Applied Energy 115 (2014) 405–410

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

# A high-performance alkaline exchange membrane direct formate fuel cell

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## 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
Available online 7 December 2013

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

## 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.

## 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 acid 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

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http://dx.doi.org/10.1016/j.apenergy.2013.11.039

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 ($PdCl_2$) 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 $PdCl_2$ was dissolved in deionized (DI) water and carbon powers were dispersed in the solution under vigorous stirring. 3 wt.% $NaBH_4$ (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 alkalization [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 $cm^2$, 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 a magnetic stirrer (RH basic, IKA). The solution was bubbled nitrogen gas (high-purity) for one hour before each testing to remove the dissolved oxygen. The CV tests were performed with the potential range from −1.1 V to 0.2 V at a scan rate of 50 mV $s^{-1}$ and stable curves were recorded after 20 cycles of continuous scanning. To eliminate the temperature influence on the potential, the potential of the Ag/AgCl electrode was regulated through:

$$E(T) = 0.2223 - 0.0006 \times (T - 25) \tag{1}$$

where $T$ represents the temperature (°C).

### 2.3. Ionic conductivity and formate permeability

Home-made quaternized polysulfone solutions (5 wt.%) were cast into thin films with a thickness of around 60.0 μm. The ionic conductivity of the as-prepared membrane was determined with a potentiostat (EG&G Princeton, model M2273) through an AC impedance method. A four-electrode conductivity cell was used to clamp the samples. To prevent possible interference from $CO_2$, the test apparatus was placed in a home-made container filled with nitrogen gas (high-purity) during the measurement process. The samples were sandwiched between two pieces of PTFE plate and placed in deionized water (DI water), which had been deaerated by bubbling nitrogen gas for 30 min. A frequency range from 100 Hz to 1 kHz with a wave amplitude of 5 mV was applied to the conductivity clamp to obtain the AC impedance spectra. The ionic conductivity $\sigma$ was obtained from:

$$\sigma = \frac{L}{d \times W \times R_\Omega} \tag{2}$$

where $R_\Omega$ is the membrane resistance obtained from AC impedance spectra, $W$ represents the width of the potential electrodes, $L$ is the distance of the potential electrodes; and $d$ is the membrane thickness.

HCOOK disperses through the membrane by diffusion and electro-osmotic drag (EOD), which is similar to that of methanol [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]. Compartment A was filled with 45 ml of 1 M or 6 M HCOOK, while Compartment 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