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On the role of the silica-containing catalyst layer for proton exchange membrane fuel cells

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The performance of a PEMFC (proton exchange membrane fuel cell) severely decreases as the relative humidity decreases. Herein, we present size-controlled SiO_2 (silica) nanoparticles in the CLs (catalyst layers) to provide sufficient water to the Nafion ionomer. It is found that the microstructure of the agglomerated CL is notably improved using the SiO_2 particles with smaller diameter. In addition, as the SiO_2 particle diameter decreases, both the electrochemical surface area and ohmic performance are improved, as well as the wettability, for the PEMFC application. The highest performance is achieved for the CL with the 8 nm SiO_2 particle, which results in 2.93 times increased current density at 0.5 V relative to the 80 nm SiO_2-containing CL, when SiO_2-to-carbon ratio was fixed to 0.20. Consequently, it is more effective to improve the electrode morphology of the SiO_2 CL than simply increase the SiO_2 content, in order to enhance the fuel-cell performance under low relative humidity.

1. Introduction

A PEMFC (proton exchange membrane fuel cell) is highly efficient and green energy-conversion device, regarded as one of the promising next-generation power suppliers in the 21st century. In order to use atmospheric air as an oxidizer in the fuel-cell system, a stable performance must be achieved in a wide range of RH (relative humidity) [1]. However, typical perfluorosulfonic acid membranes require external humidification, because their proton transport mechanism is strongly dependent on the membrane WU (water uptake) [2]. For successful commercialization, the US DOE (Department of Energy) focuses on producing a MEA (membrane electrode assembly) that can yield at least 0.6 V at 1.5–2.0 A cm^{-2} with a total platinum (Pt) loading of 0.125 mg cm^{-2} under 0–100% RH conditions [3]. To present, water management is still regarded as an important issue in operation of the PEMFC [4,5].

Since Watanabe et al. [6,7] have invented a new concept of the self-humidifying PEM (proton exchange membrane) that contained Pt and metal-oxide particles, which initiated the chemical oxidation of H_2 (hydrogen) and O_2 (oxygen) and retention of moisture, respectively, a number of researchers [8–10] have investigated the self-humidifying membranes to obtain superior low-humid performance by improving the membrane WU. However, increasing the WU in the anode CL (catalyst layer) may be more required than in the membrane and cathode CL, because the anode dehydration can be severed by the electro-osmotic drag [11]. Therefore, several designs of the self-humidifying CLs [12–15], mostly with hygroscopic additives, have been constructed. Han et al. [12] fabricated a thin SiO_2 (silica)–Nafion functional layer between the PEM and CL, by airbrushing deposition, to increase the WU in the CL under dehumidified condition. However, the fuel-cell performance of the MEA under sufficiently humidified condition should be decreased relative to the conventional one because of the increased proton-transfer resistance. Recently, Inoue et al. [13,14] have provided a facile procedure on SiO_2-containing CL, which conducts both hydrolysis/condensation of SiO_2 sol and catalyst ink preparation in a single vial. These authors reported that the ESA (electrochemical surface area) is increased as the SiO_2 content increases, although others [15,16] argued that the ESA mostly decreased as the SiO_2 blocks the electrocatalytic sites of the Pt. Besides Han et al. [12] and Inoue et al. [14] have argued that SiO_2-containing CL has reduced performance fluctuation in not only low RH but also high RH condition. Despite these efforts, the electrode morphology of the SiO_2 CL has not been clarified yet. In addition, the influences of hygroscopic material in the CL on the chemical and electrochemical performance were either not clarified or controversial.

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To best of our knowledge, the Pt/C–Nafion suspension forms an agglomerated structure covered with thin Nafion film with a thickness below 50 nm (Fig. 1) [17]. In order to improve the CL WU, it is important to make a close contact between the SiO_2 particle and Nafion ionomer in the central part of the agglomerate, which is mainly formed by the micropores. Therefore, the electrode morphology may vary with different SiO_2 particle diameters, hence dominating the chemical and electrochemical performance of the SiO_2 CL. Under dehumidified condition, an intimate contact between SiO_2 and Nafion ionomer can be of great importance to improve the ohmic polarization. Herein, the SiO_2 particles with three different diameters of 8 nm, 30 nm and 80 nm were employed as a hygroscopic additive in the CLs with different SiCRs (SiO_2-to-carbon ratios) of 0.01, 0.04 and 0.20. By using sufficiently small-sized SiO_2 particles, an improved fuel-cell performance under low RH was obtained with increased ESA. In addition, the wettability of the CL was successfully controlled by varying the specific surface area of SiO_2, which may affect the concentration polarization of the PEMFCs.

2. Experimental

2.1. Materials

The 20 wt% Pt/C (Pt on carbon black) and 40 wt% TBAOH (tetrabutylammonium hydroxide) were purchased from Alfa Aesar. The 99.5 wt% TEOS (tetraethyl orthosilicate), ammonia, methanol, propane-1,2,3-triol and 1,5-pentanediol were purchased from Sigma Aldrich. The Nafion 212 membrane was purchased from Ion Power and solely used as a PEM. The 5 cm^2, three-serpentine cell fixture was purchased from CNL Co. to measure the fuel-cell performance.

2.2. Preparation of the spherical SiO_2 particle

Preparation of the SiO_2 particles was performed by the hydrolysis/condensation method [18], which is originally proposed by Stöber et al. [19]. The 1.2 g of TEOS was added into a 3.0 M ammonia solution in a 1-propanol/methanol mixture. Solution was physically stirred in room temperature to form spherical colloidal SiO_2 by the sol–gel reaction. Then, the mixture was centrifuged and washed three times and dried in the vacuum oven at 50 °C over 24 h to separate the SiO_2 particles. Then, the 10 wt% aqueous mixture of SiO_2 dispersion with different particle diameter of 8 nm, 30 nm and 80 nm was obtained as a hygroscopic agent. Molar concentration of the TEOS and ammonia was controlled to obtain different diameters of the SiO_2 particles (Table 1).

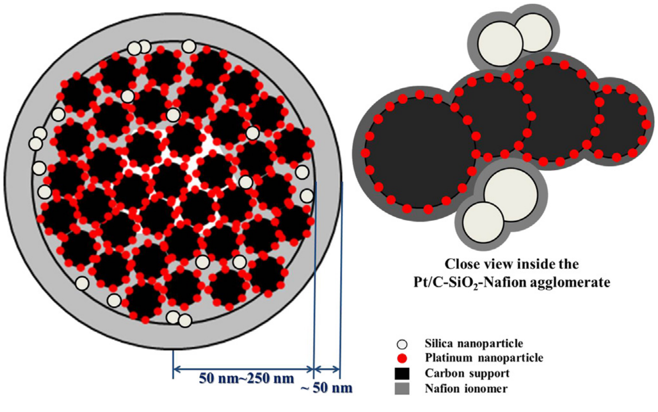

Fig. 1. Conceptual illustration of the Pt/C–SiO_2–Nafion agglomerate.

Table 1
Synthetic variables used in the modified Stöber method to prepare nano-sized SiO_2 colloids with three different particle diameters.

Sample	Molar concentration of TEOS (M)	Molar concentration of ammonia (M)
80 nm SiO_2	0.35	2.0
30 nm SiO_2	0.20	1.0
8 nm SiO_2	0.10	0.5

As reported in the previous literature [17], diameter of the Pt/C–Nafion agglomerate varies in between 100 and 500 nm (Fig. 1) while the thickness of Nafion ionomer covering layer is only a few 10 nm. In order to reveal true behavior of the size effect, the SiO_2 particle of three different diameters that represent for smaller (8 nm), similar (30 nm) and larger (80 nm) than the Nafion covering layer thickness is needed for the CL preparation.

2.3. Fabrication of SiO_2-containing membrane electrode assembly

In a 50 mL vial equipped with a magnetic stirrer, the 2.24 g of 5 wt% Nafion dispersion was added into 3.1 g of a propane-1,2,3-triol, followed by an addition of the prepared 10 wt% colloidal SiO_2 solution to adjust the SiO_2-to-carbon mass ratio to be 0.01, 0.04 and 0.20. After that, the 0.2 g of 20 wt% carbon-supported Pt catalyst was added into the mixture and homogenized at 50 °C. Then, the 0.1 g of 40 wt% TBAOH was applied, followed by 24-h stirring.

The 0.3 T PTFE (polytetrafluoroethylene) film was thoroughly cleansed and repeatedly painted with the SiO_2-containing catalyst ink and annealed in the convection oven at 130 °C until the Pt loading reached 0.2 mg cm^{-2}. After the CL is formed, a sufficient amount of 1,5-pentanediol was applied onto the CL surface in order to obtain a high transfer rate of over 99%. Prior to the decal transfer, the Nafion membrane was converted into the sodium form by lightly boiling in 1 wt% sodium hydroxide aqueous solution, followed by boiling in deionized water. After that, the CL-coated decal was assembled by sandwiching the sodium-form Nafion membrane and hotpressing at 140 °C [20,21] for 10 min. After the PTFE film was peeled off, the MEA was boiled in deionized water at 100 °C, in order to remove any residual 1,5-pentanediol, and 0.5 M sulfuric acid solution at 70 °C, followed by cleansing in a lightly boiling water. After the cleansing, the MEA was wiped and dried in atmospheric condition less than 30 min in order to promote the pre-activation process of the cell performance [22].

2.4. Chemical characterization

Size of the prepared SiO_2 nanoparticle was examined by TEM (transmission electron microscopy) (JEM-2000EXII) at an accelerated voltage of 200 kV. Microstructures of the SiO_2 particles and SiO_2-containing CL were characterized by SEM (scanning electron microscopy) (Jeol JSM-6330F) equipped with an energy dispersive spectrometer. SEM images of the electrode morphology were verified with 100,000× magnification. The thickness and contact between membrane and electrode were verified by cross-section analysis.

Contact angle of the SiO_2-containing CL was measured by the static sessile drop method (KRUSS DSA100 Drop Shape Analysis System). The contact angle image was taken by a digital camera (Phillips SPC900NC) at 5 s after the water drop was put on the CL surface. In order to obtain a completely flat surface, the CL was coated on the PTFE sheet, which is tightly attached to the slide glass using an acid-resistant adhesive. For accuracy, an averaged value