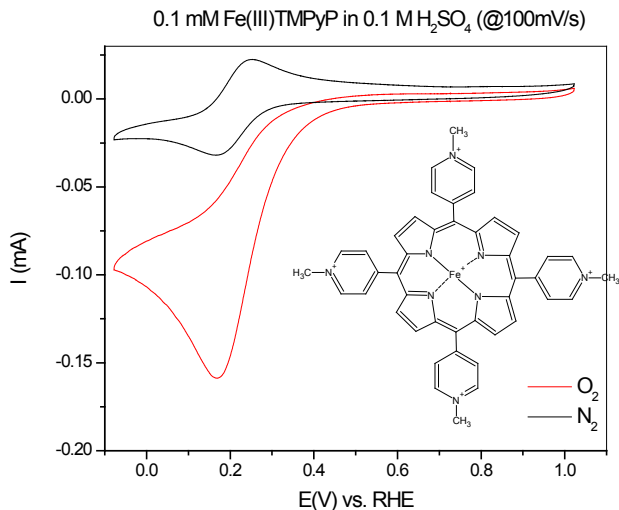
Qinggang He,
Robert Kostecki

Fe catalysts - 4 electron reduction at high concentrations, 2 electrons at low concentrations.

Co catalysts tend to give 2 electron reductions.

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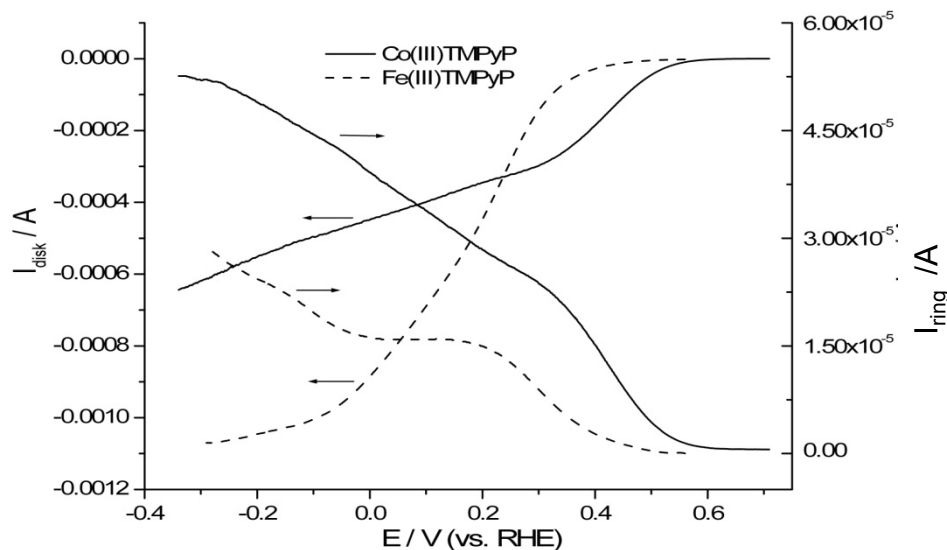
Polarization curves for GC disk and Pt ring electrodes and peroxide yield for O_2 saturated 0.1M TFMSA + 0.8 mM Fe(III)TMPyP and 0.1M TFMSA + 0.8 mM Co(III)TMPyP, rotation speed: 400 rpm, scan rate: 20mV/s.

Qinggang He,
Robert Kostecki

Outer-sphere Redox catalysis mechanism (Marcus-Hush)

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

$$TPyPFe(II) + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} TPyPFe(III) + \overset{\bullet}{O_2^-}$$

$$\overset{\bullet}{O_2^-} + H^+ \rightleftharpoons O_2\overset{\bullet}{H}$$

$$TPyPFe(II) + O_2\overset{\bullet}{H} \longrightarrow TPyPFe(III) + O_2H^-$$
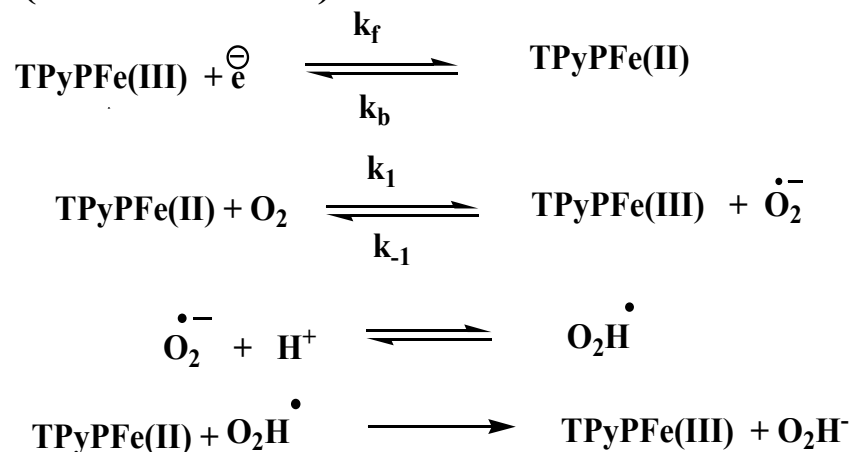
Quasi-redox inner-sphere mechanism.

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

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

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

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.

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Technical Accomplishments
Catalysis Mechanism Diagnosis

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
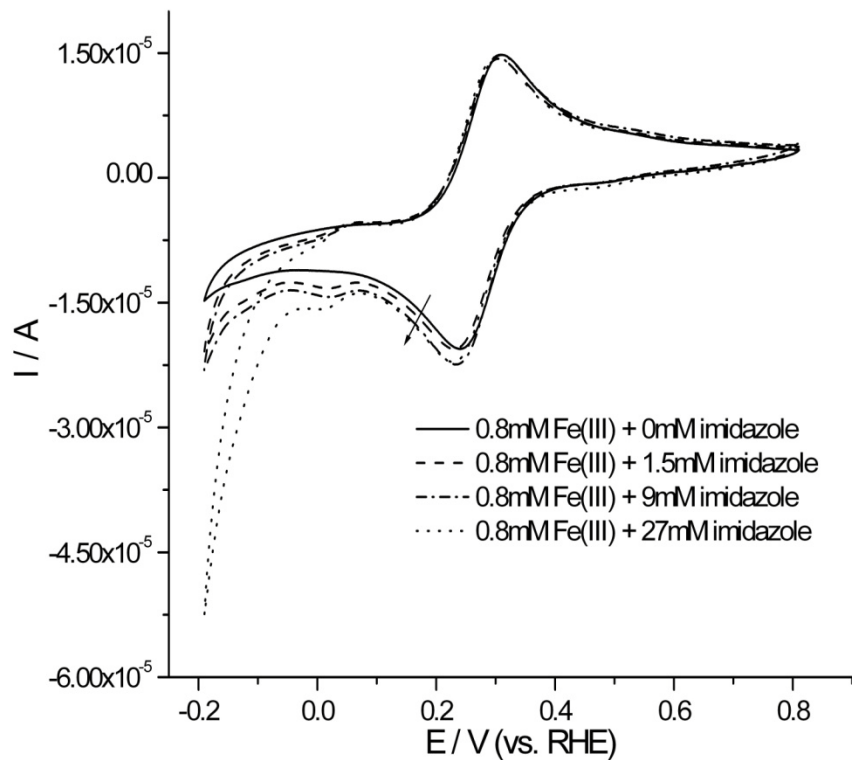
Addition of imidazole base to solution does not change Redox potential of catalyst. Base is protonated and does not bind to the metal center.
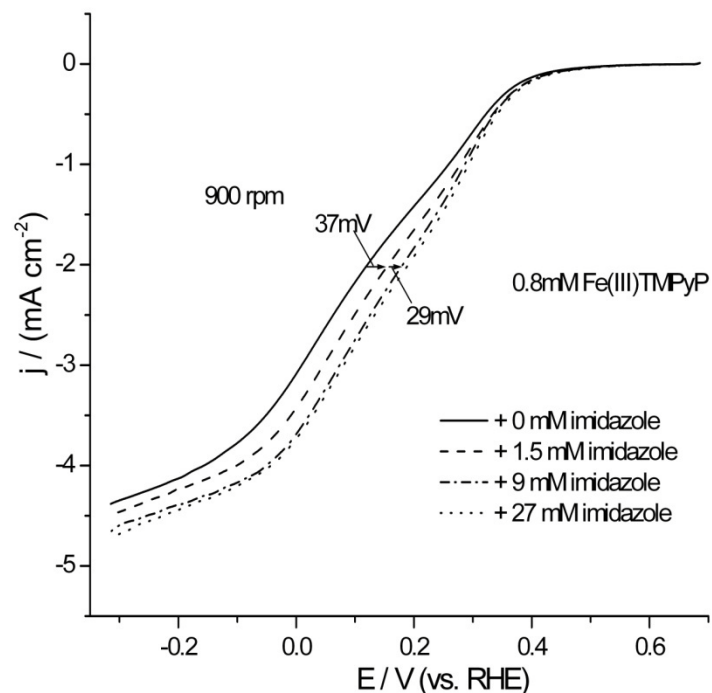
Addition of base does not change onset potential but apparently increases rate of catalyst regeneration and catalyst turnover frequency (TOF).

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Technical Accomplishments

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

Fe(III)TMPyP
under Ar in 0.1M HTFSA

Added to Fe(III)TMPyP
under O_2 in 0.1M HTFSA

E/V vs. NHE
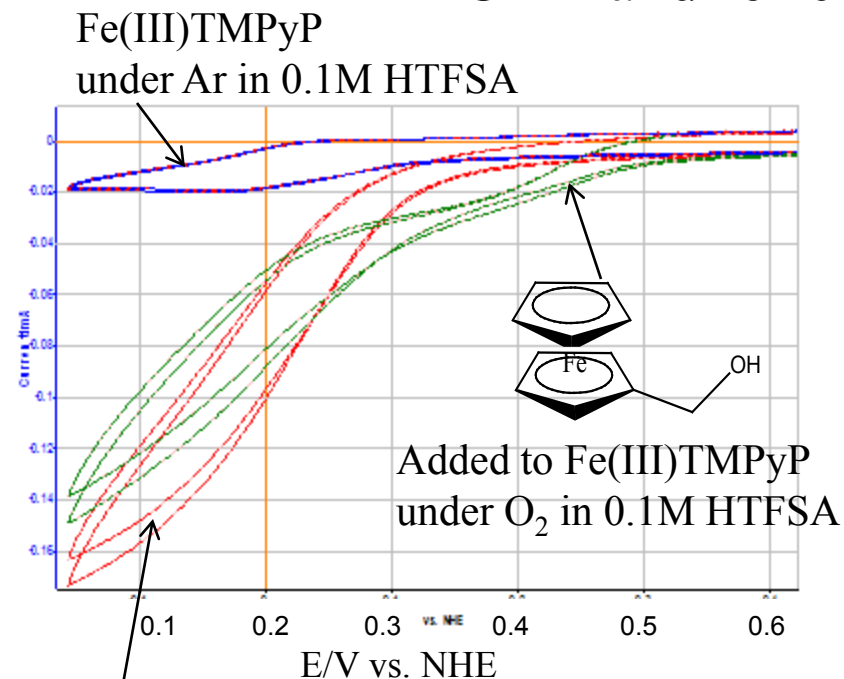
Fe(III)TMPyP
under O_2 in
0.1M HTFSA

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

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

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

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

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

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

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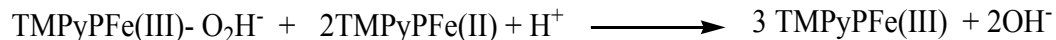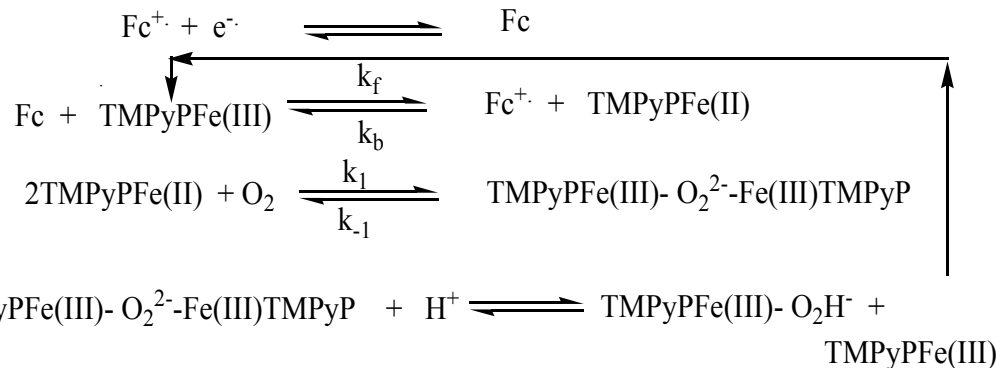
Tethering porphyrins to polyelectrolytes

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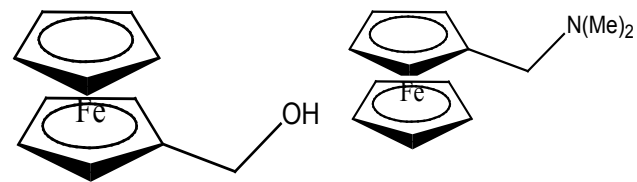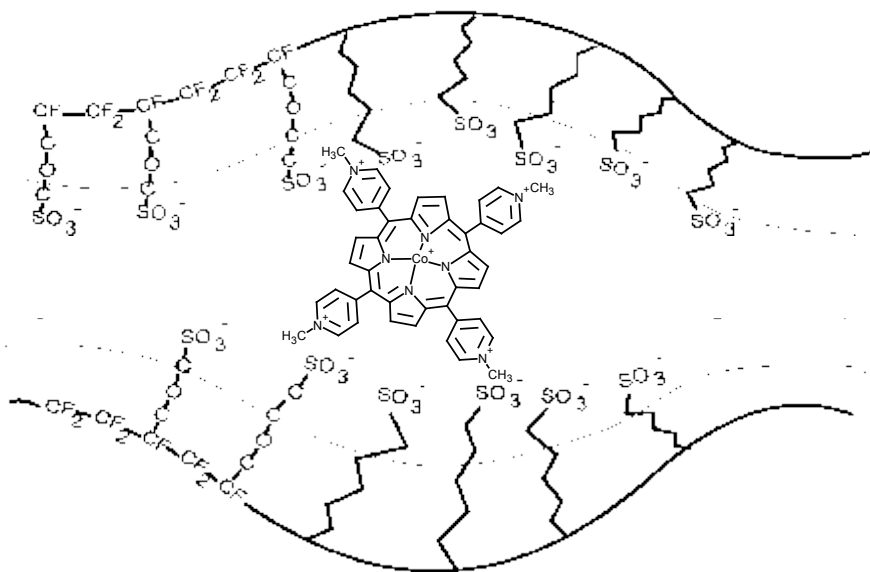
Ferrocenes added as electron carriers
-More mobile in polymer catalyst layer
due to lower charge and smaller volume.

Co and Fe TMPyP complexes tethered in Nafion®

Lior Elbaz, Piotr Zelenay
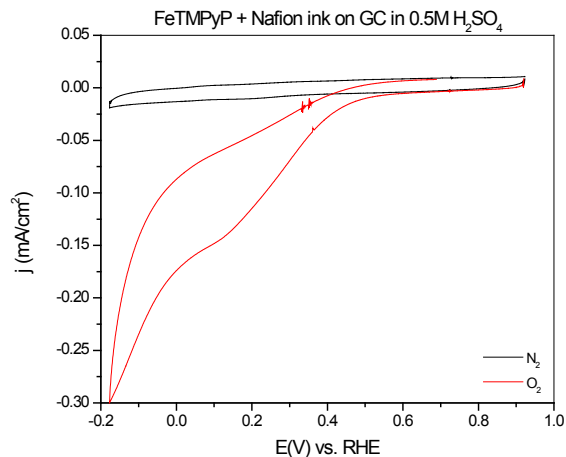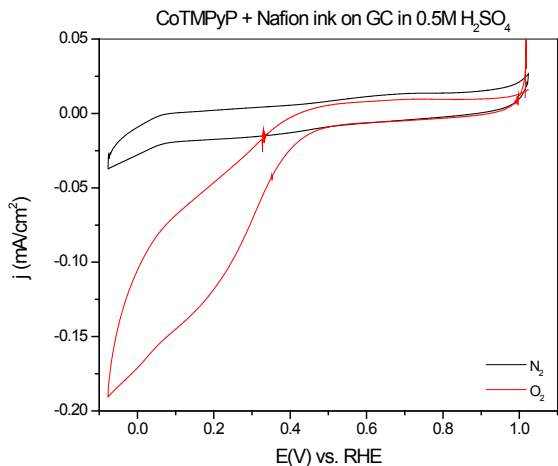
Nafion® ink cast on glassy carbon electrodes
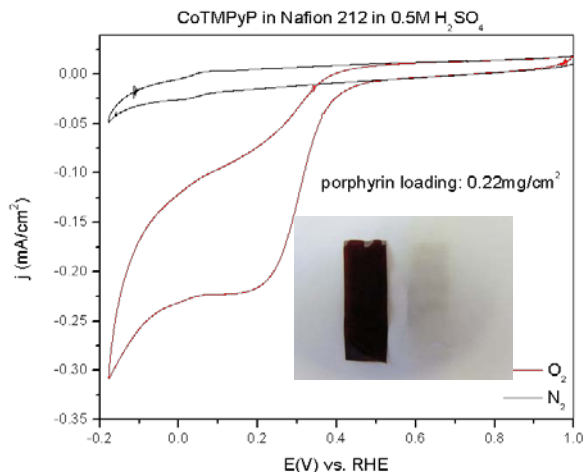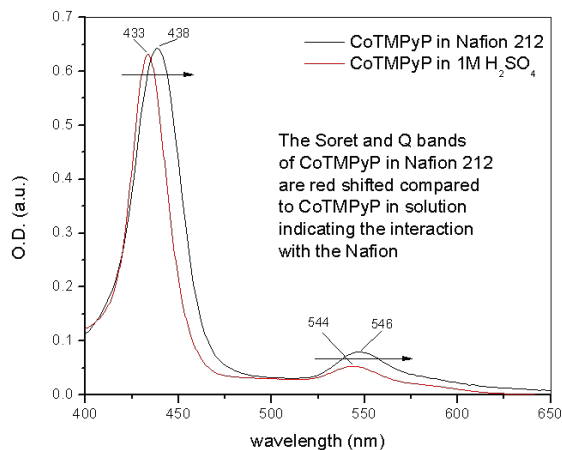
Proton conductivity:
Nafion® -CoP – 58 mS/cm
Nafion® – 115 mS/cm
Lower H_2O uptake with CoP
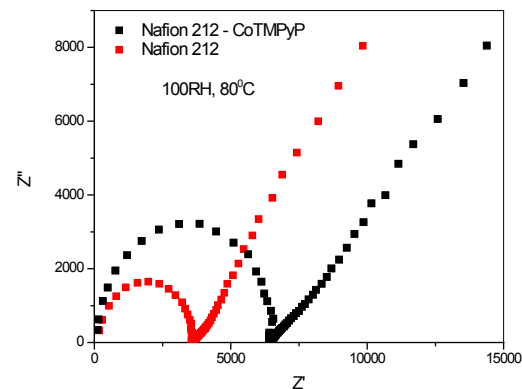
Nafion® 212 membrane with CoTMpyP.

Technical Accomplishments
Tethering porphyrin catalysts and electron "Molecular Wires" to polyelectrolytes
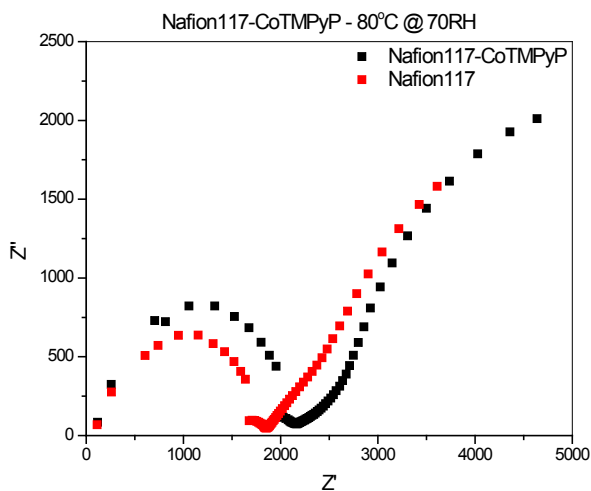

Under Ar

Freshly cast film

Film after 2 days in solution

E/V vs. RHE

Film after 2 days in solution

Under O$_2$

Freshly cast film

E/V vs. RHE
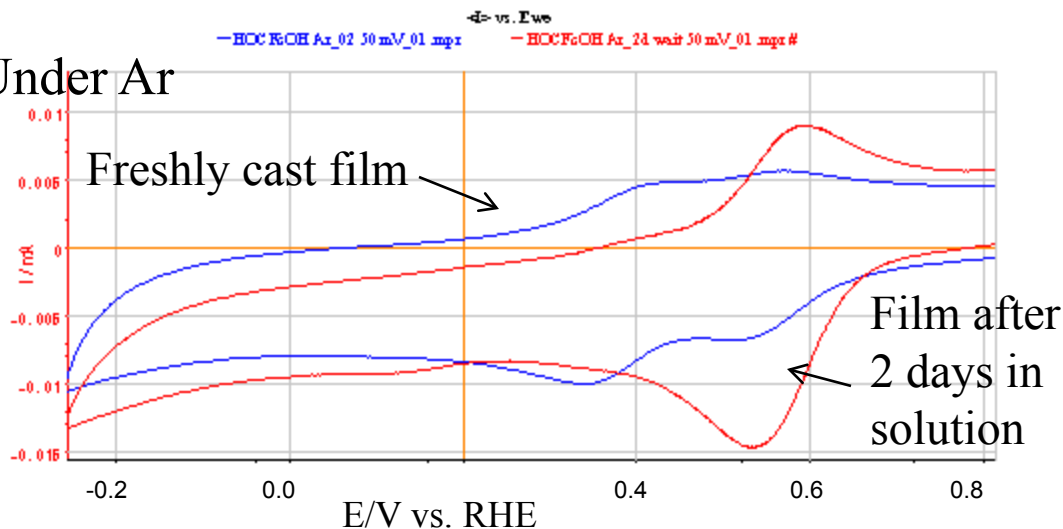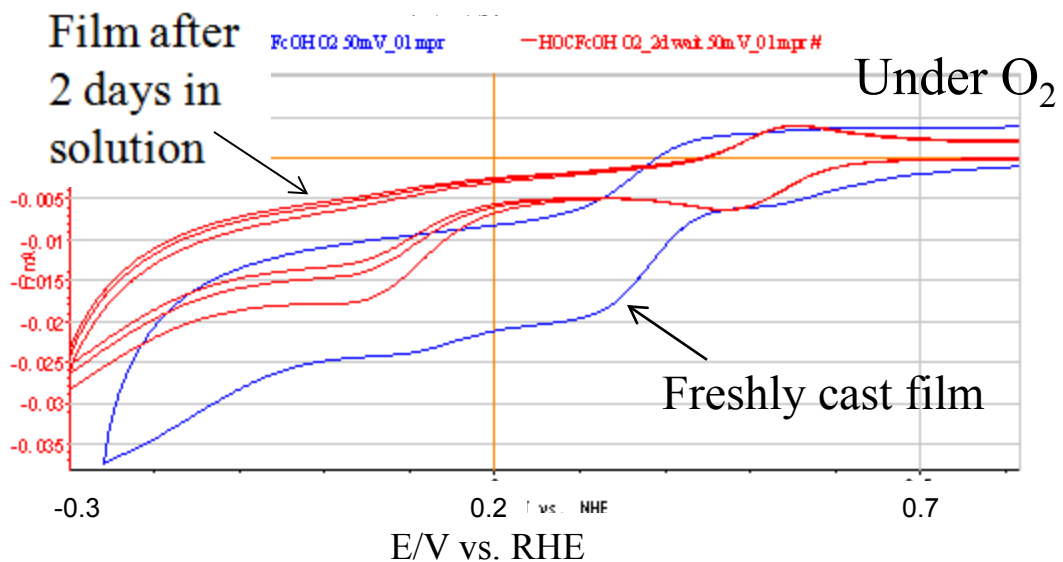
- Initial CV shows two peaks for FcCH$_2$OH, one peak after two days. Reacts with sulfonic acid of Nafion® to form ester and potential shifts positively.

- Freshly cast film shows strong catalysis of ORR.
- Bound ester shows little or weak catalysis.
- FeTMPyP and FcCH$_2$OH stay in film.

Nafion® ink containing FeTMPyP and hydroxymethylferrocene (FcCH$_2$OH) cast on GC electrodes - ~ 1 micron dry film. CV recorded in 0.1 M TFMSA.

Tethering porphyrin catalysts and "Molecular Wires" to polyelectrolytes

Under O_2
+0.4V; -0.3V

Under Ar
E = +0.4V
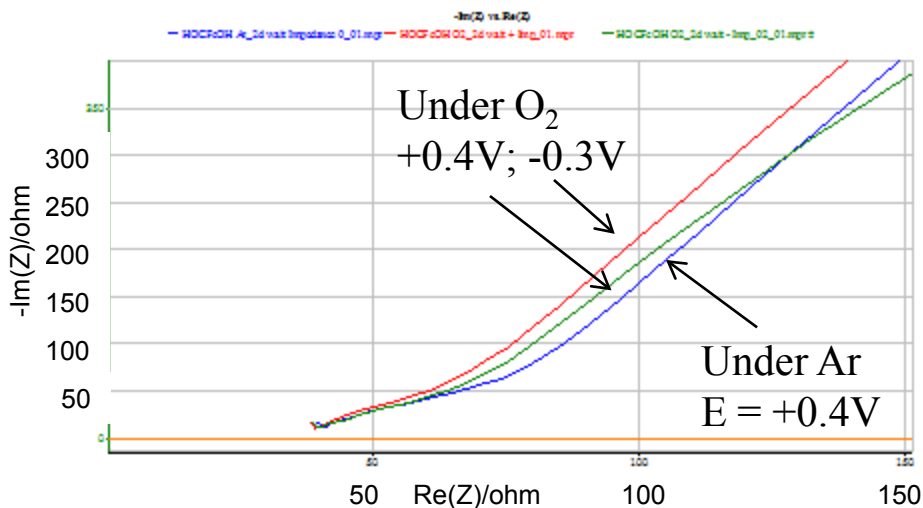
Impedance measurements of coated GC electrode vs. Ag/AgCl

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

Nafion117-CoTMPyP - 80°C @ 70RH

■ Nafion117-CoTMPyP
■ Nafion117

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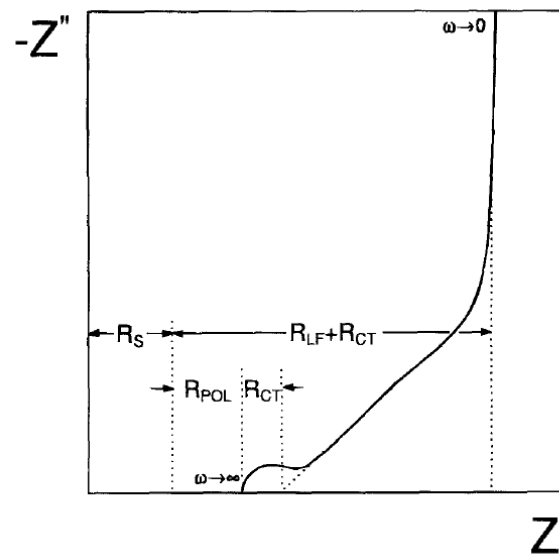
R_S = solution (HTFMSA) resistance
R_{POL} = polymer-phase resistance
R_{CT} = charge-transfer resistance
R_{LF} = low frequency resistance from ac impedance.

New Catalysts
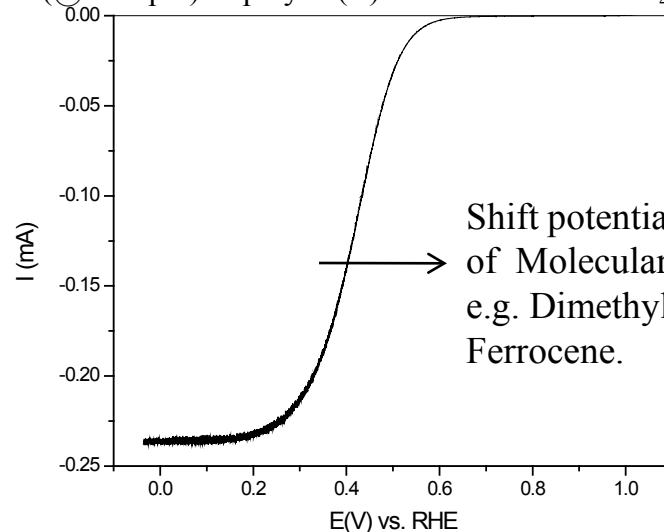
Electropolymerization of dipyrromethane (DiPM):
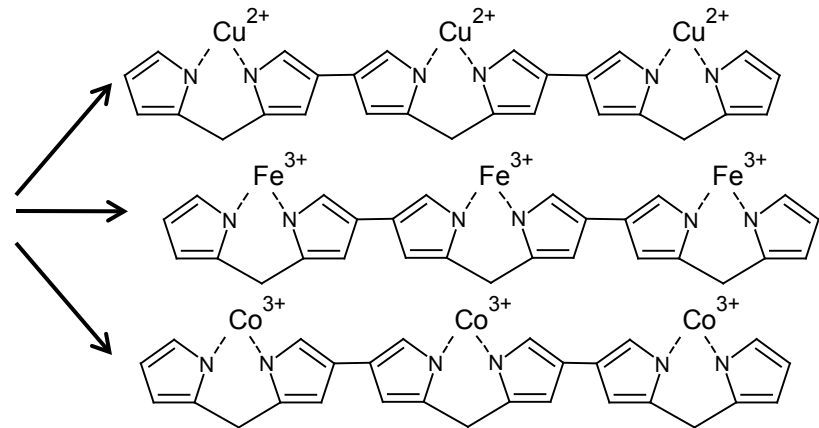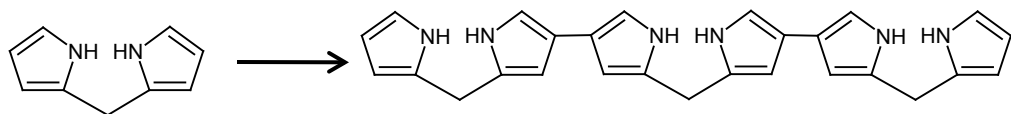
CV of polyCo(II)DiPM in 0.1 M $HClO_4$
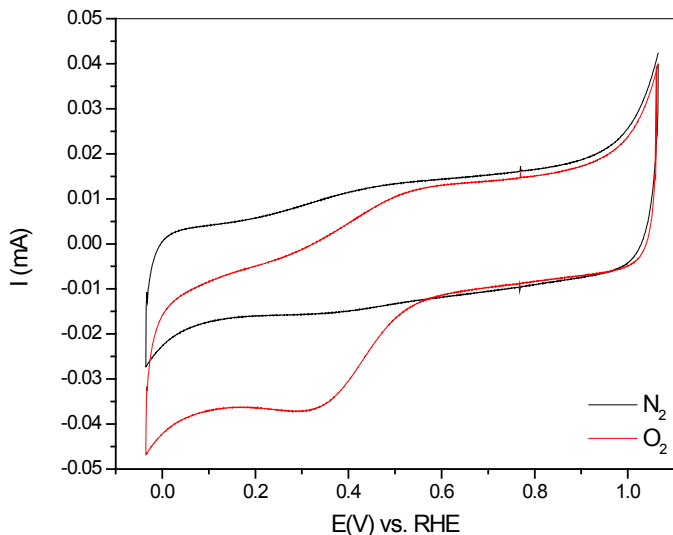
- Electropolymerization of DiPM + Co(II) appearing different from that of DiPM alone.
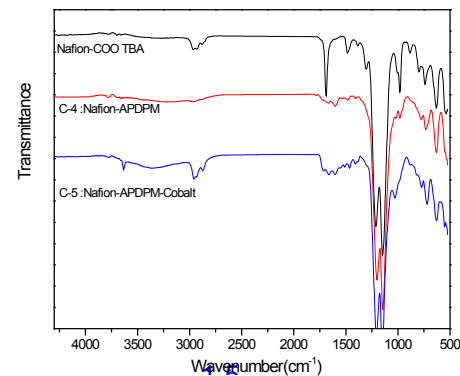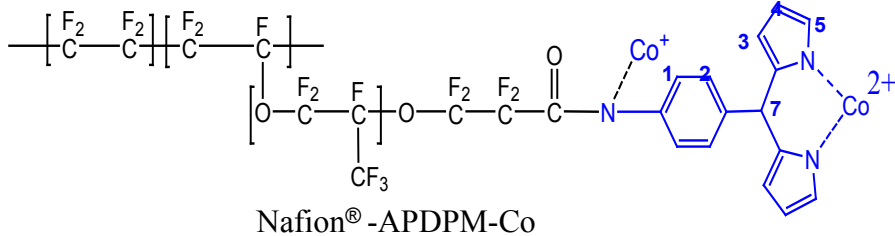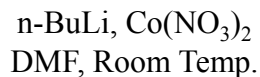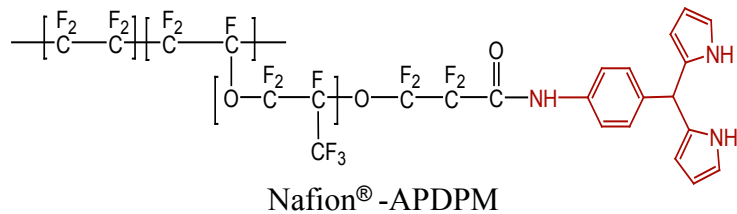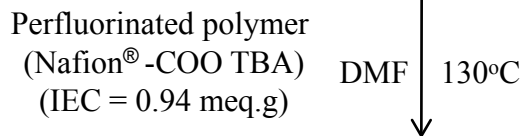
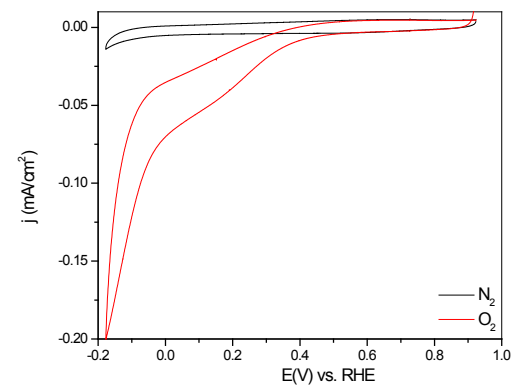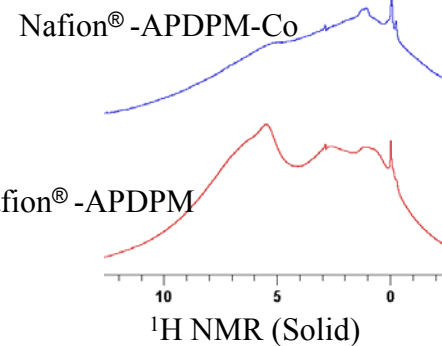RDE (@ 400rpm) of polyCo(II)DiPM in 0.1 M $HClO_4$

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

Co-catalyzed polymer showing ORR activity ($E_{onset} \sim 0.68$ V, $E_{1/2} \sim 0.45$ V)

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

5-(4-aminophenyl) dipyrromethane
(APDPM)

DMF | 130°C

Nafion® -APDPM

n-BuLi, Co(NO$_3$)$_2$
DMF, Room Temp.

Nafion® -APDPM-Co

^{1}H NMR of APDPM
in CDCl$_3$

Nafion® -APDPM-Co

Nafion® -APDPM

^{1}H NMR (Solid)

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MEA Preparation

Yu Seung Kim

3D catalyst

Nafion-APDPM-Co
or Nafion-APDPM (w/o Cobalt)

Carbon black (XC72)

Mixing → Nafion 5wt% NMP

Catalyst Ink

Painting drying →

Membrane painted Electrode
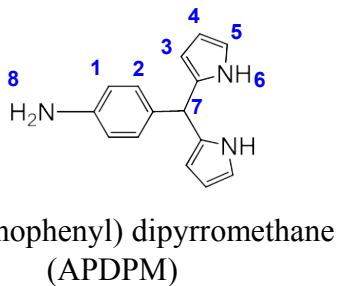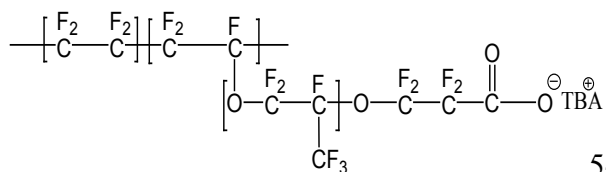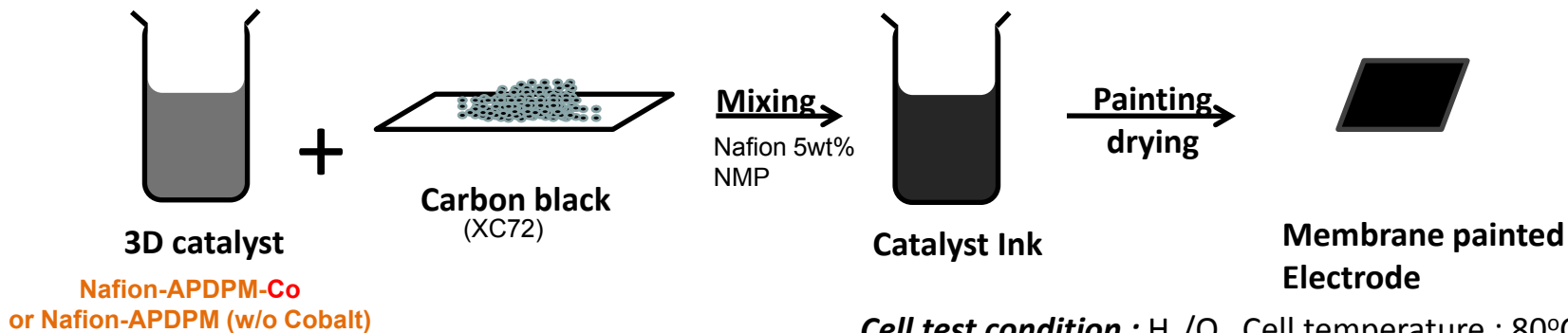
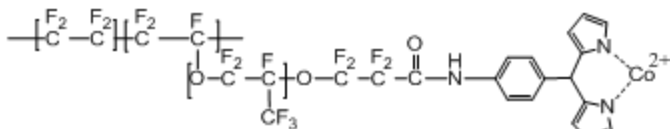*Cell test condition :* H_2/O_2, Cell temperature : 80°C
Membrane: Nafion® 212 (H^+ form)
Anode catalyst layer: LANL Standard (0.2 mg Pt/cm²)
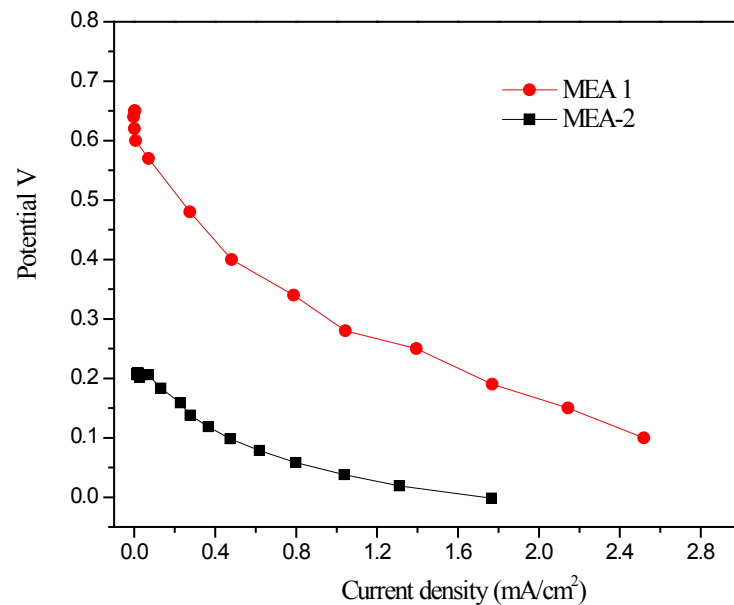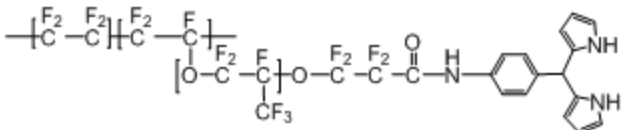
MEA 1
-Cathode : 26 µg Co^{2+}/cm² and 0.6mg XC72/cm²
 Nafion-APDPM-Co : XC72 = 1:1wt%

MEA 2
-Cathode : 0.6 mg XC72/cm²
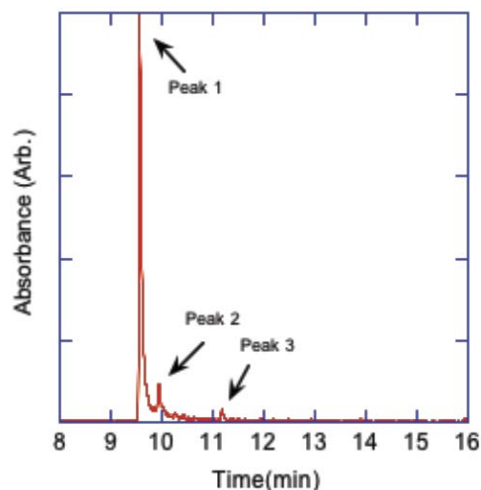 Nafion-APDPM : XC72 = 1:1wt% (W/O Cobalt)

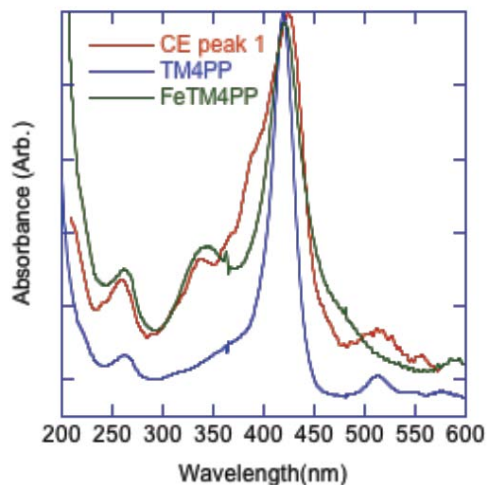A long way to go! Packing density low

Stability and Degradation Studies

John Chmiola

- 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
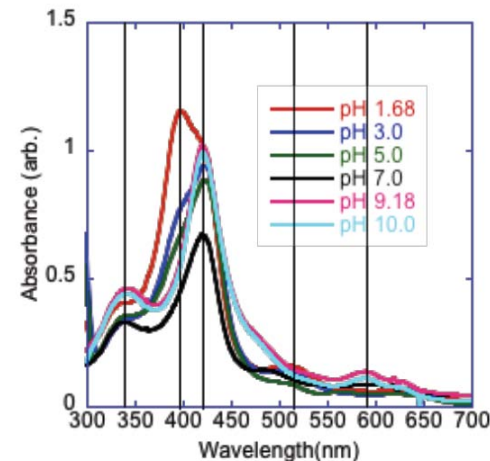
UV/vis Spectra of FeTMPyP as fn. of pH

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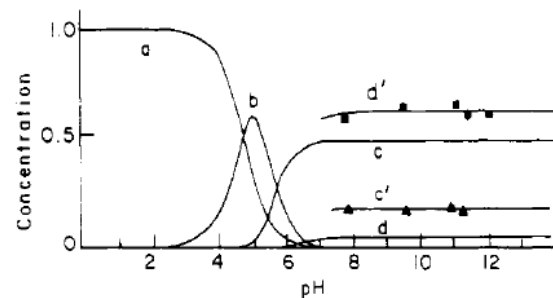
Speciation of FeTMPyP with pH
a, [Fe'''TMPyP(H,O)]; b, [Fe'TMPyP-(H,O)(OH)]; c = c', [[Fe'''TMPyP(H2O)1,O]; d = d', [Fe'''TMPyP(OH),].

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Technical Accomplishments

Molecular Modeling and Synthesis of Catalysts.

- Calculate stabilities of complexes with pH and binding to ligands.

- Calculate energy barriers to oxygen reduction.

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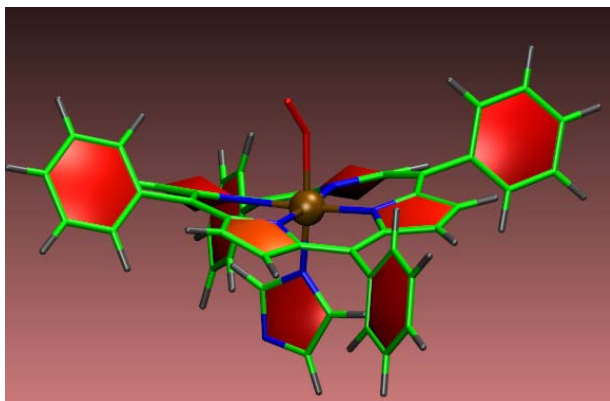
Fe(II)TMPyP bound with imidazole and oxygen. Geometry changes with ligands.

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.

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.
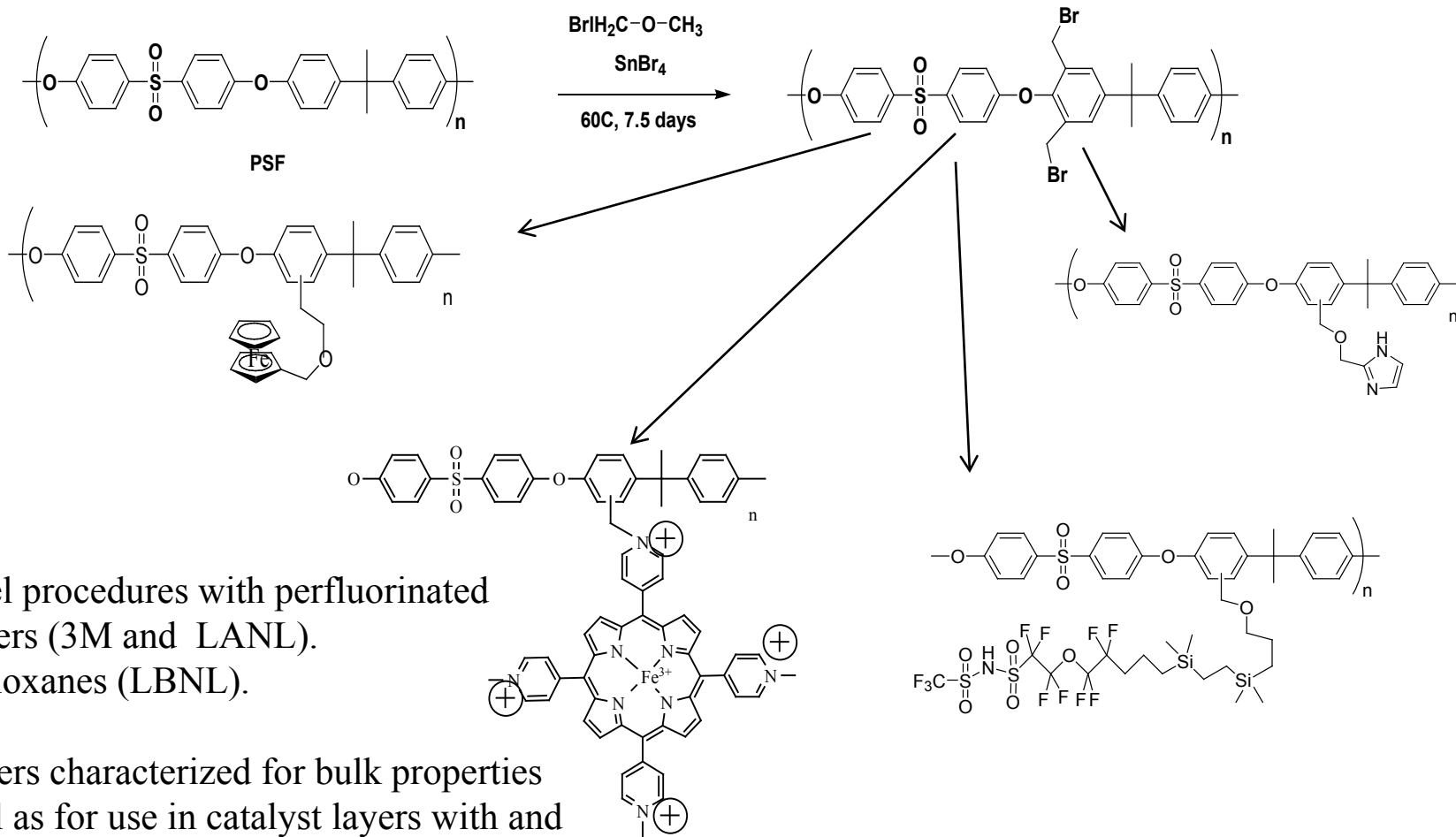
Collaborations

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.
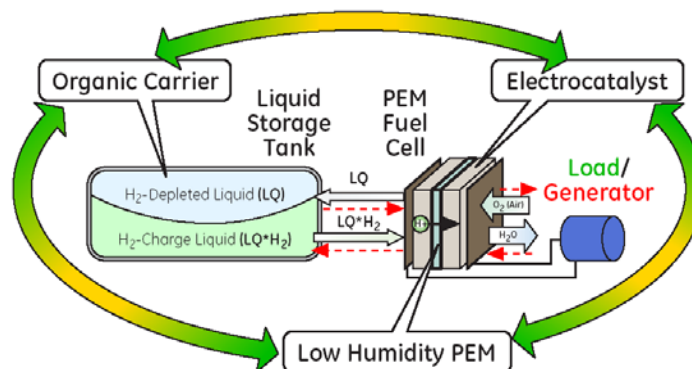
Future Work

- 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.

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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
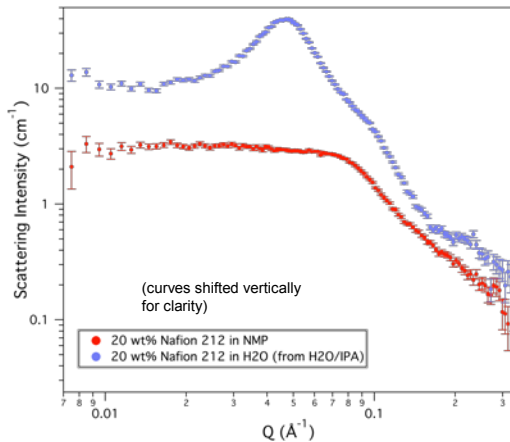Neil Henson- Molecular modeling/computation

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 27 Management tools (see Supplementary slides).

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

SANS: NMP- vs. H2O-Based Gels

(curves shifted vertically for clarity)

- 20 wt% Nafion 212 in NMP
- 20 wt% Nafion 212 in H2O (from H2O/IPA)

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)

120 Å
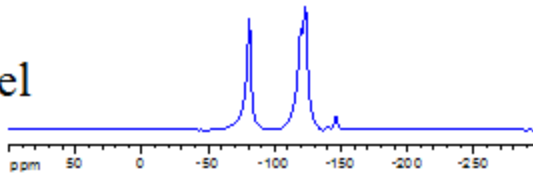
16 Å

9 Å
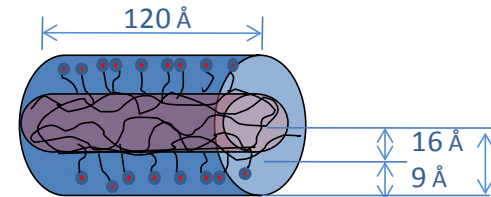
Aqueous mixture: Highly swollen particles

– SANS data cannot be fit to any particle shape form factor

– Data fits well to clustering / solvation model

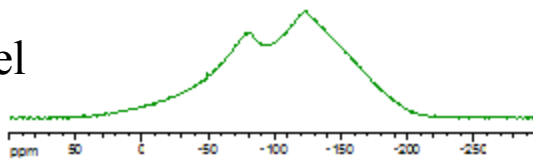Highly Swollen Nafion® Particle
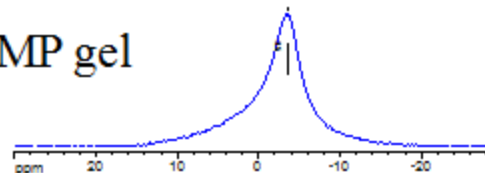
> 200 nm
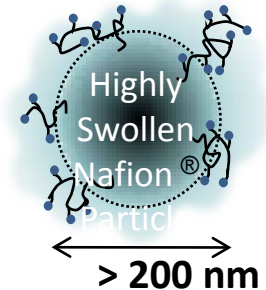
^{23}Na NMR
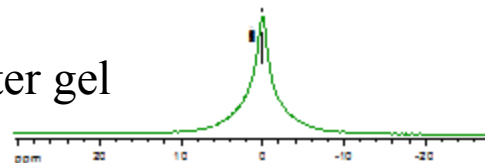
^{19}F NMR

NMP gel

water gel

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	0.6×10^{-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	4.31×10^{-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