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Short Communication

Accelerated testing of polymer electrolyte membranes under open-circuit voltage conditions for durable proton exchange membrane fuel cells

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ABSTRACT

Nafion NRE212, Nafion HP, and a hydrocarbon-based membrane were used in an accelerated open-circuit voltage (OCV) test to examine their oxidative stability. The catalyst layer and the gas permeability were analyzed to apply the same experimental conditions for each electrolyte membrane. The accelerated OCV test was conducted for ~800 h, and the states of the membrane electrode assembly (MEA) were investigated by measuring the electrolyte membrane resistance, cyclic voltammograms, and linear sweep voltammograms with respect to time. Typically, the sulfonated poly(arylene ether), which has a low oxidative stability, showed the best performance in the OCV test, followed by the Nafion HP membrane and Nafion NRE212 membrane. The inherent oxidative durability of the electrolyte membrane and the gas permeability likely play a crucial role in the oxidative stability during MEA operation. The results further confirmed that the gas permeability affects the stability of the electrode in the catalyst layer.

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Introduction

Proton exchange membrane fuel cells (PEMFCs) have been studied as an alternative energy technology for clean power generation because of their high efficiency and lack of carbon emissions [1,2]. Polymer electrolyte membranes, which act as a proton conductor and barrier between hydrogen and air, are a key component in PEMFCs. Perfluorinated sulfonic acid (PFSA) membranes (Nafion®, DuPont) are a commercial benchmark because of their high proton conductivity and excellent mechanical strength. Nonetheless, PFSA membranes are expensive and show low glass transition temperatures [3–5].

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Despite the advantages of PFSA membranes, their chemical stability is an important issue for commercializing PEMFC systems [6–8]. During the oxygen reduction reaction (cathode side), reactive chemical species (RCSs), such as hydroxyl radicals and hydrogen peroxide, are generated. RCSs easily diffuse into the membrane and accelerate its chemical degradation [6,8–10] (e.g., by attacking and degrading the polymer backbone of the PFSA membranes). The unstable carboxylic acid terminal groups of the PFSA membrane are important in the degradation mechanism [11,12]. However, a new degradation mechanism associated with the sulfonic acid functional groups was recently suggested [13,14]. Both acidic functional groups lose hydrogen atoms upon attack by RCSs, and $-COO\bullet$ or $-SO_3\bullet$ radicals can induce an unzipping reaction in the PFSA membrane.

Although studies on the long-term chemical stability are crucial for commercializing PEMFCs, few practical evaluations of the electrolyte membrane have been performed. Evaluating the long-term stability of the electrolyte membrane and the interference affected by the catalyst layer is a time-consuming testing process; therefore, accurately diagnosing the membrane is difficult. Generally, long-term constant current tests and accelerated open-circuit voltage (OCV) tests are used to evaluate the long-term stability of the membrane [2,15]. The Fenton test and hydrogen peroxide exposure test are possible test protocols; however, they do not directly evaluate the electrolyte membrane of the membrane electrode assembly (MEA) [16]. Nevertheless, the time-consuming process for typical long-term constant current tests are not easily accessible in the laboratory. Therefore, the United States Department of Energy and Japan's New Energy and Industrial Technology Development Organization (NEDO) developed standardized long-term stability evaluation methods by creating evaluation protocols for OCV acceleration.

OH radicals and hydrogen peroxides are typically produced by two competing reaction mechanisms during fuel cell operation [17]; the oxygen reduction reaction does not occur in the accelerated OCV test. Thus, RCSs are only generated according to Eqs. (1)–(3) [18]. The reaction can occur in both the anode and cathode catalysts; therefore, the decomposition reaction can be initiated at the anode and cathode during the accelerated OCV test. Considering the RCS generation mechanism, the concentration of hydrogen and oxygen permeability in each electrode, significantly affects the number of generated RCSs. Furthermore, the activity and electrochemical surface area (ECSA) of the catalyst are important because RCSs are generated on the surface of the platinum catalyst on the cathode and anode. Thus, the number of generated RCSs varies according to the catalyst and its support.

$$H_2 + O_2 \rightarrow 2HO \text{ (on catalyst surface)} \quad (1)$$

$$2HO\cdot + H_2 \rightarrow H_2O_2 + 2H\cdot \quad (2)$$

$$H\cdot + O_2 \rightarrow HOO\cdot \quad (3)$$

We conducted an OCV test under NEDO conditions using three different electrolyte membranes. We used Nafion NRE212 as a reference material and investigated the effect of its reinforced structure on the oxidative stability using Nafion HP. Furthermore, hydrocarbon electrolyte membranes (Fig. S1), which typically have a low oxidative stability, were selected to analyze the effects of different properties from the PFSA on the oxidative stability. Most previous studies observed changes in OCV and did not examine how the components of the MEA specifically affected the changes. We observed the real-time ECSA, linear sweep voltammograms (LSVs), and ohmic resistance with respect to time during an accelerated OCV test; changes in the gas permeability, catalyst layer, and MEA were simultaneously monitored. We report the effects of changes in gas permeability and cyclic voltammetry (CV) behavior on the oxidative stability of MEAs with different electrolyte membranes using the electrochemical properties of the MEA.

Experimental

Sulfonated poly(ether sulfone) (SPES50) (50% sulfonation) was purchased from Yanjin Chemical (China) (Fig. S1). Nafion NRE212 and HP membranes (DuPont) were used as received. The SPES50 membranes were prepared by the solution-casting method to produce a homogeneous membrane (50-μm thick).

The fuel cell electrodes were prepared as follows. A metal catalyst layer (ionomer: 20 wt% against supported catalyst) was prepared using the decal transfer method. A platinum-supported catalyst (HISPEC4000, Johnson Matthey Catalysts) and Nafion ionomer were mixed to form a slurry, which was coated onto the polymeric substrate. The dried catalyst layer was thermally transferred to the membranes by compression for 4 min at 140 °C. Finally, an MEA (25 cm^2 electrode area) was obtained by edge sealing.

The OCV of each cell was observed using a potentiostat (ZIVE SP2, WonATech, Korea), and the high-frequency resistance (HFR) was monitored using a 1-kHz resistance meter (Hioki) every 24 h. The cell was operated at 90 °C and 30% relative humidity (RH) under atmospheric conditions (NEDO conditions). CVs, and LSVs were measured using a potentiostat (HCP-803, Bio-Logic Science Instruments, France). Detailed conditions for ECSA and LSV test are available in Supporting information.

Results and discussion

The MEAs (prepared using Nafion NRE212, Nafion HP, and SPES50 membranes) use the same electrode layers for accurate OCV comparisons. The weight of the electrode layers coated onto the polyethylene terephthalate films using thermal transfer was measured, confirming that all platinum loadings are 0.20 mg cm^{-2} for each electrode layer. Prior to the long-term test of the prepared MEA in the OCV, the states of the catalyst layer were examined by measuring CVs (90 °C, 30% RH; Fig. S2); the ECSAs of NRE212, Nafion HP, and SPES50

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