

## **DIRECT METHANOL FUEL CELLS**

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## Major Contributors to DMFC Effort in FY 2002

<b>Eric Brosha</b> (TSM)	- Ultrasonic spray/freeze dry
<b>John Davey</b> (Tech)	- MEA research; technical support
<b>Christian Eickes</b> (PD)	- Electrocatalysis
<b>Robert Fields</b> (TSM)	- Controls & software
<b>Michael Hickner</b> (GRA)	- Membrane & MEA research
<b>François Le Scornet</b> (GRA)	- Single cell & stack testing
<b>Don McMurry</b> (Tech)	- Controls & software
<b>Bryan Pivovar</b> (TSM)	- Membrane & MEA research
<b>Gerie Purdy</b> (Tech)	- Testing & general support
<b>John Ramsey</b> (GRA)	- Flow & hardware modeling
<b>John Rowley</b> (Tech)	- Technical support
<b>Mahlon Wilson</b> (TSM)	- Cell/stack design & engineering
<b>Christine Zawodzinski</b> (TSM)	- Cell/stack design & engineering
<b>Tom Zawodzinski</b> (TSM)	- Membrane & MEA research
<b>Piotr Zelenay</b> (TSM)	- Project management & electrocatalysis
<b>Yimin Zhu</b> (PD)	- Electrocatalysis

## Status by the End of FY 2001

- Composition of anodes with reduced catalyst loading optimized
- **5 gPt/kW** successfully demonstrated in a 45-cm<sup>2</sup> five-cell stack with a total Pt loading of 0.53 mg cm<sup>-2</sup>
- Several membranes with higher selectivity and lower electro-osmotic drag of water identified; improved overall efficiency demonstrated with several alternative membranes
- Fourth-generation 30-cell 80-W DMFC stack delivered and integrated by Ball Aerospace into a complete demonstration system for the military
- Design/modeling study of a ~500 W APU stack initiated

## Response to Selected Reviewers' Comments

**R** *“Need more emphasis on automotive applications.”*

*Manufacturing capability resulting from the likely market-entry of DMFCs for portable power applications should reduce the cost and facilitate commercialization of PEM fuel cells for higher power applications, automotive transportation in particular. Portable power-transportation synergy in fuel cell R&D appears to be the best commercialization strategy.*

**R** *“Not sure that LANL should be developing fuel cell stacks.”*

*Fundamental research has been and will remain the focus of direct methanol fuel cell program at LANL. Few stack prototypes have been built to prove practical viability of core DMFC technology developed at LANL, identify possible scale-up issues and verify adaptability of the technology to complete systems.*

## Major Collaborations & Commercial Interactions (C)

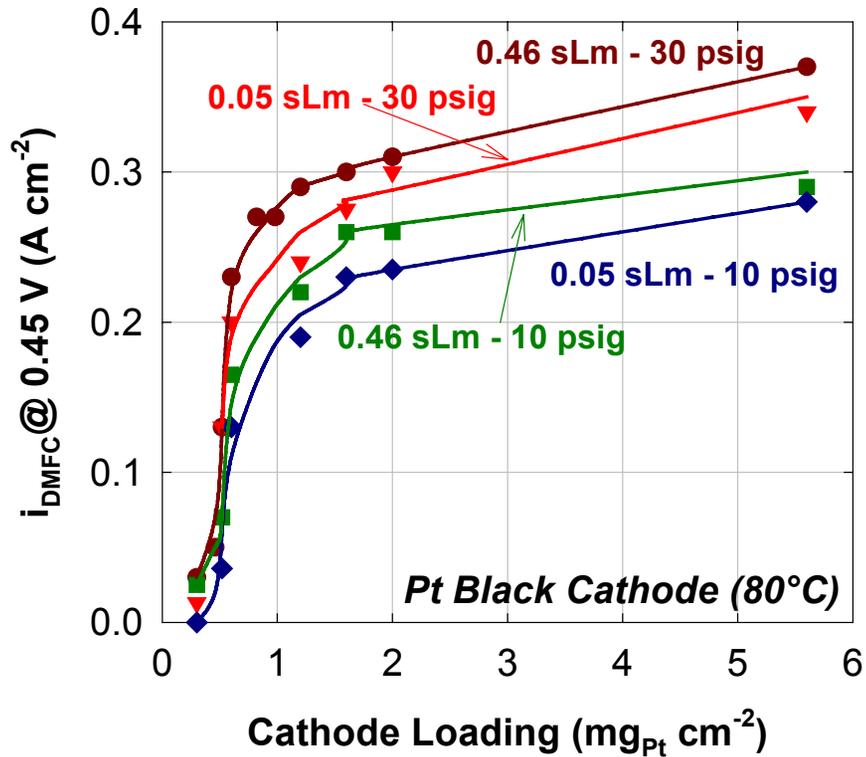
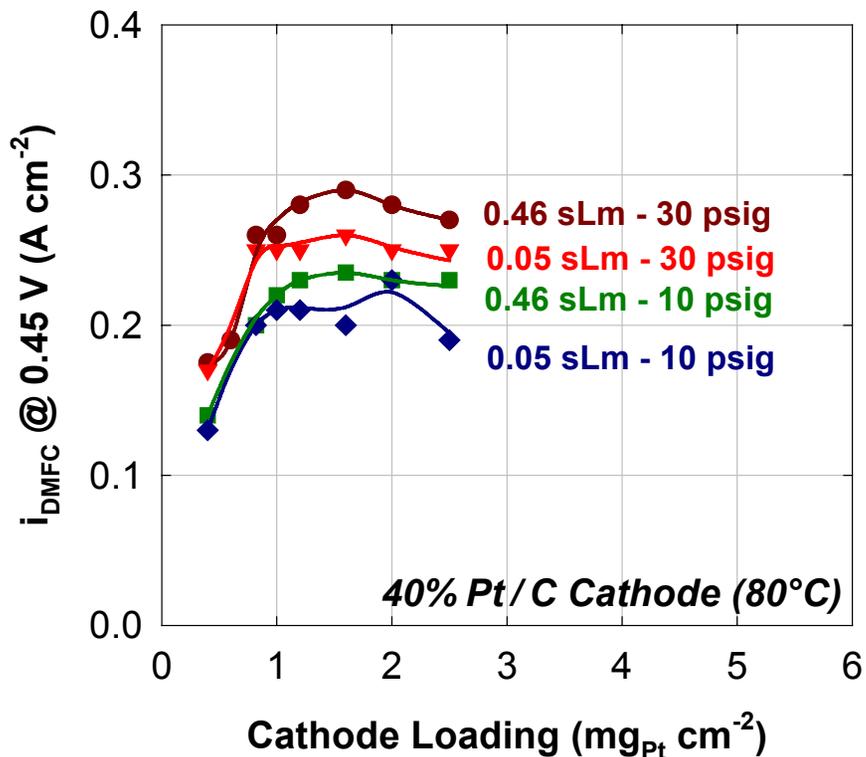
- Collaboration with Motorola on fundamental DMFC technology and high-temperature RHFC membrane for portable power in final stage of re-instating *via* CRADA; common research to begin in mid-May.
- Partnership with Ball Aerospace in FY 2002:
  - ✓ Complete 60 W (*net power*) DMFC system demonstrated to the military;
  - ✓ Three-year Palm Power research project started in mid-2001, focusing on fundamental research as well as stack development; first 22 W stack delivered to Ball for system integration in March 2002;
  - ✓ Operating conditions for the APU system agreed upon; first stack will be shipped from LANL in the fall of 2002.

## Major Collaborations & Commercial Interactions (II)

- Catalyst research:
  - ✓ Johnson Matthey – Effect of atomic composition, morphology and crystallography of Pt-Ru blacks on DMFC anode activity;
  - ✓ OMG – New carbon-supported cathode catalyst with improved methanol tolerance;
  - ✓ Superior MicroPowders – Carbon-supported catalysts for PEM and DMFC cathodes; DMFC MEAs (*planned*).
- Membrane/MEA research & development; polymer fabrication:
  - ✓ Virginia Tech – Development of alternative polymers (BPSH) and MEAs with significantly improved selectivity;
  - ✓ Hydrosize Technologies, Inc. – Fabrication of BPSH initiated; first two batches of BPSH polymer ordered and synthesized; polymer to be shipped to LANL within a week.

# Cathode Research

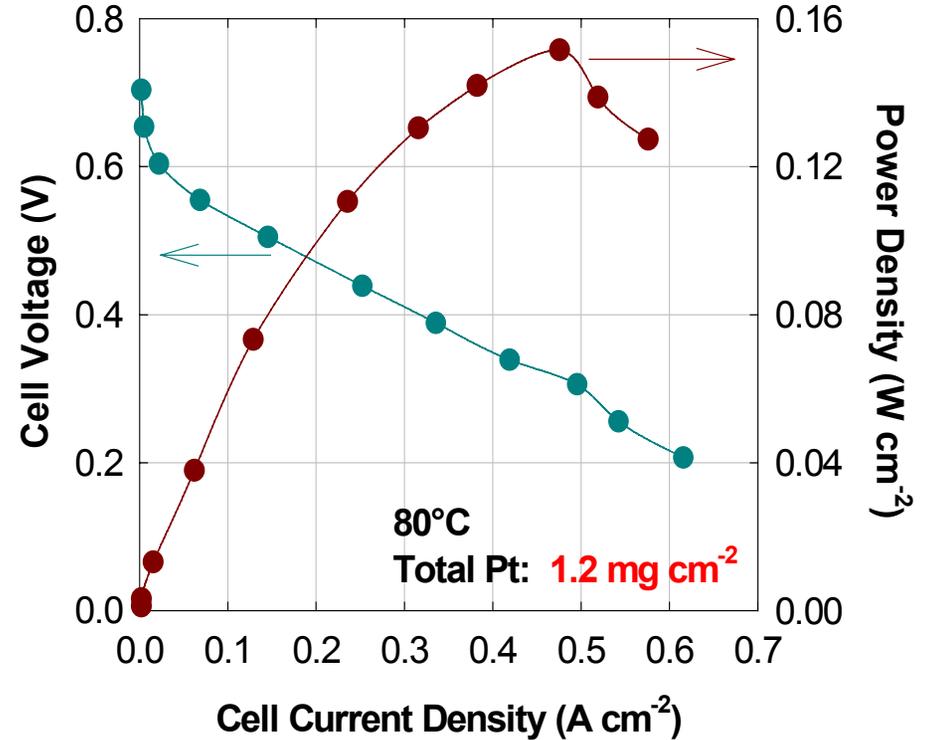
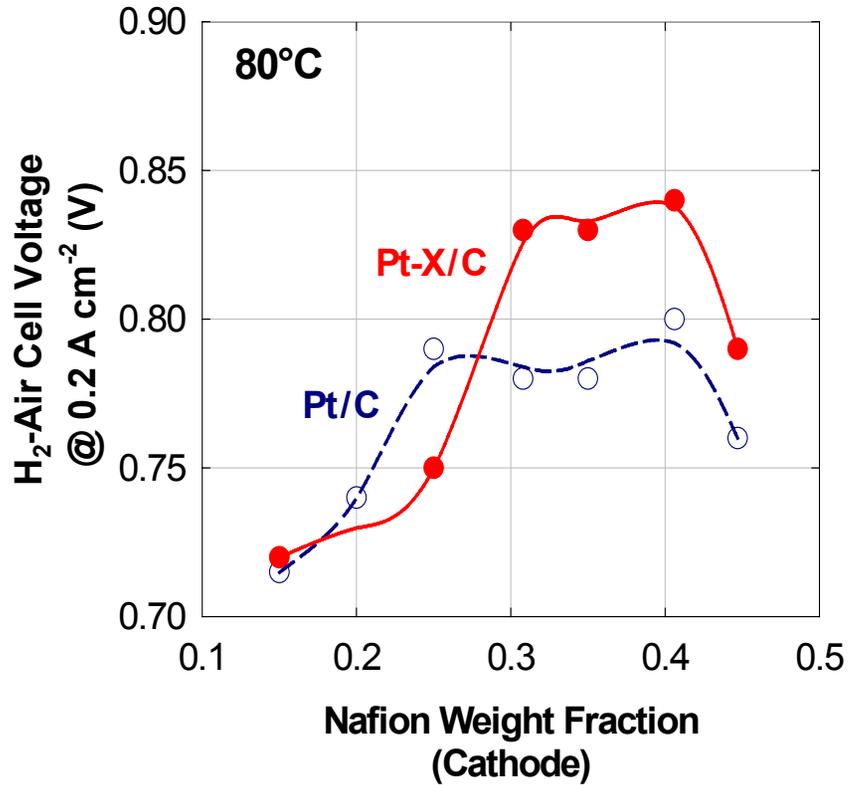
## Carbon-Supported vs. Unsupported Pt Catalysts



**Pt < 1.0  $mg cm^{-2}$  - Pt / C catalyst**  
**Pt > 1.0  $mg cm^{-2}$  - Pt black catalyst**

# Cathode Research

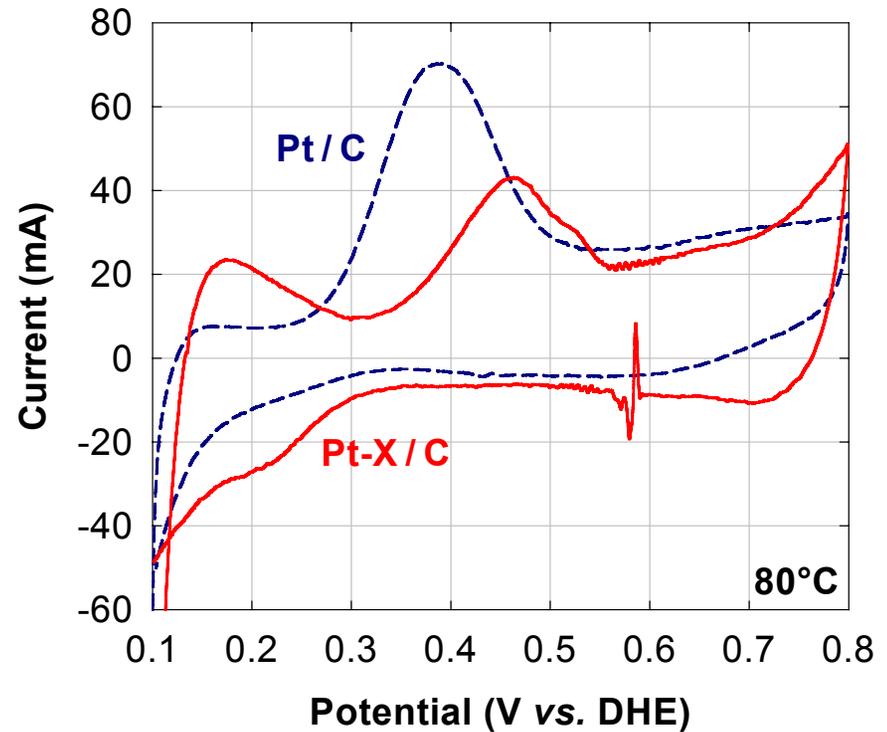
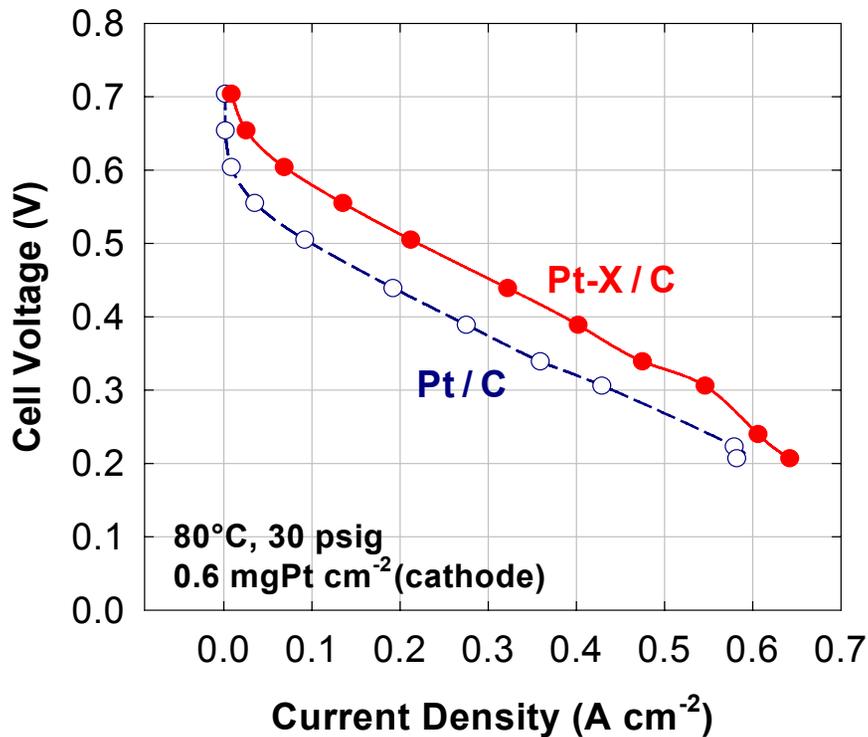
## Nafion Content; Improved Cell Performance with Low Total Pt Loading



**Achievements:** (1) Nafion content in the cathode optimized at a low Pt loading (0.6 mg cm<sup>-2</sup>)  
(2) Very good performance demonstrated at 80°C with 1.2 mg cm<sup>-2</sup> total Pt loading

# Cathode Research

## New Binary Catalyst with Improved $O_2$ Activity & Methanol Tolerance



**Achievement:** Even at low a Pt loading of  $\sim 0.6$  mg cm<sup>-2</sup>, the new binary Pt-X/C catalyst shows significantly better activity in oxygen reduction and improved methanol-tolerance over commercial Pt/C catalyst (E-Tek).

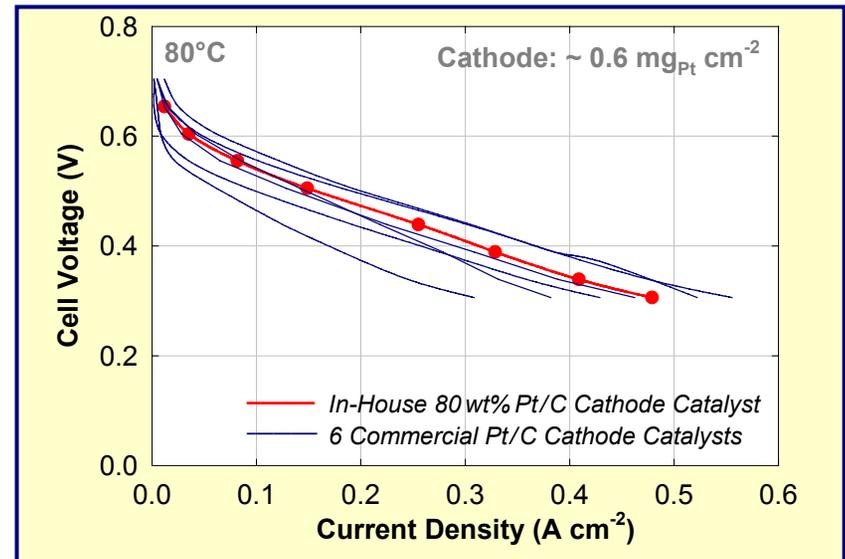
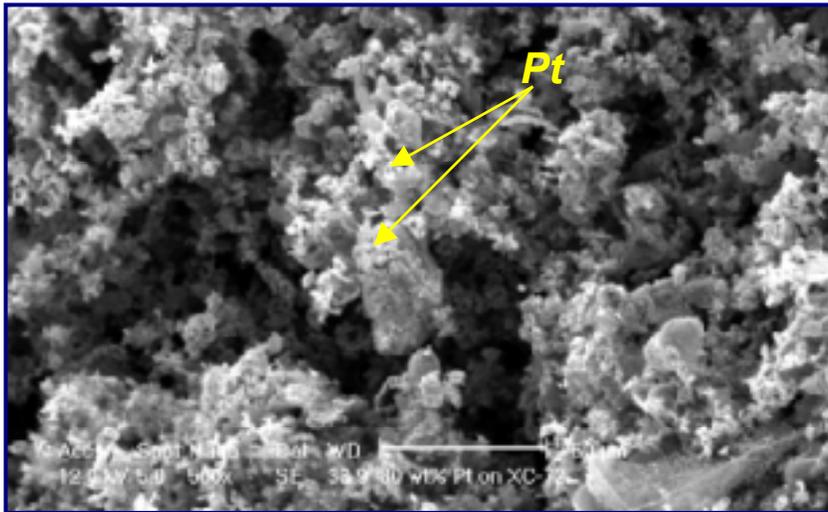
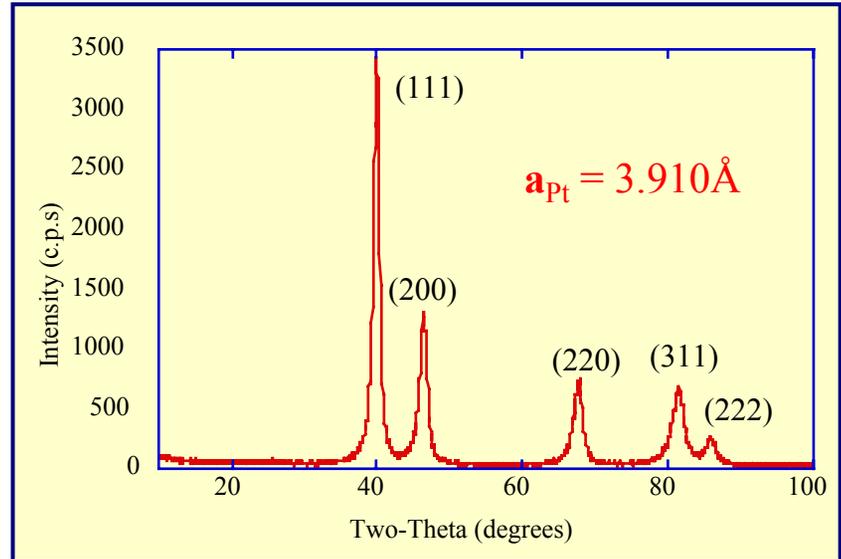


Collaboration with OMG (formerly Degussa-dmc<sup>2</sup>)

# In-House Catalyst Effort

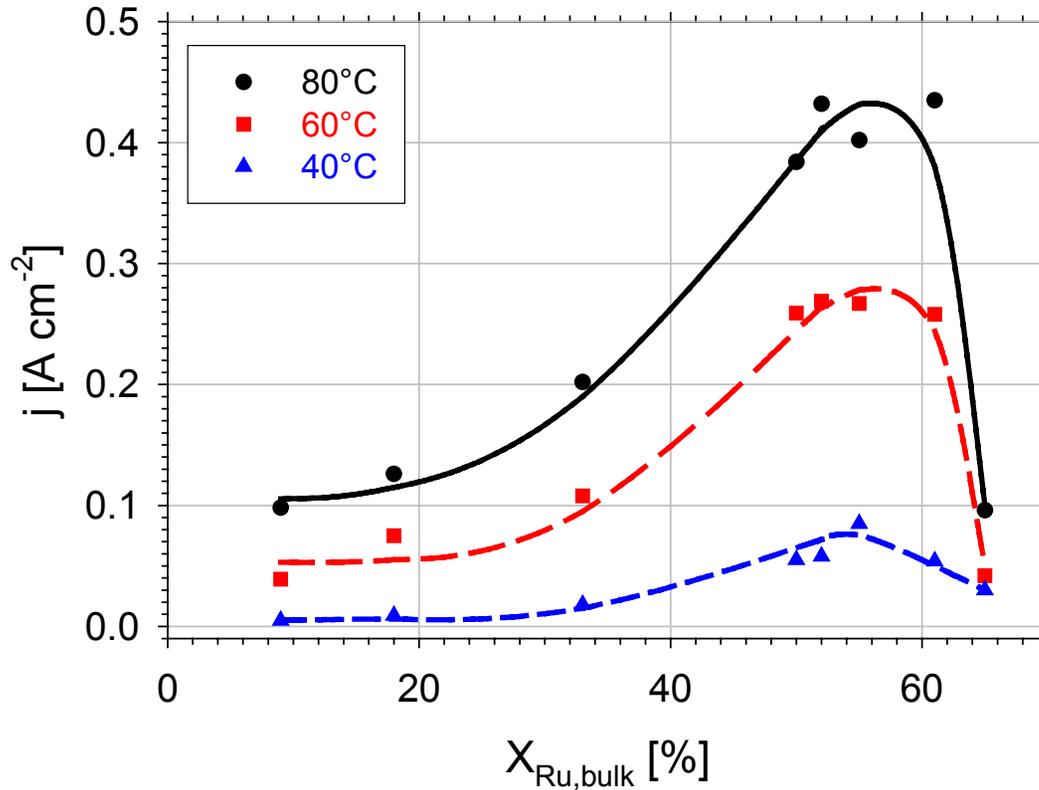
## New Carbon-Supported Pt Catalyst: 80wt%Pt/C

- ✓ Ultrasonic-spray / free-dry method
- ✓ 10- $\mu\text{m}$  droplets quickly frozen in  $\text{LN}_2$
- ✓ 6.1 nm Pt particle size determined by whole-profile fitting of XRD data
- ✓ Pt very well dispersed Pt (SEM)
- ✓ *DMFC performance very close to that of best cathode catalysts commercially available!*



# Anode Research

## *Pt-Ru Blacks: Catalytic Activity vs. Atomic Ratio*



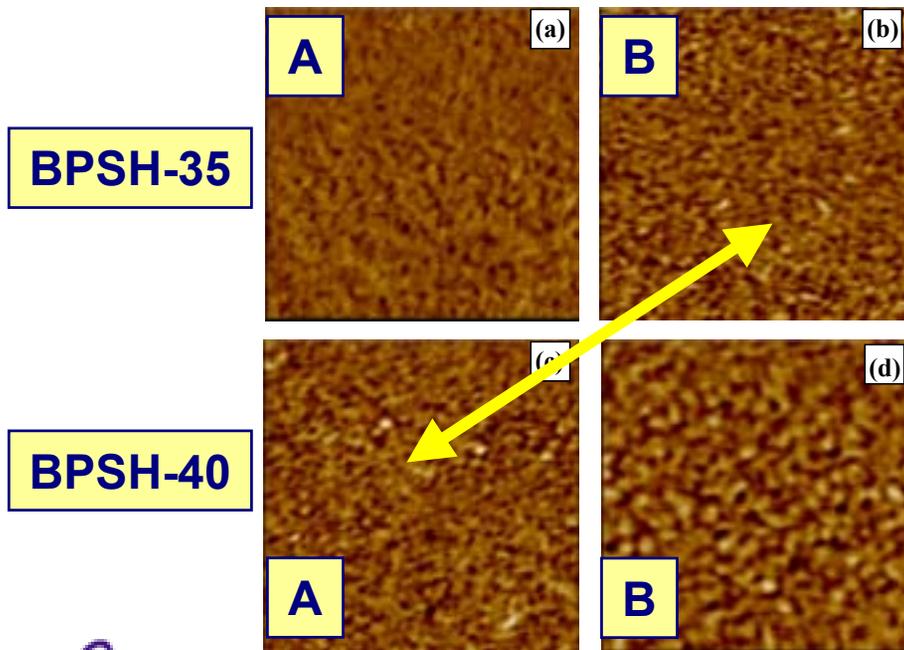
**Achievement:** Optimum bulk composition of the anode catalyst found to be  $55 \pm 5$  at% Ru, regardless of temperature.

© Collaboration with Johnson Matthey

# Membrane / MEA Research

## Effect of Processing on Membrane Performance

Membrane	MeOH Permeability $10^6$ (cm <sup>2</sup> /s)	Conductivity mS/cm	Selectivity $10^{-6}$ mS s/cm <sup>3</sup>	Relative Selectivity	$E_D$
N117	2.73	84.7	31.0	1.0	~3.3
BPSH-40 (A)	0.50	38.5	76.3	2.5	~1.5
BPSH-35 (B)	0.81	43	53.1	1.7	1.3
BPSH-40 (B)	1.40	38.1	27.2	0.9	2.7

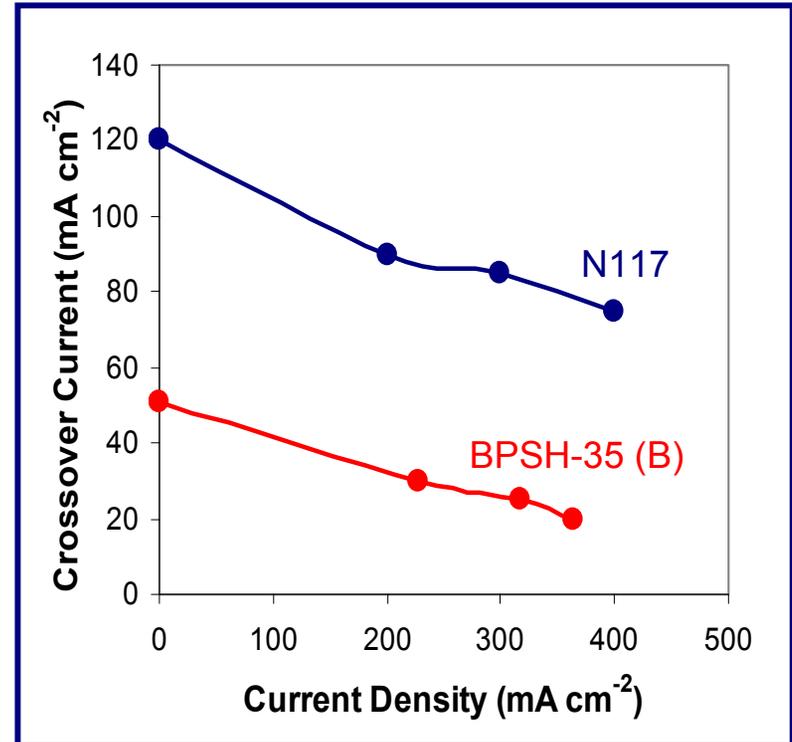
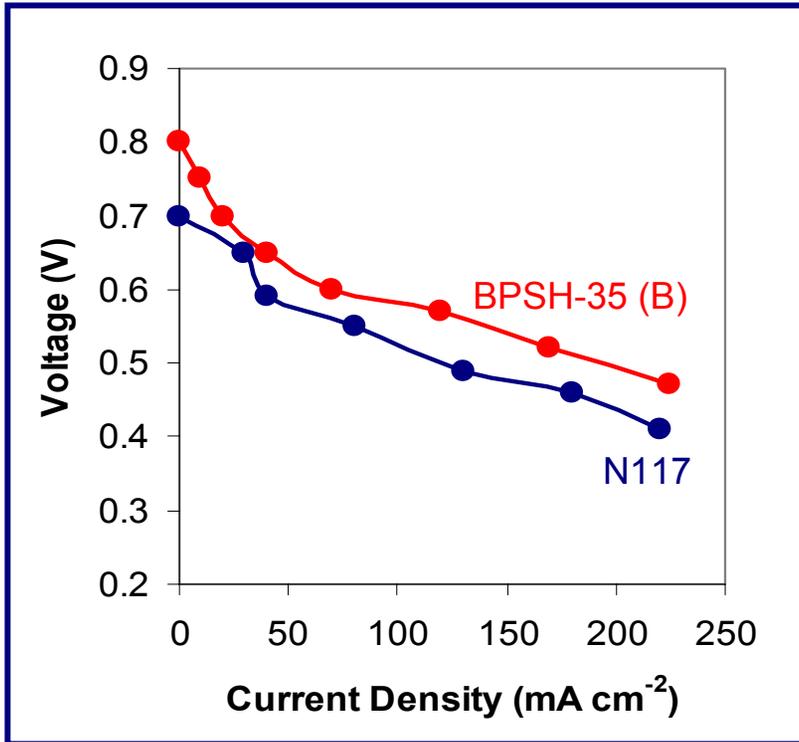


A – Membrane before processing  
B – Membrane after processing

Processing greatly affects BPSH polymer properties and morphology; after processing, BPSH-35 (B) becomes similar to BPSH-40 (A).

# Membrane / MEA Research

## DMFC MEAs with Alternative Polymers



**Achievement:** In short-term testing, with ambient air at 80°C and 1.0 M MeOH anode feed, BPSH-35 (B) offers significantly reduced methanol crossover and comparable performance to Nafion 117.



*Collaboration with Virginia Tech*

# Membrane / MEA Research

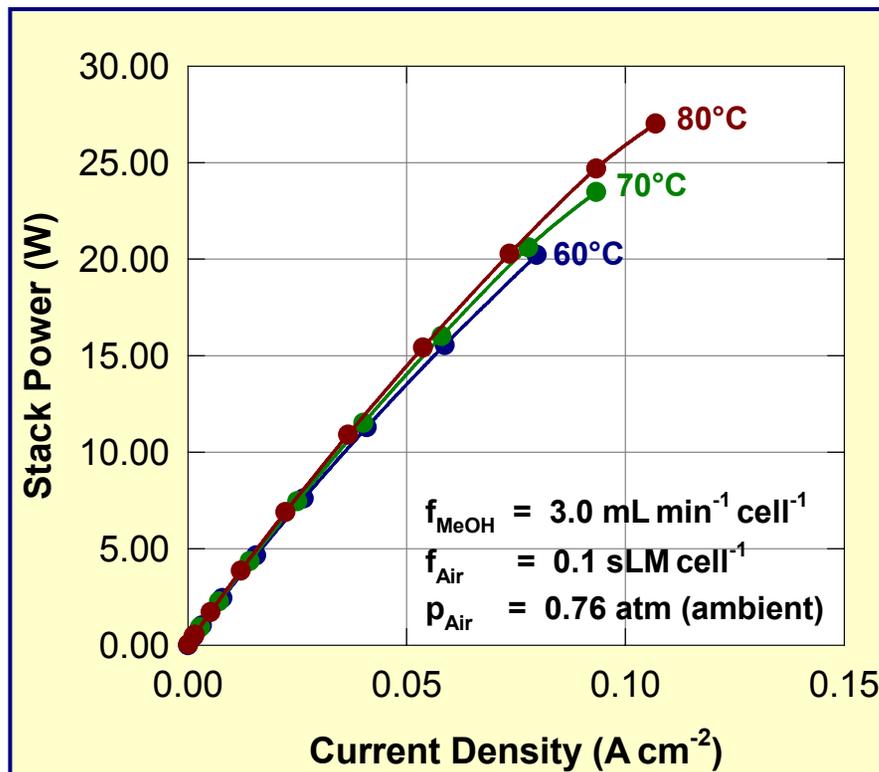
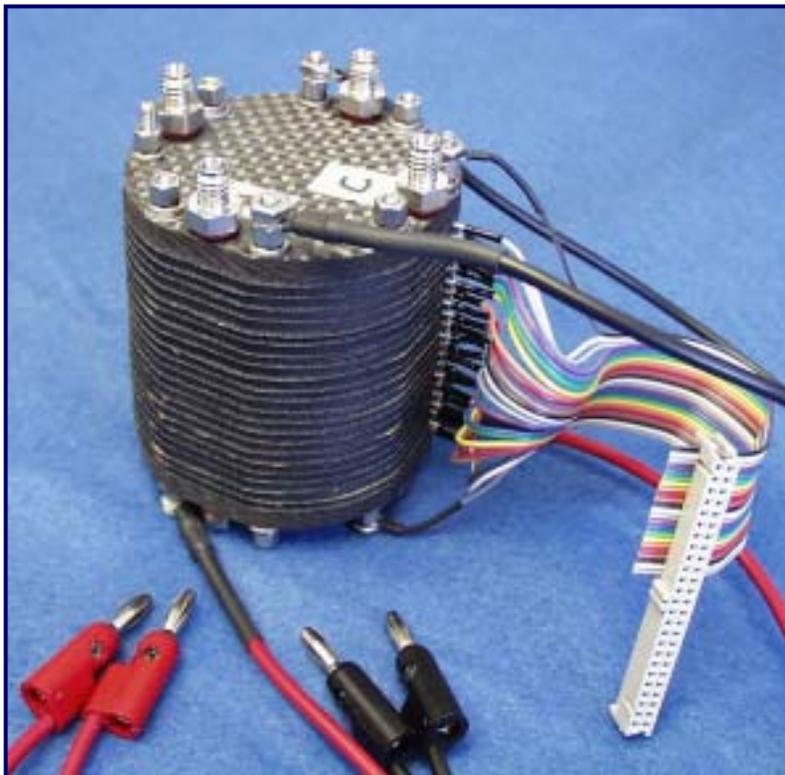
## MEA Issues Critical to Further Progress

Membrane	Fuel Cell Conductivity (mS cm <sup>-1</sup> )	Membrane Conductivity (mS cm <sup>-1</sup> )	Fuel Cell Relative Selectivity	Membrane Relative Selectivity
<i>Nafion 117</i>	85	110	1.0	1.3
BPSH-40 (A)	38	80	2.5	4.4
BPSH-50 (A)	40	100	1.3	3.8
BPSH-60 (A)	52	170	1.1	2.5
Ion Clad	26	130 <sup>Tricoli</sup>	1.5	5.7

- Based on membrane properties alone, relative selectivity of “alternative” MEAs should be higher than observed in DMFC testing.
- “Fuel cell conductivity” needs to be improved.
- More research required - with Nafion-free catalyst layers in particular.

# 22 W DMFC Stack for Portable Power

*High Efficiency, Ambient Pressure & Low Cathode Air Flow*

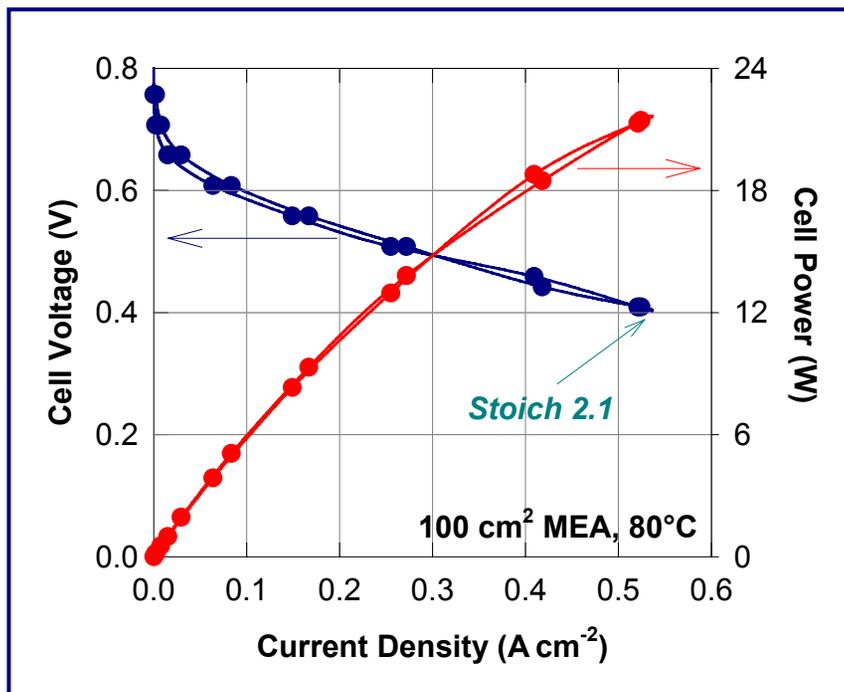


**Achievement:** Very good performance demonstrated at ambient cathode pressure (**0.76 atm**), low air flow ( $\lambda < 3$ ) and relatively high stack voltage of  $\sim 12 \text{ V}$  (**0.55 V cell<sup>-1</sup>**).

© Collaboration with Ball Aerospace

# 500 W Prototype Stack / System Development for APU

On Track with Stack Deliverable in Fall 2002

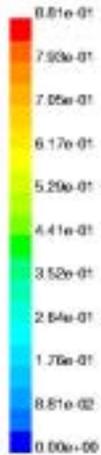
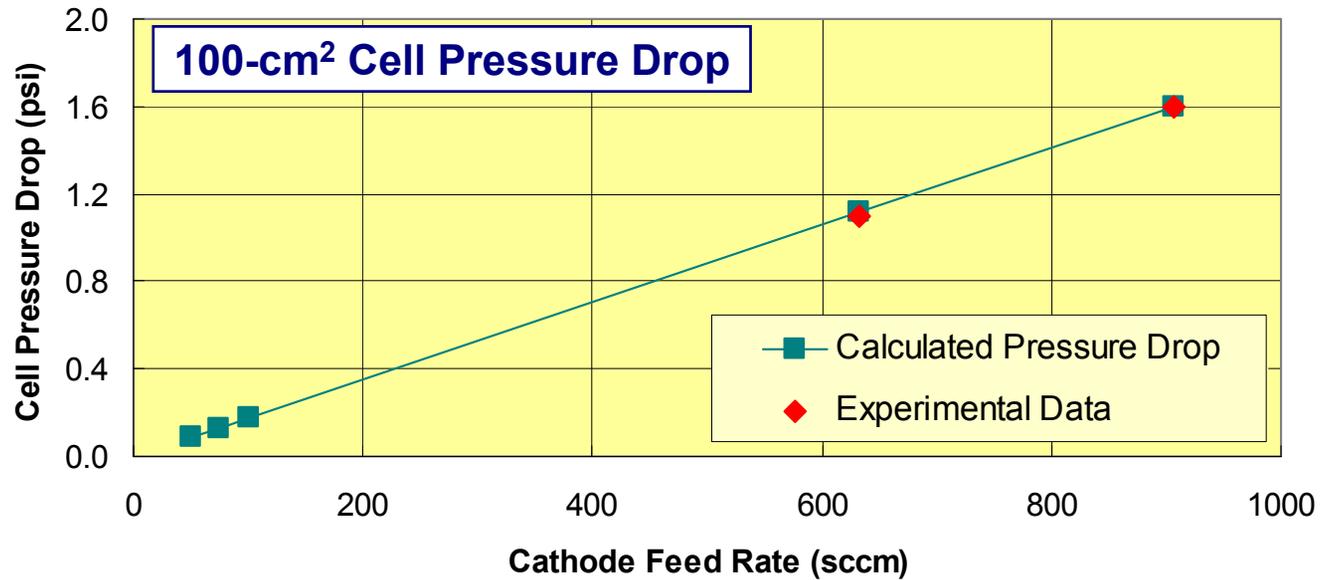


**APU Stack:** High-conductivity 100-cm<sup>2</sup> graphite hardware used in the first-generation APU cell. Performance recorded:

**2.1 air stoich, 30 psig cathode back pressure: ~ 21 W**  
**1.3 air stoich, ambient cathode pressure: ~ 11 W**

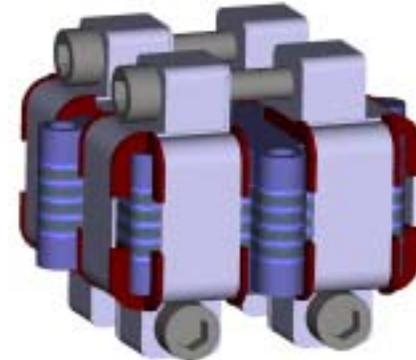
# APU Hardware & Flow Modeling

## Pressure Drop – Air Flow – Stack Hardware



*Air flow: 0.6 m/s*

**Manifold Flow Models**



**Alternative Compression Approach**

## FY 2002: Summary

### Reduction in Catalyst Loading:

- ✓ Composition of cathodes with reduced Pt loading optimized; good performance with a total precious metal loading of 1.2 mg cm<sup>-2</sup> demonstrated at 80°C – *task completed*

### Catalyst Research:

- ✓ Alternative Pt-X cathode catalyst identified (*patent pending*)
- ✓ In-house catalyst fabrication capability established; system used to make - commercially unavailable - 80 wt% Pt/C cathode catalyst
- ✓ Study of the effect of Pt-to-Ru atomic ratio on anode performance at different cell operating temperatures – *task completed*

## FY 2002: Summary (II)

### Membrane Research:

- ✓ Well-performing BPSH (sulfonated poly(arylene ether sulfone)) MEAs with significantly reduced methanol crossover demonstrated – **task completed**
- ✓ Demonstration of short stack with 3× better selectivity – **pending**

### Stack R&D:

- ✓ Components for 22 W DMFC stack for portable power applications designed, fabricated and optimized in single-cell and short-stack testing; first 22 W stack built and delivered to Ball Aerospace
- ✓ Components for 500 W stack for auxiliary power applications under development; single cell operation of 100-cm<sup>2</sup> hardware demonstrated with good results – **task on schedule (stack delivery planned for the fall of 2002)**

## FY 2003 Plans

- Continue fundamental research and development in electrocatalysis of methanol oxidation and oxygen reduction; improve performance by optimizing hydrophilic/hydrophobic properties of the cathode (*Sep 03*)
- Study and report on the effect of sulfonation on performance of BPSH membranes in direct methanol fuel cells; narrow the gap between bench-top and fuel-cell selectivity of alternative membranes to no more than 30% (*May 03*)
- Demonstrate for at least 500 hours durability of Nafion and alternative MEAs (no more than 15% performance loss) (*May 03*)
- Demonstrate for at least 100 hours sustained operation of a “portable power” DMFC stack with air stoich below two (*May 03*)
- Investigate composition of the DMFC cathode exhaust as a function of cell operating conditions (*Sep 03*)