

Resonance-Stabilized Anion Exchange Polymer Electrolytes

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Project ID: FC043

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Overview

Timeline

- Project start – September 2009
- Project end – September 2011
- Percent complete (as of March 5, 2011) – 80%
 - Polymer & ionomer synthesis (90%)
 - Catalyst synthesis (70%)
 - MEA processing & Testing (60%)

Budget

- Total Project Funding: \$ 1,320k
 - Funding for FY 10: \$ 528k
 - Funding for FY 11: 330k
- No cost share

Barriers

- B. Cost
- C. Electrode Performance
- A. Durability

Partners

Project Lead:



- Yu Seung Kim (PI)
- Dae Sik Kim
- Andrea Labouriau
- Piotr Zelenay
- Hoon Jung

Collaborators:



- Cy Fujimoto (Ext. PI)
- Michael Hibbs



- Chuck Hays (Ext. PI)
- Daneil Konopka
- Michael A. Johnson
- Adam Kisor
- Poyan Bahrami
- Michael Errico

Interactions:

- Celler Technologies (S. Gottesfeld)
- Ovonic Fuel Cell Company (R. Privette)
- Cornell University (Geoff Coates)
- U. Southern California (S. Narayan)

Relevance – Objective and Technical Target

Objectives

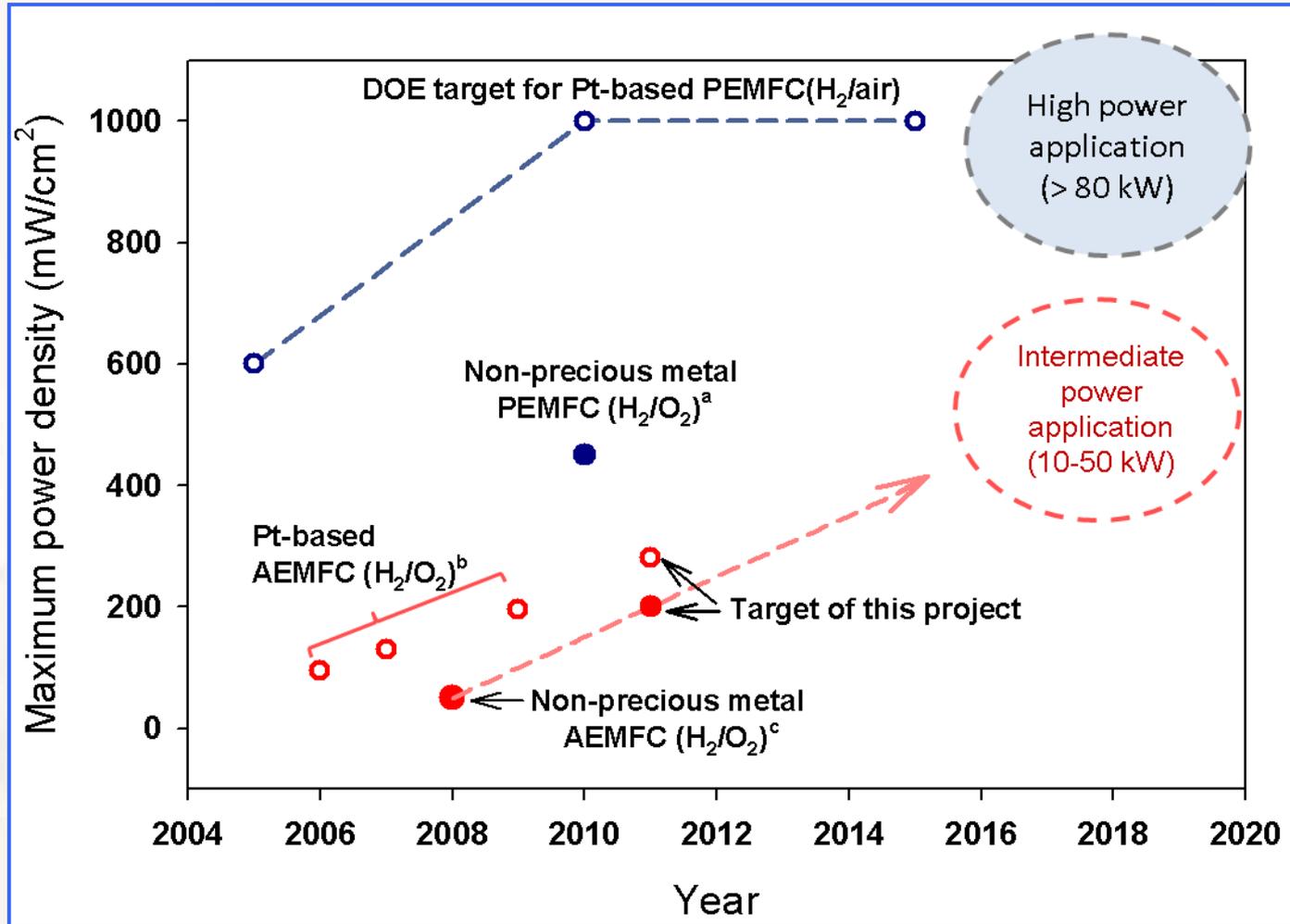
- Demonstrate an improved alkaline membrane fuel cell (AMFC) performance using novel *polymer electrolytes* and *non-precious metal catalysts*.
- *FY 10*: Anion exchange polymer electrolytes
- *FY 11*: Catalyst development and integration of AMFC MEAs

Barriers and FY 10 Status

ISSUES	Technical Barriers	Technical Target	FY 2010 status*
Membrane	Conductivity	σ : > 50 mS/cm	× (32-39 mS/cm)
	Stability	Stability : > 500 h in NaOH soln.	× (382 h, 30% loss)
	Mechanical property	Yield stress: > 10 MPa, Strain : > 10%	× ×
Ionomer	Conductivity	σ : > 50 mS/cm	× (40 mS/cm)
	Stability	Stability : > 500 h in NaOH soln.	×
	Gas permeability	<i>Perfluorinated ionomer</i>	✓
	Cat.-ionomer interface	<i>Cation optimization</i>	×
Electro-catalysts	Non-precious metal	<i>Non platinum based cat.</i>	×
	ORR activities	> 0.85 V ($E_{1/2}$)	×

* Y.S.Kim 2010 DOE AMR meeting June 7-11 (2010)

Relevance – Impact on DOE Hydrogen & Fuel Cell Program

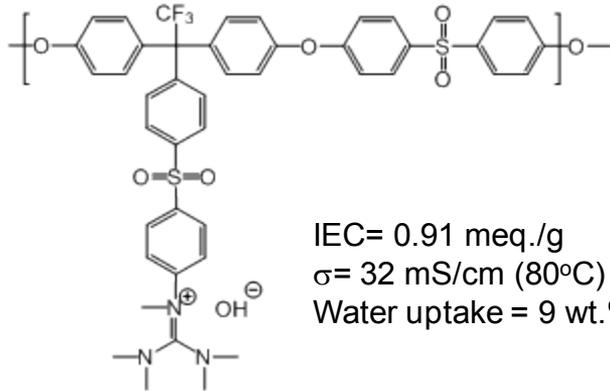


a: P. Zelenay, 2010 DOE AMR Meeting, June 7-11, 2010; b: Y. Yan et al., *Angewandte Chem.* **121**, 6621-6624, (2009); Varcoe et al., *Chem. Mater.* **19**, 2686-2693, (2007); Varcoe et al., *Electrochem. Comm.* **8**, 839-843, (2006); c: Lu et al. *PNAS*, **105**, 20611-20614, (2008);

Approach – Hydrocarbon Based Anion Exchange Membranes

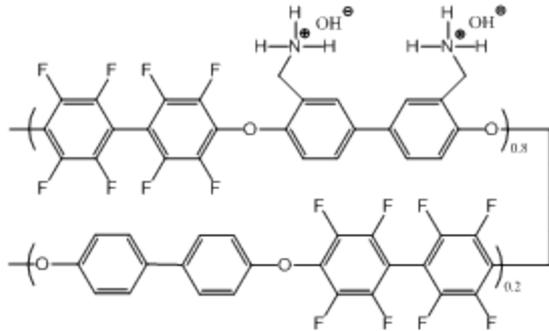
FY 10 Results

Guanidinium base homopolymer



IEC= 0.91 meq./g
 σ = 32 mS/cm (80°C)
Water uptake = 9 wt. %

Tetra-alkylammonium base copolymer

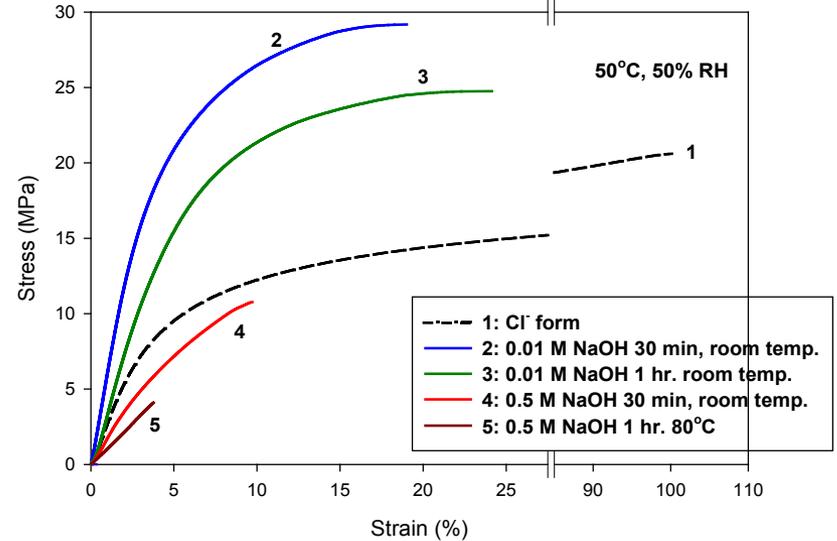


IEC= 2.7 meq./g
 σ = 60 mS/cm (80°C)
Water uptake = 63 wt. %

issue



Tetra-alkylammonium base random copolymer



Cause of mechanical property degradation

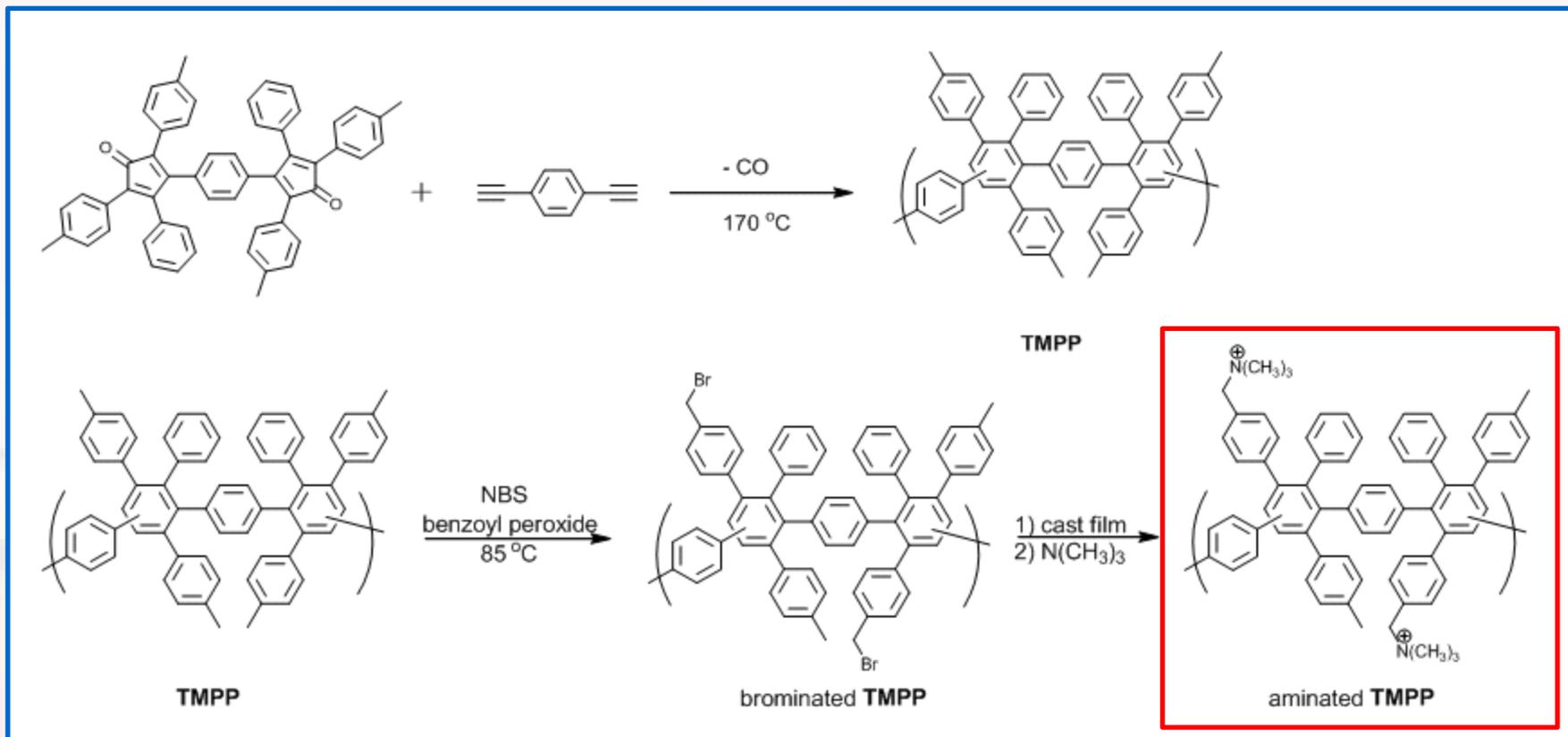
- ✓ Nucleophilic attack of OH⁻ to polymer backbone ether linkage
- ✓ Low electron density due to electron-withdrawing fluorine moiety

approach



Poly(phenylene) based AEM (SNL)

Synthesis of Poly(Phenylene) Anion Exchange Membranes



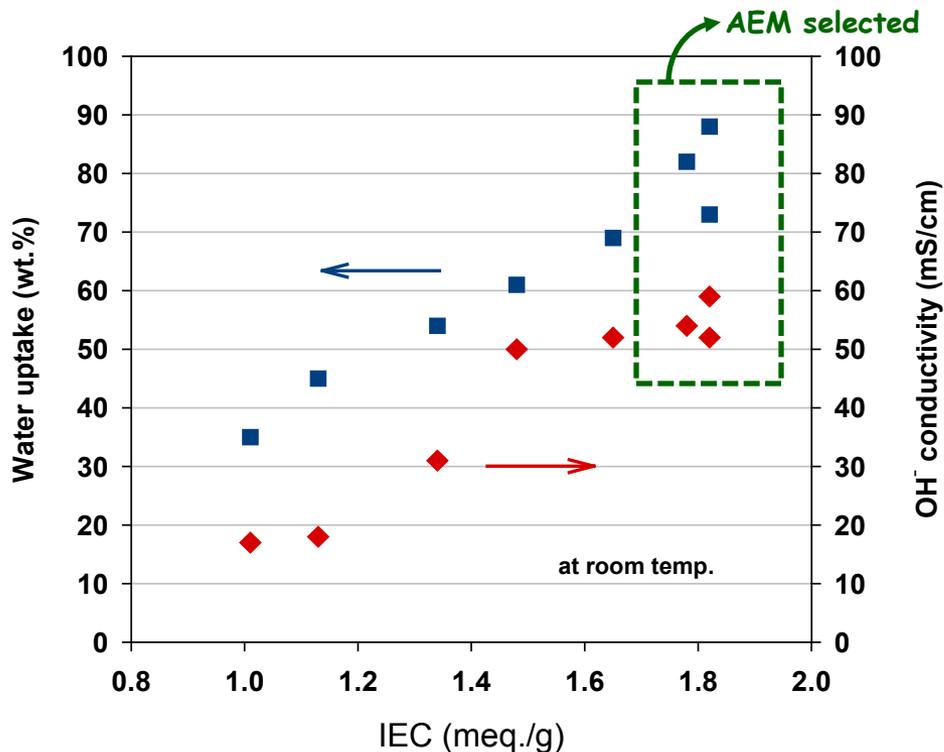
- ✓ **Extremely good chemical stability** due to the wholly aromatic structure
- ✓ **No ether or fluorine** linkages which are susceptible to nucleophilic degradation
- ✓ Number average molecular weight is $\sim 35,000$ gm/mol
- ✓ **Uniform distribution of tri-methyl functional groups** reduces water uptake at a given IEC

Structure analysis of these polymers is provided in the supplement slide (slide no. 23)

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Water Uptake and Conductivity of Aminated TMPP

Water uptake and OH⁻ conductivity



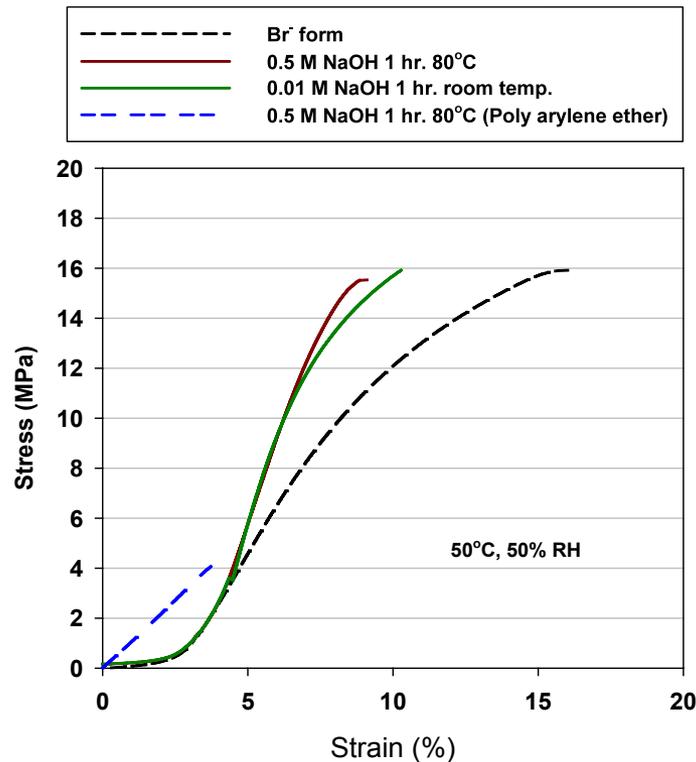
IECs measured by Volhard titration of bromide ions
Conductivity measure in degassed liquid water



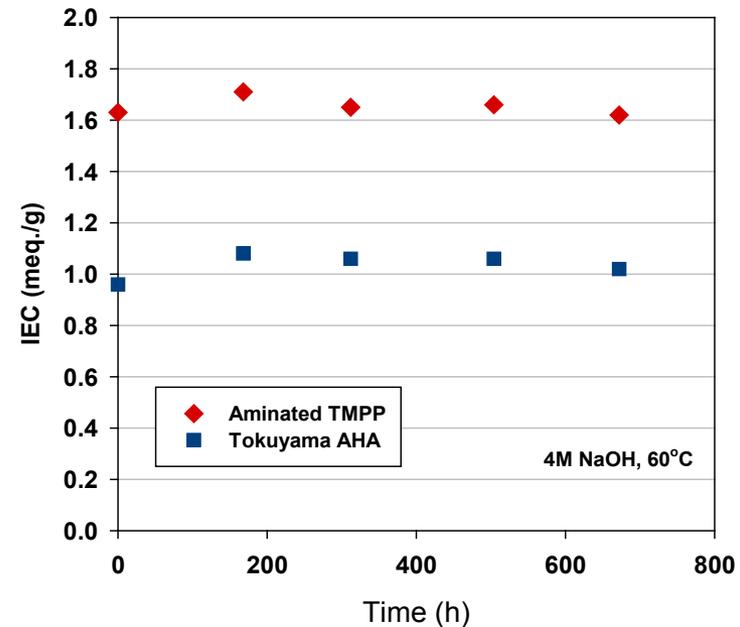
- ✓ AEM selected based on conductivity and water uptake
- ✓ Degree of functionality (number of -CH₂Br groups/repeat unit) is typically 2-2.5
- ✓ **Selected AEM meets the conductivity and water uptake target for 2011**

Mechanical Property and Stability of Aminated TMPP

Stress-strain curves



AEM stability under high pH conditions



* Poly(arylene ether sulfone) with benzyl trimethylammonium Groups became too brittle to handle after 1-2 days.

- ✓ **Mechanical properties of poly(phenylene) did not change with different NaOH treatment**
- ✓ The mechanical stability of poly(phenylenes) was superior to those of poly(arylene ether)s
- ✓ The IEC of poly(phenylene)s **did not change over 700 h in 4 M NaOH soln. at 60°C**
- ✓ Further improving mechanical properties of poly(phenylene) is under investigation

Approach – Perfluorinated Anion Exchange Ionomers

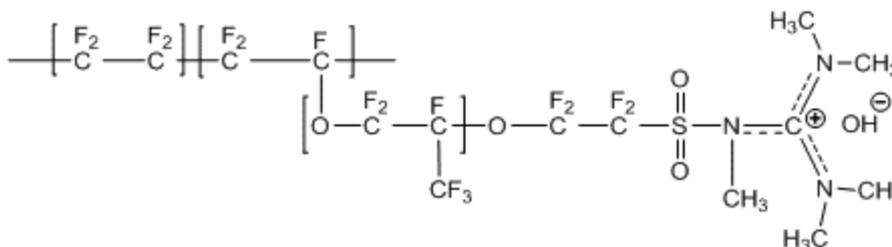
FY 10 Results

Guanidine functionalized perfluorinated ionomer

IEC= 0.9 meq./g

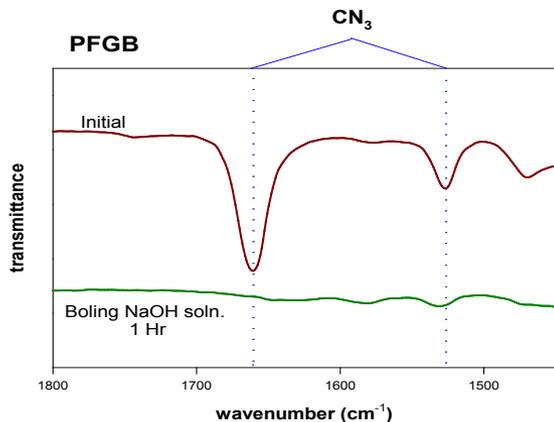
$\sigma = 52 \text{ mS/cm (50}^\circ\text{C)}$ ✓

Water uptake = 15 wt.% ✓

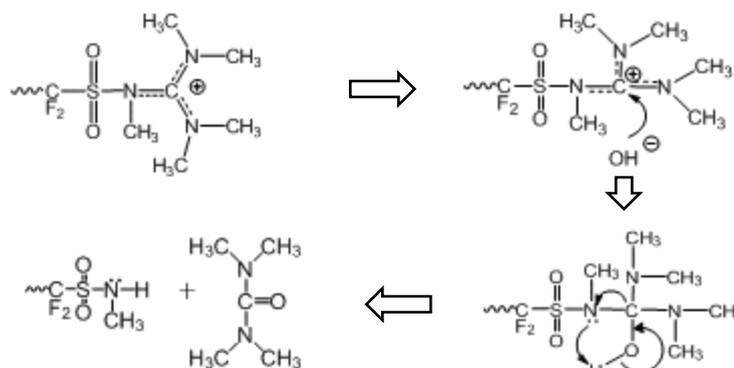


issue

Poor Stability



Degradation Mechanism

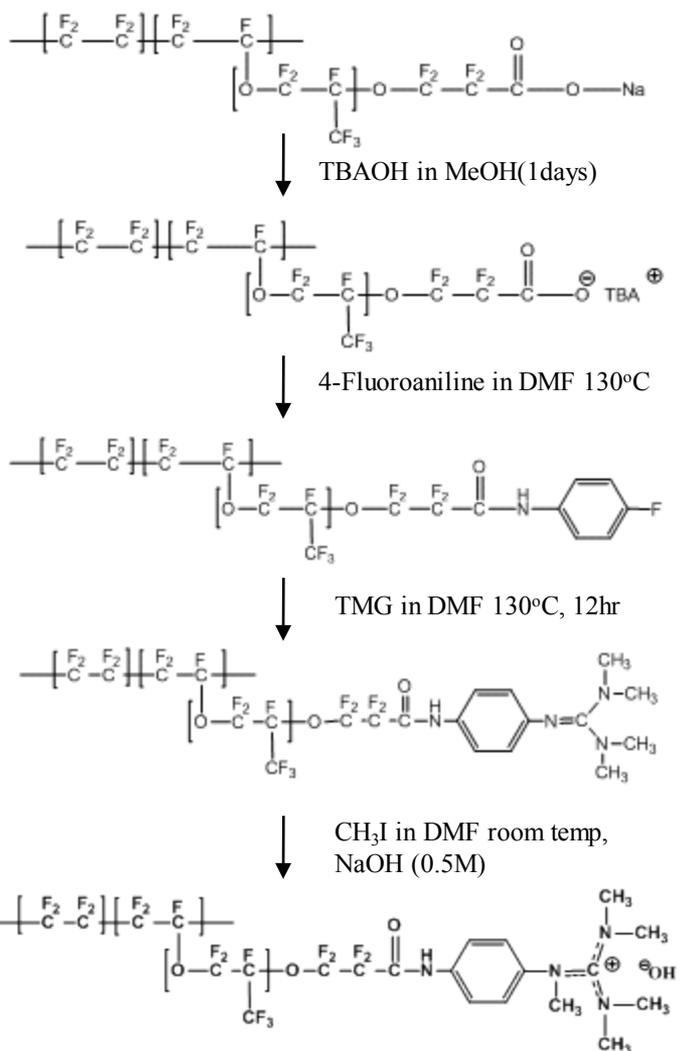


approach

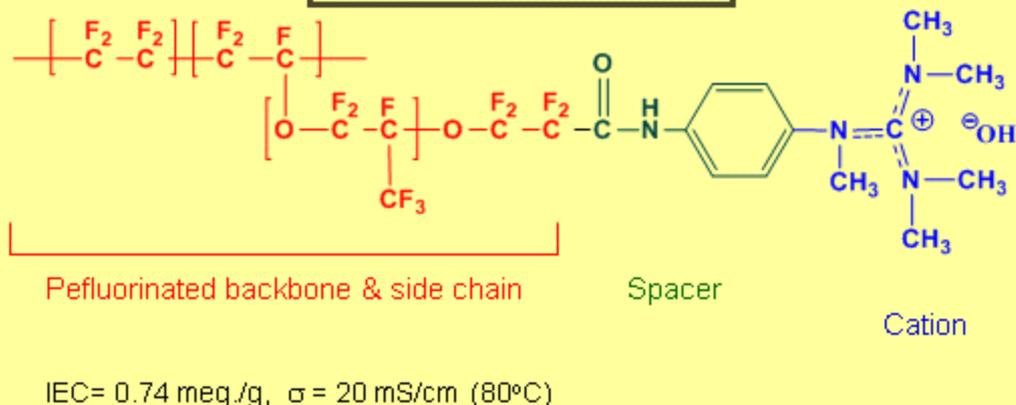
Stabilizing cation by electron donating spacer (LANL)

Synthesis of Guanidinium based Perfluorinated Ionomers

Synthesis



Perfluorinated ionomer*



Perfluorinated backbone & side chain

- ✓ Provide high gas permeability
- ✓ Inert to electro-catalytic reaction
- ✓ Chemically and oxidative stability

Spacer

- ✓ Cation stability by increasing electron density

Cation

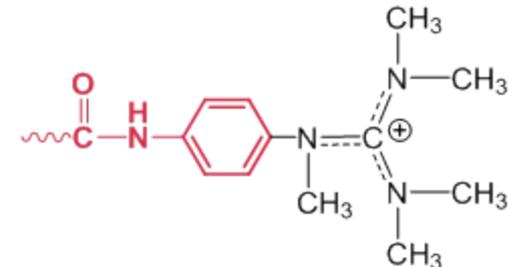
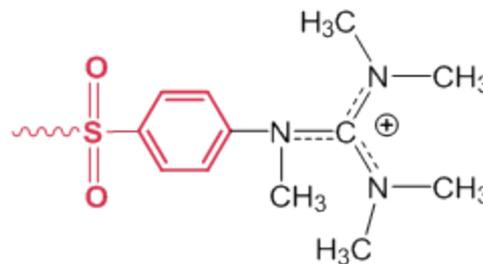
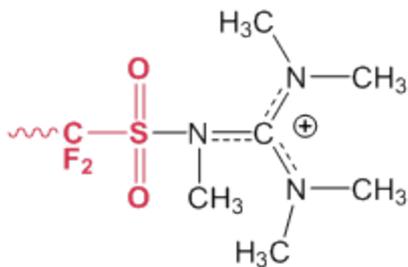
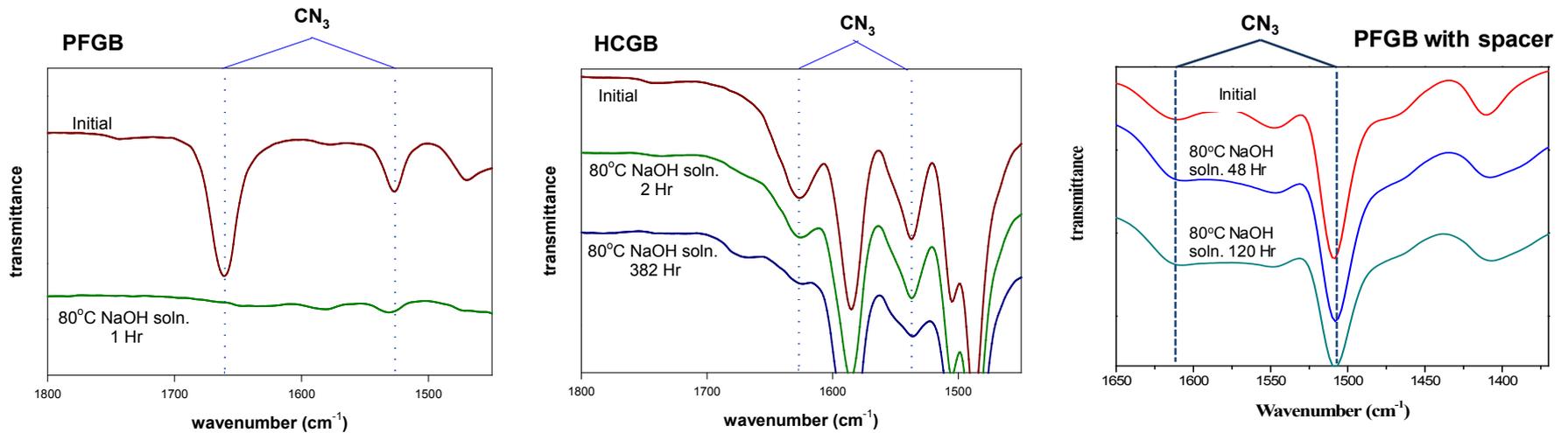
- ✓ Cation stability by resonance structure
- ✓ Provide highly active catalyst-electrolyte interface

*LANL patent pending (2011)

Structure analysis of these polymers is provided in the supplement slide (slide no. 24)

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Effect of Electron Density on Cation Stability



Local electron density & stability

- ✓ The cation stability of perfluorinated AEM significantly improved by the electron donating spacer
- ✓ This is a proof of principle for utilizing perfluorinated ionomer for AMFC

Approach – Non-Precious Metal ORR Electrocatalysts

ORR activity of electro-catalysts is largely dependent on electrolytes (see right Fig)



In acid membrane fuel cells, relatively active sulfonated groups are tethered to polymers, while in alkaline membrane fuel cells, tetra-alkylammnium groups are used.



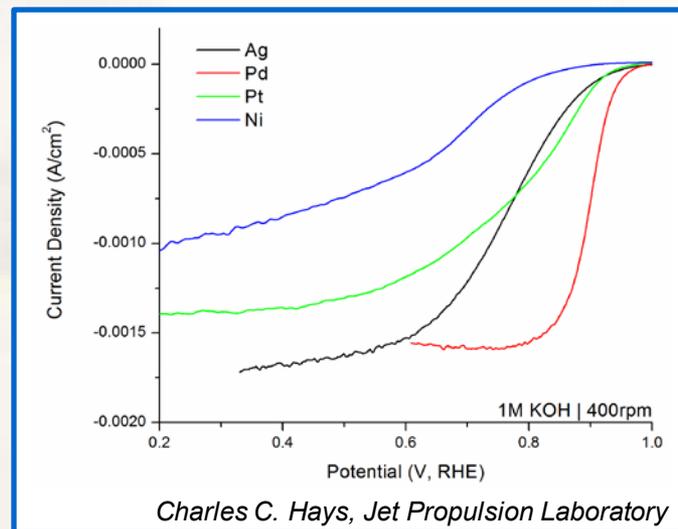
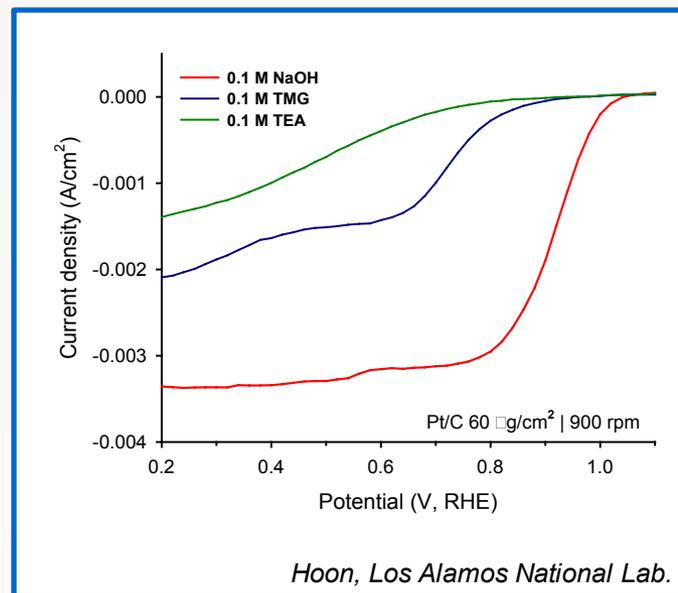
ORR activity also strongly depends on the type of electro-catalysts (see right Fig)



Understanding ORR activities of different cation and alternative catalysts



Development of highly active ORR catalysts



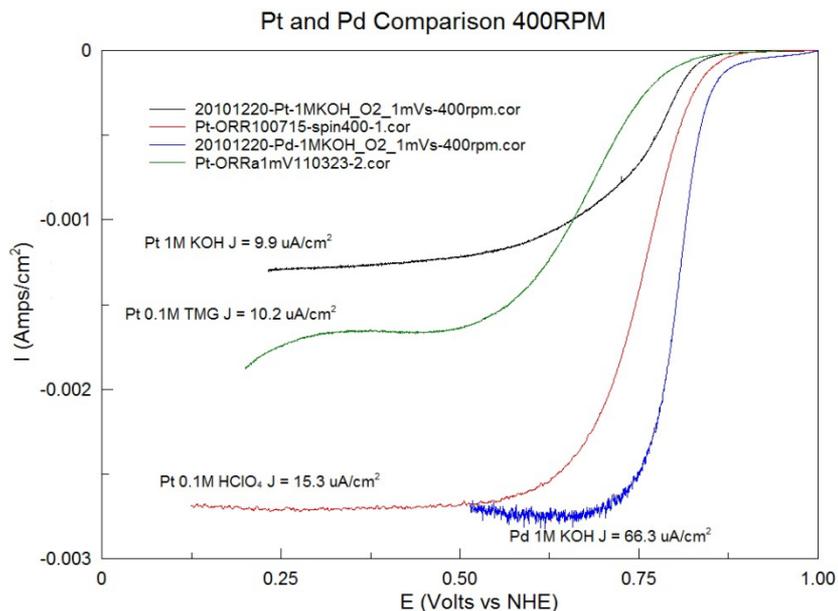
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2011 DOE Hydrogen and Fuel Cells Program Review

ORR and HER Activities of Pt and Pd Catalysts in TMG

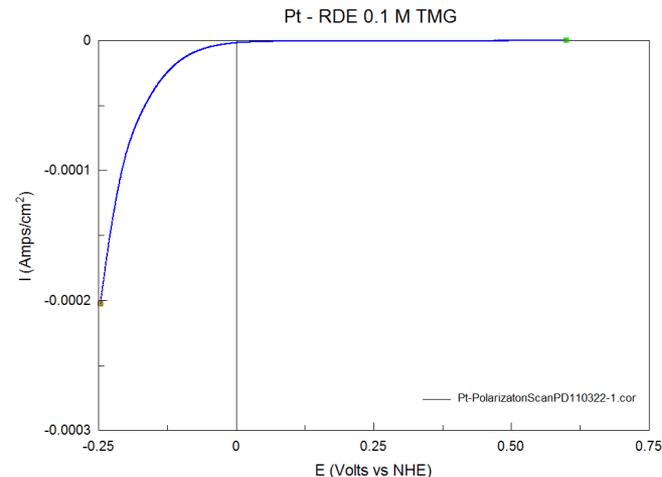


ORR Activity



ORR Catalyst	Electrolyte	i at 0.9 V ($\mu\text{A/cm}^2$)
Pt	1 M KOH	-9.9
	0.1 M TMG	-10.2
	0.1 M HClO ₄	-15.3
Pd	1 M KOH	-66.3
	0.1 M TMG	-50.9

HER Activity

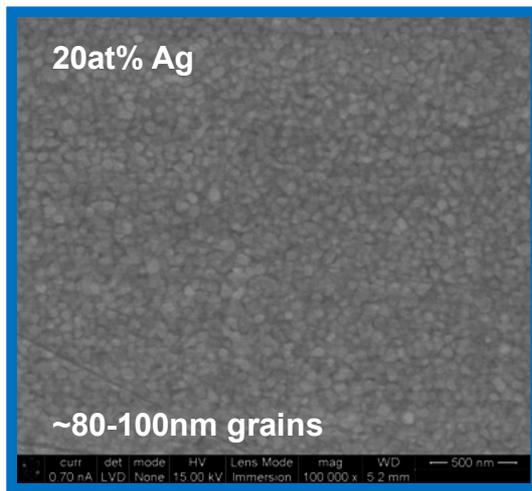
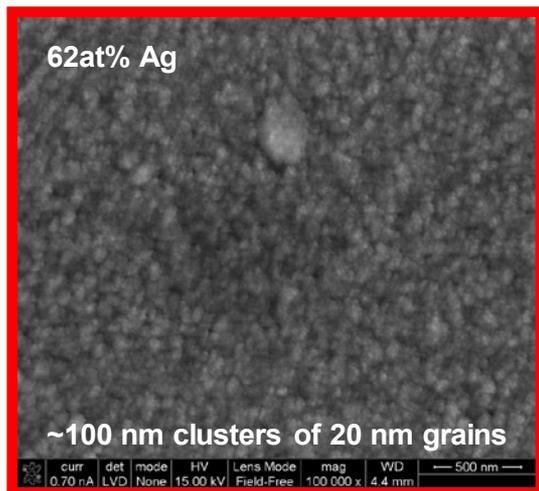


- ✓ Performed electrochemical tests via RDE on elemental electrodes in 0.1 M TMG + H₂O electrolyte
- ✓ Pt, Pd, tested so far, ORR current densities in TMG rival those in KOH
- ✓ RDE measurements of the HER on Pt in 0.1 M TMG indicates a good catalytic activities at the interface with TMG electrolytes

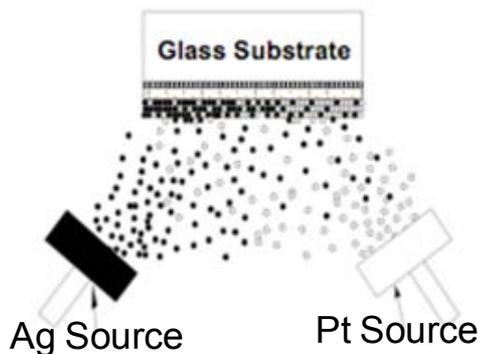
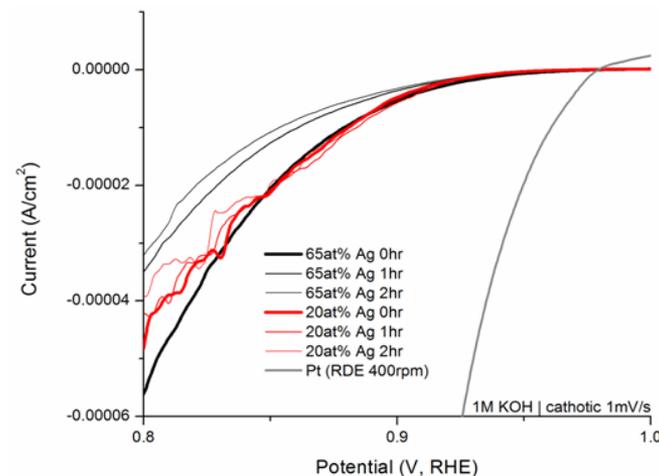
Synthesis of Ag-Pt based Binary Electro-catalysts



Thin film synthesis by co-evaporation



Potential cycling (0-1.1 V (250 mV/s))

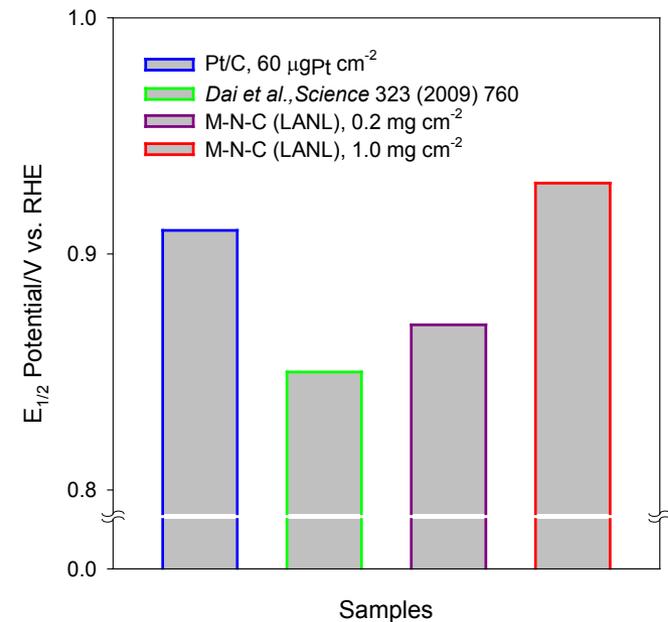
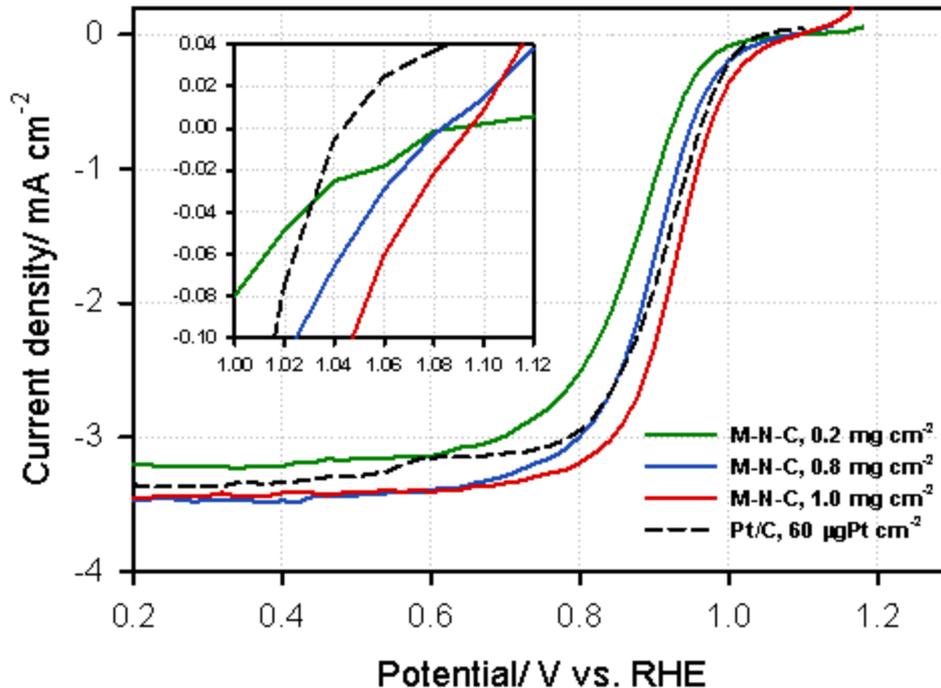


dc-Magnetron sputtering: Pt, Ni, Ag targets; Pdep ~ 10⁻⁷ Torr

- ✓ Ag-Pt and Ag-Ni catalysts were prepared from co-evaporation technique
- ✓ Higher Ag content results in finer grain structure, ~20 nm grains: higher Pt content results in more coarse grains.
- ✓ XRD indicates all Ag-Pt films exhibit a strong (111) crystallographic orientation and no chemical ordering (supplementary slide 25)
- ✓ **Ag is not stable in the Ag-Pt array (> 20 at.% Ag) due to the formation of AgO sublayers**

ORR Activity of M-N-C Catalysts in NaOH Solution

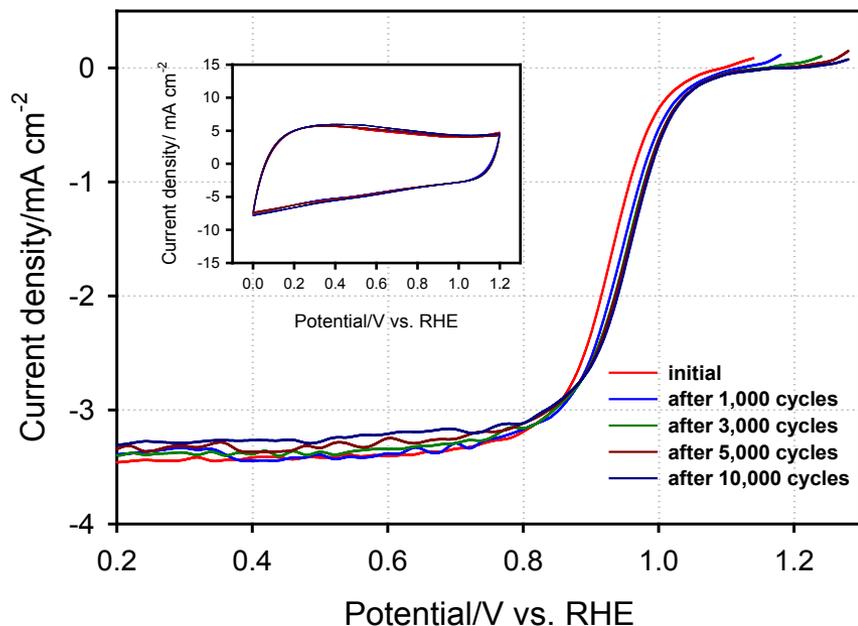
RDE: 0.1 M NaOH; 900 rpm; room temperature; steady state potential (OCP, 120 s, 20 mV steps, 25 s/step)



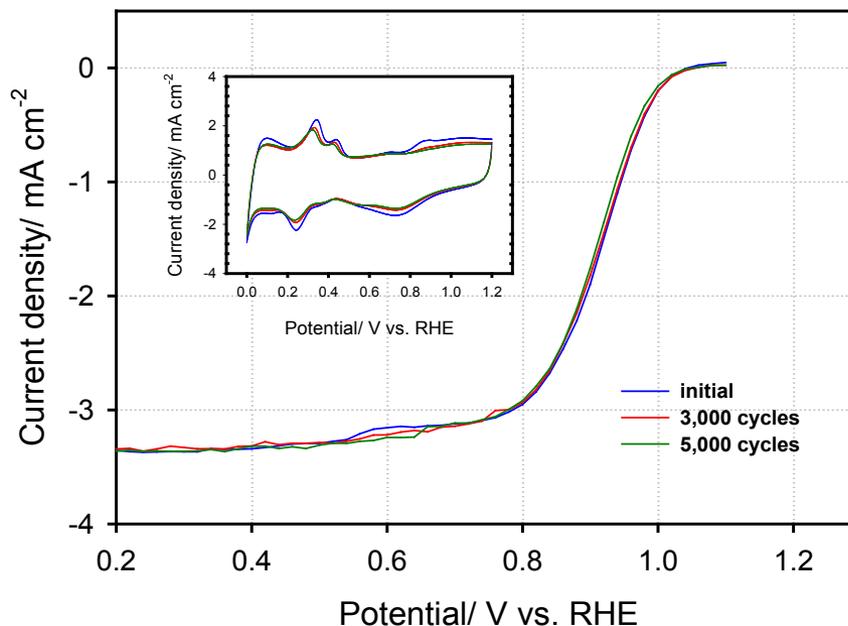
- ✓ Dai et al. reported high activity of N doped carbon nanotube catalyst in alkaline solutions (supplementary slide no 26)
- ✓ Highly-active and durable M-N-C catalyst was prepared using commercial carbon black rather than expensive CNT as a starting material
- ✓ **Excellent ORR activities with M-N-C catalyst** was obtained; E_{1/2} increased with catalyst loading
- ✓ Onset potential of M- N-C catalyst higher than that of Pt/C

Durability of M-N-C Catalysts during Potential Cycling

M-N-C catalyst (1.0 mg cm^{-2})



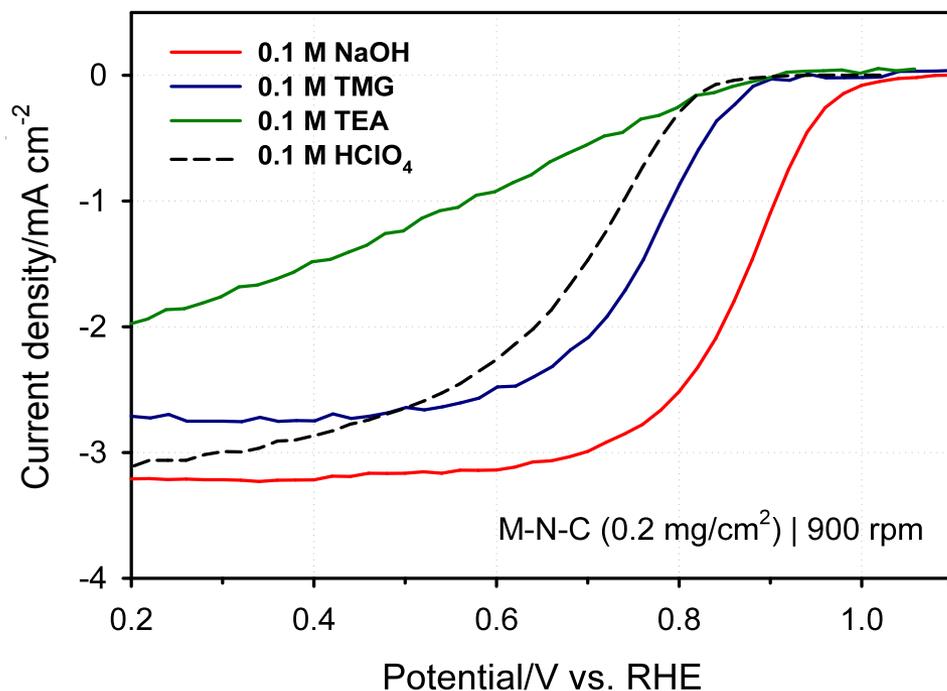
Pt/C catalyst ($60 \mu\text{g cm}^{-2}$)



RDE: 0.1 M NaOH; 900 rpm; room temperature; steady state potential (OCP, 120 s, 20 mV steps, 25 s/step); cycling condition, 0.6 to 1.0 V, 50 mV s^{-1} in saturated O_2

- ✓ **Excellent stability of M-N-C catalysts** (ORR activities of M-N-C catalysts increased with potential cycling)
- ✓ **$E_{1/2}$ of M-N-C catalyst was 0.95 V while $E_{1/2}$ of Pt/C catalyst was 0.90 V after 5,000 cycles**

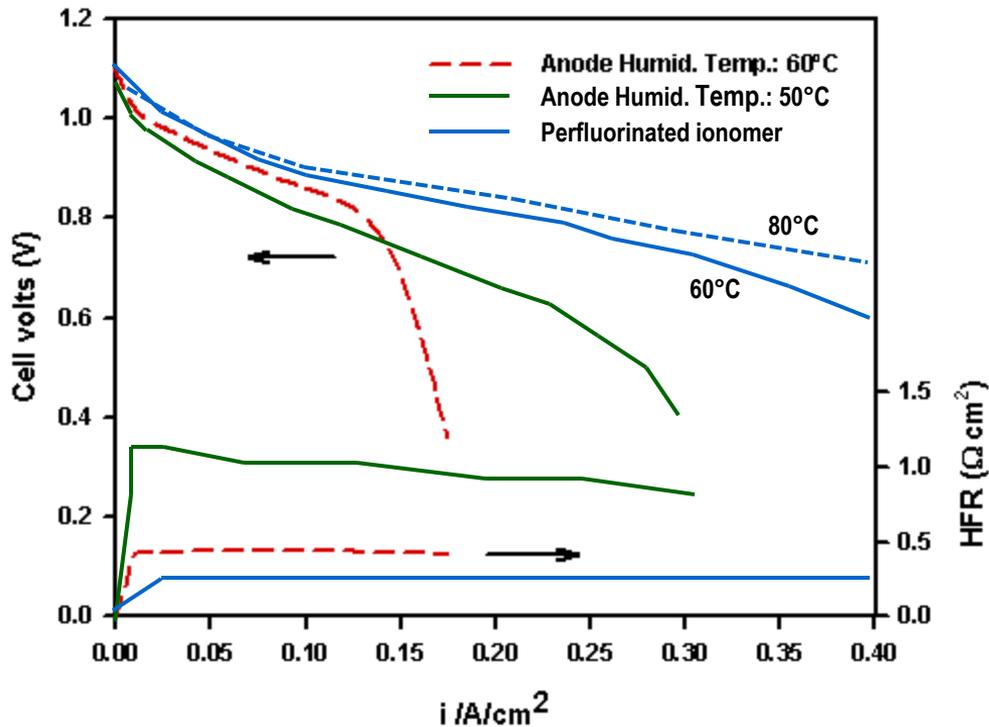
ORR activities of M-N-C Catalysts in Different Electrolytes



ORR Catalyst	Electrolyte	Onset potential (V)
M-N-C (0.2 mg/cm^2)	NaOH	1.06
	TEA	0.90
	TMG	1.03
	HClO_4	0.91
Pt/C ($60 \mu\text{g/cm}^2$)	NaOH	1.03
	TEA	0.90
	TMG	0.95
	HClO_4	0.96

- ✓ The ORR activity of the M-N-C catalyst (0.2 mg/cm^2) in TMG is superior to that in tetraalkylammonium
- ✓ The onset potential of the M-N-C catalyst in TMG is equivalent to that of the Pt/C in NaOH.

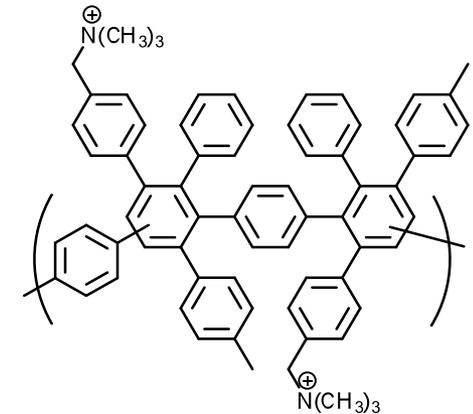
H₂/O₂ Performance of Alkaline Membrane Fuel Cells



Catalyst: Pt black (3 mg/cm²), Cell temp. 60° C, Cathode humidification: 60° C, back pressure: 30 psig, high stoic. Catalyst: ionomer weight composition (9:1, not optimized); MEAs were prepared from direct painting.

Membrane/ionomer

IEC = 1.8 meq./g
 σ = 55 mS/cm
 Thickness: 50 μ m



aminated TMPP

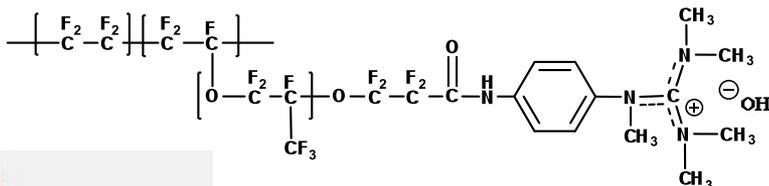
Fully hydrated conditions (anode humid. temp.: 60°C)

- Mass transport issue due to flooding
- Possibly poor cation – catalyst structure

Partial hydrated conditions (anode humid. temp.: 50°C)

- Improved performance with removing mass transport issue
- Poor membrane hydration/remaining issue with cation

Ionomer (IEC = 0.74 meq./g, σ = 20 mS/cm)



Perfluorinated ionomer (anode humid. temp.: 60°C)

- Improved performance with removing mass transport issue
- No membrane hydration problem
- Maximum power density:
 236 (at 60°C) and 278 mW/cm² (at 80°C)

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Collaborations

Sub Contractors

- Sandia National Laboratories: Polymer Synthesis, extensive collaboration.
- Jet Propulsion Laboratory: Electrode Preparation, extensive collaboration.

Industry

- Ovonic Fuel Cell Company (R. Privette): Material characterization, occasional.
- Cellera Inc. (S. Gottesfeld): Electrode design, occasional.

University

- Cornell University (Geoff Coates): Polymer synthesis, occasional.
- University of Southern California (S. Narayan): Electro-catalysis, occasional.

Federal/National Laboratory

- Los Alamos National Laboratory (P. Zelenay) through DOE Advanced Catalyst Program: Catalyst issue in alkaline fuel cells, moderate interaction.
- Canada NRC (M. Guiver) through DOE Technical Assistant Program: Polymer synthesis, occasional.
- National Renewable Energy Laboratory (B. Pivovar) through DOE BES program: cation stability, occasional.

Summary

<i>Anion Exchange Membrane: Aminated poly(phenylene)</i>		Target	March 1, 2010	March 1, 2011
Conductivity (mS/cm)		> 50	32 ^a	51-59 ^b
Water uptake (wt.%)		< 10	9-46	73-98
Chemical stability in NaOH soln. (h)		> 500	< 1	> 670
Yield stress (MPa)/strain (%)		> 10/>10	4/4	16/8
<i>Anion Exchange Ionomer: Guanidinium functionalized perfluorinated polymer</i>		Target	March 1, 2010	March 1, 2011
Conductivity (mS/cm)		> 50	40	20 ^b
Chemical stability in NaOH soln. (h)		> 500	< 1	> 120
<i>ORR catalyst: M-N-C catalyst (0.2 mg/cm²)</i>		Target	March 1, 2010	March 1, 2011
E _{1/2} potential (V)	NaOH or KOH	> 0.85	-	0.87
	TMG	> 0.75	-	0.77
<i>AMFC performance^d</i>		Target	March 1, 2010	March 1, 2011
Maximum power density (mW/cm ²)	Pt based	> 300	-	280
	Non-Pt based	< 200	-	-
Durability under continuous operations (< 10% loss)		> 500	-	-

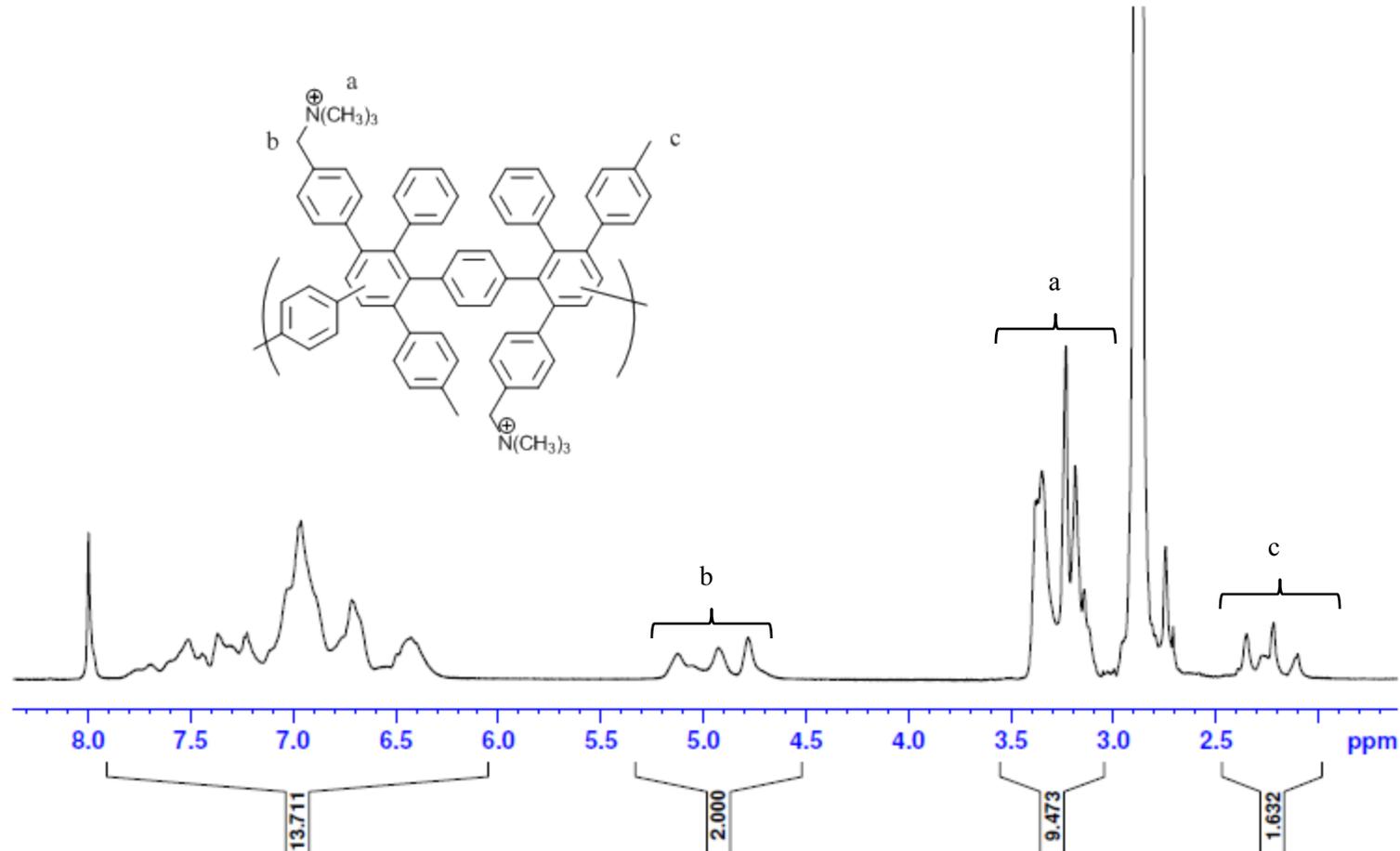
^a Measured at 80°C; ^{b,c} Measured at 30°C; ^d at 60°C

Future Research (April 1- Sep. 30, 2011)

- **Poly(phenylene) anion exchange membranes (SNL)**
 - Synthesis of high MW membranes (target MW > 50,000 g/mol)
- **Perfluorinated ionomer (LANL)**
 - Synthesis of high IEC polymers (target IEC = 0.9 meq./g)
 - Stability study
- **M-N-C catalysts (LANL)**
 - Effect of cation on ORR mechanism of M-N-C catalysts
- **Ag based catalysts (JPL)**
 - ORR activity of Ag catalyst in TMG solution
- **MEA fabrication (LANL and JPL)**
 - Optimization of electrode composition and MEA processing condition
- **Fuel cell testing (LANL)**
 - H₂/O₂ and H₂/air conditions
 - Durability test (target: 500 h with < 10% performance loss)

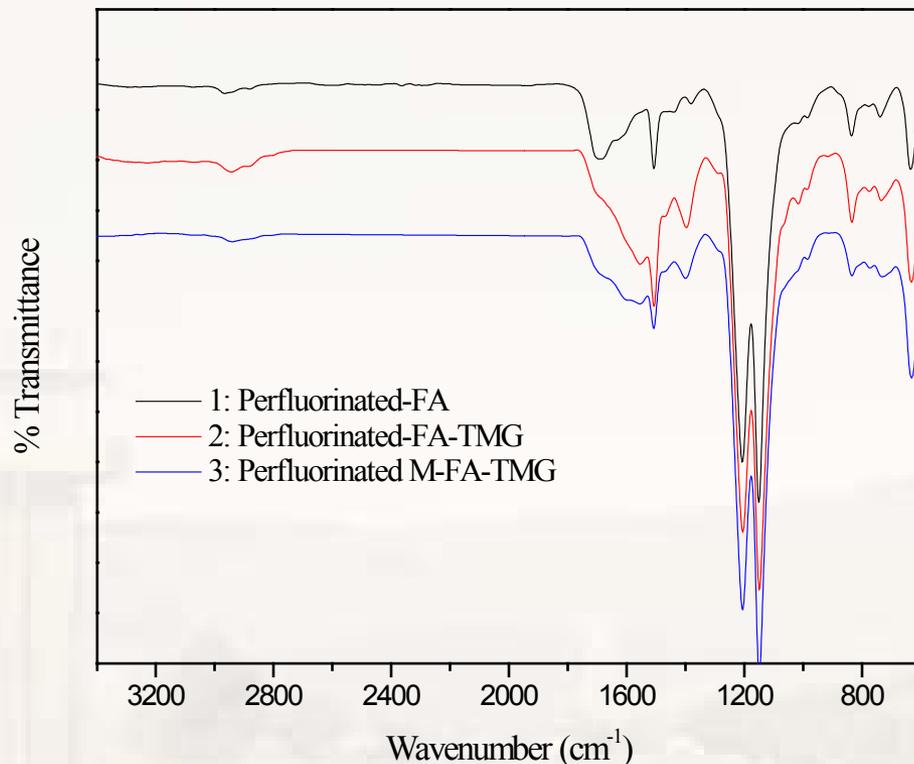
Technical Back-up Slides

^1H NMR of Aminated TMPP

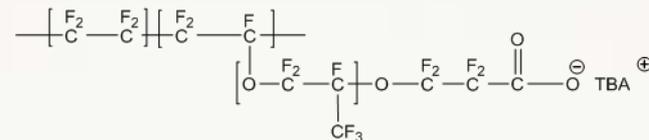


Protons a, b, and c are represented by groups of peaks due to varying probabilities for methyl and ammonium groups at each of four positions on each repeat unit.

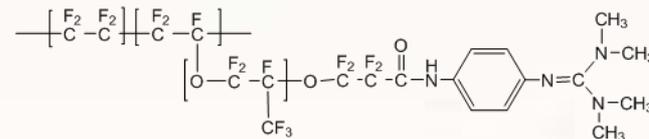
FT-IR of PFGB



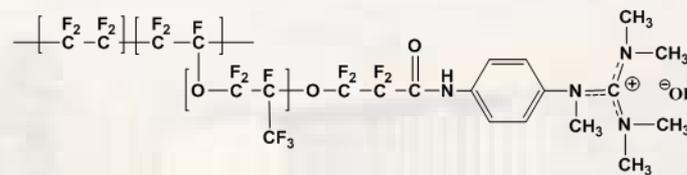
1. Perfluorinated-FA



2. Perfluorinated-FA-TMG



3. Perfluorinated M-FA-TMG

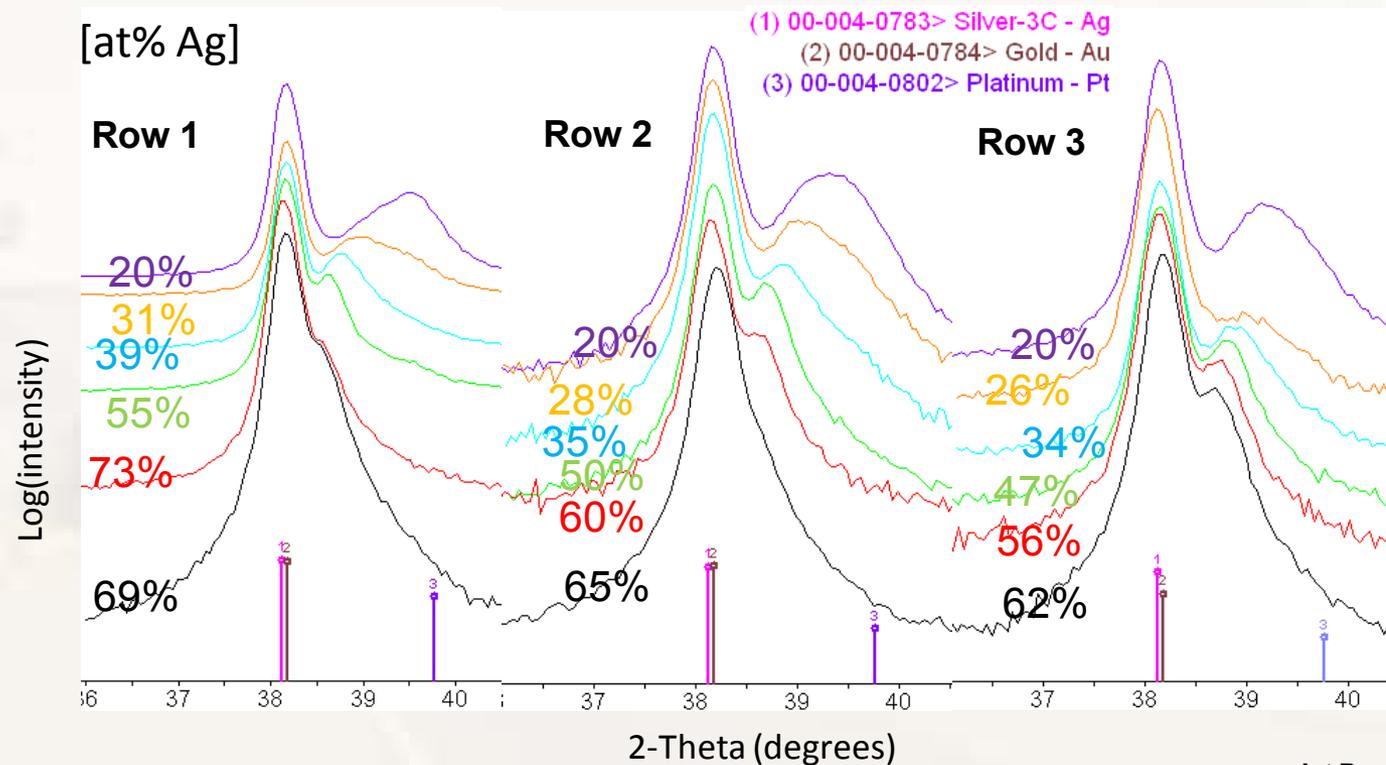


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XRD of Ag-Pt Array

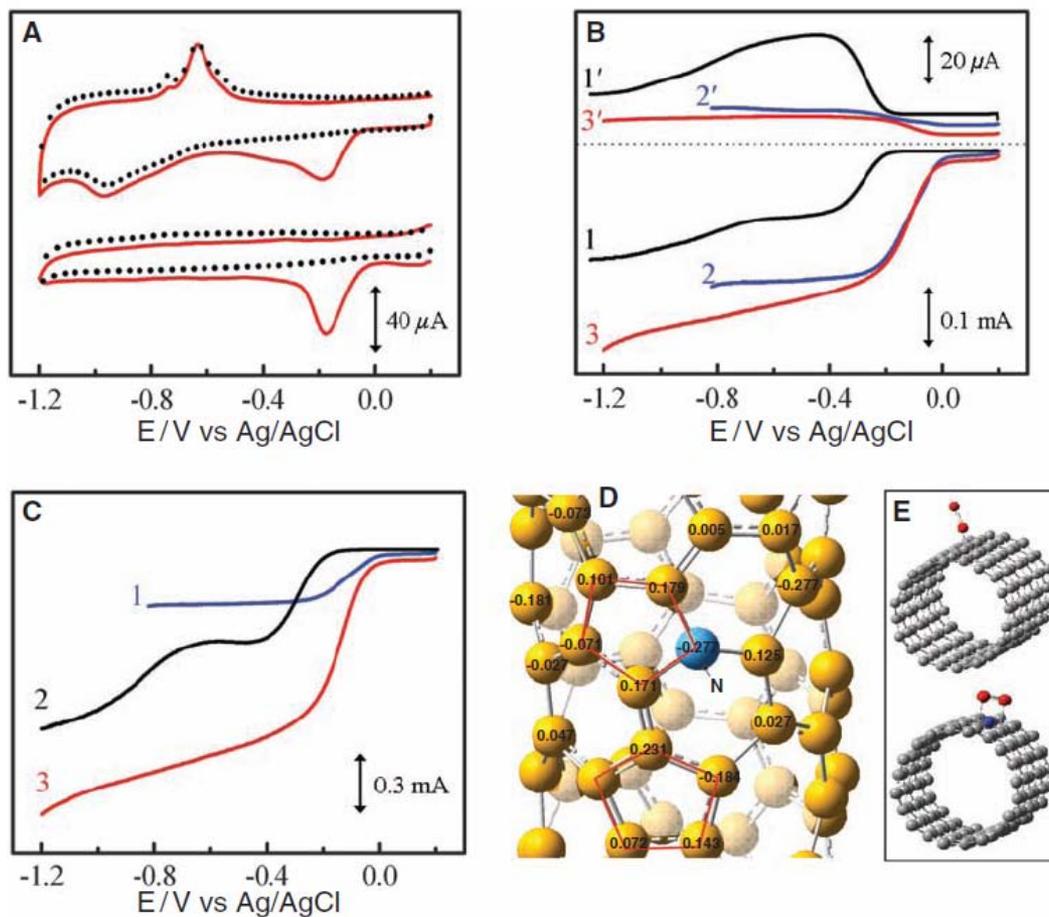
Synthesized two multi-electrode arrays for electrochemical tests
In both libraries, Pt-Ag and Ni-Ag, the thin films are single phase
- All films exhibit a strong (111) crystallographic orientation
- No chemical ordering



Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

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ORR Enhancement with N Doping into Carbon in Alkaline Media



Dai et al., *Science* 323
(2009) 760