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Hydrogen crossover through perfluorosulfonic acid membranes with variable side chains and its influence in fuel cell lifetime

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ABSTRACT

In this study, hydrogen crossover in long side chain Nafion 211 membrane and short side chain Aquivion membrane is studied under different conditions. It is found that both temperature and relative humidity significantly influence the hydrogen crossover in the polymer electrode membranes (PEMs). The difference in hydrogen crossover behavior between Nafion 211 membrane and Aquivion membrane is revealed. The influence of hydrogen crossover on the fuel cell lifetime is also investigated under open circuit voltage (OCV). It is proved hydrogen crossover in the PEM would lead to possible degradation of the PEM and the decrease of electro-chemical surface area in the catalyst of the single cell. Single cell assembled with Aquivion membrane shows slower OCV and ECSA decay compared to the Nafion 211 single cell. Our results suggest that the PEM fuel cell lifetime is closely related to the hydrogen crossover in the PEM. The current study also highlights the possibility of improving the fuel cell durability by rational design of the PEM morphology. Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Perfluorosulfonic acid (PFSA) membrane has been widely used in proton exchange membrane fuel cell due to their high proton conductivity and relatively good stability [1–3]. In order to avoid the performance loss associated with the membrane resistance during fuel cell operation, PFSA membranes with low thickness were commonly used. One of the main problems arises from the application of such thin PFSA membranes is the poor mechanical properties of the

membrane [4]. This problem can be solved by using a reinforced PFSA membrane [5,6]. Another major concern for using the thin PFSA membrane in fuel cell is the fuel (such as hydrogen) crossover across the membrane during fuel cell operation. The fuel crossover in the PFSA membranes not only leads to the loss of fuel cell performance but also causes severe degradation of the membrane. For example, hydrogen crossover through the PFSA membrane in fuel cell would lead to the development of mixed potentials at electrodes and thus a decreased open circuit potential [7]. The performance of the fuel cell and fuel efficiency decreases greatly due to the

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hydrogen crossover. Membrane degradation resulted from the hydrogen crossover has been also demonstrated. Heat generated from the reaction of the crossover fuels results in localized overheating on the PFSA membrane. Deformation and thermal degradation of the membrane could be induced because of the overheating. In addition, fuel crossover facilitates the formation of peroxide radicals [8]. These radicals also degrade the PFSA membrane by unzipping the main chain and side chain of the membrane [9]. This degradation process causes the formation and development of pinhole in PFSA membrane and ultimate failure of fuel cell [4].

A lot of work has been done to develop the methods for the measurements of gas permeability through PFSA membranes. The gas permeability of PFSA membrane was first studied with time-lag technique [10]. Gas chromatography based methods have been also employed to study the gas permeability in PFSA membrane [11–14]. Broka et al. investigated oxygen permeability in recasted Nafion membranes using gas chromatography [11]. They found gas permeability in Nafion membrane depended on temperature and humidity and therefore concluded that both the hydrophobic phase and the hydrophilic phase in Nafion membrane are important for its gas permeability [11]. More recently, the measurement of gas crossover through PFSA membrane using a mass spectroscopy was demonstrated [15,16]. Electrochemical techniques have been widely used nowadays for the quantification of fuel crossover in PFSA membranes [17,18]. This methods allows for facile and *in-situ* measurements of the fuel crossover. Moreover, results obtained with this fuel cell set-up based method can be better correlated to the results from the fuel cell experiments.

It was shown that the gas crossover in PFSA membrane was a complex process in which many factors (e.g. humidity and temperature) play important roles [14]. Despite the progress in understanding the gas crossover in PFSA membrane, systematic investigation of the gas crossover in PFSA membrane and its potential impact on fuel cell lifetime is still rare. In this paper, the hydrogen crossover in PFSA membranes was carefully studied with the *in-situ* electrochemical techniques. Nafion 211 membrane and Aquivion membrane were studied and compared to investigate the impact of membrane properties on the hydrogen crossover in the PFSA membranes. The impact of fuel crossover in PFSA membranes on the fuel cell durability was also evaluated.

2. Experimental

2.1. Pretreatment of the PFSA membranes

Nafion 211 membranes (25 μm thick, EW value (defined as the weight of membrane per mole sulfonic acid) 1100 g/mol, DuPont) and Aquivion membranes were used in this study. The Aquivion membrane was fabricated using a casting method similar to that of Nafion 211 membrane [9]. In brief, Aquivion PFSA (Solvay Soleix, EW 790) solution was applied in a Petri dish. A membrane was obtained by evaporation the solvents at 70 $^{\circ}\text{C}$ for 2 h. The membrane was then annealed at 100 $^{\circ}\text{C}$ and 150 $^{\circ}\text{C}$ for 30 min and 20 min, respectively. The thickness of the Aquivion membrane was controlled by the

volume of the Aquivion solution used. In this study, the thickness of the Aquivion membrane was kept at $\sim 26 \mu\text{m}$. The single cell performance of the casted Aquivion membrane was reported previously [5]. Prior to experiments, all the membranes were protonated by sequentially soaking in 5 wt% H_2SO_4 solution and deionized water for 1 h. The soaking procedure was repeated once to fully protonate the membranes.

2.2. Preparation of the single cell

A catalyst layer was formed on the PFSA membranes by coating a water solution consisting of 40 wt% Pt/C (Pt/Vuclan XC72, Johnson Matthey) and 5 wt% Nafion DE520 solution (DuPont) on both sides of the membranes. To prepare the membrane electrode assembly (MEA), hydrophobic carbon paper (90 μm thick, TGP-H-060, Toray) was subsequently hot pressed onto both sides of the catalyst coated membrane. The MEA was mounted in a single cell test fixture with a serpentine flow field and a fuel cell clamp with two heating sheets on both sides. The active area of the single cell is 5 cm \times 5 cm.

2.3. Water uptake of the PFSA membranes

Water uptake of the membrane was quantified by weight change of the membrane after 8 h incubation in a thermo-humidity controlled chamber for 8 h. The weight of the dry membrane was measured after drying the membrane at 100 $^{\circ}\text{C}$ for 24 h. The water uptake was calculated with Equation (1), where W_2 and W_1 are the weight of the hydrated membrane and the weight of the dry membrane, respectively.

$$\Delta W(\text{wt}\%) = \frac{W_2 - W_1}{W_1} \times 100\% \quad (1)$$

2.4. Electrochemical characterizations

The hydrogen crossover in the PFSA membrane was measured using linear sweep voltammetry (LSV). The diffusion-limited hydrogen oxidation current density of the hydrogen crossover was measured using the Autolab PG30/FRA (Eco chemie B.V.). The single cell for hydrogen crossover measurement was activated with G50 fuel cell test station (Greenlight) at 65 $^{\circ}\text{C}$ and 100% RH before the measurement. During the measurement, hydrogen and nitrogen was fed to the anode and cathode of the single cell, respectively. The flow rate is 300 sccm/min for both hydrogen and nitrogen. By applying a dynamic potential from 0 to 0.7 V (scanning rate: 2 mV/s), the limiting hydrogen oxidation current density was measured. The measurements were performed at different temperature and different RH.

The electro-chemical surface area (ECSA) per unit area of both the anode and cathode in the catalyst layer was measured by *in-situ* cyclic voltammetry (CV) using Auto lab (PGSTAT 30, Eco chemie B.V.). The ECSA of the cathode was first measured. The anode, which serves as reference/counter electrode, was fed with hydrogen at 300 sccm/min. The cathode was fed with nitrogen at 300 sccm/min and served as working electrode. The CV measurements were carried out with a scan rate of 50 mV/s from 0.05 V to 1.25 V. After the cathode CV test was finished, the flow path was changed to

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