Preparation of flexible inorganic-organic hybrid proton-conducting membranes via sol-gel processing

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Attention has focused on fuel cells as a next-generation clean energy source, particularly systems using proton-conducting electrolytes for a wide range of applications. Nafion® membranes are an example of ion-exchange membranes with sulfonate groups that have developed as proton-conducting electrolytes and display high proton conductivity below 373 K. Despite this, these membranes still have problems for practical use because of their chemical and mechanical degradation during long-term use. As alternative candidates, the sol-gel-derived SiO_2-P_2O_5 binary glasses reported by Nogami *et al*. provide high proton conductivity and chemical stability [1], but their inherent brittleness has thus far prevented practical application. To improve the disadvantage, we focused on an organic-inorganic hybrid. Sol-gel-derived inorganic-organic hybrids are watched with interest as they allow homogenous mixing and solidification of inorganic and organic components at the nanometric level without damaging the properties of organic polymers. Since this process begins with colloidal suspension of solid particles, it provides a high degree of compositional control and is thus considered a promising approach to proton conductor synthesis because it makes dispersal of conductive ions in the matrix possible at the molecular level.

In this paper we report on inorganic-organic hybrid proton-conducting membranes prepared by sol-gel processing to achieve both durability and flexibility using polyethylene glycol (PEG) as the organic component in light of the favorable characteristics it has demonstrated for application to polymer electrolyte materials.

All SiO_2-P_2O_5 binary glasses in this study were prepared through the hydrolysis of tetraethoxysilane ($Si(OC_2H_5)_4$, TEOS), phenyltriethoxysilane ($C_6H_5Si(OC_2H_5)_3$, PhTEOS), and trimethylphosphate ($PO(OCH_3)_3$, TMP). The compositions of binary glasses were $90SiO_2$-$10P_2O_5$, $80SiO_2$-$20P_2O_5$ and $70SiO_2$-$30P_2O_5$. The sol compositions are shown in Table I. First, TEOS and PhTEOS were hydrolyzed for 3 hrs at room temperature with a solution of H_2O, C_2H_5OH, and HNO_3. Next, $PO(OCH_3)_3$ was added to the solution and refluxing was started. After further hydrolyzing, a solution of C_2H_5OH containing PEG (average formula weight of 600) was added followed by refluxing overnight. The obtained clear sol was poured into a Teflon petri-dish and dried in a dry oven at 313 K until it formed a stiff gel. Higher P_2O_5 ratios were directly proportional to slower gelation rates. For example, the gelation time of the $90SiO_2$-$10P_2O_5$ was 4 days, but that of the $70SiO_2$-$30P_2O_5$ was 9 days. Hypothetically speaking, triesters of $PO(OR)_3$ (R = Me, Et, Bu) are slowly hydrolyzed at low pH levels [2, 3]. In this sol, however, nitric acid is used as the catalyst of hydrolysis, so the gelation time is lengthened due to the slow hydrolysis rate of $PO(OCH_3)_3$. The gel was dried by heating to 373 K at 0.5 K/min, kept at that temperature for 6 hrs, and cooled to room temperature at 0.5 K/min. The resulting membrane was transparent and flexible. Thickness of the membrane was 0.2–0.5 mm.

Fig. 1 shows FT-IR spectra of (a) $90SiO_2$-$10P_2O_5$, (b) $80SiO_2$-$20P_2O_5$, and (c) $70SiO_2$-$30P_2O_5$ recorded with a Shimadzu FT-IR spectrophotometer in the range 4000–400 cm^{-1} using KBr disk methodology. All spectra have a strong and broad band at about 1200–1000 cm^{-1}. The band near 1100 cm^{-1} is assigned to P—O stretching vibration in P—O—P and P—O—Si bridging units, and the band near 1040 cm^{-1} is assigned to Si—O stretching vibration in Si—O—Si and P—O—Si bridged units [4]. As the ratio of P_2O_5 increases, the band at about 1100 cm^{-1} becomes more pronounced due to increase of P—O—P and P—O—Si bridging units. All spectra in Fig. 1 also feature a band at 3000–2800 cm^{-1}. An absorption band near 2900 cm^{-1} is assigned to C—H stretching vibration caused by PEG, and thus PEG is thought to be present in the inorganic matrix of these membranes. A strong and broad band at about 3700–3000 cm^{-1} is assigned to hydroxyl groups of Si—OH, P—OH, and PEG. However, amounts of OH

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TABLE I Sol compositions of the prepared membranes

Composition (mol%)	Materials (molar ratios)					
	TEOS	PhTEOS	TMP	H_2O	HNO_3	C_2H_5OH
$90SiO_2$-$10P_2O_5$	0.654	0.164	0.182	4	0.01	10
$80SiO_2$-$20P_2O_5$	0.534	0.133	0.333	4	0.01	10
$70SiO_2$-$30P_2O_5$	0.430	0.108	0.462	4	0.01	10

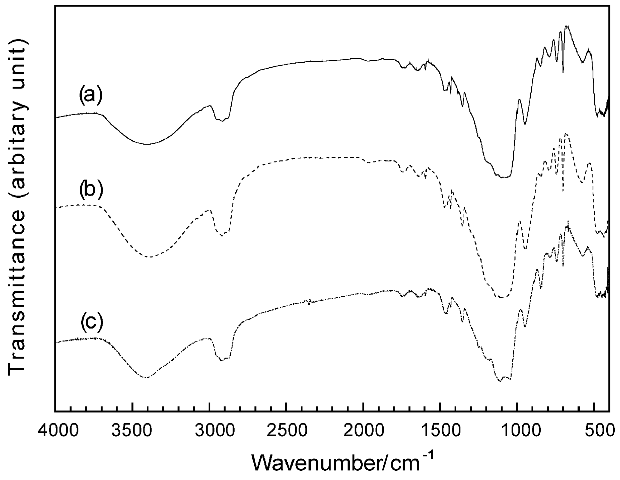

Figure 1 FT-IR spectra of (a) $90SiO_2$-$10P_2O_5$, (b) $80SiO_2$-$20P_2O_5$, and (c) $70SiO_2$- $30P_2O_5$ membranes.

in PEG was smaller than that in Si—OH and P—OH. Accordingly, this band is deemed to be related to hydroxyl groups of Si—OH, P—OH.

The greatest characteristic of our membranes is the flexibility. Phosphate materials are lacking in chemical durability [1], so higher P_2O_5 ratios were directly proportional to weaker membrane strengths: $90SiO_2$-$10P_2O_5$ glass were the hardest, and $70SiO_2$-$30P_2O_5$ glasses were the weakest. But all glasses were flexible. The flexibility of the prepared hybrid membranes is illustrated in Fig. 2. This membrane ($90SiO_2$-$10P_2O_5$) could be wrapped around a stick with a radius within 6 mm. Other membranes also had the same flexibility. Flexibility is a novel property of these hybrids and important for making an electric cell stack. This characteristic is thought to be due to the adoption of the organic component (PEG) and the effect of $C_6H_5Si(OC_2H_5)_3$. The aging process of acid-catalyzed silica gels begins with the hydrolysis, the production of Si—OH from Si—OC_2H_5, and is followed by the condensation reaction. As these reactions make progress, new bonds (Si—O—Si) are formed, creating additional cross-linking and surface area between pores in the gel network. But, when organic molecules, here PEG, are added in this type of silica gel, these molecules can hydrogen bond to the Si—OH. Without the available Si—OH groups, condensation reactions cannot form the bridging bonds and syneresis is halted. The same goes for POH formed by $PO(OCH_3)_3$. These prevent the gel from being brittle. $C_6H_5Si(OC_2H_5)_3$, with acid catalysts, was hydrolyzed and condensed with simultaneously hydrolyzing $Si(OC_2H_5)_4$. The influence of $C_6H_5Si(OC_2H_5)_3$, however, resulted in membranes with small void spaces due to the steric hindrances of phenyl groups, thus enabling membranes whose size can be easily altered with a pair of scissors.

Conductivity of these hybrid membranes was measured with an impedance meter (Hioki LCR 3532-50

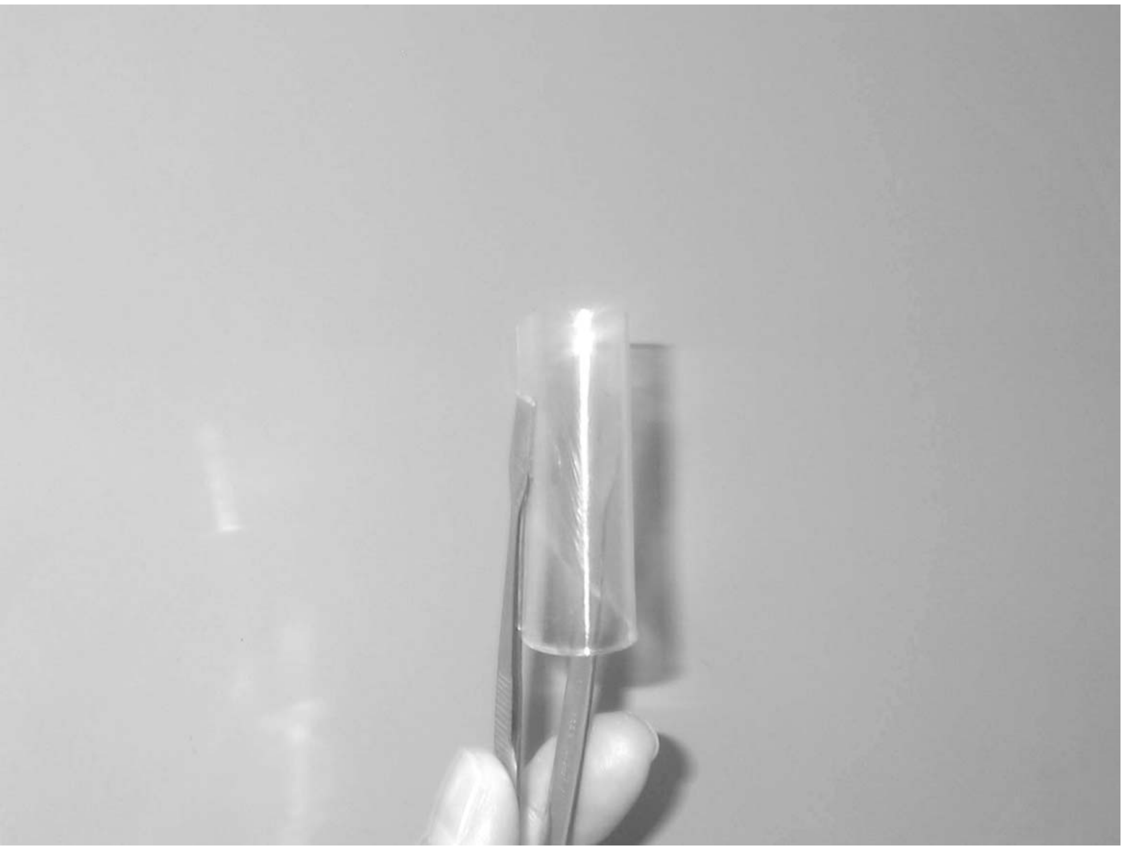

Figure 2 Photograph of the $90SiO_2$-$10P_2O_5$ membrane.

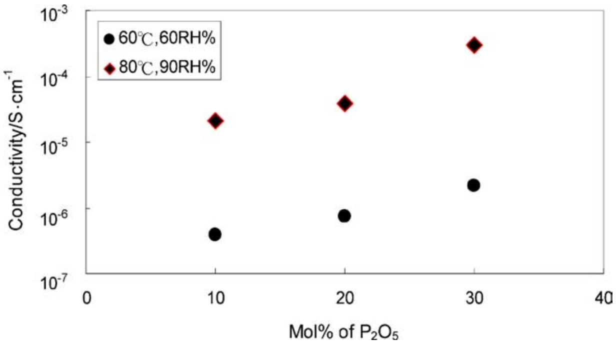

Figure 3 Change in proton conductivity due to variance of P_2O_5 molar percent.

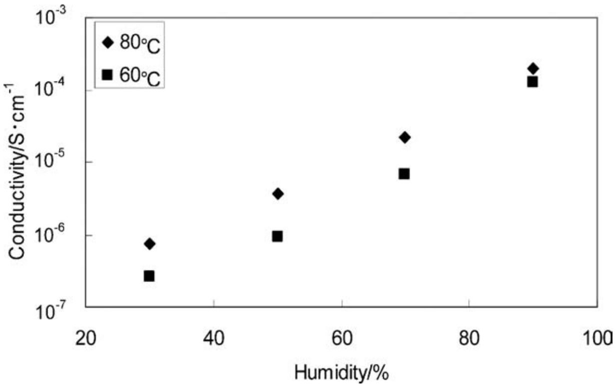

Figure 4 Change of proton conductivity with relative humidity in $70SiO_2$-$30P_2O_5$ glass.

HiTESTER) over a frequency range of 50 Hz to 5 MHz according to an alternating current impedance method. The samples were kept in a constant temperature/humidity chamber for 1 hr at various temperatures and relative humidities (RH). After measurement, conductivity was determined from the first real axis intercept point in the complex impedance plot.

Fig. 3 shows the change of proton conductivity due to different P_2O_5 ratios. The chamber was set at 333 K, 60% RH (circles) and 353 K, 90% RH (diamonds). To obtain high proton conductive glass, the glass must have a large number of protons that are strongly hydrogen bonded [1, 5]. The proton in a SiOH bond is strongly bonded with oxygen, so it is free of hydrogen bonding. In contrast, the hydrogen bond with P—OH and water is strong [6]. Accordingly, proton conductivity becomes higher when molar percent of P_2O_5 is increased, as represented by the corresponding results represented in Fig. 3. All membranes did not break at 353 K, 90% RH. This is evidence that the chemical durability of phosphate materials is lowered owing to absorbed water [1].

Fig. 4 shows the change of proton conductivity with RH for the $70SiO_2$-$30P_2O_5$ membrane. Proton conductivity increases as RH becomes higher at each temperature so that membrane conductivity is seen to depend on the amount of molecular water absorption. At high RH there was a strong probability that the membranes included water, thus leading to high conductivity. Considering Figs 3 and 4 together, the proton conduction is thought to be associated with proton hopping between hydroxyl groups and water molecules [1].

In conclusion, sol-gel processing with polyethylene glycol and metal alkoxides produced flexible inorganic-organic hybrid proton-conducting membranes that displayed a moderately high proton conductivity of 10^{-4} S·cm^{-1}.

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