2011 Hydrogen Program Annual Merit Review and Peer Evaluation Meeting
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Advanced Materials and Concepts for Portable Power Fuel Cells

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Project ID: FC091

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Overview

Timeline

- **Start date:** September 2010
- **End date:** Four-year duration
- **Completion:** *ca.* 15%

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

– Radoslav Adzic

University of California, Riverside

– Yushan Yan

Virginia Tech

– James McGrath

Johnson Matthey Fuel Cells

– Nadia Permogorov

Smart Fuel Cell Energy

– Verena Graf

Oak Ridge National Laboratory

– 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)

$$V_{cell} = V_{th} [\eta_\Sigma (\eta_{fuel}\, \eta_{BOP})^{-1}] = 0.6\text{-}0.7\ V$$

The ultimate project goal!

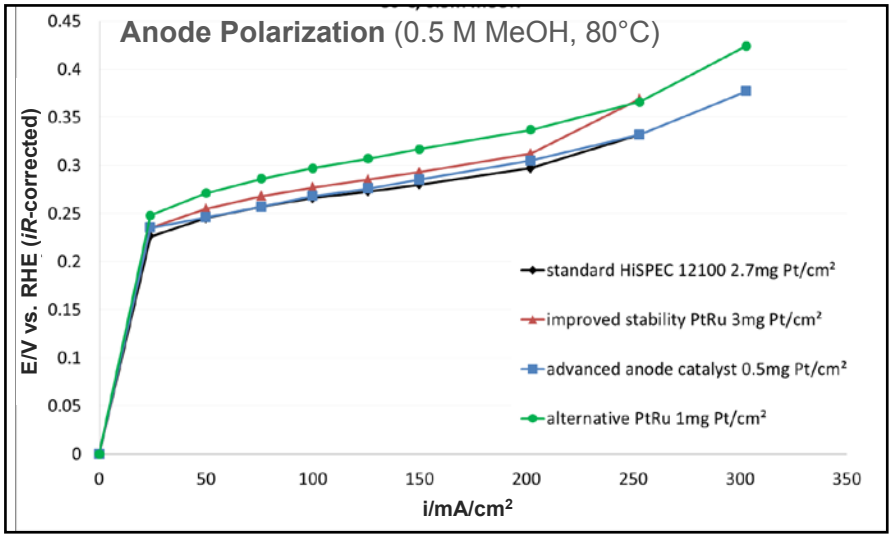
Approach: Focus Areas

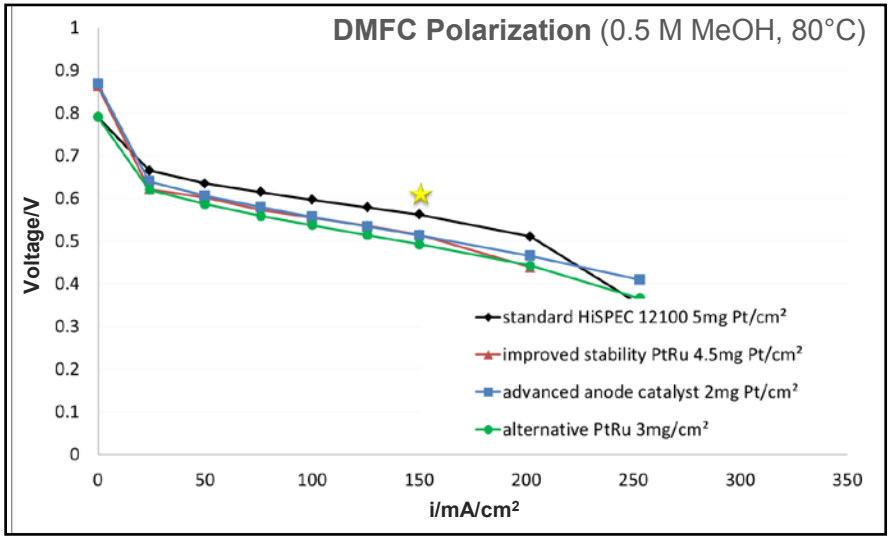
- **DMFC anode research:**
  - catalysts with improved activity and reduced cost (BNL, JMFC, LANL)
  - development of catalysts with improved durability (LANL, JMFC)
- **Innovative electrode structures for better activity and durability** (UCR)
- **Hydrocarbon membranes for lower MEA cost and enhanced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

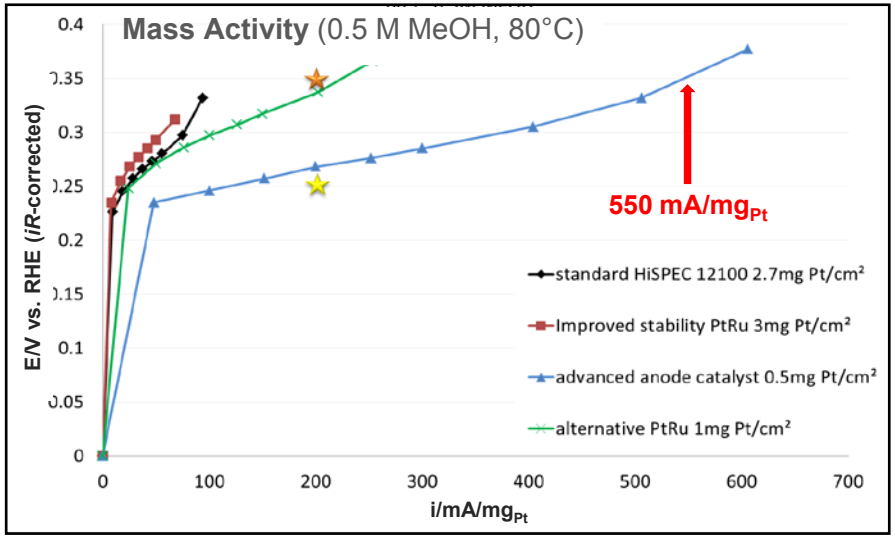
Approach: Milestones

DATE	MILESTONE	STATUS	COMMENTS
Feb 11	Complete preliminary electrochemical characterization of methanol and DME oxidation on state-of-the-art anode catalysts (performance baseline determination).	**Complete**	Characterization completed on both carbon-supported and support-free PtRu catalysts from Johnson Matthey.
Mar 11	Complete evaluation of at least three PtRu catalysts of different composition for DME oxidation.	**Complete**	Fuel cell study of DME oxidation completed at six PtRu catalysts.
Apr 11	Conclude synthesis of trisulfonated hydrophilic (SQS) 6F copolymers.	**Complete**	6FPAEB-BPS100 copolymer synthesized; structure confirmed using ^{1}H NMR.
Apr 11	Demonstrate a nanotube catalyst with MeOH oxidation activity within 0.05 V of the state-of-the-art PtRu catalysts.	**Complete**	Two PtRu nanotube catalysts demonstrated with the onset MeOH oxidation potential of ~ 0.33 V *vs.* RHE (the same as measured with HiSPEC 12100 reference catalyst)
Jun 11	Complete equipment set-up for stack evaluation; adapt stack hardware to testing hydrocarbon membranes of different thickness.	**Pending**	Delay possible due to late implementation of SFC subcontract.
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).	**Complete**	Milestone exceeded; 550 mA/cm^2 at 0.35 V measured at 80°C with JMFC's "advanced anode catalyst" for MeOH oxidation.
Sep 11	Demonstrate high-activity $Pt_{ML}/Pd_{alloy}/C$ electrocatalyst with Pt mass activity of 2.5 A/mg and specific activity of 1.2 mA/cm^2 (both at 0.9 V)	**Pending**	On schedule.
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.	**Pending**	On schedule.

MeOH Oxidation: Pt-Thrifted Anode Catalysts Performance







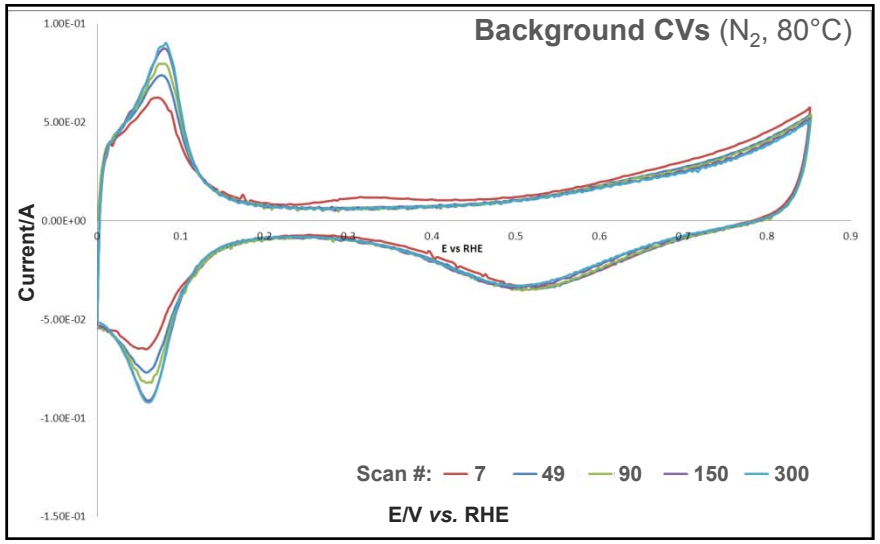
- **Highlight: "Advanced MeOH oxidation catalyst" matching the performance of benchmark HiSPEC® 12100 catalyst at a much higher loading; mass activity of 550 mA/mg$_{Pt}$ reached at 0.35 V (80°C)**

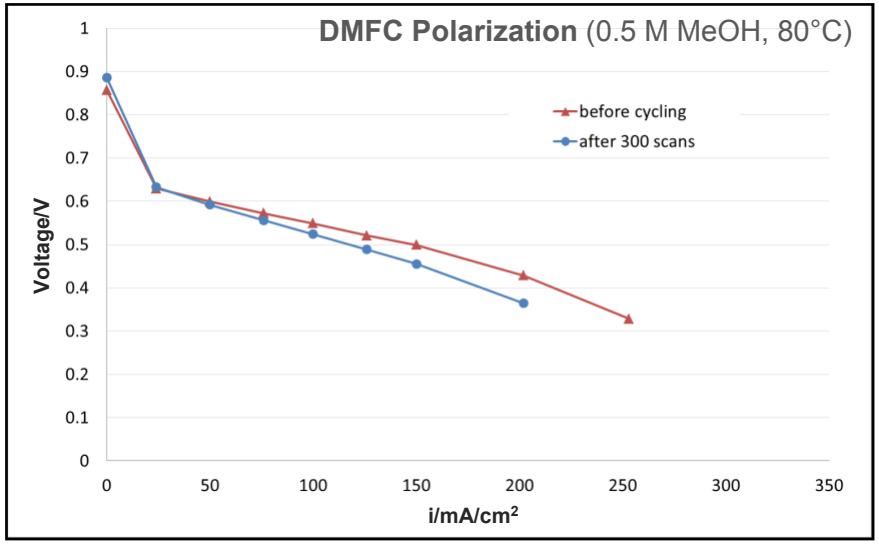
  Mass activity milestone achieved and exceeded by 175%

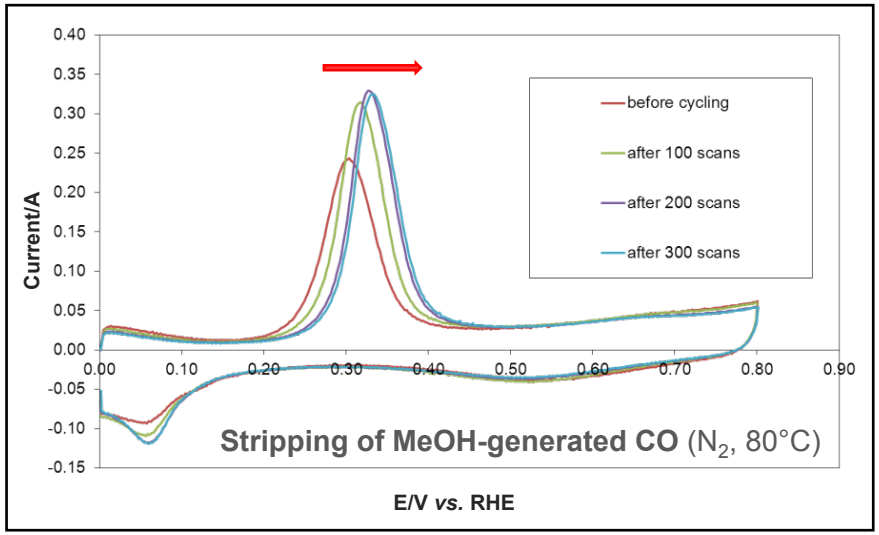
- **Anode research on track to reach final project goal of 150 mA/cm² at 0.60 V (DMFC) using lower precious metal content**

MeOH Oxidation: Pt-Thrifted Catalyst Stability

Cycling of Advanced MeOH Catalyst (0.0-0.85 V, 20 mV/s, 80°C)





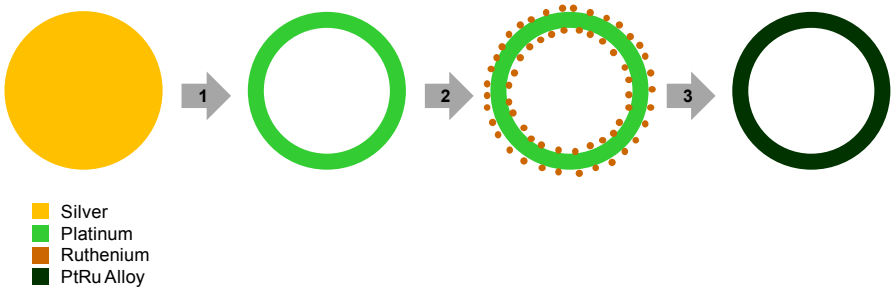


Surface CO generation: *0.5 M MeOH, 0.125 V, 15 min, 80ºC*
Stripping scan rate: *20 mV/s*

- **Background and CO-stripping CVs showing noticeable changes to catalyst properties during the first 200 cycles, little thereafter (a steady-state reached)**
- **Increase in Pt-character observed during the first 200 cycles, virtually no change thereafter**
- **300 cycles resulting in 20-30 mV fuel cell performance loss at 0.50 V, attributable to the anode (based on the anode polarization)**
- **Benchmarking *vs.* HiSPEC® 12100 planned**

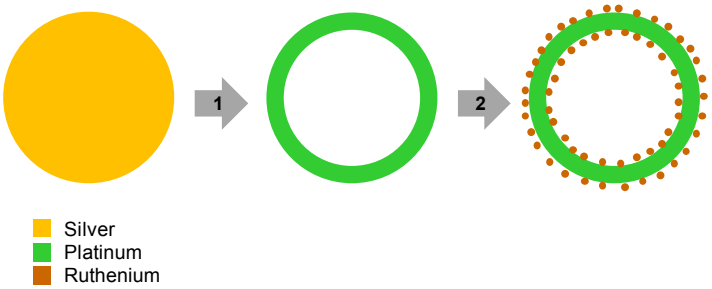
Innovative Electrode Structures: PtRu Nanotube Catalysts for MeOH Oxidation

PtRu Nanotubes from Ag Template (Chemical)



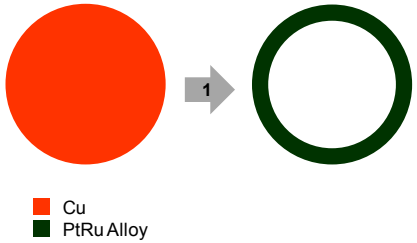
1. Displacement of Ag in AgNW with Pt to form PtNT;
2. Ru deposition from $RuCl_3$ (reduction with ethylene glycol in the presence of polyvinyl pyrrolidone for shape control);
3. Annealing to form PtRu alloy.

PtRu Nanotubes from Ag Template (Electrochemical)

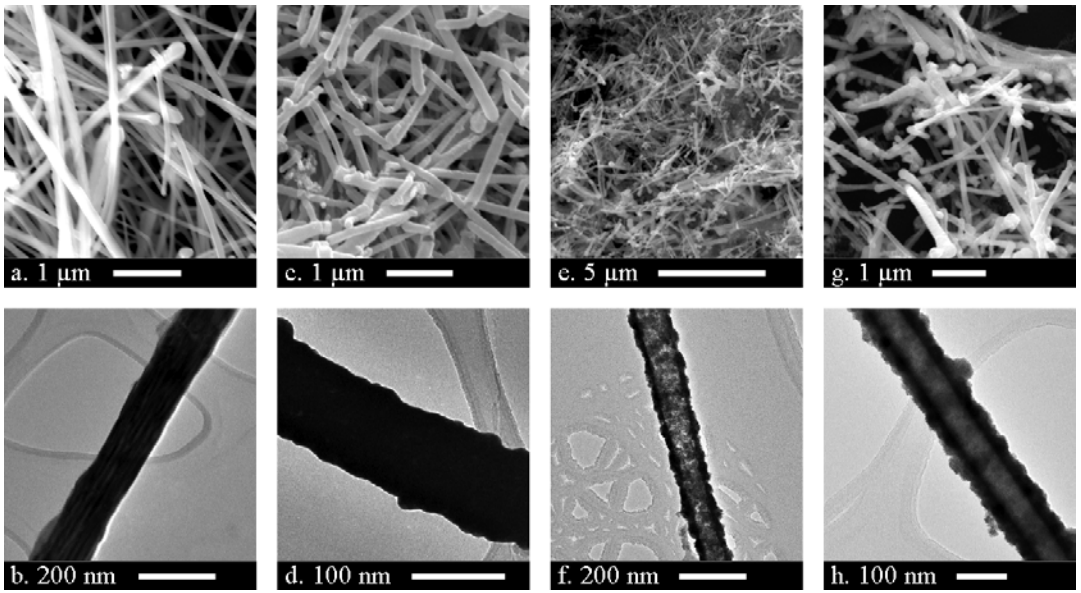


1. Displacement of Ag in AgNW with Pt to form PtNT;
2. Electrochemical deposition of Ru from $RuCl_3$ in H_2SO_4 at 0.3 V for 2 minutes.

PtRu Nanotubes from Cu Template



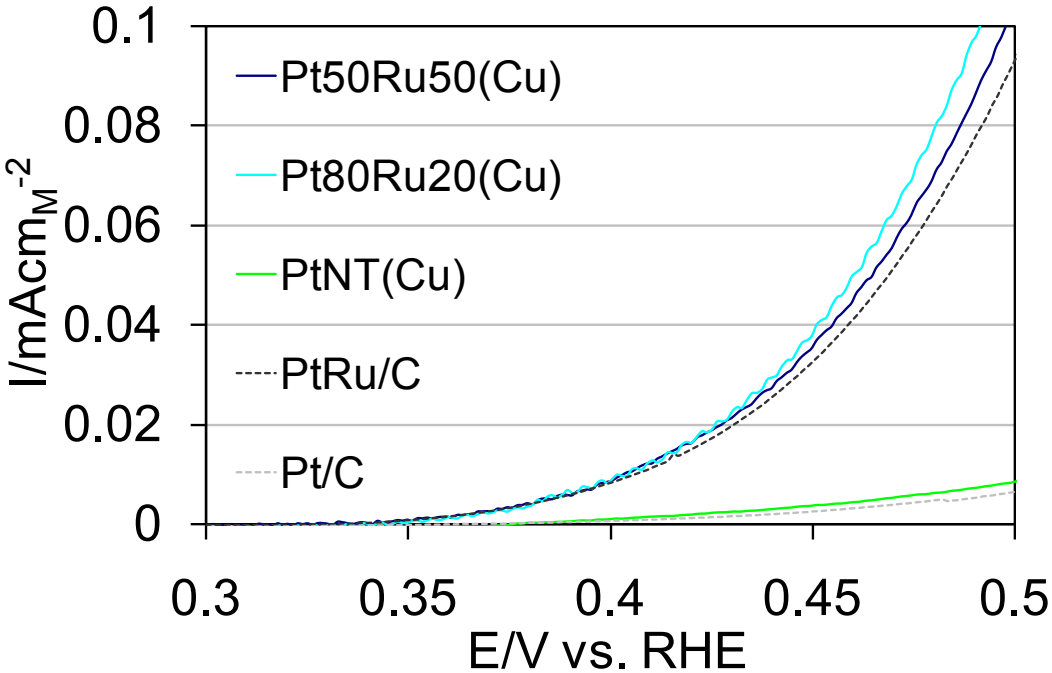
1. Simultaneous displacement of Cu in CuNW with Pt and Ru to form PtRuNT;
2. Annealing to form PtRu alloy.



SEM images: (a) CuNW; (c) PtNT; (e) $Pt_{80}Ru_{20}$ (Cu); (g) $Pt_{50}Ru_{50}$ (Cu).
TEM images: (b) CuNW; (d) PtNT; (f) $Pt_{80}Ru_{20}$ (Cu); (h) $Pt_{50}Ru_{50}$ (Cu).

Innovative Electrode Structures: PtRu Nanotube Catalyst Performance

Electrode preparation: *Catalysts coated onto a 5 mm glassy-carbon electrode at a total metal (Pt, Ru) loading of 80 µg cm^{-2}, followed by addition 10 µL of a 0.05 wt % Nafion® solution to ensure catalyst adhesion.*
Solution: *1.0 M MeOH in 0.5 M H_2SO_4;* ***Scan rate:*** *5 mV s^{-1}* ***Reference electrode:*** *RHE* ***Cell:*** *25ºC*



	E_{Onset} (V vs. RHE)
PtNT (Cu)	0.486
$Pt_{80}Ru_{20}$NT (Cu)	0.328
$Pt_{50}Ru_{50}$NT (Cu)	0.325
Pt/C	0.497
PtRu/C *	0.327

* HiSPEC® 12100

- **Highlight: Excellent specific activity for MeOH oxidation demonstrated with several PtRuNT catalysts; onset potential already matching the one measured with a state-of-the-art commercial catalyst (HiSPEC® 12100)**

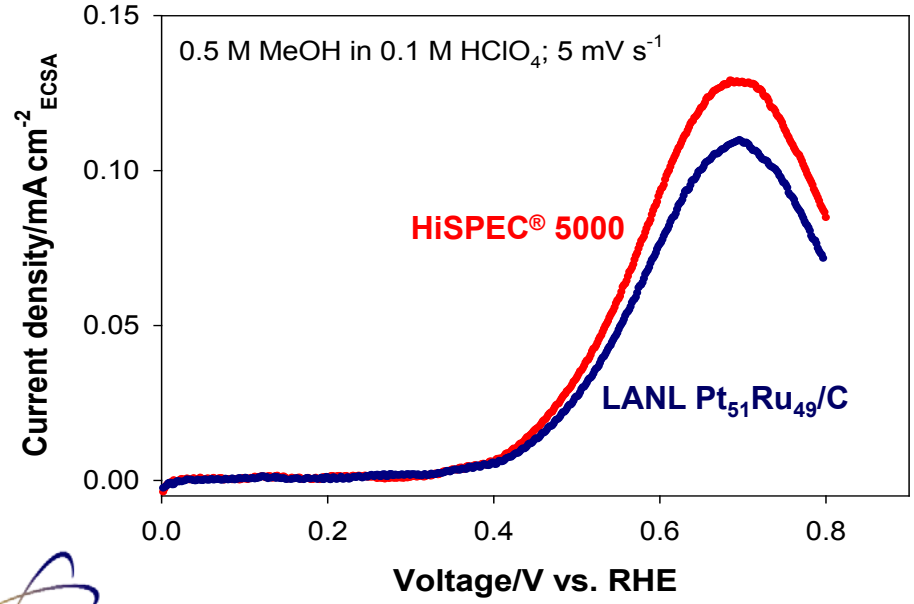
MeOH activity milestone achieved with PtRu nanotube catalysts

- **Mass activity of PtRu nanotube catalysts in need of improvement, for example, via thinning of the tube wall (presently *ca.* 11 nm)**

MeOH Oxidation: LANL PtRu/C Catalyst (for Improved Alloying)

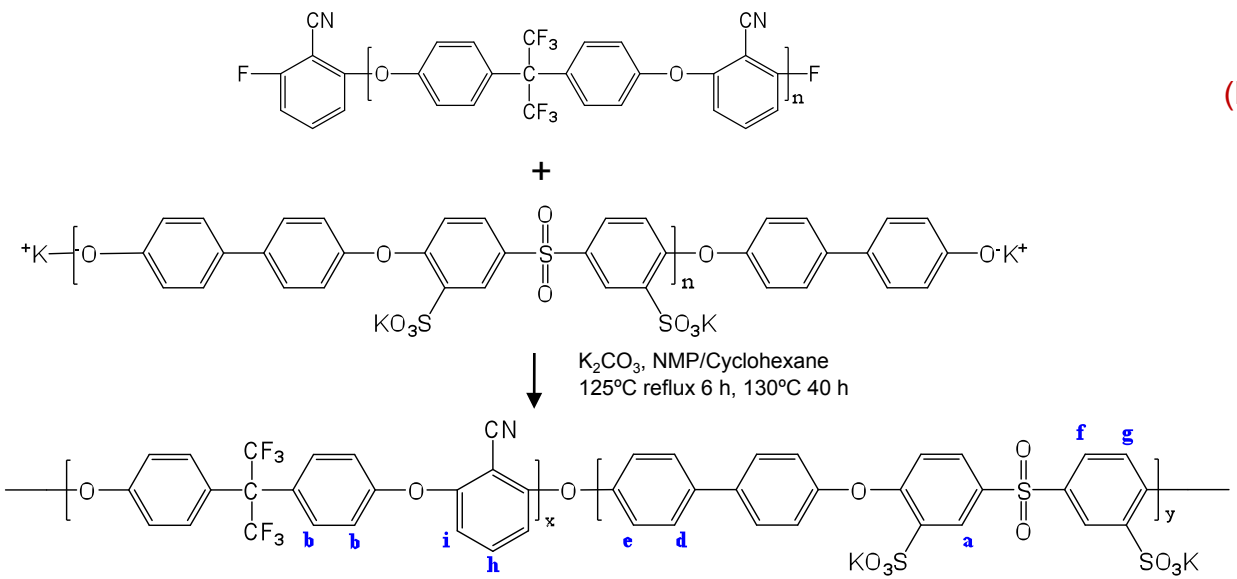
Characteristics	HiSPEC® 5000	LANL PtRu Catalyst
Metal loading by TGA in air (wt%)	23	27
Pt:Ru mass ratio by XRF	63:37 (50:50 at%)	64:36 (51:49 at%)
ECSA by CO stripping (m^2/g_{PtRu})	92	77
Onset potential [a] of MeOH oxidation (V vs. RHE)	0.34	0.34

[a] *Determined at a current equal to of 3× the standard deviation of background current*



- **Highlight: PtRu/C synthesized with the same onset potential for MeOH oxidation as that of the state-of-the-art commercial catalyst and possibly with improved alloying**
- **Next: XRD verification of alloying; study of catalyst stability under DMFC operating conditions; impact on ruthenium crossover**

Multiblock Copolymers for Reduced MeOH Crossover: Synthesis



Hydrophobic block

Partially fluorinated and CN functionality (Hexa**F**luoro **P**oly**A**rylene **E**ther **B**enzonitrile (6FPAEB))

+

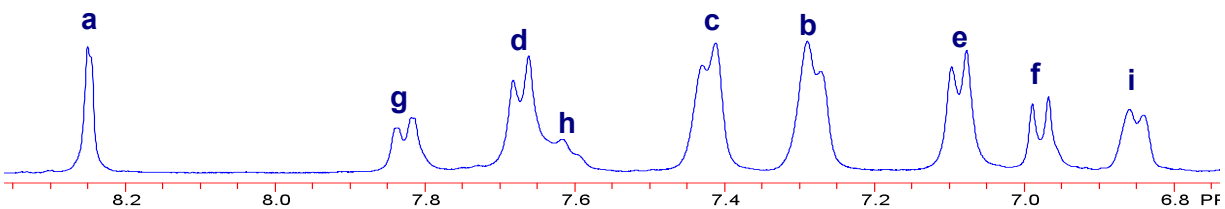
Hydrophilic block

Sulfonated groups (**B**iphenol based **P**olysulfone with **100**% di**S**ulfonation (BPS100))

↓

Multiblock copolymer

(6FPAEB-BPS100 *x-y*, *x* and *y* stand for M_W of each block in g/mol)



^{1}H NMR spectrum of 6FPAEB-BPS100 15k-15k

- **Partial fluorination of hydrophobic block to enhance proton conductivity via better phase separation and to improve adhesion (intactness) to Nafion® ionomer in electrodes**
- **Benzonitrile used to reduce MeOH permeability via complexation with H_2O molecules**
- **Highly-sulfonated hydrophilic block increasing proton conductivity**
- **^{1}H NMR confirming the chemical structure of multiblock copolymer**

Copolymer synthesis milestone achieved

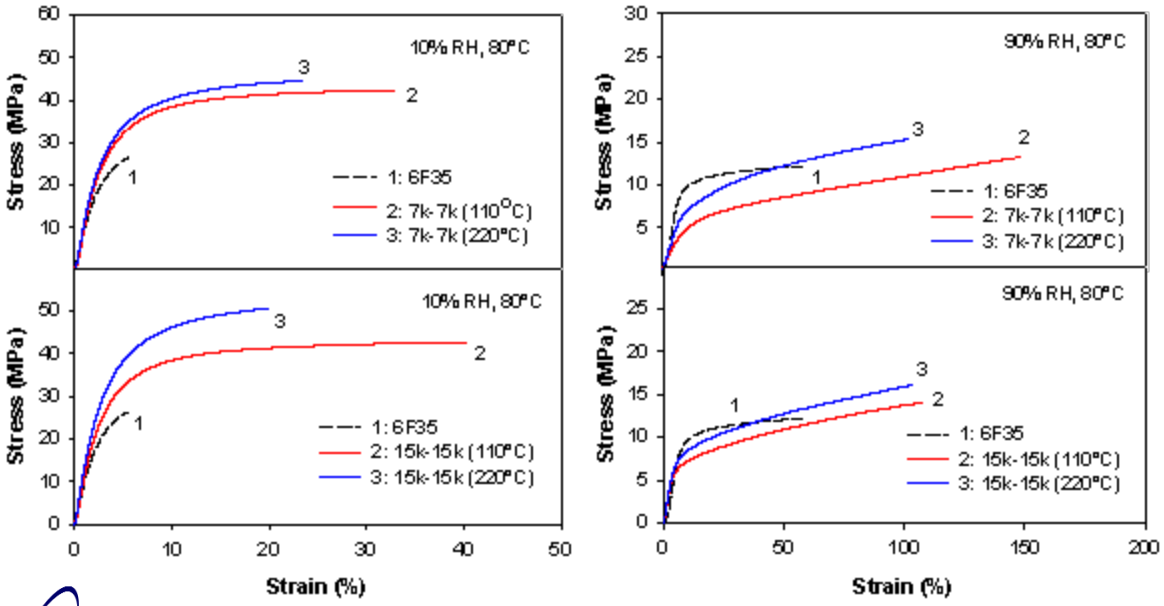
Multiblock Copolymers for Reduced MeOH Crossover: Properties

Polymer	IV (dL/g) [b]	IEC (meq/g) [c]	Water Uptake (wt%)	Conductivity[d] (mS/cm)
Nafion® 212	n/a	1.00	22	120
6FPAEB35 (random)[a]	0.62	1.50	32	80
6FPAEB-BPS 7k-7k[a]	0.61	1.55	42	137
6FPAEB-BPS 15k-15k[a]	1.01	1.55	46	147

[a] Annealed at 220ºC; [b] Measured by GPC with 0.05 M LiBr/NMP as mobile phase at 60ºC; [c] From ^1H NMR; [d] Measured in liquid water at 30ºC.

- **Higher water uptake (undesirable) and proton conductivity (desirable) observed with multiblock than random copolymer**
- **Highlight: Proton conductivity increase much larger than rise in water uptake**
- **Next: Reduction in water uptake by e.g., lowering the annealing temperature and block length**

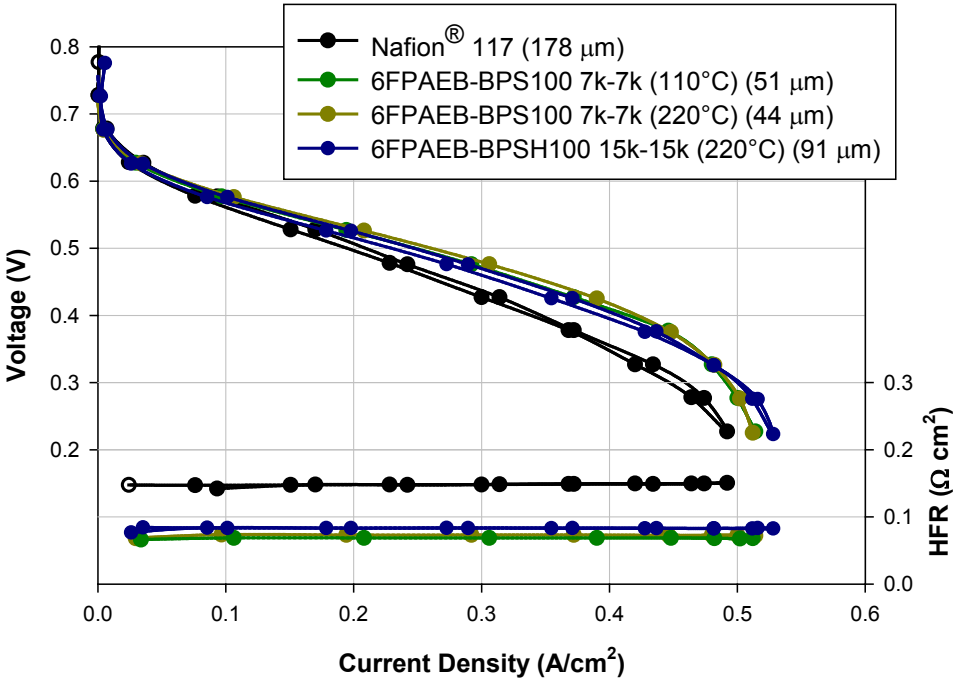
Stress-Strain Curves



Annealing temperature given in parenthesis

- **Highlight: Mechanical properties successfully improved by using multiblock-copolymer approach**
- **At 10% RH and 90% RH, higher toughness (integral of stress-strain curves) measured for all multiblock copolymers compared to random copolymer**
- **Lower annealing temperature giving better elongation, especially for the 15k-15k material; higher annealing temperature giving higher stress value**

Multiblock Copolymers for Reduced MeOH Crossover: DMFC Performance



Anode: *6 mg cm^{-2} $Pt_{50}Ru_{50}$ black, 1.8 mL/min 0.5 M MeOH solution;* ***Cathode:*** *4 mg cm^{-2} Pt black; 500 sccm air;* ***Membrane:*** *Multiblock copolymers and Nafion® 117;* ***Cell:*** *80ºC;* ***Dwell time:*** *60 s*

PEM	MeOH crossover[a] (mA/cm²)	MeOH permeability (cm²/s)
Nafion® 117	72	4.6×10^{-6}
6FPAEB-BPS 7k-7k (110ºC)	114	1.6×10^{-6}
6FPAEB-BPS 7k-7k (220ºC)	110	1.5×10^{-6}
6FPAEB-BPS15k-15k (220ºC)	90	1.8×10^{-6}

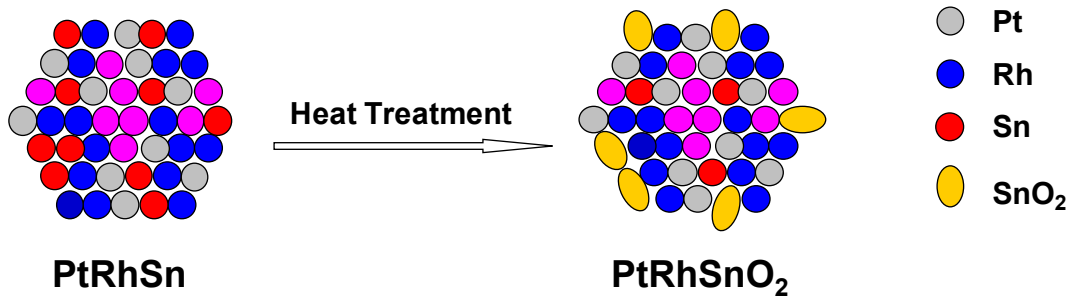
[a] *Measured in limiting-current experiments*

- **Good adhesion (intactness) of multiblock-copolymer membranes and Nafion®-bonded electrodes observed during MEA processing and DMFC testing**
- **Three times lower MeOH permeability of multiblock-copolymer membranes allowing for the use of thinner membranes in DMFC testing**
- **Highlight: Multiblock-copolymer membranes outperforming Nafion® 117 in DMFC testing, even at a relatively low MeOH concentration of 0.5 M MeOH; even larger improvement expected at higher MeOH concentrations**

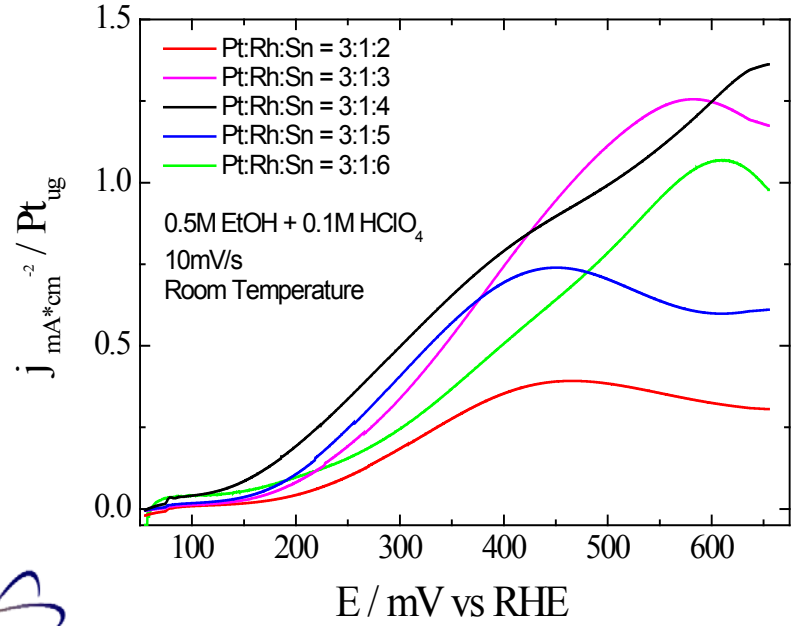
Ethanol Oxidation: Ternary $PtRhSnO_2$ Catalyst

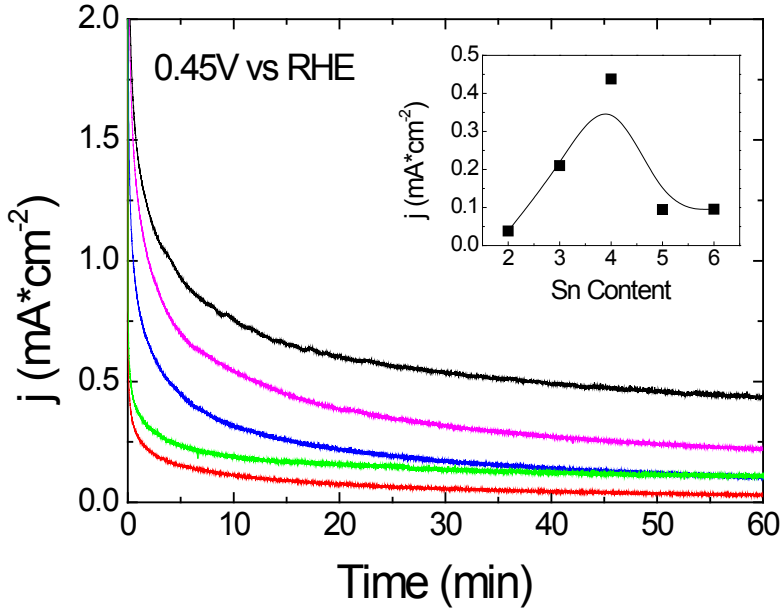
Ternary $PtRhSnO_2$ <u>model</u> catalyst capable of oxidizing EtOH to CO_2 (at 25°C):

- 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

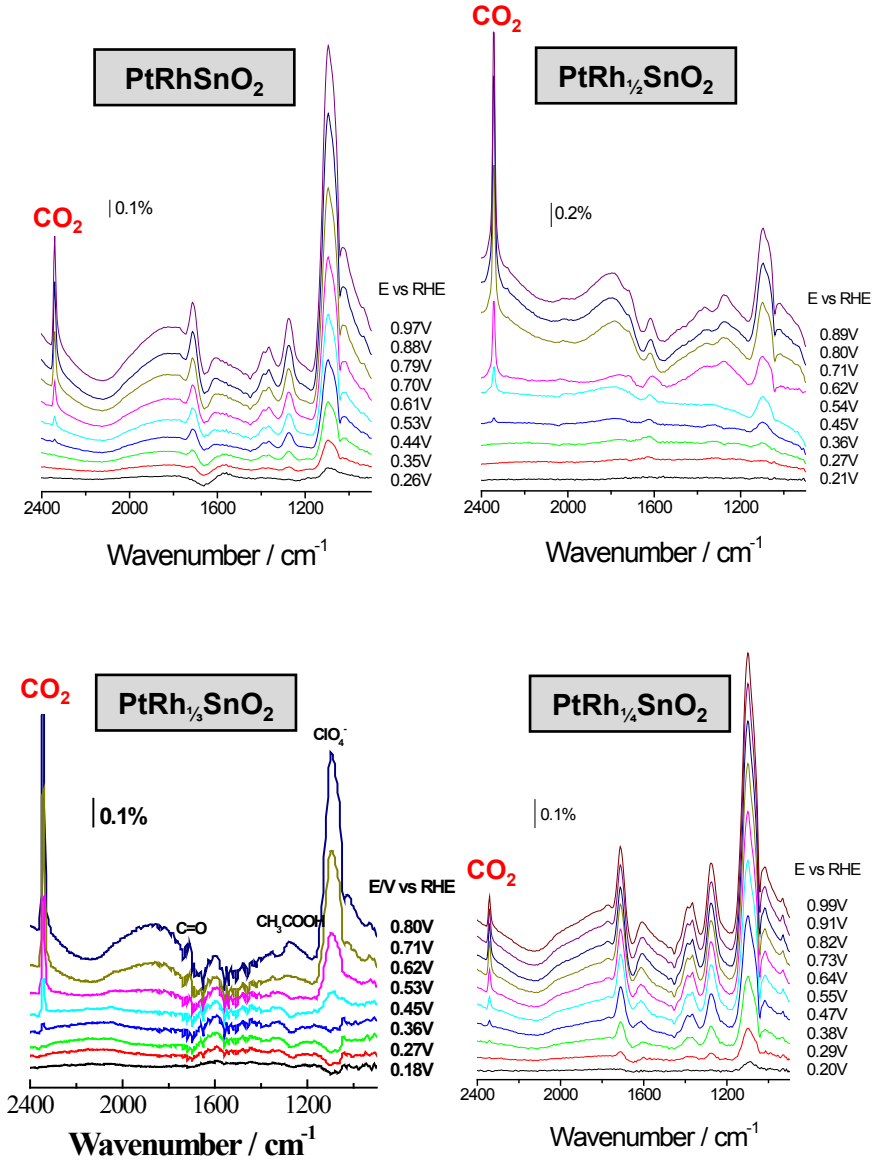


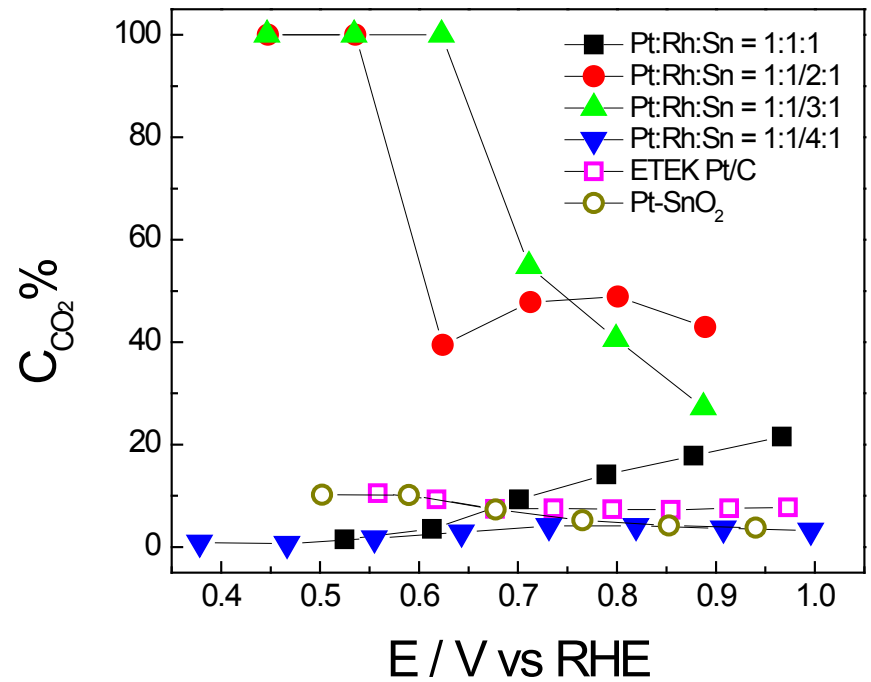
Pt:Rh:Sn = 3:1:[Sn Content]





Ethanol Oxidation: $PtRhSnO_2$ Catalyst Optimization

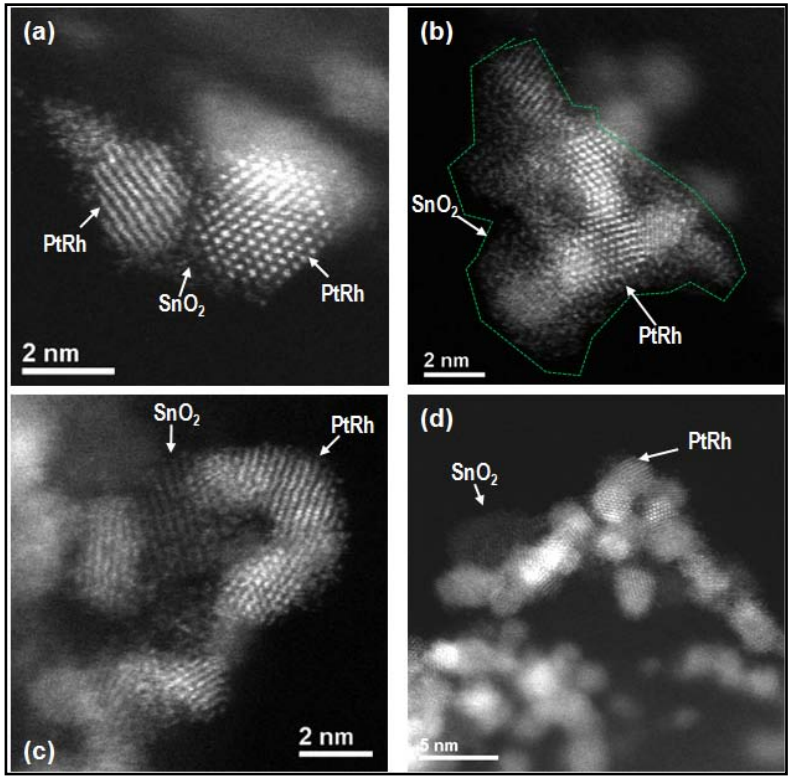




- **At low potentials, CO_2 generation dominant with the most active ethanol oxidation catalysts ($PtRh_{1/2}SnO_2$ and $PtRh_{1/3}SnO_2$)**
- **<u>Highlight</u>: Best $PtRhSnO_2$ catalysts showing unprecedented activity in ethanol oxidation**

Ethanol Oxidation: $PtRh_{1/2}SnO_2$ Catalyst Characterization

Aberration-corrected DF-STEM

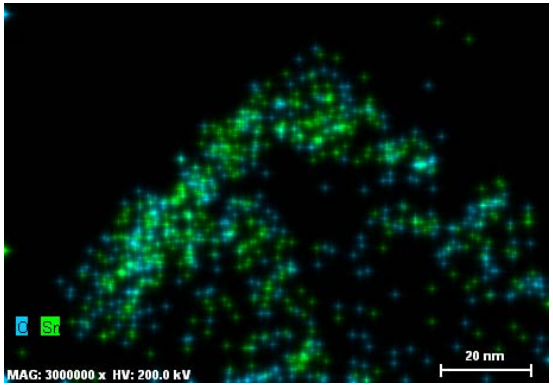


(a), **(b)** – 1-2 nm PtRh particles on amorphous SnO_2 (Pt ensembles likely too small for optimal EtOH adsorption)

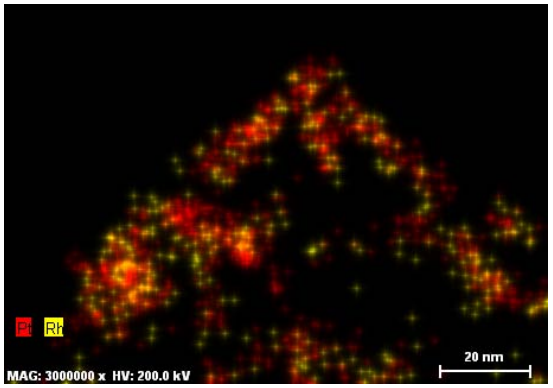
(c) - PtRh nanoparticles on crystalline SnO_2; PtRh(111) spacing 2.27 Å; SnO_2 spacing *ca.* 2.78 Å, corresponding to the (011) SnO_2 lattice planes

(d) - discrete 1-2 nm PtRh nanoparticles on amorphous SnO_2 used for EDS mapping (*on the right*)

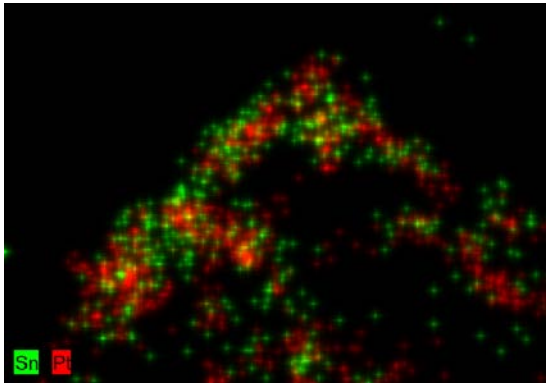
EDS Elemental Mapping



Broad oxygen signal associated with Sn confirming formation of broad SnO_2 fragments

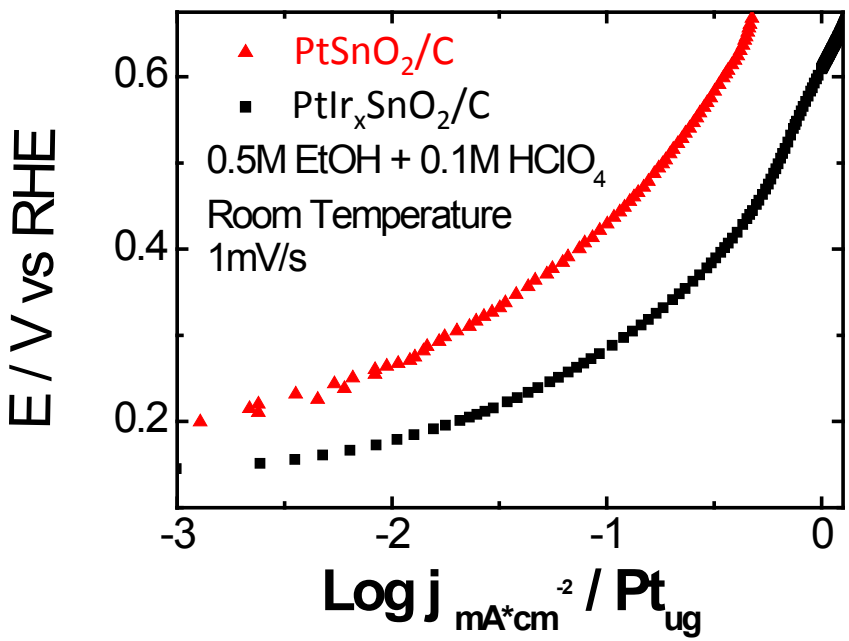


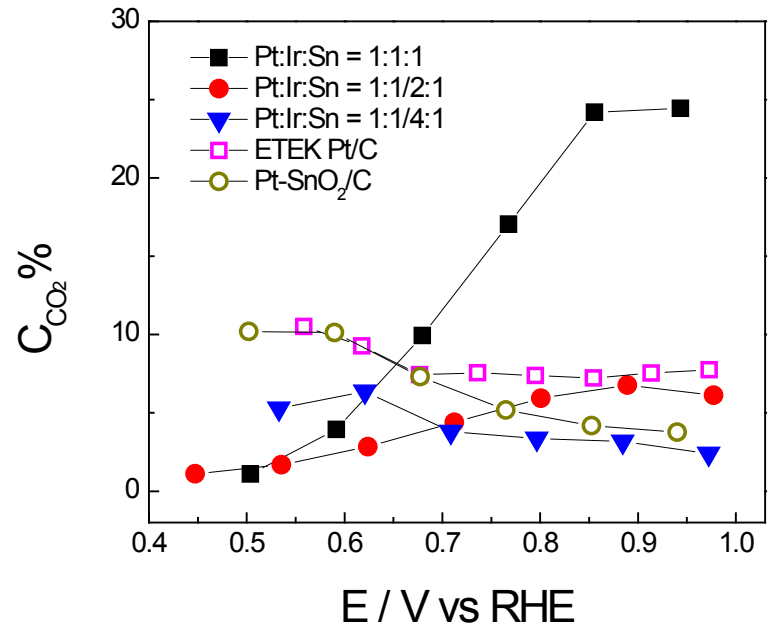
Pt-Rh map suggesting random alloying (in agreement with EXAFS)

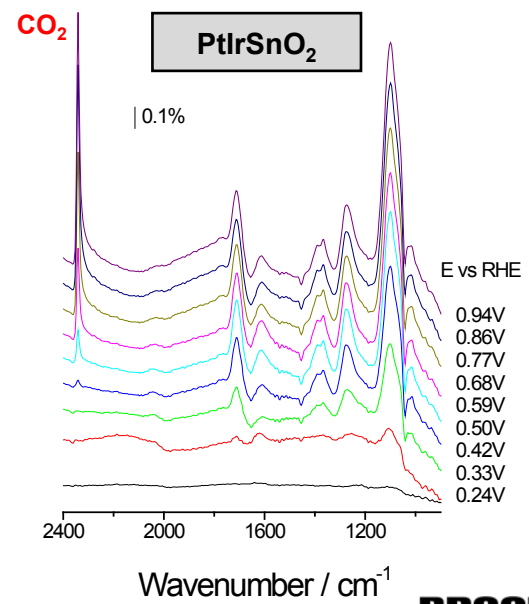


Sn-Pt map indicating decoration of SnO_2 by PtRh nanoparticles

Ethanol Oxidation: $PtIr_xSnO_2$ Catalysts

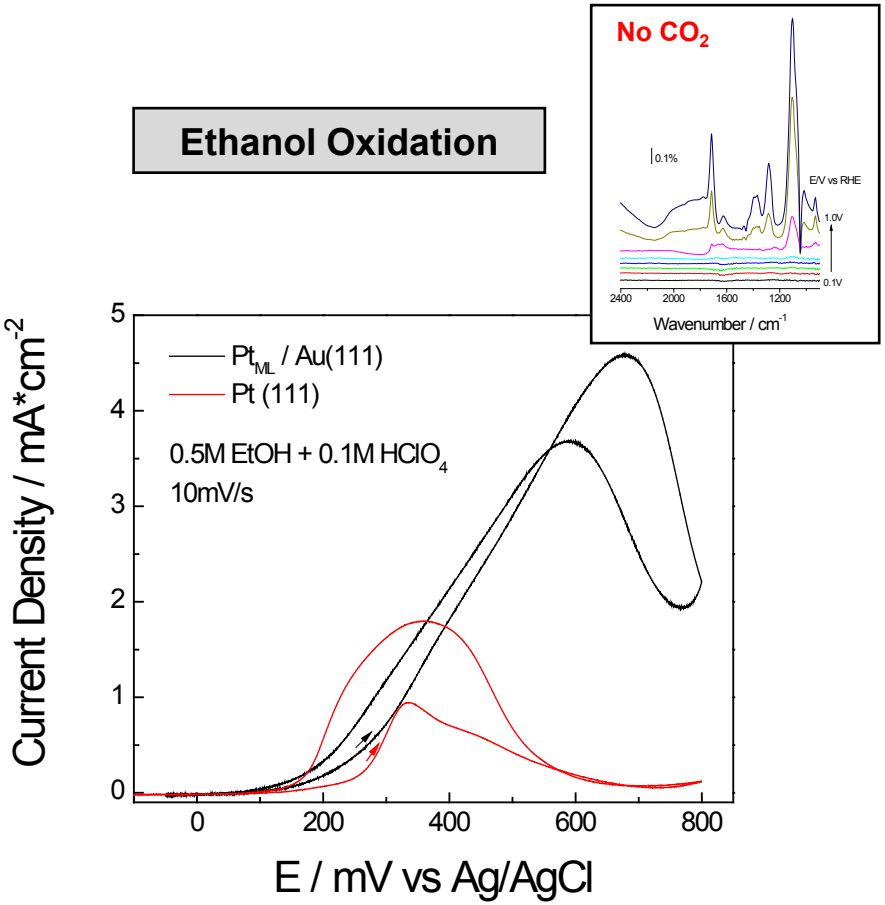


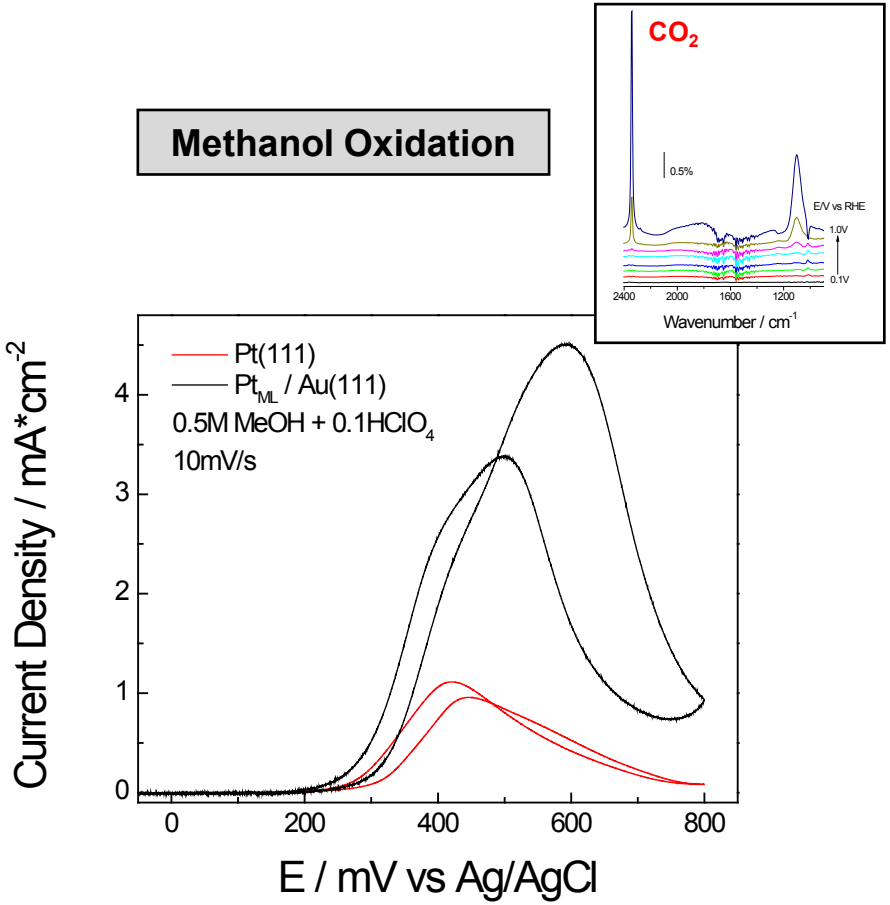




- **Ir-based ternary catalysts exhibiting significant catalytic activity in EtOH oxidation to CH_3COOH**
- **Selectivity of Ir-based ternary catalysts for CO_2 formation much lower than that of the best $PtRhSnO_2$ catalysts**

Ethanol and Methanol Oxidation: Pt_{ML}/Au(111) Catalyst Study





- **IRRAS data attesting to high CO_2 production at a Pt_{ML}/Au(111) catalyst from MeOH (but not EtOH); low oxidation onset potentials values observed**
- **<u>Highlight</u>: Au showing promising characteristics as support for EtOH and MeOH; worth further investigation**

Direct Dimethyl Ether Fuel Cell (DDMEFC)

DME Advantage

- Higher energy density than MeOH (12 e^-/molecule; 8.2 kWh/kg)
- No C-C bond to split
- Possibly lower crossover compared to MeOH (lower dipole moment)
- Storable as high density liquid at *ca.* 75 psig
- Amenable to gaseous, pump-less feed (handling similar to propane and butane); existing infrastructure usable
- Low toxicity, comparable to liquid propane; not spreadable into groundwater; decomposable in atmosphere within tens of hours

Muller *et al.*, *J. Electrochem. Soc.* **147**, 4058, 2000.
Mench *et al.*, *J. Electrochem. Soc.* **151**, A144, 2004.

$$CH_3-O-CH_3 + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$$

$$3O_2 + 12H^+ + 12e^- \rightarrow 6H_2O$$

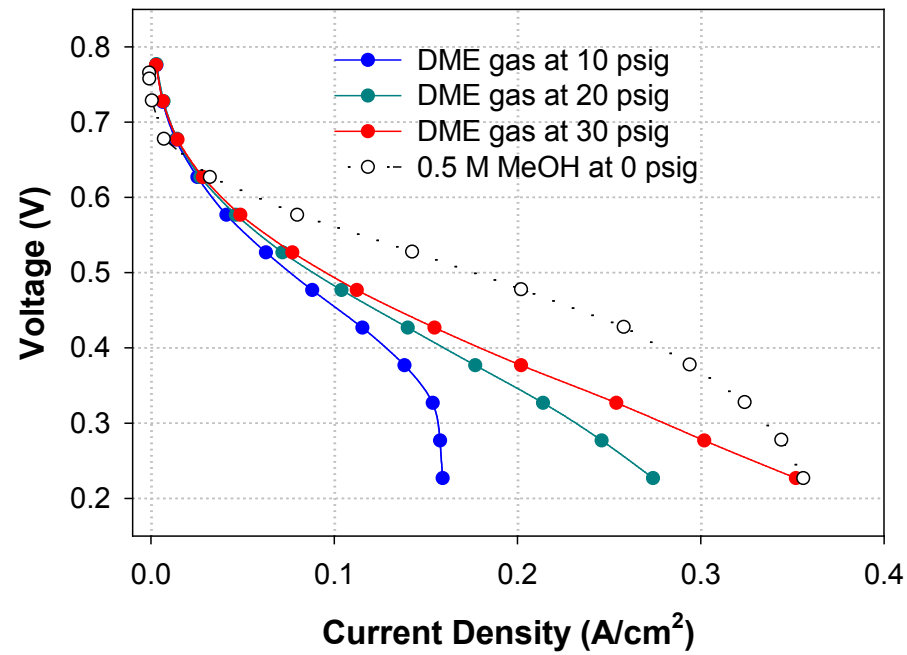
$$CH_3-O-CH_3 + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

Anode: *6 mg cm^{-2} $Pt_{50}Ru_{50}$ black, 1.8 mL/min MeOH solution or 40 mL/min DME gas;* ***Cathode:*** *4 mg cm^{-2} Pt black, 30 psig (with DME) or 0 psig (with MeOH), 500 sccm air;* ***Membrane:*** *Nafion® 117;* ***Cell:*** *80ºC*

- **Lower DDMEFC than DMFC performance measured with MEAs optimized for methanol (but many paths for improvement exist)**

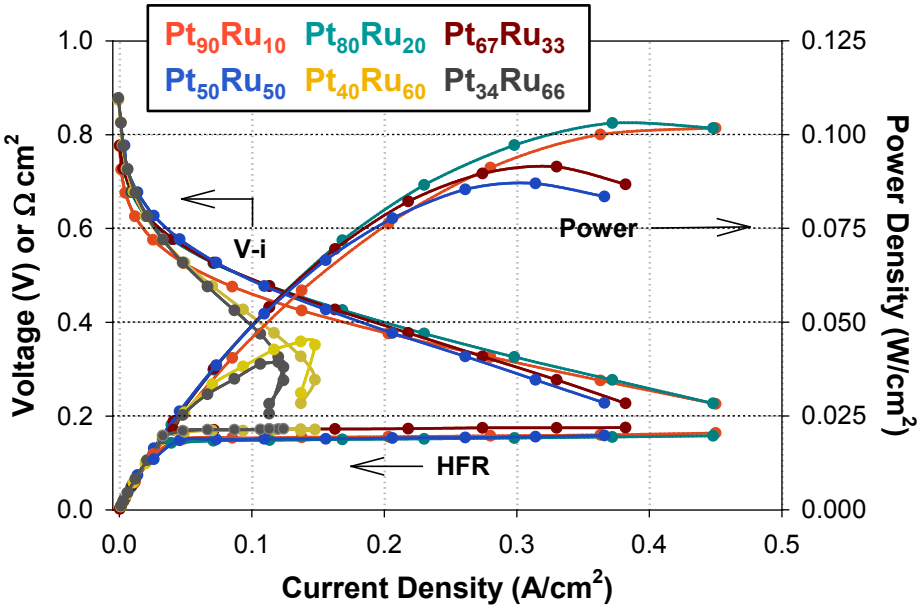
  Baseline milestone achieved

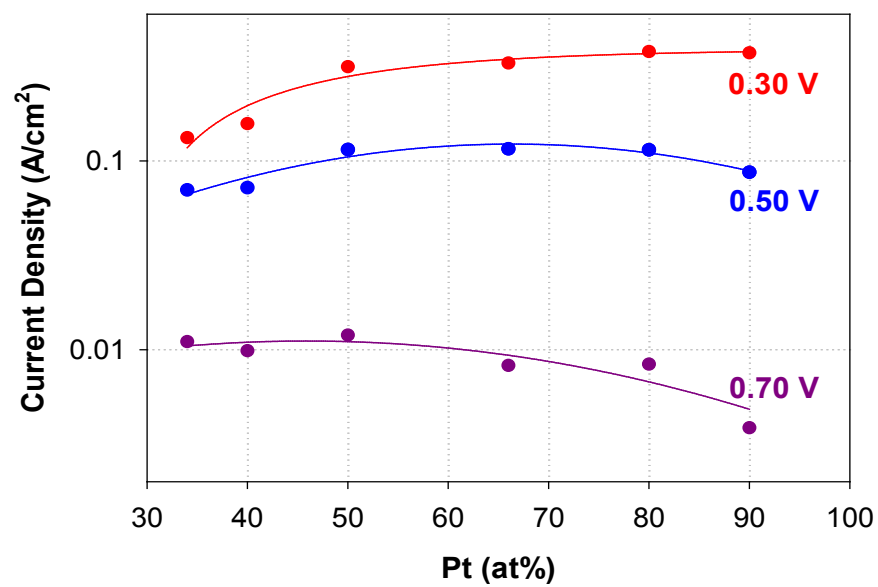
- **DDMEFC performance strongly depending on pressure; only slight dependence on fuel flow rate observed (40-200 sccm)**
- **Next: Assess DDMEFC feasibility versus DMFC after further optimization of the DME anode (go/no-go decision in FY12)**



DME Fuel Cell: Anode Catalysts with Different Pt-to-Ru Ratios

Anode: *6 mg cm^{-2} PtRu, 40 sccm DME gas, 30 psig;* ***Cathode:*** *4 mg cm^{-2} Pt, 20 psig, 500 sccm air;* ***Membrane:*** *Nafion® 117;* ***Cell:*** *80°C*





- **Highlight: Wide range of Pt-to-Ru ratios screened for DME anode performance for the first time**

  Milestone achieved with a higher number of PtRu catalysts (six instead of three)

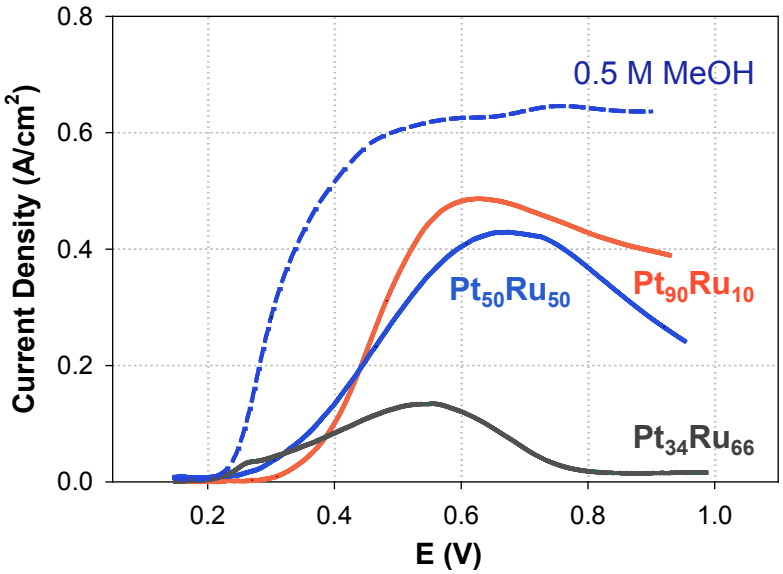
- **Highlight: $Pt_{50}Ru_{50}$ exhibiting overall best performance in high and middle voltage ranges; Pt-rich catalysts performing better at low voltages (near peak power); behavior more complex than that of DMFC anode catalysts** (technical backup slide)

- **Next: Effect of anode catalyst composition on Ru crossover and cathode performance (relevant to both DDMEFC and DMFC); half-cell DME studies with PtRu catalysts (far fewer prior reports on DME catalysis exist compared to MeOH catalysis)**

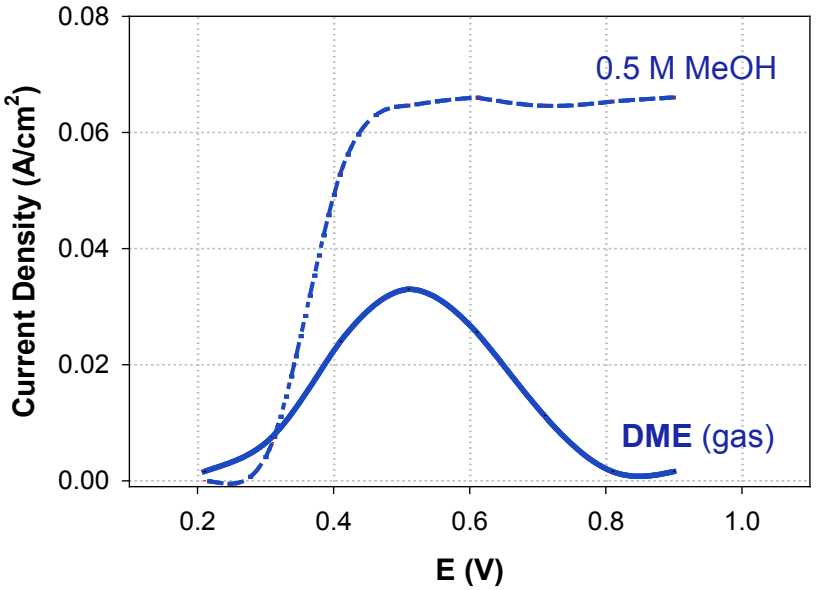
DME Fuel Cell: PtRu Anode Activity and Fuel Crossover

Anode: *6 mg cm^{-2} $Pt_{50}Ru_{50}$ black, 40 sccm DME, 30 psig or 6 mg cm^{-2} $Pt_{50}Ru_{50}$ black, 0.5 M MeOH, 1.8 mL min^{-1};* ***Cathode:*** *4 mg cm^{-2} Pt black, 20 psig, 200 sccm H_2;* ***Membrane:*** *Nafion® 117;* ***Cell:*** *80ºC*

DME Anode Polarization Plots



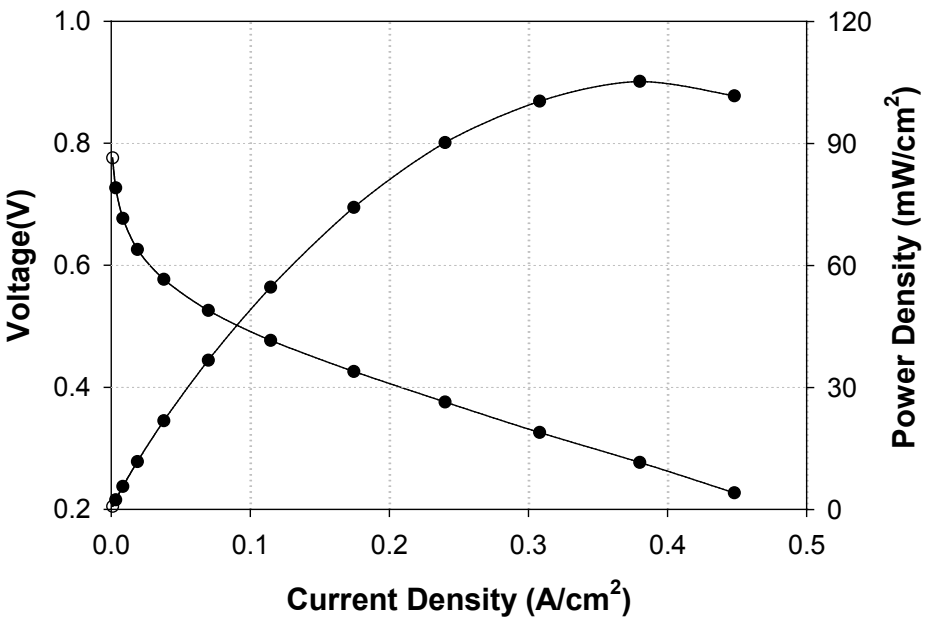
DME and MeOH Crossover Plots



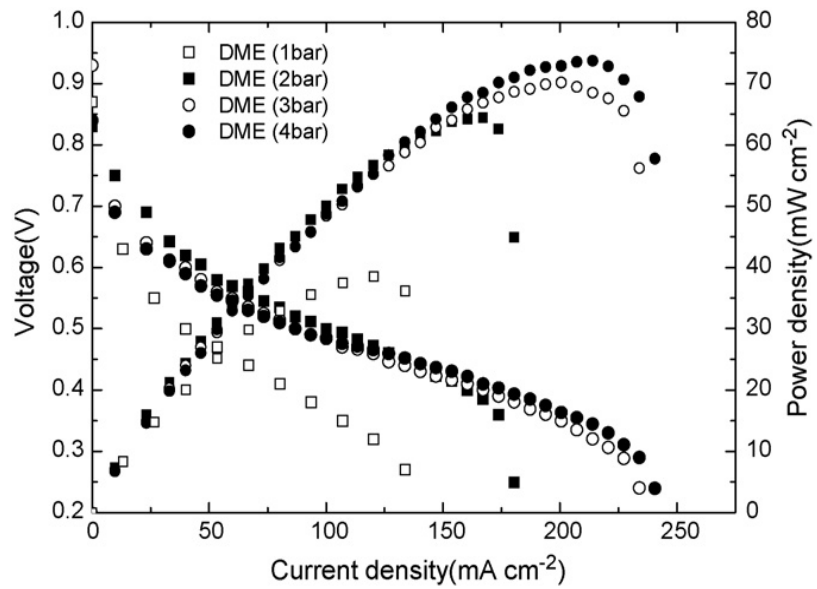
- **PtRu anode deactivation occurring at high potentials, likely due to the surface oxide formation**
- **Highlight: Anode deactivation more pronounced at high Ru content (likely more oxophilic and thus less active surface)**
- **Highlight: DME oxidation current at the cathode is much lower than that of MeOH, especially at higher potentials**
- **Next: Half-cell study to verify the impact of surface oxide(s) on DME oxidation on PtRu catalysts**

DME Fuel Cell: Performance Relative to Previous Work

Anode: *6 mg cm^{-2} $Pt_{80}Ru_{20}$ black, 40 sccm DME gas, 30 psig;* ***Cathode:*** *4 mg cm^{-2} Pt black, 20 psig, 500 sccm air;* ***Membrane:*** *Nafion® 117;* ***Cell:*** *80ºC*



Anode: *5 mg cm^{-2} PtRu black, DME-saturated aqueous solution, 1.2 mL min^{-1};* ***Cathode:*** *5 mg cm^{-2} Pt black, 300 sccm air;* ***Membrane:*** *Nafion® 117;* ***Cell:*** *80ºC*



Im *et al., J. Power Sources* **179**, 301, 2008

Highlight: In spite of using gaseous DME feed, the performance of LANL DDMEFC at 80ºC exceeding the best previous published result

Collaborations

- **Seven organizations with highly complementary skills and capabilities in catalyst development, electrode-structure design, materials characterization, MEA fabrication, and portable fuel cell development and commercialization:**
  - ✓ Los Alamos National Laboratory and Brookhaven National Laboratory – *direct DOE-EERE contracts*
  - ✓ University of California-Riverside and Virginia Tech – *subcontracts to Los Alamos National Laboratory*
  - ✓ Johnson Matthey Fuel Cells and SFC Energy – *subcontracts to Brookhaven National Laboratory*
  - ✓ Oak Ridge National Laboratory – *no cost partner*
- **Collaborations outside Fuel Cell Technologies Program:**
  - ✓ University of Iceland, Reykjavik, Iceland and The School of Renewable Energy Science, Akureyri, Iceland – ruthenium crossover research project completed at LANL in January 2011 by Anna Trendewicz, an exchange graduate student from Iceland
  - ✓ University of Waterloo, Waterloo, Ontario, Canada – initial phase of collaboration in the development of nanostructured methanol oxidation catalysts
  - ✓ Ballard Power Systems, Burnaby, British Columbia, Canada – preliminary collaborative discussions; two common presentations on catalyst crossover in fuel cell systems

Proposed Future Work: Remainder of FY11 and FY12

Methanol oxidation catalysis:

- Perform comprehensive activity and stability study of advanced MeOH oxidation catalysts versus HiSPEC®12100 as a benchmark
- Complete evaluation of PtSnX catalysts for upcoming go/go-no decision on PtSn catalysts in FY12
- Evaluate the degree of Ru crossover resulting from advanced MeOH oxidation catalysts

Innovative membranes and electrode structures:

- Determine durability of multiblock copolymers in an operating fuel cell; reduce polymer water uptake
- Improve dimension control and eliminate oxidation of CuNW (before galvanic displacement)
- Significantly reduce wall thickness of PtRu nanotubes to at least double the catalyst surface area

Ethanol oxidation catalysis:

- Increase the size of PtRh nanoparticles to enhance the size of Pt ensembles in $PtRhSnO_2$ catalyst and to facilitate adsorption an dehydrogenation of the EtOH molecule
- Scale up the synthesis of a selected ternary catalyst to 2 g per batch for MEA testing
- Evaluate Au clusters and/or supported Au-monolayers as catalyst supports
- Complete DEMS instrument set-up

DME research:

- Determine the effect of anode catalyst composition on Ru crossover and cathode performance (relevant to both DDMEFC and DMFC)
- Complete half-cell DME studies with PtRu catalysts
- Assess DDMEFC feasibility versus DMFC following full optimization of the DME anode (go/no-go decision on DME research in FY12)

Summary

- Thrifted PtRu catalyst of MeOH oxidation meets and significantly exceeds 2011 mass activity target (200 mA/mg_{Pt})
- PtRu nanotube catalysts exhibit promising methanol oxidation activity; however, mass activity needs to be increased by, for example, thinning tube walls
- Multiblock 6FPAEB-BPS100 copolymers with improved mechanical properties and high proton conductivity show lower MeOH permeability and better DMFC performance compared to Nafion®
- Ternary $PtRhSnO_2$ electrocatalysts exhibit unprecedented activity for ethanol oxidation and produce large amounts of CO_2
- Ternary catalysts with a Rh-to-Pt ratio between 1:3 and 1:2 have the highest activity in EtOH oxidation; an increase in the catalyst particle size may be required for efficient EtOH adsorption and dehydrogenation
- Au represents potentially promising support for EtOH and MeOH oxidation catalysts
- Unlike in MeOH oxidation, the optimal PtRu catalyst composition varies depending on the operating voltage of the DME fuel cell (anode potential)
- DME crossover is less than that of MeOH under typical testing conditions
- A LANL DDMEFC operating with a $Pt_{50}Ru_{50}$ anode catalyst has shown the highest performance reported to date at 80°C
- All project milestones have been achieved or are on track to completion

Co-Authors

- **ethanol and methanol anode catalyst research**

  R. R. Adzic (PI), M. Li, K. Sasaki, M. Vukmirovic

- **anode catalyst and membrane research; characterization**

  P. Zelenay (Project Lead), H. Chung, Z. Ding, C. Johnston, Y. S. Kim, Q. Li, A. Trendewicz, P. Turner, G. Wu

- **nanostructure catalyst structures**

  Y. Yan (PI), S. Alia

- **hydrocarbon membrane research**

  J. McGrath (PI), Y. Chen, C. H. Lee, M. Lee

- **methanol anode catalyst research; MEA integration**

  N. Permogorov (PI), G. Hards, G. Spikes

- **MEA integration and testing; final deliverable**

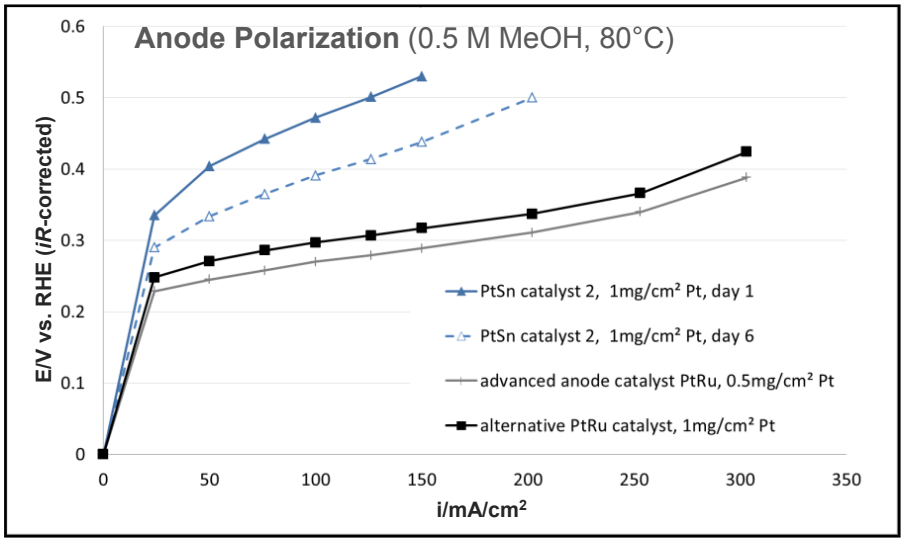
  V. Graf (PI), C. Böhm, J. Stephens

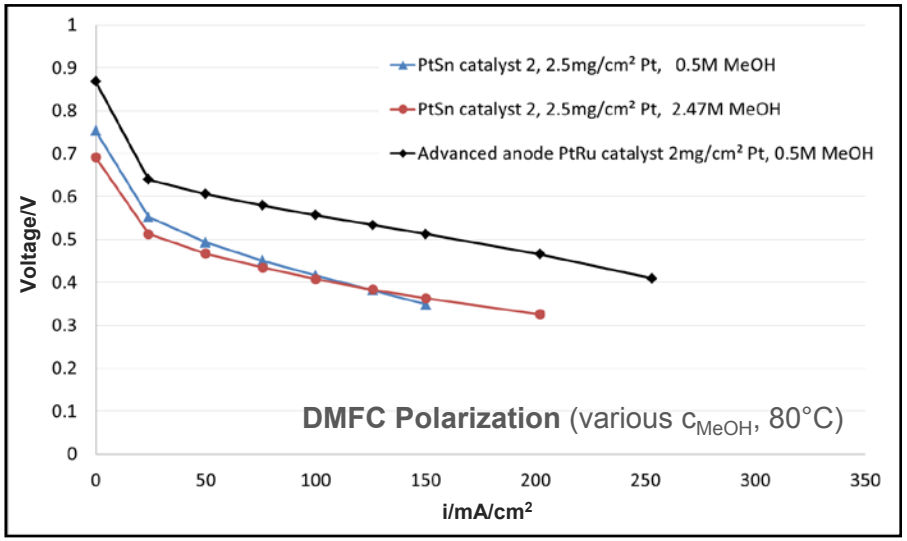
- **microscopic characterization** (no-cost partner)

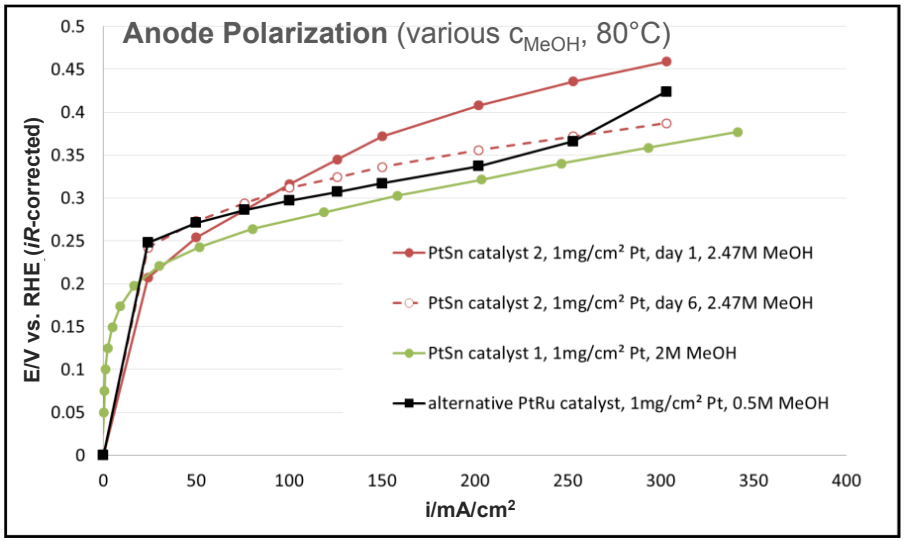
  K. More (PI), D. Cullen

Technical Back-Up Slides

MeOH Oxidation: PtSn Catalysts

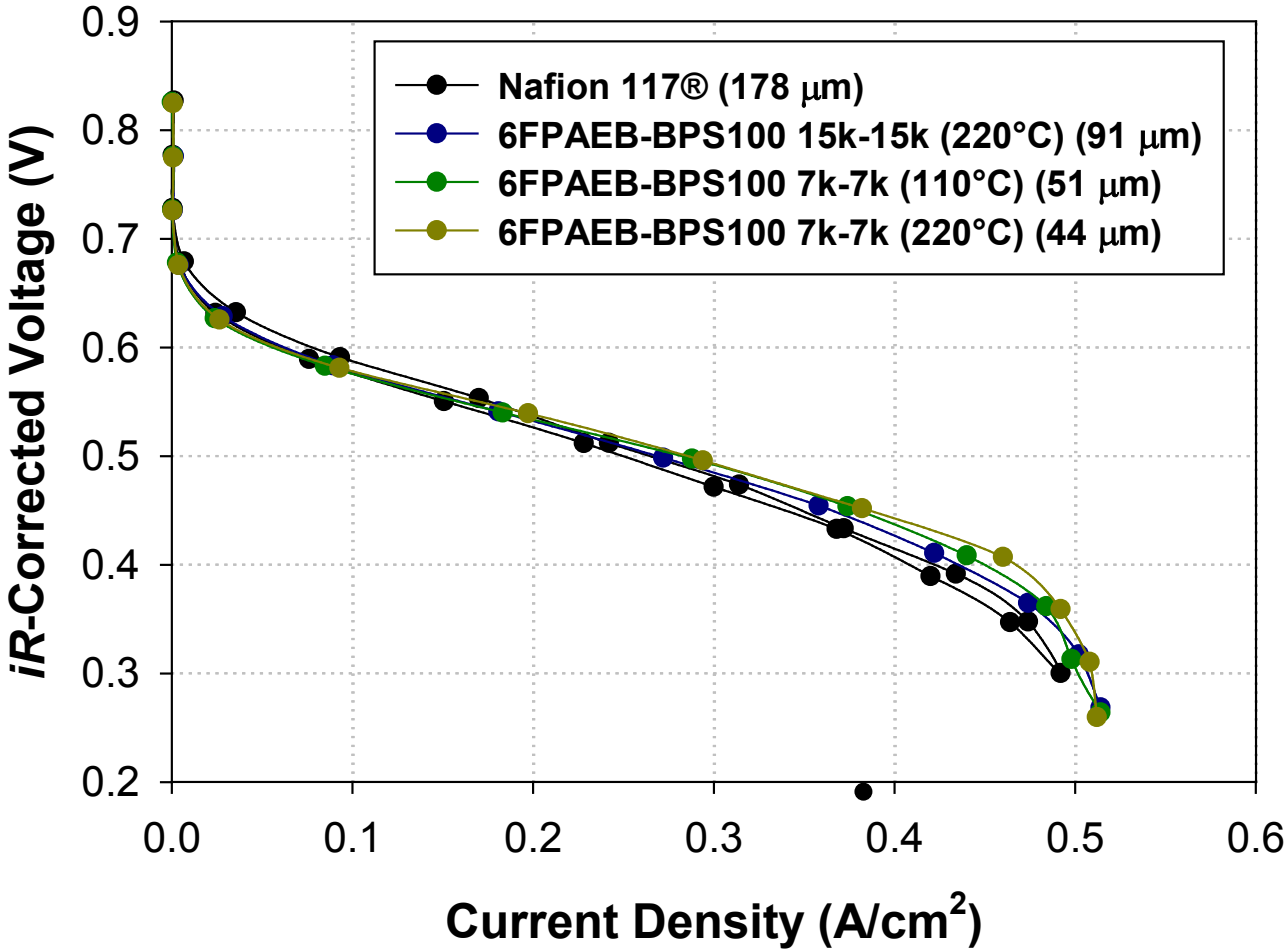






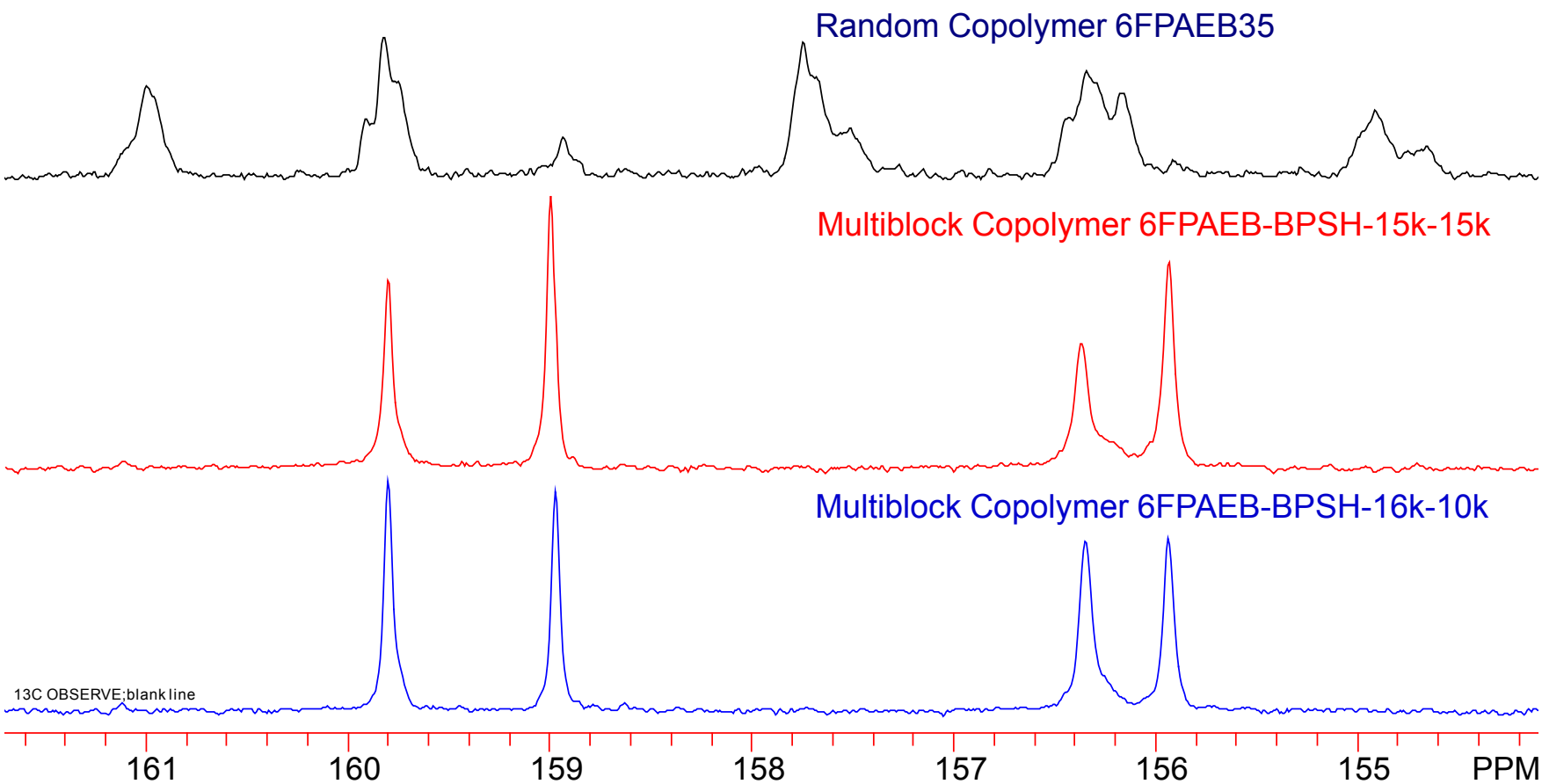
- **At 0.5 M MeOH, PtSn catalyst performing very poorly; anode performance improved at higher MeOH concentrations (2.0 and 2.47 M)**
- **Different rate limiting step of MeOH oxidation on PtSn catalysts than PtRu catalysts**
- **High fuel crossover responsible for poor DMFC performance at high MeOH concentrations**
- **Even before durability testing PtSn catalysts offering little promise for DMFC anode application**

Multiblock Copolymers for Reduced MeOH Crossover: DMFC Performance



***iR*-corrected data**

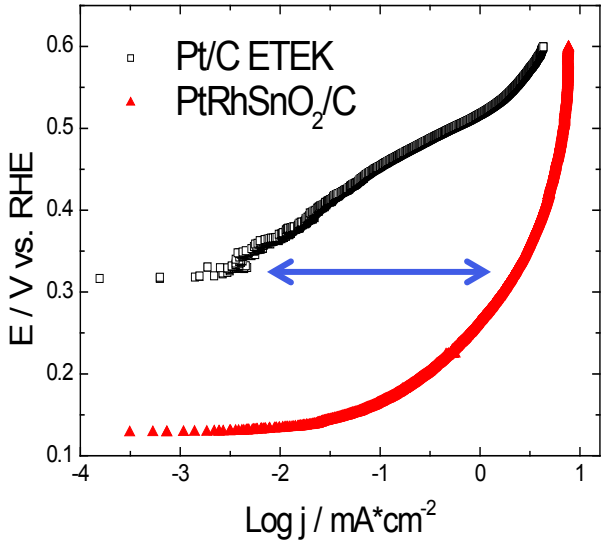
^{13}C NMR of Random and Multiblock Copolymers



Increased phase separation of multiblock copolymers apparent from sharp peaks

Ethanol Oxidation: $PtRhSnO_2$ Catalyst (Overview)

Electrochemical Activity

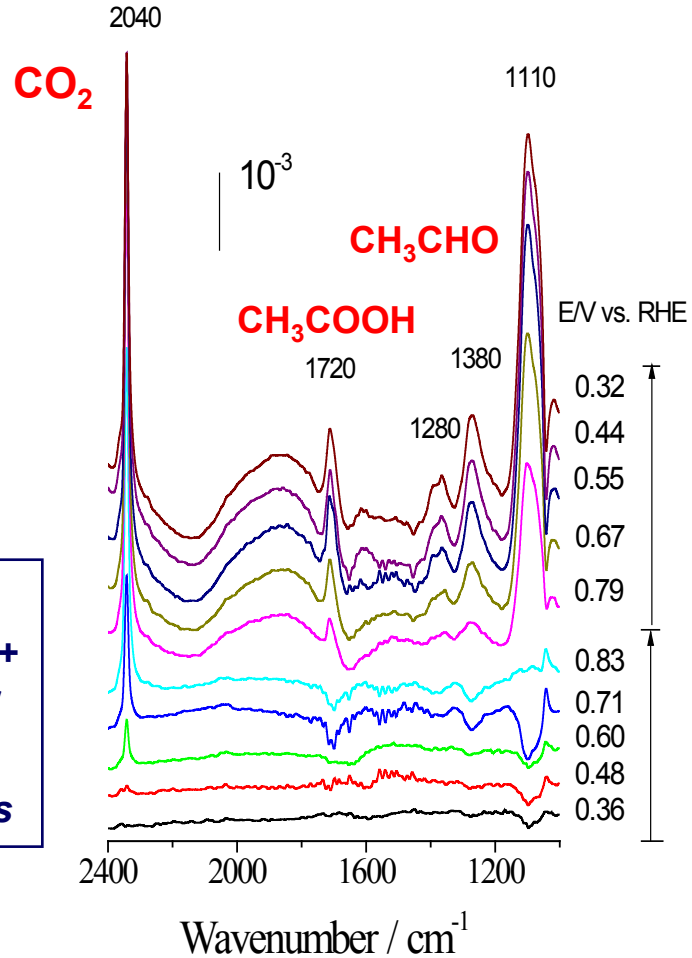


Modified polyol synthesis method

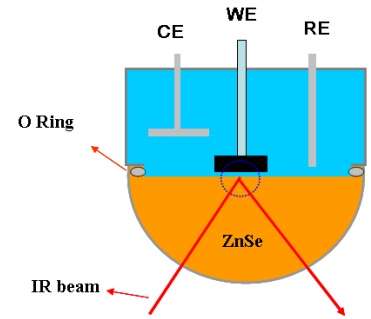
$PtRhSnO_x$ colloid: H_2PtCl_6 + $RhCl_3$ + $SnCl_2$+ NaOH + EG + H_2O 200ºC, Ar

Homogeneous distribution of Pt and Rh throughout 1-3 nm particles

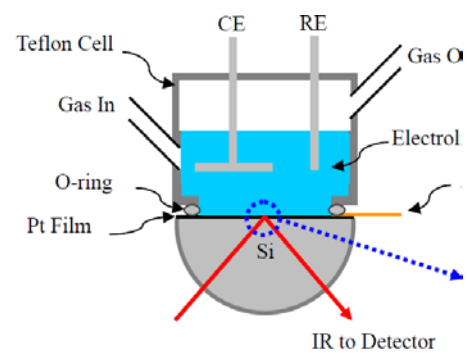
In situ IRRAS Study



IRRAS



SEIRRAS



Ethanol Oxidation: *In situ* EXAFS Analysis of $PtRhSnO_2$

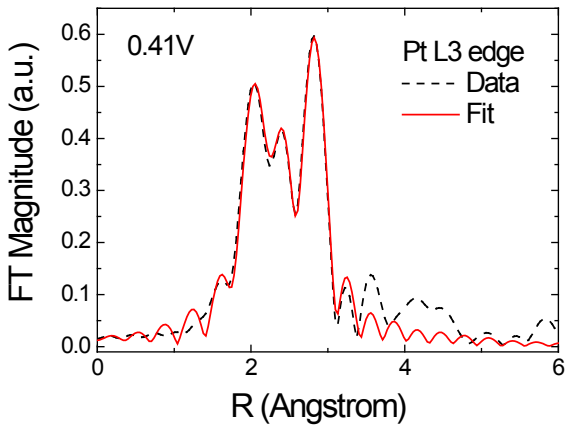
Fit Pt L3 and Rh K data concurrently with no constraints

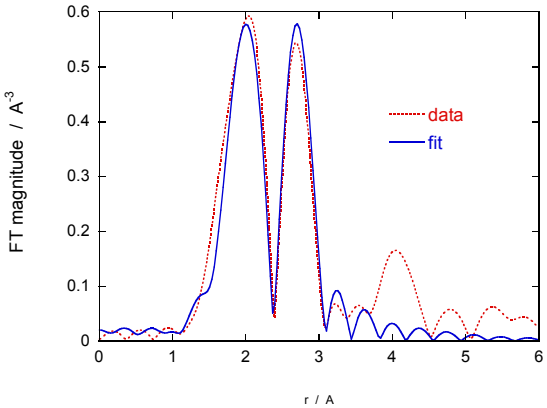
$N_{Pt\text{-}Pt}$ = 5.1 (1.0)
$N_{Pt\text{-}Rh}$ = 1.7 (±1.1)
$N_{Rh\text{-}Rh}$ = 1.9 (±0.9)
$N_{Rh\text{-}Pt}$ = 5.5 (±1.6)

$r_{Pt\text{-}Pt}$ = 2.740 Å (±0.012) (< Pt 2.76 Å)
$r_{Pt\text{-}Rh}$ = 2.714 Å (±0.005)
$r_{Rh\text{-}Rh}$ = 2.683 Å (±0.028)
$r_{Rh\text{-}Pt}$ = 2.714 Å (±0.019)

$r_{Pt\text{-}Pt} > r_{Pt\text{-}Rh} \cong r_{Rh\text{-}Pt} > r_{Rh\text{-}Rh}$

$N_{Pt\text{-}Rh}/N_{Rh\text{-}Pt} = 0.31 \cong x_{Pd}/x_{Pt}$ (0.33 from ICP!)
$N_{Pt\text{-}Pt} + N_{Pt\text{-}Rh}$ = 6.8 (±2.1)
$N_{Rh\text{-}Rh} + N_{Rh\text{-}Pt}$ = 7.4 (±2.6)





PtRh solid-solution-alloy nanoparticles with a diameter of *ca.* 1-2 nm