Conducting Materials

A Biopolymer Composite Material as an Anhydrous Proton-Conducting Membrane**

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Chitin is a biopolymer famous as a natural mucopolysaccharide resource and is present in the exoskeleton of crustaceans and insects, as well as in chitin-enriched materials, such as crab and shrimp shells. These are generally discarded as industrial waste around the world,[1] and so chitin can be considered to be an extremely low-cost, nonhazardous, and environmentally benign polymer. The use of chitin and its derivatives as biomedical materials has been reported, for example as tissue engineering materials, surgical tape, and artificial skin.[2,3] However, their use in electronically or optically active materials has not been reported. Application of these biopolymers in electrical devices would be attractive not only in terms of product cost and environmental safety but also from a materials science point of view.

Recently, polymer electrolyte membrane fuel cells (PEMFCs) that operate under anhydrous conditions (or extreme low humidity) and intermediate temperature (100–200 °C) have attracted much attention as clean, advanced energy conversion systems with high efficiencies.[4] The operation of the PEMFCs at higher temperatures improves the tolerance of the Pt electrode for carbon monoxide and provides higher energy efficiency, simplified heat management, and co-generation.[4] However, the customary perfluorinated sulfonic acid membranes that are used, such as nafion, are unstable at higher temperatures, which result in proton conductivity abruptly decreasing as a result of the evaporation of water from the electrolyte membrane and destruction of the polymer structure. Additionally, the production cost of perfluorinated membranes is extremely high, which makes industrialization of the PEMFCs difficult. Therefore, highly conducting proton membranes composed of inexpensive materials that conduct at intermediate temperatures are necessary for advanced PEMFC technology. In particular, composite materials of strong acids and basic polymers have been proposed as novel polymer electrolytes of single proton conductors under anhydrous and intermediate temperature conditions.[4–8]

In this study we prepared an anhydrous proton-conducting membrane using a composite of chitin phosphate (CP;

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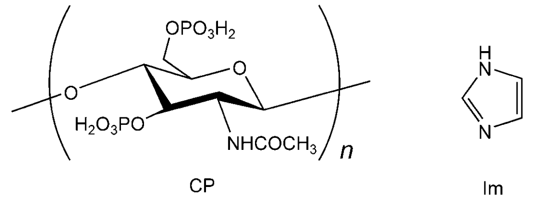
chitin modified with a phosphonic acid group) and the basic heterocycle imidazole (Im). A composite material of CP and 200 wt% Im showed a high proton conductivity of $7\times10^{-3}\,\mathrm{S\,cm^{-1}}$ at 150 °C under anhydrous (water-free) conditions. Additionally, the thermal stability of CP/Im composite material was found to increase with the doping ratio of the imidazole.

Chitin phosphate (CP) was synthesized by a previously reported procedure.[9] The CP/heterocycle composite materials were prepared as follows: a mixed aqueous solution of CP/Im was cast onto a teflon plate and dried at room temperature or 70 °C for 1–3 days. The dried-membrane was then stripped from the teflon plate.[10] The molecular structures of CP and imidazole are shown in Scheme 1. Figure 1 a and b show the thermogravimetric (TG) and differential thermal analyses (DTA) of pure chitin phosphate (**1**), CP/20 wt% Im (**2**), CP/50 wt% Im (**3**), CP/100 wt% Im (**4**), CP/200 wt% Im (**5**), and CP/500 wt% Im (**6**) composite materials, respectively, measured at the heating rate of $10\,^{\circ}\mathrm{C\,min^{-1}}$ under a dry nitrogen flow. The pure CP and composite materials showed a TG weight loss of a few percent at 160 °C. This TG weight loss is due to the evaporation of solvent or imidazole from the material (Figure 1 a) and dehydration of the phosphate group. An exothermic peak at 167.9 °C corresponding to thermal decomposition was evident in the DTA analysis of the pure chitin phosphate (line (1) in Figure 1 b). Surprisingly, this exothermic peak disappeared on doping with imidazole (lines (2)–(4), Figure 1 b). It is indicated from these results that the CP/Im composite material formed an acid/base complex through electrostatic interactions in the composite membrane. As a result, the composite becomes more stable than the pure CP. The large TG weight loss of the CP/Im composite material above 200 °C is because of evaporation of imidazole from the membrane or thermal decomposition.



Scheme 1. Molecular structures of chitin phosphate (CP) and imidazole (Im).

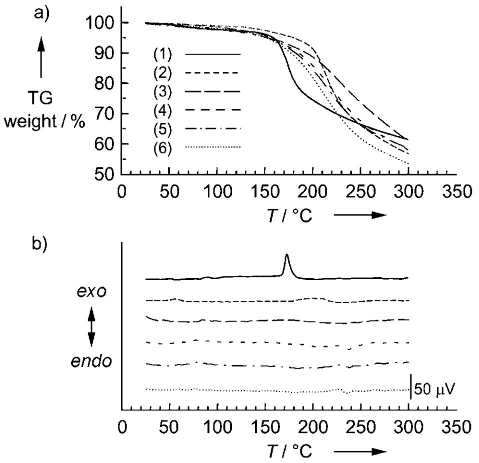


Figure 1. a) Thermogravimetric (TG) and b) differential thermal analyses (DTA) curves of CP/Im composite materials. (1) pure CP, (2) CP/20 wt% Im, (3) CP/50 wt% Im, (4) CP/100 wt% Im, (5) CP/200 wt% Im, and (6) CP/500 wt% Im composite materials.

The molecular structure of the acid/base complex in the CP/Im composite material was characterized by infrared (IR) spectroscopic analysis with a diamond attenuated total reflection prism with a resolution of $4\,\mathrm{cm^{-1}}$. Figure 2 shows the IR spectra of the CP/Im composite materials of a) pure CP, b) CP/20 wt% Im, c) CP/50 wt% Im, d) CP/100 wt% Im, e) CP/200 wt% Im, f) CP/500 wt% Im, and g) pure imidazole, respectively. The absorption band at $1011\,\mathrm{cm^{-1}}$, attributed to the asymmetric stretching vibration of the P–OH group (dashed line in Figure 2),[11,12] decreased when imidazole was mixed in the CP. In addition, two new absorption bands appeared at 1028 and $967\,\mathrm{cm^{-1}}$, the stretching vibration bands of $-\mathrm{HPO_4}^-$ and $-\mathrm{PO_4}^{2-}$ (dashed line in Figure 2),[13] respectively. These results indicated that the P–OH group of CP is deprotonated on doping of imidazole and forms the P–O$^-$ group. Alternatively, the absorption band at approximately $3100\,\mathrm{cm^{-1}}$ in the composite materials, which corresponding to the stretching band of the N–H group,[11] moderately increased in comparison with the spectrum of pure imidazole. These results suggest that the P–OH groups of CP are deprotonated on doping with imidazole and form P–O$^-$ groups. This free proton strongly interacts with the nonprotonated imidazole –N= atom. Therefore, the composite material of CP and imidazole is an acid/base salt (Scheme 2).

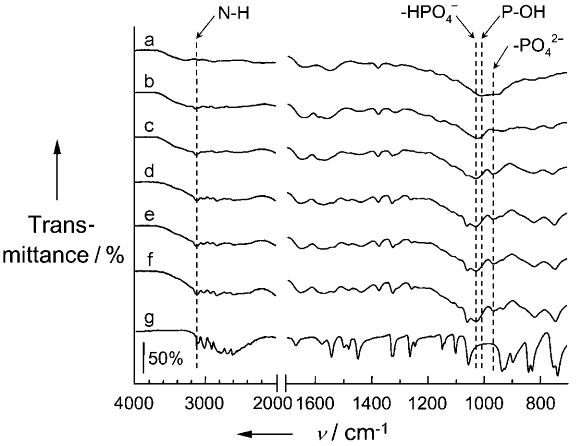
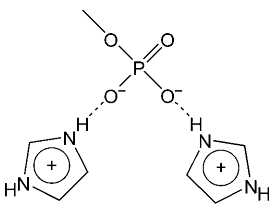


Figure 2. IR spectra of CP/Im composite materials with different doping ratios of imidazole. a) pure CP, b) CP/20 wt% Im, c) CP/50 wt% Im, d) CP/100 wt% Im, e) CP/200 wt% Im, f) CP/500 wt%Im, and g) pure Im materials.

The proton conductivity measurements of the CP/Im composite materials were demonstrated by the a.c. impedance method over the frequency range 1 Hz–1 MHz under a



Scheme 2. Acid–base composite material.

dry nitrogen flow. Thus, the measured impedance response indicates the anhydrous proton conductivity. A typical impedance response, as shown by Cole–Cole plots, of the CP/Im composite materials was similar to that of highly conducting proton membranes, such as humidified nafion, organic/inorganic hybrid membranes mixed with heteropolyacids,[14] monododecylphosphate (MDP)/benzimidazole,[5] 2-undecylimidazole (UI)/MDP,[6] uracil (U)/MDP,[7] and poly(vinylphosphonic acid) (PVPA)/heterocycle[8] composite materials (Figure 3 a). The proton conductivity measurements were carried out on the same sample four times under anhydrous conditions, with the temperature being varied from ambient to 160 °C. The conductivity decreased slightly on repeated measurements and reached a steady state after three. The anhydrous, steady-state proton conductivities of the CP/Im composite materials and their variation with the imidazole doping level and temperature are shown in Figure 3 b. The anhydrous proton conductivity of the CP/Im composite materials increased with temperature and reached a maximum at 150 °C. Additionally, the conductivity of the composite material became larger as the imidazole doping ratio increased. The CP/200 wt % Im composite material indicated the largest anhydrous proton conductivity of $7\times 10^{-3}\,\mathrm{S\,cm^{-1}}$ at 150 °C, while the pure CP membrane did not show any measurable proton conductivity ($<10^{-8}\,\mathrm{S\,cm^{-1}}$ at 150 °C). Additionally, the anhydrous proton conductivity of pure imidazole could not be measured by melting and evaporation at intermediate temperatures.[15] These results indicate that the biopolymer/heterocycle composite material becomes proton-conductive by forming acid/base ionic pairs and constructs a proton-conductive pathway with fast proton transfer.

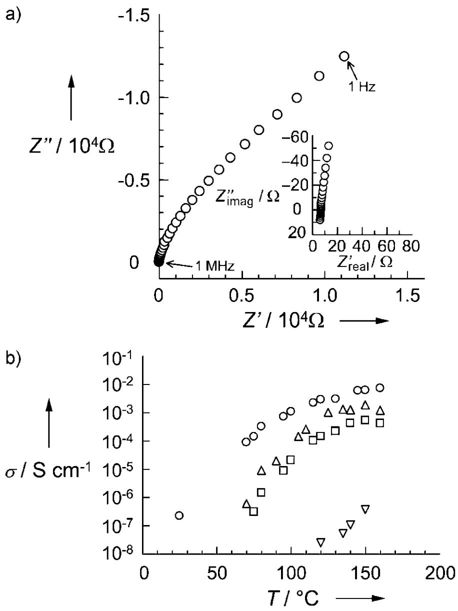


Figure 3. a) Typical impedance response (Cole–Cole plots) of CP/200 wt% Im composite material under anhydrous conditions. The frequency range is 1 Hz–1 MHz. The insert indicates the impedance response at the frequency range of 2 kHz–1 MHz. b) Proton conductivities of CP/Im composite materials with different imidazole doping ratios under anhydrous conditions. The doping ratios of Im are: ▽: 20 wt% Im, □: 50 wt% Im, ○: 200 wt% Im, and △: 500 wt% Im, respectively.

Previously, we reported a acid/base composite material with a heterocycle that acted as a proton-conducting membrane under anhydrous conditions.[5–8] In this case, a Grotthuss-type mechanism was proposed, in which proton transport by basic heterocycles can occur by movement from protonated molecules to nonprotonated neighbor molecules with a small activation energy of approximately 0.5 eV.[5,6,8] Namely, the protonated and nonprotonated nitrogen atoms in the heterocycle can act as donors and acceptors in proton-transfer reactions, respectively. In our investigations, the calculated activation energy (E_a) from the Arrhenius plots of the conductivities is approximately 0.6–0.4 eV (see the Supporting Information). This value is almost the same as other materials reported as anhydrous single proton conductors of UI/MDP composite materials[6] and PVPA/heterocycle composite materials.[8] These results suggest that proton conductivity in the CP/Im composite materials is based on proton transport by a Grotthuss-type mechanism[16,17] between imidazole groups. Therefore, the proton-conducting mechanism was proposed to be as follows: protonated imidazole centers are formed by proton transfer from the phosphonic acid group of the CP. These acid/base complexes composed of imidazole and the phosphonic acid groups can be confirmed by the IR spectroscopic analysis (see Figures 2 and Scheme 2). The phosphonic acid groups in CP appears to act as proton donors[16,17] to the imidazole centers, and the proton conductivity occurs between the imidazole centers by a Grotthuss-type mechanism. As a result, the CP/Im composite material gives a high proton conductivity of $7\times 10^{-3}\,\mathrm{S\,cm^{-1}}$ at 150 °C under anhydrous conditions. These biocomposite proton-conducting materials without the presence of water molecules are novel and could be applicable as an advanced electrolyte membrane for PEMFCs operated above 100 °C.

In summary, we have prepared an anhydrous proton conductor consisting of a commonly discarded biopolymer, chitin phosphate, and imidazole. The CP/200 wt % Im composite material showed a large proton conductivity of $7\times 10^{-3}\,\mathrm{S\,cm^{-1}}$ at 150 °C under anhydrous conditions. The utilization of a biopolymer such as CP for PEMFC technologies is novel and challenging as it is inexpensive, nonhazardous, and environmentally benign. Besides its superior ion-conducting properties under anhydrous or extremely low-humidity conditions, this biopolymer composite material may have the potential for application in bioelectrochemical devices, including implantable batteries and biosensors.

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[15] The melting point of pure imidazole is 90–91 °C. Namely, imidazole is in the liquid state at the intermediate temperature. In our experiments, the proton conductive measurements were performed by the sandwich of two Pt electrodes. Therefore, the conductivity of imidazole at the intermediate temperature could not be measured.

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