VII.K.8 Direct Methanol Fuel Cells

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Start Date: October, 1997
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)]

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
<th>DOE Targets – Complete System</th>
<th>LANL 2005</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2006</td>
<td>2010</td>
</tr>
<tr>
<td>Specific Power</td>
<td>W/kg</td>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>Power Density</td>
<td>W/L</td>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>Energy Density</td>
<td>Wh/L</td>
<td>500</td>
<td>1,000</td>
</tr>
<tr>
<td>Lifetime</td>
<td>hours</td>
<td>1,000</td>
<td>5,000</td>
</tr>
</tbody>
</table>

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
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 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
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 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
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 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, (Pt-Ru)$_1$, or before application, (Pt-Ru)$_2$, leads to less Ru accumulation at the cathode surface than observed in the cells using standard untreated MEA, (Pt-Ru)$_{ref}$.

**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**


**Patents Issued**

FY 2005 Publications

FY 2005 Presentations


