Hybrid Organic–Inorganic Material as New Matrices of Proton-conducting Membranes

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Organic–inorganic composite proton-conducting membranes were prepared by using a hybrid organic–inorganic matrix Compoceran® E201 that consists of an epoxy prepolymer and a siloxane part. It was demonstrated that the compound disperses proton-conducting Cs-substituted phosphotungstic acid (Cs-PWA) particles uniformly in spite of the large difference in densities. Relatively high proton conductivity of $10^{-3}\,\mathrm{S\,cm^{-1}}$ was obtained at 160 °C and at RH of 80% for the membrane with the weight ratio Cs-PWA/E201 = 1.6.
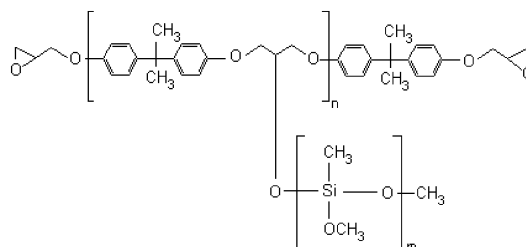
The increase of the operation temperature of polymer electrolyte membrane fuel cells (PEMFCs) above 100 °C is a great concern for their application in electric vehicles or distributed cogeneration systems.[1] The higher operation temperatures would result in reduction of amount of expensive and rare Pt used as catalysts on electrodes, protection of the inactivation of Pt catalyst by CO contained in fuel gases, and improvement of the quality of exhaust gases as heat sources. However, prevailing Nafion® or its analogs cannot be applied above 120 °C due to evaporation of water. Very recently, Matsuda et al. reported that Cs^+-substituted phosphotungstic acid (Cs-PWA) exhibits very high proton conductivity of $3.3 \times 10^{-3}\,\mathrm{S\,cm^{-1}}$ at 100 °C in dry atmosphere.[2] This material may be a promising proton conductor that can be used in intermediate temperature fuel cells. However, this material is in particle form and it is difficult to fabricate a gas-blocking membrane only with Cs-PWA. In order to protect the gas permeation and to handle easier, Cs-PWA should be dispersed in a matrix. As matrices, organic polymers are preferable because some of them provide flexible composite membranes.

Some research on organic–inorganic composite proton conductors have been reported.[1,3,4] Most of them employed PWA, $Zr(HPO_4)_2$, or H_3PO_4 as proton conductors. They are cluster, nanosheet, and ion, respectively, and are relatively easily dispersed in organic matrices due to their small sizes. A study on powdery inorganic conductors dispersed in an organic matrix is reported by Heo et al.[4] A scanning electron microscope (SEM) image of their sample showed inhomogeneous aggregation of inorganic particles in the matrices, which may result in poor network of proton conduction in the membrane. To disperse inorganic proton conductors homogeneously, high affinity of organic matrices to the inorganic compounds is required. In this context, we noticed a commercial hybrid organic–inorganic material "Compoceran®" (Arakawa Chemical Industries, Ltd.). Compoceran® consists of siloxane and organic components, which are phenol–formaldehyde oligomer, epoxy prepolymer, polyimide, and polyamide. In this study, we used Compoceran® E201 (Figure 1, hereafter abbreviated as E201) that contains bisphenol-A epoxy prepolymer with the aim of fabricating flexible membranes. In this letter, preparation and proton

Figure 1. Structural formula of Compoceran® E201.

conductivity of membnanes consisting of E201 and Cs-PWA are reported.

Cs-PWA:E201 composite membranes were prepared as follows: First, Cs-PWA was synthesized by mechanochemical reaction of Cs_2SO_4 and PWA by using a planetary ball mill in N_2 atmosphere with a rotation speed of 600 rpm for 10 min.[5] Next, Cs-PWA and E201/acetone solution were mixed and stirred for 30 min. During the stirring, adsorbed water on Cs-PWA particles and atmospheric water caused partial hydrolysis and polymerization of siloxane. Then acetone solution of 2-ethyl-4-methyl-imidazole was added as a hardener of epoxy prepolymer. After stirring for 30 min, the homogeneous solution was spread on a PTFE dish, dried at 60 °C for 4 h, and heated at 150 °C for 2 h. The composite membranes were prepared for the weight ratio of Cs-PWA/E201 (x) ranging from 0.1 to 2.0. The prepared membranes were studied by X-ray diffraction (XRD), thermogravimetry analysis (TGA), and field-emission scanning electron microscopy (FE-SEM). Proton conductivity was obtained from ac impedance spectra measured on a frequency response analyzer for frequencies from 1 MHz to 0.1 Hz with an oscillation voltage of 100 mV. The impedance spectra were recorded on cooling processes in a temperature range from 80 to 160 °C and in an atmosphere with a relative humidity (RH) of 20% to 80%. The apparatus used for the impedance measurement is described in Supporting Information, in detail.[7]

XRD patterns of mechanically milled mixture of Cs_2SO_4 and PWA showed shifts of diffraction peaks to higher angles compared with PWA, which was accounted for by partial substitution of Cs ions for protons of PWA.[5] For Cs-PWA:E201, flexible, smooth and pale brown membranes were obtained for $x \leq 1.6$, as shown in Figure 2a. The membrane with $x = 2.0$ was a hard, fragile, and rough film. TGA confirmed the obtained membranes were thermally stable up to 200 °C. The weight ratio estimated from TGA of parts of membranes well agreed with the mixed value, indicating the homogeneity of the membranes. In a FE-SEM image of the cross section of Cs-PWA:E201($x = 1.6$) (Figure 2b), it was confirmed that particles of 1–3 µm in a diameter were uniformly dispersed in the matrix. For comparison, we also prepared a membrane using a bisphenol-A epoxy prepolymer without siloxane (JER828, Japan
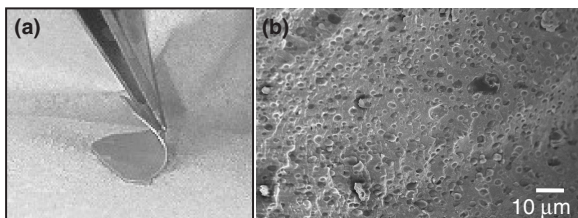
Figure 2. (a) Appearance and (b) a cross-section FE-SEM images of Cs-PWA:E201 composite membranes ($x = 1.6$).
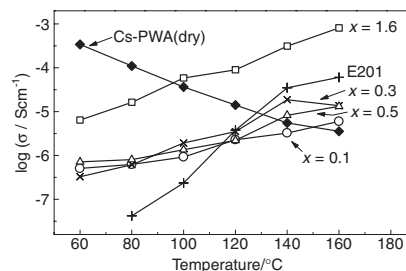

Figure 3. Temperature dependence of proton conductivity of Cs-PWA:E201 composite membranes with several compositions at RH of 80%. Conductivity of a E201 membrane and a Cs-PWA pellet is also shown. Conductivity of Cs-PWA was measured in dry air.

Epoxy Resins Co., Ltd.) as a matrix. In the composite membrane without siloxane parts in the matrix, severe aggregation and precipitation of Cs-PWA in the membrane were observed (Figure S2).[7] It is supposed that E201 molecules surround Cs-PWA particles due to the high affinity between siloxane and Cs-PWA, which facilitated the homogeneous dispersion.

Nyquist plots of the membranes showed two semicircles at a higher frequency range and an inclined straight line at a lower frequency range (Figure S3).[7] The impedance spectra were analyzed by assuming an equivalent circuit shown in Figure S4, consisting of components related to bulk impedance of proton conduction (R_b and C_b), grain-boundary impedance of proton conduction (R_{GB} and C_{GB}), and impedance of ion-blocking electrodes (R_{el} and C_{el}).[7] For impedance spectra obtained at higher temperatures, the two semicircles were hardly distinguished, and the proton conductivity of the membrane (σ) was calculated from total resistance ($R_b + R_{GB}$) for all spectra. Figure 3 shows temperature dependence of the σ of Cs-PWA:E201 composite membranes measured at RH = 80%. For all samples, σ increased with increasing temperature. For $x = 0.1$–0.5, no significant dependence on composition was observed; however, a membrane of $x = 1.6$ exhibited higher conductivity by 1–2 orders of magnitude than other samples. The membrane of $x = 1.6$ showed high conductivity of ca. $1 \times 10^{-3}\,\mathrm{S\,cm^{-1}}$. However, at 60 °C, the conductivity of Cs-PWA:E201($x = 1.6$) at RH of 80% is lower by 2 orders of magnitude than that of Cs-PWA in dry atmosphere, which indicates poor network of Cs-PWA particles. Figure 3 shows that E201 itself exhibits proton conductivity, which may be ascribed to the proton conduction via hydroxy groups of SiO_2. The conductivity of Cs-PWA:E201($x = 0.1$–0.5) was lower than a pristine E201 membrane above 140 °C. This is accounted for by voids in the composite membranes, which result from vaporization of methanol produced by the hydrolysis of the methoxy groups. The apparent activation energy of Cs-PWA:E201($x = 1.6$) was $57\,\mathrm{kJ\,mol^{-1}}$, which is much higher than that of pristine Cs-PWA. Figure S5 shows humidity dependence of σ of Cs-PWA:E201($x = 1.6$) and E201($x = 0$) membranes.[7] It should be noted that both membranes exhibited the same humidity dependence of proton conductivity, which suggests that the rate-determining step of the proton conduction is the same for both membranes, i.e., proton conduction through the matrix. Calculated from densities of dry E201 ($1.2\,\mathrm{g\,cm^{-3}}$) and dry Cs-PWA ($4.9\,\mathrm{g\,cm^{-3}}$) at a room temperature, the volume fraction of Cs-PWA in the Cs-PWA:E201($x = 1.6$) was 27%. This value is close to the threshold of percolation networks in three-dimensional systems (31% for a simple cubic lattice).[6] Therefore, it is assumed that in the composite membrane of $x = 1.6$, proton pathways are partially interconnected, which

increase the total conductivity; however the properties of the membrane are dependent on E201 matrix filling the gaps (Figure S6).[7]

From the above results, it is necessary to increase the volume fraction of Cs-PWA particles to obtain higher proton conductors. Although flexible membranes with higher Cs-PWA composition ($x = 2.0$, volume fraction = 33%) could not be prepared with the current method, we have succeeded in fabricating flexible homogeneous membranes with higher Cs-PWA compositions by reducing the Cs-PWA particle size to about 100 nm. The structure and the proton conductivity of the Cs-PWA:E201 membranes consisting of Cs-PWA nanoparticles will be described in the following report.

In summary, we succeeded in preparing homogeneous flexible organic–inorganic composite proton-conducting membranes by using a hybrid organic–inorganic material. The siloxane part of the precursor facilitates homogeneous dispersion of Cs-PWA particles with large density, and the epoxy prepolymer part resulted in the dense and flexible membranes, which are easily handled and assembled in fuel cells. Relatively high proton conductivity of $10^{-3}\,\mathrm{S\,cm^{-1}}$ was obtained for $x = 1.6$ at 160 °C and at RH of 80%, but the proton conduction was limited by the matrix. Proton-conducting membranes with higher conductivity, lower temperature dependence, and lower humidity dependence are anticipated by improving the preparation process.

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7 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.