

Crystalline Maricite NaFePO₄ as a Positive Electrode Material for Sodium Secondary Batteries Operating at Intermediate Temperature

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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 $\text{Na}[\text{FSA}][\text{C}_2\text{C}_1\text{im}][\text{FSA}]$ ($\text{C}_2\text{C}_1\text{im}^+$ = 1-ethyl-3-methylimidazolium, FSA^- = bis(fluorosulfonyl)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 m- $\text{NaFePO}_4/\text{m-}\text{NaFePO}_4$ 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.

Keywords:

Sodium secondary batteries, Olivine, Maricite, Ionic liquid, Intermediate-temperature operation

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, 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]. NaFePO₄, 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, NaFePO₄ 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 NaFePO₄ (t-NaFePO₄) can be prepared by chemical and electrochemical Li-Na exchange process (i.e. delithiation of LiFePO₄ and sodiation of FePO₄, respectively) [28, 29]. However, there are no reports of the direct synthesis of t-NaFePO₄ for a practical use, even though it delivers a reversible capacity of 120 mAh g⁻¹ based on Fe³⁺/Fe²⁺ redox activity [29]. Maricite NaFePO₄ (m-NaFePO₄) can be synthesized by conventional solid-state methods because it is thermodynamically stable phase [28]. However, m-NaFePO₄ 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-NaFePO₄ during the first charge, transforming the maricite phase into electrochemically active amorphous FePO₄. 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-NaFePO₄ [31-33], no detailed reaction mechanism has been clarified and no improvements in performance for practical applications have not sufficiently been achieved.

Our recent preliminary report demonstrated that m-NaFePO₄ 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-NaFePO₄, *ex-situ* XRD measurements suggested some crystalline m-NaFePO₄ 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-NaFePO₄ positive electrodes for intermediate-temperature sodium secondary batteries. Since ball-milling of m-NaFePO₄ 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 Na₂FeP₂O₇ positive electrodes indicated that imidazolium-based ILs enable better rate performance by decreasing both bulk and interfacial impedances [20]. Here, m-NaFePO₄ electrodes prepared by three different conditions methods (as-synthesized, ball-milled, and re-calcined) were examined at 298 K and 363 K using the a Na[FSA]-[C₂C₁im][FSA] (C₂C₁im = 1-ethyl-3-methylimidazolium, FSA = bis(fluorosulfonyl)amide) IL electrolyte in order to clarify the activation mechanism of m-NaFePO₄. Furthermore, the effects of temperature and ball-milling conditions on the activation of m-NaFePO₄ were investigated by electrochemical impedance spectroscopy (EIS) using m-NaFePO₄/m-NaFePO₄ symmetric cells.

2. Experimental

2.1 Synthesis

A powdery sample of m-NaFePO₄ was synthesized by a conventional solid-state method [25]. Stoichiometric amounts of Na₂CO₃ (Wako Pure Chemical Industries, purity 99.8%), FeC₂O₄·2H₂O (Wako Pure Chemical Industries, purity 99%), and (NH₄)₂HPO₄ (Wako Pure Chemical Industries, purity > 99%) were ball-milled in acetone for 12 hours at 600 rpm using a Fritsch Pulverisette 7 Premium Line. The mixture was collected and dried under vacuum for 24 hours at 393 K and then thoroughly ground using a mortar and pestle. This precursor mixture was then calcined at 623 K for 3 hours and heated at 873 K for 12 hours under Ar flow, followed by cooling to room temperature. X-ray diffraction (XRD) patterns were measured using a Rigaku Smart Lab diffractometer with Cu-K α radiation (40 kV and 30 mA) to confirm the

purity of the m-NaFePO₄. Rietveld refinement confirmed the absence of detectable impurities in the prepared m-NaFePO₄ in our previous report [34].

2.1.1 Fabrications of the synthesized m-NaFePO₄

Three types of m-NaFePO₄ were prepared: as-synthesized, ball-milled, and re-calcined. The ball-milling was performed using 1 mm diameter of zirconium oxide balls for 12 hours at 600 rpm using a Fritsch Pulverisette 7 Premium Line in 20 mL of acetone to reduce the particle size of the m-NaFePO₄. (m-NaFePO₄ : zirconium balls = 3 : 1 in volume). The ball-milled (24 hours) m-NaFePO₄ 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 hours under Ar atmosphere. XRD patterns were measured again after the fabrications. The morphologies of the three types of m-NaFePO₄ 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-NaFePO₄ samples described above. The working electrode sheet was prepared by mixing m-NaFePO₄, 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 Na[FSA] (Mitsubishi Materials Electronic Chemicals, purity > 99%) and [C₂C₁im][FSA] (Kanto Chemical, purity > 99.9%) were dried under vacuum for 24 hours at 353 K. The Na[FSA]-[C₂C₁im][FSA] (3:7 molar 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 hours prior to the assembly of the test cell.

Electrochemical properties were measured using a HJ1001SD8 charge-discharge test device (Hokuto Denko). All the measurements were conducted at least 3 hours after temperature adjustment in an ESPEC thermostatic chamber. The symmetric cells for EIS were prepared using 2032 coin-type cells using three different m-NaFePO₄ samples. The cells were assembled as shown in Fig. S1 under a dry Ar atmosphere. The measurements were performed with a VSP potentiostat (Bio-Logic) at 298 K, 323 K, 343 K, and 363 K over a frequency range from 1 MHz to 1 mHz with a perturbation amplitude of 10 mV. In order to prepare samples for *ex-situ* XRD and X-ray absorption fine structure (XAFS) measurements, cells were disassembled in an Ar-filled glovebox and the electrodes were rinsed three times with dehydrated tetrahydrofuran (Wako Pure Chemical Industries, water content ≤ 10 ppm) in the glovebox and dried under vacuum at 333 K.

2.3 X-ray diffraction and absorption measurements

Ex-situ XRD measurements were performed using a Rigaku Smart Lab diffractometer. After electrochemical analysis, each dried electrode material was loaded into an airtight sample holder for measurement. XAFS measurement was performed using beam line BL-3 at the SR center, Ritsumeikan University. The electrode material was removed from the Al current collector, mixed with boron nitride powder, and pressed into a pellet for these measurements. Fe *K*-edge spectra were measured in transmission mode.

2.4 Particle size distributions and surface areas

Particle size distributions of the as-prepared m-NaFePO₄, the ball-milled (12 hours) m-NaFePO₄, the ball-milled (24 hours) m-NaFePO₄, and the re-calcined m-NaFePO₄ were measured using a Microtrac MT3300 II. N₂ gas adsorption measurement was carried out on a Micromeritics Tristar II. The samples were dried at 373 K under vacuum for 12 hours before adsorption. The adsorption was performed at 77 K, and BET method was analyzed by Micromeritics software.

3. Results and discussion

Figs. 1 and 2 show the XRD patterns and SEM images of the as-synthesized, ball-milled, and re-calcined m-NaFePO₄ samples (see Fig. S2 for SEM images at different magnification). The XRD pattern of ball-milled m-NaFePO₄ for 12 hours (Fig. 1b) confirms that it comprises pure maricite phase. However, some peak broadening compared to the pattern of the as-synthesized sample is observed (Fig. 1a) which is due to reduction of the crystallite size, as confirmed by the SEM images in Fig. 2b. The broad background may indicate that the ball-milled NaFePO₄ partly contains amorphous phase. However, longer ball-milling (24 hours) did not result in complete amorphization (see Fig. S3, Supplementary data).

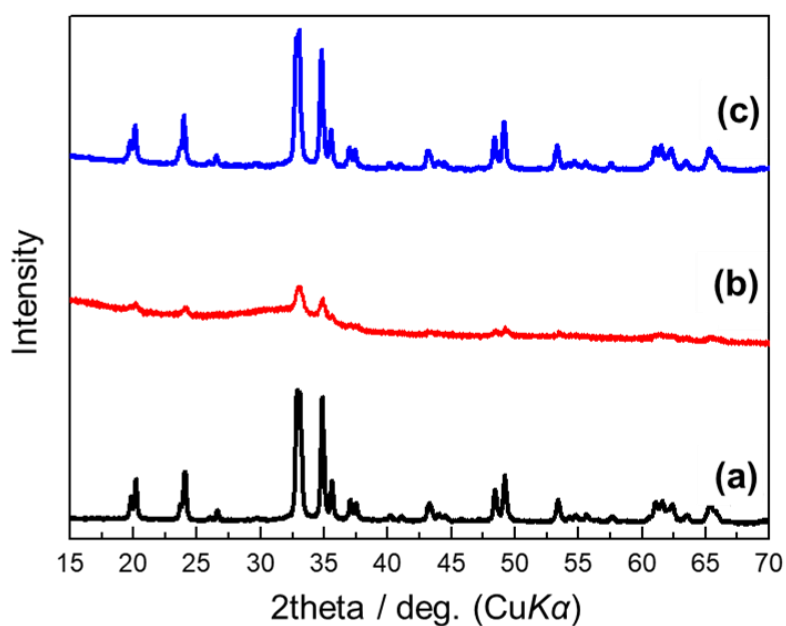


Fig. 1. X-ray diffraction patterns of (a) as-synthesized m-NaFePO₄, (b) ball-milled m-NaFePO₄, and (c) re-calcined m-NaFePO₄.

The SEM image of the as-synthesized m-NaFePO₄ (Fig. 2a) indicates that the crystallite size ranges from 100 nm to 200 nm. The size is reduced to 50–100 nm upon ball-milling treatment (Fig. 2b). The XRD pattern of the re-calcined m-NaFePO₄ indicates a recovery of crystallinity to the same level as that of the as-prepared m-NaFePO₄ (Fig. 1c). After re-calcination,

secondary particles grow more tightly than those in the original state (Fig. 2a and 2c), which is reflected in the poor charge-discharge performance of the re-calcined m-NaFePO₄, as discussed below. The precise particle size distribution of the samples was measured by the laser diffraction particle size analyzer (see Fig. S4 for particle size distribution). According to the results, the as-prepared m-NaFePO₄ mostly has the particle distribution range from 10 μm to 500 μm. After ball-milling treatment, the particle size distribution range shifted from 1 μm to 50 μm (longer ball-milling (24 hours) shows similar result). After re-calcination, particle size distribution ranges from 100 μm to 1000 μm which is significantly larger than the size of the ball-milled NaFePO₄.

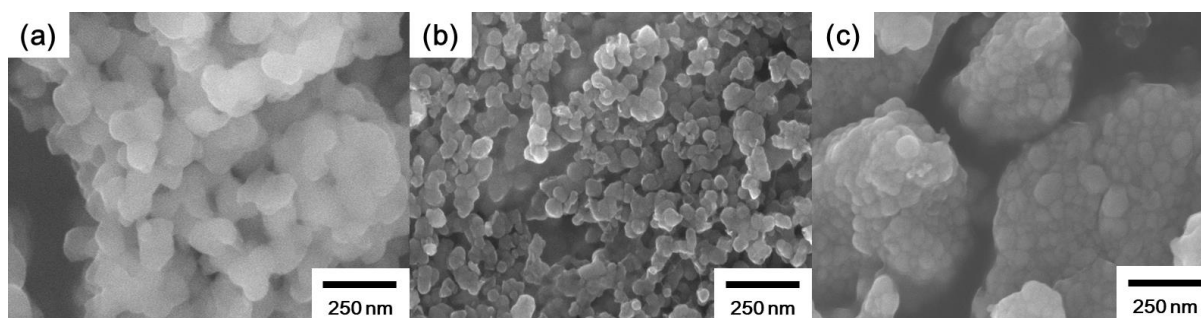


Fig. 2. FE-SEM images of (a) as-synthesized m-NaFePO₄, (b) ball-milled m-NaFePO₄, and (c) re-calcined m-NaFePO₄.

Fig. 3 shows the results of galvanostatic charge-discharge tests at a C-rate of C/10 ($1C = 155 \text{ mA g}^{-1}$) under a cutoff voltage of 2.0 V–4.0 V. The as-synthesized m-NaFePO₄ electrode exhibits the very limited reversible capacity of 10 mAh g⁻¹ at 298 K (Fig. 3a). This result is in agreement with previous recognition of that m-NaFePO₄ is an inactive positive electrode material at room temperature [28, 29, 31-34]. Although the reversible capacity of the as-synthesized m-NaFePO₄ is doubled upon elevating operating temperature to 363 K, the capacity is still only 20 mAh g⁻¹ (Fig. 3b). Thus, although the elevation of operation temperature improves Na⁺ diffusion in m-NaFePO₄, it is still very limited.

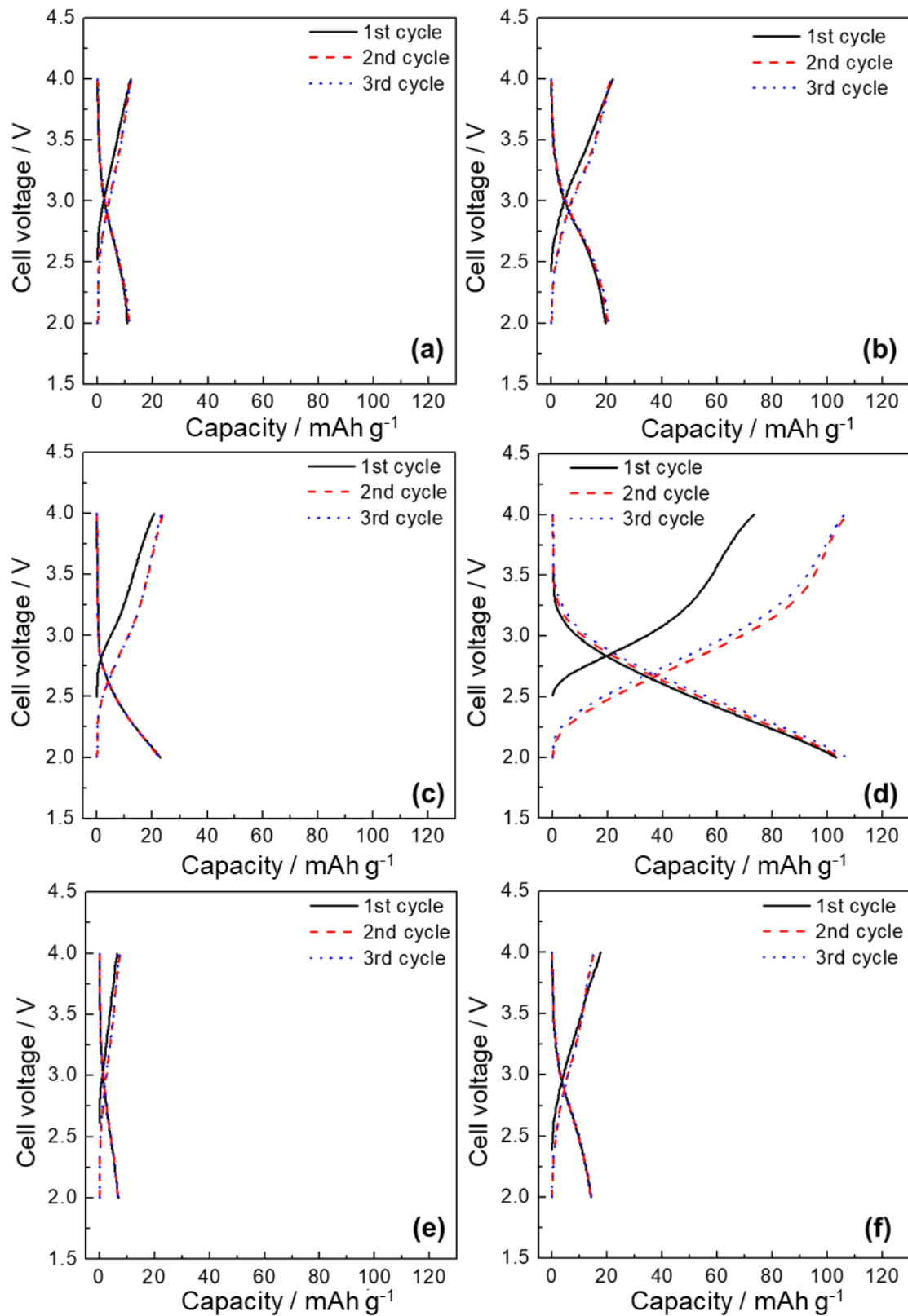


Fig. 3. Charge-discharge curves of Na/as-synthesized $m\text{-NaFePO}_4$ cells at (a) 298 K and (b) 363 K, Na/ball-milled $m\text{-NaFePO}_4$ cells at (c) 298 K and (d) 363 K, and Na/re-calcined $m\text{-NaFePO}_4$ cells at (e) 298 K and (f) 363 K. Electrolyte: $\text{Na}[\text{FSA}]\text{-}[\text{C}_2\text{C}_{11}\text{im}][\text{FSA}]$, charge-discharge rate: $C/10$, and cutoff voltage: 2.0 V–4.0 V.

The ball-milled m-NaFePO₄ exhibits a reversible capacity of 23 mAh g⁻¹ at 298 K (Fig. 3c) and 107 mAh g⁻¹ at 363 K (Fig. 3d), demonstrating that the reversible capacity of m-NaFePO₄ is dramatically improved by the combination of the elevation of operating temperature ball-milling treatment. Although the coulombic efficiency for the initial cycle is 140.7% at 363 K, suggesting partial oxidation of the before charge electrode material (see XAFS analysis below), it reaches 98.1% for the second cycle. The ball-milling treatment in acetone efficiently reduces crystallite size, which shortens Na⁺ diffusion paths in the solid state and increases surface area. Elevation of operating temperature also contributes to the improvement of Na⁺ diffusion, both in the solid state and in the electrolyte. Prolonged ball-milling (24 hours) does not significantly improve the reversible capacity of m-NaFePO₄ (104 mAh g⁻¹ at 0.1 C and 113 mAh g⁻¹ at 0.05 C, both at 363 K (Fig. S5, Supporting Information). After re-calcination of the ball-milled m-NaFePO₄, the particles strongly aggregate each other, which makes the material inactive again and limits the reversible capacity to 6.9 mAh g⁻¹ at 298 K and 14.2 mAh g⁻¹ at 363 K (Fig. 3e and 3f). Surface area of the as-prepared, ball-milled, and re-calcined m-NaFePO₄ was measured by the N₂ gas adsorption method, since it can also affect the electrochemical activity. The resulting surface areas are 4.27, 7.15, and 3.24 m² g⁻¹, respectively (see Fig. S6 and S7 for details of surface area measurements). This result indicates that the surface area of the ball-milled m-NaFePO₄ is roughly twice larger than those of the as-prepared and re-calcined m-NaFePO₄, which does not contradict the SEM observation and suggests the increase of the electrochemically active sites in the ball-milled NaFePO₄. In our previous report [34], since ball-milling with conductive carbon resulted in unstable discharge behavior, the lower cutoff voltage had to be set above 2.2 V. On the other hand, ball-milling was performed without conductive carbon, enabling stable discharge down to 2.0 V in the present work. The conductive carbon ball-milled with active materials is thought to cause the reductive decomposition of ILs at 363 K.

The discharge rate and cycling performance of the ball-milled NaFePO₄ at 363 K are shown in Figs. 4 and 5, respectively. The charging rate was 0.1 C for the first 5 cycles and was increased to 0.2 C for the rest of rate tests. The discharge current ranges from 0.1 C to 10 C. After the rate capability test, three cycles of charge-discharge were measured at 0.2 C to see recuperation of the cell.

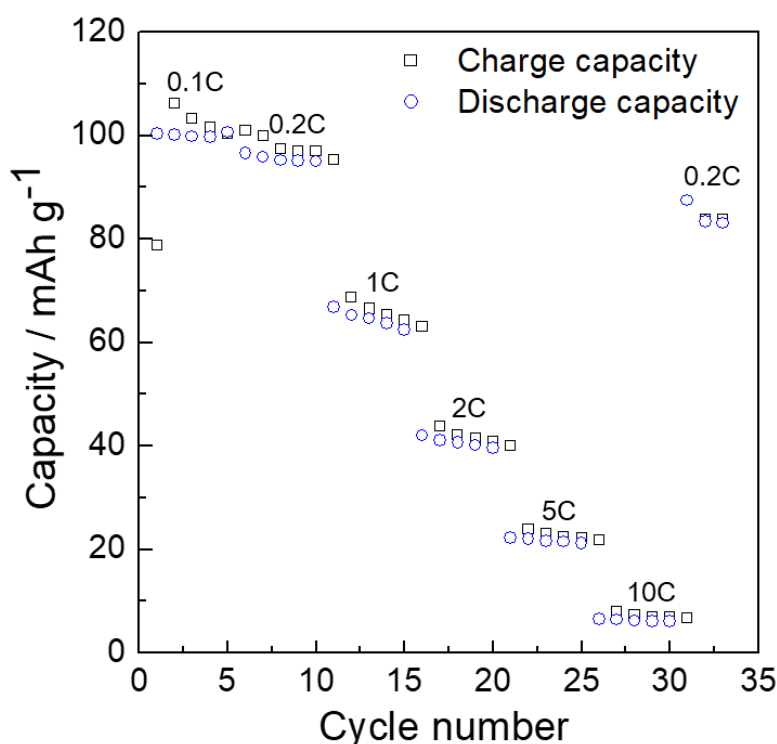


Fig. 4. Rate capability of a Na/ball-milled m-NaFePO₄ cell at 363 K. Cutoff voltage: 2.0 V–4.0 V.

The discharge capacity monotonously decreases with increasing current rate. Although the electrode reaction is constrained at high discharge rates because of the high activation energy for Na⁺ diffusion, the discharge capacities are still 95.0 mAh g⁻¹ at 0.5 C (10th cycle), 62.5 mAh g⁻¹ at 1 C (15th cycle), and 40.0 mAh g⁻¹ at 2 C (20th cycle). The capacity recuperation of the cell after rate capability test was about 87.4% in Fig. 4 (33rd cycle vs. 10th cycle). The cycling performance of the ball-milled m-NaFePO₄ was evaluated at 1 C with cutoff voltages

of 2.0 V and 4.0 V. The cell is stabilized and the coulombic efficiency reaches 99% by the 10th cycle, and the coulombic efficiency exceeds 99.8% after the 50th cycle (Fig. 5). The capacity retention of the ball-milled m-NaFePO₄ is 67.2% after the 100th cycle.

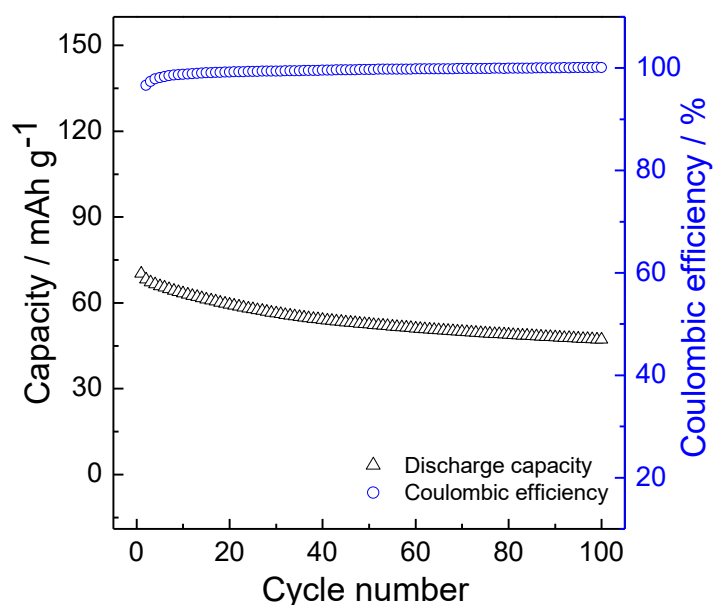


Fig. 5. Cyclability of a Na/ball-milled m-NaFePO₄ cell at 363 K. Black triangles indicate discharge capacity and blue circles indicate coulombic efficiency. Cutoff voltage: 2.0 V–4.0 V, C-rate: 1 C.

To elucidate the reasons for the capacity enhancement by ball-milling and elevation of operating temperature, EIS was conducted at 298 K, 323 K, 343 K, and 363 K with symmetric cells using the as-synthesized, ball-milled, and re-calcined m-NaFePO₄. As shown in Fig. 6, each impedance plot is composed of two semicircles. The small semicircle at the higher frequency region (~10 kHz) is related to the resistance of the composite material (R_e) and is also observed in a control cell without active materials (i.e., prepared with acetylene black and PTFE only).

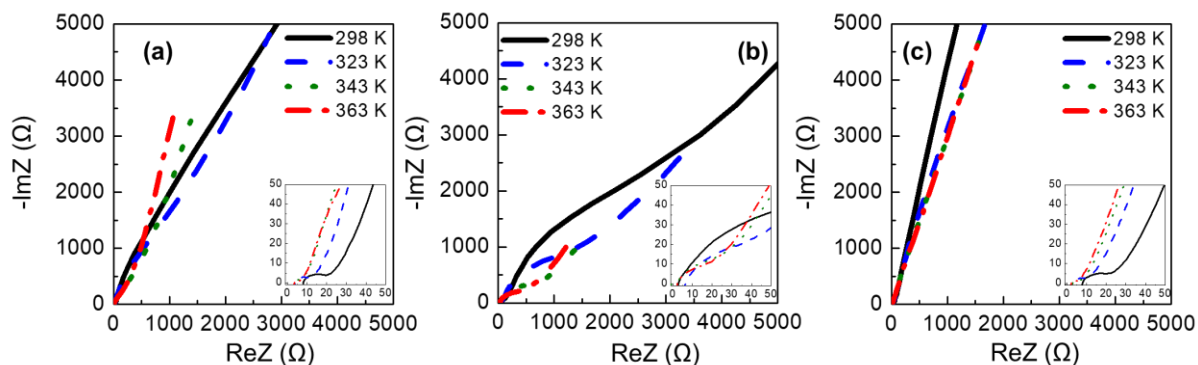


Fig. 6. Nyquist plots for (a) as-synthesized NaFePO₄/Na[FSA]-[C₂C₁im][FSA]/as-synthesized NaFePO₄, (b) ball-milled NaFePO₄/Na[FSA]-[C₂C₁im][FSA]/ball-milled NaFePO₄, and (c) re-calcined NaFePO₄/Na[FSA]-[C₂C₁im][FSA]/re-calcined NaFePO₄ symmetric cells in the temperature range between 298 K and 363 K. AC perturbation: 10 mV, frequency range: 1 MHz–10 mHz.

The other semicircle in the lower frequency region originates from the interfacial resistance on the electrode (R_{in}). The impedance spectra obtained were fitted by the equivalent circuit as shown in Fig. S8 (Supplementary data). The same circuit was uniformly used for the three different fabricated samples at four different temperatures, and the Warburg impedance was not considered in the present cases since introduction of the Warburg impedance destabilizes the fitting especially for the re-calcined sample. According to the fitted parameters in Table S1 (Supplementary data), the R_{in} value for the as-synthesized m-NaFePO₄ is considerably large at 298 K (15448 Ω), and the plot appears to be almost straight (Fig. 6a). With increasing temperature, the size of R_{in} decreases (1340 Ω), corresponding to the doubled capacity at 363 K from that at 298 K. The same trend is observed for the ball-milled and the re-calcined m-NaFePO₄ in Fig 6b and 6c. Comparing the R_{in} values for the as-synthesized and ball-milled m-NaFePO₄ reveals that R_{in} dramatically decreases with ball-milling. After re-calcination, R_{in} increases again (Fig. 6c) to a value even higher than that of the as-synthesized m-NaFePO₄, which corresponds with the lower reversible capacity of the re-calcined m-NaFePO₄ than that of the as-synthesized sample (Fig. 3a, 3b, 3e, and 3f). These observations confirm that both the

elevating temperature and ball-milling contribute to the reduction of R_{in} for the positive active material.

The *ex-situ* XRD data for the ball-milled m-NaFePO₄ indicate that the maricite phase is preserved, even after 50 cycles (Fig. S9, Supplementary Data). In addition, there seems to be some slight peak shifting to higher angles after charging followed by shifting back upon discharging (Fig. S9, Supplementary Data). However, the XRD peaks of the ball-milled m-NaFePO₄ are too weak and broad to ascertain whether the peak shifting originates from desodiation and sodiation of the maricite phase. Thus, the as-synthesized m-NaFePO₄, which exhibits higher crystallinity (Fig. 1a), was used to investigate the desodiation and sodiation mechanisms. Structural change was monitored by obtaining XRD patterns from the as-synthesized m-NaFePO₄ at different states of charge (SOCs). Four samples were prepared at 363 K for *ex-situ* XRD (Fig. S10, Supplementary Data).

After charge-discharge at a slow constant current rate (0.05 C), prolonged constant voltage charging was additionally applied until the cells exhibited a certain capacity. One of two cells was charged to 4.0 V at 0.05 C and maintained at 4.0 V for 10 hours, reaching an SOC of 30%, and the other was charged to 4.0 V at 0.05 C and maintained at 4 V for 150 hours reaching an SOC of 67%. The obtained XRD patterns are shown in Fig. 7. Slight peak

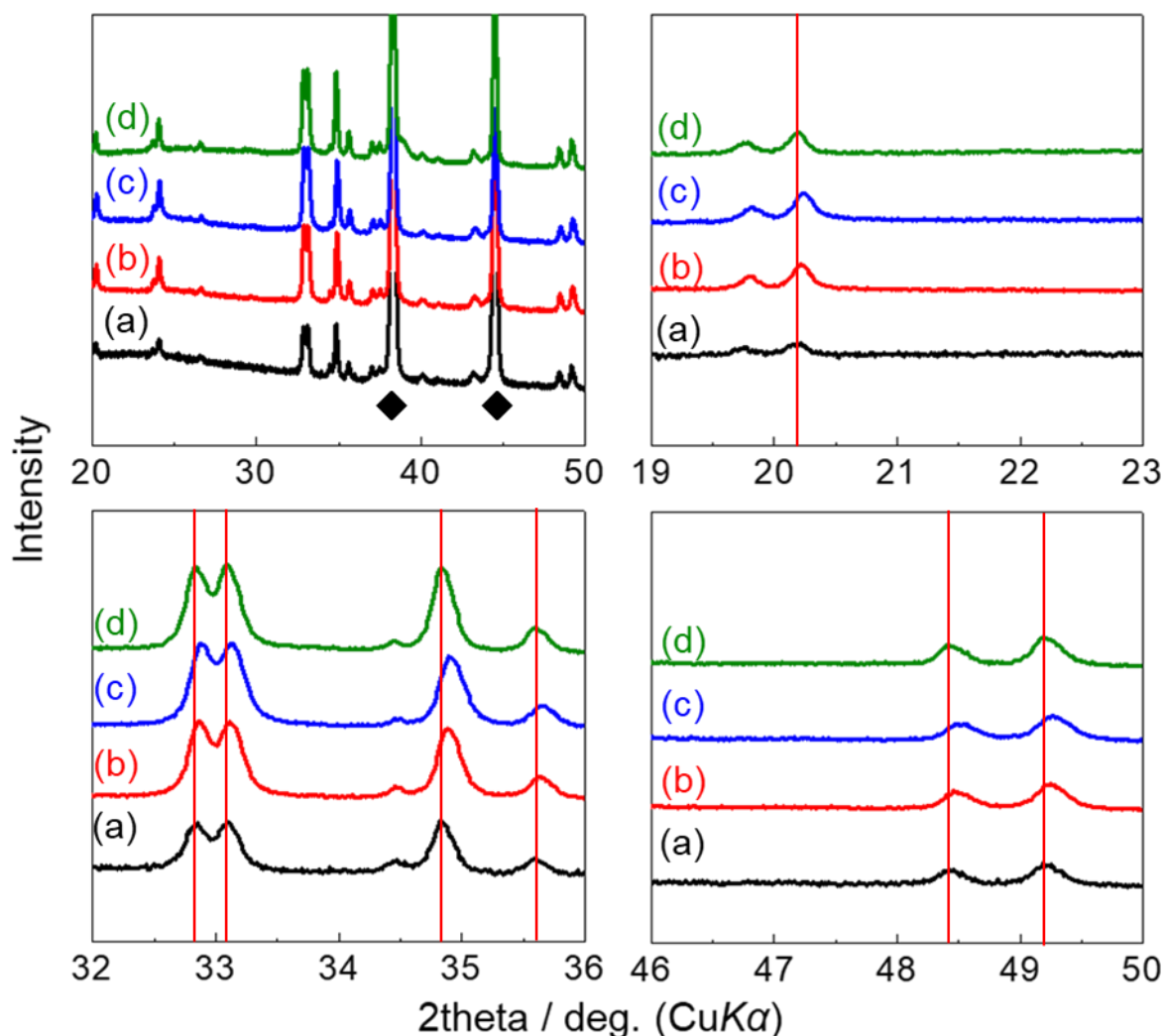


Fig. 7. *Ex-situ* XRD patterns of the as-synthesized $m\text{-NaFePO}_4$ electrode (a) before charge-discharge testing, (b) charged to 4 V at 0.05 C and maintained at constant current, constant voltage (CCCV) for 10 hours, (c) charged to 4 V at 0.05 C and maintained at CCCV for 150 hours, and (d) charged to 4 V at 0.05 C, maintained at CCCV for 150 hours, discharged to 2 V at 0.05 C, and maintained at CCCV for 150 hours. All electrochemical measurements were performed at 363 K. The \blacklozenge symbols indicate the peaks for Al. The red perpendicular lines are reference lines to clarify XRD peak shifting. The charge-discharge profile used to prepare *ex-situ* XRD samples are shown in Fig. S10.

shifting to higher angles is observed upon charging to SOC 30 % and 67% (Fig. 7b and 7c), which indicates a decrease in d-spacing owing to desodiation. The peaks return to their original positions upon discharging at 0.05 C to 2.0 V followed by constant voltage discharging at 2.0 V for 150 hours (Fig. 7d), indicating that sodiation of the maricite phase proceeds at 363 K.

Fig. S11 shows the *ex-situ* XRD pattern of the as-synthesized $m\text{-NaFePO}_4$ at 298 K, and no

peak shifting is observed. This result further demonstrates that m-NaFePO₄ is an inactive material at room temperature, which is consistent with the lack of sodiation-desodiation demonstrated in Fig. 4a. However, elevating the temperature changes m-NaFePO₄ into an active material, and ball-milling can further improve its electrochemical performance.

The X-ray absorption near edge structure (XANES) spectra of the ball-milled m-NaFePO₄ (before charge, charged, and discharged) are shown in Fig. 8. The main edge at

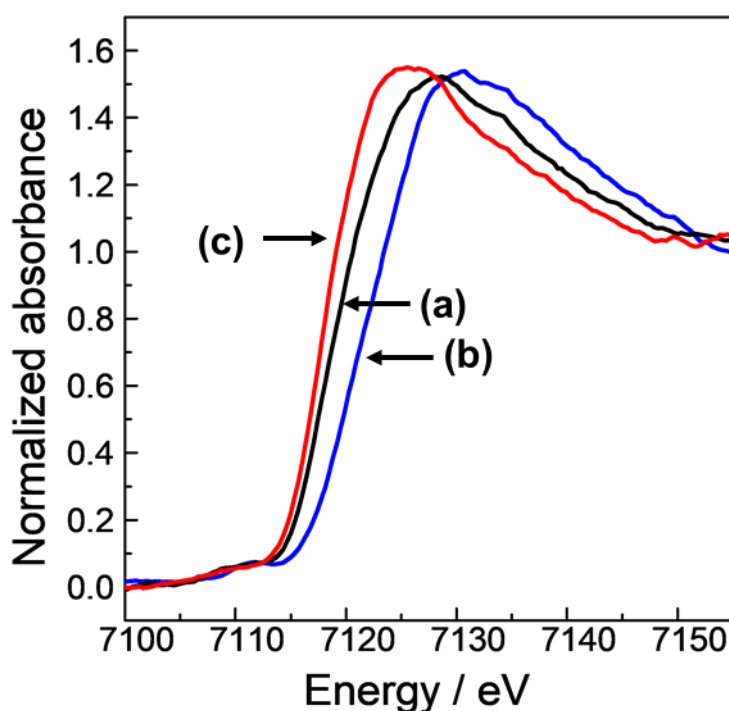


Fig. 8. Fe *K*-edge XANES spectra of ball-milled NaFePO₄ electrodes: (a) before charge, (b) charged to 4.0 V, and (c) discharged to 2.0 V.

7120 eV shifts to the higher energy upon charging, which is explained by the oxidation of iron to Fe³⁺ during desodiation. Conversely, the main edge of the sample discharged to 2.0 V is shifted to lower energy, which indicates the reduction of Fe³⁺ to Fe²⁺ by sodiation. However, the main edge for the discharged sample is located at a lower energy than that of the before

charge sample. The energy difference between the samples before charge and after the first cycle is thought to originate from partial oxidation of Fe^{2+} to Fe^{3+} in the sample before charge during the prolonged ball-milling treatment since reduction of iron to the lower oxidation state than +2 leads to the unstable conversion reaction. This is also reflected in the small charge capacity in the first cycle, as shown in Fig. 3d. In order to prove that air atmosphere oxidizes the electrodes, XANES of the ball-milled m- NaFePO_4 samples that were kept in the air for two weeks were measured. After the exposure to the air, the main edges of the ball-milled m- NaFePO_4 before charge and after first cycle were located at the same position which was higher than that of the sample before charge (Fig. S12, Supplementary Data).

4. Conclusion

We have investigated the electrochemical properties of m- NaFePO_4 as a positive electrode material for sodium secondary batteries using $\text{Na}[\text{FSA}]-[\text{C}_2\text{C}_{1\text{im}}][\text{FSA}]$ IL electrolytes. The charge-discharge profiles show that the reversible capacity of m- NaFePO_4 is increased by ball-milling and elevation of the cell operation temperature. The ball-milled m- NaFePO_4 delivers a reversible capacity of 107 mAh g^{-1} at C/10 at 363 K. The reason for the capacity increase was elucidated by the results of EIS using symmetric cells. The interfacial impedance is significantly reduced with elevating temperature and with decreasing crystallite size. Finally, peak shifting in the *ex-situ* XRD patterns has been confirmed for the first time, indicating that sodiation and desodiation proceed in the maricite phase at elevated temperature. Thus, the elevation of operation temperature using ILs, not only improves the performance of an electrode, it can transform an inactive electrode material into a promising active electrode material for intermediate-temperature operating sodium secondary batteries.

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