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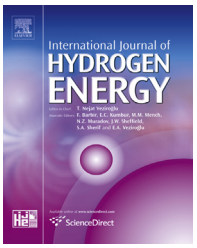

Investigation of porous structure formation of catalyst layers for proton exchange membrane fuel cells and their effect on cell performance

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ABSTRACT

The porous structure formation of a catalyst layer used for proton exchange membrane fuel cells was investigated with respect to the control of mass transport in the electrode. The fabrication process involves blending the materials and solvents to form a catalyst slurry, applying the slurry on a substrate, drying to evaporate the solvents, and decal transferring onto the polymer electrolyte membrane by hot pressing. In this study, hot-pressing and drying processes were investigated to control the porous structure. The hot-pressing pressure was varied from 0.5 to 10 MPa. The porous structure was evaluated by cross-sectional visualization and a nitrogen physisorption measurement, and it was found that the pressure affects both pore size and porosity. A drastic voltage drop appeared in the polarization curve when the hot-pressing pressure was over 2 MPa. The temperature and humidity during drying were controlled to change the drying rate. The drying behavior was monitored by in-situ visualization and weight measurements. The drying rate slightly affected porosity, although it did not significantly affect the pore size, which was reflected in the polarization curves. These results indicate that the pore size is a more significant factor than the porosity with respect to overpotential in the polarization curve.

Introduction

In proton exchange membrane fuel cells (PEMFCs), catalyst layers (CLs) are one of the most important components for achieving both high performance and cost reduction. However, controlling the porous structure during the fabrication of CLs is a key challenge. The mass transport properties of CLs depend strongly on the structure involved [1–3]. Typical CLs consist of platinum-supported carbon (Pt/C), an ionomer, and pores. They have nano- and microscale porous structures and their components are responsible for the transport of

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electrons, protons, reactant gases, and the water generated. CLs are electrodes and are thus indispensable components in PEMFCs. Especially under operating conditions, a correlation between reactant transport and water generation should be considered. Water should be discharged from the CLs to avoid condensation and prevention of oxygen transport.

Structural characterization has been conducted for a fundamental understanding of the transport phenomena in CLs. Several well-known techniques exist for determining the nano- and microscale porous structures. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) facilitate the visualization of two-dimensional porous structures. Mercury intrusion porosimetry and nitrogen physisorption measurements can be used to determine the pore-size distributions [4]. In addition, new ways of determining the porous structure of CLs are being developed and applied. For example, a combined apparatus comprising a focused ion beam and SEM called FIB-SEM has been developed and applied to the CLs of PEMFCs [5]. Nanometer-scale X-ray computed tomography called nano-CT can visualize the three-dimensional structure of CLs [6], although the resolution is still under development.

The effects of the structure and components of CLs on cell performance have been investigated [7–10]. However, the porous structure strongly correlated with the blending ratio of components such as carbon particles and ionomers. Additionally, solvents in the catalyst ink affect the resultant porous structure. The type of the solvents affects the state of the ink such as solution and colloidal states [3,11]. Solvent ratio such as water to alcohol weight ratio affect the ionomer and agglomeration in the ink [12]. Therefore, independent control of the material distributions and porous structure is necessary to clarify their effect on the performance and develop well-ordered CLs.

Although there are a number of studies on the structure and performance of CLs, a method of generating a porous structure has not yet been established and the relation between the microscopic porous structure and the macroscopic cell performance remains unclear. Several methods of fabricating CLs are in common use [13–15]. The fundamental process involves blending the materials to produce a slurry called catalyst ink, which is then applied to form a thin layer, followed by drying to evaporate the solvents, leaving a porous structure. The fabrication techniques are mainly categorized by the coating methods, such as doctor blading, spray coating, and ink-jet printing [16]. The coating is conducted in two ways: direct coating on a PEM or a combination of coating on a substrate and decal transferring to the PEM. The decal transfer method is often used to prevent solvents from swelling into the PEM. Hot pressing is conducted to transfer the CLs from the substrate to the PEM. Although there are a number of coating techniques, drying and hot pressing are common key techniques for CL fabrication. CLs have been fabricated using a trial and error approach, because they have both nano- and microscale complex structures and many parameters are involved in the fabrication process. An understanding of the mechanism and key parameters of the structure formation is necessary for the development of high-performance CLs.

We focused on the fabrication process and investigated the effects of the fabrication conditions on the porous structure of CLs [10,17,18]. In this study, we focused particularly on the use of drying and hot pressing to modulate the porous structure. Hot pressing is conducted at more than 120 °C, which is the glass transition temperature of the Nafion ionomer, to attach CLs to a PEM. Particles are then displaced, allowing plastic deformation to occur. The hot-pressing pressure can therefore affect the porous structure by compressing the pores. Yim et al. reported that secondary pores in CLs are compressed by hot pressing and affect cell performance [19]. Drying is the other key process that controls the porous structure because it affects the rate of solvent evaporation and volume reduction, thus affecting the formation of the porous structure. Physical processes involved in the drying of slurries, such as migration [20–22], shrinkage [23], and cracking [24], have been investigated in a wide range of engineering studies.

The objective of this study is to clarify the porous structure formation during drying and hot pressing of CLs for PEMFCs and to establish a relationship between the porous structure and the cell performance. To clarify the effects of these fabrication conditions on the resultant porous structure, cross-sectional visualization by SEM and nitrogen physisorption measurements of the CLs were conducted to evaluate the porosity and pore size distribution. For a fundamental understanding of the drying process, in-situ visualization by atmospheric SEM and weight measurements to determine the drying rate were conducted. Performance evaluation was conducted to clarify the effect of the fabricated porous structure on the cell performance.

Experimental

Fabrication and performance evaluation of the CCMs

The CLs were fabricated according to the following procedure. The catalyst ink was composed of 20 wt.% Nafion solution (DE2020, Wako Pure Chemical Industries), Pt/C (TEC10E50E, Tanaka Kikinzoku Kogyo), water, and n-propanol in the following blending ratios. The ionomer to carbon (I/C) ratio was 1.0, the non-volatile to solvent ratio was 0.1, and the propanol to water ratio was 0.8. The catalyst ink was applied to a polytetrafluoroethylene (PTFE) film by doctor blading and then dried to form the CLs. Two CLs and a Nafion membrane (NRE-212, 50 μm thickness, DuPont) were assembled as a catalyst-coated membrane (CCM) by hot pressing. The hot-pressing pressure was controlled by a load cell and confirmed using a pressure-detecting sheet (Prescale, Fujifilm). The precise fabrication conditions were modulated according to the objective of the experiments. The fabricated CLs all contained the same amount of platinum (0.3 mg/cm^2) in order to compare their polarization curves.

The PEMFC used for performance evaluation had an active area of 5 cm^2 and a single serpentine channel, with a channel and rib width of 1 mm and depth of 1 mm. Gas diffusion layers with a microporous layer were used on both sides of the CCMs. The cell operated at 80 °C with H_2 at 200 mL min^{-1} and air or O_2 at 500 mL min^{-1} under ambient pressure. The relative humidity (RH) of both the anode and the cathode was set at 40% or 90%. High-frequency resistance (HFR, 10 kHz) was measured by an AC mΩ tester (365E, Tsuruga Electric Corporation). Cyclic voltammetry (CV) was carried out at 30 °C and

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