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Effects of catalyst layer on the structural change of a membrane electrode assembly under humidity cycle tests

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HIGHLIGHTS

- We examined effects of catalyst layer on the structural change of an MEA.
- Swelling deformation becomes small by enlarging the catalyst layer thickness. Decrease of storage elastic modulus of MEA was prevented by the catalyst layer.
- Catalyst layer reduce the structural change of an MEA under the humidity cycle test.

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ABSTRACT

Structural changes in a polymer electrolyte membrane (PEM) and a membrane electrode assembly (MEA) of different catalyst thickness under humidity cycle tests were investigated. Nafion211 membrane was used in this study. The catalyst layer thickness of MEAs was set to 2–10 μm using catalyst paste of the same composition. Dimensional changes in the PEM and MEA due to swelling were measured, and dynamic mechanical analysis (DMA) of the membrane and MEA were carried out. Moreover, humidity cycle tests for the MEA were carried out according to the conditions specified in the FCCJ protocol, and structural changes in the MEA after the tests were examined. It was shown that the membranous structural change under humidity cycle tests tends to become small when the thickness of the catalyst layer is large.

1. Introduction

With growing public interest in environmental protection and energies other than oil, research and development is under way on polymer electrolyte fuel cells (PEFCs) as a substitute for the internal combustion engine. Improved durability and cost reduction of fuel cell stacks are two important issues to enable widespread use of fuel cell vehicles. Polymer electrolyte membrane fuel cells, especially for automotive applications, must operate over a wide range of conditions. The Fuel Cell Commercialization Conference of Japan (FCCJ) proposed several methodologies for testing MEAs and their materials [1–5]. We have applied the protocols of FCCJ to standard materials and verified their validity using a JARI standard single cell [6,7]. The JARI standard single cell has an electrode surface area of 25 cm^2 and one serpentine flow channel in each separator of anode and cathode [6]. This cell has a large gas flow rate in a channel, and is characterized by being easy to produce a pressure distribution. The JARI standard single cell is suitable for simulating the phenomena that may actually occur in a PEFC stack, and so is suitable for material evaluation under conditions near the operating condition of an actual stack. Humidity cycle tests that simulate the operation of a fuel cell vehicle are widely used to test the mechanical durability of a membrane in the form of membrane electrode assemblies (MEAs). In perfluorosulfonic acid membranes, sufficient membrane hydration contributes to good proton conduction. The membrane swells through the absorption of water produced by an electrochemical reaction. Conversely, the membrane shrinks via desorption of water in low-humidity fuel cell operation. The membrane swells and shrinks repeatedly according to the fuel cell environment, which changes with the automotive operating conditions. As a result, the repeated expansion and shrinkage affects the deformation of the polymer electrolyte membrane and decreases its mechanical durability. The humidity cycle test is a means of accelerating mechanical degradation of the membrane, which is an important subject for researchers studying the mechanical behavior of electrolyte membranes. Many

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researchers have studied the mechanical behavior of fuel cell membranes under conditions of cycling humidity using numerical models. Compressive, plastic deformation occurs during hygro-thermal loading, resulting in tensile residual stress after unloading [8]. These residual in-plane stresses are the major stress component in the membrane [9,10]. The simulation results of in situ fuel cell hygro-thermal cycling in a simplified two-dimensional fuel cell model supports the theory of hygro-thermal driven mechanical stress causing the formation of pinholes in the channel [11]. Humidity cycling leads to mechanical failure of the membrane due to in-plane swelling strain where the fastening force is lower within the channel portions of grooved gas flow fields. A methodology to predict the durability of PEM under humidity cycling was presented, and such testing can be used to evaluate membrane failure [12]. Mechanical stress in the membrane is caused by the restriction of its swelling by the gas diffusion layer (GDL) and cell assembly, both of which influence the compressive stress distribution [13–15]. From the results of research on MEA wrinkle deformation, caused by compressive stress along with in-plane swelling as an initial phase of the degradation, a lower swelling ratio in the in-plane direction and a thicker membrane prevent membrane buckling [16]. Most of the above-mentioned literature investigated the effects of fastening force distribution caused by the gas flow field configuration or by imperfect geometry of the GDL surface [17]. The effects of the MEA catalyst layer have not been sufficiently discussed. In this study, we experimentally investigated the effects of the catalyst layer on the swelling characteristics, thermal deformation behavior, and structural change of a membrane electrode assembly under humidity cycle tests.

2. Experimental

2.1. MEA preparation

MEAs were prepared using a commercial Pt/C catalyst (TEC10E50E), polymer dispersion (DE2020) and polymer electrolyte membrane (NR211). The catalyst paste was applied onto a Teflon sheet using the doctor-blade method and was heat-treated at 125 °C for 1 h. The weight ratio of electrolyte polymer to carbon support in the paste was 1.0. The Pt metal loading was calculated based on the chemical composition of the catalyst paste. A sheet of electrolyte membrane (8 × 8 cm) was sandwiched between catalyst sheets of 25 cm^2 (5 × 5 cm), with the catalyst layer side of the sheets in contact with the membrane. The sheet-membrane unit was hot-pressed at 135 °C for 10 min, after which the Teflon sheets were removed to obtain an MEA. The thickness of the catalyst layers of an MEA anode and cathode was set at 2–10 μm at the same time. The composition of the catalyst layer was the same regardless of the thickness of the catalyst layer, and the thickness of the catalyst layer was adjusted by varying the clearance gap of the blade. That is, a catalyst layer with larger thickness had a greater Pt loading. MEA specifications as prepared in this study are shown in Table 1.

Table 1
MEA specifications.

Catalyst	Pt/CB (TEC10E50E), TKK
Thickness of anode/cathode catalyst layer (anode/cathode Pt loading mg cm^{-2})	0/0 μm (without catalyst layer) 2/2 μm (0.05/0.05) 10/10 μm (0.3/0.3)
Ionomer	D2020, Dupont
I/*C*	1
Electrolyte membrane	NR211, Dupont
GDL	SGL 24-BCH

2.2. Measurement of dimensional changes in the MEA

We investigated the effects of the thickness of the catalyst layers of an MEA on the deformation characteristics of the membrane by water absorption swelling. Dimensional changes in the PEM and MEA due to swelling were measured. The PEM sample before swelling was cut into a 5-cm square from a PEM sheet. The MEA sample before swelling was cut into a 5-cm square from the electrode area of the MEA prepared by the method described in 2.1 above. The dimensions of the samples before swelling (initial value) were measured at 23 °C and 50% RH. The samples were soaked in deionized water at 80 °C for 1 h, and then the dimensions after swelling were measured. The dimensions along the in-plane direction of the membrane were measured by ruler with a minimum scale value of 0.5 mm. The dimensions along the transverse direction of the membrane were measured by micrometer. From the measurement results, the swelling ratio was calculated by:

$$\text{Swelling ratio} = (X1 - X0)/X0 \times 100\% \quad (1)$$

x, *y*: in-plane direction of membrane; *z*: transverse direction of membrane
0: before swelling; 1: after swelling

2.3. Dynamic mechanical analysis of PEM and MEA

We investigated the effects of the thickness of the catalyst layers of an MEA on the deformation characteristics of the membrane by repeated loading. As for the measurement of physical properties relevant to the glass transition point and tensile strength of an MEA, dynamic mechanical analysis (DMA) of the membrane and the MEA was carried out. The PEM sample was cut into a 50 × 5 mm square from a PEM sheet. The MEA sample was cut into the same size as the PEM from the electrode area of the MEA. The dimensions of the samples before DMA were measured at 23 °C and 50% RH. The samples were soaked at 23 °C and 50% RH for 24 h. The conditions of DMA in this study are shown in Table 2.

2.4. Humidity cycle tests

The deformation by swelling test and the storage elastic modulus in DMA analysis may influence the mechanical durability of the membrane in a humidity cycle test. In order to investigate the effect of the catalyst layer thickness on the mechanical durability of a membrane in the humidity cycle tests under fuel cell operation, the humidity cycle tests proposed by FCCJ were carried out in the form of membrane electrode assemblies (MEAs). Testing was done on a JARI standard single cell, the specifications of which are shown in Table 3.

Table 2
Measurement conditions of dynamic mechanical analyzer.

Sample size	50 × 5 mm
Testing equipment	DMS6100 Dynamic Mechanical Analyzer (Hitachi High-Tech Science Corporation)
Temperature span	−70 °C–200 °C
Rate of temperature increase	2 °C min^{-1}
Frequency	10 Hz
Initial tensile force	50 mN
Measurement mode	Tensile
Distance between chucks	25 mm
Nitrogen flow rate	300 mL min^{-1}
Target distortion	25 μm
Atmospheric gas	Nitrogen flow 300 mL min^{-1}