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3 **Charge–discharge behavior of a $\text{Na}_2\text{FeP}_2\text{O}_7$ positive electrode**
4 **in an ionic liquid electrolyte between 253 and 363 K**
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Abstract

The electrochemical properties of a $\text{Na}_2\text{FeP}_2\text{O}_7$ positive electrode were investigated in the ionic liquid sodium bis(fluorosulfonyl)amide (NaFSA)–*N*-methyl-*N*-propylpyrrolidinium bis(fluorosulfonyl)amide ($\text{C}_3\text{C}_1\text{pyrrFSA}$). A stable charge–discharge behavior was obtained over the temperature range 253–363 K. The cell offered nearly a one-electron theoretical capacity of about 90 mAh g^{−1} at 298–363 K. The rate capability showed considerable enhancement with increasing temperature, delivering 50 mAh g^{−1} at a very high rate of 4000 mA g^{−1} (*ca.* 41 C) at 363 K. Furthermore, the $\text{Na}_2\text{FeP}_2\text{O}_7$ positive electrode demonstrated excellent cyclability, exceeding 300 cycles, in terms of both capacity retention and coulombic efficiency at 298–363 K, as only negligible capacity fade (<1%) was observed. This good performance over a wide temperature range will meet the requirements of the versatile applications expected for Na secondary batteries.

Key words: Sodium secondary battery; $\text{Na}_2\text{FeP}_2\text{O}_7$; Positive electrode; Ionic liquid; Bis(fluorosulfonyl)amide

1. Introduction

Owing to significant cost advantages stemming from abundant Na resources, Na secondary batteries have recently drawn heightened interest as next-generation energy storage devices in the fields of renewable energy and sustainable vehicular transport [1–4]. To facilitate practical applications, efforts have addressed the development of electrode materials. The chemistry of intercalation compounds [5–8], as well as carbonaceous [9–11] and alloy materials [12–14], has been explored to date. In addition, for Li-ion batteries, the choice of electrolytes is generally recognized as critical for both their performance and safety [15–18]. However, electrolytes for Na batteries have received less attention and very limited choices are available [19, 20].

It is understood that batteries for automotive use must function over a broad temperature range. A reasonable, practical requirement for hybrid electric vehicles (HEVs) and plug-in hybrid electric vehicles (PHEVs) ranges from 243 to 343 K [17]. It is suggested that the technological bottleneck limiting the wide temperature operation of Li-ion batteries is the electrolyte itself [15–18, 21]. Due to recent advances, the temperature span for the operations of some Li-ion systems has been extended to between 233 and 333 K [17, 18, 22]; however, high-temperature operation still remains a significant challenge. These limitations are due to the exacerbated solvent evaporation/decomposition and solid–electrolyte interface (SEI) formation at elevated temperatures [15,16], and the thermal instability of the lithium salt LiPF_6 [23]. The safety features of commercially produced Li batteries are also insufficient for large-scale applications [15]. Since Na batteries are being actively developed as complements to the Li-based technology, electrolytes for Na batteries meeting the requirements

of wide temperature operation without compromising battery performance and safety are worth exploring.

Ionic liquids (ILs) are characterized as task-specific reaction media and provide several attractive properties when exploited as electrolytes for secondary batteries [24–26]. Their merits include (i) an inherent thermal stability and wide liquid range that enable the device to operate in extreme temperature conditions; (ii) nonflammability, which provides the battery with a level of safety that is important for large-scale application; and (iii) nonvolatility, which prevents the electrolyte from drying or generating pressure at elevated temperatures. We have investigated a series of ILs based on bis(fluorosulfonyl)amide (FSA) anions and bis(trifluoromethylsulfonyl)amide (TFSA) anions, proposed for battery applications at 340–440 K [27–30]. For instance, the NaFSA–KFSA system is suitable for battery operation around 363 K [31–33]; while the NaTFSA–CsTFSA system can be employed at 423 K [34]. In an attempt to fulfill the need for room-temperature operation, we have recently focused on NaFSA–C₃C₁pyrrFSA IL mixtures (C₃C₁pyrr = *N*-methyl-*N*-propylpyrrolidinium) because of the low melting point (264 K), high conductivity, and good thermal stability of C₃C₁pyrrFSA [35, 36]. It has been demonstrated that NaFSA–C₃C₁pyrrFSA mixtures exhibit an electrochemical window of 5.2 V and an ionic conductivity of 15.6 mS cm^{−1} at 353 K [37]. By utilizing this IL as the electrolyte, good electrochemical properties have been obtained for NaCrO₂ positive electrodes over 298–353 K and hard carbon negative electrodes at 363 K [37, 38].

In terms of cost and mass production, economic active materials built from abundant elements are highly desirable. For Li-ion battery research, the report on olivine LiFePO₄ in 1997 caused a paradigm shift for positive electrode materials

from oxides to polyanionic compounds [39]. Inspired by this pioneering study, there has been increasing interest in identifying new electrode materials for Na batteries centered around phosphate-based polyanions such as $(\text{PO}_4)^{3-}$, $(\text{P}_2\text{O}_7)^{4-}$, or $(\text{PO}_4)_2\text{P}_2\text{O}_7^{10-}$ [40–45]. The common characteristic of these compounds is their remarkable thermal stability that imparts enhanced safety at elevated temperatures. Among them, the pyrophosphates ($\text{A}_2\text{MP}_2\text{O}_7$, A = Li, Na; M = Fe, Mn, Co, etc.) constitute a class of potential electrode candidates for both Li [46] and Na batteries [41–43]. Pyrophosphates offer many positive attributes such as favorable electroactivity without the need for nanosizing or carbon-coating, high volumetric energy density, and the possibility of two-electron redox reactions. Recently, solid-solution phases of the formula $\text{Na}_{2-x}\text{Fe}_{1+x/2}\text{P}_2\text{O}_7$ ($0 < x < 0.44$) were synthesized and tested in organic electrolytes at 298 K [47, 48]. Due to the low cost of its components, we have focused on the $\text{Na}_2\text{FeP}_2\text{O}_7$ and studied its electrochemical properties in the NaFSA–KFSA electrolyte at 363 K. This positive electrode shows a good rate capability together with an impressive cycle life exceeding 1000 cycles [49]. However, the high melting point (330 K) of the NaFSA–KFSA IL limits the operation temperature range of its batteries.

In this work, we report the electrochemical properties of $\text{Na}_2\text{FeP}_2\text{O}_7$ in NaFSA–C₃C₁pyrrFSA IL over a wide temperature range, 253–363 K. The temperature dependence of the rate capability and cyclability from room temperature to 363 K is also investigated. The interfacial resistance at the electrode surface is evaluated by electrochemical impedance spectroscopy (EIS).

2. Experimental

Sodium iron pyrophosphate $\text{Na}_2\text{FeP}_2\text{O}_7$ was synthesized by a solid-state method as described in ref. [49]. X-ray diffraction (XRD) data were collected using a Rigaku SmartLab diffractometer equipped with Cu $K\alpha$ radiation (40 kV and 30 mA) and a one-dimensional high-speed detector (D/teX Ultra) in the Bragg-Brentano geometry. The structure refinement was carried out by the Rietveld method in an iterative procedure using the RIETAN-FP software package [50]. The morphology of the sample was observed by field-emission scanning electron microscopy (FE-SEM, Hitachi SU-8020). The working electrode was prepared by mixing $\text{Na}_2\text{FeP}_2\text{O}_7$, acetylene black (AB) as a conductive additive, and polytetrafluoroethylene (PTFE) as a binder in a weight ratio of 75:20:5. Metallic sodium discs (Aldrich, purity 99.95%) pressed onto aluminum current collectors were used as reference and counter electrodes. A NaFSA- $\text{C}_3\text{C}_1\text{pyrrFSA}$ (20:80 molar ratio) ionic liquid was utilized as the electrolyte. Glass microfiber filters (Whatman GF/A) were used as the separators. NaFSA (Mitsubishi Materials Electronic Chemicals Co. Ltd, purity >99%) and $\text{C}_3\text{C}_1\text{pyrrFSA}$ (Kanto Chemical Co., Inc., purity >99.9%) were dried under vacuum for 24 h at 353 and 333 K, respectively. The separator was impregnated under vacuum with the electrolyte at 333 K for 2 d prior to the test.

Charge-discharge properties were evaluated using 2032 type coin cells with a Bio-Logic VSP potentiostat in the temperature range 253 to 363 K. Temperature was controlled by an ESPEC Environmental Test Chamber. In a typical set of experiments, measurements were first performed on the cells at 363 K at a current density of 20 mA g^{-1} for 5 cycles, after which the temperature was lowered. At each temperature step, charge-discharge tests were performed after equilibration for 2 h. Since a battery may heat up due to delays in cooling, the resulting capacity

measurement may depend on the cooling conditions. In this work, the test chamber was equipped with an active flow of air to avoid this problem. Electrochemical impedance spectroscopy (EIS) measurements were carried out using a VSP potentiostat over a frequency range from 200 kHz to 5 mHz with an AC perturbation voltage of 10 mV. The EIS measurements were taken after several charge–discharge cycles for the Na/NaFSA–C₃C₁pyrrFSA/Na₂FeP₂O₇ cell and several deposition–dissolution cycles for the Na/NaFSA–C₃C₁pyrrFSA/Na cell. The theoretical capacity of Na₂FeP₂O₇ is defined as 97 mAh g^{−1}, corresponding to a one-electron transfer.

3. Results and discussion

The XRD pattern and Rietveld refinement results of the Na₂FeP₂O₇ sample are shown in Fig. 1a. This Na₂FeP₂O₇ sample exhibits an XRD pattern consistent with that reported in the literature [42] and crystallizes in the space group *P*-1, with $a = 6.4299(4)$ Å, $b = 9.4145(8)$ Å, $c = 11.0110(9)$ Å, $\alpha = 64.403(5)^\circ$, $\beta = 85.465(3)^\circ$, $\gamma = 72.818(3)^\circ$, and $V = 573.39(8)$ Å³. No obvious diffraction peaks from impurities were detected. The morphology of the sample was observed by FE-SEM. As shown in Fig. 1b, Na₂FeP₂O₇ particles are agglomerated with grain sizes ranging from 0.1 to 1 μm. It was reported that nanosizing is not necessarily required for Na₂FeP₂O₇ because it has a high ionic conductivity due to spacious diffusion pathways, unlike most of the other polyanion-type positive electrode materials [41, 43, 47].

The initial two cycling profiles of the Na₂FeP₂O₇ electrode at a current density of 10 mA g^{−1} at 298 and 363 K are shown in Fig. 2. A shift of the plateau potential from the first to the subsequent charging processes is observed for both

temperatures. Thereafter, well-overlapped charge–discharge profiles are observed, reflecting the good reversibility of the $\text{Na}_2\text{FeP}_2\text{O}_7$ electrode. Reversible capacities are 90 and 94 mAh g^{-1} at 298 and 363 K, respectively. Compared to our previous study using the NaFSA–KFSA electrolyte [49], the electrochemical performance of the $\text{Na}_2\text{FeP}_2\text{O}_7$ electrode shows no apparent difference in these two ionic liquids at 363 K. The differences in the electrochemical features observed between the first cycle and those in subsequent cycles were also reported for the same material tested in organic electrolytes at 298 K, which were ascribed to the presence of Na defects in the initial structure [43]. Yamada et al. examined the changes in the Fe oxidation state in $\text{Na}_2\text{FeP}_2\text{O}_7$ by a Mössbauer study, in which desodiated $\text{Na}_{2-x}\text{FeP}_2\text{O}_7$ samples were prepared via chemical oxidation using NO_xBF_4 [41]. In our previous study, the reversible change of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple and the variation of the Fe–O bond length upon electrochemical cycling were confirmed by X-ray absorption spectroscopy [49].

A crucial requirement for a battery intended for the powering of electric vehicles, as mentioned above, is the capability to sustain efficient operations over a wide temperature range. As shown in Fig. 3, the $\text{Na}_2\text{FeP}_2\text{O}_7$ electrode in the NaFSA– $\text{C}_3\text{C}_1\text{pyrrFSA}$ electrolyte functions well over a temperature range that spans from 363 K to as low as 253 K. At temperatures greater than 298 K, no appreciable change in the charge–discharge profiles is observed. The reversible capacities are over 90 mAh g^{-1} at a rate of 20 mA g^{-1} (*ca.* C/5) within 298–363 K, which is close to the theoretical capacity. Although larger potential polarization is observed at 253–273 K, 43% of the theoretical capacity can still be delivered at 253 K. Furthermore, its capacity is fully recovered upon returning to 363 K, indicating that cell components remain intact upon cycling in this temperature

1 range. To the best of our knowledge, no other studies have been dedicated to Na
2 battery performance at such extreme temperatures. In this context, the
3 NaFSA–C₃C₁pyrrFSA IL represents a promising electrolyte for wide-temperature
4 Na battery applications. Importantly, the upper temperature measureable in this
5 study is constrained by the Na metal electrode (m.p.: 371 K). An even higher
6 operating temperature might thereby be expected by utilizing an alternative
7 negative electrode material such as hard carbon [38].

16 The rate capability of the Na₂FeP₂O₇ electrode was evaluated over 298–363
17 K. The cells were charged to 4.0 V at a constant current of 10 mA g⁻¹ and then
18 discharged to 2.0 V at various current densities. The results are shown in Fig. S1
19 in the Supporting Information. The capacities at 20 mA g⁻¹ are 90, 94, 94, and 94
20 mAh g⁻¹ at 298, 323, 348, and 363 K, respectively. Defining these values as the
21 reference capacities (*C*₀) for each temperature, the ratios between the practical
22 capacity (*C*) and the reference value are plotted as a function of rate, as shown in
23 Fig. 4. No capacity decline is observed when the rate increases from 20 to 200 mA
24 g⁻¹ for the cell tested at 363 K, and the value of *C*/*C*₀ remains at 87% at 1000 mA
25 g⁻¹ (*ca.* 10 C). Even at a very high current rate of 4000 mA g⁻¹ (*ca.* 41 C), 53% is
26 still retained. For the cells tested at 348 and 323 K, similarly, almost no capacity
27 decline is observed at 200 mA g⁻¹. At a rate of 1000 mA g⁻¹, the *C*/*C*₀ values
28 remain at 82% and 68% at 348 and 323 K, respectively. For the cell measured at
29 298 K, full capacity is retained at 100 mA g⁻¹ but rapidly drops when the current
30 increases to 200 mA g⁻¹. For reference, the charge-discharge curves and the cycle
31 dependence of discharge capacity at high rates of 200, 500 and 1000 mA g⁻¹ at
32 363 K are shown Fig. S2. The greatly enhanced rate performance at temperatures
33 higher than 323 K is attributed to the good thermal stability of

NaFSA–C₃C₁pyrrFSA IL, enabling the full utilization of thermal benefits. Although the ionic conductivities of conventional electrolytes also increase as temperatures rise, the evaporation and degradation problems of organic solvents can offset the thermal effects, or even result in deteriorated electrochemical performance [25].

It should be noted that the temperature performance of a battery system is complicated and may not depend on the behavior of a single component. For example, the kinetic limitation at low temperatures may result from solution conductivity, interfacial impedance, or activation-controlled solid-state diffusion [17]. To clarify the rate-limiting factor in the present case, electrochemical impedance measurements were performed on the Na/Na₂FeP₂O₇ half cell and the Na/Na symmetric cell using the same electrolyte over 298–363 K. Typical Nyquist plots of the former cell are given in Fig. 5a. Each plot consists of a semicircle and an inclined line on a complex plane. The high frequency limits refer to the bulk electrolyte resistance (R_b). The semicircle at the middle frequency region is derived from the charge-transfer process (R_{ct}) at the electrode/electrolyte interface. The straight line in the low frequency region is attributed to Warburg diffusion associated with finite sodium motion [51]. As shown in Fig. 5a, the charge-transfer resistance exhibits a significant sensitivity to temperature. As might have been expected, both R_b and R_{ct} drastically decrease as the temperature is raised, confirming that the transfer of ions in the electrolyte and electrons at the electrode surface is facilitated at elevated temperatures. These findings are consistent with previous studies on Li-ion cells [52, 53]. Nyquist plots of the Na/Na symmetric cell are shown in Fig. 5b. The most significant difference from the Na/Na₂FeP₂O₇ half cell occurs in the mid-frequency range, namely, the

interfacial resistance. A significantly larger interfacial impedance is acquired at 298 and 323 K. Thus, it is concluded that the major component of the R_{ct} observed for the Na/Na₂FeP₂O₇ cell originates from the Na counter electrode, especially at lower temperatures. For Li-ion batteries, the formation of an SEI on the lithium metal surface is well accepted in organic electrolytes as well as ionic liquids [54]. It is unclear whether the highly resistive component observed in the present case is associated with the SEI or not. Further investigation is now underway.

After the initial electrochemical characterizations, the long-term cycling performance of the Na₂FeP₂O₇ electrode was examined at 100 mA g⁻¹ (*ca.* 1 C) at 298, 323, and 363 K. As shown in Fig. 6, a remarkably stable charge–discharge behavior extending 300 cycles with negligible capacity decay is observed for all temperatures. The average coulombic efficiencies over the whole test are 99.3, 99.9, and 99.6% at 298, 323, and 363 K, respectively. These values further approach 100% at the end of the test, indicating no undesirable side reactions occur, even at elevated temperatures. In a recent report, pristine Na₂FeP₂O₇ and its charged states (NaFeP₂O₇) were characterized by in situ thermal XRD and thermogravimetric (TG) analyses [42, 43]. Both studies showed no indication of decomposition, phase transformation, or oxygen evolution up to about 833 K. The excellent thermal stability far exceeds those of layered oxides, which can be attributed to the robust pyrophosphate (P₂O₇)⁴⁻ building blocks. Furthermore, the full extraction of Na from Na₂FeP₂O₇ is accompanied by approximately 3% volume shrinkage [42]. This volume change is smaller than that of several positive electrodes such as LiFePO₄ (6.8%) [55], Na₂FePO₄F (4%) [56], and Na₄Fe₃(PO₄)₂(P₂O₇) (4%) [44]; thus, an intercalation/deintercalation process with lower strain is expected. These appealing properties can be fully utilized in

conjunction with a chemically stable IL electrolyte. The good thermal stability and low melting point of NaFSA–C₃C₁pyrrFSA ionic liquid enable the cell to operate at extreme temperatures. The satisfactory electrochemical properties over a wide temperature range demonstrated here are thus originated from both the excellent electrode active material of Na₂FeP₂O₇ and the compatible electrolyte of NaFSA–C₃C₁pyrrFSA. To our knowledge, the Na₂FeP₂O₇ electrode tested in the NaFSA–C₃C₁pyrrFSA (and NaFSA–KFSA) IL electrolyte shows the best cycling performance in terms of capacity retention among the reported phosphate-based positive electrode materials for Na secondary batteries, as shown in our previous and present work [49]. Since ILs are practically nonflammable, the change from the inorganic IL (NaFSA–KFSA) electrolyte to the organic one (NaFSA–C₃C₁pyrrFSA) does not cause significant safety issues in the present temperature range.

4. Conclusions

To enhance safety and extend their operating temperature range, Na batteries utilizing the Na₂FeP₂O₇ positive electrode and the NaFSA–C₃C₁pyrrFSA ionic liquid electrolyte were proposed. Fairly stable capacity was observed over 253–363 K: a nearly one-electron capacity was delivered for temperatures greater than 298 K, and 43% of their capacity was retained at 253 K. Furthermore, such a cell exhibited remarkable cyclability and flexibility when operating conditions were switched from low to high rates at 298–363 K. The results obtained in this work demonstrate that combining the economically viable positive electrode Na₂FeP₂O₇ with the nonflammable NaFSA–C₃C₁pyrrFSA electrolyte could be a

promising platform for the broad spectrum of applications expected for Na secondary batteries.

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Fig. 1. (a) X-ray diffraction with Rietveld refinement of $\text{Na}_2\text{FeP}_2\text{O}_7$ ($R_{\text{wp}} = 0.93\%$, $R_{\text{p}} = 0.73\%$, $R_{\text{F}}^2 = 1.67\%$), with the experimental data (red dots), calculated pattern (black line), Bragg positions (green bars), and difference curve (blue line). (b) SEM image of as-synthesized $\text{Na}_2\text{FeP}_2\text{O}_7$.

Fig. 2. Galvanostatic charge–discharge curves of the initial two cycles for the Na/NaFSA–C₃C₁pyrrFSA/Na₂FeP₂O₇ cell at a current density of 10 mA g⁻¹ in the voltage range 2.0–4.0 V at (a) 298 K and (b) 363 K.

Fig. 3. (a) Galvanostatic charge-discharge curves for the Na/NaFSA-C₃C₁pyrrFSA/Na₂FeP₂O₇ cell at 20 mA g⁻¹ over 253–363 K. (b) Discharge capacities of the Na₂FeP₂O₇ positive electrode as a function of operating temperature and cycle number. Cut-off voltage: 2.0–4.0 V.

Fig. 4. The ratios between the discharge capacity (C) and the reference capacity (C_0) as a function of rate at 298–363 K. The charging was conducted at 10 mA g^{-1} . The reference capacities were 90, 94, 94, and 94 mAh g⁻¹ at 298, 323, 348, and 363 K, respectively. Cut-off voltage: 2.0–4.0 V.

Fig. 5. Nyquist plots for (a) the Na/NaFSA- C_3C_1 pyrrFSA/ $Na_2FeP_2O_7$ cell and (b) the Na/NaFSA- C_3C_1 pyrrFSA/Na symmetric cell at 298–363 K. The AC perturbation was 10 mV, and the frequency range was from 200 kHz to 5 mHz.

Fig. 6. Cycling performance and coulombic efficiency (C.E.) of the $\text{Na}_2\text{FeP}_2\text{O}_7$ positive electrode at 298, 323, and 363 K. Cut-off voltage: 2.0–4.0 V. Current density: 100 mA g^{-1} .