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Composite proton conducting membranes based on Nafion and sulfonated SiO_2 nanoparticles

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ABSTRACT

Sulfonated SiO_2 nanoparticles with uniform core–shell structure are synthesized and used as functional fillers for preparing composite proton conducting membranes for direct methanol fuel cells (DMFCs). Poly(4-styrenesulfonic acid) in the shell of SiO_2 nanoparticle contributes well-dispersion of the SiO_2 nanoparticle in the Nafion membrane. The addition of core–shell SiO_2 nanoparticles into Nafion matrix is very effective in improving membrane performance, including ion exchange capacity, proton conductivity, mechanical strength and methanol permeability. As a result, the DMFC assembled with a composite membrane exhibits superior performance as compared to a Nafion-based cell.

1. Introduction

Direct methanol fuel cells (DMFCs) that generate electricity using methanol as a fuel are attractive as power source for portable applications due to low temperature operation, low emission and compact cell design [1–3]. The protons generated from methanol at the anode are transported through a proton conducting membrane to the cathode, followed by combination with oxygen and an electron to complete the electrochemical reaction. Perfluorosulfonic polymers such as Nafion are widely used in DMFCs as the proton conducting membrane, because they exhibit high proton conductivity and good mechanical, chemical and thermal stability [4–7]. However, the high methanol crossover from the anode to the cathode not only decreases fuel utilization but also causes mixed potentials at the cathode, which reduces cell voltage and decreases the efficiency of the fuel cell system. Modification of proton conducting membranes through the addition of inorganic particles such as silica is a common approach to reduce methanol crossover [2,8–14]. The presence of inorganic particles in the polymer membranes also allows not only the enlarged hydrophilic channels but also the increase in number of water molecules [15]. Moreover, the addition of inorganic fillers into the polymer membrane is very effective in improving the mechanical, thermal and electrical properties of proton conducting membrane [16–21]. However, an incorporation of these inorganic fillers can lower membrane ion exchange capacity (IEC) that contributes to proton conductivity. It has been reported that some inorganic fillers such as SiO_2 and ZrO_2 could act as the source of proton ions by suitable surface modification [22–25]. The acidic moieties on the surface of modified fillers allow them to contribute directly to the charge carrier concentration in the composite polymer membrane. In our previous study, the core–shell structured SiO_2 particles containing charge carriers in their shell were synthesized and used as functional fillers in Li^+-conducting composite polymer electrolytes [26]. These fillers are unique, because they have a very uniform spherical shape and the SiO_2 core is covalently bonded to poly(lithium 4-styrenesulfonte) in the shell layer.

With the goal of developing proton conducting membranes with high proton conductivity, low methanol permeability and good mechanical property, we prepared the composite polymer membranes based on Nafion and core–shell structured SiO_2 nanoparticles containing sulfonic acid groups. The core–shell structured SiO_2 nanoparticles have a thin shell layer of poly(4-styrenesulfonic acid) (PSSA) surrounding a SiO_2 core. Proton conductivity, water uptake, mechanical strength and methanol permeability of the composite membranes are investigated and compared with those of a Nafion membrane. Finally, the electrochemical performance of DMFC assembled with the composite membrane is evaluated and compared to that of DMFC with a Nafion membrane under the same operating conditions.

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2. Experimental

2.1. Synthesis of core–shell structured SiO_2 nanoparticles

The sulfonated SiO_2 nanoparticles with core–shell structure were synthesized by radical polymerization of vinyl-functionalized silica powders and 4-styrenesulfonic acid sodium salt (SSNa), as depicted in Fig. 1. Monodisperse vinyl-functionalized silica particles were prepared through sol–gel reaction of vinyltrimetoxysilane (VTMS) [27]. VTMS (10 ml) was added into 150 ml of water with stirring until the oil droplets completely disappeared. After vigorous stirring for 30 min, 0.1 ml of NH_4OH was added to the solution, then the reaction progressed for 12 h at room temperature. After completion of the reaction, the resulting precipitate was centrifuged and washed with ethanol. The vinyl-functionalized silica particles (1.5 g) were dispersed in *n*-methyl pyrrolidone (NMP) via ultrasonication for 30 min. A solution consisting of SSNa (6.0 g) and azobisisobutyronitrile (0.4 g) dissolved in NMP was added to the solution containing vinyl-functionalized silica. The reaction mixture was heated to 60 °C to induce polymerization with stirring for 72 h. After polymerization, the solution was precipitated into a large excess of diethyl ether. The precipitate was filtered and washed with methanol several times. The core–shell structured SiO_2 powders were obtained as a final product after vacuum drying at 100 °C for 12 h.

2.2. Preparation of composite polymer membranes

Nafion resin (equivalent weight: 1100, DuPont) and sulfonated SiO_2 core–shell particles were mixed in *N*,*N*-dimethylacetamide (DMAc) using ball milling and sonication. The solution was cast onto a glass plate and dried in a vacuum oven at 60 °C for 12 h. The thickness of composite membranes ranged from 100 to 120 μm. The obtained composite membranes were treated with a 1.0 M NaCl solution for 24 h to avoid thermal decomposition of the sulfonic acid group in Nafion on further heat treatment. The membranes in sodium form were rinsed with de-ionized water, vacuum dried at 60 °C and thermally treated at 150 °C for 6 h. The acid form of the composite membranes was obtained by boiling the sodium form of the membranes in 0.5 M H_2SO_4 for 2 h, followed by washing with boiling water to remove excessive H_2SO_4.

2.3. Characterization and measurements

Morphologies of silica powders and composite polymer membranes were examined using a field emission scanning electron microscope (SEM, JEOL JSM-6300) and a transmission electron microscope (TEM, JEOL 2010). Fourier transform infrared (FT-IR) spectra were recorded on a Magna IR 760 spectrometer in the range of 400–4000 cm^{-1} with KBr powder-pressed pellets. The elemental composition of the core-shell structured SiO_2 particles was determined using energy dispersive X-ray (EDAX). The mechanical properties of the composite polymer membranes in wet states were measured using a universal test machine (AGS-J, Shimadzu) in accordance with the ASTM D882 method. IEC values of the membranes were determined by titration with 0.01 M NaOH solution, and the methanol permeability was measured using a liquid diffusion cell composed of two compartments, as reported earlier in detail [28]. For measurements of water uptake and swelling ratio, the membranes were first vacuum dried at 100 °C overnight. After measuring the weight and dimension of the dried membranes, the membranes were immersed in de-ionized water for 24 h. The water-swollen membranes were taken out, wiped with tissue paper and weighed immediately. Water uptake was calculated using the Eq. (1):

$$\text{water uptake}(\%) = (W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}} \times 100. \qquad (1)$$

where W_{dry} and W_{wet} are the weight of the dried and hydrated membranes, respectively. The swelling ratio was calculated by Eq. (2):

$$\text{swelling ratio}\,(\%) = (A_{\text{wet}} - A_{\text{dry}})/A_{\text{dry}} \times 100. \qquad (2)$$

where A_{dry} and A_{wet} are the areas of the dried and hydrated membranes, respectively. The water uptake and swelling ratio of each sample were measured at least five times to ensure data reproducibility. Proton conductivity was measured using a four-electrode *AC* impedance method using an impedance analyzer (ZAHNER, IM6) over a frequency range of 1–100 kHz with an oscillating voltage of 10 mV. Single-cell tests were performed on cells with an active area of 9 cm^2. The membrane-electrode assembly (MEA) was fabricated with a composite membrane, PtRu/C (HISPEC 12100, Johnson Matthey) as the anode catalyst, and Pt/C (HISPEC 13100, Johnson Matthey) as the cathode catalyst. The gas diffusion layer of the anode was Toray TGP-H-060 carbon paper (Toray Co., Japan) treated with 5 wt% PTFE, and that of the cathode was 25BC carbon paper (SGL, Germany). Pt loadings were 2.0 mg cm^{-2} for both anode and cathode. The polarization curves were obtained with an electrochemical measurement system capable of recording the voltage, current and temperature of the cell. Performance of the cells was measured with a 1.0 M methanol solution under an air atmosphere at 60 °C.

3. Results and discussion

Fig. 2(a) shows the FE-SEM image of vinyl-functionalized silica nanoparticles prepared by the sol–gel reaction of VTMS in aqueous solution. The silica particles have a uniform spherical shape with an average diameter of 420 nm. Fig. 2(b) shows the TEM image of core–shell structured SiO_2 nanoparticle containing poly(sodium 4-styrenesulfonate) (PSSNa) in the shell. The particle has a core–shell morphology with a 210-nm-thick shell layer of PSSNa (in gray) surrounding a core SiO_2 particle (black in the image). The core diameter was measured to be about 420 nm, which is consistent with the SEM image shown in Fig. 2(a). From the EDAX result of core–shell structured SiO_2 nanoparticle, the atomic ratio of sulfur and sodium was estimated to be 1.0. These results suggest that the SiO_2 particles in Fig. 2(a) are well encapsulated by PSSNa with a uniform thickness.

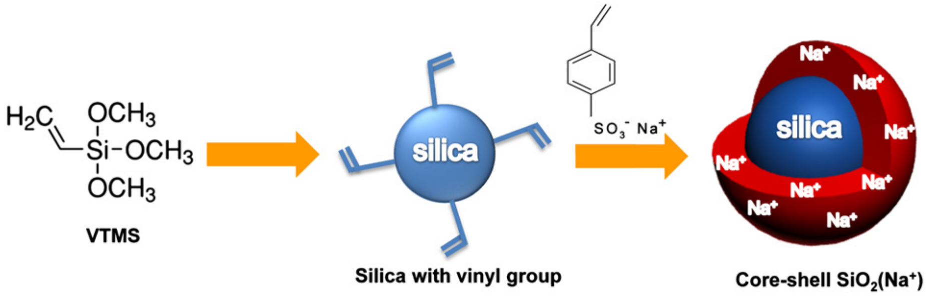

Fig. 1. Reaction scheme for sythesis of core–shell structured SiO_2 nanoparticles containing poly(sodium 4-styrenesulfonate).

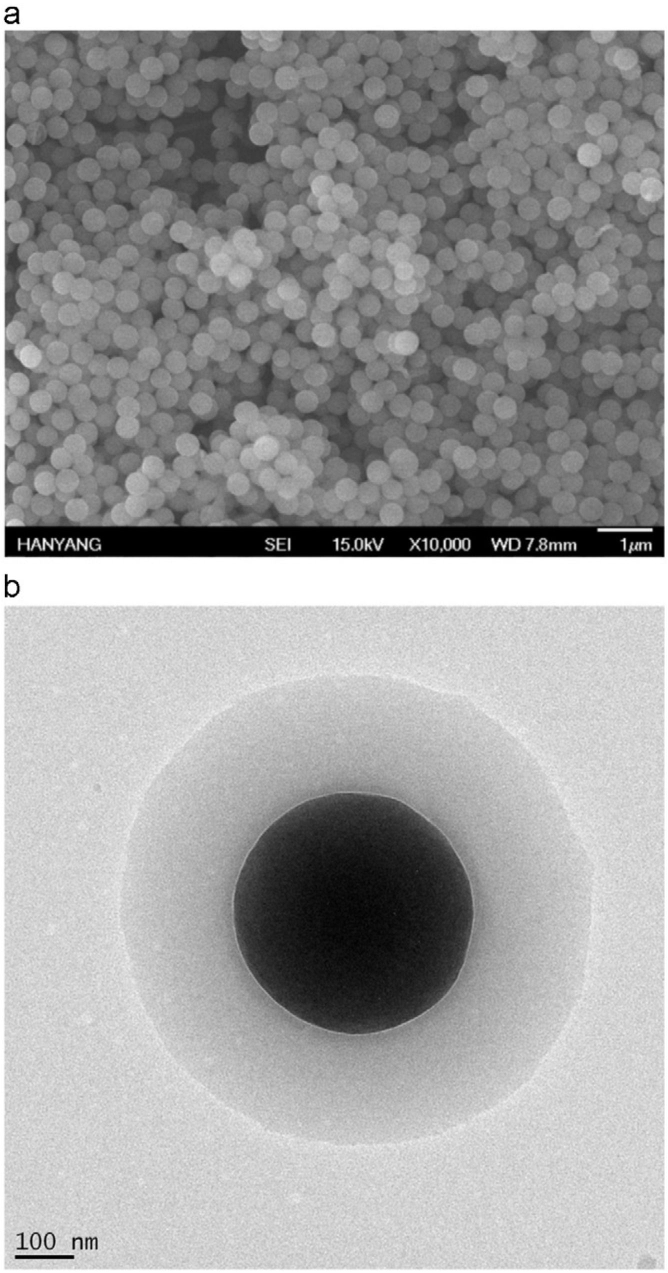

Fig. 2. (a) FE-SEM image of vinyl-functionalized silica particles, and (b) TEM image of a core–shell structured SiO_2 nanoparticle encapsulated by poly(sodium 4-styrenesulfonate).

The chemical structure of vinyl-functionalized SiO_2 powders and core–shell SiO_2 nanoparticles was investigated by FT-IR spectra, as presented in Fig. 3. In the FT-IR spectrum of SiO_2 core (Fig. 3(a)), symmetric stretching vibrations of the siloxane (Si–O–Si) group appeared at 766 cm^{-1}, while asymmetric stretching vibrations of siloxane were observed between 1200 and 1000 cm^{-1} [29]. The presence of C=C double bonds introduced by the covalently bonded VTMS molecules in the SiO_2 particles was confirmed by observing two sharp peaks at 1603 and 1410 cm^{-1}, which are known to be characteristic of C=C double bonds [30,31]. In the core–shell SiO_2 particles (Fig. 3(b)), the intensities of these peaks were significantly decreased, indicating the reactive vinyl groups on the cored SiO_2 particles was reacted with SSNa monomer by radical polymerization to produce core–shell structured SiO_2 particles. New peaks were observed at 1040 and 1186 cm^{-1}, which can be assigned to the symmetric and asymmetric vibration of SO_3^- group, respectively, as shown in PSSNa of Fig. 3(c). In-plane skeleton vibration peak of aromatic group was appeared at 1129 cm^{-1}, while in-plane bending vibration peak of aromatic group was observed at 1009 cm^{-1} [32]. Also, two bands at about 2925 and 2852 cm^{-1} can be assigned to the C–C single bond arising from radical polymerization of vinyl groups between cored SiO_2 particle and SSNa monomer. The broad absorption peak at around 3400 cm^{-1}

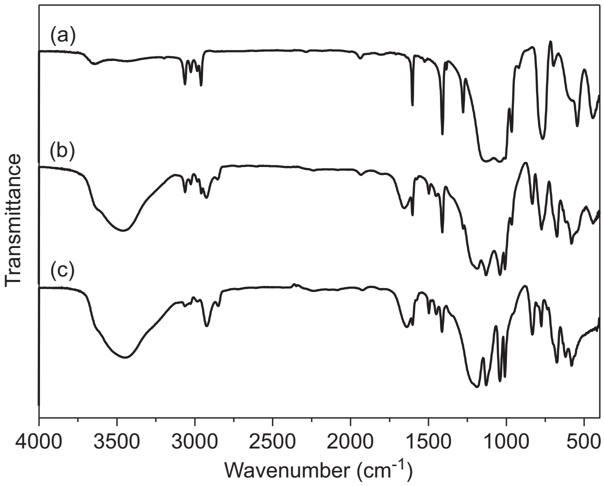

Fig. 3. FT-IR spectra of (a) SiO_2 core particles with vinyl groups, (b) core–shell structured SiO_2 particles encapsulated by poly(sodium 4-styrenesulfonate) and (c) poly(sodium 4-styrenesulfonate).

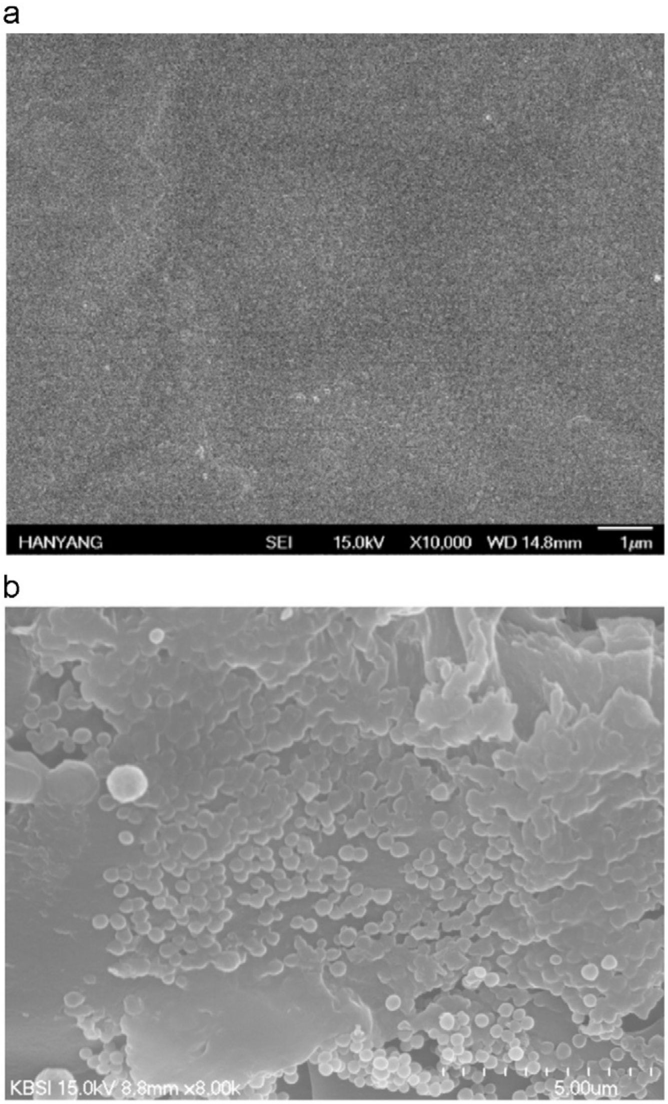

Fig. 4. (a) SEM image of surface and (b) cross-section of the composite polymer membrane containing 12 wt% core–shell structured SiO_2 nanoparticles.

(O–H stretching) in Fig.3(b) and (c) indicates that there are a number of –OH groups due to physically absorbed water molecules in core–shell SiO_2 particles and PSSNa, respectively. From the above results, it is confirmed that PSSNa is covalently bonded to SiO_2 core particle by copolymerization of vinyl-functionalized silica powders and SSNa monomer.

Composite polymer membranes were prepared from Nafion and core–shell structured SiO_2 nanoparticles. Fig. 4(a) shows the FE-SEM image of the composite polymer membrane containing 12 wt% core–shell SiO_2 nanoparticles. As shown in figure, the membrane showed a very homogeneous and smooth surface. No silica agglomeration could be observed on the membrane surface. Fig. 4(b) shows the cross-sectional image of the composite polymer membrane. The presence of the silica particles was confirmed, and the average diameter of SiO_2 particles in the membrane was smaller than 500 nm, indicating a good interfacial contact between PSSA in the shell of the SiO_2 nanoparticles and Nafion matrix. It is expected that the silica particles embedded in the composite polymer membrane act a methanol barrier that reduces methanol permeability. The EDAX mapping images shown in Fig. 5(a), (b) and (c) illustrates the homogeneous distributions of chosen elements (fluorine, silicone, sulfur) across the image, which suggests that the sulfonated SiO_2 nanoparticles are homogeneously distributed in the composite membrane without agglomeration. It is plausible that $-SO_3H$ group of PSSA in the shell of core–shell structured SiO_2 particle has a high affinity with Nafion. The introduction of the covalent bonding between SiO_2 core and PSSA shell resulted in reinforcing interfacial interaction between two phases. As a result, homogeneous silica dispersion could be successfully obtained in the composite polymer membrane.

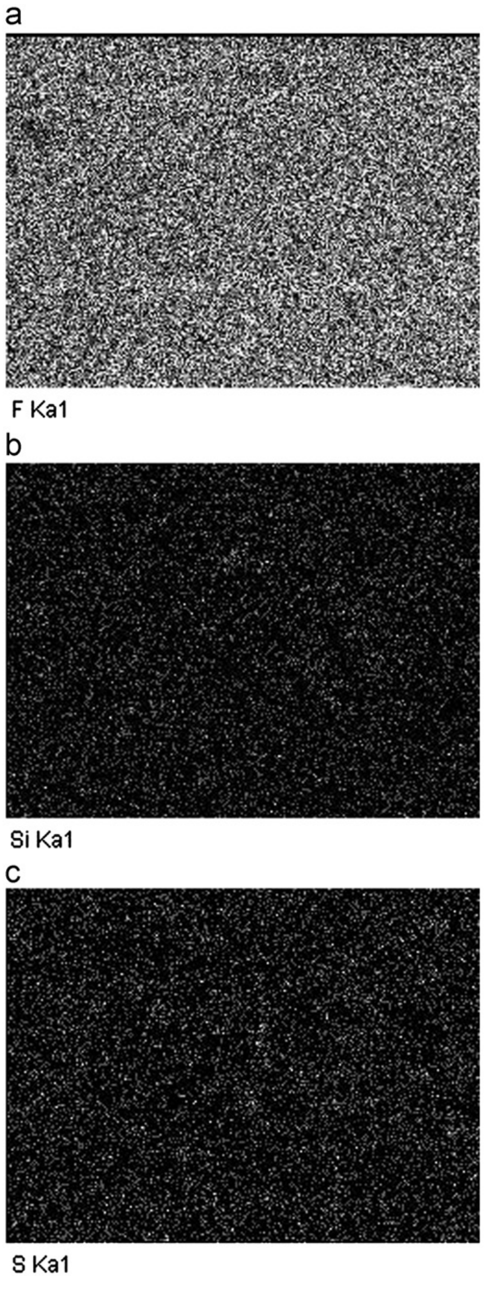

Fig. 5. EDXS mapping images of (a) fluorine, (b) silicone and (c) sulfur in the composite polymer membrane containing 12 wt% core–shell structured SiO_2 nanoparticles.

IEC provides an indication of the ion exchangeable groups present in the membrane, which plays an important role for proton conductivity. IEC values of the composite polymer membranes prepared with core–shell structured SiO_2 particles are shown in Fig. 6(a). The IEC values of Nafion-115 and Nafion-recast membrane (i.e., 0 wt% core–shell SiO_2) were about 0.90 mequiv g^{-1}. The IEC values of the composite membranes increased with increasing core–shell SiO_2 particle content due to the incorporation of additional acidic functional groups of PSSA in the shell. This presumption was confirmed from the fact that the IEC value of sulfonated SiO_2 core–shell particles was measured to be 1.70 mequiv g^{-1}. The mechanical properties of membranes in the fully hydrated state were evaluated because the membranes are operated under humidified conditions. Fig. 6(b) shows the tensile strength of the composite polymer membranes. This figure illustrates that the incorporation of core–shell structured SiO_2 nanoparticles into Nafion membrane improves the mechanical properties. The enhancement of tensile strength can be ascribed to homogeneous distribution of core–shell structured SiO_2 nanoparticles with high mechanical strength. Strong ionic interactions between sulfonic acid groups covalently bonded to SiO_2 particles and sulfonic acid groups in Nafion might form ionic cross-linking structures in the presence of water molecules, which increase the mechanical properties of the composite polymer membranes.

Water uptake and swelling behavior of the composite polymer membranes are examined as a function of the core–shell SiO_2 content at room temperature, and the results are shown in Fig. 7. It can be seen that water uptake gradually increased with the content of core–shell SiO_2 particle. As explained earlier, the sulfonic acid groups in the shell of core–shell structured SiO_2 particle are highly hydrophilic, resulting in enhanced water absorption with addition of sulfonated SiO_2 particles. The swelling behaviors of the composite polymer membranes were similar to those of their water uptake; however, the dimensional change was not serious at high content of sulfonated SiO_2 particles. Moreover, the composite polymer membranes did not exhibit any loss in mechanical strength, due to the strong $-SO_3H/-SO_3H$ interactions between core–shell structured SiO_2 particle and Nafion, as illustrated in Fig. 6(b).

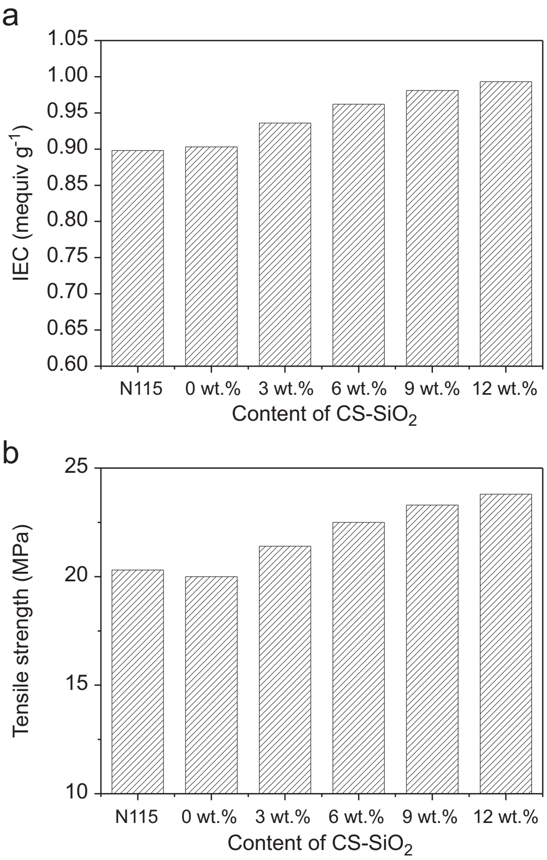

Fig. 6. (a) IEC values and (b) tensile strength of composite polymer membranes as a function of core–shell structured SiO_2 content.

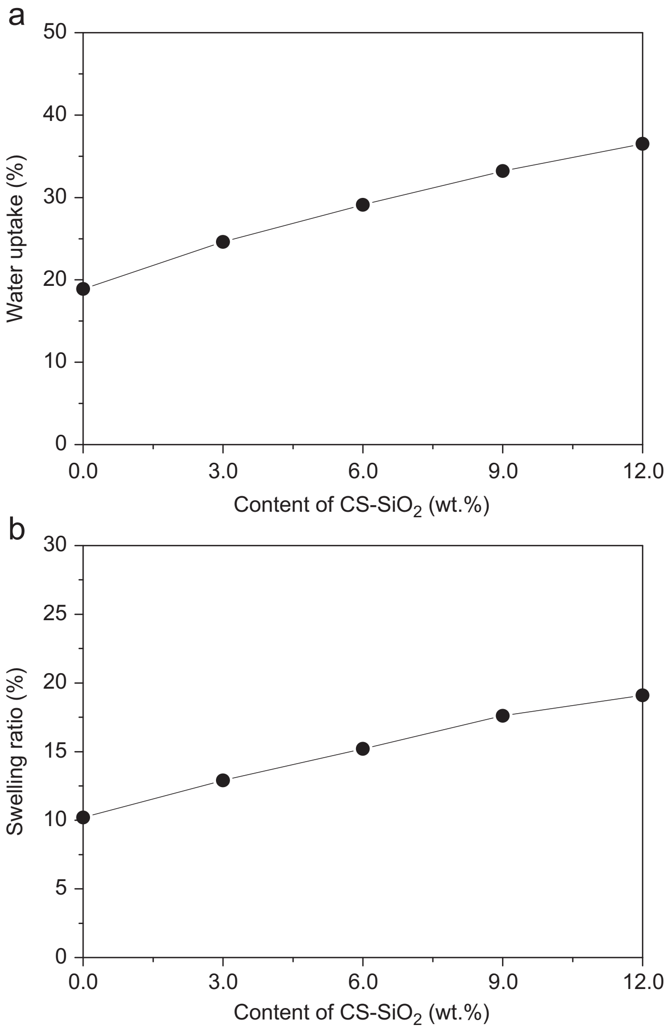

Fig. 7. (a) Water uptake and (b) swelling ratio of composite polymer membranes as a function of core–shell structured SiO_2 content.

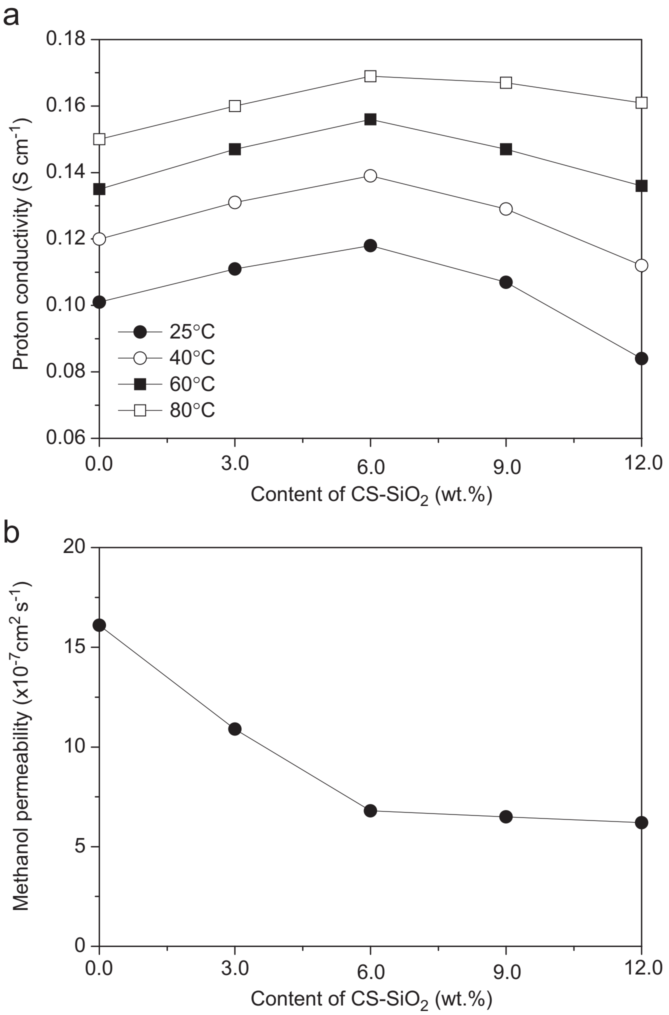

Fig. 8. (a) Proton conductivities of composite polymer membranes measured at different temperatures, and (b) methanol permeability of composite polymer membranes as a function of core–shell SiO_2 particle content.

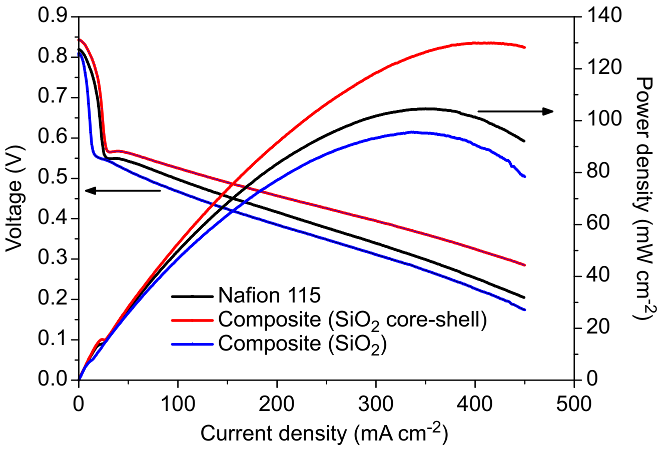

Fig. 9. Polarization and power density curves of a single cell assembled with different polymer membranes. (Nafion 115, composite polymer membrane containing 6 wt% core–shell SiO_2 particles and composite polymer membrane containing 6 wt% unmodified SiO_2 particles).

Proton conductivities of composite polymer membranes were measured at 100% relative humidity and are plotted as a function of the core–shell SiO_2 particle content at different temperatures, as presented in Fig. 8(a). Proton conductivity increased with increasing core–shell SiO_2 particle content, reaching a maximum around 6 wt%, followed by a decrease. An increase in proton conductivity with the addition of sulfonated SiO_2 particle is related to an increase in IEC due to the introduction of additional sulfonic acid groups. Moreover, core–shell SiO_2 particles absorb water on the surface through a strong interaction with surface $-SO_3H$ groups and the formation of hydrogen bonds, thus increasing water retention and proton conductivity, as reported earlier [33]. A decrease in proton conductivity beyond 6 wt% may be related to the physical cross-linking effect of core–shell SiO_2 particles restricting mobility of the polymer chain and decreasing the free volume. Also, the connectivity of proton conducting phase becomes more tortuous at high content of SiO_2 particles. It is thus believed that the addition of 6 wt% SiO_2 powders provides the most desirable environment for proton conduction in the composite polymer membrane under study. The methanol permeability of composite membranes is shown in Fig. 8(b), which illustrates that the methanol permeability decreases with the addition of core–shell SiO_2 particles. The decrease in methanol permeability might result from the well-dispersed silica particles in the composite membrane acting as methanol barrier, which inhibit methanol crossover through the membranes [18,34,35]. In addition, the strong $-SO_3H/-SO_3H$ interactions between core–shell SiO_2 and Nafion suppress segment motions of polymer chain in aqueous methanol solution so as to depress the methanol diffusion in the composite membrane, as reported in the composite polymer membrane prepared with sulfonated poly (phthalazinone ether ketone) and sulfonated SiO_2 nanoparticles [23].

Electrochemical performance of DMFC assembled with a composite polymer membrane is evaluated at 60 °C under feed flow rates of 3 cc min^{-1} of 1.0 M methanol and 400 cc min^{-1} air at atmospheric pressure. Based on the properties of membranes described above, the composite membrane containing 6 wt% core–shell SiO_2 particles exhibiting the highest proton conductivity was chosen as a membrane in preparing MEA. In order to investigate the effect of core–shell structured SiO_2 particles, a composite polymer membrane containing same content of unmodified SiO_2 particle (without PSSA shell layer) with same particle size (average diameter: 420 nm) was also tested under the same operation conditions. Fig. 9 compares the cell performance of DMFCs assembled with Nafion and composite polymer membranes. It was encouraging that the cell prepared with composite polymer membrane based on core–shell SiO_2 exhibited better cell performance than that of Nafion-based cell in the whole range of current density. The maximum power density of the cell reached 129.9 $mW\,cm^{-2}$, which is much higher than the value obtained for a Nafion-based cell (104.6 $mW\,cm^{-2}$). Proton conductivity and methanol permeability of the membrane are two main factors affecting the DMFC performance. Thus, a selectivity that is defined as the ratio of proton conductivity to methanol permeability has to be maximized for achieving good cell performance. From the proton conductivity at 60 °C and methanol permeability data shown in Fig. 8, the composite membrane has a much higher selectivity ($22.9\times10^4\,S\,s\,cm^{-3}$) than that of Nafion ($8.4\times10^4\,S\,s\,cm^{-3}$), which results in improved cell performance. On the other hand, the cell prepared with composite polymer membrane based on unmodified SiO_2 exhibited poor cell performance as compared to Nafion-based cell, mainly owing to the lower proton conductivity (0.05 $S\,cm^{-1}$ at 60 °C) of the composite membrane, in spite of its reduced methanol permeability ($6.5\times10^{-7}\,cm^2\,s^{-1}$). That is, the composite polymer membrane prepared with unmodified SiO_2 has lower selectivity ($7.7\times10^4\,S\,s\,cm^{-3}$) than that of Nafion. These results demonstrate that the addition of sulfonated SiO_2 nanoparticles with uniform core–shell structure as fillers is very effective in improving cell performance, by increasing proton conductivity as well as reducing methanol crossover.

4. Conclusions

The core–shell structured SiO_2 nanoparticles with uniform spherical shape were successfully synthesized from vinyl-functionalized silica powders and 4-styrenesulfonic acid sodium salt. The sulfonated SiO_2 nanoparticles were homogeneously distributed in the Nafion membrane without agglomeration. The composite polymer membranes prepared with Nafion and core–shell SiO_2 nanoparticles exhibited higher proton conductivity, better mechanical strength and lower methanol permeability compared to Nafion membrane. Evaluation of single-cell performance showed that the cell assembled with the composite membrane exhibited better performance than that of Nafion-based cell.

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