

**2012 Hydrogen and Fuel Cells Program
Annual Merit Review and Peer Evaluation Meeting**
Arlington, VA – May 14-18, 2012

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. 40%

Budget

- **Total funding estimate:**
 - DOE share: \$3,825K
 - Contractor share: \$342K
- **FY11 funding received:** \$1,000K
- **FY12 funding estimate:** \$975K

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 Delaware

Dare to be first.



– Yushan Yan

Virginia Tech



– James McGrath

VIRGINIA POLYTECHNIC INSTITUTE
AND STATE UNIVERSITY

Johnson Matthey Fuel Cells



Johnson Matthey Fuel Cells

the power within

– Noelia Cabello-Moreno

SFC Energy



– Christian Böhm

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

Technical Targets: Portable Power Fuel Cell Systems (< 2 W; 10-50 W; 100-250 W)				
Characteristics	Units	2011 Status	2013 Targets	2015 Targets
Specific power	W/kg	5; 15; 25	8; 30; 40	10; 45; 50
Power Density	W/L	7; 20; 30	10; 35; 50	13; 55; 70
Specific energy	Wh/kg	110; 150; 250	200; 430; 440	230; 650; 640
Energy density	Wh/L	150; 200; 300	250; 500; 550	300; 800; 900
Cost	\$/W	150; 15; 15	130; 10; 10	70; 7; 5
Durability	Hours	1,500; 1,500; 2,000	3,000; 3,000; 3,000	5,000; 5,000; 5,000
Mean time between failures	Hours	500; 500; 500	1,500; 1,500; 1,500	5,000; 5,000; 5,000

Original project technical targets (may be relaxed given modified targets above):

- **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 $\rightarrow \eta_{\Sigma} = 0.42-0.52$ (1.6-2.0 \times improvement over the state of the art, ~ 1.250 kWh/L)

(2) If $\eta_{\text{fuel}} = 0.96$, $\eta_{\text{BOP}} = 0.90$, $V_{\text{th}} = 1.21$ (at 25°C)

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

The ultimate project goal!

Approach: Focus Areas

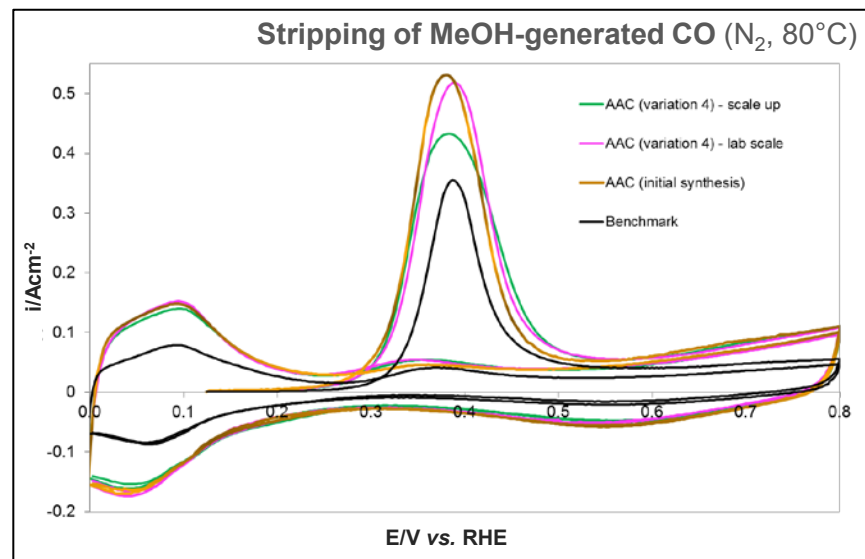
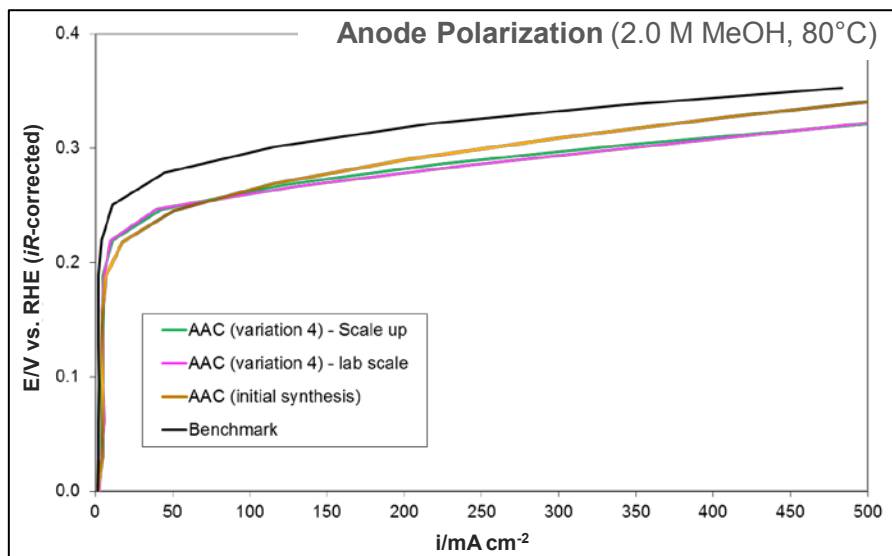
- **DMFC anode research:**
 - new catalysts with improved activity and reduced cost (BNL, JMFC, LANL)
 - improved catalyst durability (JMFC, LANL, BNL)
- **Innovative electrode structures for better activity and durability (UD)**
- **Hydrocarbon membranes for lower MEA cost and enhanced fuel cell performance (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 or Go/No-Go Decision	Status	Comment
Dec 11	Complete equipment set-up for fuel cell testing with liquid feed of DME; improve the DDMEFC performance to reach $\geq 250 \text{ mA/cm}^2$ at 0.40 V at 80°C. Go/no-go decision on DME research.	Complete	Set-up completed; a “go” decision for DME research based on anode activity and path forward for catalyst development.
Dec 11	Assess activity and stability in half-cell and fuel-cell testing of the PtRu benchmark HiSPEC® 12000 and at least one developmental PtRu catalyst over the DMFC anode potential range 0.0-0.85 V.	Pending	HiSPEC® 12100 and PtRu black testing completed; developmental catalysts to arrive soon at LANL for testing.
Jan 12	Go/no-go on PtSn catalysts development for methanol oxidation: PtSn catalyst exceeding half-cell mass activity of 200 mA/mg _{Pt} at 0.35 V at 80°C (<i>iR</i> -corrected) and demonstrating durability at least matching that of the HiSPEC 12100 benchmark catalyst.	Complete	“No-go” decision for PtSn development; a “go” for ternary PtRuSn catalyst; 200 mA/mg _{Pt} milestone exceeded with ternary PtRuSn by at least 150%.
Jan 12	Demonstrate a ternary PtRhSnO ₂ electrocatalyst capable of oxidizing ethanol to CO ₂ with an efficiency of 50% at 0.4 V vs. RHE at 80°C.	Pending	Further catalyst optimization and DEMS set-up for CO ₂ determination needed to complete task; expected in October 2012.
Mar 12	Synthesize at least one multiblock copolymer allowing for (i) current density $\geq 0.28 \text{ A/cm}^2$ at 0.5 V, (ii) methanol utilization of $\geq 95\%$ at peak power, and (iii) less than 10% DMFC performance degradation for 100 h in a preliminary life-test at 80°C.	Complete	Current density greater than 0.28 A/cm ² at 0.5 V; crossover reduced by 55% relative to Nafion® 212 and by 40% relative to the best earlier multiblock copolymers.
Mar 12	Complete kinetic study of DME adsorption and oxidation on PtRu catalysts to assess DDMEFC potential to deliver 1.25 kWh/L (conditional upon a “go” decision on DME research in Dec 11).	Complete	1.25 kWh/L (fuel) deliverable already at maximum power; 1.25 kWh/L (system) achievable at long operating times.
Aug 12	Complete equipment set-up for the evaluation of the stack with selected alternative membranes; adapt stack hardware to testing hydrocarbon membranes of different thickness.	Pending	Set-up for short-stack test stand ongoing at SFC ENERGY facility at Rockville, Maryland; timely completion planned.
Sep 12	Demonstrate improved methanol oxidation activity of a thrifted PtRu catalyst with durability at least matching that of the HiSPEC® 12100 benchmark catalyst.	Pending	On track; durability of new JMFC’s thrifted PtRu catalysts under evaluation.
Sep 12	Scale up the synthesis of PtRu platelets for methanol oxidation to 0.5 g batch to allow MEA testing.	Pending	Scale-up synthesis underway.
Sep 12	Develop PtRu core-shell nanowires with methanol oxidation onset potential of $\leq 0.325 \text{ V}$ vs. RHE at room temperature and 5-fold improvement in mass activity relative to that of PtRu nanotubes in FY11.	Complete	Methanol oxidation onset potentials of 0.30 V and 0.31 V and 5-fold mass activity improvement demonstrated.

Methanol Oxidation: Advanced Anode Catalyst Performance & Scale-Up

Benchmark: HiSPEC® 12100 (50% Pt), 1.0 mg_{Pt} cm⁻²; **ACC variation 4:** PtRu/C (18% Pt), 1.0 mg_{Pt} cm⁻²; **Scale-up:** 100 g ACC



- **Highlight:** PtRu “advanced anode catalyst” (AAC) exceeding the performance of benchmark HiSPEC® 12100 catalyst by *ca.* 40 mV
- **Highlight:** ACC (variation 4) successfully scaled-up to 100 g without performance loss (in spite of a slightly lower specific surface area)
- Anode research on track to reach the target of improved activity of thrifed PtRu catalysts without a durability loss and to reach the project goal of 150 mA cm⁻² at 0.60 V (DMFC)

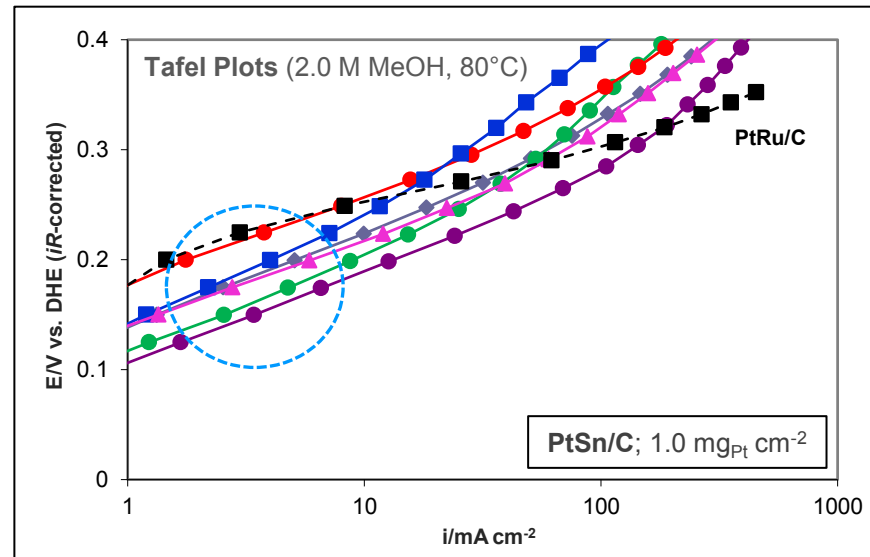
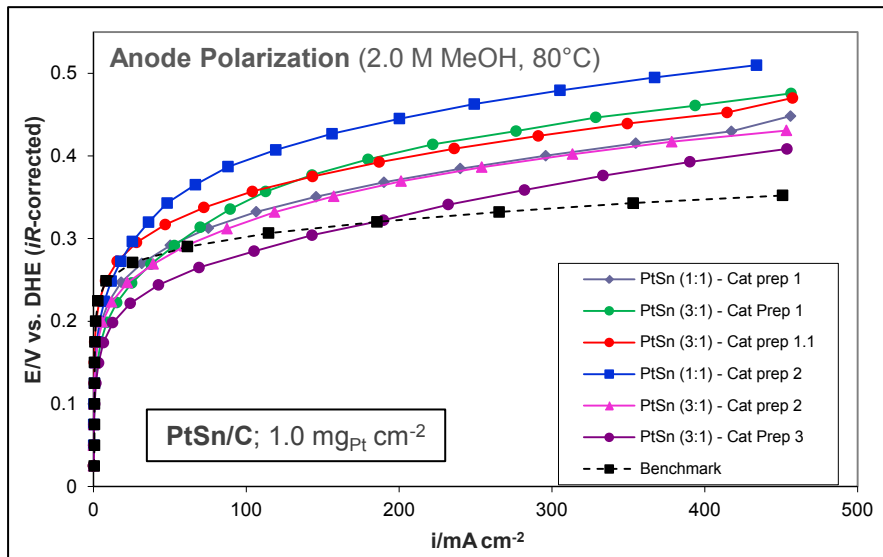
Methanol Oxidation: Binary PtSn/C Catalysts

Cat prep 1 → base hydrolysis

Cat prep 1.1 → base hydrolysis, modified firing step

Cat prep 2 → complex route

Cat prep 3 → new preparation route



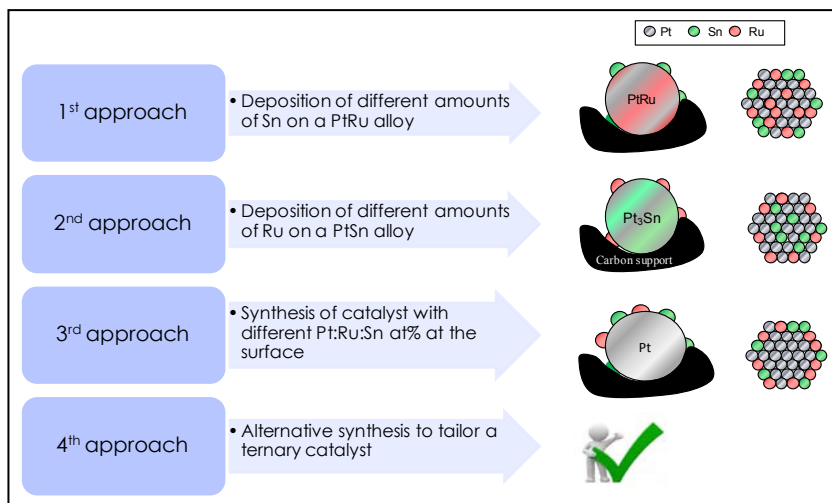
- Methanol-oxidation activity advantage of PtSn/C catalysts, Pt(3:1) in particular, relative to PtRu/C in the kinetic region (at low current densities, up to 150 mA cm⁻²)
- PtSn/C performance limited at potentials higher than 0.2 V due to SnO₂ formation and resulting decrease in the OH availability*

No-go for the binary PtSn catalyst research

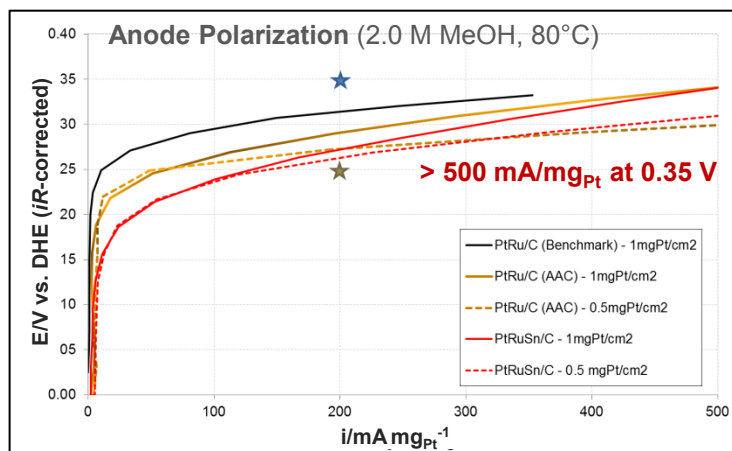
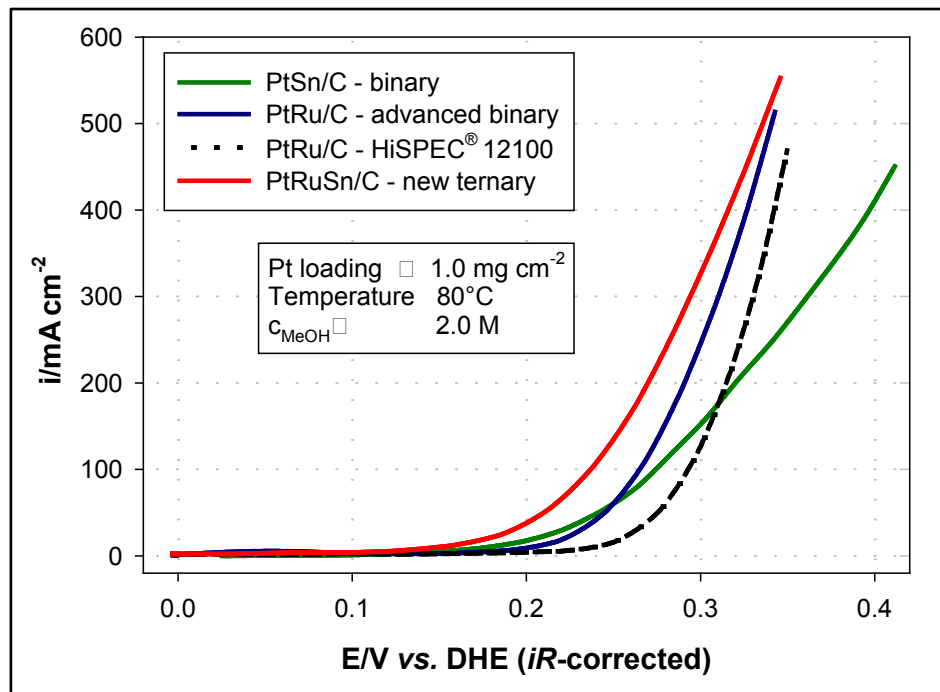
- Could PtSn/C be combined with a third metal to reduce methanol oxidation overpotential in the high current-density region?

* The effect of Sn content on MeOH oxidation activity in a Technical Backup Slide

MeOH Oxidation: Ternary PtRuSn/C Catalysts



Catalyst	Pt at%	Ru at%	Sn at%
PtRu/C - HiSPEC® 12100	50	50	-
PtRu/C - advanced binary	20	80	-
PtSn/C - binary	77	-	23
PtRuSn/C - new ternary	19	71	10

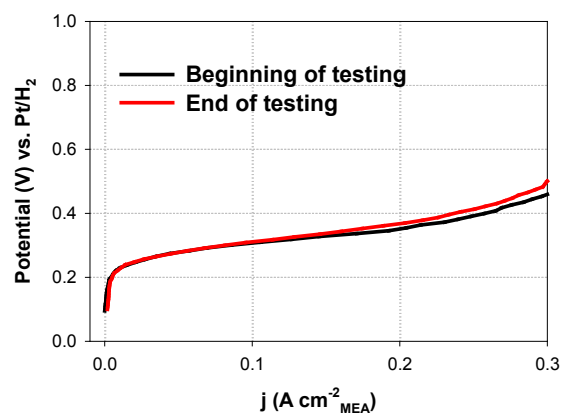
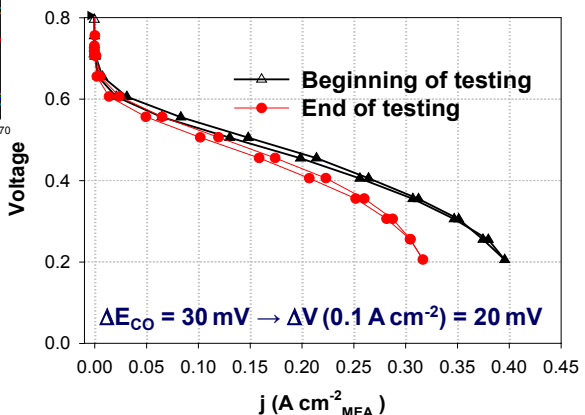
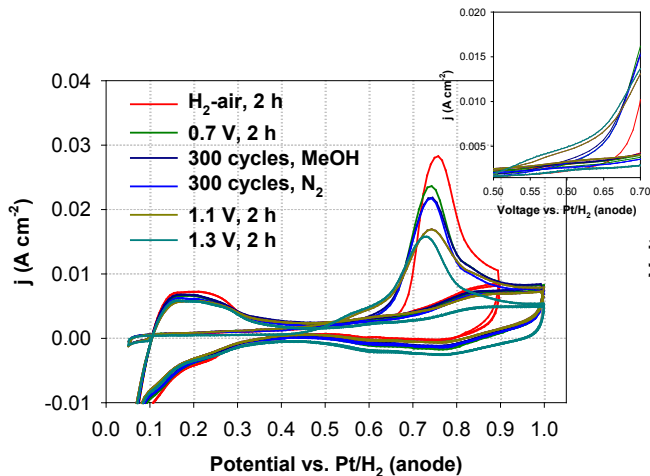
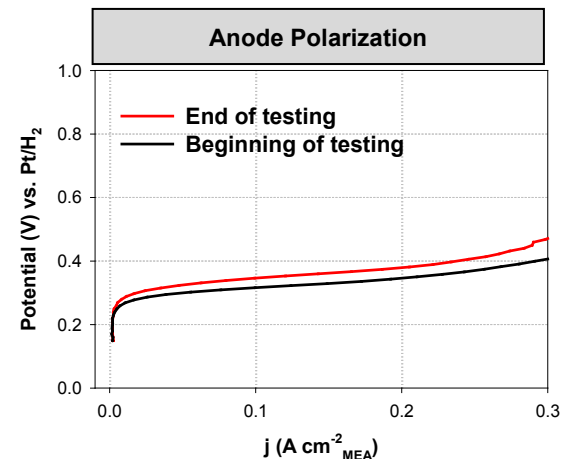
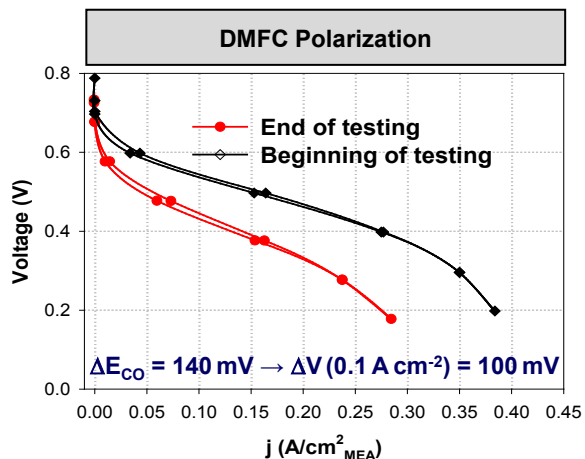
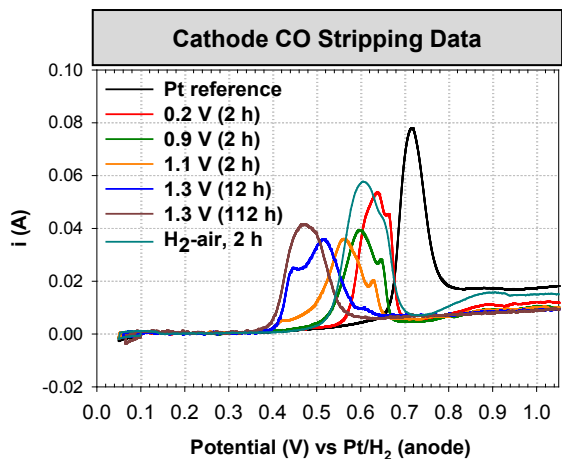


- **Highlight:** JMFC's ternary PtRuSn/C catalyst combining unique activity of PtSn/C at low overpotentials with superior performance of PtRu/C at high overpotentials
- **Highlight:** Significantly higher MeOH oxidation activity of PtRuSn/C catalyst than most active thrifed PtRu/C catalysts

Mass-activity milestone for Sn-containing catalysts exceeded by approximately 150%

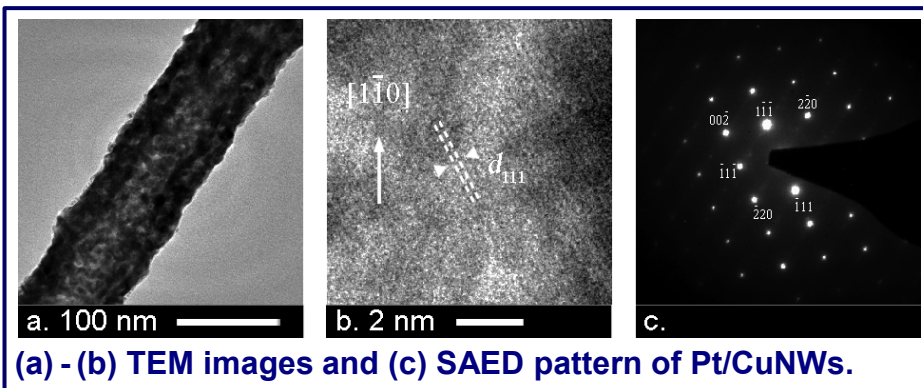
MeOH Oxidation: PtRu and PtRu/C Anode Stability

Anode: PtRu (5 mg cm⁻²) or PtRu/C (3 mg cm⁻²), 0.5 M MeOH; Cathode: Pt (3 mg cm⁻²) or Pt/C (5 mg cm⁻²); Membrane: Nafion® 117 or 2×Nafion® 212; Cell: 80°C



- Performance losses with both systems attributed to Ru cathode contamination; only small anode losses observed
- Data after humidification and 2 h polarization: Ru contamination less severe and more difficult to induce with carbon-supported catalysts (PtRu/C - Pt/C) than with the blacks (PtRu - Pt) due to (i) the larger amount of unalloyed Ru phase in PtRu black at higher catalyst loading in the PtRu - Pt system (alloyed fraction similar based on XRD, cf. a Reviewer-Only Slide) and, though less likely, (ii) contribution of the carbon surface area in Pt/C (PtRu/C - Pt/C)

Methanol Oxidation: Innovative PtRu Nanostructure Catalysts



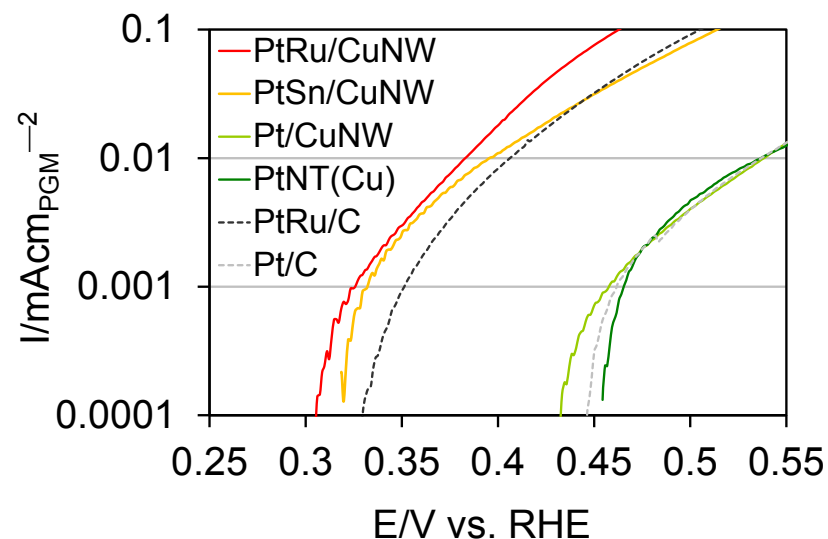
- **Highlight:** Onset potential of methanol oxidation improved by 30 mV and 20 mV with PtRu/CuNWs and PtSn/CuNWs relative to the benchmark PtRu/C catalyst (HiSPEC® 12100)

Oxidation onset potential target of < 0.325 V and improvement in PGM mass activity at low overpotentials achieved with two catalysts

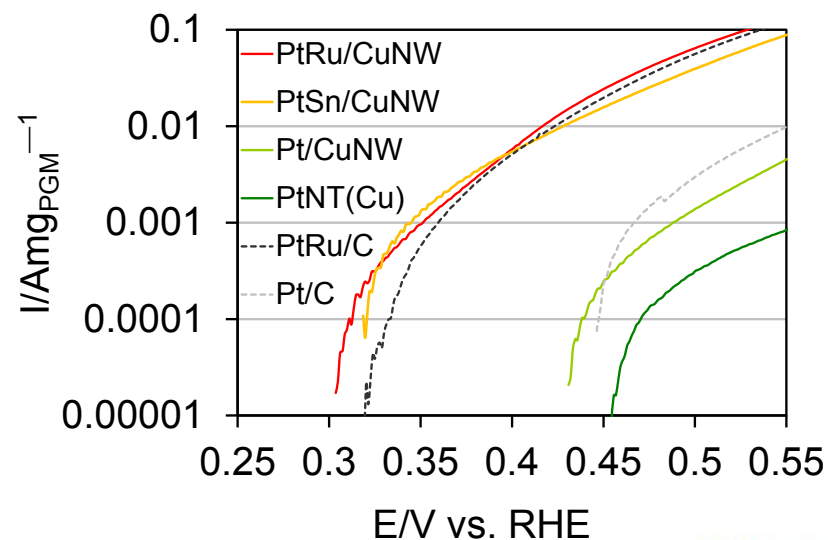
- **Performance stability demonstrated to be on par with the benchmark catalyst** (data included in a Technical Backup Slide)

Solution: 1.0 M MeOH in 0.5 M H₂SO₄; Scan rate: 5 mV s⁻¹
Benchmark PtRu/C catalyst: HiSPEC® 12100

Specific Activity of PtRu Nanostructures (per cm²_{PGM})

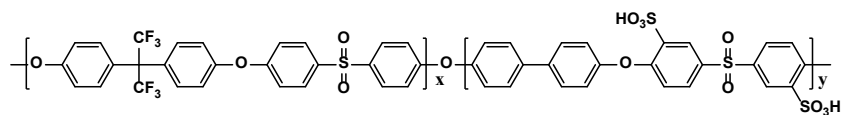


Mass Activity of PtRu Nanostructures (per mg_{PGM})

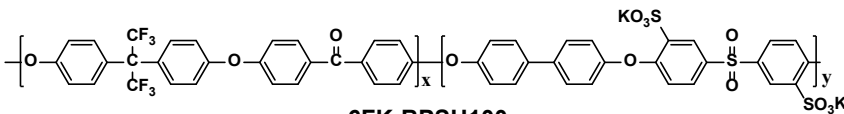


DMFC Multiblock Copolymers: Properties and Performance

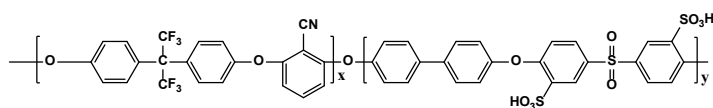
Multiblock Copolymers: Structure and Properties



6FBPS-BPSH100



6FK-BPSH100



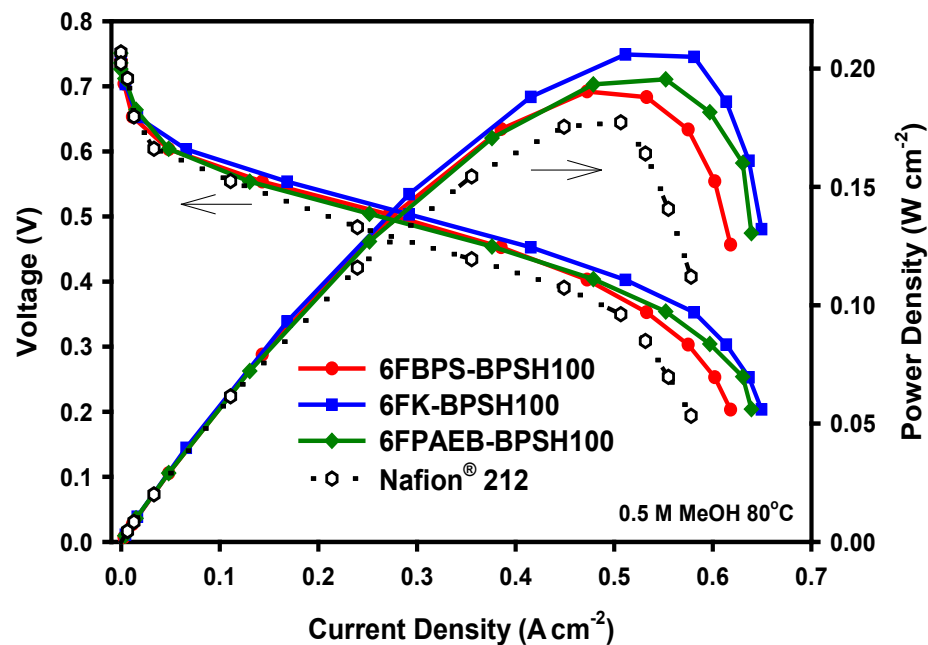
6FPAEB-BPSH100

Characteristics	6FBPS-BPSH100	6FK-BPSH100	6FPAEB-BPSH100	Nafion® 212
Block size (g)	15,000	7,000	11,000	-
Thickness (mm)	44	31	34	50
HFR (W cm ²)	0.073	0.070	0.063	0.066
Crossover (A cm ⁻²) ^a with 0.5 M MeOH	0.150	0.149	0.173	0.181
<i>i</i> at 0.5 V (A cm ⁻²)	0.272	0.292	0.252	0.240

^a Crossover limiting current density at zero DMFC current .

Anode: 6.0 mg cm⁻² Pt₅₀Ru₅₀ black, 0.5 M 1.8 mL/min MeOH solution; **Cathode:** 4.0 mg cm⁻² Pt black; 500 sccm air; **Membrane:** multiblock copolymers and Nafion® 212; **Cell:** 80°C

DMFC Performance with 0.5 M MeOH

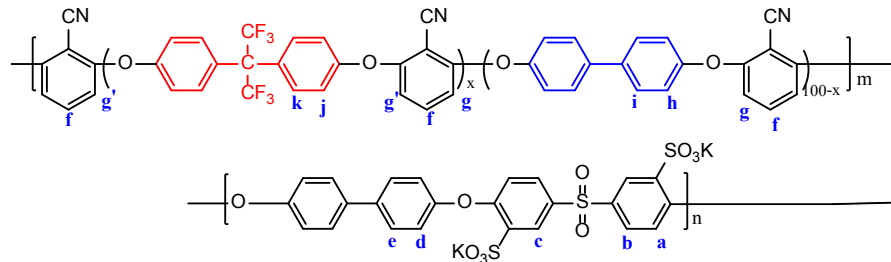


- **Highly conductive multiblock copolymers prepared using telechelic BPSH-100 oligomers ***
- **Highlight:** Multiblock copolymer membranes outperforming Nafion® 212 in DMFC testing (0.5 M MeOH)
DMFC milestone performance (> 0.28 A/cm² at 0.5 V) achieved with 3 out of 11 multiblock copolymers
- **Next:** Further reduction in methanol crossover

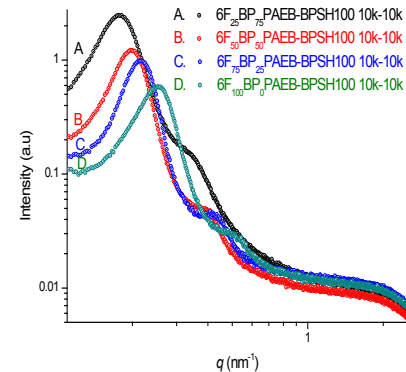
* Synthesis details and spectroscopic data in a Technical Backup Slide

DMFC Multiblock Copolymers: MeOH Crossover Reduction

6F_xBP_{100-x} PAEB-BPSH100 Multiblock copolymers



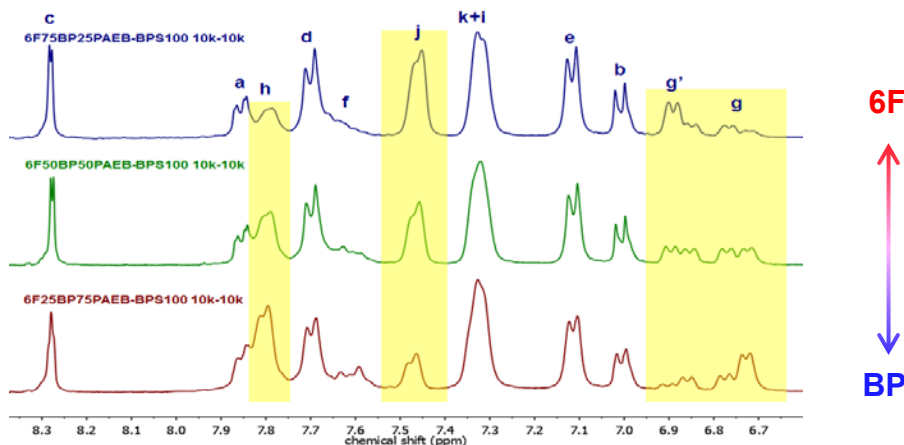
SAXS Profiles



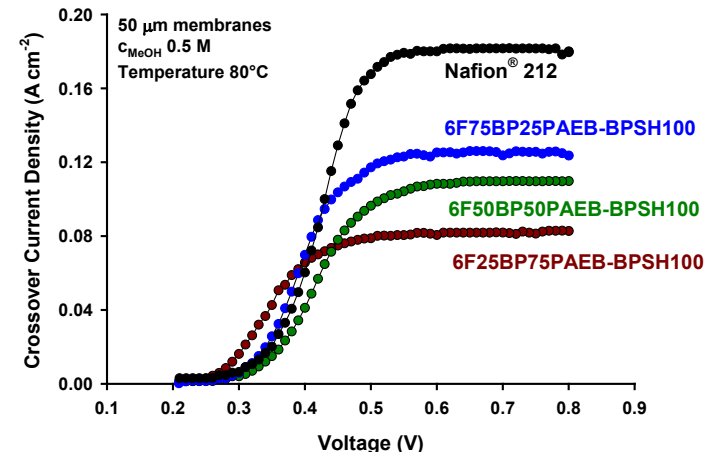
Interdomain distance increasing with the 6F-BPA moiety decrease

6F_xBP_{100-x} PAEB-BPSH100 showing 2nd order peaks → lamellar structure

¹H NMR of Multiblock Copolymers (10K-10K)



Methanol Crossover with Various Membranes

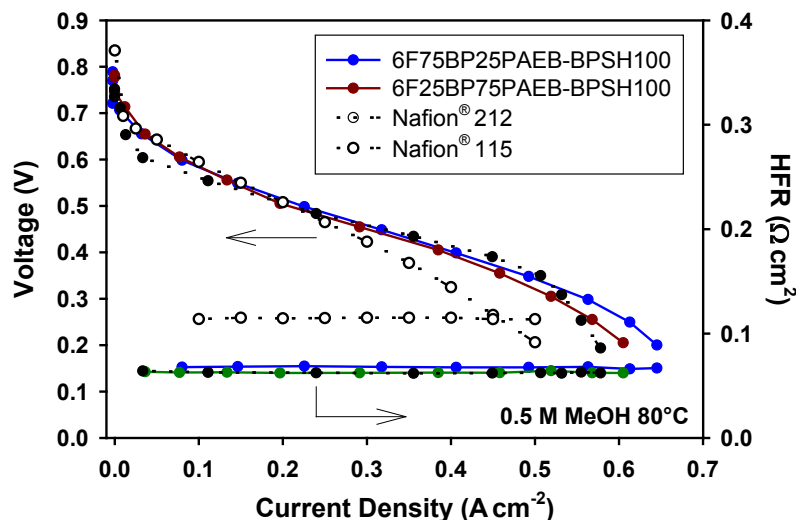


- Methanol permeability controlled by introducing BP and varying BP-to-6F ratio
- SAXS profile indicating highly ordered structure of multiblock copolymers with decreasing interdomain distance (anisotropic behavior confirmed by NMR)
- **Highlight: 55% reduction in methanol crossover compared to Nafion[®] 212**

DMFC Multiblock Copolymers: Performance and Fuel Utilization (0.5 M MeOH)

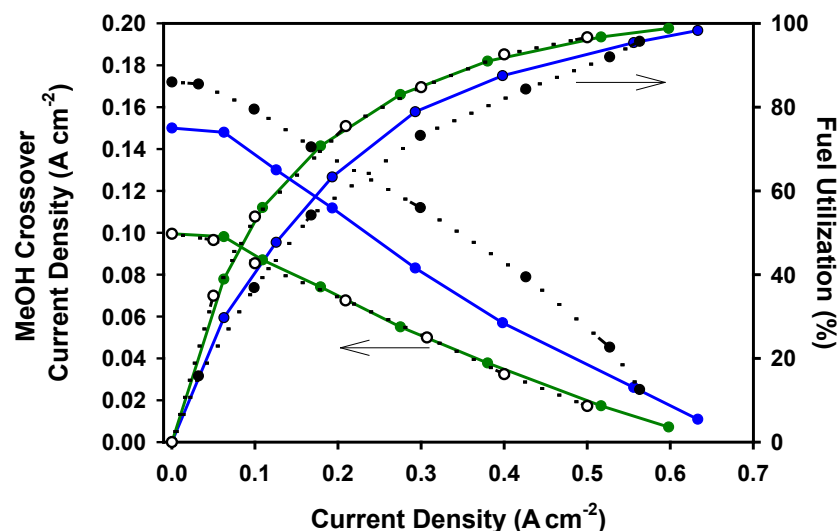
Anode: PtRu black (4.0 mg cm⁻²);
Cathode: Pt black (3.0 mg cm⁻²); Cell: 80°C

DMFC Polarization (0.5 M MeOH)



Characteristics	Multiblock		Nafion®	
	6F75 (50 μm)	6F25 (47 μm)	212 (50 μm)	115 (125 μm)
η_{fuel} at 0.5 V, %	69	77	62	75
η_{fuel} at peak power, %	92	95	90	88

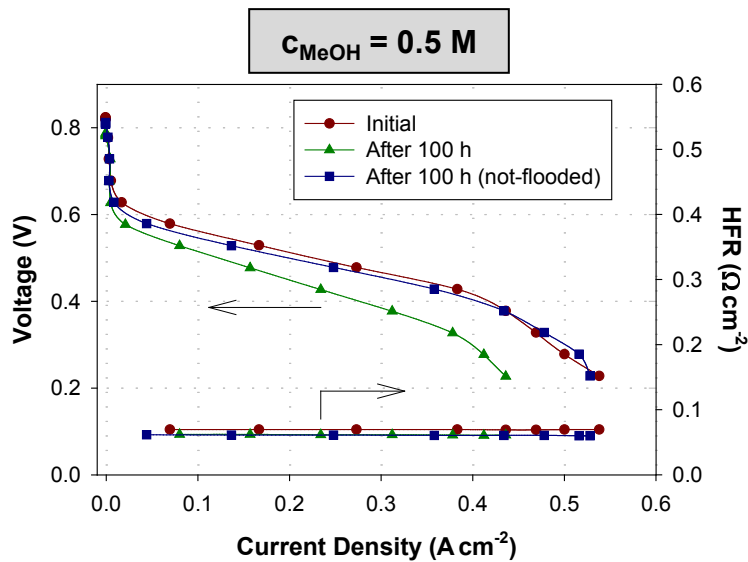
MeOH Crossover and Fuel Utilization



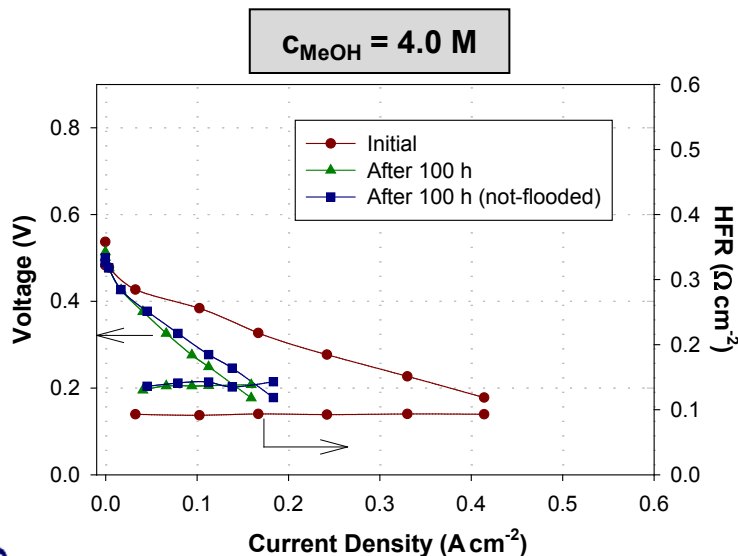
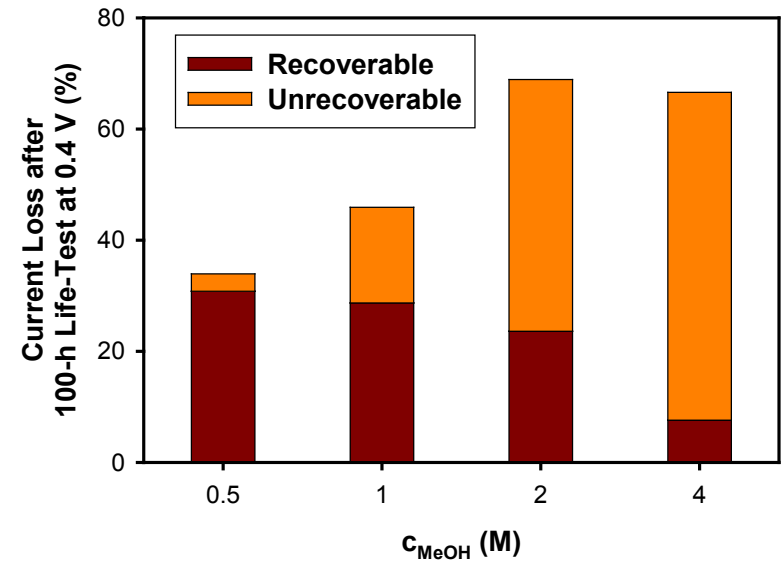
- MEAs with multiblock-copolymer membranes showing superior performance to Nafion® 212 at DMFC voltages higher than ca. 0.55 V while maintaining similar resistance
- **Highlight:** Better fuel utilization obtained with multiblock copolymers MEAs than Nafion®
DMFC fuel utilization milestone of $\geq 95\%$ at peak power achieved with 6F25BP75PAEB-BPS100 copolymer
- **Next:** Further reduction of methanol crossover by replacing 6F and BP with hydroquinone

* Performance with 2.0 M MeOH feed in a Technical Backup Slide

DMFC Performance Degradation: 100-Hour Life Test



Anode: $6.0 \text{ mg cm}^{-2} \text{ Pt}_{50}\text{Ru}_{50}$ black, 1.8 mL/min MeOH solution;
Cathode: 4.0 mg cm^{-2} Pt black; 500 sccm air; **Membrane:** Nafion® 212; **Cell:** 80°C ; **Life test:** constant voltage at 0.45 V

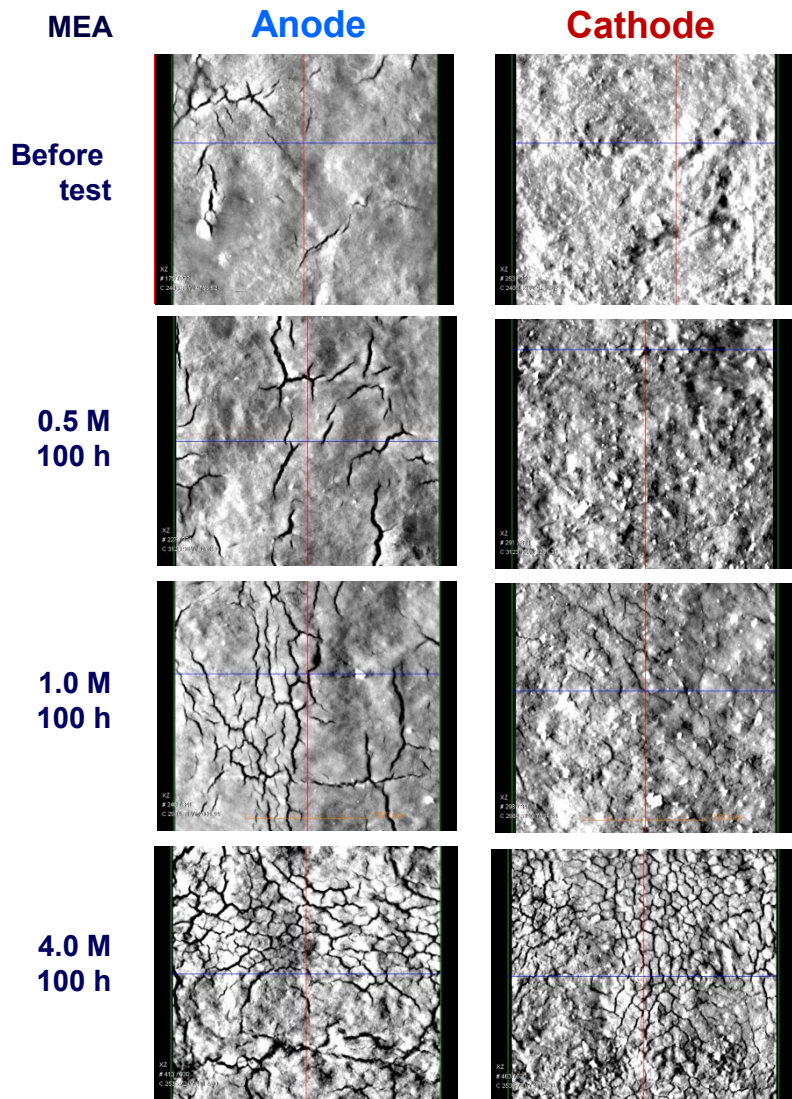


- **Unrecoverable performance loss significantly increasing with methanol concentration; recoverable performance decreasing***
- **Post-life-test HFR increasing with methanol concentration; loss of ionomer possible**
- **Highlight: 3% unrecoverable performance measured with 0.5 M MeOH at 0.4 V after 100 hours**
- **Next: Perform detailed degradation study**

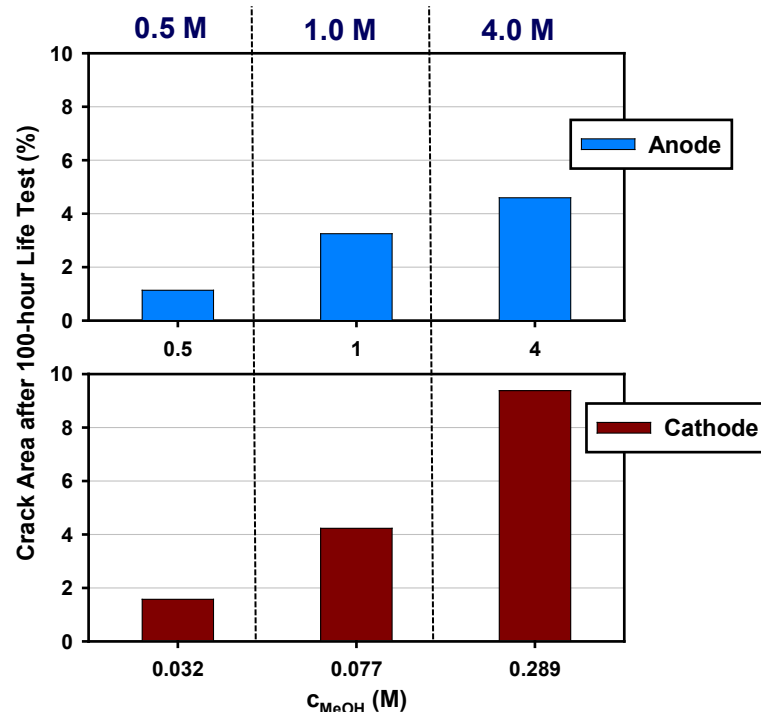
* Current and HFR changes during the life test in a Technical Backup Slide

DMFC Performance Degradation: Crack Formation in Electrodes

X-Ray Tomography after 100-hour Test (1x1 mm)



Anode: 6.0 mg cm⁻² Pt₅₀Ru₅₀ black, 1.8 mL/min MeOH solution;
Cathode: 4.0 mg cm⁻² Pt black; 500 sccm air; **Membrane:** Nafion® 212; **Cell:** 80°C; **Life test:** constant voltage at 0.45 V



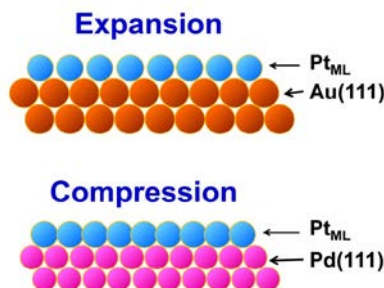
- Anode and cathode cracking increasing with MeOH concentration; * cathode more vulnerable
- **Highlight:** Potentially important factor for DMFC performance degradation determined
- **Next:** Develop mitigation strategy for cracking

* Effect of other life-test conditions in a Reviewer-Only Slide

Ethanol Oxidation: Monolayer Catalysts for Alcohols Oxidation (Approaches)

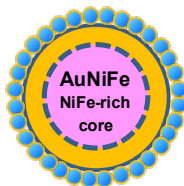
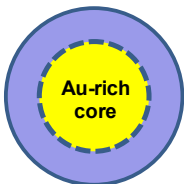
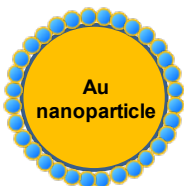
Geometric and Ligand Effects: Pt_{ML} on Substrates

1. Decrease in Pt content to a single monolayer
2. Tuning of the catalytic properties of Pt monolayer
3. Establishment of predictive base for oxidation reactions



Carbon-Supported Nanoparticle Catalysts: Pt_{ML}/Au

1. **Pt_{ML}/Au/C**: Pt_{ML} supported on Au nanoparticles
2. **Au-Pt/C**: Au-rich core and Pt-rich shell
3. **Pt_{ML}/AuNi_{0.5}Fe/C**: Pt_{ML} supported on nanoparticles containing Au-rich shells and NiFe-rich cores to reduce noble metal loading



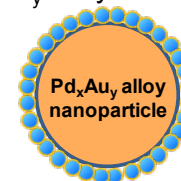
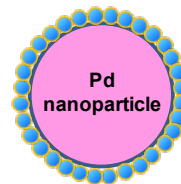
Combination of Bifunctional and Electronic Effects

1. Further modification of Pt_{ML}/Au(111) via bi-functional mechanism to tune catalytic properties of Pt monolayer
2. Incorporation of oxophilic elements (e.g., Ru, Ir) and hydroxides species (e.g., Sn(OH)_x) into Pt_{ML}

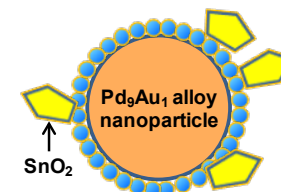


Carbon-Supported Nanoparticle Catalysts: Pt_{ML}/Pd

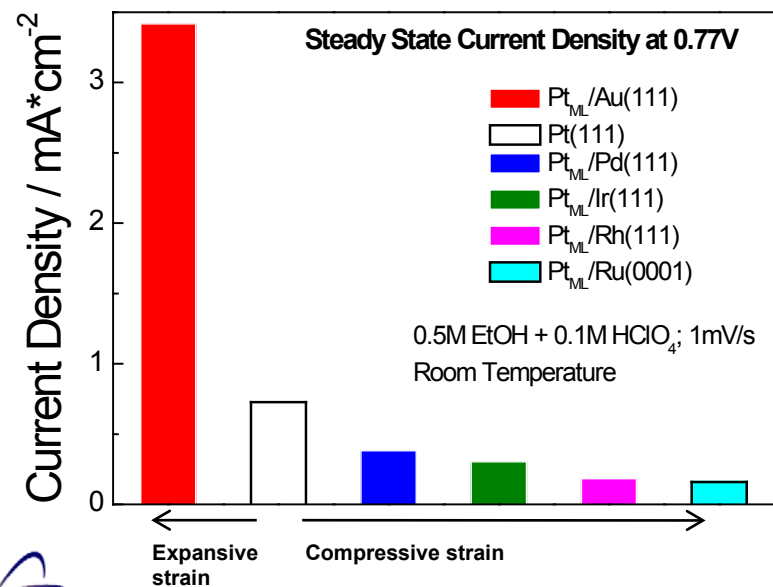
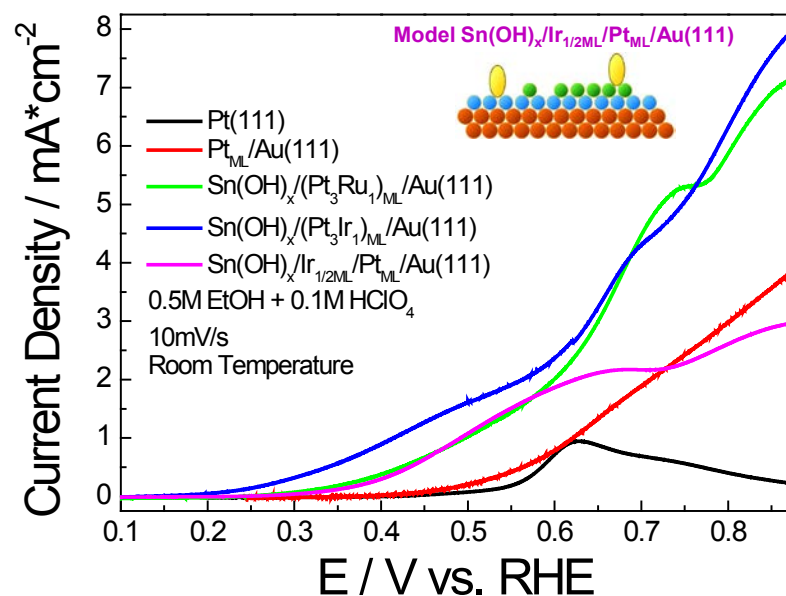
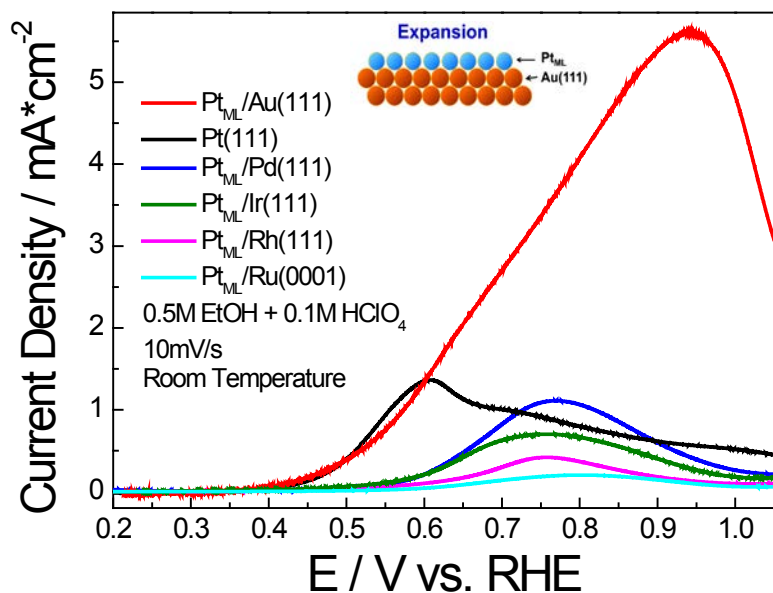
1. **Pt_{ML}/Pd/C**: Pt_{ML} supported on Pd nanoparticles
2. **Pt_{ML}/Pd_xAu_y/C**: Pt_{ML} supported on Pd_xAu_y alloy nanoparticles



2. **SnO₂/Pt_{ML}/Pd₉Au₁/C**: SnO₂-modified Pt_{ML} supported on Pd₉Au₁ alloy nanoparticles



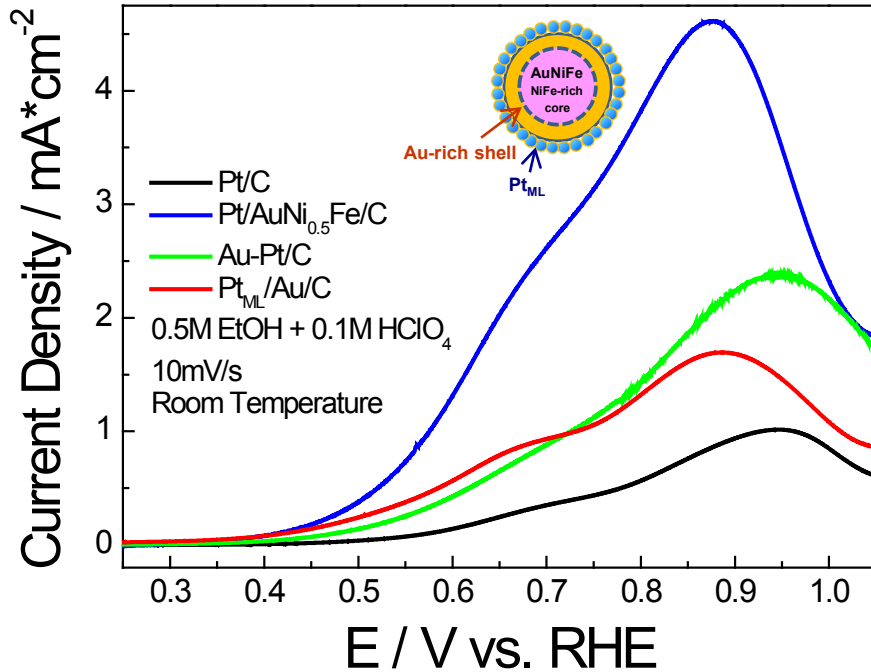
Ethanol Oxidation: Expanded/Compressed and “Engineered” Surfaces



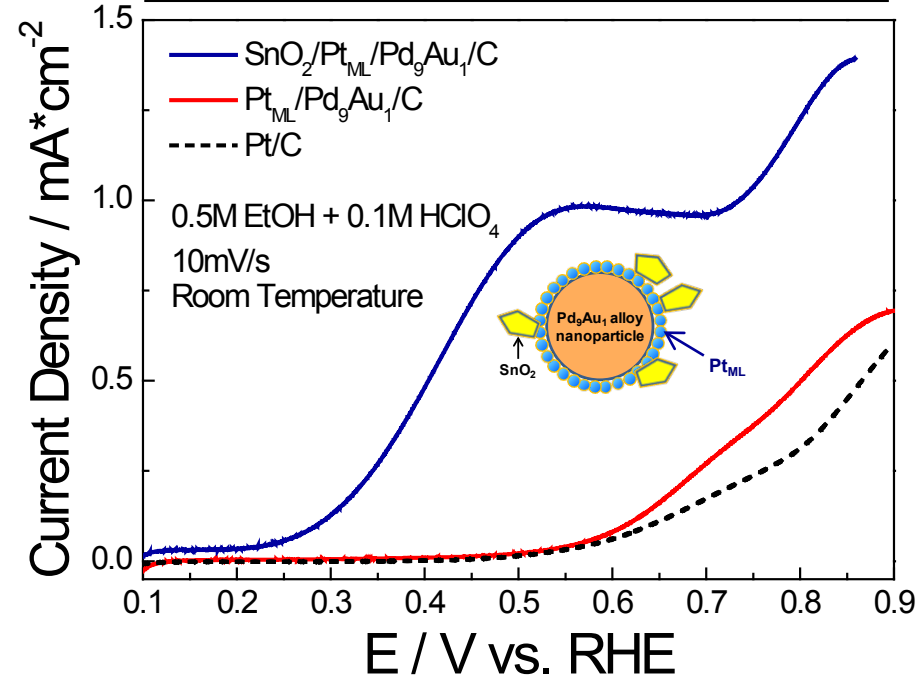
- Lattice expansion in Pt_{ML} supported on $\text{Au}(111)$ leading to significantly enhanced EtOH oxidation current relative to $\text{Pt}(111)$ and to likely improved selectivity in CO_2 generation
- **Highlight:** Further “engineering” of $\text{Pt}_{\text{ML}}/\text{Au}(111)$ surface resulting in additional shift in the onset EtOH oxidation potential to below 0.2 V vs. RHE at the $\text{Sn}(\text{OH})_x/(\text{Pt}_3\text{Ir}_1)_{\text{ML}}/\text{Au}(111)$ catalyst
- Cost-effective core materials needed

Ethanol Oxidation: Carbon-Supported Nanoparticle Pt_{ML} Catalysts

Carbon-Supported Pt_{ML}/Au Catalysts

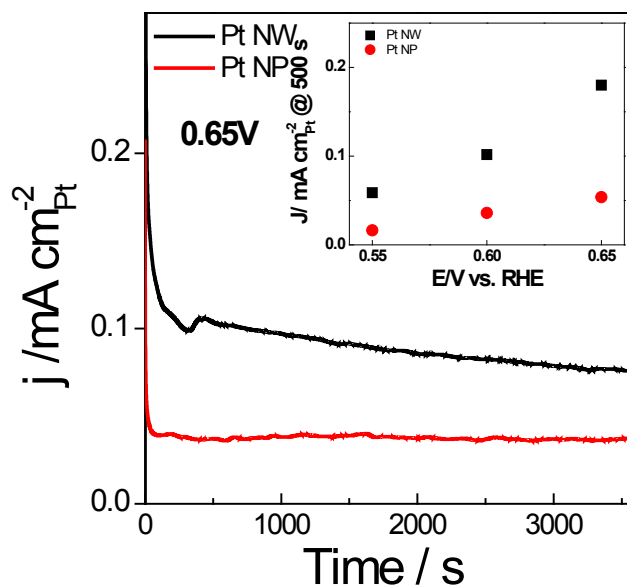
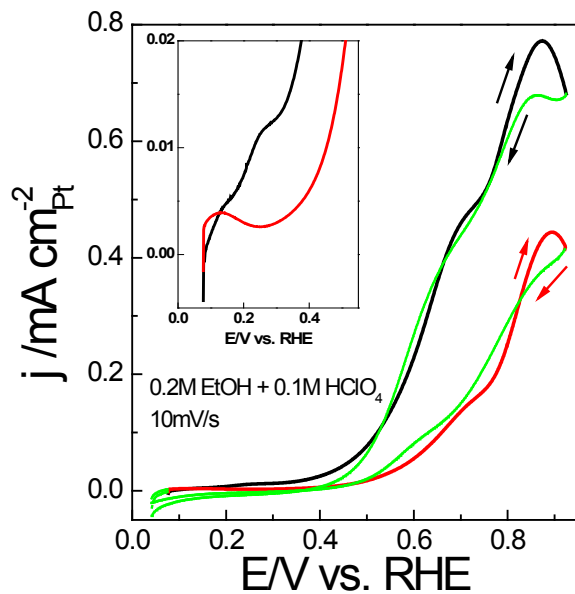
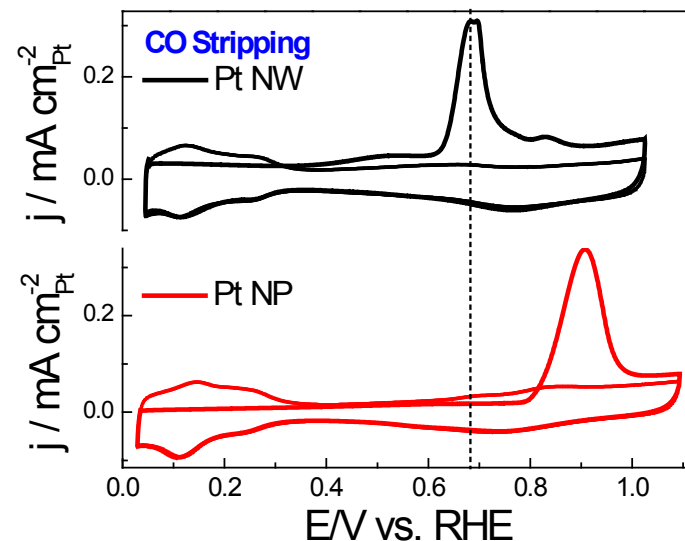
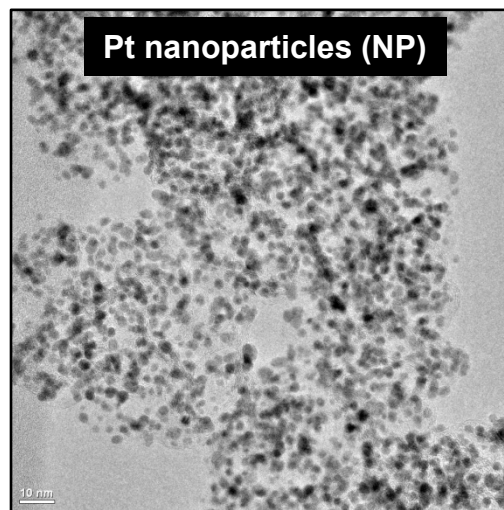
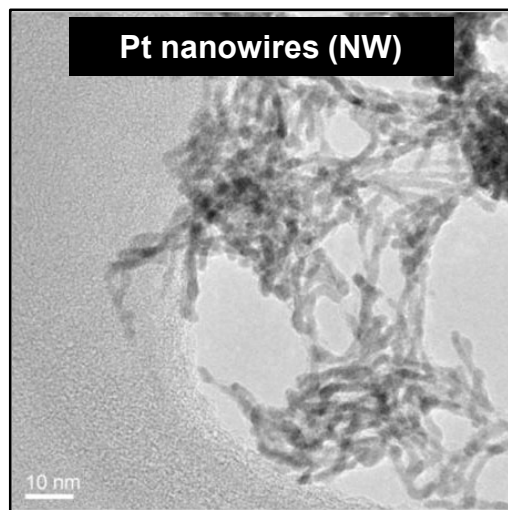


Carbon-Supported Pt_{ML}/Pd Catalysts



- **Highlight:** Very promising activity demonstrated using Pt_{ML}/AuNi_{0.5}Fe/C catalyst with reduced noble metal loading in the nanoparticle core
- **Highlight:** SnO₂/Pt_{ML}/Pd₉Au₁/C catalyst exhibiting the lowest onset potential among carbon-supported catalysts, comparable to that measured with the most active single-crystal catalysts; high CO₂ yields possible
- In-situ infrared reflection-absorption spectroscopy (IRRAS) and on-line differential electrochemical mass spectroscopy (DEMS) being set up to study the substrate-induced change in Pt_{ML}'s selectivity for the oxidation of ethanol

Ethanol Oxidation: The Effect of Nanocatalyst Morphology



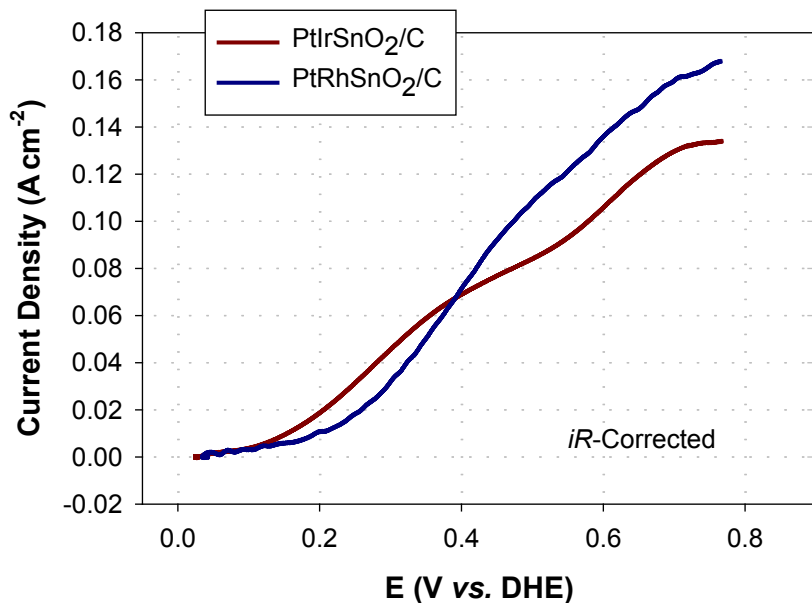
- **Highlight: A pronounced morphology effect in EtOH and CO_{ads} oxidation on Pt nanowires and nanoparticles**
- **Higher activity of nanowires caused by a weaker bonding of CO_{ads} and its more facile removal from the catalyst surface**
- **Effect potentially important for catalyst design**

Ethanol Oxidation: Anode and DEFC Performance

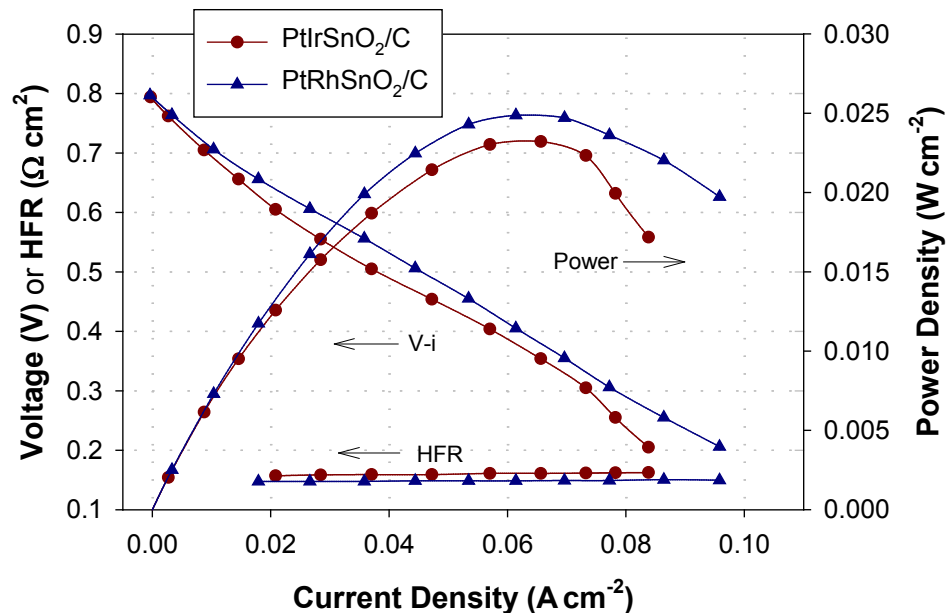
Anode: 1 mg cm⁻²_{metal} 12 wt% PtIrSnO₂/C or 13% PtRhSnO₂/C, 0.5 M ethanol, 1.8 ml/min; **Cathode:** 4 mg cm⁻² Pt black, 200 sccm H₂; **Membrane:** Triple Nafion® 212 sandwich; **Cell:** 80°C

Anode: 1 mg cm⁻²_{metal} 12 wt% PtIrSnO₂/C or 13% PtRhSnO₂/C, 0.5 M ethanol, 1.8 ml/min; **Cathode:** 4 mg cm⁻² Pt black, 500 sccm air; **Membrane:** Triple Nafion® 212 sandwich; **Cell:** 80°C

Anode Polarization Plots



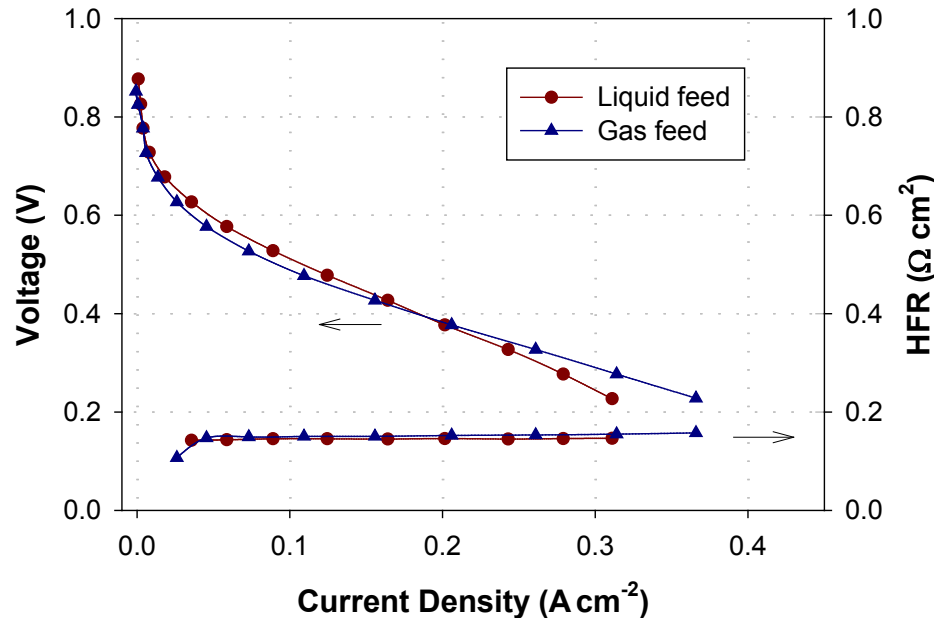
DEFC Performance



- **Highlight:** Excellent activity demonstrated with two ternary catalysts; onset potential of EtOH oxidation very close to the thermodynamic value of ca. 0.04 V at 80°C
- While exceeding the best DEFC performance published, the fuel cell performance of both catalysts greatly impacted by possible cathode contamination; reduction in non-noble metal migration from the anode likely needed

DME Fuel Cell Research: Liquid Feed

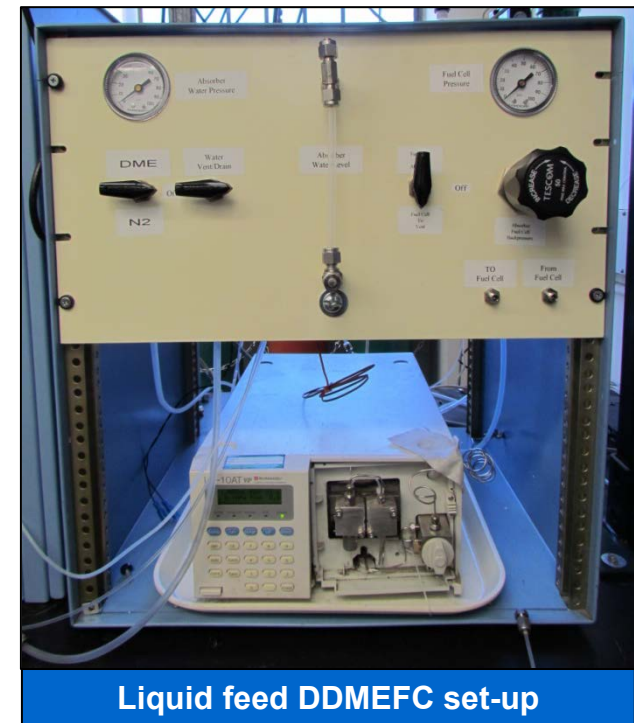
Anode: 6 mg cm⁻² Pt₅₀Ru₅₀, 40 sccm DME gas, 30 psig, anode humidifier at 85°C or DME-saturated solution (1.65 M)*, 2.5 ml/min; **Cathode:** 4 mg cm⁻² Pt, 500 sccm air, 20 psig; **Membrane:** Nafion® 117; **Cell:** 80°C
 * Muller et al., *J. Electrochem. Soc.* **147**, 4058, 2000.



Performance	Liquid Feed	Gas Feed
OCV (V)	0.877	0.852
DME-crossover peak current (mA cm ⁻²)	50	48

- **DME-to-H₂O ratio of 1.4:1 in FY11 DME fuel cell with anode humidifier at 85°C larger than stoichiometric (1:3), possibly resulting in water deficiency at the anode**
- **Highlight:** Liquid-feed DME fuel cell showing higher OCV and slightly improved performance in the kinetic region compared with the fuel cell operating on gaseous DME

Liquid-feed DME fuel cell milestone achieved

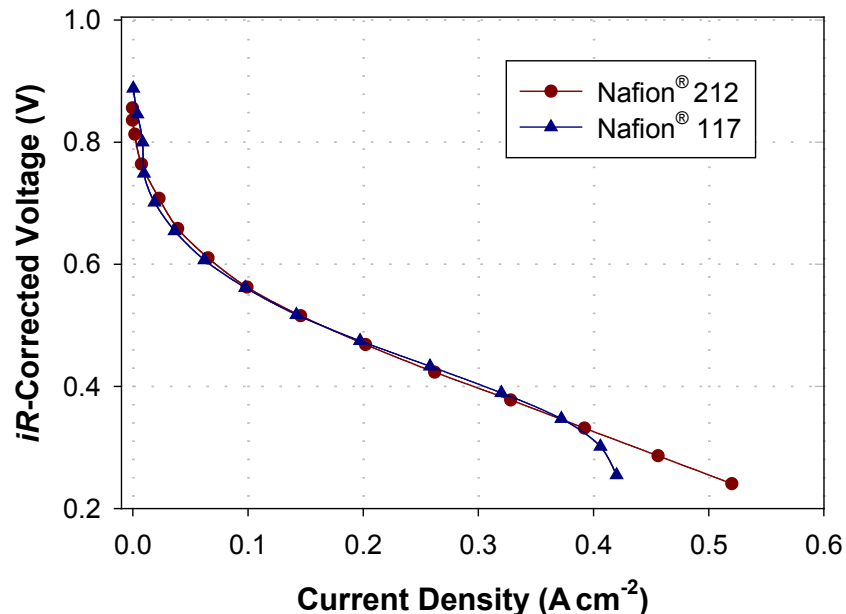
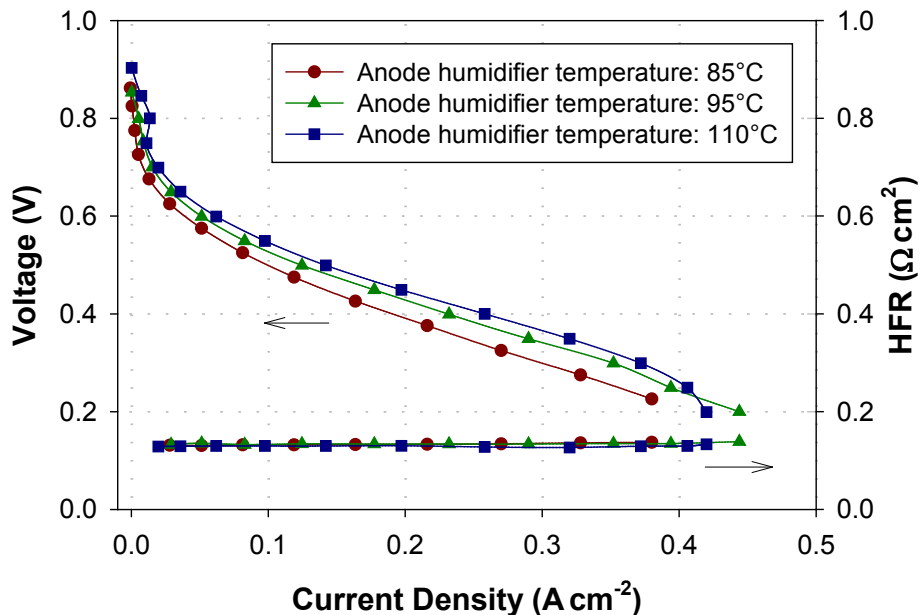


Liquid feed DDMEFC set-up

DME Fuel Cell: Effects of Anode Humidification and Membrane Thickness

Anode: 6 mg cm⁻² Pt₅₀Ru₅₀ black, 40 sccm DME gas, 30 psig; **Cathode:** 4 mg cm⁻² Pt black, 500 sccm air, 20 psig; **Membrane:** Nafion® 117; **Cell:** 80°C

Anode: 6 mg cm⁻² Pt₅₀Ru₅₀ black, 40 sccm DME gas, 30 psig, anode humidifier at 110°C; **Cathode:** 4 mg cm⁻² Pt black, 500 sccm air, 20 psig; **Membrane:** Nafion® 212 or Nafion® 117; **Cell:** 80°C



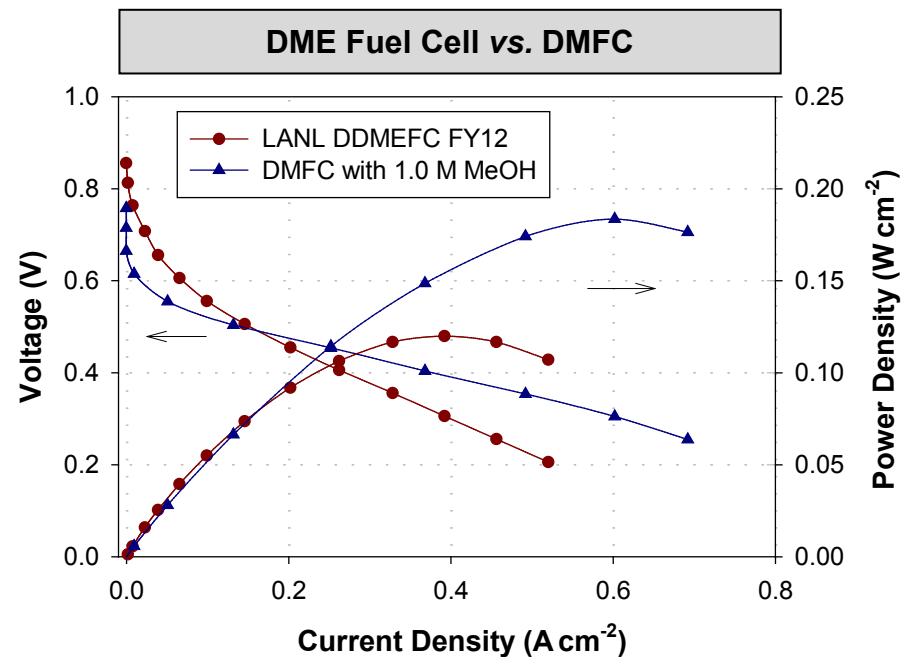
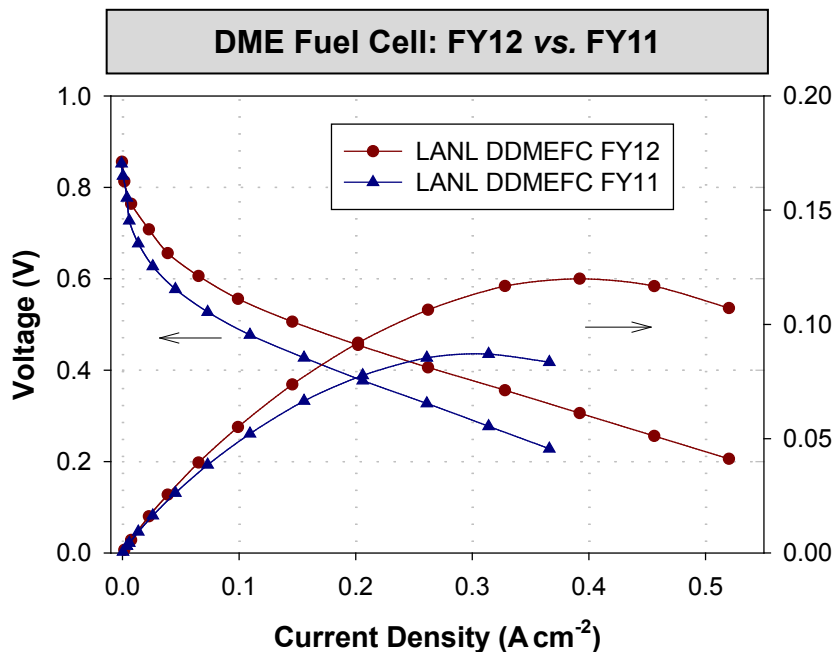
Humidifier temperature (°C)	Total pressure (kPa)	H ₂ O vapor pressure (kPa)	DME partial pressure (kPa)	DME-to-H ₂ O ratio (molar)
85	143	58	85	1.4 : 1
95	177	84	93	1.1 : 1
110	191	143	48	1 : 3

- **Highlight:** DDMEFC performing better with the molar ratio of DME to H₂O closer to stoichiometric
- Gas-feed DDMEFC with anode humidifier at 110°C outperforming liquid-feed DME fuel cell
- Unlike DMFC performance, the *iR*-corrected DDMEFC performance shown to be independent of the membrane thickness, indicating relatively low fuel crossover and/or lower activity of the Pt cathode towards DMFE than MeOH at high potentials

DME Fuel Cell: Performance Comparisons

Anode: 6 mg cm⁻² Pt₅₀Ru₅₀ black, 40 sccm DME gas, 30 psig, anode humidifier at 85°C (FY11) or 110°C (FY12); **Cathode:** 4 mg cm⁻² Pt black, 500 sccm air, 20 psig; **Membrane:** Nafion® 117 (FY11) or Nafion® 212 (FY12); **Cell:** 80°C

Anode: 6 mg cm⁻² Pt₅₀Ru₅₀ black, 1.8 mL/min 1 M MeOH or 40 sccm DME, 30 psig, anode humidifier at 110°C; **Cathode:** 4 mg cm⁻² Pt black, 20 psig (with DME) or 0 psig (with MeOH), 500 sccm air; **Membrane:** Nafion® 212; **Cell:** 80°C



- **Highlight:** FY12 performance of the DME fuel cell reaching more than 250 mA cm⁻² at 0.40 V and exceeding the FY11 performance at 0.50 V by ca. 65%

DME fuel cell performance milestone achieved

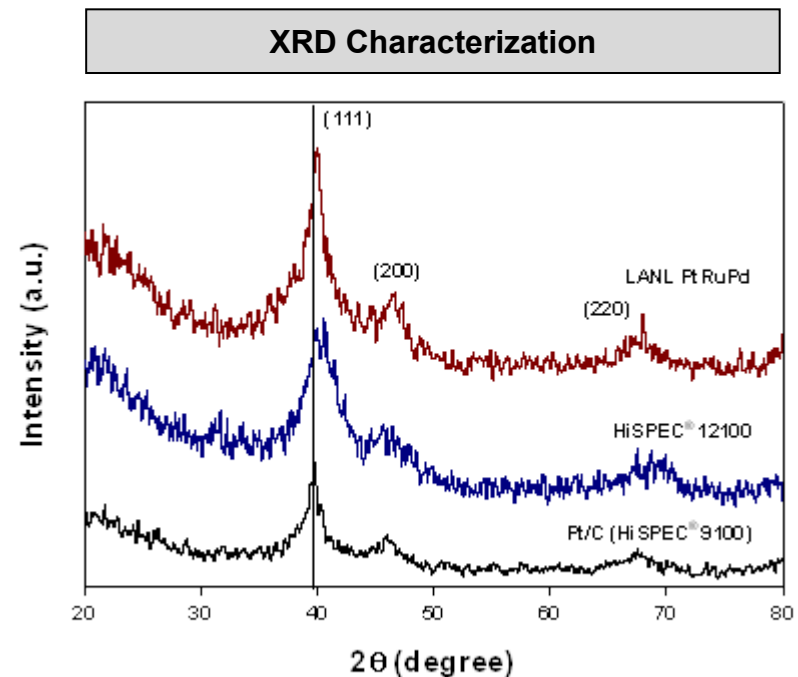
- At voltages higher than 0.49 V, DME fuel cell performance superior to that of the DMFC, mainly due to reduced effect of DME crossover compared to that of MeOH

“Go” decision for further DME research

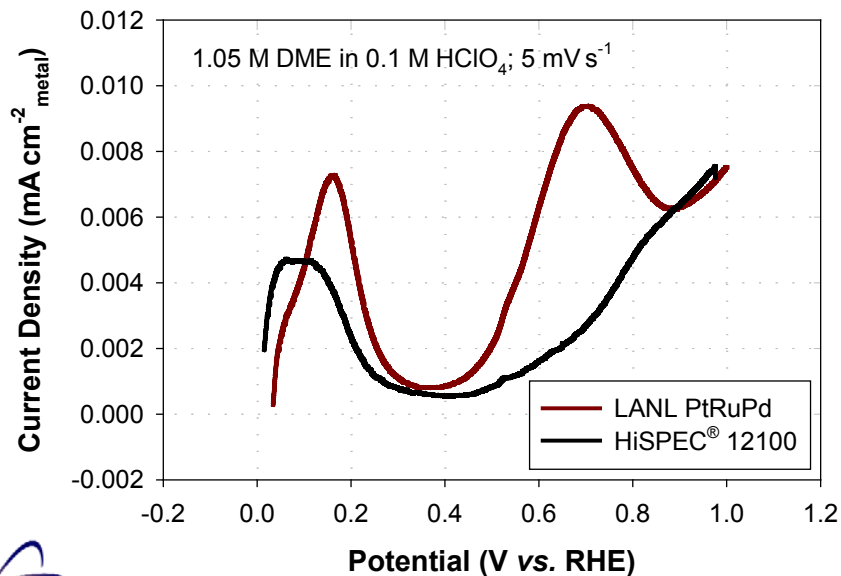
DME Fuel Cell: New Ternary PtRuPd Catalyst for DME Oxidation

Characteristics	HiSPEC® 12100	LANL PtRuPd
Metal loading by TGA in air (wt%)	73	24
Pt:Ru:Pd mass ratio by XRF	67:33:0 (51:49:0 at%)	74:10:16 (60:15:25 at%)
ECSA by H ₂ adsorption/desorption (m ² /g _{metal})	51	103
Onset potential of DME oxidation (V vs. RHE) ^a	0.43	0.38
Particle size from XRD (nm)	3.6	4.3

^a Determined at a current exceeding the background current by 3δ (δ - the standard deviation of the background current)



Electrochemical Cell Test



- Pd aiding in the C-O bond cleavage
- Alloying verified by the right shift in the (111) XRD peak for PtRuPd vs. Pt
- **Highlight:** LANL PtRuPd ternary catalyst exhibiting significant catalytic activity in DME oxidation in half-cell testing
- **Next:** Ternary catalyst optimization for maximum activity and stability under DME fuel cell operating conditions

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 Delaware 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:**
 - ✓ Oorja Protonics, Fremont, California, USA – next-phase research and development aimed specifically at reducing cost of the direct methanol fuel cell components and system for applications in excess of 1 kW in power (early phase)
 - ✓ Warsaw University, Warsaw, Poland – dimethyl ether oxidation on platinum-free electrocatalysts
 - ✓ University of Waterloo, Waterloo, Ontario, Canada – development of nanostructured methanol oxidation catalysts (early phase)

Proposed Future Work: Remainder of FY12 and FY13

Methanol oxidation catalysis:

- Further develop PtRuSn ternary catalysts to improve the kinetic performance at low Pt loadings
- Develop protocols for stack testing under SFC Energy conditions (75-80°C, 0.5 M MeOH)
- Evaluate stability and durability of new MeOH oxidation catalysts; meet durability milestone (durability of thrifted PtRu catalyst matching that of HiSPEC® 12100 w/o activity loss); carry out breakdown of performance losses in DMFCs and initiate development of mitigation strategies
- Optimize accelerated corrosion test to mimic decay mechanisms in long-term stack testing

Innovative membranes and electrode structures:

- Continue reducing methanol crossover by introducing hydroquinone into multiblock copolymers
- Improve durability of alternative membranes in the presence of higher concentrations of MeOH
- Develop PtSn/CuNW structure to achieve the onset potential of methanol oxidation of 0.29 V and 20% improvement in PGM mass activity of innovative nanostructure catalysts

Ethanol oxidation catalysis:

- Establish methodology for the synthesis of Pt_{ML}-nanoparticle catalysts with cost-effective core materials for deposition of Pt_{ML} and active promoters (SnO_x, SnO₂, Ru, etc.); scale-up the synthesis
- Implement in-situ IRRAS and on-line DEMS to determine substrate-induced selectivity of Pt_{ML}'s in EtOH (and MeOH) oxidation and EtOH oxidation at ternary PtRhSnO₂/C and PtIrSnO₂/C catalysts
- Determine the mechanism of cathode performance loss in DEFCs operating with ternary anode catalysts; develop a mitigation strategy

DME research:

- Develop a comprehensive model of the DME oxidation mechanism and catalyst requirements
- Optimize the ternary PtRuPd catalyst for maximum activity and stability at the DME fuel cell anode

Summary

- The latest PtRu “advanced anode catalyst” exceeds performance of the HiSPEC[®] 12100 benchmark by 40 mV; the catalyst synthesis has been successfully scaled up to 100 g
- A “no-go” decision has been made for further PtSn catalyst research; effort redirected towards PtRuSn catalyst, already showing unprecedented MeOH oxidation activity
- Carbon-supported PtRu catalysts cause less cathode contamination by Ru than blacks
- PtRu/CuNW catalyst exhibits a 30 mV improvement in the onset potential of MeOH oxidation relative to the HiSPEC[®] 12100 benchmark, similar stability maintained
- Multiblock copolymers, e.g. 6F25BP75PAEB-BPS100, allow for up to 55% reduction in MeOH crossover relative to the Nafion[®] 212 benchmark; fuel utilization up to 95% has been reached with 0.5 M MeOH feed near the peak-power point
- While DMFC performance strongly depends on methanol concentration, the unrecoverable performance loss with 0.5 M MeOH feed is relatively small
- Several Pt_{ML} catalysts with expanded lattice and “engineered” catalysts have onset potential of EtOH oxidation near 0.2 V vs. RHE (20°C -25°C); EtOH oxidation is very strongly dependent on catalyst morphology (e.g. nanowires vs. nanoparticles)
- Both PtIrSnO₂/C and PtRhSnO₂/C ternary catalysts allow to reach in MEA the onset potential of MeOH oxidation close to the thermodynamic value of 0.04 V at 80°C
- DME performance has been improved by 65% vs. FY11, resulting in a “go” decision for DME further research; new PtRuPd/C catalyst promises to aid in C-O bond cleavage



– **ethanol and methanol anode catalyst research**

R. R. Adzic (PI), S. Bliznakov, M. Li, P. Liu, K. Sasaki, W.-P. Zhou



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

P. Zelenay (Project Lead), H. Chung, C. Johnston, Y. S. Kim, Q. Li, D. Langlois, D. Spornjak, P. Turner, G. Wu

Dare to be first.



– **nanostructure catalyst structures**

Y. Yan (PI), S. Alia, J. Zheng



– **hydrocarbon membrane research**

J. McGrath (PI), Y. Chen, J. Rowlett

VIRGINIA POLYTECHNIC INSTITUTE
AND STATE UNIVERSITY



Johnson Matthey Fuel Cells
the power within

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

N. Cabello-Moreno (PI), G. Hards, G. Spikes



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

C. Böhm (PI), V. Graf, P. Hassell

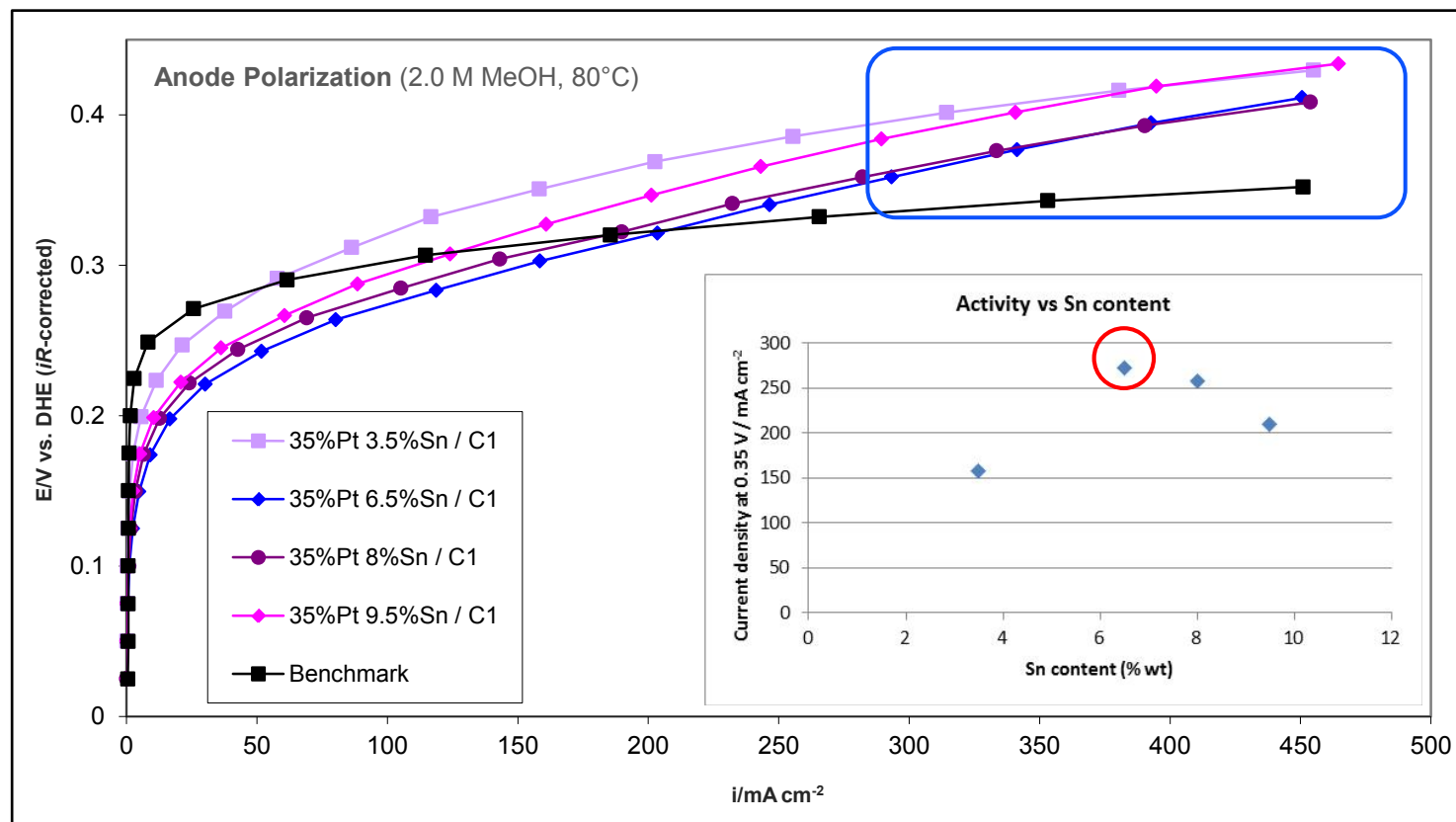


– **microscopic characterization (no-cost partner)**

K. More (PI), D. Cullen

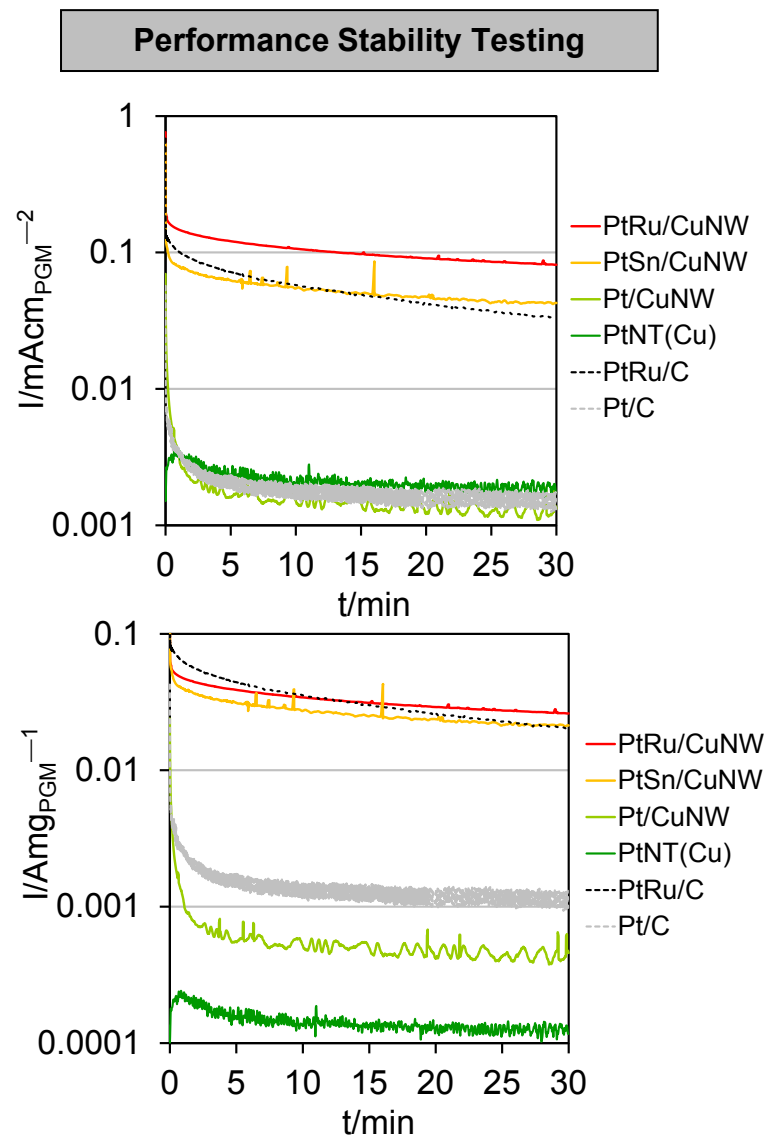
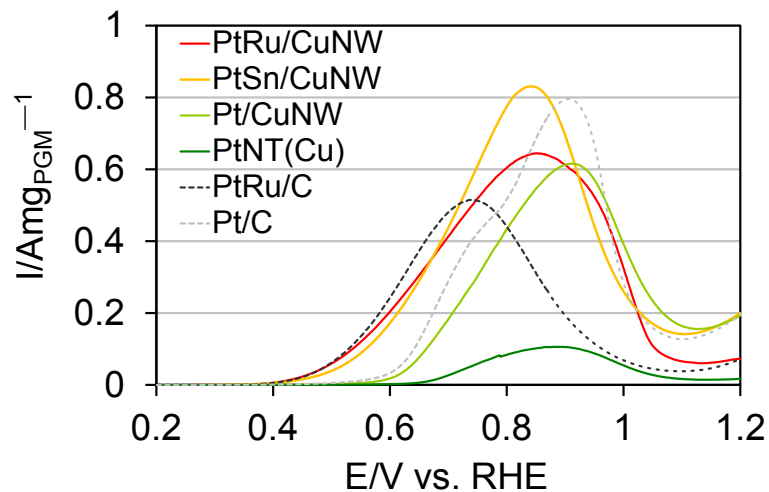
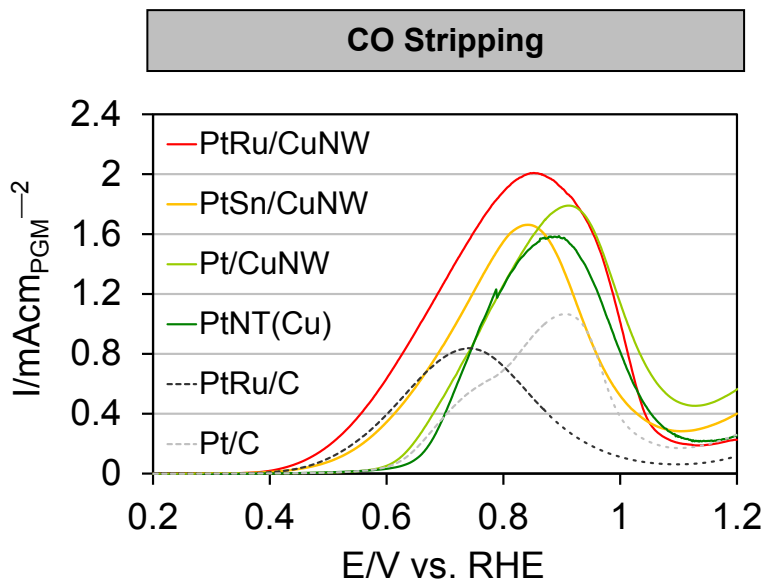
Technical Backup Slides

MeOH Oxidation: Binary PtSn/C Catalysts – Sn Content Study



- A series of PtSn (3:1) catalysts with variable Sn content prepared by Cat prep 3 route
- The plot of activity vs. Sn content revealing a volcano plot with a maximum at 6.5 wt% Sn

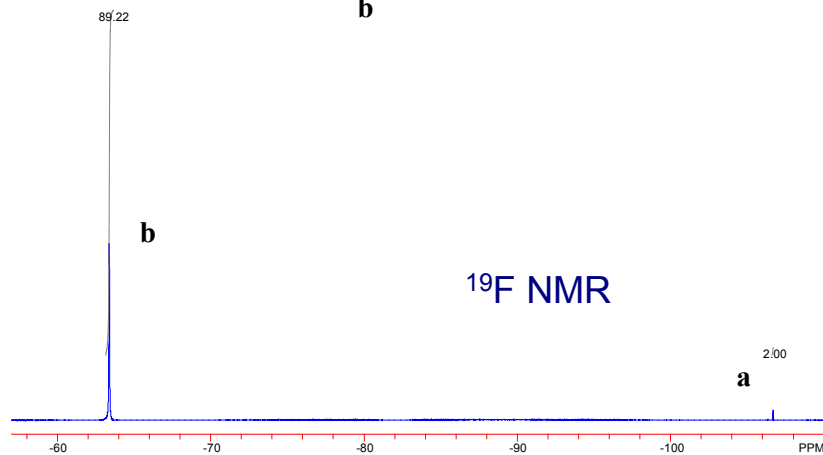
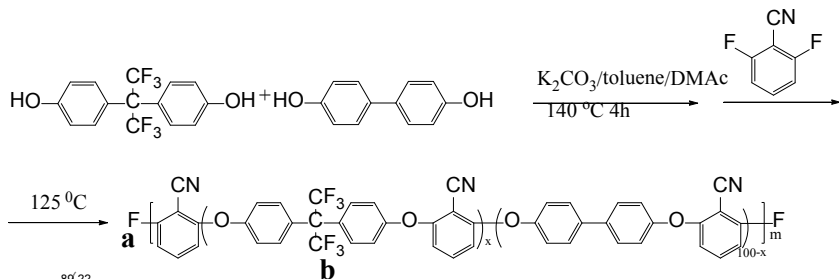
Methanol Oxidation: Innovative PtRu Nanostructure Catalysts



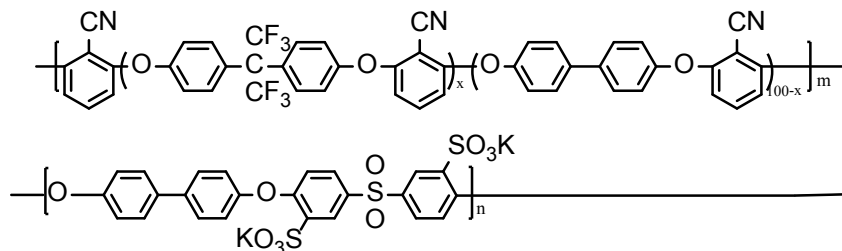
Solution: 1.0 M MeOH in 0.5 M H_2SO_4 ; **Voltammetry:** scan rate 5 $mV s^{-1}$; **Benchmark PtRu/C catalyst:** HISPEC® 12100

DMFC Multiblock Copolymers: Synthesis and Characterization

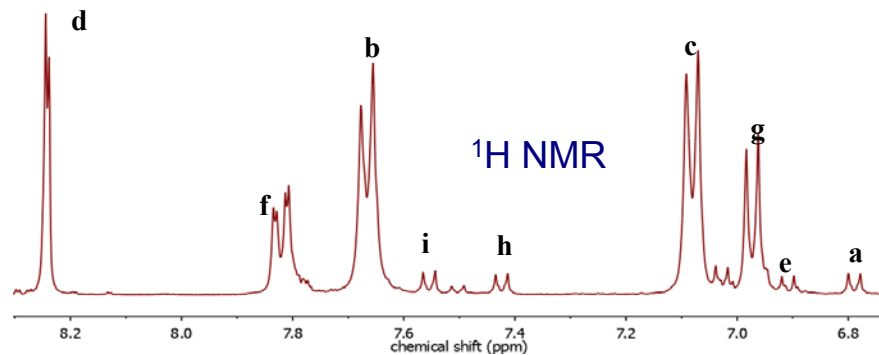
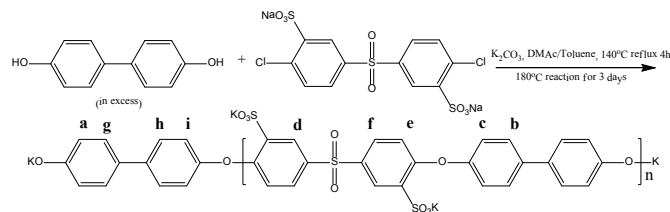
^{19}F NMR of $6\text{F}_{50}\text{BP}_{50}\text{PAEB}$ 10k Oligomer



Multiblock copolymer
with reduced methanol permeability

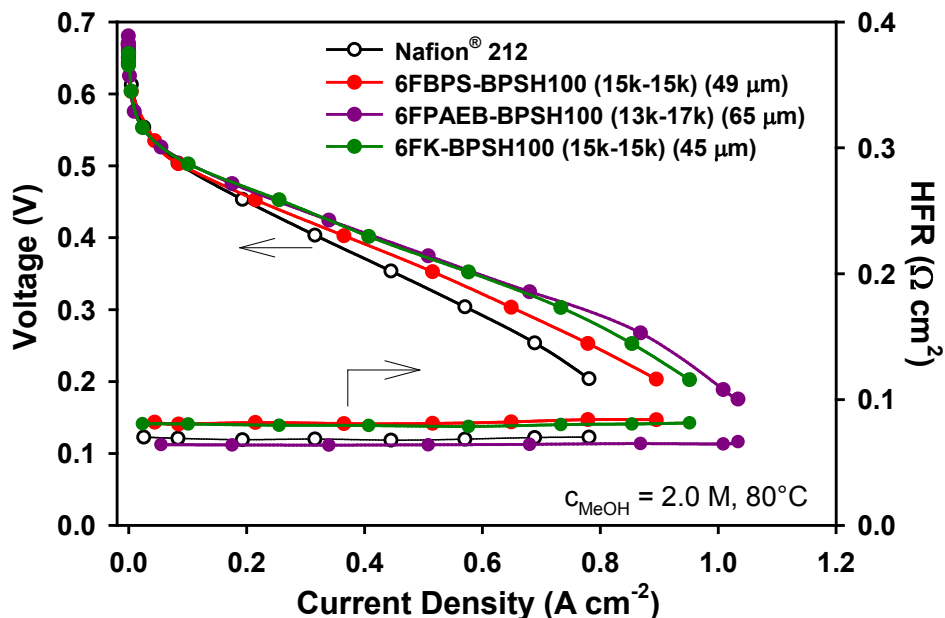


Hydrophilic Telechelic BPSH-100 Oligomers

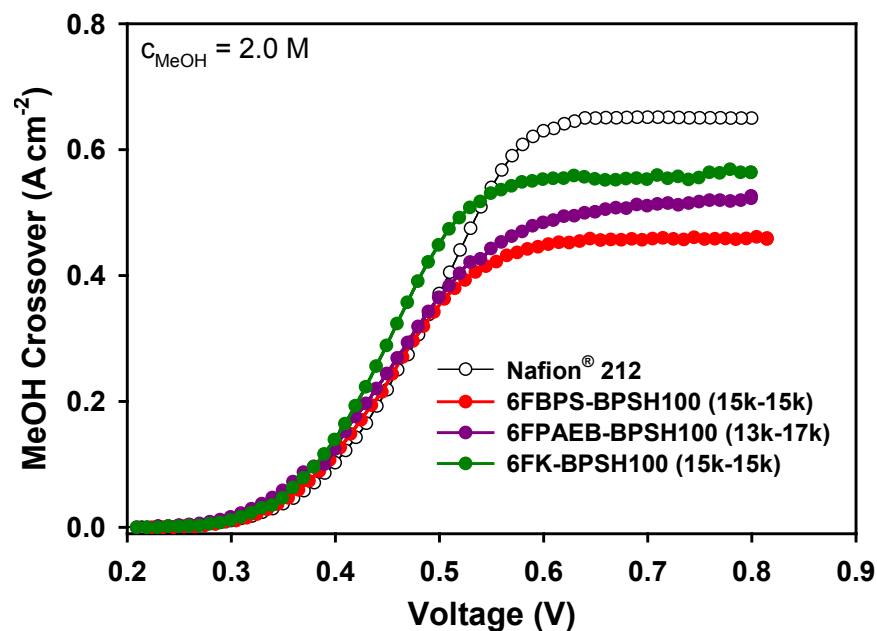


DMFC Multiblock Copolymers: Performance and Fuel Utilization (2.0 M MeOH)

DMFC Polarization (2.0 M MeOH)



MeOH Crossover and Fuel Utilization



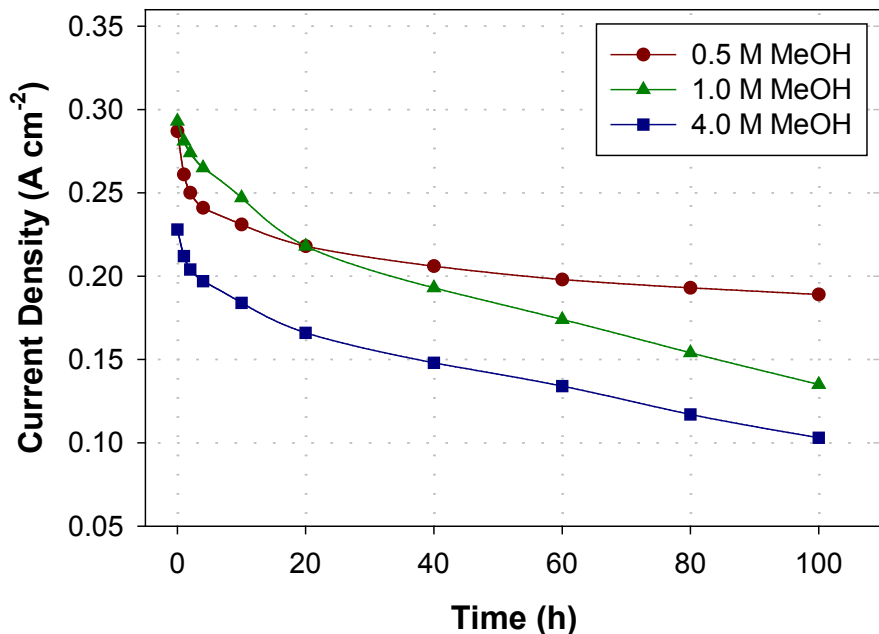
Methanol Concentration	Characteristics	Multiblock	Nafion®
		6FBPS (49 μm)	212 (50 μm)
0.5 M	η_{fuel} at 0.5 V, %	69	62
	η_{fuel} at peak power, %	92	90
2.0 M	η_{fuel} at 0.5 V, %	27	12
	η_{fuel} at peak power, %	79	57

- MEAs with multiblock copolymer membranes showing better performance and lower methanol crossover with 2.0 M methanol feed than the control Nafion® MEA
- Low fuel utilization (no more than 80%) caused by high methanol feed concentration

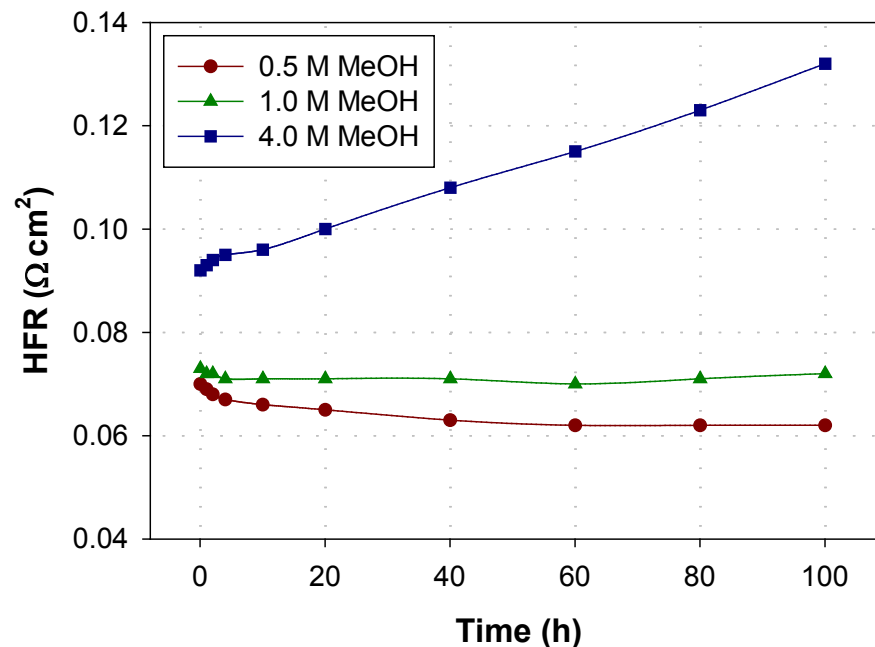
DMFC Performance Degradation: Current Density and HFR Changes

Anode: 6 mg cm⁻² Pt₅₀Ru₅₀ black, 1.8 mL/min MeOH solution; Cathode: 4 mg cm⁻² Pt black; 500 sccm air; Membrane: Nafion® 212; Cell: 80°C

Current Density in 100-Hour Life Test at 0.40 V



HFR in 100-Hour Life Test at 0.40 V



- Higher initial HFR value observed in more concentrated MeOH
- Little time-dependence of HFR with 0.5 M and 1.0 M MeOH feed concentrations
- Continuous HFR increase with 4.0 M MeOH feed, most likely due to structural MEA degradation