A Flexible CsH₅(PO₄)₂-Doped Composite Electrolyte Membrane for Intermediate-Temperature Fuel Cells

Xiaojing Chen^a, Wen Wen^b, Jing Hu^c, Hejia Su^d, Haibin Li^{e*}, Xiangyang Kong^a, Marta Boaventura^f

^a School of Materials Science and Engineering, Shanghai Jiao Tong University, 800 Dong Chuan Road, Shanghai 200240, China

^b School of Mechanical Engineering, Shanghai Institute and Technology, 100 HaiQuan Road, Shanghai 200240, China

^c The Fifth Research Laboratory, Northwest Institute of Mechanical and Electrical Engineering, 5 Biyuan Road, Xianyang 712000, Shaanxi, China

^d Computer and Information Science, University of California, Santa Cruz, 1156 High Street, Santa Cruz, CA 95064, USA

^e Institute of Fuel Cells, School of Mechanical Engineering, Shanghai Jiao Tong University, 800 Dong Chuan Road, Shanghai 200240, China

^f LEPABE, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

*Corresponding author: haibinli@sjtu.edu.cn (H. Li); Tel.: +86 21 34206249; fax: +86 21 34206249

ABSTRACT: Based on CsH₅(PO₄)₂, sulfonated poly(ether ether ketone) (SPEEK), and phosphosilicate sol, proton-conducting CsH₅(PO₄)₂/phosphosilicate/SPEEK composite electrolyte membranes have been prepared by a sol–gel method followed by mechanical ball-milling. The chemical structures, morphologies, thermal performances, stability, and

proton conductivities of the composite electrolyte membranes were investigated. After incorporating the SPEEK polymer, these composite membranes exhibited adequate flexibility and mechanical performance; despite inorganic content of up to 80 wt%, a tensile strength of 6.2 MPa was maintained. Specifically, the composite electrolyte membrane displays a high proton conductivity of 14.6 mS cm^{-1} at 250°C under 47% $\text{H}_2\text{O}/\text{N}_2$ atmosphere. A fuel cell equipped with the composite electrolyte membrane showed a stable output voltage over the continuous measurement of 50 h under a constant output current density of 40 mA cm^{-2} .

Keywords: Cesium pentahydrogen diphosphate; Intermediate-temperature fuel cells; Phosphosilicate sol; Solid acids; Sulfonated poly (ether ether ketone).

1. Introduction

Fuel cells are electrochemical devices that directly convert chemical energy (e.g., hydrogen and methanol) into electrical energy [1,2]. Intermediate-temperature fuel cells (ITFCs), which operate at $200\text{--}600^\circ\text{C}$, are superior to low- and high-temperature fuel cells in many aspects [3-7]. For example, they offer reduced electrode catalyst poisoning by carbon monoxide [7,8], lower Pt electrode material requirements [9], less complicated water management, and more responsive kinetics and diffusion rates [7,10,11]. ITFCs broaden the range of applicable materials and extend material lifespans compared to high-temperature fuel cell.

Due to their stability at high temperatures (between 100 and 250°C) and their high protonic conductivity, solid acids can be used as ITFC electrolyte application material. CsHSO_4 and CsH_2PO_4 are solid acid compounds that can be used as electrolytes at intermediate temperatures. As these materials heat, a phase transition occurs, accompanied by an increase of several orders of magnitude in their ionic conductivity. This change is referred to as the

superprotonic phase transition. CsHSO_4 displays a superprotonic phase transition at 141°C and its decomposition/melting at approximately $200\text{--}230^\circ\text{C}$, having proton conductivity of $8 \times 10^{-3} \text{ S cm}^{-1}$ at 160°C [12]. CsH_2PO_4 experiences a superprotonic phase transition at around 230°C , having a proton conductivity of $2.2 \times 10^{-2} \text{ S cm}^{-1}$ at 240°C [13].

Cesium pentahydrogen diphosphate, $\text{CsH}_5(\text{PO}_4)_2$, melts at around 154°C and has a broader operating temperature range, making it a promising alternative solid acid electrolyte for use at intermediate temperatures. Its melting facilitates anhydrous proton transport and its proton conductivity increases rapidly up to 200 mS cm^{-1} above 160°C under 30% $\text{H}_2\text{O}/\text{Ar}$ atmosphere [14]. To maintain high proton conductivity and prevent $\text{CsH}_5(\text{PO}_4)_2$ from dehydrating, humidified conditions are necessary [15]. Since chemical bonds do not exist between the matrix particles in $\text{CsH}_5(\text{PO}_4)_2$ -based electrolytes, $\text{CsH}_5(\text{PO}_4)_2$ offers unsatisfactory mechanical integrity at temperatures higher than 154°C [16]. The thicknesses of these pellet electrolytes normally exceed 1 mm [15], which is necessary to maintain an acceptable mechanical strength [17] as well as to prevent gas leakage [18]. As is well known, the area-specific resistance (ASR) of an electrolyte membrane is given by t/σ , where t is the electrolyte thickness and σ is the conductivity. Area-specific resistance of pellet-form electrolytes is very high, hindering their application in ITFCs [15]. Hibino et al. reported several works on the topic of inorganic/organic composite electrolytes using metal phosphates as the proton conductor for ITFCs [7,19-22]. By adding organic binders, they prepared $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$ composite membranes with a thickness of less than $150 \text{ }\mu\text{m}$, having a relatively low ASR of $0.24 \text{ }\Omega \text{ cm}^2$ [7]. Therefore, the reduction of electrolyte thickness and the development of a new matrix that offers an interconnected network and stability at

intermediate temperatures is necessary for the practical application of $\text{CsH}_5(\text{PO}_4)_2$ in ITFCs.

Many polymers are regarded as promising matrices that can be cast from organic solutions in a convenient and inexpensive process. Qing et al. [23] reported an organic/inorganic composite electrolyte with conductivity up to 10 mS cm^{-1} that was based on polyvinylidene fluoride and CsH_2PO_4 . Boysen et al. [24] reported composite electrolytes composed of CsHSO_4 and polyvinylidene fluoride that showed conductivities up to 3 mS cm^{-1} . The superprotonic transition temperatures of these composite electrolytes proved to be unaffected by the presence of the polymer, and these materials exhibited a certain degree of flexibility.

Due to its excellent mechanical properties, acceptable proton conductivity, and thermal stability up to 250°C , SPEEK was used as the polymer matrix in this work [25-27]. Additionally, SPEEK is soluble in several polar solvents, such as DMF [26], resulting in good membrane-forming ability, and thus it can be used to prepare composite electrolyte membranes by a solution-casting method. In the present work, composite electrolyte membranes have been fabricated by combining $\text{CsH}_5(\text{PO}_4)_2$, SPEEK, and phosphosilicate sol in a mechanical ball-milling process followed by casting from solution. In these composite electrolyte membranes, $\text{CsH}_5(\text{PO}_4)_2$ serves as the proton conductor, SPEEK as the supporting polymer matrix, and phosphosilicate sol as a binder.

2. Experimental

2.1. Materials

$\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS, >96.0%, Shanghai Sinopharm Chemical Reagent Co. Ltd., Shanghai, China), H_2SO_4 (95–98 wt%, Shanghai Sinopharm Chemical Reagent Co. Ltd.), H_3PO_4 (85 wt% in water, Shanghai Sinopharm Chemical Reagent Co. Ltd.), *N*,

N-dimethylacetamide (DAMc, Shanghai Lingfeng Chemical Reagent Co. Ltd., Shanghai, China), Cs_2CO_3 (99.9% trace metals basis, Aladdin, CA, USA), poly(ether ether ketone) (PEEK, Grade 450-P, Victrex Inc., UK), and silver paste (DAD-40, Shanghai Research Institute of Synthetic Resins of China, Shanghai, China) were used as received without further purification.

2.2. Preparation

$\text{CsH}_5(\text{PO}_4)_2$ was synthesized from Cs_2CO_3 and H_3PO_4 as starting materials. An aqueous solution of $\text{Cs}_2\text{CO}_3/\text{H}_3\text{PO}_4$ in a molar ratio of 1:4 was concentrated to dryness overnight at 100°C and the residue was protected from moisture prior to use. SPEEK with a degree of sulfonation (DS) of 69.3% was obtained by sulfonating PEEK according to a procedure described in detail elsewhere [28]. A phosphosilicate sol was prepared by a sol–gel method as described in our previous publication [29]. Briefly, the requisite amounts of TEOS, hydrochloric acid, and deionized water were mixed and stirred for 1 h in an ice-bath until the solution became transparent. The requisite amount of H_3PO_4 was then added to the transparent solution in a molar ratio of 3:7 (H_3PO_4 : TEOS), and stirring was continued for 30 min in an ice-bath to form the phosphosilicate sol.

To obtain the composite electrolyte membranes, SPEEK was dissolved in DMAc to produce a 12.5 wt% solution. The phosphosilicate sol was then added to batches of this solution and the mixtures were stirred for 1 h at room temperature. The requisite amounts of $\text{CsH}_5(\text{PO}_4)_2$ were then combined with the mixed solutions of SPEEK and phosphosilicate sol. The resulting mixture was stirred magnetically for 20 min at room

temperature, and then milled in a planetary ball-milling apparatus (QM-3SP2, NanDa Instrument Plant) for 72 h at 580 rpm. Next, the resulting slurries were cast onto cleaned glass plates using a casting knife and dried at 70°C for 5 h to form membranes. After detaching the membranes from the glass plates, the membranes were subjected to hydrothermal treatment at 155°C for 5 h to produce the final composite electrolyte membranes. (See Figure 1 for a flowchart of this procedure.) Phosphosilicate sol (PSi) composition was calculated in terms of P_2O_5 (from H_3PO_4) and SiO_2 (from TEOS). Membranes prepared with different amounts of $CsH_5(PO_4)_2$ and PSi are denoted as $(xCs/(10-x)PSi)/SPEEK$; the total weight ratio of inorganics (PSi and $CsH_5(PO_4)_2$) to organics (SPEEK) was kept fixed at 8:2, while, among the inorganics, the amounts of $CsH_5(PO_4)_2$ and PSi were varied. The values of x are listed in Table 1.

Other samples mentioned in the characterization and discussion sections were also prepared. (1) Pure SPEEK membrane: To form a membrane, SPEEK was dissolved in DMAc to form a 15 wt% solution, and then cast onto a glass plate and dried at 70°C for 8 h. (2) Composite membrane of phosphosilicate sol and SPEEK (designated as PSi/SPEEK): SPEEK was dissolved in DMAc to form a 15 wt% solution, and then the phosphosilicate sol was mixed with this solution in a weight ratio of SPEEK: PSi = 7:3. The mixture was agitated for 1 h at room temperature, and then milled in a planetary ball-milling apparatus for 72 h at 580 rpm. Finally, the slurry was cast onto a cleaned glass plate using a doctor blade and dried at 70°C for 7 h to form the membrane.

2.3. Characterization

The crystalline structures of the various samples were characterized by XRD (Bruker D8 Advance, Cu- K_{α} , $6^{\circ} \text{ min}^{-1}$). FTIR spectra of the respective samples were recorded in the range $4000\text{--}400 \text{ cm}^{-1}$ on a Nicolet 6700 FTIR spectrometer using KBr pellets composed of 3 wt% samples and 97 wt% KBr. Thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC) were performed on a simultaneous DSC-TGA apparatus (TA Q600). All samples were pre-heated to 150°C , cooled to 90°C , and then heated to 500°C at a rate of $10^{\circ}\text{C min}^{-1}$ in a flow of air of 100 mL min^{-1} . The mechanical properties of the composite membranes were assessed on a Perkin-Elmer dynamic mechanical analyzer (DMA 8000) using a DMA-controlled force module with a stretching speed of 0.3 N min^{-1} at room temperature. Composite membrane samples, with a surface size of $25 \times 5 \text{ mm}^2$, were used for the tests. The elemental compositions of the composite membranes were analyzed by means of a scanning electron microscopy (SEM, JSM-7800F) equipped with an energy-dispersive X-ray detector (EDS, Thermo Scientific). The method of liquid nitrogen brittle fracture was used to acquire cross-sections of the membranes.

The conductivities of composite electrolyte membranes were determined by means of an impedance/gain phase analyzer (SI 1260, Solartron) controlled by Z-plot electrochemical impedance software over the frequency range from 10^{-1} to 10^7 Hz with a voltage amplitude of 20 mV. Measurements were carried out over the temperature range from 100°C to 250°C under a 47% $\text{H}_2\text{O}/\text{N}_2$ atmosphere generated by bubbling dry N_2 through water held at 80°C . A two-electrode a.c. method described in a

previous study [30] was applied to the measurement. Two parallel silver stripe electrodes connected with gold wires were obtained by painting silver paste on the composite electrolyte membrane. To obtain a steady state, a time interval of 1 h between adjacent temperatures (testing temperature elevated by 10°C) was selected. The electrolyte resistance was approximated from the intercept on the real axis at the high-frequency end in the impedance spectra. The electrolyte conductivity was determined according to the following equation:

$$\sigma = a/tLR \quad (1)$$

where σ is the conductivity, a is the distance between the two parallel electrodes, L is the length of the silver stripe electrodes, t is the thickness of the composite membrane, and R is the known resistance of the composite membrane.

A single fuel cell was fabricated by using the (9Cs/1PSi)/SPEEK composite electrolyte membrane. The composite electrolyte membrane was sandwiched between two gas diffusion electrode (GDEs) with Pt loading of 0.5 mg cm⁻² (S10CC, SGL Group) without hot-pressing procedure to form a membrane-electrode assembly (MEA) with an active area of 5 cm².

The fuel cell was fuelled with humidified hydrogen at the anode and dry oxygen at the cathode, respectively. The gas flow rates of H₂ and O₂ were both set to 60 cm³ min⁻¹. Humidification of H₂ at the anode was obtained by feeding water with a flow rate of 0.026 ml min⁻¹ into the gas flow. The durability test of the fuel cell was conducted by operating under a constant output current density of 40 mA cm⁻² at 180°C.

3. Results and discussion

3.1. Crystalline and chemical structures of the composite electrolyte membranes

XRD was employed to investigate the crystalline structures of the composite electrolyte membranes. Figure 2 shows the XRD patterns of the various membranes and $\text{CsH}_5(\text{PO}_4)_2$ powder. The XRD pattern of the $\text{CsH}_5(\text{PO}_4)_2$ powder is in good agreement with that in a previous report [15], and no signals due to any by-products can be observed. The patterns of the pure SPEEK and PSi/SPEEK membranes showed these samples to be amorphous. For the composite electrolyte membranes with different amounts of $\text{CsH}_5(\text{PO}_4)_2$, the peaks assigned to $\text{CsH}_5(\text{PO}_4)_2$ bore a striking resemblance to those of $\text{CsH}_5(\text{PO}_4)_2$ powder. This implies that the crystalline structure of $\text{CsH}_5(\text{PO}_4)_2$ in the composite electrolyte membranes was not affected by the membrane-forming process or the amount of phosphosilicate.

FTIR was used to characterize the functional groups present in the different solid acid materials. As shown in Figure 3, the infrared spectrum of $\text{CsH}_5(\text{PO}_4)_2$ powder features broad absorption bands at $\nu = 2800, 2348, \text{ and } 1644 \text{ cm}^{-1}$, which indicate strongly hydrogen-bonded systems at the corresponding positions [31-33]. $\text{CsH}_5(\text{PO}_4)_2$ has five robust hydrogen bonds per formula unit; while the fifth is shorter, four are nearly identical, such that the salt formula might be written as $\text{CsH}(\text{H}_2\text{PO}_4)_2$ [32]. The intense absorption bands observed at $\nu = 1286, 1213, 1128$ (with a shoulder at 1086), 982, and 870 cm^{-1} correspond to the stretching vibrations of the acid phosphate (H_2PO_4^-) ions, while the bands at $\nu = 580, 546, 522, 496, 469, \text{ and } 421 \text{ cm}^{-1}$ correspond

to their bending vibrations. For the pure SPEEK membrane, the absorption peaks at $\nu = 1079, 1030, \text{ and } 688 \text{ cm}^{-1}$ can be assigned to the O=S=O stretching vibrations of the sulfonic acid group, confirming successful sulfonation [32,34,35]. The band at $\nu = 1642 \text{ cm}^{-1}$ corresponds to the carbonyl group of SPEEK [36], and the broad band at around $\nu = 3439 \text{ cm}^{-1}$ can be allocated to the O–H vibration of sulfonic acid groups engaging with water molecules [34,37]. Aside from the bands assigned to sulfonic acid groups and O–H vibration, other bands types can also be observed in the spectra of the PSi/SPEEK membranes. The bands at around $\nu = 480 \text{ and } 848 \text{ cm}^{-1}$ can be assigned to the characteristic peaks of Si–O–Si, and that at around $\nu = 974 \text{ cm}^{-1}$ can be ascribed to the stretching of Si–OH. These features provide evidence for the formation of a silicate network during the gelation. Furthermore, the bands at around $\nu = 1259 \text{ and } 1333 \text{ cm}^{-1}$ can be assigned to P=O stretching originating from the introduction of H_3PO_4 [38-41]. The spectrum of the composite electrolyte membranes is much more complex than those of its components; however, identifying each band characteristic type of the bonds discussed above is still effortless. In addition, bands at $\nu = 1083 \text{ and } 1115 \text{ cm}^{-1}$ can be ascribed to P–O–Si bonds.

3.2. Morphology of the composite electrolyte membranes

The morphologies of the composite electrolyte membranes were observed by SEM/EDS. Figure 4 shows the SEM results of all the investigated samples. Figure 4 (a), (c), and (e) show the cross-sectional morphologies of (7Cs/3PSi)/SPEEK, (8Cs/2PSi)/SPEEK, and (9Cs/1PSi)/SPEEK composite electrolyte membranes before the conductivity tests. Figure 4 (b), (d), and (f) show the cross-sectional morphologies

of the respective composite electrolyte membranes after the conductivity tests (from 100 to 250°C; test time 11 h). From Figure 4 (a), (c), and (e), we can easily see many block-like particles embedded within the composite membranes, and their numbers increase notably with the increase of the amount of added $\text{CsH}_5(\text{PO}_4)_2$. Figure 4 (g) and (h) are high-magnification SEM images at different scales of (7Cs/3PSi)/SPEEK membrane. Figure 4 (g) shows that block-like particles were entangled within the matrix, in which no accumulation of the glass particles was determined, and Figure 4 (h), at higher magnification, shows that the matrix consisted of a net-like structure with globular structures embedded therein.

In order to investigate the chemical compositions of the three structures (block-like, net-like, and globular), EDS analysis was conducted. Figure 5(a) is the SEM image of (7Cs/3PSi)/SPEEK composite electrolyte membrane. Figure 5 (b), (c), and (d) show the EDS results at the selected sites: Area1, Area2, and Point1 in Figure 5 (a). From the EDS results in Figure 5 (b) and the XRD patterns in Figure 2, we have determined that the block-like structure was composed of $\text{CsH}_5(\text{PO}_4)_2$, and the small amounts of C and Si may be due to the slight quantity of phosphosilicate containing unhydrolyzed TEOS, which frequently happens in a typical sol–gel process. The small amount of phosphosilicate may attach to the surfaces of the $\text{CsH}_5(\text{PO}_4)_2$ blocks. From Figure 5 (c), the net-like structure evidently contained quite a lot of C and S. The net-like structure may have been formed as follows: SPEEK may have been covered or wrapped by the incorporated phosphosilicate sol. During the mixing and milling processes, some fine powder of $\text{CsH}_5(\text{PO}_4)_2$ may have become attached on the SPEEK skeleton with the

help of the adhesiveness of the phosphosilicate sol. Such a continuous net-like matrix containing dispersed block-like $\text{CsH}_5(\text{PO}_4)_2$ particles could provide the composite membrane with sufficient mechanical flexibility, which is essential for membrane electrode assembly (MEA) for fuel cells, and with potential intermediate-temperature proton conducting ability. Figure 5 (d) shows that the globular structure contained Si, P, and Cs as well as trace amounts of C and S. It is deduced that the globular structure may have stemmed from the aggregated phosphosilicate particles, which were bound by small amounts of $\text{CsH}_5(\text{PO}_4)_2$ and SPEEK.

By comparison of SEM images before (Figure 4 (a), (c) and (e)) and after (Figure 4 (b), (d) and (f)) the conductivity tests, it is evident that the $\text{CsH}_5(\text{PO}_4)_2$ blocks became more connected. This may be due to the melting and agglomeration of $\text{CsH}_5(\text{PO}_4)_2$ during the conductivity test. The sizes of $\text{CsH}_5(\text{PO}_4)_2$ particles shown in Figure 4 (a)–(f) are considerably smaller than those in Figure 4 (i). This implies that the ball-milling process was very helpful for reducing the size of $\text{CsH}_5(\text{PO}_4)_2$ particles. In the composite electrolyte membranes, a high content of $\text{CsH}_5(\text{PO}_4)_2$ should be beneficial for improving the conductivity, but it could also lead to excessive agglomeration of $\text{CsH}_5(\text{PO}_4)_2$ particles, making the membrane more fragile.

3.3. Thermal and Mechanical Properties of the Membranes and $\text{CsH}_5(\text{PO}_4)_2$ Powder

Figure 6 (a) and (b) show normal TGA and DSC curves of SPEEK, PSi/SPEEK, $\text{CsH}_5(\text{PO}_4)_2$, and the composite membranes with varying amounts of $\text{CsH}_5(\text{PO}_4)_2$. The TGA curve of the SPEEK membrane displays two typical degradation stages that

correspond to the degradation of the sulfonic acid groups and thermal oxidation of the polymer main chain. The first weight loss step is mainly associated with loss of the sulfonic groups in the range of 180–300°C. The second weight loss step is attributable to thermal degradation of the main SPEEK chain beyond 300°C. In contrast to pure SPEEK, the degradation of the PSi/SPEEK membrane was considerably delayed due to the incorporation of the phosphosilicate component. For $\text{CsH}_5(\text{PO}_4)_2$, weight loss commenced at 165°C, and only one degradation step was observed, which presumably corresponded to its dehydration. For the composite electrolyte membranes with various contents of $\text{CsH}_5(\text{PO}_4)_2$, the three curves show similar trends, and resemble that of the SPEEK membrane. Therefore, their degradations are likely caused in large part by degradation of the SPEEK membrane, combined with the dehydration $\text{CsH}_5(\text{PO}_4)_2$.

As shown in Figure 6 (b), in the DSC curves of SPEEK and PSi/SPEEK membranes, the peaks at around 310°C were in accordance with decomposition of the PEEK main chain. For $\text{CsH}_5(\text{PO}_4)_2$, a large endothermic peak appeared at 150°C, attributable to its melting [32,42]. The endothermic peak of (9Cs/1PSi)/SPEEK was noted at 143°C, which was lower than that of $\text{CsH}_5(\text{PO}_4)_2$; this indicates a lower melting point than that of pure $\text{CsH}_5(\text{PO}_4)_2$. Furthermore, the corresponding endothermic peaks of (8Cs/2PSi)/SPEEK and (7Cs/3PSi)/SPEEK almost disappeared. Melting point depression has also been viewed in a $\text{CsH}_5(\text{PO}_4)_2$ -doped glass membrane [10], pellet electrolytes of $\text{CsH}_5(\text{PO}_4)_2/\text{SiO}_2$ [15,43,44], $\text{CsH}_5(\text{PO}_4)_2/\text{SiP}_2\text{O}_7$ [45], and $\text{CsHSO}_4/\text{SiO}_2$ [46]. In these structures, $\text{CsH}_5(\text{PO}_4)_2$ and CsHSO_4 are the proton conductors, while SiO_2 and SiP_2O_7 are the matrices. Interaction between two components at the

contacting interface is normally the cause of melting point depression [43,44,46]. In this work, the $\text{CsH}_5(\text{PO}_4)_2/\text{PSi}/\text{SPEEK}$ composite electrolyte membranes contained $\text{CsH}_5(\text{PO}_4)_2$ and phosphosilicate. As confirmed by SEM and EDS studies, these components were in contact, with an extensive interface between them. As a result, the interfacial interaction between $\text{CsH}_5(\text{PO}_4)_2$ and phosphosilicate leads to melting point depression.

Figure 7 depicts the stress–strain curve measurement of the composite electrolyte membranes at room temperature. As can be seen, the (7Cs/3PSi)/SPEEK membrane displayed the best mechanical properties, with a maximum tensile strength of 6.2 MPa and a maximum elongation of 4.8%, despite the fact that the inorganic content in this composite electrolyte membrane was as high as 80 wt%; the total weight ratio of inorganics (PSi and $\text{CsH}_5(\text{PO}_4)_2$) to organics (SPEEK) was kept fixed at 8:2. This indicates that the mechanical properties of the composite electrolyte membrane is capable of satisfying the needs of MEA fabrication in fuel cells.

3.4. Proton conductivity of the composite electrolyte membranes

Figure 8 depicts the proton conductivities of the composite electrolyte membranes with various quantities of $\text{CsH}_5(\text{PO}_4)_2$, the pure SPEEK membrane, and a PSi/SPEEK membrane measured under humidified 47% $\text{H}_2\text{O}/\text{N}_2$ conditions.

The conductivity of the pure SPEEK membrane first increased and then decreased with increasing temperature, and a maximum conductivity of $5.32 \times 10^{-6} \text{ S cm}^{-1}$ was obtained at 200°C. The decrease in the conductivity of the pure SPEEK membrane may be related to the loss of chemically bound water molecules and degradation of the

pure SPEEK. The conductivity of the PSi/SPEEK membrane showed a slow increase from 100 to 190°C, then a rapid increase from 190 to 240°C, and finally a slight decrease between 240 and 250°C. The maximum conductivity at 240°C was 1.7×10^{-4} S cm⁻¹. Comparison of the conductivities of PSi/SPEEK and pure SPEEK membranes shows that the incorporation of phosphosilicate greatly increases the conductivity. This is because phosphosilicate is strongly hygroscopic, resulting in the absorption of more water molecules under the same conditions; it also contributes additional functional groups (i.e., SiOH and POH, which can furnish pathways for proton transfer) [29]. The decrease in conductivity of the PSi/SPEEK membrane above 240°C may be attributed to the desorption of chemical bound water molecules, which are important for water-mediated proton conduction.

Unlike for the pure SPEEK and PSi/SPEEK membranes, the conductivities of the composite electrolyte membranes with various contents of CsH₅(PO₄)₂ showed rapid increases in the low temperature range, and then showed slow and sustained increases in the high temperature range. Furthermore, their conductivities were higher in the high temperature range but lower in the low temperature range with increasing CsH₅(PO₄)₂ content. This led to the appearance of feature points in each of these curves, and the temperatures of these feature points for the (9Cs/1PSi)/SPEEK, (8Cs/2PSi)/SPEEK, and (7Cs/3PSi)/SPEEK composite electrolyte membranes were 140, 130, and 120°C, respectively. These feature points should correspond to the melting point of CsH₅(PO₄)₂, which was confirmed by the DSC curves in Figure 6 (b). In the low temperature range below the melting point, CsH₅(PO₄)₂ is in the solid state

and has low proton-conducting capability, but phosphosilicate possesses high proton conductivity under humidified conditions [47,48]. Consequently, the predominant proton-conducting carriers should be derived from phosphosilicate, rather than from $\text{CsH}_5(\text{PO}_4)_2$, so that the conductivities of the $\text{CsH}_5(\text{PO}_4)_2/\text{PSi}/\text{SPEEK}$ composite electrolyte membranes increase with increasing phosphosilicate content. In the high temperature range above the melting point, $\text{CsH}_5(\text{PO}_4)_2$ is in the liquid state, resulting in a high proton conductivity [42,43]. Consequently, $\text{CsH}_5(\text{PO}_4)_2$ is primarily accountable for the proton conduction of the composite electrolyte membranes; thus, their conductivities increase relative to the increasing of $\text{CsH}_5(\text{PO}_4)_2$ content. Among the prepared composite electrolyte membranes, (9Cs/1PSi)/SPEEK showed the highest conductivity of 14.6 mS cm^{-1} at 250°C . It is worth noting that the composite electrolyte membranes showed no decrease in conductivity up to 250°C in the measured temperature range. However, at temperatures higher than 250°C , they softened and became deformed.

The ASR value is more important than proton conductivity itself in evaluating the practical performance of fuel cells [49]. The cross-section SEM image in Fig. 4(e) show that the (9Cs/1PSi)/SPEEK composite membrane has thickness of $97 \text{ }\mu\text{m}$. From the proton conductivity data in Figure 8, the ASR values of the composite electrolytes at 250°C can be calculated to be $0.664 \Omega \text{ cm}^2$. The ASR value is lower than that of $\text{CsH}_5(\text{PO}_4)_2/\text{SiP}_2\text{O}_7$ pellets of thickness 1–2 mm with a conductivity of 116 mS cm^{-1} at 230°C [15], but higher than $0.37 \Omega \text{ cm}^2$ of solid acid/phosphate ($\text{CsH}_5(\text{PO}_4)_2/\text{Si-P-O}$

matrix) thin film with a thickness of 106 μm , which was prepared by utilizing electrostatic spray deposition [16].

3.5. The stability of the composite electrolyte membranes

As shown in Figure 9, reproduction of the conductivity for (9Cs/1PSi)/SPEEK composite electrolyte membrane was evaluated in heating–cooling cycles under humidified 47% $\text{H}_2\text{O}/\text{N}_2$ conditions. The interval time between both heating–cooling cycles was 24 h. Upon heating for a first time, the conductivity showed a steep increase by 3 orders of magnitude in the low temperature range of 100–140°C, and a slow increase in the high temperature range of 140–250°C. In the cooling process, the composite electrolyte membrane kept relatively high conductivity with a slight decrease. It is reasonable that, during heating $\text{CsH}_5(\text{PO}_4)_2$ is in the liquid state in temperatures above the melting point, resulting in a high proton conductivity, and during cooling $\text{CsH}_5(\text{PO}_4)_2$ exists as supercooled liquid, keeping the high conductivity [50]. In the second heating–cooling cycle, the conductivity was slightly lower than those in the first cycle, due to the degradation of SPEEK, which was associated with loss of the sulfonic groups. It is confirmed that the conductivity of the composite electrolyte membrane was reproducible upon heating–cooling cycles.

In order to evaluate the stability of the composite electrolyte membrane operating in a fuel cell, a longevity experiment was conducted. The fuel cell was assembled by using (9Cs/1PSi)/SPEEK composite electrolyte membrane. Figure 10 shows the stability of the output voltage with time under a constant output current density of 40 mA cm^{-2} . After an initial increase from ca. 0.37 to 0.45 V, during the continuous

measurement up to 50 h, the fuel cell equipped with (9Cs/1PSi)/SPEEK composite electrolyte membrane showed a good stability at around 0.45 V. This result demonstrates the high stability of the composite electrolyte membrane under fuel cell conditions.

4. Conclusions

Composite electrolyte membranes were constructed by combining $\text{CsH}_5(\text{PO}_4)_2$, SPEEK, and phosphosilicate sol in a simple sol–gel method, followed by mechanical ball-milling. These membranes exhibited outstanding mechanical, thermal, and conductivity achievement, making them favorable electrolytes for ITFCs. Moreover, they were macroscopically flexible, meeting the requirements of MEA fabrication. Namely, the composite electrolyte membranes were in the solid state at temperatures above 150°C, the melting point of pure $\text{CsH}_5(\text{PO}_4)_2$, likely because SPEEK with phosphosilicate matrices fostered the melt. The (9Cs/1PSi)/SPEEK membrane showed a high conductivity of 14.6 mS cm^{-1} at 250°C under 47% $\text{H}_2\text{O}/\text{N}_2$ atmosphere. The fuel cell equipped with a composite electrolyte membrane showed a stable output voltage over the continuous measurement of 50 h under a constant output current density of 40 mA cm^{-2} . These composite electrolyte membranes with high conductivities above $10^{-3} \text{ S cm}^{-1}$ over broad temperature range of 120–250°C provide a comprehensive temperature range for ITFCs.

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References

- [1] K. Scott, C. Xu, X. Wu, WIREs Energy Environ. 3 (2014) 24-41.
- [2] T.Norby, Nature 410 (2001) 877-878.
- [3] E. Fabbri, L. Bi, D. Pergolesi, E. Traversa, Mater. Views 24 (2012) 195-208.
- [4] J.-D. Kim, T. Mori, I. Honmac, J. Electrochem. Soc. 153 (2006) A508-A514.
- [5] A. Aguadero, L. Fawcett, S. Taub, R. Woolley, K.-T. Wu, N. Xu, J.A. Kilner, S.J. Skinner, J. Mater. Sci. 47 (2012) 3925-3948.
- [6] T.Norby, Nature (2001) 877-878.
- [7] Y. Jin, B. Lee, T. Hibino, J. Jpn. Pet. Inst. 53 (2010) 12-23.
- [8] M. Nagao, A. Takeuchi, P. Heo, T. Hibino, M. Sano, A. Tomitab, Electrochemical and Solid-State Letters 9 (2006) A105-A109.
- [9] M. Mamlouk, J.H. Jang, K.S. J, J. Fuel Cell Sci. Tech. 9 (2012) 1-9.
- [10] G. Qing, R. Kikuchi, A. Takagaki, T. Sugawara, S.T. Oyama, J. Power Sources 272 (2014) 1018-1029.
- [11] G. Qing, R. Kikuchi, A. Takagaki, T. Sugawara, S.T. Oyama, J. Electrochem. Soc. 161 (2014) F451-F457.
- [12] A.I. Baranov, L.A. Shuvalov, N.M. Shchagina, JETP Lett. 36 (1982) 459-462.
- [13] A.I. Baranov, V.P. Khizriichenko, V.A. Sandier, L.A. Shuvalov, Ferroelectrics 81 (1998) 1147-1150.
- [14] H. Muroyama, K. Kudo, T. Matsui, R. Kikuchi, K. Eguchi, Solid State Ionics 178 (2007) 1512-1516.
- [15] T. Matsui, T. Kukino, R. Kikuchi, K. Eguchi, Electrochim. Acta 51 (2006) 3719-3723.
- [16] T. Matsui, T. Noto, H. Muroyama, M. Iijima, K. Eguchi, J. Power Sources 196 (2011) 9445-9450.
- [17] T. Uda, S.M. Haile, Electrochem. Solid State Lett. 8 (2005) A245-A246.
- [18] P. Heo, T.Y. Kim, J. Ha, K.H. Choi, H. Chang, S. Kang, J. Power Sources 198 (2012) 117-121.
- [19] Y. Jin, K. Fujiwara, T. Hibino, Electrochem. Solid-State Lett. 13 (2010) B8-B10.
- [20] Y. Jin, T. Hibino, Electrochim. Acta 55 (2010).
- [21] P. Heo, M. Nagao, T. Kamiya, M. Sano, A. Tomita, T. Hibino, J. Electrochem. Soc. 154 (2007).
- [22] P. Heo, N. Kajiyama, K. Kobayashi, M. Nagao, M. Sano, T. Hibino, Electrochem. Solid State Lett. 11 (2008) B91.
- [23] G. Qing, R. Kikuchi, A. Takagaki, T. Sugawara, S.T. Oyama, J. Electrochem. Soc. 161 (2014) F451-F457.
- [24] D.A. Boysen, C.R.I. Chisholm, S.M. Haile, S.R. Narayanan, J. Electrochem. Soc. 147 (2000) 3610-3613.
- [25] S.D. Mikhailenko, K. Wang, S. Kaliaguine, P. Xing, G.P. Robertson, M.D. Guiver, J. Membr. Sci. 233 (2004) 93-99.
- [26] M. Rikukawa, K. Sanui, Prog. Polym. Sci. 25 (2000) 1463-1502.
- [27] T. Kobayashi, M. Rikukawa, K. Sanui, N. Ogata, Solid State Ionics 106 (1998) 219-225.
- [28] P. Xing, G.P. Robertson, Michael D. Guiver, S.D. Mikhailenko, K. Wang, S. Kaliaguine, J. Membr. Sci. 229

(2004) 95-106.

- [29] Q. Xie, Y. Li, X. Chen, J. Hu, L. Li, H. Li, J. Power Sources 282 (2015) 489-497.
- [30] Q. Xie, Y. Li, J. Hu, X. Chen, H. Li, J. Membr. Sci. 489 (2015) 98-105.
- [31] K. Jaouadia, N. Zouaria, T. Mhiria, M. Giorgib, Phase Transit. 78 (2005) 627-638.
- [32] G.V. Lavrova, E.B. Burgina, A.A. Matvienko, V.G. Ponomareva, Solid State Ionics 177 (2006) 1117-1122.
- [33] P. Colomban, J. Raman Spectrosc. 27 (1996) 747-758.
- [34] N. Intaraprasit, P. Kongkachuichay, J. Taiwan Inst. Chem. Eng. 42 (2011) 190-195.
- [35] Z. Di, Q. Xie, H. Li, D. Mao, M. Li, D. Zhou, L. Li, S.A. Chae, J. Power Sources 273 (2015) 688-696.
- [36] H.K. Kim, H.T. Ju, J.W. Hong, Eur. Polym. J. 39 (2003) 2235-2241.
- [37] N. Zhang, G. Zhang, D. Xu, C. Zhao, W. Ma, H. Li, Y. Zhang, S. Xu, H. Jiang, H. Sun, H. Na, Int. J. Hydrog. Energy 36 (2011) 11025-11033.
- [38] A. Epiphanova, O. Magaev, O. Vodyankina, J. Sol-Gel Sci. Technol. 61 (2012) 509-517.
- [39] P. Massiot, M.A. Centeno, I. Carrizosa, J.A. Odriozola, J. Non-Cryst. Solids 292 (2001) 158-166.
- [40] V.G. Plotnichenko, V.O. Sokolov, V.V. Koltashev, E.M. Dianov, J. Non-Cryst. Solids 306 (2002) 209-226.
- [41] P. Innocenzi, J. Non-Cryst. Solids 316 (2003) 309-319.
- [42] H. Muroyama, T. Matsui, R. Kikuchi, K. Eguchi, J. Electrochem. Soc. 155 (2008) B958-B962.
- [43] T. Matsui, H. Muroyama, R. Kikuchi, K. Eguchi, J. Jpn. Pet. Inst. 53 (2010) 1-11.
- [44] G.V. Lavrova, V.G. Ponomareva, Solid State Ionics 179 (2008) 1170-1173.
- [45] T. Matsui, T. Kukino, R. Kikuchi, K. Eguchi, J. Electrochem. Soc. 153 (2006) A339-A342.
- [46] V.G. Ponomareva, G.V. Lavrova, L.G. Simonova, Solid State Ionics 118 (1999) 317-323.
- [47] H. Li, D. Jin, X. Kong, H. Tu, Q. Yu, F. Jiang, Microporous Mesoporous Mat. 138 (2011) 63-67.
- [48] S. Suzuki, Y. Nozaki, T. Okumura, M. Miyayama, J. Ceram. Soc. Jpn. 114 (2006) 303-307.
- [49] Steele, B.C. H., H. A., Nature 414 (2001) 345-352.
- [50] T. Tezuka, K. Tadanaga, A. Hayashi, M. Tatsumisago, Solid State Ionics 177 (2006) 2463-2466.

Table 1. Composite electrolyte membranes with various amounts of $\text{CsH}_5(\text{PO}_4)_2$.

Sample	x	$\text{CsH}_5(\text{PO}_4)_2$ (wt %)	$\text{P}_2\text{O}_5\text{-SiO}_2$ (wt %)	the molar ratio of P: Si
$(9\text{CsH}_5(\text{PO}_4)_2/1\text{PSi})/\text{SPEEK}$	9	90	10	3:7
$(8\text{CsH}_5(\text{PO}_4)_2/2\text{PSi})/\text{SPEEK}$	8	80	20	3:7
$(7\text{CsH}_5(\text{PO}_4)_2/3\text{PSi})/\text{SPEEK}$	7	70	30	3:7

Figure Captions

Figure 1. Flow chart of the preparation of the composite electrolyte membranes.

Figure 2. XRD patterns of pure SPEEK, $\text{CsH}_5(\text{PO}_4)_2$, PSi/SPEEK, and the composite electrolyte membranes with different amounts of $\text{CsH}_5(\text{PO}_4)_2$.

Figure 3. FTIR spectra of $\text{CsH}_5(\text{PO}_4)_2$ powder and SPEEK, PSi/SPEEK, and the composite electrolyte membranes with different amounts of $\text{CsH}_5(\text{PO}_4)_2$.

Figure 4. SEM cross-sectional morphologies of (a) (7Cs/3PSi)/SPEEK, (c) (8Cs/2PSi)/SPEEK, and (e) (9Cs/1PSi)/SPEEK membranes before the conductivity tests, and (b), (d), and (f) the corresponding membranes after the conductivity tests; (g) and (h) are partially enlarged images of (a), and (i) is an image of $\text{CsH}_5(\text{PO}_4)_2$ powder.

Figure 5. SEM image (a) and EDS results of the (7Cs/3PSi)/SPEEK composite electrolyte membrane; (b) corresponds to Area 1, (c) to Area 2, and (d) to point 1 in SEM image (a).

Figure 6. Typical TGA and DSC curves of SPEEK, PSi/SPEEK, $\text{CsH}_5(\text{PO}_4)_2$, and the composite electrolyte membranes with different amounts of $\text{CsH}_5(\text{PO}_4)_2$.

Figure 7. Stress–strain curves of the composite electrolyte membranes with different amounts of $\text{CsH}_5(\text{PO}_4)_2$.

Figure 8. Temperature dependences of the conductivities of SPEEK, PSi/SPEEK, and (9Cs/1PSi)/SPEEK, (8Cs/2PSi)/SPEEK, and (7Cs/3PSi)/SPEEK composite electrolyte membranes, under 47% $\text{H}_2\text{O}/\text{N}_2$ atmosphere.

Figure 9. Temperature dependence of proton conductivity of (9Cs/1PSi)/SPEEK composite electrolyte membrane upon two heating and cooling cycles.

Figure 10. Output voltage of a fuel cell with the (9Cs/1PSi)/SPEEK composite electrolyte membrane as a function of time for 50 h under an output current density of 40 mA cm^{-2} . The fuel cell was operated at 180°C under humidified H_2 and dry O_2 gases at the anode and the cathode, respectively.