TITLE:
Full Utilization of Superior Charge-Discharge Characteristics of Na1.56Fe1.22P2O7 Positive Electrode by Using Ionic Liquid Electrolyte

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Recently, it has been recognized that Na secondary batteries can offer a performance comparable to that of Li batteries, at a more reasonable cost. Developing commercial Na secondary batteries that are economically viable, safe, and have a long life will definitely require the development of new electrode materials and electrolytes. Layered oxides in the form of Na₂MO₃ (where M is a transition metal) have been extensively tested as Na host materials, and some of the oxides have exhibited considerably high Na storage capacities by suitably tailoring the stoichiometric ratio of Na to M. However, most of these materials undergo complicated phase transitions during cycling and may result in limited cyclability, which is an obstacle for practical applications.

In order to overcome such limitations in electrode performance, phosphate-based framework materials have been proposed as positive electrode materials in Na secondary batteries. The robust framework undergoes a topotactic Na insertion/extraction reaction with a small volume change upon electrochemical cycling. Among them, pyrophosphates (Na₃MP₂O₇, where M = Fe, Mn, or Co) have attracted interest owing to their favorable electrochemical activity and good thermal stability. However, they are less appealing in terms of theoretical capacity (ca. 97 mAh g⁻¹, 1 Na per formula unit) as compared to layered oxides (ca. 120 mAh g⁻¹, 0.5 Na per formula unit), owing to the presence of the P₂O₇ units that induce a weight penalty.

Recently, Naₙ₋ₓFeₓ₁₋ₓP₂O₇ compounds (where, 0 < x < 0.44) were synthesized and evaluated as positive electrodes for Na secondary batteries using organic electrolytes at room temperature. The substitution of Na with Fe would directly influence the active Na sites and the coordination environment of the redox center, resulting in distinct electrochemical characteristics. Notably, the theoretical capacity for the extreme stoichiometric composition, Na₈.₄Fe₇P₂O₁₇ (x = 0.44), is estimated to be increased to the highest value of 118 mAh g⁻¹, assuming that 1.22 Na is reversibly intercalated/deintercalated via the redox reaction of 1.22 Fe^{II}/Fe^{III}. A comparison between the end members of Na₂FeP₂O₇ and Na₈.₄Fe₇P₂O₁₇ (i.e., x = 0 and 0.44) is therefore of importance, as it would provide an avenue for the electrochemical properties of the pyrophosphates to be maximized through composition design. However, the full theoretical capacity of Na₈.₄Fe₇P₂O₁₇ has not been realized so far. The capacity values typically reported in the literature are ca. 85 mAh g⁻¹ and generally include only results of limited cycles.

Ionic liquids (ILs) have been proposed as replacements for conventional electrolytes because of its advantages such as nonflammability, good thermal and electrochemical stability compared to organic solvents. Recent advances in the field of Li secondary batteries have suggested that ILs represent a viable alternative to overcome the disappointing compromises between performance and safety features with organic electrolytes. However, the adoption of IL electrolytes for Na batteries has received less attention so far.

In our previous studies, the charge–discharge behavior of Na₂FeP₂O₇ electrodes in Na[FSO₃][C₃C₁pyrr][FSO₃] IL electrolytes was investigated over a wide temperature range of 253–363 K. The results revealed a considerable enhancement in rate capability with increasing temperature along with an outstanding cyclability, implying that there are significant opportunities to improve the performance of Na secondary batteries by utilizing an IL electrolyte. Another advantage of using IL electrolytes is that the operation of the batteries at high temperatures is favorable to fully draw the potential capacity of the electrode material.

In the present work, the electrochemical properties of Na₈.₄Fe₇P₂O₁₇ in the Na[FSO₃][C₃C₁pyrr][FSO₃] IL electrolyte system at 298–363 K are investigated and compared to those of Na₂FeP₂O₇ under the same conditions, in order to understand the effect of altering the stoichiometric ratio of Na to Fe, in a pyrophosphate-type positive electrode. The dependence of the rate capability and the cyclability of these electrodes on temperature are also examined.

**Experimental**

Naₙ₋ₓFeₓ₁₋ₓP₂O₇ with extreme compositions, (namely, x = 0 and 0.44) were synthesized using a solid-state method. Stoichiometric amounts of Na₂CO₃, Fe₂O₃, 2H₂O and (NH₄)₃HPO₄ were mixed thoroughly by ballmilling for 8 h. The mixture was then heated at 573 K for 6 h and then heated at 873 K for 12 h under Ar flow. X-ray diffraction (XRD) data were collected using a Rigaku SmartLab diffractometer equipped with a one-dimensional high-speed Si strip detector (D/teX Ultra), utilizing Cu Kα radiation (40 kV and 30 mA). The structural refinement was carried out by the Rietveld method in an iterative procedure using the RIETAN-FP software package. The obtained structure was evaluated based on R_w and R_p defined as follows:

\[
R_w = \left( \frac{\sum w_i |y_i - y_{i, \text{calc}}|}{\sum w_i |y_i|} \right)^{1/2}
\]

\[
R_p = \frac{\sum |y_i - y_{i, \text{calc}}|}{\sum y_i}
\]
using 2032 type coin cells with a Bio-Logic VSP potentiostat. The separator was impregnated under vacuum with the electrolyte at 333 K for 48 h prior to the test. The theoretical capacity of Na2FeP2O7 was assessed using 2032 type coin cells with a Bio-Logic VSP potentiostat. The positive electrode was prepared by mixing Na2−xFe1+2/3P2O7, acetylene black and polytetrafluoroethylene in a weight ratio of 75:20:5. The mass loading and thickness of the active material were around 2.0 mg cm−2 and 50 μm, respectively. A metallic sodium disc pressed onto an aluminum current collector was used as the negative electrode. A Na[FSA]–[C3C1pyrr][FSA] (in a 20:80 molar ratio) ionic liquid was utilized as the electrolyte. Na[FSA] and [C3C1pyrr][FSA] were dried under vacuum for 24 h at 353 K and 333 K, respectively. The separator was impregnated under vacuum with the electrolyte at 333 K for 48 h prior to the test. The theoretical capacity of Na2FeP2O7 and Na1.56Fe1.22P2O7 were defined as 97 mAh g−1 and 118 mAh g−1, respectively, corresponding to a one-electron transfer per redox-active metal.

Results and Discussion

Although Na1.56Fe1.22P2O7 was first synthesized and characterized using single crystal X-ray diffraction by Angenault et al. in 1995, no electrochemical data was reported in that work. The XRD pattern and the Rietveld refinement results of the as-synthesized Na1.56Fe1.22P2O7 are shown in Fig. 1. No obvious diffraction peaks from impurities are detected. The Na1.56Fe1.22P2O7 sample crystallizes into the space group P1, with a = 6.4215(3) Å, b = 9.390(4) Å, c = 10.978(4) Å, α = 64.546(10)°, β = 86.091(12)°, γ = 73.013(13)°. The lattice parameters of Na1.56Fe1.22P2O7 are in good agreement with previously reported microcrystalline and single crystal data. Unit cell parameters are presented in Table S1 (Supplementary material).

A compositional analysis of the as-synthesized Na1.56Fe1.22P2O7 was conducted using ICP-AES and AAS. The atomic ratio of Na/Fe/P is determined to be 1.47:1.22:2. The consistency between the analytical result obtained above and the expected compound verifies the feasibility of solid-state method adopted. Na1.56Fe1.22P2O7 exhibits a broad size distribution ranging from hundreds of nanometers to a few micrometers (Fig. 1, inset) and no distinct differences in the morphology are found when compared with Na5Fe2P2O7. The Rietveld refinement results for Na5Fe2P2O7, synthesized by the same solid-state method have been reported in our previous study.

A comparative study of the crystal structures of Na1.56Fe1.22P2O7 and Na5Fe2P2O7 reveals the similarities and the differences between them. According to the structural models proposed for Na1.56Fe1.22P2O7 and Na5Fe2P2O7, both the compounds possess a similar framework in which the FeO6 octahedra interconnect with the P2O7 units resulting in three-dimensional and large interstitial spaces through which Na ions can diffuse (Fig. 2). On the other hand, compared to Na5Fe2P2O7, the occupancy of Na6 sites is reduced to 0 and the occupancy of Na4 sites is increased from 0.333 to 0.60% in the case of Na1.56Fe1.22P2O7. The Na5 sites are partially occupied by Fe with an occupancy of 0.118 in addition to one Na site in the large tunnel along the a axis (Na1) being partly replaced by Fe in Na5Fe2P2O7, whereas no site mixing is found in Na5Fe2P2O7. The presence of co-occupied sites results in a much larger mean value for the cation–oxygen bond length compared to that of the other FeO6 octahedra in Na5Fe2P2O7.

The galvanostatic charge–discharge curves of the Na5Fe2P2O7 and Na5Fe2P2O7 electrodes at a current density of 10 mA g−1 at 298 and 363 K are compared in Fig. 3. Na5Fe2P2O7 delivers reversible capacities of 90 mAh g−1 and 94 mAh g−1 in the voltage range of 2.0–4.0 V at 298 K and 363 K, respectively. In addition, an apparent shift in the plateau potential from the first charging to the subsequent charging cycles is observed at both temperatures. This phenomenon has been ascribed to a Na deficiency in the pristine state caused by oxidative contamination on the particle surface upon ambient exposure. In comparison with Na5Fe2P2O7, Na1.56Fe1.22P2O7 clearly shows better electrochemical characteristics under the same
the operating voltage is influenced by the local environment of the altered as the ratio of Na to Fe is varied. The results also indicate that files are altered. Besides, the distinct voltage profiles imply that the sites and their ordering lead to multistep voltage-capacity profiles.\(^\text{11}\)

Experimental conditions. At 298 K, the Na\(_{1.56}\)Fe\(_{1.22}\)P\(_2\)O\(_7\) electrode exhibits a smooth charge–discharge profile, a smaller voltage shift during the first charging cycle, and a reversible capacity of 90 mAh g\(^{-1}\). For Na\(_{2}\)FeP\(_2\)O\(_7\), a new plateau appears at 3.8 V (Fig. 3b). For Na\(_{3.42}\)Fe\(_{2.44}\)(P\(_2\)O\(_7\))\(_{2.05}\). They concluded that the sample was comprised of a Na-rich Na\(_{5.66}\)Fe\(_{1.17}\)P\(_2\)O\(_7\) phase and an inactive NaFePO\(_4\) phase.\(^\text{18}\) For the composites, a reversible capacity of about 85 mAh g\(^{-1}\) was obtained in NaClO\(_4\)/EC:DEC at C/20 at 303 K. The room temperature capacity (ca. 90 mAh g\(^{-1}\)) obtained in the present IL electrolyte is slightly higher than those obtained in the organic electrolytes under similar conditions, which could be explained by the successful synthesis of Na\(_{5.66}\)Fe\(_{1.17}\)P\(_2\)O\(_7\). More importantly, the present result confirms that a moderately elevated operating temperature can effectively enhance the utilization ratio of the active materials, resulting in a higher capacity.

Honma et al. has reported that while Na\(_{2-x}\)Fe\(_{1+x/2}\)P\(_2\)O\(_7\)/C composites with different stoichiometries (i.e., x values of 0, 0.22, and 0.44) can be synthesized by glass-ceramic routes, their reversible discharge capacities remain constant at ca. 86 mAh g\(^{-1}\) in NaPF\(_6\)/EC:DEC electrolytes at 298 K.\(^\text{17}\) Ha et al. has performed an off-stoichiometric synthesis with a nominal composition of Na\(_{2-x}\)Fe\(_{1+x/2}\)P\(_2\)O\(_7\). They concluded that the sample was comprised of a Na-rich Na\(_{5.66}\)Fe\(_{1.17}\)P\(_2\)O\(_7\) phase and an inactive NaFePO\(_4\) phase.\(^\text{18}\) For the composites, a reversible capacity of about 85 mAh g\(^{-1}\) was obtained in NaClO\(_4\)/EC:DEC at C/20 at 303 K. The room temperature capacity (ca. 90 mAh g\(^{-1}\)) obtained in the present IL electrolyte is slightly higher than those obtained in the organic electrolytes under similar conditions, which could be explained by the successful synthesis of Na\(_{5.66}\)Fe\(_{1.17}\)P\(_2\)O\(_7\). More importantly, the present result confirms that a moderately elevated operating temperature can effectively enhance the utilization ratio of the active materials, resulting in a higher capacity.

Fig. S1 (Supplementary material) shows ex-situ XRD patterns of as-synthesized, fully charged and fully discharged Na\(_{5.66}\)Fe\(_{1.17}\)P\(_2\)O\(_7\). For the fully charged sample, there are several splits and shifts of diffraction peaks when compared with the as-synthesized Na\(_{5.66}\)Fe\(_{1.17}\)P\(_2\)O\(_7\). However, the overall framework of crystal structure seems to be preserved. For the fully discharged sample, the diffraction pattern coincides with that for as-synthesized Na\(_{5.66}\)Fe\(_{1.17}\)P\(_2\)O\(_7\), confirming that the reaction is reversible. The diffraction pattern of charged sample is in agreement with the previous report by Ha et al. in which they prepared a series of Na\(_{5.66}\)Fe\(_{1.17}\)P\(_2\)O\(_7\) via chemical sodiation and desodiation.\(^\text{18}\) They concluded that there were no apparent evidences for the formation of a new phase in the fully charged state, indicating that the Na\(_{5.66}\)Fe\(_{1.17}\)P\(_2\)O\(_7\) electrode undergoes a single-phase reaction.\(^\text{18}\)

The rate capability of the Na\(_{5.66}\)Fe\(_{1.17}\)P\(_2\)O\(_7\) electrode was evaluated over a temperature range of 298–363 K. The cells were charged to 4.0 V at a constant current density of C/10 (11.8 mA g\(^{-1}\)), and subsequently discharged to 2.0 V at various rates. The discharge capacity of the Na\(_{2-x}\)Fe\(_{1+x/2}\)P\(_2\)O\(_7\) electrode plotted as a function of the discharge rates and temperatures is shown in Fig. 4. The capacities decrease with increasing current densities for all the cells because the reactions are kinetically constrained at high rates. Nevertheless, the capacities remain at 77%, 89%, and 90% for the cells tested at 323, 348, and 363 K, respectively when the discharge rate is increased from C/5 to 10 C. The reversible capacities at 363 K are 106, 97, 88, 78, and 64 mAh g\(^{-1}\) at discharge rates of 2 C, 10 C, 20 C, 30 C, and 40 C, respectively. It may be noted that carbon coating and/or nanosizing are not necessary to obtain such electrode performance. Clark et al.

**Figure 3.** Galvanostatic charge–discharge curves for the Na/Naf[FSA]–[C\(_3\)C\(_6\)pyrr][FSA]/Na\(_{2-x}\)Fe\(_{1+x/2}\)P\(_2\)O\(_7\) (x = 0 and 0.44) cells 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. Na\(_{1.56}\)Fe\(_{1.22}\)P\(_2\)O\(_7\): Red line. Na\(_2\)FeP\(_2\)O\(_7\): black line.

**Figure 4.** The rate capability of the Na\(_{2-x}\)Fe\(_{1+x/2}\)P\(_2\)O\(_7\) (x = 0 and 0.44) positive electrodes over the 298–363 K temperature range. The cell was charged at C/10. Cut-off voltage: 2.0–4.0 V. Na\(_{1.56}\)Fe\(_{1.22}\)P\(_2\)O\(_7\): Red line. Na\(_2\)FeP\(_2\)O\(_7\): black line.
The outstanding cyclability is attributed to the present result is reminiscent of the well-known zero-strain Li$_4$Ti$_5$O$_12$.

Na$_2$FeP$_2$O$_7$ (2.6%).$^{11}$ Their results revealed that Na$_2$FeP$_2$O$_7$ provides quasi-three-dimensional (3D) Na ion diffusion paths with acceptably low activation energies in all crystallographic directions. Ion blocking by Na/Fe antisite defects is therefore much less likely to impede its transport properties when compared to other materials such as NaFePO$_4$ and Na$_2$FePO$_4$F in which only 1D and 2D conduction pathways are allowed, respectively.$^{34}$ Consequently, high Na$^+$ mobility is expected for pyrophosphates including Na$_{1.56}$Fe$_{1.22}$P$_2$O$_7$. In our previous study, it has been demonstrated that the charge transfer between the ions in the electrolyte and the electrons at the electrode surface is facilitated at elevated temperatures.$^{24}$ Overall, an enhanced high rate performance is achieved for Na$_{1.56}$Fe$_{1.22}$P$_2$O$_7$ compared to Na$_2$FeP$_2$O$_7$. The charge–discharge curves for the rate capability test are shown in Fig. S2 (Supplementary material).

The long term cycling performance of the Na$_{1.56}$Fe$_{1.22}$P$_2$O$_7$ electrode at a current density of 1 C (118 mA g$^{-1}$) at 298, 323, and 363 K is shown in Fig. 5. A remarkably stable cycling behavior with negligible capacity decay (<1.5%) over 300 cycles is observed in all the cases. The average coulombic efficiencies over the course of the entire test are 99.9%, 99.8%, and 99.7% at 298 K, 323 K, and 363 K, respectively, indicating the absence of undesirable side reactions. When cycled at a high rate of 20 C (2360 mA g$^{-1}$) at 363 K, 71% of the initial capacity is retained after 300 cycles and the coulombic efficiency averages at 99.9%, 99.8%, and 99.7% at 298 K, 323 K, and 363 K, respectively, according to its low sensitivity to Na insertion/extraction as well as the use of a chemically stable IL electrolyte (Na$^+$/[C$_3$C$_1$pyrr][FSA]). The positive electrode for Li secondary batteries, which highlights the importance of using electrode materials exhibiting small volume change in order to achieve high cycle stability.$^{34}$ Although the theoretical capacity of Na$_{1.56}$Fe$_{1.22}$P$_2$O$_7$ is lower than the recently reported layered oxides,$^{7,8}$ the rate capability and cyclability achieved here recommend this material as a strong candidate as positive electrode for Na secondary batteries.

**Conclusions**

The electrochemical properties of the end members of Na$_{2-x}$Fe$_{1+x/2}$P$_2$O$_7$ (Na$_{2-x}$FeP$_2$O$_7$ and Na$_{1.56}$Fe$_{1.22}$P$_2$O$_7$ where $x = 0$ and 0.44, respectively) have been investigated and compared in Na$^+$/[C$_3$C$_1$pyrr][FSA] IL electrolytes over the temperature range of 298–363 K. By altering the Na/Fe stoichiometric ratio, Na$_{1.56}$Fe$_{1.22}$P$_2$O$_7$ exhibits a reversible capacity of 108 mAh g$^{-1}$ at 363 K, which is 15% improved than that of Na$_2$FeP$_2$O$_7$ at the same condition. In addition, it also exhibits an enhanced high rate performance and a remarkably stable cyclability. These superior charge–discharge characteristics have been demonstrated for the first time by adopting a thermally and chemically stable IL electrolyte. The positive electrode material is composed of abundantly available elements including Fe, P, and Na, and can be prepared by a scalable solid-state method, which encourages further development of polyvanionic compounds through composition design.

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