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Short communication

Optimization of an anode fabrication method for the alkaline Direct Formate Fuel Cell

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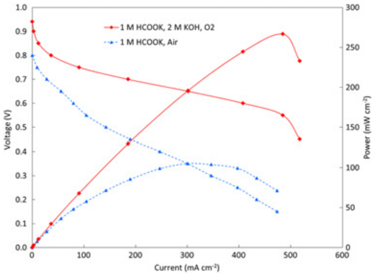
HIGHLIGHTS

- ► We show significantly improved performance in a Direct Formate Fuel Cell.
- ► This fuel cell produces power density greater than other alkaline liquid fuel cells.
- ► This fuel cell still produces competitive power without KOH and using air as oxidant.
- ► The alkaline environment is advantageous for catalysts and reaction rates.

GRAPHICAL ABSTRACT



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ABSTRACT

The performance of an alkaline Direct Formate Fuel Cell (DFFC) employing a polymer anion exchange membrane has been greatly improved by optimization of the method and amount of catalyst loading at the anode. An optimum anode for this DFFC was obtained by a combination of direct-membrane spray painting and gas diffusion layer brush painting. When this fuel cell was operated at 60 °C with 1 M HCOOK, 2 M KOH, and oxygen, its current density at 0.6 V was 408 mA cm^{-2}, and its maximum power density was 267 mW cm^{-2}. When KOH was removed from the fuel stream, a power density of 157 mW cm^{-2} was achieved. Both of these power densities are very competitive with recent reports of alkaline direct liquid fuel cells (DLFC). We also demonstrate the DFFC when air was used at the cathode and no KOH was added to the fuel; the maximum power density was 105 mW cm^{-2} in this case.

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1. Introduction

Direct liquid fuel cells (DLFCs) are being commercialized for use in portable electronic devices due to their high energy density [1–3]. Optimized DLFCs afford simple, liquid storage for the fuel and an air-breathing cathode for the oxidant. The majority of DLFCs employ acid chemistry, in which protons are conducted across a Nafion® polymer electrolyte membrane from anode to cathode. However, the recent development of alkaline anion exchange membranes, which conduct hydroxide ions from cathode to anode, has renewed interest in the application of alkaline chemistry to DLFCs [4–11].

Within the past year, there have been two demonstrations of a Direct Formate Fuel Cell (DFFC), which uses dissolved potassium formate as the fuel. Jiang and Wieckowski demonstrated a DFFC which could produce 170 mW cm^{-2} at 120 °C with 6 M HCOOK and 2 M KOH using a polybenzimidazole-based membrane [12]. Bartrom and Haan demonstrated an alkaline DFFC which produced the following maximum power densities at 60 °C using a Tokuyama A201 membrane: [13].

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1) 144 mW cm^{-2} using 1 M HCOOK, 2 M KOH, and oxygen
2) 125 mW cm^{-2} using 1 M HCOOK, 2 M KOH, and air
3) 51 mW cm^{-2} using 1 M HCOOK and oxygen

Our report also demonstrated that the formate oxidation rate does not degrade overnight in an electrochemical cell, suggesting stability for the catalyst and the reaction rate. In addition, the membrane used in our study has been demonstrated recently to possess long-term stability; the small rate of performance decline with time was attributed primarily to slow anode catalyst degradation due to particle size growth [14].

Until this year, ethanol was the leading fuel reported for alkaline DLFCs in terms of power density; ethanol is also a very attractive fuel from a viewpoint of renewability [5,6,11]. The use of ethanol was impractical in an acid fuel cell, but several reports have demonstrated the viability of the alkaline direct ethanol fuel cell (DEFC), and its best performance at 60 °C was shown to be 185 mW cm^{-2} when assembled with a polymer anion exchange membrane [6–9,11]. Although it is still difficult to oxidize ethanol completely to carbon dioxide, it partially oxidizes more readily than in an acid environment, making it a viable candidate for the fuel of an alkaline DLFC [15]. However, formate is also an interesting fuel for alkaline DLFCs for a variety of reasons. Formate is known to oxidize readily on palladium at a lower potential than ethanol without formation of catalyst poison [16–18]. The theoretical cell voltage is 1.45 V, which is greater than that of DLFCs employing alcohol fuels. Formate salts have advantages for storage and transportation, and they are already approved for use in the environment [19]. There is also potential for formate to be produced as a renewable fuel from the reduction of carbon dioxide [20–22]. Formate is also of interest on a fundamental surface science level. Researchers are investigating the possible role of formate as an intermediate in the oxidation of methanol in alkaline environments. Methanol is another small organic fuel with the potential to be used in alkaline DLFCs, but its oxidation mechanism is complex. Formate is of particular interest in methanol oxidation due to its role as a surface species which is competitive with the strongly adsorbed CO intermediate [4,10].

In this paper, we report on: 1) steps taken at the anode in order to optimize the DFFC from our first report and 2) electrochemical measurements in which we seek to answer questions about the anode reaction and its relevance to overall performance of the DFFC. We report a significantly higher power density in all fuel and oxidant configurations. We attempt to draw correlation between the dependence on fuel concentration, KOH concentration, and temperature between the fuel cell and an electrochemical half cell. We also demonstrate the possibility of employing the DFFC under conditions of no alkaline KOH in the fuel stream and air at the cathode; this key condition has not yet been reported to our knowledge for an alkaline DFFC.

2. Experimental

2.1. Fuel cell

The fuel cell assembly and testing procedure are the same as previously described [13] except for the following modifications. The palladium black anode catalyst was spray painted directly onto the A201 membrane using a 2 × 2 cm template which produced an active area of 4 cm^2. This spray painting technique produces a more uniform coverage than brush painting and better overall catalyst-membrane adhesion. Various palladium loadings were attempted with a range from 2 to 12 mg cm^{-2}. In addition, palladium (up to 4 mg cm^{-2}) was brush painted onto carbon cloth to form a gas diffusion electrode in some variations of the fuel cell assembly. Variations on the mass ratio of AS-4 ionomer to catalyst were explored from a range of 1:3–1:12. Finally, the cathode gas was heated and humidified. We continue to use Pt black at the cathode in order to optimize the anode without introducing potential cathode limitations at this time.

2.2. Electrochemical cell

The electrochemical experiments were carried out in a standard three electrode glass cell as described previously but with the following modifications [13]. The reference electrode was a standard calomel electrode (CH Instruments) stored in saturated potassium chloride (0.244 V vs SHE).

3. Results and discussion

3.1. Optimization of the Direct Formate Fuel Cell

In order to optimize the DFFC using the materials at hand, we varied the anode catalyst loading (2–12 mg cm^{-2}), location of anode catalyst (direct spray on membrane; brush paint on gas diffusion layer), and mass ratio of ink ionomer to catalyst (1:3–1:12). We determined the most efficient loading to be 4 mg cm^{-2} spray paint on membrane, 4 mg cm^{-2} brush paint on GDL, and 1:6 ionomer to catalyst ratio. The voltage–current plots from this loading combination are demonstrated in Fig. 1. This DFFC was operated with 1 M HCOOK anode fuel, oxygen as the oxidant, and the fuel cell operating at 60 °C. Addition of 2 M KOH was used in one of the DFFCs shown. The maximum power density of 267 mW cm^{-2} for this first membrane electrode assembly (MEA1) is significantly greater than that of the recent DFFC reports in the literature [12,13]. When the KOH was removed from the fuel stream, the maximum power density decreased to 157 mW cm^{-2}. Even this power density achieved without KOH is 85% of the maximum power density reported to date for alkaline direct alcohol fuel cells at this temperature, but alcohol fuels require KOH added to the fuel stream to reach this level of performance [11]. The use of formate as a fuel therefore provides a key advantage in that KOH is not needed in the fuel stream to achieve competitive performance.

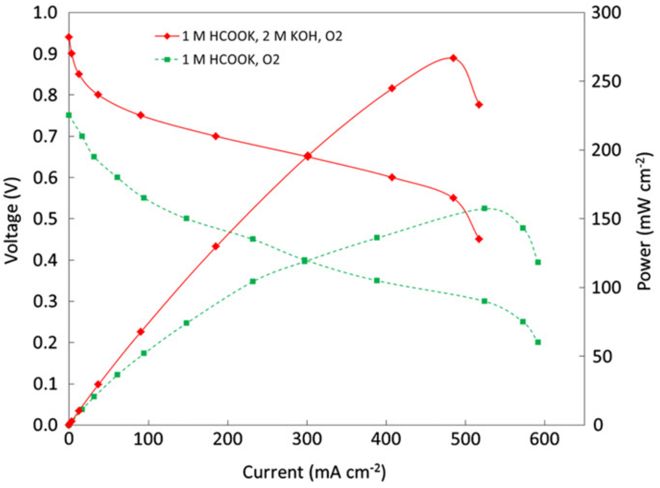

Fig. 1. VI plots demonstrating current and power densities at optimum conditions with 2 M KOH in fuel stream and without KOH in fuel stream. Power density of 267 mW cm^{-2} is achieved with KOH and 157 mW cm^{-2} is achieved without KOH. Fuel: 1 mL min^{-1} 1 M HCOOK + 0 or 2 M KOH. Oxidant: 100 sccm humidified oxygen. Fuel cell temperature: 60 °C.

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