Sodium-Ion Diffusion and Voltage Trends in Phosphates Na₄M₃(PO₄)₂P₂O₇ (M= Fe, Mn, Co, Ni) for Possible High Rate Cathodes

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Abstract

Polyanionic phosphates have the potential to act as low cost cathodes and stable framework materials for Na-ion batteries. The mixed phosphates Na₄M₃(PO₄)₂P₂O₇ (M=Fe, Mn, Co, Ni) are a fascinating new class of materials recently reported to be attractive Na-ion cathodes, which display low volume changes upon cycling, indicative of long lifetime operation. Key issues surrounding intrinsic defects, Na-ion migration mechanisms and voltage trends have been investigated through a combination of atomistic energy minimization, molecular dynamics (MD) and density functional theory (DFT) simulations. For all compositions, the most energetically favourable defect is calculated to be the Na/M antisite pair. MD simulations suggest Na⁺ diffusion extends across a 3D network of migration pathways with an activation barrier of 0.20-0.24 eV, and diffusion coefficients (D_{Na}) of 10⁻¹⁰-10⁻¹¹ cm²s⁻¹ at 325K, suggesting good rate capability. The voltage trends indicate that doping the Fe-based cathode with Ni can significantly increase the voltage, and hence energy density.
1 Introduction

Rechargeable lithium batteries have come to dominate portable energy storage over the past two decades, primarily due to their light weight and high energy density.\(^1,2\) However, there are concerns over the abundance and cost of lithium, and the safety of Li-ion batteries. Na-ion batteries have been touted as alternatives to Li-ion batteries because of a higher natural abundance, and lower cost of sodium, as well as its similar intercalation chemistry to lithium.\(^3\)-\(^8\) Hence, there is renewed interest in electrode materials that can easily intercalate and transport Na-ions at suitable potentials.

Electrode selection is critical in the development of Na-ion batteries and cathode materials research has followed similar paths to that of Li-ion battery systems. Various layered oxide compounds have drawn attention including Na\(_{0.44}\)MnO\(_2\)\(^9,10\), Na\(_x\)CoO\(_2\)\(^11\), Na\(_x[\text{Fe}_0.5\text{Mn}_0.5]O_2\)\(^12\) and Na\(_{0.85}\)Li\(_{0.17}\)Ni\(_{0.21}\)Mn\(_{0.64}\)O\(_2\).\(^13\) These materials have an advantage over their lithium analogues as the larger ionic radius of the Na\(^+\) ion inhibits transformations to spinel polymorphs upon cycling, which leads to improved stability. However, a rich variety of intermediate phases leads to an intricate set of phase transitions upon cycling, adding to the complexity of ion migration upon charge/discharge.\(^14,15\) Polyanionic cathodes have also garnered notable recent interest. These materials typically demonstrate better capacity retention and cycle stability than for layered oxides, due to their robust and stable frameworks with tightly bound polyanions. In addition, voltage response upon cycling is generally simpler than layered oxides, as two-phase behaviour, with a well-defined phase boundary, is usually favoured.\(^16\) Polyanionic materials of interest include NASICON-type compounds (such as Na\(_3\)V\(_2\)(PO\(_4\))\(_3\)),\(^17\) NaVPO\(_4\)F,\(^18\) NaFePO\(_4\)\(^19-21\) and Na\(_2\)FePO\(_4\)F.\(^16,22-24\)

More recently, mixed phosphates of the formula Na\(_4\)M\(_3\)(PO\(_4\))\(_2\)P\(_2\)O\(_7\) (where M is a transition metal) have been considered as potential cathodes. The Co system, Na\(_4\)Co\(_3\)(PO\(_4\))\(_2\)P\(_2\)O\(_7\), has been synthesized through a sol-gel process by Iba et al\(^25\) and was shown to reversibly intercalate Na-ions at high voltage (~4.7 V), with a capacity of ca. 99 mAhg\(^-1\) at 0.2 C rate. Furthermore, the material demonstrated excellent rate performance, retaining 89 mAhg\(^-1\) capacity at 5C rate.\(^25\) The Na\(_4\)Fe\(_3\)(PO\(_4\))\(_2\)P\(_2\)O\(_7\) material has been studied by Kang et al\(^26,27\) using combined experimental and DFT techniques. A theoretical capacity of 129 mAhg\(^-1\) delivered at approximately 3.2 V vs Na/Na\(^+\) is highly competitive with other Na-ion cathodes.\(^8\)

It has been shown that Na\(_4\)Fe\(_3\)(PO\(_4\))\(_2\)P\(_2\)O\(_7\) does not undergo a phase change upon Na-ion extraction, with a small volume change of just 4% upon cycling. This value compares favourably with other Na-ion battery materials, such as NaFePO\(_4\) and NaFeSO\(_4\)F, which exhibit
a volume change of 15% and 14.5% respectively upon cycling.\textsuperscript{16,28} The low volume change in Na\textsubscript{4}Fe\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}P\textsubscript{2}O\textsubscript{7} is important for good long-term cycle life.\textsuperscript{26,27}

Our focus here is in probing the defect, diffusion and voltage trends of the Na\textsubscript{4}M\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}P\textsubscript{2}O\textsubscript{7} (M=Fe, Mn, Co, Ni) class of materials. In this study, we have applied a combination of atomistic energy minimization and molecular dynamics methods to examine the processes governing the defect chemistry and ion migration. In addition, we have employed DFT methods to study the trends in cell voltage across a variety of transition metal configurations.

2 Methods

Atomistic modelling techniques have been widely used in the study of defect and transport properties of solids. These have been detailed elsewhere\textsuperscript{8,29-31} and as such only a brief outline will be given here.

Interatomic interactions were represented by a long-range electrostatic term plus a function representing the short-range repulsive and van der Waals interactions. Since charged defects will polarize other ions in the lattice it is important to incorporate electronic polarization into the potential model and this was achieved through inclusion of the shell model.\textsuperscript{29,30} A crucial feature of defect simulations is the treatment of lattice relaxation about the charged defect or migrating Na\textsuperscript{+} ion. The Mott-Littleton approach was used, whereby the crystal lattice is partitioned into two regions, implemented through the GULP code.\textsuperscript{30} This approach has previously been used effectively to explore a number of battery materials.\textsuperscript{16,32-36}

Molecular dynamics (MD) simulations were performed with DL POLY (v4)\textsuperscript{37} using a fitted version of the partial-charge potential model of Pedone et al,\textsuperscript{38} which has been explicitly developed to allow rapid simulation of finite temperature properties in complex oxides. An overview of the potentials and structural reproduction from this model is given in Table S1 and S2. A supercell consisting of 10 x 4 x 6 unit cells (~25,000 ions) was used, with 5% of Na ions removed randomly. The systems were pre-equilibrated for at least 750 ps (with a timestep of 1.5 fs) before the main simulation runs of 750 ps were performed. An NPT ensemble, with a Berendson thermostat, was used throughout to allow for thermal expansion. Sodium-ion diffusion coefficients were calculated from the mean square displacements. Such MD techniques have previously been applied to many lithium battery and solid oxide fuel cell ion conductors.\textsuperscript{39-43}
DFT calculations were performed using a plane wave basis set implemented in the VASP code. A cutoff energy of 800 eV and a k-point grid of 1x2x2 were needed to adequately converge the forces and energies. PAW potentials and spin-polarized GGA with the PBESol functional were used. DFT+U methodology was used to account for the metal d-orbitals with an effective Hubbard \( U_{\text{eff}} = U - J = 4.3, 3.9 \) and 6.0 eV (\( J = 1.0 \) eV) for Fe, Mn and Ni respectively. These values are consistent with those previously derived for cathode materials. See supplementary information Table S3 for a tabulated list of published U values from battery cathode studies. In addition van der Waals interactions were considered as these have been shown to influence cell voltage in some polyanionic systems. However, for these materials, they were found to have a negligible effect on calculated voltages, probably due to the paucity of unscreened dispersion interactions.

Previous DFT studies on a range of oxide electrode materials have shown such methods to be well suited to simulating precise trends in cell voltages. For all materials the Na\(^+/\)Na cell voltages for the \( M^{2+}/M^{3+} \) redox couples were calculated from:

\[
V = \frac{\varepsilon(Na_4M_3(PO_4)_2P_2O_7) - \varepsilon(Na_xM_3(PO_4)_2P_2O_7) - (4-x)\mu(\text{Na})}{4-x}
\]  

where \( \varepsilon(Y) \) is the total energy of composition \( Y \) and \( x \) is the number of sodium atoms remaining per formula unit, which was taken as \( x=1 \) to produce the end member \( \text{NaM}_3(\text{PO}_4)_2\text{P}_2\text{O}_7 \). The chemical potential of sodium, \( \mu(\text{Na}) \), was calculated using metallic sodium, which is standard practice for cell voltage calculations.

3 Results and Discussion

3.1 Structures and Intrinsic Defects

The starting point for our simulations is the reproduction of the observed crystal structures. The structures of \( \text{Na}_4\text{M}_3(\text{PO}_4)_2\text{P}_2\text{O}_7 \) (where \( M=\text{Fe, Co, Mn, Ni} \)) all adopt a similar crystal structure with a Pna2\(_1\) space group. The \( \text{Na}_4\text{Fe}_3(\text{PO}_4)_2\text{P}_2\text{O}_7 \) structure is shown in figure 1. The transition metals reside in octahedral sites which are joined by phosphate (\( \text{PO}_4 \))\(^3-\) groups to form layers in the \( bc \) plane. These layers are bridged parallel to the \( a \) axis by pyrophosphate (\( \text{P}_2\text{O}_7 \))\(^4+\) groups, forming a 3D framework. The Na\(^+\) ions are found in four non-equivalent sites with Na1 and Na4 residing in two channels in the phosphate framework parallel to the \( b \) axis.
The interatomic potentials for all four systems Na$_4$M$_3$(PO$_4$)$_2$P$_2$O$_7$ (where M=Fe, Mn, Ni, Co) were derived simultaneously, which is not trivial for such complex structures. A comparison between the calculated structures based on these effective potentials (Table S4) and experimental data is given in Table 1.

The calculated unit cell parameters differ from experiment by at most 1.74% and in most cases the deviations are substantially less. The mean deviations in bond lengths are 0.071 Å, 0.103 Å and 0.097 Å for the M-O, P-O and Na-O bonds respectively. The shorter average Na-O bond lengths (2.38 Å compared to 2.48 Å) found in the Fe material from experiment makes reproduction of the series of complex structures challenging when using the same Na-O and P-O potentials. Nevertheless, the accurate reproduction of all structures, including the iron analogue, with the same interatomic potentials gives us confidence that the model can be used reliably in subsequent defect and migration simulations to explore trends in properties.

To investigate the intrinsic defect chemistry a series of isolated point defect energies (vacancy, interstitial and impurity) were calculated for all four transition metals in Na$_4$M$_3$(PO$_4$)$_2$P$_2$O$_7$ (M= Fe, Mn, Ni and Co). Combining the energies of these point defects, energies of formation for Frenkel and Schottky-type disorder can be derived. The corresponding equations in Kroger-Vink notation are given in supplementary information. We also examined Na/M "antisite" pair defects involving the exchange of positions of a pair of Na$^+$ (radius 1.02Å$^{50}$ and M$^{2+}$ (radius Fe=0.61Å, Mn=0.83Å, Co=0.65Å and Ni=0.69Å$^{53}$ ions. This type of defect is worth considering as it has been observed in other polyanionic battery systems, such as NaFePO$_4$ and Li$_2$MnSiO$_4$. It has also been predicted to have significant impact on the electrochemical performance of some materials. The defect formation results are presented in Table 1 from which three main points emerge.

Firstly, the high energies associated with M Frenkel, O Frenkel, P Frenkel and Schottky defects (for all transition metals) suggest that such intrinsic defects are unfavorable. Hence such defects are unlikely to exist in significant concentrations in the undoped materials.

Secondly, the most favorable type of intrinsic defect is predicted to be the Na/M antisite pair for all materials; as has been found in previous studies of NaFePO$_4$ and Na$_2$FeP$_2$O$_7$. Furthermore, from the energetics the concentration of antisite defects would be expected to be greatest in Na$_4$Fe$_3$(PO$_4$)$_2$P$_2$O$_7$ and least in Na$_4$Ni$_3$(PO$_4$)$_2$P$_2$O$_7$. This may have an impact on electrochemical performance as antisite defects have the potential to "block" sodium-ion migration especially in 1D Na$^+$ conductors.
Third, Na Frenkel defects also have a relatively low energy, suggesting a minor intrinsic population of Na interstitials and vacancies. As with the antisite defects the Fe-based material is predicted to have the highest defect concentration, whilst the Ni-based material should display the lowest defect population.

### 3.2 Na-ion Diffusion

Sodium diffusion properties are of vital interest when examining the electrode kinetics. Our MD simulations focused on the Fe and Mn based materials, as these two are of greatest practical interest because of their high natural abundance. Simulations over significant timescales and various operating temperatures have been conducted for the compositions Na$_{3.8}$M$_3$(PO$_4$)$_2$P$_2$O$_7$ for (M = Fe, Mn).

Initially the mean square displacement (MSDs), $<[r(t)]^2>$, of sodium ions was resolved, and then used to derive Na-ion diffusion coefficients ($D_{Na}$) from the relation:

$$D = \frac{1}{6} \frac{d<[r(t)]^2>}{dt}$$

yielding $D_{Na}$ values of $6.1 \times 10^{-11}$ cm$^2$s$^{-1}$ and $3.1 \times 10^{-10}$ cm$^2$s$^{-1}$ at 325 K for the Fe and Mn materials respectively. Although no experimentally measured diffusion data are available for direct comparison, these values compare well to other Na-ion cathodes; these include layered oxides Na$_3$MnO$_2$ ($10^{-11}$cm$^2$s$^{-1}$)$_{55}$ and polyanionic materials such as Na$_3$V$_2$(PO$_4$)$_2$F ($10^{-10}$cm$^2$s$^{-1}$).$^{56}$ See Table S5 in supplementary information for a selection of Na diffusion coefficients from the published literature. Our diffusion data can also be used to estimate activation barriers ($E_a$) of Na-ion migration form an Arrhenius plot ($ln \ D$ vs $1/T$), shown in Figure 2. A diffusion barrier of 0.2-0.24 eV is predicted for two materials, indicative of fast Na-ion mobility and high rate performance in the polyanion framework. Comparable activation barriers between Li and Na-ion cathodes have been found in various materials,$^{16,27,36,57}$ despite the larger ionic radius of Na$^+$ ion (1.02 Å) compared to the Li$^+$ ion (0.76 Å).$^{53}$ This is typically rationalized by the tendency of sodium to form longer Na-O bonds, providing a more open framework structure. Previous DFT analysis$^{27}$ of the Fe material found a higher activation barrier (~ 0.5 eV), although this was determined from nudged elastic band (NEB) calculations for a single migrating Na-ion.
A useful means of visualizing diffusion trajectories is plotting accumulated Na-ion densities, which indicates the lattice sites most frequently traversed over the course of the simulation run. These plots are shown in Figure 3 for the Fe system; we note that the same behaviour is found for the Mn-based material. The broad distribution and significant overlap of Na-ion densities demonstrates the highly mobile nature of Na-ions in this material involving all Na sites. This diffusion extends over a 3D network throughout the material, in which b-axis channels (containing sites Na1 and Na4) are connected by intralayer migration through Na2 and Na3 sites. Within this context, the low antisite defect energy is likely to have less of an impact than would be expected in the case of 1D diffusion where it would block the 1D channel. The 3D network and low activation barriers, as well as the low volume change upon cycling, are promising features for good rate capability of these cathodes.

Closer analysis indicates that the topology of the migration paths varies throughout the diffusion network. The pathways involving only Na2 and Na3 are essentially linear, i.e. span a shortest path trajectory, as can be seen in Fig 3 (a). Conversely, for diffusion involving Na1-Na1 and Na4-Na4 paths down the b-axis channels, a curved trajectory is found, which provide the lowest energy pathways, as shown in Fig 3 (b). Such curved trajectories have also been observed in other polyanion materials, such as NaFePO4.16 The trajectories for Na-ion diffusion are largely consistent with previous DFT analysis of the Fe material.27

3.3 Voltage Trends

Tailoring the cell voltage is key to achieving optimal battery performance and maximizing energy density. DFT calculations were thus used to explore transition metal doping of the Na4Fe3(PO4)2P2O7 material and its influence on the cell voltage. To calculate the cell voltage the relevant sodium ions are removed from the structure, which is subsequently energy minimized to determine the most stable structure. Numerous vacancy configurations were tested based on the results of both screening using potentials-based simulations and previous DFT studies.26 The voltage was extracted from the lowest energy configurations using equation 1.

As with potentials-based calculations, the Na4M3(PO4)2P2O7(M=Fe, Ni, Mn) experimental structures have been reproduced to a high degree of accuracy (Table S6). Furthermore the cell voltage for Na4Fe3(PO4)2P2O7 is calculated to be 3.0 eV vs Na/Na+, in good agreement with the experimental value of 3.2V vs Na/Na+.27 The voltage, and energy density, of Na4Fe3(PO4)2P2O7 would generally be considered too low for optimal battery
performance. Therefore, to raise the calculated voltage, doping with Mn and Ni has been explored, as both cations typically display higher voltages than Fe containing materials.

The trend in voltage across transition metal compositions is detailed in Figure 4 as a function of Fe content. The transition metal end members (Na₄Fe₃(PO₄)₂P₂O₇, Na₄Mn₃(PO₄)₂P₂O₇ and Na₄Ni₃(PO₄)₂P₂O₇) follow the series Fe (3.0 V) < Mn (3.5 V) < Ni (4.9 V); this trend is consistent with other battery material series such as LiMPO₄, Li₂MP₂O₇ and Na₂MPO₄F, which are known experimentally to follow a similar pattern. In addition, the voltage of the Ni end member (4.9 eV) is outside the stability window of standard electrolytes. Whilst the voltage of the Mn material is more attractive, Mn-based phosphates often experience problems with redox cycling typically on account of Jahn-Teller effects.

Compositions Na₄Fe₃₋ₓMnx(PO₄)₂P₂O₇ (for x=1,2) are calculated to have a voltage of 3.2V, suggesting Mn doping provides a relatively minor increase in cell voltage and energy density. Conversely, Ni doping is predicted to deliver a significant increase in cell voltage, providing a high degree of voltage control by varying the doping concentration. Furthermore, the composition Na₄Fe₂Ni(PO₄)₂P₂O₇ is predicted to have a cell voltage of 3.7 V, close to the upper limit on voltage set by typical electrolyte stability windows. Therefore, we predict that doping Na₄Fe₃(PO₄)₂P₂O₇ with a relatively modest level of Ni would lead to a ~25% enhancement in voltage; this is a significant increase to a viable voltage in terms of energy density and electrolyte stability.

4 Conclusions

A combination of atomistic energy minimization, molecular dynamics (MD) and DFT simulation techniques has been used to provide insights into the defect chemistry, Na-ion diffusion and voltage trends in the Na-ion battery materials Na₄M₃(PO₄)₂P₂O₇ (M = Fe, Mn, Ni, Co).

First, our atomistic potential model provides an accurate reproduction of the complex structures for all four compositions. In all materials the most favorable intrinsic defect is found to be the Na/M antisite pair. Large-scale MD simulations allowed us to explore Na-ion diffusion kinetics and transport mechanisms. Na⁺ diffusion coefficients (DNa) are of the order 10⁻¹⁰-10⁻¹¹ cm²s⁻¹ at 325 K and activation barriers are found to be 0.20-0.24 eV in the Fe- and Mn-based materials. These values compare favourably to successful Li-ion cathodes indicating rapid Na-ion transport which, coupled with the small volume change observed on cycling, suggests high rate capability and good cycle life. In addition, the MD trajectories suggest a 3D
network of migration pathways, with all sodium ions diffusing. Closer analysis indicates that all pathways involving Na2 and Na3 sites are essentially linear, whilst for diffusion down the b-axis channels (Na1 and Na4 sites) curved trajectories are found.

Finally, DFT methods have been used to explore voltage trends. The experimental voltage of Na4Fe3(PO4)2P2O7 is reproduced and higher cell voltages for Na4Mn3(PO4)2P2O7 and Na4Ni3(PO4)2P2O7 are predicted. Moreover, we demonstrated that doping Na4Fe3(PO4)2P2O7 with Ni can lead to a significant increase in voltage.

These results will assist in developing strategies for optimizing these novel phosphates as possible high-rate Na-ion cathodes, especially for the more cost-sensitive stationary storage sector.

Acknowledgments

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Supporting Information Available

Potential parameters employed in simulations and deviation between calculated and experimental structures from all simulation techniques. Tabulated $U_{eff}$ values from computational studies of Li-ion and Na-ion battery materials. Tabulated Na$^+$ diffusion coefficients from studies of Na-ion battery materials. Thermodynamic stability data and calculated Density of States from DFT simulations. This information is available free of charge via the Internet at http://pubs.acs.org.
Figure 1: Experimental structure of $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ as a representative system for all materials studied; $\text{FeO}_6$ units are brown, $\text{PO}_4$ and $\text{P}_2\text{O}_7$ units are grey and $\text{Na}^+$ ions are yellow.
Figure 2: Arrhenius plot of Na ion diffusion coefficients in Na$_{3.8}$Fe$_3$(PO$_4$)$_2$P$_2$O$_7$ and Na$_{3.8}$Mn$_3$(PO$_4$)$_2$P$_2$O$_7$.

Figure 3: Na-ion density plots for Na$_{3.8}$Fe$_3$(PO$_4$)$_2$P$_2$O$_7$ overlaid on initial lattice sites. (Key: Na=yellow, Fe=brown, P=grey and O=red; yellow details Na-ion migration pathways.) (a) demonstrates 3D network view down b axis revealing linear regions (involving Na2 and Na3 sites) and (b) magnified view showing the curved paths along the b axis channels (involving Na1 and Na4 sites).
Figure 4: Trends in cell voltage (vs Na/Na⁺) as a function of increasing Mn and Ni concentrations on the Fe site in Na₄Fe₃(PO₄)₂P₂O₇.
## Tables

Table 1: Deviation (Δ) between calculated and experimental structures\textsuperscript{26,52} of Na₄M₃(PO₄)₂P₂O₇ (where M=Fe, Mn, Ni and Co).

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Bond Length

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Table 2: Calculated intrinsic defect energies in eV for Na₄M₃(PO₄)₂P₂O₇ for M=Fe, Mn, Ni and Co.

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39. Lee S. and Park S. S., Atomicistic Simulation Study of Mixed-Metal Oxide Li(Ni0.5Co0.5Mn0.5)O2 Cathode Material for Lithium Ion Battery, J. Phys. Chem. C, 2012, 116, 6484-6489.
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