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<th>Full Utilization of Superior Charge-Discharge Characteristics of Na1.56Fe1.22P2O7 Positive Electrode by Using Ionic Liquid Electrolyte</th>
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<tr>
<td>Citation</td>
<td>Journal of the Electrochemical Society (2014), 162(1): A176-A180</td>
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<tr>
<td>Issue Date</td>
<td>2014-11-25</td>
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<td>URL</td>
<td><a href="http://hdl.handle.net/2433/196870">http://hdl.handle.net/2433/196870</a></td>
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<td>Type</td>
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Kyoto University
Na_{1.56}Fe_{1.22}P_2O_7 was synthesized via a conventional solid-state method and evaluated as a positive electrode for Na secondary batteries using Na[FSA]·[C_3C_1pyrr][FSA] (C_3C_1pyrr = N-methyl-N-propylpyrrolidinium and FSA = bis(fluorosulfonyl)amide) ionic liquids (IL) as electrolytes, over the temperature range of 298–363 K. A reversible capacity as high as 108 mAh g\(^{-1}\) has been achieved for the first time with a thermally stable IL at 363 K. This value is close to the theoretically calculated capacity of 118 mAh g\(^{-1}\) and is significantly higher than the previously reported values of ca. 85 mAh g\(^{-1}\) in organic electrolytes at 298 K. The capacity of 108 mAh g\(^{-1}\) also exceeds the value obtained for NaFeP_2O_7 electrodes (94 mAh g\(^{-1}\)) under the same experimental conditions. Moreover, excellent rate capability and superior cyclability exceeding 3000 cycles have been achieved by using the IL electrolyte over a wide temperature range of 298–363 K.

In our previous studies, the charge–discharge behavior of Na_{2-x}Fe_{1/2}P_2O_7 in Na[FSA]·[C_3C_1pyrr][FSA] (where FSA = bis(fluorosulfonyl)amide and C_3C_1pyrr = N-methyl-N-propylpyrrolidinium) IL electrolyte 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 Na_{1.56}Fe_{1.22}P_2O_7 in the Na[FSA]·[C_3C_1pyrr][FSA] IL electrolyte system at 298–363 K are investigated and compared to those of Na_{2-x}Fe_{1/2}P_2O_7 under the same conditions, in order to understand the effect of altering the stoichiometric ratio of Na to Fe, in a polyanion-type positive electrode. The dependence of the rate capability and the cyclability of these electrodes on temperature are also examined.

Experimental

Na_{2-x}Fe_{1/2}P_2O_7 with extreme compositions, (namely, x = 0 and 0.44) were synthesized using a solid-state method. Stoichiometric amounts of Na_2CO_3, Fe_2O_3, 2H_2O and (NH_4)_2HPO_4 were mixed thoroughly by ballmilling for 8 h. The mixture was initially 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_{wp} and R_{p}, defined as follows:

\[
R_{wp} = \sqrt{\frac{\sum w_i |Y_i - Yo_i|^2}{\sum w_i Y_o^2}}
\]

\[
R_{p} = \frac{\sum \left| Y_i - Yo_i \right|}{\sum Yo_i}
\]
Results and Discussion

Although Na\textsubscript{1.56}Fe\textsubscript{1.22}P\textsubscript{2}O\textsubscript{7} 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.\textsuperscript{29} The XRD pattern and the Rietveld refinement results of the as-synthesized Na\textsubscript{1.56}Fe\textsubscript{1.22}P\textsubscript{2}O\textsubscript{7} are shown in Fig. 1. No obvious diffraction peaks from impurities are detected. The Na\textsubscript{1.56}Fe\textsubscript{1.22}P\textsubscript{2}O\textsubscript{7} sample crystallizes into the space group P-1, with $a = 6.4215(3)$ Å, $b = 9.390(4)$ Å, $c = 10.978(4)$ Å, $\alpha = 64.546(10)^\circ$, $\beta = 86.091(12)^\circ$, $\gamma = 73.013(13)^\circ$, $V = 569.8(4)$ Å$^3$, and $Z = 4$. The lattice parameters of Na\textsubscript{1.56}Fe\textsubscript{1.22}P\textsubscript{2}O\textsubscript{7} are in good agreement with previously reported microcrystalline and single crystal data.\textsuperscript{18,29} Unit cell parameters are presented in Table S1 (Supplementary material).

A compositional analysis of the as-synthesized Na\textsubscript{1.56}Fe\textsubscript{1.22}P\textsubscript{2}O\textsubscript{7} was conducted using ICP-AES and AAS. The atomic ratio of Na/Fe/P is determined to be 1:4.7:1.2:2. The consistency between the analytical result obtained above and the expected compound verifies the feasibility of solid-state method adopted. Na\textsubscript{1.56}Fe\textsubscript{1.22}P\textsubscript{2}O\textsubscript{7} 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 Na\textsubscript{3}FeP\textsubscript{2}O\textsubscript{7}. The Rietveld refinement results for Na\textsubscript{3}FeP\textsubscript{2}O\textsubscript{7}, synthesized by the same solid-state method have been reported in our previous study.\textsuperscript{24}

A comparative study of the crystal structures of Na\textsubscript{1.56}Fe\textsubscript{1.22}P\textsubscript{2}O\textsubscript{7} and Na\textsubscript{2}FeP\textsubscript{2}O\textsubscript{7} reveals the similarities and the differences between them. According to the structural models proposed for Na\textsubscript{1.56}Fe\textsubscript{1.22}P\textsubscript{2}O\textsubscript{7} and Na\textsubscript{2}FeP\textsubscript{2}O\textsubscript{7},\textsuperscript{11,29} both the compounds possess a similar framework in which the FeO\textsubscript{6} octahedra interconnect with the P=O units resulting in three-dimensional and large interstitial spaces through which Na ions can diffuse (Fig. 2). On the other hand, compared to Na\textsubscript{2}FeP\textsubscript{2}O\textsubscript{7}, the occupancy of Na\textsubscript{6} sites is reduced to 0 and the occupancy of Na\textsubscript{4} sites is increased from 0.333 to 0.882 in the case of Na\textsubscript{1.56}Fe\textsubscript{1.22}P\textsubscript{2}O\textsubscript{7}. The Na\textsubscript{5} sites are partially occupied by Fe with an occupancy of 0.118 in addition to one Na site in the large tunnel along the $c$ axis (Na1) being partly replaced by Fe in Na\textsubscript{1.56}Fe\textsubscript{1.22}P\textsubscript{2}O\textsubscript{7}, whereas no site mixing is found in Na\textsubscript{2}FeP\textsubscript{2}O\textsubscript{7}. 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 FeO\textsubscript{6} units ($r_{\text{Na}^{+}} = 1.02$ Å > $r_{\text{Fe}^{2+}} = 0.78$ Å).\textsuperscript{29} Therefore, polyhedral units are considered to be more distorted in Na\textsubscript{1.56}Fe\textsubscript{1.22}P\textsubscript{2}O\textsubscript{7} than in Na\textsubscript{2}FeP\textsubscript{2}O\textsubscript{7}.

The galvanostatic charge–discharge curves of the Na\textsubscript{1.56}Fe\textsubscript{1.22}P\textsubscript{2}O\textsubscript{7} and Na\textsubscript{2}FeP\textsubscript{2}O\textsubscript{7} electrodes at a current density of 10 mA g$^{-1}$ at 298 and 363 K are compared in Fig. 3. Na\textsubscript{2}FeP\textsubscript{2}O\textsubscript{7} 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.\textsuperscript{12,30,31} In comparison with Na\textsubscript{2}FeP\textsubscript{2}O\textsubscript{7}, Na\textsubscript{1.56}Fe\textsubscript{1.22}P\textsubscript{2}O\textsubscript{7} clearly shows better electrochemical characteristics under the same conditions.

$\text{C}_{1}$ and $\text{O}_{1}$ are intensity values of diffraction data, where C and O indicate computed and observed values. The weight is labeled as $w_i$. The crystal structures were visualized using the VESTA software.\textsuperscript{27} The morphology of the sample was observed using field-emission scanning electron microscopy (FE-SEM, Hitachi SU-8020). The composition of the sample was analyzed for Na, and Fe and P using atomic absorption spectrometry (AAS, Hitachi Z2300) and inductively coupled plasma atomic emission spectroscopy (ICP-AES, SII SPS4000), respectively.

The electrochemical properties of Na\textsubscript{2}–xFe\textsubscript{1}P\textsubscript{2}O\textsubscript{7} were assessed using 2032 type coin cells with a Bio-Logic VSP potentiostat.\textsuperscript{24,28} The positive electrode was prepared by mixing Na\textsubscript{2}Fe\textsubscript{1.22}P\textsubscript{2}O\textsubscript{7}, 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]–[C\textsubscript{3}C\textsubscript{1}pyrr][FSA] (in a 20:80 molar ratio) ionic liquid was utilized as the electrolyte. Na[FSA] and [C\textsubscript{3}C\textsubscript{1}pyrr][FSA] were dried under vacuum for 24 h at 353 K and 333 K, respectively.

Figure 1. X-ray diffraction pattern with the Rietveld refinement results of Na\textsubscript{1.56}Fe\textsubscript{1.22}P\textsubscript{2}O\textsubscript{7} ($R_{wp} = 0.88\%$ and $R_{F} = 0.60\%$); experimental data (red dots), calculated pattern (black line), Bragg positions (green bars) and the difference curve (blue line). (Inset) SEM image of the as-synthesized Na\textsubscript{1.56}Fe\textsubscript{1.22}P\textsubscript{2}O\textsubscript{7}.

Figure 2. Crystal structures of (a) Na\textsubscript{2}FeP\textsubscript{2}O\textsubscript{7} and (b) Na\textsubscript{1.56}Fe\textsubscript{1.22}P\textsubscript{2}O\textsubscript{7}, with FeO\textsubscript{6} and PO\textsubscript{4} polyhedra shown in blue and gray, respectively. Na, Fe, P and O are green, blue, gray and orange, with the shading indicating occupancy.
Polyanions. An upward shift in the discharge curves is observed for the operating voltage is influenced by the local environment of the active Na intercalation/deintercalation sites of the two compounds are altered. Besides, the distinct voltage profiles imply that the polys are different between Na1.56Fe1.22P2O7 and Na2FeP2O7, the voltage pro-

Figure 3. Galvanostatic charge–discharge curves for the Na/Na[FSA]–[C6.C7pyrt][FSA]/Na2–Fe1+x/2P2O7 (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. Na1.56Fe1.22P2O7: Red line. Na2FeP2O7: black line.

Notably, the voltage profiles of Na1.56Fe1.22P2O7 and Na2FeP2O7 also exhibit a smooth charge–discharge profile, a smaller voltage shift during the first charging cycle, and a reversible capacity of 90 mAh g−1 at 298 K and 363 K. Na1.56Fe1.22P2O7: Red line. Na2FeP2O7: black line.

The rate capability of the Na1.56Fe1.22P2O7 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 subse-

Figure 4. The rate capability of the Na2–Fe1+x/2P2O7 (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. Na1.56Fe1.22P2O7: Red line. Na2FeP2O7: black line.

Honma et al. has reported that while Na2–Fe1+x/2P2O7/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 NaPF6/EC/DEC electrolytes at 298 K. Ha et al. has performed an off-stoichiometric synthesis with a nominal composition of Na2–Fe1+x/2P2O7. They concluded that the sample was comprised of a Na-rich Na1.56Fe1.22P2O7 phase and an inactive NaFePO4 phase. For the composites, a reversible capacity of about 85 mAh g−1 was obtained in NaClO4/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 Na1.56Fe1.22P2O7. 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 Na1.56Fe1.22P2O7. For the fully charged sample, there are several splits and shifts of diffraction peaks when compared with the as-synthesized Na1.56Fe1.22P2O7. 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 Na1.56Fe1.22P2O7, 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 Na1.56–Fe1.22P2O7 via chemical sodiation and desodiation. They concluded that there were no apparent evidences for the formation of a new phase in the fully charged state, indicating that the Na1.56Fe1.22P2O7 electrode undergoes a single-phase reaction.

The rate capability of the Na1.56Fe1.22P2O7 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 Na2–Fe1+x/2P2O7 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.
The outstanding cyclability is attributed to the present result is reminiscent of the well-known zero-strain Li4Ti5O12 indicating the absence of undesirable side reactions. When cycled at a current density: 1 C (118 mA g−1), 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, showing 15% improved than that of Na2FeP2O7 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 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 polyaniomone compounds through composition design.

### Conclusions

The electrochemical properties of the end members of Na2–xFe1+x/2P2O7 (NaFeP2O7 and Na3–xFe1+x/2P2O7 where x = 0 and 0.44, respectively) have been investigated and compared in Na[FSA]–[C3C1pyrr][FSA] IL electrolytes over the temperature range of 298–363 K. By altering the Na/Fe stoichiometric ratio, Na0.56Fe1.22P2O7 exhibits a reversible capacity of 108 mAh g−1 at 363 K, which is 15% improved than that of Na2FeP2O7 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 polyaniomone compounds through composition design.

### Acknowledgments

This study was partly supported by Advanced Low Carbon Technology Research and Development Program (ALCA) of Japan Science and Technology Agency (JST) and Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT) program “Elements Strategy Initiative to Form Core Research Center”.

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