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The direct formate fuel cell with an alkaline anion exchange membrane

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We demonstrate for the first time an operating Direct Formate Fuel Cell employing formate salts as the anode fuel, air or oxygen as the oxidant, a polymer anion exchange membrane, and metal catalysts at the anode and cathode. Operation of the DFFC at 60 °C using 1 M KOOCH and 2 M KOH as the anode fuel and electrolyte and oxygen gas at the cathode produces 144 mW cm^{-2} of peak power density, 181 mA cm^{-2} current density at 0.6 V, and an open circuit voltage of 0.931 V. This performance is competitive with alkaline Direct Liquid Fuel Cells (DLFCs) previously reported in the literature and demonstrates that formate fuel is a legitimate contender with alcohol fuels for alkaline DLFCs. A survey of the literature shows that a formate–oxygen fuel cell has a high theoretical potential, and the safe, renewable formate fuel does not poison the anode catalyst.

1. Introduction

Development of the first commercial fuel cells in the 1960s revolved around two different hydrogen–oxygen fuel cells which possess the same overall chemistry:

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \quad E^0_{\mathrm{cell}} = 1.23\ \mathrm{V} \tag{1}$$

A fuel cell with an *acid* electrolyte passes H^+ from anode to cathode:

$$H_2 \rightarrow 2H^+ + 2e^- \quad E^0_{\mathrm{anode}} = 0.00\ \mathrm{V} \tag{2}$$

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad E^0_{\mathrm{cathode}} = 1.23\ \mathrm{V} \tag{3}$$

while a fuel cell with an *alkaline* electrolyte passes OH^- from cathode to anode:

$$H_2 + 2OH^- \rightarrow 2H_2O + 2e^- \quad E^0_{\mathrm{anode}} = -0.83\ \mathrm{V} \tag{4}$$

$$\tfrac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad E^0_{\mathrm{cathode}} = 0.40\ \mathrm{V} \tag{5}$$

The oxygen reduction reaction (Equation (3) or (5)) limits the efficiency of a hydrogen–oxygen fuel cell [1]. Since the reaction proceeds more rapidly in alkaline media, the alkaline fuel cell (AFC) is more efficient. Hydrogen–oxygen fuel cells containing liquid or solid electrolytes were used in the space program but suffered from engineering difficulties which were remedied by the development of Nafion®, a polymer ion exchange membrane which replaced a liquid or solid electrolyte. Nafion® permitted the miniaturization of fuel cells and improved their performance and durability. However, since Nafion® is a proton exchange membrane (PEM), it is only capable of replacing the electrolyte in an *acid* fuel cell. Therefore, its creation shifted scientists' attention toward acid fuel cells, for which most research of the past several decades has been focused [2].

While hydrogen–oxygen fuel cells are very energy efficient, they are impractical for many portable power applications such as transportation and portable electronic devices. Hydrogen compression is energy inefficient, and safe hydrogen storage requires high-mass components. Therefore direct liquid fuel cells (DLFCs) are currently being commercialized for portable electronic devices such as mobile phones and laptop computers, and they are being researched for transportation applications [3–5]. State of the art *acid* DLFCs possess a PEM and are fed by small organic molecule fuels such as methanol or formic acid:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad E^0_{\mathrm{anode}} = 0.02\ \mathrm{V} \tag{6}$$

$$HCOOH \rightarrow CO_2 + 2H^+ + 2e^- \quad E^0_{\mathrm{anode}} = -0.22\ \mathrm{V} \tag{7}$$

However, DLFCs using such fuels have several engineering challenges [6,7]. First, the oxidation reactions are kinetically

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sluggish in acid media, especially in comparison to hydrogen oxidation. Second, the catalysts, which must be noble metals to survive the acid environment, are susceptible to poisoning. Third, the fuel tends to be dragged across the membrane along with the protons, particularly in the methanol fuel cell. Finally, the methanol fuel is toxic and the environment of both fuel cells is corrosive.

The *alkaline* environment of an AFC is ideal for direct operation using a small organic molecule fuel. For decades, the major roadblock to commercialization has been the lack of a practical polymer electrolyte anion exchange membrane (AEM). However, within the past few years, Tokuyama developed an AEM which has been demonstrated by a few scientists to operate a DLFC fueled by small organic molecules [7–11]. There are two key advantages of the polymer AEM membrane. First, the fuel cell membrane is not susceptible to carbonation, which would lead to formation of precipitates if an alkaline fuel cell was operated using a liquid electrolyte. Second, the membrane permits operation of a direct liquid fuel cell in an *alkaline* environment, where in comparison to an acid environment: (1) the oxidation of small organic molecules is more facile, (2) less expensive catalysts are stable, and (3) the fuel does not cross the membrane. The alkaline environment is significantly less corrosive to the catalysts, which would permit the use of less noble catalysts. However, two main drawbacks to AEMs are significant and are being addressed in development: (1) thermal stability, and (2) chemical stability (nucleophilic replacement of ammonium by hydroxide, although this mechanism is less likely at lower temperatures). Development of this polymer AEM is rapidly removing engineering barriers to development of practical direct liquid alkaline fuel cells.

An example of an alkaline DLFC is shown in Fig. 1, where the fuel, F, is oxidized to carbon dioxide and water at the anode, while oxygen is reduced at the cathode. The alkaline anion exchange membrane is a key component and passes hydroxide ion from cathode to anode; the combination of fuel and hydroxide at the anode releases electrons, which flow out of the fuel cell to do the work of powering a wireless phone, for example. As electrons flow to the cathode, the oxygen is reduced and hydroxide is released and transferred across the membrane. The electrodes consist of catalysts in direct contact with the membrane via painting or indirect contact via a gas diffusion electrode hot pressed to the membrane.

The most popular fuel to date, in part due to its renewability, is ethanol:

$$CH_3CH_2OH + 12OH^- \rightarrow 2CO_2 + 9H_2O + 12e^- \quad E^0_{\text{anode}} = 0.74\ \text{V} \tag{8}$$

As expected, the ethanol oxidation reaction is facile in alkaline media, but it still exhibits a high overpotential and the oxidation to CO_2 is generally incomplete [12]. Despite these drawbacks, alkaline direct ethanol fuel cells (DEFCs) with polymer AEMs have been demonstrated to produce significant power density with optimization of catalysts (including non-platinum metals) and fuel/electrolyte concentrations [7].

Methanol also has been studied as a fuel for an AFC:

$$CH_3OH + 6OH^- \rightarrow CO_2 + 5H_2O + 6e^- \quad E^0_{\text{anode}} = -0.81\ \text{V} \tag{9}$$

A major advantage to using methanol in an alkaline fuel cell rather than an acid fuel cell (Equation (6)) is that water is produced (rather than required) at the anode. The water requirement in the acid methanol fuel cell demands a prohibitive water management system which significantly reduces the net power output of the fuel cell. In addition, the methanol oxidation reaction is more likely to go to completion than ethanol oxidation due to the lack of carbon–carbon bond, and its oxidation mechanism is currently the focus of much research [6]. However, methanol oxidation is also subject to high overpotential, which limits its power density [8,10]. In addition, its toxicity and flammability reduce its attractiveness as a fuel.

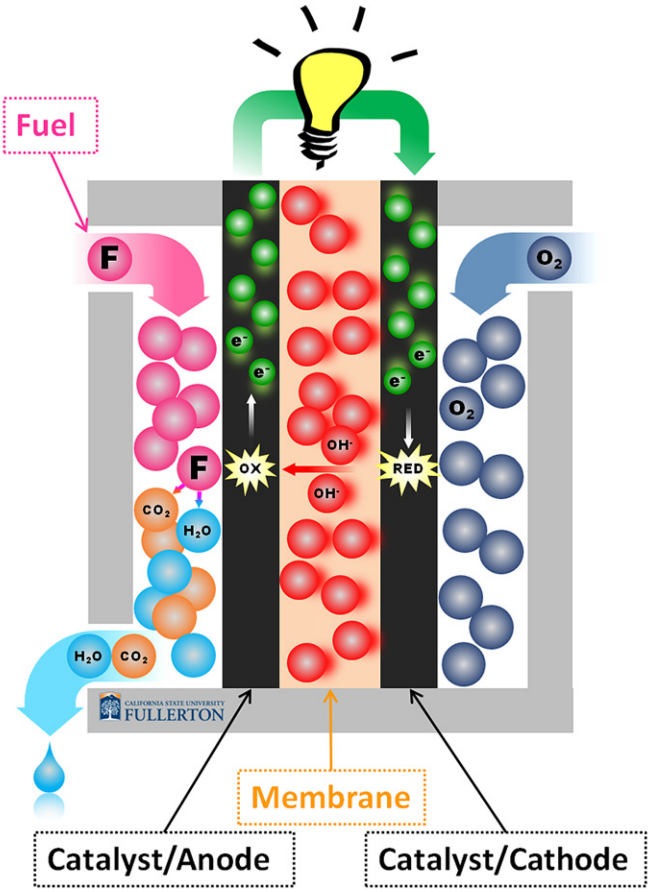

Fig. 1. A conceptual diagram of an alkaline direct liquid fuel cell showing the fuel oxidizing to water and carbon dioxide at the anode and oxygen reducing at the cathode. The key component of this fuel cell is the polymer membrane which transfers hydroxide ions from the cathode to anode.

The oxidation of sodium formate and potassium formate was studied several decades ago and shown in alkaline media to oxidize readily on palladium, which is less costly than platinum [13–15]:

$$COOH^- + 3OH^- \rightarrow CO_3^{2-} + 2H_2O + 2e^- \quad E^0_{\text{anode}} = -1.05\ \text{V} \tag{10}$$

Combination of Equations (5) and (10) would produce an overall theoretical E^0_{cell} of 1.45 V, which is 0.31 V higher than an alkaline DEFC and 0.24 V higher than an alkaline DMFC. In alkaline media, formate salts do not exhibit any poisoning and are expected to oxidize efficiently on even less costly catalysts than palladium.

One can envision a formate fuel which is transported conveniently in a solid form and dissolved in water at the point of energy demand to produce a usable fuel. These two formate salts are not dangerous to humans or the environment. Formate solutions are used as airplane and road de-icing agents due to their environmentally-friendly and non-corrosive properties; chloride salts currently used in road de-icing contaminate aquifers and corrode vehicles and bridges [16]. Sodium formate is approved as a food additive in the United States [17]. There is current research on conversion of carbon dioxide to small organic molecule fuels such as formic acid and methanol; these fuels are ideal for such