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

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3M Company

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Project ID #
FC 011

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Overview

Timeline

- Project start –September 2009
- Project end –August 2012
- Percent complete – 90%
- Project in close-out due to failure to meet Go/No-Go Milestone.

Budget

Total project funding

- DOE share $5,175k
- Contractor share - in-kind (up to $1,000k) plus NSF studentships (UCB)

Funding received in FY 10-11

- $4660k

Closeout Funding for FY12

-$515k

Barriers Addressed

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

Milestones & Go/No-Go Decisions.

All milestones met except the voltage for the Go/No-Go Decision.

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). >20 hr lifetime demonstrated Interim goal is 100 A/cm^3 of supported catalyst at 800 $mV_{ir\text{-}free}$ with at least 10 hours operational lifetime. Achieved current density & lifetime but not voltage.

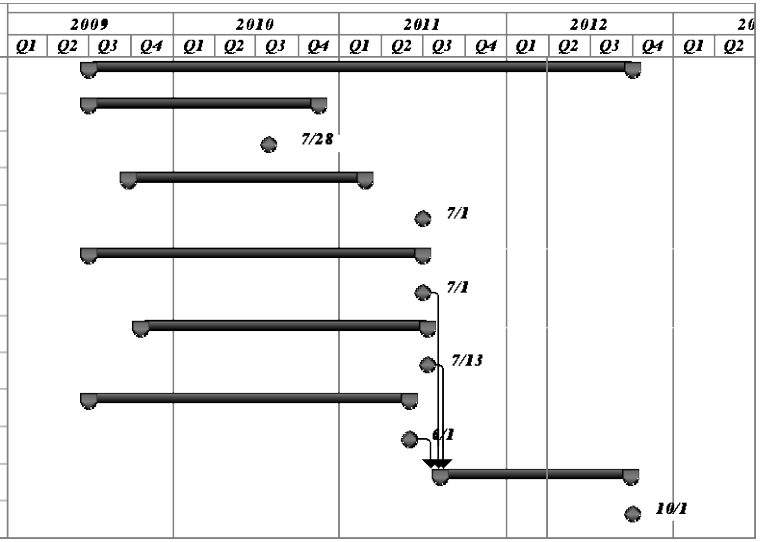
Milestone 3. Methods of optimization of catalysts demonstrated in MEAs (24 mo). Complete.

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

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

Milestone 6. Final report, project closeout and recommendation for future work, if any (9/12).

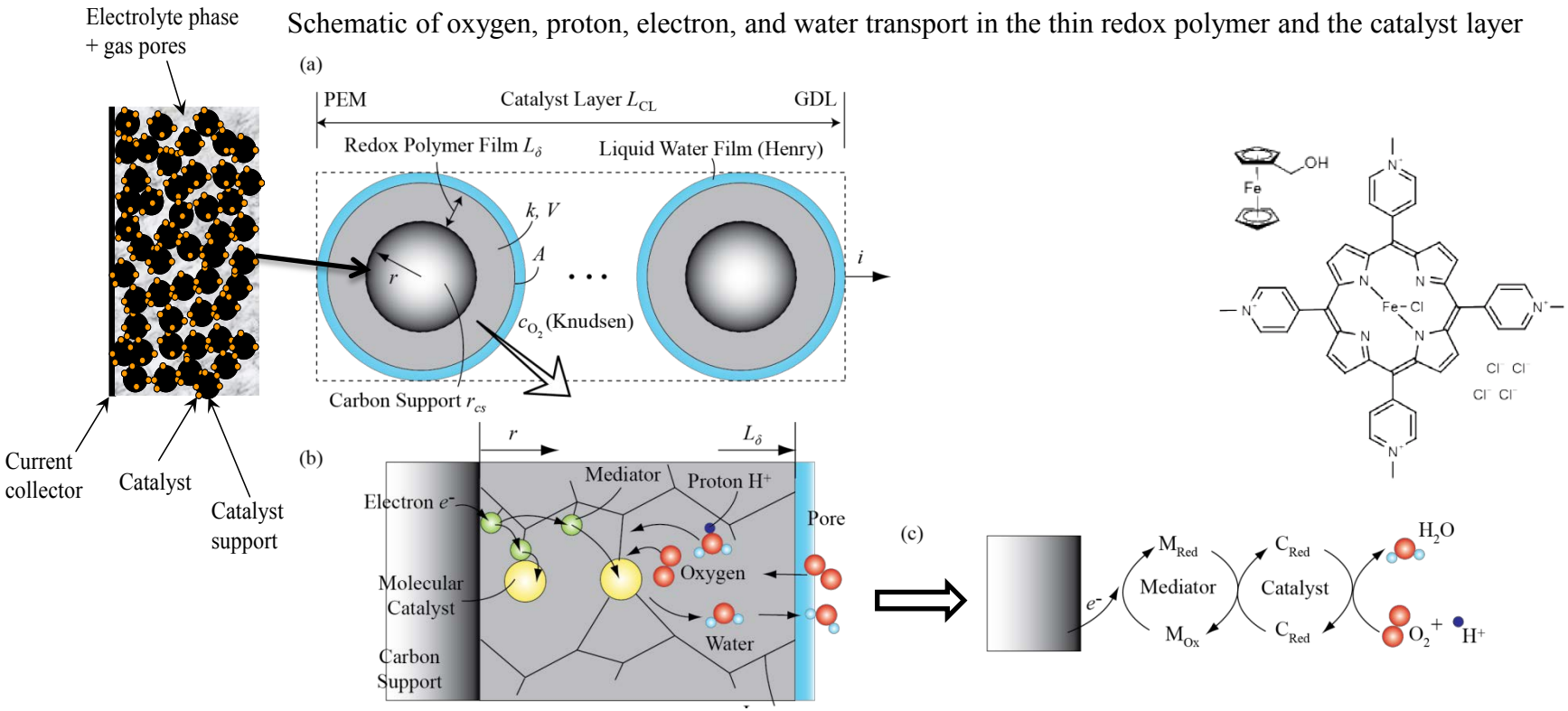
ID	Task Name
1	Non-PGM Electrodes for Catalysis of Fuel Cell Reactions
2	Development of synthesis, and electrochemical screening methods
8	***Oxygen reduction catalysis demonstrated with polymer coated electrodes***
9	MEA fabrication and testing methods development
13	***Go/No-Go Decision(do tethered 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
31	***Project completion -Final Report and Proposal for Further Work.***



Strategy/Approach

3D Non-PGM Catalyst Concept

Molecular catalysts dispersed in ionomer film over carbon particles



- Similar to traditional fuel-cell catalyst layers but put the catalysts into the ionomer film
  - Homogeneous 3D catalysis – geometric effects make up for large catalyst size

Questions: Can this work? Is it durable?

Strategy/Approach.

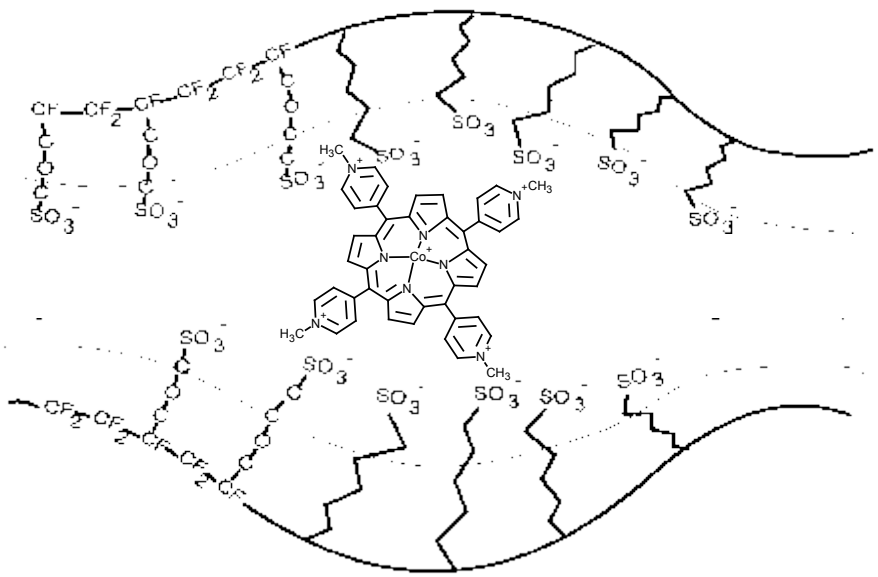
Tether Porphyrin Catalysts to Polyelectrolytes by Ionic Bonds (Anson, Saveant, 1984.)

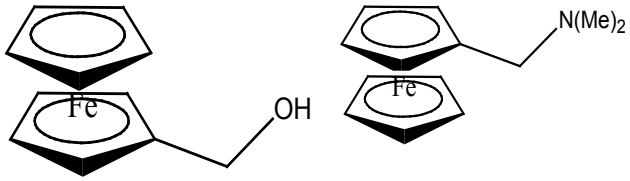
•Different metalloporphyrins :

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 were attached to the polymer by electrostatic interaction between their positively charged substituents and the negatively charged sulfonic acid groups on the polymer.





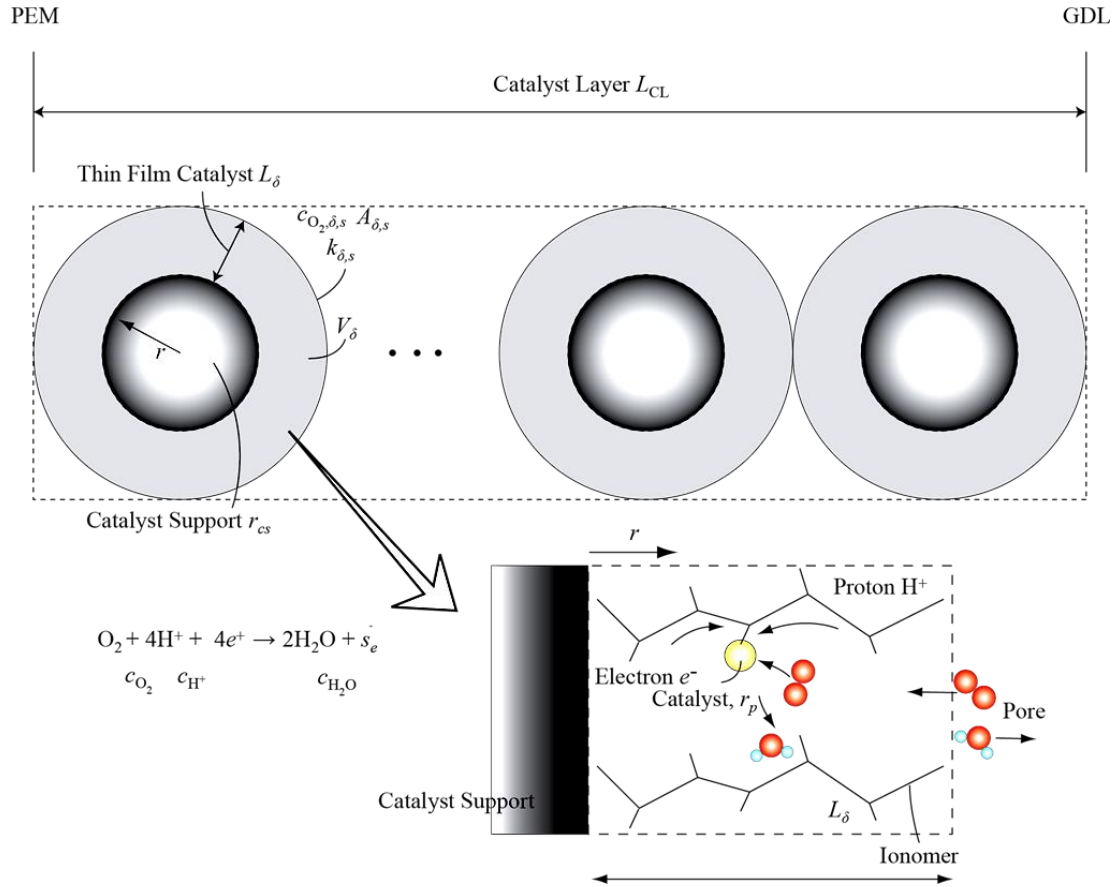
Ferrocenes added as electron carriers
-More mobile in polymer catalyst layer due to lower charge and smaller volume.

Electron hopping, vehicle and segmental motion mechanisms

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)



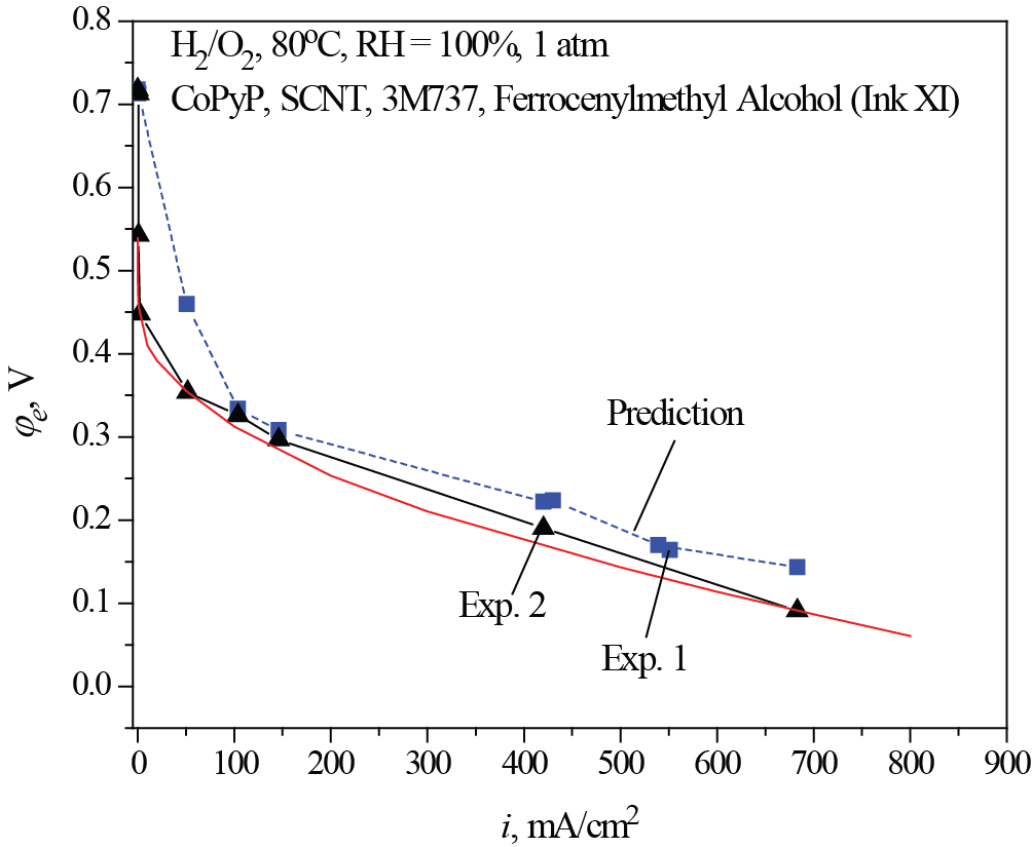
Schematic drawing of oxygen, proton, electron, and water transport though the thin metal catalyst layer through a catalyst layer.

Technical Accomplishments.

Model Validation (Ink XI)

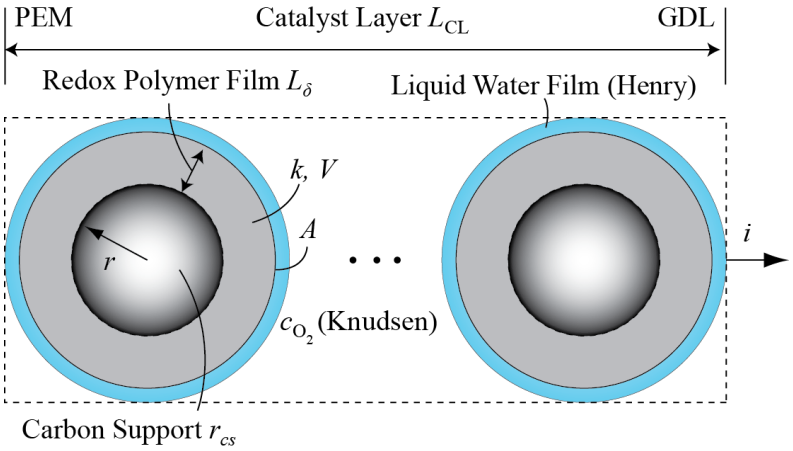
Catalyst Composite (Ink XI)

Ionomer	Carbon	Catalyst	Mediator
3M737	SWCNT	CoPyP	FeMeOH
I/C=0.6, Cat/Ion=5.5, FeMeOH/CoPyP=1			



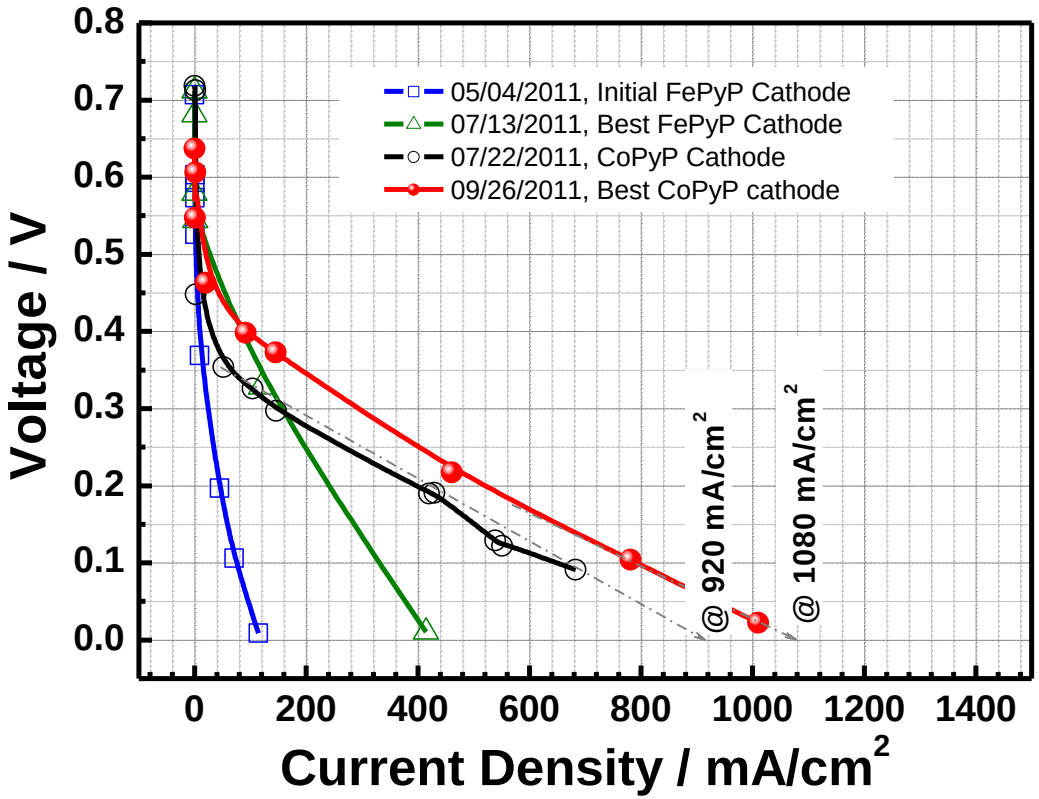
Volume Ratio and Geometry

Composite	Volume ratio
Gas Phase (Assumed)	0.3
Carbon	0.43
Redox Polymer	0.26
Thickness, L_δ	2 nm
Thickness, L_{CL}	20 µm



Technical Accomplishments.

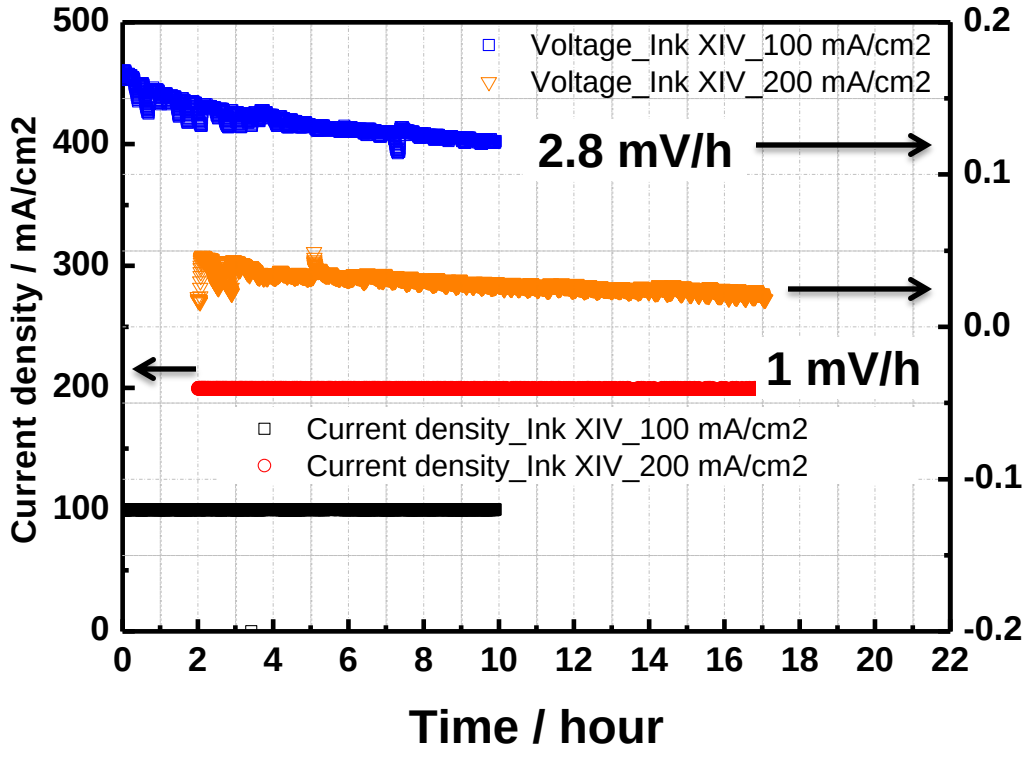
MEA Activity



- Over past 12 months have dramatically increased performance
- Current density achieved implies high TOF for non-PGM catalyst
- Architecture works and can achieve high performance

Technical Accomplishments.

Progress – MEA Lifetime



- Very good stability and initial lifetime of the system
- Good stability through voltage and humidity cycling

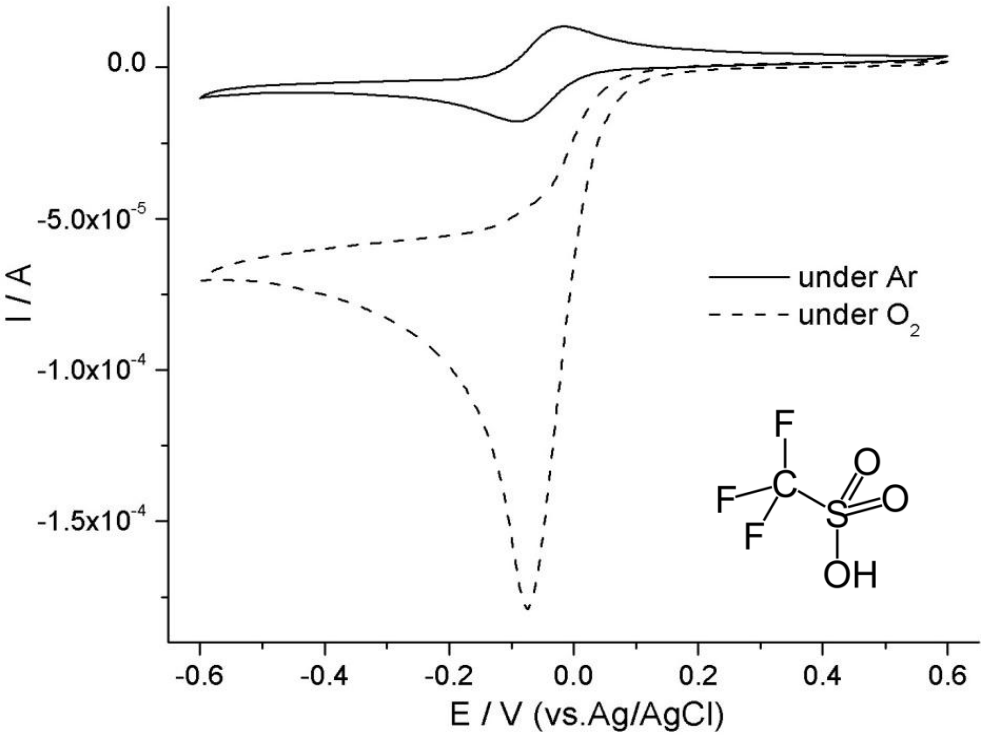
Have good lifetime and current density, now need to increase the voltage

Technical Accomplishments.
Increasing Voltage

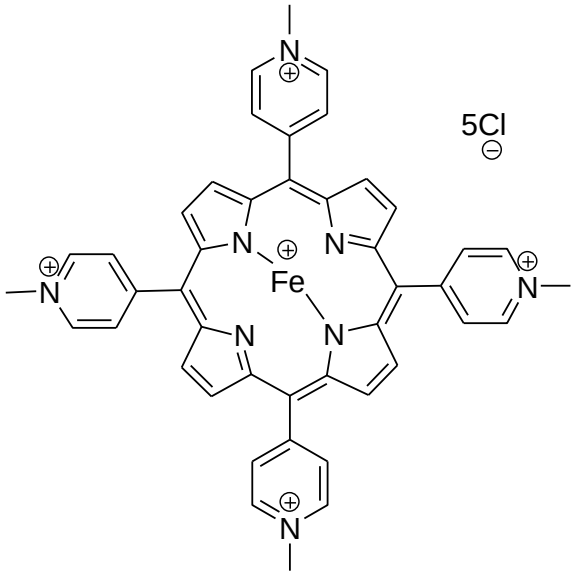
- Different mediators and catalysts
  - Determined with input from molecular modeling of catalyst redox potential, activity towards oxygen reduction and stability to H^+
  - Up to 500 mV gain is theoretically possible from use of mediators which is favored by high concentrations as is found in thin films of polymer (2-100 nm) containing catalyst and mediator
- Increase mediator and catalyst concentration
  - Need to make thicker polymer films (not thicker electrodes)
    - Gain co-operativity
    - Better catalyst efficiency (similar to enzymes)
    - More efficient mediation over larger voltages
  - Change ionomer in the layer
  - Change ink conditions and solvents to optimize electrode morphology

Technical Accomplishments.

Kinetics study of ORR by homogeneous catalysis



Cyclic voltammograms on a glassy carbon in 0.1M TFMSA containing 0.8 mM Fe(III)TMPyP in the presence and absence of O_2, scan rate = 50mV/s.

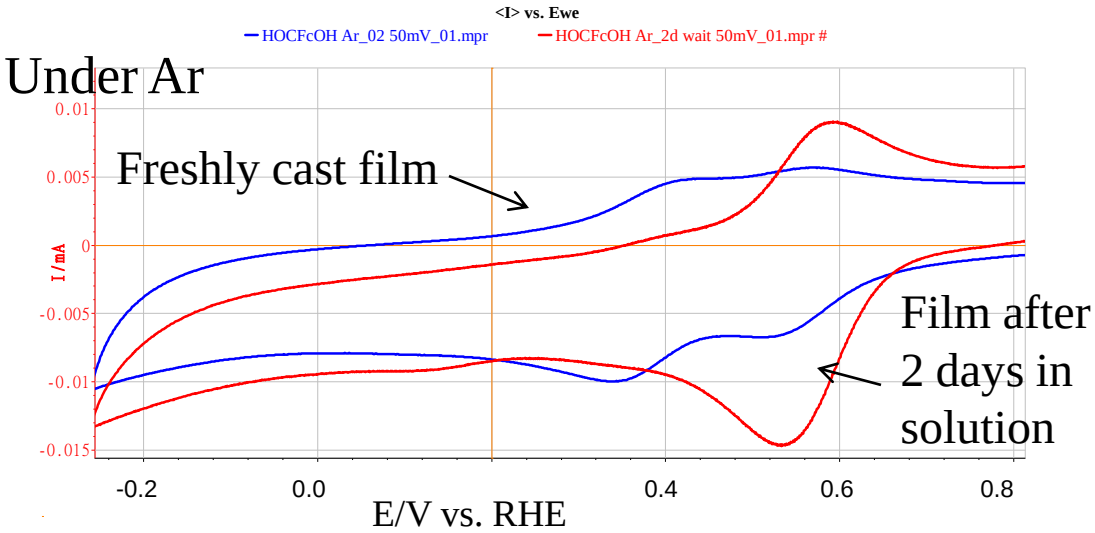


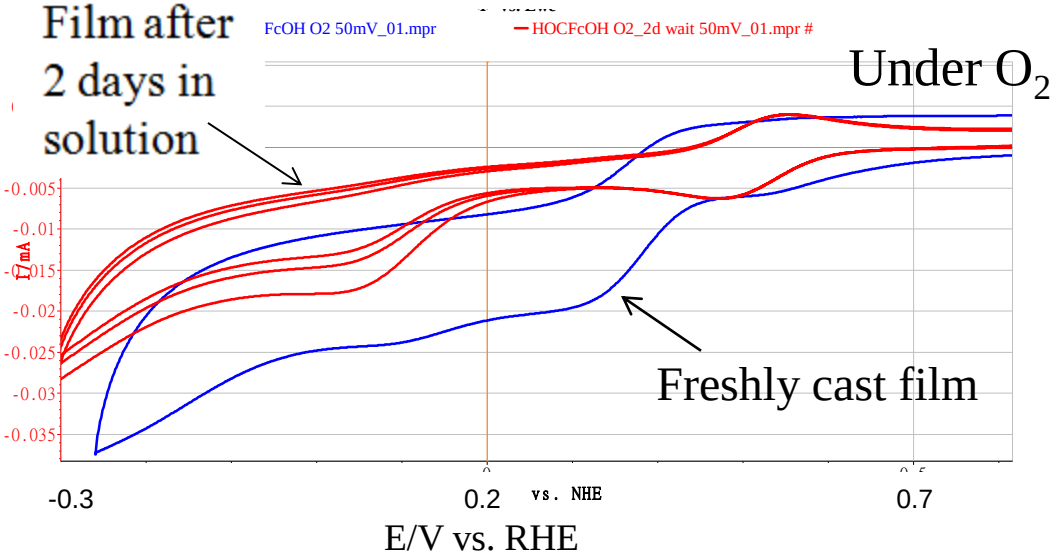
$C_{44}H_{36}Cl_5FeN_8$
Mol. Wt.: 909.92

Structure of Fe(III)TMPyP

Technical Accomplishments.

Tether porphyrin catalysts and "Molecular Wires" to polyelectrolytes – Electroanalytical Tests





- 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.

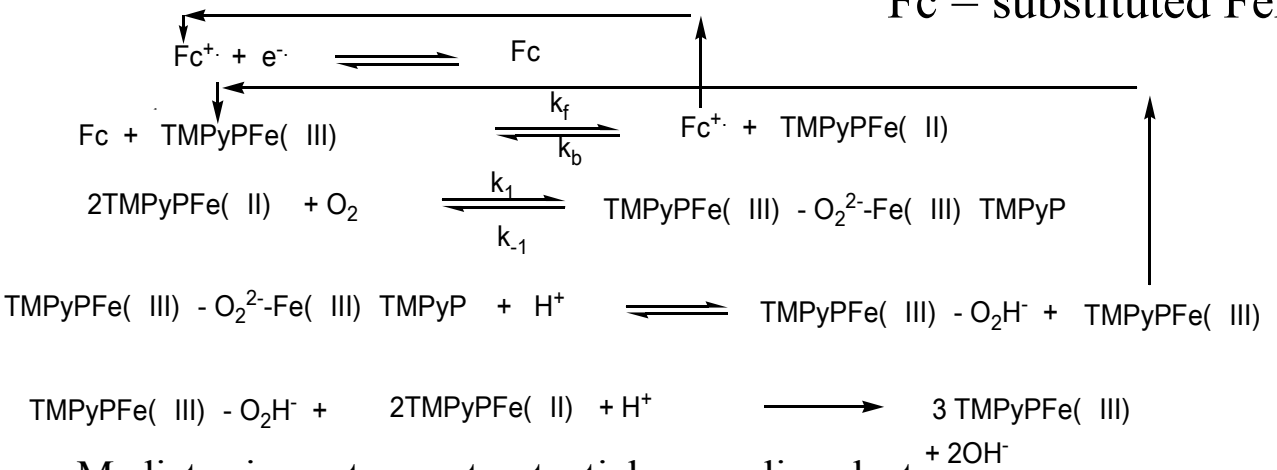
Nafion® ink containing FeTMPyP and hydroxymethylferrocene ($FcCH_2OH$) cast on GC electrodes - ~ 1 micron dry film. CV recorded in 0.1 M TFMSA.

Technical Accomplishments.

Mediator Approach

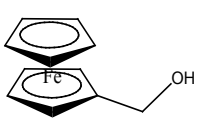
- Catalyst reacts with O_2 in a quasi-redox inner-sphere mechanism

Fc = substituted Ferrocene

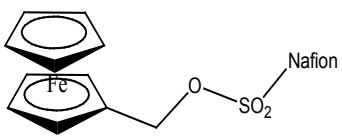


Mediation rate and voltage gain controlled by redox potential of catalysts and mediators and by k_1, rate of reaction with O_2(activity)

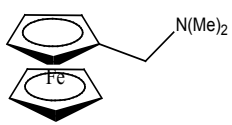
–Mediator impacts onset potential – supplies electrons to the 3D matrix in outer-sphere mechanism
Change mediator type and can gain up to a maximum of 0.5 V theoretically



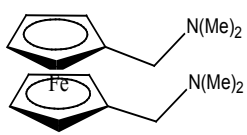
E° ~0.4V



E° ~0.55V



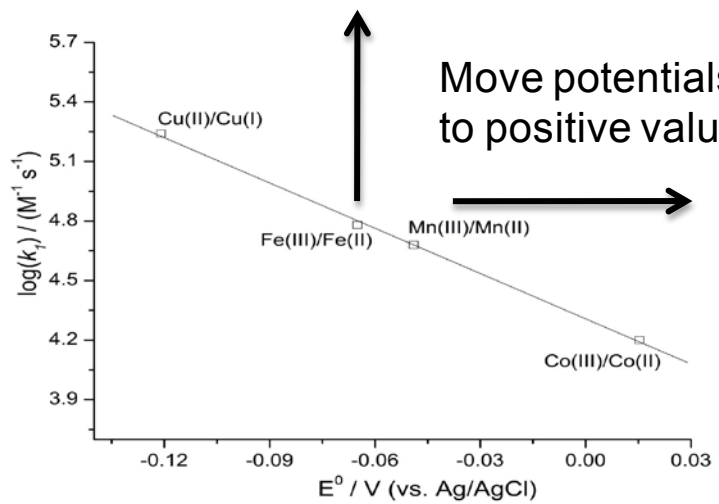
E° ~0.6V



E° ~0.85V Meets DOE goals if catalyst connected

Increase rate

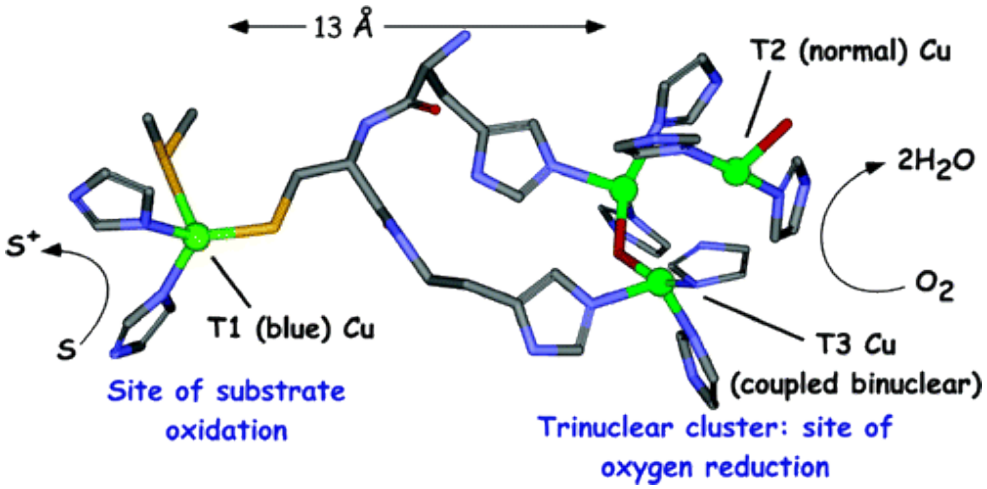
Move potentials to positive values



Technical Accomplishments.
Multi-center Catalysts for better Activity?

Enzyme ORR catalysts.

Copper catalyst centers are held in place by IMIDAZOLE



Nature chooses imidazole as a base to tether metal ions in the presence of oxygen.

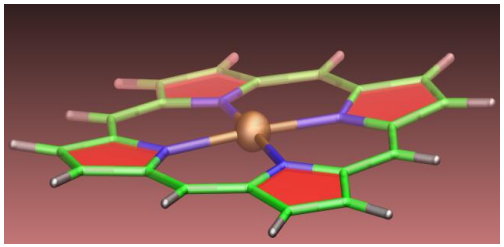
Copper or iron catalysts better than platinum?

- Three metal centered O_2 reaction site more active? – does this lead to faster reaction rates? – Can this be mimicked by high metal loading in the polymer?
- 4th metal center serves as mediator to transport electrons.
- Fast rates combined with mediator gives low overpotentials – pathway to non-PGM catalysts.

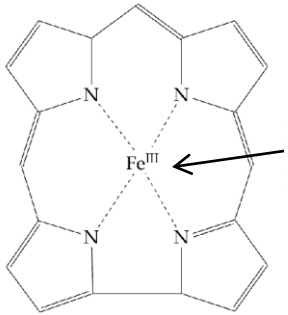
Technical Accomplishments.

Molecular Modeling of Porphyrin & Corrole Systems to improve Voltage & Activity (Rate)

Flat ring

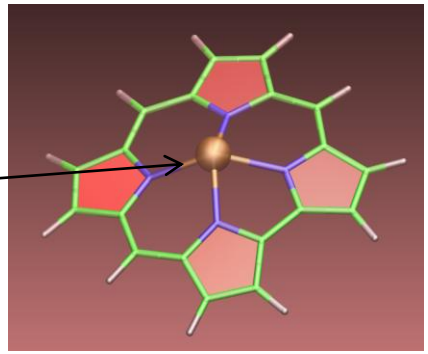


Porphyrin



Corrole

Puckering of ring increases reactivity?



Corrole

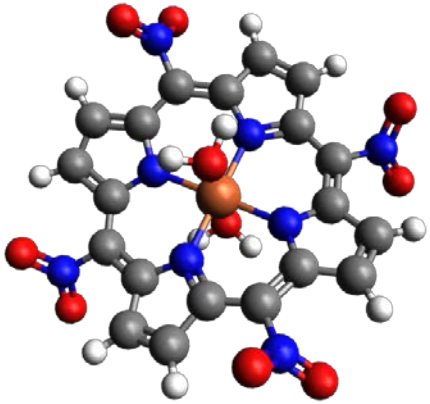
- Several convenient anchor points on the corrole ring system appropriate for introducing functional groups, as indicated
- Prediction carried out of a number of interesting structural changes, most notably exemplified by the relative position of the metal ion with respect to the plane of the corrole ring, with oxidation state and substituents

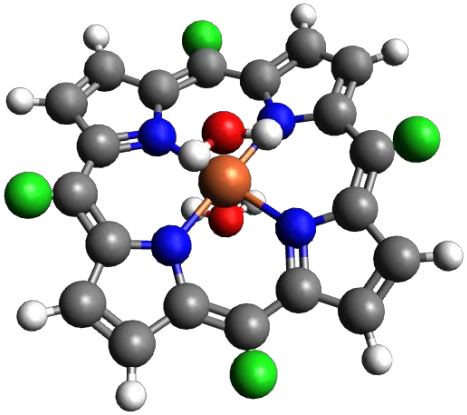
	$-NH_2$	$-NO_2$	-Cl	-F	$-CF_3$
	-M	+M	-I	-I, +M	-I
heme	-0.87	+1.08	+0.44	+0.26	+0.46
corrole	-0.62	+2.10	+0.39	+0.36	+0.47

Technical Accomplishments.

Effects of Direct Substitution on the Porphyrin Ring

Substituent	Estimated Relative Shift (V)
Nitro	1.076
Amine	-0.875
Chlorine	0.445
Fluorine	0.260
CF_3-	0.463





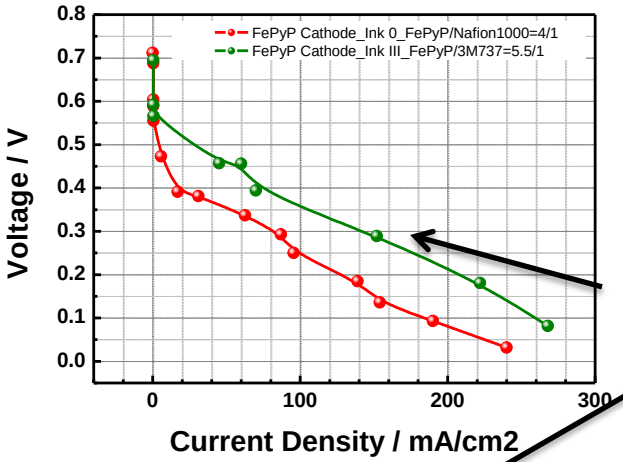
Voltage shifts like this combined with strong mediation gives voltages of > 0.8V

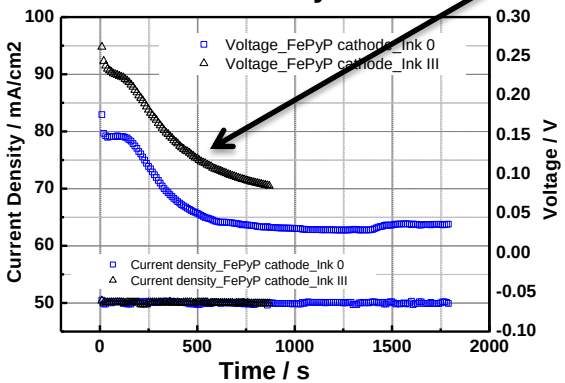
Mulliken charge analysis for Iron under substituent modification of Porphyrin

Charge	Spin Multiplicity	Unsubstituted	Nitro	Amine	Chlorine	Fluorine	CF_3-
0	3	1.108	1.242	1.045	1.156	1.107	1.156
1	4	1.280	1.292	1.168	1.298	1.282	1.280

Technical Accomplishments.
Electrode Effects(Ionomer)

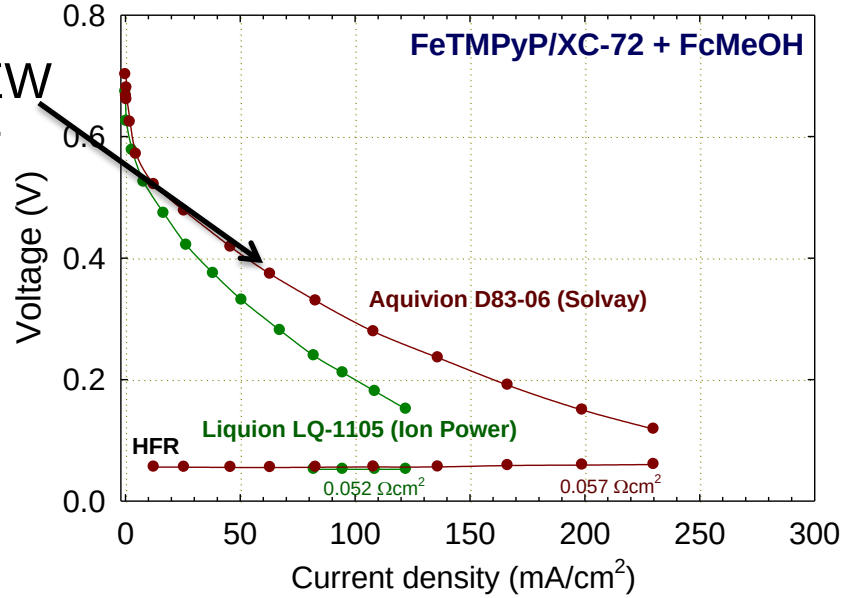
- Increase onset potential by changing ionomer, particularly EW





Lower EW ionomer

Anode: 0.25 mg cm^{-2} Pt/C (E-TEK GDE), 10 psig, 100 ml/min; Cathode: MeTMPyP catalyst (Me = Fe or Co), 0.66 mg/cm^2, 15 psig, 200 ml/min; Membrane: Nafion® 212; Cell: 80℃

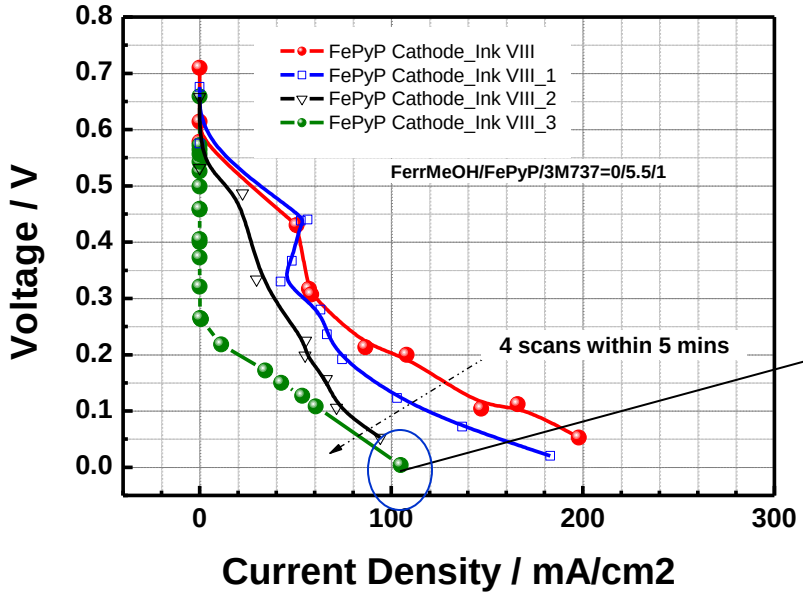


- Shorter side-chain and lower equivalent-weight ionomer (3M, Acquivion®, Solvay) performs significantly better than Nafion®-based MEA
- Ionomer ratio impacts performance

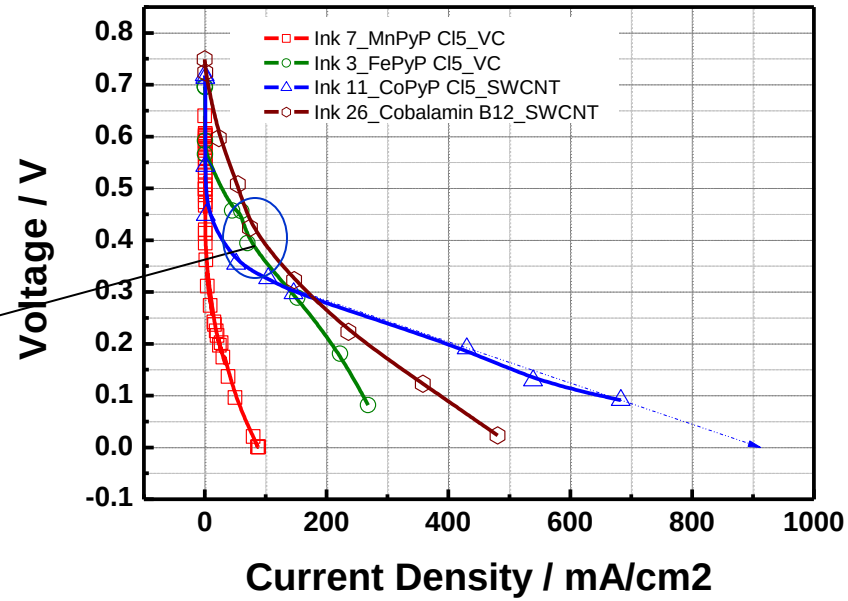
Technical Accomplishments.

Effect of Mediator on MEA Performance

No mediator



With mediator

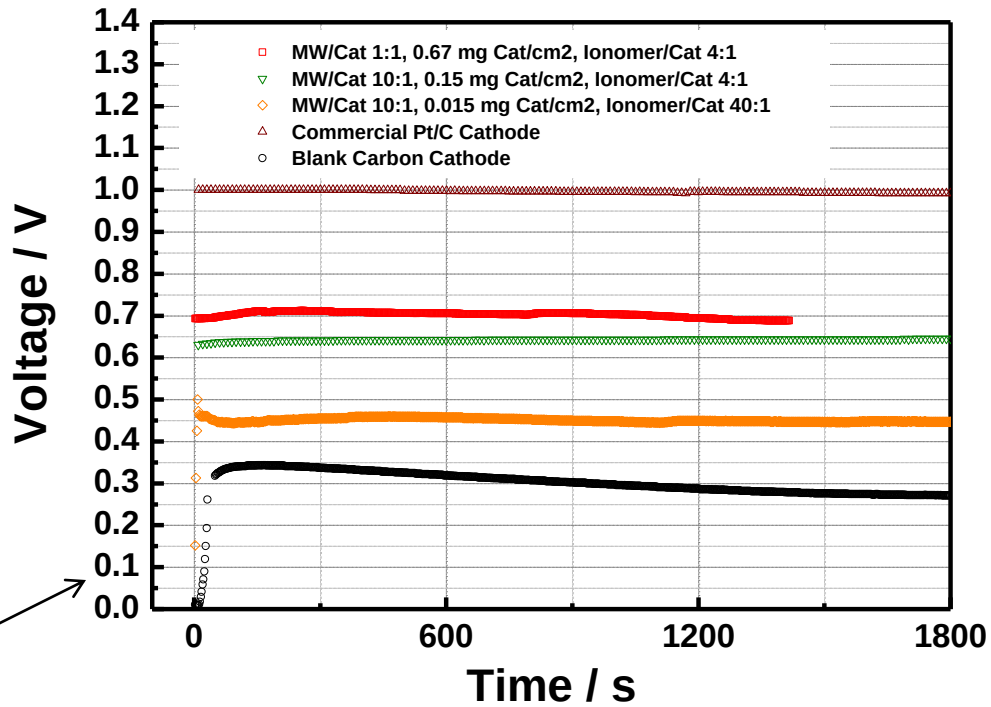


- Mediator increases current density and voltage (350 mV at 200 mA/cm^2)

Technical Accomplishments.

Concentration Effects-Catalyst Loading

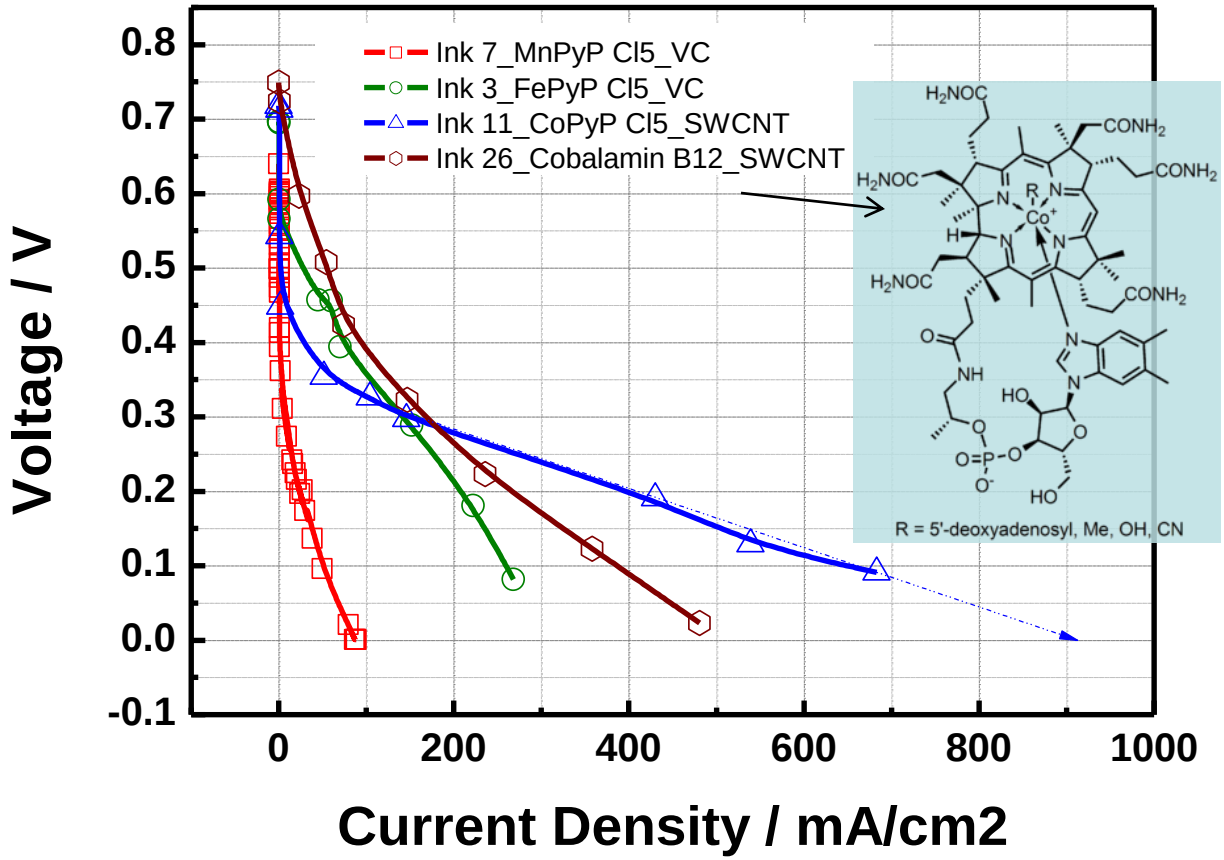
- Optimizing MEA formulation and structure can also increase onset potential.
  - 3D and concentration effect
  - Increase mediation effect (up to 500mV)
- 3D catalyst arrays provide potential for co-operative effects (source of enzyme effectiveness).
- To date, catalyst loadings used are much lower than other non-PGM MEA's. See effect of loading on OCV values



Catalyst loadings are 10-100 times less than the published LANL non-PGM catalysts on the basis of metal centers added to the formulation. Higher loading requires improvements to ink formulations and better morphology

Technical Accomplishments.

Catalyst effect



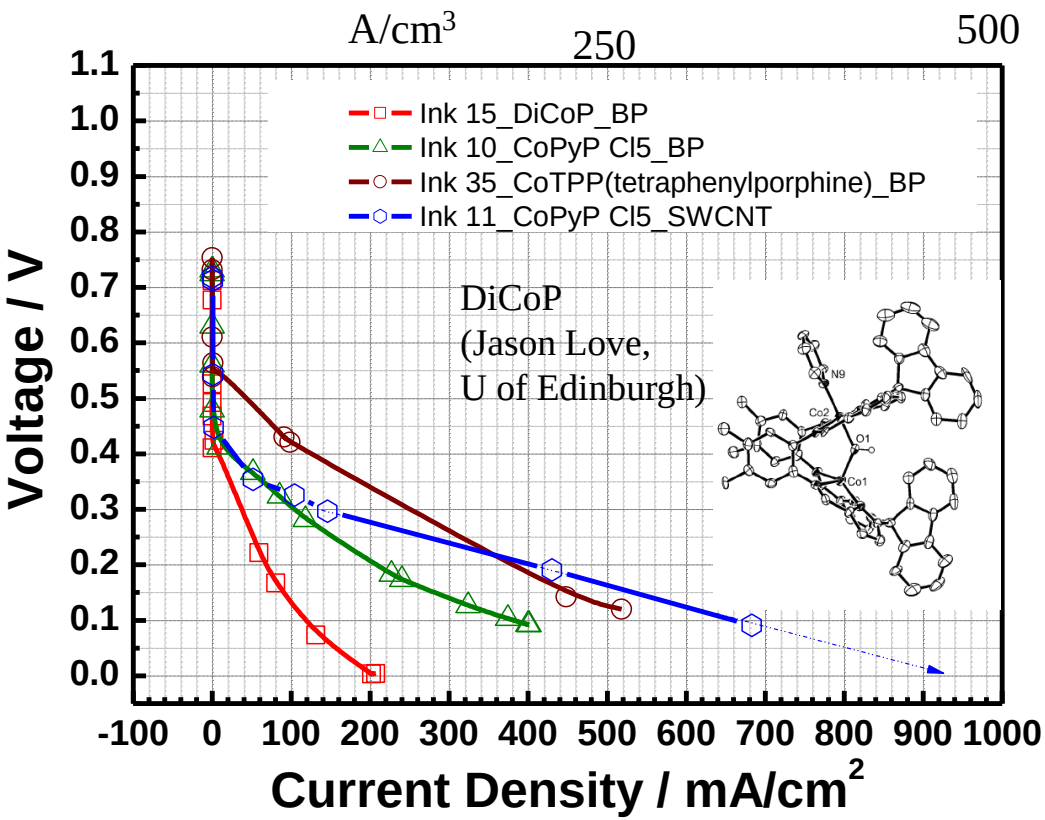
- Results illustrate the ease of changing catalysts so they can be rapidly evaluated.
- Catalysts from many sources can be rapidly mounted & tested.
- Performances observed here in MEA tests track the results observed in voltammetry & RDE experiments.

-Mn catalyst performance reflects speciation issues observed in voltammetry.

- Result with Cobalamin (Vitamin B_{12}) illustrates ease of testing biological Catalysts.

Technical Accomplishments.

Surface catalysis effect - Control experiments

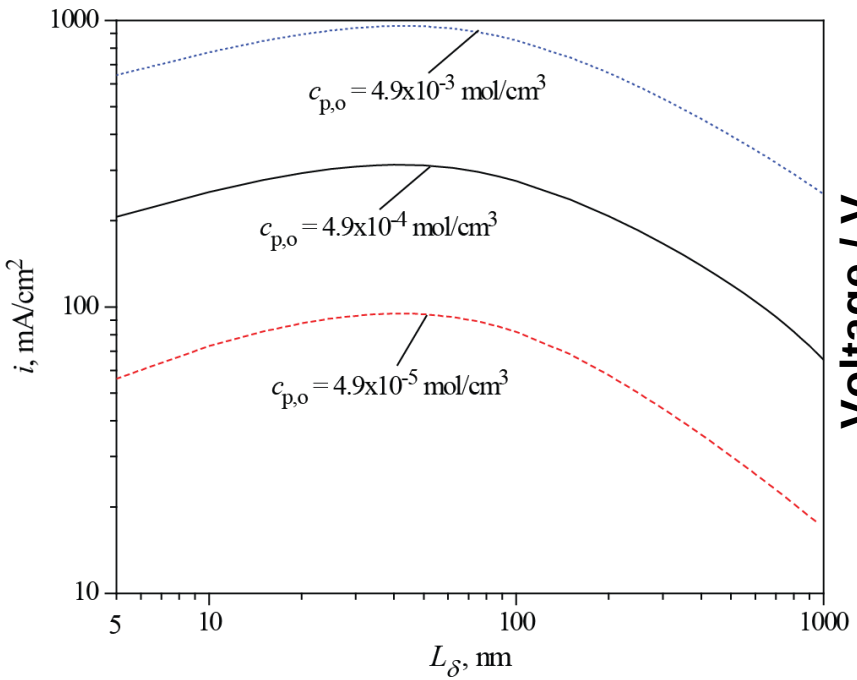


- Inks 15 and 35 contain catalysts that are completely insoluble in water – implies that water solubility is not a necessary property.
- Comparison of inks 10 and11 show effect of surface on performance.
- These results imply that the catalysts are close to the surface and the polymer layer is thin and probably non-uniform. Similar conclusions are drawn from the results of transport modeling
-Polymer film appears to be 2-5nm thick.

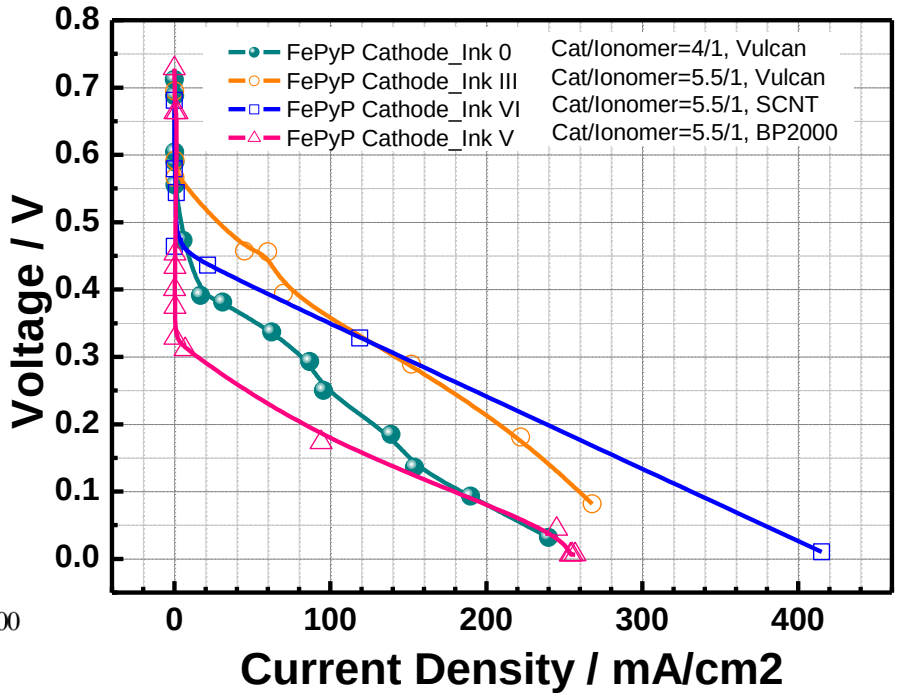
Technical Accomplishments.
MEA Optimization

- Guided by macroscopic modeling and applied science efforts
- Need to optimize film thickness, loadings, ionomers, solvents, etc.
- Develop novel diagnostic for transport properties within electrode layers.

Model predictions of effect of catalyst concentration and polymer film thickness



Ionomer and Carbon Effect – different carbons have large effect on performance

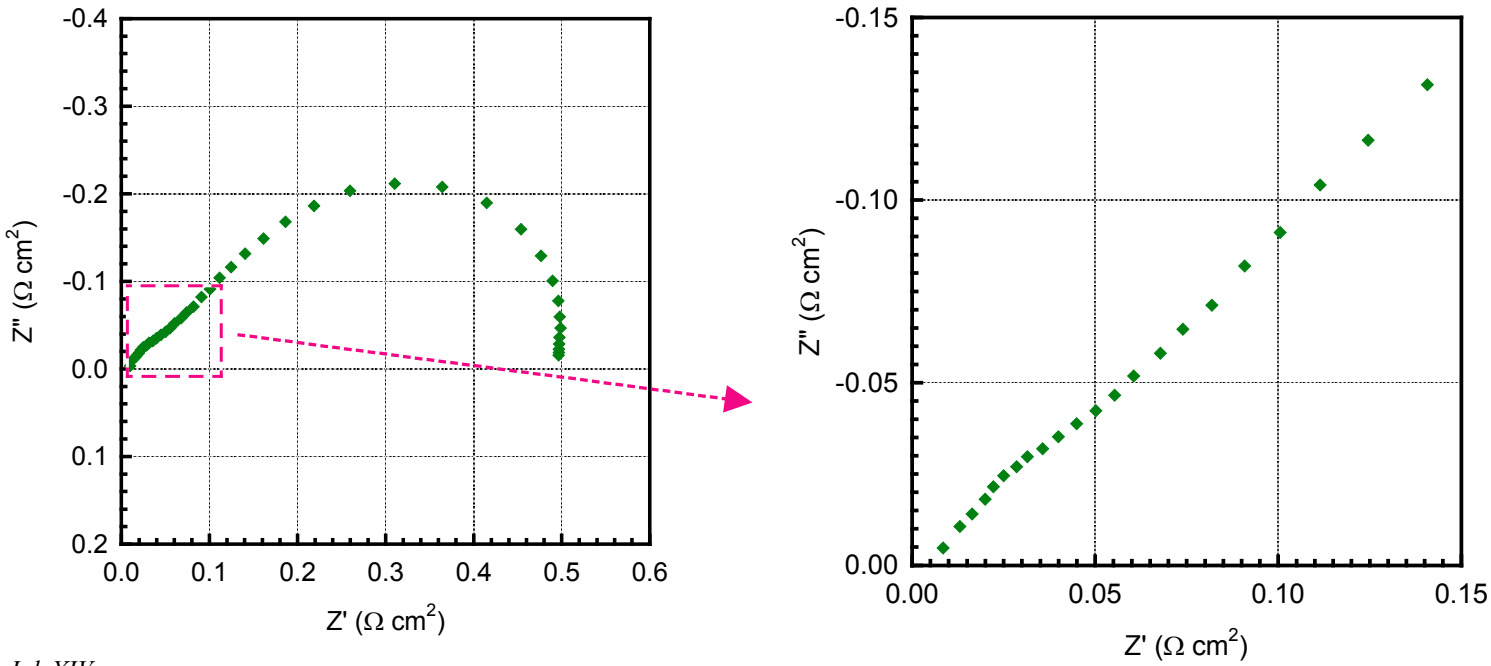


BP2000 is very high surface area – more adsorption of catalysts on the surface – less 3D catalysis.

Technical Accomplishments.

MEA Impedance Analysis

Impedance measurement of an MEA made using Ink XIV;
galvanostatic mode, 200 mA/cm2 DC, 20 mA/cm2 AC, 10 kHZ to 100 mHZ;

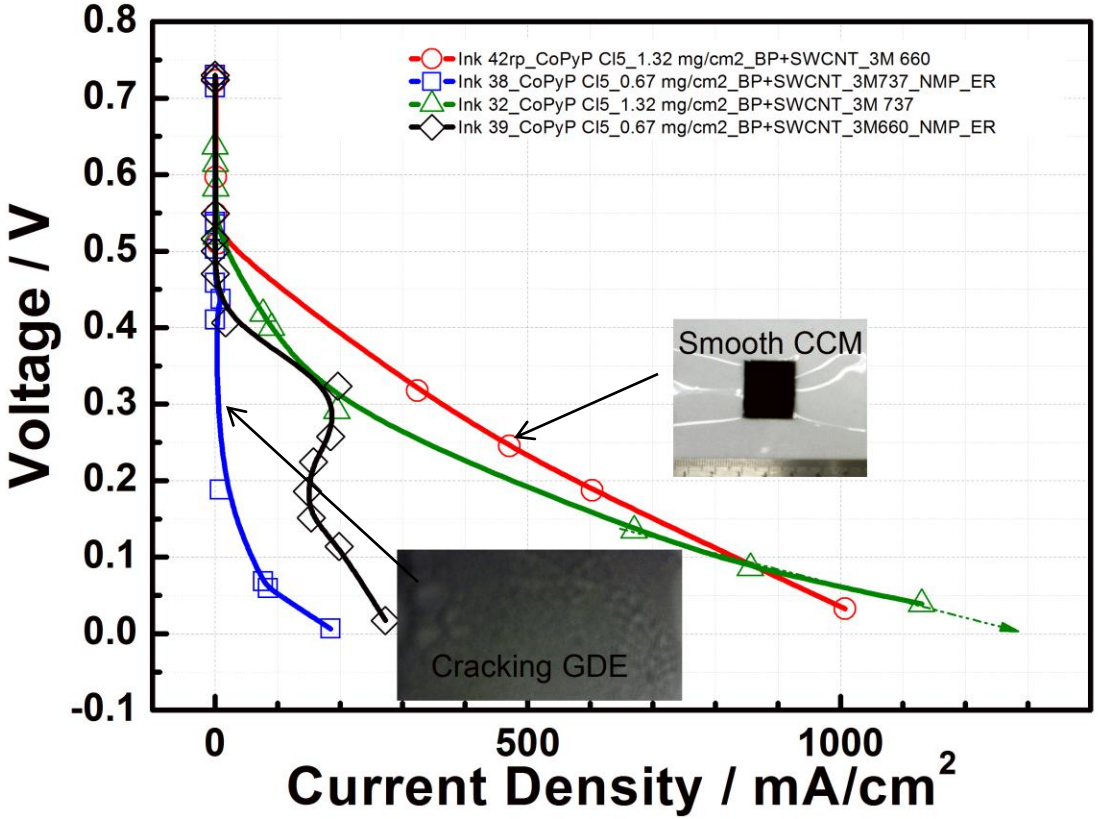


Ink XIV:
Catalyst: Co(III) meso-tetra(N-Methyl-4-Pyridyl)Porphinepentachloride (0.00669g)
Mediator: Ferrocenylmethyl alcohol (0.00158g), mediator/catalyst = 1:1
Binder: 3M 737 (0.149 g)
Carbon: BP + SCNT, 1:1 (0.05 g), I/C = 0.6

- Impedance shows higher charge transfer impedance & much higher electrolyte resistance in electrode layer –consistent with catalyst & mediator consuming acid groups and reducing proton concentration

Technical Accomplishments

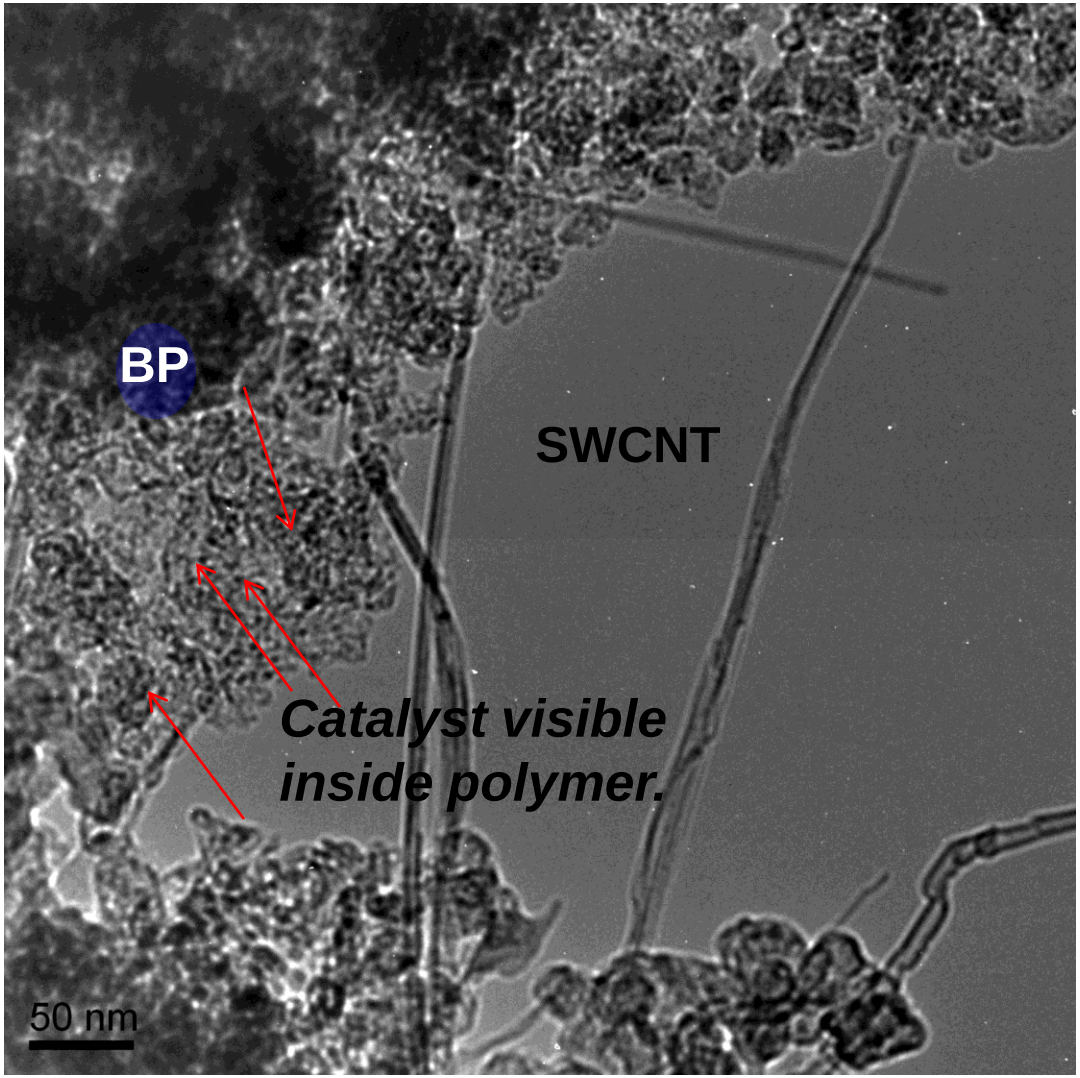
Lower EW Ionomer and Different Ink Solvents to Optimize Electrode Morphology



- Further reduction in EW leads to better performance due to:
  -better dispersion of catalyst?
  -different morphology of polymer layer due to better solubility in electrode ink solvents?
  -Better mediation occurs as a function of thicker layers and Better morphology?
- Replacement of ink solvents with different solvents (NMP, DMSO, PC) leads to different Morphologies but also new problems due to cracking as solvents evaporate.
- Need considerable study to optimize morphology.

Technical Accomplishments

TEM of MEA Electrode Layer



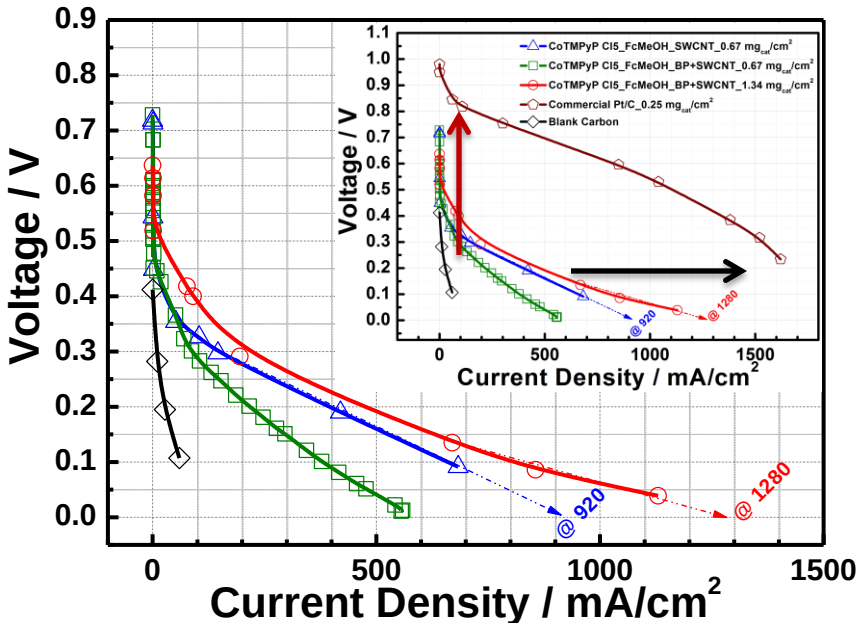
- Catalysts are visible along with carbon substrate and polymer
- Polymer morphology results from shape of polymer particles in electrode ink dispersion – see LANL work on inks in Supplementary slides.
  - Optimize for better dispersion of catalysts in polymers and thicker, more uniform polymer layers in electrode catalyst layers.

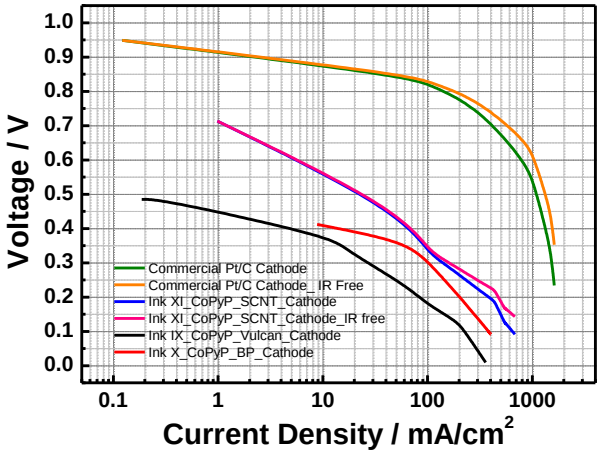
By Dr. Nana Zhao

Technical Accomplishments.

ORR Catalysis Status

- Three main issues remain
  - **Onset potential or OCV is too low with current catalyst/mediator**
    - Minimum value to enable 100 A/cm^3 (catalyst volume) at 0.80 V with fully realized 3D diffusion profile estimated at ~0.85 V
    - Need higher catalyst loading
    - Different non-PGM catalysts
    - Different mediators.
  - **Need to optimize transport and MEA structures**
    - Develop polymer coated electrodes to provide scaffold to test different non-PGM catalysts once MEA is optimized
    - Stabilize MEA morphology to support mediation.
  - **Understand lifetime and durability**





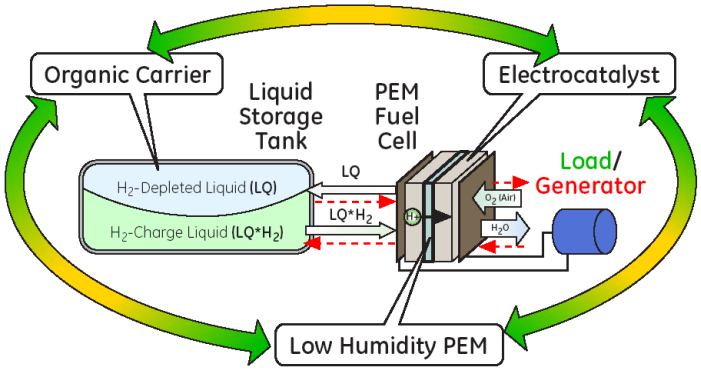
Collaborations

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.

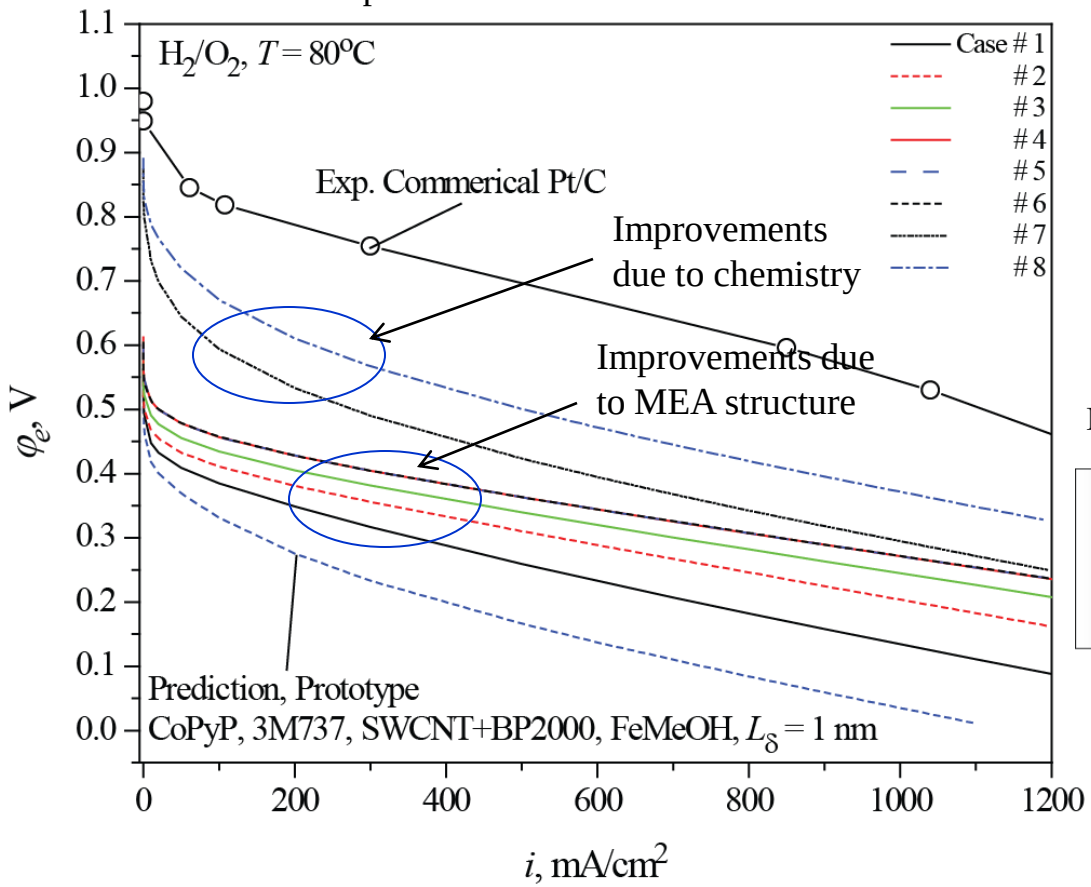


Future Work

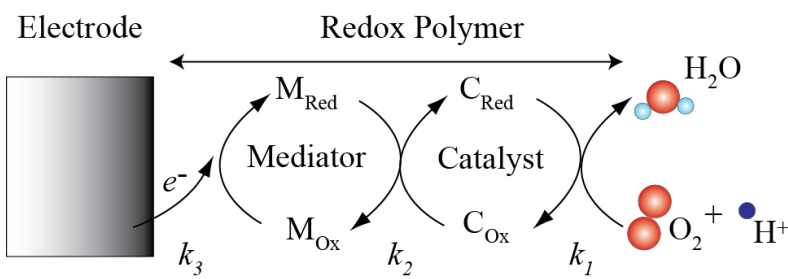
Improve Geometry, Kinetics, Transport & Chemistry

- Incremental improvements from geometry, reaction rates and transport can reach higher current and potential but step-change comes from better catalyst chemistry in combination with mediators.

Eight design improvements towards commercial Pt/C catalyst performance.



Prototype 20μm CL thickness.
#1: 10 x L thickness
#2 :10 x σ_H+
#3: 10 x k_1
#4: 100 x k_1
#5: 100 x k_1; 10 x D_{O2}
#6: 100 x k_1; 10 x D_e
#7: 10 X k_1 ; E_m^o = 0.8V
#8: 100 X k_1 ; E_m^o = 0.8V



Future Activities

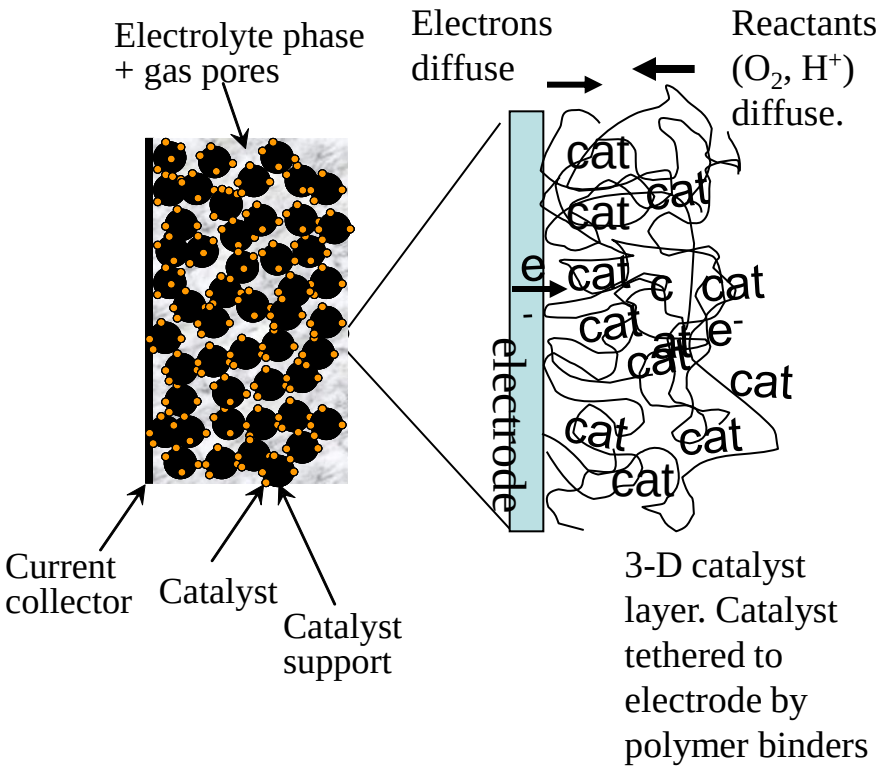
- Degradation analysis and lifetime testing development
  - MEA accelerated stress testing (Modified FCTT protocols)
    - Impedance methods and analyses
- Optimize MEA fabrication methods to provide most reliable test platform for catalysts and mediators
  - Improve and validate macroscopic model –incorporate mediators.
  - Provide more accurate transport data for the model
- Synthesis and screening of new catalysts guided by molecular modeling/computation
  - NSF proposal submitted for catalyst design and synthesis.
  - Incorporation of mediators.
  - Catalyst tethering to polymers
- Procure new catalysts from the entire chemical community to test in developed architecture.
- Move on to other reactions (e.g. anode reactions(dehydrogenation)).

Summary

- The concept of the 3D Molecular-scale Catalyst layer has been shown to work and to work well in MEA's. High turnover rates (> 200 s^{-1}) with sufficient catalysts loadings have been shown to support high current densities (> 1A/cm^2).
- The stability of the catalyst and catalyst layer has been shown to be surprisingly good and sufficient to warrant further investigation provided a pathway to higher voltages is found.
- All milestones have been accomplished except for the voltage criterion. Since that is a Go/No-go decision criterion the project is in close out.
- A pathway to meet the voltage criterion has been identified which involves a combination of MEA optimization combined with better chemistry of catalysts and electron transfer mediators.
  - All of the steps involved in the pathway to meet the voltage criterion are based on validated transport and molecular models. There are no "magical" effect of surface to invoke.
  - Since the chemistry of the catalysts is known in solution their performance can be studied much more easily than with expensive surface techniques.
- Extended lifetime at high current densities and high voltages will depend upon proper electrode morphology that can be maintained indefinitely.

Technical Back-Up Slides

Rationale



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

- 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 site
- **Geometric effects compensate for catalyst size**

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		

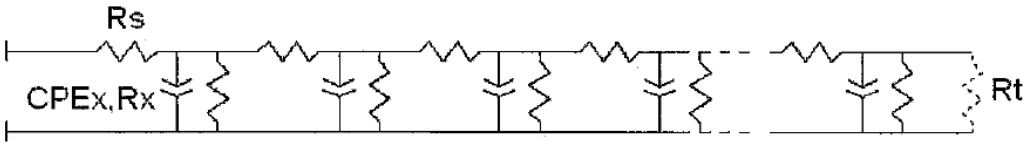
Table 2. Geometrical/transport properties used for a catalyst layer and GDL.

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

Data From Impedance Analysis

Transmission Line:



Fitting:

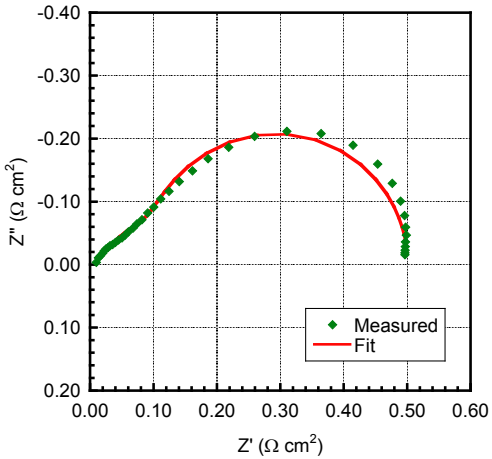


Table I: Values determined from equivalent circuit fitting of MEA using Ink XIV.

Current Density (mA/cm²)	Ohmic Resistance, R_{ohmic} (Ω • cm²)	Electrolyte Resistance, R_s (Ω • cm²)	Double-Layer Capacitance, C_{dl} (mF/cm²)	Charge-Transfer Resistance, R_{ct} (Ω • cm²)	HFR at 1 kHz (Ω • cm²)	R_s/R_{ct}
200	0.0741	0.00291 (*5.89*)	0.291 (*5.56*)	40.68 (*2.44*)	0.1064	7.15e-5
150	0.0723	0.00383 (*6.93*)	0.359 (*6.61*)	53.95 (*3.12*)	0.1083	7.10e-5
100	0.0851	0.00332 (*4.69*)	0.367 (*3.96*)	81.45 (*2.29*)	0.1132	4.08e-5
75	0.0899	0.00403 (*4.71*)	0.394 (*3.91*)	110.5 (*2.34*)	0.1172	3.65e-5
50	0.0995	0.00377 (*5.97*)	0.463 (*4.44*)	177.0 (*3.41*)	0.1183	2.13e-5
30	0.1121	0.00408 (*7.43*)	0.528 (*5.02*)	330.9 (*4.91*)	0.1216	1.23e-5
Average	0.0888	0.00369 (*5.94*)	0.400 (*4.92*)	-----	0.1143	

Numbers in parenthesis are the error % from the fitting result.

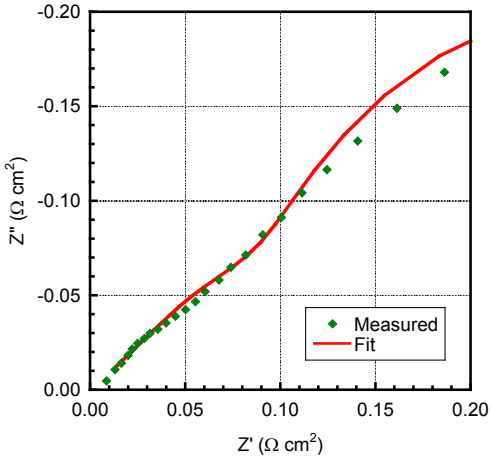


Table II: Values determined from equivalent circuit fitting of commercial Pt/C MEA.

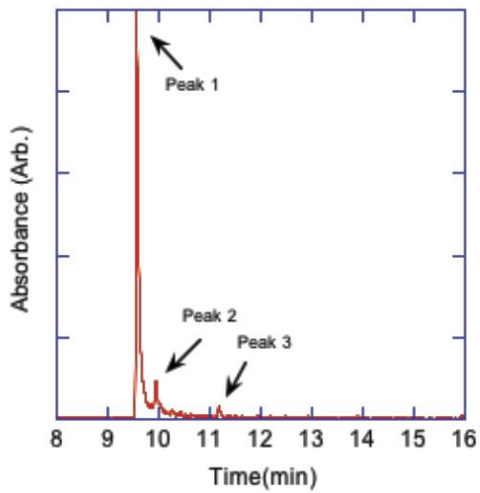
Current Density (mA/cm²)	Ohmic Resistance, R_{ohmic} (Ω • cm²)	Electrolyte Resistance, R_s (Ω • cm²)	Double-Layer Capacitance, C_{dl} (mF/cm²)	Charge-Transfer Resistance, R_{ct} (Ω • cm²)	HFR at 1 kHz (Ω • cm²)	R_s/R_{ct}
200	0.0109	1.059e-5 (*10.56*)	0.199 (*3.71*)	18.62 (*3.09*)	0.0119	9.95e-5
150	0.0109	1.065e-4 (*10.07*)	0.201 (*3.49*)	24.85 (*2.91*)	0.0118	9.83e-4
120	0.0112	5.074e-5 (*16.35*)	0.187 (*3.04*)	30.98 (2.90)	0.0118	1.64e-6
100	0.0112	4.537e-5 (*17.78*)	0.190 (*3.00*)	37.00 (*3.11*)	0.0118	1.23e-6
75	0.0113	4.016e-5 (*19.76*)	0.195 (*3.01*)	49.55 (*3.37*)	0.0115	8.10e-7
50	0.0115	6.457e-5 (*21.95*)	0.213 (*2.62*)	77.75 (*2.62*)	0.0111	8.30e-7
30	0.0112	1.422e-4 (10.86)	0.230 (*2.77*)	140.9 (*2.69*)	0.0108	1.01e-6
10	0.0114	1.932e-4 (*17.79*)	0.260 (*3.19*)	381.5 (3.27)	0.0119	5.06e-7
Average	0.0112	8.167e-5 (*15.64*)	0.209 (3.10)	------	0.0116	

Numbers in parenthesis are the error % from the fitting result.

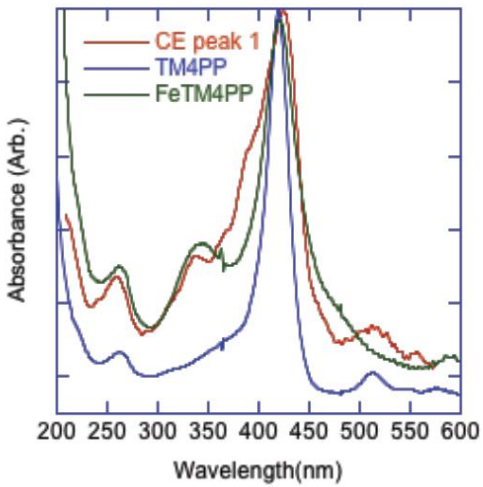
Technical Accomplishments.

Stability and Degradation Studies

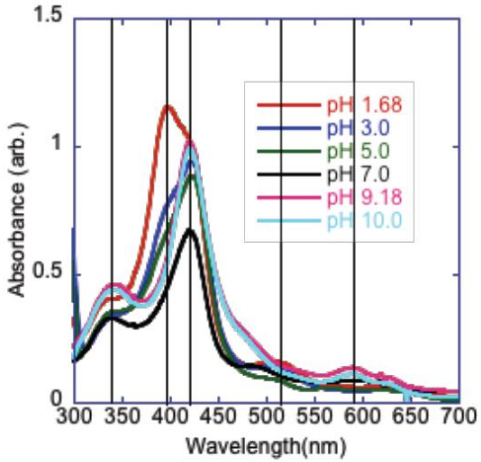
- FeTMPyP measured to be stable to ORR conditions by UV/vis test.
  - Kuwana, Inorg. Chem., 22 (1983), 699.



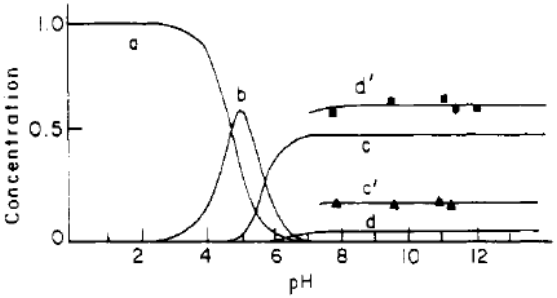
Capillary Electrophoresis(CE) Analysis of FeTMPyP using UV/vis detector



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



UV/vis Spectra of FeTMPyP as fn. of pH



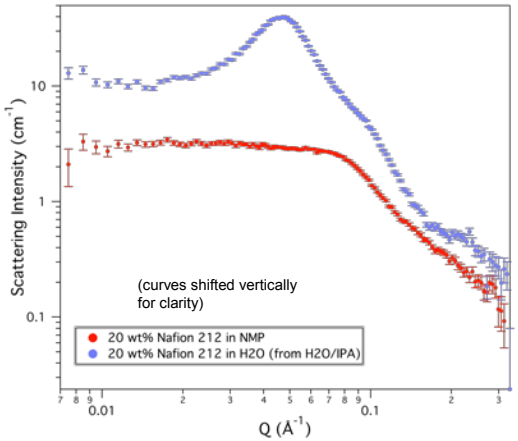
Speciation of FeTMPyP with pH
a, [Fe'''TMPyP(H_2O)]; b, [Fe'TMPyP-(H_2O)(OH)]; c = c', [[Fe'''TMPyP(H2O)]$_2$O]; d = d', [Fe'''TMPyP(OH)$_2$].

CE analysis shows impurities and degradation products. UV/vis provides spectral confirmation. CE/Ion Trap Mass Spectroscopy used to identify products from O_2 attack. Analysis of fuel cell product water detects degradation products.

Collaboration

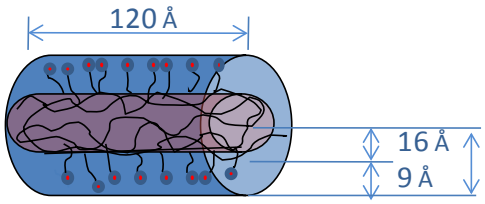
Polymer ink characterization for electrode fabrication (LANL Applied Science Program)

SANS: NMP- vs. H2O-Based Gels



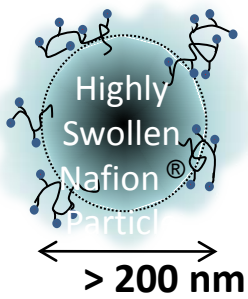
NMP dispersion: Core-Shell Cylinder

- 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)



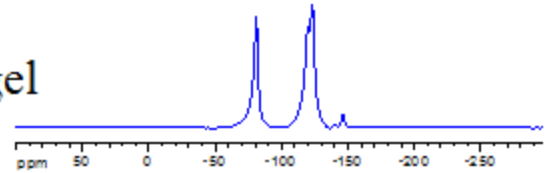
Aqueous mixture: Highly swollen particles

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

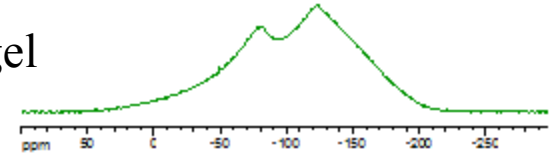


^{19}F NMR

NMP gel

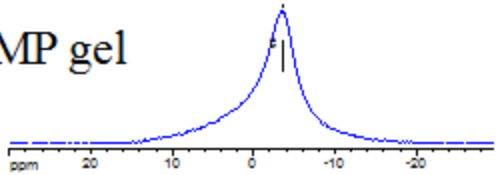


water gel

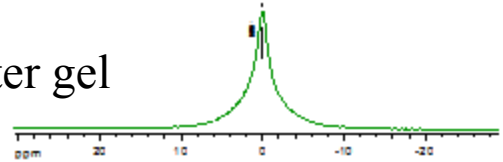


^{23}Na NMR

NMP gel



water gel



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

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