Synthesis of calcium phosphate hydrogel from waste incineration fly ash and its application to fuel cell

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Abstract

Waste incineration fly ash was successfully recycled to calcium phosphate hydrogel, a type of fast proton conductor. The crystallized hydrogel from incineration fly ash had a lower electric conductivity and a lower crystallinity than that from calcium carbonate reagent. However, the difference in electric conductivity between these crystallized hydrogels decreases with temperature. This was due to the presence of potassium in the incineration fly ash. The fuel cell with a membrane electrode assembly (MEA) using the calcium phosphate hydrogel membrane prepared from incineration fly ash was observed to generate electricity. The performance of this fuel cell was almost equal to that of a mixture of K_2CO_3 and $CaCO_3$ reagents; further, the performance of the former was superior to the fuel cell with perfluorosulfonic polymer membrane at temperatures greater than approximately 85 ˚C.

1. Introduction

In Japan, over 7 millions tons of waste incineration fly ash generated by garbage incineration plants are discharged every year, and this amount has been increasing (Government of Japan, 2006). The main component of waste incineration ash is Ca because $Ca(OH)_2$ or CaO powder is blown into the incinerator in order to prevent the generation of dioxins. The synthesis methods of tobermorite (Yao et al., 1999; Tamura et al., 2000), zeolite (Murayama et al., 2001; Miyake et al., 2002), and calcium apatite (Tanaka et al., 2005) have been proposed as new ways of reusing waste incineration fly ash. However, reports on process that reuse waste incineration fly ash are less than on techniques for reusing coal fly ash (Querol et al., 2002; Fukui et al., 2006, 2007; Penilla, 2006). A minor portion of waste incineration fly ash is used as cement fillers but the major portion is reclaimed from the sea. 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 obligate to reuse waste incineration fly ash. Thus, there is a need to rapidly develop new effective ways of reusing waste incineration fly ash.

The fuel cell is one of the most important key technologies for supplying clean energy. In the development of fuel cells, the focus must be on reducing the cost in order to facilitate their widespread use. Many methods have been investigated to reduce the cost of fuel cells and to improve the efficiency of their performance (Matsuda et al., 2000; Chandra et al., 2002). Since calcium phosphate hydrogel (Kasuga et al., 2001, 2002; Akamatsu et al., 2005) is cheaper and shows a higher proton conductivity and greater heatresistance than perfluorosulfonic polymers such as Nafion (Colomban et al., 1992), it

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is thought to be one of the candidates for the electrolyte of fuel cells. Furthermore, as this hydrogel can be also applied to electric double-layer capacitors, and hydrogen sensors, the demand for it is expected to increase in future. Here, this hydrogel is a kind of ionic hydrogels, which are not hydrophilic networks that can be absorb large amount of water.

We have proposed the synthesis of calcium phosphate hydrogel from incineration fly ash (Fukui et al., 2008a). And we have also reported that using calcium phosphate hydrogel from incineration fly ash might contribute to the reduction of the cost of the fuel cell though the cost of the electrolyte occupied about 10 % of the cost of the fuel cell (Fukui et al., 2009). The present study deals with the characterization of the electric conductivity of calcium phosphate hydrogel obtained from incineration fly ash and the determination of the fuel cell performance for calcium phosphate hydrogel membrane prepared from incineration fly ash. Further, the electric conductivity and fuel cell performance are compared with those of calcium phosphate hydrogel synthesized from pure reagents.

2. Experimental

2.1 Preparation of calcium phosphate hydrogel

Waste incineration fly ash with a mass median diameter of 60.0 μm was obtained from an incineration plant in Higashi-Hiroshima, Japan. The composition of incineration fly ash was 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**; it mainly comprises Ca apart from containing K, Si, S, and so on. In order to clarify effects of K component in incineration fly ash, waste incineration fly ash, $CaCO_3$ reagent, and a mixture of K_2CO_3 and $CaCO_3$ reagents ($K_2CO_3/CaCO_3 = 0.08$) were used as the

raw materials. **Fig.1** shows the X-ray diffraction patterns for incineration fly ash and it comprises KCl, $CaSO_4$, and $Ca(OH)_2$ and so on in the crystalline phase.

A volume of 6.8 cm^3 of phosphoric acid reagent (85% liquid) was added to 5.0 g of a raw material. The batch mixture was melted in air at 1200 ˚C for 30 minutes and it was poured onto an iron plate. The intermediate, calcium phosphate glass, was acquired by quenching the melt. The glass powder was crushed with a hammer, and powder particles in the diameter range of 0.125-2.38 mm was obtained by sieving. This glass powder was pulverized with a stainless ball mill to obtain a median diameter of 11.0 μm. Here, the rotational speed of the ball mill was set at 125 rpm.

A mixture of the pulverized powder and distilled water was placed in a Petri dish at 35 ˚C and 95% RH for 48 hours to prepare amorphous calcium phosphate hydrogel. In order to crystallize the derived amorphous hydrogel, it was heat-treated in saturated vapor at 90 ˚C for 6 hours. Here, the moisture content of hydrogel was defined by the mass ratio of distilled water to the derived hydrogel.

2.2 Characterization of measurements

The particle size of the calcium phosphate glass powder was measured by a 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 a chemical impedance analyzer (Hioki, 3532-80) by using the Cole-Cole plot method; 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 whose height, depth, and width were 5.0 mm, 10.0 mm, and 50.0 mm, respectively. The distance between the two electrodes for

the current measurement was set at 50.0 mm and that for the applied voltage was set at 26.0 mm. For the measurements, the cell was protected by covering with a polystyrene cover using a vinyl tape in order to prevent the drying of the hydrogel.

2.3 Preparation of membrane electrode assembly and determination of fuel cell performance

For the fabrication of a membrane electrode assembly (MEA), a 50.0 μm thick layer of crystallized calcium phosphate hydrogel which had a moisture content of 50% was coated onto a carbon electrode with a Pt catalyst layer and a thin gas diffusion layer by a controlled coater (Matsuo K-101). The area of the carbon electrode was 4.0 cm^2. The calcium phosphate hydrogel layer on the anode was dried for 24 hours at room temperature to increase its mechanical strength. Subsequently, the dried hydrogel layer on the anode was press-joined to the wet hydrogel layer on the cathode by adding 10 μL of distilled water for 1 minute.

A schematic diagram of the fuel cell performance is given in **Fig.2**. The prepared MEA, which has a square-shaped working electrode area of 2.0 cm^2, was placed in a single-cell test station fixture set in a temperature and humidity controlled box to determine the fuel cell performance. The fuel cell temperature was controlled to be in the range of 15-90 ˚C. Humidified hydrogen gas was heated in a buffer volume and supplied to the anode side at 1.0 kPa (gauge pressure). The air at atmospheric pressure was fed to the cathode side. The change in the cell voltage was measured for various values of the output current, which was controlled by an electronic load (Array, 3710A).

As a control experiment, the performance of the fuel cell containing the commercial supplied perfluorosulfonic polymer membrane whose moisture content was optimized was also measured under the same experimental conditions.

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3. Results and discussions

3.1 Characterization of calcium phosphate hydrogel

Fig.3 shows the appearance of the intermediate formed from various raw materials and phosphoric acid. The intermediate that is synthesized from incineration fly ash appears as vitrified transparent green calcium phosphate glass. Furthermore, it can be observed that the same transparent calcium phosphate glass is synthesized from the mixture of K_2CO_3 and $CaCO_3$ reagents, and that from $CaCO_3$ reagent. It was confirmed by X-ray diffraction patterns that any obtained glass is completely amorphous, though the results are not shown here. Consequently, it can be staked that incineration fly ash can be reused as calcium phosphate glass.

The electric conductivity of calcium phosphate hydrogels synthesized from various raw materials will now be discussed. Amorphous calcium phosphate hydrogels, which have various moisture contents, are prepared by varying the volume of distilled water added to the pulverized glass powder. **Fig.4** shows the relationship between the moisture content and the electric conductivity of calcium phosphate hydrogel synthesized from various raw materials. In all the cases, the alternating current conductivity of amorphous calcium phosphate hydrogel increases exponentially and subsequently remains almost constant. It is thought that this result is a consequence of the destruction of the calcium phosphate hydrogel structure. In other words, calcium phosphate hydrogel retains water between long-chain phosphate structures, as shown in **Fig.5** (Fukui et al., 2008b). The distance between the long chains in the structure increases with the moisture content, which corresponds to the amount of water in the hydrogel. This increase causes the destruction of calcium ion bridges between the long chains. For this reason, the conductivity of

amorphous calcium phosphate hydrogel is almost constant when the moisture content is relatively high. Moreover, for the calcium phosphate hydrogel synthesized from $CaCO_3$ reagent, the critical moisture content at which the destruction of the gel structure begins is larger than that of the hydrogel synthesized from other raw materials. This may be because potassium ion present in the incineration fly ash and the mixture of K_2CO_3 and $CaCO_3$ reagents breaks the long-chain phosphate structures as shown in Fig.5(c). The validity of this phenomenon is investigated now and we will report it in future. It can be observed that calcium phosphate hydrogels synthesized from incineration fly ash and the mixture of K_2CO_3 and $CaCO_3$ reagents have a higher conductivity than the calcium phosphate hydrogels synthesized from $CaCO_3$ reagent. Hardly any difference can be found in the conductivity change between the amorphous calcium phosphate hydrogels synthesized from incineration fly ash and that obtained from the mixture of K_2CO_3 and $CaCO_3$ reagents. This fact indicates that the electric conductivity of amorphous calcium phosphate hydrogel obtained from incineration fly ash is strongly affected by potassium ions and both ion conduction due to the potassium ions and proton conduction occurs. The 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.

In this study, crystallized calcium phosphate hydrogel which had a moisture content of 50% was characterized. **Fig.6** shows the relationship between the measurement temperature and the electric conductivity of crystallized calcium phosphate hydrogel. The conductivity of crystallized calcium phosphate hydrogels obtained from all raw materials increases exponentially with the temperature. The conductivity of the crystallized hydrogel obtained from incineration fly ash is almost similar to that synthesized from the mixture of K_2CO_3 and $CaCO_3$ reagents. Though crystallized

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hydrogel from $CaCO_3$ reagent has the highest conductivity, its increasing rate in the conductivity, which corresponds to the activation energy for conduction, is smaller than that for hydrogel synthesized from any other raw materials. Accordingly, an increase in the temperature decreases the difference in the conductivity between the hydrogel obtained from $CaCO_3$ reagent and that synthesized from other raw materials. This fact implies that it is effective to reuse incineration fly ash as crystallized calcium phosphate hydrogel at relatively high temperatures. Furthermore, hardly any difference can be observed in the conductivity change between crystallized calcium phosphate hydrogel synthesized from incineration fly ash and those obtained from the mixture of K_2CO_3 and $CaCO_3$ reagents. Therefore it can be staked that in addition to amorphous hydrogel, crystallized hydrogel synthesized from incineration fly ash is also mainly subjected to K element in incineration fly ash.

Fig.7 shows X-ray diffraction patterns of crystallized calcium phosphate hydrogels synthesized from various raw materials. It is found that hydrogels that contain calcium phosphate hydrate $Ca(H_2PO_4)_2H_2O$ in the crystalline phase can be obtained from all raw materials. Crystallized calcium phosphate hydrogel synthesized from $CaCO_3$ reagent has the highest degree of crystallinity. The degree of crystallinity for crystallized calcium phosphate hydrogel synthesized from incineration fly ash is almost equal to that for the hydrogel synthesized from the mixture of K_2CO_3 and $CaCO_3$ reagents. This fact suggests that impurities, especially K element, contained in incineration fly ash prevent the crystallization of $Ca(H_2PO_4)_2H_2O$. For these reasons, crystallized hydrogel from $CaCO_3$ reagent has a higher conductivity than that obtained from any other raw material.

3.2 Fuel cell performance

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The change in the cell voltage was measured for various values of the current density, and the power density was calculated from the measurement. **Fig.8** shows the cell voltage and power density as a function of the current density. In any case, the cell voltage decreases monotonously as the current density increases. Further, an increase in the cell temperature causes an increase in the cell voltage and power density. Hence, it can be observed that the fuel cell with a MEA fabricated by using the calcium phosphate hydrogel synthesized from incineration fly ash successfully generates electricity. However, the performance of this fuel cell is lower than that containing a MEA fabricated by calcium phosphate hydrogel synthesized from $CaCO_3$ reagent. This is because calcium phosphate hydrogel synthesized from incineration ash has a lower electric conductivity than that obtained from $CaCO_3$ reagent, as shown in Fig.6.

The dependence of the fuel cell performance on the cell temperature was evaluated with the power density for a current density of 30.0 mA/cm^2. The result is shown in **Fig.9**. An increase in the cell temperature causes an increase in the cell voltage of fuel cells fabricated with a calcium phosphate hydrogel membrane prepared from any raw material. The fuel cell using the hydrogel membrane prepared from $CaCO_3$ reagent has the highest cell voltage at all measured temperatures. However, its gradient of in the cell voltage is smaller than that of fuel cells using hydrogel membranes prepared from other raw materials. Consequently, the difference in the cell voltage among fuel cells with a hydrogel membrane decreases with the cell temperature. Moreover, it can be also found that the cell voltage of the fuel cell containing the hydrogel membrane prepared from incineration fly ash is almost equal to that of the fuel cell processing a hydrogel membrane synthesized from the mixture of K_2CO_3 and $CaCO_3$ reagents. This result shows good agreement with the change in the electric conductivity shown in Fig.6. On the other hand, the cell voltage of the fuel cell fabricated with perfluorosulfonic polymer

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decreases with the cell temperature; in particular, it decreases rapidly at temperatures above 80 ˚C. At temperatures above approximately 85 ˚C, the cell voltage of the fuel cells comprising a hydrogel membrane synthesized from any raw material is higher than that of the cell containing perfluorosulfonic. Thus, it can be concluded that it is quite effective to use calcium phosphate hydrogel synthesized from incineration fly ash in a fuel cell when it is used at relatively high temperatures.

4. Conclusions

  The properties of calcium phosphate hydrogels derived from incineration fly and reagents were investigated. The performance of the fuel cells fabricated with these calcium phosphate hydrogels was determined. The results obtained in this study can be summarized as follows.

1.   Waste incineration fly ash, whose Ca content is 66.8% can be successfully recycled into amorphous and crystallized calcium phosphate hydrogel, a type of fast proton conductor.

2.   Crystallized calcium phosphate hydrogel synthesized from incineration fly ash has a lower degree of crystallinity than that obtined from $CaCO_3$ reagent.

3.   Potassium in incineration fly ash reduces the degree of crystallinity and the conductivity of the crystallized hydrogel and it promotes the destruction of the amorphous gel structure.

4.   The fuel cell with a MEA fabricated from calcium phosphate hydrogel synthesized from incineration fly ash could successfully generate electricity.

5.   The performance of the fuel cell containing a hydrogel membrane fabricated with calcium phosphate hydrogel synthesized from incineration fly ash is almost equal to

that of the fuel cell containing a hydrogel membrane obtained from pure reagents at temperatures above approximately 85 ˚C; further the performance of this cell is superior to the fuel cell with a perfluorosulfonic polymer membrane.

Acknowledgements

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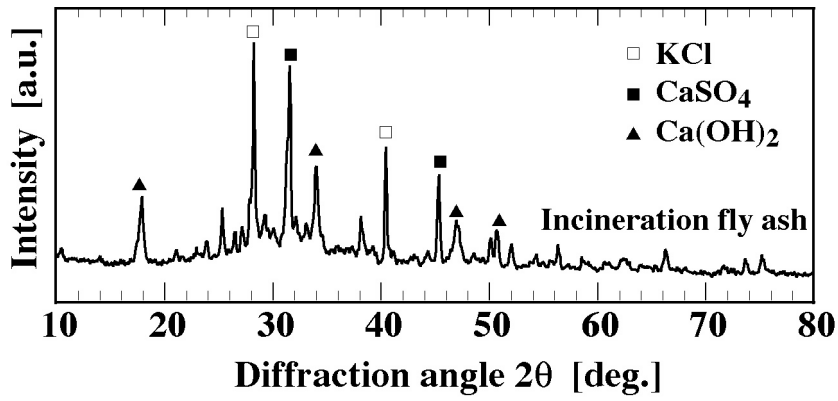
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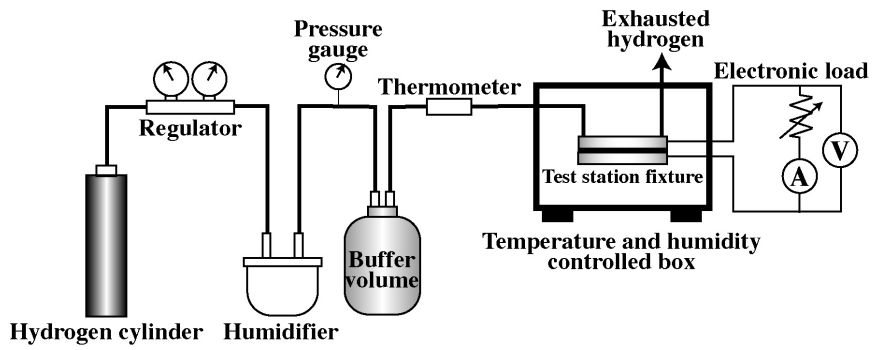
Fig.1 XRD peak chart of incineration fly ash

Fig.2 Schematic diagram of cell performance measurement set-up
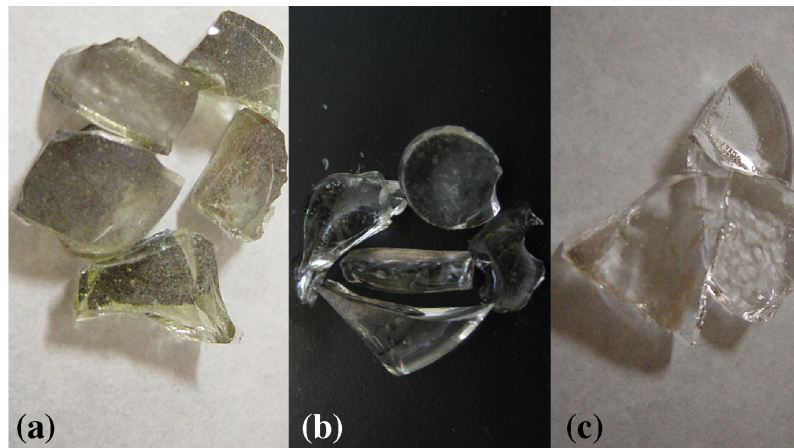

Fig.3 Appearance of intermediates synthesized from incineration fly ash and reagents
((a) From incineration fly ash, (b) From mixture of K_2CO_3 reagent with $CaCO_3$ reagent,
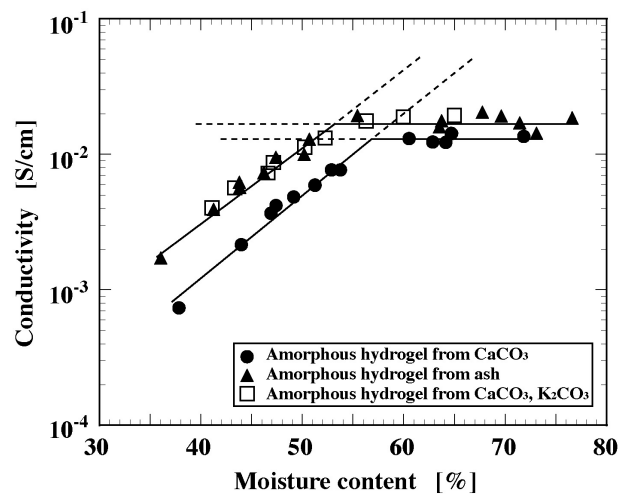(c) From $CaCO_3$ reagent)

Fig.4 Electric conductivity of amorphous calcium phosphate hydrogel at 25 ℃ as a
function of moisture content for various raw materials

Fig.5 Structure of calcium phosphate hydrogel

Fig.6 Conductivity of crystallized calcium phosphate hydrogel as a function of
temperature for various raw materials

Fig.7 XRD peak charts of crystallized calcium phosphate hydrogel synthesized from
reagents and incineration fly ash

Fig.8 Voltage and power density of the fuel cell having the calcium phosphate hydrogel
membrane from various raw materials as a function of current density

Fig.9 Voltage of the fuel cell having various types of MEAs as a function of current
density (at current density = 30.0 mA/cm^2)

Table 1   Properties of tested incineration ash

Chemical component	Content [wt%]
Ca	66.8
P	-
K	8.0
Si	6.1
Al	5.8
S	4.9
Zn	3.0
Fe	2.1
Ti	1.9
Others	1.4

Fig.1 XRD peak chart of incineration fly ash

Fig.2 Schematic diagram of cell performance measurement set-up

Fig.3 Appearance of intermediates synthesized from incineration fly ash and reagents ((a) From incineration fly ash, (b) From mixture of K$_2$CO$_3$ reagent with CaCO$_3$ reagent, (c) From CaCO$_3$ reagent)

Fig.4 Electric conductivity of amorphous calcium phosphate hydrogel at 25 °C as a function of moisture content for various raw materials
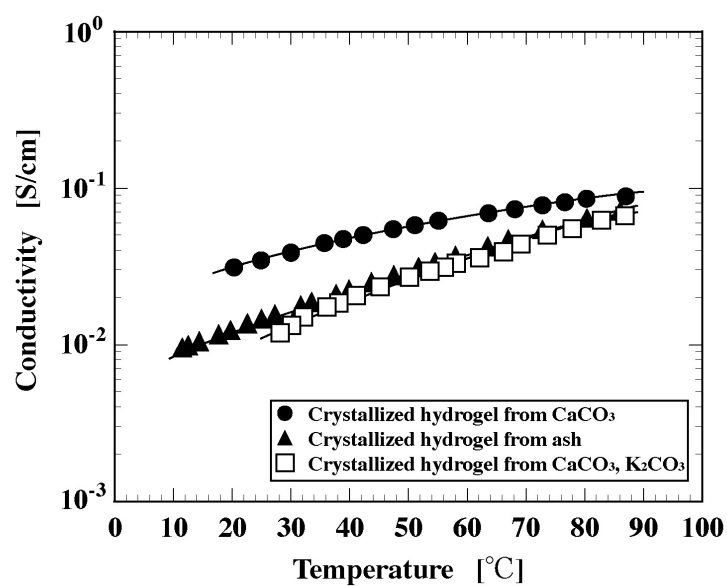
(a) Calcium phosphate glass

(b) Calcium phosphate hydrogel

(c) Calcium phosphate hydrogel with potassium ion

Fig.5 Structure of calcium phosphate hydrogel

**Fig.6 Conductivity of crystallized calcium phosphate hydrogel
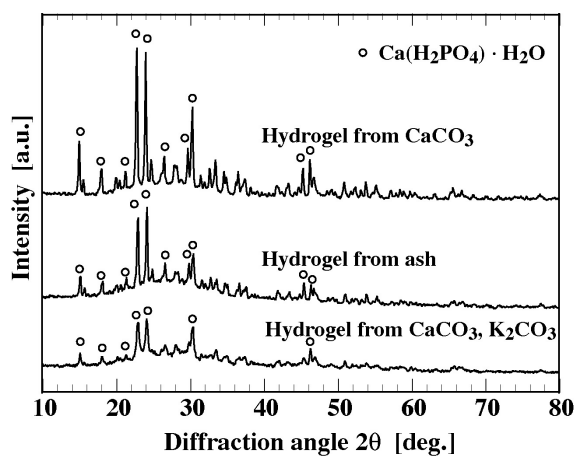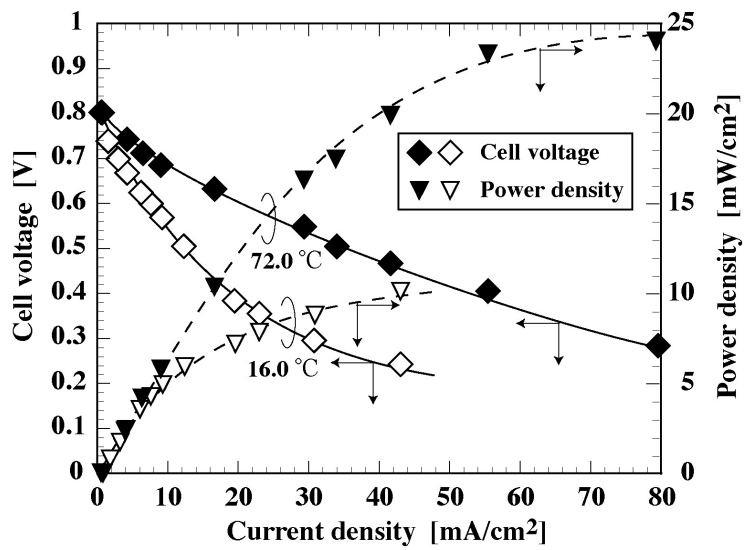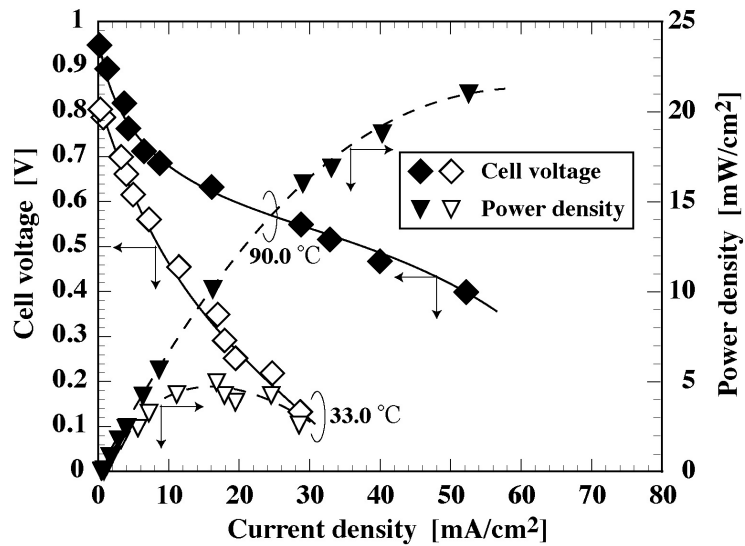as a function of temperature for various raw materials**

**Fig.7 XRD peak charts of crystallized calcium phosphate hydrogel
synthesized from reagents and incineration fly ash**

(a) From CaCO3 reagent

(b) From incineration fly ash

Fig.8 Voltage and power density of the fuel cell having the calcium phosphate hydrogel membrane from various raw materials as a function of current density
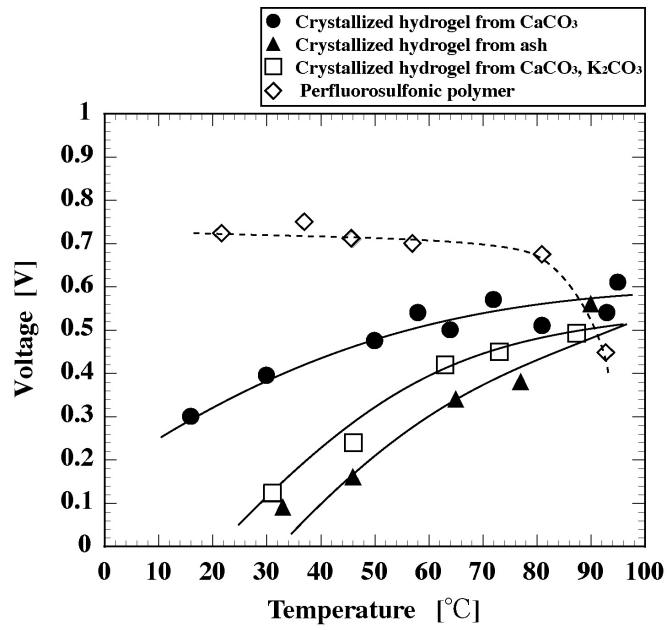
Fig.9 Voltage of the fuel cell having various types of MEAs as a function of temperature (at current density = 30.0 mA/cm²)