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Methods for Optimization on Direct Methanol Fuel Cells to Increase Peak Power Density

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I. Abstract
Fuel cells are important devices for the transition to renewable energy technology. Fuel cells are electrochemical devices, meaning they transform the chemical energy stored in fuel into electrical energy. Many fuels used in fuel cells come from renewable sources and have low emissions, resulting in high power generation with minimal environmental impact. The many applications of fuel cells include but are not limited to, use in transportation for cars, trucks, shipping, and planes and stationary power generation. In the lab, I utilized low-temperature direct methanol fuel cells (DMFC), a type of polymer electrolyte fuel cell with methanol used as the fuel. Over the semester, the goal of my independent study was to optimize the peak power density of the fuel cell as a proxy for performance by changing multiple design variables and testing. Many of these variables included vapor feed flow rate and many different aspects of membrane electrode assembly (MEA) construction. In this process, I, along with master’s degree candidate Ryan Spragg and Ph.D. candidate Guilherme Maia, determined the optimal feed flow rate for vapor phase methanol fuel and optimal use of water management layers (WMLs).

II. Introduction
The DMFC is a type of fuel cell that has emerged as an alternative to hydrogen fuel cells with fuel that is significantly easier to transport. In the basic structure of a fuel cell, fuel is supplied continuously to the anode while an oxidant (usually oxygen from the air) is supplied continuously to the cathode. When this reaction occurs while the fuel cell is connected in a closed circuit, the fuel cell produces electricity. The primary components of the DMFC MEA are the anode, usually platinum ruthenium (PtRu) catalyst coated onto a carbon paper or carbon cloth gas diffusion layer (GDL); the cathode, also usually made of a conductive carbon paper or cloth GDL coated in platinum (Pt) catalyst. Between the electrodes is an ion exchange membrane, a polymeric membrane that ideally only allows for the transfer of charged ions across the MEA. Additional components of the fuel cell are the polytetrafluoroethylene (PTFE) gasket which holds the MEA in place, the graphite plates with flow channels etched into them for optimal mass transfer between fed fuel and the MEA, and the current collectors. For a DMFC, the electrochemical reaction is:

\[ CH_3OH + \frac{3}{2}O_2 \rightarrow 2H_2O + CO_2 \]
With the half-reaction at the anode being:

\[ CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \]

And the half-reaction at the cathode being:

\[ \frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \]

As seen in the above reaction, electrons are allowed to flow through the circuit from anode to cathode and protons flow through the MEA to the cathode. One of the major limitations of DMFCs is methanol crossover, in which the methanol fuel fed to the anode does not react and flows across the membrane, reducing fuel efficiency. This paper explores the methods used in the lab to improve fuel efficiency by improving the stoichiometric ratio of reactants at the anode to maximize the electrochemical reaction and therefore improve efficiency, especially at high power density high concentration methanol feedstocks.

### III. Materials and Methods

#### a. MEA Construction

All MEAs were constructed in the lab. First, the GDL material (substrate) was chosen, which was generally carbon paper or carbon cloth, some of which came pre-treated with a PTFE microporous layer (MPL). The GDL was then cut into a 25 cm² square. To create the coating, deionized water to isopropyl alcohol ratio of 1 to 2 was used, and then the liquid catalyst ratio, using PtRu as the catalyst for the anode and Pt as the catalyst for the cathode. Then, the slurry would be sonicated until well mixed (at least 2 hours) and poured into the spray gun for spray coating. Using the pressurized spray gun, the catalyst layer would be applied to the substrate by spraying one even layer at a time, allowing it to dry for about 5-10 minutes, and then spraying another layer on. This process was repeated along with massing the electrode intermittently until the desired catalyst loading was achieved. Once completed, the electrodes were allowed to dry. To finally construct the MEA, the electrodes (one anode and one cathode) were each punched into 5 cm² squares. The electrodes and membrane were placed into a PTFE template with a slightly larger than 5 cm² cutout with first the anode facing up, the Nafion® membrane in the middle, followed by the cathode facing down. The PTFE template was then closed and wrapped in two layers of aluminum foil with care to ensure none of the electrodes or the membrane moved out of place from the PTFE cutout. Finally, the MEA was hot pressed at 275ºF creating the final MEA.

#### b. Fuel Cell Test Setup

All MEA constructions were tested using one of two fuel cell test setups - one for liquid-feed methanol and one for vapor-feed methanol. All tests were done using the Scribner 890c fuel cell test system. The fuel cell test system collected data on voltage, current density, high-frequency resistance (HFR), and power density. Additionally, it was used to step the voltage for MEA activation and the production of polarization and power
curves. Wires connected the fuel cell to the fuel cell test system. For all tests, humid air flowed into the cathode at 0.25 L/min by sending dry air from the fume hood through a bottle of DI water sitting in an 80°C water bath. For liquid feed tests, a flow controller and tubing connected the bottle of fuel to the fuel cell, pumping in fuel at 1 mL/min for 1 M methanol and at 0.33 mL/min for all other higher methanol concentrations. For vapor feed tests, nitrogen gas was bubbled through the fuel bottle which was connected to the fuel cell by tube, with the flow rate of nitrogen controlled by an Airgas flowmeter.

IV. Results

After many tests conducted on many different MEAs, most of which were unpromising, throughout the majority of the first part of the semester, we concluded that the optimal MEA to try and replicate had an I:PtRu ratio of 0.4 on the anode with a loading of about 4.77 mg PtRu/cm² and an I:Pt ratio of 0.455 on that cathode with a loading of about 1.5 mg Pt/cm². We conducted many tests using this MEA design, specifically involving water management layers and vapor feed flow rates.

The water management layer used was an additional piece of hydrophobic carbon cloth. For all tests, the addition of a WML increased the peak power density of the fuel cell. This was especially powerful at high-concentration methanol vapor feeds. At the higher concentrations of methanol, less water is present which means the stoichiometric ratio for the anode half reaction decreases. If there is not enough water, the power production of the fuel cell will be limited by the amount of water present in the MEA for the methanol to react with. The water management layer ensures that the reaction can continue, especially when less water is being fed, like in

![Figure 1: Power Curves, Polarization Curves (top), and HFR (bottom) for liquid feed tests on the MEA created on November 2](image)
the 75 wt% or pure methanol vapor feeds. For these high-concentration vapor feeds, it can be seen in figure 2 that adding two WMLs was beneficial, as peak power density increased. However, as seen in figure 1, peak power density decreased for the liquid feed when using two WMLs. This makes sense because, for the liquid feed at lower concentrations, there is already a significant amount of water being fed to the fuel cell, so the fuel cell is not water-limited and therefore the additional WML adds resistance but does not improve performance.

![Power Curves, Polarization Curves, and HFR](image)

*Figure 2: Power Curves, Polarization Curves (top), and HFR (bottom) for vapor feed tests on the MEA created on November 2 with variations in water management layers.*

As seen in figure 3, for optimizing the vapor feed flow rate, the optimal nitrogen flow rate was 30 mL/min. The peak power density was lower for flow rates higher than this (500 mL/min, 250 mL/min) and for flow rates lower than this. At lower nitrogen flow rates, the stoichiometric ratio is closer to one, improving the efficiency of the fuel cell (a higher percentage of the methanol fed is consumed). This allows for more of the methanol to react, resulting in higher peak power density. However, when the nitrogen flow rate is decreased below this, the amount of methanol being fed to the fuel cell is so much less that there are fewer moles of the reaction, generating less electric power.
Figure 3: Power Curves, Polarization Curves (top), and HFR (bottom) for vapor feed tests on the MEA created on November 2 with variations in vapor feed flow rate.

V. Conclusions

After many rounds of testing and experimentation, we determined ideal vapor feed flow rates, water management layers, anode and cathode catalyst loading, and Ionomer:Catalyst ratios. While these are important developments for the continued testing of DMFCs, they are just the start. Moving forward we were planning on conducting vapor feed methanol crossover tests using a newly acquired carbon dioxide detector. Future horizons also include testing PGM-free catalysts that free the fuel cell from dependency on the critical raw material of platinum. The importance of fuel cells to create a sustainable future is not to be underestimated, and to have well-functioning fuel cells, it is imperative to optimize their performance.
VI. References
