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# Dynamics of direct hydrocarbon polymer electrolyte membrane fuel cells

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Abstract. Hydrocarbons have 50-100 times higher energy per unit weight compared to commercially available batteries, thus harvesting only 10% of the energy from hydrocarbons could provide a far lighter energy source for portable electronic devices. With this motivation, the feasibility of using polymer electrolyte membrane fuel cells with propane fuel, operating at low temperatures (< 100°C), was explored. It was interesting to note that there was a significant influence of the current history on the fuel cell performance. In particular, at higher current densities (>24 mA/cm<sup>2</sup>) the power output gradually decreases then rapidly "extinguishes" (i.e., produces no power). However, by employing an unconventional operating mode (loadinterrupt) where the current is shut off for a short period of time and then reapplied, the average maximum power density increased to 11.6 mW/cm<sup>2</sup>. Furthermore, the extinction of the fuel cell can be further improved by seeding a small amount of unsaturated hydrocarbons (~2000ppm) into the fuel stream and can extend the lifetime of the fuel cell by more than 10 times.

#### 1. Introduction

It is well known that most fuels contain far more energy per unit mass than batteries [1], hence in recent years many attempts have been made to create portable electrical power sources using fuels as the energy storage mediums [2]. Such sources could replace batteries in some applications, with the advantages of far greater power and/or lifetime, instant recharge ability, no "memory effect" and having no toxic material disposal issues. Polymer electrolyte membrane (PEM) fuel cells, electrochemical devices that convert chemical enthalpy directly into electricity, are a natural choice for fuel-based portable power devices because of their low operating temperatures, rapid startup, simple construction, efficiency, quietness, and clean exhaust compared to other forms of electrical power generators [3-4]. Currently, hydrogen is the most common fuel for PEM fuel cells because of low operating temperature and high power density ( $\approx 0.7$  W/cm<sup>2</sup>). However, hydrogen is highly reactive, extremely flammable and difficult to store at high ratios of energy/mass or energy/volume ratios when the mass or volume of the storage medium is included [5]. Thus, the direct methanol PEM fuel cells have been introduced to avoid the difficulties of fuel storage and many improvements have been made over the past decade [6-8], but one main challenge of direct methanol PEM fuel cells is that methanol closely resembles water (which the membrane must allow to flow across) leading to fuel crossover losses from the anode to cathode. The toxicity of aldehydes formed during methanol oxidation is another concern. In addition, they are both manufactured from natural gas using complex reactor

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systems that have large capitol cost and have high cost and weight infrastructure for distribution and storage [9].

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The direct hydrocarbon PEM fuel cells could be the most practical type of fuel cells for portable electrical power systems because of the storability (inexpensive and easily available infrastructure), relatively low flammability hazard, and lack of toxicity of many hydrocarbons. Some portable power systems have been proposed using hydrocarbons or alcohols that are reformed into hydrogen (H<sub>2</sub>) and carbon monoxide (CO) and then fed into the fuel cell after eliminating CO, but the reformer system adds considerable weight, volume, complexity, and additional cost of at least 30% of the total cost of the fuel cell system [10-11]. Despite many advantages over other types of fuel cells, the direct hydrocarbon PEM fuel cells have been overlooked because hydrocarbon reaction rates on fuel cell anodes at low temperature are one or more orders of magnitude slower than those of methanol and hydrogen [12].

## 2. Experimental methodology

#### 2.1. Experimental setup and procedures

The experimental setup consists of; (1) distilled water and pump to provide water for the humidifiers (2) lab made humidifiers with heat pads and temperature controller to operate humidifiers at desired operating temperature (3) flow meters (Matheson FM 1050-602-E300) to control the flow rate of incoming fuel and oxygen (4) fuel cell apparatus.

Prior to testing, the fuel cell was preconditioned with humidified nitrogen for one hour to humidify the membrane electrode assembly (MEA) for better proton conductivity and to purge the fuel cell system and humidifiers. The temperature of the fuel cell was measured and recorded with a thermocouple. After the fuel cell reached the desired operating temperature, the nitrogen was shut off and humidified fuel (propane chemically pure grade 99%, otherwise noted) and oxygen flew into anode and cathode, respectively. The catalyst was platinum black with loadings of 15 mg/cm<sup>2</sup> on anode and 8 mg/cm<sup>2</sup> on cathode. The operating temperature of the fuel cell was held at 85°C for all tests, and the flow rate of humidified fuel and oxygen were set at 1.2 L/min for anode and 0.8 L/min for cathode with no back pressure on anode or cathode.

#### 3. Results and discussion

#### 3.1. Current dynamics

The direct hydrocarbon PEM fuel cells work at low temperatures (< 100°C), but it is suspected that anode catalyst is being poisoned by some intermediate species during fuel oxidation. One operating scheme to circumvent adsorption of intermediate species on platinum surface is to employ unconventional mode of operation, where the fuel cell is operated for a certain period of time and the current is shut off and once again apply the current (load-interrupt mode). Remarkably, it was observed that merely setting the current to zero for a few seconds "reset" the fuel cell in the sense that when the same current was applied again, the power density was restored to the value at the beginning of the test, as if the first test and subsequent extinction event had never occurred. With the loadinterrupt operating scheme, it has shown that the performance can significantly increase compared to that of the constant current scheme. One explanation to this improvement is that when the current is shutoff the platinum surface might be getting deadsorbed with intermediate species that might be blocking the propane from reaching the platinum surface.

As shown in figure 1 (upper left and upper right), the average power densities for 12 mA/cm<sup>2</sup> and 24 mA/cm<sup>2</sup> with constant current operating scheme were 6.23 mW/cm<sup>2</sup> and 7.61 mW/cm<sup>2</sup>, respectively. Similarly, with load-interrupt operating scheme the average power densities were 6.04 mW/cm<sup>2</sup> and 9.36 mW/cm<sup>2</sup> for 12 mA/cm<sup>2</sup> and 24 mA/cm<sup>2</sup>, respectively. At low currents, the loadinterrupt operating scheme was not beneficial but as current increases, load-interrupt operating scheme benefit amplifies. It was observed that at any higher currents above 24 mA/cm<sup>2</sup>, the fuel cell extinct

before 1000 seconds, but with load-interrupt operating scheme, the current density can be increased to  $40 \text{ mA/cm}^2$  and still be able to provide power for more than 1000 seconds. The average maximum power density was 11.5 mW/cm<sup>2</sup> as shown in figure 1 (lower right), which is almost 1.5 times higher than the average maximum power density obtained with constant current operating scheme at 24 mA/cm<sup>2</sup> (7.61 mW/cm<sup>2</sup>).



**Figure 1.** Constant current and load-interrupt mode of a 25cm<sup>2</sup> direct propane fuel cell. The current was applied for 20 seconds and shut off for 5 seconds for 1000 seconds (only until 250 seconds shown). Upper Left: Low current test. Upper Right: Medium current test. Lower Left: High current test. Lower Right: Polarization curve of scan current, constant current, and load-interrupt mode

As shown in figure 1 (lower right), polarization curve of load-interrupt and constant current operating schemes at various currents were plotted. With this unconventional mode of operation, the load-interrupt mode yields higher average maximum power density than that of the constant current operating scheme, especially at higher currents. The current working hypotheses is that there may be occasional alternate reaction pathways leading to formation of intermediate species or CO on the anode which eventually poisons the anode catalyst, but gets deadsorbed once the current is turned off.

#### 3.2. Unsaturated hydrocarbons and carbon monoxide poisoning

It has been verified by many researchers and investigators that even a small trace amount of CO can poison the catalyst sites, therefore significantly reduce the performance of PEM fuel cells. With this motivation, higher purity grade propane was tested because 1% of impurity in the CP grade propane might be responsible for the extinction of direct hydrocarbon PEM fuel cells. However, extremely pure (research grade, >99.99%) propane fuel does not produce any power whatsoever; the PEM fuel cells simply does not "start" or "ignite" at temperatures up to 90°C. With addition of unsaturated hydrocarbons (UH) (ethylene, propylene, isobutylene or acetylene) bleed into the fuel stream enables

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the fuel cell to "start" and the cell continues to operate even after small trace of UH gas is removed. The most effective tested UH thus far is ethylene as shown in figure 2 (left). As shown in figure 2 (right), it is also interesting to note that without any addition of UH (0ppm, first started with UH and removed), the fuel cell extinguishes ~70 seconds, but with addition of only 2000ppm (0.2%) of ethylene can increase the lifetime of the fuel cell by more than 10 times. Furthermore, with unsaturated hydrocarbon addition, the fuel cell can start even at room temperature, though with low open circuit voltage (0.6V) and maximum power density of 0.5 mW/cm<sup>2</sup>.



Figure 2. Dynamics of direct hydrocarbon PEM fuel cells at 85°C using research-grade propane. Left: effect of addition of 2540 ppm (0.254%) of unsaturated hydrocarbons on power production at constant current 36 mA/cm<sup>2</sup> (without the addition, no power is produced); Right: effect of ethylene concentration on power production at constant current 36 mA/cm<sup>2</sup> (for 0 ppm, the cell was first "ignited" with ethylene then the ethylene flow was stopped.). Note logarithmic time scale.

After the fuel cell is started with UH and removed, significant amount of CO (~14.28%) was bleed into the fuel stream. It has been found that CO does not "poison" (render inoperative) these PEM fuel cells as shown in figure 3 (left). It can be expected for the fuel cell would extinguish faster with significant amount of CO in the fuel stream, but similar to those of UH, it helps to avoid extinction. CO as an additive to hydrocarbon fuels has the same qualitative effect as UH, but UHs are effective in much smaller concentration and yield higher power densities. Instead, CO can actually be used as fuel, albeit with much lower power densities (~4 mW/cm<sup>2</sup>) than those of hydrocarbons as shown in figure 3 (right)



**Figure 3.** Left: Bleeding carbon monoxide into the fuel stream (~14.3%) at constant current 36 mA/cm<sup>2</sup> Right: Polarizaton curve of pure research grade propane and pure CP grade carbon monoxide scanning at 0.133 mA/cm<sup>2</sup>s.

#### 4. Conclusion

This work successfully demonstrated working direct hydrocarbon PEM fuel cells despite low reactivity of hydrocarbons at low temperatures (<  $100^{\circ}$ C) compared to those of methanol and hydrogen. The extinction of the fuel cell can be avoided by operating the fuel cell in the load-interrupt mode where the load is applied on and off. The working hypothesis is that turning off the load somehow deadsorbing intermediate species on platinum surfaces that might be impeding fuel from reaching the catalyst sites. By employing this operating scheme, the average maximum power density can be 1.5 times higher than that of constant current operating scheme. The extinction of the fuel cell can also be prolonged by bleeding small amount of UH (~ 2000ppm) into the anode fuel stream. It is suspected that UH is interacting with intermediate species or retards the polymerization process on the platinum surface. Out of four UHs tested, ethylene seems to yield the best result and carbon monoxide, a well known specie for catalyst poisoning, did not contribute to the extinction of the fuel cell.

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