

The Current Density on Electrosynthesis of Hydroxyapatite with Bipolar Membrane

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Abstract. Synthesis of hydroxyapatite by electrochemical method has been successfully done. The novelty of this research is used of the bipolar membrane to separate electrolysis chamber. The bipolar membrane is used to keep the cations still around the cathode and react to form hydroxyapatite. The aim of this paper was to compare the current density on electrosynthesis of hydroxyapatite with and without bipolar membrane and the effect of current density on electrosynthesis. The electrosynthesis was performed at 2 hours at 400 to 600 mA/cm² at room temperature. The bigger the current density, the more pure HA formed. The electrosynthesis of hydroxyapatite with bipolar membrane more effective than without bipolar membrane. The formation of HA is very effective in the cathode chamber. HA can be formed at low current density. In electrosynthesis with the bipolar membrane, particles of HA are nanosheet flower-like. The nanosheet flower-like HA growth at 1.6 A to 2 A.

1 Introduction

Hydroxyapatite (hydroxylapatite, HA) is the most potential material to be used as a substitute for human bone and teeth [1]. Actually, the formula of HA is Ca₅(PO₄)₃(OH) but usually written as Ca₁₀(PO₄)₆(OH)₂. HA has been used for the biomedical application [2], scaffolding for new bone formation [3], and as matrices for drug release control [4]. HA is also used for the nonbiomedical application such protein adsorption [5], gas sensors [6], hydrogen production [7], biodiesel production [8] and catalysts [9].

There are several methods for HA synthesis, e.g. mechanochemical method [10], emulsion method [11], the sol-gel process [12], chemical precipitation method [13], and hydrothermal technique [14, 15]. Mechanochemical treatment is suitable for large-scale hydroxyapatite production but the disadvantage of this method is the possibility of being contaminated. Emulsion method is a simple process method with the good product that is high crystallization without high temperature and crystalline size with the narrow distribution. The sol-gel method for HA production can process in low temperature and results high product purity. Chemical precipitation method is simple, low cost, and the low-temperature but difficult to control particle size. The particles have the wide particle size

distribution. The hydrothermal method needs the high temperature for the high degree of crystallinity. The alternative method for synthesis of HA is the electrochemical method. The electrochemical methods were originally used for HA coatings on metals. The electrochemical method is known to assemble fine particles. Synthesis of nanosized hydroxyapatite by electrochemical method explained in reference [16].

The synthesis of hydroxyapatite by electrochemical method has been developed using pulsed direct current [17]. In this method, the pulsed direct current is periodically interrupted. When the current is interrupted, HA particles around cathode move away to bulk solution. This condition is to avoid high concentration of HA particles and agglomeration process. This method requires the longer process.

In another our work [18, 19], we conclude that water reduction at cathode to produce hydroxide ions is very important process in HA formation. The problem in the electrochemical method is the concentration of OH⁻ ions produced by water reduction difficult increase due they move away from the cathode and react with H⁺ ions produced by water oxidation in the anode. In this work, we used the bipolar membrane to separate chamber system in the electrochemical cell.

The novelty of this work is used of the bipolar membrane to separate electrolysis chamber at hydroxyapatite synthesis by the electrochemical method. The bipolar membrane is used to keep the cations still

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around the electrode and react to form hydroxyapatite. The effect of current density on electrosynthesis of HA with the bipolar membrane was studied.

2 Experimental

A bipolar membrane was installed in the electrochemical cell (Fig. 1). The bipolar membrane is Fumasep FBM from FUMATECH BWT GmbH. The bipolar dimension is 2×5 cm and 0.2 – 0.25 mm in thickness.

The solution used for the HA synthesis by electrochemical method was consisted of Na₂H₂EDTA.2H₂O (Merck, reagent grade), KH₂PO₄ (Merck, reagent grade) and CaCl₂ (Merck, reagent grade). The concentration of Ca²⁺/EDTA/PO₄³⁻ as homogeneous solution was 0.25/0.25/0.15 M. All chemicals were used without further treatment. The electrolysis was done in a electrochemical cell. There are two carbon sheet with dimensions of (2×1) cm as the anode and the cathode. The acrylic material was used to the electrochemical cell. The anode and the cathode were within 3 cm and immersed in the solution at a depth of 2 cm. The anode and the cathode were connected to a DC power supply (Zhaoxin PS-3005D). The bipolar membrane was installed between the anode and cathode. The solution was electrolysed at 2 hours at 400 to 600 mA/cm² at room temperature and under ultrasonic cleaner to void agglomeration.

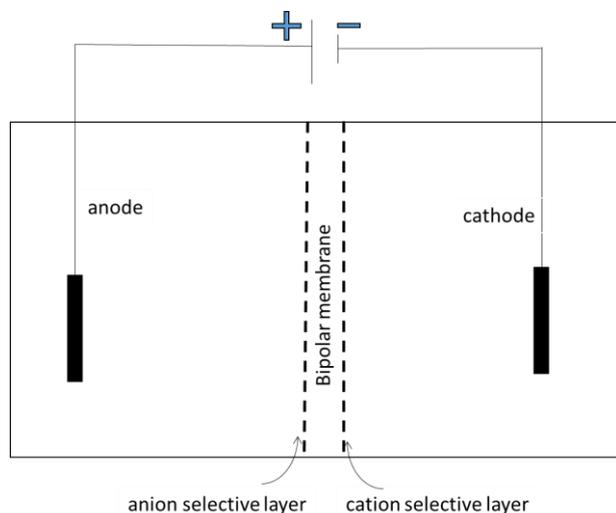


Fig. 1. The electrochemical cell for HA synthesis with bipolar membrane

The suspension produced was filtered. The particle was washed with demineralized water and dried at 110°C for 2 days. The X-ray diffraction (XRD) pattern of the particles was detected using an X-ray diffractometer (Shimadzu 6000). The morphologies of the particles analysis were observed using scanning electron microscopy (Inspect S40, FEI). Fourier transform infrared spectroscopy (FTIR) (Shimadzu 8400s) was performed to evaluate the functional groups of

specimens. The FTIR spectra were obtained over the region 500–4,000 cm⁻¹.

3 Result and Discussion

The XRD patterns of particle resulted in electrosynthesis of HA without and with bipolar membrane at various current density were compared. Fig. 2 show the XRD patterns of particles obtained at various the current density at 2 hrs without the bipolar membrane. Fig. 3 show XRD patterns at the same condition with the bipolar membrane at cathode chamber and Fig. 4 at the anode chamber.

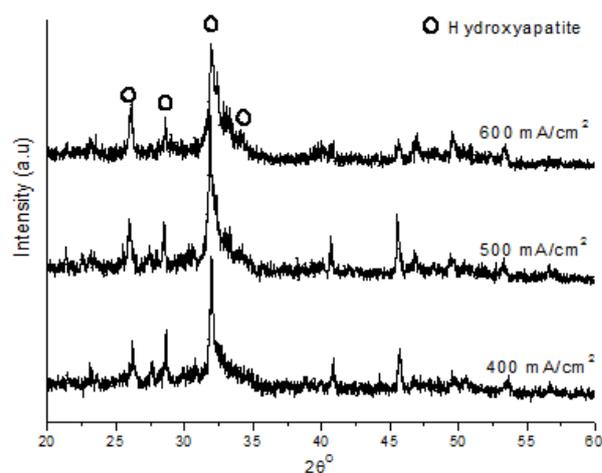


Fig. 2. The effect of current density at XRD patterns for particles prepared without bipolar membrane

At electrosynthesis of HA without bipolar membrane, the particle products are HA. There are four characteristic peaks at 26° (002), 29° (210), 32° (300), and 34° (202). These peaks match with the standard pattern of HA (JSPDS 09-0432). The 34° (202) peak is not clear at 400 mA/cm² and is clear at 500 and 600 mA/cm². The bigger the current density, the higher purity of HA product. The crystalline properties of the HA particles increase with the increase of current density. The final pH of solution shows the phase of calcium phosphate. If final pH of solution < 8, the phase product is brushite. If final pH of solution > 8, the phase product is HA [18]. In this work, we find that the final pH of solution for 400, 500, and 600 mA/cm² are 8.1, 9.1, and 9.5.

At the cathode of electrosynthesis of HA with the bipolar membrane (Fig. 3), the particle products are HA. There are four characteristic peaks at 26° (002), 29° (210), 32° (300), and 34° (202). They match with the standard pattern of JSPDS 09-0432. All of product is pure HA. The final pH solution for 400, 500, and 600 mA/cm² are 12.5, 13.4, and 13.7.

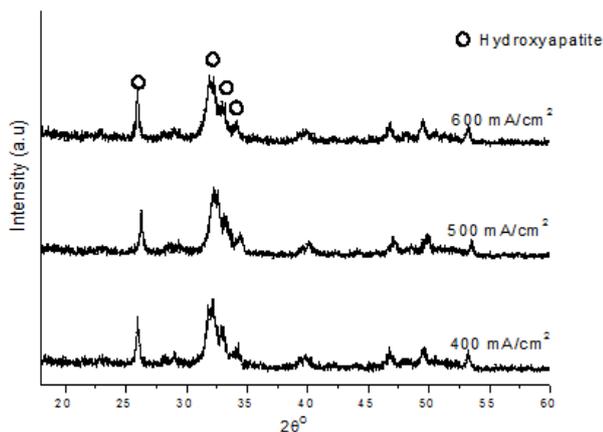


Fig. 3. The effect of the current density at XRD patterns for particles prepared with the bipolar membrane at the cathode

At the anode of electrosynthesis of HA with the bipolar membrane (Fig. 4), the particle products are brushite (at 400 and 500 mA/cm²) and hydroxyapatite (at 600 mA/cm²). At current density 400 and 500 mA/cm², the patterns have 7 characteristic peaks at 21°, 25°, 27°, 29°, 32°, 37°, and 42° which the standard of brushite. The final pH solution at anode for 400, 500, and 600 mA/cm² are 4.5, 5.6, and 7.8.

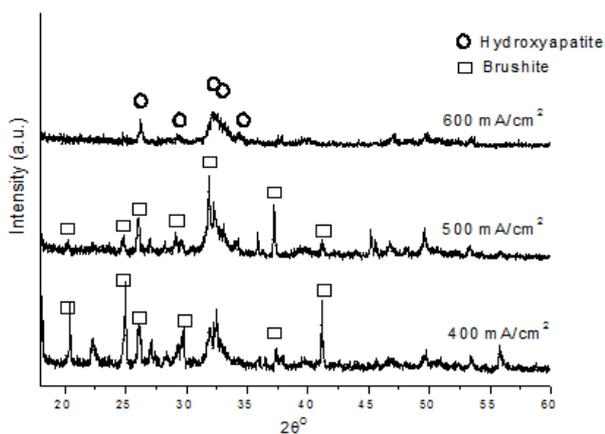


Fig. 4. The effect of the current density at XRD patterns for particles prepared with the bipolar membrane at the anode.

The reactions occurred in the cell without bipolar membrane can be explained in Fig. 5. The reduction of water in cathode produce OH⁻ ions. The hydroxyde ions is very important in the formation of HA. The hydroxyde ions change the equilibrium of phosphate and EDTA-Ca. In this case, hydroxyde ions produced by reduction of water move away from the cathode and react with H⁺ ions produced by oxidation of water in the anode. We will find HA formation if we can produce OH⁻ ions more than react with H⁺.

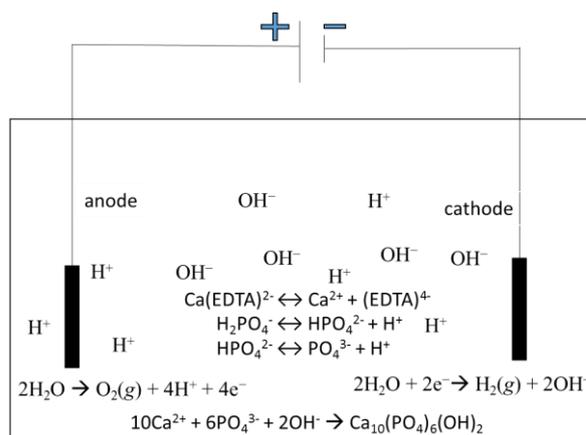


Fig. 5. The reactions occurred in the cell electrochemical for HA synthesis without the bipolar membrane

Fig 6. shows the movement of ions when the bipolar membrane installed in the cell electrochemical.

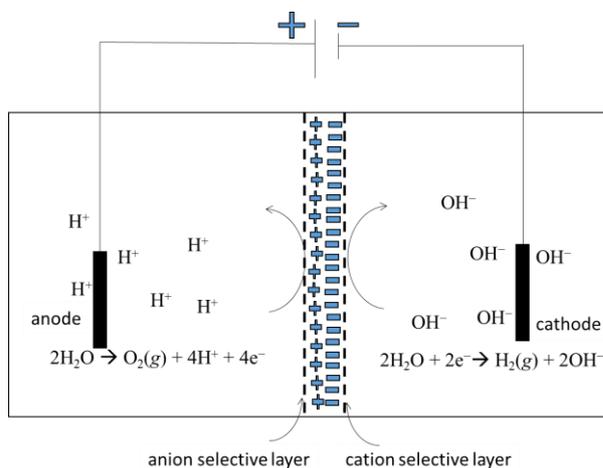


Fig. 6. The movement of ions in cell electrochemical for HA synthesis with bipolar membrane

In the cathode chamber, OH⁻ ions do not move away from the cathode because the bipolar membrane prevents OH⁻ ions to the anode chamber. The pH solution rapidly increases and the formation of HA increase. The formation of HA is very effective in this chamber. HA can be formed at low current density and low time electrolysis. In the anode chamber, H⁺ ions do not move away from the anode chamber to the cathode chamber. In this chamber, pH solution increases very slowly. The pH solution still can increase due to the equilibrium condition from ions in solution. HA can be formed if the pH solution more than 8.

The FTIR analysis used to identify the HA product. The Fig. 7 shows the FTIR spectra of the particle with and without the bipolar membrane. According of the FTIR spectra, there is no significant difference of HA product with and without the bipolar membrane. The spectra were analyzed in the 4,000 to 500 cm⁻¹ wavenumber.

The FTIR spectra of particle prepared without and with the bipolar membrane show that there are the phosphate and hydroxide groups. The characteristic bands for phosphate was seen at 493 cm^{-1} , 559 cm^{-1} , 976 cm^{-1} , and $1,032\text{ cm}^{-1}$. The broadband of low intensity in the range $3,000\text{--}3,500\text{ cm}^{-1}$ can be attributed to traces of water.

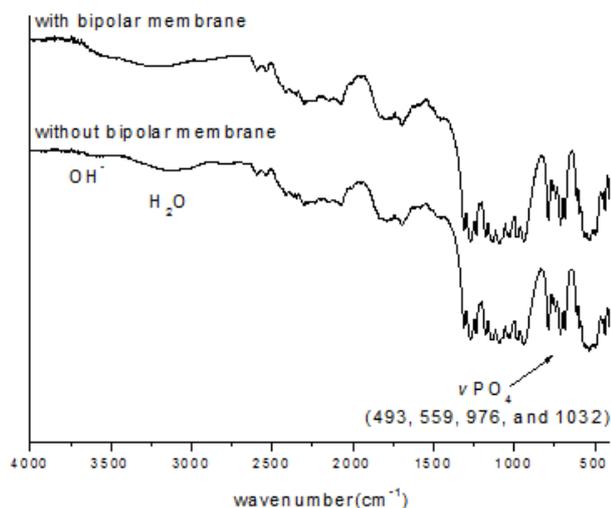


Fig. 7. The comparison of FTIR spectra of the HA particles without and with the bipolar membrane

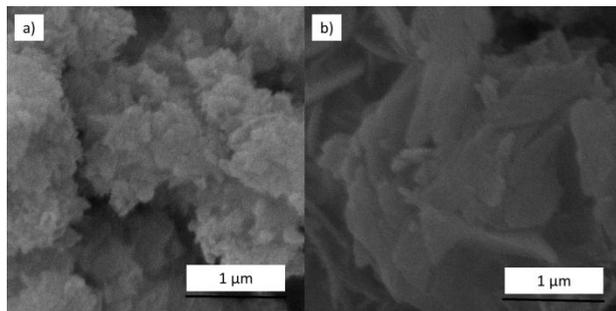


Fig. 8. The morphology of HA particles by SEM without the bipolar membrane. (a) 1.6 A and (b) 2 A

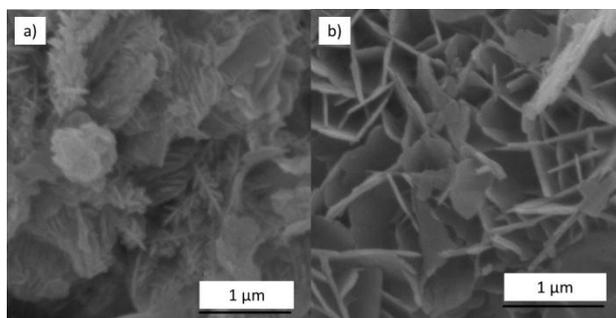


Fig. 9. The morphology of HA particles by SEM with the bipolar membrane at cathode chamber. (a) 1.6 A and (b) 2 A

The SEM images of HA product with and without the bipolar membrane at high magnification is provided in Fig. 8 and Fig. 9. The particles of HA without the bipolar

membrane at 1.6 A (Fig. 8 (a)) are the spherical-like shape. The growth of particles at 2 A (Fig. 8 (b)) forms plate sheet-like. In electrosynthesis with the bipolar membrane, particles of HA are nanosheet flower-like. The nanosheet flower-like HA growth at 1.6 A to 2 A (Fig. 9).

4 CONCLUSION

The synthesis of HA was performed by electrochemical method at 2 hours at 400 to 600 mA/cm² at room temperature. We compare the current density on electrosynthesis of hydroxyapatite with and without the bipolar membrane. The increase of current density results higher purity of HA. The electrosynthesis of hydroxyapatite with bipolar membrane more effective than without bipolar membrane. The bipolar membrane is used to keep the cations (OH⁻ ions) still around the electrode and react to form hydroxyapatite. The formation of HA is very effective in the cathode chamber. HA can be formed at low current density. In electrosynthesis with the bipolar membrane, particles of HA are nanosheet flower-like. The nanosheet flower-like HA growth at 1.6 A to 2 A

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