Hydroxyapatite-imidazole-polymer composite films as a proton conductor under no humidified condition

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ABSTRACT

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp)-imidazole (Im)-poly(vinylidene fluoride) (PVdF) composite films were prepared by casting the HAp dispersed solution that included Im and PVdF. Their conducting behaviors under no humidified condition and various temperatures were investigated. Two kinds of HAp (a-HAp and n-HAp) with different particle size were used. The average particle size of a-HAp was 1.25 μm in diameter and that of n-HAp was 0.61 μm in diameter. The conductivity for a-HAp-Im-PVdF (1:2:5, by weight) film at 120°C was 8.4 μS cm^{-1} and that for n-HAp-Im-PVdF (1:2:5, by weight) was 298 μS cm^{-1}. The particle size of HAp and the amount of Im and HAp in the films affected their conducting behavior and their mechanical properties.

Keywords: proton conductor, dry condition, polymer electrolyte membrane fuel cell

1 INTRODUCTION

Solid polymer electrolyte type fuel cell (PEFC) is one of the candidates for an energy generator with high performance and low production of carbon dioxide [1]. Higher temperature operation (> 100°C) of PEFC will offer higher energy conversion performance [2]. However, typical solid polymer electrolytes (SPE) for PEFC, such as Nafion™, base on the conduction mechanism through the water molecules in the SPE. To keep the water molecules in the SPE, the operation temperature of the fuel cells with the SPE should be lower than 100°C. SPE for the fuel cells with higher operation temperature (> 100°C) requires other proton conduction mechanism that is not depended on water molecules. Some investigations were performed with various systems, Nafion-imidazole (Im)-phosphoric acid [3], Teflon™-Im-phosphoric acid [3], polymer electrolyte membranes based in the polybenzimidazole (PBI) doped with phosphoric acid [4], and PBI doped with Im or 1-methylimidazole and phosphoric acid [5]. Previously, we reported preparation of SPE films based on hydroxyapatite (HAp), Im, and poly(ethylene oxide) (PEO) and their temperature dependence of conductivity and their proton conduction mechanism without water molecules [6]. However, the HAp-Im-PEO films were not stable over 60°C, because the melting point of PEO is about 60°C. Crosslinking of PEO (c-PEO) with tolylene 2, 4-diisocyanate as a cross-linking reagent was effective to keep the dimension of the film. However, the SPE with c-PEO matrix was not acceptable because of their dimension and mechanical instability over 100°C. In this paper we report that preparation of HAp-Im-poly(vinylidene fluoride) (PVdF) composite films and their conductive performance at the temperature over 100°C. PVdF acts as a binder to improve the thermal and mechanical stability of the composite films.

2 EXPERIMENTAL

2.1 Materials

Poly(vinylidene fluoride) (PVdF), average molecular weight 534,000 (Aldrich) and imidazole (Im) (Wako) were used as received. Other chemicals were also purchased and used as received.

2.2 Preparation of hydroxyapatite

Two types of HAp (a-HAp and n-HAp) were prepared [7, 8]. One type of HAp, a-HAp was prepared according to the reported procedure [7] with some modification. The pH of calcium chloride aqueous solution ($[Ca^{2+}] = 0.2$ mol dm^{-3}]) was adjusted to 9.01 by addition of Tris-HCl buffer (Solution A). Diammonium hydrogenphosphate aqueous solution ($[PO_4^{-3}] = 0.12$ mol dm^{-3}) was prepared and the pH of the solution was adjusted to 9.30 by addition of NH_3-NH_4Cl buffer (Solution B). The solution B (40 ml) was added to 40 ml of the solution A at room temperature. After the addition the mixed solution was stirred for 2 h at room temperature. The white participate was filtered off from the solution and the solid was dried at 80°C for 24 h and then at room temperature for 24 h under dynamic vacuum conditions (*ca.* 0.13 kPa).

Another type of HAp, n-HAp was prepared according to the method in the paper [8] with some modification. Phosphoric acid (2.03 g) was added to 150 ml of water. Dispersion of calcium hydroxide (2.22 g / 150 ml of water) was added into the phosphoric acid aqueous solution at room temperature (addition rate 7.5 ml min^{-1}). After the addition of the $Ca(OH)_2$ dispersion, the reaction mixture was stirred 2h and then the mixture was left at rest for 15 h at room temperature. The participated solid was dried at 80°C for 24 h and then at 80°C for 24 h under dynamic vacuum condition (*ca.* 0.13 kPa). The n-HAp solid was grinded in an

agate mortar and the grinded powder was riddled with 200 mesh sieve. Calcinated HAp (c-HAp) was prepared from n-HAp by heating at 800°C, for 2 h in the air.

2.3 Preparation of HAp-Im-PVdF composite

Typical preparation procedure of the composite was as follows. Hydroxyapatite (a-HAp or n-HAp), 0.1 g was dispersed into 3 mL of *N, N*-dimethylformamide (DMF). Imidazole (0.2 g) was added into the HAp dispersed DMF. The HAp dispersed DMF solution containing Im was stirred for 24 h (Dispersed solution C). PVdF (0.5 g) was dissolved in 5 mL of DMF and stirred for 24 h (Solution D). The dispersed solution C was added to the solution D and the HAp dispersed solution was stirred at room temperature for 24 h. The HAp dispersed solution containing PVdF and Im was poured into an Al foil dish and the DMF was removed at 50°C for 24 h under atmosphere pressure and then at 55°C, for 6 h under dynamic vacuum condition (*ca.* 0.13 kPa). The resulted film was presented as HAp-Im-PVdF (1:2:5) composite film. Resulted film was referred as HAp-Im-PVdF (x:y:z) composite film. The x, y, and z in the parenthesis express the weight ratio of each component in the composite film. The HAp particles in the films were dispersed homogeneously under the visual observation.

2.4 Measurements

A composite film for conductance measurement was sandwiched with two stainless steel plates (13 mm in diameter). Conductivity for the composite film was measured with an LCR meter (HIOKI 3531 Z Hi tester, 10-100 mV_{p-p}, 1-100 kHz) under various temperature conditions from 50 to 120°C. Infrared spectra of samples were recorded with an FTIR spectrophotometer (IRPrestige-21, Shimadzu). XRD patterns of HAp and the composites films were recorded with an X-ray diffraction meter (XD-D1, Shimadzu, CuKα, λ=0.1542 nm). DSC measurements of the samples were preformed with a differential scanning calorimeter (DSC5100S, Bruker AXS); heating rate was 10 K min⁻¹. The mechanical properties of the composite films under heating condition (100°C) were recorded with a thermal mechanical analysis instrument (EXSTAR6000 TMA/SS, SII). Typical sample size was 10.0 mm × 3.0 mm, 100 μm thickness. All the tests were conducted at a crosshead speed of 50 μm/min and offset load of 50 mN. The percentage strain (λ) was calculated as follows:

$$\lambda = [(L - L_0)/L_0] \times 100 \tag{1}$$

where L is the total extension measured from the grip displacement and L_0 is the grip distance. The initial Young's modulus was calculated from the initial slope of the stress–strain curve obtained. SEM observation of HAp particles that were Au sputtered with an Ion Sputter (E101, Hitachi) was performed with an SEM equipment (JSM-T300, JEOL).

3 RESULTS AND DISCUSSION
3.1 Structure of hydroxyapatite

Characterization of a-HAp and n-HAp was performed with XRD, FTIR, and SEM measurements. FTIR spectra of a-HAp and n-HAp showed the peak at 875 cm⁻¹ that is attributed to HPO_4^{2-}. This suggests that a-HAp and n-HAp are partially calcium deficient hydroxyapatite [9]. Fig. 1 shows the XRD patterns of HAp used in this investigation. The XRD pattern of c-HAp powder indicates that c-HAp is crystalline form. The XRD pattern of a- or n-HAp powder suggests that the structure of a-HAp or n-HAp is mainly hydroxyapatite structure containing partially amorphous phase. The average particle size of a-HAp was 1.25 μm and that of n-HAp was 0.61 μm determined from SEM observations of them.
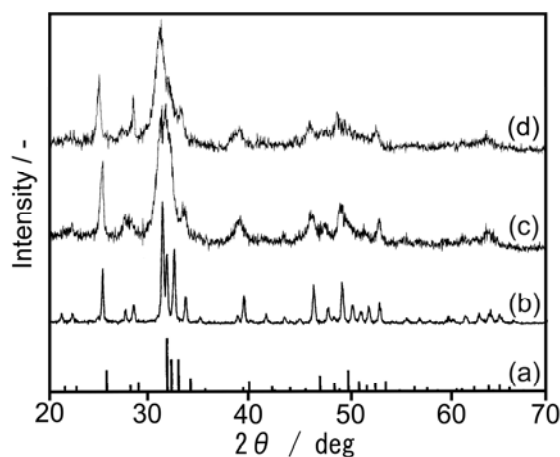

Fig. 1 XRD patterns of (a) JCPSD card (Card No.90432), (b) a-HAp, (c) n-HAp, and (d) c-HAp (Calcinated at 800°C for 2h in the air).

3.2 Temperature dependence of conductivity for HAp-Im-PVdF composite films

PVdF-based composite films were prepared from HAp dispersed DMF solution containing Im and PVdF, and the resulted films with HAp were free-standing, flexible, and opaque. Conductivity for c-HAP-Im-PVdF film was very low, under 10⁻⁹ S cm⁻¹, which is the limitation on measurement of our equipment. Fig. 2 shows temperature dependence of conductivity for a-HAp-Im-PVdF and n-HAp-Im-PVdF composite films. The conductivity clearly increases with temperature for all the samples because of the higher diffusivity of the Im molecules and the higher flexibility in the chains of the PVdF matrix. Conductivity at 120°C of a-HAp-Im-PVdF (1:2:5) was 8.4 μS cm⁻¹ and that of n-HAp-Im-PVdF (1:2:5) was 298 μS cm⁻¹. Conductivity of the SPE film with n-HAp was about 35 times higher than that with a-HAp. At all temperatures, the conductivity for n-

HAp-Im-PVdF films with other composition was also higher than that for a-HAp-Im-PVdF films. This suggests that conductivity for the SPE film depends on the kind of HAp. Optical microscope observation of the films suggested that dispersion of n-HAp particles in the SPE films was not similar to that of a-HAp. The n-HAp particles were well dispersed in the composite film and a-HAp particles were not in the matrix.
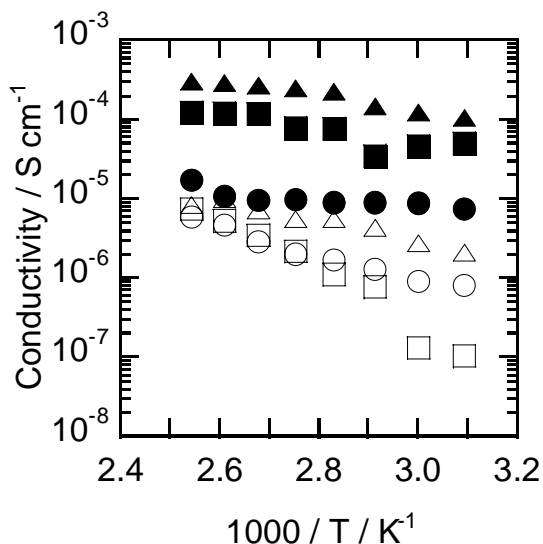

Fig. 2 Temperature dependence of conductivity for HAp-Im-PVdF composite films.

a-HAp-Im-PVdF (x:y:z): △ (1:2:5), □ (2:2:5), ○ (5:2:5)

n-HAp-Im-PVdF (x:y:z): ▲ (1:2:5), ■ (2:2:5), ● (5:2:5)

The Arrhenius plots show linear lines irrespective of type of HAp and concentration of Im and PVdF. They can be interpreted by normal Arrhenius relationship, eq 2.

$$\log \sigma = \log \sigma_0 - E_a/RT \qquad (2)$$

where σ_0 is the conductivity at infinite T, R is gas constant, E_a is activation energy, the results are illustrated in Table 1.

Table 1 Parameters of Arrhenius plots calculated from temperature dependence of conductivity for HAp-Im-PVdF composite films

Sample	σ_0 / S cm^{-1}	E_a / kJ mol^{-1}
a-HAp-Im-PVdF(1:2:5)	6.09×10^{-2}	9.15
a-HAp-Im-PVdF(2:2:5)	1.88×10^{-4}	28.0
a-HAp-Im-PVdF(2:5:5)	1.50×10^{-3}	21.3
n-HAp-Im-PVdF(1:2:5)	1.19×10^{-1}	6.96
n-HAp-Im-PVdF(2:2:5)	1.69×10^{-1}	5.81
n-HAp-Im-PVdF(2:5:5)	8.01×10^{-2}	8.25
Im-PVdF(2:5)	1.20×10^{-4}	29.5

The E_a for the composite films, n-HAp-Im-PVdF is 5.81 - 8.25 kJ mol^{-1}. The E_a for hydrated pure Nafion obtained by NMR is 11.0 kJ mol^{-1} [10] and by themacroscopic conductivity measurements is 9.34 kJ mol^{-1} [11]. The E_a for the n-HAp-Im-PVdF is lower than that for Nafion.

The parameter, σ_0 is closely related with the number of charge carriers in the composite film. The σ_0 for the composite film with n-HAp is the one or two orders in magnitude larger than that for the film with a-HAp. Thus, the conductivity for the composite film with n-HAp is higher than that for the film with a-HAp.

3.3 Mechanical property of the composite films

Mechanical property of an SPE film for a PEFC operated under higher temperature (> 100°C) condition is also important for its long-life operation. Fig. 3 describes the stress–strain results at 100°C obtained on the HAp-Im-PVdF films as well as for a pure PVdF film. Specific values of the mechanical properties of HAp-Im-PVdF films are summarized in Table 2. A yielding phenomenon was observed clearly with the PVdF film. The maximum stress appeared at the yield point (36%, 7.1 MPa). The breaking elongation of PVdF film was 102%. Strain-stress curves of a-HAp-Im-PVdF films were difference with that of PVdF. The yield point of a-HAp-Im-PVdF (1:2:5) was 2.8% and 3.9 MPa. The breaking elongation of the film was 18% and the values of other films with a-HAp were 15 and 10%. The n-HAp-Im-PVdF (1:2:5) film showed a yielding phenomenon, however, the maximum stress (6.8 MPa) appeared over the first yield point (21%, 5.7 MPa). The breaking elongation of the film was 99%. Mechanical toughness of the films is reduced by addition of a-HAp particles. Addition of n-HAp particles to the PVdF film almost preserves the mechanical strength of an original PVdF film.
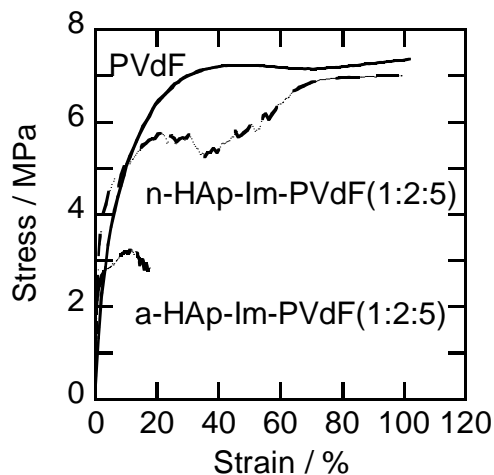

Fig. 3 Strain-stress curves of PVdF and HAp-Im-PVdF composite films at 100°C.

3.4 Effects of dispersion of HAp in PVdF matrix to conductivity and mechanical property

We reported the charge carriers in HAp-Im-PEO or HAp-Im-c-PEO (Crosslinked PEO) are imidazolium ions that are produced by acid-base reaction between imidazole and the phosphate groups on the surface of HAp [6]. We also checked the PVdF-based composite films with FTIR measurements. Infrared spectra of the composite films suggest that the charge carriers in them are imidazolium ions that are produced by acid-base reaction between imidazole and the phosphate groups on the surface of HAp.

Depersiveness of HAp in the PVdF matrix is also concerned with conductivity and mechanical property of HAp-Im-PVdF composite films. Distance (d) between particles (r is radius of the particles) in a matrix is calculated as follows [12]:

$$d = [(4\pi \times \sqrt{2} / 3V)^{1/3} - 2] \times r \qquad (3)$$

where V is volume fraction of the particles in the matrix. When the content of HAp in the a-HAp-Im-PVdF composite film is equal to that in the n-HAp-Im-PVdF film, the estimated distance between an HAp particle and another one in the n-HAp-Im-PVdF composite film is about 2 times shorter than that in the a-HAp-Im-PVdF film. The shorter distance between the HAp particles will provide higher conductivity and enhanced mechanical property for the n-HAp-Im–PVdF composite films. Detail investigation about the effect of dispersibility of HAp on the composite film system is now in progress.

ACKNOWLEGEMENT

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Table 2 Mechanical property of PVdF and HAp-Im-PVdF composite films at 100°C

Sample [a]	Modulus / MPa	Yield stress / MPa	Yield strain / %	Breaking elongation / %
PVdF	120	7.1	36	102
a-HAp-Im-PVdF (1:2:5)	390	2.8	3	18
a-HAp-Im-PVdF (2:2:5)	440	3.8	15	34
a-HAp-Im-PVdF (5:2:5)	330	3.1	10	16
n-HAp-Im-PVdF (1:2:5)	160	5.7, 6.8	21, 72	99
n-HAp-Im-PVdF (2:2:5)	350	6.0	20	98
n-HAp-Im-PVdF (5:2:5)	590	5.5	9	96

a) Typical sample size is 10.0 mm × 3.0 mm, 100 µm thickness. Cross head rate 50 µm min^{-1}