Sodium-Ion Battery Cathodes Na₂FeP₂O₇ and Na₂MnP₂O₇: Diffusion Behaviour for High Rate Performance

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Na-ion batteries are currently the focus of significant research interest due to the relative abundance of sodium and its consequent cost advantages. Recently, the pyrophosphate family of cathodes has attracted considerable attention, particularly Li₂FeP₂O₇ due to its high operating voltage and enhanced safety properties; in addition the sodium-based pyrophosphates Na₂FeP₂O₇ and Na₂MnP₂O₇ are also generating interest. Herein, we present defect chemistry and ion migration results, determined via atomistic simulation techniques, for Na₂MnP₂O₇ (where \( M = \text{Fe}, \text{Mn} \)) as well as findings for Li₂FeP₂O₇ for direct comparison. Within the pyrophosphate framework the most favourable intrinsic defect type is found to be the antisite defect, in which alkali cations (Na/Li) and M ions exchange positions. Low activation energies are found for long-range diffusion in all crystallographic directions in Na₂MnP₂O₇ suggesting three-dimensional (3D) Na-ion diffusion. In contrast Li₂FeP₂O₇ supports 2D Li-ion diffusion. The 2D or 3D nature of the alkali-ion migration pathways within these pyrophosphate materials means that antisite defects are much less likely to impede their transport properties, and hence important for high rate performance.

1. Introduction

Li-ion batteries have dominated the portable energy storage market during the past two decades due to their lightweight, high energy density and high power, which all depend critically on fast Li-ion mobility. Despite the widespread use of Li-ion cells, batteries based on alternative carrier ions such as sodium ions could be more suitable for large-scale energy storage systems. Whilst the higher gravimetric capacity afforded by Li-ion cells is critical for portable applications, the relative abundance and low cost associated with Na-ion batteries now make them an attractive alternative for grid storage.

Substantial research effort has been invested during the previous decades to produce electrode materials for sodium batteries that will allow for facile intercalation of Na-ions at suitable potentials. Amongst the cathode materials investigated, a variety of layered oxides (e.g. Na₅Co₂O₄, NaCrO₂, NaVO₂, NaₓFeₓMn₁₋ₓO₂) and polyanionic compounds (e.g. NaFePO₄, NaₓVₓPO₄, NaFePO₄F, NaFeSO₄F) have been reported.

Recently lithium pyrophosphate-based materials including Li₂FeP₂O₇ and Li₂Fe:Meₙ₋₁P₂O₇ (0 ≤ x ≤ 1) have been examined, which show good electrochemical and thermal properties. It was found that Li₂FeP₂O₇ exhibited a redox-potential of 3.5 V vs Li/Li⁺ while showing a reversible capacity of ~105 mAh g⁻¹ whilst for the mixed-metal pyrophosphate it was found that the partial substitution with Mn was observed to increase the Fe³⁺/Fe²⁺ redox potential. This pyrophosphate structure can offer partial upshift of the Fe³⁺/Fe²⁺ redox potential approaching 4 V (vs Li/Li⁺) independent of cationic size and redox activity of 3d metal substituents. In addition to this high-voltage redox tunability, it is expected that the framework provided by the pyrophosphate anion will give rise to cathode materials with enhanced thermal stabilities.

Motivated by the significance of Na-ion batteries for large-scale storage systems in addition to the promising properties of Li₂FeP₂O₇, attempts were made to synthesise a sodium version of the Fe-based pyrophosphate (Na₂FeP₂O₇), as well as other Na-analogues with different transition-metal active redox species such as a new Mn-based polymorph, \( \beta\)-Na₃MnP₂O₇. Pammi et al. were able to prepare Na₃FeP₂O₇ via a conventional one-step solid-state synthesis, and found it to be electrochemically active, delivering a reversible capacity of 82 mAh g⁻¹ with an operating voltage around 3 V (vs Na/Na⁺). The combination of low cost materials, moderate theoretical capacity (~100 mAh g⁻¹), high rate kinetics and good thermal stability makes Na₂FeP₂O₇ a highly promising Na-ion battery material. From a crystal structure view-point, the change of alkali ions from Li to Na results in different crystal frameworks: while Li₂FeP₂O₇ adopts the monoclinic \((P2_1/c)\) structure, Na₂FeP₂O₇ adopts the triclinic \((P-1)\) structure.

Recently \( \beta\)-Na₃MnP₂O₇ has also been proposed as a new pyrophosphate cathode for sodium-ion batteries, and found to offer similar (if not slightly superior) electrochemical...
performance to Na$_2$FeP$_2$O$_7$. Na$_2$MnP$_2$O$_7$ exhibits a discharge capacity close to 80 mA h g$^{-1}$ (at 25 °C) with a voltage of 3.6 V, the highest Mn$^{2+}$/Mn$^{3+}$ redox potential amongst all Mn-based cathodes. The electrochemical activity of the Mn-containing cathode material is noteworthy, when compared to the Li counterpart (Li$_2$MnP$_2$O$_7$), which is almost inactive at room temperature owing to its sluggish kinetics. The β-Na$_2$MnP$_2$O$_7$ polymorph crystallises in the triclinic (P1) space group, isostructural to the rose-polymorph of Na$_2$CoP$_2$O$_7$.

The present study uses advanced simulation techniques to investigate important atomic-scale issues related to point defects and alkali (Na/Li) ion migration in Na$_2$MP$_2$O$_7$ (M = Fe, Mn.) and Li$_2$FeP$_2$O$_7$. The present work extends our previous simulation studies of lithium battery electrodes such as Li$_2$MPO$_4$ (M = Mn, Fe, Co, Ni), and our investigations of sodium-based cathodes such as NaFeSO$_4$F$_8$ and Na$_2$FePO$_4$F$_4$.

2. Simulation Methods

This investigation uses well established simulation techniques based on the Born model of solids. As these techniques are described in detail elsewhere, only a general outline will be given here. All systems were treated as crystalline solids, with interactions between ions consisting of a long-range Coulombic component and a short-range component representing electron-electron repulsion and van der Waals interactions. The short-range interactions were modelled using the Buckingham potential, and the well-known shell model was employed to account for the polarizability effects. As argued previously, interatomic potential methods are assessed primarily by their ability to reproduce observed crystal properties. Indeed, they are found to work well, even for phosphate and silicate cathodes, where there is undoubtedly a degree of covalency. The Fe–O, Mn–O, P–O and O–O interatomic potentials were taken directly from the study of the related Li$_2$P$_2$O$_7$ (to which we compare our defect and migration results), whilst the Na–O potential was taken from the recent study of the Na$_2$FePO$_4$F cathode material. The resulting potential parameters are listed in Table S1 (supporting information).

The inclusion of lattice relaxation about defects (such as Na vacancies) and migrating ions was simulated via an implementation of the Mott-Littleton scheme incorporated within GULP (v4.0). This methodology considers the crystal lattice as two separate regions, with explicit relaxation of the ions in the inner region immediately surrounding the defect (~1000 ions). In contrast, the remainder of the crystal (~3000 ions), where the defect forces are relatively weak, is treated by more approximate quasi-continuum methods.

3. Results and Discussion

3.1 Structural Modelling and Intrinsic Defects

Reproduction of the experimentally observed crystal structures (Figure 1) provided the starting point for the current study. The structure exhibited by Na$_2$FeP$_2$O$_7$ is triclinic (P-1), comprised of corner-sharing FeO$_6$ octahedra creating Fe$_2$O$_{11}$ dimers, which are interconnected by both corner-sharing and edge-sharing with P$_2$O$_7$ pyrophosphate groups. The FeO$_6$ octahedra and PO$_4$ tetrahedra are connected in a staggered fashion thus creating large tunnels along the [011] direction within which the Na atoms are present. The Na ions occupy six distinct crystallographic sites; three of which are fully occupied (Na1, Na2, Na3), whilst the other three adopt sites that are partially occupied (Na4, Na5, Na6). To account for the partial occupancy it was necessary to employ a 3×1×1 supercell approach considering different cation ordering schemes as used in previous simulations. The energetics of the different cation configurations were investigated through a series of geometry optimizations performed under P1 symmetry. We note that the lattice energy differences were found to be very small (< 15 meV), suggesting that any ordering of the Na4, Na5 and Na6 sites may not be significant.
calculated and experimental crystal structures are given in Table 1.

<table>
<thead>
<tr>
<th>Param</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\alpha$ (°)</th>
<th>$\beta$ (°)</th>
<th>$\gamma$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Na$_2$FeP$_2$O$_7$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>calc.</td>
<td>6.449</td>
<td>9.483</td>
<td>10.993</td>
<td>64.85</td>
<td>86.24</td>
<td>73.13</td>
</tr>
<tr>
<td>expt.$^{25}$</td>
<td>6.433</td>
<td>9.458</td>
<td>11.143</td>
<td>65.16</td>
<td>85.49</td>
<td>73.49</td>
</tr>
<tr>
<td>$\Delta$ (±)</td>
<td>0.016</td>
<td>0.025</td>
<td>0.150</td>
<td>0.31</td>
<td>0.75</td>
<td>0.36</td>
</tr>
</tbody>
</table>

| **Na$_2$MnP$_2$O$_7$** | | | | | | |
| calc. | 9.917 | 11.169 | 12.489 | 148.77 | 121.26 | 69.00 |
| expt.$^{27}$ | 9.922 | 11.084 | 12.473 | 148.39 | 121.95 | 68.42 |
| $\Delta$ (±) | 0.017 | 0.085 | 0.017 | 0.38 | 0.68 | 0.58 |

| **Li$_2$FeP$_2$O$_7$** | | | | | | |
| calc. | 11.017 | 9.754 | 9.805 | 90.00 | 101.54 | 90.00 |
| expt. | 11.200 | 9.715 | 9.791 | 90.00 | 102.85 | 90.00 |
| $\Delta$ (±) | 0.183 | 0.039 | 0.014 | 0.00 | 1.31 | 0.00 |

For all pyrophosphate systems, the calculated unit cell parameters deviate from experiment by at most 0.18 Å, and in most cases much less; the same is found for the individual bond lengths. The excellent reproduction of the crystal structures gives us confidence that the interatomic potential models can be used reliably in the defect and migration calculations.

Investigation of the defect properties of cathode materials is essential in order to gain a full understanding of their electrochemical behaviour, particularly the possibility of “blocking” antisite defects in structures showing 1D ion conduction. A series of isolated point defect (vacancy and interstitial) energies were calculated for both Li$_2$FeP$_2$O$_7$ and Na$_2$MP$_2$O$_7$ ($M = Fe, Mn$). By combining these energies, the relative energies of formation of Frenkel and Schottky type defects were determined. These take the following general forms (using Kröger-Vink notation and where $A = Li, Na$):

A Frenkel: $A^X \rightarrow V_A^+ + A^+_1$  
$M$ Frenkel: $M^X \rightarrow V_M^{**} + M_i^*$  
O Frenkel: $O^X \rightarrow V_O^{**} + O_i^*$  
Full Schottky: $2A^X + M^X + 2P^X + 7O^X \rightarrow 2V_A^+ + V_M^{**} + 2V_O^{**} + 7V_O^{**} + A_2MP_2O_7$  

Calculation of the $M/A$ antisite pair defect, involving the exchange of an $A^+$ ion (Li$^+$ radius 0.76 Å, Na$^+$ radius 1.02 Å) with an $M^{2+}$ ion (Fe$^{2+}$ radius 0.78 Å and Mn$^{2+}$ radius 0.83 Å) $^{45}$, was considered according to:

$M/A$ Antisite: $M^X + A_2^X \rightarrow A^X + M^*_2$  

Analysis of the resulting defect energies listed in Table 2 reveals three main points. First, the magnitude of the calculated energies for $M$ Frenkel, O Frenkel and Schottky defects suggests their formation is unfavourable. Further to which, it is found that O$^2-$ vacancies and interstitials are particularly unfavourable, and highly unlikely to occur in any significant concentration in these undoped materials, thus confirming the structural stability of the pyrophosphate framework in accord with thermal stability experiments.$^{25}$

Second, the intrinsic defect type found to be most favourable for the Na$_2$MP$_2$O$_7$ material is the Na/M antisite pair as was predicted for the Li/Fe antisite pair in the analogous study of the Li analogue (Li$_2$FeP$_2$O$_7$)$^{39}$. The formation energy for the Na/M antisite within the Na$_2$MP$_2$O$_7$ materials is of greater magnitude, suggesting lower but still significant concentrations of antisite defects within Na$_2$MP$_2$O$_7$. Since Na$^+$ is significantly larger than Li$^+$, Fe$^{2+}$ and Mn$^{2+}$ $^{45}$, it is perhaps suggestive that Na/M antisite defect will be less prominent within the pyrophosphate framework than the analogous Li/Fe antisite as revealed by the calculations. Overall our expectations for such defects is that their concentration of antisite disorder would be temperature dependent and therefore sensitive to the experimental conditions imposed during synthesis.

Lastly, the second lowest energies found for the Na$_2$MP$_2$O$_7$ cathode materials were for the Na Frenkel defect formation (Table 2). This result is in accordance with the value calculated for the Li Frenkel defect within Li$_2$FeP$_2$O$_7$. This suggests that a very minor population of such Li/Na vacancy and interstitial defects could be present at high temperatures. It should be noted that in terms of ion diffusion, the antisite defects will have greater significance within the olivine materials since their presence will block the only available channel for 1D alkali ion migration.$^{31,40}$

### Table 2 Energies of Intrinsic Atomic Defect Processes in Na$_2$MP$_2$O$_7$ ($M = Fe, Mn$) and Li$_2$FeP$_2$O$_7$.

<table>
<thead>
<tr>
<th>Disorder Type</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li or Na Frenkel</td>
<td>1.14</td>
</tr>
<tr>
<td>FeP$_2$O$_7$</td>
<td>1.34</td>
</tr>
<tr>
<td>O Frenkel</td>
<td>1.21</td>
</tr>
<tr>
<td>Full Schottky</td>
<td>5.03</td>
</tr>
<tr>
<td>A/M antisite</td>
<td>3.95</td>
</tr>
</tbody>
</table>

3.2 Na Ion Migration

Examination of the Na$^+$ mobility and pathways in Na$_2$MP$_2$O$_7$ is of vital importance when considering their respective charge/discharge rates and any differences with Li$^+$ mobility. Na-diffusion pathways were considered between all neighbouring Na positions within the Na$_2$MP$_2$O$_7$ ($M = Fe, Mn$) materials along each of the three principal axes via conventional vacancy hopping. Energy profiles for Na migration along each of the pathways considered can be mapped out, and the migration energies derived; such an approach has been used in numerous previous studies on oxide ion and cation migration in complex oxides.$^{31,32,46}$ The resulting lowest migration energies for Na diffusion along the three principal axes of the Na$_2$MP$_2$O$_7$ materials are reported in Table 3 with the corresponding lowest migration energies for Li diffusion within Li$_2$FeP$_2$O$_7$ reported for comparison.$^{39}$

From the results presented in Table 3, it would appear that both Na$_2$MP$_2$O$_7$ structures support quasi-three dimensional (3D) Na$^+$ diffusion with activation energies of 0.49 eV and 0.58 eV for Na$_2$FeP$_2$O$_7$, and Na$_2$MnP$_2$O$_7$ respectively. The final calculated paths for long-range Na$^+$ diffusion are shown in Figures 2 and 3. The Li$_2$FeP$_2$O$_7$ compound shows 2D Li$^+$ diffusion in the bc-plane with an activation energy of 0.40 eV.$^{39}$ Therefore in all cases the pyrophosphate framework appears to show high alkali-ion (Na$^+/Li^+$) mobility. Although
there are no Li⁺/Na⁺ conductivity data for direct comparison, our calculated values for alkali-ion migration are consistent with experimental activation energies for Li/Na ion conductivity in other framework-structured phosphate materials.⁴⁷⁻⁴⁹ We note that in a recent theoretical study of a different Na₂FeP₂O₇ polymorph (triclinic, P1) Na⁺ diffusion was found to be 2D with migration barriers of ~0.54 eV.³⁶

Table 3 Calculated Migration Energies for Most Favourable Paths of Alkali-Ion Diffusion: Na⁺-ion Migration in Na₃FeP₂O₇ and Na₃MnP₂O₇ and Li⁺-ion Migration in LiₓFeP₂O₇.

<table>
<thead>
<tr>
<th>Net Diffusion Direction</th>
<th>Na₃FeP₂O₇ Migration Energies (eV)</th>
<th>Na₃MnP₂O₇ Migration Energies (eV)</th>
<th>LiₓFeP₂O₇ Migration Energies (eV)³⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-axis</td>
<td>0.33</td>
<td>0.58</td>
<td>0.73</td>
</tr>
<tr>
<td>b-axis</td>
<td>0.42</td>
<td>0.58</td>
<td>0.40</td>
</tr>
<tr>
<td>c-axis</td>
<td>0.49</td>
<td>0.58</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Fig. 2 Calculated paths for long-range Na⁺ migration within Na₃FeP₂O₇ along the a-axis, b-axis and c-axis directions with activation energies ≤ 0.49 eV; a) view of the ac-plane; b) view of the bc-plane.

The 2D and 3D transport behaviour in the pyrophosphates contrasts with that in olivine LiFePO₄ and NaFePO₄ which only allow Li⁺/Na⁺ migration along 1D channels parallel to the b-axis.³¹,⁴⁰ In addition, ion blocking by antisite defects is much less likely to make a significant difference to the alkali (Na/Li) ion migration in these pyrophosphate materials. Electrochemical studies indicate that Na₂FeP₂O₇ has excellent rate kinetics, superior to that of Li₂FeP₂O₇;³⁹ this may be related to the high dimensionality (3D) and low migration energy for Na⁺-ion diffusion in Na₂FeP₂O₇.

Our simulations also reveal curved paths between adjacent Na/Li sites within each of the pyrophosphate materials studied (Figures 2 and 3). It is worth noting that analogous, curved migration pathways were first predicted for Li⁺ diffusion within LiFePO₄ based on atomistic calculations,³¹ which were subsequently confirmed by neutron diffraction maximum entropy method (MEM) analysis.³⁰

Fig. 3 Calculated paths for long-range Na⁺ migration within Na₃MnP₂O₇ along the a-axis, b-axis and c-axis directions with activation energies ≤ 0.58 eV; a) view of the ac-plane; b) view of the ab-plane.

There has been recent debate about the volume difference between the reduced and oxidized phases as a significant factor in determining electrochemical performance of cathode materials.⁴⁰,⁵¹⁻⁵² For two-phase processes, a phase boundary between oxidized and reduced phases is formed during charge/discharge. Electrochemical performance could be affected by the amount of strain generated in this phase boundary, as well as by the activation energy barrier for Li⁺- or Na⁺-ion transport.

The difference in the unit cell volume (ΔV) of the oxidized and reduced phases is only ~3.26 % for Na₃FeP₂O₇, but > 15 % for NaFePO₄ and NaFeSO₄F. We note that while the majority of the compounds undergo volume contraction on Li/Na extraction, Li₂FeP₂O₇ shows a small volume expansion, although de(lithiation) has been found to be via a solid-solution mechanism in this pyrophosphate.⁵² Although the interplay of all factors is still under investigation, materials with a large volume difference between the end member phases could lead to poor rate capability as discussed by Tripathi et al.⁴⁰ In contrast, promising electrochemical properties can be anticipated for Na-based cathode materials with low volume change on cycling (e.g. < 7 %) and low ion migration activation barriers (e.g. < 0.5 eV) as in the case of Na₂FeP₂O₇ and Na₂FePO₄F.

4. Conclusions
We have investigated Fe- and Mn-based pyrophosphate materials which offer promising high rate cathodes that are potentially low cost and thermally stable for sodium-ion batteries. This survey of Na$_2$FeP$_2$O$_7$ ($M$ = Fe, Mn) with comparison to Li$_2$FeP$_2$O$_7$ used atomistic simulation techniques to provide insights into their defect and ion migration properties.

First, the simulations show good reproduction of the observed complex structures of Na$_2$FeP$_2$O$_7$ and Na$_2$MnP$_2$O$_7$. The defect calculations indicate the stability of the pyrophosphate framework towards oxygen evolution, which is important for operational safety. The most favourable intrinsic defect type is the Na/M and Li/Fe antisite, with the relative energies suggesting greater Li/Fe disorder in the Li$_2$FeP$_2$O$_7$ material as observed.

Secondly, both Na$_2$FeP$_2$O$_7$ and Na$_2$MnP$_2$O$_7$ are predicted to exhibit curved diffusion pathways parallel to the a-, b- and c-axes with low migration energies (<0.50 eV). Hence, the pyrophosphate framework appears to support 3D Na$^+$ diffusion in Na$_2$MnP$_2$O$_7$, and 2D Li$^+$ diffusion in Li$_2$FeP$_2$O$_7$, which is consistent with the high rate kinetics observed for Na$_2$FeP$_2$O$_7$.

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Notes and references
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$^e$ Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b0000000x/