

# V.D.5 Facilitated Direct Liquid Fuel Cells with High Temperature Membrane Electrode Assemblies

Emory S. De Castro  
 Advent Technologies, Inc.  
 One Mifflin Place, Suite 400  
 Cambridge, MA 02138  
 Phone: (857) 264-7035  
 Email: EmoryDeCastro@Advent-Energy.com

DOE Manager: Gregory Kleen  
 Phone: (240) 562-1672  
 Email: Gregory.Kleen@ee.doe.gov

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Subcontractors:  
 Piotr Zelenay (PI), Hoon T. Chung, Gerie Purdy, Xi Yin,  
 Los Alamos National Laboratory (LANL), Los Alamos, NM

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## Technical Barriers

This project addresses the following technical barriers from the Fuel Cell section 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)

## Technical Targets

This program falls under DOE’s incubator initiative, which explores high impact research in new areas. Thus, the technical targets for this program 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).

## FY 2016 Accomplishments

- Confirmed equivalent performance using standard commercial materials at the two different test sites: successful down-scaling of test setup from 50 cm<sup>2</sup> to 5 cm<sup>2</sup>.
- Successful design and construction of a test apparatus that allows precise control of DME to water ratios, critical for optimizing reaction conditions.
- Early results with a binary benchmark catalyst demonstrates nearly 50% decrease in platinum group metal (PGM), leading to nearly double the specific power (W/g<sub>PGM</sub>) when comparing the same catalyst at low temperature to high temperature operation (80°C vs. 180°C).



## Overall Objectives

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

## Fiscal Year (FY) 2016 Objectives

- Establish equivalent test results between Advent Technologies Inc. and LANL.
- Construct test apparatus that controls DME/water ratio in a fuel stream.
- Evaluate benchmark binary PtRu/C catalysts for high temperature DME fuel cells.

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

Key Performance Indicator	Current DMFC	Target	Program Status (after six months)
Maximum power (>)	0.180 W/cm <sup>2</sup>	0.270 W/cm <sup>2</sup>	0.062 W/cm <sup>2</sup>
Total precious metal loading	5 mg <sub>PGM</sub> /cm <sup>2</sup>	3 mg <sub>PGM</sub> /cm <sup>2</sup>	2.7 mg <sub>PGM</sub> /cm <sup>2</sup>
Degradation rate	19 μV/h at a 0.2 A/cm <sup>2</sup>	10 μV/h at a 0.2 A/cm <sup>2</sup>	Not applicable this phase
Loss in start/stop cycling	1.5 mV/cycle; cycle	0.75 mV/cycle; cycle	Not applicable this phase
Anode mass-specific activity	50 A/g at 0.5 V	75 A/g at 0.5 V	25 A/g at 0.5 V

## INTRODUCTION

In searching for an exemplary carbon-neutral fuel, DME may be one of the most appealing. This simplest of the ethers can be readily produced from renewably sourced hydrogen and CO<sub>2</sub>, making it essentially a hydrogen carrier. Both nontoxic and easy to liquefy under moderate pressure, DME closely matches diesel and has been run in trucks. Recently, LANL demonstrated the potential for direct oxidation of DME in a fuel cell [2]. Thus, one fuel 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 or 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

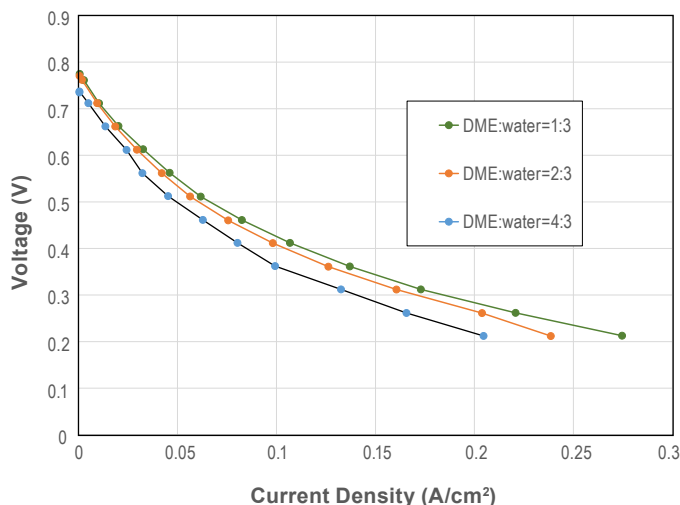
The project consists of three phases. In the first phase, we will demonstrate direct oxidation of DME at a small-scale (5 cm<sup>2</sup>) MEA without the advanced catalyst. The second phase will focus on the development of a small-scale gas diffusion electrode matched for the advanced LANL catalyst; however, we will first use a binary catalyst that has good activity for DME oxidation. In the last phase, we will scale up MEA to a 50 cm<sup>2</sup> size and optimize the gas diffusion electrode structure for the use in practical devices. We initially employ 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<sup>®</sup>, 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 and incorporated as project milestones.

## RESULTS

- *Verified baseline testing at Advent and LANL.* Due to the novelty of this system and the nuances of operating

MEAs at temperatures higher than 160°C, the first task in this program is to verify that test systems perform as expected. Since the purpose of this program is to demonstrate proof of concept, we need to keep the test scale small but relevant, thus, 5 cm<sup>2</sup> MEAs were tested in H<sub>2</sub>-air fuel cells. The results verified that both TPS and PBI 5 cm<sup>2</sup> MEAs tested at LANL showed performance within the variation of commercial materials (45 cm<sup>2</sup>), tested at Advent.

- *Achieved precise control of the DME-to-H<sub>2</sub>O molar ratio in fuel stream.* For every mole of DME oxidized, three moles of water are needed to support the reaction. This stoichiometry is critical, and early attempts to control water content in the DME vapor via flowing the fuel through humidification bottles was not precise enough to obtain relevant data. During this project, by designing a steam generator/mixer in together with a precision water pump, we were able to control the molar ratio of DME to H<sub>2</sub>O and study the impact of this ratio on power from the test cell. Figure 1 shows the polarization curve of PtRu/C PBI MEA at 180°C at different DME-to-H<sub>2</sub>O molar ratios, with the best performance achieved with the DME-to-H<sub>2</sub>O ratio of 1:3.
- *Demonstrated higher direct DME fuel cell performance with increased operation temperature.* PBI and TPS MEAs with both Pt/C and PtRu/C anode catalysts were tested at various temperatures. Direct DME fuel cell performance was improved with the increase in cell temperature. A monotonic increase of the DME oxidation current in PtRu/C PBI MEA was observed with the increase of temperature from 150°C to 180°C



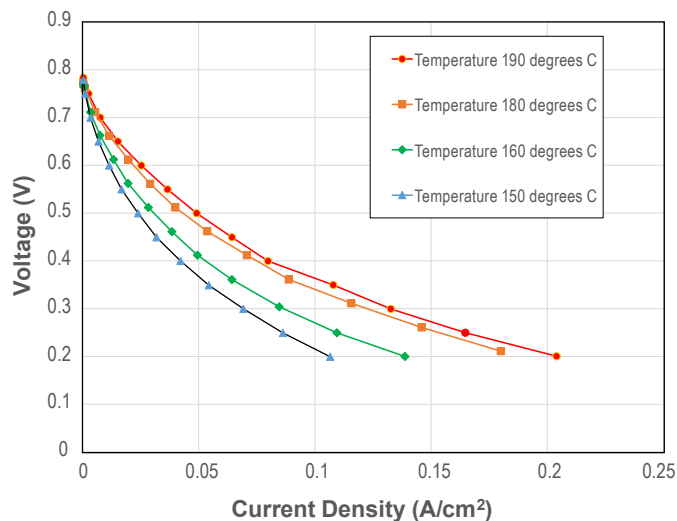
**FIGURE 1.** DME fuel cell performance of PBI-based MEA with different DME-to-H<sub>2</sub>O molar ratios. Cell temperature 180°C. Anode: PtRu/C, HiSPEC<sup>®</sup> 12100 PtRu/C, 4.5 mg/cm<sup>2</sup>; DME 500 sccm, backpressure 3.5 psig. Cathode: Pt-alloy/C 1.0 mg/cm<sup>2</sup>; air 500 sccm, backpressure 3.5 psig.

(Figure 2). At 0.5 V, the current density increased from 0.024 A/cm<sup>2</sup> to 0.053 A/cm<sup>2</sup> when temperature increased from 150°C to 180°C.

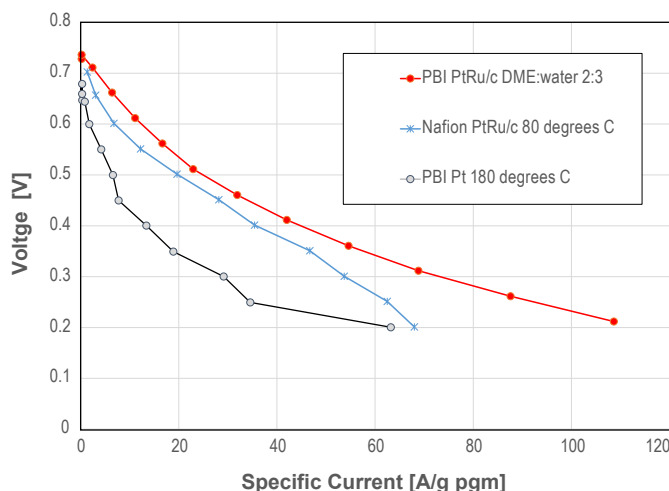
- Lowered PGM content. A more relevant comparison than polarization curves is calculating the power of current normalized to the amount of PGMs employed in the assembly (Figure 3). The reference data of Nafion<sup>®</sup> membrane PtRu/C catalyst at lower temperature (80°C) is still better than the PBI membrane Pt/C catalyst at high temperature (180°C). However, the PBI membrane PtRu/C catalyst at high temperature (180°C) exhibits higher specific current than the reference Nafion<sup>®</sup> membrane PtRu/C catalyst at lower temperature (80°C). While our final target is to show mass-specific current density higher than 50 A/g<sub>PGM</sub> at 0.5 V, the state-of-the-art DMFC specific current, even in this early stage we are at 25 A/g<sub>PGM</sub> at 0.5 V. A specific power comparison is listed in Table 2, where the maximum power is measured at 0.2 V and normalized to PGM loading. The highest specific power is obtained with the PBI membrane PtRu/C catalyst at 180°C.

**TABLE 2.** Specific Power at 0.2 V for Direct DME Oxidation

MEA	Specific power W/gPGM
Nafion <sup>®</sup> PtRu (80°C)	14
PBI Pt (180°C)	13
PBI PtRu (180°C)	23



**FIGURE 2.** DME fuel cell performance of PBI-based MEA at various temperatures. Anode: PtRu/C, HiSPEC<sup>®</sup> 12100 PtRu/C, 4.5 mg/cm<sup>2</sup>; DME 500 sccm, DME-to-H<sub>2</sub>O molar ratio 1:3, backpressure 3.5 psig. Cathode: Pt-alloy/C 1.0 mg/cm<sup>2</sup>; air 500 sccm, backpressure 3.5 psig.



**FIGURE 3.** Specific current density (A/g<sub>PGM</sub>) for Nafion<sup>®</sup> membrane HiSPEC<sup>®</sup> 12100 PtRu/C 4.0 mg<sub>metal</sub>/cm<sup>2</sup> anode at 80°C (DME 40 sccm, backpressure 26 psig), PBI membrane Pt/C 1.0 mg/cm<sup>2</sup> anode at 180°C (DME 500 sccm, backpressure 30 psig), and PBI membrane HiSPEC<sup>®</sup> 12100 PtRu/C 1.9 mg/cm<sup>2</sup> anode at 180°C (DME 500 sccm, backpressure 20 psig).

## CONCLUSIONS AND FUTURE DIRECTIONS

Although early in the program, these results support our basic concept that DME can be directly oxidized through the use of tuned catalysts and operation at higher temperatures. It is important to note that the data of the Figures 1 and 2 are derived from MEA assembly conditions optimized for fuels such as reformat (a mix of hydrogen, carbon monoxide, and carbon dioxide). There is no reason to suspect these conditions are best for direct DME oxidation, and the bulk of our efforts in this next period is to understand and fabricate MEAs that facilitate this reaction. Variables that we will investigate include phosphoric acid loading in the catalyst layer, hydrophobicity and porosity gradients, and compression during lamination of the MEA. We anticipate demonstrating direct DME oxidation key performance indicators that exceed that for the state of the art DMFC.

## FY 2016 PUBLICATIONS/PRESENTATIONS

- De Castro, E.S., Zelenay, P. and Gregoriou, V., “A Disruptive Fuel in the System: Electricity from a Carbon-Neutral Fuel,” A paper presented at the Fuel Cell Seminar and Energy Exposition, Los Angeles, CA, USA, November 16–19, 2015; Abstract 104.

## REFERENCES

- 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\\_d\\_fuel\\_cells\\_0.pdf](http://energy.gov/sites/prod/files/2016/06/f32/fcto_myrd_d_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.