A liquid-electrolyte-free anion-exchange membrane direct formate-peroxide fuel cell

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Conventionally, two critical issues that limit the steady-state discharge of alkaline liquid fuel cells are the pH-dependant problem at anode and the carbonation problem at cathode. The present work addresses these two issues by reporting an anion-exchange membrane direct liquid fuel cell that uses a pH-insensitive fuel, formate, as the reductant, and a CO₂-free reactant, hydrogen peroxide, as the oxidant, referred to as anion-exchange membrane direct formate-peroxide fuel cell (AEM DFFPC). Theoretically, the cell voltage of the AEM DFFPC can be as high as 1.92 V. It has been experimentally demonstrated that a conceptual half-hour constant-current discharge of the AEM DFFPC almost remains unchanged, even eliminating the supporting electrolytes at both anode and cathode. In contrast, an anion-exchange membrane direct ethanol fuel cell (AEM DEFC) shows a sharp decline in constant discharge within a few seconds.

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Introduction

Presently, the global environmental crisis, especially for the greenhouse gas and smog outputs, has become one of the most pressing issues that hinder the rapid development of the world economies. An effective way to address partial crisis is to reduce the carbon emissions by lowering burning of fossil fuels. Apparently, to meet the ever-increasing global energy demand, it is essential to develop high-efficiency and renewable energy conversion systems. Direct liquid fuel cells (DLFCs) that directly convert chemical energy stored in liquid fuels into electricity can satisfy the aforesaid requirements [1–3], primarily because in comparison with combustion the DLFC is not limited by the Carnot cycle, and hence allowing more efficient, not to mention its zero-emission. Therefore, the DLFCs have received increasing attention [4–6].

In developing DLFCs, owing to the fact that the electrochemical kinetics of electrode reactions is quicker in an alkaline environment than that in an acid media, the anion-exchange membrane (AEM) DLFCs, especially for the AEM direct ethanol fuel cell (DEFC), have recently attracted growing concerns [7–9]. Although the AEM-based system seems appealing, currently, an critical issue that limits the steady-state discharge of AEM DEFCs is the pH-dependant problem at anode: the rate of ethanol oxidation reaction (EOR) is significantly determined by the adsorption of the OH⁻ ions at the surface of the catalysts [10], leading to adding additional alkali (typically, KOH/NaOH) to fuel solution. Another potential issue that limits the development of the alkaline fuel cell is...
the carbonation problem at cathode: carbon dioxide from air in a longer operation causes the cathode carbonation, resulting in adding CO2-scrubbing process to cathode. The addition of both supporting electrolytes and CO2 scrubber not only lowers the system energy density but also increases the system complexity. Clearly, an ideal solution is to eliminate the addition from cell system. To this end, herein, an anion-exchange membrane direct formate-peroxide fuel cell (AEM DFPFC) that uses a pH-insensitive fuel, formate, as the oxidant, was reported. It has been demonstrated that a conceptual half-hour constant-current discharge of the AEM DFPFC almost remains unchanged, even eliminating the supporting electrolytes at both anode and cathode. Moreover, using hydrogen peroxide makes the AEM DFPFC not only possess a high theoretical cell voltage, but also work in an oxygen-free environment.

Setup and working principle in DFPFC

Fig. 1 illustrates the schematic of an AEM DFPFC. The core of the AEM DFPFC is the membrane electrode assembly (MEA), which consists of an anion-exchange membrane sandwiched between anode and cathode electrodes. In this type of DFPFC, the anion-exchange membrane not only conducts hydroxide ions from the cathode to anode, apparently, it also as an electronic insulator separates anode and cathode compartments. Both electrodes are composed of a diffusion layer backing a catalyst layer, wherein the triple-phase boundary, comprising of electron-conducting phase, ion-conducting phase and liquid phase, is created by an anion ionomer [11]. The possible electrode reactions in AEM DFPFC are as follows.

On the cathode, the peroxide aqueous solution in the absence of additional supporting electrolyte (typically, KCl/H2SO4 [12,14]) is electrochemically reduced in the cathode active sites to produce hydroxyl ions. The cathodic hydrogen peroxide reduction reaction according to:

\[ \text{H}_2\text{O}_2 + 2e^- \rightarrow 2\text{OH}^- \quad E^\circ_{\text{cathode}} = 0.87 \text{ V vs. SHE} \quad (1) \]

The generated hydroxyl ions at cathode as the charge carrier migrate through membrane to the anode. Subsequently, on the anode, the formate, usually potassium/sodium formate in aqueous solution without additional hydroxide electrolyte (typically, KOH/NaOH [13–16]), reacts with hydroxyl ions in anode active sites to generate electrons. The anodic formate oxidation reaction (FOR) is possibly expressed as:

\[ \text{COOH}^- + 2\text{OH}^- \rightarrow \text{HCO}_3^- + \text{H}_2\text{O} + 2e^- \quad E^\circ_{\text{anode}} = -1.05 \text{ V vs. SHE} \quad (2) \]

Accordingly, the overall reaction in the AEM DFPFC using hydrogen peroxide as oxidant is:

\[ \text{COOH}^- + \text{H}_2\text{O}_2 \rightarrow \text{HCO}_3^- + \text{H}_2\text{O} \quad E^\circ_{\text{overall}} = 1.92 \text{ V vs. SHE} \quad (3) \]

In conclusion, theoretically, the cell voltage of the H2O2-based AEM DFPFC can be as high as 1.92 V, which is 0.47 V higher than that of the O2-based anion-exchange membrane direct formate fuel cell (AEM DFFC) [14]. Using hydrogen peroxide as oxidant makes the AEM DFPFC not only possess a high theoretical cell voltage, but also work in an oxygen-free environment.

Experimental

The in-house fabricated MEA was composed of an anion-exchange membrane (A201, Tokuyama) sandwiched between a pair of electrodes. The A201 anion-exchange membrane is composed of hydrocarbon polymer backbones and quaternary ammonium groups. Both anode and cathode were prepared by the catalyst coated substrate (CCS) method as reported in detail elsewhere [9]. The anode electrode, consisting of 30 wt.% anion ionomer (I2, Acta S.p.A.) and Pd/C (Aldrich) catalyst with a Pd loading of 2.0 mg cm\(^{-2}\), was directly applied to backing layer made of carbon paper (E-TEK). The cathode electrode, comprising 30 wt.% I2 ionomer and Pt/C (Johnson Matthey Corp.) catalyst with a Pt loading of 2.0 mg cm\(^{-2}\), was attached to a diffusion layer made of wet-proofing micro-porous layer and carbon paper.

An Autolab PGSTAT302N electrochemical test station (Eco Chemie, Netherlands) was employed to adjust the discharging condition and record the voltage–current curves [17]. The fresh aqueous solutions were supplied to anode and cathode by a peristaltic pump. The electrical heating rod was installed in the fixture to control the operating temperature at 40 °C. All the solutions were prepared from analytical grade reagents and DI water.

Results and discussion

Fig. 2 shows the cell performance of the AEM DFPFC consists of an anion-exchange membrane as the OH\(^-\) conductor, a Pd/C coated carbon-paper anode, and a Pt/C coated wet-proofing micro-porous layer-based carbon-paper cathode, a 1.0-M...
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