

VII.K.8 Direct Methanol Fuel Cells

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Projected End Date: Project continuation and direction determined annually by DOE

Objectives

The main research tasks of the project are to develop materials and cell components and to optimize operating conditions of direct methanol fuel cells for maximum power density and fuel conversion efficiency at a minimum cost. Individual objectives include:

- Design and optimize membrane-electrode assemblies (MEAs) for enhanced direct methanol fuel cell (DMFC) performance.
- Advance electrocatalysts for methanol oxidation and oxygen reduction to increase power density and lower total precious metal loading.
- Characterize and optimize non-Nafion[®] polymers with reduced crossover and improved performance.
- Model, design and demonstrate advanced cell components.
- Identify main routes of cell performance degradation and improve cell (stack) performance durability.
- Collaborate with fuel cell industry on efficient system integration and technology transfer to facilitate commercialization of direct methanol fuel cells.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- A. Durability
- B. Cost
- C. Electrode Performance
- D. Thermal, Air and Water Management
- F. Fuel Cell Power System Integration

Technical Targets

Table 1. LANL Progress Toward Meeting DOE Requirements for Consumer Electronics [Table 3.4.8 Technical Targets: Consumer Electronics (sub-Watt to 50-Watt)]

Characteristics	Units	DOE Targets – Complete System		LANL 2005
		2006	2010	
Specific Power	W/kg	30	100	230 (stack specific power)
Power Density	W/L	30	100	~150 (stack power density)
Energy Density	Wh/L	500	1,000	~2,400 (energy density of fuel at 0.55 V/cell – stack design voltage)
Lifetime	hours	1,000	5,000	3,000 (single cell, 15% performance loss)

Approach

- Build, operate and test electrochemical cells and fuel cells with advanced materials, such as anode and cathode catalysts, membranes and MEAs.
- Through experimentation, develop a thorough understanding of the key factors impacting cell performance and durability.
- Maximize efficiency, power, and energy density of DMFCs via creative design of stack components and experimental verification of the hardware performance.

Accomplishments

Electrocatalysis:

- Fabricated and characterized Pt-Co black catalyst with average particle size reduced by 55% relative to the best Pt blacks for DMFC cathodes.
- Developed MEAs with two types of cathode catalysts tolerant to 5-17 M methanol (MeOH); demonstrated high oxygen reduction reaction (ORR) activity and respectable performance durability of both catalyst types.

Membrane & MEA:

- Demonstrated biphenyl sulfone H form (BPSH)-based MEA with better conversion efficiency than Nafion[®].
- Developed new biphenol-based phenyl phosphine oxide copolymer (BPPPO) MEA (hydrocarbon-based) with remarkable long-term stability (11% performance loss over 800 hours).

Durability Research:

- Developed four methods for significantly lowering Ru crossover.
- Introduced novel Nafion[®]-based MEA with 15% performance loss over 3000 hours of operation (vs. 40% loss with the standard MEA); finished detailed comparative performance loss study of both MEAs.

High-Specific-Power Stack for Portable Applications:

- Designed, built and integrated high-specific-power stack; licensed technology to industry.

Future Directions

Remainder of FY 2005:

- Improve oxygen reduction activity of highly dispersed Pt-Co blacks.
- Further minimize ruthenium crossover in DMFCs by combining various methods of Ru stabilization identified to date.

FY 2006 Objectives (crucial to the success of DMFCs for portable power):

- Develop MEAs based on alternative membranes that would enable the use of methanol feed concentration as high as 5.0 M without loss in cell performance and performance durability.
- Through fundamental mechanistic research, eliminate ruthenium crossover from direct methanol fuel cells.
- Improve performance of DMFC anode and cathode by developing better “secondary” catalyst structures.
- Explore mixed-conducting intercalated nanocomposites as DMFC cathode materials with potentially high catalytic activity, full methanol tolerance and good stability.

Introduction

Direct methanol fuel cell research at Los Alamos has focused on developing materials and optimizing performance of direct methanol fuel cells for portable power devices (*e.g.*, commercial electronics, battery replacement for the military) and transportation (*e.g.*, on-board auxiliary power units). The main objective of the DMFC research has been to develop the technology that would allow methanol-based systems to meet performance (power density, energy conversion efficiency, durability) and cost targets.

Approach

At the heart of the Los Alamos National Laboratory (LANL) approach is building, operating and testing electrochemical cells and fuel cells with advanced materials developed onsite and elsewhere. Through experimentation, we attempt to develop a thorough understanding of the key factors that impact DMFC performance and performance durability of Nafion[®] and non-Nafion[®] membranes, methanol-oxidation and oxygen-reduction catalysts, and MEAs. The effort targets maximum fuel conversion efficiency, specific power and energy density at a minimum cost.

Results

In FY 2005, our effort in electrocatalysis has concentrated on developing (i) new supported and unsupported cathode catalysts with average particle size reduced by at least 40% and performance

superior to the best commercial cathode catalysts, and also (ii) methanol-tolerant oxygen-reduction catalysts for mixed-reactant DMFCs. By using carbon-supported and support-free catalyst synthesis methods introduced earlier, we obtained a 60 wt% Pt-Co/C catalyst with average particle size of 6.2 nm and a Pt-Co black catalyst with an even smaller average particle size of 2.7 nm (*cf.* X-ray diffraction patterns in Figure 1a). At low current densities, Pt-Co black catalyst matches the performance of the state-of-the-art anode commercial catalyst (HiSPEC 1000 from Johnson Matthey), but it trails the reference at higher current densities (Figure 1b). Since this is most likely indicative of a problem with catalyst utilization, further effort in Pt-Co electrocatalysis at LANL will focus on improving the anode catalyst structure.

In collaboration with the University of New Mexico, University of Illinois Urbana-Champaign and University of Poitiers in France, we have initiated a study of methanol-tolerant cathode catalysts. The materials developed in this study involve several types of metal porphyrins and chalcogenides. Catalysts in both these classes exhibit good performance and methanol tolerance up to 17 M in concentration.

Membrane/MEA research at LANL has focused on (i) hydrocarbon membranes with enhanced interfacial stability, (ii) improvements in the energy conversion efficiency by using membranes alternative to Nafion[®], and (iii) the impact of methanol concentration on MEA properties. In this

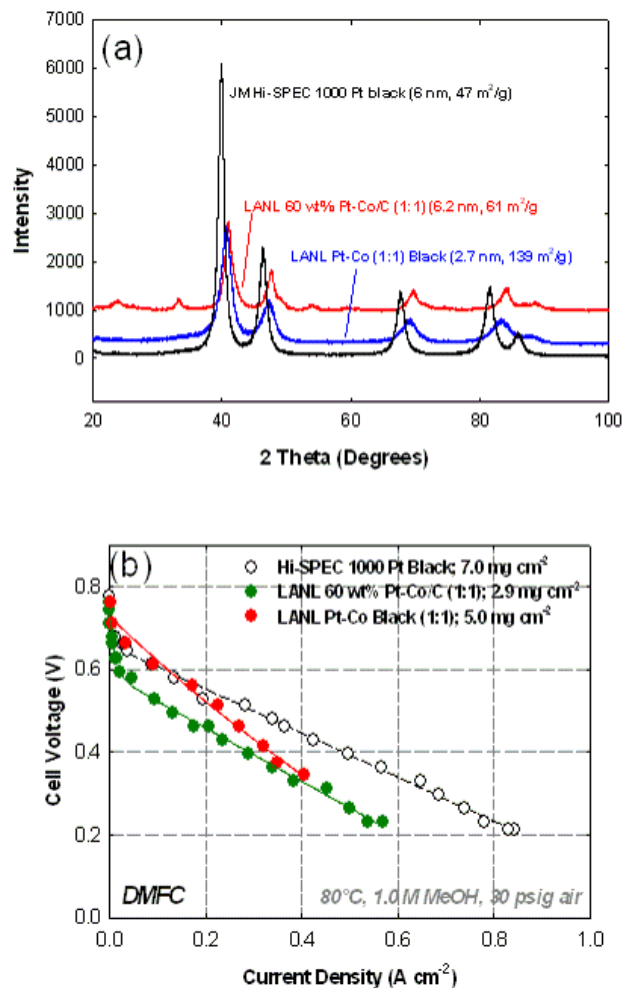


Figure 1. Pt-Co Cathode Catalysts with Reduced Particle Size (a) X-ray diffraction patterns for LANL 60% Pt-Co/C (carbon supported) catalyst, LANL Pt-Co black (unsupported) catalyst, and Johnson Matthey's HiSPEC 1000 reference Pt black catalyst; (b) DMFC performance plots recorded with all four catalysts

work, often performed in close collaboration with Virginia Polytechnic Institute, we have demonstrated for the first time the new membrane based on biphenol phenyl phosphine oxide (BPPPO). Relative to the previously tested BPSH MEAs, the BPPPO-based MEA shows very good durability over 800 hours of DMFC operation (Figure 2), which is comparable to the best Nafion[®]-based systems.

We have also demonstrated that the use of alternative membranes, such as BPSH-30, improves energy conversion efficiency in a DMFC compared

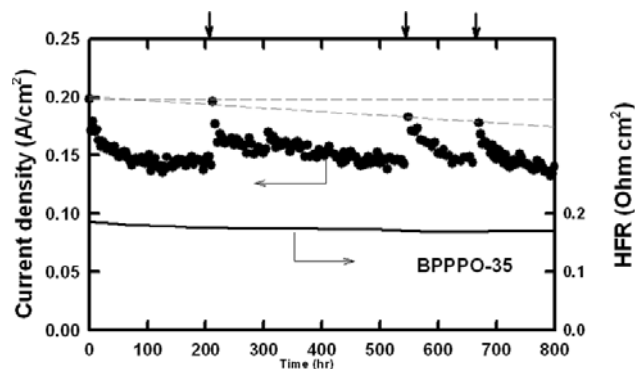


Figure 2. 800-Hour Life Test of the MEA with BPPSO-35 Membrane at 80°C (Total unrecoverable performance loss: 21 mA/cm²; ~11%)

to that provided by a “standard” Nafion[®] 117 MEA. Thanks to the lower crossover and high maintained DMFC performance, the BPSH-30 MEA offers an overall efficiency improvement of 2-3% across the entire range of cell operating currents.

In another membrane/MEA-related effort, we have shown the impact of feed concentration of methanol on membrane conductivity and interfacial resistance. A tenfold increase in concentration, from 0.5 M to 5.0 M, leads to a 30% drop in the membrane/MEA conductivity and even greater (50%) rise in the resistance at the membrane-electrode interface.

This year, in the research effort supported internally by Los Alamos National Laboratory under a technology maturation initiative and by our industrial partner Mesoscopic Devices, Inc., we have achieved substantial progress in the design of a high-specific-power DMFC stack for portable power. After confirming very good performance of newly developed hardware in a short six-cell DMFC stack, we built several full-size 25-cell stacks (Figure 3a). These stacks, weighing 250 g each, have already generated up to 55 W in power (Figure 3b) that translates to a specific power of 230 W/kg. This performance is very close to the level required by the 2006 and 2010 DOE system targets for consumer electronics (*cf.* Technical Targets table above). The high-specific-power stacks from LANL have been integrated by Mesoscopic Devices in their 20-W systems for portable power and demonstrated, among

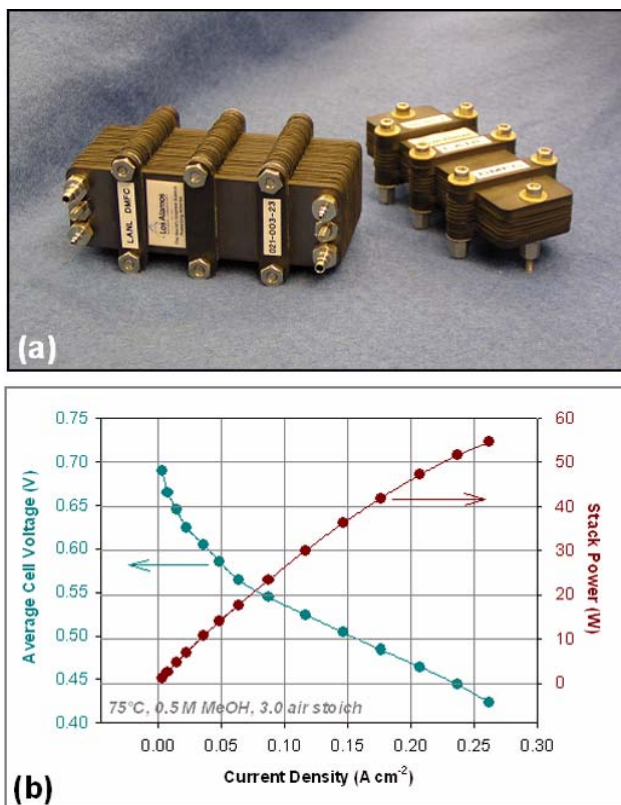


Figure 3. High-Specific-Power DMFC Stacks for Portable Applications (a) Photograph of a short six-cell stack and a full-size 25-cell stack; (b) Polarization and power-density plots recorded for the 25-cell stack

others, at the 2004 Fuel Cell Seminar in San Antonio in November 2004.

DMFC performance durability has become one of the main focal areas of the direct methanol fuel cell research at Los Alamos. Recently, we have implemented a novel approach to making Nafion[®]-based MEAs that includes thermal treatment of the MEA before it is used in the cell. This novel approach has resulted in significantly better performance stability than that of standard Nafion[®] MEAs in use at LANL for DMFC research (Figure 4). Non-recoverable performance loss of the new MEA over 3,000 hours has been ~15%, significantly less than the 40% loss incurred by the standard MEA. A detailed breakdown of electrode performance losses in the two cases has revealed that the new procedure helps both the anode and the cathode to maintain performance over long operating times (Figure 5). The novel MEA anode exhibits virtually

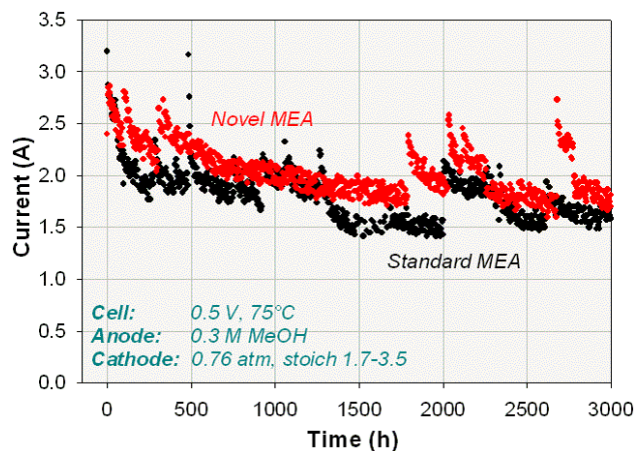


Figure 4. 3000-Hour Life Tests of the Novel and Standard DMFC MEAs

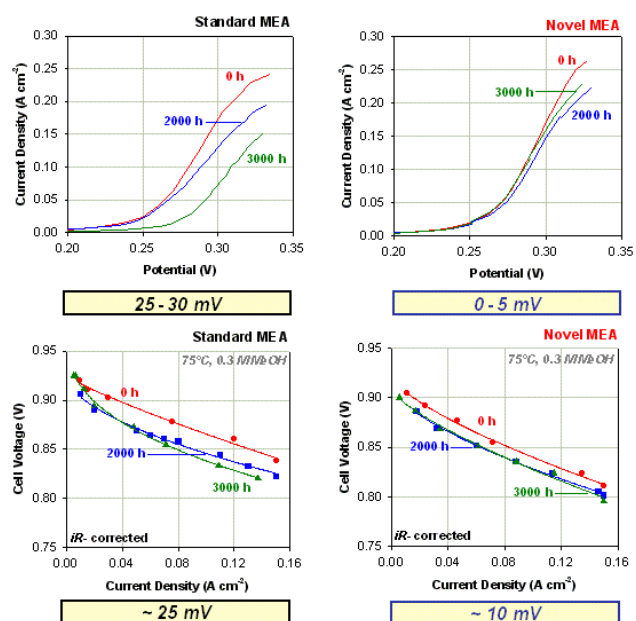


Figure 5. Breakdown of the Anode (top) and Cathode (bottom) Performance Losses with Standard and Novel MEAs over 3000 Hours of DMFC Operation

no performance drop during the life test, while the reference cell's anode loses as much as 25 mV over the same time. Most of the difference in the anode performance can be ascribed to faster decrease in the electrochemical surface area of the standard anode. Similarly, there is a difference in the rate of performance loss of both cathodes, with the reference cell's cathode losing 25 mV versus only a 10-mV performance loss of the novel MEA cathode. In this

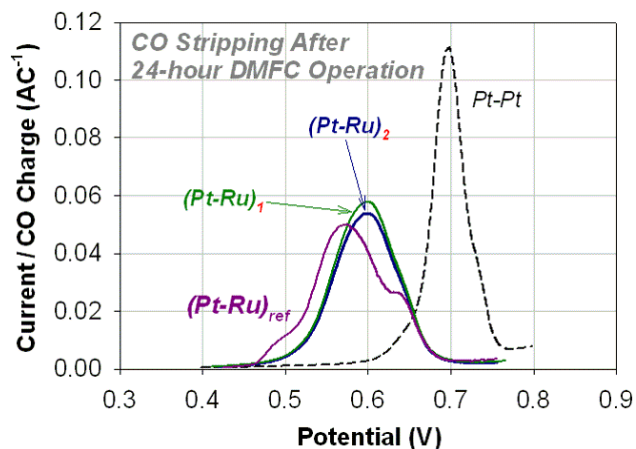


Figure 6. CO stripping data showing the impact of acid pretreatment on the accumulation of crossover Ru at the Pt cathode after 24 hours of DMFC operation. CO stripping from the cathode in cells with untreated anode catalyst, $(\text{Pt-Ru})_{\text{ref}}$, and in Pt anode (no Ru), Pt-Pt, is shown for reference. (See text for further details.)

case, the novel MEA fabrication approach leads to substantial reduction in ruthenium crossover, which is likely to be related again to better stability of the Pt-Ru anode catalyst in the novel MEA. Reduced Ru crossover helps the Pt cathode maintain good ORR activity, otherwise lowered by Ru deposition.

The use of the novel MEA approach represents one of four methods recently tested at LANL in order to minimize Ru crossover in DMFCs with Pt-Ru anodes. The other three are (i) acid pretreatment of the anode catalyst, (ii) acid pretreatment of the membrane with the anode catalyst applied already to it, and (iii) curing catalyst layers via decal transfer to the membrane. As shown by CO stripping data in Figure 6, acid pretreatment of the anode catalyst either already applied to the membrane, $(\text{Pt-Ru})_1$, or before application, $(\text{Pt-Ru})_2$, leads to less Ru accumulation at the cathode surface than observed in the cells using standard untreated MEA, $(\text{Pt-Ru})_{\text{ref}}$.

Conclusions

The key conclusions from the DMFC research performed at LANL in the past year can be summarized as follows:

- Reduction in average particle size of Pt-Co catalyst, the unsupported catalyst in particular, leads to improved oxygen reduction kinetics.

Mass-transfer properties of the Pt-Co black catalyst need improvement before that catalyst can become practical.

- Fully methanol-tolerant cathode catalysts with good long-term stability are achievable. However, ORR activity of these catalysts needs to be enhanced.
- Membrane-electrode assemblies based on alternative polymers, such as BPPPO-35, provide good performance and durability, no worse than those of Nafion[®]-based MEAs. Thanks to lower methanol crossover, alternative polymers offer better overall fuel conversion efficiency.
- DMFC stacks with specific power as high as 350-400 W/kg can be manufactured, possibly bringing performance of the entire DMFC system close to the DOE targets for not only FY 2006 but also FY 2010.
- Durability of Nafion[®]-based MEAs can be substantially improved via a novel MEA fabrication and curing process.
- There are several ways of reducing ruthenium crossover and protecting DMFC cathodes from the negative impact of Ru on the ORR rates. The acid treatment of the anode catalyst, either alone or after it has been applied to the membranes, is one of them.

Special Recognitions & Awards

1. Individual Los Alamos National Laboratory Patent & Licensing Awards for E. Brosha, M. S. Wilson and P. Zelenay, February 2005.
2. J. C. Ramsey and P. Zelenay, "Compact Direct Methanol Fuel Cell Stack," Los Alamos National Laboratory Technology Maturation Award, August 1, 2005.

Patents Issued

1. "Direct Methanol Fuel Cell and System," M. S. Wilson, U.S. Patent 6,808,838 B1, October 26, 2004.
2. "Direct Methanol Fuel Cell Stack," M. S. Wilson and J.C. Ramsey, U.S. Patent 6,864,004 B2, March 8, 2005.
3. "High Specific Power Direct Methanol Fuel Cell Stack," J.C. Ramsey and M. S. Wilson, U.S. Patent 20050118491 A1, June 2, 2005.

FY 2005 Publications

1. "Researchers Redefine the DMFC Roadmap," P. Piela and P. Zelenay, *The Fuel Cell Review*, 1, 17-23 (2004).
2. "Ruthenium Crossover in the Direct Methanol Fuel Cell with a Pt-Ru Anode," P. Piela, C. Eickes, E. Brosha, F. Garzon and P. Zelenay, *J. Electrochem. Soc.*, 151, A2053-A2059 (2004).
3. "Direct Methanol Fuel Cell Performance of Disulfonated Poly(Arylene Ether Benzonitrile) Copolymers," Y. S. Kim, M. Sumner, W. Harrison, J. E. McGrath, B. S. Pivovar, *J. Electrochem. Soc.* 151, 12, A2150 (2004).
4. "Sulfonated Poly(Arylene Ether Sulfone) Copolymer Proton Exchange Membranes: Composition and Morphology Effects on Methanol Permeability," Y. S. Kim, M. Hickner, L. Dong, B. Pivovar and J. E. McGrath, *J. Membrane Sci.*, 243, 317-326 (2004).
5. "New Proton Conducting Sulfonated Poly(Arylene Ether) Copolymers Containing Aromatic Nitriles," M. J. Sumner, W. L. Harrison, R. M. Weyers, Y. S. Kim, J. E. McGrath, J. S. Riffle, A. Brink, M. H. Brink, *J. Membrane Sci.*, 239, 2, 199-211 (2004).
6. "Sulfonated Naphthalene Dianhydride Based Polyimide Copolymers Proton Exchange Membrane Fuel Cells (PEMFC): I. Monomer and Copolymer Synthesis," B. Einsla, Y. T. Hong, Y. S. Kim, F. Wang, N. Gunduz and J. E. McGrath, *J. Polym. Sci. Pol. Chem.*, 42, 862 (2004).
7. "Alternative Polymer Systems for Proton Exchange Membranes (PEMs)," M. Hickner, H. Ghassemi, Y. S. Kim, B. Einsla, and J. E. McGrath, *Chem. Rev.*, 104, 4587-4612 (2004).
8. "Electrochemical and XRD Characterization of Pt-Ru Blacks for DMFC Anodes," C. Eickes, E. Brosha, F. Garzon, G. Purdy, P. Zelenay, T. Morita and D. Thompsett, in *Proton Conducting Membrane Fuel Cells III*, M. Murthy, T. F. Fuller, J. W. Van Zee, S. Gottesfeld (Eds.), ECS Proceedings, Electrochemical Society, Pennington, New Jersey, vol. 2002-31, pp. 450-467 (2005).
9. "A Six-Cell 'Single-Cell' Stack for Stack Diagnostics and Membrane Electrode Assembly Evaluation," B. Pivovar, F. Le Scornet, C. Eickes, C. Zawodzinski, G. Purdy, M. Wilson, and P. Zelenay, in *Proton Conducting Membrane Fuel Cells III*, M. Murthy, T. F. Fuller, J. W. Van Zee, S. Gottesfeld (Eds.), ECS Proceedings, Electrochemical Society, Pennington, New Jersey, vol. 2002-31, pp. 481-489 (2005).
10. "Optimization of Carbon-Supported Platinum Cathode Catalysts for DMFC Operation," Y. Zhu, E. Brosha and P. Zelenay, in *Proton Conducting Membrane Fuel Cells III*, M. Murthy, T. F. Fuller, J. W. Van Zee, S. Gottesfeld (Eds.), ECS Proceedings, Electrochemical Society, Pennington, New Jersey, vol. 2002-31, pp. 490-505 (2005).
11. "The Effect of BPSH Post Treatment on DMFC Performance and Properties," M. Hickner, Y. Kim, J. McGrath, P. Zelenay and B. Pivovar, in *Proton Conducting Membrane Fuel Cells III*, M. Murthy, T. F. Fuller, J. W. Van Zee, S. Gottesfeld (Eds.), ECS Proceedings, Electrochemical Society, Pennington, New Jersey, vol. 2002-31, pp. 530-540 (2005).
12. "Poly(Arylene Ether Sulfone) Copolymers from Sulfonated Monomers Building Blocks: Synthesis, Characterization and Performance – A Review," W. L. Harrison, Y. S. Kim, M. Hickner, J. E. McGrath, *Fuel Cells*, 5, 201-212 (2005).

FY 2005 Presentations

1. 206th Meeting of the Electrochemical Society, Honolulu, Hawaii, October 3 – 8, 2004. Title: "Novel Process for Improved Long-Term Stability of DMFC Membrane-Electrode Assemblies," C. Hamon, G. Purdy, Y. S. Kim, B. Pivovar and P. Zelenay* .
2. 206th Meeting of the Electrochemical Society, Honolulu, Hawaii, October 3 – 8, 2004. Title: "Direct Measurement of *iR*-Free Individual-Electrode Overpotentials in PEFC," P. Piela, T. Springer, M. Wilson, J. Davey and P. Zelenay* .
3. 206th Meeting of the Electrochemical Society, Honolulu, Hawaii, October 3 – 8, 2004. Title: "Non-Platinum Electrocatalysts for Polymer Electrolyte Fuel Cells: Methanol-Tolerant Cathode Catalyst," S. Levendosky, P. Atanassov* , B. Piela and P. Zelenay.
4. 206th Meeting of the Electrochemical Society, Honolulu, Hawaii, October 3 – 8, 2004. Title: "The Importance of Interfaces in Membrane Optimization for DMFCs," Y. S. Kim, J. E. McGrath, B. S. Pivovar* .
5. 206th Meeting of the Electrochemical Society, Honolulu, Hawaii, October 3 – 8, 2004. Title: "The Effect of Methanol Concentration on Membrane Conductivity and Interfacial Resistance in DMFCs," Y. S. Kim and B. S. Pivovar.
6. 206th Meeting of the Electrochemical Society, Honolulu, Hawaii, October 3 – 8, 2004. Title: "Zirconium Phenylphosnate/Poly(arylene ether sulfone) Composite Membranes for Proton Exchange Membrane Fuel Cells," M. Hill, B. Einsla, Y. S. Kim, J. McGrath.

7. 206th Meeting of the Electrochemical Society, Honolulu, Hawaii, October 3 – 8, 2004. Title: “Membrane-Electrode Interfacial Degradation in Nafion based PEMFCs and DMFCs,” A. Siu, Y. S. Kim, B. S. Pivovar.
8. 206th Meeting of the Electrochemical Society, Honolulu, Hawaii, October 3 – 8, 2004. Title: “Sulfonated Poly(arylene ether sulfone) as Candidates for Proton Exchange Membranes: Influence of Substitution Position on Membrane Properties,” J. E. McGrath, W. L. Harrison, B. Einsla, N. Arnett, Y. S. Kim, B. Pivovar.
9. Fuel Cell Seminar, San Antonio, Texas, November 1 – 5, 2004. Title: “Influence of Membrane-Electrode Interface on Long-Term Performance of Direct Methanol Fuel Cells,” Y. S. Kim, B. Pivovar.
10. 4th IUPAC World Polymer Congress, Paris, France, July 4 – 9, 2004. Title: “New PEM Membranes, Catalyst Layer Materials, and MEAs for Fuel Cells,” J. E. McGrath, W. L. Harrison, B. Einsla, M. Hickner, B. Pivovar, Y. S. Kim, A. Brink, H. Brink, and R. S. Ward, MACRO 2004.
11. 2004 International Taipei Power Forum & Exhibition, Taipei, Taiwan, December 1 – 3, 2004. Title: “DMFC Research and Design Trends in Los Alamos National Laboratory and Other US Fuel Cell Centers,” P. Zelenay* (invited keynote lecture).
12. Industrial Technology Research Institute, Hsinchu, Taiwan, December 6, 2004. Title: “Selected Aspects of Direct Methanol Fuel Cell Research at LANL,” P. Zelenay* (invited lecture).
13. Industrial Technology Research Institute, Hsinchu, Taiwan, December 7, 2004. Title: “Direct Measurement of iR -free Individual Electrode Overpotentials in PEFC,” P. Zelenay* (invited lecture).
14. Samsung Advanced Institute of Technology, Suwon, Korea, December 9, 2004. Title: “Direct Methanol Fuel Cell Research at Los Alamos National Laboratory,” P. Zelenay* (invited lecture).
15. Catalysis Club of Chicago, Chicago, Illinois, January 10, 2005. Title: “Electrocatalysis: The Key to Polymer Electrolyte Fuel Cell Success,” P. Zelenay* (invited lecture).
16. Tactical Power Sources Summit, Arlington, Virginia, February 1 – 2, 2005. Title: “Research and Design Trends in Direct Methanol Fuel Cells for Portable Power,” J. Ramsey* and P. Zelenay (invited keynote lecture).
17. Advances in Materials for Proton Exchange Membrane Fuel Cell Systems 2005, Asilomar Conference Grounds, Pacific Grove, California, February 20 – 23, 2005. Title: “Direct Methanol Fuel Cell Performance of Partially Fluorinated Disulfonated Poly(Arylene Ether Sulfone) Random (Statistical) Copolymers,” M. Hill, B. R. Einsla, Y. S. Kim, W. Harrison, B. S. Pivovar, and J. E. McGrath.
18. Advances in Materials for Proton Exchange Membrane Fuel Cell Systems 2005, Asilomar Conference Grounds, Pacific Grove, California, February 20 – 23, 2005. Title: “Disulfonated Poly(Arylene Ether Benzonitrile) Copolymers (PAEB) for Proton Exchange Membrane Fuel Cells (PEMFC),” M. Sankir, Y. S. Kim, J. E. McGrath.
19. Advances in Materials for Proton Exchange Membrane Fuel Cell Systems 2005, Asilomar Conference Grounds, Pacific Grove, California, February 20 – 23, 2005. Title: “Optimizing Alternative Membranes in DMFCs – Actual Performance Improvements,” B. S. Pivovar, Y. S. Kim.
20. Small Fuel Cells 2005, Washington, DC, April 27 – 29, 2005. Title: “Advancements in DMFC MEAs and Stacks for Portable Power Applications,” P. Zelenay* and J. Ramsey (invited lecture).
21. IDGA: New and Alternative Energy Sources, Next Generation Power for the Military, Tysons Corner, Virginia, June 28 – 29, 2005. Title: “Advancements in Direct Methanol Fuel Cell Technology at Los Alamos National Laboratory,” J. Ramsey* and P. Zelenay.
22. First Symposium on MEA Manufacturing for Hydrogen Applications, Edison Materials Technology Center (EMTEC), Dayton, Ohio, August 9 – 11, 2005. Title: “Overview of Fuel Cell Membrane Electrode Assemblies (MEAs) at Los Alamos National Laboratory (LANL),” J. Davey*, M. Wilson, P. Zelenay, J. Valerio, and G. Bender (invited lecture).