

Phosphoric Acid-Functionalized Mesoporous Silica/Nafion Composite Membrane for High Temperature PEMFCs

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The proton exchange membrane fuel cell (PEMFC) has received a great attention as a clean power generator to convert the chemical energy of hydrogen to electric energy electrochemically. It has major advantages for the portable electronic devices and transportation/stationary power systems^{1,2} such as the high power density and high energy efficiency, rapid start-up, *etc.* One of the most widely used proton exchange membrane is perfluorosulfonic acid (Nafion, DuPont Co.). It has excellent thermal and chemical stability and high proton conductivity below 80 °C. However, PEMFC with Nafion membrane shows the poor performance at higher temperature due to the dehydration and low proton conductivity of the membrane. Recently, many studies have been performed to develop proton conducting membrane for operation above 100 °C³⁻⁶ because the high temperature operation of PEMFC has the advantages of low CO poisoning of Pt catalyst and simple thermal and water management.⁷ Even if the Nafion composite membranes with incorporation of water retentive and inherent proton conductive fillers have been studied extensively under elevated temperature and low humidity conditions,^{4,8} the proton conductivity of the composite membrane is occasionally lower than the pristine Nafion because the well-connected ionic domain of the Nafion is deformed by the inorganic fillers.³⁻⁶

In this paper, we report the physico-chemical and electro-chemical properties of the phosphoric acid-functionalized mesoporous silica/Nafion composite membrane. The mesopore of silica increases the water retention capacity more effectively, and the phosphor-silicate has thermally and chemically stable silica networks and the surface-terminated phosphate interacts strongly with the water molecules. Therefore, the phosphoric acid-functionalized mesoporous silica/Nafion composite membrane shows the higher proton conductivities and cell performance than the pristine Nafion at high temperature and low humidity.

The morphology and particle size of the prepared inorganic materials were investigated by TEM, and the data are shown in Figure 1. The shape of mesoporous SiO₂ is spherical with a diameter of ~45 nm and their pore size is ~5 nm as shown in Figure 1(a). The specific surface area and the mean

pore size of the mesoporous SiO₂ are 560 m²·g⁻¹ and 4.82 nm, respectively. However, the morphology of the phosphoric acid-functionalized mesoporous SiO₂ was quite different from that of pristine one. As shown in Figure 1(b)-(d), the porous structure is destructed and particle size increases as the annealing temperature increases after the mixing of mesoporous SiO₂ with phosphoric acid. Figure 1(b) shows the sample heated at 80 °C in the vacuum, and the result shows that the porosity of the sample is slightly reduced. With an annealing at 200 °C, the morphology change is significant in that the mesopore disappears and large pore is formed. Interestingly, the further annealing above 200 °C, the pore completely disappears and their particle size also increases, because of the formation of phosphor silicate through the reaction of silica and phosphoric acid, and the bulk-like phosphor silicate phase is confirmed by XRD (not shown for brevity).

In order to elucidate the chemical structure of the prepared

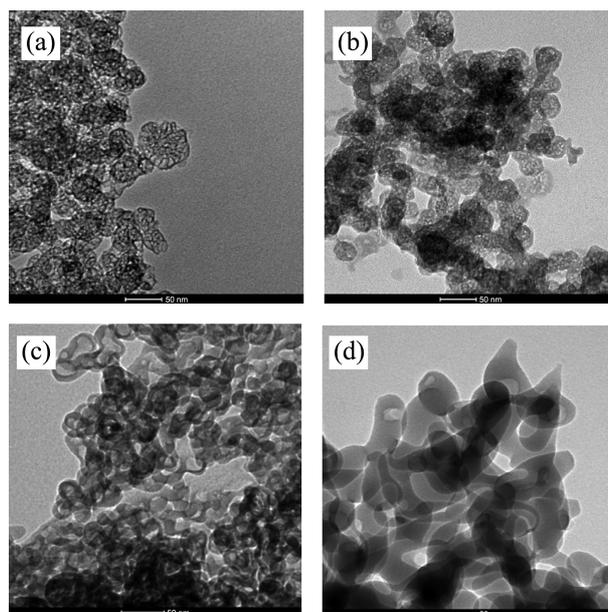


Figure 1. TEM images of mesoporous SiO₂ (a) and phosphoric acid-functionalized mesoporous SiO₂ annealed at 80 °C (b), 200 °C (c), and 600 °C (d).

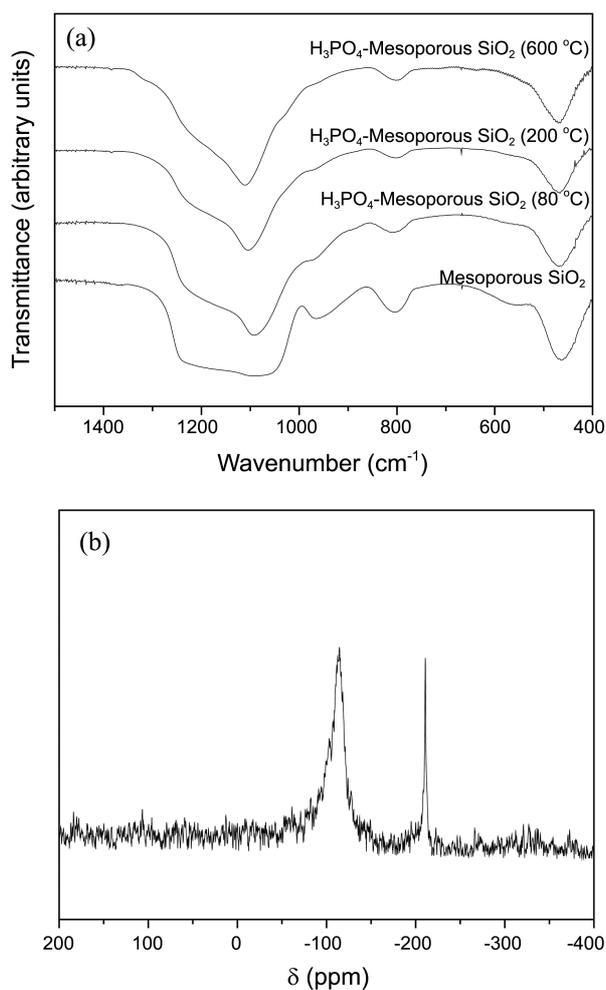


Figure 2. (a) FT-IR spectra of the mesoporous silica and phosphoric acid-functionalized mesoporous silica heated at various temperature and (b) Si MAS-NMR spectrum of the phosphoric acid-functionalized mesoporous SiO₂.

samples, FT-IR and MAS-NMR spectroscopy were performed. Figure 2(a) shows the FT-IR spectra of pristine and modified mesoporous silica annealed at 80, 200, and 600 °C. The IR spectrum of mesoporous silica shows its characteristic vibrational features at 465 (Si-O-Si symmetric bending), 803 (Si-O-Si symmetric stretching), 960 (Si-OH stretching), 1086 and 1214 cm⁻¹ (Si-O-Si asymmetric stretching).⁹⁻¹⁰ After phosphoric acid treatment, the band at 1086 cm⁻¹ for the pristine mesoporous silica is blue-shifted with an increase in the annealing temperature, and this shift is also observed in the phosphosilicate glass due to the characteristic vibrational features of the P-O-P, Si-O-P and Si-O-P.¹⁰ In addition, the shoulder peaks at 1320 and 1020 cm⁻¹ can be assigned to Si-O-P=O and Si-O-P stretching vibration, respectively.¹¹ The ²⁹Si MAS-NMR spectrum of phosphoric acid-functionalized mesoporous SiO₂ annealed at 80 °C is shown in Figure 2(b). For the pristine mesoporous SiO₂, NMR spectrum has a single broad resonance feature centered at ~ -100 ppm assigned to the tetra-coordinated silicon in amorphous silica (Si(OSi)₄).¹² However, after the reaction of mesoporous silica with phosphoric acid, an additional

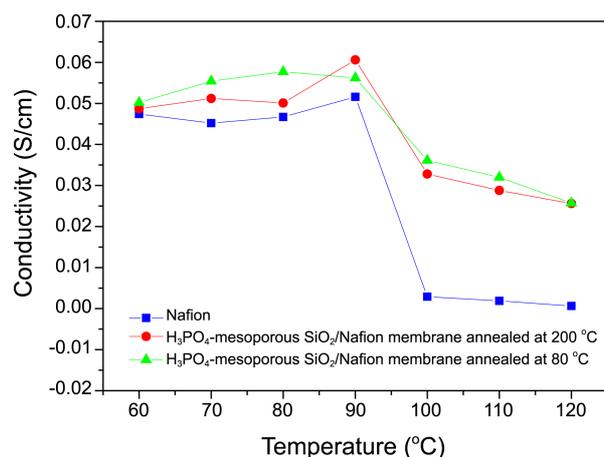


Figure 3. The proton conductivities of the pristine Nafion and the phosphoric acid-functionalized mesoporous SiO₂/Nafion composite membranes at various temperatures. The temperature of humidifier is fixed to 60 °C.

resonance feature appears at ~ -210 ppm, as shown in Figure 2(b), assigned to the formation of Si₃(PO₄)₄ and/or Si(HPO₄)₂.¹³ Moreover, the resonance feature at ~ -100 ppm nearly unchanged after the reaction. It indicates that there is not significant bulk-type reaction between mesoporous silica and phosphoric acid but the surface modification of mesoporous silica by phosphoric acid.

The water uptakes of the pristine Nafion and modified SiO₂ annealed at 80 and 200 °C/Nafion composite membranes were 20.4, 24.8, and 23.5%, respectively. The higher water uptakes of the composite membranes are due to the strong hydrophilicity of the modified SiO₂ and the presence of the excess amount of absorbed water within the pores. As shown in Figure 3, the proton conductivity of the composite membrane is much higher than that of the pristine Nafion membrane, and it is good agreement with water uptake results. In spite of the reduction of the relative humidity with an increase in the cell temperature, the proton conductivity increases due to the higher mobility of the proton and the enhanced catalytic activity of the catalyst at 60-90 °C. In this temperature range, the proton conductivity of the membrane is determined by the water in Nafion because the absorbed water as a proton carrier is kept in Nafion and therefore, the pristine Nafion and composite membranes show similar conductivity. However, the further increase in the cell temperature (≥ 100 °C) causes the decrease in the conductivity of Nafion because of the evaporation of water absorbed in the membrane. On the other hand, the conductivity of composite membrane does not significantly reduced because the surface phosphate group can play a role in conducting proton at high temperature (≥ 100 °C). It is noteworthy that the composite membranes have the high proton conductivity at high temperature despite the reduction of water content because it has the enhanced water retention property than the pristine Nafion membrane. Therefore, the phosphoric acid-functionalized SiO₂ can act as the material with much improved proton conduction under high temperature and low humidity conditions.

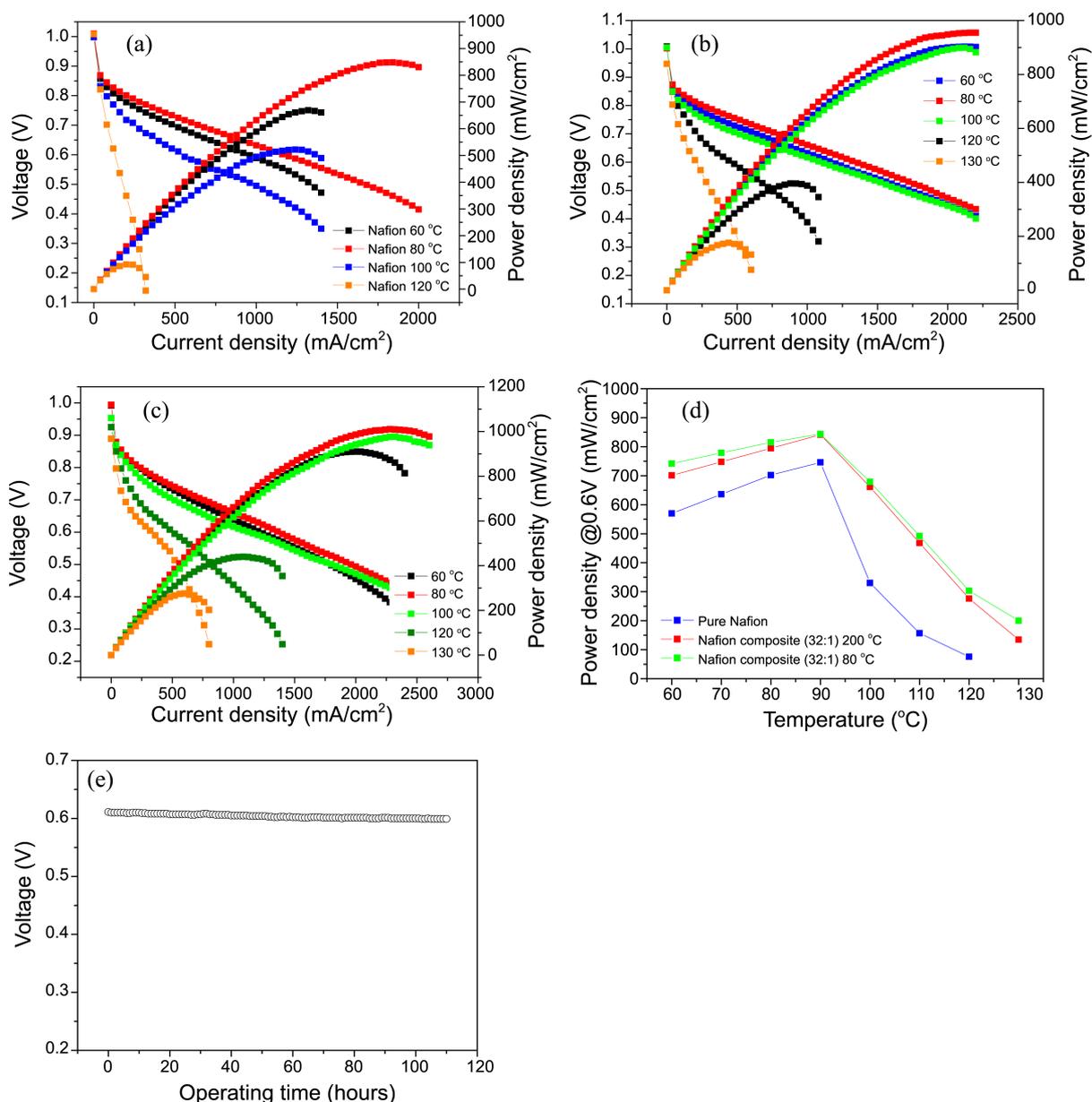


Figure 4. The I-V curves of the pristine Nafion (a), phosphoric acid-functionalized mesoporous SiO₂ annealed at 200 °C (b) and 80 °C (c) Nafion composite membranes. (d) The comparison of the power densities at 0.6 V of the all membranes. (e) The longevity test results of the composite membrane.

The cell performance of the prepared membranes was investigated, and the current density (i) – voltage (V) curves and the longevity test result are shown in Figure 4. The power densities at 0.6 V of the prepared membranes monotonically increase as a function of the cell temperature in the range of 60–90 °C as expected the proton conductivity results. Even though the cell performance decreases with a further increase in the cell temperature, the cell with composite membrane shows much higher power density under elevated temperature condition in comparison with the cell having the pristine Nafion membrane. The phosphoric acid-functionalized mesoporous SiO₂ has the inter-connected pores (~5 nm size) and the water absorbed in the pores can be kept efficiently. In addition, thus excess amount of water

in the membrane causes to the higher proton conductivity. These results are corresponding to the recent reports^{14,15} that the vapor pressure of the water in the smaller pores is lower than the normal vapor pressure of the water. The longevity test was performed on the the phosphoric acid-functionalized mesoporous SiO₂/Nafion composite membrane, and it shows sufficiently high performance as shown in Figure 4(e).

The novel Nafion-based composite membrane with phosphoric acid-functionalized mesoporous SiO₂ was prepared successfully by the direct solvent casting. There is a significant morphology change of phosphoric acid-functionalized mesoporous SiO₂ as a function of annealing temperature. The electrochemical properties such as the conductivity, cell performance, and longevity, were evaluated at various temper-

atures. The inter-connected mesopore of the phosphoric acid-functionalized SiO₂ acts as strong water absorber and proton transfer channels without interrupting the proton transfer pathway. Due to the enhanced water retention and proton conductivity, the composite membranes have the higher power density and conductivity than the pristine one at high temperature and low humidity. Hence, the phosphoric acid-functionalized mesoporous SiO₂/Nafion composite membrane shows the enhanced electrochemical properties. Therefore, this Nafion-based composite membrane may be useful for the application in the high temperature PEMFCs.

Experimental Section

The mesoporous silica was prepared by the procedure described in elsewhere.¹⁶ The obtained mesoporous silica was mixed with the stoichiometric amount of phosphoric acid in an ethanol medium. After evaporation of the solvent, the dried mixture was heated at 80 °C for 24 hours in vacuum or at various temperatures for 6 hours in air atmosphere. The phosphoric acid-functionalized mesoporous silica/Nafion composite membranes were prepared by the direct casting method. The prepared phosphoric acid-functionalized mesoporous silica 0.0156 g was mixed with the 5 wt % Nafion solution 10 g (Aldrich), and the slurry was casted onto a glass dish under ambient condition. The obtained composite membrane was dried at 120 °C for 3 hours. In order to fabricate MEA, the prepared membrane was placed in between the two commercial Pt/C electrodes (E-tek) with 0.5 mg·cm⁻² Pt loading, and subsequently hot-pressed (40 kgf·cm⁻²) at 130 °C for 5 minutes.

The morphology of the inorganic materials was investigated by transmission electron microscopy (TEM, FEI Co, Tecnai G2 20 S-TWIN). The specific surface area and pore size distribution of the mesoporous silica were measured by BET analysis (BEL Japan Inc., BEL SORP-mini). The chemical structure was identified by Fourier transform-infrared spectroscopy (FT-IR, Nicolet 380), and the solid state magic angle spinning-nuclear magnetic resonance spectroscopy (MAS-NMR, Bruker, Avance 500). The water uptakes of the membrane were determined by the difference of mass of membrane before and after immersing into water. The proton conductivity was measured by *in-situ* electrochemical impedance spectroscopy (EIS) method using IM6 impedance analyzer (Zahner elektrik Co.), and the detailed procedure is

described in elsewhere.^{17,18} The unit cell test was performed at 60-130 °C and the temperature of humidifier is fixed to 60 °C throughout this study. Therefore, the relative humidity (RH) is significantly decreased from 100 to 7.4% as an increase in the cell temperature from 60 to 130 °C. The unit cell was operated with H₂ and O₂ as 120 cm³·min⁻¹ flow rate introduced into the anode and cathode, respectively. For a longevity test, the cell voltage with the composite membrane was measured at 120 °C with the fixed current density of 500 mA·cm⁻².

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