Synthesis of nickel – hydroxyapatite by electrochemical method

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Abstract. The electrochemical method in two chambers with the bipolar membrane has been used to produce the nickel – hydroxyapatite particle. Hydroxyapatite is used as the supported catalyst for nickel catalyst. In this work, in-situ electrochemical synthesis in two chambers with bipolar membrane has been used in the formation of nickel-hydroxyapatite. A simple electrolysis cell from acrylic was used. The anode and the cathode were set parallel with a distance of 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. The particle was produced in the electrolysis cell. In the anode chamber, the pH solution decreases for the time of electrolysis while in the cathode chamber the pH solution increases. The nickel – hydroxyapatite particle is formed in the cathode chamber. There is no particle in the anode chamber. At the lower current density, the first formed is brushite. At the higher current density, brushite converts to HA. The higher current density the greater the chances of HA formation. The increase in the initial concentration of NiCl\textsubscript{2} accelerates the increase of the pH of the electrolysis solution.

1. Introduction

Hydroxyapatite (HA) is a very attractive calcium phosphate because of its many applications. HA has been used as the coating for metallic implants [1, 2], as the bone filler [3], bone tissue engineering [4], and drug delivery [5]. In addition, HA may be used as a supported catalyst. Hydroxyapatite has attractive properties as a supported catalyst such as the ability of ion exchange, adsorption ability, acid-base properties, not toxic, and good thermal stability. The several methods for HA synthesis methods that have been commonly used are hydrothermal [6], emulsion [7, 8], mechanochemical [9, 10] and chemical precipitation [11, 12]. Among several methods of HA synthesis, electrochemical method is the most promising method. The advantages of the electrochemical method are the ease of controlling the product by regulating the current or potential system. The electrochemical methods for HA synthesis have been developed using the bipolar membranes. The bipolar membrane is used to separate the cell into two chambers, namely the anode chamber and the cathode chamber. The formation of HA is very effective in the cathode chamber because the cations (OH\textsuperscript{-} ions) still around the electrode and react to form hydroxyapatite. HA can be formed at low current density [13, 14].
Nickel is one of the potential candidates that exhibit good catalyst properties. Nickel as a catalyst has been widely used in some industries such as for the production of hydrogen [15] and syngas [16]. The support of the catalyst is required to increase the catalyst dispersion and prevent the catalyst being lost out with the gas bubbles.

The impregnation of Ni catalyst to HA as a supported catalyst by the electrochemical method in two chambers and the bipolar membrane becomes an interesting challenge. The electrosynthesis of HA with the bipolar membrane, HA was produced in the cathode. In the other side, the Ni$^{2+}$ ions were oxidized in the anode to produce Ni and NiO. Synthesis of HA electrochemically requires the solution in the high pH because at low pH it tends to form brushite [17]. The OH$^-$ ions produced by water reduction at the cathode is very important in HA formation [18]. The addition of nickel to the electrolysis solution of HA causes a decrease in pH. This condition causes the formation of HA getting slower.

In this work, in-situ electrochemical synthesis in two chambers with bipolar membrane has been used in the formation of nickel-hydroxyapatite. The novelty of this research is the electrochemical synthesis in situ of nickel-hydroxyapatite as catalysts in the two chamber and the bipolar membrane. The optimal conditions of the electrolysis process have been studied i.e. the current density, the electrolysis time, and the initial concentration of nickel.

2. Experimental

The electrochemical cell is separated into 2 chambers i.e. the anode chamber and the cathode chamber using a bipolar membrane (Figure 1). The bipolar membrane used is Fumasep FBM from FUMATECH BWT GmbH. It consists of an anion layer and a cation layer. On the borderline between anion membrane (AEM) and cation membrane (CEM) water is split into OH$^-$ and H$^+$ ions when exceeding a potential difference of approximately 0.8 V. The bipolar dimension is 2×5 cm and 0.2 – 0.25 mm in thickness.

![Figure 1. A schematic presentation of the electrolysis cell for synthesis of Ni-HA](image)

The electrolysis solution for the electrosynthesis of HA was obtained from Na$_2$H$_2$EDTA.2H$_2$O (Merck, reagent grade), KH$_2$PO$_4$ (Merck, reagent grade) and CaCl$_2$ (Merck, reagent grade). The concentration relationship of Ca$^{2+}$/EDTA/PO$_4^{3-}$ is 0.25/0.25/0.15 M. The NiCl$_2$ (Merck, reagent grade) was dissolved in the electrolysis solution at the initial concentration of 0.2 to 1 M. All chemicals were used as supplied with no further treatment. Two carbon electrodes with dimensions of (2×1) cm were used as the anode and the cathode. A simple electrolysis cell from acrylic was used. The anode and the cathode were set parallel with a distance of 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 the cathode. The electrosynthesis was performed for 30 to 60 minutes at 80 to 240 mA/cm$^2$ at room temperature. The ultrasonic cleaner was used in the
electrolysis cell to void agglomeration. The pH of the electrolysis solution was measured by the portable pH meter (ST300 Ohaus).

The particle was produced in the electrolysis cell. The particle was separated from the solution by filtration. The particle was washed with demineralized water and dried in the oven at 110°C overnight. The X-ray diffraction (XRD) pattern of the particles was detected using an X-ray diffractometer (Shimadzu 6000). 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

3.1. The current density

The study on the effect of the current density on the particle produced was done at the initial concentration 0.5 M NiCl₂ for 1 hour the electrolysis time. The green particle was obtained by the electrochemical method of the bipolar membrane under the condition described above. These particles were found in the cathode chamber and no particle in the anode chamber. The XRD patterns of the particle produced were shown in Figure 2.

![Figure 2. The XRD patterns of the particles produced at various the current density](image_url)

At the current density 80 mA/cm², there are five characteristic peaks matched the standard pattern of brushite (JCPDS 72-0713). They are 11.71° (020), 20.99° (12-1), 29.35° (14-1), 30.53° (121), 34.21° (150). The peak at 31.71° (211) matches the standard pattern of hydroxyapatite (JCPDS 09-0342) and the peak at 45.45° match the standard pattern of Ni (JCPDS 04-0850). At the current density 160 mA/cm², the characteristic peaks of the brushite disappear and the peaks of HA and Ni still appear. At the higher current density (240 mA/cm²), there are four characteristic peaks matched the standard pattern of HA. They are 25.99° (002), 28.37° (210), 31.73° (211), and 33.23° (300). At the lower current density, the first formed is brushite. At the higher current density, brushite converts to HA. The higher current density the greater the chances of HA formation.
Figure 3. The profile of the solution pH for the electrolysis time at various the current density at the anode chamber (a) and the cathode chamber (b).

The profile of the pH solution for the electrolysis time at the anode chamber and the cathode chamber was shown at Figure 3. In the anode chamber, the pH solution decreased for the time of electrolysis. The decrease in the pH of the solution at the anode chamber is due to the formation of H$^+$ ions in the anode as the result of water oxidation.

$$2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \quad (1)$$

The formation of O$_2$ was shown by the gas bubble formed in the anode for the electrolysis time. The lower the current density the lower the pH of the solution. At the condition of the pH is very low the solution can damage the bipolar membrane. No particle was formed in the anode chamber because of low the solution pH. In the cathode chamber, the pH solution increased for the time of electrolysis. The increase in the cathode chamber is due to the formation of OH$^-$ ions in the cathode as the result of water reduction.

$$2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq) \quad (2)$$

The formation of H$_2$ was confirmed by the gas bubble formed in the cathode for the electrolysis time. The higher the current density the higher the pH of the solution. At 80 mA/cm$^2$, the final pH solution was 4. This pH causes the calcium phosphate to consist of brushite and HA. At 160 and 240 mA/cm$^2$, the final pH solution was more than 4. The HA was formed at this pH or higher.

3.2. The initial concentration of NiCl$_2$

The influence of the initial concentration of NiCl$_2$ on the particle produced was performed at 240 mA/cm$^2$ for 30 minutes. The initial concentrations of NiCl$_2$ were 0.2 M, 0.5 M, and 1 M. Figure 4 shows the XRD patterns of particle produced for various of the initial concentration of NiCl$_2$.

The characteristic peaks of HA are shown at the XRD patterns of the particles produced at the 0.2, 0.3, and 0.5 M initial concentration of NiCl$_2$. The characteristic peaks of HA are 25.99$^\circ$ (002), 28.37$^\circ$ (210), 31.73$^\circ$ (211), and 33.23$^\circ$ (300). The characteristic peaks of Ni appear at 45.5$^\circ$.

The crystallite sizes of HA and Ni were calculated using the Scherrer Formula, which is presented as

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (3)$$
Figure 4. The XRD patterns of the particles produced at various the initial concentration of NiCl$_2$.

In this formula, $K$ is the shape coefficient for reciprocal lattice point (assuming $K = 0.9$), $\lambda$ the wavelength of the X-ray radiation (0.1540 nm), $\beta$ is full width at half maximum (FWHM) of the peak, and $\theta$ is the diffraction angle. The crystallite size of the HA and Ni at several of the initial concentration of NiCl$_2$ is shown in Table 1. The higher the initial concentration of NiCl$_2$ the higher the crystallite size of HA and Ni particles.

Table 1. The Crystallite size of the particle produced at various the initial concentration of NiCl$_2$.

| The initial concentration of NiCl$_2$ (M) | The Crystallite Size (nm) |
|----------------------------------------|---------------------------|
|                                        | HA ($2\theta = 31.7^\circ$) | Ni ($2\theta = 45.5^\circ$) |
| 0.2                                    | 52.5                       | 36.4                        |
| 0.5                                    | 59.9                       | 43.7                        |
| 1                                      | 59.9                       | 54.7                        |

3.3. The electrolysis time

Figure 5. The XRD patterns of the particles produced at various the electrolysis time.
The study of the electrolysis time was done at 0.5 M the initial concentration of NiCl$_2$ and 240 mA/cm$^2$ for 30, 45, and 60 minutes the electrolysis time. The particle produced was analyzed by X-ray diffractometer. The XRD patterns of the particle produced at various the electrolysis time shown in Figure 5. The HA particle was produced at 30 min the electrolysis time. In the high current density (240 mA/cm$^2$), the formation of HA at the bipolar membrane was very effective. Both the high current density and the bipolar membrane caused the formation of HA was very fast.

Figure 6 show the profile of solution pH for the electrolysis time. In the anode chamber, the pH solution decreases for the time of electrolysis while in the cathode chamber the pH solution increase. The pH of the solution increases fast in 15 minutes. This condition causes the formation of HA is fast. In the anode chamber, the pH of the solution is very low. The low of the solution pH cause there is no particle formed.

![Figure 6. The profile of the solution pH for the electrolysis time.](image)

4. Conclusions
The electrochemical method in two chambers with the bipolar membrane can produce the nickel – hydroxyapatite particle. In the anode chamber, the pH solution decreases for the time of electrolysis while in the cathode chamber the pH solution increases. The nickel – hydroxyapatite particle is formed in the cathode chamber. There is no particle in the anode chamber. At the lower current density, the first formed is brushite. At the higher current density, brushite converts to HA. The higher current density the greater the chances of HA formation. The increase in the initial concentration of NiCl$_2$ accelerates the increase of the pH of the electrolysis solution.

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