2013 Hydrogen and Fuel Cells Program
Annual Merit Review and Peer Evaluation Meeting
Arlington, Virginia – May 13-17, 2013

Advanced Materials and Concepts for Portable Power Fuel Cells

Piotr Zelenay

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Project ID: FC091

Overview

Timeline

- **Start date:** September 2010
- **End date:** Four-year duration
- **Completion:** *ca.* 70%

Budget

- **Total funding estimate:**
  - DOE share: $3,948K
  - Contractor share: $342K
- **FY12 funding received:** $975K
- **FY13 funding received:** $1,048K

Barriers

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

Partner Organization – Principal Investigator

Partner Organization	Principal Investigator
Brookhaven National Laboratory	– Radoslav Adzic
University of Delaware	– Yushan Yan
Virginia Tech (Virginia Polytechnic Institute and State University)	– James McGrath
Johnson Matthey Fuel Cells	– Alex Martinez Bonastre
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 $\rightarrow$ 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

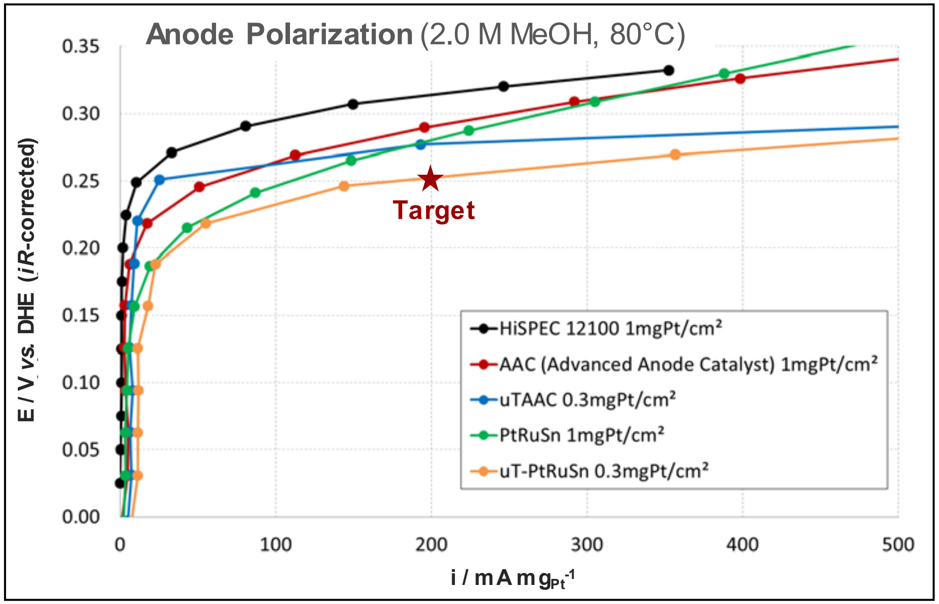
- **DMFC anode research:**
  - new catalysts with improved activity and reduced cost (JMFC, LANL, BNL)
  - improved catalyst durability (JMFC, LANL, BNL)
- **Innovative electrode structures for better activity and durability** (UD)
- **Hydrocarbon membranes for lower MEA cost and enhanced fuel cell performance** (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	Milestones	Status	Comment
Jan 13	Complete construction of the DEMS instrument.	**Complete**	DEMS instrument has been constructed.
Feb 13	Improve the ternary $PtRhSnO_2$ electrocatalyst to oxidize ethanol to CO_2 with an efficiency of 30-50% at E = 0.4 V at 60-80°C.	**Delayed**	More time required to verify and, if needed, resolve possible SnO_2 stability problem in ternary catalysts.
Mar 13	Demonstrate 150 mA cm^{-2} at 0.50 V in a DDMEFC operating with a new-generation PtRuPd/C anode catalyst at a loading of < 3.0 mg_{Pt} cm^{-2} (80°C).	**Complete**	0.15 A cm^{-2} at 0.50 V achieved with new high-metal content $Pt_{45}Ru_{45}Pd_{10}/C$ catalyst; catalysts outperforming PtRu/C reference by catalyst by *ca.* 50 mV at 0.15 A cm^{-2}.
Apr 13	Demonstrate PtRu or PtRuSn methanol oxidation catalyst that exceeds final project anode mass activity-target of 200 mA mg_{Pt}^{-1} at ≤ 0.25 V at 80°C (*iR*-corrected), with durability at least matching that of the state of the art (HiSPEC® 12100).	**Mass-activity target complete** **Durability target pending**	Mass-activity target of 200 mA mg_{Pt}^{-1} at ≤ 0.25 V (80°C) achieved with ultra-thrifted PtRuSn/C catalyst (uT-PtRuSn); durability of uT-PtRuSn in need of improvement; several other advanced anode catalysts showing better durability than the benchmark HiSPEC® 12100 catalyst.
May 13	Synthesize multi-block copolymer with methanol permeability reduced by at least 50% relative to Nafion® and maintained ionic conductivity and water uptake.	**Complete**	MeOH crossover in tetramethylbisphenol A (TM) copolymer reduced by more than 50% without ionic-conductivity or water-uptake penalties.
Aug 13	Characterize the most promising new DMFC anode catalyst and/or membrane developed in the project in a short stack under conditions simulating SFC's commercial products.	**On schedule**	Testing of JMFC's AAC catalyst in a 50-cm^2 five-cell stack planned by SFC Energy for the summer of 2013.
Sep 13	Develop PtRu/CuNWs based methanol oxidation catalysts with the onset potential < 0.3 V *vs.* RHE and mass activity at 0.40 V *vs.* RHE at least matching that of the benchmark PtRu catalyst (HiSPEC®12100).	**Complete**	Onset potential of methanol oxidation of 0.288 V *vs.* RHE has been achieved by tuning Pt-to-Ru ratio in PtRu/CuNWs catalyst; mass activity is comparable to that of the benchmark catalyst.

Methanol Oxidation: New Ultra-Thrifted Anode Catalysts

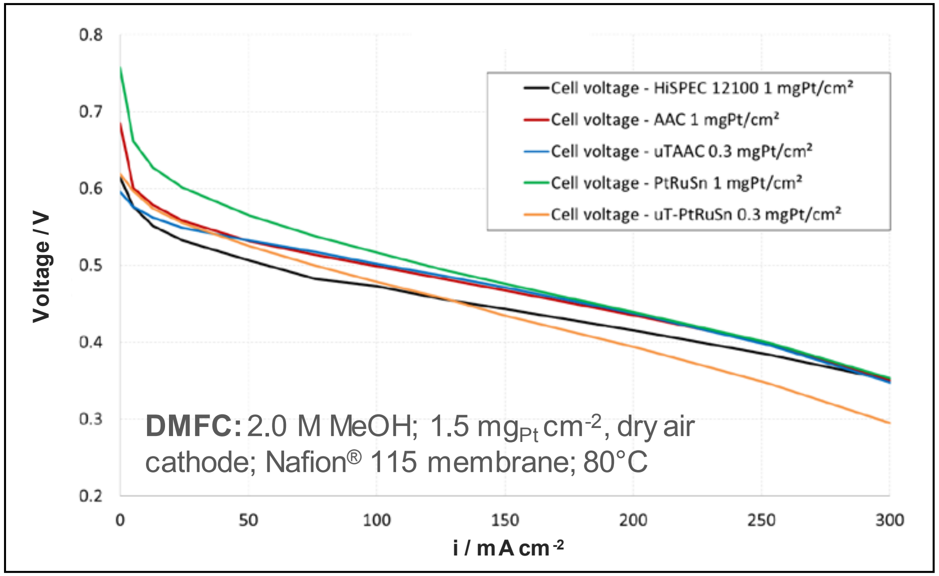
Catalyst Code	Atomic Ratio		
	Pt	Ru	Sn
HiSPEC® 12100 PtRu/C – JMFC benchmark	50	50	-
PtRu/C (Advanced Anode Catalyst, AAC) – FY12	20	80	-
Ultra-thrifted PtRu/C (uTAAC) – FY13	**10**	**90**	**-**
PtRuSn/C – FY12	20	73	7
Ultra-thrifted PtRuSn/C (uT-PtRuSn) – FY13	**10**	**85**	**5**



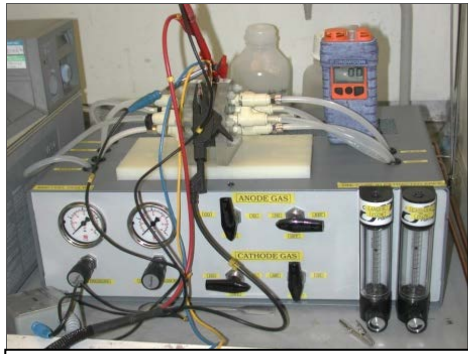
- **Highlight: New ultra-thrifted PtRu/C catalyst (uTAAC) outperforming the HiSPEC® 12100 benchmark and ACC in terms of MeOH oxidation onset potential and mass activity; matching AAC in DMFC testing at a loading of only 0.3 mg_{Pt} cm^{-2}**

Mass-activity target of 200 mA mg_{Pt}^{-1} at ≤ 0.25 V (80°C) achieved with uT-PtRuSn catalyst

- **Highlight: PtRuSn/C catalyst performing by far the best in DMFC testing at current densities < 150 mA cm^{-2} (Sn effect at low MeOH oxidation overpotentials)**



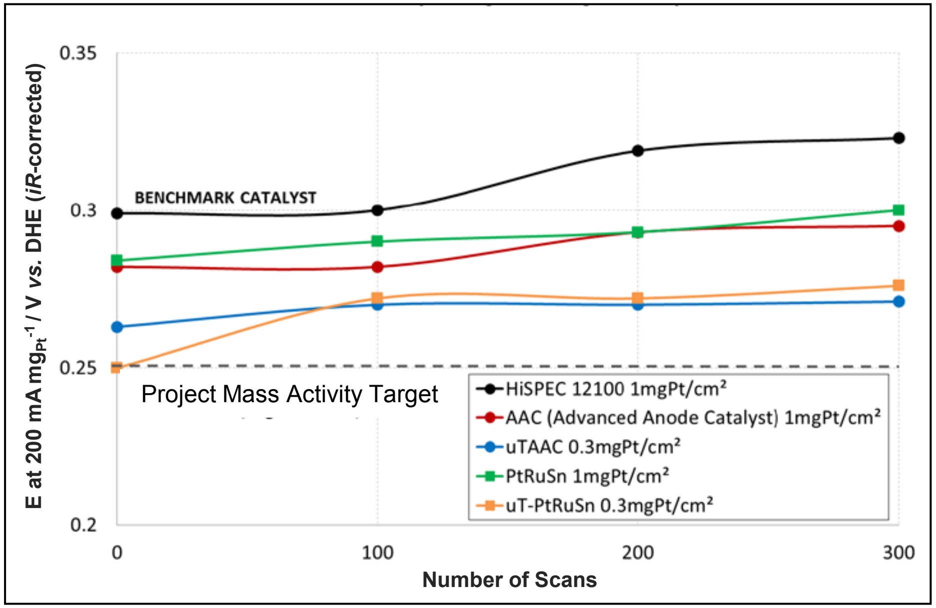
Methanol Oxidation: In-Situ Accelerated Anode Stability Testing (2.0 M MeOH)



Cell performance: H_2-air fuel cell polarization and DMFC anode polarization plots. **Catalyst surface probing:** Stripping of MeOH-generated CO from anode and cathode.

Catalyst	Loss after 300 Cycles / mV	E Increase after 300 Cycles, %
HiSPEC® 12100 1.0 mg_{Pt} cm^{-2}	24	8
Advanced Anode Catalyst (AAC) 1.0 mg_{Pt} cm^{-2}	13	5
Ultra-thrifted PtRu (uTAAC), 0.3 mg_{Pt} cm^{-2}	**8**	**3**
PtRuSn 1.0 mg_{Pt} cm^{-2}	16	6
Ultra-thrifted PtRuSn (uT-PtRuSn), 0.3 mg_{Pt} cm^{-2}	26	10

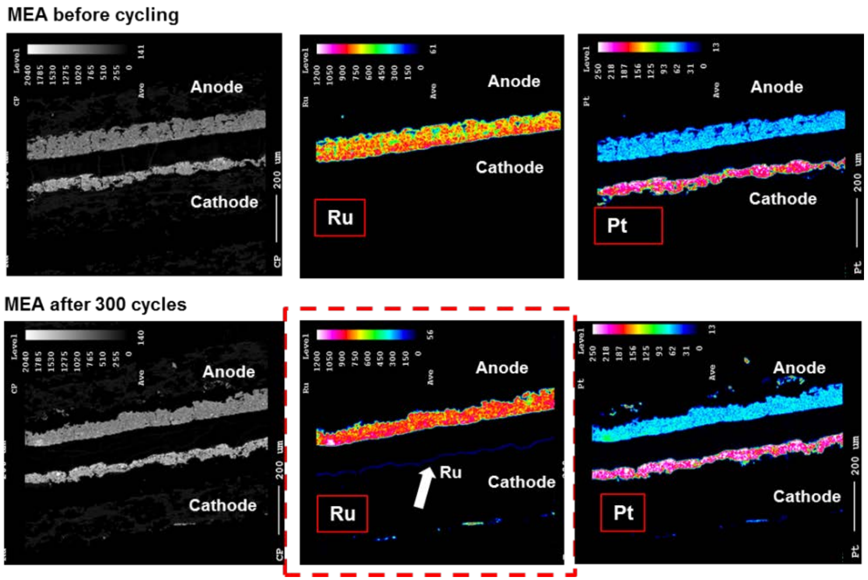
Anode: H_2O; **Cathode:** H_2; **Cycling:** 0.05 – 0.85 V, 300 cycles; 80°C



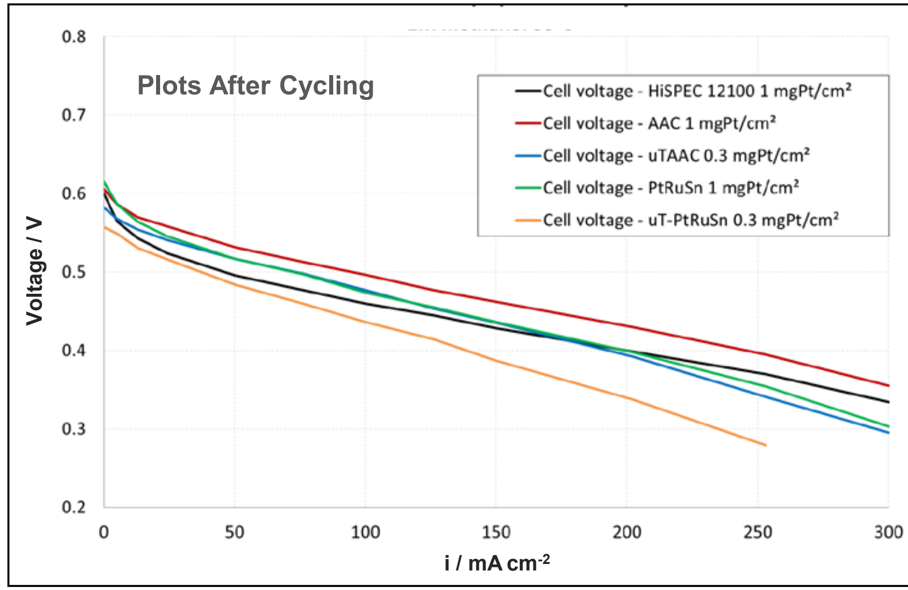
- **Highlight: Ultra-thrifted PtRu catalyst (uTAAC) maintaining excellent mass activity (only 13 mV off the project target) throughout the stability testing**
- **Ultra-thrifted PtRuSn catalyst (uT-PtRuSn) in need of stability improvement at high operating anode potentials encountered during stability testing**

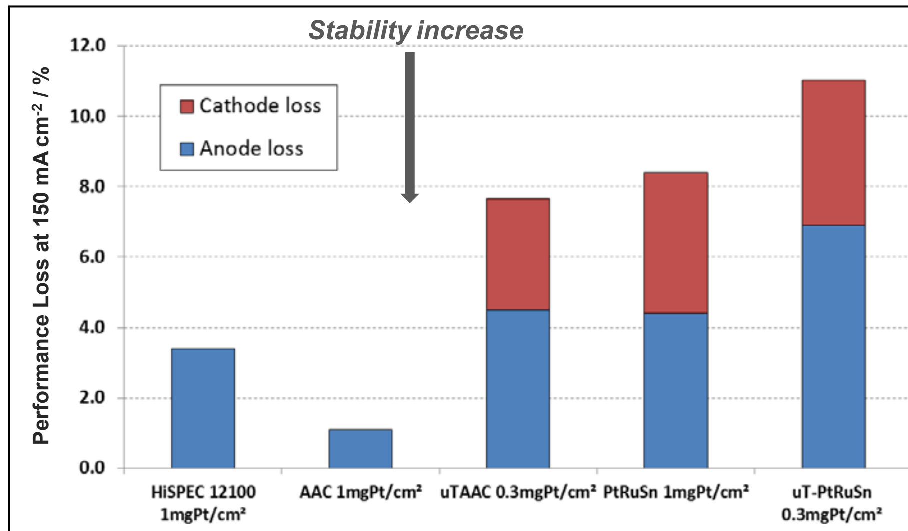
Methanol Oxidation: In-Situ MEA Accelerated Stability Testing (2.0 M MeOH)

Anode: Thrifted PtRu/C advanced anode catalyst (AAC), H_2O; **Cathode:** H_2; **Anode Cycling:** 0.05 – 0.85 V, 300 cycles total



Anode: H_2O; **Cathode:** H_2; **Cycling:** 0.05 – 0.85 V, 300 cycles, 80°C

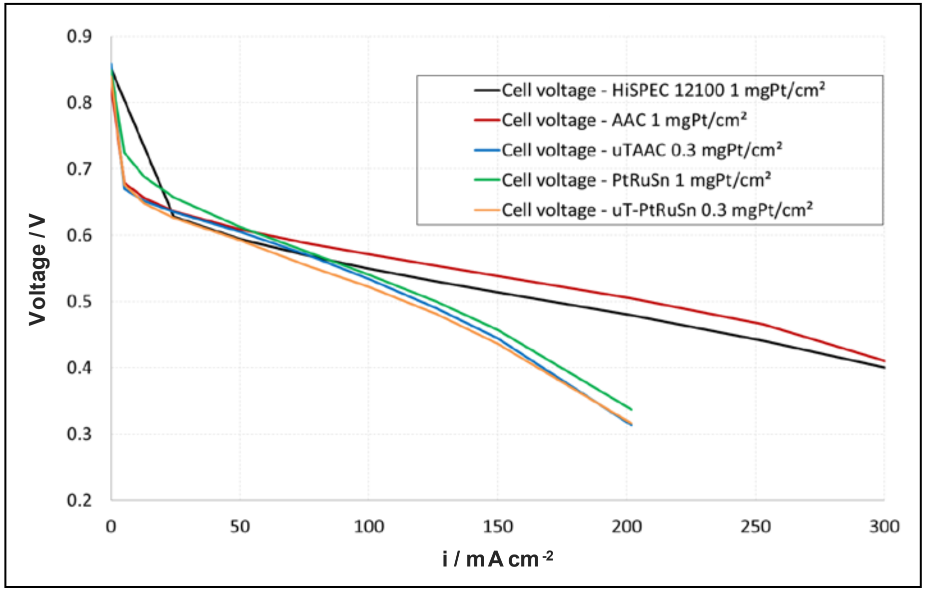




- **Highlight: Thrifted PtRu/C catalyst (AAC) showing excellent cycling durability at *ca.* 1% overall performance loss after 300 cycles (no cathode loss in spite of small Ru migration)**
- **Ultra-thrifted PtRuSn catalyst (uT-PtRuSn) in need of stability improvement at high potentials; Ru migration to the cathode detected in cathode CO stripping (see *Technical Backup Slides*) with a clear impact on cathode performance**

Methanol Oxidation: DMFC Polarization Plots with 0.5 M MeOH

Anode: PtRu/C or PtRuSn/C, 0.5 M MeOH; **Cathode:** Pt/C (1.5 mg_{Pt} cm^{-2}), dry air; **Membrane:** Nafion® 115; **Cell:** 80°C

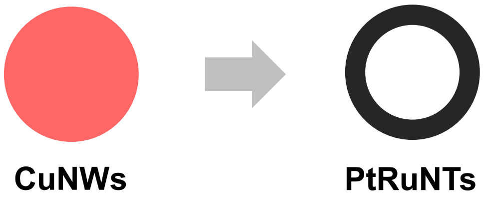


- **Highlight:** **PtRu/C catalyst (AAC) at only 1.0 mg_{Pt} cm^{-2} 0.54 V at 150 mA cm^{-2}, close to the project target of 0.6 V at 150 mA cm^{-2}; further optimization of anode expected to lead to further performance gains**
- **At 0.5 M MeOH, PtRuSn catalysts not offering a performance advantage over Pt/Ru**

AAC performance within 60 mV of the overall project DMFC target!

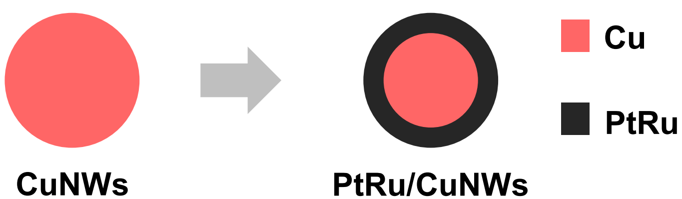
Methanol Oxidation: Innovative PtRu Nanostructure Catalysts (Synthesis)

Synthesis of PtRuNTs



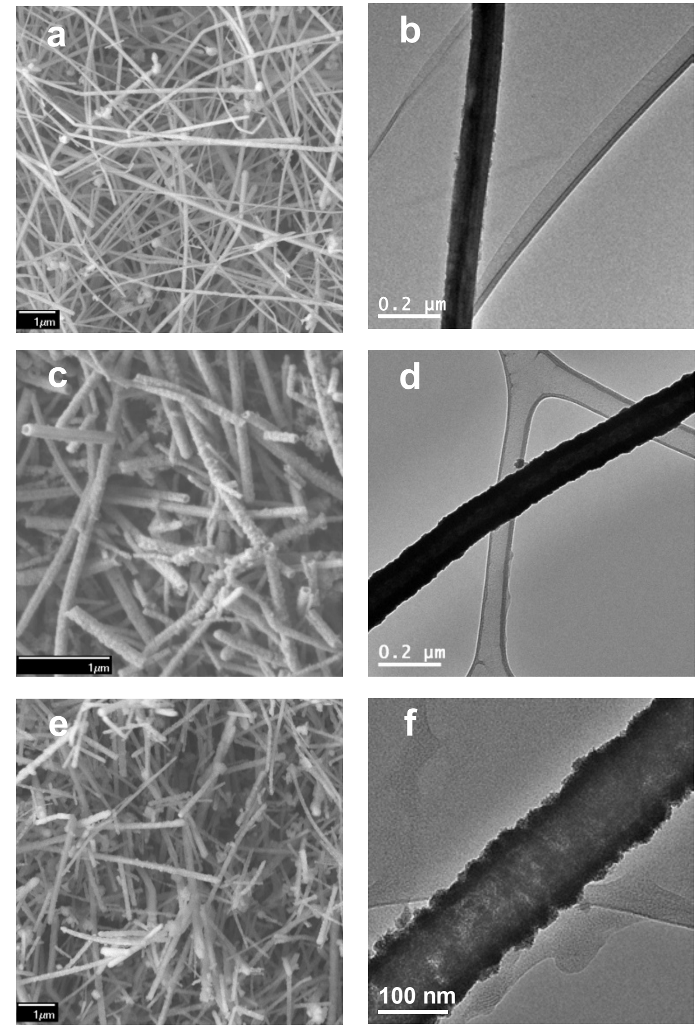
Simultaneous complete displacement of Cu in CuNWs with Pt and Ru to form PtRuNT

Synthesis of PtRu/CuNWs



Simultaneous partial displacement of Cu in CuNWs with Pt and Ru to form PtRu coated on CuNWs structure

Catalyst	wt%			
	Pt	Ru	Cu	C
PtRu/C (HiSPEC® 12100)	50	25	0	25
PtRu/CuNWs	23	7	70	0
Pt_3Ru/CuNWs	**23**	**5**	**72**	**0**
Pt_6Ru/CuNWs	28	2	70	0



SEM images: (a) CuNWs, (c) PtRuNTs, (e) PtRu/CuNWs. **TEM images:** (b) CuNWs, (d) PtRuNTs, (f) PtRu/CuNWs

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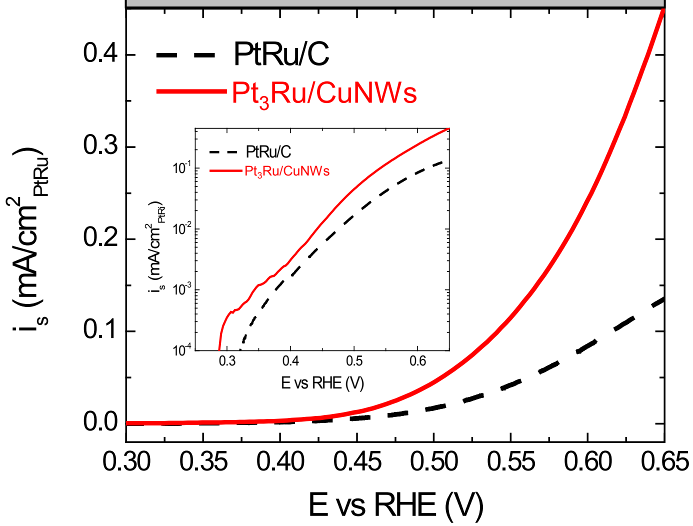
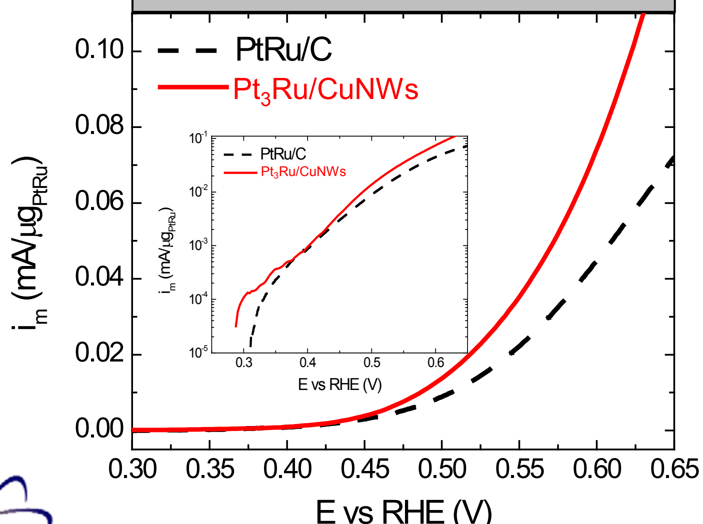
Methanol Oxidation: Innovative PtRu Nanostructure Catalysts (Highlights)

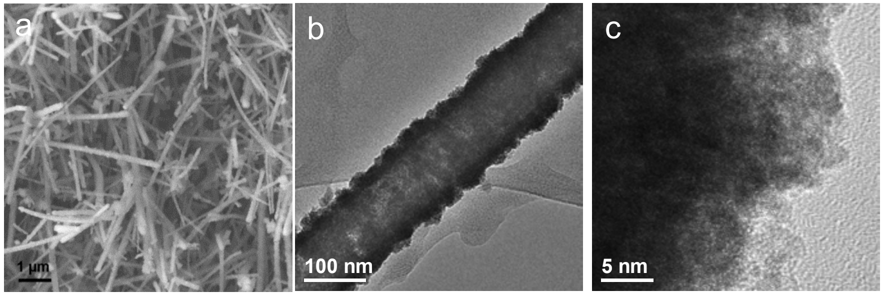
Solution: 1.0 M MeOH in 0.1 M $HClO_4$; **Scan rate:** 5 mV s^{-1}; **PtRu/C:** HiSPEC® 12100

Specific Activity



Mass Activity





(a) SEM, (b) TEM and (c) HRTEM images of PtRu/CuNWs

Catalyst	Onset Potential of MeOH Oxidation (V *vs.* RHE)
PtRu/C (HiSPEC® 12100)	0.320
Pt_3Ru/CuNWs	**0.288**

- **Highlight: Very low onset potential of methanol oxidation of 0.288 V vs. RHE achieved by tuning the Pt-to-Ru ratio in PtRu/CuNW catalysts**

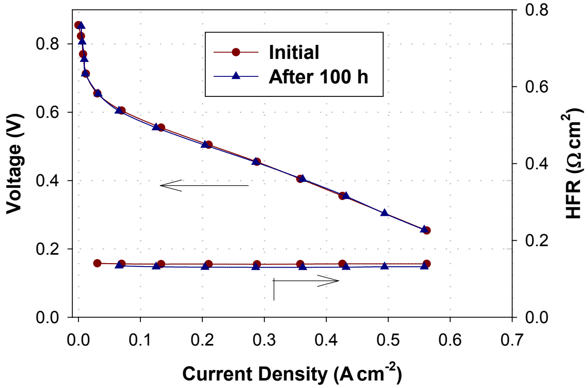
Onset potential target of ≤ 0.3 V vs. RHE achieved with a PtRu/CuNW catalyst

- **Mass activity of PtRu/CuNWs based on total precious metal content higher than that of PtRu/C benchmark catalyst (HiSPEC® 12100)**

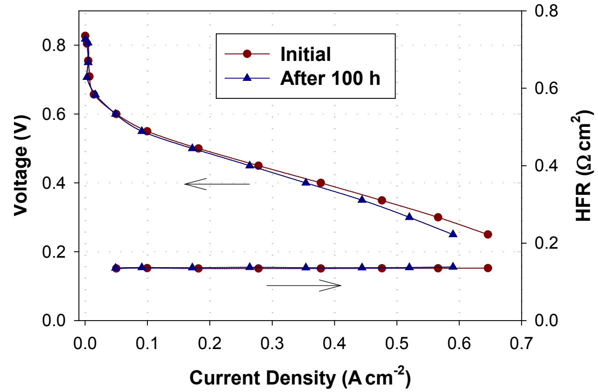
DMFC Durability: 100-Hour Life Test with Metal Black Catalysts

Anode: 6 mg cm^{-2} $Pt_{50}Ru_{50}$ black, 1.8 mL/min MeOH; **Cathode**: 4 mg cm^{-2} Pt black, 500 sccm air; **Membrane**: 3 × Nafion® 212; **Cell**: 75ºC; **Life test**: 0.45 V, 100 hours

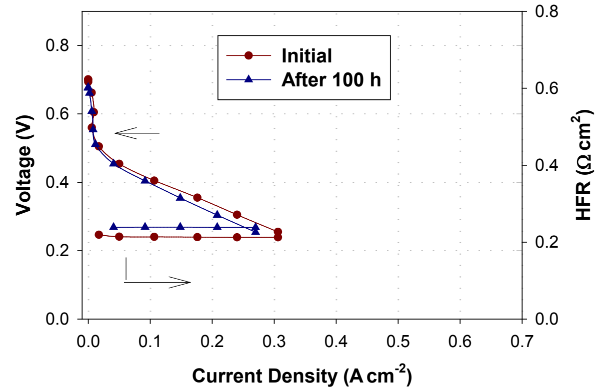
0.5 M MeOH



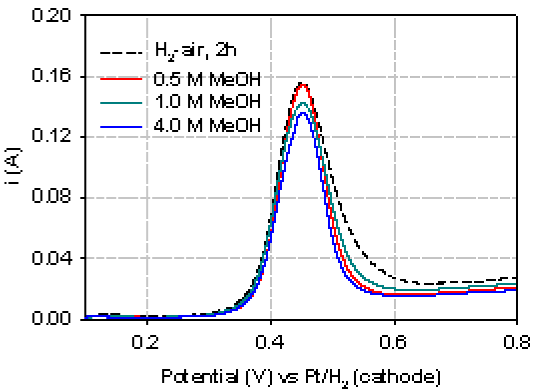
1.0 M MeOH



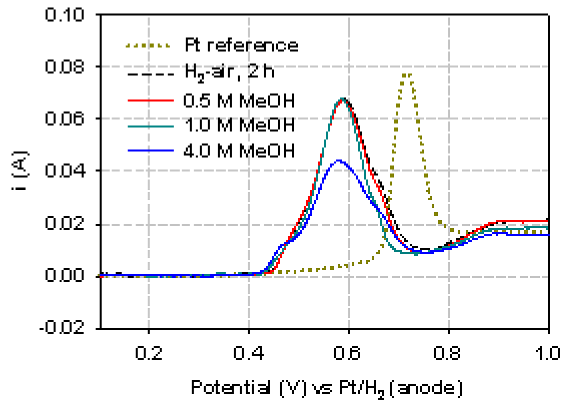
4.0 M MeOH



Anode CO Stripping



Cathode CO Stripping

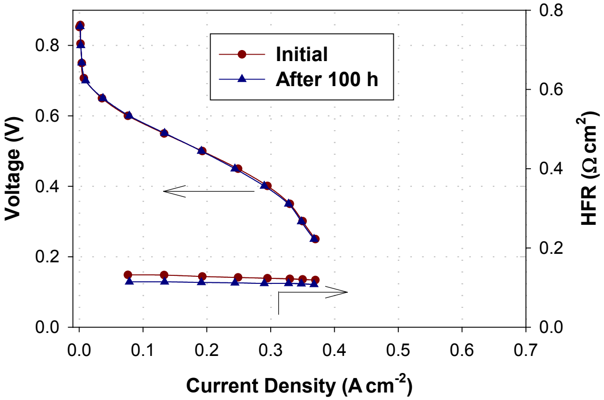


- **Most Ru crossover taking place during 2-hour H_2-air break-in; potential of CO stripping from the cathode virtually independent of methanol concentration**
- **Surface composition of the anode not affected by the concentration of MeOH in the 100-hour test**

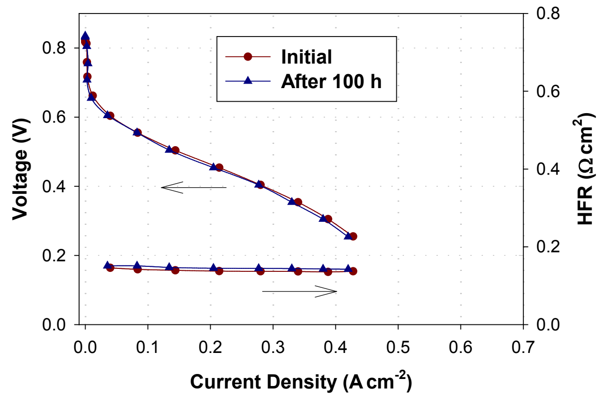
DMFC Durability: 100-Hour Life Test with Carbon-Supported Catalysts

Anode: 4 mg_{metal} cm^{-2} HiSPEC® 12100, 1.8 mL/min MeOH; **Cathode**: 2 mg_{Pt}/cm^2 HiSPEC® 9100; 500 sccm air; **Membrane**: 3×Nafion® 212; **Cell**: 75ºC; **Life test**: 0.45 V, 100 hours

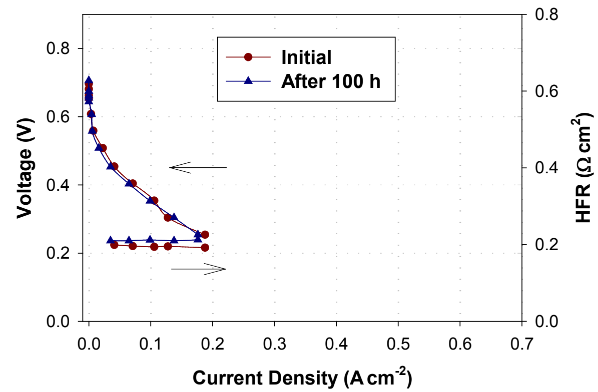
0.5 M MeOH



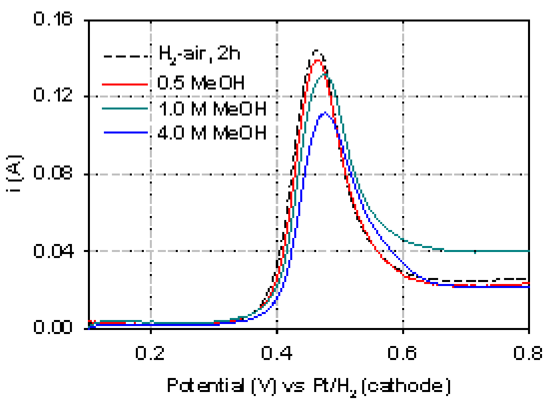
1.0 M MeOH



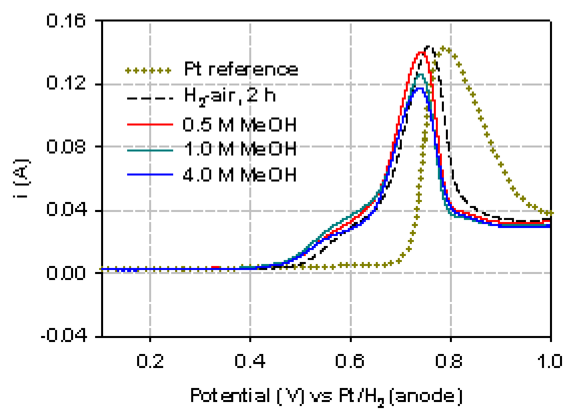
4.0 M MeOH



Anode CO Stripping



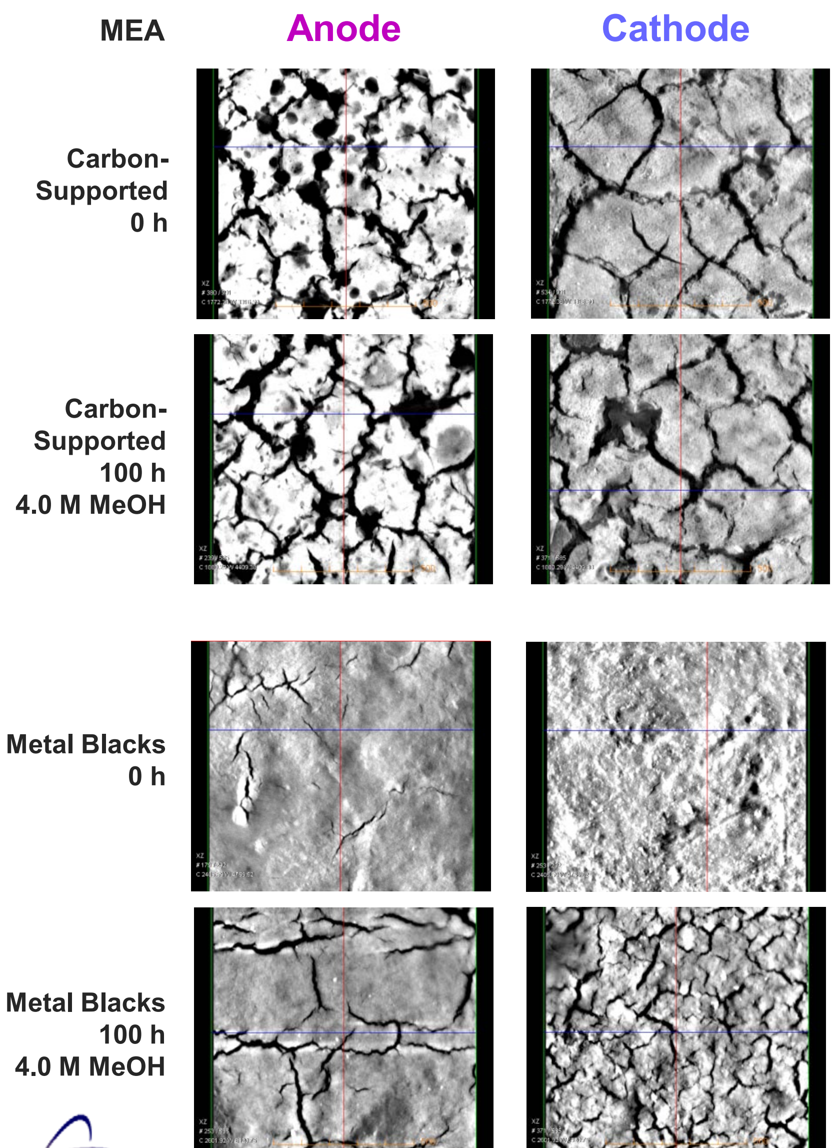
Cathode CO Stripping



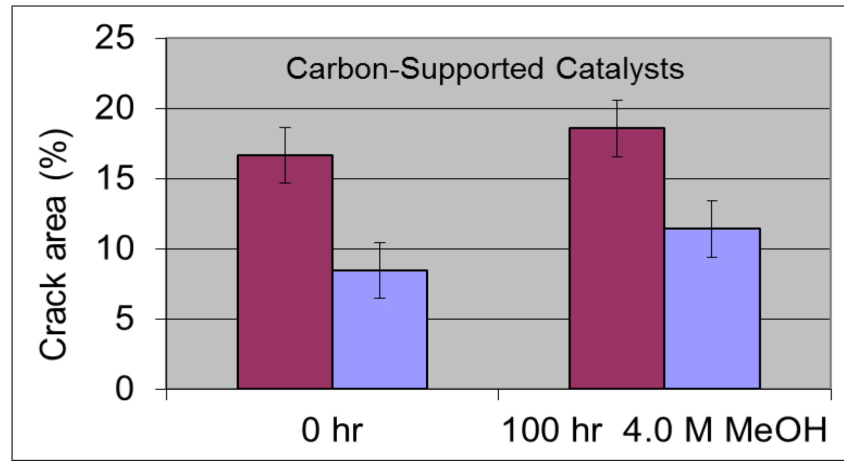
- **High-frequency resistance gain at the highest MeOH concentration also observed with carbon-supported catalysts**
- **Very small Ru contamination of the cathode (in agreement with JMFC results)**

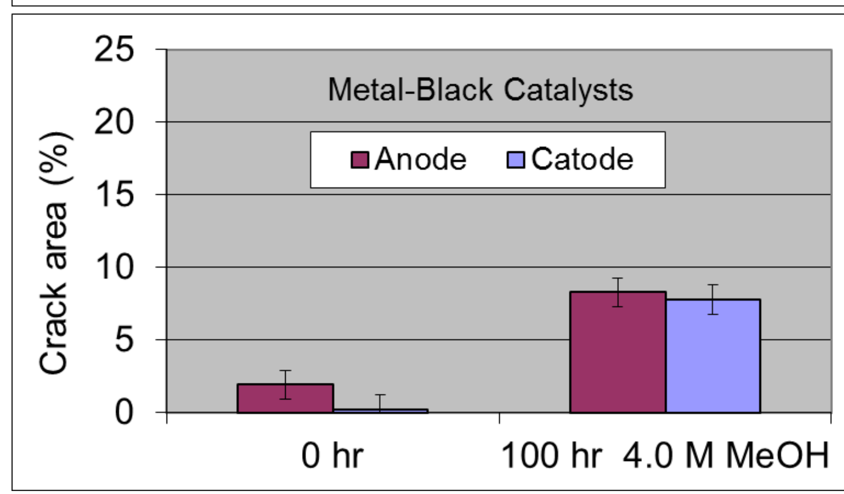
DMFC Durability: Electrode X-Ray Tomography

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



- **JMFC carbon-supported electrodes:** Significant presence of cracks in as-prepared and tested MEAs (16-19% anode, 8-12% cathode); possible benefit to mass transport
- **LANL metal-black electrodes:** Virtually crack-free initially; crack formation during life test not causing any significant performance loss of metal-black electrodes

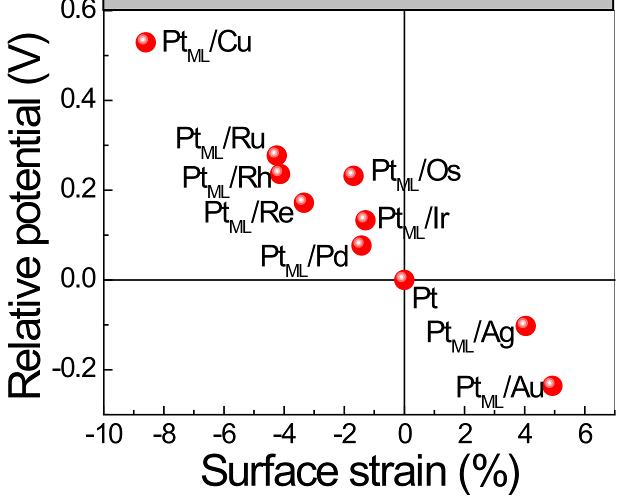




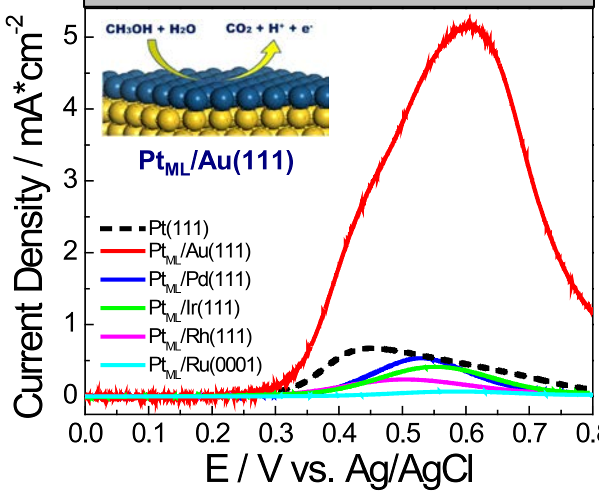
Ethanol Oxidation: Pt-Monolayer Catalysts Enhanced by Au Nanocore

Approach: Theoretical Prediction → Pt_{ML}/Au(111) Model Catalyst → Pt_{ML}/Au/C Nanocatalyst → ($RhSnO_2$, Ru)-Modified Pt_{ML}/Au/C

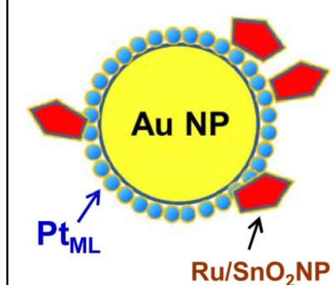
DFT Simulation (MeOH Oxidation)



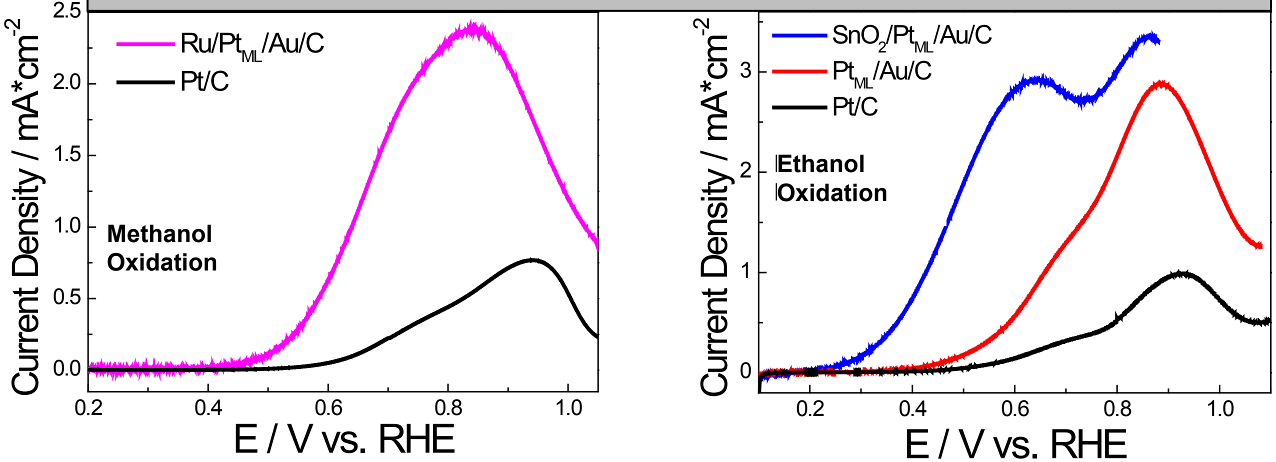
Single-Crystal Model Catalysts



Ru/Pt_{ML}/Au/C and SnO_2/Pt_{ML}/Au/C

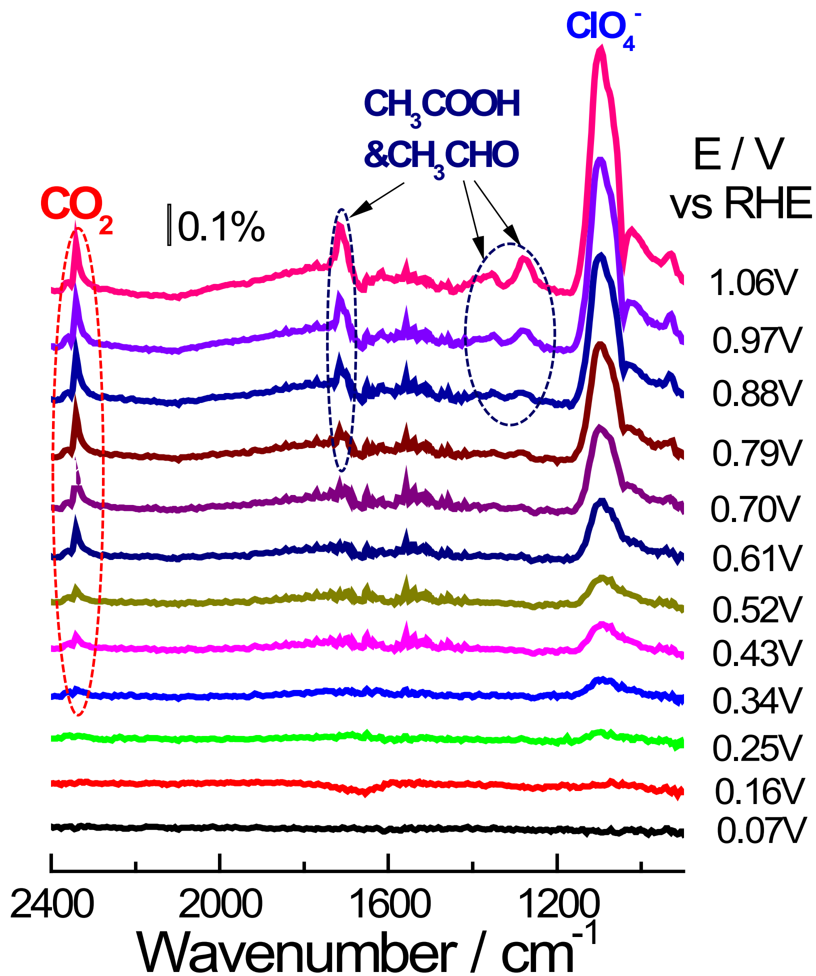


Pt_{ML} Catalysts with MeOH and EtOH Oxidation Activity Enhanced by Au Nanocore



- Model catalyst study confirming DFT prediction of the expansive strain effect of underlying Au on the Pt_{ML} activity
- **Highlight:** Pt_{ML}/Au/C nanocatalyst synthesized by displacing Cu UPD layer pre-deposited on Au/C; Pt_{ML}/Au/C further modified with SnO_2 to achieve high ethanol oxidation activity of bifunctional catalyst

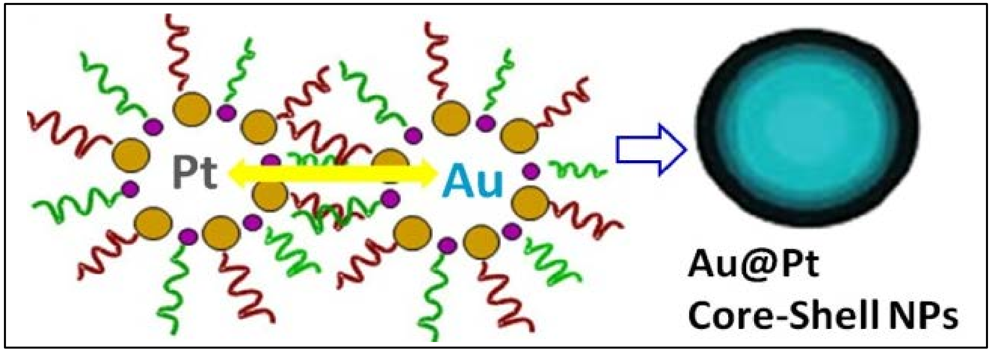
Ethanol Oxidation: Selectivity of $RhSnO_2/Pt_{ML}/Au/C$ Catalyst (In-Situ IR Study)



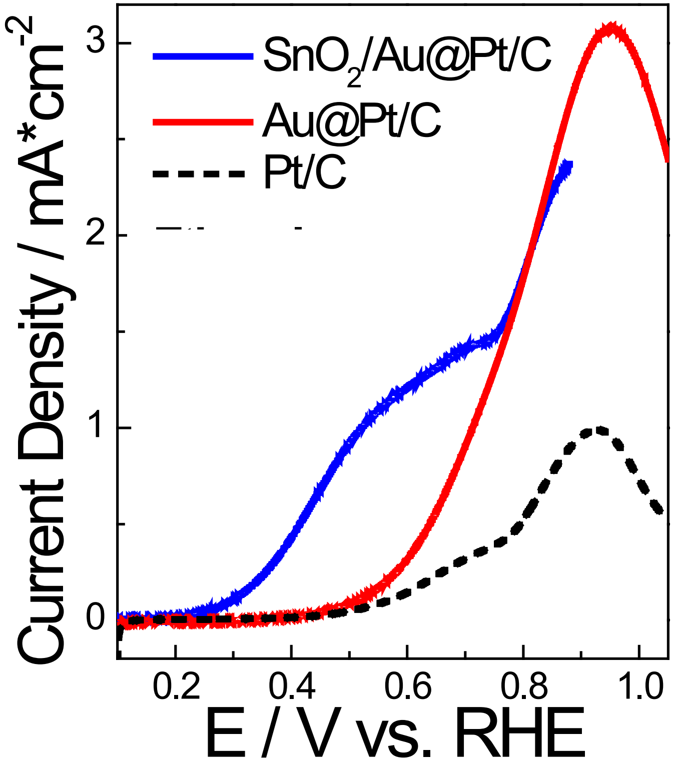
- **Highlight:** CO_2 is the only product observed by IR in the potential range of 0.30 - 0.70 V
- CH_3COOH and CH_3CHO showing at potentials higher than 0.70 V

Ethanol Oxidation: Microemulsion Synthesis of Au@Pt/C Catalyst

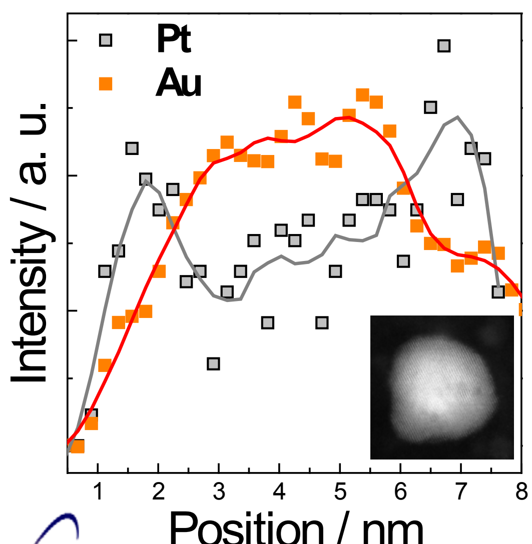
Microemulsion Synthesis of Au@Pt Core-Shell Nanoparticles

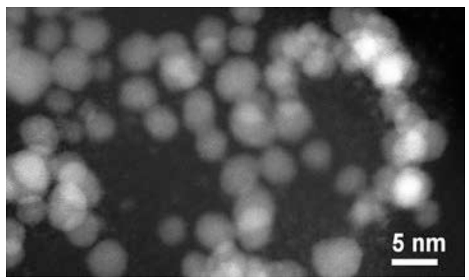


Ethanol Oxidation



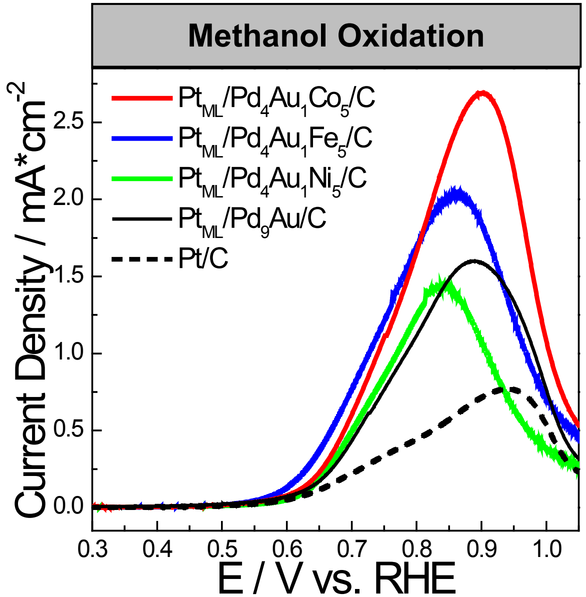
HAADF-STEM and EDX



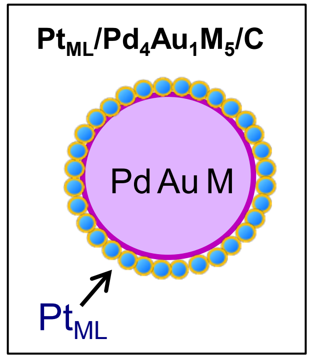


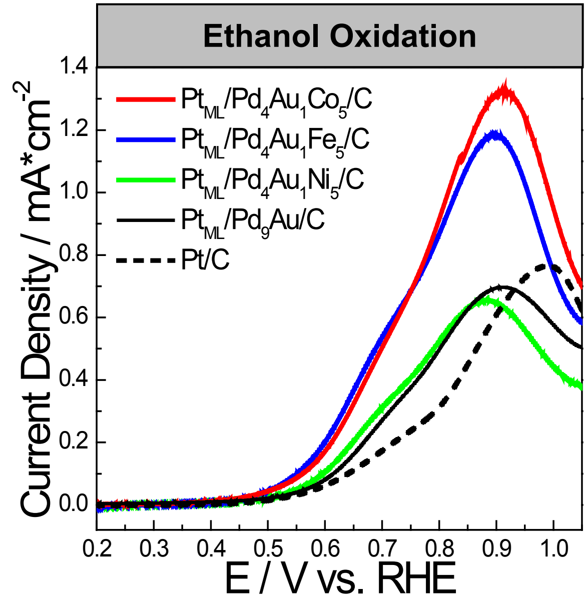
- **Highlight:** **One-pot, easily scalable synthesis, less complex than the Cu UPD method; effective control of the core-shell architecture achieved**
- **Au@Pt nanoparticles obtained, ~ 4 nm in average particle size; SnO_2-modfied bifunctional catalyst performing similarly to the catalyst obtained using the Cu UPD approach**

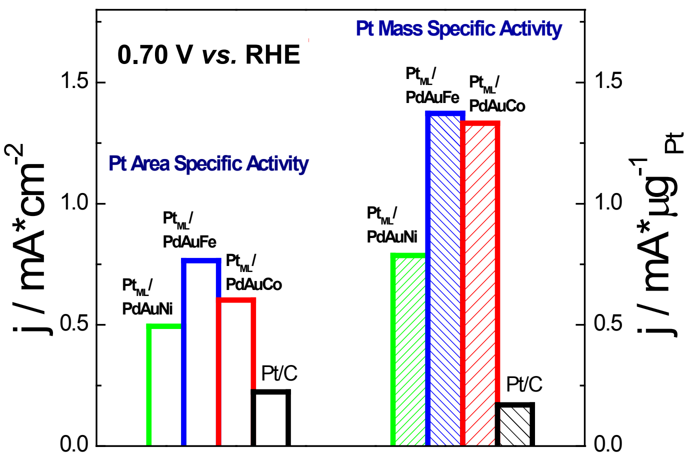
Ethanol Oxidation: $Pt_{ML}/Pd_4Au_1M_5/C$ Nanocatalysts (M = Ni, Fe, Co)



Solution: 0.5 M MeOH/EtOH in 0.1 M $HClO_4$; **Scan rate:** 5 mV s^{-1}; **Electrode:** GC, 0.2 cm^2

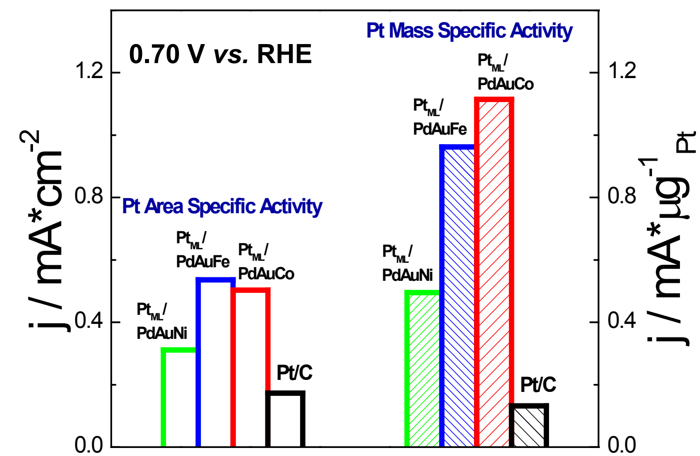






Highlight:

$Pt_{ML}/Pd_4Au_1Fe_5/C$ and $Pt_{ML}/Pd_4Au_1Co_5/C$ demonstrating more than 8-fold increase in Pt and 2-fold increase in total PGM mass activity in ethanol oxidation at 0.70 V



DMFC Membranes: Barriers, Approach, Milestone

- **Technical Barriers**

  Low proton conductivity → addressed in FY11 with multi-block copolymers (> 0.1 S cm^{-1})

  High methanol permeability → addressed in FY12 with nitrile moiety (≥ fuel utilization 95% at peak power)

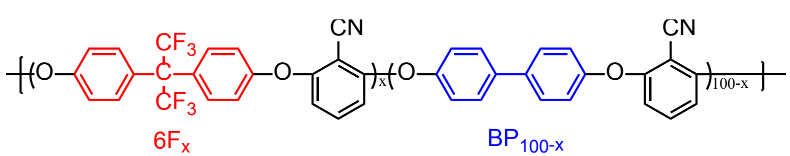
  Poor membrane-electrode interface → <u>this year</u>

- **Approach**

  Interfacial delamination between hydrocarbon membrane and Nafion®-bonded electrode typically caused by excessive membrane swelling.

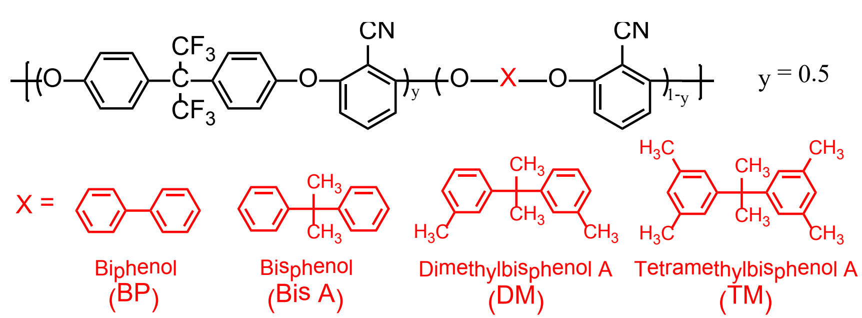
  Approach used here to improve interfacial compatibility: Reduce water uptake by modifying chemical structure of hydrophobic blocks.

Approach 1: Control fluorination level



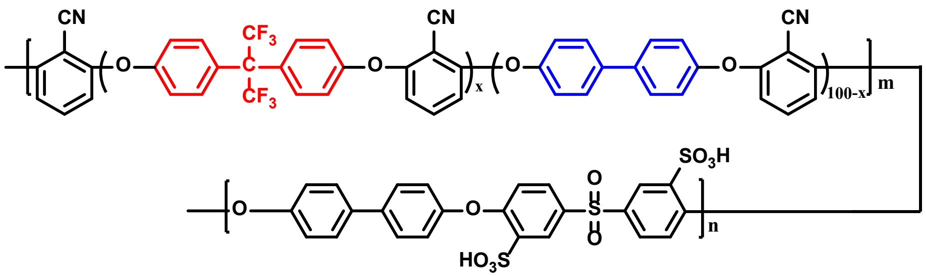
6F to BP ratio: 6F100 BP0, 6F75 BP25, 6F50 BP50, 6F25 BP75

Approach 2: Control bisphenol structure



DMFC Membranes: Nitrile Multi-Block Copolymers with Controlled Fluorination

$6F_xBP_{100-x}$PAEB-BPSH100 Multi-Block Copolymers

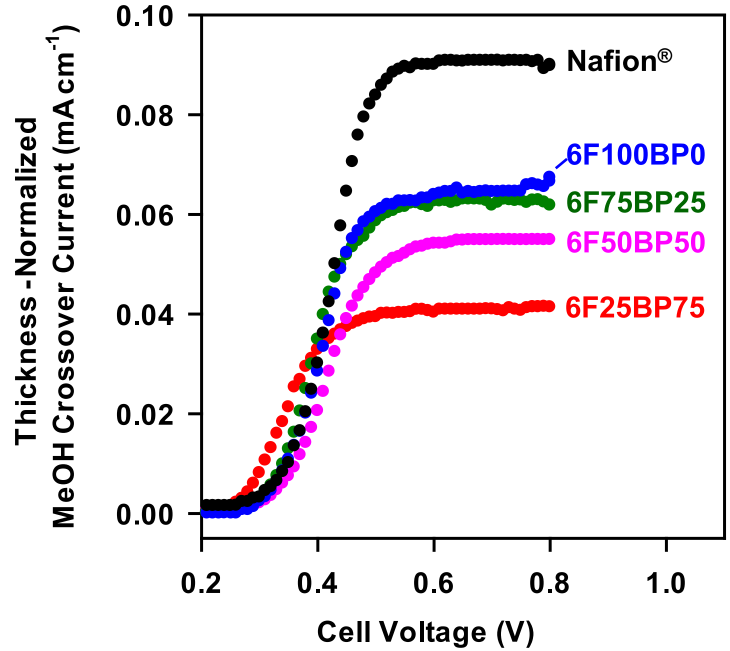


$6F_xBP_{100-x}$ (10K-10K)	IEC[a] (meq g^{-1})	Proton conductivity (S cm^{-1})	Methanol permeability[b] (cm^2 s^{-1})	Water uptake (wt%)
Nafion®	0.91	0.11	3.14	22
6F100BP0	1.53	0.14	2.23	45
6F75BP25	1.55	0.14	2.18	44
6F50BP50	1.55	0.13	1.89	52
6F25BP75	**1.50**	**0.13**	**1.41**	**54**

[a] From ^{1}H NMR; [b] From limiting-current experiment (80°C)

MeOH Crossover Current (0.5 M MeOH)

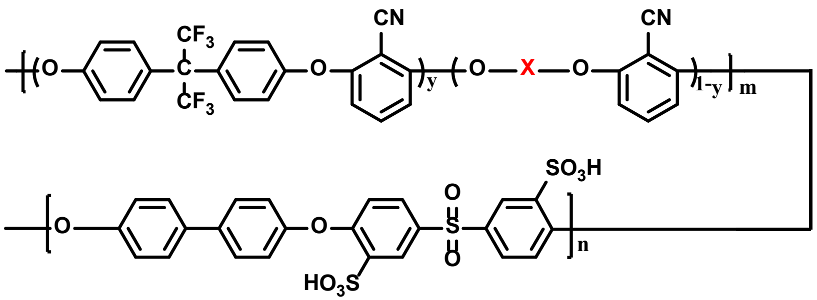
Anode: 6.0 mg cm^{-2} $Pt_{50}Ru_{50}$ black, 0.5 M MeOH,1.8 mL/min; **Cathode:** 4.0 mg cm^{-2} Pt black; 500 sccm N_2; **Cell:** 80ºC, 5 cm^2 single cell hardware



- No significant effect of fluorination level on proton conductivity and water uptake
- Highlight: **Higher conductivity (by 18%) and reduced MeOH permeability (by 55%) compared to Nafion® 212 achieved with 6F25BP75 thanks to an increase in biphenol (BP) moiety content**

DMFC Membranes: Multi-Block Copolymers with Controlled Hydrophobicity

$6F_yX_{100-y}$ PAEB-BPSH100 Multi-Block Copolymers

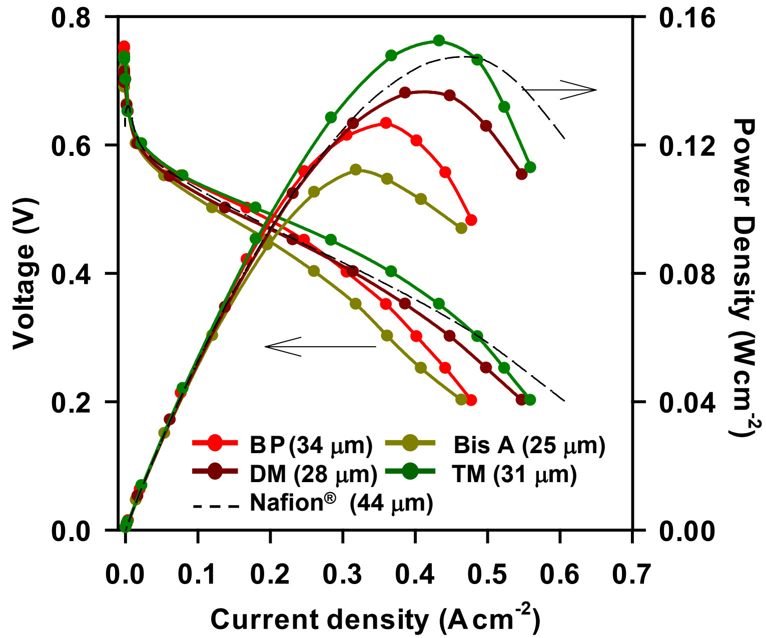


$6F_{50}X_{50}$	IEC (meq g^{-1})	Proton conductivity (S cm^{-1})	Methanol permeability[a] (cm^2 s^{-1})	Water uptake (wt%)
Nafion®	0.91	0.11	2.36	22
BP*	1.50	0.13	1.47	54
Bis A	1.74	0.12	1.30	40
DM	1.65	0.15	1.42	35
TM	**1.50**	**0.10**	**1.09**	**20**

* 6F25BP75, [a] From limiting-current experiment (75°C)

Preliminary DMFC Data (1.0 M MeOH)

Anode: 2.7 mg cm^{-2} $Pt_{50}Ru_{25}/C$, 1.0 M MeOH, 1.8 mL/min; **Cathode:** 2.0 mg cm^{-2} Pt/C; 500 sccm, N_2; **Cell:** 75ºC, 5 cm^2 single cell hardware



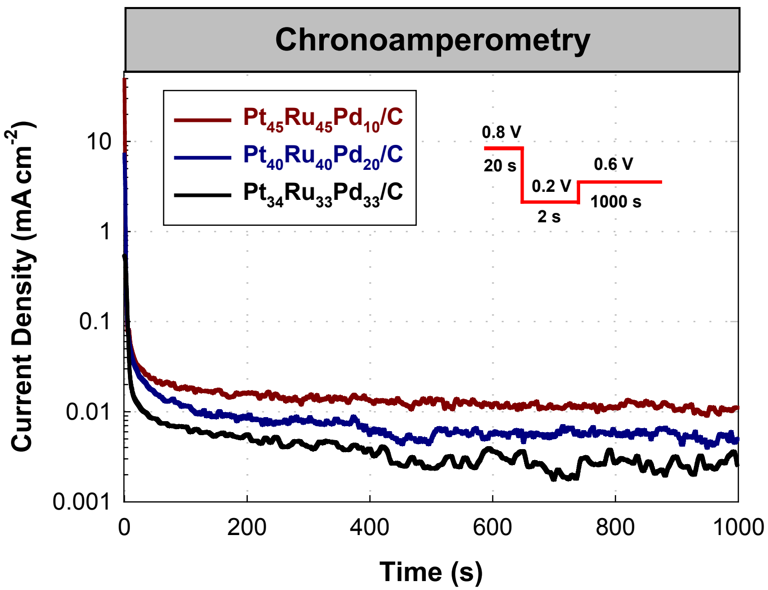
- Significant performance improvement by reducing water uptake of multi-block copolymer
- **Highlight:** Structural changes to bisphenol unit proven very effective in controlling membrane water uptake

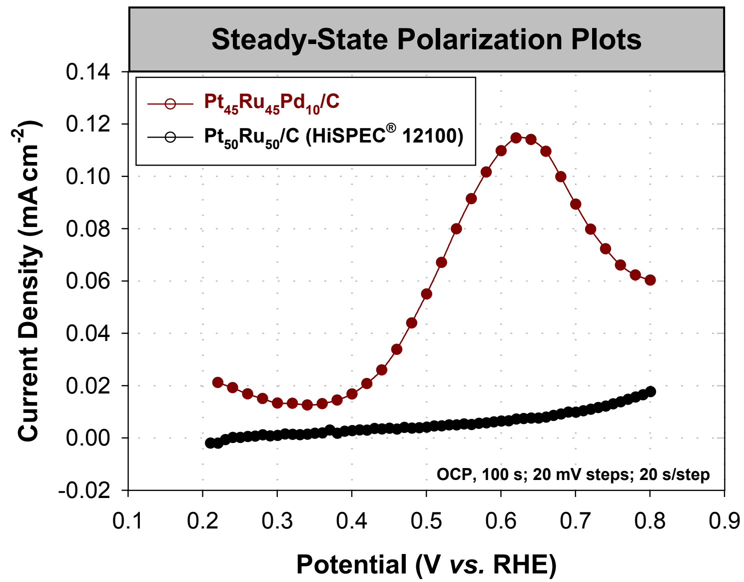
MeOH crossover reduced in TM-based multi-block copolymer by 54%
(membrane milestone achieved)

DME Oxidation: PtRuPd/C Catalysts with High Metal Content

Characteristics	PtRuPd/C	$Pt_{50}Ru_{50}/C$ (JM HiSPEC® 12100)
Metal loading by TGA in air (wt%)	65 ± 2	72
Pt:Ru:Pd atomic ratio by XRF	46:44:10	51:49:0
Crystalline size from XRD (nm)	3.2	3.6
Specific surface area (m^2/g_{metal})	60	49

Catalyst : PtRuPd/C or HiSPEC® 12100 on GCE (0.196 cm^2); **Loading**: 60 μg_{Pt} /cm^2; **Electrolyte**: 0.1 M $HClO_4$; **Concentration of DME-saturated solution**: 1.05 M

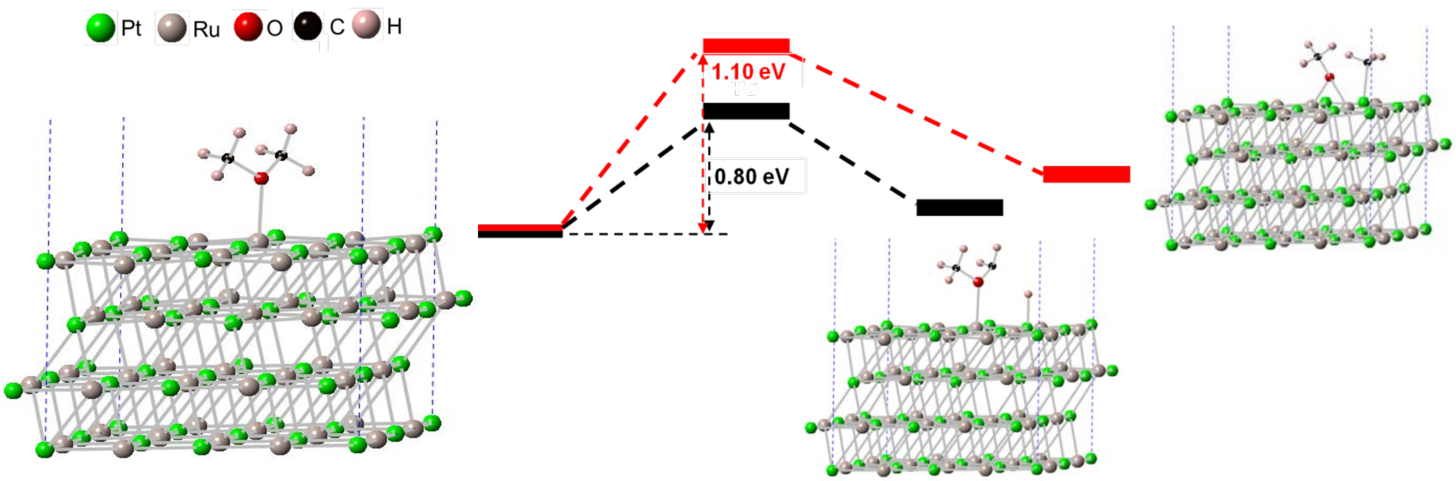




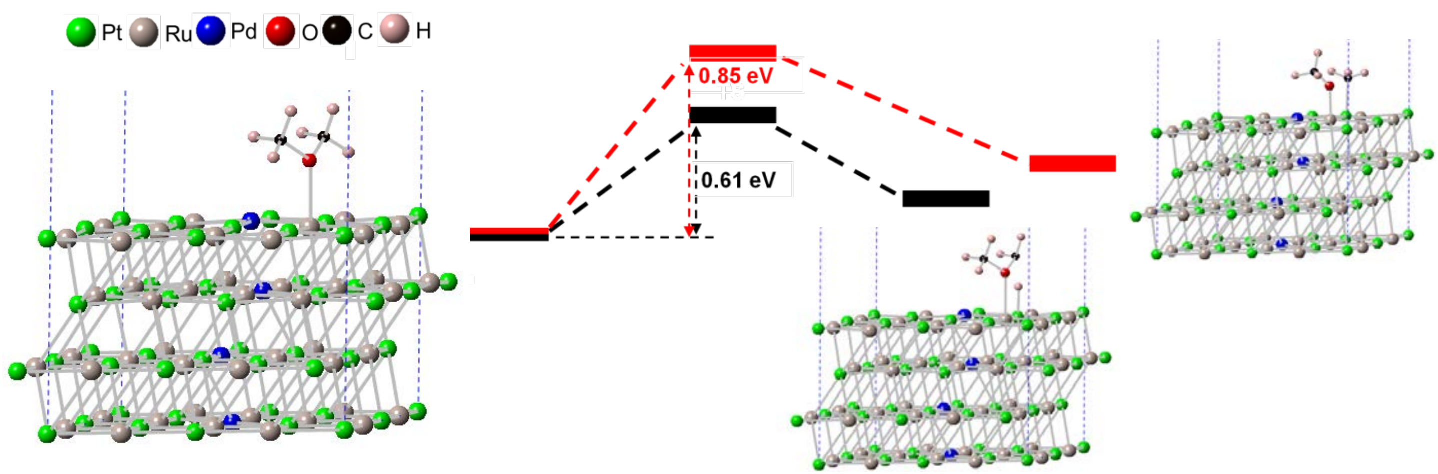
- **Highlight: PtRuPd/C catalysts with high metal content synthesized by a modified polyol method**
- **$Pt_{45}Ru_{45}Pd_{10}/C$ outperforming HiSPEC® 12100; 10 at% Pd assuring efficient C-O bond scission without inhibiting removal of surface CO by Ru hydroxide/oxides**

DME Oxidation: PtRu *vs.* PtRuPd (DFT)

Activation Energy for Breaking C-H (black) and C-O (red) Bonds on $Pt_{50}Ru_{50}(111)$



Activation Energy for Breaking C-H (black) and C-O (red) bonds on $Pt_{45}Ru_{45}Pd_{10}(111)$



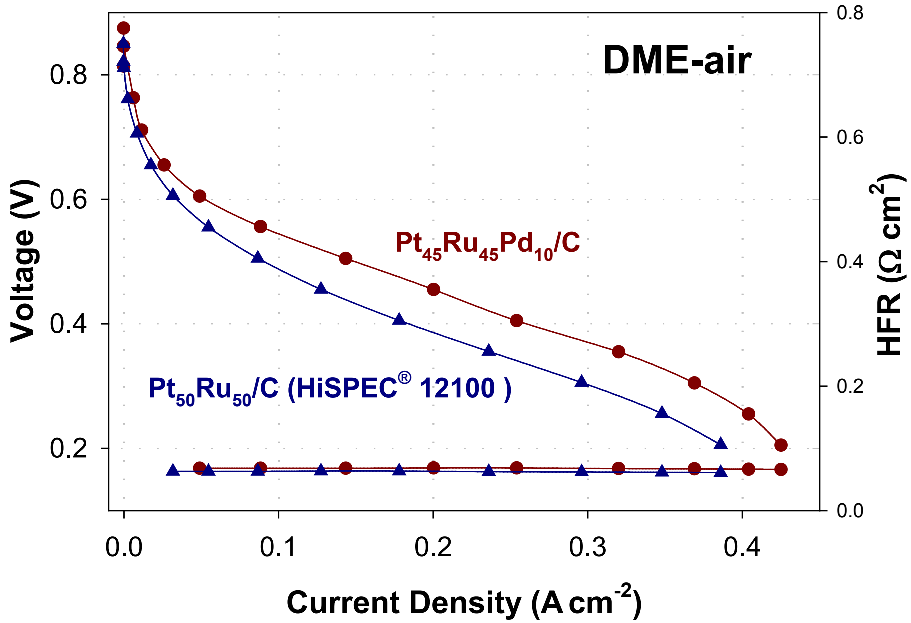
Highlight: Pd addition to PtRu resulting in significant lowering of the activation energy for C-H and C-O bond breaking during DME oxidation, by 0.19 eV and 0.25 eV, respectively

DME Oxidation: $Pt_{45}Ru_{45}Pd_{10}$/C Catalyst Fuel Cell Performance

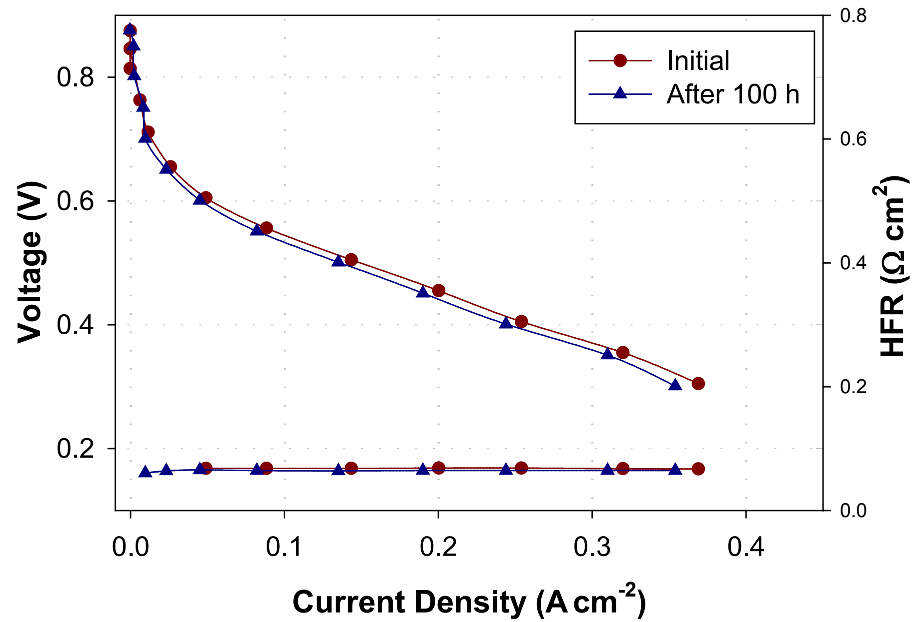
Anode: 2.7 mg_{Pt} cm^{-2} PtRuPd/C or HiSPEC® 12100, 40 sccm DME gas, 30 psig; **Cathode**: 4.0 mg cm^{-2} Pt black, 500 sccm air, 20 psig; **Membrane**: Nafion® 212; **Cell**: 80ºC

Anode: 2.7 mg_{Pt} cm^{-2} PtRuPd/C, 40 sccm DME gas, 30 psig; **Cathode**: 4.0 mg cm^{-2} Pt black, 500 sccm air, 20 psig; **Membrane**: Nafion® 212; **Cell**: 80ºC; **Life test**: constant voltage 0.4 V, 100 h

DDMEFC Performance



Durability Test



- **Highlight: Cell voltage value measured with $Pt_{45}Ru_{45}Pd_{10}$/C at 0.15 A cm^{-2} by *ca.* 70 mV higher than voltage measured with PtRu/C reference catalyst**

DME fuel cell performance milestone of 0.15 A cm^{-2} at 0.50 V achieved

- **No significant performance loss observed for 100 hours**

Collaborations

- **Seven organizations with 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 – reduction in cost of direct methanol fuel cell components and system for applications in excess of 1 kW in power (common program development phase)
  - ✓ Warsaw University, Warsaw, Poland – dimethyl ether oxidation on platinum-free electrocatalysts
  - ✓ University of Waterloo, Waterloo, Ontario, Canada – development of nanostructured methanol oxidation catalysts

Proposed Future Work: Remainder of FY13 and FY14

Methanol oxidation catalysis:

- Improve anode mass activity of thrifted (AAC) and ultra-thrifted (TAAC) PtRu/C catalysts
- Stabilize nano-particulate structures of PtRu/C and PtRuSn/C to minimize Ru and Sn dissolution
- Optimize AAC-based anodes; complete 50 cm^2 five-cell stack testing by SFC Energy
- Scale-up and test in MEAs PtRu platelets and Pt monolayer catalysts

Innovative membranes and electrode structures:

- Optimize membrane thickness and MEA processing for better performance of membranes with controlled hydrophobicity
- Improve durability of alternative membranes in the presence of higher concentrations of MeOH
- Identify the mechanism of DMFC performance degradation in prolonged life tests, up to 500 h, and develop mitigation strategies
- Further improve mass activity of PtRu/CuNWs; scale up nanostructured catalyst synthesis

Ethanol oxidation catalysis:

- Develop catalysts based on expanded Pt monolayers decorated by SnO_2 and Rh islands and optimized for ethanol oxidation
- Scale-up ternary and Pt-monolayer catalysts for ethanol oxidation and test in MEAs

DME research:

- Optimize composition and morphology of ternary DME oxidation catalysts for efficiency and power at high and intermediate DDMEFC voltages, respectively

Summary

- **Ultra-thrifted catalysts (uTAAC and uT-PtRuSn) of MeOH oxidation have been synthesized in 25 g batches; uT-PtRuSn meets the project anode activity target of 200 mA mg_{Pt}^{-1} at 0.25 V while ultra-thrifted Pt/Ru/C catalyst (uTAAC) is only 13 mV away from that target**
- **Thrifted PtRu/C catalysts (AAC) has come within 40 mV of the overall DMFC performance target of 0.15 A cm^{-2} at 0.60 V; AAC is ready for 50 cm^2 stack testing by SFC Energy in the summer of 2013**
- **A very low MeOH oxidation onset potential target of 0.288 V *vs*. RHE has been achieved with a PtRu/CuNW catalyst with optimized Pt-to-Ru ratio; catalysts synthesis scale-up is ongoing**
- **JMFC and LANL data indicate that Ru crossover in MEAs with state-of-the-art carbon-supported PtRu catalysts, though detectable, is much reduced and does impact ORR activity of the cathode**
- **Under conditions used, up to 4.0 M MeOH, cracking of metal-black or carbon-supported catalyst layers has little, if any, effect on performance; cracks may facilitate anode operation at high currents**
- **Structural changes to bisphenol unit are very effective in controlling membrane water uptake and reducing MeOH crossover (by as much as 54% in TM-based multi-block copolymer)**
- **Pt_{ML}/Au/C catalysts EtOH oxidation have been synthesized by displacing Cu UPD layer on Au/C and by microemulsion approach; catalysts have been further modified with various modifiers to enhance activity via bifunctional approach; Pt_{ML} supported on such nanocores as PdAuFe and PdAuCo show interesting potential as lower-cost EtOH catalysts**
- **$RhSnO_2/Pt_{ML}$/Au/C catalyst exhibits high ethanol oxidation selectivity; CO_2 is the only product in the potential range of 0.3-0.7 V; non-CO_2 byproducts are observed at very high potentials (above 0.7 V)**
- **Current density of 0.15 A cm^{-2} at DDMEFC voltage of 0.50 V has been reached with a new high metal-content ternary catalyst of DME oxidation ($Pt_{45}Ru_{45}Pd_{10}$/C); DFT calculations confirm the effect of Pd addition on the kinetics of both the C-O and C-H bond scission**

Co-Authors

- **ethanol and methanol anode catalyst research**

  Radoslav Adzic (PI), Meng Li, Miomir Vukmirovic

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

  Piotr Zelenay (Project Lead), Hoon Chung, Yu Seung Kim, Qing Li, Gerie Purdy, Dusan Spernjak, Xiaodong Wen, Gang Wu

- **nanostructure catalyst structures**

  Yushan Yan (PI), Jie Zheng

- **hydrocarbon membrane research**

  James McGrath (PI), Yu Chen, Jarrett Rowlett, Andy Shaver

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

  Alex Martinez Bonastre (PI), Noelia Cabello Moreno, Graham Hards, Emily Price, Jonathan Sharman, Geoff Spikes

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

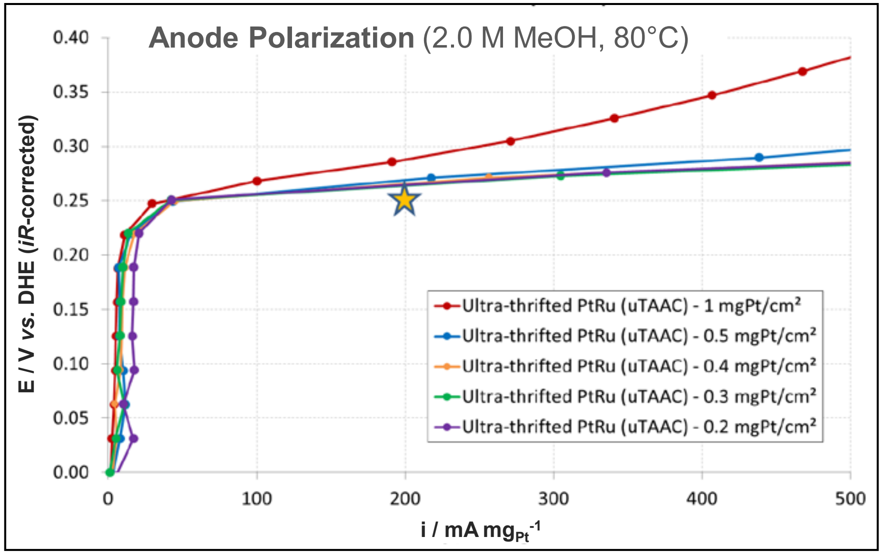
  Christian Böhm (PI)

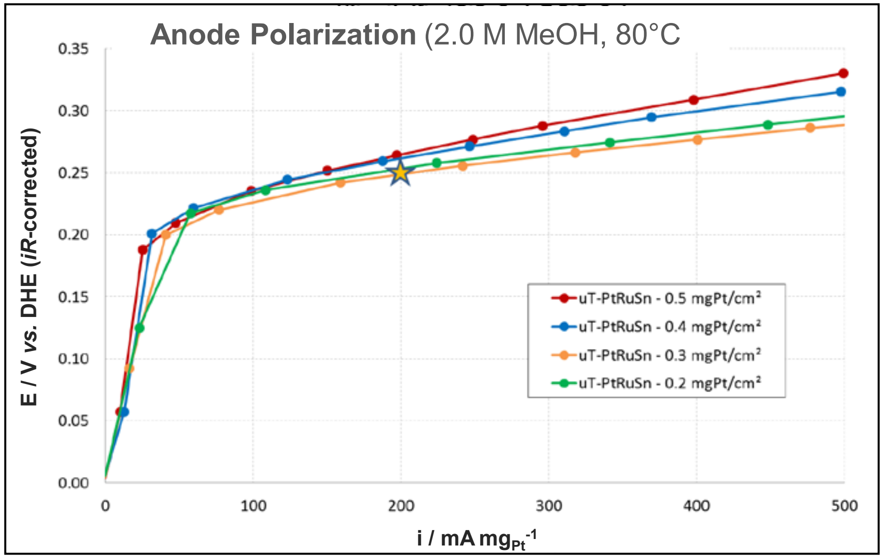
- **microscopic characterization** (no-cost partner)

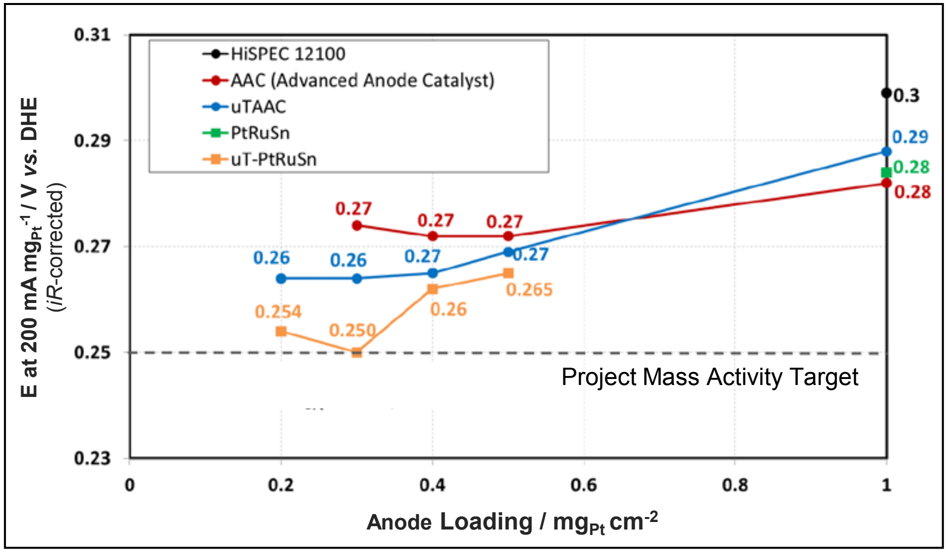
  Karren More (PI), David Cullen

Technical Backup Slides

Methanol Oxidation: Loading Dependence (uTAAC and uT-PtRuSn)





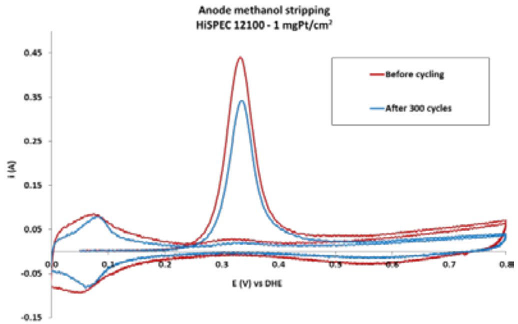


- Loading studies performed in the range from 0.2 to 1.0 $mg_{Pt}\ cm^{-2}$ with uTAAC and from 0.2 to 0.5 $mg_{Pt}\ cm^{-2}$ with uT-PtRuSn; thinner layers benefiting from better catalyst utilization
- **Highlight:** At the optimum catalyst loading of 0.3 $mg_{Pt}\ cm^{-2}$, the ultra-thrifted carbon-supported PtRuSn catalyst reaching the mass activity target of the project (200 mA mg_{Pt}^{-1})
- Significant improvement on the benchmark DMFC anode catalyst (HiSPEC® 12100) achieved with several new materials

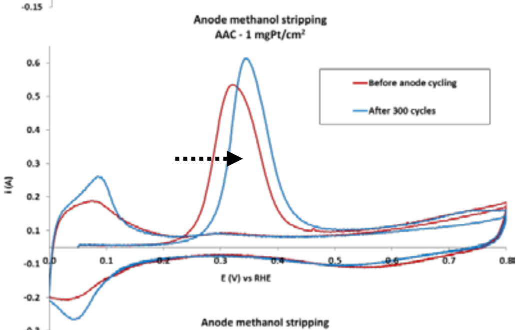
Methanol Oxidation: Stripping of MeOH-Derived CO (PtRu Catalysts)

Anode CO Stripping

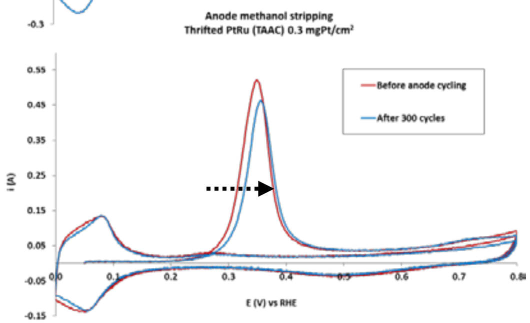
HiSPEC ® 12100



Thrifted PtRu/C (AAC)

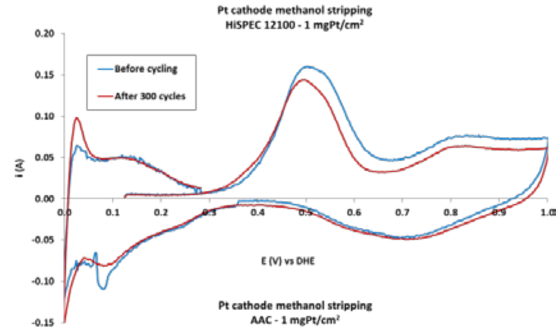


Ultra-thrifted PtRu/C (uTAAC)

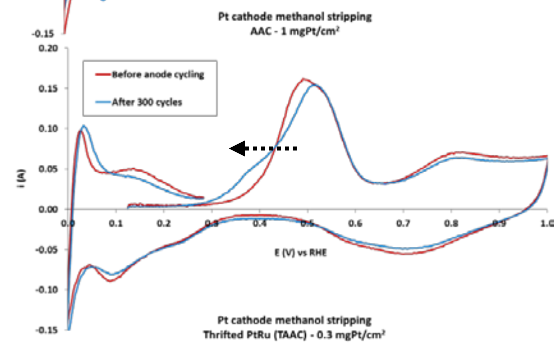


Cathode CO Stripping

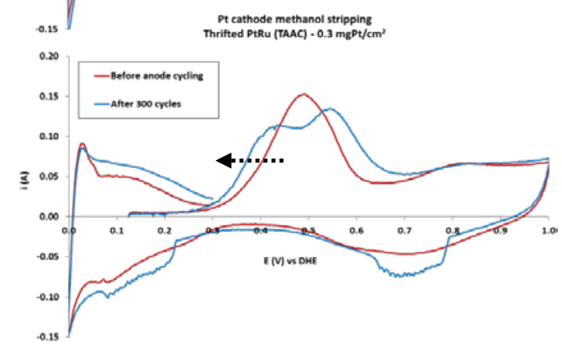
HiSPEC ® 12100



Thrifted PtRu/C (AAC)



Ultra-thrifted PtRu/C (uTAAC)

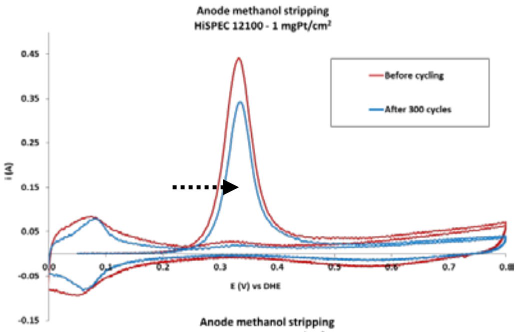


- **Largest increase in Pt character observed with AAC anode**
- **Cathode in MEA with uTAAC indicating the largest Ru crossover**

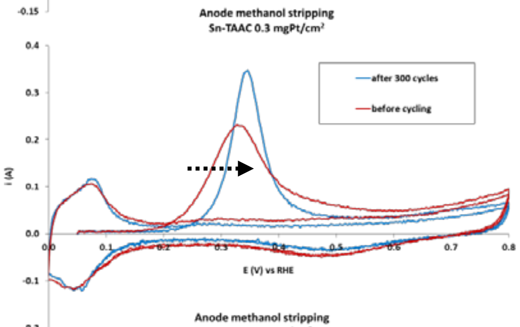
Methanol Oxidation: Stripping of MeOH-Derived CO (PtRuSn Catalysts)

Anode CO Stripping

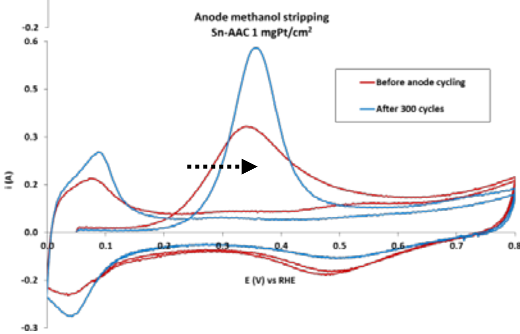
HiSPEC ® 12100



PtRuSn/C

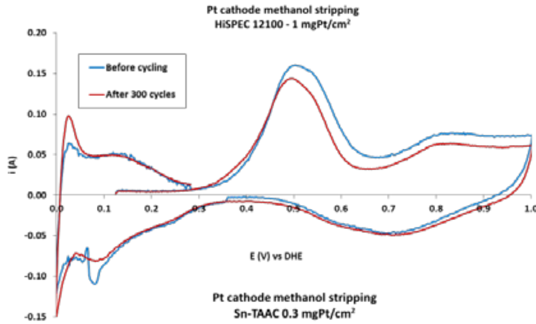


Ultra-thrifted PtRuSn/C (uT-PtRuSn)

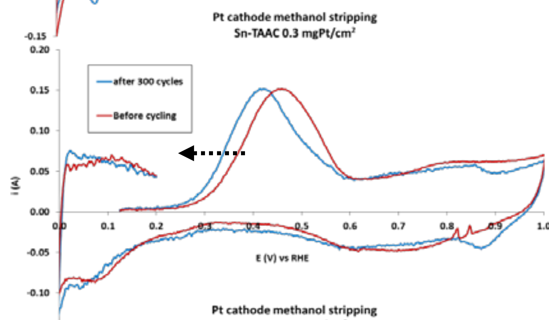


Cathode CO Stripping

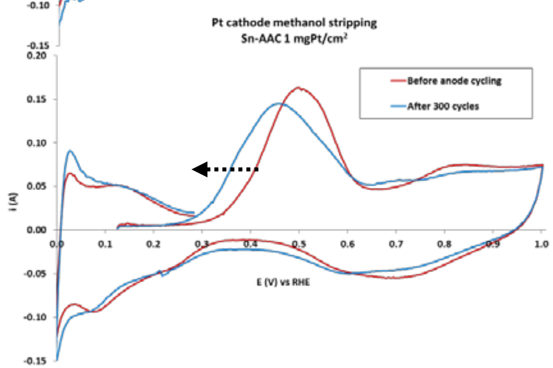
HiSPEC ® 12100



PtRuSn/C



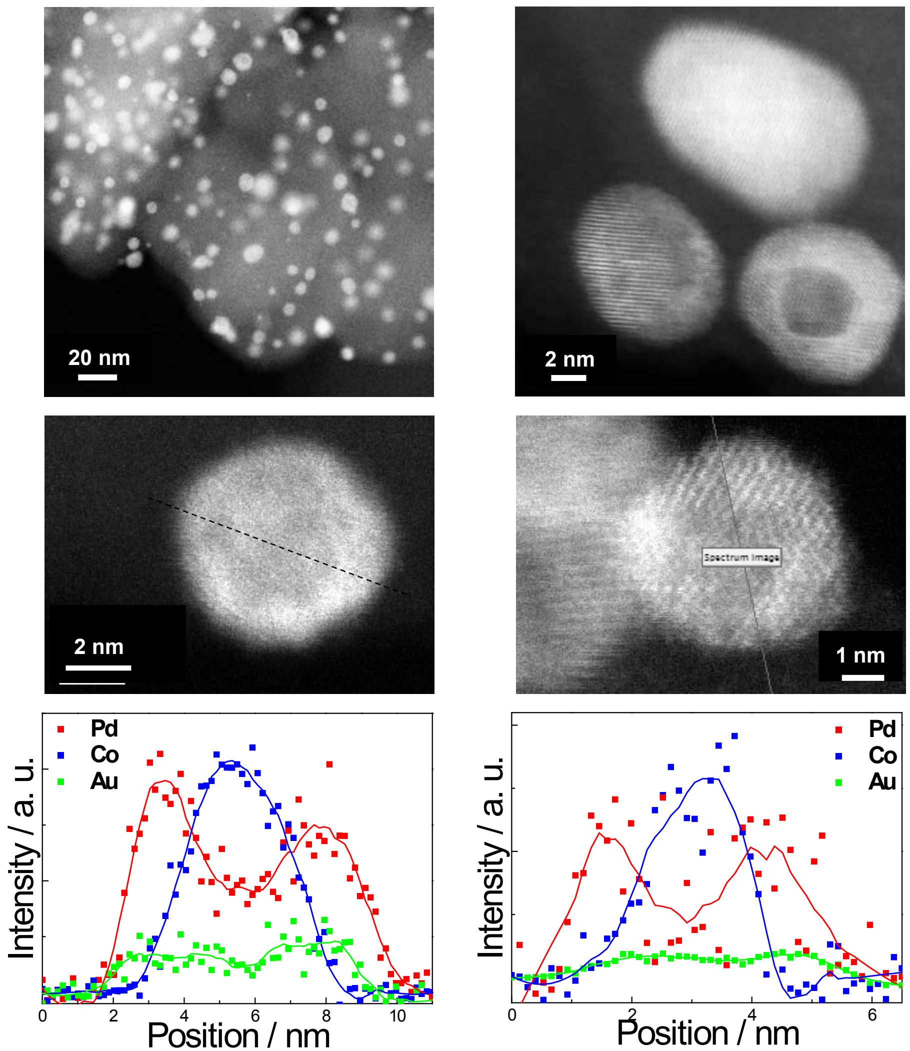
Ultra-thrifted PtRuSn/C (uT-PtRuSn)



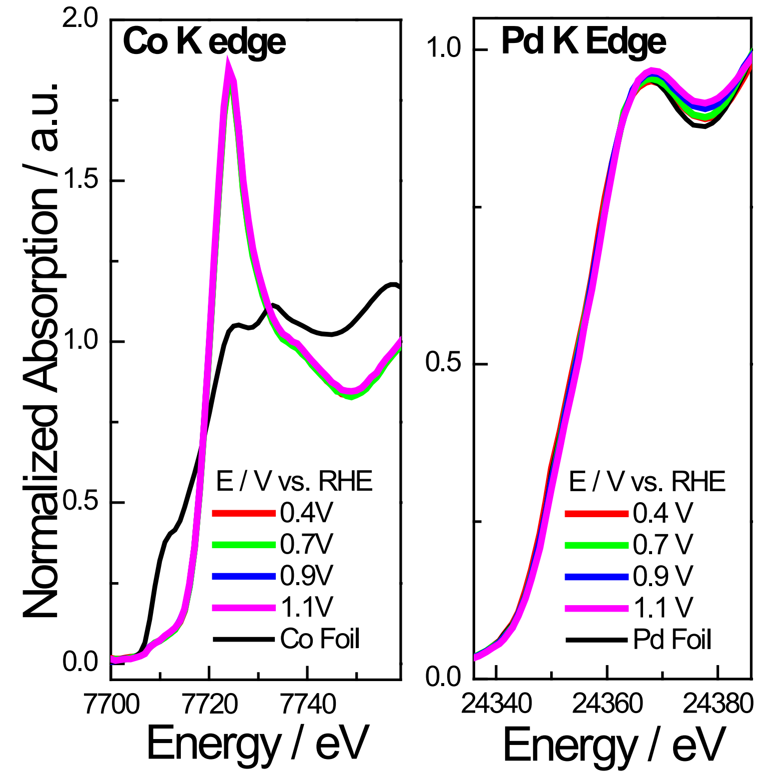
- CO-stripping peak on Sn-containing anodes becoming much narrower after cycling (Sn loss?)
- Possible accumulation of Sn on cathodes in MEAs with Sn-containing anodes

Ethanol Oxidation: $Pd_4Au_1M_5$/C Particles as Nanocores (STEM and XAS)

HRTEM, HAADF-STEM, and EELS

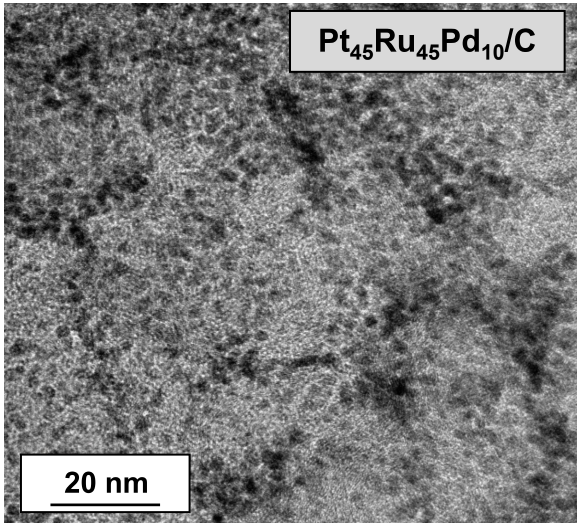


In-situ XAS: Co and Pd K Edges

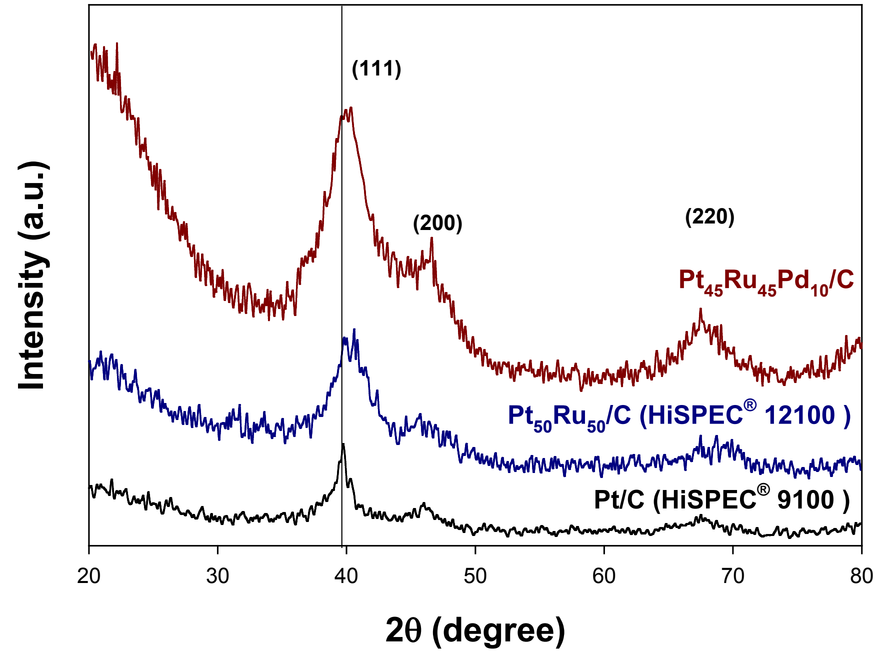


- STEM and EELS studies confirming core-shell structure of $Pd_4Au_1Co_5$ nanoparticles, with Co-rich core and PdAu-rich shell
- In-situ XAS attesting to good protection of Co core by PdAu shell and stabilization of Pd

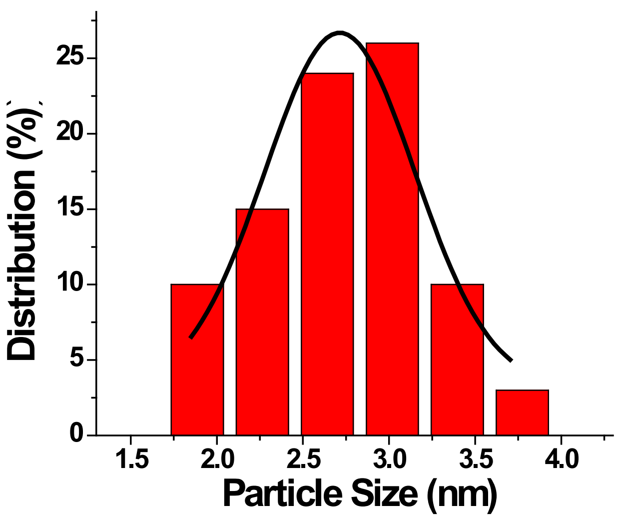
DME Oxidation: $Pt_{45}Ru_{45}Pd_{10}/C$ Catalyst (Characterization)



XRD Characterization



Size Distribution of $Pt_{45}Ru_{45}Pd_{10}/C$



- Uniform and narrow distribution of PtRuPd nanoparticles on carbon support (average size ~ 2.7 nm)
- Alloying verified by the positive shift of the (111) XRD peak for PtRuPd *vs.* Pt (atomic radii: r_{Pt} = 1.39 Å, r_{Ru} = 1.34 Å, r_{Pd} = 1.37 Å)