Performance of fuel cell using calcium phosphate hydrogel membrane prepared from waste incineration fly ash and chicken bone powder

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(Keywords)
Waste incineration fly ash ; Bone Powder ; Calcium phosphate hydrogel ; Fuel cell

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Abstract

Waste incineration fly ash and bone powder could be successfully recycled to calcium phosphate hydrogel, a type of fast proton conductor. The electric conductivity of the crystallized hydrogel from them was compared with that from calcium carbonate reagent. It was found that the conductivity of the hydrogel from bone powder is almost equal to that from calcium carbonate reagent, which is higher than that from incineration fly ash. Because the crystallized hydrogel from incineration ash has a lower crystallinity than that from bone powder and calcium carbonate reagent. However, the difference of the conductivity among them can be hardly observed above 100 ˚C. The fuel cell with membrane electrode assembly (MEA) using the calcium phosphate hydrogel membrane prepared from incineration fly ash and bone powder was observed to generate electricity. The performance of fuel cells having the hydrogel membrane obtained from all raw materials increases with the cell temperature, and the fuel cell containing the hydrogel membrane from incineration fly ash has the highest dependence of the fuel cell performance. For this reason, the difference in the cell performance among them can be hardly observed above 120 ˚C. This tendency agrees with the change in the electric conductivity with the temperature. Further, the performance of all fuel cells with the hydrogel membrane is superior to that of the fuel cell with perfluorosulfonic polymer membrane at temperatures greater than approximately 85 ˚C.

1. Introduction

In Japan, over 7 million tons of waste incineration fly ash generated by garbage incineration plants is discharged every year, and this amount has been increasing [1]. 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 [2, 3], zeolite [4, 5], and calcium apatite [6] 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 [7-10]. A small portion of waste incineration fly ash is used as cement fillers and so on.

Over 4 millions tons of chicken bone is also discharged per year from chicken meat processing plants for industrial wastes in Japan [11]. Chicken bone consists of Ca and P. Some part of chicken bone is used as the raw material of the fertilizer.

A large portion of these industrial wastes are reclaimed from the sea. The large daily output and the limited landfill capacity have caused various social and environmental problems. Thus, there is a need to rapidly develop new effective ways of reusing these industrial wastes.

On the other hand, the fuel cell is one of the most important key technologies for supplying clean energy. Many methods have been investigated to reduce the cost of fuel cells and to improve the efficiency of their performance. Since calcium phosphate hydrogel [12-14] is cheaper and shows a higher proton conductivity and greater heatresistance than perfluorosulfonic polymers such as Nafion [15], it 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.

As a new effective method for reusing them, we have proposed the synthesis of calcium phosphate hydrogel from incineration fly ash and chicken bone powder [16-17]. Our previous paper [17] has reported the characterization of the electric conductivity of calcium phosphate hydrogel obtained from incineration fly ash and chicken bone powder in the temperature range of 15-70 ˚C. The present study deals with the determination of the fuel cell performance for calcium phosphate hydrogel membrane prepared from incineration fly ash and chicken bone powder. Further, the electric conductivity and fuel cell performance are compared with those of calcium phosphate hydrogel synthesized from pure reagents in the temperature range of 15-130 ˚C.

2. Experimental

2.1 Preparation and characterization of calcium phosphate hydrogel

Waste incineration fly ash, bone powder and $CaCO_3$ reagent was used as a raw material. Waste incineration fly ash and chicken bone powder was obtained from an incineration plant and a chicken meat processing plant in Higashi Hiroshima, Japan, respectively.

Phosphoric acid reagent, which has a concentration of 85wt%, was added to 5.0 g of a raw material. Based on our previous paper [17], the additive volume of phosphoric acid was optimized (incineration fly ash and $CaCO_3$ reagent : 6.8 cm^3, bone powder : 5.1 cm^3). 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 pulverized with a hammer and a stainless ball mill to obtain a median diameter of 11.0 μm.

A mixture of the pulverized powder weighting 2.0 g and distilled water with a volume of 2.0 cm^3 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.

The alternating current conductivity of the hydrogel was measured by using the chemical impedance meter (Hioki, 3532-80) with 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 radius and depth were 5.0 mm and 7.0 mm, respectively. The two disk electrodes for the current and the applying voltage measurement were set at the top and the bottom of the cell, respectively. For the measurements, the cell was sealed tightly in order to prevent the evaporation of water from the hydrogel.

2.2 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 was coated onto a carbon electrode with a Pt catalyst layer and a thin gas diffusion layer (Chemix, TGP-H06H) by a controlled coater (Matsuo, K-101). The area and the Pt catalyst load of the carbon electrode were 4.0 cm^2 and 1.0 mg cm^{-2}, respectively. 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 measurement set-up is given in **Fig.1**. 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 30-140 ˚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 (Chemix, NE112) whose thickness was 51 μm was also measured using the same electrodes under the same experimental conditions.

3. Results and discussions

3.1 Characterization of calcium phosphate hydrogel

The metallic element compositions of incineration fly ash and bone powder as determined by EDX (Shimadzu, EDX-800), are listed in **Table 1**. Incineration fly ash is mainly composed Ca and it also contains K, Si, S and so on. Bone powder is mainly composed Ca and P, impurities can not be almost detected in it. **Fig.2** shows the X-ray diffraction (Rigaku, RINT-2000) patterns for incineration fly ash and bone powder. Incineration fly ash comprises KCl (JCPDS No.:41-176), $CaSO_4$ (JCPDS No.:37-0184) and $Ca(OH)_2$ (JCPDS No.:84-1268) and so on in the crystalline phase, while bone powder has crystalline phase of only $Ca_{10}(PO_4)_6(OH)_2$ (JCPDS No.:74-0566).

The metallic element compositions of the intermediate, calcium phosphate glass synthesized from various raw materials are listed in **Table 2**. Any calcium phosphate glass is mainly composed Ca and P. Although the calcium phosphate glass obtained from incineration fly also contains some impurities, impurities can not be almost detected in the calcium phosphate glass obtained from bone powder and $CaCO_3$ reagent. However, the content of P in any calcium phosphate glass is almost equal to about 40 %. This result reveals that the element P present in bone powder can be used effectively as a substitution for H_3PO_4 reagent. Consequently, bone powder provides a 25% reduction in the usage of H_3PO_4 reagent. On the contrary, the calcium phosphate glass from incineration fly ash provides the lowest content of Ca. This result suggests that impurities such as Al, Si, and K react with H_3PO_4 as a substitution for Ca. Furthermore, any calcium phosphate glass was confirmed to be completely amorphous by X-ray diffraction.

Crystallized calcium phosphate hydrogels from various raw materials were characterized. **Fig.3** 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 to a maximum, and then it decreases gradually with the temperature. This decline of the conductivity may be induced by the evaporation of water from hydrogel and the heat decomposition of hydrogel. The conductivity of crystallized hydrogel from bone powder almost agrees with that from $CaCO_3$ reagent, though a decrease in the temperature raises the difference in the conductivity between them. Further, the conductivity of them reaches a maximum at 80 ˚C. On the other hand, crystallized hydrogel from incineration fly ash has the lowest conductivity since potassium ion present in the incineration fly ash breaks the long-chain phosphate structures [17, 18]. An increase in the temperature decreases the difference in the conductivity between the hydrogel obtained from incineration fly ash and that synthesized from other raw materials. Because the conductivity of crystallized hydrogel from incineration fly ash continues to increase with temperature until 100 ˚C. This fact implies that crystallized hydrogel from incineration fly ash has a greater heatresistance and higher water-holding ability than that synthesized from other raw materials. Therefore, it is effective to reuse incineration fly ash as crystallized calcium phosphate hydrogel above 80 ˚C. These results agree with the conductivity measured at 15-70 ˚C in our previous work [18].

Fig.4 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 $Ca(H_2PO_4)_2\ H_2O$ (JCPDS No.:09-0347) in the crystalline phase can be obtained from all 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 fact suggests that impurities contained in incineration fly ash prevent the crystallization of $Ca(H_2PO_4)_2H_2O$. For these reasons, crystallized hydrogel from $CaCO_3$ reagent and bone powder has a higher conductivity than that obtained from incineration fly ash.

3.2 Determination of fuel cell performance

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.5** shows the cell voltage and power density as a function of the current density. In any case of fuel cell having the calcium phosphate hydrogel membrane, the cell voltage decreases monotonously as the current density increases. The power density increases to the maximum and then decreases gradually with the current density. 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 an MEA fabricated by using the calcium phosphate hydrogel synthesized from incineration fly ash successfully generates electricity.

However, the durability of these hydrogel membranes was not confirmed sufficiently. It is necessary to investigate the chemical and mechanical degradation of these hydrogel membranes during prolonged usage.

The performance of this fuel cell is lower than that containing an MEA fabricated by calcium phosphate hydrogel synthesized from $CaCO_3$ reagent and bone powder. This is because calcium phosphate hydrogel synthesized from incineration ash has a lower electric conductivity than that obtained from $CaCO_3$ reagent and bone powder, as shown in Fig.3. Moreover, it can be found that hydrogel synthesized from incineration ash shows the highest dependence of the fuel cell performance on the cell temperature. This tendency also agrees with the change in the electric conductivity with the temperature.

On the other hand, the power density of the fuel cell having the perfluorosulfonic polymer membrane increases monotonously as the current density increases in our measurement range. It can be found that the fuel cell with an MEA fabricated by using the perfluorosulfonic polymer has a higher performance than any other fuel cell having the calcium phosphate hydrogel membrane at 57 ˚C. Namely, the fuel cell having the perfluorosulfonic polymer membrane has the maximum power density and the lowest decreasing rate in the cell voltage which corresponds to the lowest inertial resistance. However, the cell performance of this fuel cell is not so high as the result in the literature [19]. Because hydrogen gas was fed into fuel cell at relatively lower pressure in order to prevent from breaking the hydrogel membrane. Moreover, the cell temperature reduces the cell voltage and power density remarkably.

The dependence of the fuel cell performance on the cell temperature was evaluated with the power density for a current density of 300 A m^{-2}. The result is shown in **Fig.6**. An increase in the cell temperature causes an increase in the power density 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 power density at all measured temperatures. However, its gradient of in the power density is smaller than that of fuel cells using hydrogel membranes prepared from other raw materials. Consequently, the difference in the power density among fuel cells with a hydrogel membrane decreases with the cell temperature. The difference in the power density among them can not be observed above 120 ˚C. Accordingly, this result suggests that the hydrogel membranes prepared from incineration fly ash and bone powder can be substituted sufficiently above 120 ˚C for that from $CaCO_3$ reagent.

Moreover, these results show good agreement with the change in the electric conductivity shown in Fig.3.

On the other hand, the power density of the fuel cell fabricated with perfluorosulfonic polymer decreases with the cell temperature; in particular, it decreases rapidly at temperatures above 80 ˚C. At temperatures above approximately 85 ˚C, the power density of the fuel cells comprising a hydrogel membrane synthesized from any raw material is higher than that of the cell containing perfluorosulfonic polymer. 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 bone powder 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. 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. However, the difference of the conductivity among them can be hardly observed above 100 ˚C.
2. Crystallized calcium phosphate hydrogel synthesized from incineration fly ash has a lower degree of crystallinity than that obtined from $CaCO_3$ reagent and bone powder.
3. The fuel cells with an MEA fabricated from calcium phosphate hydrogel synthesized from incineration fly ash and bone powder can successfully generate electricity.
4. The dependence of the fuel cell performance prepared by the hydrogel from incineration fly ash is higher than that of fuel cells having the hydrogel membrane obtained from $CaCO_3$ reagent and bone powder. This tendency agrees with the change in the electric conductivity with the temperature.
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 cells containing a hydrogel membrane obtained from pure reagents and bone powder at temperatures above approximately 120 ˚C; further the

performance of these cells are superior to the fuel cell with a perfluorosulfonic polymer membrane.

Acknowledgements

This study was financially supported by the JFE 21st Century Foundation and Electric Technology Research Foundation of Chugoku.

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Figures and Tables

Fig.1 Schematic diagram of cell performance measurement set-up

Fig.2 XRD peak charts of incineration fly ash and bone powder

Fig.3 Conductivity of crystallized calcium phosphate hydrogel as a function of temperature for various raw materials

Fig.4 XRD peak charts of crystallized calcium phosphate hydrogel synthesized from various raw materials

Fig.5 Voltage and power density of the fuel cell having the calcium phosphate hydrogel membrane from various raw materials and perfluorosulfonic polymer membrane as a function of current density

Fig.6 Voltage of the fuel cell having various types of MEAs as a function of current density (at current density = 300 A m^{-2})

Table 1 Properties of tested incineration ash and bone powder

Table 2 Chemical composition of calcium phosphate glass synthesized from various raw materials

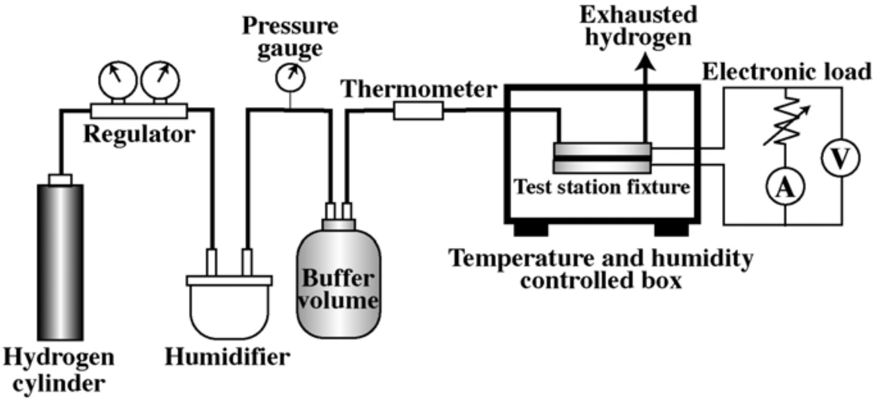


Fig.1 Schematic diagram of cell performance measurement set-up

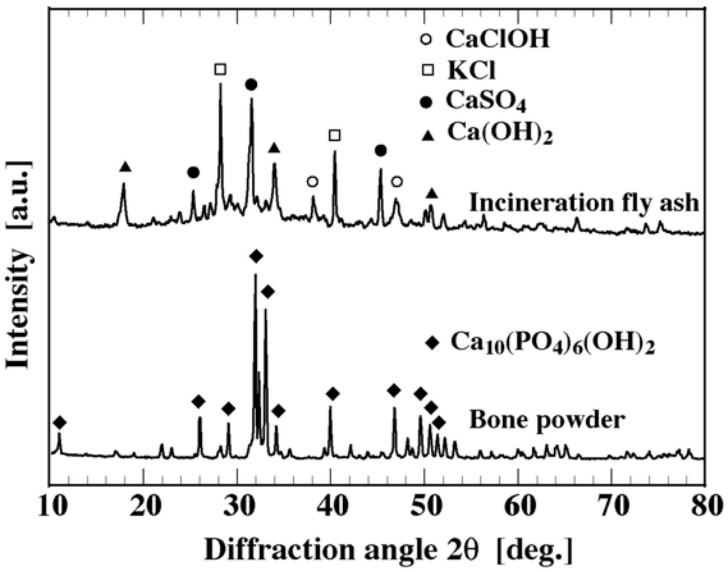


Fig.2 XRD peak charts of incineration fly ash and bone powder

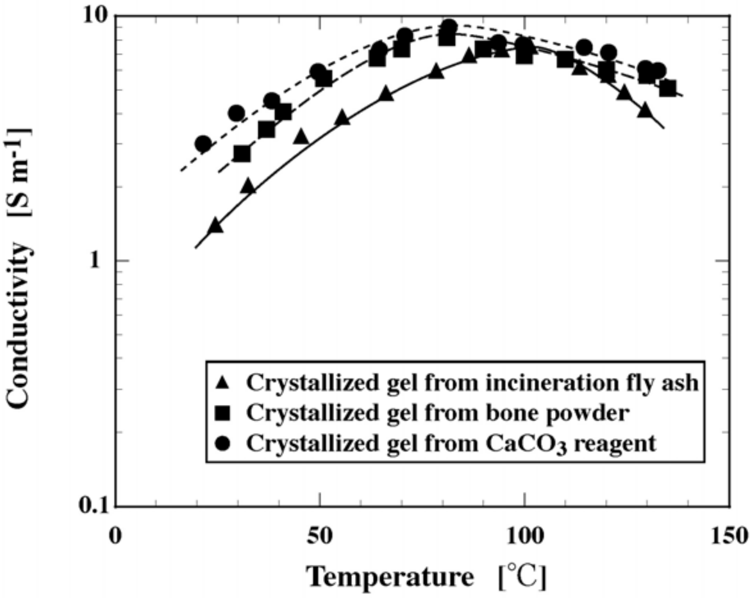


Fig.3 **Conductivity of crystallized calcium phosphate hydrogel as a function of temperature for various raw materials**

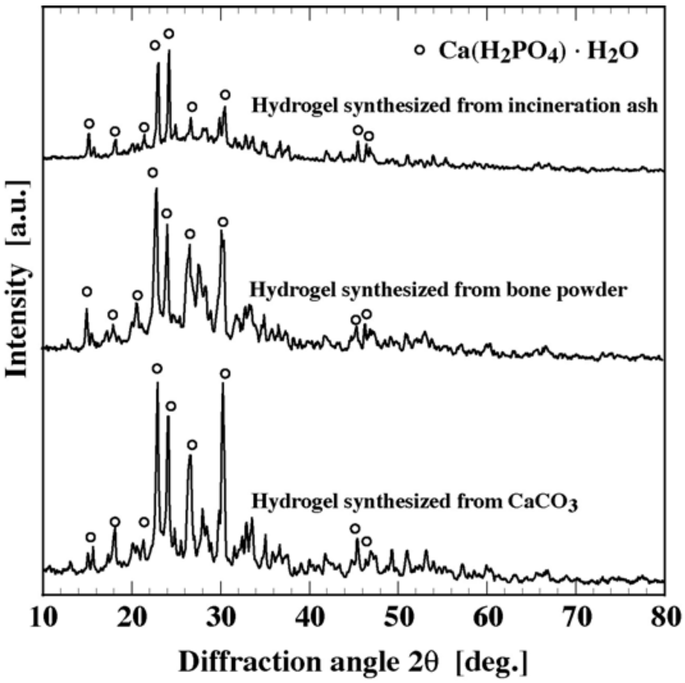
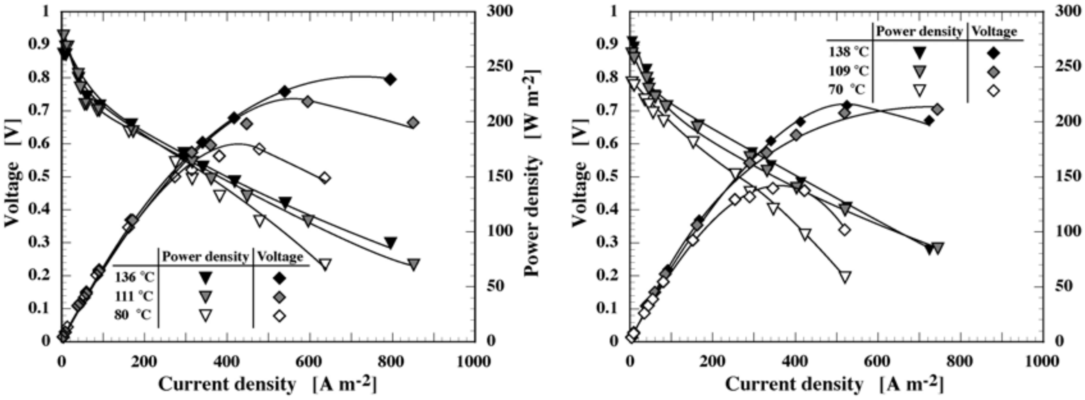
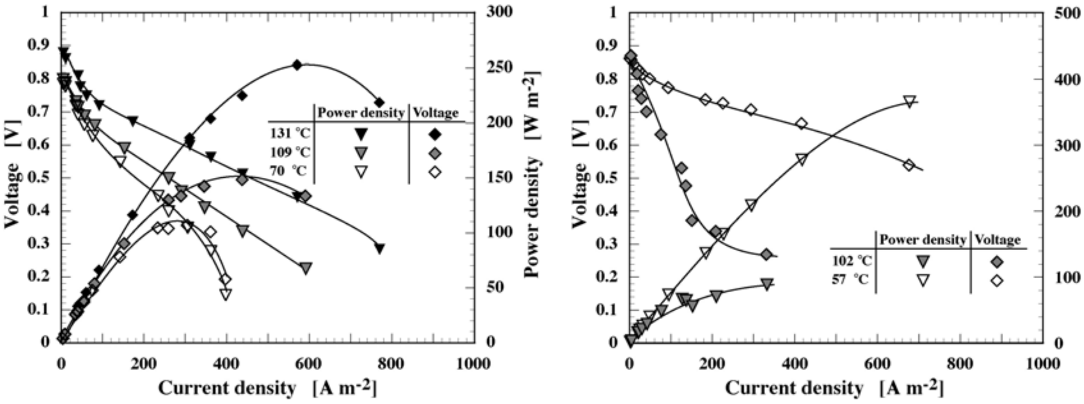


Fig.4 XRD peak charts of crystallized calcium phosphate hydrogel synthesized from various raw materials



(a) Incineration fly ash

(b) Bone powder



(c) $CaCO_3$ reagent

(d) Perfluorosulfonic polymer

Fig.5 Voltage and power density of the fuel cell having the calciumphosphate hydrogel membrane from various raw materials and the perfluorosulfonic polymer membrane as a function of current density

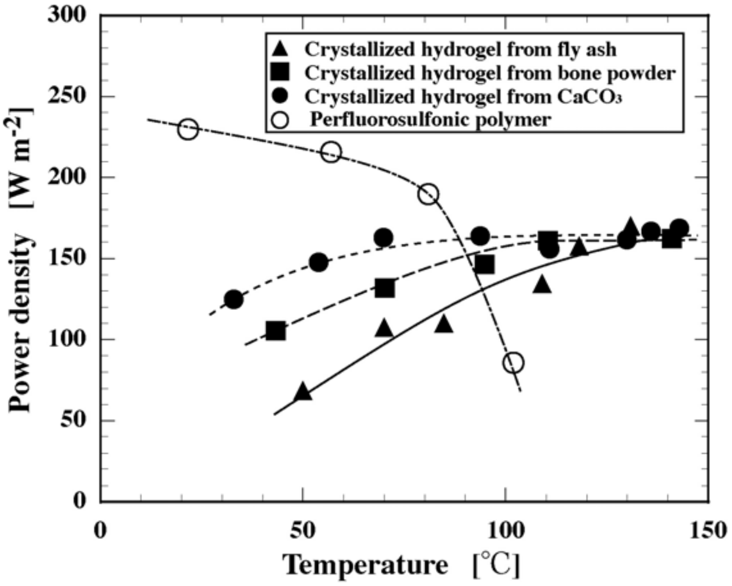


Fig.6 Power density of the fuel cell having various types of MEAs as a function of temperature (at current density = 300 A m^{-2})

Table 1 Properties of tested incineration ash and bone powder

Metallic element	Content [wt%]	
	Incineration 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

Table 2 Chemical composition of calcium phosphate glass synthesized from various raw materials

Component		Ca	P	Si	K	Al	Zn	Others
Content [wt%]	$CaCO_3$ reagent	58.5	41.5	-	-	-	-	-
	Incineration ash	40.5	39.8	6.4	5.5	3.6	1.8	2.4
	Bone powder	55.5	40.1	1.9	1.1	-	0.1	1.3