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Synthesis of calcium phosphate hydrogel from waste incineration fly ash and bone powder

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ABSTRACT

Waste incineration fly ash and bone powder could be successfully recycled into calcium phosphate hydrogel, a type of fast proton conductor. Various properties of the intermediate and calcium phosphate hydrogel from them were characterized and compared with that from calcium carbonate reagent. It was found that the intermediate from the incineration fly ash and calcium phosphate glass was more brittle than that from bone powder and calcium carbonate reagent. The electric conductivity of crystallized hydrogel obtained from all raw materials increases exponentially with temperature. However, the crystallized hydrogel from incineration fly ash has lower electric conductivity and lower crystallinity than that from bone powder and the reagent. Moreover, the difference in electric conductivity between these crystallized hydrogels decreases with temperature. Compared with using the reagent as a raw material, bone powder provides a 25% reduction in the usage of H_3PO_4 to acquire the crystallized hydrogel which has the highest conductivity. These experimental results suggest that the incineration fly ash and bone powder are useful calcium sources for the synthesis of calcium phosphate hydrogel.

1. Introduction

Waste incineration fly ash is generated by garbage incineration plants. Over 7 million tons of waste incineration fly ash is discharged per year in Japan [1]. The amount of waste increases annually. Since $Ca(OH)_2$ or CaO powder is blown into an incinerator in order to prevent the formation of dioxins, the main component of waste incineration ash is Ca. Although synthesis methods of tobermorite [2,3], zeolite [4,5] and calcium apatite [6] were proposed as new methods of reusing waste incineration fly ash, reported literature on such methods is still less when compared to those on reusing coal fly ash [7–10]. A small portion of waste incineration fly ash is used as cement fills, while a large portion is reclaimed from the sea [1]. The large daily output and the limited landfill capacity have caused various social and environmental problems. "Law for the Promotion of Effective Utilization of Resources [1991]" and "Fundamental Law for Establishing a Sound Material-Cycle Society [2000]" established by the Japanese government makes it obligatory to reuse waste incineration fly ash. Thus, new effective ways to reuse it should be quickly developed.

Over 4 million tons of chicken bone is also discharged per year from chicken meat processing plants as industrial wastes in Japan [11]. Some amount of chicken bone is used as a raw material for fertilizers. Chicken bone consists of Ca and P. New methods to reuse chicken bone are also required.

Fuel cells are one of the most important technologies for supplying clean energy. Many types of methods have been investigated in order to reduce the cost of fuel cells and to improve the efficiency of the cell performance. Calcium phosphate hydrogel [12,13] is thought to be one of the promising candidates for the electrolyte of fuel cells because it has higher proton conductivity and greater heat resistance than perfluorosulfonic polymers such as Nafion [14]. Furthermore, calcium phosphate hydrogel is a viscous material and it easily forms films and plates. Since it can be also applied to an electric double layer capacitor and a sensor for hydrogen, its demand is expected to increase.

Therefore, the synthesis of calcium phosphate hydrogel from incineration ash and chicken bone powder is proposed as a new effective method for reusing them [15]. The performance of calcium phosphate hydrogel synthesized from $CaCO_3$ reagent and from incineration ash and bone powder has been compared.

2. Experimental

2.1. Synthesis method of calcium phosphate hydrogel

Waste incineration fly ash, bone powder and $CaCO_3$ reagent were used as the raw material. Waste incineration fly ash and

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Table 1
Properties of tested incineration ash and bone powder

Metallic element	Content (wt.%)	
	Incinerations ash	Bone powder
Ca	66.8	80.0
P	–	14.9
K	8.0	0.3
Si	6.1	1.0
Al	5.8	–
S	4.9	–
Zn	3.0	1.0
Fe	2.1	0.2
Ti	1.9	–
Others	1.4	2.6

chicken bone powder were obtained from an incineration plant and a chicken meat processing plant in Higashi Hiroshima, Japan, respectively. The metallic element compositions of incineration fly ash and bone powder were determined by EDX (Shimadzu, EDX-800). Ten samples were measured by EDX, and measurement error margin was plus or minus 15%. The result is listed in Table 1; here, its content is defined as the ratio of metallic element. Incineration fly ash mainly consists of Ca and includes K, Si, S and so on. On the contrary, bone powder mainly consists of Ca and P, and its impurities cannot be almost detected. Fig. 1 shows the X-ray diffraction patterns of incineration fly ash and bone powder. Incineration fly ash has a crystalline phase of KCl, $SiCl_4$, and $Ca(OH)_2$, while bone powder has a crystalline phase of only $Ca_{10}(PO_4)_6(OH)_2$.

The volume of 3.4–8.5 cm^3 phosphoric acid reagent, which has a concentration of 85 wt.%, was added to 5.0 g of as-received incineration ash. Here, a ratio of 6.8 cm^3 of phosphoric acid reagent to 5.0 g of a raw material was defined as the additional ratio of H_3PO_4, $R = 1$, which is equal to the stoichiometric ratio of calcium phosphate. Namely, phosphoric acid reagent was added with R ranging from 0.5 to 1.25. A batch mixture of them was melted under air at 1200 °C for 30 min and poured onto an iron plate. The intermediate calcium phosphate glass was acquired by quenching the melt. The glass powder, which was crushed using a hammer, was adjusted to a diameter of 0.125–2.38 mm by sieving. The resulting glass powder was pulverized with a stainless ball mill, which had an inner diameter of 12.0 cm. Here, the rotational speed of the ball mill was set to 125 rpm.

A mixture of the pulverized powder weighting 2.0 g and distilled water with a volume of 2.0 cm^3 was placed on a petridish at 35 °C and 95% RH for 48 h in order to prepare amorphous calcium phosphate hydrogel. In order to crystallize the derived amorphous hydrogel, it was heat-treated at 90 °C for 6 h in saturated vapor.

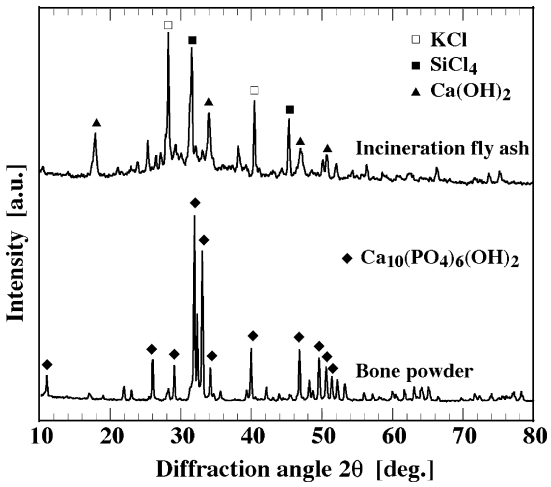

Fig. 1. XRD peak charts of incineration fly ash and bone powder.

2.2. Measurement methods

The particle size of calcium phosphate glass powder was measured by using the laser scattering particle size analyzer (Horiba, LA-920). The crystalline phase was identified by XRD (Rigaku RINT-2000) and the chemical component was quantified by EDX (Shimadzu, EDX-800). The alternating current conductivity of the hydrogel was measured by using the chemical impedance meter (Hioki, 3532-80) with the Cole–Cole plot method, where the applied voltage was 1.0 V and the measurement frequency was varied from 100 Hz to 1.0 MHz. The hydrogel was filled in the measurement cell to a height of 5.0 mm, depth of 10.0 mm, and width of 50.0 mm width. The distance between the two electrodes for the current measurement was set to 50.0 mm and the distance of the two electrodes for the applying voltage was 26.0 mm. For the purpose of measurements, the cell was shielded with a polystyrene cover using vinyl tape in order to prevent serious drying of the hydrogel.

3. Results and discussion

Fig. 2 shows the appearance of the intermediate from various raw materials and phosphoric acid. The intermediate that is synthesized from incineration fly ash at the additional ratio of H_3PO_4, $R = 0.5$ is unvitrified. This intermediate has the crystalline phase of CaO, $Ca_2P_2O_7$ and $Ca(PO_3)_2$, as shown in Fig. 3(a). On the other hand, in the case of the additional ratio of H_3PO_4, $R = 1.0$, a transpar-

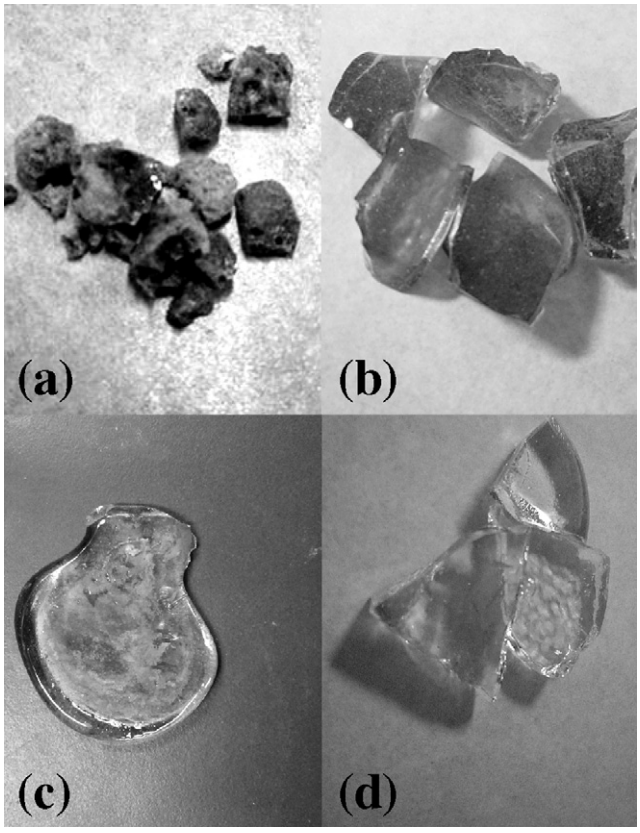

Fig. 2. Appearance of intermediates synthesized from various raw materials ((a) from incineration fly ash, $R = 0.5$, (b) from incineration fly ash, $R = 1.0$, (c) from bone powder, $R = 1.0$, and (d) from $CaCO_3$ reagent, $R = 1.0$).

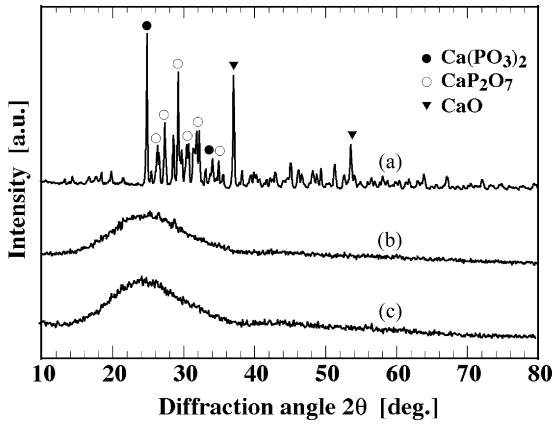

Fig. 3. XRD peak charts of intermediates synthesized from various raw materials ((a) from incineration fly ash, $R = 0.5$, (b) from incineration fly ash, $R = 1.0$, and (c) from bone powder, $R = 1.0$).

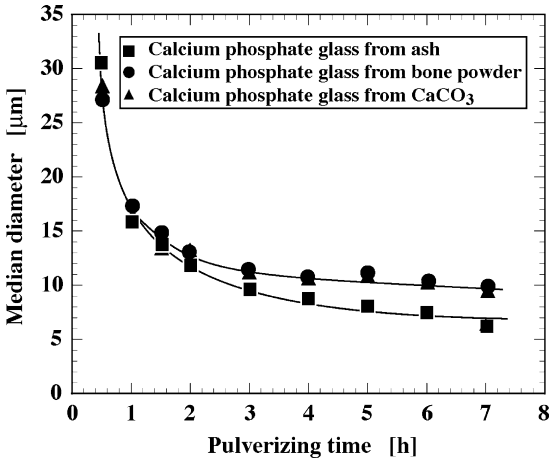

Fig. 5. Change in median diameter of calcium phosphate glass powder with pulverization time for various raw materials.

ent green calcium phosphate glass is obtained, which is completely amorphous, as shown in Fig. 3(b). It is believed that impurities in the incineration fly ash impart a green color to the glass. Furthermore, it can be observed that the same transparent calcium phosphate glass is synthesized from bone powder at the additional ratio of H_3PO_4, $R = 1.0$ that is synthesized from $CaCO_3$ reagent (Fig. 2(c) and (d)). The glass from $CaCO_3$ reagent is also completely amorphous, as shown in Fig. 3(c).

Fig. 4 shows the relationship between the additional ratio of H_3PO_4 and the content of P in the intermediate, where the content of P is defined as the ratio of P to all the metallic elements present in the intermediate. In any case, the content of P in the intermediate increases with the additional ratio of H_3PO_4. Since bone powder contains the P element, the intermediate from the bone powder provides the highest content of P. Further, bone powder requires least additional ratio of H_3PO_4 in order to vitrify the intermediate. This result suggests that the element P present in the bone powder is effectively used to synthesize calcium phosphate glass. A change in the content of P for incineration fly ash is similar to that for $CaCO_3$ reagent. This result suggests that impurities such as Al, Si, and K react with H_3PO_4 as a substitution for Ca.

The change in the particle size with pulverizing time during ball milling with respect to calcium phosphate glass powders obtained from various raw materials that have 40% of the P content (incineration fly ash and $CaCO_3$ reagent: $R = 1.0$, bone powder: $R = 0.75$) is shown in Fig. 5. The mass median diameter of all glass powders decreases to a constant value with an increase in the pulverizing time. The difference in the median diameter change between the glass powders synthesized from bone powder and $CaCO_3$ reagent is negligible. Furthermore, incineration fly ash provides the minimum median diameter at a steady state. This result indicates that the glass powder synthesized from incineration fly ash is more brittle and easier to grind as compared to the glass powders synthesized from bone powder and $CaCO_3$ reagent.

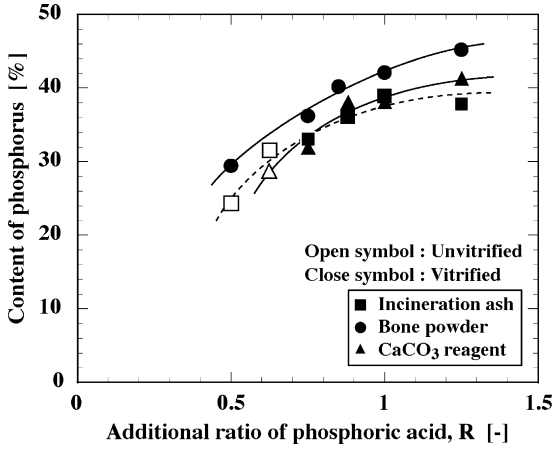

Fig. 4. Relationship between the additional ratio of H_3PO_4 and content of phosphorus in the intermediate.

It is believed that calcium phosphate glass consists of long-chain phosphate structures and bridging calcium ions between the longchains, as shown in Fig. 6(a) [16]. In the case of calcium phosphate glass from incineration fly ash, K^+, Al^{3+} and so on which are present in the incineration fly ash, also bridge between the longchains substituting for some part of Ca^{2+}. As the ion diameter of these ions differ from that of Ca^{2+}, it is thought that calcium phosphate glass from incineration fly ash has the strain and deformation as shown in Fig. 6(b). For this reason, the glass from incineration fly ash is more brittle than that from bone powder and $CaCO_3$ reagent.

The above-mentioned hydrogelation process from calcium phosphate glass powders was studied. Fig. 7 shows a change in the alternating current conductivity of amorphous calcium phosphate hydrogel with the gelation time. Here, the median diameter of any glass powder was adjusted to 11.0 μm. In any case, the conductivity increases to a maximum value, it subsequently decreases to a constant value with the gelation time. This result suggests that the hydrogelation process mechanism does not depend on any type of glass powder. Immediately after calcium phosphate glass powder is added to distilled water, Ca^{2+}, PO_4^{3-} and so on are dissolved in distilled water. Hence, the ionic conduction induced by these ions increases the conductivity of calcium phosphate hydrogel. However, the viscosity of hydrogel increases and the proton conduction of hydrogel occurs as the hydrogelation progresses. Therefore, the ionic conduction is restrained. Hence, the conductivity decreases to a constant value with the gelation time.

The characteristics of crystallized calcium phosphate hydrogels from various raw materials were examined. Fig. 8 shows the X-ray diffraction patterns of crystallized calcium phosphate hydrogels obtained from various raw materials. It is found that hydrogels; which have the crystalline phase of calcium phosphate hydrate, $Ca(H_2PO_4)_2{\cdot}H_2O$; can be obtained from all the raw materials. Although the degree of crystallinity for crystallized calcium phosphate hydrogels synthesized from $CaCO_3$ reagent and bone powder is almost equal, crystallized calcium phosphate hydrogel from incineration fly ash has the lowest degree of crystallinity. This

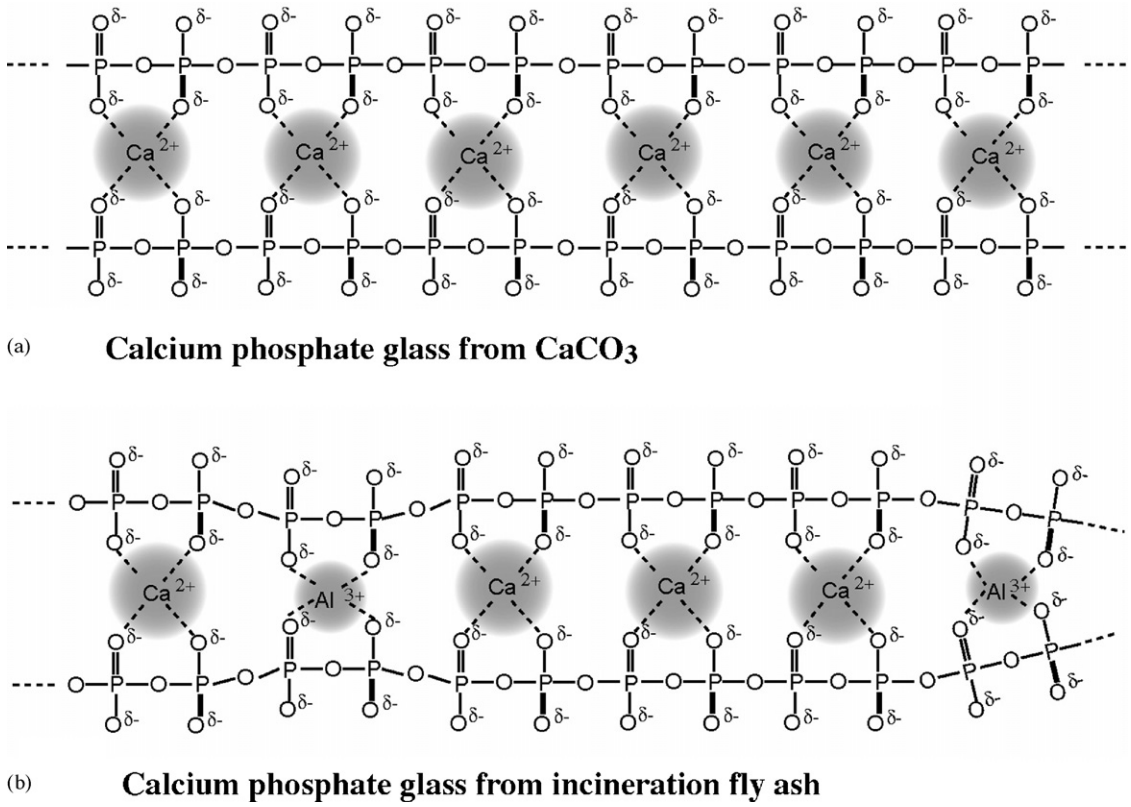

Fig. 6. Structure of calcium phosphate glass ((a) calcium phosphate glass from $CaCo_3$ and (b) calcium phosphate glass from incineration fly ash).

is because impurities contained in incineration fly ash disturb the crystallization to $Ca(H_2PO_4)_2{\cdot}H_2O$.

Fig. 9 shows the relationship between the measurement temperature and the conductivity of crystallized calcium phosphate hydrogels. The conductivity of crystallized calcium phosphate hydrogels from all raw materials increases exponentially with temperature. The high proton conduction in the hydrogel can be explained as the hopping of numerous protons dissociated from the P–OH groups between hydroxyl groups and water molecules. The conductivity of crystallized hydrogel from bone powder almost agrees with that from $CaCO_3$ reagent. Although crystallized hydrogel from incineration fly ash has the lowest conductivity, its gradient in the conductivity, which corresponds to the activation energy for conduction, is steeper than others. However, we have not clarified effects of metallic impurities in incineration fly ash on the conductivity sufficiently. We are now investigating it and will report it in the future. Accordingly, an increase in the temperature lessens the difference in the conductivity between incineration fly ash and the others. This fact signifies that it is effective to reuse incineration fly ash into crystallized calcium phosphate hydrogel when it is used at a relatively high temperature.

The effects of the content of P in calcium phosphate glass on the conductivity of crystallized calcium phosphate hydrogel were

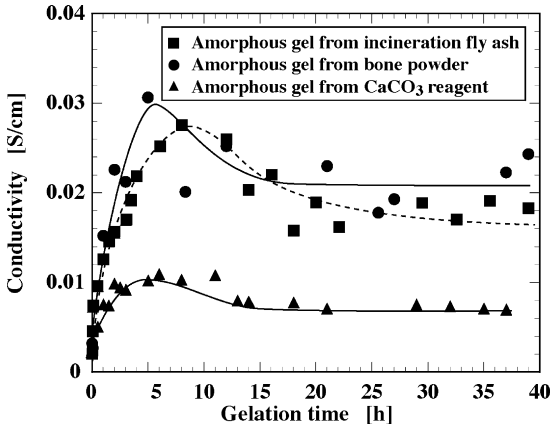

Fig. 7. Change in conductivity of amorphous calcium phosphate hydrogels from various raw materials with gelation time.

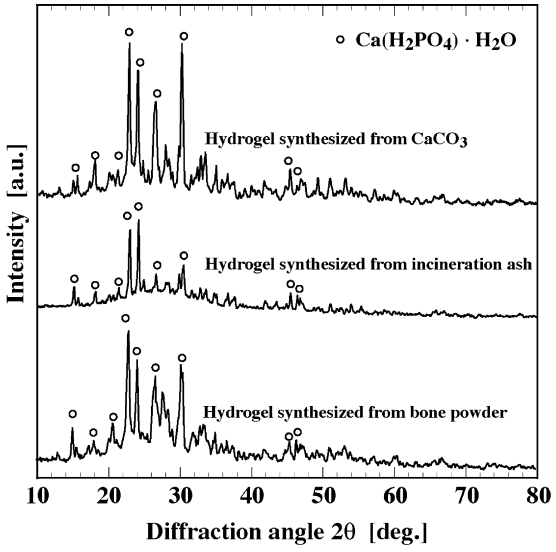

Fig. 8. XRD peak charts of crystallized calcium phosphate hydrogel synthesized from various raw materials.

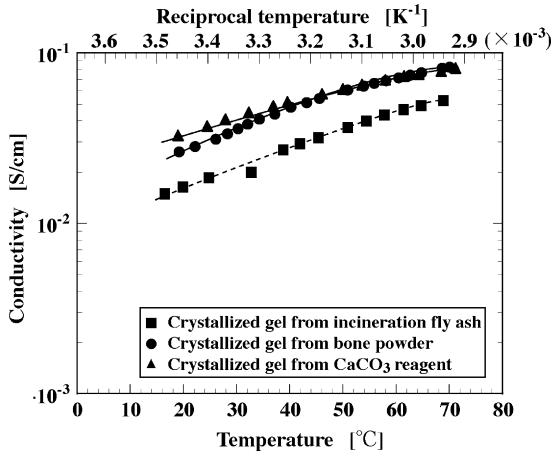

Fig. 9. Conductivity of crystallized calcium phosphate hydrogel as a function of temperature for various raw materials.

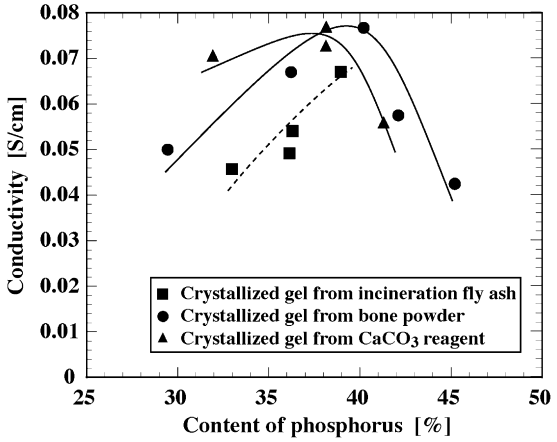

Fig. 10. Relationship between the content of phosphorus in calcium phosphate glass powder and the conductivity of crystallized calcium phosphate hydrogels for various raw materials.

measured. As shown in Fig. 10, crystallized calcium phosphate hydrogel has maximum conductivity at approximately 40% content of P, which is independent of the type of raw material. It was confirmed that the crystalline phase of crystallized calcium phosphate hydrogel acquired below 35% was $CaHPO_4$ and the crystallized calcium phosphate hydrogel has crystalline phases of both $Ca(H_2PO_4)_2{\cdot}H_2O$ and a by-product of $Ca_2P_2O_7{\cdot}H_2O$ ranging above 45%. Hence, it can be said that in order to maximize the conductivity of crystallized calcium phosphate hydrogel, the optimum content of P in calcium phosphate glass is about 40%. Figs. 4 and 5 reveal that bone powder provides a 25% reduction in the usage of H_3PO_4 in order to maximize the conductivity of crystallized calcium phosphate hydrogel. Further, the difference in the dependence of the conductivity of crystallized calcium phosphate hydrogel on the temperature between the bone powder and the $CaCO_3$ reagent is hardly observed, as shown in Fig. 9. Consequently, bone powder is extremely suitable as a raw material for crystallized calcium phosphate hydrogel.

4. Conclusions

The properties of calcium phosphate hydrogels derived from incineration fly ash and bone powder were investigated. The results obtained in this study can be summarized as follows:

(1) Waste incineration fly ash, which has a Ca content of 66.8%, and bone powder can be successfully recycled into amorphous and crystallized calcium phosphate hydrogels, a type of fast proton conductor.
(2) The intermediate calcium phosphate glass synthesized from incineration fly ash has a lower mechanical strength than that from $CaCO_3$ reagent and bone powder.
(3) The hydrogelation process mechanism from calcium phosphate glass powder to amorphous calcium phosphate hydrogel does not depend on the type of raw materials.
(4) Crystallized calcium phosphate hydrogel from incineration fly ash has a lower degree of crystallinity than that from $CaCO_3$ reagent and bone powder.
(5) The conductivity of crystallized hydrogel from bone powder is almost equal to that from $CaCO_3$ reagent, which was higher than that from incineration fly ash.
(6) Bone powder provides a 25% reduction in the usage of H_3PO_4 to acquire the high conductivity for the crystallized calcium phosphate.
(7) In order to maximize the conductivity of crystallized calcium phosphate hydrogel, the optimum content of P in calcium phosphate glass should be approximately 40%.

Acknowledgements

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