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Effect of membrane thickness on the performance and efficiency of passive direct methanol fuel cells

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Abstract

The use of various Nafion membranes, including Nafion 117, 115 and 112 with respective thicknesses of 175 μm, 125 μm and 50 μm, in a passive direct methanol fuel cell (DMFC) was investigated experimentally. The results show that when the passive DMFC operated with a lower methanol concentration (2.0 M), a thicker membrane led to better performance at lower current densities, but exhibited lower performance at higher current densities. When the methanol concentration was increased to 4.0 M, however, the three membranes exhibited similar cell voltages over a wide range of current densities. In contrast, this work also shows the polarization behaviors in an active DMFC when the three membranes were substantially different. Finally, the test of fuel utilization indicates that the passive DMFC with a thicker membrane exhibited higher efficiency.

Keywords: Passive direct methanol fuel cell; Air breathing; Nafion membrane; Cell performance; Methanol crossover; Fuel utilization

1. Introduction

Compared with hydrogen, methanol, as a liquid non-fossil fuel for fuel cells, offers many advantages, such as high energy density (6100 Wh kg^{-1} at 25 °C), ease in storage and transport, as well as low cost. Therefore, direct methanol fuel cells (DMFCs) based on Nafion membranes are more suitable for powering small portable devices such as telecommunications, laptop and other consumable electronic devices. Over the past decade, DMFCs have been extensively studied [1–7]. More recently, a so-called passive DMFC has been proposed and investigated [8–15]. In passive-feed DMFCs, since external pumps and other ancillary devices are completely removed, the fuel supply relies on the diffusion from a built-in fuel reservoir only, while the oxidant is supplied from the ambient air. Therefore, the most striking feature of the passive DMFC is that it has much simpler structure and more compact system design than active DMFCs. Moreover, the parasitic power loss from ancillary devices, which is significant in active DMFCs, is eliminated in passive DMFCs. For these reasons, the passive DMFC has been considered as a more promising power source for future advanced electronic devices.

Presently, one of the most challenging issues for DMFCs (both active and passive) that employ Nafion membranes is methanol crossover, which results not only in a fuel loss, but also a decrease in the overall cell voltage due to the mixed potential on the cathode. Methanol crossover from the anode compartment through the membrane to the cathode compartment occurs in part because of molecular diffusion and in part because of the electro-osmotic drag. It has been shown that the former mechanism dominates under the open circuit condition and at low current densities, whereas the latter one becomes more important at high current densities [16]. Methanol crossover depends on a number of factors; the most important ones are the membrane permeability/thickness, the concentration of methanol in the fuel feed, the operating temperature and the performance of the anode itself. The membrane is a very important factor regarding the methanol

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crossover problem. Thicker membranes give a lower rate of methanol crossover but tend to have higher resistances, degrading the cell performance. Therefore, there exists an optimal thickness for the current Nafion membranes, which gives the best performance.

The use of three kinds of commercially available Nafion membranes, including Nafion 117, 115 and 112 with respective thicknesses of 175 μm, 125 μm and 50 μm, in active DMFCs has been extensively studied [17–21]. Ren et al. [19] and Jung et al. [20] tested these membranes in an active DMFC operating at 110–130 °C. Their experiments revealed that the cell performance increased with decreasing membrane thickness as a result of lower resistances. The best performance was obtained using the Nafion 112 membrane. They also found that at higher operating temperatures, the performance difference between the different membranes became much larger. An improvement in more than 100 mW cm^{-2} at 0.5 V could be achieved when Nafion 112 replaced Nafion 117 at 130 °C. Hikita et al. [21] found that the rate of methanol crossover decreased with increasing current density, indicating that the influence of methanol crossover becomes less important at high current densities.

To the best of our knowledge, the effect of Nafion membrane thickness on the performance of passive DMFCs has never been reported in the literature. Most recently, we tested Nafion 115 in a passive DMFC operated with different methanol concentrations [15] and found that the cell performance was improved substantially with the increased methanol concentration. We further found that the better performance with higher methanol concentrations was mainly attributed to the increased cell operating temperature as a result of the exothermic reaction between the permeated methanol and oxygen on the cathode. Therefore, it can be speculated that the effect of membrane thickness on the performance of a passive DMFC is different from that on an active DMFC, as the cell operating temperature is inherently coupled with the rate of methanol crossover in the passive DMFC. In this work, we tested the effect of membrane thickness on the performance of a passive DMFC and show how the rates of methanol crossover and the cell operating temperatures associated with different membranes affect the polarization behavior of the cell. Moreover, we also show the effect of membrane thickness on fuel utilization.

2. Experimental

2.1. Membrane and electrode assembly (MEA)

Three Nafion membranes, including Nafion 117, 115 and 112, whose thicknesses in the dry state are 175 μm, 125 μm and 50 μm, respectively, were used in this work. These membranes were pretreated before final fabrication in 5 vol.% H_2O_2, DI water, 0.5 M H_2SO_4 and DI water for 1 h in turn, and were kept in DI water prior to the fabrication of MEAs. Single-side ELAT electrodes, by E-TEK Corp., were employed in both the anode and the cathode. The catalyst loading on the anode was 4.0 mg cm^{-2} with PtRu black (1:1, a/o), while the catalyst loading on the cathode was 2.0 mg cm^{-2} using 40 wt.% Pt on Vulcan XC-72. In addition, the loading of dry Nafion® ionomer on the surface of each electrode was 0.8 mg cm^{-2}. MEAs with an active area of 4.0 cm^2 were fabricated by hot pressing at 135 °C and 8 MPa for 3.0 min. More detailed information about the MEA fabrication can be found elsewhere [2].

2.2. Single cell fixture

As shown in Fig. 1, the MEA mentioned above was sandwiched between two electrical current collectors, which were made of 316 stainless steel plates of 1.0 mm in thickness. A plurality of parallel channels was machined by a wire cutting technique for both current collectors, serving as the passages of fuel and oxidant, which resulted in an open ratio of 48%. A 200-nm platinum layer was sputtered onto the surface of 316 stainless steel plates to reduce the contact resistance with the electrodes. The cell was held together between an anode and a cathode fixture, both of which were made of transparent acrylic plates. A 3.0 mL methanol solution reservoir was built in the anode fixture. 2.0 M or 4.0 M methanol was diffused into the catalyst layer from the built-in reservoir, while oxygen, from the surrounding air, was diffused into the cathode catalyst layer through the opening of the cathode fixture. The cell temperature was measured by a miniature thermocouple (0.0005-in. thick, CO-1T, OMEGA), which was installed between the anode current collector and the MEA.

The limiting current density method [22] in the permeation cell was employed to evaluate methanol crossover of the three membranes in this work. Humidified nitrogen at room temperature was passed through the cathode side in the permeation cell at a rate of 100 mL min^{-1}, while 2.0 M or 4.0 M methanol was passed through the anode side at 1.0 mL min^{-1}. An external voltage of polarization at 1 mV s^{-1} by 273A EG&G potentiostat was imposed on the cell. The value of current density at 0.9 V was chosen to represent the limiting current density.

2.3. Electrochemical instrumentation and test conditions

An Arbin BT2000 electrical load interfaced to a computer was employed to control the condition of discharging and record the voltage–current curves. For each discharging current point along the *I–V* curve, a more than 40-s waiting time was used to obtain the stable voltage. The internal resistance of the cell was measured by the Arbin BT2000 built-in function. To this end, ten continuous current pulses with amplitude of 0.2 A were applied to the cell; the internal resistance reported in this work are the average data over the ten pulses.

All the experiments of the passive DMFCs were performed at room temperatures of 20–22 °C and the relative humidity of 50–70%. Prior to the passive DMFC performance test,