DIRECT HYDROCARBON PEM FUEL CELLS

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Abstract: A study of Proton Exchange Membrane Fuel Cells (PEMFCs) using hydrocarbon fuels (propane and butane) is reported. Power densities of 22 mW/cm^2 were enabled using a novel hydrazine-treated Pt-based catalyst. This catalyst also improved the performance of dimethyl ether and hydrogen PEMFCs, though not to the extent as with hydrocarbons. An usual feature unique to hydrocarbons is that average power densities could be increase substantially using a "current interrupt" operating scheme where the cell was shut off for short periods of time. Applications to portable power devices are discussed.

Keywords: proton exchange membrane fuel cells; catalysts; platinum; hydrocarbons

INTRODUCTION

Proton Exchange Membrane Fuel Cells (PEMFCs) are the most practical and convenient type of fuel cell for portable electrical power generation because of their low operating temperatures, simple construction and rapid startup [1, 2]. However, PEMFCs require very low operating temperatures (generally < 100˚C) and thus have been limited to a small number of very reactive fuels, specifically hydrogen, which is difficult to store efficiently, or methanol, which has relatively low energy density (40% of hydrocarbons) and has issues with "crossover" from the anode to cathode which limits efficiency. For portable power applications, it is desirable to employ hydrocarbon fuels because of their low cost, convenient storage, high energy density and lack of crossover. This work discusses the development of hydrocarbon-fueled PEMFCs.

One approach to utilizing hydrocarbons in PEMFCs is via a separate upstream reformer to convert the hydrocarbon into H$_2$ and CO then remove the CO that would otherwise poison the PEMFC anode catalyst [3], however, the size and "balance of plant" required limits the value of this scheme for portable power applications. <u>Direct</u> (reformer-less) hydrocarbon PEMFCs have generally been considered impractical due to the low reactivity of hydrocarbons on PEMFC catalysts at the low temperatures and CO "poisoning," however, recent work [4] has shown that ammonia-treated platinum-based catalysts enable self-sustaining <u>combustion</u> of hydrocarbons at temperatures as low as 60˚C, which is entirely compatible with PEMFCs. With this motivation, ammonia and hydrazine-treated Pt catalysts were evaluated for use in direct hydrocarbon PEMFC anodes.

EXPERIMENTAL METHODS

Membrane electrode assemblies (MEAs) with a 25 cm^2 active cell area were fabricated using a 'direct paint' technique to apply the catalyst layer. The 'catalyst inks' were prepared by dispersing the catalyst nanoparticles into appropriate amounts of Millipore® water and a 5% Nafion® solution (1100EW, Sigma-Aldrich). Anode and cathode 'catalyst inks' were directly painted onto Teflon® coated carbon papers (E-TeK). For all MEAs in this study, the cathode consisted of platinum black (PtBl) nanoparticles (surface area 27 m^2/g, Alfa Aesar) at a standard loading of 8 mg/cm^2. The anode consisted of either treated or untreated PtBl catalysts at a loading of 15 mg/cm^2. The painted anode and cathode were hot-pressed onto a Nafion® N-117 or N-112 membrane at 120 °C and 500 lbs. for 25 min to form a MEA. The fabricated MEAs were assembled into the hardware and evaluated for electrical performance.

Three different anode catalysts were investigated in this study: (i) high surface area Pt black (PtBl) from Premetek; (ii) ammonia treated PtBl (Pt(NH$_3$)); (iii) hydrazine treated PtBl (Pt(N$_2$H$_4$)). Two methods were tried to treat PtBl with ammonia. First approach was to burn PtBl in ammonia/air mixture, as it did for Pt foil treatment in Swiss-roll combustion study. However, the nanoparticles severely agglomerated after treatment, which dramatically reduced active surface areas for electrochemical reaction. In second approach, PtBl was immersed in aqueous ammonia and oil bathed at 80^0 C for 5 hours. It then washed with de-ionized Milipore water and naturally dried. The agglomerations of PtBl were not significantly noticed and ready for MEA fabrication. Similar method was used to treat PtBl with hydrazine. 0.6g PtBl was added into the 100mL 25% hydrazine aqueous solution (anhydrous 98%, Sigma-Aldrich) with continuous stirring. The solution was heated to

40^{0}C and kept at this temperature for 4 hours. The reaction mixture was heated to 100 ^{0}C for one hour and then refluxed for another hour. After the solution was cooling down to room temperature, the treated Pt was washed with de-ionized Milipore water and naturally dried before being used as fuel cell catalysts. Sulfonated tetrafluorethylene based copolymer (Nafion®) is the most widely used electrolyte material for PEMFCs. Nafion® N-112 (51 µm) is one of the thinnest commercially available films, and Nafion® N-117 (183 µm) is the most commonly used and one of the thickest. Both membranes were used in this study to evaluate the effect of thickness on fuel cell performance. The membranes were pretreated prior to the fabrication in 5% Sulfuric acid solution at 100 ^{0}C for half an hour, and then rinsed with DI water and kept in boiled water for one hour. The purpose of this treatment is to exchange Na^+ with H^+ in the sulfonic acid chains for better proton conductivity as commercial Nafion® were purposely built in $SO_3^-Na^+$ form for easy processing, storage and transportation. Likewise, a certain amount of Nafion® solution was added in catalyst ink to create binding between catalyst and membrane. During fuel cell operation, protons will be produced on the catalyst surface. In order to carry the protons into the membrane, proton conductor like Nafion® is needed to reduce the resistance. It also helps to bind Pt particles and carbon paper to the membrane mechanically.

The MEA (Fig. 1) was held in a single cell test fixture consisted of machined graphite flow fields with direct gas or liquid feeds and gold plated copper plates to avoid corrosion (Fuel Cell Technologies Inc.) Fuels and oxidants were pumped into humidifier chambers before fed to the cell, and the flow rates were controlled by flow meters (Fig. 2). Cell potential was controlled by a fuel cell testing station (Fuel Cell Technologies Inc.). The cell temperature was measured by a thermocouple which was installed between the anode current collector and the MEA.

RESULTS

With propane fuel, cells with hydrazine-treated catalysts showed significantly better performance than cells with conventional platinum black or ammonia-treated catalysts (Fig. 3). The maximum power density of 22 mW/cm^2 was achieved at ≈ 85˚C (Fig. 4) probably due to membrane dryout as temperatures approached 100˚C. Similar results (not shown) were obtained using n-butane fuel. No significant differences were found using air or O_2 cathode streams indicating that, as expected, cell performance is cathode-limited.
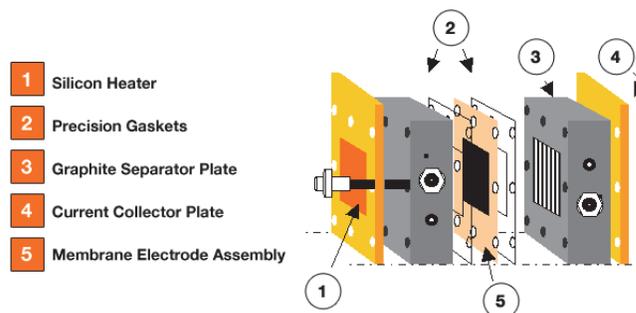

Figure 1. Schematic of a single fuel cell test fixture: 1) silicon heater to heat the cell externally; 2) gaskets to prevent gas or liquid leakage; 3) machined graphite flow fields with direct fuel/oxidant feeds; 4) gold plated copper plates to collect current and avoid corrosion; 5) lab fabricated MEA (Fuel Cell Technologies Inc.)
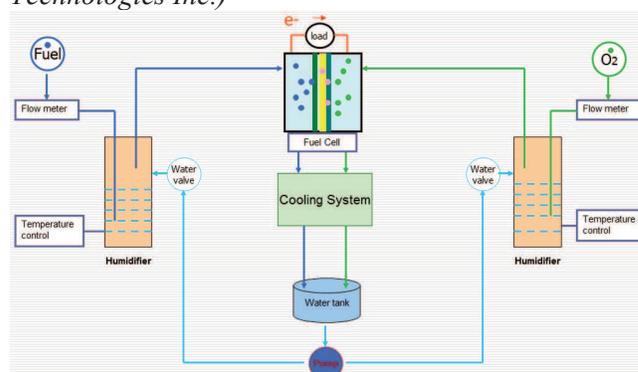

Figure 2. Schematic of direct hydrocarbon fuel cell set-up: fuels and oxidants were pumped into a humidifier chamber before fed to the cell, and the flow rates were controlled by flow meters.
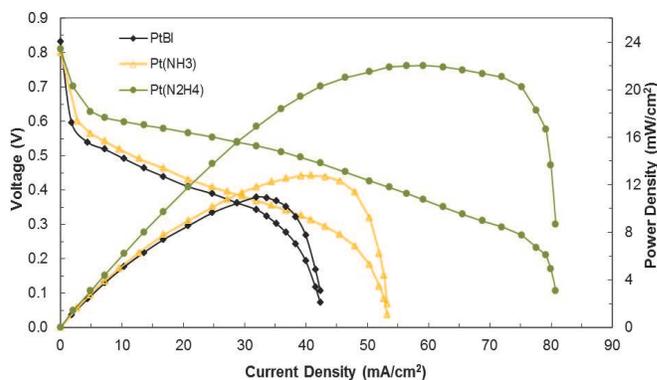

Figure 3. Performance of C$_3$H$_8$-fueled PEMFCs at 85˚C using untreated platinum black (PtBl), NH$_3$-treated and N$_2$H$_4$ treated cathode catalysts.

An unusual dynamic behavior of hydrocarbon-fueled PEMFCs was observed, namely that the attainable power was substantially dependent the cell operating history (Fig. 5). For a quick-scan polarization curve generated in ≈ 2 minutes, the maximum power of 22 mW/cm^2 was obtained whereas for steady-state operation, at sufficiently high current

draw the PEMFC would shut down (i.e. produce zero power) after several minutes of constant-current operation. Based on the power density and Pt loading, it can be estimated that over this period of time each Pt site has reacted $> 10^4$ propane molecules, yet the cell condition was still evolving over this time period.
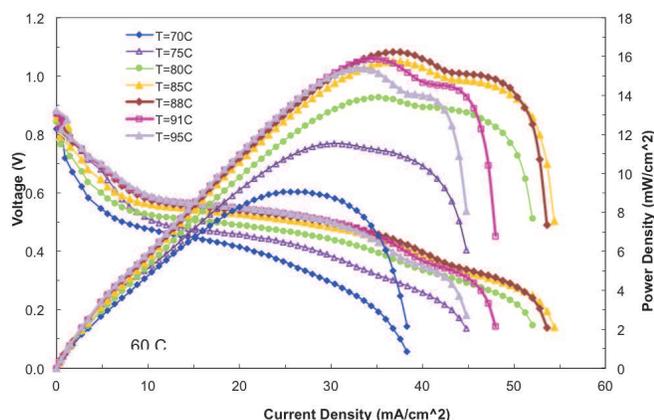

Figure 4. *Performance of a C_3H_8-fueled PEMFC at different temperatures with N_2H_4-treated cathode catalyst.*
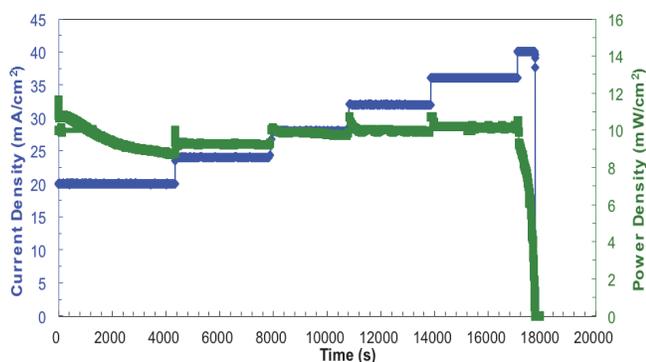

Figure 5. *Sustainable steady-state operation with propane fuel.*

This shut-down could be avoided by intentionally open-circuiting the cell for short periods of time every few minutes (Fig. 6). In this way the <u>average</u> power could be doubled compared steady-state operation, i.e. comparable to the peak power measured in a quick-scan polarization curve (Figure 7).

Dimethyl ether (Figs. 8, 9) and hydrogen (Figs. 10, 11) exhibited maximum power densities of 90 mW/cm^2 and 550 mW/cm^2, respectively, and also benefitted from the hydrazine anode catalyst treatment, but did not benefit from the load-interrupt mode of operation.
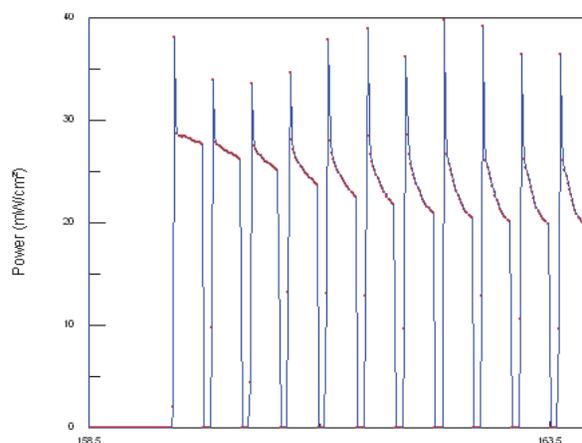

Figure 6. *Transient performance of C_3H_8-fueled PEMFCs at 85˚C with N_2H_4-treated cathode catalysts in "load interrupt" mode (20 s on, 5 s off).*
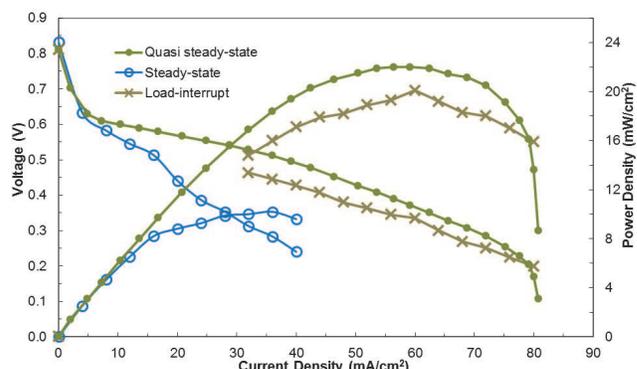

Figure 7. *Comparison of propane-fueled PEMFCs operating in steady-state, transient quick-scan and "load interrupt" modes.*
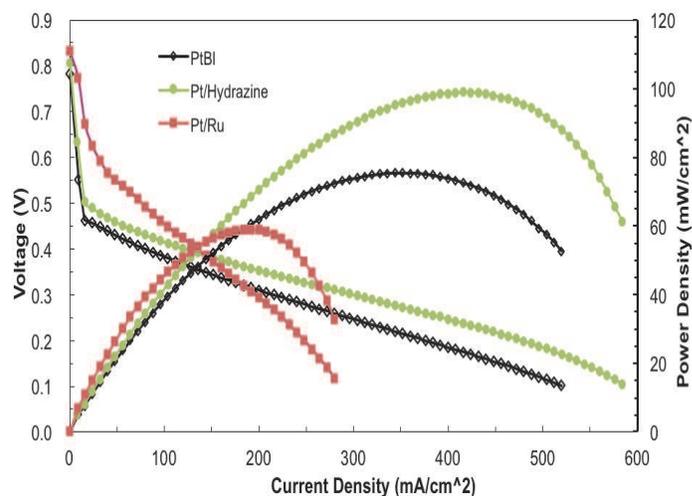

Figure 8. *Polarization curves and power density curves of a 25 cm^2 single direct DME fuel cell with various anode catalysts at 85 °C. DME pressure and flow rate: 1 atm and 1.2 L/min, oxygen pressure and flow rate: 1 atm and 1.0 L/min. Both streams were humidified at 85 °C.*
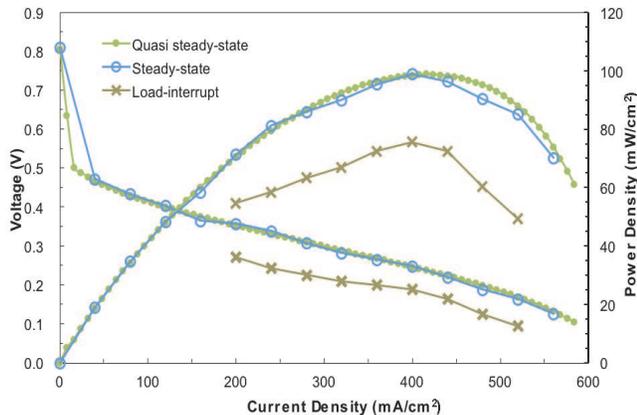
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Figure 9. Polarization and power density curves of a 25 cm² single direct DME fuel cell under different operating conditions. The cell temperature was 85 °C. DME pressure and flow rate: 1 atm and 1.2 L/min, oxygen pressure and flow rate: 1 atm and 1.0 L/min. Both streams were humidified at 85 °C.
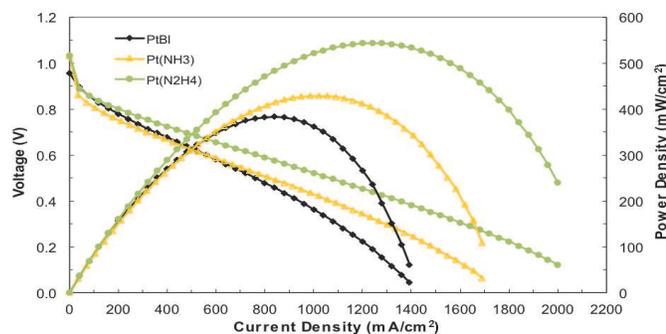

Figure 10. Polarization curves and power density curves of a 25 cm² single direct propane fuel cell with various anode catalysts at 75 °C. Hydrogen and flow rate: 1 atm and 1.2 L/min, oxygen pressure and flow rate: 1 atm and 2.0 L/min. Both streams were humidified at 70 °C.
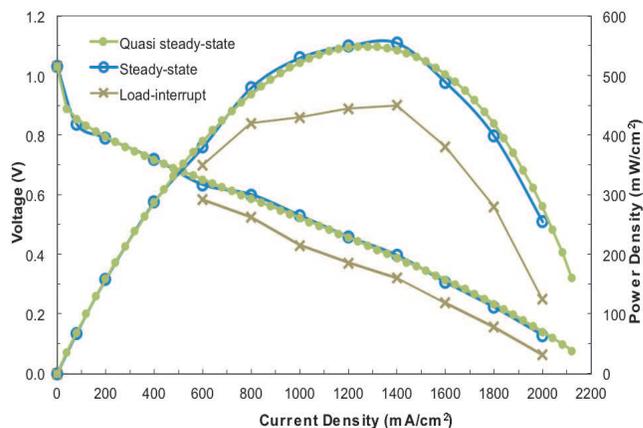

Figure 11. Polarization and power density curves of a 25 cm² single direct H₂ fuel cell under different operating conditions. The cell temperature was 75 °C. Hydrogen pressure and flow rate: 1 atm and 1.2 L/min, oxygen pressure and flow rate: 1 atm and 1.0 L/min. Both streams were humidified.

DISCUSSION

We propose that this unusual behavior may be due to an occasional alternate reaction pathway leading to the formation of a deactivating species (perhaps CO) on the anode catalyst sites which eventually accumulates to the point of rendering the cell ineffective. In future work we will isolate the deactivating specie and identify means to further increase power from these hydrocarbon PEM fuel cells.

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