



Crystalline maricite NaFePO_4 as a positive electrode material for sodium secondary batteries operating at intermediate temperature

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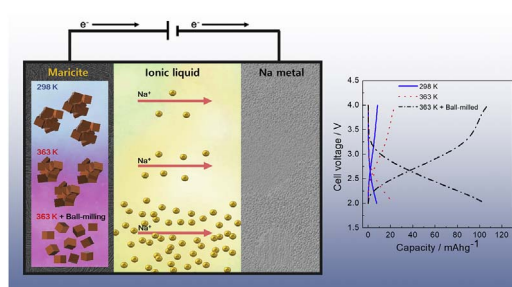
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HIGHLIGHTS

- A maricite NaFePO_4 positive electrode is employed for sodium secondary batteries.
- Crystalline m-NaFePO_4 is electrochemically active at intermediate temperature.
- XRD reveals that m-NaFePO_4 undergoes desodiation-sodiation reaction.
- The interfacial resistance of m-NaFePO_4 is evaluated by EIS using symmetric cells.

GRAPHICAL ABSTRACT



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ABSTRACT

Maricite NaFePO_4 (m-NaFePO_4) was investigated as a positive electrode material for intermediate-temperature operation of sodium secondary batteries using ionic liquid electrolytes. Powdered m-NaFePO_4 was prepared by a conventional solid-state method at 873 K and subsequently fabricated in two different conditions; one is ball-milled in acetone and the other is re-calcined at 873 K after the ball-milling. Electrochemical properties of the electrodes prepared with the as-synthesized m-NaFePO_4 , the ball-milled m-NaFePO_4 , and the re-calcined m-NaFePO_4 were investigated in $\text{Na}[\text{FSA}]\text{-}[\text{C}_2\text{C}_1\text{im}][\text{FSA}]$ ($\text{C}_2\text{C}_1\text{im}^+ = 1\text{-ethyl-3-methylimidazolium}$, $\text{FSA}^- = \text{bis}(\text{fluorosulfonyl})\text{amide}$) ionic liquid electrolytes at 298 K and 363 K to assess the effects of temperature and particle size on their electrochemical properties. A reversible charge-discharge capacity of 107 mAh g^{-1} was achieved with a coulombic efficiency $> 98\%$ from the 2nd cycle using the ball-milled m-NaFePO_4 electrode at a C-rate of 0.1 C and 363 K. Electrochemical impedance spectroscopy using $\text{m-NaFePO}_4/\text{m-NaFePO}_4$ symmetric cells indicated that inactive m-NaFePO_4 becomes an active material through ball-milling treatment and elevation of operating temperature. X-ray diffraction analysis of crystalline m-NaFePO_4 confirmed the lattice contraction and expansion upon charging and discharging, respectively. These results indicate that the desodiation-sodiation process in m-NaFePO_4 is reversible in the intermediate-temperature range.

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1. Introduction

Lithium secondary batteries have been widely adopted as power sources for small devices owing to their high energy density [1–3]. However, this advantage of lithium secondary batteries is offset for large-scale energy storage applications by their high cost, including potential problems for constituent elements, and safety issues regarding the use of organic electrolytes. Thus, electrode materials free from trace elements have drawn attention as a means to strengthen the economic viability of sodium secondary batteries. Post-lithium secondary batteries have to be economically affordable and safe, and provide good electrochemical performance [4–8]. Owing to these factors, there is currently considerable interest in sodium secondary batteries for large-scale energy storage applications [9]. A number of reports have stated that the safety problems associated with lithium secondary batteries can be mitigated using ionic liquid (IL) electrolytes owing to their non-flammability, low volatility, and high thermal and electrochemical stabilities [10–13], and this is also true for sodium secondary batteries [14,15].

According to our previous studies, the elevation of operating temperature using IL electrolytes can enhance Na^+ diffusion both in the solid active material and the electrolyte, which effectively improves the electrochemical performances of positive and negative electrodes [16–21]. Thus, sodiation/desodiation into/from materials that are inactive at room temperature may be realized by elevating the operation temperature. Such elevated-temperature operation of secondary batteries is not impracticable for real applications. Indeed, it is even preferable in some cases considering the self-heating of batteries and their use in hot environments such as the engine compartments of automobiles.

Iron-based phosphates family such as $\text{Na}_2\text{FePO}_4\text{F}$, $\text{Na}_2\text{FeP}_2\text{O}_7$, and $\text{Na}_4\text{Fe}(\text{PO}_4)_2\text{P}_2\text{O}_7$ have been studied as potential positive electrode materials for sodium secondary batteries [22–27]. NaFePO_4 , which is known to adopt an olivine structure with two polymorphs triphylite and maricite [28], has the highest theoretical capacity of 155 mAh g^{-1} among the iron-based phosphates. However, NaFePO_4 has not been deeply studied in detail owing to its difficult preparation (in the case of triphylite) or electrochemical inactivity (in the case of maricite). Triphylite NaFePO_4 (t- NaFePO_4) can be prepared by chemical and electrochemical Li-Na exchange process (i.e. delithiation of LiFePO_4 and sodiation of FePO_4 , respectively) [28,29]. However, there are no reports of the direct synthesis of t- NaFePO_4 for a practical use, even though it delivers a reversible capacity of 120 mAh g^{-1} based on $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox activity [29]. Maricite NaFePO_4 (m- NaFePO_4) can be synthesized by conventional solid-state methods because it is thermodynamically stable phase [28]. However, m- NaFePO_4 was considered to be electrochemically inactive for a long time until a recent study by Kang's group [30], in which Na^+ was proved to be desodiated from nano-sized m- NaFePO_4 during the first charge, transforming the maricite phase into electrochemically active amorphous FePO_4 . This phase exhibits a reversible capacity of 142 mAh g^{-1} at room temperature [30]. Although other research groups have also investigated the charge-discharge behavior of m- NaFePO_4 [31–33], no detailed reaction mechanism has been clarified and no improvements in performance for practical applications have sufficiently been achieved.

Our recent preliminary report demonstrated that m- NaFePO_4 exhibits a reversible capacity of 80 mAh g^{-1} at a C-rate of 0.2 C in a pyrrolidinium-based IL at 363 K [34]. Although it did not directly show the electrochemical activity of “crystalline” m- NaFePO_4 , *ex-situ* XRD measurements suggested some crystalline m- NaFePO_4 is preserved, even after 100 cycles [34]. Since the reversible capacity achieved in this previous study was far from the theoretical value, further improvement was required.

In the present study, the ball-milling conditions have been reexamined in order to improve the performance of m- NaFePO_4 positive electrodes for intermediate-temperature sodium secondary batteries.

Since ball-milling of m- NaFePO_4 with conductive carbon leads to irreversible capacity and degradation of battery performance, ball-milling was performed without adding conductive carbon [34]. Another improvement was the use of imidazolium-based IL electrolytes. Our previous study on $\text{Na}_2\text{FeP}_2\text{O}_7$ positive electrodes indicated that imidazolium-based ILs enable better rate performance by decreasing both bulk and interfacial impedances [20]. Here, m- NaFePO_4 electrodes prepared by three different conditions (as-synthesized, ball-milled, and re-calcined) were examined at 298 K and 363 K using the a $\text{Na}[\text{FSA}][\text{C}_2\text{C}_1\text{im}][\text{FSA}]$ ($\text{C}_2\text{C}_1\text{im} = 1\text{-ethyl-3-methylimidazolium}$, $\text{FSA} = \text{bis}(\text{fluorosulfonyl})\text{amide}$) IL electrolyte in order to clarify the activation mechanism of m- NaFePO_4 . Furthermore, the effects of temperature and ball-milling conditions on the activation of m- NaFePO_4 were investigated by electrochemical impedance spectroscopy (EIS) using m- $\text{NaFePO}_4/\text{m-NaFePO}_4$ symmetric cells.

2. Experimental

2.1. Synthesis

A powdery sample of m- NaFePO_4 was synthesized by a conventional solid-state method [25]. Stoichiometric amounts of Na_2CO_3 (Wako Pure Chemical Industries, purity 99.8%), $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Wako Pure Chemical Industries, purity 99%), and $(\text{NH}_4)_2\text{HPO}_4$ (Wako Pure Chemical Industries, purity > 99%) were ball-milled in acetone for 12 h at 600 rpm using a Fritsch Pulverisette 7 Premium Line. The mixture was collected and dried under vacuum for 24 h at 393 K and then thoroughly ground using a mortar and pestle. This precursor mixture was then calcined at 623 K for 3 h and heated at 873 K for 12 h under Ar flow, followed by cooling to room temperature. X-ray diffraction (XRD) patterns were measured using a Rigaku Smart Lab diffractometer with $\text{Cu-K}\alpha$ radiation (40 kV and 30 mA) to confirm the purity of the m- NaFePO_4 . Rietveld refinement confirmed the absence of detectable impurities in the prepared m- NaFePO_4 in our previous report [34].

2.1.1. Fabrications of the synthesized m- NaFePO_4

Three types of m- NaFePO_4 were prepared: as-synthesized, ball-milled, and re-calcined. The ball-milling was performed using 1 mm diameter of zirconium oxide balls for 12 h at 600 rpm using a Fritsch Pulverisette 7 Premium Line in 20 mL of acetone to reduce the particle size of the m- NaFePO_4 (m- NaFePO_4 : zirconium balls = 3: 1 in volume). The ball-milled (24 h) m- NaFePO_4 was prepared in the same condition except for the longer ball-milling time. The re-calcination was made by heating the ball-milled sample at 873 K for 12 h under Ar atmosphere. XRD patterns were measured again after the fabrications. The morphologies of the three types of m- NaFePO_4 were observed by field-emission scanning electron microscopy (FE-SEM, Hitachi SU-8020).

2.2. Electrochemical measurements

The electrochemical properties of the electrode materials were measured using 2032 coin-type cells at 298 K and 363 K. Sodium metal (Aldrich, purity 99.95%) cut into a disk (16 mm in diameter) and fixed on an Al plate current collector was used as the negative electrode. Positive electrodes were prepared using the three different m- NaFePO_4 samples described above. The working electrode sheet was prepared by mixing m- NaFePO_4 , Super C65 as a conductive additive, and PTFE as a binder (75:20:5 wt%), and spreading the mixture with a pestle and mortar. The sheet was pressed onto an Al mesh to have a coating density of approximately 4 mg cm^{-2} . The salts $\text{Na}[\text{FSA}]$ (Mitsubishi Materials Electronic Chemicals, purity > 99%) and $[\text{C}_2\text{C}_1\text{im}][\text{FSA}]$ (Kanto Chemical, purity > 99.9%) were dried under vacuum for 24 h at 353 K. The $\text{Na}[\text{FSA}][\text{C}_2\text{C}_1\text{im}][\text{FSA}]$ (3:7 M ratio) IL was used as the electrolyte [14]. A glass microfiber filter (Whatman GF/A) was impregnated with the electrolyte at 333 K under vacuum for 24 h prior to the assembly of the test cell.

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