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High Ionic Conductivity of Transparent Film of Hydroxyapatite and Poly(vinyl alcohol) Nanocomposite

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Summary: Hydroxyapatite (HAp)-polyvinyl alcohol (PVA) nanocomposite film containing Li^+ was designed as a solid polymer electrolyte. A composite was prepared by reacting $Ca(OH)_2$ with H_3PO_4 in the presence of PVA which is denatured in order to have the carboxyl group, and a $LiN(CF_3SO_2)_2$ was added. HAp particles were commonly formed in the shape of spindles (long axis ca. 80 nm and short axis ca. 25 nm). The obtained nanocomposite film, in which HAp particles were dispersed uniformly, is transparent, flexible and drawable. Its ionic conductivity is about 10^{-3} S/m at room temperature. This value is very large. This high ionic conductivity is considerable on the basis of the dynamic percolation theory.

Keywords: films; hydroxyapatite; Ionic conductivity; nanocomposite

Introduction

At a present, polymer film with a high conductivity is in great demand, because a polymer with a high dc conductivity is required for realizing a the thin fuel cell.[1,2] However, it is difficult to obtain a polymer film in which ion transport is stable and dc conductivity is high. For the realization of a polymer film with a high conductivity, we focus on a composite of inorganic materials and polymers. On the other hand, a traditional micrometer-scale composite is far too limited to obtain excellent properties. However, recently, there have been many reports indicating that a nanocomposite shows unique characteristics. It is known that the characteristics of the interface between a polymer matrix and inorganic particles in a composite are different from those of bulk materials. That is, new properties appear at the interface. When particle size decreases into nanometer size and without aggregation, surface-to-bulk ratio increases markedly.[1,2] This phenomenon is called the nanoeffect.[1,2] Consequently, the nanoeffect induces different properties compared with traditional composites.[1,2] In this study, in order to realize the high ionic conductivity caused by nanoeffect, a new nanocomposite film with Li^+ was prepared by a in situ method. The results obtained are reported.

Sample Preparation

It is well known that mere mixing a polymer matrix and inorganic particles leads to particle aggregation. In contrast, with interactions between the polymer matrix and the inorganic particles, we speculate that the inorganic particles can be uniformly dispersed in the polymer matrix. On the basis of this concept, we used the interactions between calcium cations and carboxyl groups. A nanocomposite film was fabricated by the following in situ method. Here, in all experiments, a polyvinyl alcohol (PVA) containing 1 mol% itaconic acid units (Kuraray Co., Ltd.: KM 118) was used. First, in the in situ preparation of hydroxyapatite (HAp), calcium hydroxide $Ca(OH)_2$ was added to an aqueous PVA solution and then phosphoric acid H_3PO_4 was fed for 1 h. Second, lithium salt (35 wt%, $LiN(CF_3SO_2)_2$), was poured to the colloidal solution. Third, we cast and

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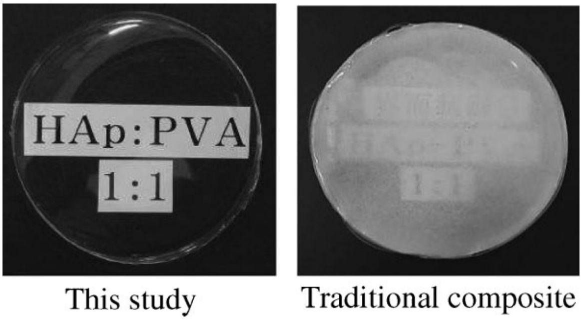

Figure 1.
Fabrication of new nanocomposite material.

then dried the colloidal solution. Finally, a transparent composite film with Li^+, was obtained, as shown in Figure 1. On the other hand, the HAp content in the film was determined quantitatively from the weight change around the burning at 800 °C.

The composite film which was dried at 110 °C for 2 h was kept at 800 °C for 6 h in the electric furnace. Then, the weight of remained ash was measured. The result showed that the weight ratio of HAp to PVA is one. We also confirmed that the ash is HAp by IR measurement. On the other hand, a traditional composite film was fabricated. Only mixing the PVA solution, HAp powder and $LiN(CF_3SO_2)_2$ results in the formation of a two-layer solution with the deposition of white powder ($PVA{:}HAp{:}LiN(CF_3SO_2)_2 =$ 32.5 wt%:32.5 wt%:35 wt%). The opaque film is the traditional composite film, as shown in Figure 1. Typically, the drawing of a traditional HAp-PVA composite film is impossible.

However, the HAp-PVA composite film obtained from the in situ method is transparent and flexible; thus, it can be drawn. This is a very important point in this study.

Morphology of Composite Film Obtained from the in Situ Method

The formation of HAp particles in the transparent film fabricated by our in situ method was measured using an X-ray diffraction (XRD) system. The peaks of the freeze-dried powder of the transparent composite film are consistent with those peaks corresponding to the HAp crystal. Thus, the obtained XRD pattern indicates the formation of HAp particles in the in situ method. Here, first, the obtained transparent film, as shown in Figure 1, was confirmed as a "HAp-PVA" composite film. Then, we investigated the morphology of the HAp-PVA composite film by transmission electron microscopy (TEM). Figure 2 shows the TEM image of the HAp-PVA composite film obtained from the in situ method. HAp particles were observed as black spindles. Particle size is obtained by graphic data processing from the TEM images. The length and width of the particles were estimated to be about 80 nm and 25 nm, respectively. Nanometer-sized HAp particles uniformly dispersed in the PVA matrix. From these results, we concluded that the HAp-PVA "nanocomposite" film was successfully fabricated by our in situ method. On the other hand, the primary particle diameter of HAp used for fabricating the traditional composite film is about 30 nm. However, HAp particle coheres, and the secondary particle diameter is about 2 μm in the traditional composite.

Ionic Conductivity of HAp-PVA Nanocomposite Film

We measured the ionic conductivity of this film. Figure 3 shows the relationship between ionic conductivity and HAp content. Triangles indicate the data of

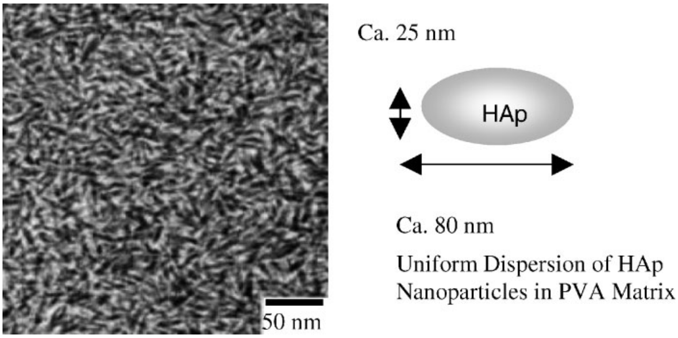

Figure 2.
TEM image of nanocomposite film.

the HAp-PVA nanocomposite film. As HAp content increased, ionic conductivity increased. When HAp content of was 50 wt %, the ionic conductivity of the HAp-PVA nanocomposite film was approximately 10^{-3} S/m. Also, the ionic conductivity of HAp-PVA nanocomposite (PVA:HAp:$LiN(CF_3SO_2)_2 = 50{:}50{:}0$) in which is not added lithium salt is 2.2×10^{-11} S/m. In contrast, the ionic conductivity of the traditional composite was only 10^{-8} S/m. The nanodispersion of HAp led to a high ionic conductivity.

Nonlinear Complex Conductivity of HAp-PVA Nanocomposite Film

A model of the ion transfer mechanism of a polymer, in which the dynamic percolation theory proposed first by Ratner et al.,[3] reflects dynamics based on the segmental motion of a chain molecule,[4] attracts attention. The conductivity on the angular frequency ω, $\sigma(\omega)$, in this model, is characterized by the ion-hopping probability through a bond between sites, a fraction of the bond, and the bond renewal rate λ.

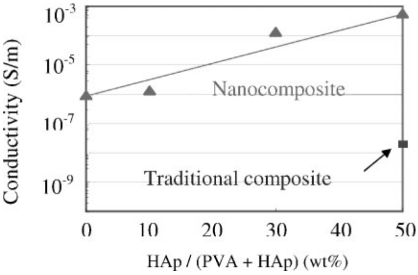

Figure 3.
Nanodispersion of HAp leading to high ionic conductivity.

$$\sigma(\omega) = \frac{n_e e^2}{kT} \int_0^{\infty} e^{-j\omega t} \sum s^2 e^{-\lambda t} p_0(s,t)\,dt \qquad (1)$$

Here, $p_0(s,t)$ is the conditional probability at site s at time t, e is the elementary charge, n_e is the carrier density, k is the Boltzmann constant, and T is the absolute temperature. In this model, for the ions to contribute to ion conduction, a long-distance motion is necessary, which is realized not only by the local motion of polymer chains (hopping motion), but also by repeated coordination exchanges assisted by the segmental motion of chain molecules (represented by λ).[3,4] However, Eq. (1) is very complex; thus, we have already reported the approximate expansion equation, Eq. (2), which is based on Eq. (1), in the case of $\omega \to 0$.[5,6] Using the approximate equation, we obtain the following equation.[5,6] Here, I is the current, σ_1 is linear conductivity, and σ_n $(n > 1)$ is nonlinear conductivity.

$$I = \sigma_1 E + \sigma_3 E^3 + \sigma_5 E^5 + \cdots \qquad (2)$$

$$\sigma_1 = \frac{n_d n_e e^2 \langle r^2 \rangle_0}{kT} \left(\lambda - \frac{\lambda^2 kT e^{\frac{\Delta U}{kT}}}{\alpha_0 f(s) n_s e P_a} \right) \qquad (3)$$

$$\sigma_3 = \frac{\lambda^2 e n_d n_e \langle r^2 \rangle_0 e^{\frac{\Delta U}{kT}}}{3 P_0 f(s) n_s P_a} \left(\frac{e n_s P_a}{2kT} \right)^3 \qquad (4)$$

$$\sigma_5 = \frac{3\lambda^2 e n_d n_e \langle r^2 \rangle_0 e^{\frac{\Delta U}{kT}}}{1420 P_0 f(s) n_s P_a} \left(\frac{e n_s P_a}{2kT} \right)^5 \qquad (5)$$

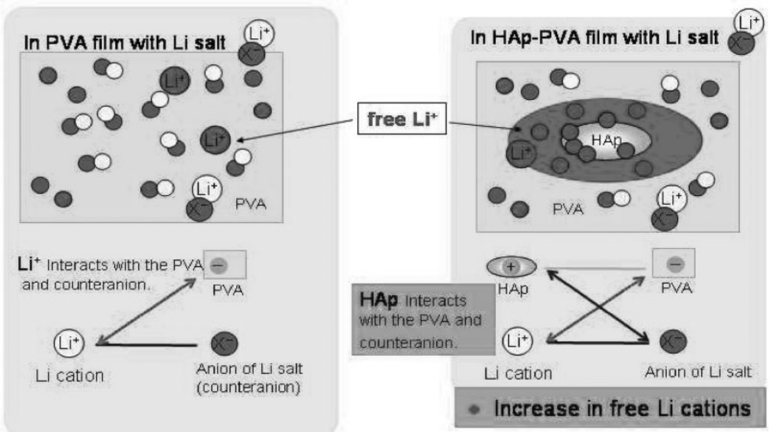

Figure 4.
Enhancement mechanism of ionic conductivity.

Here, P_a ($>\lambda$) is the elementary hopping distance, $\langle r^2\rangle_0$ is the mean-squared displacement on the static percolation lattice, α_0 is the transformation coefficient, n_s is the effective carrier density, n_d is the dimensional constant, and $f(s)$ is fraction bonds. However, it is impossible to obtain the important parameters, such as n_sP_a, in Eqs. (3)–(5), using the observed linear conductivity σ_1, because there are many unknown constants, if some assumptions are not introduced. However, the ratio of σ_3 to σ_5 becomes the very simple equation,

$$\frac{\sigma_5}{\sigma_3} = \frac{9e^2n_s^2P_a^2}{5680k^2T^2} \tag{6}$$

Using Eq. (6), it becomes possible to obtain n_sP_a, if σ_3 and σ_5 could be measured experimentally, without establishing assumptions.

Thus, we measured σ_3 and σ_5 of HAp-PVA nanocomposite film using the system of nonlinear conductivity measurements following previous study.[5,6] As a result, we obtained values of $\sigma_3 = 2.5 \times 10^{-17}$ SmV^{-2} and $\sigma_5 = 1.8 \times 10^{-32}$ Sm^{3}V^{-4} of HAp-PVA nanocomposite film. Using these σ_3 and σ_5, $n_sP_a = 3.2 \times 10^{-8}$ was obtained from Eq. (6). In contrast, n_sP_a is eightfold as large as 4×10^{-9} for polyethylene oxide (PEO) with Li$^+$ which is a very famous ion-conducting polymer, as previously reported.[5,6] Following to Ratner's papers,[3] the increase in n_sP_a means that effective career density becomes larger.[4] Why is the effective carrier density large in the HAp-PVA nanocomposite film? We propose the following model on the basis of Croce's theory.[7] First, we consider, in the case of the PVA film with lithium salt without HAp, lithium cations could form complexes with the matrix PVA and counter anions, as shown in Figure 4. On the other hand, in the case of the HAp-PVA film with Li$^+$, the other interaction exists. The Ca^{2+} ions on the HAp particle surface might interact with the anion site of PVA and the counter anion of lithium salt (Figure 4). We speculate that such interaction between HAp particles and counter-anions induces an increase in free lithium cations on the surface of HAp particles. This is reason why the effective carrier density is large in the HAp-PVA nanocomposite. As a result, HAp-PVA nanocomposite shows the high ionic conductivity.

Summary

Preparation of nanocomposite by in situ method

The HAp-PVA nanocomposite film was fabricated by an in situ method by the interaction between HAp and PVA.

Transparent and drawable thin film can be easily fabricated.

High ionic conductivity of HAp-PVA nanocomposite film with Li^+

From the results of nonlinear conductivity measurements, we conclude that effective carrier density is very large in HAp-PVA nanocomposite film. We speculate that its high ionic conductivity was caused by the increase in free lithium cations, that was induced by the ionic interaction of HAp particles.

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