Research Article

n-Hexadecane Fuel for a Phosphoric Acid Direct Hydrocarbon Fuel Cell

Yuanchen Zhu, 1,2 Travis Robinson, 1 Amani Al-Othman, 2,3 André Y. Tremblay, 1 and Marten Ternan 4

1 Chemical and Biological Engineering, University of Ottawa, 161 Louis Pasteur, Ottawa, ON, Canada K1N 6N5
2 Catalysis Centre for Research and Innovation, University of Ottawa, 30 Marie Curie, Ottawa, ON, Canada K1N 6N5
3 Chemical Engineering, American University of Sharjah, Sharjah, UAE
4 EnPross Incorporated, 147 Banning Road, Ottawa, ON, Canada K2L 1C5

Correspondence should be addressed to Marten Ternan; ternan@bell.net

Received 8 January 2015; Accepted 17 March 2015

Academic Editor: Michele Gambino

Copyright © 2015 Yuanchen Zhu et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The objective of this work was to examine fuel cells as a possible alternative to the diesel fuel engines currently used in railway locomotives, thereby decreasing air emissions from the railway transportation sector. We have investigated the performance of a phosphoric acid fuel cell (PAFC) reactor, with n-hexadecane, \( \text{C}_{16}\text{H}_{34} \) (a model compound for diesel fuel, cetane number = 100). This is the first extensive study reported in the literature in which n-hexadecane is used directly as the fuel. Measurements were made to obtain both polarization curves and time-on-stream results. Because deactivation was observed hydrogen polarization curves were measured before and after n-hexadecane experiments, to determine the extent of deactivation of the membrane electrode assembly (MEA). By feeding water-only (no fuel) to the fuel cell anode the deactivated MEAs could be regenerated. One set of fuel cell operating conditions that produced a steady-state was identified. Identification of steady-state conditions is significant because it demonstrates that stable fuel cell operation is technically feasible when operating a PAFC with n-hexadecane fuel.

1. Introduction

Fuel cells offer many advantages for the conversion of the chemical energy in a fuel into electrical energy. Fuel cell energy efficiencies can be greater than those of conventional combustion engines. For example, because Carnot heat engines are limited to the maximum temperature that their materials can withstand, their theoretical energy efficiency is close to 67%. In contrast, fuel cells do not have materials limitations and can have larger theoretical energy efficiencies. Often emissions from fuel cells are generally less than those from combustion engines. In some applications fuel cells are competing successfully with batteries in part because they can use fuel continuously whereas batteries stop providing electrical power as soon as their charge has been exhausted.

Fossil fuels are usually the lowest cost source of energy and that is not apt to change in the foreseeable future. Unfortunately emissions from fossil fuels have a negative effect on the earth’s climate. Direct hydrocarbon fuel cells (DHFCs) can have theoretical energy efficiencies near 95%. Their large energy efficiencies mean that a smaller quantity of fuel is required and therefore they will emit fewer emissions and have a smaller impact on climate change than heat engines or the more technological advanced fuel cells that use hydrogen or methanol as their fuels.

The purpose of this work was to decrease both greenhouse gas emissions (\( \text{CO}_2, \text{CH}_4, \text{and} \text{N}_2\text{O} \)) and air contaminants (\( \text{NO}_X, \text{CO}, \text{HC}, \text{and} \text{SO}_X \)) by replacing locomotive diesel engines with fuel cell engines. n-Hexadecane (cetane number = 100) was used as a model compound to represent commercial diesel fuels. A phosphoric acid fuel cell was used because its temperature is high enough to ensure that the n-hexadecane would be in the vapour phase if an appropriate steam/n-hexadecane ratio is used. Therefore the existence of two liquid phases within the fuel cell could be avoided.
Direct hydrocarbon fuel cells have other advantages. DHFC systems have lower capital costs than other fuel cell systems because the fuel processing systems (steam reforming, etc.) for hydrogen and methanol fuels are not required. In addition, the infrastructure already exists for diesel fuel and other petroleum derived fuels. That is not the case for hydrogen or methanol fuels. Storage of liquid fuels, such as diesel fuel, is much easier than storage of gaseous fuels such as hydrogen.

Unfortunately DHFCs have one major disadvantage. Their current densities are much smaller than those of hydrogen and methanol fuel cells. Work in our laboratory is being performed to understand the characteristics of DHFCs with a long-term objective of improving their performance.

William Grove demonstrated the first fuel cell operation in 1839 using hydrogen as the fuel. He was also credited with suggesting possible commercial opportunities if coal, wood, or other combustibles could replace hydrogen [1] which would be DHFCs. Direct hydrocarbon fuel cells were investigated intensely in the 1960s. Three reviews of the DHFC work up to that time are available [2–4].

Research on DHFCs has continued. Low-temperature fuel cell studies (<100°C) were performed on methane by Bertholet [5] and on propane by Cheng et al. [6] and by Savadogo and Rodriguez Varela [7, 8]. Heo et al. [9] performed intermediate temperature fuel cell studies (100–300°C) using propane. A larger number of DHFC studies have been performed on solid oxide fuel cells. Studies using low molecular weight hydrocarbons from methane to butane were performed by Steele et al. [10], Murray et al. [11], Zhu et al. [12], Gross et al. [13], and Lee et al. [14]. Larger molecules were studied by Ding et al. [15] (octane), Kishimoto et al. [16] (n-dodecane), and Zhou et al. [17] (jet fuel). Our own work has focused on modeling the fuel cell reactor [18–20], modeling the fuel cell catalyst [21–23], experimental development of an electrolyte that is appropriate for temperatures above the boiling point of water [24–26], and experimental fuel cell studies [27, 28].

Phosphoric acid fuel cell systems have an extensive development history. A 250–400 kW fuel cell system to produce stationary electric power was developed by Pratt and Whitney/ONSI/UTC Power. 300 units were built in 19 different countries. The company was sold to ClearEdge Power and was recently acquired by Doosan Industries. The phosphoric acid fuel cell technology has been documented extensively [29–32].

The fuel in this work was n-hexadecane. There were only three data points reported previously in a fuel cell study that examined a variety of fuels [33]. This is the first fuel cell study devoted exclusively to n-hexadecane. In a direct n-hexadecane phosphoric acid fuel cell, the overall reaction is

\[
C_{16}H_{34} (g) + \frac{49}{2} O_2 (g) \rightarrow 16 CO_2 (g) + 17 H_2 O (g) \]  

(1)

The anode half-cell reaction is

\[
C_{16}H_{34} (g) + 32 H_2 O (g) \rightarrow 16 CO_2 (g) + 98 H^+ + 98 e^- \]  

(2)

The cathode half-cell reaction is

\[
\frac{49}{2} O_2 (g) + 98H^+ + 98e^- \rightarrow 49 H_2 O (g) \]  

(3)

where the (g) represents the gas phase. The anode stoichiometric ratio, SR = H_2 O/C_{16}H_{34} is 32. One mole of n-hexadecane reacts with 32 moles of water at the anode and generates 98 moles of protons and electrons. The protons migrate through the electrolyte to the cathode where the oxygen reduction reaction occurs.

Bagotzky et al. [34] described a reaction mechanism for direct hydrocarbon fuel cells using methane as a feedstock. The Bagotsky mechanism was modified, as shown in Figure 1, to describe n-hexadecane. The desired product is CO_2. However alcohols, aldehydes, carboxylic acids, and lower molecular weight hydrocarbons are possible by-products. Three reactions are shown in Figure 1: dehydrogenation (from both carbon and oxygen atoms), hydroxylation, and C–C bond cleavage. Two reactions are not shown: water dissociation (H_2 O → H + OH) and hydrogen atom ionization (H → H^+ + e^-). Hydrogen ionization is an electrochemical reaction and therefore is influenced by potential. The other four reactions are chemical reactions and are not influenced by potential.

The objective of the work described here was to identify a set of operating conditions that would permit stable continuous operation of a direct hydrocarbon phosphoric acid fuel cell using n-hexadecane as the fuel.

2. Experimental

A schematic diagram of the direct n-hexadecane fueled phosphoric acid fuel cell (PAFC) system is shown in Figure 2. The overall system consists of an air cylinder, a hydrogen cylinder, one Galvanostat, two syringe pumps, a vaporizer, a phosphoric acid fuel cell (PAFC = Electrochem FC-25-02MA), and a fuel cell test station. Both gaseous and liquid fuels can be used in this fuel cell system. Deionized water and n-hexadecane were introduced into the vaporizer by the syringe pumps. The liquid fuels were expected to vaporize before reaching the anode of the fuel cell. Air was fed to the cathode at a constant flow rate. On those occasions when hydrogen was used as the fuel, the pumps were stopped and the valve in Figure 2 was opened.

The membrane electrode assembly (MEA) used in our fuel cell work had five layers: two gas diffusion layers (GDL), two catalyst layers (CL), and a liquid electrolyte layer. The gas diffusion layers were Teflon coated Toray paper.

The liquid electrolyte was initially 85% (14.6 M) phosphoric acid, which was held in a SiC matrix between the anode and cathode catalyst layers. Platinum (0.5 mg Pt/cm^2) supported on carbon (10% Pt on C) was the catalyst in both anode and cathode catalyst layers. The fuel cells had a face area of 25 cm^2. A pin-type flow field was machined in a graphite plate. The current collectors were sheets of copper metal that had been gold plated on both sides. Silicone rubber flexible heaters were attached to each current collector.

Several types of experiments were performed. Hydrogen polarization curves were measured to determine the state...
H(CH₂)₆CH₃ = hexadecane if \( N = 15 \)

\[
\begin{align*}
&\text{H(CH₂)₆CH₃(g)} \\
&\text{H(CH₂)₆CH₃(ads)} \xrightarrow{H} \text{H(CH₂)₆CH₂} \\
&\text{H(CH₂)₆CH₂} \xrightarrow{H} \text{H(CH₂)₅CH} \\
&\text{H(CH₂)₅CH} \xrightarrow{bc} \text{H(CH₂)₄CH₂} + \text{CO} \\
&\text{H(CH₂)₄CH₂OH(g)} \leftarrow \text{H(CH₂)₄CH₂OH(ads)} \\
&\text{H(CH₂)₄CHO(g)} \leftarrow \text{H(CH₂)₄CHO(ads)} \\
&\text{H(CH₂)₄COOH(g)} \leftarrow \text{H(CH₂)₄COOH(ads)} \\
&\text{H(CH₂)₄H(g)} \leftarrow \text{H(CH₂)₄H(ads)} + \text{CO₂(ads)} \\
&\text{CO₂(g)} \rightarrow \text{O=O(ads)} \\
&N_{\text{new}} = N_{\text{old}} - 1 \\
&bc = \text{C–C bond cleavage}
\end{align*}
\]

Figure 1: Diagram of a modified Bagotsky anode reaction mechanism: H(CH₂)₆CH₃ = hexadecane if \( N = 15 \), +OH = Hydroxylation, −H = Dehydrogenation, and bc = C–C bond cleavage. Two reactions are not shown, water dissociation \( H_2O = H + OH \) and the electrochemical reaction \( H = H^+ + e^- \).

Figure 2: Diagram of a direct n-hexadecane fueled phosphoric acid fuel cell system.

of the MEA in the fuel cell. A polarization curve shows the potential difference as a function of current density. n-Hexadecane polarization curves were measured. Two types of time-on-stream experiments were performed (H₂O with n-C₁₆H₃₄ and H₂O only). The time-on-stream experiments were performed at (a) different molar ratios of water to n-hexadecane, (b) different current densities, and (c) different temperatures.

The following operating conditions were used. Separate syringe pumps were used to feed both water and n-hexadecane. The water flow rate was expressed as a function of the stoichiometric ratio (SR) of H₂O/C₁₆H₃₄ in (2) for the anode half reaction. A constant flow rate of n-hexadecane (0.2 mL/h) was used in all experiments. The two water flow rates and their stoichiometric ratios were 1 mL/h (2.5 * SR, H₂O/C₁₆H₃₄ = 80) and 5.1 mL/h (12.9 * SR, H₂O/C₁₆H₃₄ = 414). Some experiments were performed with only water being fed to the fuel cell. The experiments were performed at two temperatures, 160°C and 190°C.

A Hokuto Denko HA-301 Galvanostat was used to adjust the potential difference between the anode and cathode of the phosphoric acid fuel cell to maintain the chosen current at a constant value. The potential difference was recorded every second using a Lab View data logger.
Two hydrogen/air polarization curves obtained with a PAFC are shown in Figure 3. The upper curve was the first experiment performed with a new MEA. The lower curve was measured after some conditioning experiments had been performed with low molecular weight hydrocarbons (ethylene, propane). It is an indication of the condition of the MEA at the beginning of this investigation and will be referred to as the Reference polarization curve. The open circuit potential in Figure 3 is about 0.93 V. It is comparable to the 0.9 V value reported by Fuller et al. [35] with an air cathode half-cell having a hydrogen Reference electrode.

The results of two time-on-stream experiments at 160°C are shown in Figure 4. Both curves show deactivation, indicated by a decrease in potential difference with time. The data show that deactivation continued for at least 20 hours. The two sets of data were obtained at different current densities and different H$_2$O/n-C$_{16}$H$_{34}$ molar ratios. The deactivation reported here with n-hexadecane is consistent with deactivation reported earlier by Okrent and Heath [36] during direct hydrocarbon fuel cell experiments with decane.

Two hypotheses can be suggested to explain deactivation. Carbon monoxide, a reaction intermediate formed during the overall reaction to produce the CO$_2$, shown in Figure 1, could poison the platinum catalyst at the anode. Carbon monoxide is a well-known poison on fuel cell platinum catalysts [27]. The other possibility is the formation of carbonaceous deposits. Liebhafsky and Cairns [37] indicated the formation of dehydrogenated residues or carbonaceous materials during the operation of fuel cells with hydrocarbon fuels.

The current densities in Figure 4 were integrated with respect to time to obtain the cumulative amount of charge transferred. The potential difference in Figure 4 was plotted as a function of cumulative charge transferred in Figure 5. The data indicate that, at potential differences less than 0.4 V, the slopes of the two lines are the same. In other words, deactivation is a linear function of charge transferred. That observation suggests that deactivation, as represented by a decrease in potential difference, is related to some phenomenon that correlates with the amount of charge transferred, regardless of the H$_2$O/n-C$_{16}$H$_{34}$ molar ratio.

A hydrogen/air polarization curve was measured using the PAFC after the first TOS experiment at 160°C.
The current density was set to a constant value. Then the polarization curve was measured. The technique for measuring the polarization curve is indicated in Figure 7. The current density was set to a constant value. Then the potential difference was recorded until a steady-state value for the potential difference. For one datum point, corresponding to 0.4 mA/cm², the steady-state value of the potential difference was extrapolated from the data in Figure 7. Generally at least one hour was required to obtain a steady-state value for the potential difference. Finally, the steady-state values of the potential differences obtained in Figure 7 were used in Figure 8 to construct a polarization curve for the n-hexadecane/water-air fuel cell.

Some of the characteristics of the 190°C n-hexadecane/air polarization curve in Figure 8 are noteworthy. The open circuit potential of 0.5 V is much smaller than that of 0.93 V obtained for the hydrogen/air fuel cell in Figure 3. It suggests that the results in Figure 8 might represent the partial oxidation of carbon:

\[ \text{C} + \frac{1}{2}\text{O}_2 = \text{CO} \quad E_{298} = 0.711 \text{ V} \quad (4) \]

as the rate limiting step in the overall reaction rather than the oxidation of n-hexadecane in (2). Equation (4) is composed of two half-cell reactions:

\[ \text{C} + \text{H}_2\text{O} = \text{CO} + 2\text{H}^+ + 2\text{e}^- \quad \text{anode} \quad (5) \]

\[ 2\text{H}^+ + 2\text{e}^- + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O} \quad \text{cathode} \quad (6) \]

The difference between 0.711 V and 0.5 V might be caused by a combination of factors: a temperature of 190°C rather than 25°C, a cathode oxygen mole fraction of 0.21,
and an anode water vapour mole fraction representing equilibrium water vapour over phosphoric acid. The open circuit potential, 0.5 V, in Figure 8 is more consistent with the standard electrochemical potential of the partial oxidation of carbon to carbon monoxide reaction, 0.711 V, than with the standard electrochemical potential of the oxidation of carbon monoxide to carbon dioxide (CO + (1/2)O₂ = CO₂, E°₂₉₈ = 1.33 V). Initially two possible hypotheses were suggested to explain deactivation: either carbon monoxide poisoning or deposition of carbonaceous material. Equation (4) is consistent with the carbonaceous material hypothesis and not consistent with carbon monoxide hypothesis. On that basis the hypothesis of deposition of carbonaceous material seems to be the most likely explanation for the deactivation observed during the time-on-stream experiments.

Time-on-stream measurements were also made at 190°C. The TOS results at 190°C are compared with those at 160°C in Figure 9. A steady-state operation was achieved for the last six hours of the experiment at 190°C. A steady-state operation is a highly desirable result that is not always achieved with a comparatively large hydrocarbon molecule, such as hexadecane. For example, Okrent and Heath [36] reported unsteady cycling during which both the potential and the current oscillated over time periods of approximately 15 minutes, when octane was the hydrocarbon fuel. Although we also observed cycling in some of our experiments, that phenomenon was not the object of our investigation. The fact that a steady-state has been demonstrated here for one set of operating conditions means that in principle fuel cells can operate continuously using n-hexadecane (and presumably other diesel type fuels).

Cleaning the MEA with water was mentioned in the discussion pertaining to Figure 7. An example of water being the only reactant entering the fuel cell is shown in Figure 10. The data in Figure 10 were obtained from an MEA that had been used previously for 10 weeks in TOS experiments. When the current density was maintained constant at a value of 0.2 mA/cm² the potential difference decreased continuously for a period of 6 hours. That indicated that a progressively larger overpotential was necessary (a larger driving force was necessary) to maintain the current density at a constant value. When the current density was decreased to 0.1 mA/cm², there was an initial increase in the potential difference (smaller overpotential). The potential difference gradually decreased over the next 7 hours and then remained constant at 0.35 V for the last 6 hours.

The existence of a current density when only water was fed to the fuel cell would require that some reaction must have been occurring. Since no fuel (e.g., no n-hexadecane) was fed to the fuel cell, it is plausible that the reaction may have occurred between water and the carbonaceous material that had been previously deposited on the MEA. The existence of a current density would also require proton migration across the electrolyte. The occurrence of the anode reaction shown in (5) would be consistent with both of these requirements. The measurement of current density when only water was fed to the fuel cell is consistent with the hypothesis that carbonaceous material was formed during deactivation and was available for reaction during the water-only experiment.

After the water-only experiments in Figure 10 were completed, a hydrogen polarization curve was measured. It is compared with the Reference hydrogen polarization curve in Figure II. A comparison of the results in Figure II (after the water-only experiment) with the results in Figure 6 (after the first TOS experiment) indicates that a substantial improvement was caused by the water-only treatment. That suggests the water-only experiment cleaned the MEA. Cleaning of the MEA would be consistent with removal of a carbonaceous deposit from the catalyst surface.

The results reported here can be compared with other fuel cell systems. Two of the important criteria are capital cost and energy efficiency. The capital cost is strongly influenced by the size of the fuel cell stack that in turn is a function of current density. The theoretical energy efficiency is related to the thermodynamic efficiency of the reactions that occur.
After water-only experiments, was observed at one set of conditions. Anode: hydrogen flow rate = 9.6 mL/min. Cathode: air flow rate = 245 mL/min. Temperature = 160°C. Pressure = 1 atm. Solid circles are data obtained after a one-week experiment with water-only (on an MEA that had been used in TOS experiments for ten weeks). Open squares are data for the Reference polarization curve.

The reaction networks that occur with the particular type of fuel cell system. The operating cost of a fuel cell system is strongly influenced by the energy efficiency. Small current densities were obtained for the low-temperature (190°C) direct hydrocarbon (n-hexadecane) PAFC results without a reforming unit reported here. There are extensive reviews describing results obtained by PAFCs operating on hydrocarbons without a reforming unit [2–4]. In general the current densities are quite small. Therefore large reactors having a large capital cost would be required. In contrast Kim et al. [38] reported much larger current densities using a higher temperature (700°C) solid oxide fuel cell, SOFC, without a reforming unit when it was operating on synthetic diesel fuel. Interest in these systems, specifically the development of anodes, continues to be an active area of research [39, 40]. There have been several reviews of direct hydrocarbon SOFCs without reforming units [13, 41, 42]. Although no reforming unit was used, they indicate that internal reforming occurs [13]. Unfortunately the reforming reaction (internal or external) has a negative effect on energy efficiency. Approximately 25% of the hydrocarbon fuel must be used to provide the endothermic heat of reaction for the reforming reaction. At the low temperatures used in this study the reforming reaction is thermodynamically unfavourable and does not occur. Therefore the high-temperature SOFC systems will have a capital cost advantage over the lower temperature PAFC system used here. However, the lower temperature PAFC system used here will have a theoretical energy efficiency advantage over the SOFC system.

The use of an external reformer in combination with a PAFC system is a well-established technology that converts the hydrocarbon to hydrogen in a fuel processing system and then uses the hydrogen as the fuel in a fuel cell system. By the year 2006 more than 200 commercial plants had been sold [43]. Nevertheless research on improving the reforming process continues [44]. The reforming reaction in an external reformer has the same negative effect on energy efficiency that was mentioned above for internal reforming. The fuel processing system includes four processes: steam reforming, high-temperature water shift, low-temperature shift, and hydrogen purification. Equipment for those four processes has a substantial capital cost. In contrast there is no capital cost for a reformer/fuel processor with the low-temperature direct hydrocarbon PAFC system described here.

4. Conclusions

This study reported the first polarization curve ever measured for which n-hexadecane was the fuel at the anode of a fuel cell. The current densities were found to be very small.

Deactivation was observed in time-on-stream experiments. Deactivation, as measured by the change in potential difference, was found to be a linear function of the cumulative charge transferred across the electrolyte of the fuel cell. Deactivation during fuel cell experiments with n-hexadecane was confirmed by comparing hydrogen polarization curves before and after the time-on-stream measurements. For a given potential difference the current densities were much smaller for the hydrogen polarization curves measured after the time-on-stream experiments.

Experiments were performed in which water was the only reactant entering the fuel cell that had been used previously for 10 weeks in time-on-stream experiments. Current densities were measured during those experiments, indicating that the water must have reacted with some type of species that remained on the fuel cell catalyst at the end of the time-on-stream experiments. When a hydrogen polarization curve was measured at the end of the water-only experiments, it was close to that measured before the time-on-stream experiments. That indicates that the deactivating species on the surface of the platinum particles had been removed and that it was possible to regenerate deactivated MEAs.

A hypothesis that carbonaceous material was deposited on the platinum anode catalyst particles was suggested to explain the deactivation. Four types of observations were consistent with that hypothesis: (a) the change in potential difference during time-on-stream measurements; (b) when hydrogen polarization curves measured before and after the time-on-stream experiments were compared, the current densities measured after TOS were much smaller than those measured before TOS; (c) current densities were measured when water was the only reactant entering the fuel cell. In order to produce a current density, water must have reacted with some type of species that had been deposited on the surface of the platinum particles; and (d) the open circuit potential of a n-hexadecane fuel cell, 0.5 V, was much closer to the standard electrochemical potential for the carbonate-water reaction, 0.711 V, than to that for the carbon monoxide-water reaction, 1.33 V. Observation (d) makes a hypothesis of deactivation by carbonaceous materials more likely than deactivation by carbon monoxide poisoning.

Steady-state operation of the n-hexadecane fuel cell, without additional deactivation, was observed at one set of conditions.
Conflicts of Interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The authors gratefully acknowledge that this research and development project was supported by a grant from Transport Canada’s Clean Rail Academic Grant Program and by a Discovery Grant from the Canadian Government’s Natural Sciences and Engineering Research Council.

References

[1] J. A. A. Ketelaar, “History,” in Fuel Cell Systems, L. J. M. J. Blomen and M. N. Mugerwa, Eds., p. 20, Plenum Press, New York, NY, USA, 1993.

[2] E. J. Cairns, “Anodic oxidation of hydrocarbons and the hydrocarbon fuel cell,” Advances in Electrochemistry Science and Electrochemical Engineering, vol. 8, pp. 337–392, 1971.

[3] J. O. M. Bockris and S. Srinivasan, “Electrochemical combustion of organic substances,” in Fuel Cells: Their Electrochemistry, pp. 357–411, McGraw-Hill, New York, NY, USA, 1969.

[4] H. A. Liebhabsky and E. J. Cairns, “The direct hydrocarbon fuel cell with aqueous electrolytes,” in Fuel Cells: Their Electrochemistry, pp. 458–523, John Wiley & Sons, New York, NY, USA, 1968.

[5] S. Bertholet, Oxydation Electrolytique du Methane [Ph.D. Dissertation], Université de Poitiers, Poitiers, France, 1998.

[6] C. K. Cheng, J. L. Luo, K. T. Chuang, and A. R. Sanger, “Propane fuel cells using phosphoric-acid-doped polybenzimidazole membranes,” The Journal of Physical Chemistry B, vol. 109, no. 26, pp. 13036–13042, 2005.

[7] O. Savadogo and F. J. Rodriguez Varela, “Low-temperature direct propane polymer electrolyte membranes fuel cell,” Journal of New Materials for Electrochemical Systems, vol. 4, no. 2, pp. 93–97, 2001.

[8] F. J. Rodriguez Varela and O. Savadogo, “Real-time mass spectrometric analysis of the anode exhaust gases of a direct propane fuel cell,” Journal of the Electrochemical Society, vol. 152, no. 9, pp. A1755–A1762, 2005.

[9] P. Heo, K. Ito, A. Tomita, and T. Hibino, “A proton-conducting fuel cell operating with hydrocarbon fuels,” Angewandte Chemie—International Edition, vol. 47, no. 41, pp. 7841–7844, 2008.

[10] B. C. H. Steele, I. Kelly, H. Middleton, and R. Rudkin, “Oxidation of methane in solid state electrochemical reactors,” Solid State Ionics, vol. 28–30, no. 2, pp. 1547–1552, 1988.

[11] E. P. Murray, T. Tsai, and S. A. Barnett, “A direct-methane fuel cell with a ceria-based anode,” Nature, vol. 400, no. 6745, pp. 649–651, 1999.

[12] W. Zhu, C. Xia, J. Fan, R. Peng, and G. Meng, “Ceria coated Ni as anodes for direct utilization of methane in low-temperature solid oxide fuel cells,” Journal of Power Sources, vol. 160, no. 2, pp. 897–902, 2006.

[13] M. D. Gross, J. M. Vohs, and R. J. Gorte, “Recent progress in SOFC anodes for direct utilization of hydrocarbons,” Journal of Materials Chemistry, vol. 17, no. 30, pp. 3071–3077, 2007.

[14] J. G. Lee, C. M. Lee, M. Park, and Y. G. Shul, “Direct methanol fuel cell with La$_2$SnO$_4$–Ni–Gd$_{0.9}$Ce$_{0.1}$O$_{1.95}$ anode and electro-spin La$_{0.6}$Sr$_{0.4}$Co$_{0.1}$Fe$_{0.8}$O$_{1.9}$–Gd$_{0.6}$Ce$_{0.3}$O$_{1.5}$ cathode,” Royal Society of Chemistry Advances, vol. 3, no. 29, pp. 1816–1822, 2013.

[15] D. Ding, Z. Liu, L. Li, and C. Xia, “An octane-fueled low temperature solid oxide fuel cell with Ru-free anodes,” Electrochemistry Communications, vol. 10, no. 9, pp. 1295–1298, 2008.

[16] H. Kishimoto, K. Yamaji, T. Horita et al., “Feasibility of liquid hydrocarbon fuels for SOFC with Ni-ScSZ anode,” Journal of Power Sources, vol. 172, no. 1, pp. 67–71, 2007.

[17] Z. F. Zhou, C. Gallo, M. B. Pague, H. Schobert, and S. N. Liov, “Direct oxidation of jet fuels and Pennsylvania crude oil in a solid oxide fuel cell,” Journal of Power Sources, vol. 133, no. 2, pp. 181–187, 2004.

[18] G. Psogfojaniakkis, Y. Bourgault, B. E. Conway, and M. Ternan, “Mathematical model for a direct propane phosphoric acid fuel cell,” Journal of Applied Electrochemistry, vol. 36, no. 1, pp. 115–130, 2006.

[19] H. Khakdaman, Y. Bourgault, and M. Ternan, “Computational modeling of a direct propane fuel cell,” Journal of Power Sources, vol. 196, no. 6, pp. 3186–3194, 2011.

[20] H. R. Khakdaman, Y. Bourgault, and M. Ternan, “Direct propane fuel cell anode with interdigitated flow fields: two-dimensional model,” Industrial & Engineering Chemistry Research, vol. 49, no. 3, pp. 1079–1085, 2010.

[21] G. Psogfojaniakkis, A. St-Amant, and M. Ternan, “Ab-initio DFT study of methane electro-oxidation mechanism on platinum,” Journal of Physical Chemistry B, vol. 110, pp. 24593–24605, 2006.

[22] S. Vafaeyan, A. St-Amant, and M. Ternan, “Nickel alloy catalysts for the anode of a high temperature PEM direct propane fuel cell,” Journal of Chemistry, vol. 2014, Article ID 151638, 8 pages, 2014.

[23] S. Vafaeyan, A. St-Amant, and M. Ternan, “Propane fuel cells: selectivity for partial or complete reaction,” Journal of Fuels, vol. 2014, Article ID 485045, 9 pages, 2014.

[24] A. Al-Othman, A. Y. Tremblay, W. Pell et al., “A modified silicic acid (Si) and sulphuric acid (S)-ZrP/PTFE/glycol composite membrane for high temperature direct hydrocarbon fuel cells,” Journal of Power Sources, vol. 224, pp. 158–167, 2013.

[25] A. Al-Othman, A. Y. Tremblay, W. Pell, Y. Liu, B. A. Peppley, and M. Ternan, “The effect of glycerol on the conductivity of Nafton-free ZrP/PTFE composite membrane electrolytes for direct hydrocarbon fuel cells,” Journal of Power Sources, vol. 199, pp. 14–21, 2012.

[26] A. Al-Othman, A. Y. Tremblay, W. Pell et al., “Zirconium phosphate as the proton conducting material in direct hydrocarbon polymer electrolyte membrane fuel cells operating above the boiling point of water,” Journal of Power Sources, vol. 195, no. 9, pp. 2520–2525, 2010.

[27] C. G. Farrell, C. L. Gardner, and M. Ternan, “Experimental and modelling studies of CO poisoning in PEM fuel cells,” Journal of Power Sources, vol. 171, no. 2, pp. 282–293, 2007.

[28] R. Fonocho, C. L. Gardner, and M. Ternan, “A study of the electrochemical hydrogenation of o-xylene in a PEM hydrogenation cell,” Electrochimica Acta, vol. 75, pp. 171–178, 2012.
[29] N. Sammes, R. Bove, and K. Stahl, “Phosphoric acid fuel cells: fundamentals and applications,” *Current Opinion in Solid State and Materials Science*, vol. 8, no. 5, pp. 372–378, 2004.

[30] J. M. King and H. R. Kunz, “Phosphoric acid electrolyte fuel cells,” in *Handbook of Fuel Cells*, W. Vielstich, A. Lamm, H. A. Gasteiger, and H. Yokokawa, Eds., vol. 1, pp. 287–300, John Wiley & Sons, New York, NY, USA, 2010.

[31] S. R. Choudhury, “Phosphoric acid fuel cell technology,” in *Recent Trends in Fuel Cell Science and Technology*, S. Basu, Ed., pp. 188–216, Springer, New York, NY, USA, 2007.

[32] W. Grubb and C. J. Michalske, “A high performance propane fuel cell operating in the temperature range of 150°–200°C,” *Journal of The Electrochemical Society*, vol. 111, no. 9, p. 1015, 1964.

[33] H. A. Liebhafsky and W. T. Grubb, “Normal alkanes at platinum anodes,” *Fuel Preprints*, vol. 11, no. 2, p. 134, 1967.

[34] V. S. Bagotzky, Y. B. Vassiliev, and O. A. Khazova, “Generalized scheme of chemisorption, electrooxidation and electroreduction of simple organic compounds on platinum group metals,” *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, vol. 81, no. 2, pp. 229–238, 1977.

[35] T. F. Fuller, F. J. Luczak, and D. J. Wheeler, “Electrocatalyst utilization in phosphoric acid fuel cells,” *Journal of the Electrochemical Society*, vol. 142, no. 6, pp. 1752–1757, 1995.

[36] E. H. Okrent and C. E. Heath, “A liquid hydrocarbon fuel cell battery,” in *Fuel Cell Systems*, B. Baker, Ed., Advances in Chemistry, pp. 328–340, American Chemical Society, Washington, DC, USA, 1969.

[37] H. A. Liebhafsky and E. J. Cairns, “The direct hydrocarbon fuel cell with aqueous electrolytes,” in *Fuel Cells and Fuel Batteries*, pp. 485–510, John Wiley & Sons, New York, NY, USA, 1968.

[38] H. Kim, S. Park, J. M. Vohs, and R. J. Gorte, “Direct oxidation of liquid fuels in a solid oxide fuel cell,” *Journal of the Electrochemical Society*, vol. 148, no. 7, pp. A693–A695, 2001.

[39] S. Islam and J. M. Hill, “Barium oxide promoted Ni/YSZ solid-oxide fuel cells for direct utilization of methane,” *Journal of Materials Chemistry A*, vol. 2, no. 6, pp. 1922–1929, 2014.

[40] C. Yang, J. Li, Y. Lin, J. Liu, F. Chen, and M. Liu, “In-situ fabrication of CoFe allot nanoparticles structure (Pr₀.₄Sr₀.₆)₁₋ₓ (Fe₀.₈₅Nb₀.₁₅)ₓO₇ ceramic anode for direct hydrocarbon solid oxide fuel cells,” *Nano Energy*, vol. 11, pp. 704–711, 2015.

[41] S. McIntosh and R. J. Gorte, “Direct hydrocarbon solid oxide fuel cells,” *Chemical Reviews*, vol. 104, no. 10, pp. 4845–4865, 2004.

[42] Y. Zhao, C. Xia, L. Jia et al., “Recent progress on solid oxide fuel cell: lowering temperature and utilizing non-hydrogen fuels,” *International Journal of Hydrogen Energy*, vol. 38, no. 36, pp. 16498–16517, 2013.

[43] S. Srinivasan, *Fuel Cells: From Fundamentals to Applications*, Springer, New York, NY, USA, 2006.

[44] M. R. Walluk, J. Lin, M. G. Waller, D. F. Smith, and T. A. Trabold, “Diesel auto-thermal reforming for solid oxide fuel cell systems: anode off-gas recycle simulation,” *Applied Energy*, vol. 130, pp. 94–102, 2014.
Submit your manuscripts at http://www.hindawi.com