Preparation, Structural Characterization And Proton Conducting Properties of Novel Inorganic/Organic Hybrid Membranes with Chemically Bound Organophosphonic Acid

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Abstract: Novel proton conductive membranes based on inorganic/organic hybrid membranes were synthesized from (trimethoxysilylmethyl)styrene (TMSMS) and phenylvinylphosphonic acid (PhVPA) with various ratios using radical copolymerization followed by sol-gel process. Self-standing, homogeneous, highly transparent membranes were synthesized. TG-DTA analysis indicated that these membranes were thermally stable up to 200 °C. FT-IR and ¹³C NMR revealed that TMSMS was copolymerized with PhVPA successfully. The charged compositions of Si/P almost corresponded to the proportions of Si and P in the hybrid membranes by X-ray fluorescence spectroscopy.

The proton conductivity of the hybrid membranes increased with phosphonic acid content. The proton conductivities of the hybrid membranes of TMSMS/PhVPA=1/4 were higher than 10⁻² S/cm at medium temperatures under saturated humidity. Water was introduced into the hybrid membranes from humidified atmosphere because of hygroscopic nature of phosphonic acid group, and the contribution of H₃O⁺ transport to the proton conductivity increases with temperature under sufficient humidity.

Keywords: Inorganic-organic hybrid; Proton conductive membrane; Sol-gel process; Phenylvinylphosphonic acid; Fuel cell

1. INTRODUCTION

Fuel cell technology has been considered a promising alternative source for future energy because of their high efficiency in the direct conversion of chemical energy into electrical energy without air pollution. Growing attention has been focused on proton exchange membrane fuel cells (PEFCs) for mobile, stationary and portable electrical devices [1]. Proton-conducting perfluorosulfonic polymers, such as Nafions (Du Pont), have many attractive properties including good mechanical strength, good chemical stability and high proton conductivity, and they are widely used in commercial applications [2-3]. However, these membranes have several drawbacks such as complex water management, CO poisoning of Pt anode catalysts and high cost [4]. If PEFCs could be operated at elevated temperatures, many of these issues could be resolved [5-7]. Thus, proton-conducting materials of high conductivity at the intermediate temperature range from 100 °C to 200 °C are required.

Many investigations are carried out to develop proton conducting membranes working at intermediate temperature. The representative examples are organosiloxanes incorporated with H₃PO₄ [8-10] and PBI doped with H₂PO₄ [11]. Despite good proton conductivities, these membranes have inadequate chemical stability. The leaching out of phosphoric acid occurs during operation because of its insufficient interaction with the matrices [12].

We investigated the synthesis of organosiloxane-based inorganic/organic hybrid membranes with chemically bound phosphonic acid. (Trimethoxysilylmethyl)styrene (CH₂=CHC₆H₄CH₂Si(OCH₃)₃, TMSMS) and phenylvinylphosphonic acid (C₆H₄C(PO(OH)₂)=CH₂, PhVPA) were used as starting materials. TMSMS is a styrene derivative of tri-functionalized alkoxysilane, and has a C=C double bond for polymerization as well as Si-OCH₃ bonds. Since Si-O-Si networks are formed by the polycondensation of Si-OCH₃ bonds in the membrane, the hybrid membranes have better chemical and thermal stability than pure organic materials. Furthermore, the organic part of TMSMS includes a benzene ring which is expected to increase the thermal stability of membrane. PhVPA consists of a phenyl group and a C=C double bond for copolymerization with TMSMS. The phenyl group increases the thermal stability of product. The proton-conductive organophosphonic group is directly bound to the hybrid backbone through a carbon-carbon covalent bond as a result of copolymerization with TMSMS. Therefore, the membrane is expected to show good chemical and thermal stability and proton conductivity.

The copolymerization conditions of TMSMS with PhVPA were investigated. The structure and thermal stability of TMSMS/PhVPA were also analyzed. Finally, the proton conductivities of hybrid membranes at various temperatures and relative humidities were studied.

2. Experimental

2.1. Materials

(Trimethoxysilylmethyl)styrene (TMSMS) was synthesized according to the literature [13]. The product was a mixture of meta- and para- substituted isomers of the benzene ring. Phenylvinylphosphonic acid (PhVPA) was synthesized as described in the literature [14].

2.2. Synthesis of TMSMS/PhVPA hybrids

At first, TMSMS was copolymerized with PhVPA by
free radical copolymerization in a sealed glass capsule. The copolymerization was carried out in DMF solution including various monomer ratios of TMSMS to PhVPA at 85 °C for 8 h with azobis(isobutryronitrile) (AIBN) as an initiator. The DMF solution of the copolymer was hydrolyzed with hydrochloric acid to form Si-O cross-linking via sol-gel condensation. The obtained sol was cast onto a Teflon plate (15 mm × 30 mm²). The sol was covered with aluminum foil and heated in a dry oven at 100 °C for 12 h. After the cover was removed, the film was heated at 120 °C for 2 h and then at 140 °C for 2 h. Then, the consolidated hybrid membrane was obtained.

### 2.3. Characterization of membranes

The morphology of membranes was observed by field emission scanning electron microscopy. Thermal behavior was investigated by thermogravimetry-differential thermal analysis (TG-DTA) at a heating rate of 10 °C/min from ambient temperature to 830 °C with an air flow. The elemental composition of the membranes was analyzed using an energy dispersive X-ray fluorescence (XRF) spectrometer. Fourier transform infrared (FT-IR) spectra were measured using a single reflection ATR attachment. Solution 1H and 13C NMR spectra were measured by using CD3OD or CDCl3 as a solvent. All peaks were referred to the internal standard of tetramethylsilane (TMS). Solid-state 29Si cross-polarization (CP)/magic angle spinning (MAS) NMR spectra of the hybrid membrane were measured and the external standard of chemical shift was glycine. Solid-state 29Si magic angle spinning (MAS) NMR spectra of hybrid membranes were measured and TMS was used as the external standard for 29Si chemical shift.

### 2.4. Proton Conductivity studies

The proton conductivity of the hybrid membrane was measured by the ac impedance method using a frequency response analyzer including a potentiostat/galvanostat from 0.1 Hz to 1 MHz. Platinum meshes were used as blocking electrodes. Measurements were conducted by using a small test chamber in an electric furnace as a function of both temperature and relative humidity (R.H.). A saturated aqueous solution of MgCl2, a saturated aqueous solution of NaNO3, and water vapor were used for the control of the relative humidity. The temperature of the sample was varied from 40 to 140 °C. The direct current (DC) resistances of the membranes ($R_{dc}$) were estimated from the values of the real part of the impedance at the intersection in the complex impedance plots (Nyquist plots). The conductivity ($\sigma$) of the membrane in a transverse direction was calculated using the relation $\sigma = \frac{t}{\ln(R_{dc} S)}$, where $t$ and $S$ are the thickness and the electrode area of the membrane, respectively.

### 3. Results and discussions

#### 3.1. Synthesis of TMSMS/PhVPA copolymer and membranes

The copolymers of TMSMS/PhVPA were successfully synthesized by free radical copolymerization. The separated solid of TMSMS/PhVPA at a ratio of 1/4 was dissolved homogeneously in DMF or dimethylsulfoxide (DMSO), and the product of TMSMS/PhVPA at a ratio of 1/2 was dissolved homogeneously in DMSO.

The solutions of TMSMS-PhVPA copolymers were then hydrolyzed with water at room temperature for 24 h yielding homogeneous sols for casting. The molar ratio of water to copolymer was set to be 3 in order to hydrolyze three methoxy groups bound to Si atoms in TMSMS. The membrane was prepared from the sol after casting followed by drying at temperatures up to 140 °C.

### 3.2. Characterization of hybrid membranes

#### 3.2.1 Appearance, microstructure and composition

Fig.1 shows the typical appearance of the hybrid membrane with a composition of TMSMS/PhVPA=1/2. The obtained membranes are self-standing, homogeneous, and highly transparent. The adhesivity of the membranes increased with the increasing content of PhVPA in the copolymer. The thickness was from 200 μm to 650 μm and the membrane was yellow.

From the results of FE-SEM observations, the hybrid membrane has a dense and homogeneous microstructure. Therefore, the copolymerization and the formation of organosiloxane network through the crosslinking of methoxy groups of TMSMS constituted a homogeneous matrix without large defects, such as pores or voids.

From the results of the elemental analysis of Si and P in the hybrid membranes by energy dispersive XRF, the Si/P ratios of membranes almost reflect those of the charged composition of monomers.

#### 3.2.2. Thermal analysis

TG-DTA curves of PhVPA and membranes of TMSMS/PhVPA were measured in dry air from room temperature to 830 °C. In the TG and DTA curve of PhVPA, an intense endothermic peak appears around 113 °C and corresponds to the melting point of PhVPA. On the other hand, in TMSMS/PhVPA hybrids, no significant endothermic peak corresponding to the melting point of PhVPA is observed. The result reveals that PhVPA in the hybrid membrane is not mixed, but chemically bound to the matrix of copolymer.

In addition, only a small weight loss due to the residual solvent and the evaporation of phisically absorbed water were observed up to 200 °C.

Therefore, the hybrid membrane is stable up to 200 °C in dry air.

#### 3.2.3. FT-IR analysis of the hybrid membranes

From the results of FE-SEM observations, the hybrid membrane has a dense and homogeneous microstructure. Therefore, the copolymerization and the formation of organosiloxane network through the crosslinking of methoxy groups of TMSMS constituted a homogeneous matrix without large defects, such as pores or voids.

From the results of elemental analysis of Si and P in the hybrid membranes by energy dispersive XRF, the Si/P ratios of membranes almost reflect those of the charged composition of monomers.
Fig. 2 shows FT-IR spectra of TMSMS (Fig. 2(a)), PhVPA (Fig. 2(b)) and the hybrid membranes with two ratios of TMSMS/PhVPA=1/4 (Fig. 2(c)) and 1/2 (Fig. 2(d)).

In both hybrids, the absorption at 1633 cm\(^{-1}\) marked with \(\bullet\) in the spectra of TMSMS, corresponds to the vibration of vinyl groups, was vanished. The condensation process of the Si-OCH\(_3\) bonds of TMSMS is monitored by the absorption of 823 cm\(^{-1}\) marked with \(\blacksquare\). No absorption is observed at 823 cm\(^{-1}\) in the reaction products in Fig. 2(c) and 2(d). In addition, a new absorption of Si-O-Si bond marked with an arrow is observed at 1102 cm\(^{-1}\), which increases in intensity with increasing TMSMS in the hybrids [15-17]. From these results, the Si-OCH\(_3\) groups of TMSMS are transformed to Si-OH completely, which are subsequently condensed during the hydrolysis and drying processes, yielding a cross-linked siloxane network in the hybrid membranes. On the other hand, compared with the spectra of PhVPA, broad absorptions from 2300 to 2800 cm\(^{-1}\) due to P-OH groups and the absorption of P=O at 1260 cm\(^{-1}\) are observed for both hybrids. Therefore the copolymerization and hybridization between TMSMS and PhVPA were succeeded and the phosphonic acid group as a proton carrier was found to be incorporated in the hybrids.

3.2.4. NMR analysis of the hybrid membranes

Fig. 3 shows \(^{13}\)C NMR spectra of TMSMS, PhVPA and the reaction products (TMSMS/PA=1/2). The \(^{13}\)C CP-MAS spectrum of TMSMS/PhVPA=1/2 hybrid is shown in Fig. 3(c). Four groups of peaks are observed at around 21.4 (silylmethyl carbon), from 34.8 to 38.8 (\(\alpha\)-carbons of the organic polymer backbone), 49.2 (\(\beta\)-carbons of the organic polymer backbone), and from 127.6 to 137.3 ppm (carbons of the benzyl ring) [17-19]. Both the \(\alpha\)-carbons of the organic polymer backbone and benzene ring appear at two different chemical shifts, since the copolymer includes the unequal carbons of these groups. In addition, the signals at 112.5 and 113.5 ppm assigned to the \(\beta\)-carbon of vinyl groups of TMSMS disappear and the signal at 50.9 ppm assigned to the carbon of methoxy groups of TMSMS disappears in the hydrolyzed product. The disappearance of these signals indicates the complete polymerization of vinyl groups and the hydrolysis/condensation of methoxy groups. Combined with the results of FT-IR, the results of \(^{13}\)C NMR support the copolymerization between TMSMS and PhVPA and its subsequent hydrolysis and condensation.

From the results of \(^{29}\)Si MAS NMR spectra of the TMSMS-PhVPA hybrid, it is considered that the product is mainly a mixture of several T\(_2\) and T\(_3\) units. Therefore, the product consists of various species, including linear, multi-chain, polycyclic and branched structure. The results show that the Si-OCH\(_3\) bond undergoes the hydrolysis and condensation yielding Si-O-Si linkages as reported for the sol-gel process.

3.3. Proton conductivity of the hybrid membranes

Fig. 4 shows the temperature dependences of the proton conductivities for the hybrid membranes with ratios of TMSMS/PhVPA=1/4 and 1/2 at a medium relative humidity of 74.9 %R.H. (40 °C) - 40.0 %R.H. (120 °C) \%R.H, controlled by using NaNO\(_3\) saturated solution, and at 100 %R.H.
For all membranes studied, the proton conductivity increases with increasing PhVPA content, temperature, and relative humidity up to 120 °C. The proton conductivity of TMSMS/PhVPA=1/4 was increased up to 130 °C at 100 %R.H. Water was introduced into the hybrid membranes from a humidified atmosphere because of the hydroscopic nature of phosphonic groups, and it contributed directly to the improvement of the proton conductivity. The conductivity increases by about one order of magnitude for the change in composition from 1/2 to 1/4 under low humidity. At 130 °C and 19.2 %R.H., the conductivity of TMSMS/PhVPA=1/2 membrane is $2.5 \times 10^{-2}$ S cm$^{-1}$, while that of TMSMS/PhVPA=1/4 is $9.5 \times 10^{-3}$ S cm$^{-1}$. On the other hand, at the same composition, the difference in conductivity is about a half order lower under sufficient humidity. The proton conductivities of TMSMS/PhVPA=1/4 reached the order of $10^{-3}$ S cm$^{-1}$ under 100 %R.H. and that of about $10^{-2}$ S cm$^{-1}$ under 32.3 % R.H. (80 °C) - 19.2 % R.H. (130 °C) above 80 °C. The current hybrid membrane has great potential for applications in PEFCs operated at medium temperatures and under various humidity conditions.

**REFERENCES**