
Facilitated Direct Liquid Fuel Cells with High-Temperature Membrane Electrode Assemblies

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Overall Objectives

- Demonstrate the potential of direct liquid fuel cells by exploiting features of high-temperature membrane electrode assemblies (MEAs).
- Show feasibility that direct dimethyl ether (DME) oxidation at a high-temperature MEA performs significantly better than direct methanol fuel cells (DMFC) operating at less than 100°C when compared across metrics such as anode specific current, precious group metal (PGM) loading, power output, durability, and crossover losses.
- Leverage highly active catalysts for high-temperature direct DME fuel cells.

Fiscal Year (FY) 2019 Objectives

- Develop internal fuel cell testing for direct DME oxidation.

- Determine baseline stability profiles.
- Leverage catalyst collaborations for enhanced power production.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹, using DMFC systems as a reference fuel cell system:

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

Technical Targets

This program 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 (SOA) DMFC system, the only other viable direct fuel oxidation system at this time.

The DOE technical targets and our current project status are listed in Table 1 for comparison.

FY 2019 Accomplishments

- Converted hydrogen-air single cell test unit to DME-air.
- Established baseline decay using daily start-stop cycles.
- Demonstrated improved power with a new anode catalyst and total precious metal loading under 4.5 mg_{PGM}/cm².

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

Table 1. Progress toward Meeting Technical Targets for Direct DME Oxidation

Key Performance Indicator	Units	Current DMFC	Target	Program Status (5-cm ² cell)
Total precious metal loading	mg _{PGM} /cm ²	5	3	4.5
Anode mass-specific activity	A/g _{PGM} at 0.5 V	50	75	94
Crossover current	mA/cm ²	60–120 ^a	<60	6
Maximum power	mW/cm ²	160	270	157 ^b

^a 60 mA/cm² with 0.5 M methanol, 80°C, Nafion 117; 120 mA/cm² with 1.0 M methanol.

^b Extrapolated from actual 10 psig data to 30 psig used in prior reports using 4.4 mg_{PGM}/cm²

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 carbon dioxide, making it an effective hydrogen carrier. Being both nontoxic and easy to liquefy under moderate pressure, DME closely matches diesel and has been run in trucks. Los Alamos National Laboratory (LANL) has demonstrated the potential for direct oxidation of DME in a fuel cell [1]. 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 facile 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 power output is still not sufficient to approach commercial acceptance targets for most applications, and the precious metal cost is high. 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. The objective of 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 these MEAs in systems such 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 lab-scale (5-cm²) MEA with a commercial catalyst. In the second phase we focused on increasing the anode specific current using this commercial catalyst to achieve a key program go/no-go milestone to show concept feasibility. In this last phase, we evaluated the assemblies for durability, optimized structures for the new direct DME catalysts, and demonstrated improved power output. Throughout the program we 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 is, relative to PBI, a 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 SOA DMFC and incorporated as project milestones. The third phase is summarized in the results below.

RESULTS

Fuel Cell Test Capability

To advance the efforts, an additional Advent focus was included in this program, namely adding fuel cell testing capability for direct DME oxidation. The challenge in converting a test station from hydrogen-air (all gas) to DME-air lies in being able to inject some water into the DME gas stream in order to promote the oxidation of DME. This was done via a special metering pump and a heated pre-cell that converted the water to steam and mixed it with the DME gas. Figure 1 demonstrates that the error from three replicated tests puts Advent data within the range obtained by LANL during Phase I.

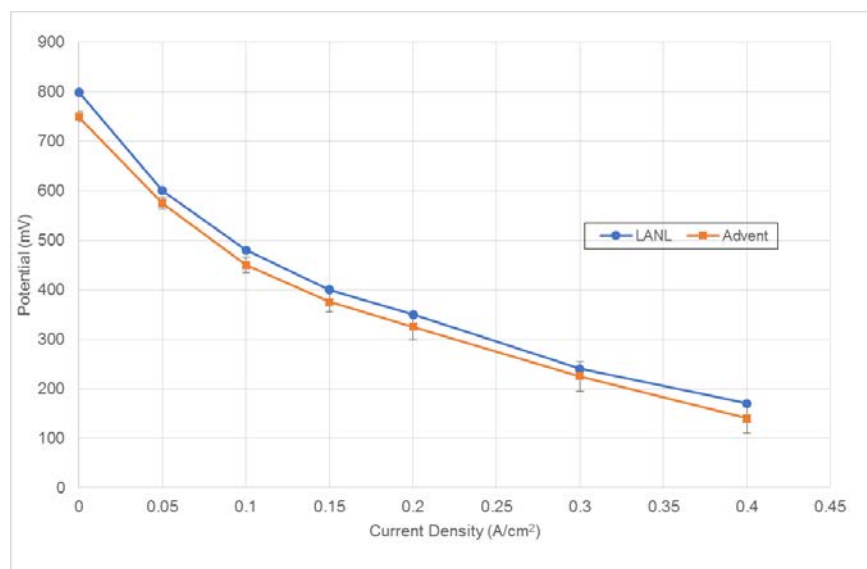


Figure 1. Advent and LANL comparative test station data in DME and air using MEAs with 1.6 mg PtRu/cm² anode, 2.9 mg Pt-alloy/cm² cathode, PBI membrane, 240 °C, and 10 psig (5-cm² test cell)

Baseline Stability

An important target for this effort is to demonstrate reasonable stability that would be appropriate for various applications. We used an excitation waveform that would simulate daily start-stop use of a device employing DME, but for this baseline, we used pure hydrogen to start. Figure 2 shows the decay of the MEA. While the daily decay is substantial, a majority of the loss is recovered in the next start-up cycle. We believe this daily decay is due to acid imbalance in the catalyst layer and can be moderated with additional optimization. The durability calculations begin with the end of the third cycle due to a break-in period and are calculated via the line drawn from the end of each day's cycle. Over the first 17 cycles, the MEA has shown a total degradation of 58.8 $\mu\text{V}/\text{cycle}$. Over that same timeframe (143 h), the degradation rate is 7.0 $\mu\text{V}/\text{h}$. The targets set forth in this work are both roughly half of the SOA DMFC (10 $\mu\text{V}/\text{h}$ vs. 19 $\mu\text{V}/\text{h}$, 0.75 mV/cycle vs. 1.5 mV/cycle), and the data shown here far exceeds even those lofty targets. While all of this data was collected under hydrogen-air, it provides an excellent baseline and proof of experimental concept for the future DME-based durability data.

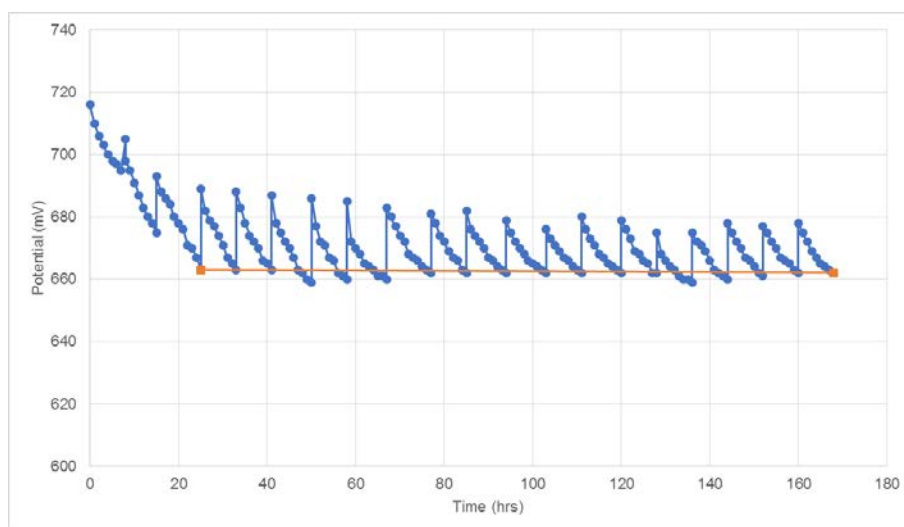


Figure 2. Baseline start-stop cycles (daily) with hydrogen-air using 1.6 mg PtRu/cm² anode, 2.9 mg Pt-alloy/cm² cathode, TPS 200X membrane, 180 °C, and ambient pressure (5-cm² test cell)

New Anode Catalyst

Our work on direct DME oxidation has attracted interest by several catalyst developers, both commercial and academic. As part of our effort to increase the power output, we have incorporated some of their anode catalysts into our MEAs. A specially developed platinum bismuth alloy was synthesized at the University of Cincinnati and then tested. The results of Figure 3 are highly encouraging as we find a nearly 20%–30% improvement over the commercial standard platinum ruthenium. Furthermore, this data was obtained at lower pressures (10 psig). When extrapolated to the standard 30 psig operational pressure established at LANL, we expect a maximum power of 157 mW/cm²—almost as much as the SOA for DMFC.

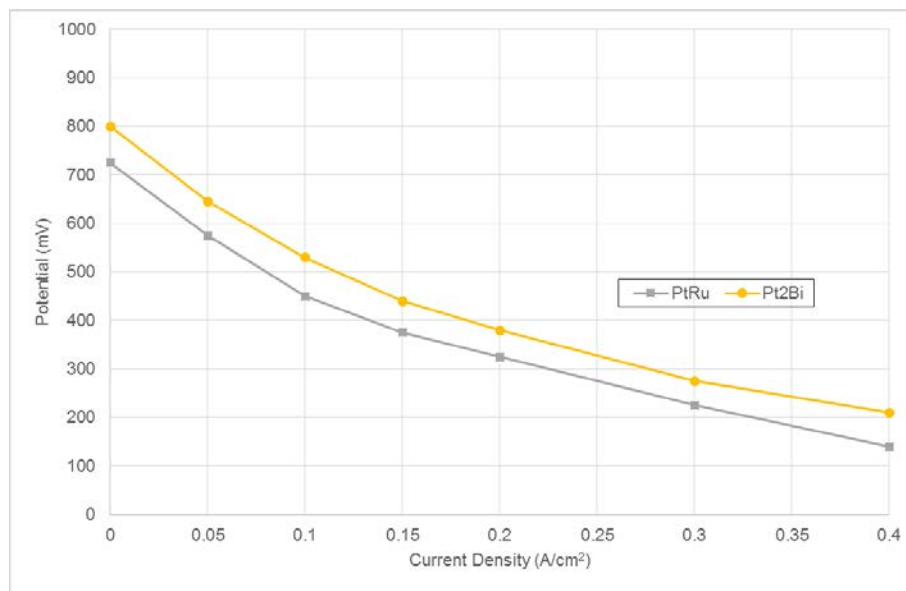


Figure 3. Comparative data using standard 1.6 mg PtRu/cm² anode (squares) vs. 1.5 mg Pt₂Bi/cm² anode (circles); 2.9 mg Pt-alloy/cm² cathode, PBI membrane, 240 °C, and 10 psig (5 cm² test cell)

CONCLUSIONS AND UPCOMING ACTIVITIES

We have shown assemblies achieving target exceeding anode mass-specific current, very low crossover, and reasonable power output. Thus, direct DME fuel cells offer great potential to exceed the performance of the SOA DMFC. While we have gone far without exceeding the power of a SOA DMFC, we have only just begun to incorporate specially developed anode catalysts and already our first sample (Pt₂Bi) performs very well. Upcoming efforts are focused on durability and further exploration of catalyst preparations from commercial sources.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. Emory S. De Castro, “Perspectives in Intermediate Temperature Fuel Cells: Past, Present, and Future,” Invited presentation at the Third International Fuel Cells Workshop, Tel-Aviv, Israel, October 29–November 1, 2018.

REFERENCES

1. Q. Li, X. Wen, G. Wu, H.T. Chung, and P. Zelenay, “High-Activity PtRuPd/C Catalyst for Direct Dimethyl Ether Fuel Cell,” *Angew. Chem. Int. Ed.* 54 (2015): 1–6.