Direct Methanol Fuel Cells

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Status by the End of FY 2002 *(Highlights)*

- **Promising performance and low methanol crossover demonstrated with BPSH MEAs in single cell testing**
- **Three-fold improvement in selectivity over Nafion achieved with alternative membranes in short stacks**
- **New binary Pt-X/C cathode catalyst identified (patent pending); composition of carbon-supported Pt cathodes optimized; respectable performance shown with 1.2 $mg_{Pt}\ cm^{-2}$ (total cell)**
- **Atomic composition of Pt-Ru blacks for DMFC anodes optimized**
- **First generation 22 W DMFC stack for portable power applications designed, fabricated, optimized, tested and delivered to Ball Aerospace for system integration**
- **Several key components for 500 W stack for auxiliary power applications developed, fabricated and demonstrated with very good results in single cell operation**

FY 2002: Reviewers' Comments (R)

Comments

- *"Good progress on all fronts – cathode, anode and membrane as well as stack development." "Astonishing productivity on variety of topics."*
- *"Probably the most successfully integrated program of those presented this year."*
- *"Funding DMFCs for portable power applications is good approach." "Performance improvement is […] very encouraging and hold promise for transportation applications."*

Recommendations

- *"Membrane work less advanced." "Solid plan – consider evaluation of other membranes."*
- *"Need preliminary durability data." "Conduct durability testing."*
- *"Use stack characterization to enhance DMFC technology."*

Response to Selected Reviewers' Comments

R ***"V-I sweeps should be done under conditions of constant or controlled air-stoich ratios and not under conditions of constant flow. Also for methanol flow at the anode."***

Constant air-stoich operation, only sporadically used a year ago, has been since introduced into all stack DMFC R&D at LANL, i.e. into all system-relevant testing. Constant air flow is still used in electrocatalysis and membrane research, which does not involve full DMFC testing.

Because of re-circulation of methanol, constant stoich operation of the DMFC anode is not very important. It is methanol concentration, not the flow rate or stoich ratio as such, that impacts anode/cell performance the most (especially at high currents). Unlike at the gas-fed cathode, high MeOH flow to the anode does not lead to significant power losses."

R ***"Why is testing at 30 psi?"***

Some testing with back-pressurized cathode (up to 30 psig) has been done for performance-vs.-pressure characteristics of larger systems, which potentially could afford a compressor (if performance warranted). No such testing is performed in research for portable power."

Major Collaborations & Commercial Interactions (C)

- **Ball Aerospace**
  - ✓ Palm Power research project continued in FY 2003 with significant effort in catalysis, membrane and MEA as well as stack development;
  - ✓ Four generations of stacks for 20 W portable system developed;
  - ✓ Four 11 W DMFC stacks delivered to Ball in January 2003 for integration in two demonstration units for DARPA.
  - ✓ Technology transfer from LANL to Ball in the final stage of negotiations
- **Motorola**
  - ✓ CRADA re-instated in the area of DMFC technology for portable electronics.

Major Collaborations & Commercial Interactions (II)

- Catalyst research:
  - ✓ <u>Johnson Matthey</u> – effect of atomic composition, morphology and crystallography of Pt-Ru blacks on DMFC anode activity;
  - ✓ <u>OMG</u> – development of novel cathode catalysts;
  - ✓ <u>Superior MicroPowders</u> – carbon-supported anode and cathode catalysts, MEAs for direct methanol fuel cells;
  - ✓ <u>University of Illinois, Urbana-Champaign</u> – fundamental research in electrocatalysis.
  - ✓ <u>TKK Tanaka</u> – carbon-supported catalysts.

- Membrane/MEA research & development:
  - ✓ <u>Virginia Tech</u> – development of alternative polymers and MEAs with significantly improved selectivity and duarbility;
  - ✓ <u>W.L. Gore</u> – new membranes and MEAs with improved performance and methanol selectivity.

September 2003 DMFC Milestones

(1) Determine optimum cathode operating conditions in the backpressure range from 0 to 30 psig

(2) Reduce air stoichiometry to no more than 3×

(3) Demonstrate DMFC cathode catalyst with performance by 15% better and long-term stability for 200 hours at least as good as a corresponding reference Pt catalyst

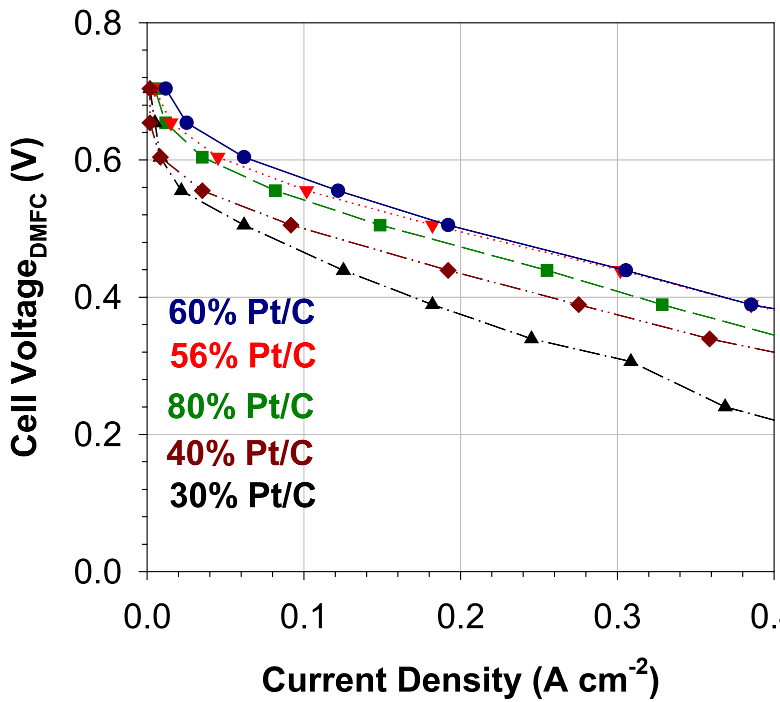
(4) Identify main routes of DMFC performance degradation

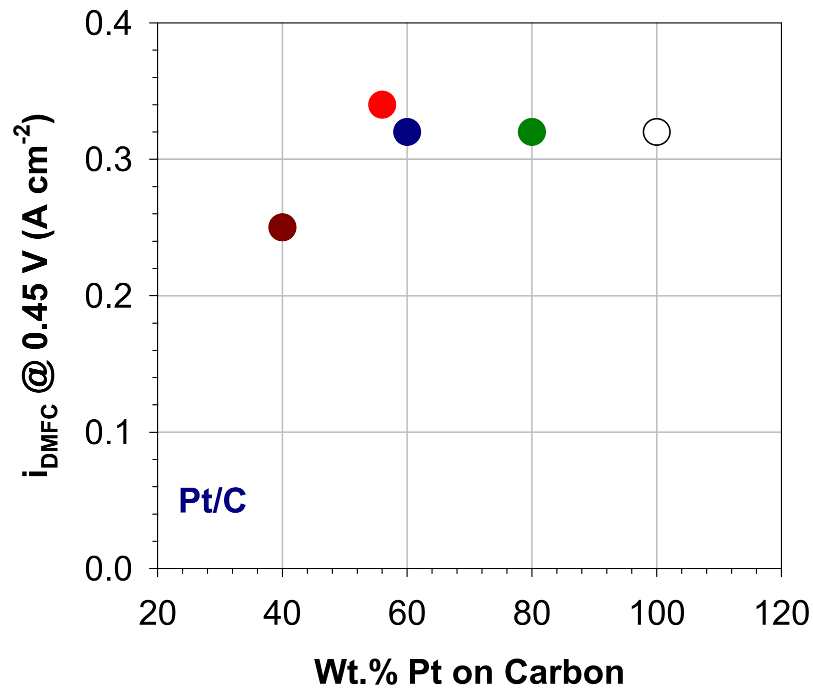
(5) Lower by a factor of two the rate of performance degradation for membranes with significantly higher selectivity than Nafion; demonstrate such membrane(s) in a cell operating for no less than 100 hours

(6) Design and build a 500 W DMFC stack

Cathode Research

Optimization of Cathode Composition at Ultra-Low Pt Loading (0.6 mg cm^{-2})



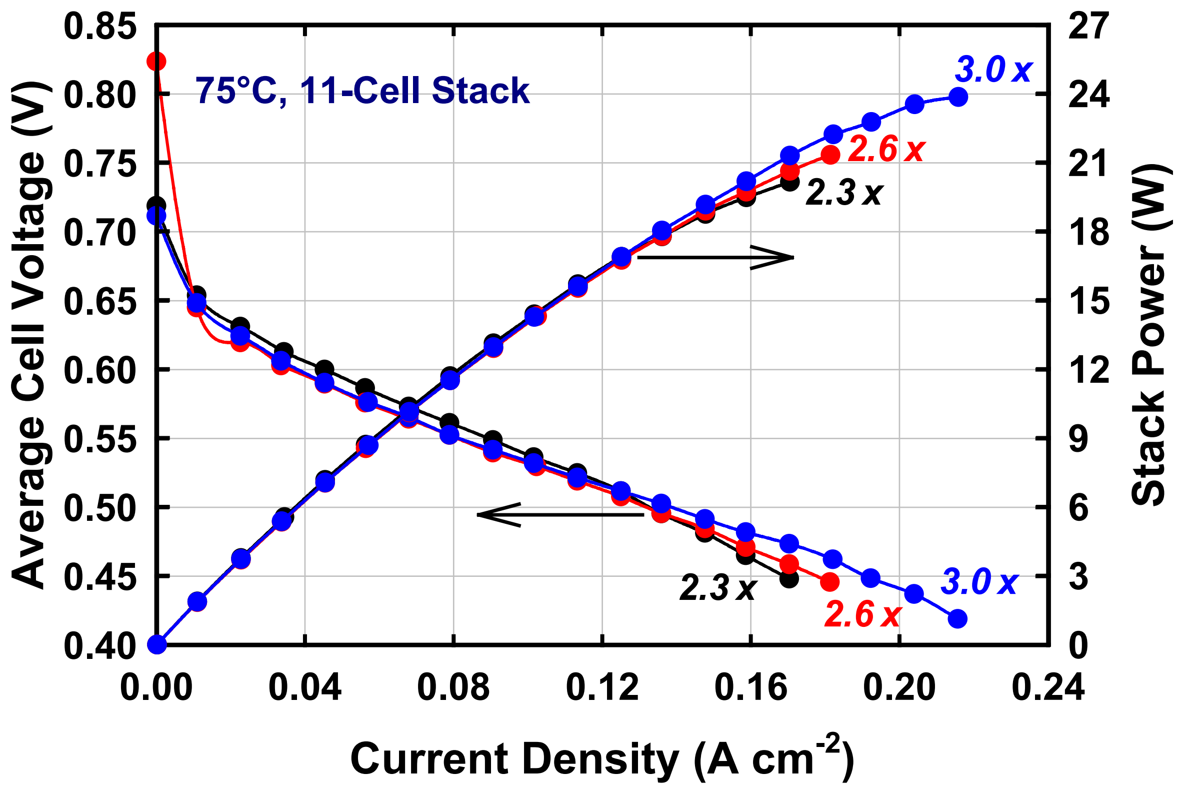


When low catalyst loading is required, such as 0.6 mg cm^{-2}, carbon-supported cathode catalysts containing between 50% and 60 wt% of Pt are best suited for DMFC operation. Two main factors determining catalyst performance are: (i) ability to handle methanol crossover and (ii) catalyst utilization.

C *Collaboration with Superior MicroPowders and TKK Tanaka*

Cathode Research

Cathode Optimization and Reduction in Air Stoichiometry



(1) ***Good performance achieved with low air stoich ratios in single cells an stacks***

(2) ***High efficiency demonstrated independently of air flow***

2003 Milestones #1 & #2 Accomplished

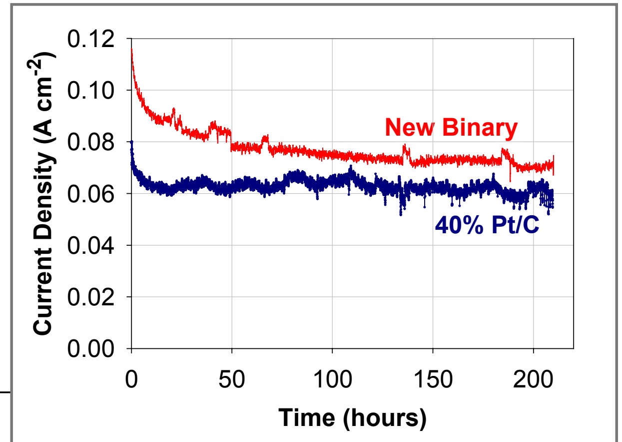
(data above relevant to Milestone #2)

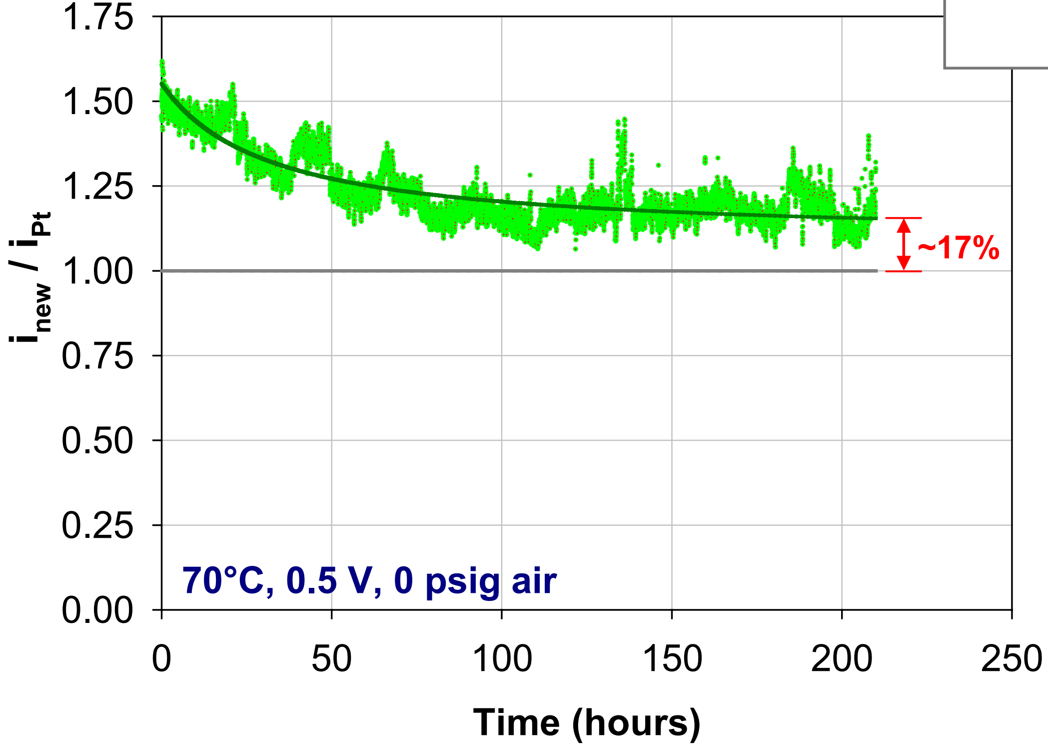
Cathode Research

200-Hour Life Test of Carbon-Supported Cathode Catalysts

Demonstrated binary carbon-supported cathode catalyst with 200-hour performance significantly better than that of corresponding 40% Pt/C catalyst.

2003 Milestone #3 Accomplished





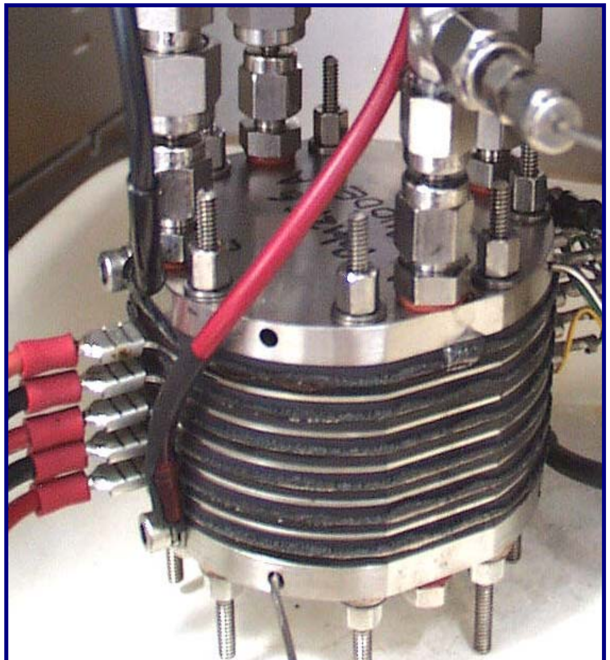
Future Research

(i) Improvement in long-term stability of the binary catalyst

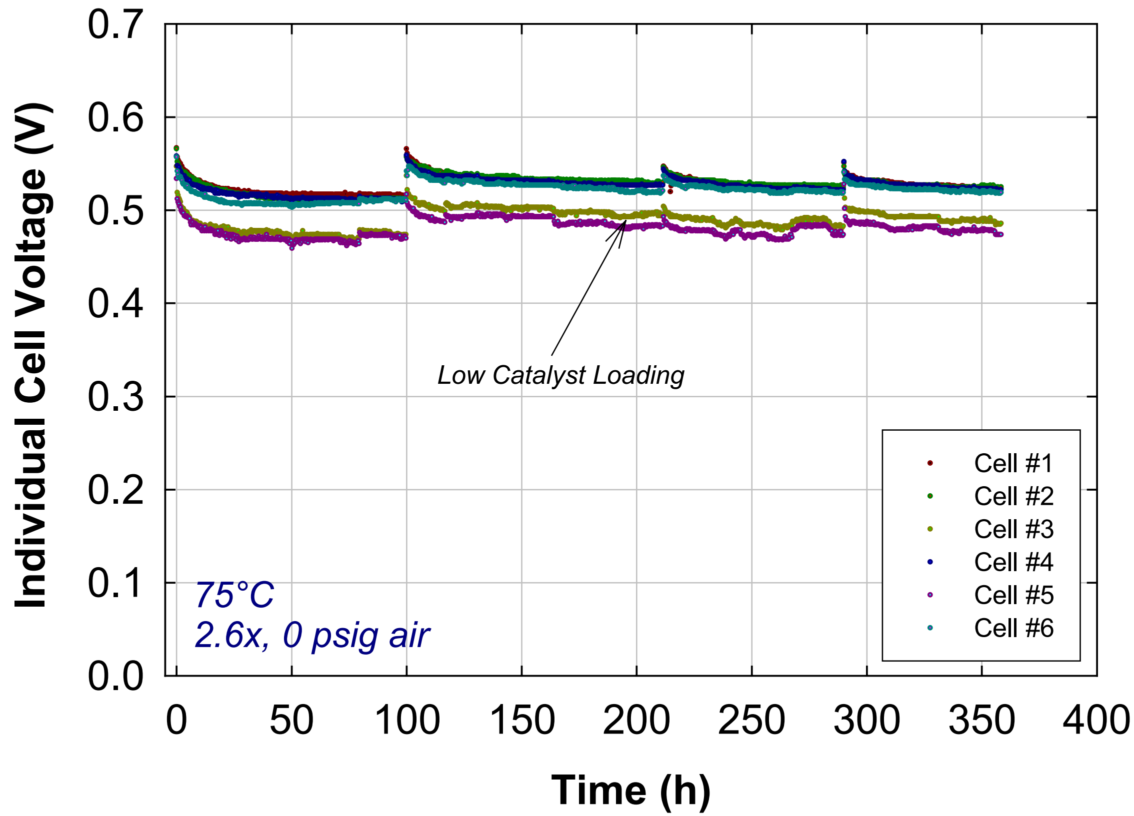
(ii) Synthesis and optimization of the unsupported binary catalyst.

Durability Research

DMFC Life Test Using Six-Cell Setup (75°C, Ambient Air)



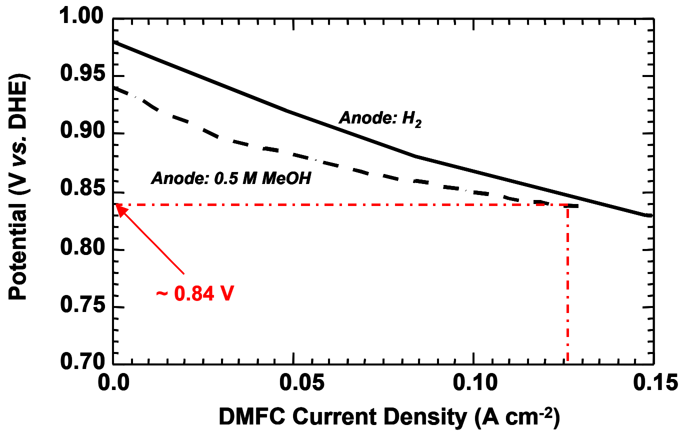
Six-Cell Setup for MEA Durability Testing

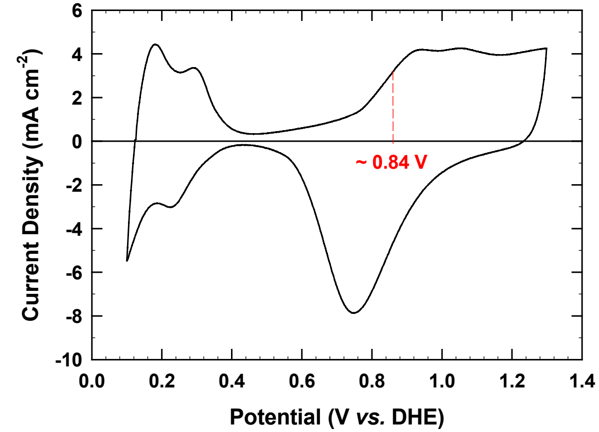


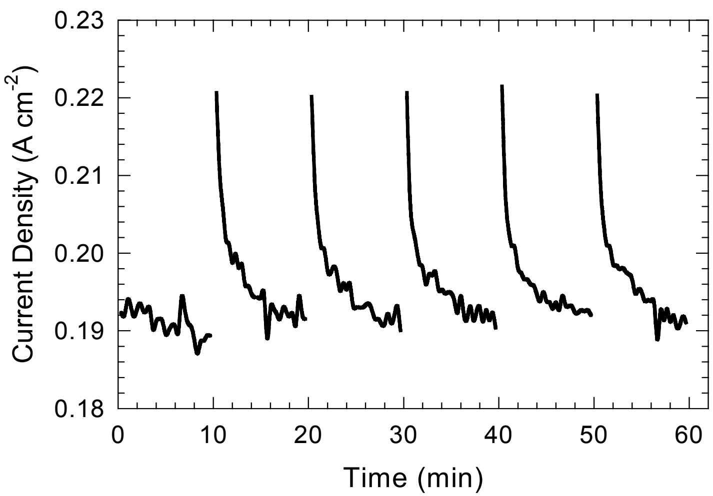
There is up to ~40 mV/cell, reversible performance loss early in the life test of "standard" MEAs operated under <u>high-efficiency conditions</u> (0.55 V/cell).

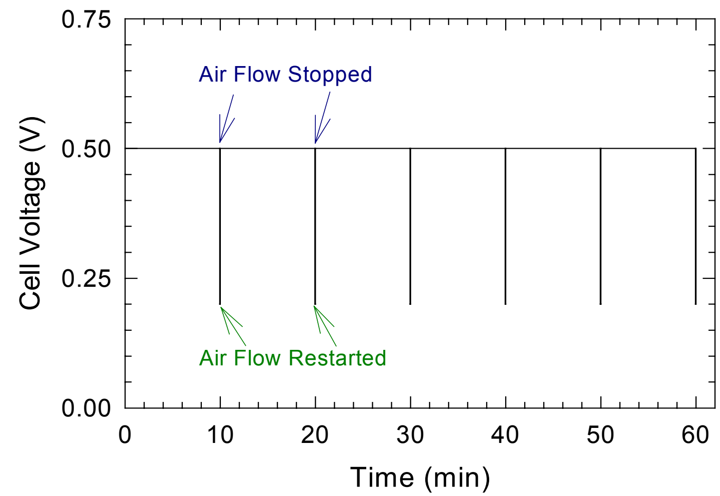
Durability Research

Short -Term Performance Loss: Why & What to Do About It?







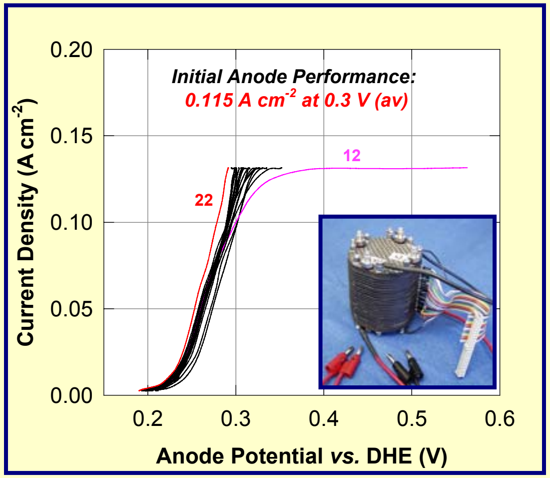


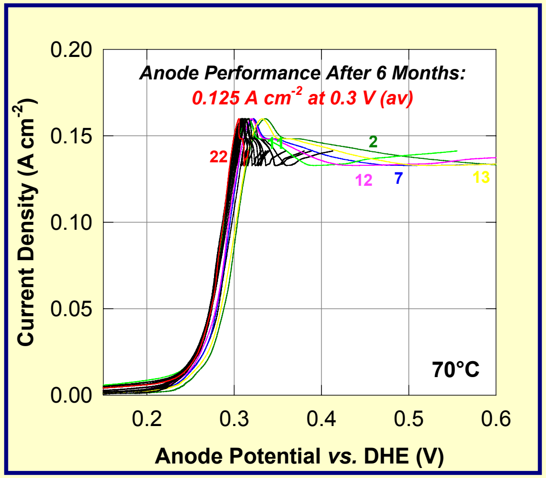
Short-term performance loss due to <u>surface oxidation of the Pt cathode</u> can be regained by voltage (cathode potential) "pulsing", e.g. via cathode air break (system-friendly approach).

Durability Research

Long-Term Performance Loss

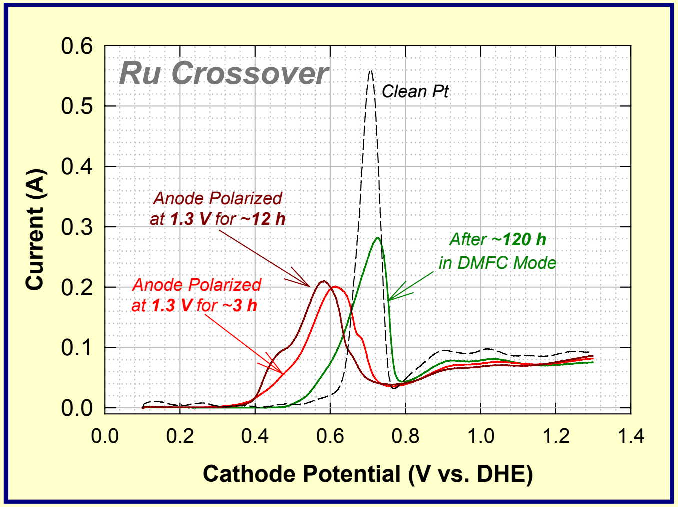
- ***There is little or no Pt-Ru <u>anode</u> performance loss in single-cells or stacks***





- ***Possible cathode losses:***
  - ✓ ***Ru crossover (electronic effects, blocking of O_2 reduction sites)***
  - ✓ ***Diminishing GDL hydrophobicity***
  - ✓ ***Nafion leaching & resulting loss of electrode integrity***

<u>Milestone #4 on Schedule</u>

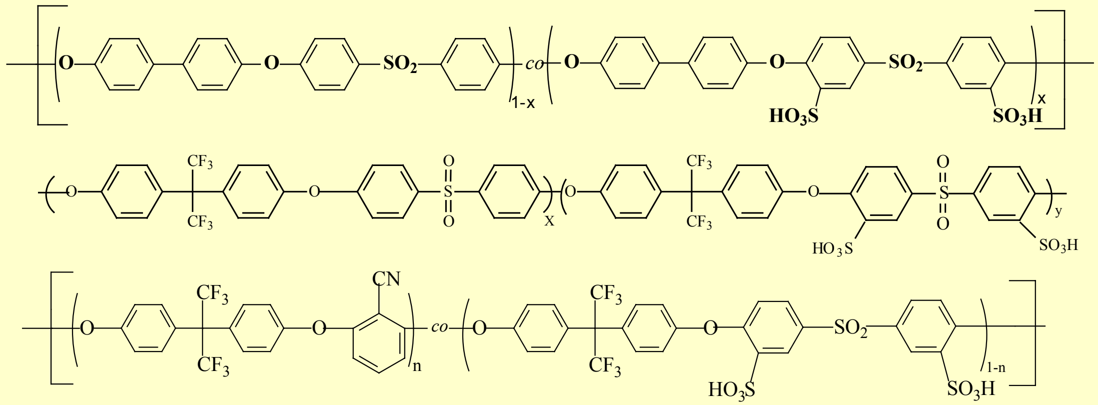


Membrane / MEA Research
Three Poly(Arylene Ether Sulfones)

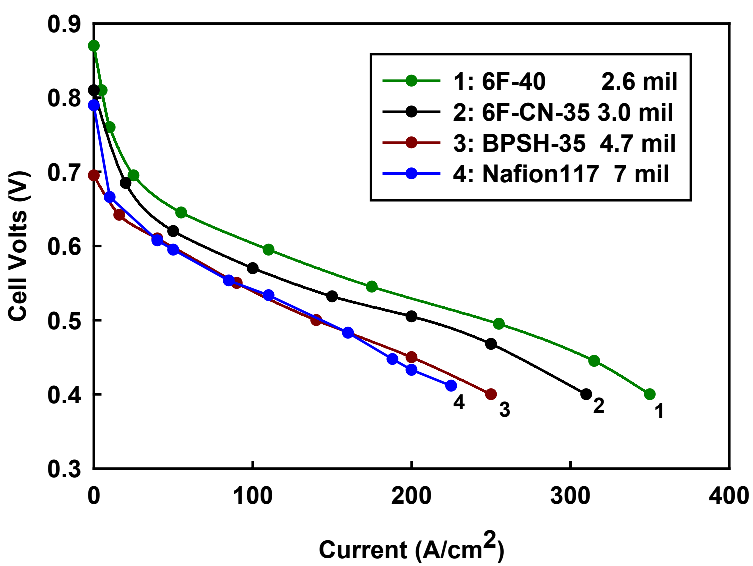
BPSH-XX

6F-XX

6F-CN-XX



XX - percentage of disulfonated monomer units

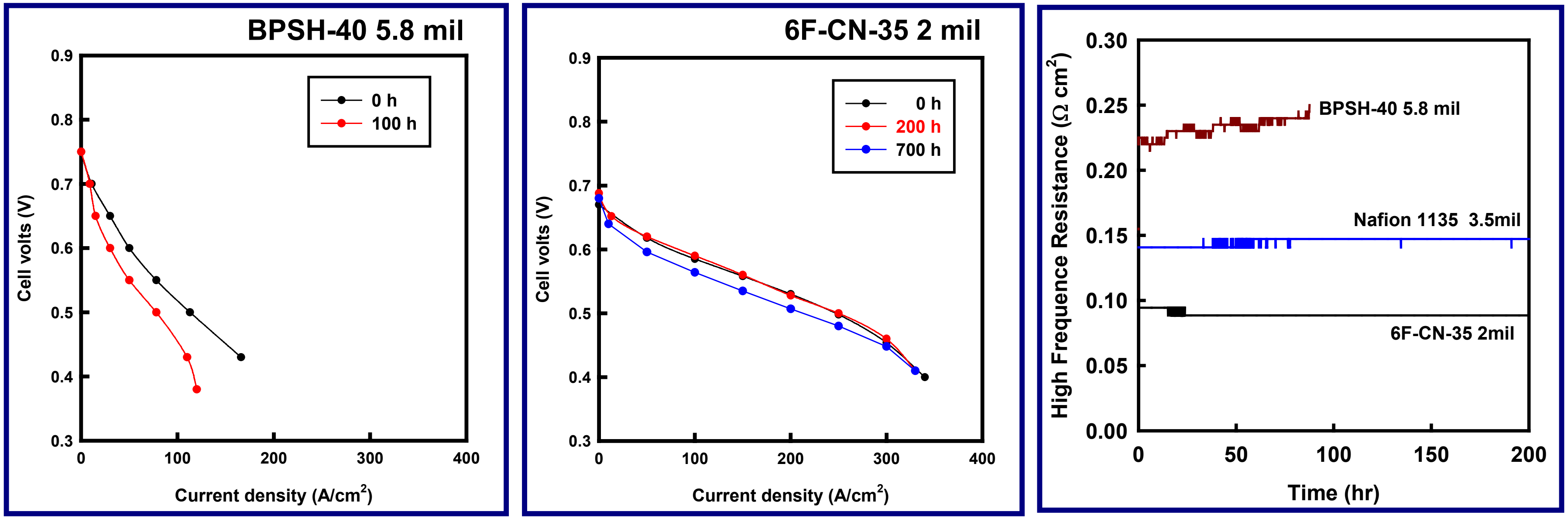


C *Collaboration with Virginia Tech*

Poly(arylene ether sulfones) exhibit either better or similar initial DMFC performance to that measured with Nafion 117.

Membrane / MEA Research

DMFC Performance of Poly(Arylene Ether Sulfones) (80°C, 0.5 V)

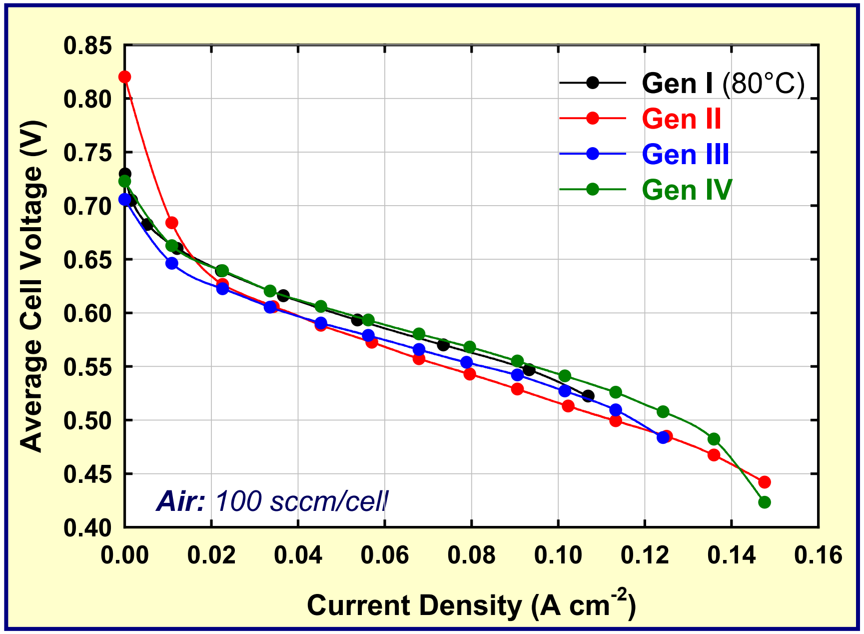


Unlike BPSH, which suffers irreversibly reduced performance after 100 hours, 6F-CN shows no degradation in the first 200 hours and only slight performance drop after 700 hours. Like Nafion (but not BPSH), 6F-CN shows no signs of resistance increase, suggesting good membrane/electrode interface. This represents a significant achievement in alternative DMFC membrane research.

2003 Milestone #5 on Schedule

DMFC Stack Prototypes for Portable Power

Three Generations of Portable 11 W Stacks

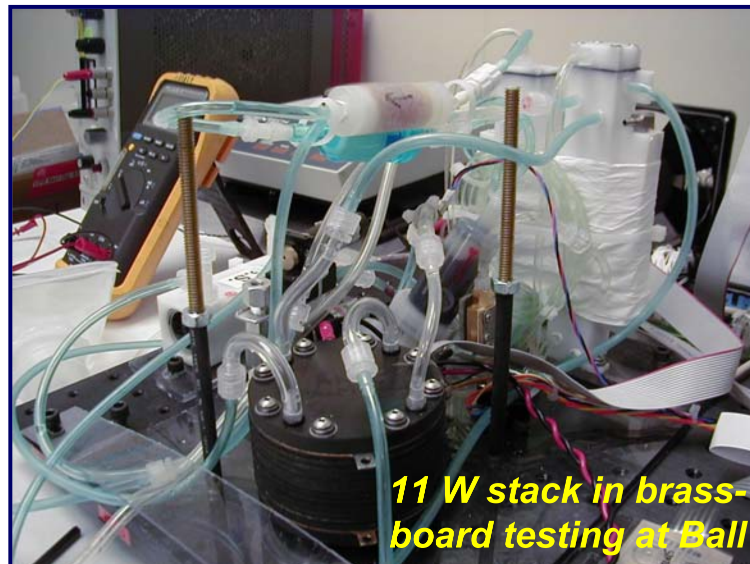


(1) **Generations II, III and IV of 11 W stacks designed, built and successfully tested in FY03**

(2) **Four Generation IV 11 W stacks delivered to Ball Aerospace in January 2003 for integration in two 20 W demo systems**

(3) **Palm Power hardware solutions extensively used in the 500 W APU stack design**

Generation IV stacks



11 W stack in brass-board testing at Ball

C *Collaboration with Ball Aerospace*

500 W APU Stack

Improvements to Hardware & Six-Cell Short Stack

Relative to the original design:

- *Compressive forces reduced and cell-to-cell distribution improved thanks to better gas-diffusion layer design and modified sealing*
- *Individual cell thickness lowered to as little as 0.055” (1.4 mm) due to new hardware used*
- *Mass-per-cell further reduced following footprint optimization*
- *Part count lowered thanks to combining functionality of various stack components*

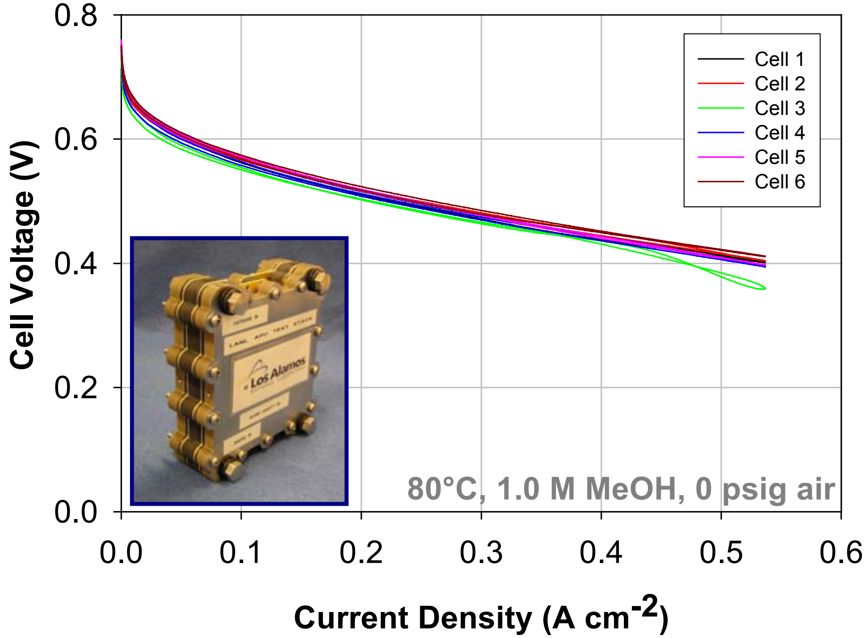
- *Predicted mass of APU stack operating with ~40% total efficiency:* ***3.2 kg***

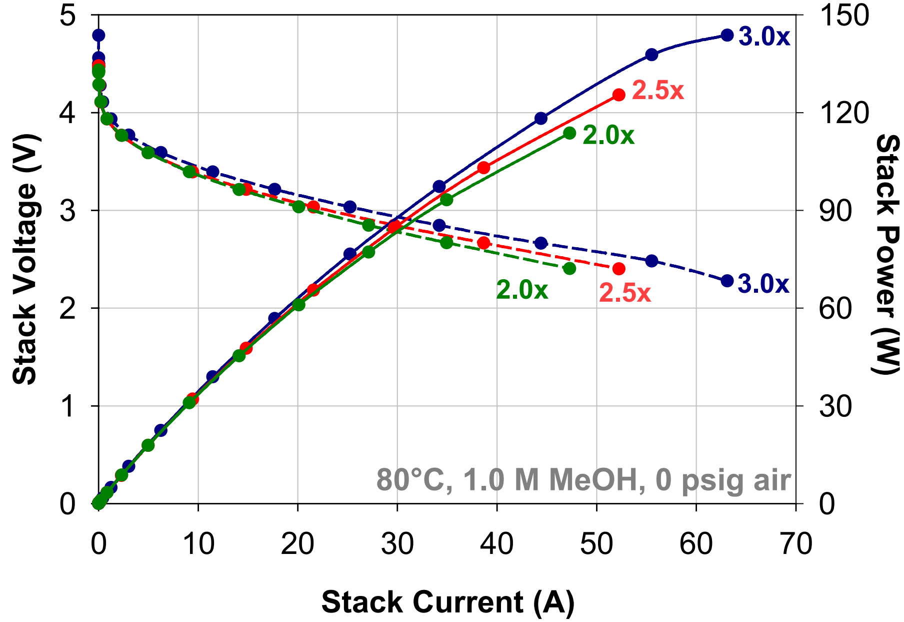
500 W Stack Model

Six-Cell Short Stack

500 W APU Stack

Short Six-Cell Stack Testing





Demonstrated uniform performance of individual cells, high power of 140 W (at 3.0x stoich & zero cathode backpressure) and negligible scale-up penalty from single cell to short stack. Expected maximum power of the full-size stack: 900 W – 1000 W (can be scaled up to 2,000 W, if required).

***2003 Milestone #6 on Schedule** (full-size stack to be built in September)*

2003 DMFC Research at Los Alamos

Summary

Cathode Research:

- ✓ Cathode operating conditions tested for optimum air back-pressure and flow rate
- ✓ Composition of carbon-supported Pt catalysts optimized for good performance at a very low loading of 0.6 mg cm^{-2}
- ✓ Low-stoich operation of cathodes in single cells and stacks achieved

Electrocatalysis:

- ✓ Alternative carbon-supported cathode catalyst demonstrated for over 200 hours with performance by ~17% better than corresponding Pt catalyst
- ✓ Study of the effect of Pt-to-Ru atomic ratio on anode performance continued using, among others, CO probing of active catalyst sites

Performance Durability:

- ✓ Effect of Pt oxide formation on short-term DMFC performance shown; a method for recovering cathode activity developed and demonstrated
- ✓ Possible reasons for long-term MEA degradation identified; Ru crossover through Nafion membrane shown for the first time

2003 DMFC Research at Los Alamos
Summary (II)

Membrane Research:

- ✓ **Novel polymers from the group of sulfonated poly(arylene ether sulfones) used in DMFCs for the first time**
- ✓ **6F and 6F-CN demonstrated to have reduced interfacial resistance relative to "regular" BPSH and superior properties to Nafion in terms of resistance and selectivity**
- ✓ **Extended DMFC lifetime shown with the 6F-CN membrane**

Stack R&D:

- ✓ **Three generations of 11 W stacks for 20 W DMFC system for portable power applications designed, built and tested; four *Generation IV* stacks delivered to Ball Aerospace in January 2003 for integration in two systems**
- ✓ **Design of all components for the 500 W - 900 W APU stack completed; six-cell 100-cm^2 stack built and found to deliver 140 W maximum power at zero cathode back-pressure and air stoich ratio not exceeding three**
- ✓ **Virtually no scale-up penalty from a single cell to six-cell stack detected**

2004 Research Plans

- Investigate mechanisms and design methods for controlling degradation of the Nafion and non-Nafion membrane-electrode assemblies
- Optimize performance and improve durability of systems based on novel alternative membranes, such as 6F and 6F-CN
- Perform theoretical and practical study of the impact of catalyst layer structure on the rate of methanol oxidation and oxygen reduction
- Investigate novel carbon-supported catalysts for low-loading DMFC operation
- Improve DMFC performance by understanding and optimizing hydrophilic/hydrophobic properties of the cathode
- Demonstrate for at least 100 hours sustained operation of a large-surface area stack with air-stoich ratio below two