Anhydrous Proton Conductive Membrane Consisting of Acid/base Complex

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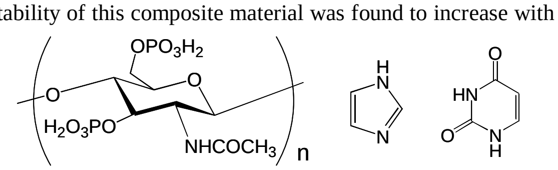
Introduction

The operation of polymer electrolyte membrane fuel cells (PEMFC) at intermediate temperature (100 - 200 °C) has been considered to provide many advantages, such as improved CO tolerance of the Pt electrode, the higher energy efficiency, fuel managements, and co-generation. However, at higher temperature, ion-exchange membranes, such as Nafion®, suffer from a reduction of proton conductivity due to a loss of water from membrane and also an irreversible change of the polymer structures. Therefore, anhydrous electrolyte materials with high proton conductivity have been investigated extensively. One of the approaches is the electrolyte membrane consisting of acid/base complexes. In particular, the hybrid material of acidic molecules, such as phosphoric acid and sulfuric acid, and basic heterocycle molecules have been reported to exhibit proton conductivity even under anhydrous condition.

In this study, we prepared an anhydrous proton conducting membrane using a composite of chitin phosphate (CP), one of discarded biopolymer, and imidazole (Im) or uracil (U) molecules, one of the basic heterocyclic molecules. This CP-200 wt% Im composite material showed the high proton conductivity of 7×10^{-3} S cm^{-1} at 150 °C under anhydrous (water-free) conditions. Additionally, the thermal stability of this composite material was found to increase with the doping ratio of the Im molecule.



CP Im U

Experimental

CP was synthesized by the previous report. The phosphorylation of chitin was confirmed by the IR spectroscopy. The degree of phosphorylation (DS) of chitin was determined by the CHN elemental analyses and ICP atomic emission spectrophotometry (P element). In this research, we have used the fully phospholated chitin (DS = 2.0, 100% phospholated).

Results and Discussion

The proton conductivity measurements of the CP-Im composite materials were demonstrated by the a.c. impedance method over the frequency range from 1 Hz to 1 MHz under dry nitrogen flow. Therefore, the measured impedance response indicates the anhydrous proton conductivity. The anhydrous proton conductivities of the CP-Im composite materials with different Im doping ratios of the (▽) CP-20 wt% Im, (□) CP-50 wt% Im, (○) CP-200 wt% Im, and (△) CP-500 wt% Im composite materials in the temperatures range from RT to 160 °C are shown in Figure 1. The anhydrous proton conductivity of the CP-Im composite material increased with the temperature and reached a maximum conductivity at 150 °C. Additionally, the conductivity of the composite material became larger with the doping ratio of the Im molecules. Especially, the CP-200 wt% Im composite material indicated the large anhydrous proton conductivity of 7×10^{-3} S cm^{-1} at 150 °C. In contrast, the pure CP membrane did not show any measurable proton conductivity (< 10^{-8} S cm^{-1} at 150 °C). These results suggest that biopolymer-heterocycle composite material becomes proton conductive by forming acid-base ionic pairs and constructs the proton conductive pathway having fast proton transfer reaction among molecules.

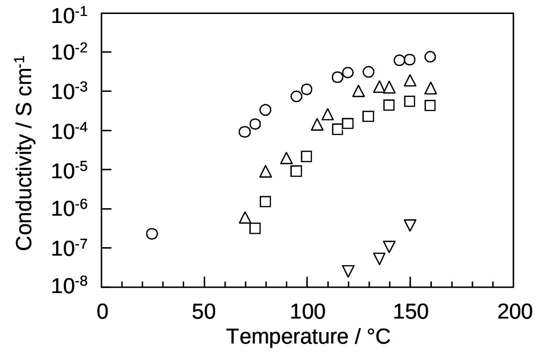


Figure 1. Anhydrous proton conductivities of CP-Im composite materials with different Im doping ratio under anhydrous condition. The doping ratios of Im are ▽, 20 wt% Im; □, 50 wt% Im; ○, 200 wt% Im; and △, 500 wt% Im, respectively.

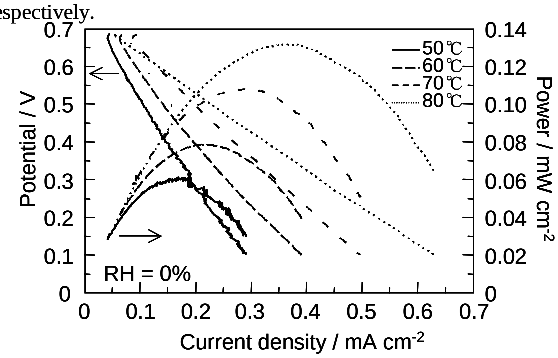


Figure 2. I–V characteristics of CP-50%U composite material with E-TEK® electrode under anhydrous condition. Pure hydrogen and oxygen were used.

Figure 2 shows I–V characteristic of the CP-U composite material with E-TEK® electrode (Pt loading 20 wt%) at different operational temperatures under anhydrous condition (dry-hydrogen and dry-oxygen). The open circuit voltage of approximately 0.8 V is a conventional potential for hydrogen/oxygen cell. The current density increased with the temperature and the power output of 130 μW cm^{-2} was obtained at 80 °C under anhydrous condition. These power densities increased with the humidity and indicated approximately 2 mW cm^{-2} at 30% relative humidity (RH). Additionally, these power output was retained under the heating of 70 °C for 24 hours.

These acid/base composite materials may have the potential for its superior ion conducting properties, in particular, under anhydrous or extremely low humidity conditions but also in bio-electrochemical devices including an implantable battery, bio-sensors, and others.

Acknowledgements

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