NOVEL FABRICATION OF POROUS HYDROXYAPATITE BY
ELECTROPHORETIC DEPOSITION PROCESS

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Abstract: We have developed the novel and simple fabrication of porous hydroxyapatite by electrophoretic deposition (EPD) method in H2O/ethanol system. In this study, the porous hydroxyapatite bulks through the controlled use of H2 gas generation in the aqueous EPD process could be successfully prepared. Especially, it was found that this aqueous EPD process in combination with a sintering process could advantageously result in unique porous bulks containing unidirectionally aligned continuous pores with some hundreds μm in diameter. These unique microstructured porous hydroxyapatite prepared by EPD process will lead to the usage of porous fillers of bone etc.

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INTRODUCTION

An application of electrophoretic deposition (EPD) of ceramics powders was first studied by Hamarker in 1939 1, 2. Some decades ago, certain applications of EPD processes were tried in various fields, such as the coating of MgO on stainless wire 3, superconductors on Ag wire 4, and the solid oxide fuel cells 5, 6. Therefore, EPD process has been an attractive process to prepare bulk and films of ceramics in structural and electro ceramics fields due to its ability of easy forming and complex shaping with a significantly fast deposition rate. Furthermore, recently, preparation of various types of ceramics and composites, such as laminate composites and functionally gradiented materials (FGM) etc, have been carried out by this EPD process, after applications of this powerful EPD process were reported by Nicholson et al 7, 8, 9 and Yamashita et al 10. In fact, most studies on the forming of ceramics in the EPD process have been carried out using organic solvents, such as amyl alcohol and dichloromethane.

Recently, much attention has been focussed on aqueous EPD processes motivated by environmental and health problems 11. This aqueous EPD process has also other advantages, such as the unnecessity of organic binders in the shaping and coating. However, when using an aqueous slurry of ceramics on the EPD process, gas formation of H2 (cathode) and O2 (anode) are frequently generated by the electrolysis of H2O, causing the bubbles to initiate defects, such as pores and voids, in the ceramics forming 12. Therefore, the gas generation during an aqueous EPD process is considered to be the most serious problem and should be avoided in the preparation of films, coatings, and shaping of ceramics with a homogeneous and dense microstructure. In the present study, the preparation of porous ceramics using the gas formation caused by the aqueous EPD process was attempted. In general, porous ceramics are prepared with using combustion or volatilation of polymer media, or sintering techniques at a low sintering temperature 13-16. Especially, a few methods for the fabrication of special porous ceramics with unidirectionally aligned continuous pores have been reported 17, 18. For example, the bulk was made by extrusion of a mixture of ceramics and organic polymers (sometimes wax) and subsequently burned out of the polymer for porous ceramics with unidirectionally aligned continuous pores. As another method for these special porous ceramics, porous ceramics could be fabricated by burning out of fiber in uniaxially carbon fiber reinforced ceramics. However, these methods are complicated, need much time and are expensive. On the contrary, the aqueous EPD process developed by authors is a simple and rapid process for the fabrication of porous bioceramics with unidirectionally aligned continuous pores 19. The purpose in the present study is to fabricate porous hydroxyapatite as a bioceramic by applying the gas generation due to electrolysis of H2O during the
EXPERIMENTAL PROCEDURES

Hydroxyapatite (HAP-200, Taihei Chemistry Co., Ltd.) powder was selected as a starting material. This HAP powder had a mean average size of 1 μm and a surface area of 2 m²/g. This HAP powder was mixed at room temperature in deionized water in a beaker using a stirrer. The pH of the slurry was adjusted with 0.1N HNO₃ or KOH aqueous solution. The zeta potential of the aqueous slurry (containing 3 vol% HAP) was measured with the ultrasonic attenuation method using the equipment (Dispersion Tech.; DT1200).

10 vol% HAP powder was mixed at pH 4 to pH 7 in the aqueous solvent of mixture of H₂O/ethanol (100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 30/70, 0/100). 200 ml of various aqueous slurry (10 vol% HAP) was added into an EPD equipment containing a carbon anode and cathode. Dimensions of carbon electrodes (G110: Tokai Carbon Co., Ltd.) were a diameter of 5 mm and length of 100 mm (a distance between carbon electrodes=10 mm). The direct current (DC) was applied with the DC controller. A constant current (100 mA) was used during the EPD process, applied with 5-500 V. The deposition time in all experiments was 5 min at room temperature. HAP deposition rate was calculated by measuring the thickness obtained during the deposition time. The deposition at the carbon cathode were dried through freeze drying for 24 hrs. The dried depositions with the carbon electrodes were sintered in an air at 1373 K. During this sintering process, all carbon electrode was oxidized and burned off. The density of the sintered ceramic deposited materials was evaluated in H₂O according to the Archimedes principle. The grain size and pore morphology of these HAP sintered samples were observed with a scanning electron microscope (FE-SEM S-800: Hitachi Co., Ltd.).

RESULTS AND DISCUSSION

Figure 1 shows the zeta potential curve of HAP. HAP showed the isoelectric point (IEP) around pH 8.1. Below this IEP, HAP particles possessed a positive surface charge with approximately 10 mV in acid aqueous solution, that was smaller than Al₂O₃ depositions. This result of zeta potential curve suggests that HAP deposition can be achieved in acid solutions by in this EPD process. In fact, the cathode surface was found to be thickly covered with layers of HAP deposition in the region of pH 4 to pH 7 (below the isoelectric point). Around the region of pH 5, HAP depositions prepared using EPD (100 mA) showed a porous microstructure having a thickness over approximately 1000 μm. On the contrary, very thin HAP deposition on the carbon anode were observed on this EPD process. At low pH region (pH 4 to 5), HAP deposition was difficult to prepare on the cathode, whereas at pH 6 to 7 the porous HAP depositions could be easily prepared on the cathode. Figure 2 shows the typical photographs of HAP depositions on the cathode using this EPD process in various solvents at pH 7.0 and a constant current of 100 mA. Bar shows 5mm.

Figure 2 Typical photographs of HAP deposition on the cathode using this EPD process in various solvents at pH 7.0 and a constant current of 100 mA. Bar shows 5mm.

Figure 1 Zeta potential curve of HAP
Nakahira A, Nishimura F, Takeda S

unidirectionally aligned continuous pores and be also controlled by the addition of ethanol to H₂O. This introduction of pores with some hundreds of µm in diameter into hydroxyapatite bulks is attractive for the interaction with living cells. The microstructure of HAP deposition was dependent on the pH and H₂O/ethanol ratio of solvent during EPD process. The microstructural features of HAP prepared by EPD process are summarized in Table 1. At low pH region of pH 4, HAP deposition was difficult to prepare on the cathode, although dense HAP deposition was obtained in ethanol. On the other hand, at pH 5 to 6 the porous HAP depositions could be easily prepared on the cathode. EPD at high pH in ethanol resulted in the dense microstructure without the unidirectionally aligned continuous pores. Nevertheless, it was obvious that the increase of pH and the ethanol fraction in H₂O/ethanol solvent

Figure 3 SEM micrographs of the surface of deposited HAP.

- a) H₂O:EtOH=100/0
- b) H₂O:EtOH=90/10
- c) H₂O:EtOH=80/20
- d) H₂O:EtOH=70/30
- e) H₂O:EtOH=50/50
- f) H₂O:EtOH=0/100

Table 1 Microstructural features of HAP prepared by EPD process under various EPD conditions.

<table>
<thead>
<tr>
<th>H₂O/ethanol</th>
<th>pH4</th>
<th>pH5</th>
<th>pH6</th>
<th>pH7</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>×</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80/20</td>
<td>×</td>
<td>×</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70/30</td>
<td>×</td>
<td></td>
<td>×</td>
<td></td>
</tr>
<tr>
<td>50/50</td>
<td>×</td>
<td></td>
<td></td>
<td>×</td>
</tr>
<tr>
<td>30/70</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0/100</td>
<td></td>
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</tbody>
</table>

Figure 4 a) Typical cross section of this porous HAP deposition by EPD at pH 7 in solvent of 70/30 (H₂O/ethanol ratio). b) Schematic drawing of EPD process.

- a) Typical cross section of this porous HAP deposition by EPD at pH 7 in solvent of 70/30 (H₂O/ethanol ratio).
- b) Schematic drawing of EPD process.
during this EPD process tend to lead to the dense microstructure without the unidirectionally aligned continuous pores.

![Figure 5](image)

Figure 5 Relation between pH and deposition rate during EPD process.

Table 2 Results of number and diameter of continuous pores in sintered HAP depositions after the sintering at 1373 K. (a) pH7 and (b) pH6

(a) pH7

<table>
<thead>
<tr>
<th>H₂O/Ethanol</th>
<th>100/0</th>
<th>90/10</th>
<th>80/20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of pore (number/mm²)</td>
<td>0.9</td>
<td>1.2</td>
<td>0.5</td>
</tr>
<tr>
<td>Pore diameter (µm)</td>
<td>520</td>
<td>514</td>
<td>596</td>
</tr>
</tbody>
</table>

(b) pH6

<table>
<thead>
<tr>
<th>H₂O/Ethanol</th>
<th>100/0</th>
<th>90/10</th>
<th>80/20</th>
<th>70/30</th>
<th>30/70</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of pore (number/mm²)</td>
<td>2.4</td>
<td>1.2</td>
<td>0.4</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Pore diameter (µm)</td>
<td>299</td>
<td>502</td>
<td>864</td>
<td>377</td>
<td>178</td>
</tr>
</tbody>
</table>

Figure 5 shows the relation between pH and deposition rate during EPD process. Samples prepared by EPD process at pH 4 to 5 showed small amount of HAP deposition. In this low pH region, the deposition rate was low. This small rate of deposition at low pH was thought to be due to large amount of gas generation caused by electrolysis of H₂O in the aqueous EPD process. On the contrary, the deposition rate was higher at pH 6 to 7, approximately 5 to 7µm/s, compared to EPD at low pH. As previous report on Al₂O₃ depositions, the pore structure, e.g. size and distribution, varied for Al₂O₃ depositions with pH of the aqueous solution. Thus, various types of pores could be controlled by the balance of deposition rate and the generation of H₂ gas. However, in the case of HAP, the thicker HAP deposition over 3 mm in thickness was difficult to prepare, since the deposition rate for HAP was very low due to lower zeta potentials than Al₂O₃. At the same time, large amount of gas generation often leads to the inhibition of deposition for HAP. Therefore, it is thought that the addition of ethanol into H₂O causes the decrease of H₂ gas generation during this EPD of HAP and consequently leads to the introduction of the pores with some hundred µm, being attractive for cells, for HAP depositions by this EPD process.

The number and diameter of continuous pores in sintered HAP depositions after the sintering at 1373 K are summarized in Table 2 for these HAP bulks. The number of unidirectionally aligned continuous pores for these sintered HAP bulks was 1 to 2. When these porous HAP deposition prepared by this EPD process is used as a filler of bone and teeth, the further increase of the number of unidirectionally aligned continuous pores is needed for real applications. The pore number, pore diameter, and pore area fraction on HAP depositions are dependent on applied current/voltage, pH, zeta potential, solvent, deposition rate, H₂ gas generation of electrolysis of H₂O on the aqueous EPD process. Nevertheless, the optimization of deposition rate and H₂ gas generation on H₂O electrolysis is under investigation for the increase of pore number and pore area fraction on the surface of depositions for the porous HAP with unidirectionally aligned continuous pores.

CONCLUSION

The preparation of porous bioceramics was carried out using an aqueous EPD process. HAP depositions were prepared with this aqueous EPD process applying 100 mA at pH 4 to pH 7 for 5 min in H₂O/ethanol system and subsequently sintered at 1373 K. These HAP depositions after sintering had unique porous microstructure with a thickness over 1000 µm, including many unidirectionally aligned continuous pores with a diameter of some hundreds µm. The pore characteristics of these porous ceramics were found to be dependent on pH and H₂O/ethanol ratio in solvent. Consequently, porous ceramics having many unidirectionally aligned continuous pores was successfully obtained already within a few minutes through this process, in which the pore structure could be controlled by H₂ gas generation during the aqueous EPD process.

REFERENCES

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