2011 DOE Hydrogen and Fuel Cells Program Review
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Resonance-Stabilized Anion Exchange Polymer Electrolytes

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Project ID: FC043

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:

Los Alamos NATIONAL LABORATORY EST.1943

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

Collaborators:

Sandia National Laboratories

- Cy Fujimoto (Ext. PI)
- Michael Hibbs

JPL

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

Interactions:

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

Relevance – Objective and Technical Target

Objectives

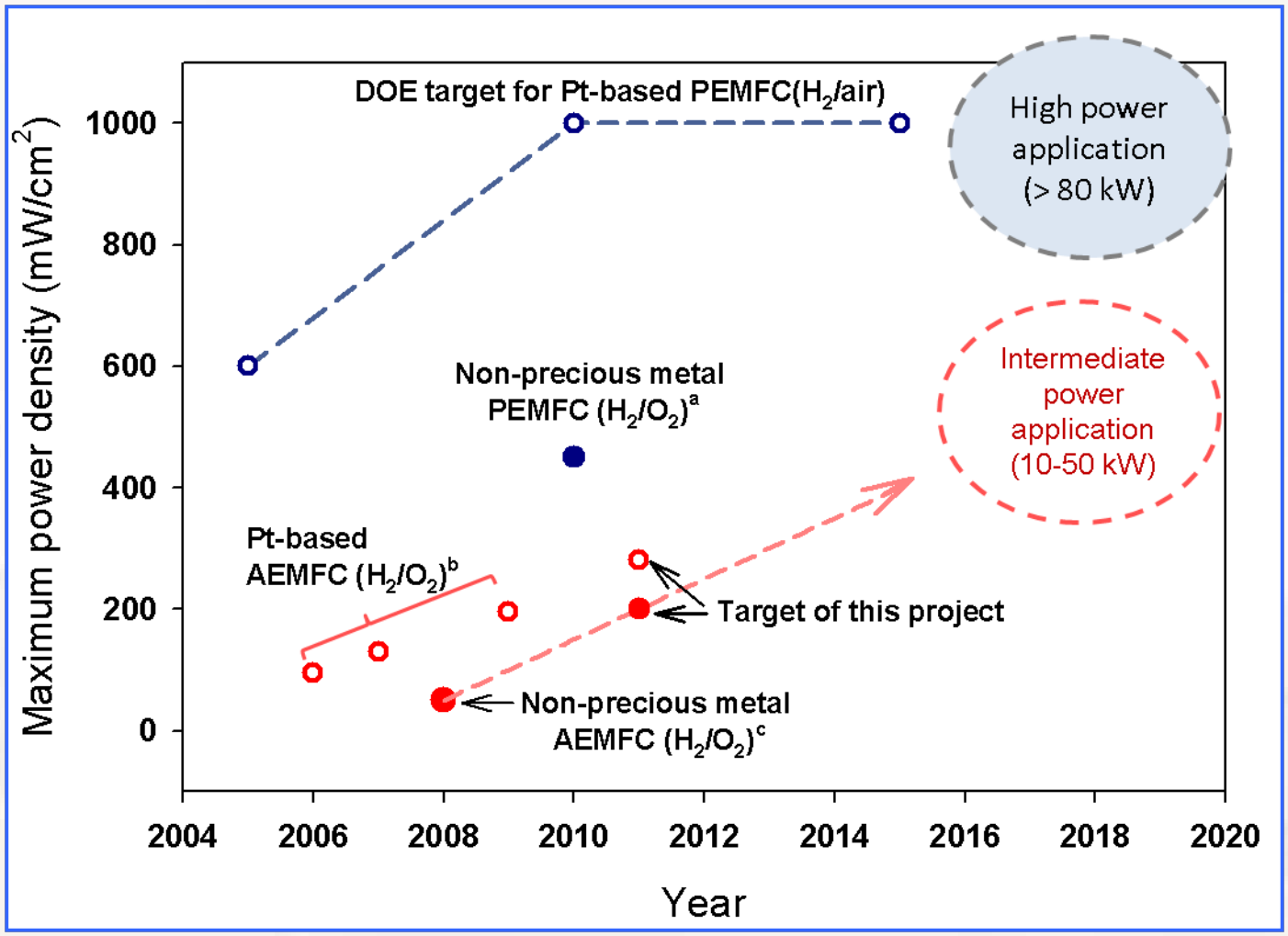
- Demonstrate an improved alkaline membrane fuel cell (AMFC) performance using novel *polymer electrolytes* and *non-precious metal catalysts*.
- *FY 10*: Anion exchange polymer electrolytes
- *FY 11*: Catalyst development and integration of AMFC MEAs

Barriers and FY 10 Status

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

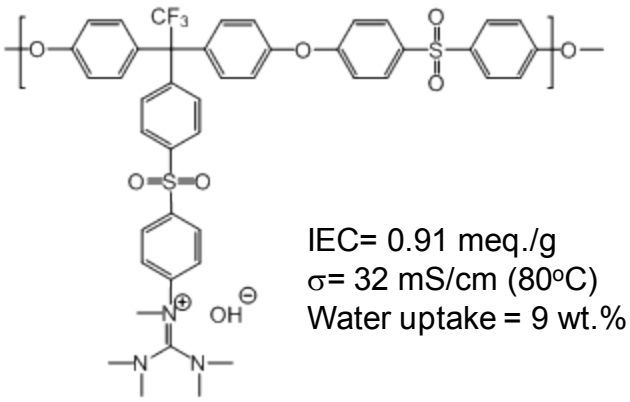


a: P. Zelenay, 2010 DOE AMR Meeting, June 7-11, 2010; **b**: Y. Yan et al., *Angewandte Chem*. **121**, 6621-6624, (2009); Varcoe et al., *Chem. Mater*. **19**, 2686-2693, (2007); Varcoe et al., *Electrochem. Comm*. **8**, 839-843, (2006); **c**: Lu et al. *PNAS*, **105**, 20611-20614, (2008);

Approach – Hydrocarbon Based Anion Exchange Membranes

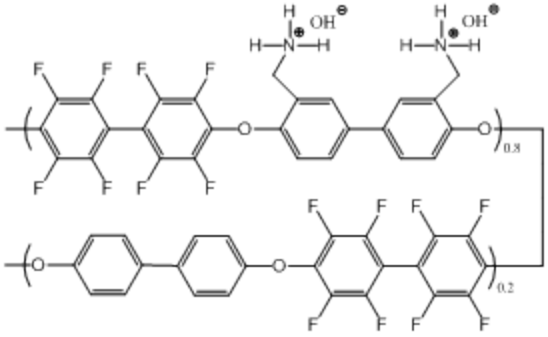
FY 10 Results

Guanidinium base homopolymer



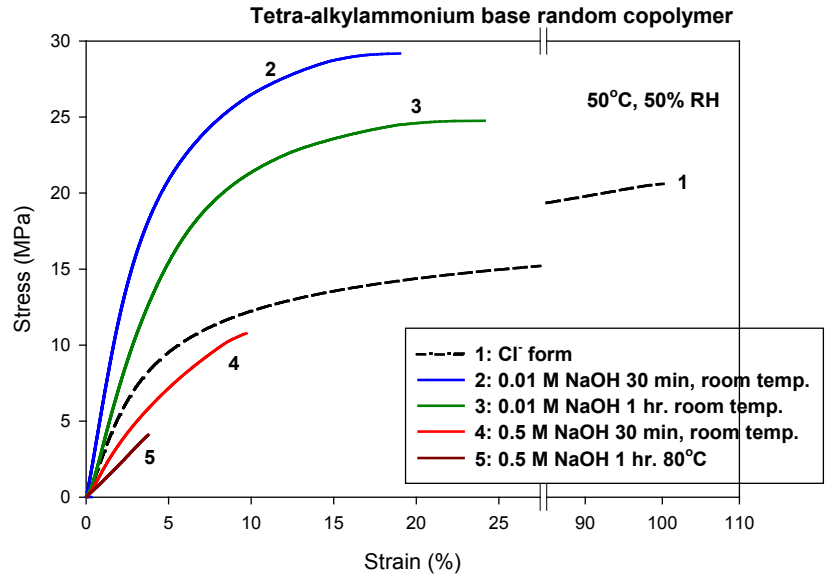
IEC= 0.91 meq./g
σ= 32 mS/cm (80°C)
Water uptake = 9 wt.%

Tetra-alkylammonium base copolymer



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

issue



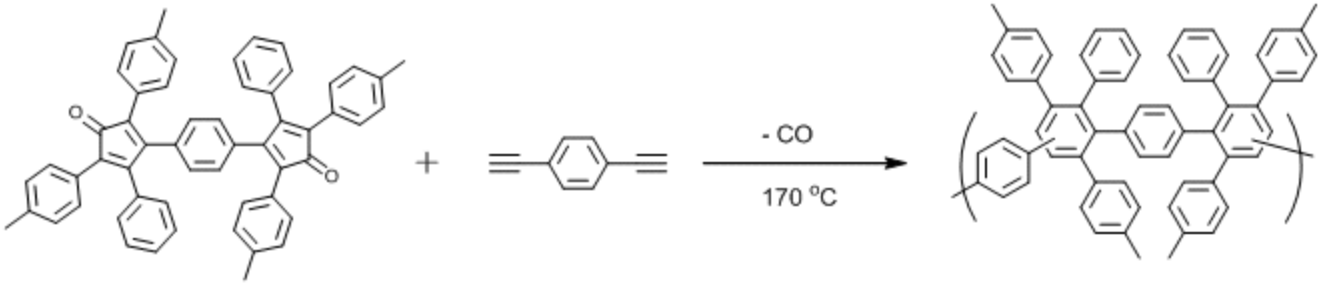
Cause of mechanical property degradation

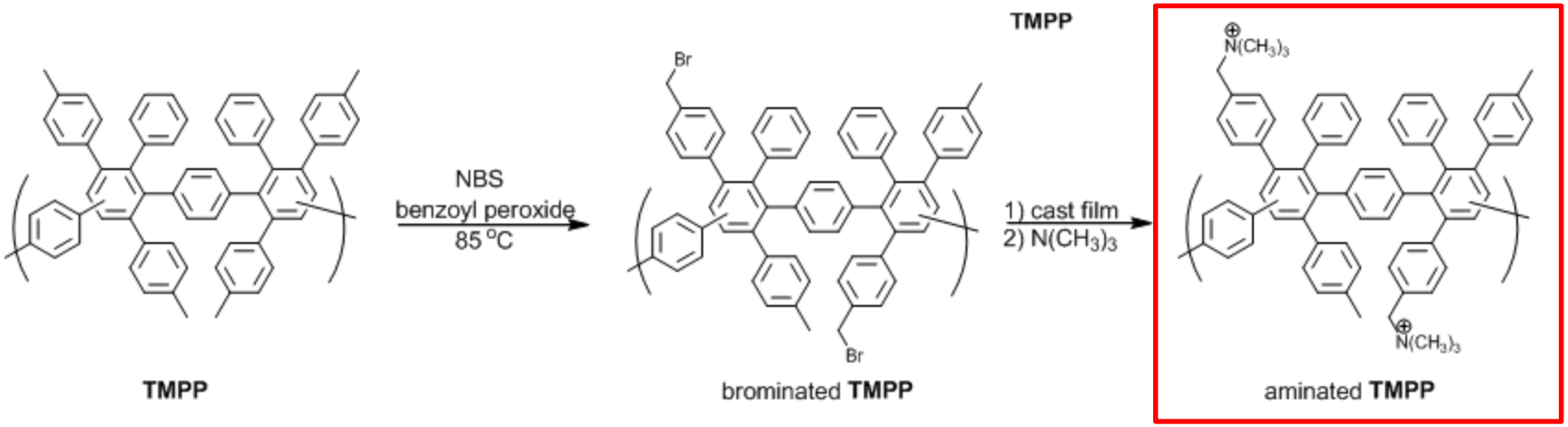
- ✓ Nucelophilic attack of OH^- to polymer backbone ether linkage
- ✓ Low electron density due to electron-withdrawing fluorine moiety

approach

Poly(phenylene) based AEM (SNL)

Synthesis of Poly(Phenylene) Anion Exchange Membranes

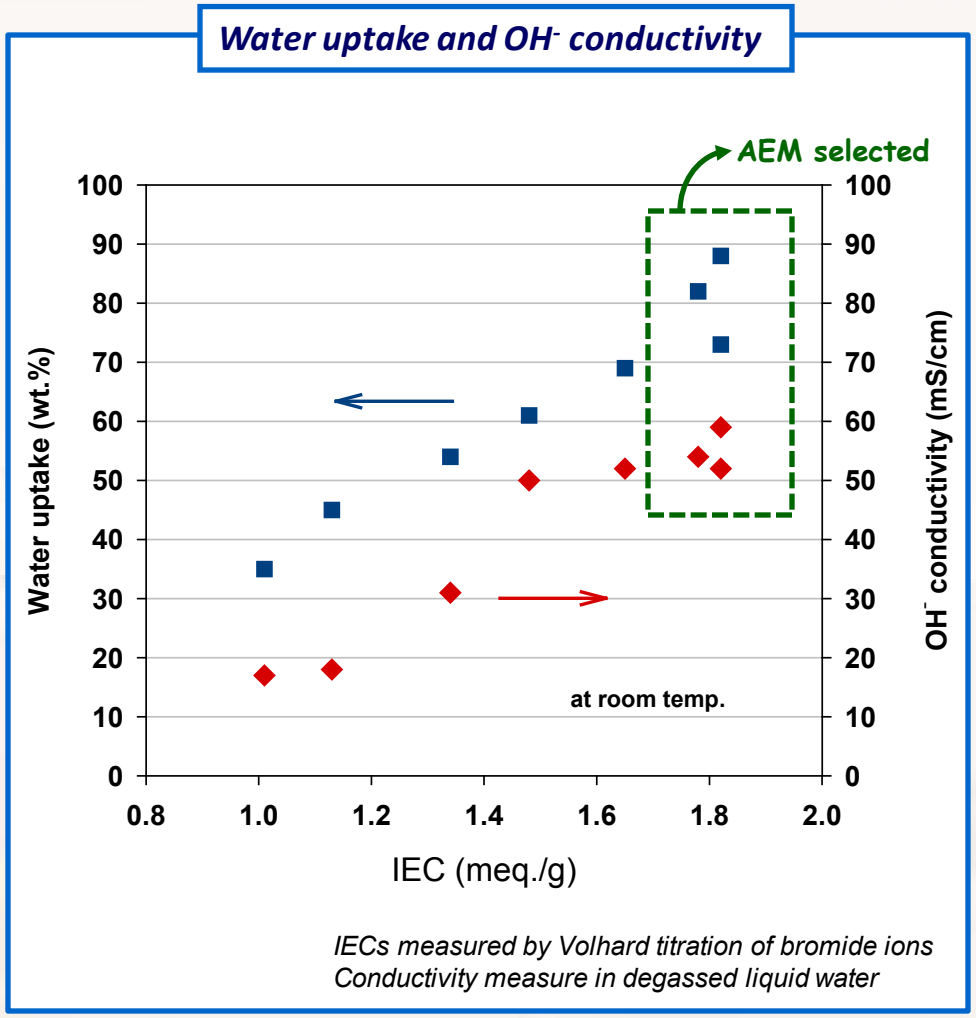




- ✓ **Extremely good chemical stability** due to the wholly aromatic structure
- ✓ **No ether or fluorine** linkages which are susceptible to nucleophilic degradation
- ✓ Number average molecular weight is ~ 35,000 gm/mol
- ✓ **Uniform distribution of tri-methyl functional groups** reduces water uptake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

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

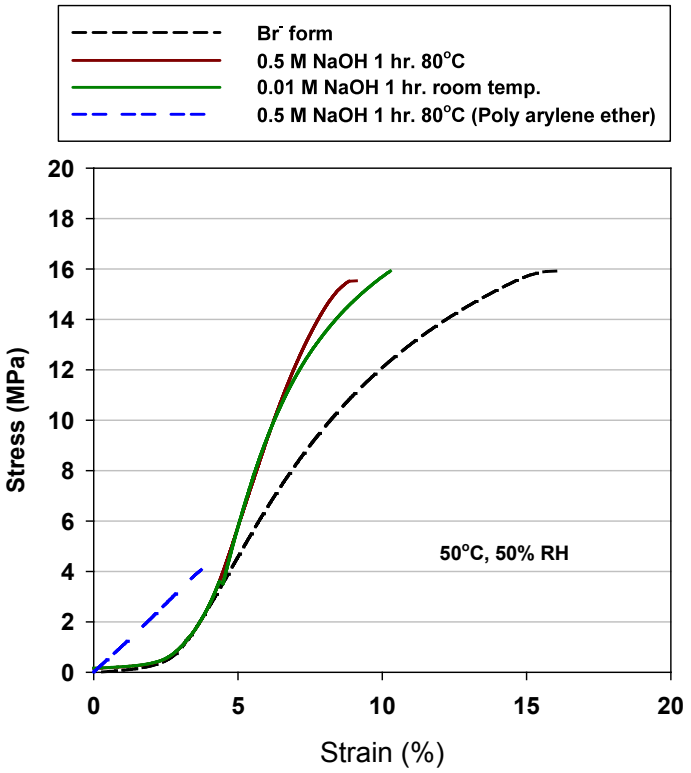
Water Uptake and Conductivity of Aminated TMPP



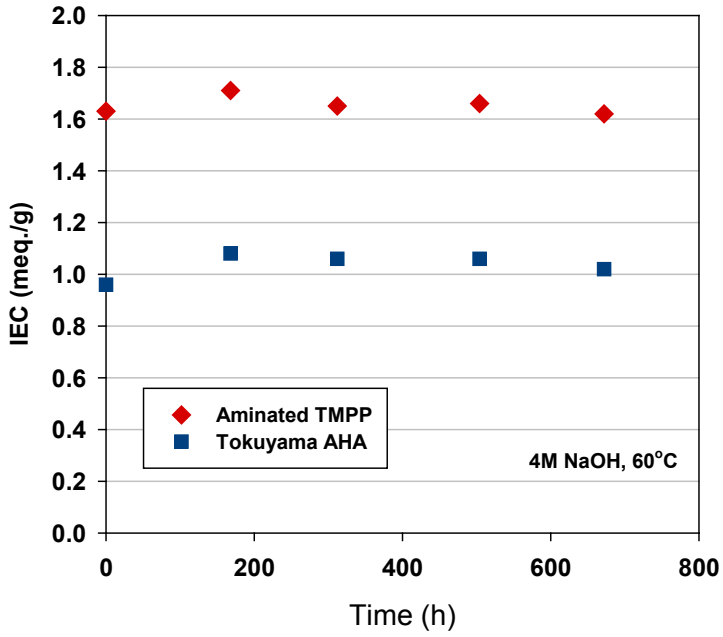
- ✓ AEM selected based on conductivity and water uptake
- ✓ Degree of functionality (number of -CH_2Br groups/repeat unit) is typically 2-2.5
- ✓ **Selected AEM meets the conductivity and water uptake target for 2011**

Mechanical Property and Stability of Aminated TMPP

Stress-strain curves



AEM stability under high pH conditions



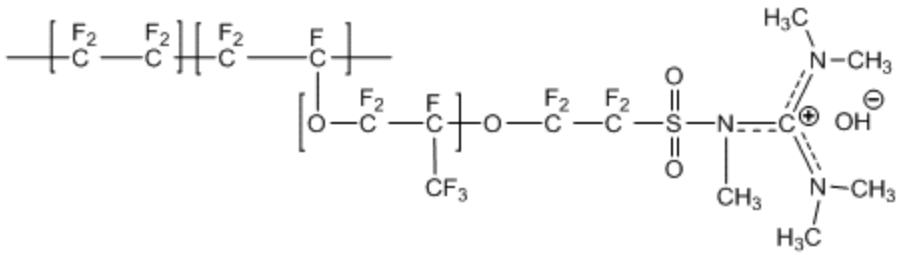
* Poly(arylene ether sulfone) with benzyl trimethylammonium Groups became too brittle to handle after 1-2 days.

- ✓ **Mechanical properties of poly(phenylene) did not change with different NaOH treatment**
- ✓ The mechanical stability of poly(phenylene)s 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

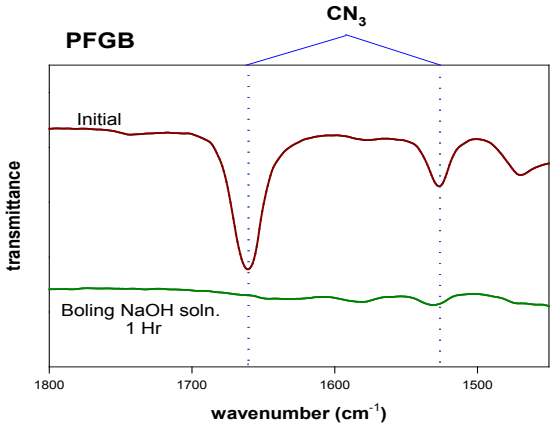
Guanidine functionalized perfluorinated ionomer



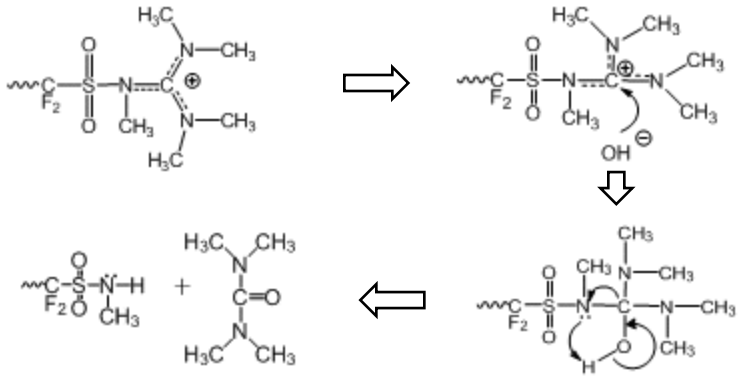
IEC= 0.9 meq./g
σ= 52 mS/cm (50°C) √
Water uptake = 15 wt.% √

issue

Poor Stability



Degradation Mechanism

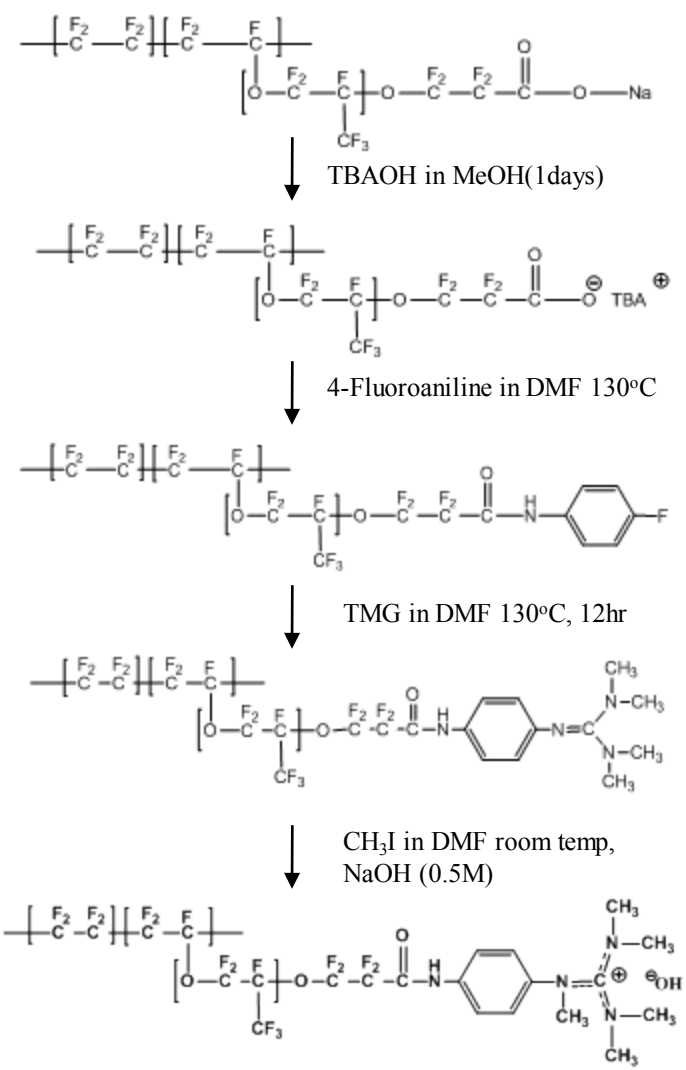


approach

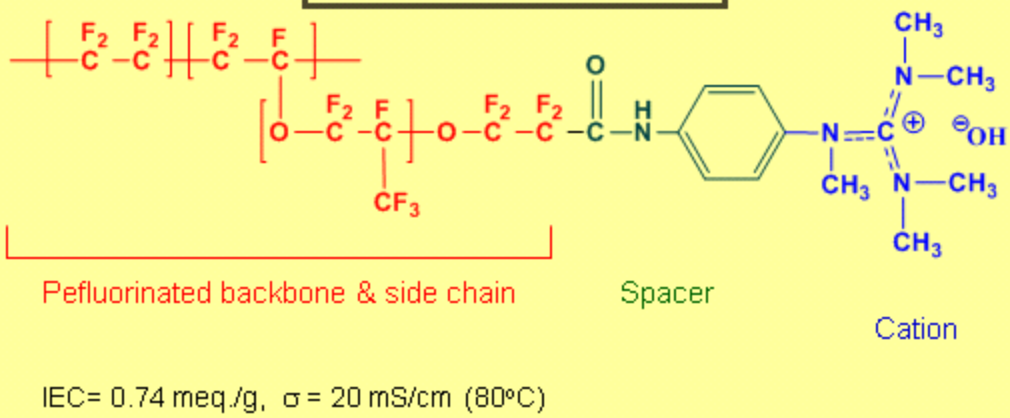
Stabilizing cation by electron donating spacer (LANL)

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**

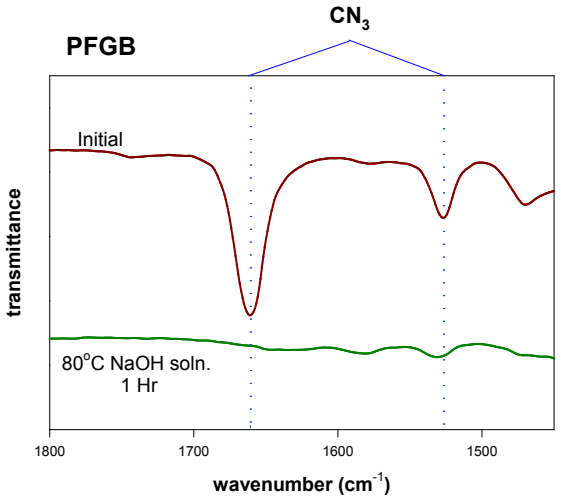
Cation

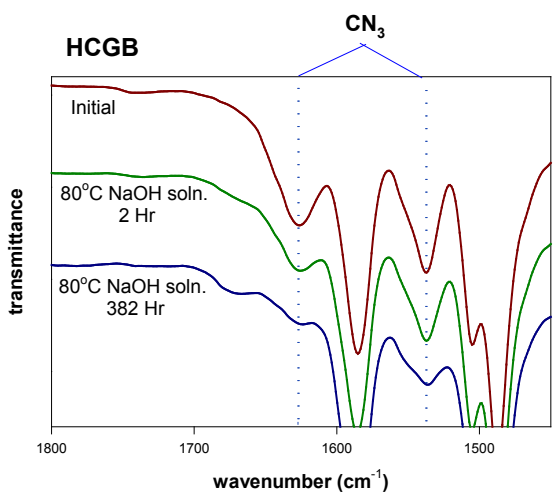
- ✓ Cation stability by resonance structure
- ✓ **Provide highly active catalyst-electrolyte interface**

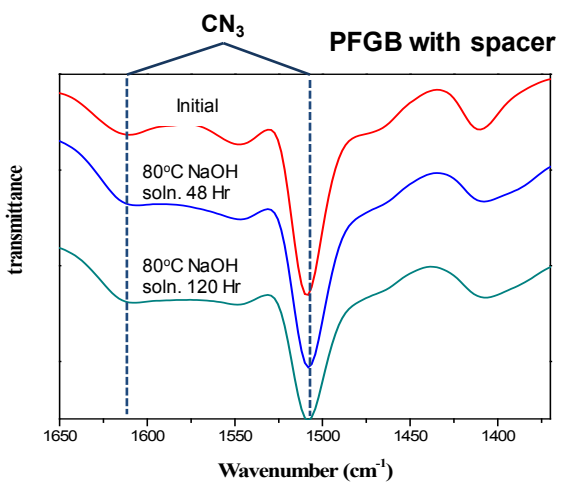
** LANL patent pending (2011)*

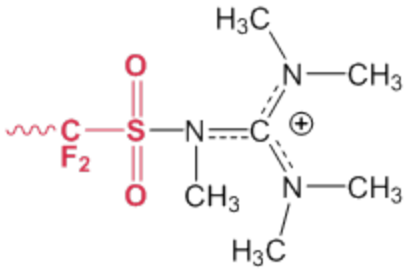
Structure analysis of these polymers is provided in the supplement slide (slide no. 24)

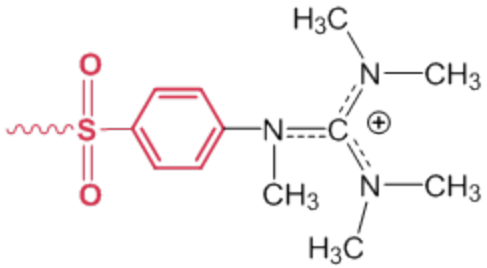
Effect of Electron Density on Cation Stability

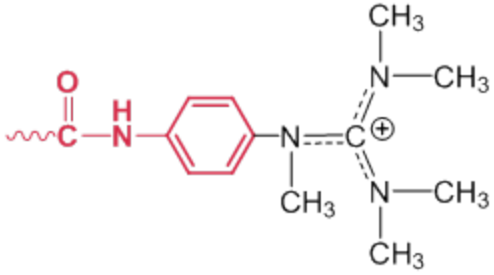












Local electron density & stability

- ✓ **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.

↓

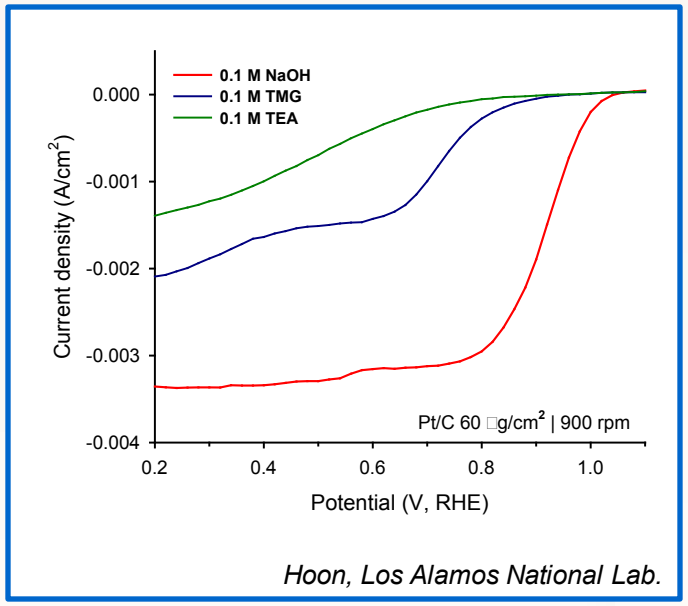
ORR activity also strongly depends on the type of electro-catalysts (see right Fig)

↓ approach

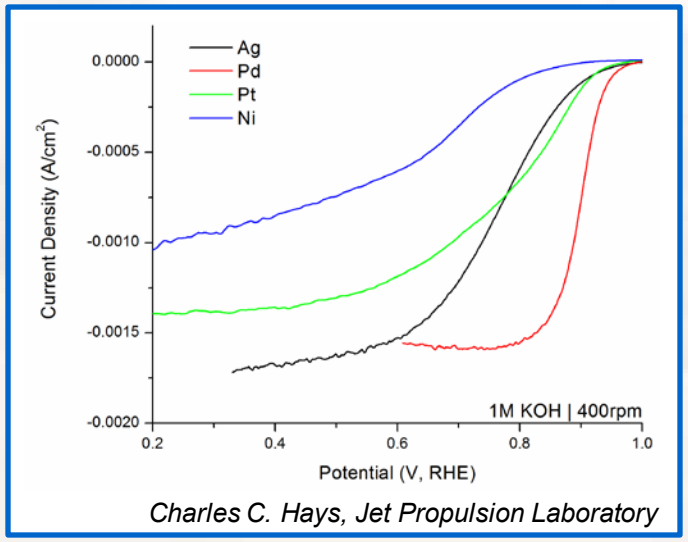
Understanding ORR activities of different cation and alternative catalysts

↓

Development of highly active ORR catalysts



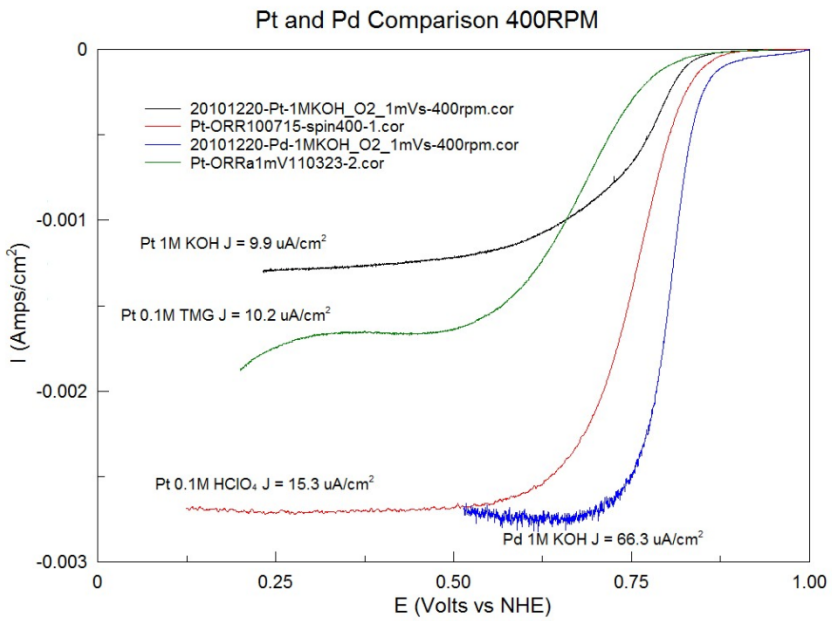
Hoon, Los Alamos National Lab.



Charles C. Hays, Jet Propulsion Laboratory

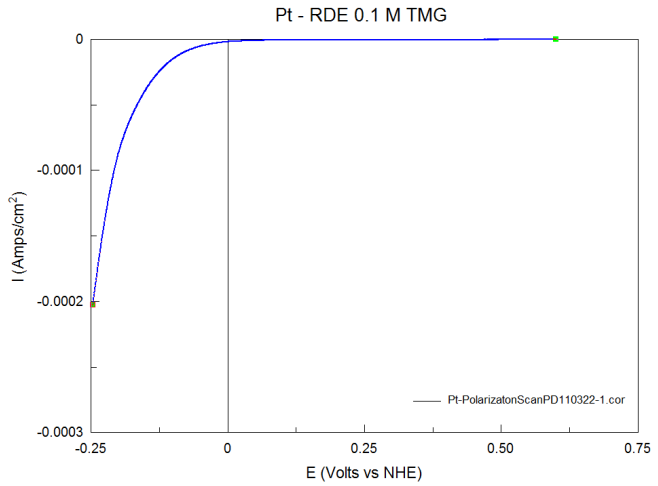
ORR and HER Activities of Pt and Pd Catalysts in TMG

ORR Activity



ORR Catalyst	Electrolyte	*i* at 0.9 V (μA/cm²)
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

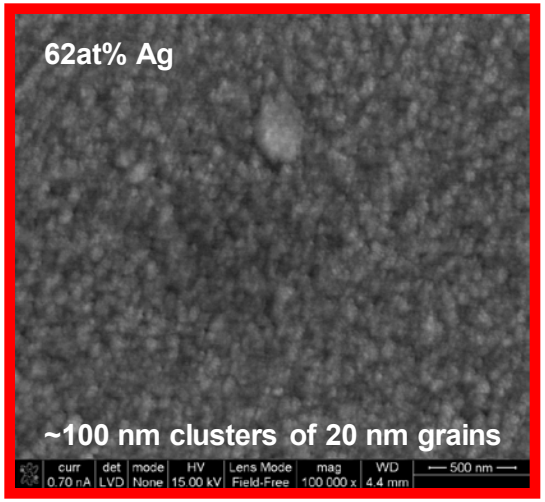
HER Activity

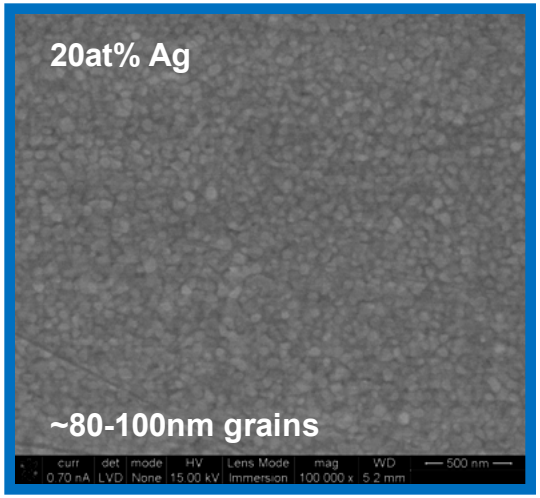


- ✓ Performed electrochemical tests via RDE on elemental electrodes in 0.1 M TMG + H_2O electrolyte
- ✓ Pt, Pd, tested so far, ORR current densities in TMG rival those in KOH
- ✓ RDE measurements of the HER on Pt in 0.1 M TMG indicates a good catalytic activities at the interface with TMG electrolytes

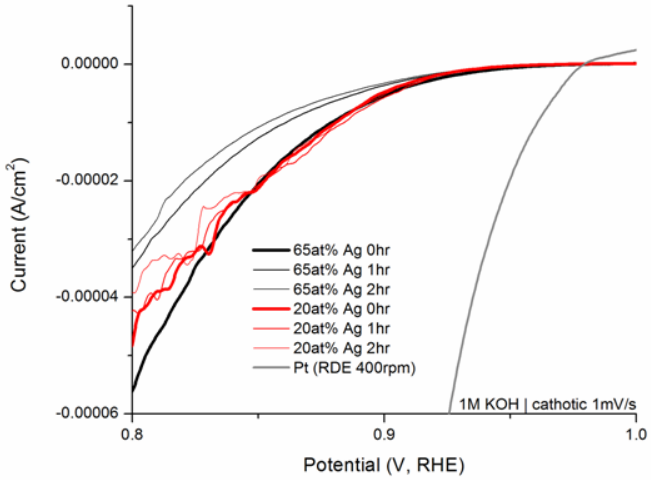
Synthesis of Ag-Pt based Binary Electro-catalysts

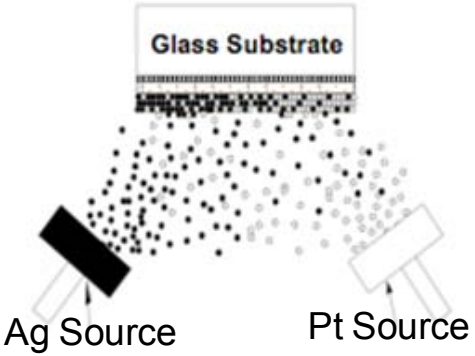
Thin film synthesis by co-evaporation





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



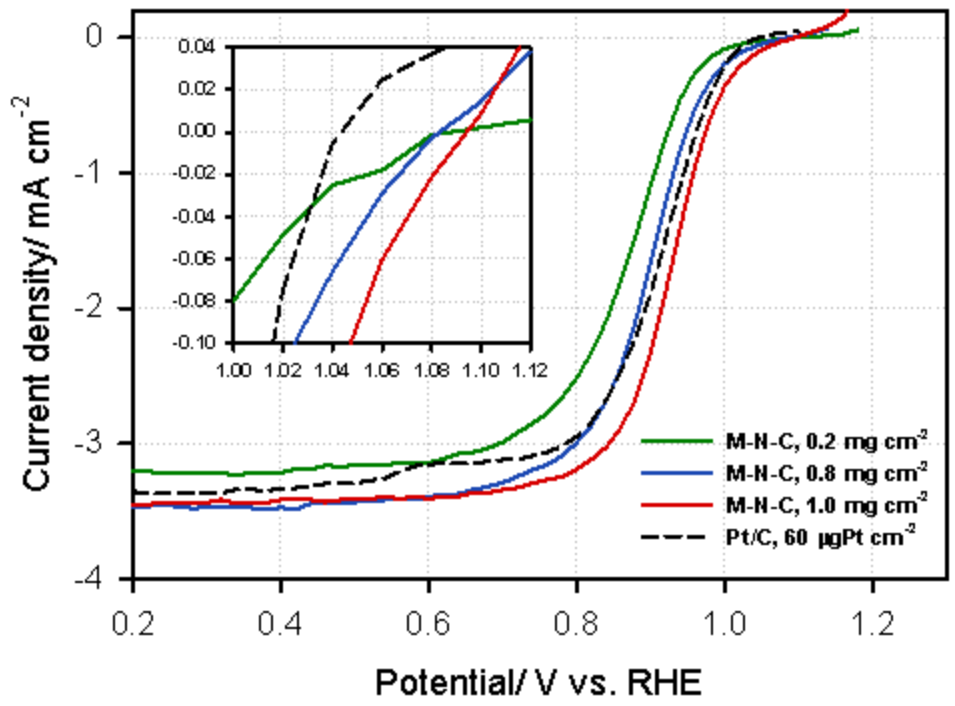


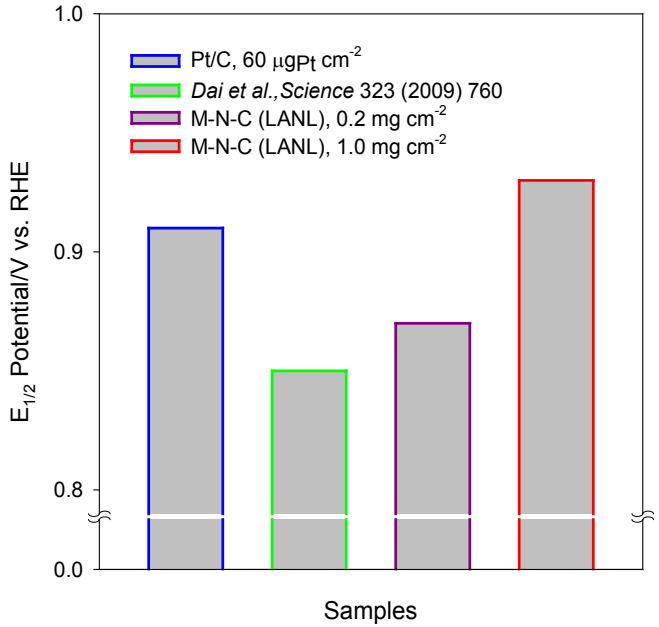
dc-Magnetron sputtering: Pt, Ni, Ag targets; Pdep ~ 10^{-7} Torr

- ✓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 course 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

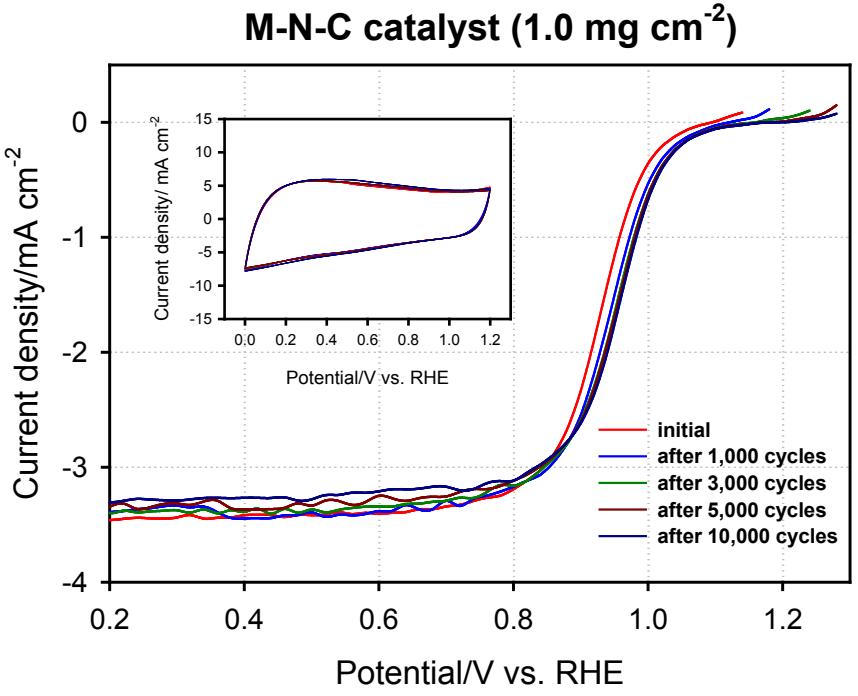
RDE: *0.1 M NaOH; 900 rpm; room temperature; steady state potential (OCP, 120 s, 20 mV steps, 25 s/step)*

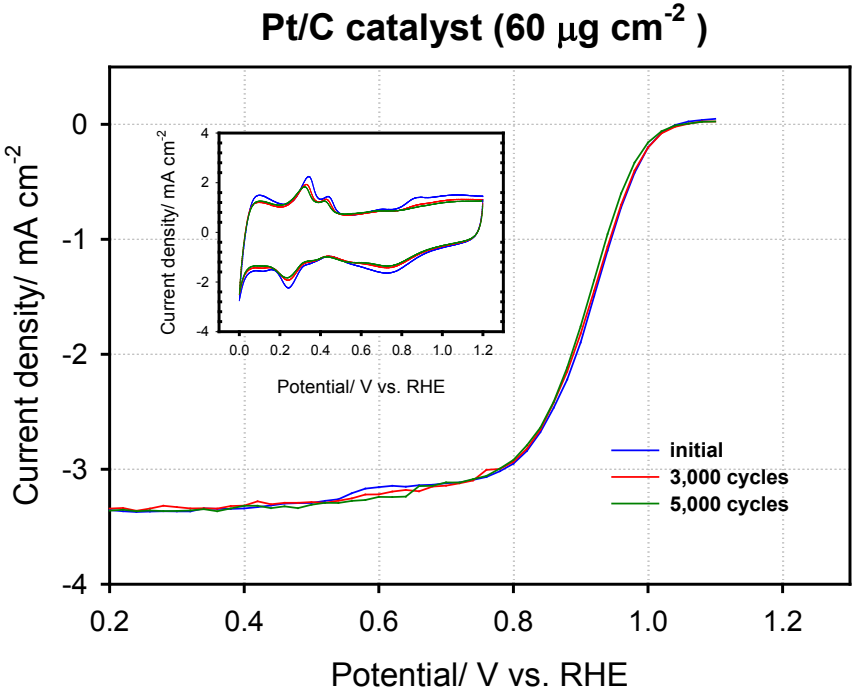




- ✓ Dai et al. reported high activity of N doped carbon nanotube catalyst in alkaline solutions (supplementary slide no 26)
- ✓ Highly-active and durable M-N-C catalyst was prepared using commercial carbon black rather than expensive CNT as a starting material
- ✓ **Excellent ORR activities with M-N-C 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

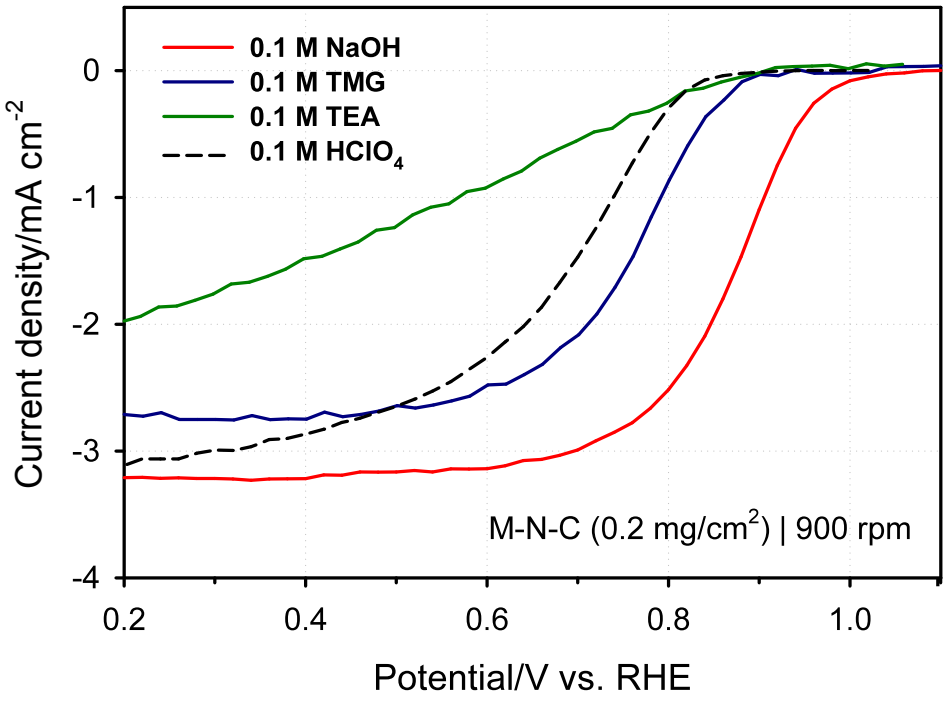




RDE: *0.1 M NaOH; 900 rpm; room temperature; steady state potential (OCP, 120 s, 20 mV steps, 25 s/step); cycling condition, 0.6 to 1.0 V, 50 mV s^{-1} in saturated O_2*

- ✓ **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**

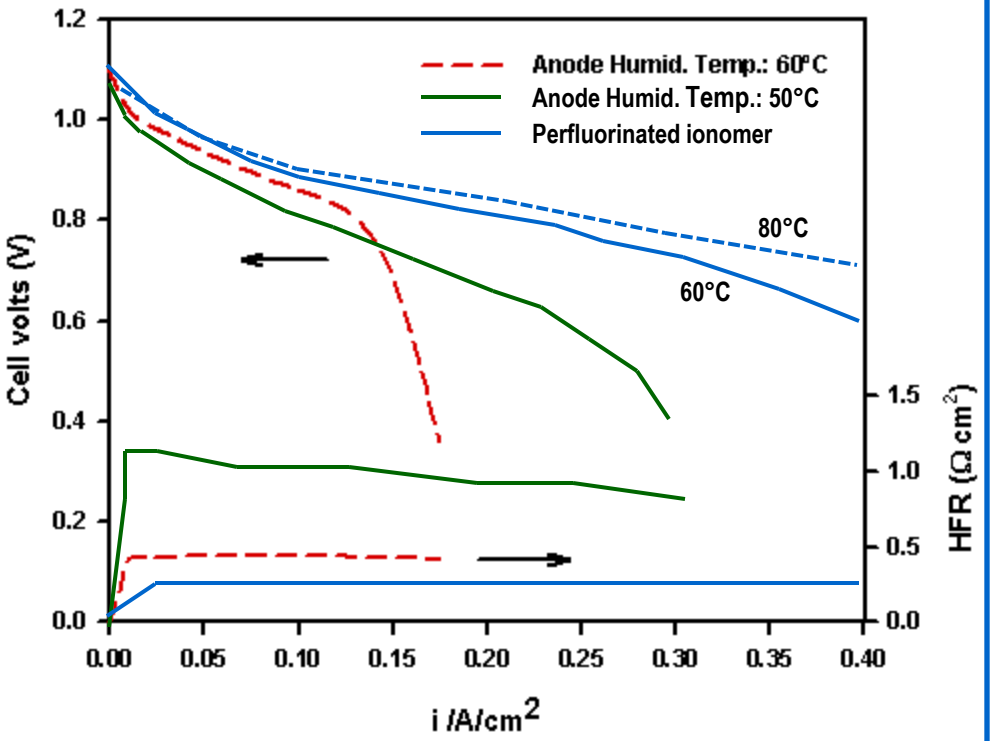
ORR activities of M-N-C Catalysts in Different Electrolytes



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 μg/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.

H_2/O_2 Performance of Alkaline Membrane Fuel Cells



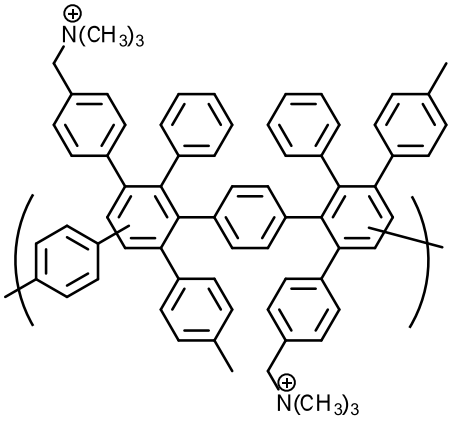
Catalyst: **Pt** black (3 mg/cm^2), Cell temp. 60° C, Cathode humidification: 60° C, back pressure: 30 psig, high stoic. Catalyst: ionomer weight composition (9:1, not optimized); MEAs were prepared from direct painting.

Membrane/ionomer

IEC = 1.8 meq./g

σ= 55 mS/cm

Thickness: 50 μm



aminated **TMPP**

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

→ Mass transport issue due to flooding

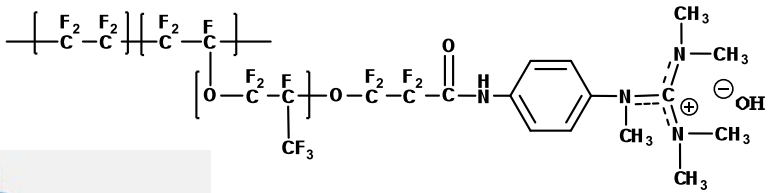
→ Possibly poor cation – catalyst structure

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/cm^2 (at 80°C)

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

Anion Exchange Membrane: Aminated poly(phenylene)		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
Anion Exchange Ionomer: Guanidinium functionalized perfluorinated polymer		**Target**	**March 1, 2010**	**March 1, 2011**
Conductivity (mS/cm)		> 50	40	20[b]
Chemical stability in NaOH soln. (h)		> 500	< 1	> 120
ORR catalyst: M-N-C catalyst (0.2 mg/cm²)		**Target**	**March 1, 2010**	**March 1, 2011**
$E_{1/2}$ potential (V)	NaOH or KOH	> 0.85	-	0.87
	TMG	> 0.75	-	0.77
AMFC performance [d]		**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	-	-

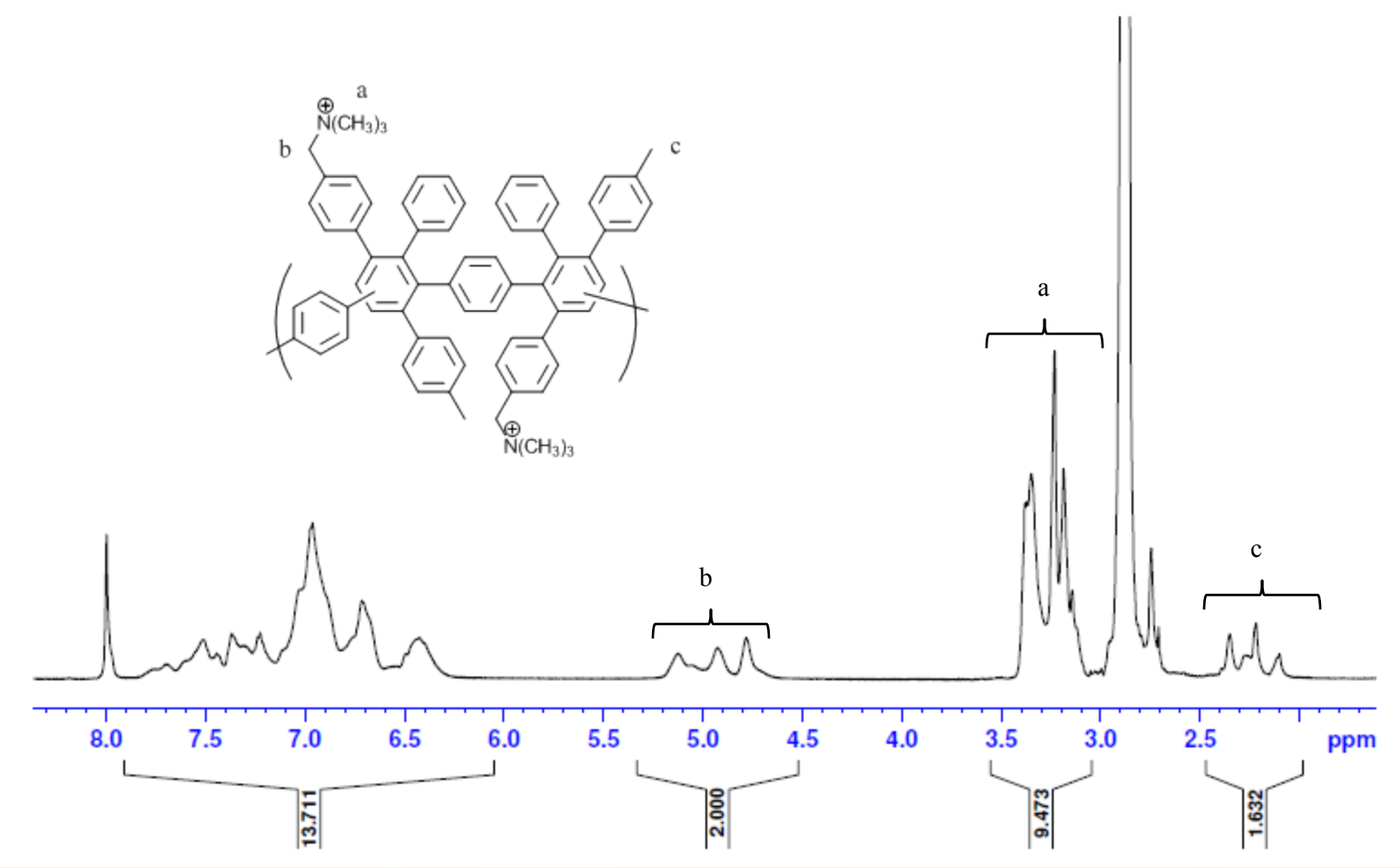
[a] Measured at 80°C: [b,c] Measured at 30°C; [d] at 60°C

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)**
  - H_2/O_2 and H_2/air conditions
  - Durability test (target: 500 h with < 10% performance loss)

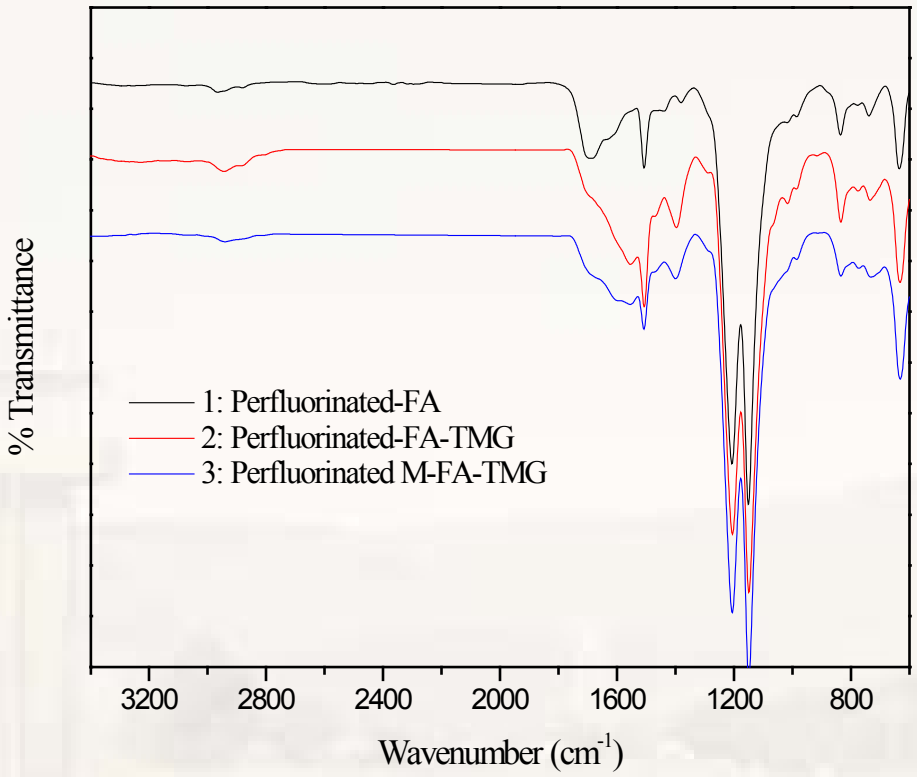
Technical Back-up Slides

^{1}H NMR of Aminated TMPP

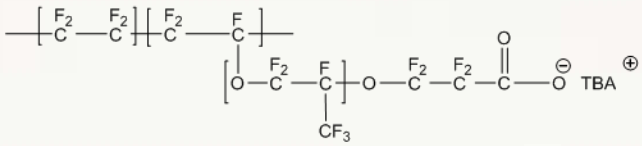


Protons a, b, and c are represented by groups of peaks due to varying probabilities for methyl and ammonium groups at each of four positions on each repeat unit.

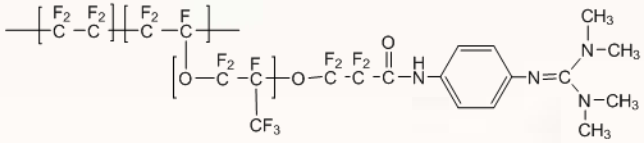
FT-IR of PFGB



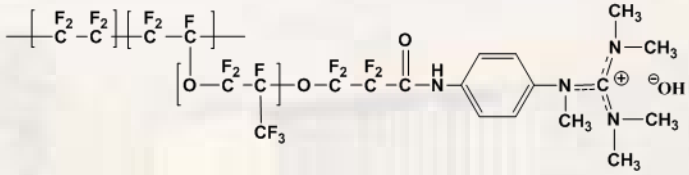
1. Perfluorinated-FA



2. Perfluorinated-FA-TMG

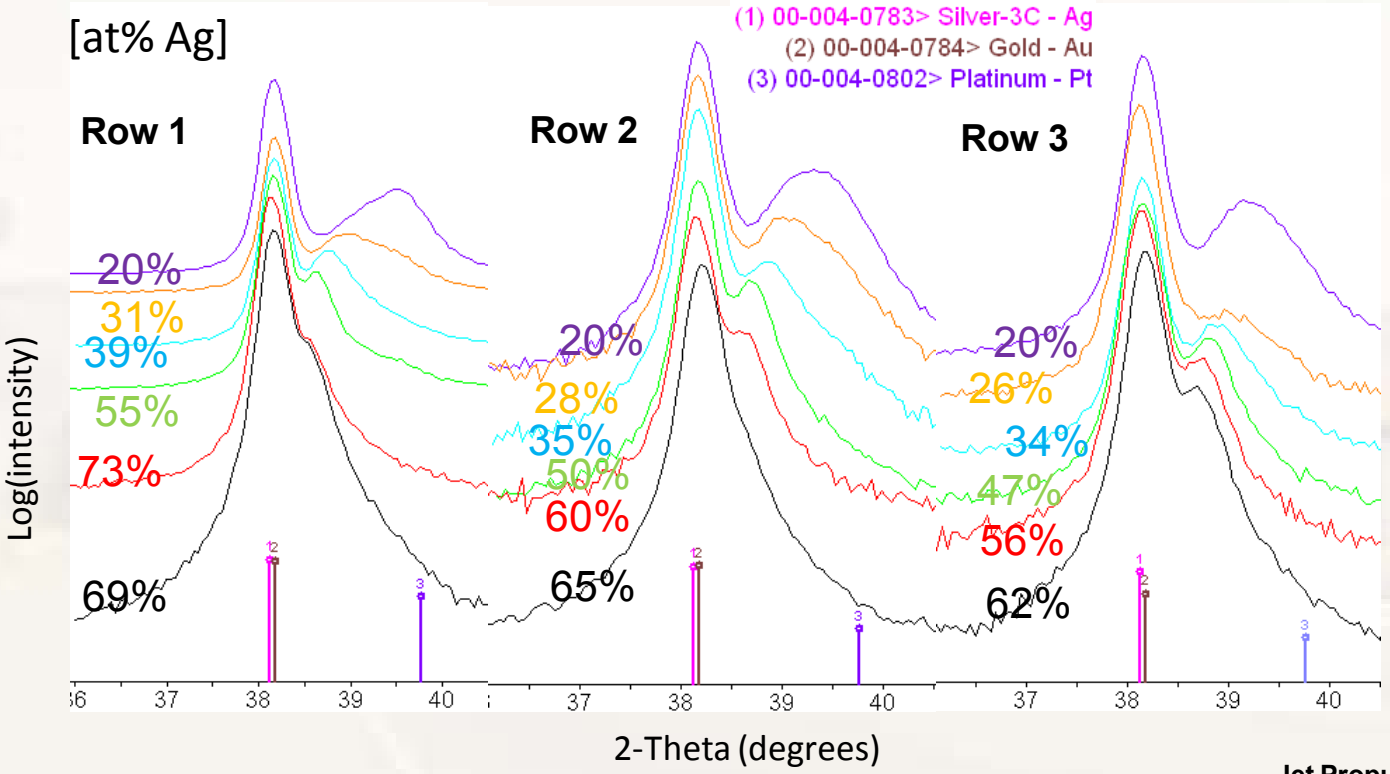


3. Perfluorinated M-FA-TMG



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



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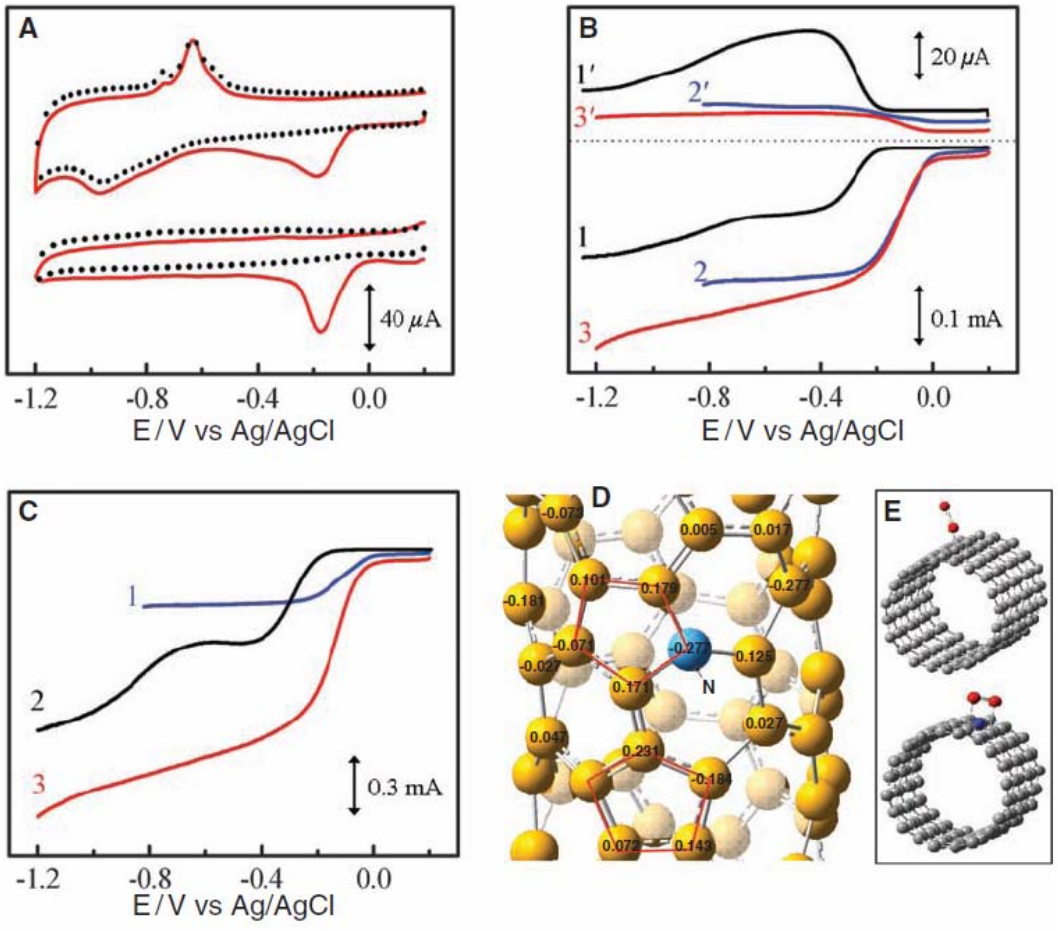
California Institute of Technology
Pasadena, California

ORR Enhancement with N Doping into Carbon in Alkaline Media



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