



Proton conductivity and fuel cell property of composite electrolyte consisting of Cs-substituted heteropoly acids and sulfonated poly(ether–ether ketone)

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ABSTRACT

Inorganic–organic composite electrolytes were fabricated from partially Cs⁺-substituted heteropoly acids (Cs-HPAs) and sulfonated poly(ether–ether ketone) (SPEEK) for application in fuel cells. Heteropoly acids, such as phosphotungstic acid (H₃PW₁₂O₄₀:WPA), and silicotungstic acid (H₄SiW₁₂O₄₀:WSiA), were mechanochemically treated with cesium hydrogen sulfate (CsHSO₄) to obtain the form of Cs-HPAs. SPEEK was prepared from PEEK by sulfonation using concentrated sulfuric acid. Water durability and surface structure of HPAs were modified by introducing Cs⁺ into HPAs. Flexible and hot water stable composite electrolytes were obtained, and their electrochemical properties were markedly improved with the addition of Cs-HPAs into the SPEEK matrix. Maximum power densities of 245 and 247 mW cm⁻² were obtained for 50WPA-50CsHSO₄ and 50WSiA-50CsHSO₄ in SPEEK (1/5 by weight) composite electrolytes, respectively, from single cell tests at 80 °C and 80 RH%. These results suggest that a three-dimensional proton-conductive path was formed among homogeneously distributed Cs-HPAs particles in the SPEEK matrix. The Cs-HPAs incorporated into the SPEEK matrix increased the number of protonate sites in the electrolyte. These observations imply that the mechanochemically synthesized Cs-HPAs, which consist of hydrogen bondings between Cs-HPAs and –HSO₄⁻, dissociated from CsHSO₄, are promising materials as inorganic fillers in inorganic–organic composite.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) have attracted much attention due to their ability to produce high-energy efficiently at low operating temperatures without harmful emissions. In recent years, perfluorinated ionomers (PFIs) have been used as electrolytes in PEFC systems, which represent a promising energy source for portable devices, automobiles, and stationary applications [1]. However, PFIs limit the large scale commercialization of PEFC systems due to the high cost and/or the poor heat resistance of the electrolytes. Consequently, an inorganic–organic composite electrolytes are attracting increasing interest as one of the key alternative materials for the development of new proton-conductive electrolytes in fuel cell applications [2–4]. Recently, chemical modifications of various aromatic polymers were attempted for use as electrolytes in fuel cell systems. Indeed, they show promising performance as not only electrolyte membranes but also as matrix for inorganic–organic composite electrolytes. High proton conductivity of poly(ether–ether ketone) (PEEK) can be attained by

sulfonation of PEEK, hence, sulfonated PEEK (SPEEK) electrolyte has good performance as a polymer electrolyte in PEFCs, but increasing degree of sulfonation (DS) leads to increased solubility in water and other solvents, and swelling [5].

On the other hand, heteropoly acids (HPAs) are well known as inorganic solid acids that show high proton conductivity and excellent catalytic property, based on their strong acidity [6–8]. However, despite the good performances of HPAs, their chemical stabilities are unsatisfactory due to their hygroscopicity. Partial Cs⁺-substituted HPAs (Cs-HPAs) have attracted significant attention because of their high catalytic activity in many acid-type reactions [9]. Such partially substituted solid acids are generally prepared by precipitation from aqueous solutions [10,11], and their composite membranes investigated as electrolytes in PEFC systems [12–14]. In contrast, we have shown that a solid state reaction involving mechanochemical treatments by using a high-energy ball mill is a promising way to improve the proton conductivity of inorganic solid acids and to synthesize a new class of inorganic solid acid-based composites [15,16]. When mixtures of cesium hydrogen sulfate (CsHSO₄) and phosphotungstic acid (H₃PW₁₂O₄₀, WPA) were mechanochemically treated, Cs_xH_{3-x}PW₁₂O₄₀ (CsWPA), was formed.

In this study, mechanochemical treatment was adopted to synthesize chemically stable Cs-HPAs. SPEEK was used as a matrix

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of the inorganic–organic composite electrolytes. The structures of the Cs-HPAs and SPEEK were investigated. Morphological study and electrochemical characterization of the composite electrolytes consisting of Cs-HPAs and SPEEK were also performed.

2. Experimental

2.1. Materials and preparation of composite electrolytes

2.1.1. Materials

Reagent-grade phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$, WPA- $n\text{H}_2\text{O}$), silicotungstic acid ($\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$, WSiA- $n\text{H}_2\text{O}$), and CsHSO_4 were purchased from Wako Pure Chemical Industries and used as starting materials for the preparation of the inorganic solid acids. Commercially available PEEK (450 P standard viscosity grade, VICTREX[®]) was used as starting material for the preparation of SPEEK. Concentrated H_2SO_4 (97.0%, NACALAI TESQUE, Inc.) and *N,N*-dimethylacetamide (DMAc, 99.0 vol.%, WAKO Pure Chemical Industries) were also used.

2.1.2. Synthesis of Cs-HPAs and SPEEK polymer

The SPEEK was prepared according to the following procedures: PEEK was initially dissolved in concentrated H_2SO_4 , with vigorous stirring, at room temperature ($25 \pm 2^\circ\text{C}$) in a nitrogen atmosphere for 24 h. Then this polymer solution was poured into a large excess of ice-cold water under continuous mechanical agitation to obtain the SPEEK polymer precipitate. The polymer precipitate thus obtained was washed several times with distilled water until a neutral pH, and then dried, initially at 100°C for 12 h in an oven, and finally at 120°C under vacuum for 12 h.

Prior to mechanical milling, WPA- $n\text{H}_2\text{O}$ and WSiA- $n\text{H}_2\text{O}$ were kept at 60°C for about 1 day to obtain WPA-6 H_2O (WPA6) and WSiA-6 H_2O (WSiA6). The mechanochemically milled WPA6- CsHSO_4 and WSiA6- CsHSO_4 (90/10, 50/50, and 10/90 by molar for both composites) were carried out in a nitrogen atmosphere using a planetary ball mill (Fritsch Pulverisette 7). The rotation speeds of the milling pot and table were kept at 720 rpm with a constant rotation ratio of 1:1, for 1 h. The volume of the pot was 45 ml and 10 balls of 10 mm diameters were used for the mechanochemical milling.

2.1.3. Preparation of composite electrolytes

The prepared Cs-HPAs and SPEEK (1/5 by weight) were put in DMAc with vigorous stirring to obtain a precursor paste. The precursor was cast onto a glass plate and developed into sheets using a casting knife. And the cast sheets were initially dried at 60°C for 10 h, then between 100 and 120°C for 10 h in an oven, and finally at 120°C under vacuum, overnight to remove the DMAc. The dried sheets were then peeled off as the prepared composite electrolytes.

2.2. Characterization of composite electrolytes

2.2.1. Powder X-ray diffraction (XRD)

XRD patterns of the mechanochemically treated composite powders were evaluated using a Rigaku RINT2000 with $\text{Cu K}\alpha$ radiation source.

2.2.2. Thermal analysis

Thermogravimetry–differential thermal analysis (TG–DTA) and differential scanning calorimetry (DSC) were carried out to determine thermostability and to calculate the water of crystallization molecules of HPAs using Rigaku Thermo Plus TG 8120 and Rigaku Thermo plus DSC 8230, respectively.

The TG–DTA of SPEEK was programmed from RT to 900°C at a rate of $10^\circ\text{C min}^{-1}$ under a N_2 atmosphere, and the DSC was

measured in a temperature range from RT to 500°C at a rate of $10^\circ\text{C min}^{-1}$ under a N_2 atmosphere.

2.2.3. Fourier transform infra-red (FT-IR) spectra

FT-IR evaluation for the sulfonation of PEEK was carried out using WS/IR-7300 (JASCO). The IR spectra of PEEK and SPEEK were measured using both pellets, formed by KBr method, and film, by casting the polymer solution on a silicon substrate.

2.2.4. Proton nuclear magnetic resonance ($^1\text{H NMR}$) and elemental analysis

Solution $^1\text{H NMR}$ was evaluated using UNITY-400P (VARIAN); and using dimethylsulfoxide- d_6 ($\text{DMSO-}d_6$, 99.8 vol.%, NACALAI TESQUE, Inc.) as solvent. Elemental evaluation using Eager 200 elemental analyzer was carried out to determine degree of sulfonation (DS) of SPEEK.

2.2.5. Water uptake (WU) and hot water stability

The electrolytes were immersed in deionized water to evaluate WU within a temperature range of $30\text{--}85^\circ\text{C}$, using the relation $\text{WU}(\%) = ((W - W_0)/W_0) \times 100(\%)$, where W_0 and W are weights of dried and wet samples, respectively. After WU measurement, the electrolytes were again immersed in hot distilled water at 90°C for 24 h to investigate hot water stability.

2.2.6. Electron microscopy

The morphologies of the composite electrolytes were characterized by transmission electron microscopy (TEM, JEOL, JEM-2100F, operating at 200 kV). Hitachi S-4800 field-emission scanning electron microanalyzer (Emax Energy EX-250, Horiba) was used to carry out the energy dispersive spectrometry (EDS) analysis of the all obtained Cs-HPAs.

2.3. Electrochemical analysis and fuel cell operation

Prior to electrochemical analysis, acid treatment was carried out to obtain fully protonated electrolytes as described below: after casting, electrolytes were immersed in 5 vol.% of H_2SO_4 solution at room temperature for 1 day, and washed several times with distilled water. Finally, electrolytes were dried in an oven at 60°C overnight.

The proton conductivity of the electrolytes was measured by AC impedance spectroscopy technique over a frequency range of $10^6\text{--}1\text{ Hz}$ using a system based on SI 1260 (Solartron). The conductivities, σ , of the samples were calculated from the impedance data, using the relation $\sigma = d/RS$, where d and S are the thickness and face area of a sample, respectively, and R was derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the real, $\text{Re}(Z)$, axis.

The current–voltage profiles in the single cells were obtained using a system based on SI 1252A with SI 1287 electrochemical measurement system (Solartron). The single fuel cell tests were carried out for the membrane electrode assemblies (MEAs). Commercially available carbon paper was used as the electrode which consisted of polytetrafluoroethylene (PTFE) treated gas diffusion layer and Pt-loaded catalyst layer (Pt: 0.5 mg cm^{-2}). The MEAs were obtained by hot pressing each electrolyte between the Pt-loaded carbon paper sheets at 130°C under a pressure of about 2 MPa for 1 min, and then blocked under 1.5 N m force at each point. Current–voltage profiles of the fuel cells were corrected using a system based on Corr ware (Scribner Associates Inc.). During a single fuel cell test, humidified H_2 of 50 ml min^{-1} and air of 100 ml min^{-1} , passing through a bubbler, were provided to the cells under ambient pressure ($P_{\text{H}_2} = P_{\text{air}} = 1\text{ atm}$). Single fuel cell tests were measured in a temperature range of RT to 80°C with relative humidity (RH) range of 50–80 RH%. The fuel cell performance

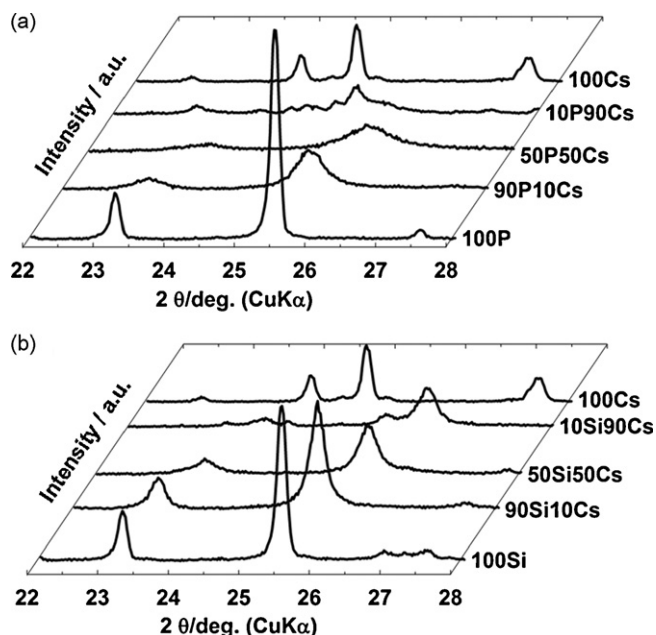


Fig. 1. Powder XRD patterns of heteropoly acid with CsHSO₄ and mechanochemically treated inorganic solid acids (720 rpm for 1 h): (a) WPA6–CsHSO₄ systems and (b) WSiA6–CsHSO₄ systems.

greatly depends on the makeup of the cell as well as on the operation conditions of temperature and humidity, so that the assembly processes of the cells and the operation conditions were optimized for each electrolyte by trial and error.

3. Results and discussion

3.1. Structure of composite electrolytes

The powder XRD patterns of heteropoly acid containing CsHSO₄ and mechanochemically treated inorganic solid acids (at 720 rpm for 1 h) are shown in Fig. 1. Fig. 1(a) and (b) are for the WPA6–CsHSO₄ and WSiA6–CsHSO₄ systems, respectively. Where, 100P, 90P10Cs, 50P50Cs, 10P90Cs and 100Cs in (a) correspond to WPA6, 90WPA6–10CsHSO₄, 50WPA6–50CsHSO₄, 10WPA6–90CsHSO₄ and CsHSO₄, respectively; and 100Si, 90Si10Cs, 50Si50Cs, 10Si90Cs and 100Cs in (b) correspond to WSiA6, 90WSiA6–10CsHSO₄, 50WSiA6–50CsHSO₄, 10WSiA6–90CsHSO₄ and CsHSO₄, respectively. Before milling, diffraction peaks of WPA6,

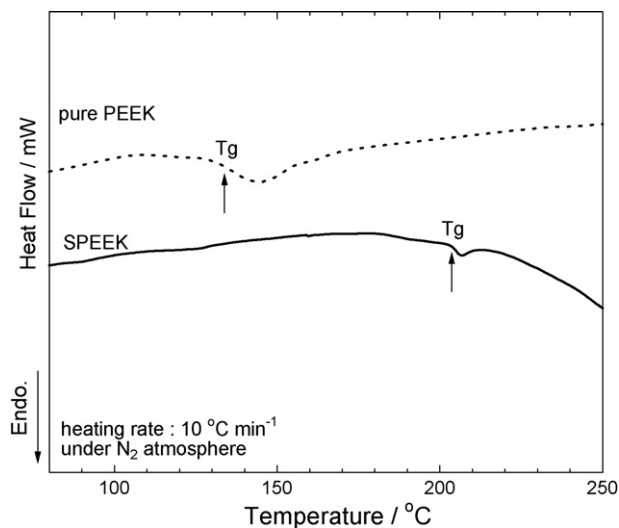


Fig. 2. DSC curves and glass transition temperatures (T_g) of pure PEEK and SPEEK cast electrolyte.

WSiA6 (bottom spectra of Fig. 1(a) and (b), respectively) and CsHSO₄ (topmost spectra of Fig. 1(a) and (b), respectively) can clearly be seen, whereas, after milling for 1 h to form CsWPA6 and CsWSiA6, significant changes are observed in the XRD patterns around 25–26°. The diffraction peaks at 25.4°, with the highest intensities, for both WPA6 and WSiA6, shift to higher angles in the composites, which indicate that H⁺ ions in WPA6 and WSiA6 were partially substituted with Cs⁺ to form Cs_xH_{3–x}PW₁₂O₄₀ and Cs_xH_{4–x}SiW₁₂O₄₀ by the mechanochemical treatment [9]. The mechanism has been described using NMR study in previous studies [15,16]. Introduced Cs was also determined by EDX analysis shown in Table 1.

Upon Cs⁺ substitution, surface structures of both WPA and WSiA were also observed to have changed, which were verified from results of BET measurement shown in Table 1. Surface structures of HPAs were modified, and the chemical durability was improved by the incorporation of Cs⁺ into the HPAs. The highest pore volumes of Cs–HPAs achieved were 19.1×10^{-3} and 19.5×10^{-3} cm³ g⁻¹ for 50P50Cs and 50Si50Cs, respectively.

Thermal stability of PEEK and SPEEK was evaluated by TG–DTA and DSC. The glass transition temperature, T_g, was obtained using DSC technique, as shown in Fig. 2, at 134 and 202 °C for PEEK and SPEEK, respectively. The higher T_g of SPEEK, compared to that of

Table 1
Structural properties of Cs-substituted HPAs composite particles by mechanochemical treatment.

Sample designation	Crystalline size (nm) ^a	Specific surface area (m ² g ⁻¹) ^b	Average pore diameter (nm) ^c	Pore volume (10 ⁻³ cm ³ g ⁻¹) ^d	Element proportions (mol%) ^e	
					Cs	S
WPA6 (P)	5.6	4.1	4.0	7.7	–	–
90P10Cs	3.1	2.8	1.2	5.9	0.3	–
50P50Cs	3.8	9.8	1.2	19.1	1.6	2.0
10P90Cs	5.0	N/A	N/A	N/A	9.1	9.4
WSiA6 (Si)	8.0	0.8	25.9	3.5	–	–
90Si10Cs	2.9	1.6	15.6	5.1	–	–
50Si50Cs	5.9	4.7	22.6	19.5	2.2	2.1
10Si90Cs	11.5	0.04	110.2	0.1	7.7	6.6
CsHSO ₄	12.6	N/A	N/A	N/A	15.3	14.9

^a Estimated by Scherrer's equation using line width of XRD peak at 25–26°.

^b BET surface area.

^c Calculated from BJH analysis.

^d Calculated from BJH analysis.

^e Estimated by EDS analysis.

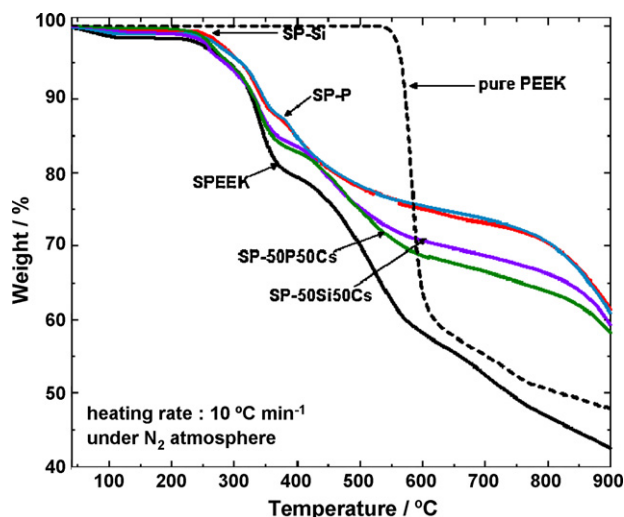


Fig. 3. TGA curves of pure PEEK, SPEEK and a few composite electrolytes.

PEEK, is explained as due to increased intermolecular interaction as a result of the introduced sulfo groups, which also hinder internal rotation of molecules. Fig. 3 shows TGA curves of pure PEEK, SPEEK and a few composite electrolytes. In the TGA study, the pure PEEK showed only one trend of weight loss, which started around 530 °C, due to the decomposition of the main chain of PEEK. In contrast, the TGA study result on the cast electrolytes showed 3 trends of weight loss: first around 120 °C, attributed to evaporation of water molecules; second between 230 and 330 °C, associated with splitting off of the sulfo groups ($-\text{SO}_3\text{H}$); and finally around 400 °C, attributed to decomposition of main chain of PEEK [18]. Furthermore, weight loss attributed to the thermal decomposition or evaporation of DMAc was not detected within the typical temperature range of 164–166 °C. This finding confirmed the removal of the DMAc from electrolytes after the casting process. However, no significant changes of Tg and thermal stability for SPEEK composite electrolytes were observed in DSC and TGA results.

Elemental analysis of both PEEK and SPEEK were carried out in order to identify their elemental proportions. The S component measured was 6.2 wt.% for SPEEK of 24 h sulfonation time, which clearly indicates the introduction of sulfo groups into the PEEK polymer backbone. Introduced sulfo groups of PEEK were identified by FT-IR spectrum; upon sulfonation, new peaks appeared at $\sim 1700\text{ cm}^{-1}$. Significant peaks at 709, 1024, and 1080 cm^{-1} are assigned to S–O stretch, S=O stretch, and symmetric O=S=O stretch, respectively. These FT-IR spectral data indicate that the sulfonation of PEEK in sulfuric acid takes place at the para position of the third substituent on phenyl ring [17].

Solution ^1H NMR spectroscopy was used to obtain structural identification. Fig. 4 shows the solution ^1H NMR spectrum of SPEEK dissolved in DMSO- d_6 , and the assignments of significant peaks are also explained in Fig. 4. The presence of sulfo groups results in a distinct signal for the proton at the H_E position. Kaliaguine and co-workers [18] reported that the DS of SPEEK can be estimated by intensity of the H_E peak in a ^1H NMR result, which is equivalent to the sulfo group content. The DS value of 66.3% for SPEEK was quantitatively estimated from combined solution ^1H NMR and elemental analysis.

Discrepancy in results between Tg and DS and/or DS and IEC for PEEK and its sulfonated form was obtained from different researchers: Rikukawa and co-workers have reported [19] that Tg for PEEK, which was supplied by ICI, is 143 °C, and SPEEK with DS of 65 mol.% was obtained after sulfonation for about 100 h; Wang and co-workers have also reported [20] that SPEEK of IEC of 1.9 meq. g^{-1}

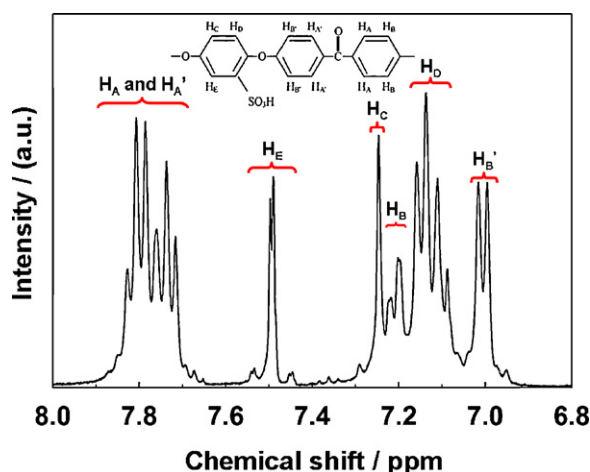


Fig. 4. ^1H NMR spectra for sulfonated PEEK (IEC = 2.218 meq. g^{-1}).

with DS of 65% was obtained after sulfonation for about 90 h using PEEK supplied from Jilin university. Kaliaguine et al. have reported [5,18] more detailed results and reasons about Tg, DS, IEC and conductivity for PEEK supplied from POLYSCIENCES, Victrex and Gharda Chemical; they mentioned that the factors that affect the final analysis results include the nature of the initial material, its molecular weight, treatment condition and experimental features of measurement technique. In this work, PEEK was used without any pretreatments; neither during sulfonation nor characterization studies. The Tg of 134 °C for pure PEEK was lower than referenced values. This discrepancy is probably due to the corrected point of DSC result; we recorded the initial point of change of trend in DSC study. On the other hand, the relation between the Tg result at 202 °C and DS result of 66.3% showed good agreement with some literature values [5,21].

The water uptake curves of the SPEEK electrolytes and a few composite electrolytes are shown in Fig. 5; and results of hot water durability tests are given in Table 2. From the results in Fig. 5 and Table 2, SPEEK shows higher water uptake and poor hot water stability, under the cited conditions. This is probably due to relatively high DS of SPEEK [19]. It can also be seen that the hot water durability of the composite electrolytes improved with the introduction of Cs-HPAs. It is noteworthy that the composite electrolytes containing Cs-HPAs show lower water uptake in a temperature range of 60–85 °C than pure SPEEK, and have sufficient hot water stability in spite of the

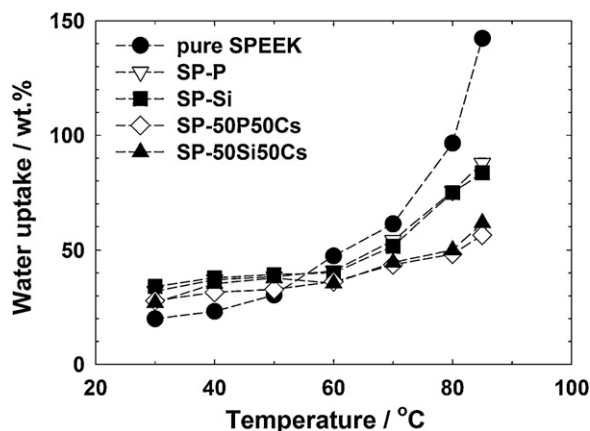


Fig. 5. The water uptake of SPEEK electrolyte and a few composite electrolytes as a function of submersion temperature.

Table 2
Physical and electrochemical characteristics of the developed composite electrolytes.

Sample designation	Thickness of dried membrane (μm)	Hot water stability ^a	Electrochemical parameters (at 80 °C under 80 RH%)		
			OCV (V)	$i_{600\text{mV}}$ (mA cm^{-2})	Conductivity (S cm^{-1})
SP	83	S	0.980	154	1.09×10^{-3}
SP-P	76	S	0.927	174	1.53×10^{-3}
SP-90P10Cs	72	Sw	0.935	218	1.90×10^{-3}
SP-50P50Cs	84	I	0.957	324	2.06×10^{-3}
SP-10P90Cs	84	I	0.946	228	1.39×10^{-3}
SP-Si	79	S	0.939	185	1.06×10^{-3}
SP-90Si10Cs	71	Sw	0.929	181	1.16×10^{-3}
SP-50Si50Cs	75	I	0.971	382	2.25×10^{-3}
SP-10Si90Cs	67	I	0.956	350	1.35×10^{-3}

Note: The ratio of composite electrolytes between Cs-HPAs and SPEEK was fixed 1/5 by weight. Hot water stability^a was determined by immersion in hot distilled water at 90 °C for 24 h, and I, Sw and S are defined as follows: I is insoluble, Sw is swollen, and S is soluble.

composite electrolytes, containing pristine heteropoly acids, showing poor hot water stability. Furthermore, weight loss of composite electrolytes containing Cs-HPAs was not observed during the hot water stability test under the cited conditions. It was probably due to the introduction of Cs-HPAs, which modified the hygroscopicity of SPEEK to improve the hot water durability of the composite electrolytes. This observation implies that the mechanochemically synthesized Cs-HPAs are promising materials as inorganic fillers in inorganic–organic composite electrolytes to improve hot water durability.

3.2. Electrochemical characteristics of composite electrolytes

Flexible and hot water stable composite electrolytes, in a thickness range of 67–84 μm , were obtained. The pure SPEEK, SPEEK containing WPA6 (SP-P), and SPEEK containing WSiA6 (SP-Si) electrolytes were transparent and yellowish, however composite electrolytes became cream-yellow and translucent with increasing CsHSO₄ amount in the mechanically milled inorganic Cs-HPAs.

The conductivities of various composite electrolytes at 80 RH% as a function of temperature are shown in Fig. 6(a) and (b), and the highest conductivities are summarized in Table 2. The conductivities of all the electrolytes increased with increasing temperature in the range of 50–80 °C. The addition of inorganic solid acids such as WPA6, WSiA6, CsWPA and CsWSiA to SPEEK increased the conductivities of the composite electrolytes. It can be seen that the mechanochemically synthesized CsWPA and CsWSiA enhanced the proton conductivity of the composite electrolytes more effectively than it did for just pure WPA6 and WSiA6. In the SP-CsWPA system, the SP-50P50Cs shows the highest conductivity, $2.06 \times 10^{-3} \text{ S cm}^{-1}$ at 80 °C and 80 RH%. In the SP-CsWSiA system, the SP-50Si50Cs achieves the highest conductivity, $2.25 \times 10^{-3} \text{ S cm}^{-1}$, under the same conditions.

The polarization curves of the H₂/Air fuel cells obtained at 80 °C under 80 RH% for SPEEK, SP-50P50Cs, and SP-50Si50Cs electrolytes are shown in Fig. 7; and the physical and electrochemical properties of all of electrolytes are summarized in Table 2. In Fig. 7, (●) is for the curve of the pure SPEEK electrolyte, (▽) and (■) are for the

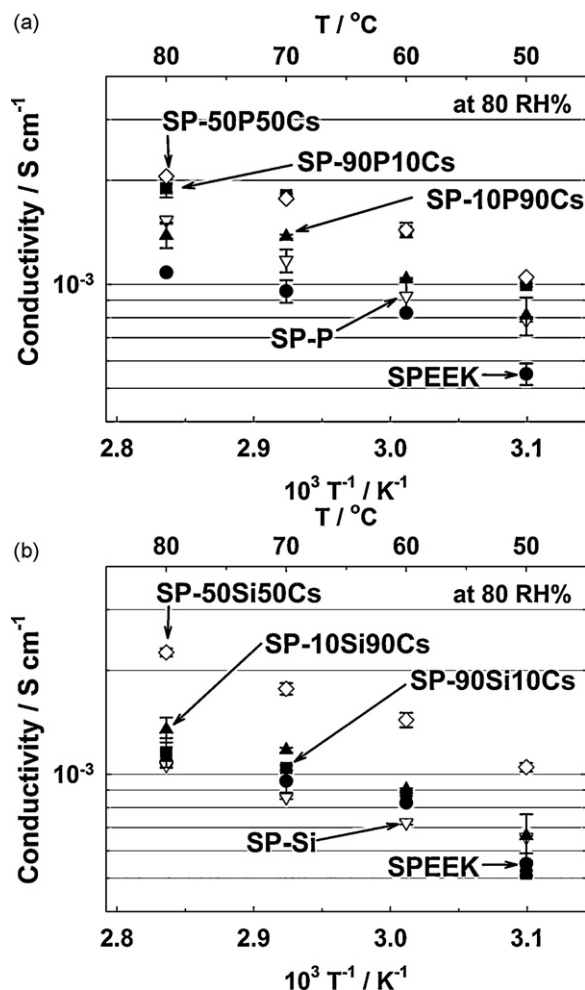


Fig. 6. Conductivity of various composite electrolytes at 80 RH% as a function of temperature: (a) WPA6-CsHSO₄-SPEEK systems and (b) WSiA6-CsHSO₄-SPEEK systems.

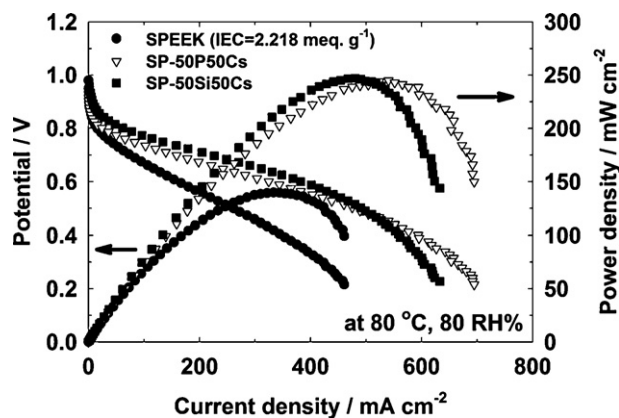


Fig. 7. The fuel cell polarization of an MEA curves at 80 °C and 80 RH%. The H₂ and air were used as fuel and oxidant, respectively; and commercially available Pt-loaded carbon paper sheet (Pt=0.5 mg cm⁻²) was used as an electrode. (●), (▽) and (■) correspond to curves for pure SPEEK, 50WPA6-50CsHSO₄-SPEEK and 50WSiA6-50CsHSO₄-SPEEK composite electrolytes, respectively.

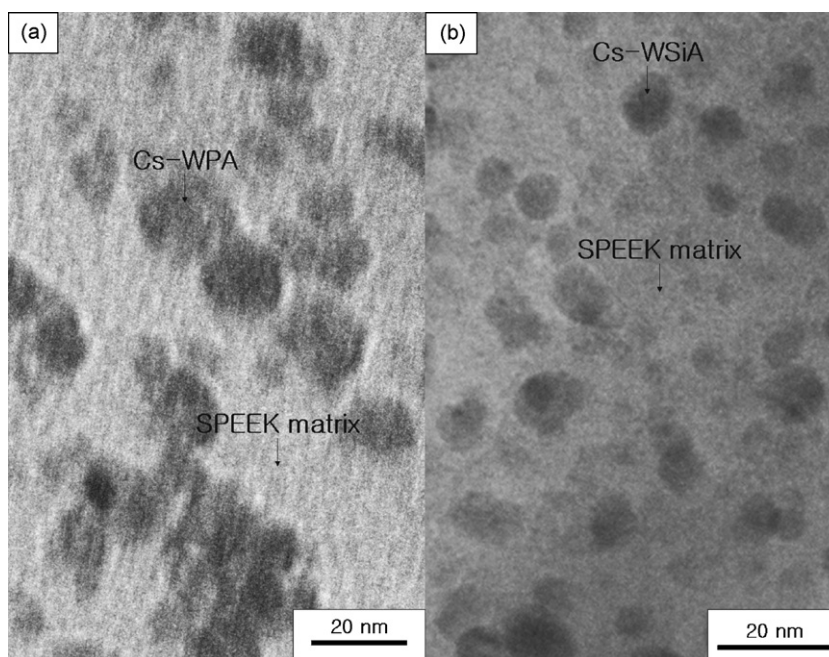


Fig. 8. TEM image for composite electrolyte membranes: (a) SP-50P50Cs and (b) SP-50Si50Cs.

curves of the SP-50P50Cs and SP-50Si50Cs composite electrolytes, respectively. The open circuit voltages (OCVs) of the pure SPEEK, SP-50P50Cs, and SP-50Si50Cs composite electrolytes are 0.980, 0.957, and 0.971 V, respectively, and the maximum power densities are 140, 245, and 247 mW cm^{-2} , respectively. From conductivity and single cell test results, better performance was obtained for 50P50Cs- and 50Si50Cs-containing SPEEK composite electrolytes. These results are consistent with the specific surface area and pore volume of 50P50Cs and 50Si50Cs, which have the highest specific surface areas and pore volumes in CsWPA and CsWSiA series (see Table 1). In Table 2, the addition of inorganic solid acids into SPEEK slightly lowered the open circuit voltage (OCV), which can be ascribed to the difference in the gas permeation property of the composite electrolytes [22]. It is noteworthy that fuel cells using composite electrolytes show higher current densities at given voltages of 700 and 600 mV than those using pure SPEEK, SP-P, and SP-Si in spite of their lower OCVs.

Fig. 8 shows the comparison of transmission electron microscopy (TEM) images for SP-50P50Cs and SP-50Si50Cs composite electrolytes. Even after the formation of electrolyte sheet, composite particles are clearly seen in both TEM images. The TEM images indicate that the particle sizes of the composites are smaller than 20 nm in diameter. Three-dimensional proton-conductive paths were formed between homogeneously distributed composite particles and $-\text{HSO}_4^-$ dissociated from CsHSO_4 in the SPEEK matrix.

A possible proton conducting pathway and mechanism in mechanochemically treated Cs-HPAs-containing SPEEK composite electrolytes under hydrous conditions are shown in Fig. 9. Initially, the proton percolates through a three-dimensional complex cluster, and then hops to the surface of Cs-HPAs particles, which consist of hydrogen bonding between surface of Cs-HPAs and $-\text{SO}_3\text{H}$ in SPEEK. This forms an activated protonated site. This site then forwards the proton to the neighboring site, which in turn passes it on to the next neighboring site, and the series continues causing proton conduction. Furthermore, the improved water uptake by modified Cs-HPAs and residual $-\text{HSO}_4^-$ which dissociated from CsHSO_4 , in the surface of composites probably support the proton transportation.

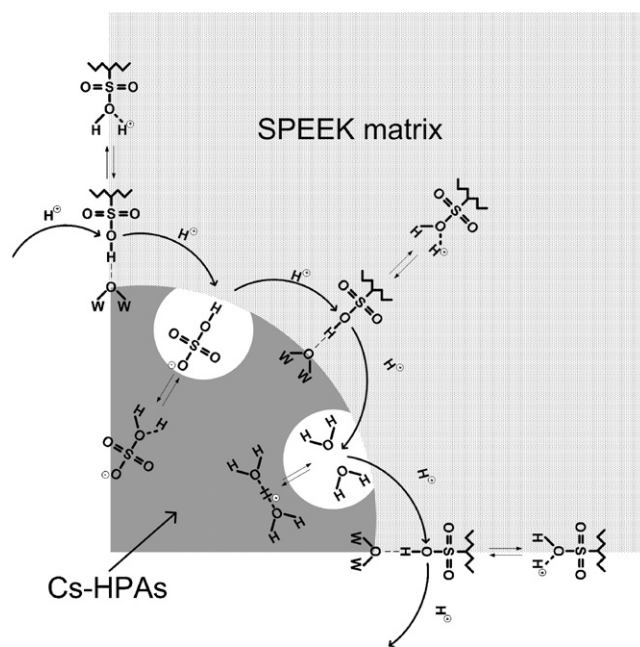


Fig. 9. Proposed proton conducting pathway and mechanism in mechanochemically treated Cs-HPAs with SPEEK system under hydrous conditions.

4. Conclusions

Cs-substituted HPAs (Cs-HPAs) were synthesized by mechanochemical treatments and subsequently incorporated into SPEEK to form composite electrolytes. Proton conductivity and fuel cell performance of these composite electrolytes were significantly improved by the introduction of the inorganic solid acids, $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ or $\text{Cs}_x\text{H}_{4-x}\text{SiW}_{12}\text{O}_{40}$, in the SPEEK matrix. Maximum power densities of 245 and 247 mW cm^{-2} were obtained for 50P50Cs- and 50Si50Cs-containing SPEEK (1/5 by weight) composite electrolytes, respectively; from single cell tests at 80 °C and 80 RH%. Mechanochemically modified Cs-HPAs

added to SPEEK caused a large increase in number of sites in the composite electrolyte for protonation, which are proposed to consist of hydrogen bondings between the surface of Cs-HPAs and, not only HSO_4^- dissociated from CsHSO_4 but also SO_3H groups in the SPEEK.

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