
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, platinum group metal (PGM) loading, power output, durability, and crossover losses.
- Leverage a highly active ternary catalyst for high-temperature direct dimethyl ether fuel cells.

Fiscal Year (FY) 2018 Objectives

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

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 Plan [1], using DMFC systems as a reference fuel cell system:

- Cost (catalyst, system)
- Performance (catalyst, electrodes, MEAs)
- 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 program were created relative to the state-of-the-art DMFC system, the only other viable direct fuel oxidation system at this time. Progress toward meeting the technical targets for direct DME oxidation is shown in Table 1.

FY 2018 Accomplishments

- Identified zero-order anode reaction kinetics impeding reaction rate.
- Overcame kinetic limitations for anode mass-specific activity for direct DME oxidation with commercial catalysts through higher-temperature operation ($>200^{\circ}\text{C}$).
- Demonstrated highest anode mass-specific activity for a direct fuel cell ($94 A/g_{\text{PGM}}$ at 0.5 V) operating with a total PGM loading less than $5 \text{ mg}_{\text{PGM}}/\text{cm}^2$.

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

Key Performance Indicator (this period)	Units	Current DMFC	Target	Program Status (5-cm ² cell)
Total PGM 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	135 ^b

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

^b Using 4.6 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 CO₂, 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 [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 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 the last phase, we will evaluate the assemblies for durability, optimize structures for the ternary catalyst, and demonstrate improved power output. Throughout the program we employ two kinds of high-temperature membranes. One is polybenzimidazole (PBI), which 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 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 state of the art DMFC and incorporated as project milestones. We currently finished the second phase, which is summarized in the results below.

RESULTS

Identification of Anode Rate-Limiting Step

The objective of this program has been to demonstrate superior anode activity for direct oxidation of a high-energy-content fuel. Last year we reported 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, implying we had not selected conditions that allowed us to isolate the anode reaction. Having achieved that goal, we evaluated the impact of DME pressure (concentration) on anode performance. If the oxidation kinetics were limited by the oxidation rate, then an increase in DME pressure should increase the current density. Figure 1 shows how changing pressure nearly eight-fold *does not* improve performance. This behavior infers the oxidation mechanism is “zero order,” meaning there is a step after the initial oxidation that limits the overall reaction. For example, DME oxidation could result in reaction products other than carbon dioxide such as carbon monoxide or other carbon-containing poisons for the anode. In this case, the reaction is limited by our ability to clear the poison from the anode catalyst.

Overcoming Rate-Limiting Anode Step

Kinetically limited processes are facilitated by increasing temperature. Thus, we systematically increased our cell temperature from 180°C to 240°C. Over this temperature range and for a given pressure of DME, the current and power output increased. Figure 2 shows this increase in power output versus temperature. Having confirmed the temperature relationship, we selected operation at the highest temperature (240°C) and

systematically varied the pressure of DME from 3.5 psig to 30 psig. Unlike that shown in Figure 1, Figure 3 now clearly shows a current dependence on DME pressure and confirms we have switched the reaction rate into first order, effectively inducing a rapid removal of electrode-blocking reaction products.

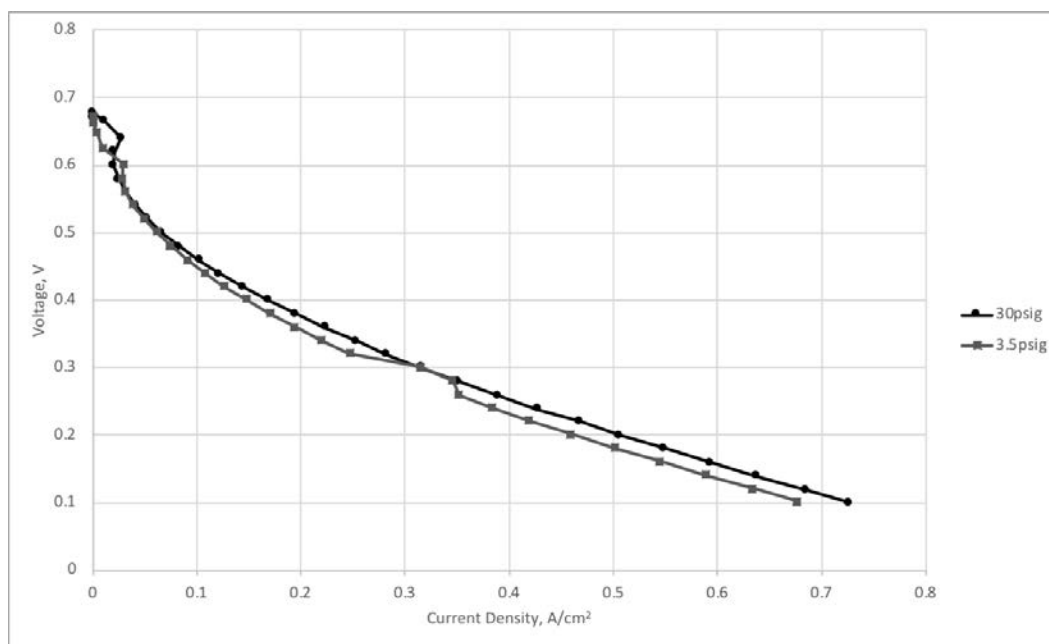


Figure 1. Lack of DME pressure dependence on current-voltage. Test MEA composed of cathode with Pt-alloy/C 2.3 mg_{Pt}/cm²; anode 12100 HiSPEC PtRu/C 2.23 mg_{Pt}/cm²; and PBI membrane. Test cell operated at 180°C with air 500 sccm, backpressure 3.5 psig and DME 125 sccm, humidified DME:water = 1:3 at the backpressure indicated.

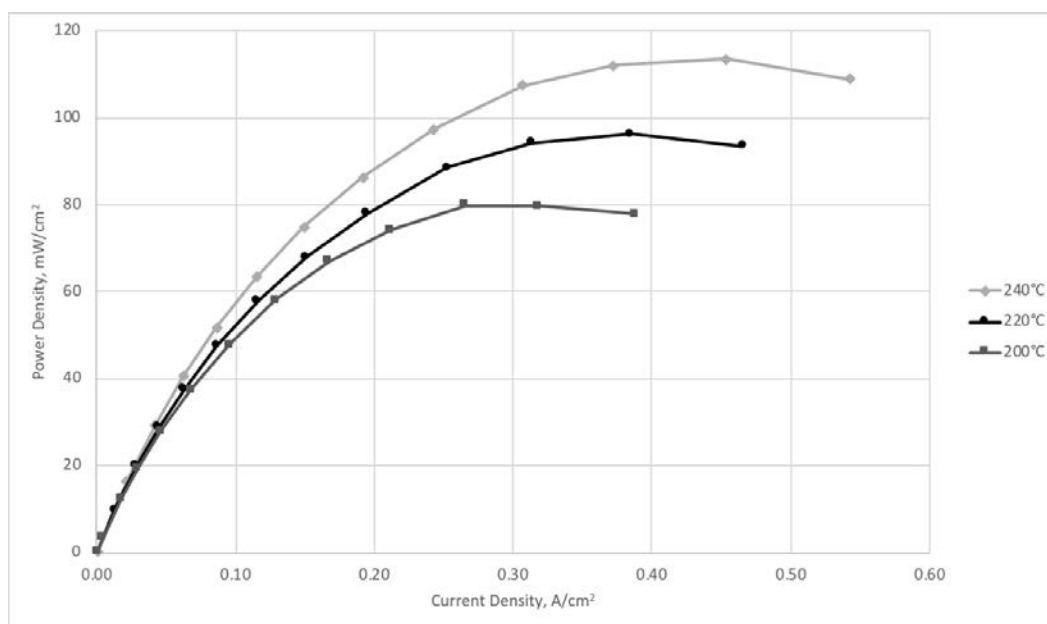


Figure 2. Power density over various temperatures. Test MEA composed of cathode with Pt-alloy/C 2.9 mg_{Pt}/cm²; anode 12100 HiSPEC PtRu/C 1.6 mg_{Pt}/cm²; and PBI membrane. Test cell operated at indicated temperatures with air 500 sccm, DME 125 sccm humidified at DME:water = 1:3 at 30 psig.

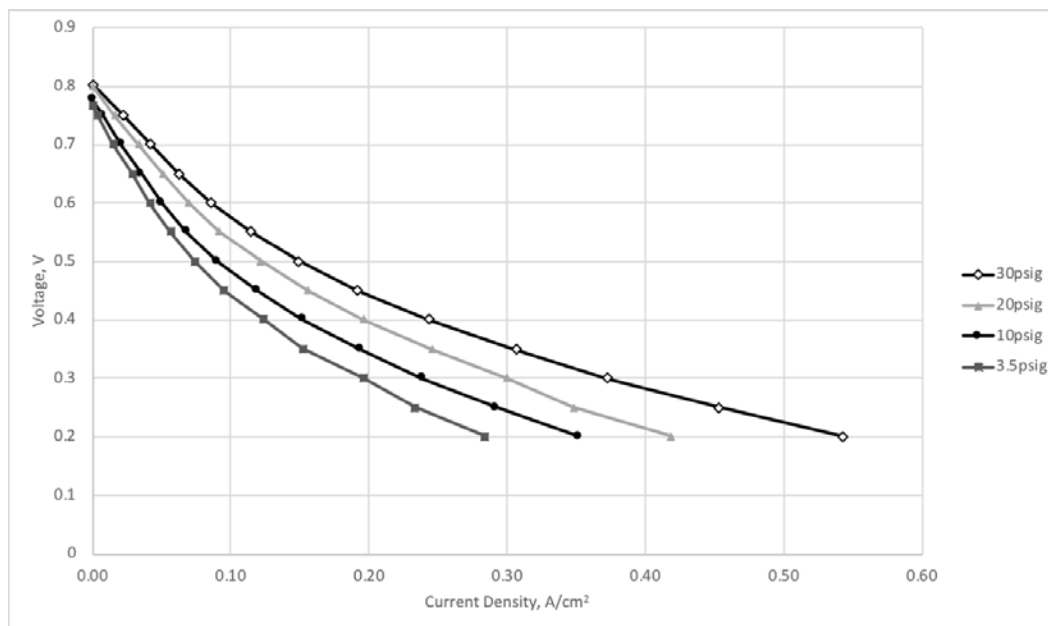


Figure 3. Current-voltage curves versus pressure of DME at higher temperature. Test MEA composed of cathode with Pt-alloy/C 2.9 mg_{PtGM}/cm²; anode 12100 HiSPEC PtRu/C 1.6 mg_{PtGM}/cm²; and PBI membrane. Test cell operated at 240 °C with air 500 sccm, DME 125 sccm humidified at DME:water = 1:3 at indicated pressures.

Improvement in Anode Mass-Specific Activity

By combining previously reported advances in the cathode configuration with operating at the higher temperature, 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 process of developing architectures for catalysts involves a materials approach whereby a key performance indicator, anode mass-specific activity, is gauged as a function of electrode-layer porosity, hydrophobicity, and phosphoric acid loading. Citing the results of Figure 4, we note several salient observations. First, we confirm that operating at higher temperature results in an improved anode mass specific activity (compare Figure 4 square “Low Temperature” with filled circle “2016”). Second, with a combination of higher cathode catalyst loading and improved electrode structure, we have almost doubled the anode specific current from 32 A/g_{PtGM} in 2016 to 50 A/g_{PtGM} at 0.5 V in 2017 (compare filled circle to triangle). And finally, when combining higher cathode loadings and higher temperature, we greatly exceeded our target of 75 A/g_{PtGM} at 0.5 V with 94 A/g_{PtGM}. This last result included two other improvements as well. One involved building thinner microporous layers to facilitate gas transport. The other improvement came from a careful balance of optimum anode and cathode catalyst loadings to optimize reaction rates while at the same time remaining under the target total catalyst loading of 5 mg_{PtGM}/cm².

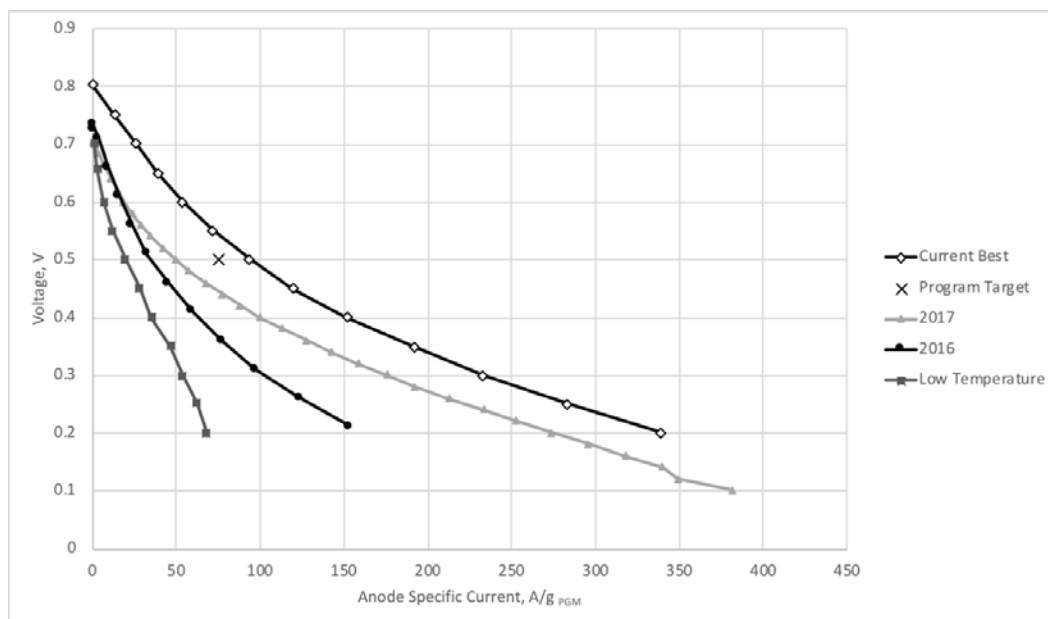


Figure 4. Improvement in anode mass-specific current

Open circles: replotted data from Figure 3 (30 psig) as anode-specific current. Single X: program target. Filled triangles: 2017 results showing impact of higher cathode catalyst loading using for anode HiSPEC 12100 PtRu/C 1.9 mg_{PGM}/cm², cathode Pt-alloy/C 2.2 mg_{PGM}/cm², at 180 °C and DME pressure 3.5 psig. Filled circles: 2016 results showing initial impact of higher operating temperature versus lower temperature using for anode HiSPEC 12100 PtRu/C 1.9 mg_{PGM}/cm², cathode Pt-alloy/C 0.8 mg_{PGM}/cm², at 180 °C and DME pressure 3.5 psig. Filled squares: LANL data from prior program, DME at HiSPEC 12100 PtRu/C, 80 °C, total 8 mg_{PGM}/cm², 26 psig. All with PBI membrane except for low-temperature black squares, which is Nafion. All with air 500 sccm, DME 125 sccm humidified at DME:water = 1:3.

CONCLUSIONS AND UPCOMING ACTIVITIES

Based on the target-exceeding anode mass-specific current, very low crossover currents, and reasonable power output, direct DME fuel cells offer great potential to exceed the performance of the state-of-the-art DMFC. While we have gone far without yet realizing the potential of the ternary catalyst, the morphology of this material is significantly different than that of our benchmark PtRu, and additional electrode optimization is needed. Upcoming efforts are focused on revising electrode processing conditions to fully realize the expected activity of the ternary catalyst, and benchmarking durability performance.

REFERENCES

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. 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.