Introduction to DMFCs

Advanced Materials and Concepts for Portable Power Fuel Cells

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The Fuel Choice

Fuels for direct-feed polymer-electrolyte fuel cells

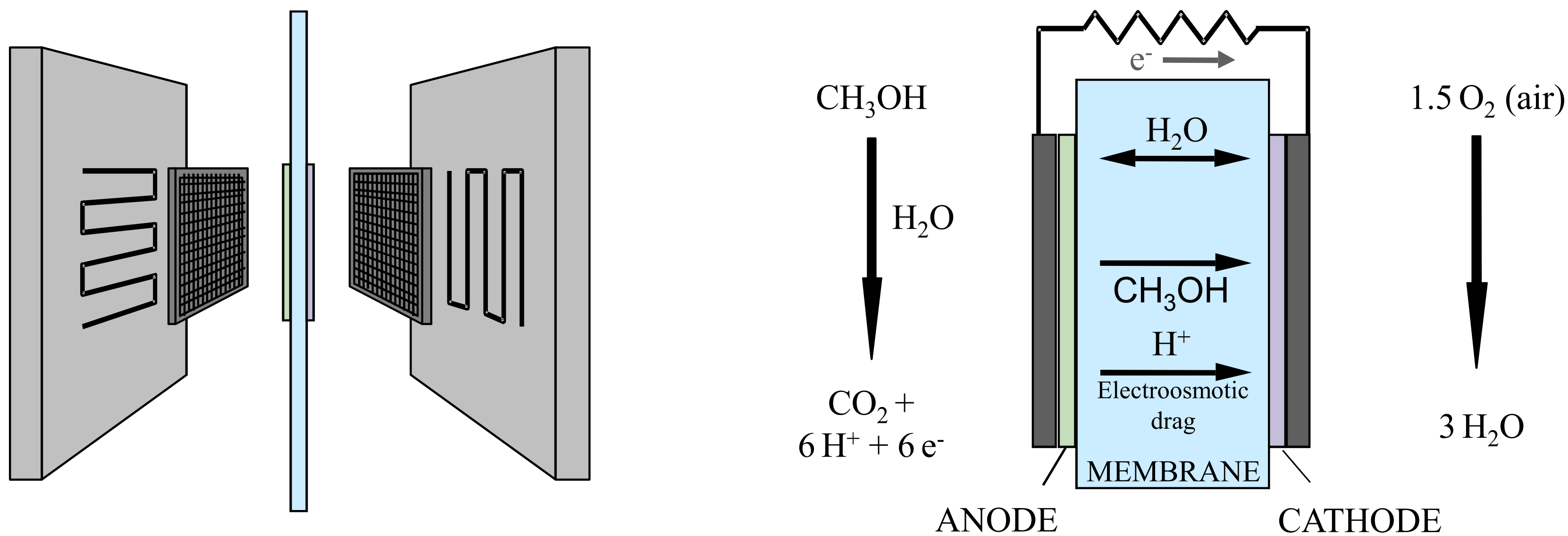
Fuel	Fuel-cell reaction	Specific energy (Wh/g)	Energy density (Wh/cm^3)
Hydrogen	$H_2 + 0.5\ O_2 \rightarrow H_2O$	33.0	2.7*
Carbon	$C + O_2 \rightarrow CO_2$	9.1	19.2
Methane	$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$	14.2	6.0*
Propane	$C_3H_8 + 5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O$	13.3	6.6*
Decane	$C_{10}H_{22} + 15.5\ O_2 \rightarrow 10\ CO_2 + 11\ H_2O$	12.9	9.4
Methanol	$CH_3OH + 1.5\ O_2 \rightarrow CO_2 + 2\ H_2O$	6.1	4.8
Ethanol	$C_2H_5OH + 3\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O$	8.0	6.3
Ethylene glycol	$C_2O_2H_6 + 2.5\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O$	5.3	5.9
Formaldehyde	$CH_2O + O_2 \rightarrow CO_2 + 2\ H_2O$	4.8	3.9*
Formic acid	$HCOOH + 0.5\ O_2 \rightarrow CO_2 + H_2O$	1.7	2.1
Oxalic acid	$C_2O_4H_2 + 0.5\ O_2 \rightarrow 2\ CO_2 + H_2O$	1.0	2.0
Ammonia	$NH_3 + 0.75\ O_2 \rightarrow 0.5\ N_2 + 1.5\ H_2O$	5.5	3.9*
Hydrazine	$N_2H_4 + O_2 \rightarrow N_2 + 2\ H_2O$	5.2	5.3

* Based on the density of liquefied gas

P. Piela and P. Zelenay, *Fuel Cell Review*, **1**, 17, 2004

Direct Methanol Fuel Cell

Anode: Pt-Ru **Cathode:** Pt **Membrane:** e.g. Nafion® 115



$CH_3OH_{(l)}$ + 1.5 O_2 $\rightarrow$ 2 $H_2O_{(l)}$ + $CO_2\uparrow$ V = 1.21 V; $\Delta G°$ = **6.1 kWh kg^{-1}** = 4.8 kWh L^{-1}

DMFC *vs.* H_2-Air PEMFC: Rates of Electrode Processes

H_2-air fuel cell (PEMFC)

Anode: $H_2 \rightarrow 2\,H^+ + 2\,e^-$ - fast, **low** η

Cathode: $0.5\,O_2 + 2\,e^- + 2\,H^+ \rightarrow H_2O$ - slow, **high** η

Overall: $\mathbf{2\,H_2 + 0.5\,O_2 \rightarrow H_2O_{(l)}}$

Direct methanol fuel cell (DMFC):

Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6\,H^+ + 6\,e^-$ - slow, **high** η

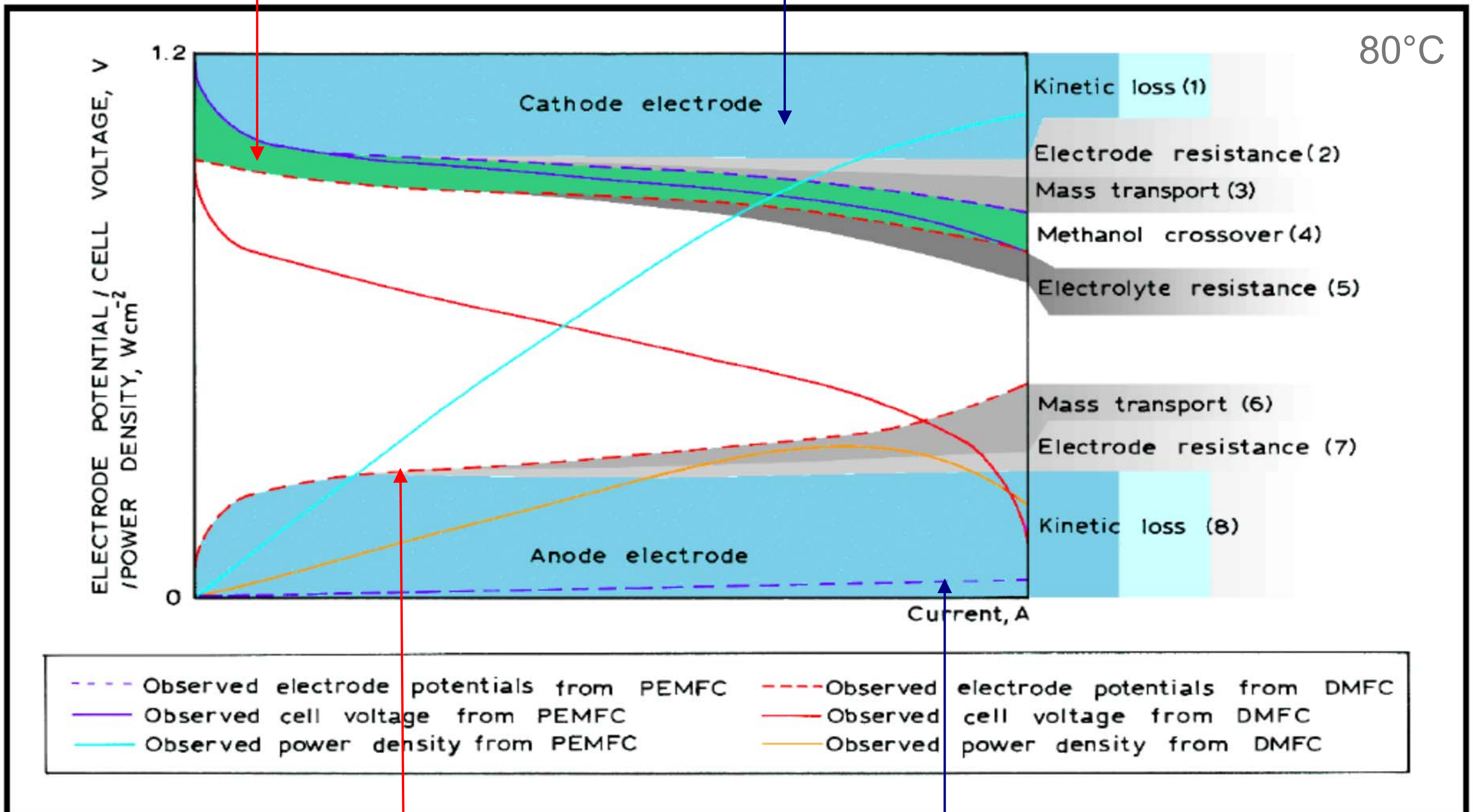
Cathode: $1.5\,O_2 + 6\,e^- + 6\,H^+ \rightarrow 3\,H_2O$ - slow, **high** η

Overall: $\mathbf{CH_3OH_{(l)} + 1.5\,O_2 \rightarrow CO_2 + 2\,H_2O_{(l)}}$

DMFC *vs.* H_2-Air PEMFC: Fuel Cell Polarization Plots

Additional DMFC cathode loss due to methanol crossover

Primary ORR kinetics loss at PEMFC cathode



Kinetic loss at DMFC anode

Kinetic loss at PEMFC anode

M. P. Hogarth and T. R. Ralph, *Platinum Metals Rev.*, 2002, **46**, 146-164

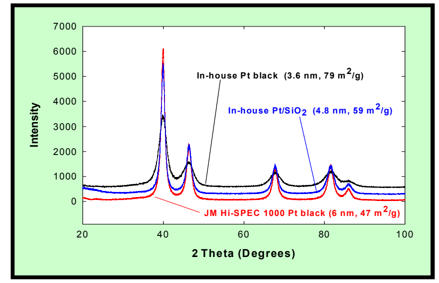
Direct Methanol Fuel Cells: R&D Focus Areas

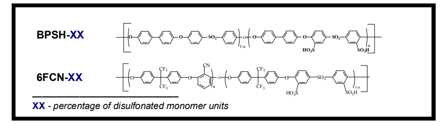
Fundamental Research

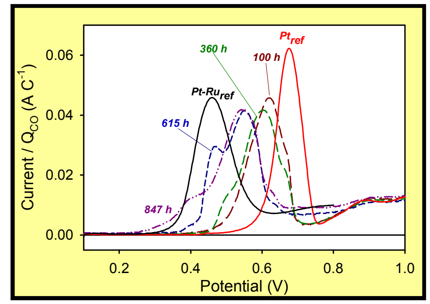
- Anode catalysts with improved methanol oxidation activity
- Methanol-tolerant cathode catalysts
- Membranes with reduced methanol permeability relative to perflurosulfonic acid polymers
- MEA assembly design and structure
- Performance durability

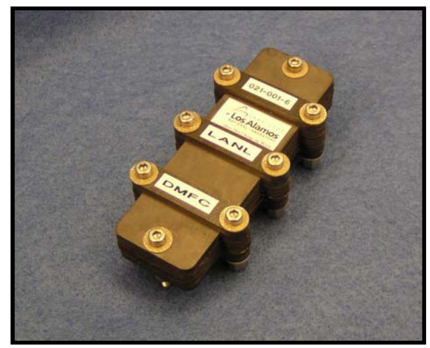
Stack and System Development

- Novel stack materials research
- Hardware modeling and design
- MEA fabrication and production scale-up
- Balance-of-plant efficiency
- Stack components durability
- Cost reduction









Portable Power Fuel Cells Systems: DOE Technical Targets

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

Advanced Materials and Concepts for Portable Power Fuel Cells: The Team

- **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. Spernjak, P. Turner, G. Wu

- **nanostructure catalyst structures**

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

- **hydrocarbon membrane research**

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

- **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

Support: DOE-EERE, Fuel Cell Technologies Program
Dr. Nancy Garland, Program Manager

Advanced Materials and Concepts for Portable Power: 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.

Project technical target:

- System cost target: $5/W
- Performance target: Overall fuel conversion efficiency (η_Σ) of 2.0 kWh/L
- Resulting DMFC operating voltage target DMFC (similar for other fuels):

(1) 2.0 kWh/L $\rightarrow$ $\eta_\Sigma = 0.42$ *1.6× improvement over the state of the art (1.25 kWh/L)*

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

$V_{cell} = V_{th} [\eta_\Sigma (\eta_{fuel}\, \eta_{BOP})^{-1}] = 0.6$ V → *the ultimate project target*

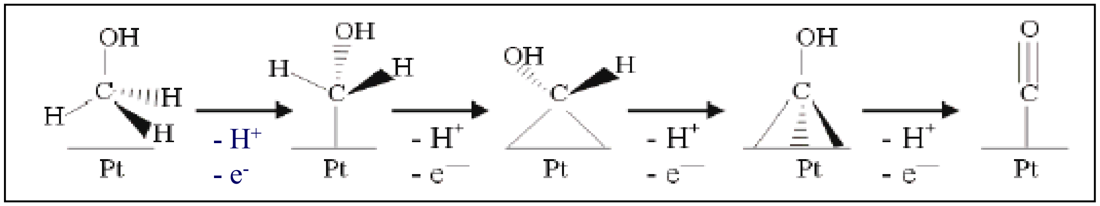
Advanced Materials and Concepts for Portable Power: Research Focus Areas

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

The Slow Process of Methanol Oxidation

Bi-functional MeOH oxidation mechanism:

First step: $CH_3OH + n\,Pt \rightarrow [n\,Pt\text{-}CH_3OH] \rightarrow CO\text{-}Pt + 4\,H^+ + 4\,e^- + (n\text{-}1)\,Pt$



V. S. Bagotzky et al., *J. Electroanal. Chem.*, 1977, **81**, 229

Second step: $CO\text{-}Pt + Ru\text{-}"O"_m \rightarrow CO_2 + Ru\text{-}"O"_{m\text{-}1} + Pt$

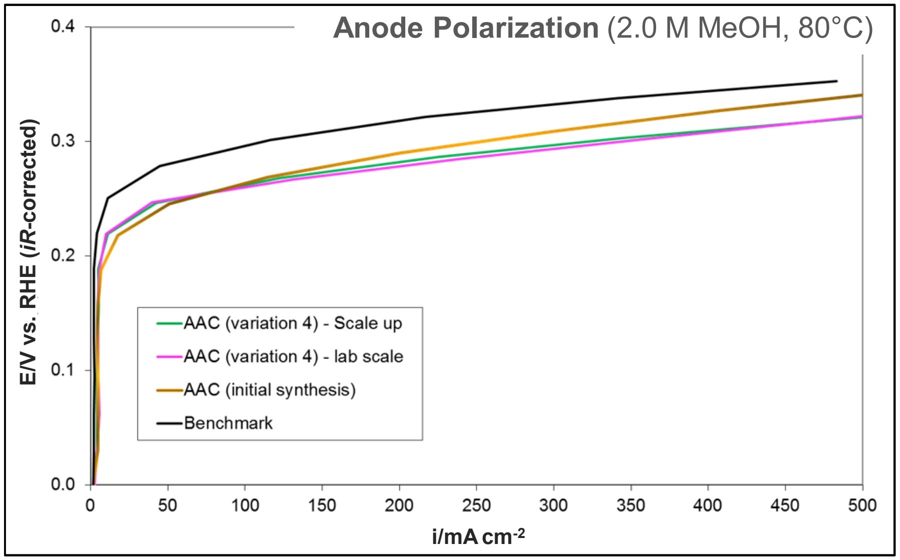
$(Ru\text{-}"O"_{m\text{-}1} + H_2O \rightarrow Ru\text{-}"O"_m + 2\,H^+ + 2\,e^-)$

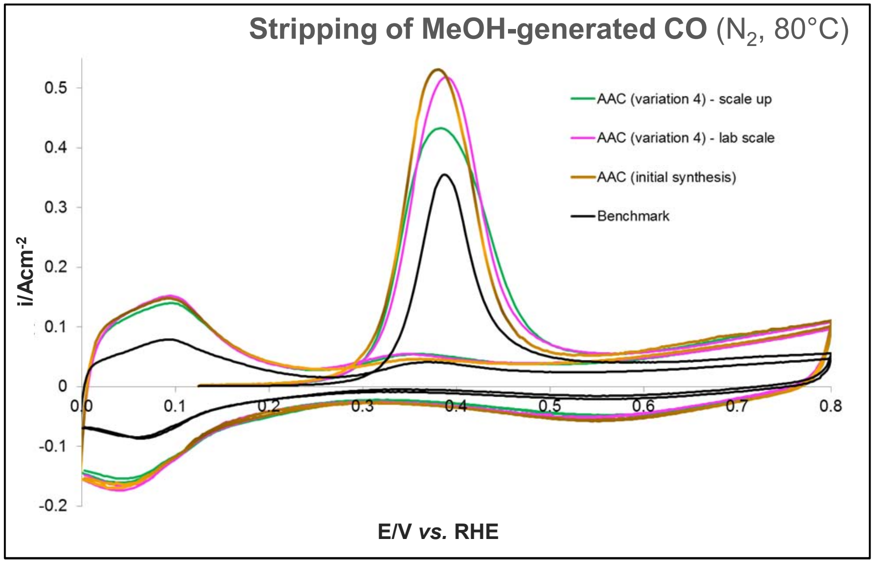
Anode catalysts:

- Binary: **PtRu** (10-40 at% surface Ru), PtSn, PtMo, PtOs, *etc.*
- Ternary (e.g., PtRuOs)
- Quaternary (e.g., PtRuOsIr, PtRuSnW)

Methanol Oxidation: Advanced Anode Catalyst Performance & Scale-Up

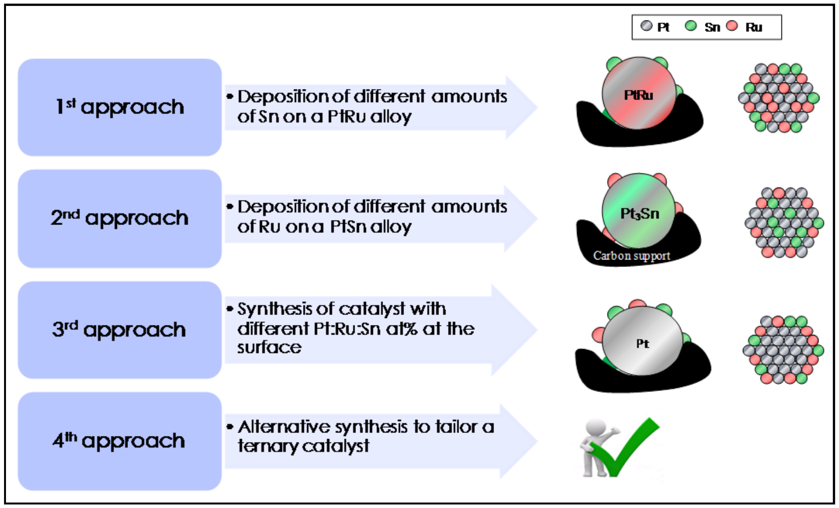
Benchmark: HiSPEC® 12100 (50% Pt), 1.0 mg_{Pt} cm^{-2}; **ACC variation 4:** PtRu/C (18% Pt), 1.0 mg_{Pt} cm^{-2}; **Scale-up:** 100 g ACC

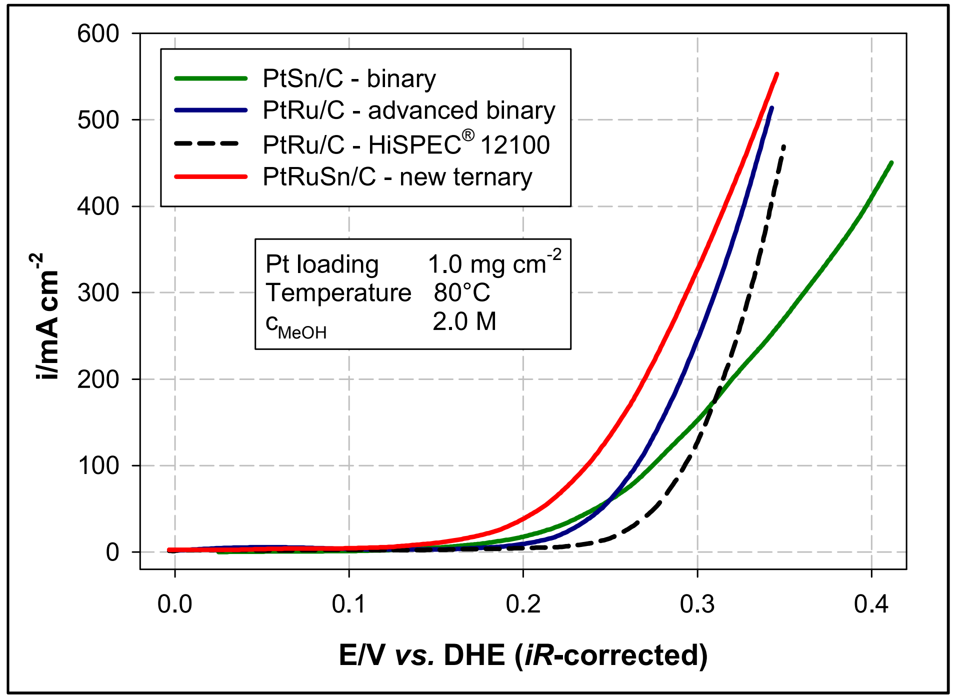




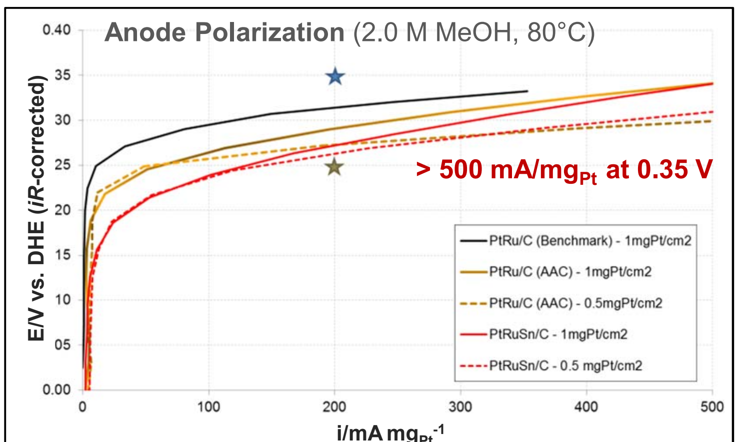
- **PtRu "advanced anode catalyst" (AAC) exceeding the performance of benchmark HiSPEC® 12100 catalyst by *ca.* 40 mV**
- **ACC (variation 4) successfully scaled-up to 100 g without performance loss (in spite of a slightly lower specific surface area)**
- **Anode research on track to reach the target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

Methanol Oxidation: Ternary PtRuSn/C Catalysts





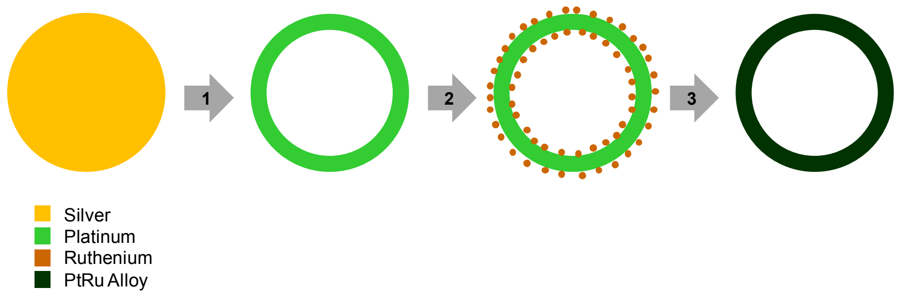
Catalyst	Pt at%	Ru at%	Sn at%
PtRu/C - HiSPEC® 12100	50	50	-
PtRu/C - advanced binary	20	80	-
PtSn/C - binary	77	-	23
PtRuSn/C - new ternary	19	71	10



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

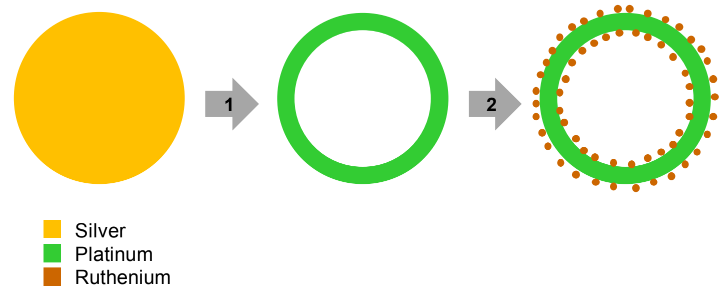
Methanol Oxidation: Innovative PtRu Nanostructure Catalysts

PtRu Nanotubes from Ag Template (Chemical)



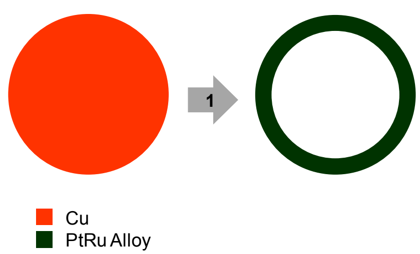
1. Displacement of Ag in AgNW with Pt to form PtNT;
2. Ru deposition from $RuCl_3$ (reduction with ethylene glycol in the presence of polyvinyl pyrrolidone for shape control);
3. Annealing to form PtRu alloy.

PtRu Nanotubes from Ag Template (Electrochemical)

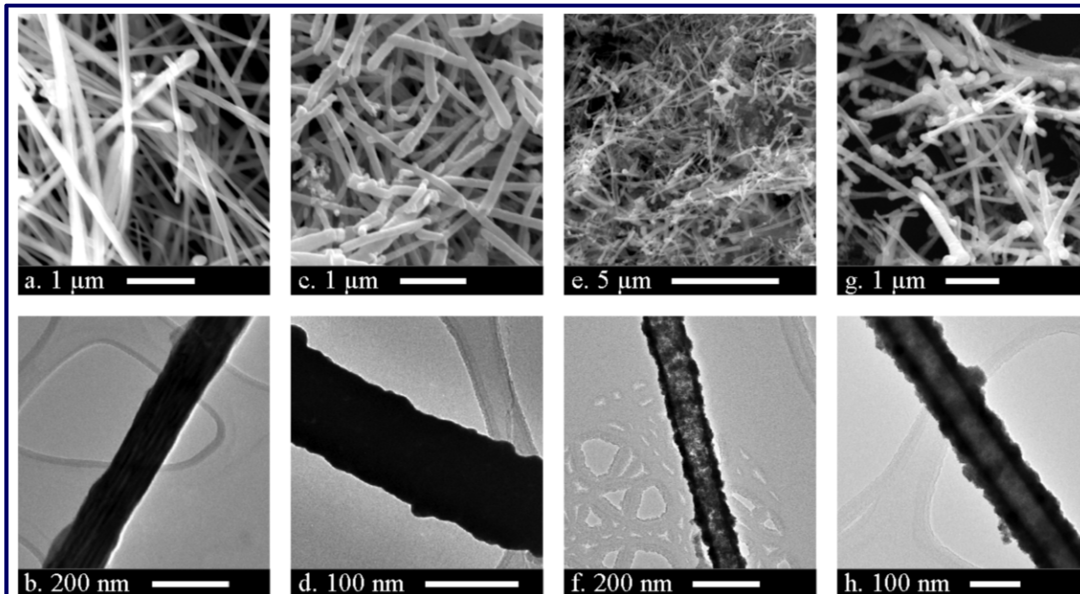


1. Displacement of Ag in AgNW with Pt to form PtNT;
2. Electrochemical deposition of Ru from $RuCl_3$ in H_2SO_4 at 0.3 V for 2 minutes.

PtRu Nanotubes from Cu Template

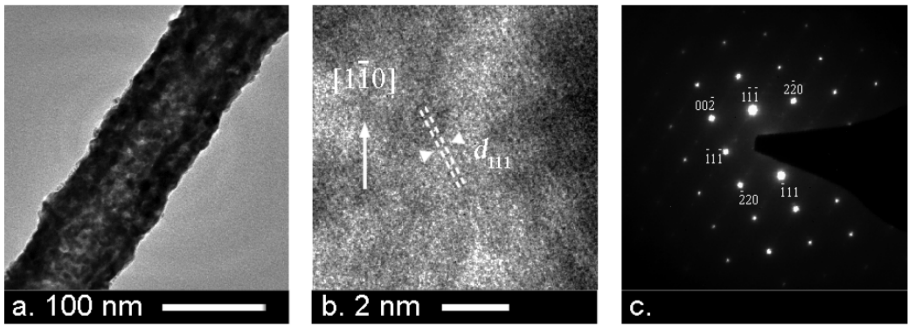


1. Simultaneous displacement of Cu in CuNW with Pt and Ru to form PtRuNT;
2. Annealing to form PtRu alloy.



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).

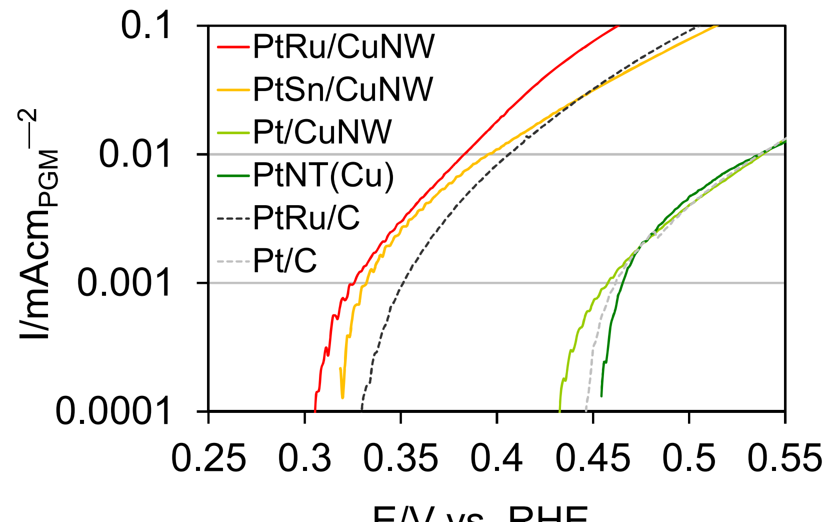
Methanol Oxidation: Innovative PtRu Nanostructure Catalysts



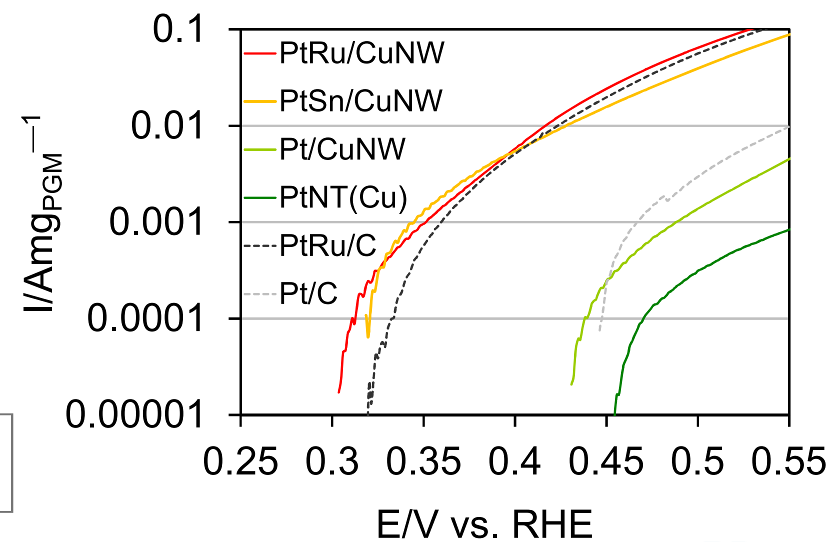
(a) - (b) TEM images and (c) SAED pattern of Pt/CuNWs.

- **Onset potential of methanol oxidation improved by 30 and 20 mV relative to the benchmark PtRu/C catalyst (HiSPEC® 12100) with PtRu/CuNWs and PtSn/CuNWs, respectively**
- **Performance stability demonstrated to be on par with the benchmark catalyst**

Specific Activity of PtRu Nanostructures (per cm^{-2}_{PGM})



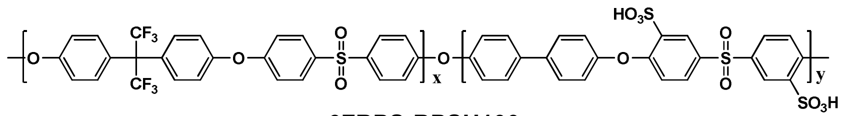
Mass Activity of PtRu Nanostructures (per mg_{PGM})



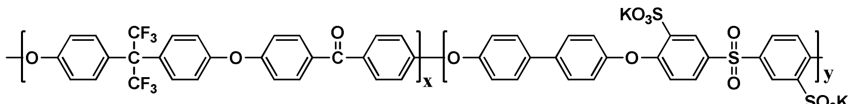
Solution: 1.0 M MeOH in 0.5 M H_2SO_4; **Scan rate:** 5 mV s^{-1}
Benchmark PtRu/C catalyst: HiSPEC® 12100

DMFC Multiblock Copolymers: Properties and Performance

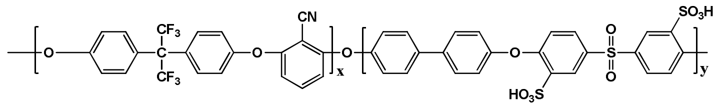
Multiblock Copolymers: Structure and Properties



6FBPS-BPSH100



6FK-BPSH100



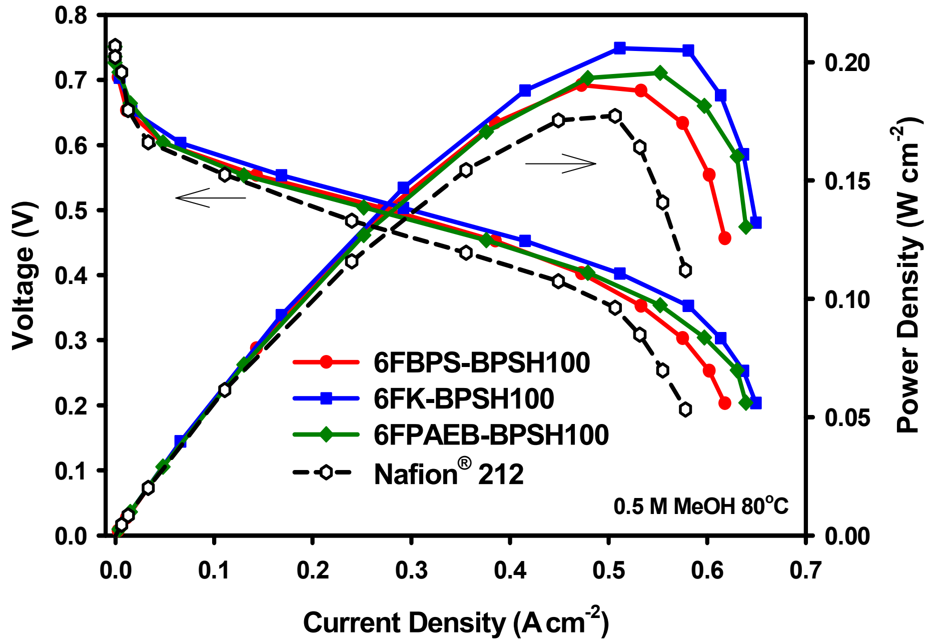
6FPAEB-BPSH100

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 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} $Pt_{50}Ru_{50}$ 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:** 80ºC

DMFC Performance with 0.5 M MeOH



- **Highly conductive multiblock copolymers prepared using telechelic BPSH-100 oligomers**
- **Multiblock copolymer membranes outperforming Nafion® 212 in DMFC testing (0.5 M MeOH)**

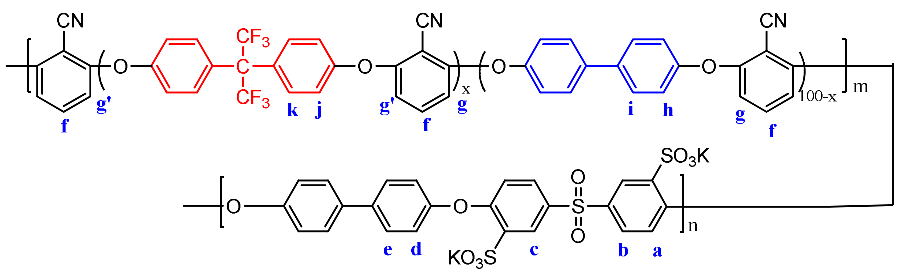
> 0.28 A/cm² at 0.5 V achieved with 3 out of 11 multiblock copolymers synthesized

Los Alamos NATIONAL LABORATORY

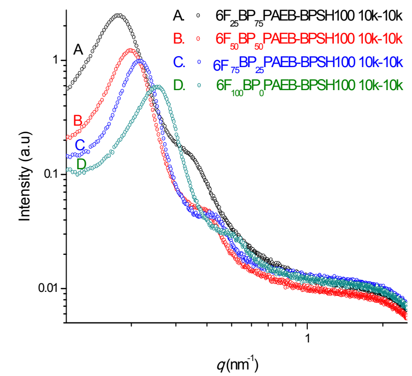
Virginia Tech
VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY

DMFC Multiblock Copolymers: MeOH Crossover Reduction

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



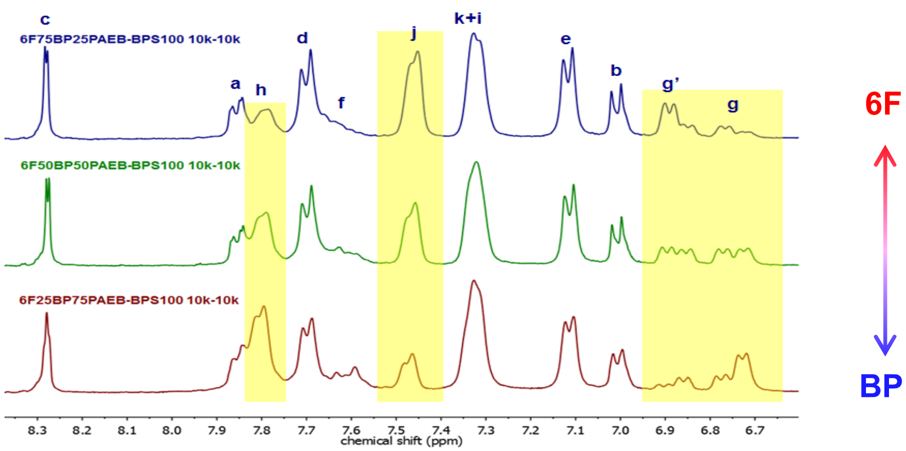
SAXS Profiles



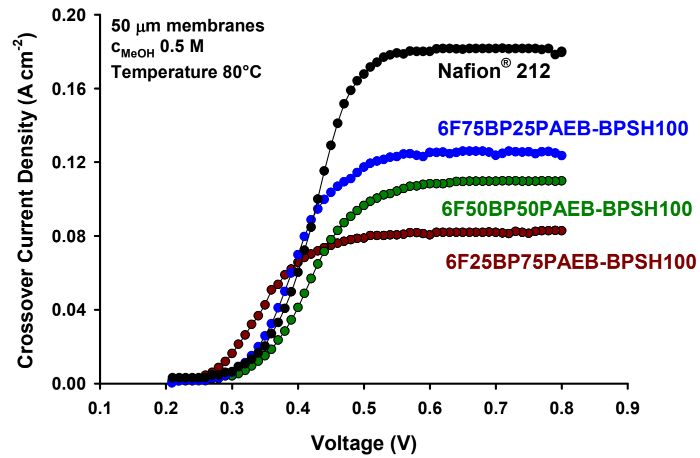
Interdomain distance increasing with the 6F-BPA moiety decrease

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

^{1}H NMR of Multiblock Copolymers (10K-10K)



Methanol Crossover with Various Membranes



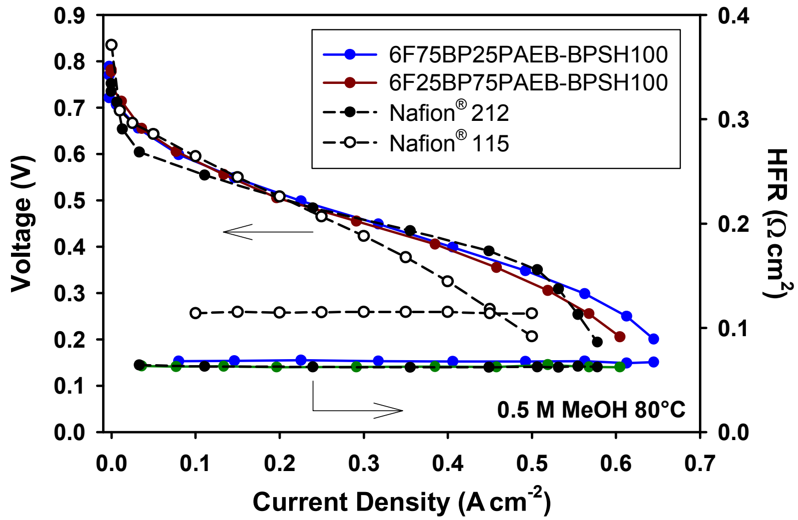
- Methanol permeability controlled by introducing BP and varying BP-to-6F ratio
- SAXS profile indicating highly ordered structure of multiblock copolymers with decreasing interdomain distance (anisotropic behavior confirmed by NMR)
- 55% reduction in methanol crossover compared to Nafion® 212

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

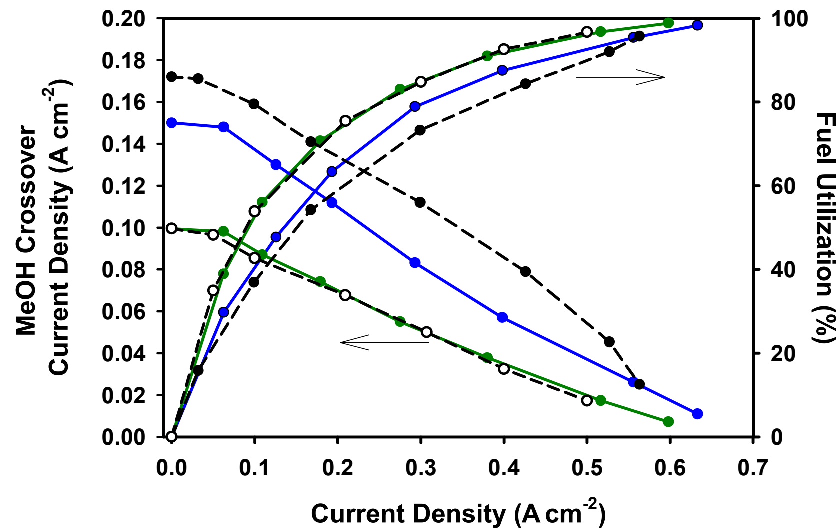
Characteristics	Multiblock		Nafion®	
	6F75 (50 μm)	6F25 (47 μm)	212 (50 μm)	115 (125 μm)
η_{fuel} at 0.5 V, %	69	77	62	75
η_{fuel} at peak power, %	92	95	90	88

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)



MeOH Crossover and Fuel Utilization

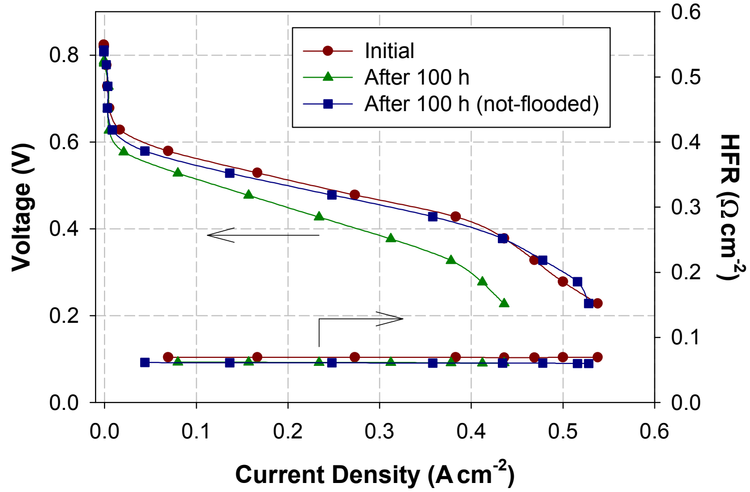


- **MEAs with multiblock-copolymer membranes showing superior performance to Nafion® 212 at DMFC voltages higher than *ca.* 0.55 V while maintaining similar resistance**
- **Better fuel utilization obtained with multiblock copolymers MEAs than Nafion®**

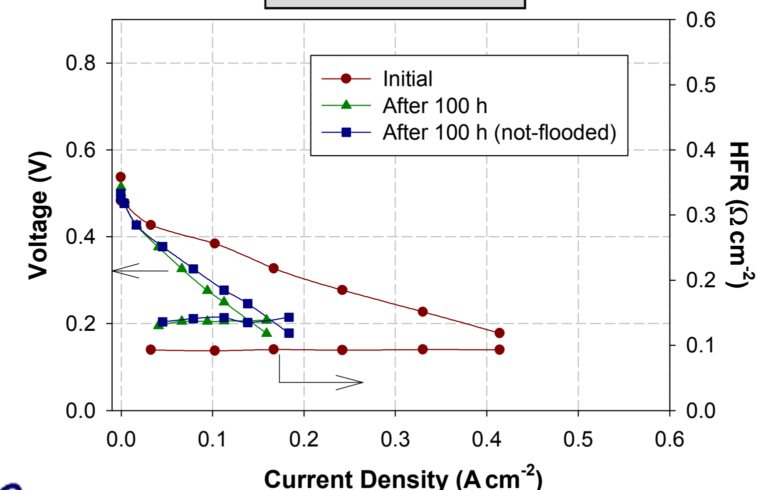
DMFC fuel utilization of ≥ 95% at peak power achieved

DMFC Performance Degradation: 100-Hour Life Test

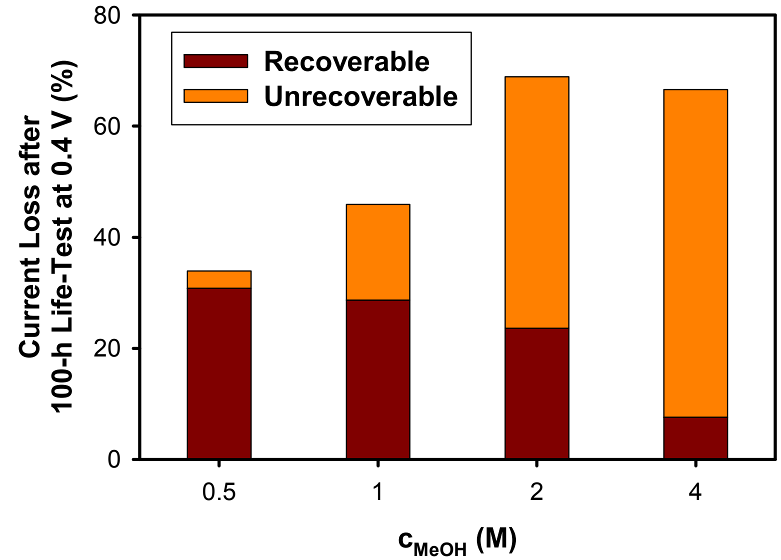
c_{MeOH} = 0.5 M



c_{MeOH} = 4.0 M



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

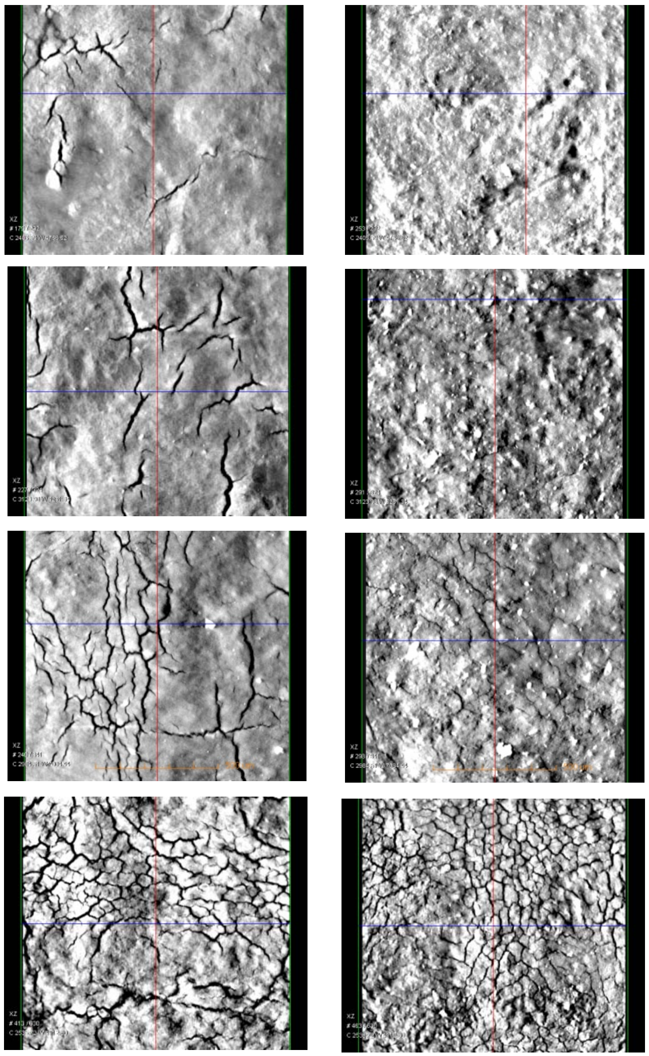


- **Unrecoverable performance loss significantly increasing with methanol concentration; recoverable performance decreasing**
- **Post-life-test HFR increasing with methanol concentration; loss of ionomer possible**
- **3% unrecoverable performance measured with 0.5 M MeOH at 0.4 V after 100 hours**

DMFC Performance Degradation: Crack Formation in Electrodes

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

MEA	Anode	Cathode
Before test		
0.5 M 100 h		
1.0 M 100 h		
4.0 M 100 h		



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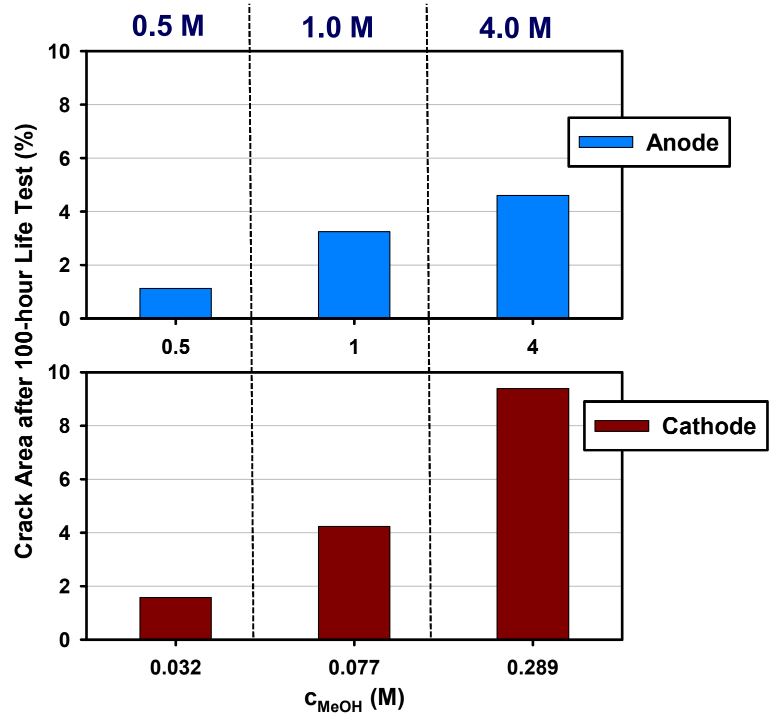
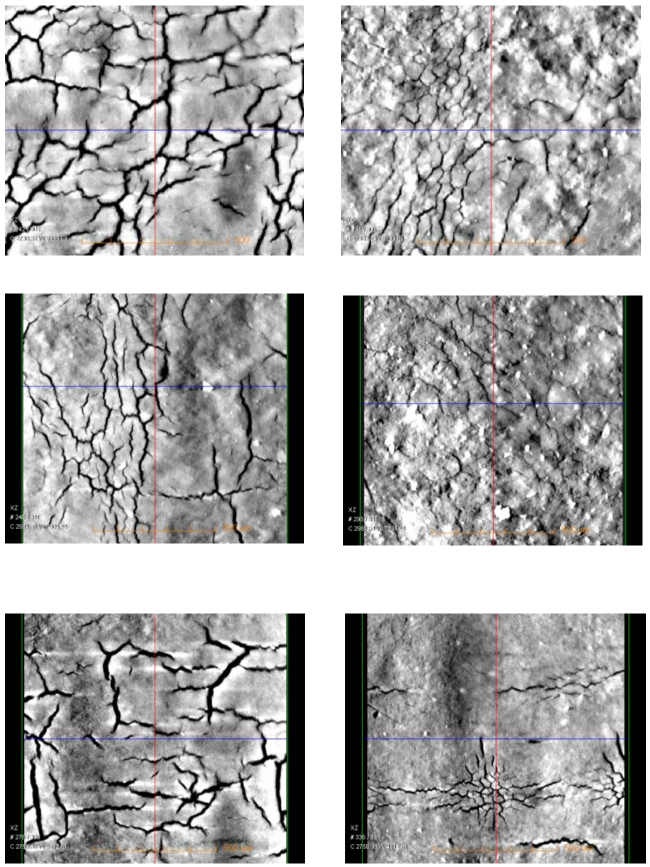


- **Anode and cathode cracking increasing with MeOH concentration; cathode more vulnerable**
- **Potentially important factor for DMFC performance degradation determined**

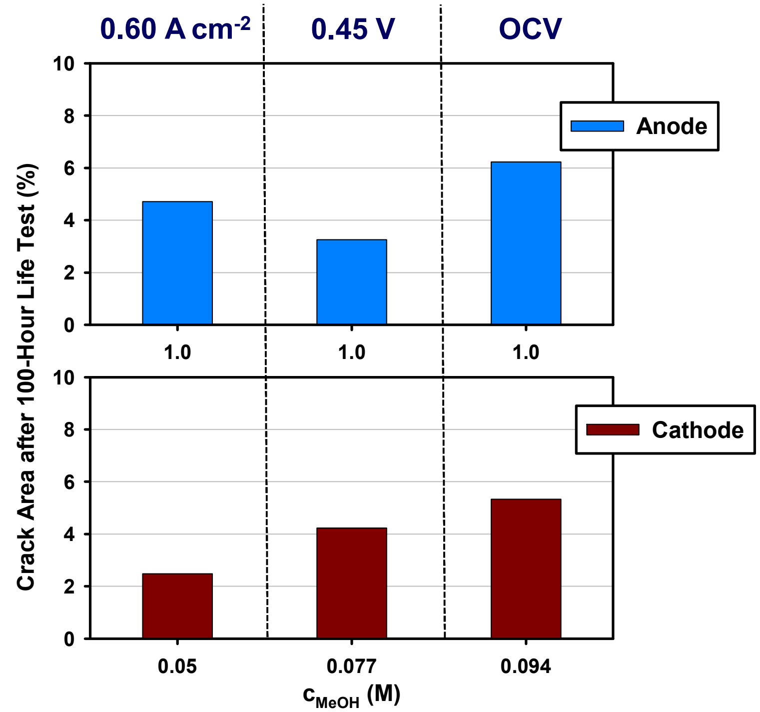
DMFC Performance Degradation: Crack Formation in Electrodes

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

MEA	Anode	Cathode
1.0 M MeOH 0.85 V		
1.0 M MeOH 0.45 V		
1.0 M MeOH 0.60 A/cm²		



Anode: 6 mg cm^{-2} $Pt_{50}Ru_{50}$ black, 1.8 mL/min 1 M MeOH solution; **Cathode:** 4 mg cm^{-2} Pt black; 500 sccm air; **Membrane:** Nafion® 212; **Cell:** 80ºC.



- **Microcrack formation depending on DMFC operating conditions subjected to the test conditions, with the most severe damage induced at OCV**
- **Mitigation strategy for cracking needed**

Summary: Advanced Materials and Concepts for Portable Power Fuel Cells

- The latest PtRu "advanced anode catalyst" exceeds performance of the HiSPEC® 12100 benchmark methanol oxidation catalyst by 40 mV, a significant performance improvement
- 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% near the peak-power point has been reached with 0.5 M MeOH feed
- While DMFC performance strongly depends on methanol concentration, the unrecoverable performance loss with 0.5 M MeOH feed is relatively small; durability improvements in the presence of higher methanol concentrations appear necessary