A high-performance alkaline exchange membrane direct formate fuel cell

L. Zeng a, Z.K. Tang b, T.S. Zhao a,*

a Department of Mechanical Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong Special Administrative Region
b Department of Physics, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong Special Administrative Region

Abstract

This paper reports on a single alkaline exchange membrane direct formate fuel cell (AEM DFFC) consisting of a carbon-supported palladium catalyst at the anode, a quaternized polysulfone membrane, and a non-precious Fe–Co catalyst at the cathode. It is demonstrated that the AEM DFFC yields a peak power density of 130 mW cm⁻² with 5 M potassium formate (HCOOK) at 80 °C. It is further shown that with the addition of KOH to the anolyte, the peak power density rises to as high as 250 mW cm⁻² at the same operating temperature. In addition, the AEM DFFC was also tested at 100 mA cm⁻² for more than 130 h and no significant degradation in performance is found. The results reported in this work suggest that formate salt (HCOOM, M⁺ = Na⁺ or K⁺) is a potential fuel for alkaline-type direct liquid fuel cells.

HIGHLIGHTS

- Alkaline exchange membrane direct formate fuel cell (AEM DFFC) has been proposed.
- The peak power density of the AEM DFFC is as high as 250 mW cm⁻² at 80 °C.
- The high performance is attributed to the use of the Pd/C catalyst and QAPSF membrane.
- The operating stability is verified with a constant current discharge at 100 mA cm⁻².

ARTICLE INFO

Article history:
Received 12 September 2013
Received in revised form 11 November 2013
Accepted 13 November 2013

Keywords:
Fuel cell
Direct formate fuel cell
Formate oxidation
Quaternary ammonia polysulfone
Alkaline exchange membrane

1. Introduction

Direct liquid fuel cells (DLFCs) have been projected as a promising power source for mobile and portable devices owing to the following advantages: high theoretical energy density, easy transportation and storage, and high solubility in aqueous electrolytes [1–9]. Formic acid is a liquid fuel that has been used as the fuel of DLFCs to form the so-called direct formic acid fuel cells (DFAFCs) [10–13]. Although considerable progress has been made in the development of DFAFCs, there still exist several technical hurdles to be cleared. At the anode, the low durability of the electrocatalyst for formic acid oxidation in acidic media represents a main technical issue, while at the cathode, the sluggish oxygen reduction kinetics in acidic media and the poisoning effect of formic acid on the cathode catalyst are two issues that should to be emphasized.

The above-mentioned issues can be addressed by changing the acid medium to the alkaline medium, which can be achieved by using formate salts as the fuel. The change from the acid medium to the alkaline medium can dramatically improve kinetics of the oxygen reduction reaction (ORR) and formate oxidation reaction (FOR) [14,15]. In addition, formate salts are renewable fuels and can be produced from the reduction of carbon dioxide by artificial photosynthesis [16]. Further, formate salts are readily transported and handled in their solid states and can be easily dissolved into water to form a liquid fuel. Recently, a proof-of-concept membrane electrode assembly (MEA) using formate salt solutions as the fuel was developed [17,18], indicating formate salt solutions are the attractive fuels for alkaline-type DLFCs. However, the high loading of precious catalysts was employed and the operating stability of the fuel cell systems, which has been shown to obtain more concern for alkaline-type DLFCs recent years [19,20], was not considered.

In this work, we demonstrate an AEM DFFC consisting of a carbon-supported palladium catalyst at the anode, a quaternized polysulfone membrane, and a non-precious Fe–Co catalyst at the...
cathode. Potassium formate solution is fed to the anode channel as the fuel. The electrochemical activity of Pd toward formate oxidation was investigated on a Pd disk electrode. The hydroxide ion conductivity and the formate permeability of a home-made anion exchange membrane were measured. We then investigated the influence of various operating parameters on the cell performance and tested the operating stability of AME DFFC at a constant current.

2. Experimental

2.1. Materials

Potassium formate (HCOOK), potassium hydroxide (KOH) and palladium chloride (PdCl₂) were purchased from Aldrich. The Pd/C catalysts (metal loading: 20 wt.%, determined by ICP-AES) were prepared as reported elsewhere [21]. Briefly, the predetermined amount of PdCl₂ was dissolved in deionized (DI) water and carbon powders were dispersed in the solution under vigorous stirring. 3 wt.% NaBH₄ (aqueous) was then added to the mixture to reduce the metal precursor. The precipitate was collected by filtration and dried at 70 °C in an oven. The non-platinum HYPERMEC™ K14 catalysts (Fe–Co alloy) were purchased from Acta. The anode and cathode supporting layers, nickel foam and carbon paper were, respectively, purchased from Hohsen and E-TEK. The membranes were cast from a home-made alkaline ionomer solution, quaternary ammonia polysulfone (QAPSF, 5 wt.%, dissolved into N,N-Dimethylformamide (DMF)). The QAPSF ionomer was synthesized through three traditional procedures: chloromethylation, quaternization and alkalinization [22]. The ion exchange capacity of QAPSF is 1.21 mmol g⁻¹. The thickness of the home-made membrane is 60 μm. QAPSF was also used as the ionomer at the both anode and cathode.

2.2. Electrochemical characterization

The electrochemical characterization was carried out with a potentiostat (Autolab PGSTAT30). Cyclic voltammetry (CV) was measured in a conventional three-electrode glass cell. The working electrode was a palladium disk electrode with an area of 0.1256 cm², while the reference and counter electrodes were an Ag/AgCl electrode and a Pt foil, respectively. The reference electrode was placed near the working electrode by a Luggin capillary. Experiments were performed in the aqueous solution containing 0.5 M HCOOK and 0.5 M KOH. The desired temperature was controlled by ICP-AES [23,24] and ethanol [25]. The permeability of HCOOK was measured by a dialysis cell containing two identical compartments separated by the home-made QAPSF membrane [26]. Compartments A was filled with 45 ml of 1 M or 6 M HCOOK, while Compartments B was filled with 45 ml of DI water. During the measurement, each compartment was continuously stirred by a magnetic stirrer. The concentration of HCOOK in compartment B was quantified by ionic chromatography (Metrohm 883 basic model with a Metrosep Organic Acids 250/7.8 column).

2.4. MEA preparation and fuel cell setup

The preparation process of the cathode and anode electrodes can be found elsewhere [27,28]. Generally, the anode catalyst ink composed of Pd/C catalysts and 5 wt.% QAPSF ionomer with ethanol as the solvent was brushed on the nickel foam. The loading of Pd/C was 2 mg cm⁻², while the QAPSF ionomer loading was maintained at 10 wt.%. Also, the cathode ink was prepared by mixing HYPERMEC™ K14 catalysts with QAPSF ionomer, and then brushed on the water-proofed carbon paper. The catalyst loading was controlled with 2 mg cm⁻², while the QAPSF ionomer loading was 15 wt.%. The QAPSF membrane was clamped between the cathode and the anode to form a MEA. The active area of MEA is 2.0 cm × 2.0 cm. The MEA was placed between two pieces of fixture plates with a single serpentine flow field on one side. An aqueous HCOOK solution or HCOOK/KOH solution was pumped to the anode channel with the flow rate of 2 ml min⁻¹ through a peristaltic pump. Simultaneously, dry oxygen (99.7%) was supplied to the cathode channel with a flow rate of 100 sccm (standard cubic centimeters per minute). An electric heating rod and a thermocouple, located adjacent the anode flow field, were applied to maintain the operating temperature. An electrical characterization system (Arbin BT2000) was used to collect polarization curves. The polarization curves were not measured until they became stable. Constant current discharge tests were performed at various current densities for several hours to determine the operating stability of the AEM DFFC.

3. Results and discussion

3.1. HCOOK oxidation on the palladium electrode

The CV curves of HCOOK oxidation at various temperatures are illustrated in Fig. 1. The CV curves during the positive scan were split into two peaks when the temperature was higher than 40 °C. The peak potentials for the formate oxidation reaction (FOR) shift to more negative with an increase in the temperature, exhibiting the accelerated kinetics of formate oxidation at elevated temperatures. While the CV curves during the negative scan shows
only one sharp peak centering at –0.29 V, it is considered that the peaks during the positive scan correspond to an oxidative pathway not involving COads (primary pathway) and the oxidation of COads accompanied by an indirect pathway of formate oxidation (secondary pathway) [29]. During the negative scan, the higher current densities are due to the quicker electro-oxidation of formate on the COads-free surface. It is seen that the oxidation currents on the palladium electrode are much higher than that reported on the platinum electrode [29], indicating the high activity of the Pd catalysts toward formate oxidation.

As observed in Fig. 1, the current density increases with temperatures, which can be ascribed to the improved kinetics of formate oxidation. Fig. 2 presents the logarithmic form of current as a function of 1000/T at a specific potential, where the apparent activation energy values are obtained from Arrhenius equation [30]:

\[ \ln i = \ln A - \frac{E_a}{RT} \]  

where \( i \) is the measured current, \( E_a \) is the apparent activation energy, \( R \) is the gas constant and \( T \) is the temperature in Kelvin. The potential-dependent activation energies are shown in Table 1. It is shown that the activation energies are lower than the literature values for formic oxidation reaction in acid media [31,32], demonstrating the high electrocatalytic activity on the palladium electrode toward FOR.

A typical TEM image of the Pd/C catalysts synthesized through a chemical reduction method is shown in Fig. 3A and the particle size distribution of as-synthesized catalysts is presented in Fig. 3B. The results indicate that Pd particles were evenly distributed on the supporting materials with a mean particle size of 3.66 ± 0.06 nm. The uniform size distribution and highly dispersed nanostructure will be favorable toward formate oxidation.

### 3.2. Ionic conductivity and formate permeability of QAPSF membrane

The ionic conductivity of QAPSF is presented in Fig. 4A. The ionic conductivity increases with the increased testing temperature range from 30 °C to 80 °C, meaning that the membrane can be stable at elevated temperatures without significant degradations. The ionic conductivity of the membrane almost increased threefold.

![Fig. 1. Cyclic voltammograms (CVs) of Pd electrode in 0.5 M HCOOK with 0.5 M KOH at different temperatures (scan rate: 50 mV s⁻¹).](image1)

![Fig. 2. Arrhenius plots of 0.5 M HCOOK with 0.5 M KOH for CVs (positive scanning) at different potentials (scan rate: 50 mV s⁻¹).](image2)

![Fig. 3. Typical TEM image (A) and histogram of particle size distribution for Pd/C catalysts (B).](image3)

![Fig. 4. Ionic conductivity of QAPSF membrane.](image4)

#### Table 1

<table>
<thead>
<tr>
<th>Potential (V)</th>
<th>0.323</th>
<th>0.373</th>
<th>0.423</th>
<th>0.473</th>
<th>0.523</th>
<th>0.276ᵇ</th>
<th>0.376ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_a ) (kJ mol⁻¹)</td>
<td>33.02</td>
<td>35.69</td>
<td>38.43</td>
<td>40.99</td>
<td>40.98</td>
<td>58.7</td>
<td>45.1</td>
</tr>
</tbody>
</table>

ᵃ The potential was referenced to reversible hydrogen electrode (RHE). The potentials versus Ag/AgCl electrode was calibrated with respect to reversible hydrogen electrode (RHE) using the following equation: \( E(RHE) = E(Ag/AgCl) + 0.9729 \) V.

ᵇ The data were adopted from Ref. [31].
when the temperature increased from 30°C to 80°C, i.e. 18.5 mS cm\(^{-1}\) at 30°C and 49.3 mS cm\(^{-1}\) at 80°C.

Another parameter related to the membrane is the rate of HCOOK permeation across the QAPSF membrane. The permeability of HCOOK was measured with a dialysis cell and the variation of HCOOK concentration in the DI water side with time is presented in Fig. 4B. The increase in the transferred HCOOK mass with a prolonged time is observed and the HCOOK flux is approximately constant when feeding 1 M or 6 M HCOOK into compartment A, i.e. 1.14 ± 0.04 \(\times\) 10\(^{-8}\) mol cm\(^{-2}\) s\(^{-1}\) and 34.08 ± 3.14 \(\times\) 10\(^{-8}\) mol cm\(^{-2}\) s\(^{-1}\). The HCOOK permeability is close to the results for the formic acid permeating Nafion membrane reported by Rhee [26] and Wang [33], but is lower than that of methanol and ethanol [28,34,35]. The low permeability of HCOOK is due to the following reasons. QAPSF membrane possesses a compact structure, which reduces the approach allowing the passage of HCOOK. In addition, HCOOK dissociates into the aqueous solution, forming a hydrated anion [HCOO]\(^{-}\), which diffuses slowly through the QPASF membrane because of the large size of hydrated anions. The benefit of the lower HCOOK permeation is that the cell performance will not be influenced by the cathode poisoning resulting from the permeated fuel.

3.3. Cell performance

The polarization curves of 1 M HCOOK mixed with KOH solutions increasing from 0.5 M to 3.0 M are shown in Fig. 5. The cell performance improves with the KOH concentration when the concentration is lower than 1 M. When the KOH concentration further increases, a high concentration overpotential in the high current density region was caused, indicating that 1 M is the optimal concentration of KOH. The influence of the KOH concentration on performance results from a competitive adsorption between HCOO\(_{ad}\) and OH\(_{ad}\) toward FOR on the Pd catalyst surface [29], therefore a high mass transport resistance in the high current density region is caused by the insufficient coverage of HCOO\(_{ad}\) when KOH concentration is above 1 M. Based on these results, subsequent experiments were implemented by feeding HCOOK with 1 M KOH as the anode fuel.

Recently, Hann et al. [36] reported that the formation oxidation reaction is not dependent on pH in the alkaline media, which indicated that the formate aqueous solution could be directly used as the fuel without added hydroxide ion in the fuel. The AEM DFFC discharged with an aqueous solution of HCOOK and the result is also illustrated in Fig. 5. The open circuit voltage (OCV) of the AEM DFFC is 0.856 V without addition of alkali in the anode, while OCV increases to 1.065 V after 1.0 M KOH is added to the anode. The voltage increases over the whole range of current density after addition of KOH, resulting from the sufficient hydroxide ions supplied from the anolyte. One significant point should be noted is that a peak power density of 42.76 mW cm\(^{-2}\) is achieved when AEM DFFC is discharged with the aqueous solution of HCOOK. The high performance should be ascribed to the excellent electrocatalytic activity of Pd/C catalysts as previously explained.

The influence of the HCOOK concentration on performance with the concentration of KOH maintained at 1.0 M is represented in Fig. 6. It is shown that the performance monotonically increases with the HCOOK concentration when it is lower than 5 M, but a further increase in the concentration to 7 M HCOOK significantly decreased the performance. The open circuit voltage (>1.0 V) is higher than the results reported elsewhere [18], indicating the well-established triple-phase boundary in the electrode due to the well dispersed Pd/C catalysts and the QPASF membrane. A power density platform of about 170 mW cm\(^{-2}\) is achieved over a current density range from 450 mA cm\(^{-2}\) to 600 mA cm\(^{-2}\). The high power density can be explained as follows. First, the homemade QAPSF membrane possesses a high ionic conductivity, leading to a reduction in the internal resistance of AEM DFFC. For instance, when the anode was fed with 5 M HCOOK and 1 M KOH, the internal resistance was 0.208 Ω cm\(^{2}\), which is lower than that of AEM DFFC using an alkaline doped polybenzimidazole membrane [17]. The variation in the internal resistance with the content of anolyte is slight, demonstrating that the QAPSF
membranes maintain sufficient ionic conductivity during the discharge process. Secondly, the Pd/C catalyst exhibits high electrocatalytic activity toward FOR. 20 wt.% Pd/C was employed as the catalysts with the loading of 2 mg cm\(^{-2}\), meaning that the metal loading in the anode was 0.4 mg cm\(^{-2}\), which is much lower than the loading reported in the literature\[17,18\]. The results indicate that an excellent performance can be obtained in AEM DFFC even when employing non-platinum catalysts in the electrode. More importantly, the power densities are comparable to those of alkaline-type DLFCs using methanol [2,37] and ethanol [38] as fuel.

As mentioned in Section 3.2, the QAPSF membrane can be stable at high temperatures. For this reason, the AEM DFFC also operated at 80 °C and polarization curves are presented in Fig. 7A. A power density platform of about 250 mW cm\(^{-2}\) is achieved over a current density range from 650 mA cm\(^{-2}\) to 800 mA cm\(^{-2}\). To the best of our knowledge, this is the highest power density for direct formate fuel cells. Moreover, a power density of 130 mW cm\(^{-2}\) can be achieved in the AEM DFFC without adding KOH into the anolyte. The anode polarization curve when fed with 5 M HCOOK and 1 M KOH in the anolyte was determined by an Hg|HgO|KOH (1.0 M) (MMO) reference electrode. The corresponding cathode polarization curve was gotten through adding the \(iR\)-corrected cell potential to the anode potential. The anode polarization curve and cathode polarization curve are represented in Fig. 7B. It is shown that the considerable overpotential is attributed to the cathode, i.e. the oxygen reduction reaction, when the current density is lower than 200 mA cm\(^{-2}\). The anode potential under an open circuit stage is \(-0.972\) V vs MMO, which is close to its theoretical value \((-1.148\) V vs MMO). The low overpotential of anode also reveals a superior electrocatalytic activity of Pd/C catalysts. When the current density is larger than 200 mA cm\(^{-2}\), the anode overpotential ranges from 200 mV to 460 mV depending on the current density whereas the cathode overpotential ranges from 700 mV to 930 mV, indicating that there is much room to improve the cell performance after oxygen reduction kinetics is further enhanced.

In summary, these results demonstrate that the AEM DFFC can be discharged at a high HCOOK concentration with elevated power density. The theoretical energy density of formate salts is calculated as:

\[
\frac{2F \times OCV}{M_W} = \frac{2 \times 96485 \times 1.45 \times 1000}{84.11 \times 3600} = 924.08 \text{ Wh kg}^{-1}
\]

where \(M_W\) is the molecular weight (kg mol\(^{-1}\)) and OCV is the open circuit voltage (V). Although the theoretical energy density is lower than that of ethanol and methanol, AEM DFFC enables to be discharged with a high concentration of formate salt, i.e. 7 M, to obtain the high performance. This merit makes AEM DFFC more competitive than other types of DLFCs.

### 3.4. Operating stability

The long-term operating stability is another concern for DLFCs. The AEM DFFC was continuously discharged at a specified current density when the anode was fed with 5 M HCOOK with 1 M KOH and the transient cell voltage is presented in Fig. 8. The cell voltage...
4. Conclusions

We demonstrate that the AEM DFFC system that is composed of a carbon-supported palladium catalyst at the anode, a quaternized polysulfone membrane, a non-precious Fe–Co catalyst at the cathode and potassium formate as the fuel. The AEM DFFC exhibited a peak power density of 250 mW cm\(^{-2}\) when the anode is fed with 5 M HCOOK with 1 M KOH at 80 °C. It is particularly interesting that even with no addition of KOH into the anolyte, the peak power density of the fuel cell can be still as high as 130 mW cm\(^{-2}\). This excellent performance is mainly attributed to: (1) the high electrocatalytic activity of the carbon-supported Pd catalysts toward FOR; (2) the excellent ionic conductivity and low formate permeability of QAPSF. Furthermore, the fuel cell can be stably discharged at 100 mA cm\(^{-2}\) for more than 130 h with no significant degradation. The high power density output with an excellent operating stability makes this alkaline-type of fuel cell a favorable power source for mobile and portable devices.

Acknowledgements

The work described in this paper was fully supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. HKUST9/CRF/11G).

References