The direct formate fuel cell with an alkaline anion exchange membrane

Amy M. Bartrom, John L. Haan*

Department of Chemistry and Biochemistry, California State University, 800 N State College Blvd, Fullerton, CA 92834, USA

ABSTRACT

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.
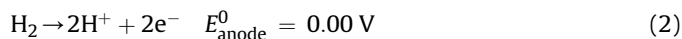
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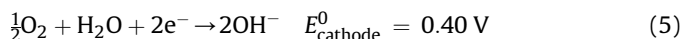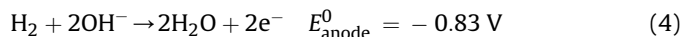
1. Introduction

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

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \quad E^0_{cell} = 1.23\,V \qquad (1)$$
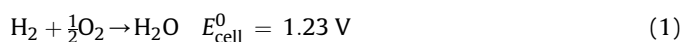
A fuel cell with an *acid* electrolyte passes H^+ from anode to cathode:

$$H_2 \rightarrow 2H^+ + 2e^- \quad E^0_{anode} = 0.00\,V \qquad (2)$$

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

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

$$H_2 + 2OH^- \rightarrow 2H_2O + 2e^- \quad E^0_{anode} = -0.83\,V \qquad (4)$$

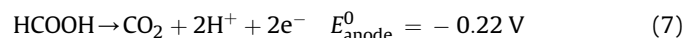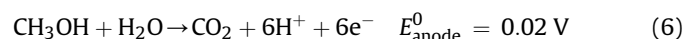$$\tfrac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad E^0_{cathode} = 0.40\,V \qquad (5)$$

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:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad E^0_{anode} = 0.02\,V \qquad (6)$$

$$HCOOH \rightarrow CO_2 + 2H^+ + 2e^- \quad E^0_{anode} = -0.22\,V \qquad (7)$$

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

* Corresponding author. Tel.: +1 6572787612; fax: +1 6572785316.
E-mail address: jhaan@fullerton.edu (J.L. Haan).

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:

$$CH_3CH_2OH + 12OH^- \rightarrow 2CO_2 + 9H_2O + 12e^- \quad E^0_{anode} = 0.74 \text{ V} \tag{8}$$
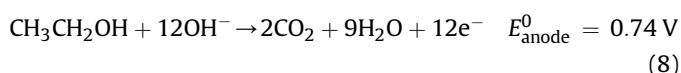
As expected, the ethanol oxidation reaction is facile in alkaline media, but it still exhibits a high overpotential and the oxidation to CO_2 is generally incomplete [12]. Despite these drawbacks, alkaline direct ethanol fuel cells (DEFCs) with polymer AEMs have been demonstrated to produce significant 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:

$$CH_3OH + 6OH^- \rightarrow CO_2 + 5H_2O + 6e^- \quad E^0_{anode} = -0.81 \text{ V} \tag{9}$$
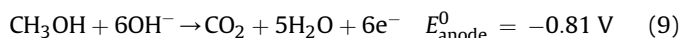
A major advantage to using methanol in an alkaline fuel cell rather than an acid fuel cell (Equation (6)) is that water is produced (rather than required) at the anode. The water requirement in the acid methanol fuel cell demands a prohibitive water management system which significantly reduces the net 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
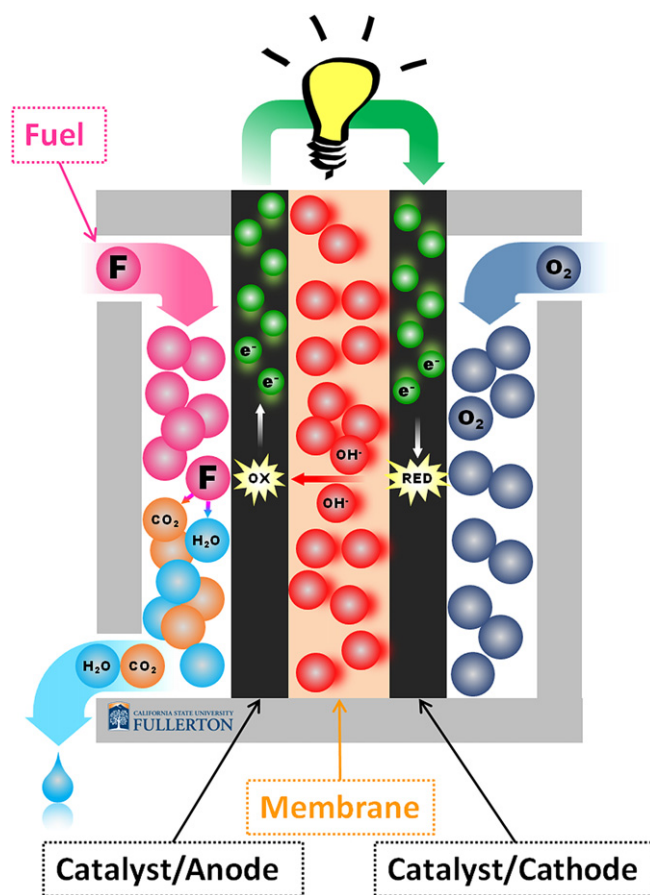

Fig. 1. A conceptual diagram of an alkaline direct liquid fuel cell showing the fuel oxidizing to water and carbon dioxide at the anode and oxygen reducing at the cathode. The key component of this fuel cell is the polymer membrane which transfers hydroxide ions from the cathode to anode.

the 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.

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]:

$$COOH^- + 3OH^- \rightarrow CO_3^{2-} + 2H_2O + 2e^- \quad E^0_{anode} = -1.05 \text{ V} \tag{10}$$
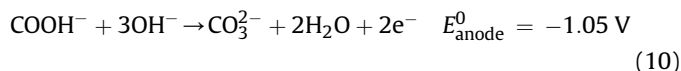
Combination of Equations (5) and (10) would produce an overall theoretical E^0_{cell} of 1.45 V, which is 0.31 V higher than an alkaline DEFC and 0.24 V higher than an alkaline DMFC. In alkaline media, formate salts do not exhibit any poisoning and are expected to oxidize efficiently on even less costly 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

a conversion since their production only requires hydrogenation, but does not require the creation of a carbon−carbon bond [18]. Combined with contemporary research on artificial photosynthesis, the conversion of carbon dioxide into usable small organic molecule fuels would directly create a renewable source of formate salts [19,20]. In addition to their safety and potential renewability, formate salts are non-flammable in contrast to alcohol fuels.

In the 1970s, formate−air fuel cells were studied using KOH and NaOH liquid electrolytes [15]. Recently, a microfluidic fuel cell was demonstrated containing formate as the fuel and hypochlorite bleach as the oxidant [21]. However, we have no knowledge of any device which demonstrates the combination of formate fuels with oxygen or air separated by an alkaline anion exchange membrane. Therefore, we present here the first report to our knowledge of a direct formate fuel cell (DFFC) employing formate salts as the anode fuel and either air or oxygen as the oxidant, with the anode and cathode separated by a polymer anion exchange membrane.

2. Experimental

2.1. Fuel cell

The fuel cell assembly consists of a test cell (Fuel Cell Technologies, 5 cm^2 active area) and a membrane electrode assembly consisting of an alkaline anion exchange membrane (Tokuyama, A201), palladium black anode catalyst (Aldrich, 99.8%), and platinum black cathode catalyst (Alfa Aesar, high surface area), and gas diffusion layers of untreated carbon cloth (Fuel Cell Stores). The catalyst ink is mixed with appropriate amounts of water and alkaline ionomer solution (Tokuyama, 5 wt% AS-4), and it is directly painted onto the membrane in order to load approximately 2 mg cm^{-2} of metal catalyst. The mass ratio of ionomer to catalyst is approximately 1:6.

The assembled fuel cell is connected to a DC load box (BK Precision, 8500). Liquid solution of KCOOH (Alfa Aesar, 99%)/KOH (Fisher), NaCOOH (Alfa Aesar, 98%)/KOH, or CH$_3$CH$_2$OH/KOH was directly fed to the anode at approximately 1 mL min^{-1} for potential−current (VI) tests and approximately 0.2 mL min^{-1} for constant current tests. The cathode was fed oxygen (Oxygen Service Company) at 100 sccm or air (Oxygen Service Company) at 400 sccm. The fuel cell assembly and the liquid fuel were both heated to 40 or 60 °C, while the cathode gas was unheated (Heating and humidifying the cathode gas only increased the fuel cell current output by approximately 1%.). For the VI experiments, the fuel cell was stepped from open circuit potential to approximately 0.4 V. The constant current experiment was set at 100 mA cm^{-2} for several hours.

2.2. Electrochemical cell

Experiments were carried out with a potentiostat (Ametek, PAR263A) in a standard three electrode glass cell. The working electrode consists of palladium black catalyst (Aldrich, 99.8%) applied to a gold tip attached to a rotating disk electrode (Pine Instruments, AFMSRCE). The counter electrode is platinum mesh (Alfa Aesar, 52 mesh). The reference electrode is Ag/AgCl (eDAQ, leakless). The reference electrode was monitored daily to insure that there was no precipitation of AgOH which would result in electrode drift.

Chronoamperometry experiments at various potentials were performed to observe the behavior of the catalysts over 15 h in three different 1 M solutions (and 1 M support electrolytes): KCOOH (KOH), CH$_3$CH$_2$OH (KOH), and HCOOH (H$_2$SO$_4$, GFS, Vicor double distilled). Each solution was degassed using argon (UHP, Oxygen Service Company). The rotating disk was operated

at 2000 rpm to remove carbon dioxide bubble formation from the working electrode and prevent concentration gradients in solution.

3. Results and discussion

3.1. Demonstration of the direct formate fuel cell

We demonstrate for the first time an operating DFFC employing formate salts as the anode fuel, air or oxygen as the oxidant, a polymer anion exchange membrane, palladium anode catalysts, and platinum cathode catalysts. Fig. 2 shows operation of the DFFC with 1 M KOOCH + 2 M KOH as the anode fuel and electrolyte, oxygen as the oxidant, and the fuel cell operating at 60 °C. Under these conditions the DFFC power density is 144 mW cm^{-2}, the current density at 0.6 V is 181 mA cm^{-2}, and the open circuit voltage is 0.931 V. This performance is competitive with alkaline DLFCs reported in the literature (up to 125 mW cm^{-2} at 60 °C) and demonstrates that formate fuel is a legitimate contender with alcohol fuels for alkaline DLFCs [7,11].

In this work we use a proof-of-concept MEA consisting of 2 mg cm^{-2} palladium black anode catalyst and 2 mg cm^{-2} platinum cathode catalyst directly painted onto a Tokuyama A201 alkaline AEM. Palladium black is used at the anode because it is known to be an excellent catalyst for formic acid oxidation [22]. Preliminary research in our lab confirms it is a powerful and stable catalyst for formate oxidation also. However, we are currently performing research to mix non-noble metals into the palladium in order to dilute and eventually replace the palladium. Platinum black is used at the cathode because it is a very reliable catalyst for oxygen reduction; however, research is progressing on non-noble metal catalysts for oxygen reduction [23]. Since the cathode reaction does not limit DLFCs, we use a reliable cathode catalyst and focus our efforts on the anode reaction. Alkaline DEFCs have been demonstrated recently using non-precious metal catalysts, so we expect future DFFCs will not require a platinum cathode catalyst either [8−10]. This MEA was also used with ethanol fuel to compare the DFFC to a DEFC since palladium has been demonstrated as a strong catalyst for ethanol oxidation in alkaline media. We anticipate that future research on the DFFC catalysts and other components will
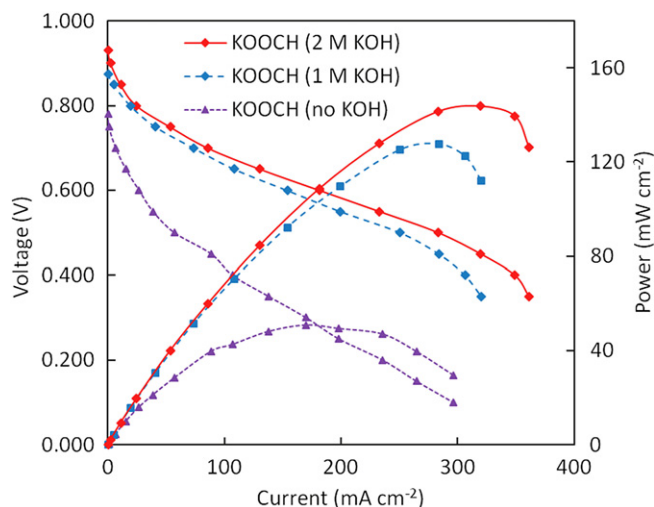
Fig. 2. VI plots comparing effects of KOH fuel electrolyte concentration in the DFFC. The optimal KOH concentration is 2 M, although significant power density can be achieved without KOH added to the fuel stream. Fuel: 1 mL min^{-1} 1 M KCOOH + 0−2 M KOH. Oxidant: 100 sccm oxygen at 25 °C. Temperature of fuel and fuel cell: 60 °C.

produce a higher-performing DFFC which will continue to compete with the DEFC.

3.2. Dependence on KOH concentration

Fig. 2 shows the role of 0−2 M KOH mixed with 1 M KCOOH as the anode fuel in a DFFC operating at 60 °C with oxygen at the cathode. A concentration of 2 M KOH was found to be optimal, therefore it was used in all other experiments. When the KCOOH anode fuel was used without any addition of KOH, the performance was significantly weakened. Current alkaline fuel cells require some hydroxide ion to be mixed with the fuel since they are a reactant in the oxidation of the fuel (Equations (8)–(10)) [11]. Theoretically, sufficient hydroxide ion is produced at the cathode and should be transferred across the membrane to the anode. However, until a more efficient membrane is developed, some hydroxide mixed with the fuel will increase efficiency. It is important to note in Fig. 2 that, although the fuel cell performance decreases when KOH is removed from the fuel, significant performance (51 mW cm^{-2}) is still achieved. This performance will be discussed again later in comparison to the ethanol fuel cell. A DFFC with a fully optimized membrane should not require any KOH in the fuel, which would be beneficial for avoiding carbonation of the anode fuel when a fuel cell is operated without an external pump as is used during testing. Therefore, a formate salt could be transported and stored in the solid form; it might even be inserted into the fuel cell in the solid form. In this case, the fuel cell would simply have the requirement to "just add water" in order to operate. Formate salts are promising fuels for alkaline DLFCs.

3.3. Dependence on KOOCH concentration

Fig. 3 shows the effect of changing the KOOCH concentration in a DFFC operating at 60 °C using oxygen at the cathode and 2 M KOH mixed with the anode fuel. A concentration of 1 M KOOCH was determined to be optimal at these conditions, while increasing the concentration to 3 M KOOCH significantly decreased DFFC performance. The solubility of potassium formate in water is 39.4 mol kg^{-1} at 18 °C; an ideal fuel cell would take advantage of this by operating at a high concentration of potassium formate [24]. Our fuel cell shows that increasing concentration of potassium

formate to 3 M, less than a tenth of its maximum solubility, significantly diminishes performance. It has been reported that 5 M ethanol is the concentration at which alkaline DEFC performance reaches a maximum, because as the ethanol concentration increases, adsorption of hydroxyls (consumed in the rate determining step) blocks ethanol adsorption [9]. It is possible that the same competitive adsorption is occurring during formate oxidation. Therefore, we are performing studies in an electrochemical cell to determine whether the diminishing power at higher concentrations is inherent to the chemistry of formate oxidation or if high performance at high concentration can be achieved by improved engineering of the alkaline fuel cell and its membrane.

3.4. Dependence on temperature and counterion

The VI plots in Fig. 4 demonstrate a significantly higher power density (144 vs. 107 mW cm^{-2}) when the DFFC is run with KCOOH at 60 °C rather than 40 °C. These results are similar to published results for the DEFC, which also requires 60−80 °C to achieve optimal performance [11]. We expect that this temperature dependence is partially due to the membrane and not entirely due to kinetics. The formic acid fuel cell was shown to be capable of operating at low temperatures (at or near room temperature) [25]. We anticipate that formate oxidation also can occur efficiently at low temperatures, and we plan to explore this in an electrochemical cell to determine how much temperature dependence should be expected independent of the membrane.

The VI plots shown in Fig. 4 also compare formate counterion when the DFFC is run with an oxygen cathode and 2 M KOH mixed with the anode fuel. A DFFC using KCOOH anode fuel produces a slightly higher power density (144 vs. 125 mW cm^{-2}) than NaCOOH anode fuel when run at 60 °C. This trend is confirmed in an electrochemical cell. Previous work years ago also demonstrated this trend, although the reason is not well understood [15]. Since potassium formate is more soluble in water, this outcome is advantageous to future optimization of the DFFC. A significant engineering issue for optimization of the DFFC will be the removal of the counterion from the anode. Previous alkaline fuel cells constructed with a liquid electrolyte suffered from issues with carbonate precipitation in the electrolyte (space between the
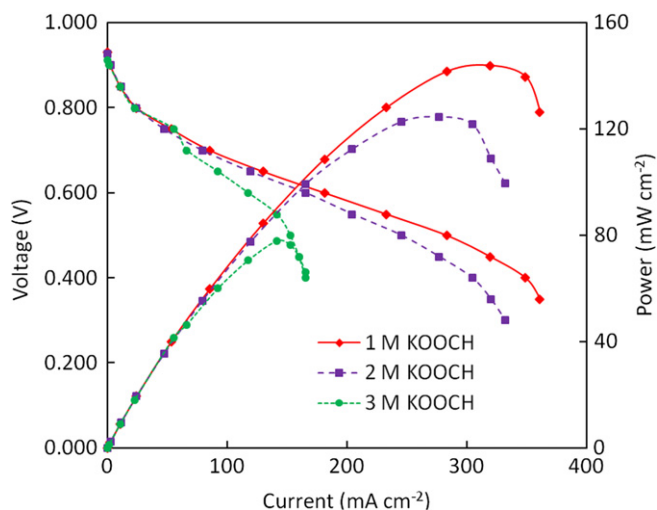

Fig. 3. VI plots comparing effects of KCOOH fuel concentration in the DFFC. The optimal KCOOH concentration is 1 M, and some decrease in fuel cell performance is demonstrated at 3 M. Fuel: 1 mL min^{-1} 1−3 M KCOOH + 2 M KOH. Oxidant: 100 sccm oxygen at 25 °C. Temperature of fuel and fuel cell: 60 °C.
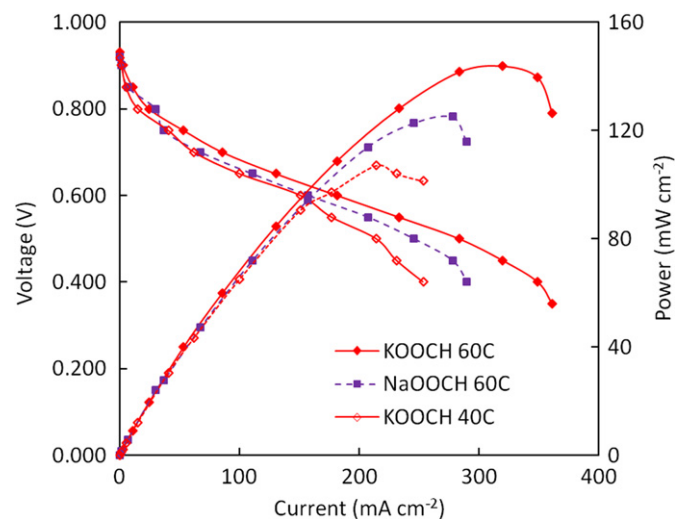

Fig. 4. VI plots comparing effects of formate counterion and temperature in the DFFC. The KCOOH fuel demonstrates a higher power density than NaCOOH at 60 °C or KCOOH at 40 °C. Fuel: 1 mL min^{-1} 1 M KCOOH + 2 M KOH − or − 1 M NaCOOH + 2 M KOH. Oxidant: 100 sccm oxygen at 25 °C. Temperature of fuel and fuel cell: 40 °C − or − 60 °C.

electrodes). The DFFC has the advantage of carbonate formation possibly occurring outside of the electrolyte and in the anode flow field. If designed carefully, this precipitation could be advantageous to removal of the counterion from the anode without interfering with fuel cell operation.

3.5. Comparison to ethanol

Fig. 5 shows _VI_ plots which compare the DFFC using KCOOH to the direct ethanol fuel cell (DEFC) operated using the same MEA at 60 °C with oxygen or air at the cathode and 2 M KOH mixed with the anode fuel. As expected, the DFFC operated with oxygen exhibits a higher power density than the DFFC operated with air. The same comparison holds for the DEFCs. Yet there are three key findings in this figure:

(1) The open circuit voltage (OCV) is significantly higher in the DFFC (0.931 V with oxygen; 0.913 V with air) compared with the DEFC (0.814 V with oxygen; 0.719 V with air). When Equation (10) is added to Equation (5) to construct the formate fuel cell, the overall theoretical E_{cell}^0 is 1.45 V. However, when Equation (8) is added to Equation (5) to construct the ethanol fuel cell, the overall theoretical E_{cell}^0 is 1.14 V, which is 310 mV lower. In practice, we find that the OCV is 117 mV higher in the DFFC when oxygen is used at the cathode, and 194 mV higher when air is used. Although the full 310 mV difference is not observed at OCV, a greater difference is observed once current is drawn.

(2) The current density at 0.6 V is nearly an order of magnitude greater in the DFFC (181 mA cm^{-2} with oxygen; 131 mA cm^{-2} with air) than the DEFC (27 mA cm^{-2} with oxygen; 17 mA cm^{-2} with air). The slope of the Ohmic region of the _VI_ curve in the formate fuel cell is similar to that of the ethanol–oxygen fuel cell, which is to be expected since the same MEA is used in each case. However, the kinetic activation losses in the initial region of the curve appear to be worse for the ethanol fuel cells (from ~0.8 to 0.6 V) than they are in the formate fuel cells (from ~0.9 to 0.8 V). Therefore, the difference in current at 0.6 V is due to the thermodynamic differences between Equations (8) and (10) in addition to kinetic losses that are observed in _VI_ curves.
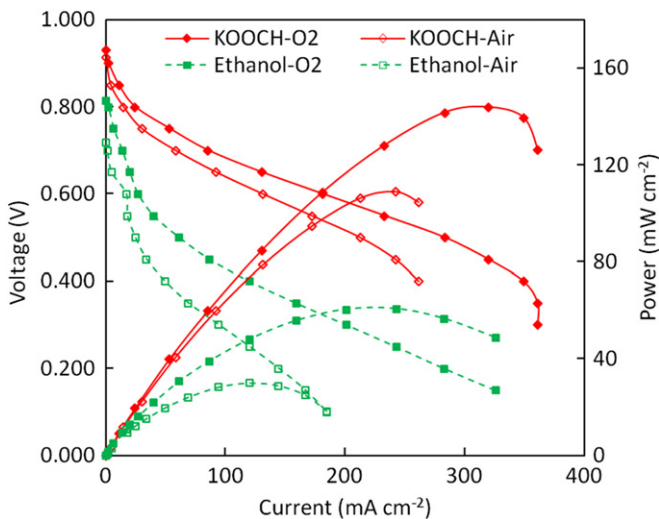

Fig. 5. _VI_ plots comparing the DFFC with air or oxygen to the DEFC with air or oxygen. The DFFC powered by KCOOH demonstrates a higher power density than a DEFC using the same MEA powered by ethanol. Each fuel cell produces more power in oxygen than in air. Fuel: 1 mL min^{-1} 1 M KCOOH + 2 M KOH − or − 2 M ethanol + 2 M KOH. Oxidant: 100 sccm oxygen − or − 400 sccm air. Temperature of fuel and fuel cell: 60 °C.
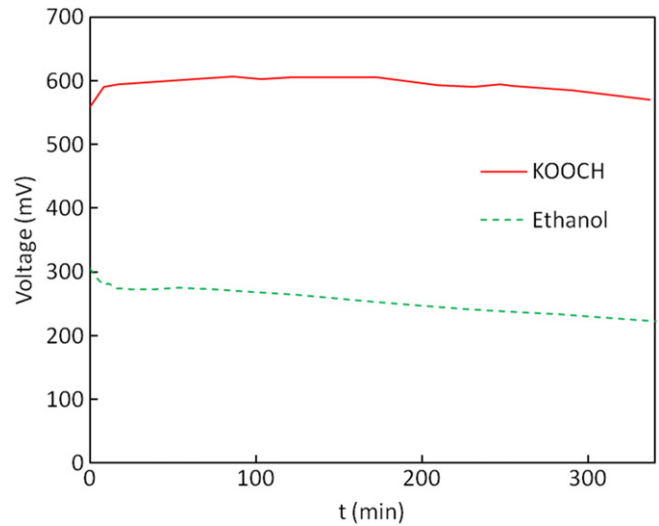

Fig. 6. Five-hour constant current test using the same MEA in a DFFC and a DEFC. The DFFC is relatively stable just below 600 mV at 100 mA cm^{-2}. Fuel: 0.2 mL min^{-1} 1 M KCOOH + 2 M KOH − or − 2 M ethanol + 2 M KOH. Oxidant: 100 sccm oxygen. Temperature of fuel and fuel cell: 60 °C.

Another perspective on the differences is to consider how many millivolts are produced by the fuel cells at the same current: ~200 mA cm^{-2}; the oxygen-DFFC produces 580 mV, the air-DFFC produces 515 mV, and the oxygen-DEFC produces 300 mV. One reason for these losses is likely due to the fact that Equation (5) is a theoretical description of what occurs in a DEFC. However, the DEFC in practice does not completely oxidize the ethanol fuel. While this was a major concern in acid fuel cells, it is less concerning in alkaline fuel cells because the oxidation reaction proceeds more rapidly in an alkaline environment. However, the ethanol is not converted completely to carbon dioxide, which would require breaking of the carbon–carbon bond; it only oxidizes to acetaldehyde or acetic acid [12]. Thus the full energy potential of the ethanol molecule is still yet to be realized.

At this point, it is important to make a different comparison: the DFFC reported here compares well with recent reports on the DEFC in literature. Using a palladium-based anode and a K-14 Hypermec (non-platinum) cathode (although in a different form than the electrodes used here) separated by a Tokuyama A201 membrane, Bianchini et al. developed a DEFC which produces 125 mW cm^{-2} at 60 °C and ~50 mA cm^{-2} at 0.6 V [8]. This is greater than our performance with ethanol, but we still find that our formate fuel cell is competitive with this well-performing DEFC.

(3) The DFFC produces more than double the power density (144 vs. 61 mW cm^{-2}) than the DEFC when oxygen is used at the cathode. Even the DFFC using cathode air produces double the power density (125 vs. 61 mW cm^{-2}) of the DEFC using cathode oxygen. Many of the alkaline AEM fuel cells reported in the literature to date require the use of oxygen at the cathode in order to achieve practical performance levels [7]. Improved polymer membranes are likely to make the use of cathode air more viable in the future, yet it is significant to observe that the DFFC performance is still substantial when air is used as the oxidant.

Fig. 6 shows a 5-h constant current test at 100 mA cm^{-2} in a DFFC and a DEFC operating at 60 °C using oxygen at the cathode

Table 1
Summary of key fuel cell data. The DFFC with 2 M KOH mixed with 1 M KCOOH produces power densities of 144 mW cm^{-2} with oxygen and 125 mW cm^{-2} with air. When KOH is removed from the fuel stream, the DFFC power density decreases to 51 mW cm^{-2}. When the same MEA is used in a DEFC with KOH added to the fuel the power density is 61 mW cm^{-2}.

Anode fuel/electrolyte	Cathode oxidant	Power density (mW cm^{-2})	Current density (0.6 V, mA cm^{-2})	OCV (V)
1 M KCOOH/2 M KOH	Oxygen	144	181	0.931
1 M KCOOH/2 M KOH	Air	125	131	0.913
2 M ethanol/2 M KOH	Oxygen	61	27	0.814
1 M KCOOH	Oxygen	51	26	0.780

and 2 M KOH mixed with the anode fuel. The DFFC using KCOOH decreases from 590 mV at 10 min to 585 mV at 5 h. The DEFC decreases from 280 mV at 10 min to 233 mV at 5 h. Therefore, at 5 h, the DFFC voltage is 2.5 times greater than the DEFC voltage. Although there is some voltage decay observed with time, full performance is regenerated after operating the fuel cell at 100 mV for up to 15 min.

Figs. 2–6 demonstrate the first DFFC employing formate salts as the anode fuel and either air or oxygen as the oxidant, with the anode and cathode separated by a polymer anion exchange membrane. Some of the key findings are summarized in Table 1. It is important to understand that the authors do not wish to discredit the ethanol fuel cell. Ethanol is a very attractive fuel due to its renewability, and the alkaline polymer membrane makes ethanol a viable fuel for a DLFC. We also understand that the DEFC used in this work is not optimized. However, we use a proof-of-concept MEA, which contains catalysts known to efficiently oxidize ethanol and reduce oxygen. The comparisons between the fuels are meant to demonstrate the fact that formate fuel is competitive with ethanol and has several theoretical advantages which are borne out in practice when the same MEA is used to create a close comparison.

3.6. Half-cell fuel comparison

Ultimately, the motivation for this work comes from Fig. 7, which shows the oxidation current on palladium at various potentials in an electrochemical cell. The following fuel (plus electrolyte) was used for these experiments: 1 M KCOOH + 1 M KOH; 1 M ethanol + 1 M
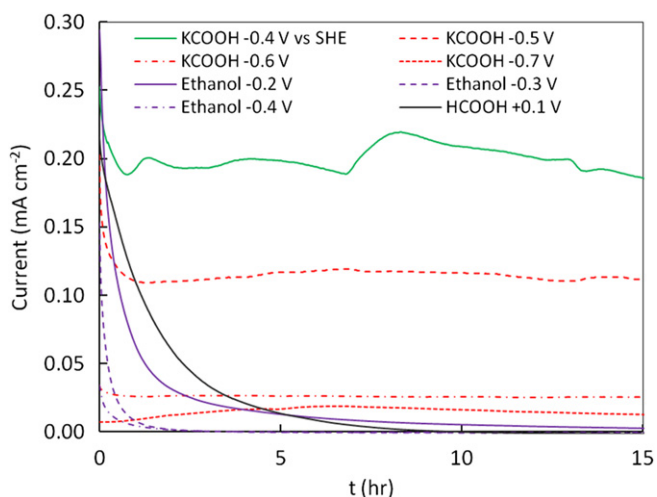

Fig. 7. Fifteen hour constant potential experiments in an electrochemical cell using a palladium black working electrode rotating at 2000 rpm. The oxidation of formate is quite stable over several hours and its oxidation rate is significantly greater than that of ethanol or formic acid at comparable applied potentials.

Table 2
The oxidation rate at 20 h for 1 M KCOOH + 1 M KOH − or − 1 M ethanol + 1 M KOH in the electrochemical cell at various potentials on palladium catalyst. The KCOOH solutions are oxidized far more efficiently than the ethanol.

Fuel	Potential (V vs. SHE)	Current density (15 h, mA cm^{-2})
KCOOH	−0.4 V	0.187
	−0.5 V	0.112
	−0.6 V	0.0255
	−0.7 V	0.0128
Ethanol	−0.2 V	0.00299
	−0.3 V	∼0
	−0.4 V	∼0

KOH; or 1 M HCOOH + 1 M H$_2$SO$_4$. We observe that, compared with ethanol, potassium formate is oxidized more efficiently, at lower potentials, and with a more stable oxidation rate. The oxidation rate after 15 h is summarized in Table 2. After 15 h, the KCOOH oxidation rate is 1–2 orders of magnitude greater than the ethanol oxidation rate at all potentials. Recall that the difference between Equations (8) and (10) is 310 mV. Therefore, one would not expect formate and ethanol to oxidize at the same rate at the same potential; one would expect to apply ∼300 mV more to ethanol to achieve a comparable oxidation rate. However, when we apply −0.5 V to KCOOH and −0.2 V to ethanol (i.e., 300 mV more), we make two important observations. First, we note that at short time periods (less than 1 h), the ethanol oxidation rate is somewhat greater, but this lasts only until ∼0.5 h. Next, we note that after approximately 1 h, the KCOOH oxidation rate stabilizes, while the ethanol oxidation rate continues to decay. After 15 h, we observe that the KCOOH oxidizes ∼40 times faster than ethanol. A poisoning intermediate has been reported for ethanol oxidation, and it is possible that is causing the decay over several hours which we observe here [26]. Note that these sluggish reactions should not be diffusion-limited in the electrochemical cell, so they are not governed by the Cottrell equation, which predicts a current decay which is inversely related to $t^{1/2}$ [27]. In addition, a rotating disk is used to 1) remove carbon dioxide bubble formation from the working electrode and 2) prevent concentration gradients in solution which might establish a diffusion-limited environment. The shape of the potassium formate curves largely supports that of a kinetically-limited reaction on a rapidly regenerated catalyst surface, but the shape of the ethanol curves indicates a fouling of the electrode surface, particularly at longer time periods.

Fig. 7 also shows that potassium formate oxidation occurs at a much more stable rate than formic acid oxidation. At 15 h, the oxidation rate of potassium formate (at pH 14) is much greater than that of formic acid (at pH 0); the analogous potentials for these methods are 0.1 V for formic acid and −0.7 V for formate, according to the Nernst equation. Formic acid is prone to poisoning by the CO molecule, particularly in the presence of Nafion®, which is used as a binder in these experiments (as well as in the formic acid fuel cell). Previous work showed that oxidation of 12 M formic acid in the presence of Nafion® resulted in poison formation which covered nearly 60% of the palladium surface after only 3 h [28]. Fig. 7 supports the hypothesis that no significant poison is forming on the palladium surface during potassium formate oxidation at potentials which are of interest to operation of the DFFC. We are investigating the possibility of a poison forming at much higher potentials (+0.6 V vs. SHE), but this potential could not be realized on the anode of an alkaline DFFC.

4. Conclusion

This is the first report of an operating DFFC 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.

When we operate the DFFC at 60 °C with 1 M KOOCH and 2 M KOH as the anode fuel and electrolyte and oxygen at the cathode, the fuel cell produces 144 mW cm^{-2} of 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 DLFCs reported in the literature and demonstrates that formate fuel is a legitimate contender with alcohol fuels for alkaline DLFCs.

Formate is an attractive fuel for alkaline DLFCs for several reasons: (1) formate is more kinetically active for electrooxidation on palladium in alkaline solution than in acid solution (formic acid), (2) the DFFC has an overall theoretical potential of 1.45 V, which is 0.31 V higher than the DEFC (which runs on ethanol) and 0.24 V higher than the DMFC (which runs on methanol), (3) formate does not poison palladium in alkaline solutions, while acid DLFCs are susceptible to severe poisoning, (4) formate salts are safe and non-flammable, and (5) formate salts can be produced from renewable sources via artificial photosynthesis.

Acknowledgments

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