The role of an anode microporous layer in direct ethanol fuel cells at different ethanol concentrations

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ABSTRACT

Ethanol crossover and ethanol electrooxidation kinetic effects on direct ethanol fuel cell (DEFC) performance were determined at different ethanol feed concentrations for cells fabricated with and without an anode microporous layer (MPL). Several characterization techniques were used, including cell performance curves, anode polarization, electrochemical impedance spectroscopy (EIS) and ethanol crossover by the voltammetric method. It was found that the optimum ethanol feed concentration depended on the anode structure design and the cell current density operation. A microporous layer could reduce ethanol crossover but induced high mass transfer resistance, resulting in a slow ethanol electrooxidation reaction rate. However, ethanol crossover was not the dominant factor affecting DEFC performance for the ethanol feed concentration range (0.5–5.0 M) studied. The MEA without an anode MPL exhibited better performance than the one with an MPL for the entire range of ethanol concentration.

1. Introduction

For direct alcohol fuel cells (DAFCs), a high alcohol feed concentration is one of the desirable operating parameters to enhance the kinetic reaction rate [1] and to maintain high specific energy of the system [2]. Nevertheless, high alcohol feed concentrations can cause the alcohol crossover problem in the anode catalyst layer (CL), especially in the case of direct methanol fuel cells (DMFCs). Many methods to diminish methanol crossover have been proposed. Feeding a dilute methanol solution could alleviate the problem; but this approach has the adverse effect of reducing the methanol electrooxidation rate, and also requires a large fuel reservoir capacity [2]. Recently, research has been conducted on modifying the electrolyte membrane to reduce methanol permeability [3–5], and on enhancing anode catalyst activity to decrease methanol concentration in the anode CL [6,7].

Besides these two approaches, several previous studies have investigated the fabrication of a membrane electrode assembly (MEA) having an anode microporous layer (MPL) to control methanol transport from the anode flow channel to the anode CL [8–11]. These anode MPLs, typically consisting of carbon powder and polytetrafluoroethylene (PTFE), were inserted between the anode CL and the anode backing.

In comparison with DMFCs, the fuel crossover problem in direct ethanol fuel cells (DEFCs) exhibits different features. The permeation of ethanol from the anode to the cathode through a Nafion® membrane was found to be lower than that of methanol due to the higher molecular weight of ethanol compared to methanol. Moreover, the negative effect of crossover on DEFC performance might be less than in the case of a DMFC because of the slower kinetic rate of ethanol reaction on the Pt catalyst employed at the cathode [12]. For these reasons, it was expected that the impact of the anode structure on the fuel crossover of a DEFC would be different from its impact on a DMFC.

On the other hand, ethanol crossover has been one of the most challenging problems to be overcome for enhancement of DEFC performance. Some researchers have proposed controlling ethanol transport at the anode side in order to mitigate ethanol crossover to the cathode: for instance, depositing an inner CL containing nanometer-sized $Pt_{50}-Sn_{50}$ particles on a Nafion membrane to serve as an ethanol filter [13], or adding an anode MPL to act as a mass transfer barrier [14]. Additionally, many efforts have been made to study the effect of ethanol feed concentration on fuel cell performance [15–23]. Some of these works have pointed out that there is an optimal ethanol concentration for maximum power density, related to the balance between ethanol oxidation kinetics and ethanol crossover [19–21]. Using a high ethanol concentration might create undesirable side effects, particularly delamination of the anode CL and the electrolyte membrane [16,23]. However, to date no systematic studies have been conducted on the effects of ethanol concentration by various characterization methods. The reason for the decrease in cell performance in relation to the optimal ethanol feed concentration is still obscure. Furthermore, the role of a microporous layer in the anode structure at several ethanol feed concentrations has never been emphasized in previous DEFC studies.

In this paper, a variety of experimental characterization techniques for investigating DEFC performance and ethanol crossover are presented under a wide range of ethanol feed concentrations. Moreover, we investigated whether adding a microporous layer in the anode structure was necessary at high ethanol feed concentrations (>1.0 M). Various characterization techniques were employed, including cell polarization and power curves, anode polarization, EIS and ethanol crossover as determined by the voltammetric method.

2. Experimental

2.1. Materials and MEA preparation

The details of MEA fabrication has been described in our previous work [24] and the preparation of the components used are explained here. A Nafion® 115 perfluorinated ion-exchange membrane (DuPont, Wilmington DE, USA) was used as a polymer electrolyte membrane for all experiments. Before use, the membrane was treated in 3% H_2O_2 solution, boiled in 0.5 M H_2SO_4 solution, and then washed in deionized water. Each treatment process was conducted at 70 °C for 1 h.

A commercial gas diffusion electrode (E-LAT®; E-TEK, Somerset NJ, USA) containing 0.5 mg Pt cm^{-2} on Vulcan XC-72 carbon powder (Johnson Matthey, London, UK) was used at the cathode, whereas the anode was made in-house. In fabricating the anode, anode catalyst ink—composed of Pt–Sn (3:1 atomic ratio) on Vulcan XC-72 catalyst, Nafion ionomer solution (5 wt% in alcohol/water) and isopropyl alcohol – was ultrasonically agitated for 1 h to obtain a homogeneous mixture. After that, the anode catalyst ink was coated onto the Nafion 115 membrane using an ultrasonic auto-spraying machine. After a 5 cm^2 CL was formed, the coated membrane was dried in a vacuum oven at 60 °C for 1 h. The loadings of catalyst metal and Nafion ionomer were 2 mg cm^{-2} and 20 wt % of dry CL, respectively.

Thereafter, a diffusion layer was prepared to attach onto the anode CL. Two different anode diffusion layers were constructed in our experiment: one was carbon cloth without an anode MPL (no PTFE; ElectroChem Inc., Woburn MA, USA), and the other was carbon cloth coated with a hydrophobic MPL (20% PTFE). The anode MPL ink, consisting of Vulcan XC-72 carbon powder, Nafion ionomer and isopropyl alcohol, was coated onto the carbon cloth by ultrasonic spraying. The thicknesses of the carbon cloth without and with the anode MPL are 226.4 ± 3.0 and 393.3 ± 8.0 μm, respectively. The surface morphology and surface contact angle of the two anode diffusion layers were characterized and confirmed the presence of the hydrophobic layer on the carbon cloth [24].

To form the MEAs, thin layers of anode and cathode electrode were applied on each side of the treated Nafion membrane and hot pressed at 6.9×10^6 Pa and 150 °C for 90 s. The single cell was sandwiched between two graphite blocks with parallel serpentine flow fields, and was clamped on both sides by current collector end-plates.

2.2. Performance testing setup and analysis

Before cell testing, a single cell was activated by feeding ultra-high purity (99.995%) hydrogen and high purity (99.99%) oxygen reactant gases to the anode and the cathode, respectively. The flow rate of both gases was 100 mL min^{-1} at 75 °C, with atmospheric pressure on each side; this first step of cell activation lasted for 4 h. After H_2/O_2 activation, a 1.0 M ethanol aqueous solution was fed to the anode by a digital micropump at a flow rate of 1 mL min^{-1}. Unhumidified oxygen gas at a flow rate of 100 mL min^{-1} was supplied to the cathode compartment at atmospheric pressure. Cell activation by ethanol solution continued for 60 min. These processes were performed to ensure a steady-state cell operation. Next, Quick-scan (cell polarization) testing was carried out by a computer-controlled fuel cell test station with an electronic load in potentiodynamic polarization mode at various ethanol concentrations (0.5, 1.0, 2.0, 3.0, 4.0, 5.0 and 6.0 M). The time interval of the test was 10 s per point.

A steady current discharging in galvanostatic mode was measured by controlling the cell current and simultaneously