The performance of sodium ion battery with NaFePO₄ cathode prepared from local iron sand

F Rahmawati, Z Faiz, D A N Romadhona, T E Saraswati and W W Lestari

Department of Chemistry, Faculty of Mathematics and Natural Sciences (FMIPA), Sebelas Maret University, Surakarta 57126, Indonesia

Corresponding author’s email: fitria@mipa.uns.ac.id

Abstract. The performance of Sodium-Ion Battery, SIB, with NaFePO₄ cathode prepared from local iron sand was investigated. The NaFePO₄ was prepared through electrochemical sodiation to FePO₄ layer on aluminium substrate. NaFePO₄ prepared from local iron sand (from NTB, Indonesia) is named as NFP_A. The result is compared to the performance of SIB with NaFePO₄ cathode prepared from a commercial FePO₄, which is named as NFP_B. The SIB was fabricated in a split cell test type and a pouch type. Battery performance was measured by Cyclic Voltammetry (CV) analysis, Galvanostatic Charge-Discharge (GCD) testing, and Electrochemical Impedance Spectroscopy (EIS) measurements. CV analysis found that sodium intercalation and de-intercalation curve in NFP_A is similar to the CV curve of NFP_B. The reduction peak presents at -2.98 V and -2.99 V for NFP_A and NFP_B, respectively. Those peaks represent Na⁺ intercalation into FePO₄ layer. The oxidation peaks, that represent de-intercalation from NaFePO₄ appears at 3.31 and 3.96 V. Split cell SIB with NFP_A as cathode provides 100 cycles under 1 C and 3 C current drawn. Meanwhile, the pouch type only provides 50 cycles before the capacity loss under 1 C current drawn. Each type has 100 % Coulombic efficiency indicates that all of the charged-ion can be completely discharged.

Keywords: Cathodes, iron sand, NaFePO₄, sodium ion battery

1. Introduction
A lithium-ion battery is the most used batteries with high operating voltage and efficiency. Nevertheless, low abundance of lithium in the earth’s crust significantly restricts the LIBs development [1]. Sodium-ion batteries (SIBs) using sodium ion as the charge carrier, which can be extracted from sea water and earth’s crust potentially replaces LIBs as the main electrical energy storage. The lack of cycle ability and structural stability of cathode materials become major problems for SIBs development. NASICON is a phosphate-based electrode which has a stable structure of open-framework, generating a high operating voltage of 3.4 V [2]. Other promising phosphate-based electrodes is NaFePO₄. It has a good structural stability and cycle ability because of the PO₄³⁻ existence as an oxygen lattice stabilizer when applied in a high current rate [3]. NaFePO₄ has two kinds of phases, olivine and maricite phase. The olivine phase needs a high temperature to synthesize but it has better electrochemical properties than the maricite phase [4]. Former studies used LiFePO₄ as the precursor to obtain olivine NaFePO₄ through the electrochemical delithiation-sodiation method [5]. The produced materials were used as a cathode for SIBs and delivered a good specific capacity (near the theoretical specific capacity of NaFePO₄ = 154 mAh/g) but showed poor cycle ability. This problem was occurred due to the large mismatch ionic
size during the Li-Na exchange process to obtain NaFePO$_4$ from LiFePO$_4$, causing severe decays in cathode capacity and cycle ability [6]. A previous research in our group conducted an electrochemical-synthesized olivine NaFePO$_4$ from FePO$_4$ layer, in which the FePO$_4$ powder was prepared from iron sand. The produced-NaFePO$_4$ showed a good electrical conductivity. Therefore, this work aims to study the performance of the prepared NaFePO$_4$ while being used as a cathode for SIBs. Split cell test and pouch cell type being used as packages for fabricated SIBs. As a comparison, an electrochemically sodiated commercial FePO$_4$ is also used as a cathode for SIBs fabrication.

2. Experimental

NaFePO$_4$ electrode material was prepared by electrochemical sodiation to a FePO$_4$ layer on Al foil. The FePO$_4$ layer on Al, FePO$_4$/Al was used as working electrode within the electrochemical system by operating cyclic voltammetry mode. Each working electrodes (WE) was prepared using 70% of the active material (FePO$_4$), 20% acetylene black (AB) and 10% polyvinylidene fluoride (PVDF) binder. N-methyl-2-pyrrolidinone (NMP) was being used as solvent to make electrode slurry. This slurry was then evenly coated using a doctor blade onto an aluminum foil as current collector to generate a 0.2 mm coating thickness. After drying in the oven for 2 h, the coated foil was cut into 5 cm x 2 cm each to create the working electrodes. These electrodes were attached onto Ag wire and placed in a three-neck rounded flask using two sodium metals, each attached onto Ag wires as the counter electrode (CE) and reference electrode (RE), and 1 M NaClO$_4$ salt in propylene carbonate solution as the electrolyte. The electrochemical sodiation was performed using cyclic voltammetry mode at a rate of 0.05 mV/s over 2 to 4 V vs Na'/Na potential window using CorrTest® Electrochemical Workstation CS150. NaFePO$_4$ (NFP) layer dried at 120 °C have been used as cathode for battery fabrication. This method produced NFP_A (from FePO$_4$ synth) and NFP_B (from FePO$_4$ comm).

3. Electrochemical tests

The batteries were fabricated using a split cell test and pouch cell packaging. Split cell test consisting of a coin cell and wrapped by set of a brass shell (figure 1). The electrochemical stack consisting of a NaFePO$_4$ cathode prepared from iron sand extraction, a graphite layer casted on a Cu foil, a polytetrafluoroethylene (PTFE) film separator and 1 M NaClO$_4$ in ethylene carbonate (EC): dimethyl carbonate (DMC) (1:1 by volume) was being used as liquid electrolyte for electrochemical measurements. The pouch cell batteries (figure 2) were fabricated using the same stack as the split cell test batteries, with the addition of a 1 cm$^2$ thin sodium metal attached to Ag wire placed between cathode layer and PTFE film. The stack was wrapped with aluminum plastic foil. For comparison, a split cell test and a pouch cell consisting of a NaFePO$_4$ cathode prepared from commercial FePO$_4$ (NFP_B) have been fabricated using the same stack as the previous fabricated batteries. Thus, the fabricated split cell test batteries were using NFP_A (SIB SC) and NFP_B (SIB KC) as cathode materials. The pouch cell batteries were also using NFP_A (SIB SP) and NFP_B (SIB KP) as cathode materials. Split cell test batteries were then galvanostatically cycled (GCD) at 1 C and 3 C (1 C = 154 mAh/g) and at 1C for the pouch cell batteries for 50 cycles each current rate using CorrTest® Electrochemical Workstation CS150. Cyclic voltammetry (CV) at a rate 0.05 mVs were performed on pouch cell batteries using CorrTest® Electrochemical Workstation CS150 over a potential window of (-3) to 4 V vs Na'/Na. The electrochemical impedance spectroscopy (EIS) measurements was carried out following the GCD testing and were conducted over a range of 20 Hz to 300 kHz with 0.2 V AC amplitude using EUCOL® U2826 LCR Meter.
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Figure 1. Scheme of split cell test SIBs: 1) Upper brass shell, 2) Cathode plate, 3) coin, 4) NaFePO₄/Al foil layer as cathode, 5) PTFE film with 1 M NaClO₄ as electrolyte, 6) Graphite/Cu foil layer as anode, 7) anode plate, 8) spring steel, 9) bottom brass shell, 10) Ag wires.

Figure 2. Scheme of pouch cell SIBs: 1) NaFePO₄/Al foil layer as cathode, 2) thin sodium metal attached into Ag wire as reference electrode, 3) PTFE film with 1 M NaClO₄ as electrolyte, 4) Graphite/Cu foil layer as anode.

4. Results and discussion

Electrochemical studies were performed by cyclic voltammetry (CV) analysis, galvanostatic charge-discharge (GCD) testing and electrochemical impedance spectroscopy (EIS) measurement. CV was conducted to determine the reduction and oxidation potentials of NaFePO₄ when cycled in the fabricated batteries. CVs for NaFePO₄ batteries are presented in figure 3. The voltammograms need to be analyzed using voltammetry analysis software to determine the reduction and oxidation potentials. The reduction potentials represent Na⁺ intercalation into FePO₄ layer, as the batteries being discharged (equation 1). The oxidation potentials represent Na⁺ de-intercalation from FePO₄ layer, as the batteries being charged (equation 2). The prediction of the total electrochemical reaction occurred inside the battery is described by equation 3.

\[
\text{NaFePO}_4 \rightarrow x\text{Na}^+ + x\text{e}^- + x\text{FePO}_4 + (1-x)\text{NaFePO}_4
\]
FePO$_4$ + xe$^-$ + xNa$^+$ → xNaFePO$_4$ + (1−x)FePO$_4$ \hspace{2cm} (2)

NaFePO$_4$ + C$_6$ ↔ $e^-$ FePO$_4$ + NaC$_6$ \hspace{2cm} (3)

NFP_A reduction-oxidation couple potential was found at (-2.98) and 3.31 V, while NFP_B was at (-2.99) and 3.96 V. These potentials were associated with Fe$^{2+}$/Fe$^{3+}$ redox couples, which means that sodium ion intercalation/de-intercalation were occurred through 1 step process. As the electrochemical potential is possibly correlated directly to the local atomic environment of the guest ions, particularly the site energy [7]. Another minor peaks could reflect the insertion or de-insertion of Na$^+$ with lower site energy [8].

Stationary energy storage applications require a long-term electrochemical cycling stability. Figure 4a shows the specific capacity of split cell test batteries which galvanostatically cycled at two charge/discharge current rates (C), 1 C and 3 C. The theoretical capacity of NaFePO$_4$ was calculated to be 154 mAh/g at 1C. SIB KC delivered a stable specific capacity of 76 mAh/g at 1C for 50 cycles, slightly lower than SIB SC which provides 77 mAh/g at 1 C for 50 cycles. These two SIBs delivered a higher specific capacity of 230 mAh/g at 3 C for further 50 cycles. This might be caused by the relation of the charging/discharging rate and electrolyte decomposition rate with the cycle numbers to reach the highest battery capacity [8]. The pouch cell batteries (SIB KP and SIB SP) delivered very small and unstable specific capacity (figure 4b). The main reasons were non-compact electrodes stacking when the batteries were fabricated and trapped gases present between electrodes layer. It also affects the SIBs operating voltage and internal battery resistance (figure 4c and figure 4d). All of the fabricated SIBs provide 100 % Coulombic efficiency that showed good reversibility properties (figure 4e and figure 4f).

The EIS measurement was performed after the GCD testing. There was no semicircle pattern in split cell test SIBs Nyquist plot (figure 5a) which means the absence of solid electrolyte interphase (SEI) layer growth between electrolyte and anode layer [9]. SEI layer provides a “barrier” preventing the electrolyte solvent molecule intercalating the anode structure, increasing the total internal resistance and decreasing the batteries’ reversibility process. However, an uncontrollable SEI layer growth would obstruct the sodium intercalation process and then decrease the battery specific capacity. The different pattern is observed at the pouch cell SIBs Nyquist plot (figure 5b). It is believed to be also caused by the electrodes stack bad contact so the ionic migration in the battery was not as good as it is supposed to be. The total internal resistance from pouch cell SIBs determined by Nyquist plot fitting were much higher than split cell test SIBs, as shown in table 1.

Figure 3. Cyclic voltammogram of SIB KP (blue line) and SIB SP (red line).
Figure 4. Specific capacity of (a) split cell test SIBs, and (b) pouch cell SIBs. Operating voltage of (c) split cell test SIBs, and (d) pouch cell SIBs. Coulombic efficiency of (e) split cell test SIBs, and (f) pouch cell SIBs.
Figure 5. Nyquist plot of (a) split cell SIBs and (b) pouch cell SIBs.

Table 1. The total internal resistance of all the fabricated SIBs.

| Battery | Total Internal Resistance (Ω) |
|---------|-------------------------------|
| SIB KC  | 5.6657                        |
| SIB SC  | 6.5297                        |
| SIB KP  | $3.7026 \times 10^4$          |
| SIB SP  | $2.5441 \times 10^{10}$       |

5. Conclusion

Sodium-Ion Battery performance with NaFePO$_4$ cathode from local iron has similar intercalation and de-intercalation trend with the SIB prepared from a commercial NaFePO$_4$. Cyclic voltammetry analysis to the SIB battery shows reduction peaks at (-2.98) and (-2.99) V, while oxidation peaks at 3.31 and 3.96 V. Split cell SIBs provides 50 cycles before dropping, whether under current drawn of 1 C or 3 C. Meanwhile, the pouch cell SIBs only performed under 1 C current drawn.

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