

## The Electrochemical Properties of the Porous Nafion Membrane for Proton Exchange Membrane Fuel Cells (PEMFCs)

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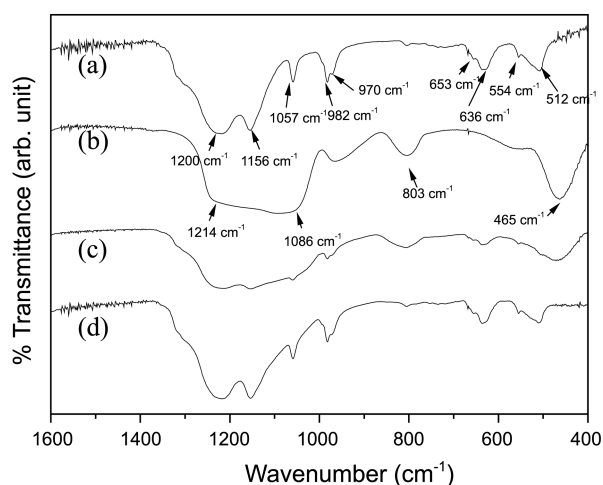
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Proton exchange membrane fuel cells (PEMFCs) have been paid a great attention as a clean power generator to convert the chemical energy of hydrogen to electric energy and they have major advantages, such as the high power density and energy efficiency, rapid start-up, *etc.*, for the portable electronic devices and transportation/stationary power systems.<sup>1,2</sup> In order to achieve the high fuel cell performance, a polymer electrolyte membrane in the PEMFCs must satisfy some requirements, for examples, high proton conductivity, zero electronic conductivity, adequate mechanical strength, chemical, and electrochemical stability. Among these properties, the proton conductivity is the most important factor because it directly affects the cell performance. Hence, the relationships between the proton conductivity and other factors have been extensively studied, and it has been reported that the proton conductivity of the membrane is closely related to its microscopic structure.<sup>3-7</sup> Early studies proposed a cluster-network structure of ionic clusters (~50 Å) interconnected with narrow ionic channels (~10 Å) in the presence of water.<sup>4,6-8</sup> Moreover, recent studies have reported that the vapor pressure of water in the small size of pores is significantly reduced and therefore the retention of water in the membrane is improved at the elevated temperature.<sup>9,10</sup> In this study, the proton conductivity and the fuel cell performance are investigated as a function of pore size in the porous Nafion membrane.

In order to investigate the chemical structure of the prepared membranes and verify the complete elimination of SiO<sub>2</sub> in the Nafion/silica nano-particle composite membranes, Fourier transform-Infrared (FT-IR) spectroscopy was performed, and the results are shown in Figure 1. The IR spectrum of the pristine Nafion membrane (Figure 1(a)) shows the characteristic vibrations of Nafion at 1220 cm<sup>-1</sup> (asymmetric C-F stretching), 1156 cm<sup>-1</sup> (symmetric C-F stretching), 1057 cm<sup>-1</sup> (S-O stretching), 982 cm<sup>-1</sup> (C-F stretching of (-CF<sub>2</sub>-CF(R)-CF<sub>2</sub>-) groups), 970 cm<sup>-1</sup> (C-O-C stretching), 653 cm<sup>-1</sup> (asymmetric O-S-O bending), 636 cm<sup>-1</sup> (C-S stretching), 554 cm<sup>-1</sup> (asymmetric C-F bending), and 512 cm<sup>-1</sup> (symmetric O-S-O bending) corresponding to the previous report.<sup>13</sup> Figure 1(b) shows the characteristic vibrational features of SiO<sub>2</sub> nano-particles at 1214 cm<sup>-1</sup> and 1086 cm<sup>-1</sup>

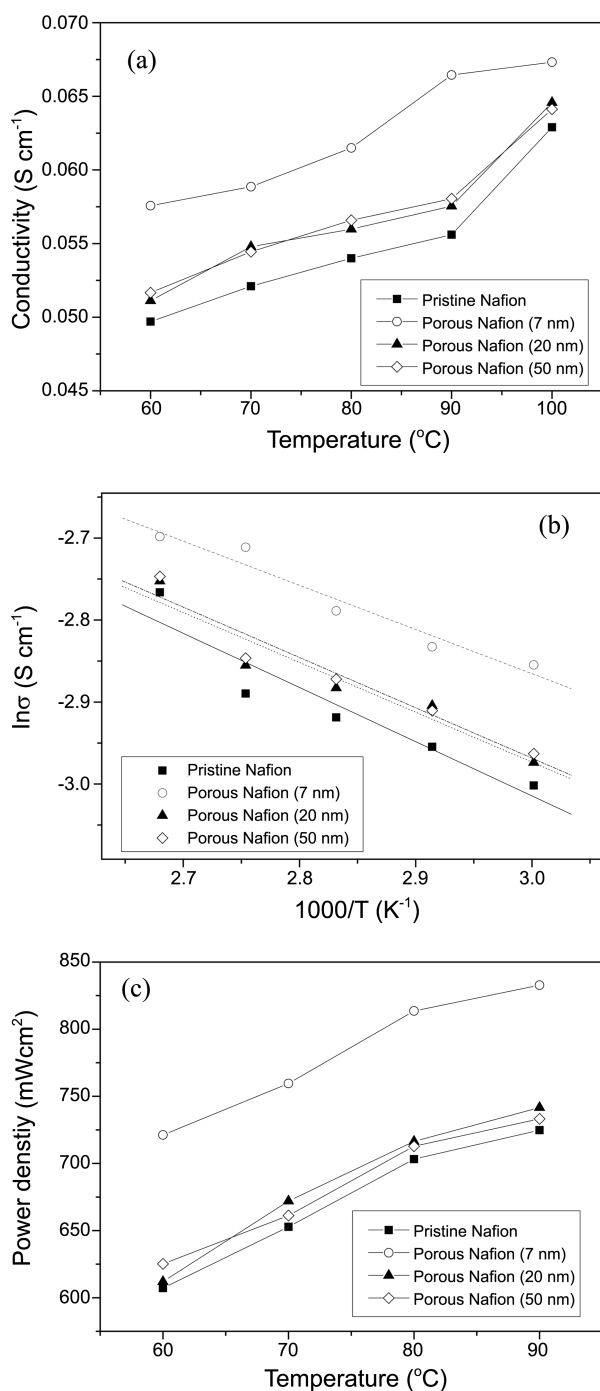
(Si-O-Si asymmetric stretching), 960 cm<sup>-1</sup> (Si-OH stretching), 803 cm<sup>-1</sup> (Si-O-Si symmetric stretching), and 465 cm<sup>-1</sup> (Si-O-Si symmetric bending).<sup>14</sup> The IR spectrum of Nafion/SiO<sub>2</sub> nano-particle composite membrane is the combination of vibrational features of the Nafion and SiO<sub>2</sub> nano-particle (Figure 1(c)). After the etching of silica in the membrane with HF solution, however, the vibrational features of SiO<sub>2</sub> completely disappear as shown in Figure 1(d). These series of IR spectra demonstrate that the SiO<sub>2</sub> nano-particles in the membrane were completely removed.

The water uptakes of the prepared membranes increase in comparison with the pristine Nafion membrane, and the increase in the water uptake is attributed to water filled in the pores of the porous membranes. The water uptakes of the porous membranes prepared with 7, 20, and 50 nm silica nano-particles are 34.0, 33.2, and 34.2%, respectively, and that of pristine Nafion membrane is 30.9%. The water uptake values for the porous membrane are not significantly different because the amount of added silica is constant. Ideally, more retained water improves the proton conduction and the cell performance under the constant temperature and



**Figure 1.** FT-IR spectra of the Nafion membrane (a), nano SiO<sub>2</sub> (b), Nafion/nano SiO<sub>2</sub> composite membrane (c), and the Nafion/nano SiO<sub>2</sub> composite membrane treated by HF aqueous solution (d).

humidity conditions. However, the proton conductivities of porous membranes were significantly different. Figure 2(a) shows the proton conductivities of the membranes measured by in-situ electrochemical impedance spectroscopy (EIS) as a function of cell temperature. The proton conductivities of all the membranes are increased as a function of the cell temperatures,<sup>15,16</sup> and the porous membrane prepared with 7 nm silica nano-particles has the most enhanced proton conductivities as shown in Figure 2(a). It can be explained



**Figure 2.** Proton conductivities (a) and Arrhenius plot (b) of the pristine Nafion membrane and porous Nafion membrane modified 7 nm, 20 nm, and 50 nm SiO<sub>2</sub> at 60–100 °C. (c) Power densities at 0.6 V of the pristine and porous Nafion membranes.

by the reduction of water vapor pressure in the small pore. As already mentioned, it is suggested that small pore ( $d < 5\text{--}10$  nm) significantly reduces the vapor pressure of water, and as a result, the proton conductivity and cell performance are enhanced.<sup>9,10</sup> As the cell temperature increases, the amount of water is maintained to be nearly constant in the membrane and the proton transfer rate is faster. Therefore, the proton conductivity of the porous membrane with small pore increases as an increase in the cell temperature. However, the conductivity of the porous membrane with the larger pore (20 and 50 nm) is not significantly enhanced because the water vapor pressure is similar to the water in the pristine membrane. In addition, the activation energies of the proton conduction for the prepared membrane were investigated by the Arrhenius equation as shown in Figure 2(b). The porous membranes with nano-sized cavities have lower activation energies (4.48–5.10 kJ/mol) than the pristine Nafion membrane (5.50 kJ/mol). It indicates that the porous membranes can transfer the protons more effectively. Moreover, the activation energies is reduced as the size of pore decreases, and the porous membrane with the cavity prepared with 7 nm silica nano-particles shows the lowest activation energy (4.48 kJ/mol) of proton-transport. In the PFSA membrane such as Nafion, the proton-transport can be explained by Grothuss and vehicle mechanism, and recent molecular dynamic simulations have reported that the bulk phase water plays an important role in proton-transport.<sup>17</sup> The proton conductivity is closely related to the activity of water. Even though the proton transfer by the Grotthuss mechanism is dominant at low activity of water vapor, the contribution of vehicle mechanism significantly increases as the activity of water increases.<sup>17</sup> Furthermore, the single cell tests for the prepared membranes were performed, and the power densities at 0.6 V of the membranes are summarized in Figure 2(c). Even though the power densities of the porous Nafion membranes, except for the membrane with 7 nm pores, are the same as that of pristine Nafion membrane, the porous membrane prepared with 7 nm SiO<sub>2</sub> nano-particles shows the highest cell performance. Therefore, the pores with nanometer-sized pore in the membrane enhanced the retention of water by the reduction of water vapor pressure, and as a result, the proton conductivity of the membrane and the fuel cell performance increases.

## Experimental Section

The porous Nafion membranes were prepared by the etching of SiO<sub>2</sub> in the Nafion/SiO<sub>2</sub> (particle size = 7, 20, and 50 nm) composite membranes. The porous Nafion membranes were prepared by an ordinary solution casting method,<sup>12</sup> and the control experiments were performed by the pristine Nafion membrane prepared by ordinary casting method without the addition of silica. For the preparation of membrane, Nafion 117 solution (Aldrich) was used and the etching solution was 25 % HF aqueous solution (J.T. Baker). The water uptakes of the Nafion and the modified Nafion membranes were determined by the measuring the difference of

masses before and after immersing them in distilled water. The proton conductivity and unit cell performance were investigated at various temperatures with the temperature of humidifier at 60 °C.

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