NaFePO$_4$ Cathode Prepared from The Caustic Fusion of A Mix Ilmenite-hematite Sand Followed by Cyclic Voltammetry for Na Insertion

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ABSTRACT

Research to prepare NaFePO$_4$ cathode material from iron sand was conducted. The iron sand consists of ilmenite FeTiO$_3$ and hematite Fe$_2$O$_3$. A caustic fusion method used to precipitate iron as Fe(OH)$_3$ and it increased Fe content up to 94.71 %. Phosphate precipitation successfully produced trigonal FePO$_4$ and monoclinic FePO$_4$ comply with ICSD#412736 and ICSD#281079. The prepared-FePO$_4$ was then used as a precursor for Na insertion by applying cyclic voltammetry mode within 2.0 – 4.0 V with 0.05 mVs$^{-1}$ of the scan rate. It produced orthorhombic olivine NaFePO$_4$ and a secondary phase of orthorhombic Na$_{0.7}$FePO$_4$. Impedance analysis at 20 Hz – 5 MHz found that the material provided a semicircle at 100 Hz peak point, indicating electrode-bulk interface with a resistance value of 1735 $\Omega$, comparable to the electrical conductivity of 5.36 x 10$^{-6}$ Scm$^{-1}$. Even though the conductivity value is quite lower than NaFePO$_4$ prepared from a commercial FePO$_4$ that has been conducted in our previous research, however the electrical conductivity still reliable for cathode.

Keywords: iron sand, ilmenite-hematite, NaFePO$_4$, caustic fusion, cyclic voltammetry, Na insertion, cathode, sodium ion-battery

INTRODUCTION

A high rate increase in electronic devices production allows a high demand of energy storage equipment, such as batteries. A movement to renewable energy sources also drives fast progress within energy storage technology. The issues are to increase the storage-specific capacity and to counter source materials limitation by searching another alternative. Until recently, Lithium Ion Battery, LIB, is the most recognized battery commercially. According to Li source limitation on earth, then Sodium-Ion Battery, SIB could be promising alternative according to high sodium abundance and uniform geographic distribution on earth [1,2]. Nowadays, research on SIB grows rapidly to increase its capacity by increasing performance of its functional materials, such as electrode (cathode, anode), or electrolyte. Iron phosphate based-cathodes are known to provide good performance cathode for SIB. Some iron phosphate based-compounds have been studied such as Na$_2$FeP$_2$O$_7$ [3], Na$_2$FePO$_4$F [4], Na$_4$Fe$_5$(PO$_4$)$_3$P$_2$O$_7$ [5], and NaFePO$_4$ [6]. The NaFePO$_4$ can be crystallized in maricite and olivine structure, in which maricite is known to more thermodynamically stable [7]. However, the olivine structure shows better performance than maricite providing 154 mAhg$^{-1}$ [16,8]. Maricite structure can be synthesized by a conventional solid-state reaction [6], meanwhile olivine structure usually synthesized by an ion-exchanged method from Li to Na. That involves
delithiation- to LiFePO$_4$ followed by sodiation to the delithiated-FPO$_4$ [7,9,10]. If the step can be driven directly to Na insertion without passing through delithiation to directly produce an olivine NaFePO$_4$, that will be an interesting option in case of eliminating delithiation step and also eliminate the possibility of lithium insertion to compete Na insertion as it occurs when LiFePO$_4$ was used as precursor [11].

Next, when SIB technology produced to fulfill market demand, a high demand on FePO$_4$ precursor will also increase. Therefore, this research initiate step from iron sand as raw material. In which Indonesia has high abundance of iron sand spread over Sumatra, Kalimantan, Sulawesi, Maluku, Jawa and also Nusa Tenggara [12]. Some oxide content within iron sand is magnetite (Fe$_3$O$_4$), ilmenite (FeTiO$_3$), hematite (Fe$_2$O$_3$) and other minerals such as alumina, silica, and other minerals depend on the area of origin [13]. Iron sand procured from Nusa Tenggara is known to have Fe content up to 68.12 %, with Ti content of 9.71 %, Al 2.00 %, and other minerals at around 19.17 % [14]. High Ti content indicates the present phase of ilmenite FeTiO$_3$. An analysis of phases inside the iron sand is conducted in this research before further steps to produce iron (II) phosphate. The prepared FePO$_4$ was then used as a precursor to insert Na directly by an electrochemical method instead of by replacing Li from LiFePO$_4$ by Na, as it was done by a previous research [15]. A low purity of raw material is also a great challenge to having an appropriate cathode performance.

**EXPERIMENT**

**Preparation of FePO$_4$ from ilmenite sand through caustic fusion method**

An XRF analysis was conducted to understand iron oxide content in the raw iron sand (PT Pacific Aristama Entebe, NTB province, Indonesia). The analysis found that the iron sand is within ilmenite and hematite types [14]. The iron sand was used as raw material to prepare Fe(OH)$_3$ by a caustic fusion method, in which the Fe(OH)$_3$ was then converted into FeCl$_3$ through acid leaching [16] followed by precipitation through reaction with NaOH solution. Meanwhile, reaction with H$_3$PO$_4$ solution produced iron phosphate. The phosphate precipitate was calcined at 700 °C under argon gas flow to produce FePO$_4$ powder, which was then analyzed by X-ray diffraction (XRD, X-Pert PAN analytical) equipped with Le Bail refinement (RIETICA software, a free edition) to investigate the phases content and their crystal structure, and by X-ray fluorescence (XRF, PAN analytical minipal 4) to analyze the elemental content.

**Electrochemical sodiation to produce NaFePO$_4$**

The intercalation of Na$^+$ ions to FePO$_4$ was conducted by cyclic voltammetry mode within the potential window of 2.0 – 4.0 V (Corrtest Electrochemical Workstation CS-150). The FePO$_4$ powder was mixed with acetylene black (AB) and polyvinylidene within the weight ratio of 0.7:0.2:0.1, for FePO$_4$ powder, AB, and polyvinylidene, respectively. The mixture was then dispersed in N-methyl-2-pyrrolidone and was stirred until homogeneous. The slurry was cast on aluminum foil and was dried at 60 °C for 2 h. The cyclic voltammetry was conducted within a three-neck flask containing 1 M NaClO$_4$/EC: DMC (1:1) electrolyte in propylene carbonate. There are three electrodes used which are the FePO$_4$ film on Al substrate (FePO$_4$/Al) as a working electrode, a sodium metal as a counter electrode, and a sodium metal as a reference electrode. Cyclic voltammetry was conducted until one cycle complete within 0.05 mVs$^{-1}$ of the scan rate. The sodiated-FePO$_4$ was then detached from its Al substrate, and the collected powder was then heated at 470 °C 1 h under Ar gas flow to release the remains NaClO$_4$. The produced powder was then characterized by XRD, SEM/EDX, impedance measurement (EUCOL U2826 LCR meter, 20 Hz – 5 MHz, 0.2 V bias). For impedance measurement, a half cell was prepared by applying one drop of NaClO$_4$ solution on the NaFePO$_4$/Al, and then while
the surface wet, an aluminum foil was attached to it to cover the surface (scheme of the half-cell is described in Figure 1). This preparation was conducted in a glove box under the Argon gas atmosphere, and then vacuum sealed with an electric hot press. Both surfaces were connected with the silver wire as a current connector, glued by silver paste. Impedance was measured within 20 Hz – 400 kHz frequency under 0.2 V of potential bias. The data was then plotted into a Nyquist plot (Z’ (real impedance) vs Z” (imaginary impedance)) and then fitted with ZView software (included within CS Studio 5 (official software of Corrtest Electrochemical Workstation) by applying R-C network (R: resistor, C: capacitor). Conductivity, σ, was calculated from equation (1) by inputting resistance, R, as the fitting result. Meanwhile, I is the thickness of half-cell (cm) and A is the active surface area (cm²).

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\sigma = \frac{1}{AR}
\]

(1)

**RESULT AND DISCUSSION**

The iron sand used in this research was analyzed by XRD to understand its specific peaks related to the phase component content inside the sand (Figure 2(a)). As described in Figure 2, the peaks show the presence of iron oxide, Fe₂O₃, iron (II) titanium (IV) oxide, FeTiO₃, a tetragonal TiO₂ and monoclinic TiO₂. The Le Bail refinement (Figure 2(b)) convinces those phases existence, as the refinement proceeds well when applying the standard diffraction data of FeTiO₃ ICSD#79278, Fe₂O₃ ICSD#15840, and TiO₂ ICSD#9161 and ICSD#154035 with a residual factor of Rp 5.62%, Rwp 9.82%.

The refinement results also predicting the composition of each phase as follows, 42.22 % of FeTiO₃, 40.32 % of Fe₂O₃, 2.81 % of rutile TiO₂ ICSD#9161, and 14.66 % of TiO₂ ICSD#154035. Table 1 provides the XRF analysis result in weight % of each element in the iron sand from the mining plan and weight % after concentrating the iron content through the caustic fusion method.
Figure 2. XRD pattern of iron sand as raw material (a), and its Le Bail plot of refinement result by inputting 4 phases of FeTiO$_3$, Fe$_2$O$_3$ and TiO$_2$ tetragonal and monoclinic.

Table 1. Elemental composition of the iron sand and the produced iron hydroxide, Fe(OH)$_3$.

| Elements | Content (%) in Iron sand | Content (%) in Fe(OH)$_3$ |
|----------|--------------------------|---------------------------|
| Fe       | 80.46                    | 94.71                     |
| Ti       | 8.50                     | 1.05                      |
| Al       | 3.00                     | -                         |
| Si       | 3.00                     | -                         |
| Ca       | 1.04                     | 0.41                      |

Figure 3 shows combined XRD patterns of iron sand, the produced-Fe(OH)$_3$, and the produced-FePO$_4$. Figure 3 shows that the green powder or FePO$_4$ calcination has a significance different peaks the calcined-one, eventhough some small peaks provided are similar with the calcined-FePO$_4$. Before calcination the green powder was washed with distilled water to remove some impurities as well as to neutralize the pH. The pretreatment seems to significantly increase the intensity of FePO$_4$ characteristic peaks, by eliminating some impurities. After calcination, the characteristic peaks are in agreement with the standard diffraction of FePO$_4$ ICSD#412736, confirming that the synthesis successfully occurred. The crystal structure is trigonal with a space group of $P3121$. A high peak at 27$^\circ$ indicates a high crystallinity. However, the unidentified peaks at 2$\theta$ 16.29$^\circ$ and 20.28$^\circ$ suggest the presence of a secondary phase. Le Bail refinement was predicting a monoclinic FePO$_4$ as the secondary phase. The refinement result is listed in Table 2.
Figure 3. Combined XRD patterns of iron sand, Fe(OH)$_3$ and the synthesized-FePO$_4$ at before and after calcination at 700 °C

Table 2. Refinement result of the prepared-FePO$_4$ from the mix ilmenite-hematite sand by applying standard diffraction of trigonal FePO$_4$ ICSD#412736 and monoclinic FePO$_4$ ICSD#281079.

| Cell Parameters | The prepared-FePO$_4$ |
|-----------------|-----------------------|
| Crystal structure | Trigonal | Monoclinic |
| Space group | $P 31 2 1$ | $P 1 21/n 1$ |
| a (Å) | 4.997(8) | 5.414(9) |
| b (Å) | 4.997(8) | 7.43(1) |
| c (Å) | 11.18(2) | 7.98(1) |
| $\alpha$ | 90° | 90° |
| $\beta$ | 90° | 95.591° |
| $\gamma$ | 120° | 90° |
| Cell volume (Å$^3$) | 241.980133 | 319.516846 |
| $R_p$ (%) | 2.05 |
| $R_{wp}$ (%) | 3.64 |

Cyclic voltammetry to FePO$_4$/Al at 0.05 mVs$^{-1}$ produced a voltammogram as depicted in Figure 4. Tafel fitting with CVview software embedded with CS Studio5 (the program for Corrtest Electrochemical workstation) found that two peaks reveal 2.4455 V vs Na$^+$/Na with a higher current density of 1.2165 $\times$ 10$^{-5}$ Acm$^{-2}$ confirming sodiation/de-sodiation, and 3.5242 V vs Na$^+$/Na confirming the activities of Fe$^{3+}$/Fe$^{2+}$ redox reaction. A previous cyclic voltammetry investigation to NaFePO$_4$ prepared by the Pechini method also provides a peak at around 3.5 V vs Na$^+$/Na indicating Fe$^{2+}$/Fe$^{3+}$ redox reaction [17]. It indicates the activity of Fe$^{2+}$/Fe$^{3+}$ will be quite prominent within sodium-ion battery with NaFePO$_4$ cathode, instead of only Na$^+$/Na activity.
Figure 4. The plot log i vs potential (left) and potential, E (volt) vs current density (Acm^{-2}) of the prepared-FePO_{4} with a potential window of 2.0 – 4.0 V vs Na^{+}/Na. The scan rate of 0.05 mV/s (right).

The XRD pattern of NaFePO_{4} is shown in Figure 5(a). Some peaks reveal agree with NaFePO_{4} pattern provide in another result, such as a high peak at 2\theta 27°, 29°, and 22° [18]. Some small peaks at 15°, 20°, 32°, 36°, 37°, 40°, and 48° are also found [10], instead of peaks at 57°, and 67.5° [19]. The diffraction data were refined by the Le Bail method of which the results are shown in Figure 5(b). The refinement was proceeded well by applying a standard diffraction data of trigonal FePO_{4} ICSD#412736, monoclinic FePO_{4} ICSD#281079, and orthorhombic Na_{0.7}FePO_{4}. The orthorhombic Na_{0.7}FePO_{4} cell parameters were taken from previous research [20]. The refinement also applied a standard orthorhombic NaFePO_{4} based on supporting information provided by other research [21]. The refinement result is listed in Table 3. Na insertion allows cell parameter increasing within a direction from 4.997(8) Å (Table 2) into 10.435(7) Å, and increasing within b direction from 4.997(8) Å to 6.229(4) Å. This is in agreement with another research on chemical Na insertion by the Pechini method which able to increase within b [010] and a [100] direction [20]. Meanwhile, another research on electrochemical Na insertion found an increasing along c direction [22], and our previous research on electrochemical Na insertion into commercial FePO_{4} layer found cell parameter increasing along a, b, and c [11]. Na insertion has changed oxidation number of Fe(III) into Fe(II) in order to keep the molecule neutralized. It was effectively increase the relative mass of the positive charge from a single Fe of 55.845 atomic unit, u [23] into 78.834 atomic unit, u. The mass increasing allows the cell parameters to change or increase along the a, b, and c axis.

SEM analysis shows the morphological change from large aggregates of FePO_{4} with a diameter larger than 500 nm (Figure 6(a)) into more homogeneous small-spherical particles with a diameter of around 50 – 65 nm (Figure 6(b)), after Na insertion. It indicates that Na insertion occurred into every single crystal structure, as it also convinced by cell parameters change (Table 2 and Table 3), and allows the insertion to break up the aggregates into dispersed-particles. Na insertion was detected by EDS analysis, in which at initial Fe available within FePO_{4} powder at around 17.43 % (atom) (Figure 7(a)), changes into 6.53 % (atom) (Figure 7(b)). Around 43.5% Fe atom was replaced by Na atom (composition within total is 2.84 % atom) (Figure 7(b)). Aluminum was detected in the prepared-material due to the Al substrate used.
The synthesized-NaFePO₄ by applying trigonal FePO₄, monoclinic FePO₄, orthorhombic Na₀.₇FePO₄, and orthorhombic NaFePO₄

| Cell parameters | The synthesized-NaFePO₄ |
|-----------------|-------------------------|
|                 | FePO₄ Trigonal P 31 2 1 | FePO₄ Monoclinic P 1 2 1/n 1 | Na₀.₇FePO₄ Orthorhombic P n m a | NaFePO₄ Orthorhombic P n m a |
| a (Å)           | 5.034(6)                | 5.460(3)                | 10.19(2)                | 10.435(7)                |
| b (Å)           | 5.034(6)                | 7.518(4)                | 6.21(5)                 | 6.229(4)                 |
| c (Å)           | 11.43(2)                | 8.109(6)                | 4.867(5)                | 4.950(3)                 |
| α (°)           | 90                      | 90                      | 90                      | 90                      |
| β (°)           | 90                      | 95.723                  | 90                      | 90                      |
| γ (°)           | 120                     | 90                      | 90                      | 90                      |

Impedance analysis to the prepared-NaFePO₄ found a high capacity of 1.103 x 10⁻⁶ Farads, indicating the electronic migration. Since a capacitance around 0.1 μF is categorized as an electrode-bulk interface [24,25]. ZView fitting (software embedded in CS Studio5) found a resistance value of 1735Ω, comparable to 5.36 x 10⁻⁶ S cm⁻¹ of electric conductivity. The resistance value is higher than NaFePO₄ prepared by a similar method to a commercial FePO₄, i.e., 1242 Ω [11]. The resistance value is also still higher than C/NaFePO₄ cathode, or a mixture of carbon with NaFePO₄ powder, which is 1300Ω [26]. The FePO₄ purity seems to decrease charge carrier migration between two electrodes.
This research found that even though NaFePO$_4$ prepared from the low purity FePO$_4$ still shows a low conductivity, however the Na insertion increases the conductivity by two order from $1.5 \times 10^{-8}$ S cm$^{-1}$ as the direct current of FePO$_4$[27] into $5.36 \times 10^{-6}$ S cm$^{-1}$ after insertion. The low conductivity of FePO$_4$ or before Na insertion because of low concentration of Fe$^{2+}$ - Fe$^{3+}$ redox pairs. Na insertion which bearing 1+ of charge has been shown to create redox pairs of Fe$^{2+}$ - F$^{3+}$ which is essential for electronic hoping. The result is in agreement with another study on investigating Li composition within Li$_x$FePO$_4$ glasses by XANES and Mössbauer
analysis which found a low concentration of Fe$^{2+}$/Fe$^{3+}$ for pure FePO$_4$, and the ratio increases with increasing x [28]. Na insertion as proven by the increasing of cell parameters as well as the change of surface morphology as depicted in Figure 6 seems having similar effect as shown by Li insertion.

**Figure 8.** Nyquist plot of impedance data along with its fitted line and R-C network model (a), and its Bode plot between frequency vs real impedance, $|Z|$.

**CONCLUSION**
Iron sand used in this research consist of ilmenite and hematite, confirmed by elemental analysis that detects 80.46 % Fe content, and 8.5 % of Ti. XRD analysis combined with Le Bail refinement confirmed the presence of ilmenite FeTiO$_3$ and hematite Fe$_2$O$_3$ phases. Caustic fusion successfully produced Fe(OH)$_3$ from the iron sand and increase Fe content up to 94.71 %. XRD analysis equipped with Le Bail refinement found the trigonal FePO$_4$ and monoclinic FePO$_4$ are formed within the iron phosphate powder. Electrochemical Na insertion by cyclic voltammetry mode within 2.0 – 4.0 V of potential windows successfully produces orthorhombic NaFePO$_4$ and orthorhombic Na$_{0.7}$FePO$_4$ as a secondary phase. Impedance analysis found that the prepared-NaFePO$_4$ provide 1735Ω resistance or comparable to 5.36 x 10$^{-6}$ Scm$^{-1}$. The result confirmed the reliability of this NaFePO$_4$ to be used as a cathode material.

**CONFLICT OF INTEREST**
Author declare no competing interest.

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