

Sulfonic-functionalized heteropolyacid–silica nanoparticles for high temperature operation of a direct methanol fuel cell

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Abstract

Sulfonic-functionalized heteropolyacid–SiO₂ nanoparticles were synthesized by grafting and oxidizing of a thiol-silane compound onto the heteropolyacid–SiO₂ nanoparticle surface. The surface functionalization was confirmed by solid-state NMR spectroscopy. The composite membrane containing the sulfonic-functionalized heteropolyacid–SiO₂ nanoparticles was prepared by blending with Nafion® ionomer. TG–DTA analysis showed that the composite membrane was thermally stable up to 290 °C. The DMFC performance of the composite membrane increased the operating temperature from 80 to 200 °C. The function of the sulfonic-functionalized heteropolyacid–SiO₂ nanoparticles was to provide a proton carrier and act as a water reservoir in the composite membrane at elevated temperature. The power density was 33 mW cm⁻² at 80 °C, 39 mW cm⁻² at 160 °C and 44 mW cm⁻² at 200 °C, respectively.

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1. Introduction

Recently, the operation of polymer electrolyte membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC) at temperatures above 100 °C is receiving worldwide attention in order to decrease the system complexity and increase the efficiency [1]. In high temperature, the catalytic activity and CO tolerance is enhanced. Furthermore, high temperature operation reduces the complexity of the reforming reactor employed for PEMFCs [2]. Unfortunately, however, currently used perfluorosulfonic acid (PFSA) membranes do not sustain prolonged operation at temperatures higher than 90 °C. This is due to dehydration phenomena occurring at high temperatures, with consequent lower conductivity and performance losses [3]. To overcome of this drawback, non-fluorinated and/or inorganic electrolyte membranes have been developed [4–6]. Haile et al. reported high temperature operation of DMFC and PEMFC at 230 °C with the performance of 50 mW cm⁻² by using a CsH₂PO₄ electrolyte. However, the catalyst loading was about 15 mg cm⁻², which is

higher than conventional loading (4 mg cm⁻²) [6]. While these new electrolyte membranes showed good water retention and high conductivity, the performances of the fuel cells have been very low compared to those based on the same amount of the catalyst [5,6]. Therefore, several researchers have made an attempt to prevent the loss of water from conventional PFSA membranes [7–10]. In particular, the incorporation of various inorganic materials has shown to significantly improve the water retention property and proton conductivity of polymer electrolyte membranes.

Heteropolyacids are one of the best proton conductive materials among the inorganic solid electrolytes [11,12]. They have already been used in PEMFCs or DMFCs with a polymer matrix [13]. However, the heteropolyacid electrolyte dissolves in the water of the hydrogen or methanol fuel [13,14]. To overcome the dissolution of heteropolyacid and the consequent short lifetime of the fuel cell, heteropolyacid should be incorporated in a host material such as silica. In our previous work, we successfully synthesized heteropolyacid–SiO₂ nanoparticles, and showed both high proton conductivity and catalytic activity [15,16]. Also, the organic–inorganic composite membranes doped with heteropolyacid showed high proton conductivity and water retention [5,14,15,17]. Antonucci et al. have investigated

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Nafion[®]-silica membranes doped with heteropolyacid for the DMFC and showed a promising result for the operation at 145 °C [8]. And, Hsing and co-workers operated PEMFC at 110 °C by using the same Nafion[®]-silica membranes doped with heteropolyacid [18]. Costamagna et al. also reported the Nafion[®]-zirconium phosphate membrane and the operation of PEMFC at 140 °C [9]. For methanol reforming and hydrogen desorption of hydrogen storage materials, however, the operational temperature of a fuel cell should be around 200 °C [1].

In this study, we report the high temperature (200 °C) operation of DMFC by using PFSA-based composite membrane. Sulfonic-functionalized heteropolyacid–SiO₂ nanoparticles were blended with Nafion ionomer to develop a high temperature composite membrane. For high dispersion of inorganic particles, the nanoparticles (heteropolyacid–SiO₂) were synthesized by a microemulsion method. The surface of the heteropolyacid–SiO₂ was further functionalized with sulfonic acid groups to improve water-retention. The incorporation of sulfonic-functionalized heteropolyacid–SiO₂ nanoparticles into the Nafion membrane was performed to make a composite membrane. This paper is the first report of an attempt to use the sulfonic-functionalized silica containing heteropolyacid as a high-temperature proton conductor and to show the performance of a DMFC at 200 °C with an acceptable loading of catalyst.

2. Experimental

2.1. Sulfonic-functionalized heteropolyacid–SiO₂ nanoparticle

Heteropolyacid–SiO₂ nanoparticles can be synthesized by a microemulsion technique as described in our previous work [15]. Sodium bis(2-ethylhexyl)sulfosuccinate (AOT, Aldrich) and heteropolyacid (12 tungsto(VI) phosphoric acid, Kanto Chemical Co.) was dissolved in cyclohexane and water, respectively. The heteropolyacid solution was added to AOT solution to form a well-defined microemulsion phase. Then, tetraethoxysilane (TEOS, Aldrich) was dropped into the microemulsion phase. The heteropolyacid–SiO₂ nanoparticles were obtained after the mixture was stirred at room temperature for 12 h. Dispersed heteropolyacid–SiO₂ nanoparticles in cyclohexane were centrifuged and the particles were repeatedly rinsed with acetone.

For the improvement of the hydrophilic and proton-conducting properties of heteropolyacid–SiO₂ nanoparticles, sulfonic acid groups were introduced onto the surface of the silica. The sulfonic-functionalized heteropolyacid–SiO₂ nanoparticles could be synthesized by grafting and oxidizing of thiol-silane compound [19]. For the synthesis of thiol-modified heteropolyacid–SiO₂ nanoparticle, 3-mercaptopropyltrimethoxysilane (MPTMS, Aldrich) was dissolved in toluene. Then, the heteropolyacid–SiO₂ nanoparticles were dispersed in this MPTMS solution, followed by reflux for 24 h at 120 °C. After reflux, the nanoparticles were washed with dry toluene several times. The surface modified nanoparticles were dried for several hours at 120 °C to evaporate toluene. The oxidation of the thiol group of nanoparticle to sulfonic acid was carried out

by treating the dried thiol-modified nanoparticles with aqueous H₂O₂ (30 wt.%). The suspension was stirred at room temperature for 12 h. After the oxidation treatment, the resulting solution was centrifuged and washed separately with water and ethanol. The wet nanoparticles were suspended in 1 M H₂SO₄ solution for 4 h. Finally, the sulfonic-functionalized nanoparticles were washed several times with water and ethanol and dried at 80 °C under vacuum. The atomic ratio of S/Si which was calculated by XPS measurement was 0.105.

2.2. Preparation of composite membrane

The sulfonic-functionalized heteropolyacid–SiO₂ nanoparticles were suspended in the Nafion[®] 5 wt.% solution to prepare the composite membrane. For the homogeneous mixing, the suspensions were sonicated at 30 °C for 1 h under an air atmosphere, using a high intensity ultrasonic probe. The composite membranes were cast then onto petri-dishes. The membranes were allowed to dry in air at 120 °C, and completely dried membranes were then peeled off. The concentration of heteropolyacid in the silica nanoparticle was 10 wt.%. The heteropolyacid–SiO₂ nanoparticles were dispersed in the Nafion[®] membrane at 10 wt.%. Therefore, the ratio of heteropolyacid:SiO₂:Nafion was 1:9:90 by weight.

2.3. Characterizations

Solid-state NMR experiments were performed on a JNM-ECP 300 JEOL spectrometer equipped with CP MAS probe. ³¹P and ¹³C NMR spectra were performed at 121.65 and 75.5 MHz at room temperature. The $\pi/2$ pulse width and pulse delay were 50 μ s and 20 s for ³¹P, and 1 μ s and 5 s for ¹³C. For confirmation of the presence of sulfonic acid groups, X-ray photoelectron spectroscopy (XPS) measurements were carried out in a ESCA LAB 2201-XL device with a Al K α source, at an operating voltage of 10 kV, and current of 15 mA. Scanning electron microscopy (SEM, JEOL) images of the membrane were taken to show the surfaces and the cross-sections. A Shimadzu thermal analyzer was used for thermal analysis combining thermogravimetry (TGA) and differential thermoanalysis (DTA) at a heating rate of 10 °C min⁻¹ in air.

2.4. Operation of direct methanol fuel cell

The performances of DMFC were obtained by using a small-scale laboratory DMFC with an external electrode area of 0.5 cm × 0.5 cm. The electrocatalysts were PtRu/C (Pt:Ru:C=40:20:40) for the anode and Pt/C (Pt:C=60:40) for the cathode. The required amount of each catalyst was 4.0 mg cm⁻² on carbon paper. Membrane-electrode assembly (MEA) was fabricated by a hot pressing method for 6 min at 125 °C, and 2.5 metric ton (2000 psi). The anode fuel was 4 M methanol solution and oxygen was fed at atmospheric pressure. The *I*–*V* curves were obtained under load from 80 to 200 °C. Methanol was initially fed in as a liquid phase with a high pressure syringe pump. The methanol/water mixture and oxygen were pre-heated to the same temperature as the cell. The

methanol/water fuel should be liquid at 80 °C and vapor at 160 and 200 °C. As the flow rate of liquid fuel was controlled by syringe pump, the vapor phase fuel could be supplied to the cell at 160 and 200 °C.

3. Results and discussion

Heteropolyacid–SiO₂ nanoparticles were minutely characterized in our previous work [15,16]. Fig. 1 shows the TEM image of heteropolyacid–SiO₂ nanoparticles. It is quite difficult to synthesize the SiO₂ nanoparticles in acid media due to the aggregation of particles. In this study, however, we successfully synthesized the silica nanoparticles containing the heteropolyacid by the combination of the sol–gel method and the microemulsion technique. Although the intermicellar collisions resulted in an aggregation of acid-catalyzed silica sol [15], the heteropolyacid–SiO₂ nanoparticle was prepared in the range of 30–80 nm as shown in Fig. 1.

The ³¹P MAS NMR spectra of the heteropolyacid and heteropolyacid–SiO₂ nanoparticles were measured to verify the presence of heteropolyacid in the SiO₂ matrix (Fig. 2). It is interesting to note that even though the signal of ³¹P MAS NMR spectra could be easily acquired, it was impossible to establish a ¹H–³¹P cross polarization. It is due to the fact that phosphorous is geometrically at the center of the Keggin anion, i.e. far away from the proton, and that the Keggin anion remained intact [20]. The heteropolyacid–SiO₂ nanoparticles showed the single sharp peak in ³¹P NMR spectra. This indicates that the heteropolyacid in the silica matrix has a uniform crystal structure, similar to pure heteropolyacid [22]. Therefore, the heteropolyacid should be successfully immobilized into the SiO₂ nanoparticles. The elution of heteropolyacid was not observed in aqueous solution for 24 h in silica matrix [15]. This led to the conclusion that the silica matrix seemed to be

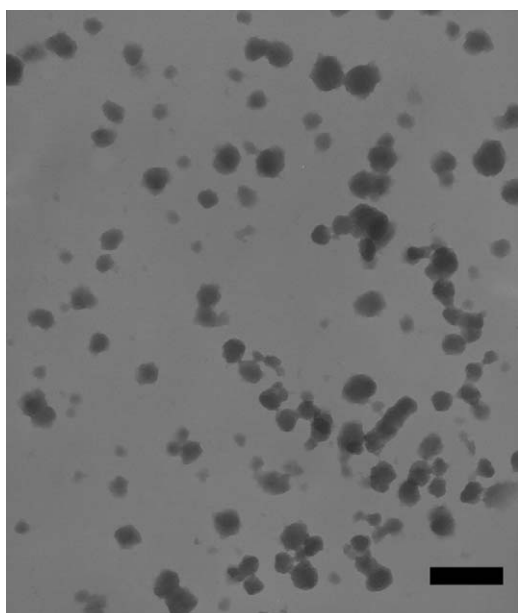


Fig. 1. TEM image of heteropolyacid–SiO₂ nanoparticles (bar: 100 nm).

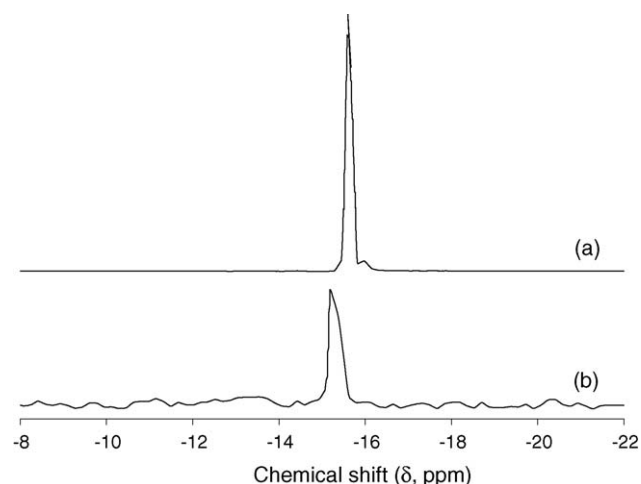


Fig. 2. ³¹P NMR spectra of (a) pure heteropolyacid and (b) heteropolyacid–SiO₂ nanoparticles.

suitable to prevent the leakage of heteropolyacid in aqueous media.

The surface functionalization of heteropolyacid–SiO₂ nanoparticles was confirmed by using solid-state NMR spectroscopy. Fig. 3 shows the ¹³C CP MAS NMR spectra of thiol- and sulfonic-functionalized heteropolyacid–SiO₂ nanoparticle. Comparing two spectra, the thiol-functionalized sample (Fig. 3(a)) presents an intense signal with chemical shifts of 27.9 ppm [19,21]. This peak corresponds to the carbon atom adjacent to the SH moiety, confirming the surface modification of mercaptopropyl groups onto the surface of heteropolyacid–SiO₂ nanoparticle. In the oxidized sample (Fig. 3(b)), which is sulfonic-functionalized, the signal corresponding to the carbon adjacent to the S atom (27.9 ppm) disappeared. However, one can observe the distinct three carbon peaks of propyl group at 54.0, 18.2, and 11.4 ppm without any evidence of the thiol resonance [19,21]. This indicates that the thiol group was successfully oxidized with H₂O₂ to form the sulfonic acid group on the surface of the nanoparticles. The presence of sulfonic acid

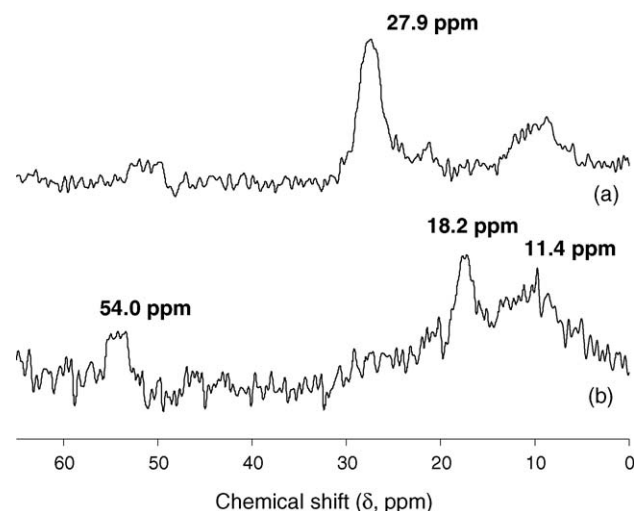


Fig. 3. ¹³C CP MAS NMR spectra of (a) thiol- and (b) sulfonic-functionalized heteropolyacid–SiO₂ nanoparticles.

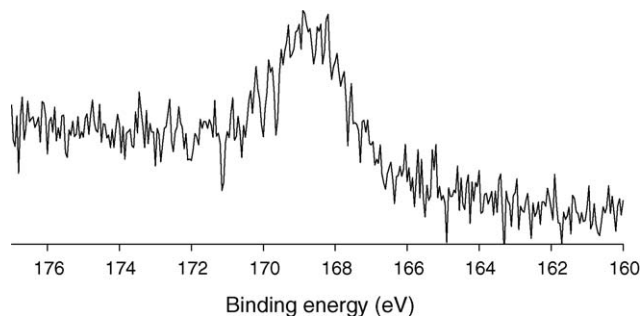
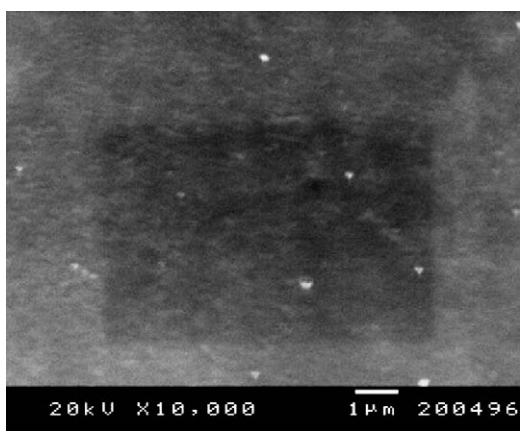


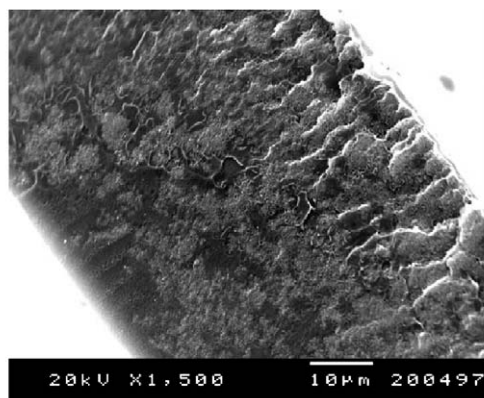
Fig. 4. XPS spectrum of sulfonic-functionalized heteropolyacid-SiO₂ nanoparticles at the S2p band.

group was confirmed by XPS analysis (Fig. 4). The peak around 169 eV is the obvious evidence of the sulfonic acid group on the surface of heteropolyacid-SiO₂ nanoparticle [21].

The sulfonic-functionalized heteropolyacid-SiO₂ nanoparticles were blended with the Nafion[®] solution to prepare the composite membrane. Fig. 5 shows the surface and cross-section of the composite membrane. The thickness of the composite membrane was about 55 μm. Sulfonic-functionalized heteropolyacid-SiO₂ nanoparticles were well-dispersed over the membrane and did not form any agglomerates. The TG-DTA curves of Nafion[®] and composite membrane are displayed in Fig. 6. Nafion[®] membrane showed a gradual mass loss of about



(a)



(b)

Fig. 5. SEM images of (a) surface and (b) cross-section of a composite membrane.

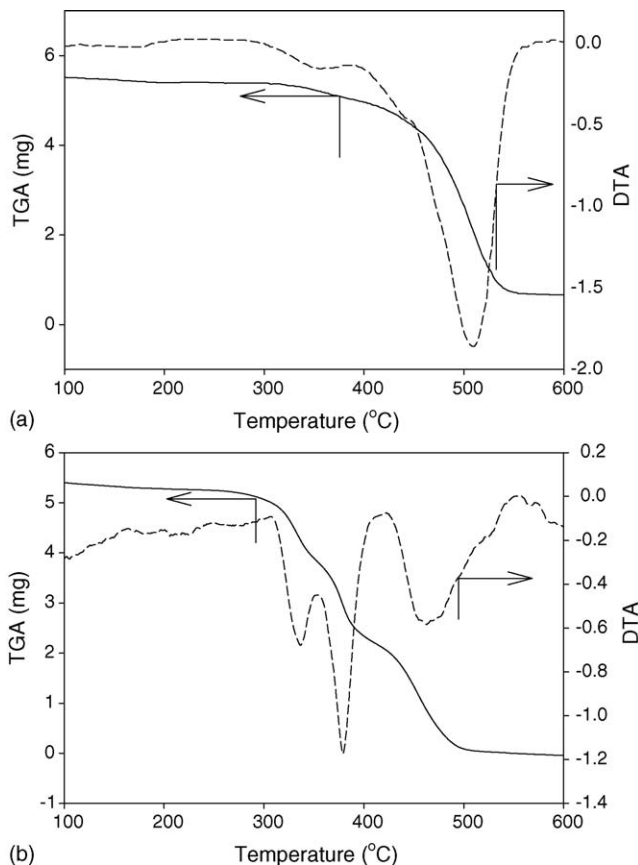


Fig. 6. TG (solid line) and DTA (dashed line) traces of (a) Nafion[®] and (b) composite membranes.

4.2% on heating from 25 to 290 °C which is attributed mainly to the loss of water [26]. Above 290 °C, the membrane started to decompose in a rapid manner. This is associated with the loosening of sulfonic acid groups. At 290–400 °C there is side-chain decomposition and at 470–560 °C PTFE backbone decomposition as reported by de Almeida and Kawano [26] occurred. In the case of the composite membrane, the amount of water loss was about 8.5% up to 290 °C. The desulfonation process started from about 290 °C similar to Nafion[®]. The high content of water might have resulted from the presence of sulfonic-functionalized heteropolyacid-SiO₂ nanoparticles in the Nafion[®] membrane.

Fig. 7 shows the polarization curves obtained for the single cell using the composite membrane. However, the performance of the composite membrane is still lower than a regular Nafion[®] membrane. We could increase the OCV and performance by changing the preparatory conditions of the MEA. Therefore, the low performances of composite membranes should be due to the lack of optimization of the electrodes/membrane interfaces. Since the composite membrane has a different surface from the Nafion membrane, the preparatory condition of the MEA can indeed be changed. However, the optimization of the MEA is a very time-consuming process and it is different for a composite membrane. Furthermore, the purpose of this study is not the development of a new electrolyte which possesses higher performance than Nafion[®] membrane but the improvement of operating temperature of a DMFC up to 200 °C. Therefore,

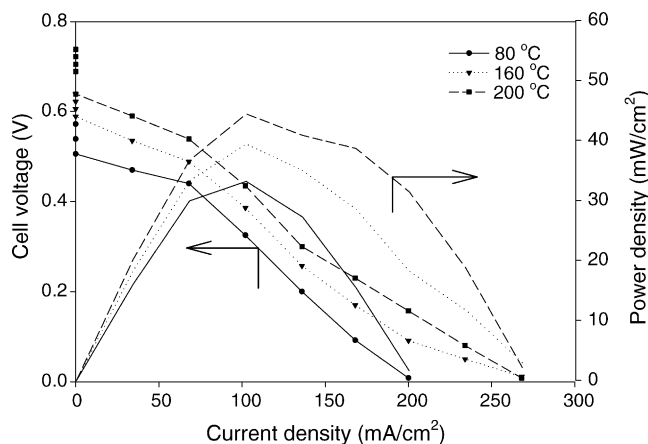


Fig. 7. DMFC performance with a composite membrane with increasing the operating temperature.

the performance of the Nafion[®] membrane is not presented. This study observed the effect of operating temperature on the performance of composite membrane. The DMFC could be successfully operated up to 200 °C with the composite membrane. The power density was 33 mW cm⁻² at 80 °C, 39 mW cm⁻² at 160 °C and 44 mW cm⁻² at 200 °C, respectively. In the case of Nafion[®]-silica recast membrane, the maximum operating temperature of DMFC was reported at 145 °C [8]. The incorporation of sulfonic-functionalized heteropolyacid-SiO₂ nanoparticle in the Nafion[®] membrane could increase the operation temperature of DMFC up to 200 °C. This might be due to the improvement of water retention of composite membrane and the highly dispersed sulfonic-functionalized heteropolyacid-SiO₂ nanoparticle in the membrane.

The heteropolyacid and sulfonic acid on the silica nanoparticles could provide high proton-conductivity at high temperature. The isolated acidic protons, i.e., three protonic species of heteropolyacid (H₃PW₁₂O₄₀) maintain a high proton mobility and proton conductivity, even though the temperature is over 200 °C. The sulfonic acid group is a well-known good protonic conductor because of extensive self-ionization and self-dehydration [23]. Arico et al. also reported that the proton conductivity was directly related to the concentration and acid strength of surface groups in the inorganic materials [24]. Therefore, the sulfonic-functionalized heteropolyacid-SiO₂ nanoparticles could play an important role as a proton conductor in the Nafion membrane. Silica could improve the water retention property of a composite membrane [7,25]. Furthermore, a silica-Nafion composite membrane could be more robust than Nafion membrane alone [25].

As shown in Fig. 7, the performance of the DMFC was increased by increasing the operating temperature. Since the electro-oxidation of methanol over a PtRu catalyst is an endothermic reaction of which the activation energy is 60 kJ mol⁻¹, the catalytic activity of electrode could be improved with increasing the operating temperature [27]. In addition, the methanol crossover, which is methanol diffusion from the anode to the cathode side across the membrane, could be reduced at high temperature [28]. The methanol crossover not

only wastes fuel but also causes performance losses at the cathode due to the consumption of oxygen and catalyst poisoning. In our previous work, the reduction of methanol crossover with increasing temperature was observed [28]. Since the methanol is partially or entirely in the vapor phase over 80 °C, the solubility and molecular activity of methanol could be decreased to reduce the methanol crossover with increasing operating temperature in a DMFC [29]. Therefore, the enhanced catalytic activity and reduced methanol crossover should improve the performance of DMFC at high temperature.

4. Conclusions

For the improvement of hydrophilic and proton-conducting properties of heteropolyacid-SiO₂ nanoparticles, sulfonic acid groups were introduced onto the surface of silica by the grafting and oxidizing of a thiol-silane compound. The incorporation of sulfonic-functionalized heteropolyacid-SiO₂ nanoparticles into a Nafion membrane could increase the operation temperature of a DMFC up to 200 °C. This might be due to the improvement of water retention in the composite membrane and the highly dispersed sulfonic-functionalized heteropolyacid-SiO₂ nanoparticles in the membrane. The sulfonic-functionalized heteropolyacid-SiO₂ nanoparticles could be both conducting carriers for protons and also act as water reservoir in the composite membrane. Finally, the high performance of a DMFC was successfully demonstrated with a composite membrane which was operated up to 200 °C.

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