Fuel Cell Projects Kick-off Meeting
Washington, DC – September 28, 2010

Advanced Materials and Concepts for Portable Power Fuel Cells

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Overview

Timeline

- **Start date:** September 2010
- **End date:** Four-year duration

Budget

- **Total funding estimate:**
  - DOE share: $3,825K
  - Contractor share: $342K
- **FY10 funding received:** $250K
- **FY11 funding estimate:** $1,000K

Barriers

- **A. Durability** (catalyst; electrode)
- **B. Cost** (catalyst; membrane; MEA)
- **C. Electrode Performance** (fuel oxidation kinetics)

Partners – Principal Investigators

Brookhaven National Laboratory

BROOKHAVEN NATIONAL LABORATORY – Radoslav Adzic

University of California, Riverside

UC RIVERSIDE UNIVERSITY OF CALIFORNIA – Yushan Yan

Virginia Tech

Virginia Tech 1872 VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY – James McGrath

Johnson Matthey Fuel Cells

JM Johnson Matthey Fuel Cells the power within – Nadia Permogorov

Smart Fuel Cell Energy

SFC ENERGY – Verena Graf

Oak Ridge National Laboratory

ornl – Karren More

Relevance: Objective & Targets

Objective: Develop advanced materials (catalysts, membranes, electrode structures membrane-electrode assemblies) and fuel cell operating concepts capable of fulfilling cost, performance, and durability requirements established by DOE for portable fuel cell systems; assure path to large-scale fabrication of successful materials

Table 3.4.7 Technical Targets: Consumer Electronics (sub-Watt to 50-Watt)				
Characteristic	**Units**	**2005 Status** [a, b]	**2006**	**2010**
Specific power	W / kg	20	30	100
Power density	W / L	20	30	100
Energy density	Wh / L	300	500	1,000
Cost	$ / W	40 [c]	5	3
Lifetime	hours	>500	1,000	5,000

Project technical targets:

- **System cost target:** $3/W
- **Performance target:** Overall fuel conversion efficiency (η_Σ) of 2.0-2.5 kWh/L

  For methanol fuel:

  (1) 2.0-2.5 kWh/L $\rightarrow$ η_Σ = 0.42-0.52 (1.6-2.0× improvement over the state of the art, ~ 1.250 kWh/L)

  (2) If η_{fuel} = 0.96, η_{BOP}= 0.90, V_{th}=1.21 (at 25°C)

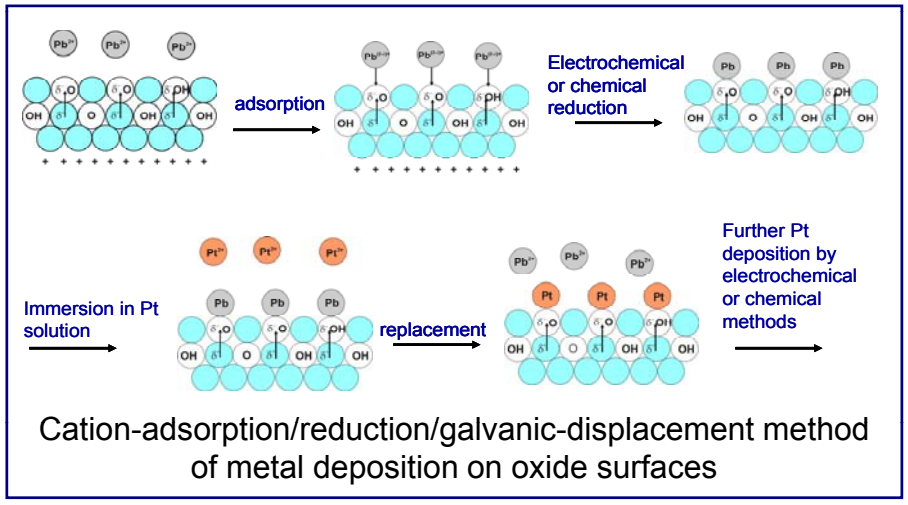
  $\mathbf{V_{cell} = V_{th}\,[\eta_\Sigma\,(\eta_{fuel}\,\eta_{BOP})^{-1}] = 0.6\text{–}0.7\ V}$ **The ultimate project goal!**

Approach: Focus Areas

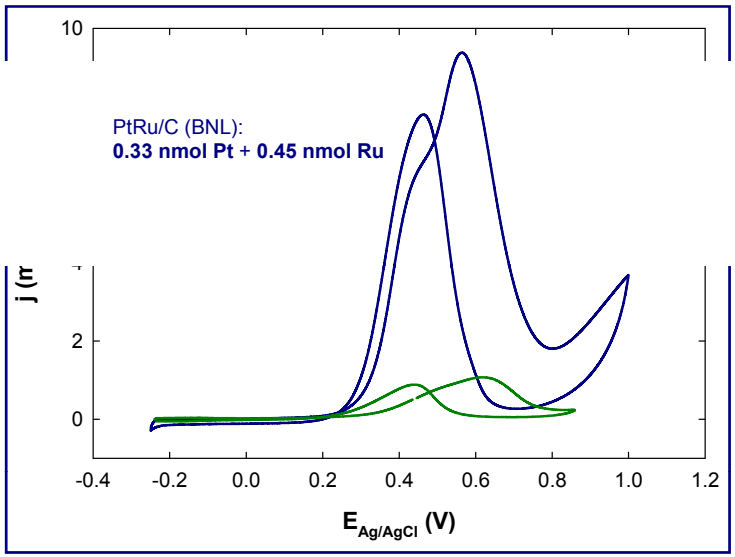
- **DMFC anode research:**
  - catalysts with improved activity and reduced cost (BNL, JMFC, LANL)
  - development of catalysts with improved durability (LANL, JMFC)
- **Alternative fuels for portable fuel cells:**
  - ethanol oxidation electrocatalysis (BNL, LANL)
  - dimethyl ether research (LANL)
- **Innovative electrode structures for better activity and durability** (UCR)
- **Hydrocarbon membranes for lower MEA cost and enhanced fuel cell performance** (VT, LANL)**:**
  - block copolymers
  - copolymers with cross-linkable end-groups
- **Characterization; performance and durability testing; multi-cell device:**
  - advanced materials characterization (ORNL, BNL, LANL)
  - MEA performance testing (LANL, JMFC, SFC)
  - durability evaluation (LANL, JMFC, SFC)
  - five-cell stack (SFC)

DMFC Anode Research: Activity

- **DMFC:** V_{th}=1.21 V (at 25°C), fuel specific energy 6.1 kWh/kg
- $CH_3OH + 2H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ $\quad E° \cong 0.02$ V (at 25°C)
- **Reduction of methanol-oxidation overpotential through atomic-level control of PtRu nanoparticle synthesis:**
  - optimal Pt-atom ensembles for MeOH adsorption and abstraction of H atoms
  - adequate Ru coverage for providing OH and O species for CO oxidation
  - submonolayer of Pt on Ru nanoparticles through galvanic replacement of Cu adlayers
- **Catalysts on oxide supports** (e.g., NbO_2, SnO_2, Magnéli phases)**:**
  - cation-adsorption/reduction/galvanic-displacement method
  - significant reduction in Pt loading expected

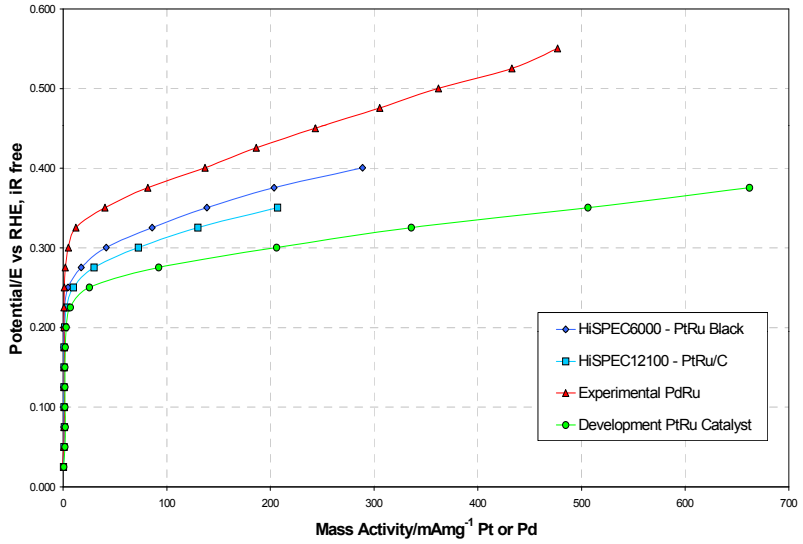


Cation-adsorption/reduction/galvanic-displacement method of metal deposition on oxide surfaces

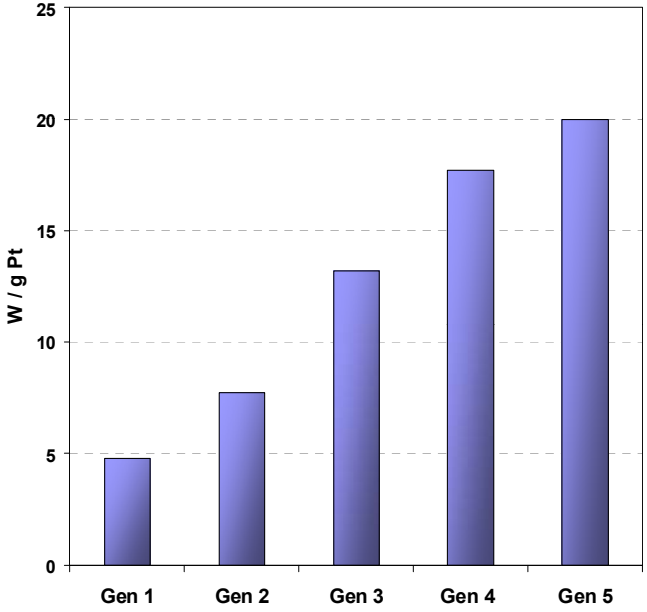


DMFC Anode Research: Activity

- **New PtRu catalysts for further thrifting of the Pt content:**
  - new formulations
  - different supports
  - performance referenced to Johnson Matthey's HiSPEC® 12100 catalyst



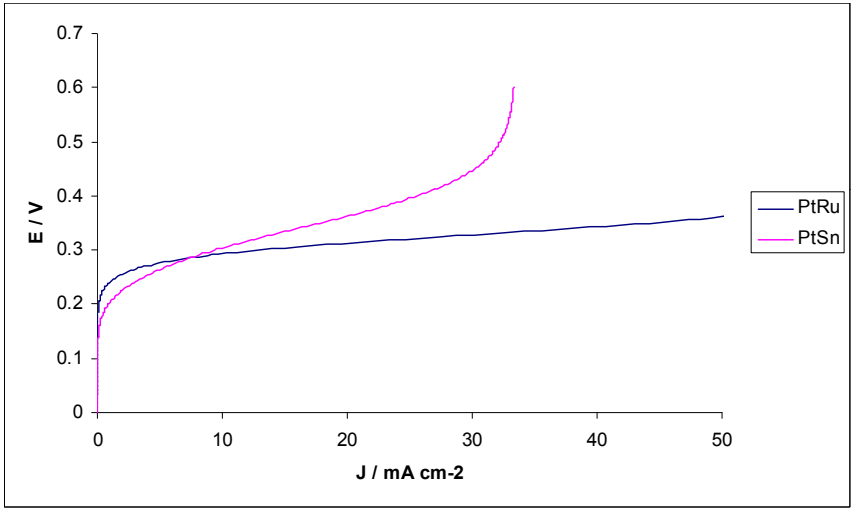
Anode polarization plots (*iR*-corrected) with various JMFC's catalysts (1.0 M MeOH, 80°C)



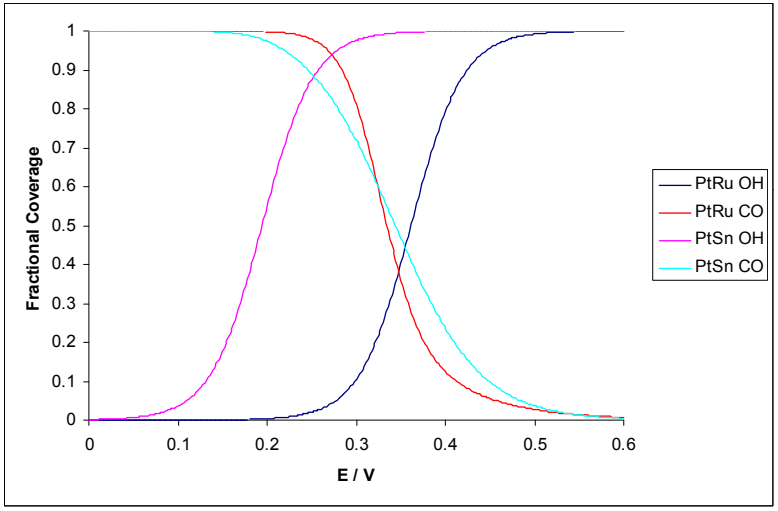
Evolution of JMFC's DMFC MEA

DMFC Anode Research: Activity

- **PtSn catalysts:**
  - PtSn catalysts showing lower onset potential for MeOH oxidation than PtRu, however, performing below PtRu at high current densities
  - model indicating OH formation on PtSn at lower potentials than on PtRu but slow decrease in CO coverage with potential (PtRu a better catalyst at higher potentials)
  - assess scope for exploiting the lower onset potentials of PtSn for methanol oxidation

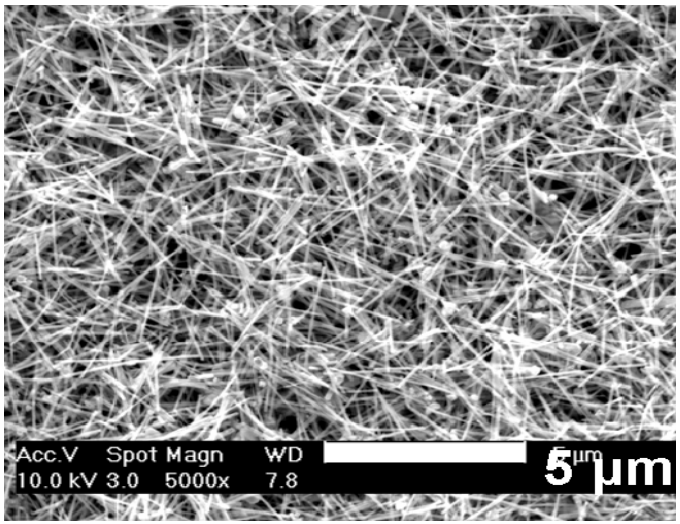


Anode polarization plots

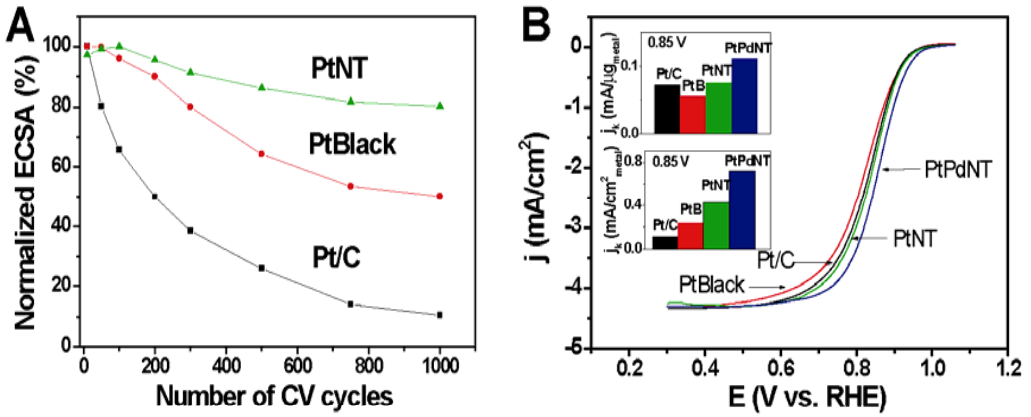


OH and CO coverage modelling

DMFC Anode Research: Innovative Nanostructures



SEM image of supportless Pt nanotubes (PtNT)



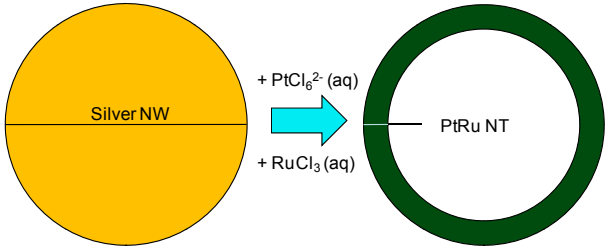
(A) ECSA loss of Pt/C (E-TEK), Pt black (E-TEK) and PtNT under cycling from 0 to 1.3 V (*vs.* RHE) at 50 mV/s in Ar-purged 0.5 M H_2SO_4 at 60°C; 50 mV/s scans between. **(B)** ORR polarization plots of Pt/C, Pt black, PtNT and PdPtNT in O_2-saturated 0.5 M H_2SO_4. Inset: Mass activity and specific activity of Pt/C, Pt lack, PtNT and PtPdNT catalysts at 0.85 V.

- **Supportless Pt nanotubes already synthesized**
- **Pt nanotubes showing improved cycling durability compared to nanoparticle catalysts and possibly higher activity**
- **Approach also applicable to the cathode**
- **Initial focus on PtRu catalysts**

DMFC Anode Research: Innovative Nanostructures

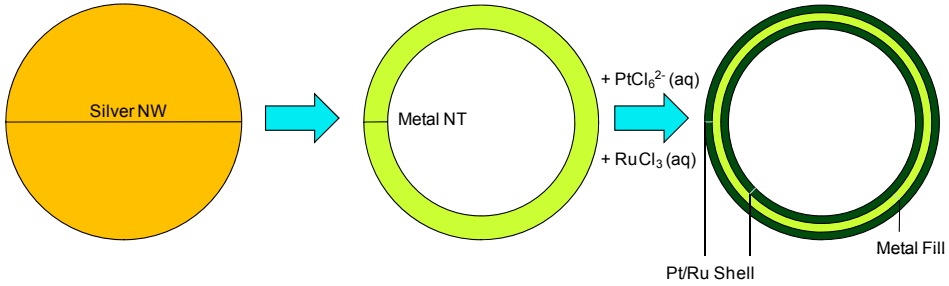
- **PtRu nanotubes**
  - Complete displacement of Ag with Pt, Ru
  - Displacement reactions: $PtCl_6^{2-}$ (aq) + 4 Ag (s) → Pt (s) + 2 Cl^- (aq) + 4 AgCl (s)

    Ru^{3+} (aq) + 3 Cl^- (aq) + 3 Ag (s) → Ru (s) + 3 AgCl (s)



Synthesis of PtRu nanotubes

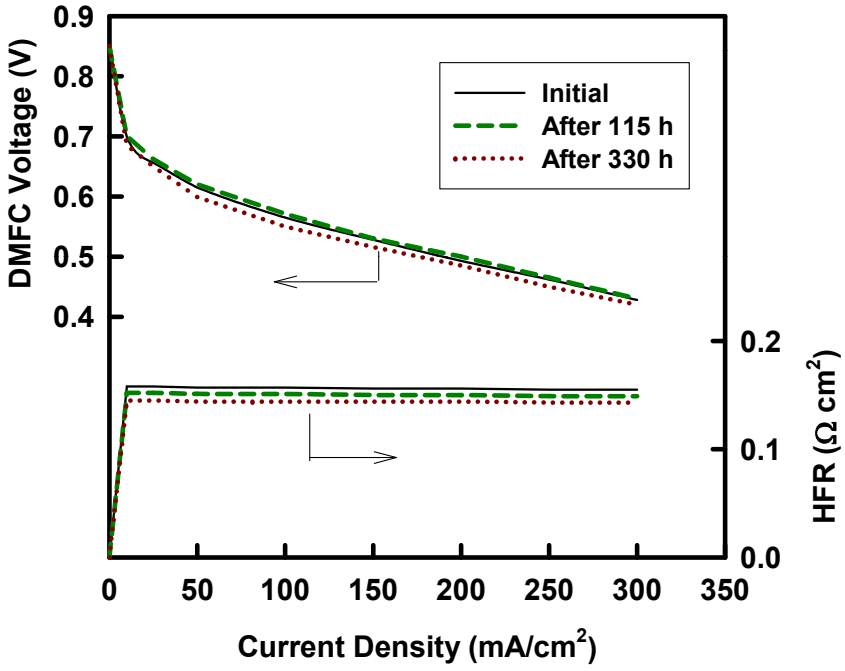
- **Metal nanotube substrate**
  - Inexpensive metal source used as template
  - Partial displacement of metal with Pt, Ru
  - Form PtRu alloy on the entire metal nanotube substrate



Synthesis of PtRu nanotubes with the aid of a metal nanotube substrate

DMFC Anode Research: Durability

- **Limiting Ru crossover as a major cause of DMFC performance loss** (mitigation methods to be applied to viable Ru-containing anode catalysts developed in the project)**:**
  - high temperature cure of anode catalyst
  - pre-leach of unstable Ru phase(s)
  - use of low-permeability membranes
  - electrochemical method of limiting ruthenium – **main focus!**



Performance of an electrochemically-treated MEA after different times of DMFC operation; 80°C

Alternative Fuels: Dimethyl Ether and Ethanol

Dimethyl ether:

- **DME fuel cell:** V_{th}=1.15 V (at 25°C), fuel specific energy 8.0 kWh/kg
- $C_2H_3OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$ $E° \cong 0.08$ V (at 25°C)
- **High fuel vapor pressure (5.9 atm at 25°C) conducive to passive fuel delivery**
- **Oxidation kinetics strongly dependent on temperature making DME a more attractive fuel at high temperatures than methanol**
- **Research:**
  - enhancement of DME oxidation through acceleration of the dissociative DME adsorption
  - effect of Pt-to-Ru ratio on the rate of DME oxidation to CO_2 (from 10:1 to 1:3)
  - the role of a third metal or non-metallic component (e.g. SnO_2)
  - go/no-go decision after Q5

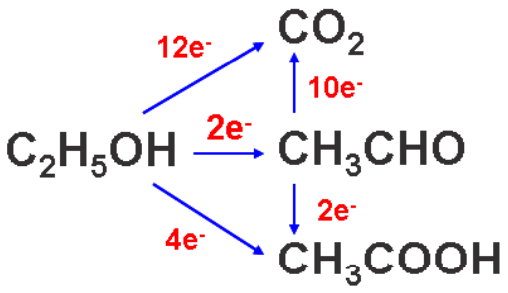
Ethanol:

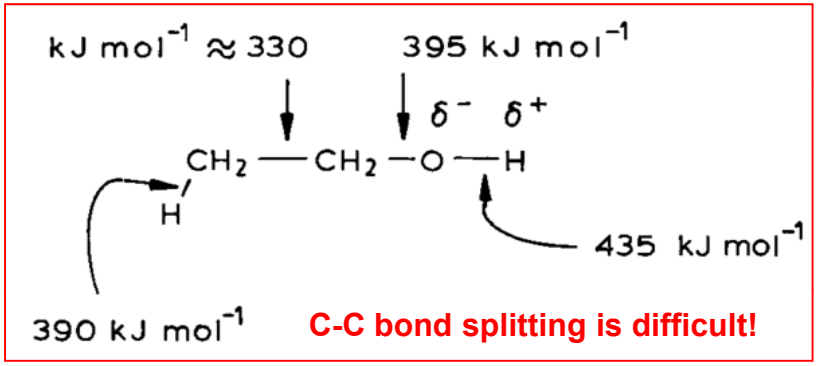
- **DEFC:** V_{th}=1.15 V (at 25°C), fuel specific energy 8.0 kWh/kg
- $C_2H_3OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$ $E° \cong 0.08$ V (at 25°C)
- **Advantages:** High energy content, renewable, non-toxic, easy to handle and distribute
- **Main challenge:** Slow, incomplete oxidation – electrocatalytic scission of the C-C bond very difficult to accomplish at low temperatures

Ethanol: Oxidation Scheme & Catalyst Concept

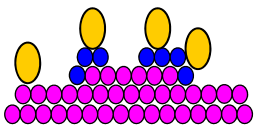
- **On Pt, EtOH oxidation is slow and limited to acetaldehyde at existing catalysts** (following the α-C-H bond dissociation)**:**

$$C_2H_5OH + Pt(H_2O) \rightarrow Pt(CH_3CHO) + H_2O + 2H^+ + 2e^-$$

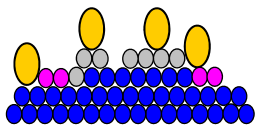




- **Ternary $PtRhSnO_2$ <u>model</u> catalyst capable of oxidizing EtOH to CO_2 (at 25°C):**
  - Pt - abstraction and oxidation of H atoms
  - SnO_2 - source of OH for oxidation of strongly bound intermediates
  - Rh - small amounts placed either on SbO_2 or Pt to aid in C-C bond scission

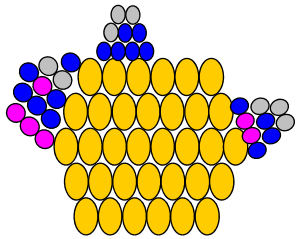


2ML SnO_2 + 1/2ML Rh / Pt(111)



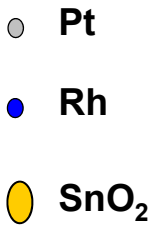
2ML SnO_2 + 1ML Pt / Rh(111)

Model Catalysts



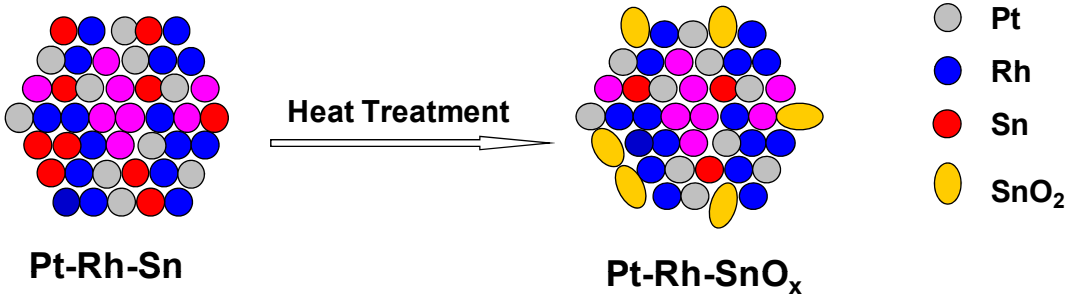
$PtRhSnO_2$/C Nanoparticles

Real Catalyst

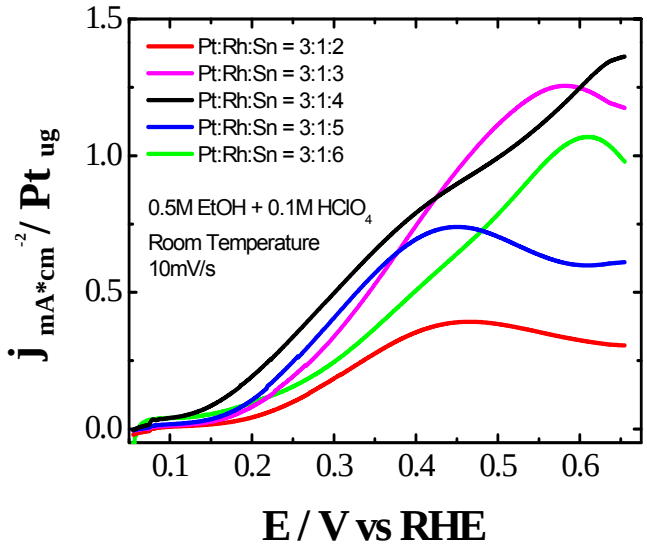


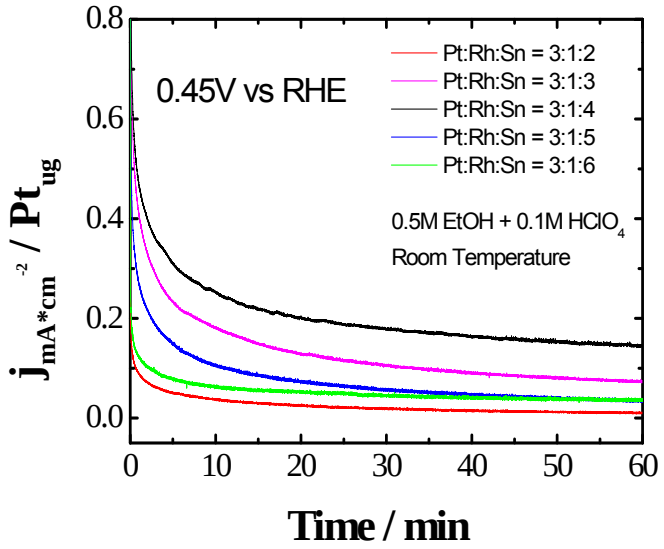
Ethanol: Improved Synthesis & Catalyst Composition Optimization

- **A modified polyol method**
  - Pt-Rh-SnO_x nanopaticles: H_2PtCl_6 + $RhCl_3$ + $SnCl_2$+ NaOH + EG + H_2O
  - Heat treatment: 200ºC, Ar, 1 hour

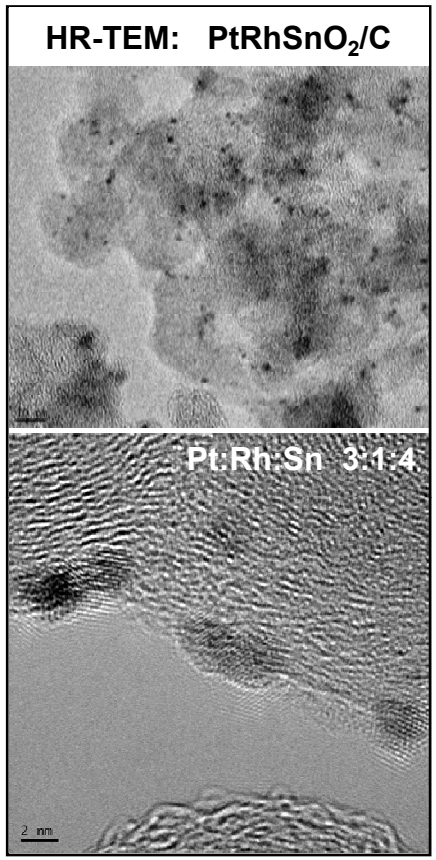


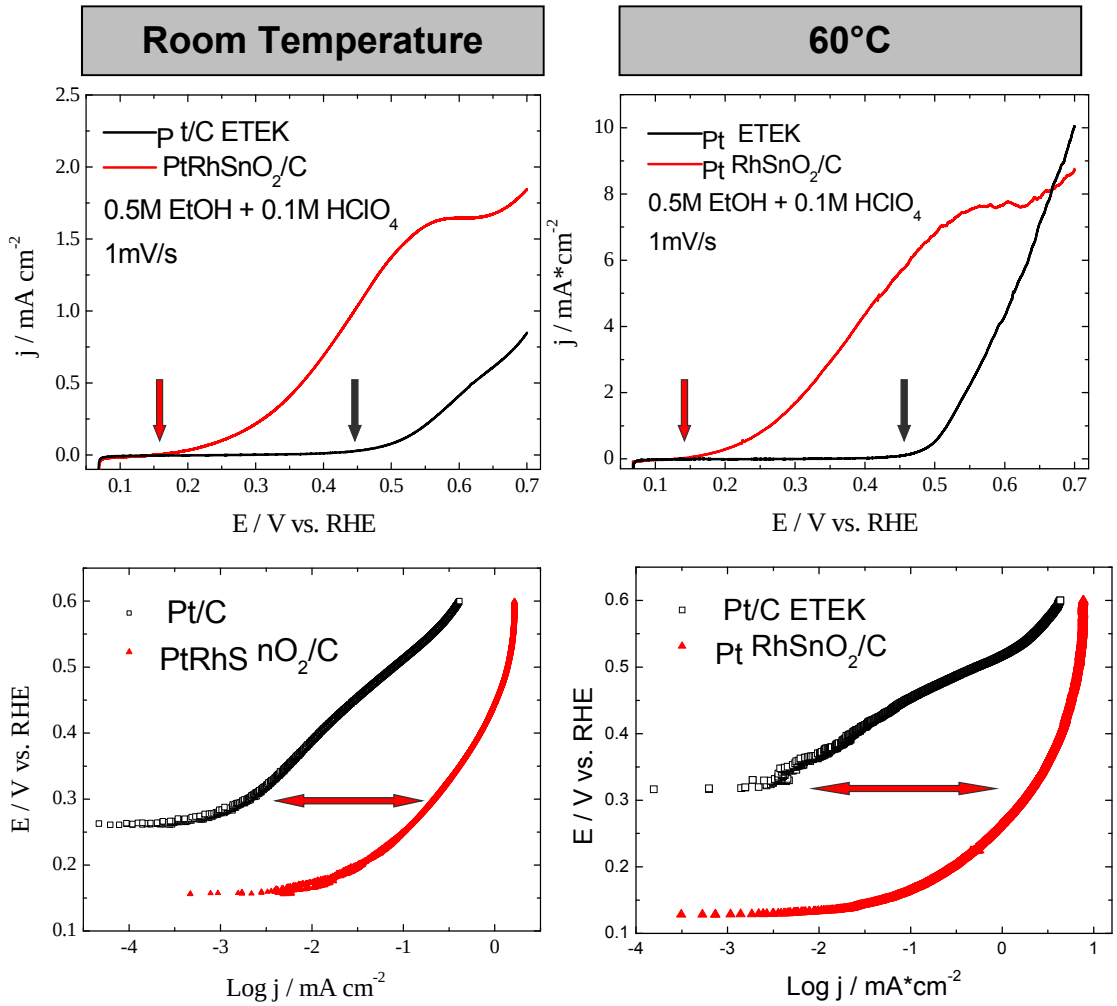
- **The effect of catalyst composition, i.e. the Pt:Rh:Sn ratio:**





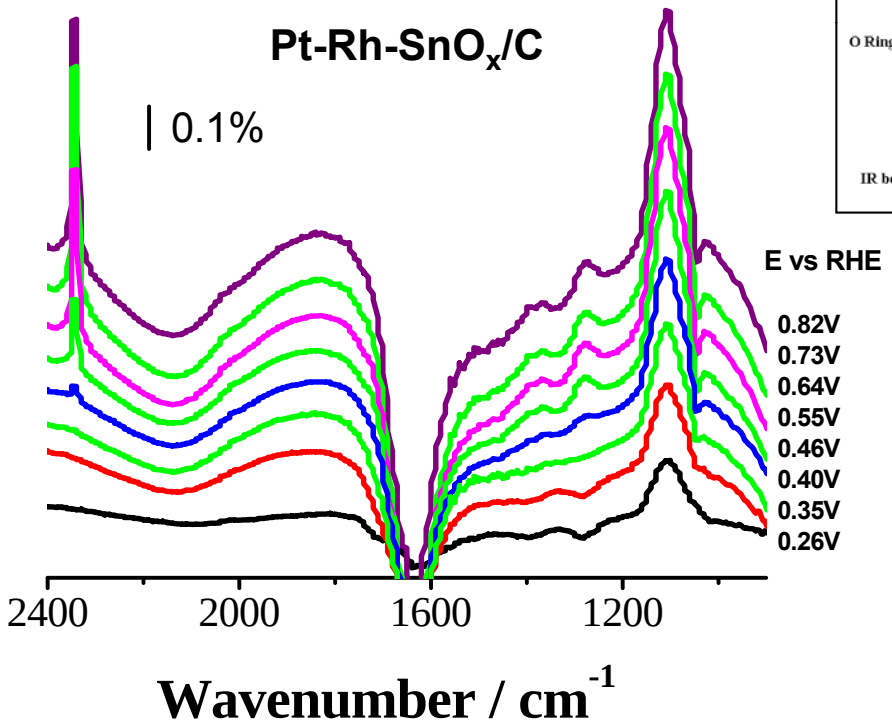
Ethanol Oxidation Performance: Ternary Catalyst vs. Pt/C

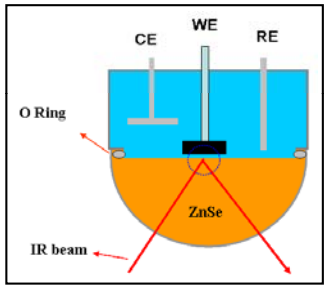


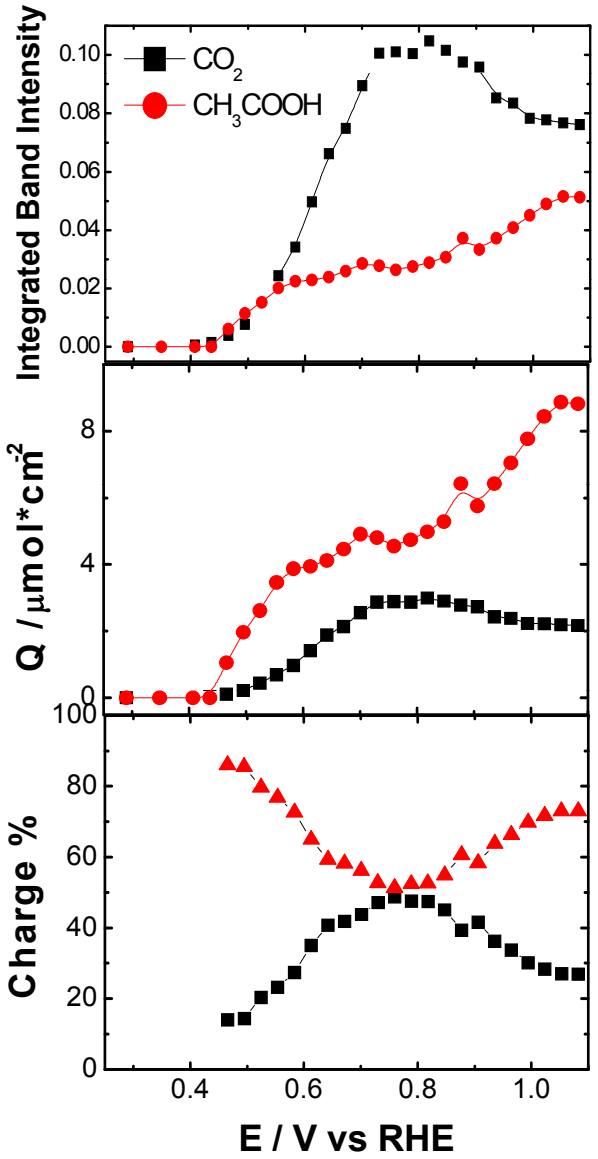


- **~ 0.3 V difference observed under voltammetric and steady-state conditions**
- **At 0.3 V, Pt-Rh-SnO_2/C offering a two-order of magnitude current-density advantage over a standard E-TEK/C catalyst**

Ethanol Oxidation: *In situ* IRRAS Quantification of Reaction Products







- **Product quantity:** $Q = A_i / \varepsilon_{eff}$

  A_i - integrated band intensity; E_{eff} - effective absorption coefficient

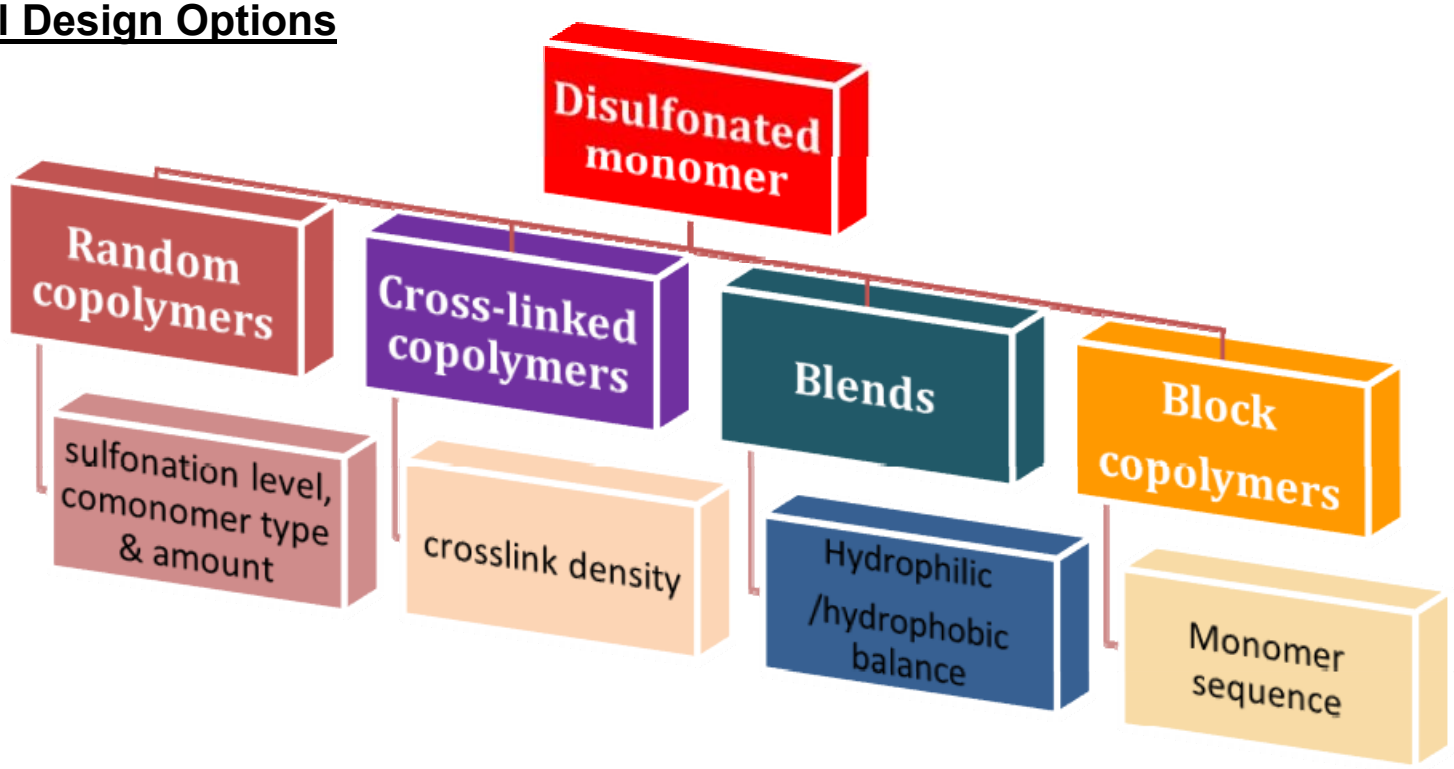
- **Charge contribution:** $C_i\% = 100\% (n_i \times Qi) / \Sigma(n_i \times Q_i)$

  CO_2 - 6e$^-$/molecule; CH_3COOH - 4e$^-$/molecule

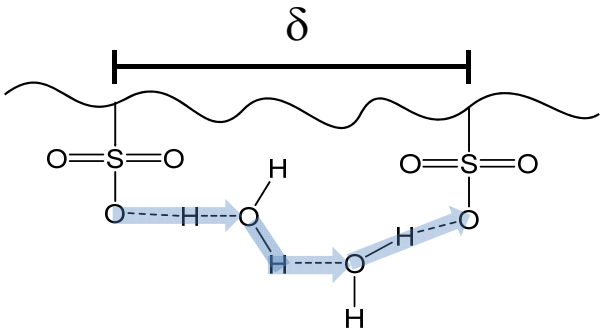
Advanced Membranes for Portable Power Fuel Cells

Issue	Objective
Selectivity	High proton conductivity but low methanol permeability
Stability	Chemical/mechanical stability of DMFC/DEFC membranes
MEA processibility	Interfacial stability between membrane and PFSA-bonded electrodes

Material Design Options



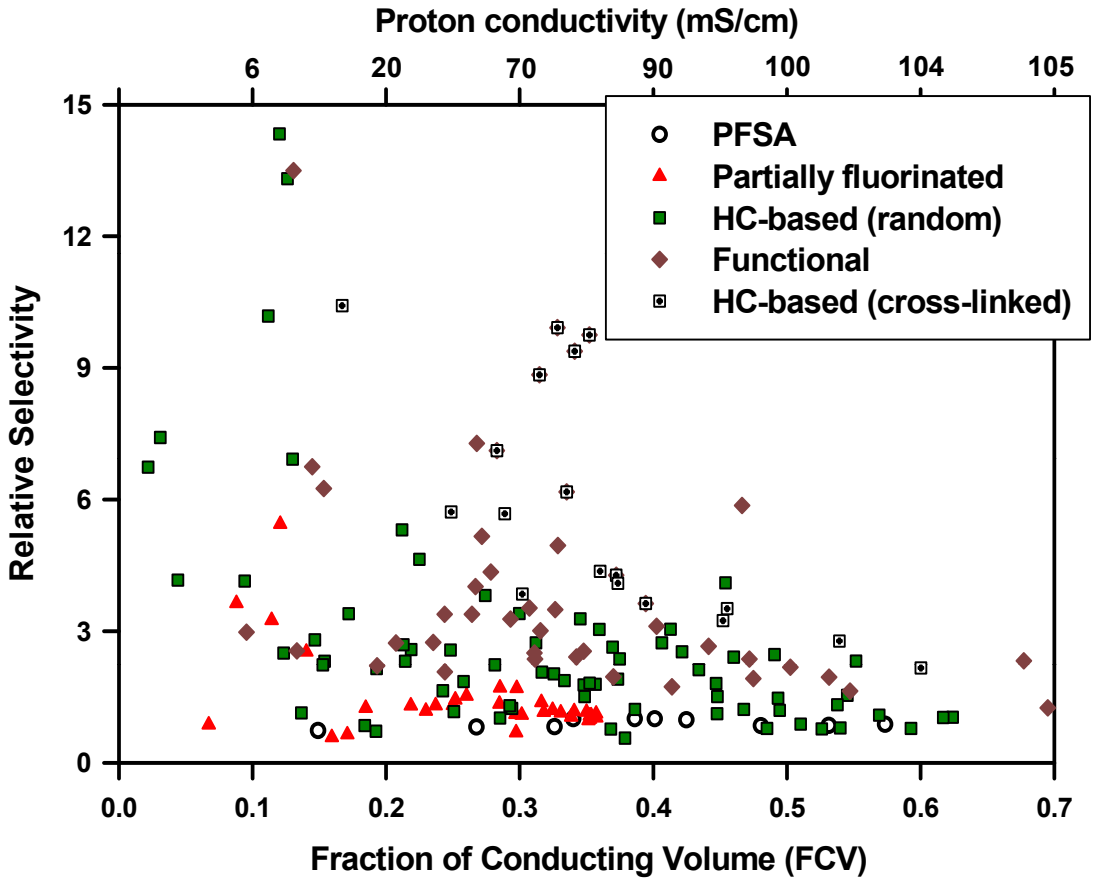
Relative Selectivity of Various Sulfonated PEMs



Fraction of conducting volume (FCV):

$$FCV = \frac{\lambda \times 18}{MVC_{(wet)}} \propto conductivity$$

MVC _ molar volume per charge



Functional: Polymer moiety resulting in a specific interaction such as hydrogen bonding, dipole-dipole or acid-base interactions. Examples: carboxylic acid group, nitirile, amide, phosphine oxide, imidazole.

Kim and Pivovar, *Ann. Rev. Chem. Biomol. Eng*. **1**, 23-148, 2010; Kim *et al.*, manuscript in preparation

Three Approaches to Advanced Membranes

1. Homogeneous thin membrane (LANL, VT)

- Relative selectivity: 2-5
- *Advantage*: Simple processing
- *Major Challenge*: PEMs with good balance of selectivity and conductivity

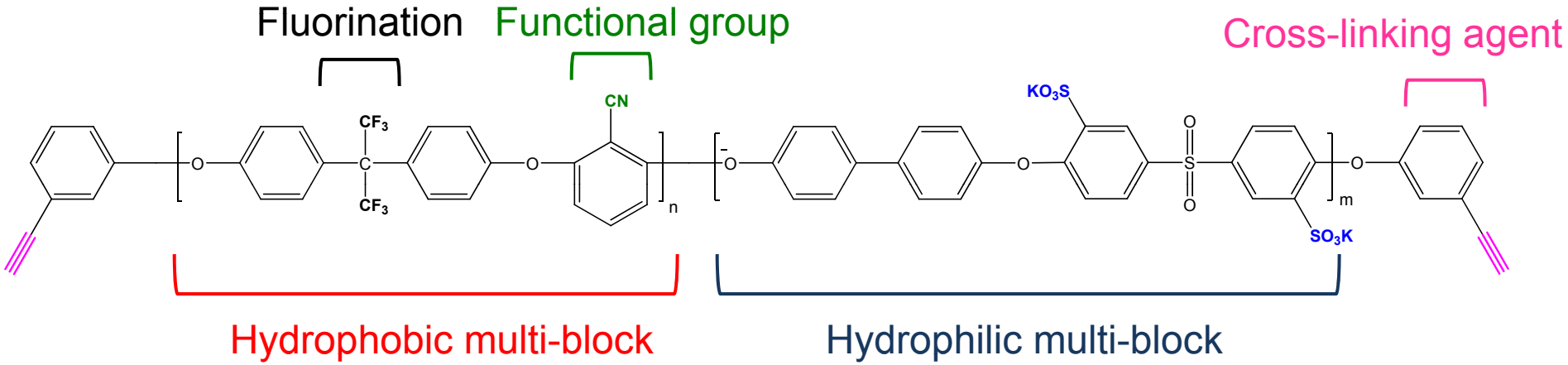
2. Multi-layer membrane (LANL)

- Thickness: 30 μm (supporter), 10 μm (selective layer)
- Relative selectivity: 5-10
- *Advantage*: High selectivity
- *Major Challenge*: Membrane processing

3. Surface treated membrane (VT)

- Relative selectivity: 2-5
- *Advantage*: Good interfacial compatibility & conductivity
- *Major Challenge*: Surface treatment

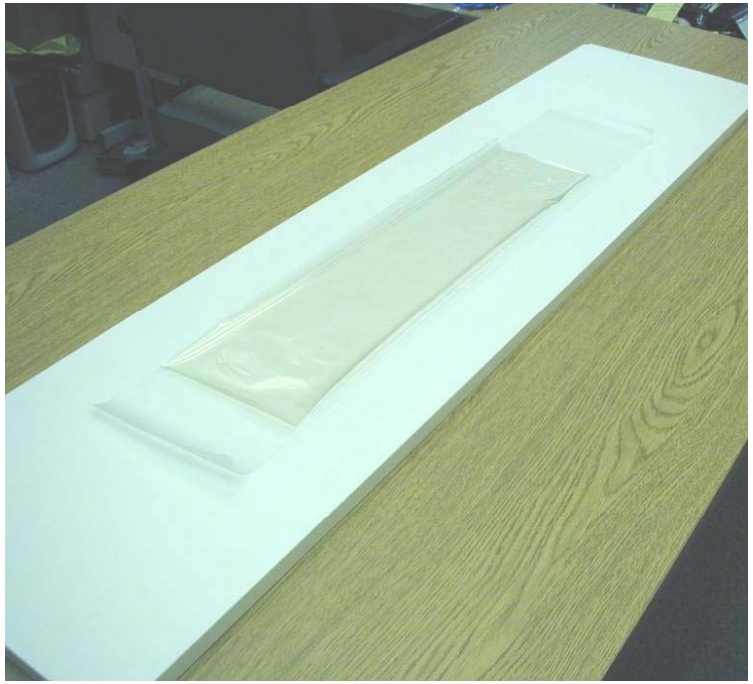
PEM Structures for Homogeneous Thin Membranes



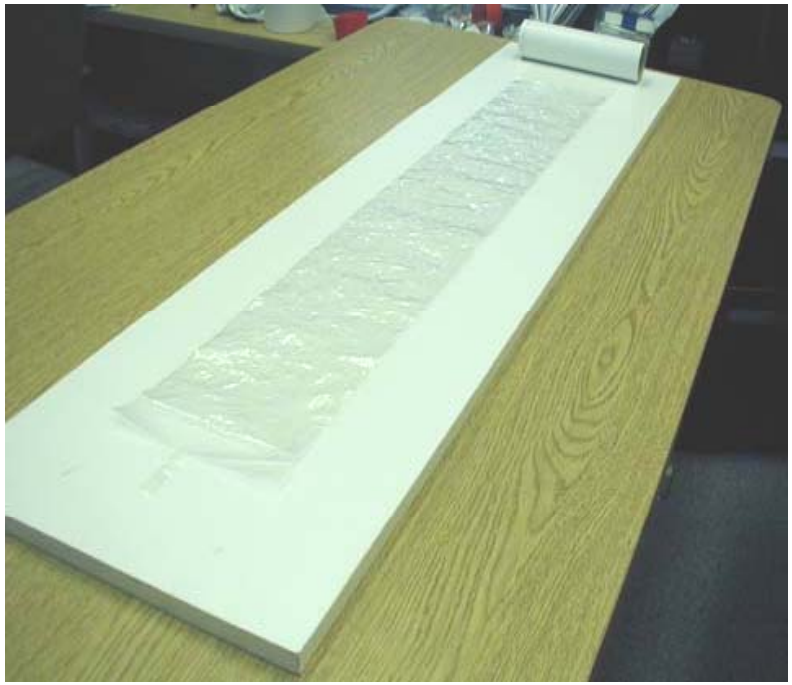
Component	Role in PEM
Functional group	Increasing selectivity
Fluorination	Increasing phase separation and conductivity
Cross-linking agent	Increasing selectivity
Multi-block structure	Increasing flexibility, phase separation, and conductivity

Polymer Processing for Homogeneous Thin Membranes

Block Copolymer Film (BisSF 17k/12k)

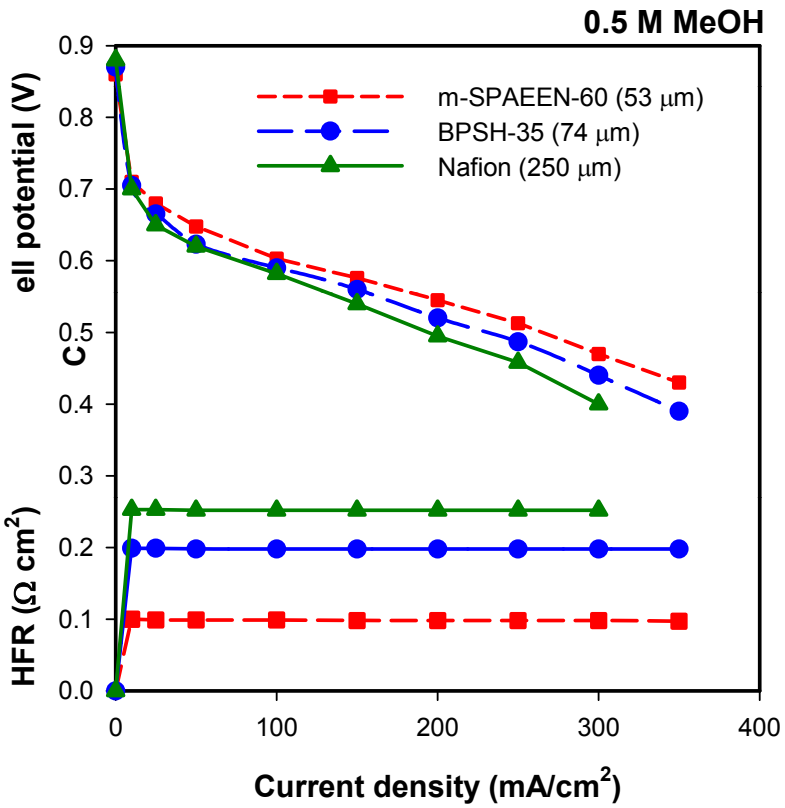


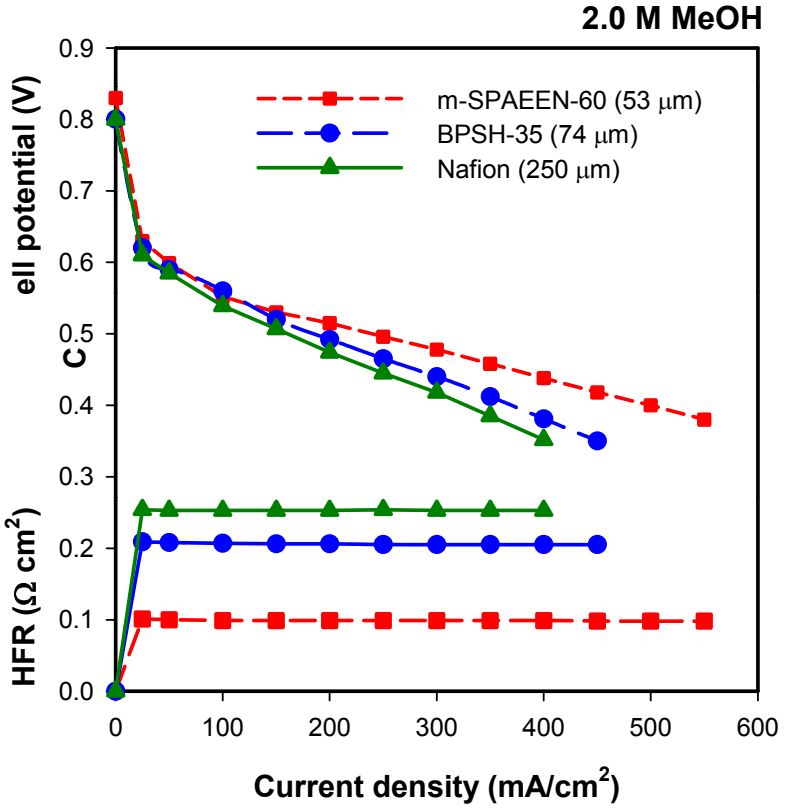
Random Copolymer Film (6F40)



Membranes with uniform thickness in the range 30-200 μm can be provided by Virginia Tech for MEA fabrication

DMFC Performance of MEAs with Homogeneous Thin Membranes



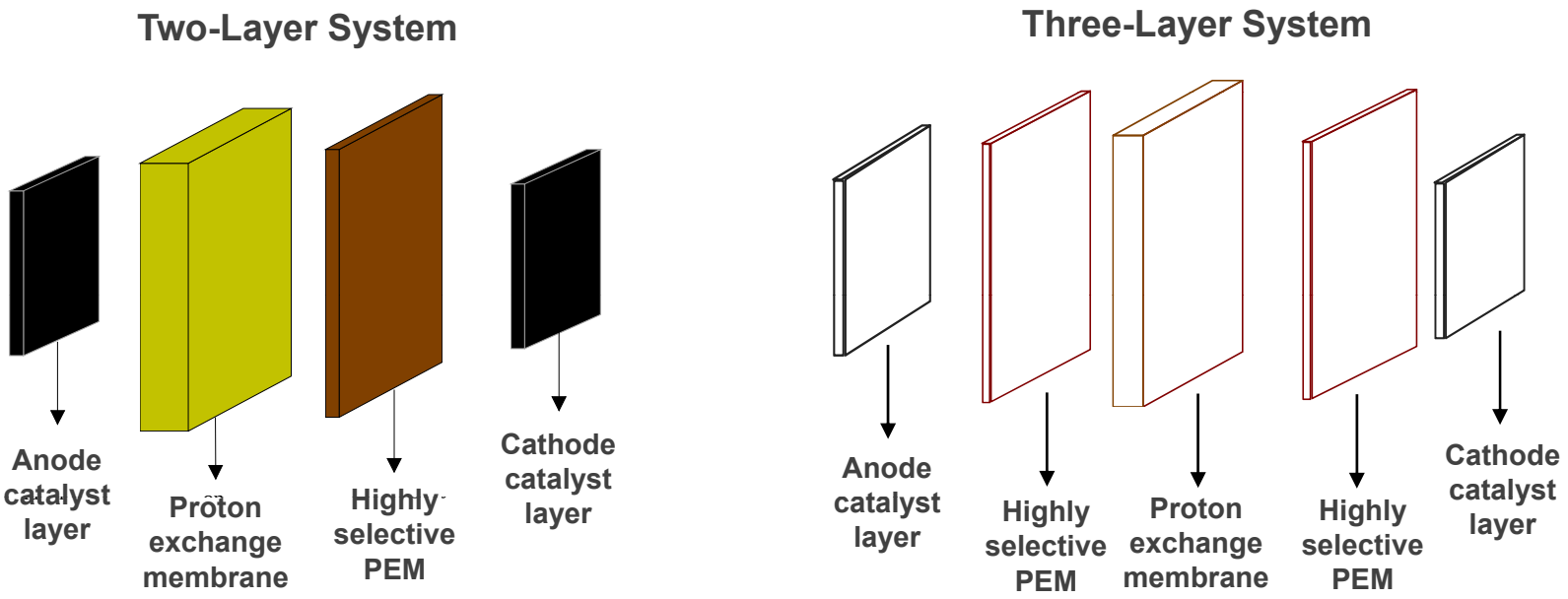


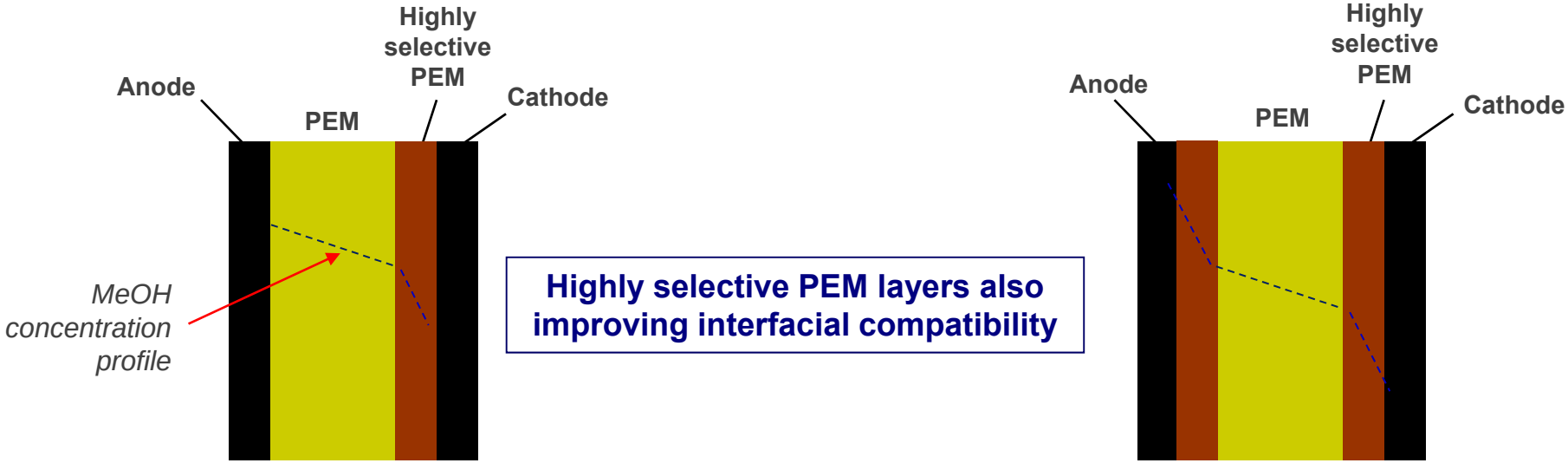
- **PEM performance comparison carried out at a fixed methanol crossover limiting current (50 mA/cm² using 0.5 M MeOH feed)**
- **Performance improvement with hydrocarbon membranes thanks to better selectivity**

Membrane	Relative Selectivity
M-SPAEEN-60	2.9
BPSH-35	1.3
Nafion®	1

Kim *et al.*, *J. Electrochem. Soc.* **155,** B21-B26, 2008

Multi-Layer Membranes

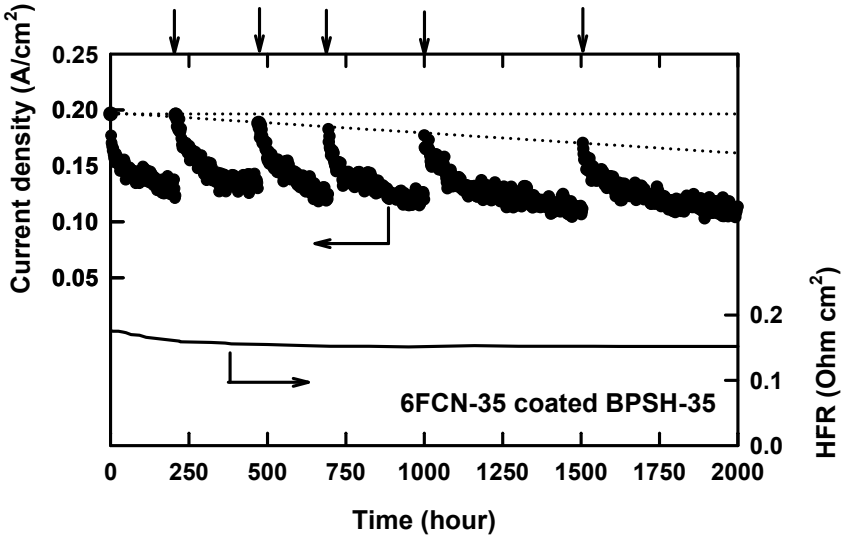




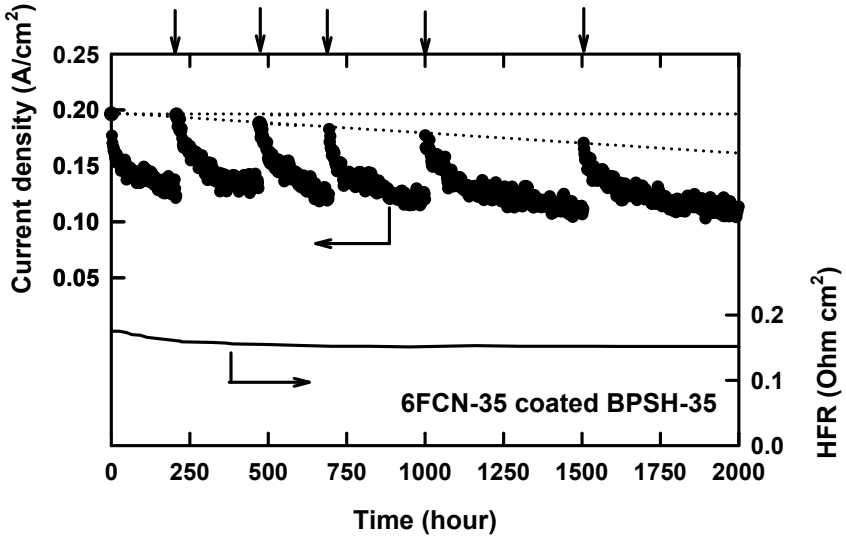
Kim and Pivovar, *US Patent Application*, LANL, 2006

Long-Term Stability of MEAs with Different Membranes

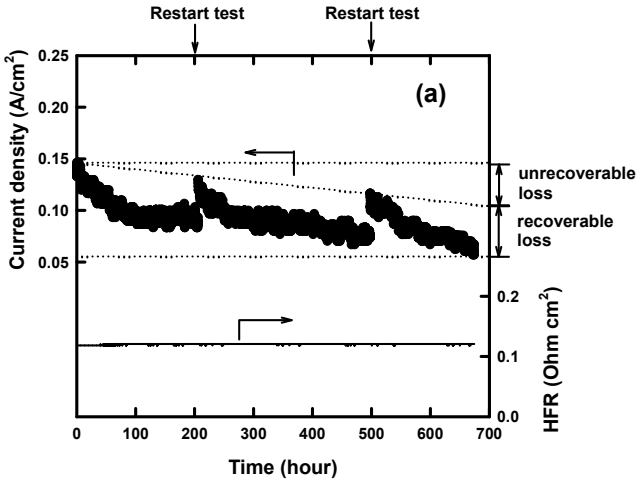
Homogenous Thin Membrane



Multilayer Membrane



Nafion® 1135 Control PEM

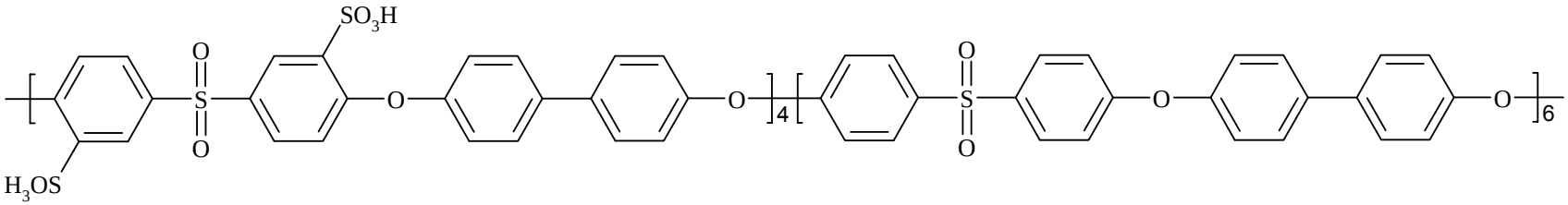


- **DMFC test conditions: 0.5 V, 80°C, 0.5 M MeOH, ambient pressure**
- **No indication of PEM or interface degradation**
- **Both membrane systems showing superior performance to the Nafion® reference system**

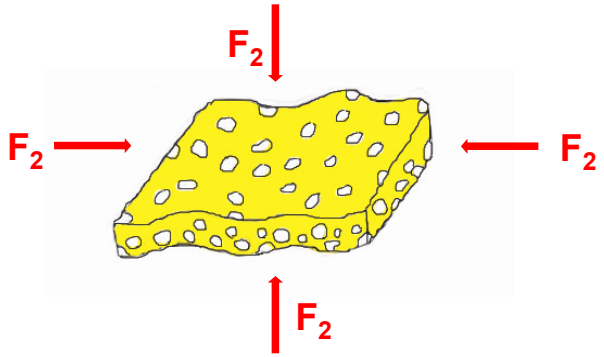
Kim *et al.*, *J. Electrochem. Soc.* **157**, B1602-B1607, B1616-B1623 (2010)

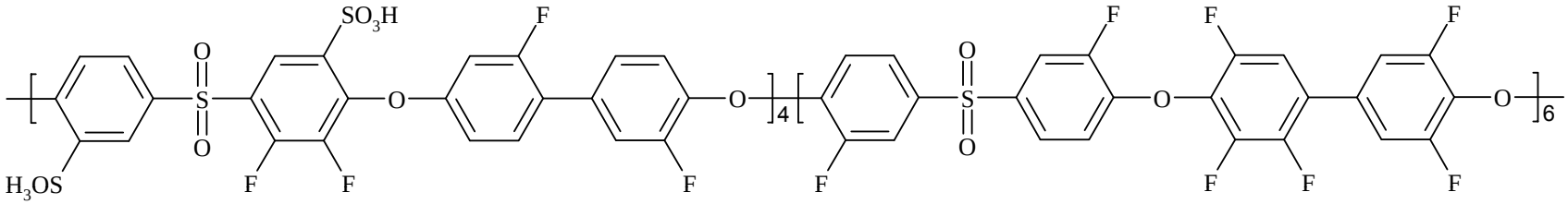
Basic Concepts of Membrane Post-Fluorination

- **No modification: Possible poor compatibility with Nafion® in electrodes**

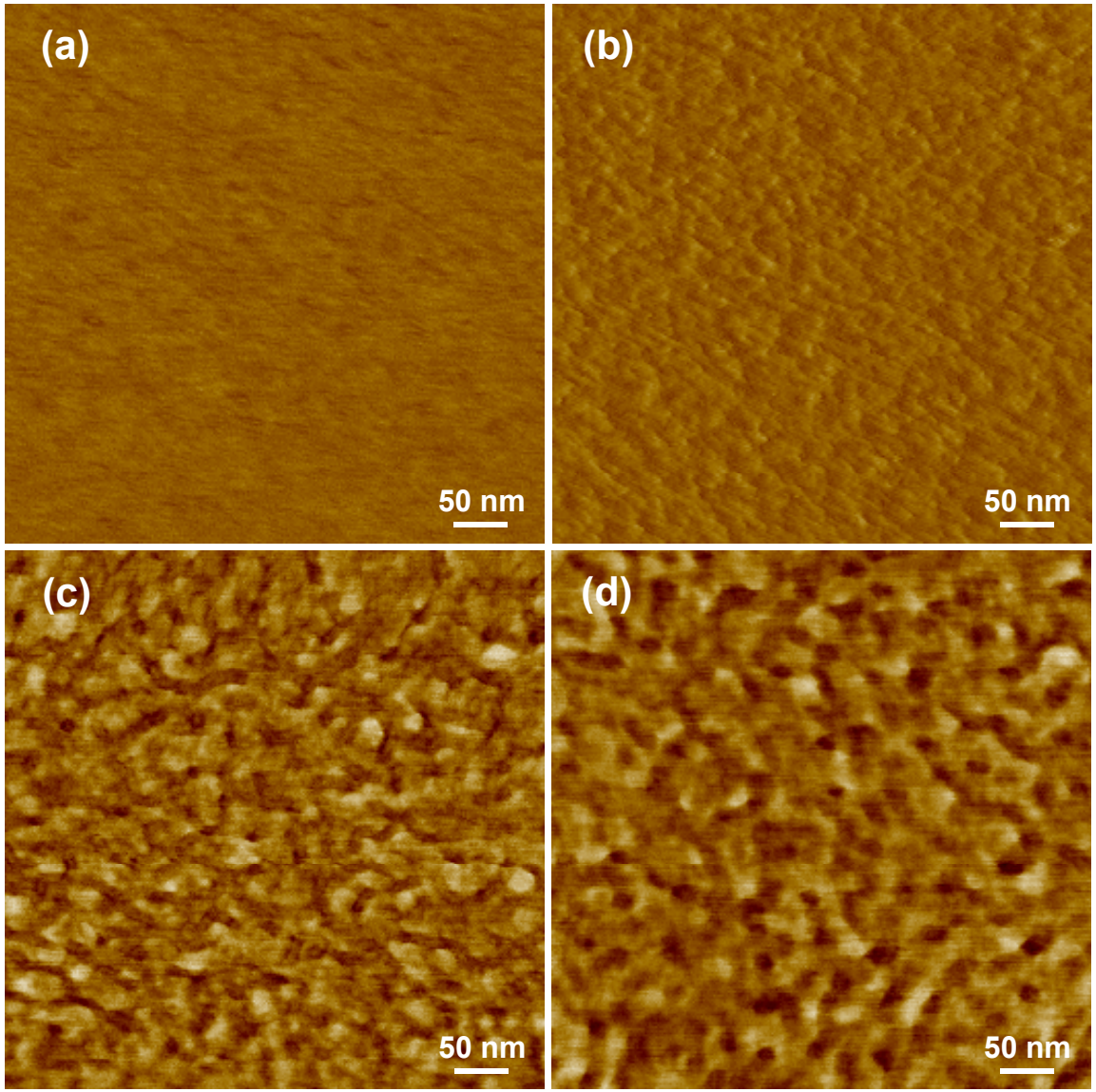


- **Fluorination: Phase separation and improved interface with Nafion® in electrodes**





Post-Fluorination of BPSH-40 Membrane



Tapping mode AFM:

(a) SPAES (BPSH-40 control)

(b) FSPAES – 10 minutes

(c) FSPAES – 30 minutes

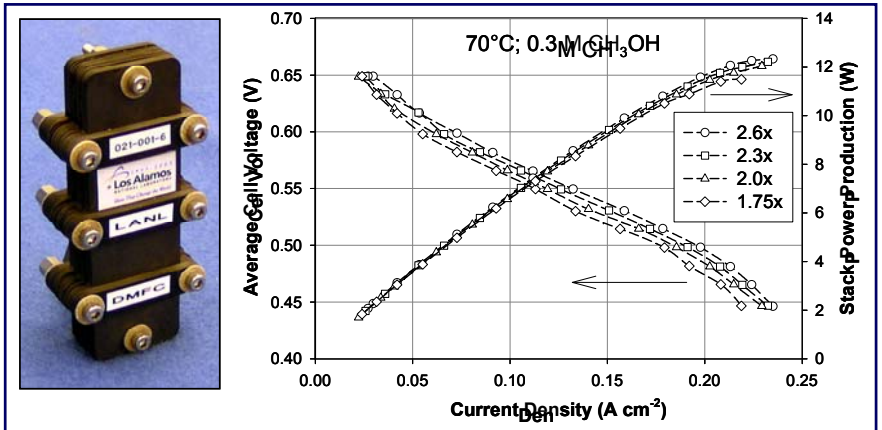
(d) FSPAES – 60 minutes

Relative humidity ~ 35%

- **Fluorination developing morphological order on the surface of BPSH-40 membrane**
- **Preliminary data indicating improved DMFC MEA performance at higher current densities**

Fuel Cell Testing & Multi-Cell Device

- **Single-cell testing of materials, including life-testing for up to 2,000 hours (LANL, JMFC)**
- **Integration of selected materials into 50 cm^2 MEAs for the five-cell stack (JMFC)**
- **Integration of MEAs into the stack and stack testing (SFC Energy)**
- **Deliverables for the Department of Energy completed by Q16**



Short-stack DMFC stack hardware developed at LANL for military power applications.

SFC stack hardware (top) and fuel cell test stands (bottom)

Tasks & Schedule

- **Task 1 DMFC Anode Research**
  - 1.1 Catalysts with Improved Activity and Reduced Cost
  - 1.2 Anode Catalyst Durability
- **Task 2 Alternative fuels for portable fuel cells**
  - 2.1 Ethanol Oxidation Electrocatalysis
  - 2.2 Dimethyl Ether Research
- **Task 3.1 Innovative Electrode Structures for Better Activity and Durability** (Metal Nanotubes)
- **Task 4 Hydrocarbon Membranes for Lower MEA Cost and Enhanced Fuel Cell Performance**
  - Block Copolymer Synthesis
  - Copolymers with Cross-linkable End-groups
- **Task 5 Characterization; performance and durability testing; multi-cell device:**
  - Fuel Cell Testing: Performance & Durability
  - Multi-cell Device(Five-Cell Stack)

Task Schedule by Quarters with Milestones (M) and Decision Points (G)

TASK	QUARTER															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1.1				MM		MG		MM	MG			M	MG	MMM		
1.2								MMG						M		M
2.1				MM	MMG	M	M	M		G		M	MMG	M		
2.2		M		MG	MG											
3.1				MMG		MG		MMG		MG		MG	MG	M		
4.1-4.2				MMG		M		MMG		M		MMG		MMG		
5.1														MM		
5.2														MM		M

** Periods after a high-risk go/no-go decisions are shown in a lighter shade.*

Approach: FY11 Milestones

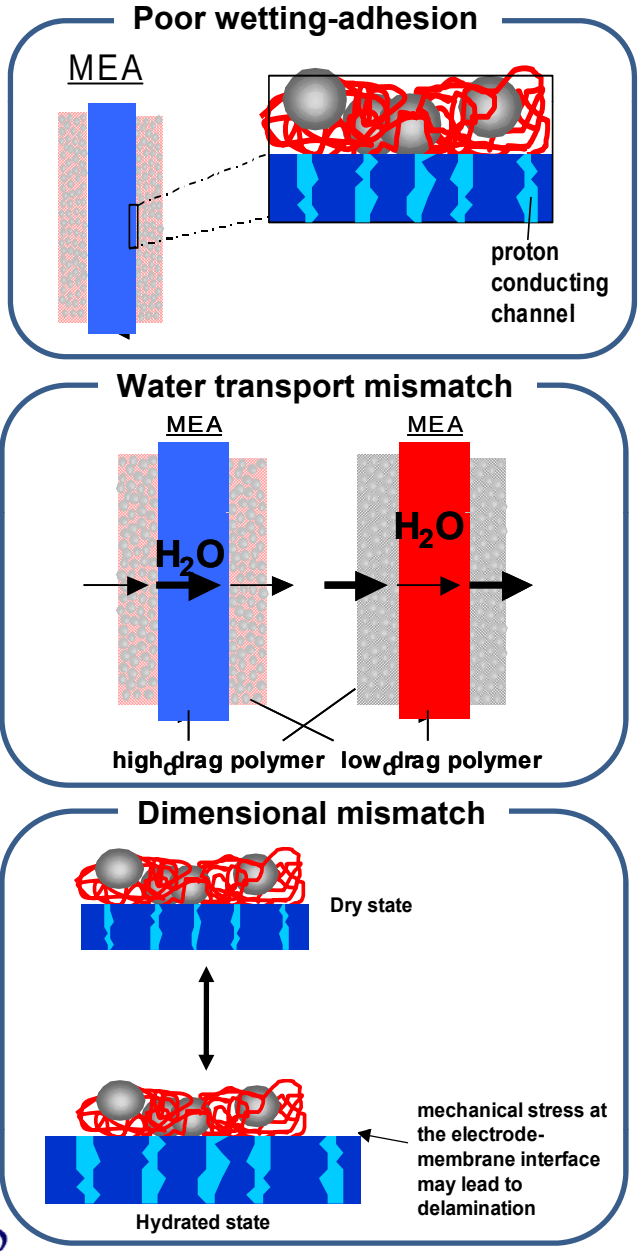
Date	Milestone
Mar 11	Complete evaluation of at least three PtRu catalysts of different composition for DME oxidation.
Apr 11	Conclude synthesis of trisulfonated hydrophilic (SQS) 6F copolymers.
Apr 11	Demonstrate a nanotube catalyst with MeOH oxidation activity within 0.05 V of the state-of-the-art PtRu catalysts.
June 11	Complete equipment set-up for stack evaluation; adapt stack hardware to testing hydrocarbon membranes of different thickness.
Sep 11	Demonstrate a new MeOH oxidation catalyst that significantly exceeds half-cell mass activity of 200 mA/mg_{Pt} at 0.35 V at 80°C (*iR*-corrected).
Sep 11	Improve the ternary $PtRhSnO_2$ electrocatalyst to oxidize EtOH to CO_2 with an efficiency of 50% at the anode potential of 0.4 V and 80°C.

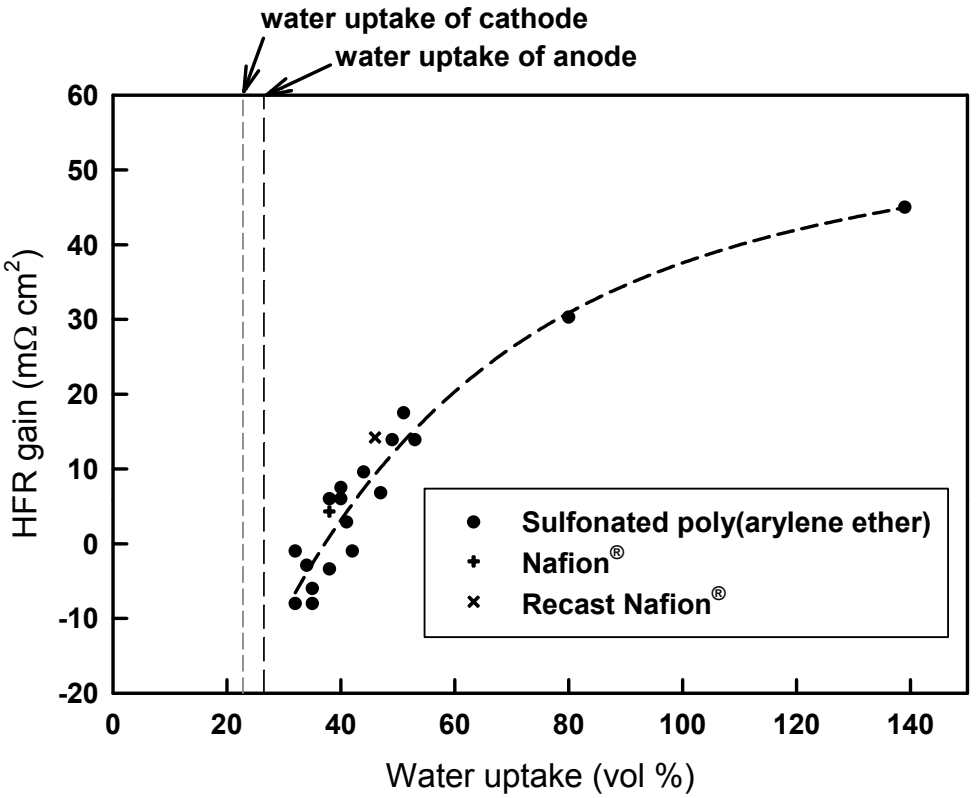
Summary

- This is a multi-partner and multi-task project targeting substantial improvements to the performance of portable fuel cells with a liquid fuel feed to the anode
- The key technical objective for the direct methanol fuel cell (DMFC) is to assure sustained operation at a cell voltage of 0.6-0.7 V (depending on specific application and cost requirements)
- The focus of the DMFC research is on (i) enhancement of the anode catalyst activity through novel catalyst composition and structure, (ii) increase in the membrane selectivity, (iii) improvement to the MEA stability, including that of the membrane-electrode interface and the catalyst itself, and (iv) reduction in the cathode loss caused by migration of unstable anode components (e.g. Ru crossover)
- Electrocatalysis of dimethyl ether oxidation is studied in the context of a system with "passive" fuel supply; DME anode performance will be referenced to that of a DMFC anode operating under similar conditions
- Ethanol research concentrates on the development of, mostly ternary, oxidation catalysts capable of breaking the C-C bond in the C_2H_5OH molecule and assuring high CO_2 yields
- Potentially viable materials developed in the project will be tested for long-term stability$_{\text{in a}}$ single fuel cell and,$_{\text{if}}$ judged practical,$_{\text{incor}}$ porated into a short fuel cell stack

Supplemental Slides

Interfacial Stability





Water uptake lower than 40 vol% assuring good stability of the membrane/electrode interface

Kim and Pivovar, *J. Electrochem. Soc.* **157**, B1616-B1623 (2010)

Effect of Chemistry on Membrane Properties

FCV=0.35

Polymer Chemistry	SO_3H Conc. (mgramequiv/cm^3)	λ (H_2O/SO_3H)	Relative Conductivity	Rel. MeOH Permeability
PFSA	1.8	16.5 (1.8)	0.85 (0.18)	0.96 (0.06)
Partially fluorinated	1.9	15.7 (1.8)	0.87 (0.23)	0.69 (0.17)
HC-based	2.3	14.1 (2.5)	0.86 (0.24)	0.38 (0.13)
Functional	2.5	12.4 (3.1)	0.83 (0.33)	0.24 (0.12)

FCV=0.25

Polymer Architecture	SO_3H Conc. (mgramequiv/cm^3)	λ (H_2O/SO_3H)	Relative Conductivity	Rel. MeOH Permeability
Random copolymer	1.6	12.0 (1.9)	0.46 (0.2)	0.19 (0.08)
Homopolymer	2.2	8.7 (1.5)	0.39 (0.1)	0.18 (0.05)
Cross-linked copolymer	3.1	5.6 (1.7)	0.66 (0.2)	0.10 (0.04)

Standard deviation given in parenthesis

Acknowledgments

- DOE-EERE Fuel Cell Technologies Program
- Technology Development Manager: Dr. Nancy Garland