Study of physicochemical characterization of potassium-doped Nafion117 membrane and performance evaluation of air-breathing fuel cell in different alkali-methanol solutions

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ABSTRACT

Direct methanol alkaline fuel cell (DMAFC) using a cation exchange membrane (CEM) was operated in passive condition and compared to passive direct methanol fuel cell (DMFC). A polymer electrolyte membrane for passive DMAFC was prepared by immersing Nafion117 membrane into KOH solution at temperature of 80 °C. The prepared membrane (potassium-doped Nafion117) exhibited higher mechanical properties and thermal stability than Nafion117. Ionic conductivity of K^+ form Nafion117 membrane was measured to be lower than that for pristine Nafion117. Single cell in alkaline condition (passive DMAFC) exhibited better cell performance than that in the cell using Nafion117 in acidic condition (passive DMFC). The open circuit voltage (OCV) of passive DMAFC reached to about 1 V which was considerably higher than that for passive DMFC (0.45 V). The methanol crossover rate through membranes was also measured and the results implied that the potassium-doped Nafion117 membrane had lower permeability to methanol.

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1. Introduction

The direct methanol fuel cell (DMFC) is currently under development as an alternative power supply source for applications ranging from portable power (passive DMFC) to medium scale power generation. Passive DMFC based on a diffusion of air by natural convection at cathode and a passive fuel delivery at anode has attracted remarkable attention as a promising candidate for power supply of portable electronic devices, which could replace the conventional batteries. One of the main advantages of the passive DMFC is the high energy content of methanol (6100 Wh.kg^{-1}), which provides an extensive scope for the development of such systems. Moreover, ability to use liquid fuel, low emission of pollutants and compact configuration, are other advantages of passive DMFCs. With the progress of DMFCs, common technical issues such as methanol crossover through the membrane, low methanol oxidation reaction kinetics at anode side, higher noble metal loading as a catalyst and water management

problems, could also affect considerably the behavior of these types of fuel cells. In DMFCs, methanol permeates through the membrane and oxidizes on the cathode side and leads to a mixed potential which finally reduces the fuel cell performance. Besides, methanol crossover through the membrane, reducing the reactant consumption, causes the fuel waste [1–5]. In order to reduce the methanol crossover, some researchers developed a methanol barrier between membrane-electrode assembly and fuel reservoir [6,7]. One of other challenges is the sluggish kinetics of methanol oxidation reaction that reduces the fuel cell performance and leads to a high loading of expensive catalyst at anode side. Actually, a major contribution to the overall polarization of the DMFC is due to the kinetic constraints in the methanol oxidation reaction [8–10]. It is reported that an excess of liquid water or a dry-out membrane will lead to remarkable durability problems. Therefore, an appropriate water balance in both anode and cathode electrodes must be achieved to ensure a successful performance of the single cell [11]. There are studies that investigate the water management problem experimentally [12] and numerically [13,14] in PEM fuel cells to enhance the performance of single cell.

In recent years, many researches on the alternatives for proton exchange membranes and electrocatalysts for DMFC, anode and cathode structures, flow plate configuration and structures have

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been carried out to improve the performance of fuel cells [15–27]. Moreover, many studies have been proposed alternative systems, such as direct methanol alkaline fuel cell (DMAFC) using anion exchange membrane (AEM) [28–32] or using cation exchange membrane (CEM) [33,34], to improve the performance of direct alcohol fuel cells.

Compared to DMFC in acidic medium, DMAFC has potential advantages in the alkaline medium. It has been suggested that the kinetics of both methanol oxidation reaction and oxygen reduction reaction can be facilitated and improved by means of alkaline media. That allows to use low catalysts loadings and to select a wide range of catalysts such as non-noble metals [35–38]. As well as that, during the operation of DMAFC, the diffused ions through the solid polymer electrolyte are not H^+ anymore, which can reduce the methanol crossover contribution induced by electro-osmosis. In the case of anion exchange membrane-DMAFC, the OH^- ions migrate from the cathode side to anode side that are opposite to the fuel crossover through the membrane and thus can reduce the methanol crossover rate [32,33]. A schematic diagram of the electrochemical reactions and transport processes in passive CEM-DMAFC is shown in Fig. 1.

Accordingly, the procedure taken in this work was to develop an alkali version of the passive DMFC, i.e. a passive direct methanol alkaline fuel cell (passive DMAFC). To investigate the feasibility of a DMAFC system, a system was planned to perform using cationic membranes, for which Nafion117 is highly applicable. A K^+ ion form of Nafion117 was made when treating with KOH solution.

As shown in Fig. 1, in passive CEM-DMAFC, the KOH solution is added to the methanol fuel reservoir. Hydroxyl anions (OH^-) will be formed at the anode fuel solution according to Eq. (1):

$$KOH \rightarrow K^+ + OH^- \tag{1}$$

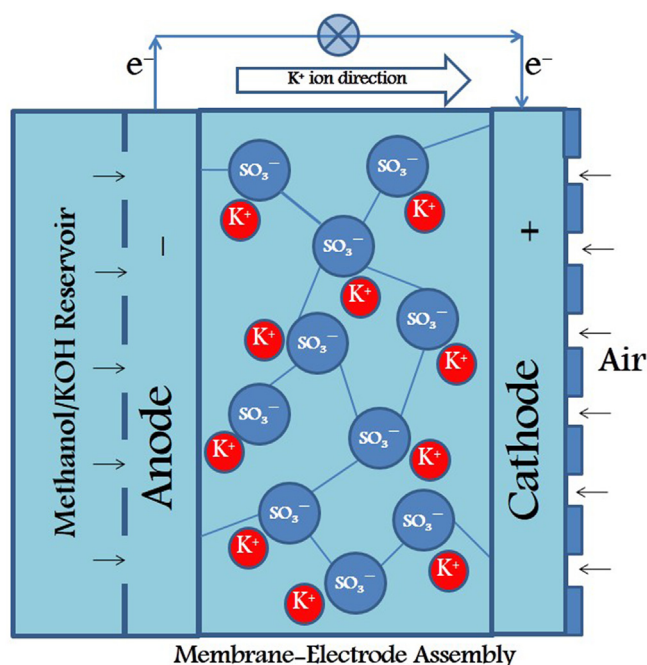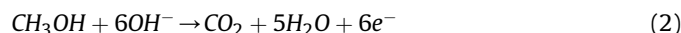Therefore, the methanol reacts with hydroxide anions which exist in methanol/KOH fuel reservoir according to Eq. (2):

$$CH_3OH + 6OH^- \rightarrow CO_2 + 5H_2O + 6e^- \tag{2}$$

The produced electrons pass through an external electrical circuit and arrive at the cathode. As well as them, K^+ ions diffuse through solid polymer electrolyte and reach to cathode catalyst layer. The oxygen reacts with H_2O and passed electrons to produce hydroxyl ions according to Eq. (3):

$$\frac{3}{2}O_2 + 3H_2O + 6e^- \rightarrow 6OH^- \tag{3}$$

The ionic conduction process in designed passive DMAFC is by the transport of K^+ ions in the direction of the anode to cathode. A practical consequence of DMAFCs operating in such a manner is that the hydroxide ions produced by oxygen reduction (Eq. (3)) react rapidly with K^+ ions leading to formation of potassium hydroxide in the cathode side of the cell. In addition, water is transported across the cell to the cathode [33].

In the present study, a passive CEM-DMAFC applying a Nafion117 membrane is fabricated and evaluated. The potassium-doped Nafion117 membrane was characterized by thermogravimetry analysis, tensile-strength test, SEM-EDX, and ionic conductivity. Besides, the methanol crossover rate through membrane-electrode assemblies (MEA) was evaluated by an electrochemical test. Finally, the single cell performances of passive DMAFC were investigated and compared with conventional DMFC, by varying the methanol and KOH solution concentrations.

2. Experimental

2.1. Preparation of potassium-doped Nafion117 membranes

Potassium-doped Nafion117 (PD-Nafion117) membrane was prepared by immersing Nafion117 (Sigma Aldrich Inc.) membrane in 15 wt% aqueous solution of potassium hydroxide (KOH; Merck) for 1 h at temperature of 80 °C, and then washed with de-ionized (DI) water for several times to remove extra alkali. As well as for the passive DMFC (acidic system), Nafion117 membrane was treated by 5 wt% H_2SO_4 aqueous solution to prepare the proton (H^+) conducting membrane. Nafion117 membrane was purified according to a three steps procedure before immersing in KOH or H_2SO_4 solutions including, i) dipping in a DI-water for 1 h at temperature of 80 °C, ii) immersing in a 3 wt% H_2O_2 aqueous solution for 1 h at temperature of 80 °C and, iii) repeating the first step to remove the extra hydrogen peroxide.

2.2. Characterization of membranes

In order to investigate the thermal stability of prepared membranes, thermogravimetry analysis (TGA) was performed on the membranes ranging from room temperature to 500 °C on a thermal analyzer (Pyris Diamond, Perkin Elmer). The heating rate of the TGA was 10 °C.min^{-1} under nitrogen atmosphere.

Tensile-strength test and water uptake measurements of the membranes were performed to investigate the mechanical properties of Nafion117 and PD-Nafion117 membranes. Mechanical tensile strength tests were performed according to the standard method (ASTM D 638) using a universal tensile-compression machine. The strips of the membrane were cut into pieces of 60 mm long and 10 mm wide. The temperature, relative humidity, gauge length and the crosshead speed were set at 25 °C, ambient condition, 30 mm and 10 mm.min^{-1}, respectively. The elongation at break point and the tensile strength of the treated Nafion117 membranes were directly obtained from the tensile tests. The elastic modulus (E) in 1% strain, the stress and strain at yield point and the stress and the strain at break point, were directly obtained from the tensile stress-elongation curves for each membrane

Fig. 1. Schematic presentation of a passive DMAFC with K^+ conducting membrane.