J Mater Sci (2007) 42:2212–2214
DOI 10.1007/s10853-006-0971-1

LETTER

Preparation of a flexible organic–inorganic hybrid proton-conducting membrane for non-humidified conditions

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Received: 23 August 2006 / Accepted: 15 September 2006 / Published online: 16 February 2007

Polymer electrolyte fuel cells (PEFCs) have recently received considerable attention as potential new energy devices. PEFCs have a proton-conducting membrane as a solid-electrolyte membrane, and Nafion© is widely used for this purpose. However, Nafion© shows high proton conductivity only when saturated with water vapor, which limits the operating temperature of these fuel cells to about 353 K. The use of solid-electrolyte membranes with high proton conductivity at an intermediate temperature range (373–473 K) with little or no dependence on humidity could greatly improve the energy efficiency of fuel cells, minimize CO poisoning of catalyst, and reduce the size of the humidifier. To develop such a high-performance solid electrolyte, organic–inorganic hybrid materials have been studied [1, 2].

A large variety of organic–inorganic hybrid membranes prepared by the sol-gel method have been reported [3–6]. Among these, the most common approach uses hydrogen bonding interactions between the polar functional groups of organic polymers and silanol groups of silica gels [4, 6]. We have reported a proton-conductive organic–inorganic hybrid membrane prepared by the sol-gel method, which showed high flexibility and moderate proton conductivity, from tetraethoxysilane, phenyltriethoxysilane, trimethylphosphate and polyethylene glycol (PEG) [7].

In this paper, we report the preparation of SiO_2–P_2O_5–PEG hybrid membranes using Gly-TMOS, polyphosphoric acid and polyethylene glycol dimethacrylate (PDE) as source materials. Polyphosphoric acid is a well-known proton-conducting material. Unfortunately, it is difficult to support and fix this compound in a membrane. To solve this problem, we proposed the use of Gly-TMOS, which contains epoxy groups in its structure, as a mediation agent. A ring-opening reaction between epoxy groups and polyphosphoric acid can help to fix polyphosphoric acid in the membrane. PDE was used to improve the membrane strength and flexibility. Hydrogen bonding interactions between PDE and the silanol groups of silica can help to disperse organic and inorganic components at a molecular level. Methacryloxy groups of PDE react with each other and polymerization proceeds by UV irradiation. This makes the membrane strong and flexible. Based on these concepts, we have prepared novel organic–inorganic hybrid membranes using the sol-gel technique.

An organic–inorganic hybrid membrane was prepared using the following molar sol composition; Gly-TMOS: polyphosphoric acid (calculated as H_3PO_4): H_2O: ethanol = 0.33: 0.67: 2: 10. PDE (NOF Corp., Blemmer PDE-400) had a molecular weight of

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ca. 400; the concentration of PDE based on the weights of Gly-TMOS and polyphosphoric acid was 50 wt%. Irgacure®184 (Ciba Specialty Chemicals) as a photo polymerization initiator was added to 4 wt% (based on the weight of PDE).

Gly-TMOS was added to a mixture of ethanol, H_2O and Irgacure®184. After the mixture was stirred for 3 h, a solution of ethanol containing polyphosphoric acid was added and the mixture was stirred for another hour. The solution of PDE was then added. The mixture was stirred overnight until a homogeneous sol was obtained. The above process was performed at room temperature. The resulting yellowish clear sol was put into a PFA petri dish, dried in an electric oven at 313 K for 1 week, and irradiated with UV light using a Photo Surface Processor (Sen Lights Corp.) for 5 min. After UV irradiation, the resulting stiff gel was heated to 373 K at a rate of 0.5 K/min, maintained at the same temperature for 6 h, and cooled to room temperature at 0.5 K/min. The prepared membrane was brownish and flexible. Thickness of the membrane was 0.4–0.6 mm. The membrane could be bent and cut to the proper size with scissors.

Figure 1 shows FT-IR spectra of (a) the prepared membrane, (b) Gly-TMOS, and (c) PDE recorded with a Shimadzu FT-IR spectrophotometer within a range of 400–4000 cm^{-1}. Spectrum (a) shows two absorption bands at 1100 cm^{-1} and 1020 cm^{-1}: the former is assigned to P–O stretching vibration in P–O–P and P–O–Si linkages, and the latter is assigned to Si–O stretching vibration in Si–O–Si, Si–O–C, and P–O–Si linkages [8]. In comparing (a) and (b), the band at 910 cm^{-1} in (b) is not seen in (a). This band is identified as epoxy rings [9]. Thus, epoxy rings were opened through the sol-gel reaction. A sharp band at about 2830 cm^{-1} in (b) is not seen in (a). This band reflects C–H symmetric stretching vibration in the case of $-OCH_3$. This is evidence that Gly-TMOS was hydrolyzed. Both (a) and (c) had a strong peak at about 1720 cm^{-1} due to C=O, so the membrane assimilated the PDE chains into the matrix. A sharp peak at about 1640 cm^{-1} was assigned to C=C in (c), but was not seen in (a). This indicates that the C=C bonds underwent photo-polymerization. Otherwise, the striking peak in (a) is the broad band at 3250–3650 cm^{-1} associated with O–H. Based on the results of IR, this is due not only to P–OH (or absorbed H_2O) containing polyphosphoric acid, but also to C–OH formed by the ring-opening reaction of the epoxy groups, and to Si–OH and Si–O–Si formed by the hydrolysis and polymerization of Gly-TMOS.

The proton conductivity of the hybrid membrane was measured using the complex impedance method with an impedance analyzer (Hioki LCR 3532–50 HiTESTER) over a frequency range of 50 Hz to 5 MHz. Plots of conductivity versus 1/*T* are shown in Fig. 2. The sample was kept in a constant-temperature chamber for 1 h at various temperatures. The chamber was not humidified but rather left open to room air. Conductivities increased with increasing temperature under these condition. This plot did not obey an Arrhenius equation, but rather showed the characteristics of Vogel–Tamman–Fulcher behavior, which demonstrates that segmental motion plays a role in proton conductivity [10]. Proton transport in the H_3PO_4 system follows a Grotthuss mechanism [10, 11]. Polyphosphoric acid was used in this study, and the membrane was flexible due to PEG chains in PDE, so

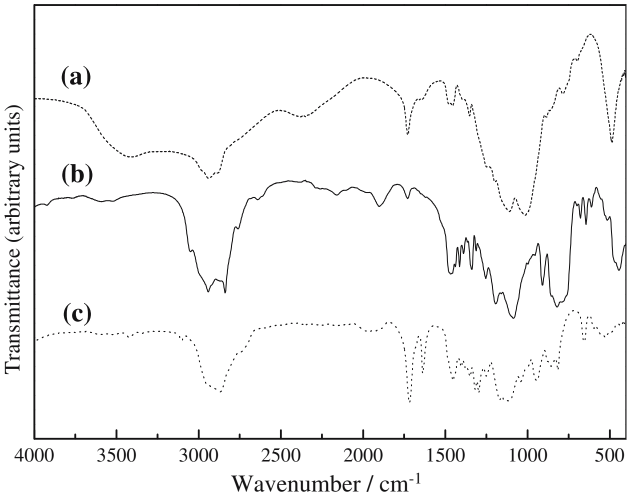

Fig. 1 IR spectra of (**a**) the prepared membrane, (**b**) Gly-TMOS and (**c**) PDE

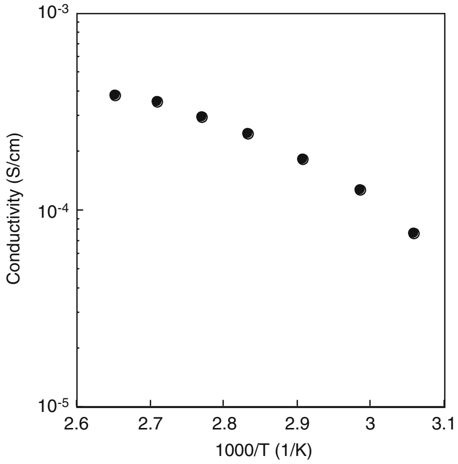

Fig. 2 Proton conductivity in the temperature region from 323 to 373 K

protons were thought to be transferred through a liquid-like phase. For organic-inorganic hybrid membranes based on Gly-TMOS, tetramethoxysilane, and H_3PO_4, it has been reported that the curvature of the dependence of proton conductivity on temperature might reflect the interaction of H_3PO_4 species and the flexible polyethylene oxide (PEO) chains formed among Gly-TMOS [10]. We used PDE, which has PEO chains in its structure. Thus, it is reasonable that the mechanism of proton transfer for the membrane also reflected the interaction PDE and polyphosphoric acid.

Our system was not humidified but rather left open to room air, and therefore it was possible that hygroscopic polyphosphoric acids absorbed small amounts of moisture from the air. To investigate the proton conductivity under dry conditions, we measured the proton conductivity in a closed system with dry N_2 flow at 378 K for about 2 weeks. The result is shown in Fig. 3. For the first few days, there was a rapid decrease in conductivity, but the rate of the decrease gradually diminished, until a steady state was reached. Based on this result, we confirmed that protons moved under anhydrous conditions in the prepared membrane.

The prepared membrane showed a moderately high conductivity of 10^{-4} S/cm under non-humidified conditions. To check the possibility of a fuel cell under non-humidified conditions, we constructed a fuel cell with the prepared membrane using the procedure described elsewhere [12]. Pure hydrogen and oxygen gases were used as the fuel. At 298 K, the current density under humidified conditions (RH 3%) was 63 mA/cm^2 and that under non-humidified conditions was 0.3 mA/cm^2 at a cell voltage of 0.1 V. The current density under non-humidified conditions at 353 K was 1.6 at the same cell voltage. The current density under humidified conditions was much higher than that under non-humidified conditions. By comparison under non-humidified conditions, the current density increased at high temperature (353 K). While the cell showed low under non-humidified conditions, we confirmed that the cell using the organic–inorganic hybrid still generated electricity under these conditions.

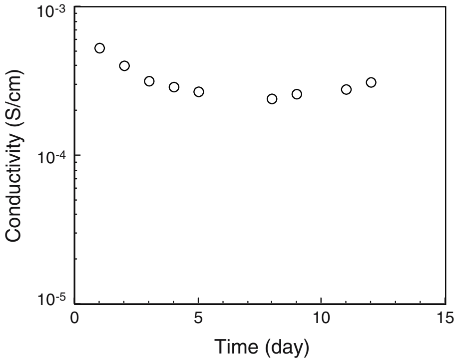

Fig. 3 Proton conductivity under dry conditions with N_2 flow

In conclusion, we have successfully stabilized polyphosphoric acid by using Gly-TMOS trough the ring-opening reaction of epoxy groups in Gly-TMOS. The photo-polymerization of a polymer, PDE, imbued the membrane with flexibility and strength. Thus, the prepared membrane displayed a moderately high proton conductivity of $10^{-4} \sim 10^{-3}$ S/cm under non-humidified conditions while remaining flexible. We also confirmed that a fuel cell with the prepared membrane generated electric power using hydrogen and oxygen as the fuel.

The present results suggest that organic–inorganic hybrid proton-conductive membranes may be useful in PEFCs at intermediate temperature, and as hydrogen or humidity sensors due to their proton conductivity under non-humidified condition. In addition, this sol-gel method can be used to make thin films on many kinds of substrates.

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