

V.D.2 Facilitated Direct Liquid Fuel Cells with High Temperature Membrane Electrode Assemblies

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Technical Targets

This project falls under DOE's incubator initiative, which explores high impact research in new areas. Thus, the technical targets for this project were created relative to the state-of-the-art DMFC system, the only other viable direct fuel oxidation system at this time (see Table 1).

TABLE 1. Progress towards Meeting Technical Targets for Direct DME Oxidation

Key Performance Indicator (this period)	Current DMFC	Target	Project Status
Total precious metal loading	5 mg _{PGM} /cm ²	3 mg _{PGM} /cm ²	4.1 mg _{PGM} /cm ²
Anode mass-specific activity	50 A/g at 0.5 V	75 A/g at 0.5 V	50 A/g at 0.5 V
Crossover current	60–120 mA/cm ² (*)	<60 mA/cm ²	6 mA/cm ²

(*) 60 mA/cm² with 0.5 M methanol, 80°C, Nafion® 117; 120 mA/cm² with 1.0 M methanol
 PGM – platinum group metal

Overall Objectives

- Demonstrate direct dimethyl ether (DME) oxidation with a high temperature membrane electrode assembly (MEA) that achieves significantly better performance than direct methanol fuel cells (DMFC).
- Leverage a highly active ternary catalyst for high temperature DME fuel cells.

Fiscal Year (FY) 2017 Objectives

- Establish enhanced kinetics for DME oxidation at the higher temperatures.
- Demonstrate DME oxidation anode specific current (A/g_{PGM}) equivalent or better than that obtained for the state-of-the-art DMFC.
- Evaluate DME crossover, compare to methanol crossover in DMFC.

Technical Barriers

This project addresses the following technical barriers from Section 3.4.5 Fuel Cells of the Fuel Cell Technologies Program Multi-Year Research, Development, and Demonstration Plan [1], using DMFC systems as a reference fuel cell system.

- (A) Durability (catalyst, membrane)
- (B) Cost (catalyst, system)
- (C) Performance (catalyst, electrodes, MEAs)

FY 2017 Accomplishments

- Identified cathode catalyst loading impeding anode activity.
- Demonstrated anode mass-specific activity for direct DME oxidation at high temperature (180°C) equivalent with benchmark PtRu catalyst equivalent to state-of-the-art DMFC (80°C).
- Demonstrated very low crossover currents for DME at high temperature compared to DMFC, at least an order of magnitude improvement.



INTRODUCTION

In searching for an exemplary carbon-neutral fuel, DME may be one of the most appealing candidates. This simplest of the ethers can be readily produced from renewably sourced hydrogen and CO₂, making it an effective hydrogen carrier. Being both nontoxic and easy to be liquefied under moderate pressure, DME closely matches diesel and has been run in trucks. Recently, Los Alamos National Laboratory (LANL) demonstrated the potential for direct oxidation of DME in a fuel cell [2]. Thus, DME could bridge both internal combustion and fuel cell technologies, while remaining carbon neutral with low or no ancillary emissions.

LANL has identified a highly active catalyst for direct oxidation of DME that already in the early phase of development allows for matching performance of the DMFC when using typical low-temperature perfluorosulfonic acid membranes. However, the output is not sufficient to approach commercial acceptance targets for higher power applications with considerable precious metal cost. More importantly, the LANL work has noted an acute sensitivity of the DME oxidation rate to temperature increase. High-temperature MEAs, based on phosphoric acid-imbibed membranes, operate at 160°C to 180°C without additional water and are highly tolerant to carbon monoxide—an intermediate of DME oxidation. This work is to exploit a novel ternary LANL anode catalyst with the features of high-temperature operation to produce high-power, low-cost direct DME MEAs. We envision the use of such systems as auxiliary electrical power for transport applications.

APPROACH

The project consists of three phases. In the first phase, we demonstrated direct oxidation of DME at a small-scale (5 cm²) MEA without the advanced catalyst. The second phase focused on the development of a small-scale gas diffusion electrode matched for the advanced LANL catalyst; however, we first used a binary catalyst that has good activity for DME oxidation. In the last phase, we will scale up MEA to a 50 cm² size and optimize the gas diffusion electrode structure for the use in practical devices. We initially employed two kinds of high-temperature membranes. One is polybenzimidazole (PBI) and is characterized as a high-acid, low-solids material. The other is referred to by a generic Advent trademark TPS[®], and, relative to PBI, is low-acid, high-solids material based on pyridine and polysulfone. Throughout the three experimental phases, key performance indicators, such as power output, amount of precious metal employed, and durability, will be compared to the state-of-the-art DMFC and incorporated as project milestones. We are currently in the second phase.

RESULTS

Cathode catalyst loading impeding anode reaction. The objective of this project has been to demonstrate superior anode activity for direct oxidation of a high energy content fuel. In actual test systems, this objective can be impeded if the cathode reaction (reduction of oxygen in air) limits whole fuel cell performance. Additionally, the project has defined a total PGM loading limit in order to be competitive with state-of-the-art DMFC, yet one method to increase current when limited by slow reactions is to increase the amount of PGM employed. Thus, initially we kept the cathode PGM loading fixed at a reasonable level and experimented with changing only the anode loading. However, as Figure 1 shows, our initial loading on the cathode limited the full

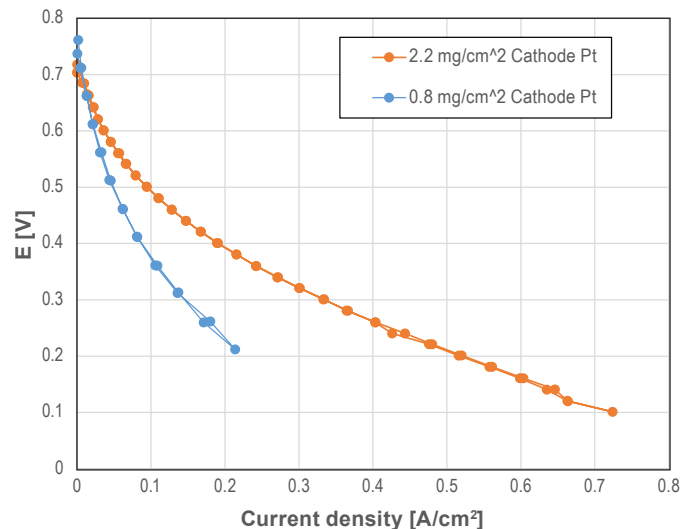


FIGURE 1. Impact of increasing cathode PGM loading for PBI-based MEA DME fuel cell performance at 180°C. Cathode: Pt-alloy/C as indicated; air 500 sccm, backpressure 3.5 psig. Anode: HiSPEC[®] 12100 PtRu/C 1.9 mg/cm²; DME 125 sccm, humidified at backpressure 3.5 psig.

reaction and fuel cell performance. Figure 1 demonstrated a substantial improvement in DME oxidation current by increasing the *cathode* platinum loading from 0.8 mg Pt/cm² to 2.2 mg Pt/cm².

Improvement in anode mass specific activity. Having established an improved cathode configuration, we were able to incorporate the benchmark PtRu anode catalyst in various configurations with the objective of maximizing activity and minimizing mass transport resistance. The general approach is to use the benchmark catalyst to develop well-performing architectures, and then use that configuration as the first trial for the LANL PtRuPd catalyst. The process of developing architectures for new catalysts involves a materials approach whereby a key performance indicator, anode mass specific activity in this case, is gauged as a function of electrode layer porosity, hydrophobicity, and phosphoric acid loading. Citing the results of Figure 2, we note several salient observations. First, with a combination of higher cathode catalyst loading and improved electrode structure, we have almost doubled the anode specific current from 32 A/g_{PGM} in 2016 to 50 A/g_{PGM} at 0.5 V. Second, when comparing direct DME oxidation at a lower temperature MEA (green squares), we obtain more than double the anode specific current but employed half the total PGM loading and nearly tenfold less pressure on the DME gas feed (26 psig vs. 3.5 psig), whereby higher pressures typically increase current. While not at our final goal of 75 A/g_{PGM}, these results confirm the potential for a direct DME fuel cell exceeding the state-of-the-art DMFC.

Crossover current. For any fuel cell employing a membrane as electrolyte, the diffusion of fuel (for example, hydrogen, methanol, or DME) from the anode to the cathode

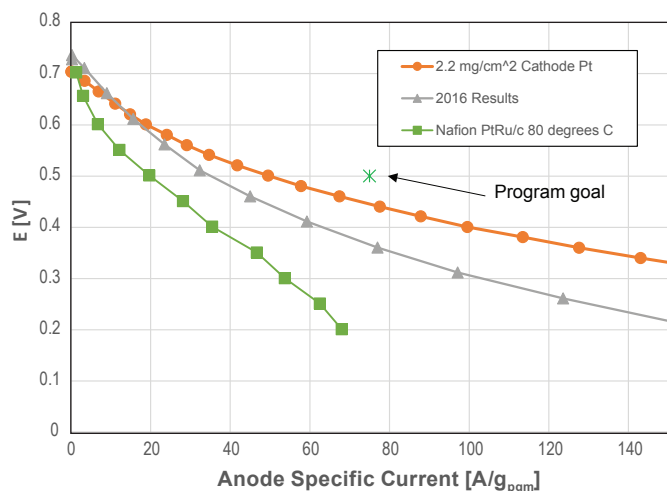


FIGURE 2. Anode-specific current for PBI-based MEA DME fuel cell performance at 180°C. Orange circles: replotted data from Figure 1 as anode-specific current; gray triangles: 2016 Results, HiSPEC[®] 12100 PtRu/C 1.9 mg PGM/cm², Pt/C 0.8 mg Pt/cm²; green squares: LANL data from prior project, DME at PtRu, 80°C, total 8 mg/cm² PGM, 26 psig vs. 3.5 psig of this project.

represents a loss in performance not only from efficiency, but also potential losses in operating voltage. One metric for fuel crossover is to measure the effective current obtained by oxidizing the fuel that diffuses through the membrane, and ultimately, relating this current to a molar flux once the reaction mechanism is understood. However, using only the current is a good approximation of loss of fuel through the membrane.

A typical crossover experiment configures the single cell MEA as a detector, that is, a voltage is applied across the anode and cathode and current is measured. For our studies, we used a high temperature MEA and introduced nitrogen to the anode compartment, and DME to the cathode. By applying a voltage bias to the MEA, DME that diffuses through the PBI membrane to the anode compartment is oxidized. Figure 3 illustrates the results of such a test. One sees that once the bias voltage is high enough to oxidize DME, current flows. In the absence of DME, no current is generated. What makes these results remarkable is that we obtain roughly 6 mA/cm² of crossover current (oxidation of DME that diffuses through the membrane), which compares

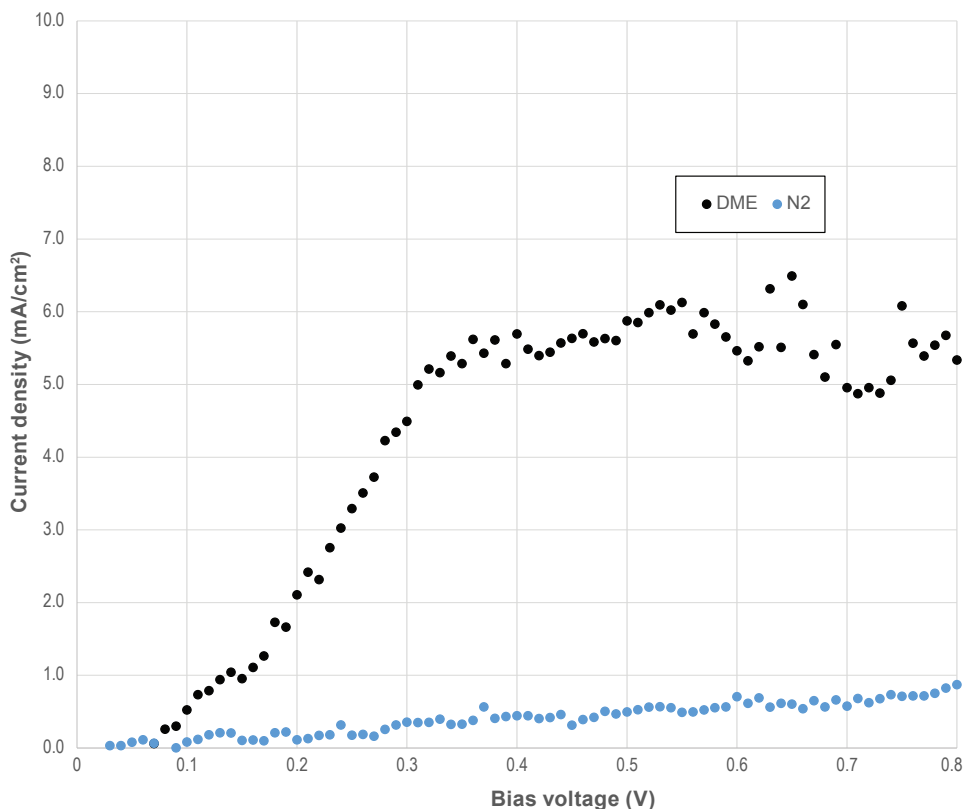


FIGURE 3. Crossover current for DME in high-temperature polymer electrolyte membrane. Anode: PtRu 2.52 mg/cm²; N₂ 3.5 psig backpressure; 100 sccm; cathode: Pt alloy; 3.5 psig DME/H₂O backpressure; DME : water = 1 : 3; DME 125 sccm; water 0.3 mL/min; membrane: PBI; 180°C. Cell size: 5 cm².

favorably to standard currents of 60–120 mA/cm² for DMFC cells operating with either 0.5 M or 1.0 M methanol.

CONCLUSIONS AND UPCOMING ACTIVITIES

Based on the improved anode specific current and very low crossover currents, direct DME fuel cells offer great potential to exceed the performance of the state-of-the-art DMFC. While we have started to evaluate assemblies with the LANL ternary catalyst, the morphology of this material is significantly different than that of our benchmark PtRu, and we do not get the immediate improvement expected. Upcoming efforts are focused on revising electrode processing conditions to fully realize the expected activity of the LANL catalyst.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. “Facilitated Direct Dimethyl Ether Fuel Cells through High Temperature Membrane Electrode Assemblies,” Emory S. De Castro, Andrew Van Dyke, Xi Yin, Hoon Taek Chung, and Piotr Zelenay, 230th Electrochemical Society Meeting, Oahu, HI, USA, October 2–7, 2016; Abstract 2396.
2. “High Temperature Membrane Electrode Assemblies for Intermediate Temperature Fuel Cells: Past, Present, and Future,” Emory S. De Castro, Brian Benicewicz, Xi Yin, Hoon Taek Chung, and Piotr Zelenay, 231st Electrochemical Society Meeting, New Orleans, MS, USA, October 2–7, 2016; Abstract 97024.

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1. Multi-Year Research, Development, and Demonstration Plan: Section 3.4 Fuel Cells, Fuel Cell Technologies Office, 2016. http://energy.gov/sites/prod/files/2016/06/f32/fcto_myrd_fuel_cells_0.pdf
2. Li, Q., Wen, X., Wu, G., Chung, H.T., and Zelenay, P., “High-Activity PtRuPd/C Catalyst for Direct Dimethyl Ether Fuel Cell,” *Angew. Chem. Int. Ed.*, **54**, 1–6, 2015.