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Degradation mechanism study of PTFE/Nafion membrane in MEA utilizing an accelerated degradation technique

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ABSTRACT

Nafion membranes are widely used for commercial membrane electrode assemblies (MEAs) in proton exchange fuel cells (PEMFCs). The polytetrafluoroethylene (PTFE)/Nafion (PN) composite membrane has the advantages of being low in cost, high in mechanical strength, and does not swell excessively. This study focuses on the properties of PTFE/Nafion membranes and PTFE/Nafion MEAs by comparing the durability and performance of the PN MEAs to commercial Nafion 211 MEAs. In an accelerated degradation test (ADT), the characterization of PTFE/Nafion and Nafion MEAs were analyzed using in-situ electrochemical methods such as polarization curves, AC impedance, cyclic voltammetry (CV), and linear sweep voltammetry (LSV). The results demonstrate an increase in the internal resistance on the PTFE/Nafion MEA only. The three mechanisms behind this unique result were proposed to be: (a) Separation of the catalyst layer from the membrane due to creep deformation; (b) Separation of the outer Nafion layer film from the core PTFE/Nafion membrane due to creep deformation; (c) Degradation of the Nafion plane (or Nafion dissolution) from the PTFE surface.

The scanning electron microscope (SEM) images indicate that only the PTFE/Nafion MEA curved after the ADT. Mechanism (a) was therefore the most possible phenomenon for the increase in internal resistance of the PN MEA.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) offer the advantages of having zero emission, scalability, high power density, and fast start-up. PEMFCs have great potential to be a green power source for computer; communication and consumer (3C) products; vehicles; and stationary power. However, cost and durability are the two main issues that are hindering the commercialization of PEMFCs. Membrane electrode assemblies (MEAs) not only play an important role in the performance of PEMFCs, but they also affect the cost and durability.

Nafion membranes (DuPont Co.) are widely used in the MEAs inside PEMFCs due to their low resistance, and excellent thermal and chemical stability. Much literature has demonstrated that the thickness of PTFE/Nafion (PN) composite membranes can be reduced to thinner than 25 μm [1]. This reduction in thickness causes PN membranes to have a lower proton resistance, which means MEAs with this PN composite membrane can cost less and generate better performance than MEAs with just Nafion membranes.

PTFE/Nafion composite membranes can be fabricated by soak, spray, or other methods [1–4]. However, the most common method in fabrication is the soak method, which is

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used in this study because its mass production is possible. Tang et al. used their homemade special soak system that could increase Nafion contents in the porous PTFE film, thus increasing the performance and durability [4].

The PTFE/Nafion composite membrane has been proved by relative humidity (R.H.) cycling tests to be a mechanically durable membrane. Tang et al. showed that while the pure Nafion membrane can only be kept in a stable condition for about 3500 R.H. cycling tests, their PTFE/Nafion composite membrane can be kept stable for over 5000 cycles, which is about 40% more cycles than the pure Nafion membrane [4]. However, there are several factors that affect the durability of PEMFCs [5–9]. Tang et al. did not evaluate the durability of the PTFE/Nafion MEA operating in PEMFC discharge mode, which meant that the experiment was undertaken without degradation of the catalyst layer. Therefore, this factor was not considered in the investigation even though electrocatalysts play an important role in affecting durability and lowering the cost of the PEMFCs [10]. Many studies have shown that no recoverable deterioration of PEMFC performance is primarily attributed to the degradation of Pt based catalysts and membranes in the MEA [11–16].

There are several accelerated degradation techniques being discussed in the test field for durability. Huang et al. simulated the mechanical behavior of fuel cell membranes under R.H. cycles [17], and also demonstrated that R.H. cycling reduces the strain-to-failure of MEA in ex-situ experiments [17]. Singaram et al. diagnosed the failure modes of the MEA via R.H. cycling [18] while Rong et al. used the finite element method to simulate the microstructural change in the catalyst layers from load cycling [19]. Mathias et al. suggested the use of material characterization tests as screening tools for automotive fuel cell materials development: (i) membrane conductivity vs. R.H. and water uptake; (ii) membrane R.H. cycling test; (iii) catalyst voltage cycling test; (iv) support corrosion test at 1.2 V [20]. According to the degradation map [21], accelerated degradation of the membrane can be achieved by dry/wet cycling, OCV hold, and operating at a high temperature with a low R.H. Accelerated degradation of the catalyst can be achieved by potential cycling.

In conclusion, durability and cost are the key issues hindering the commercialization of PEMFCs. Normally, a steady-state lifetime test can assess the lifetime of a fuel cell but this method is impractical for durability tests because it is time-consuming and costly. Instead, this study uses the accelerated degradation test (ADT) to measure the durability of PTFE/Nafion membrane and Nafion 211 membrane MEAs, and to simulate automotive fuel cell applications. As the membrane is the sole difference between PTFE/Nafion and Nafion 211 MEAs, the discussion section will focus on membrane degradation. The complex ADT includes R.H. cycling and open circuit voltage (OCV) hold, and the resulting possible membrane failure mechanisms are mechanical and chemical degradation, respectively. R.H. cycling would lead to membrane swelling/shrinking, which then results in membrane fatigue. On the other hand, the OCV would bring out the hydroxyl radicals emanating from minor H_2O_2 production which results in a reduction in membrane thickness that ultimately leads to failure [22,23].

2. Experimental

2.1. Preparation of PTFE/Nafion membrane and membrane electrode assemblies

The preparation of PTFE/Nafion membranes and membrane electrode assemblies was described in our previous papers [23–25]. The porous PTFE membrane was submerged in a Nafion solution that contained triton 3 wt%, thereby producing a PN membrane with a thickness of around 25 μm . The MEAs were fabricated by the CCM method, where one consisted of the homemade PN and the other consisted of the commercial Nafion 211. The catalyst ink consisted of a catalyst (HiSPEC 4310, Johnson Matthey Co.) comprising 39.6 wt% Pt/C, 5 wt% Nafion solution (DE520, DuPont Co.), and isopropyl alcohol as an extra solvent. The weight ratio of Pt/C loading to solid Nafion was maintained at 2:1, while the Pt loading in the anode and cathode were both 0.5 $\text{mg}_{\text{Pt}} \text{cm}^{-2}$. Each CCM was sandwiched between two gas diffusion layers (10BC, SGL Co.) without a hot press. The active area of both MEAs was 25 cm^2 . The Nafion 211 membrane was chosen for comparison as it has a similar thickness (25 μm) to the homemade PN membranes.

2.2. Experimental procedures, parameters, and apparatus

The experimental procedures, parameters, activation process, and apparatus were described in our previous studies [23–25]. After the activation process, the cell was operating at 0.6 V, 65 °C, and R.H. 100%. The polarization was checked every 30 min until it became stable. And then a complex ADT was then undertaken. The following three steps were executed for every cycle, taking approximately five minutes per cycle:

Step 1: The MEA was operated in OCV mode for 30 s under R.H. 100%;

Step 2: The MEA was operated in discharge mode at 0.6 V for 150 s under R.H. 100%;

Step 3: The MEA was operated in discharge mode at 0.6 V for 150 s under R.H. 0% (bypass).

After a certain number of cycles, the polarization curve, AC impedance, CV, and LSV were measured for analysis and comparison. The above measurements were conducted under 80 °C and R.H. 100% using FC 5100 fuel cell evaluation system (CHINO Corporation, Japan) and CHI 1127A (CH Instruments, Inc., USA).

3. Results and discussion

3.1. Electrochemical analysis

Fig. 1 shows the OCV and hydrogen crossover current (i_{loss}) results of the PTFE/Nafion and Nafion 211 MEAs during the ADT periods. Initially, the OCV of PTFE/Nafion and Nafion 211 MEAs were 0.925 V and 0.935 V, respectively. The i_{loss} of PTFE/Nafion was 0.002 A cm^{-2} , which is slightly higher than the i_{loss}

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