Topochemical Synthesis of Sodium Metal Phosphate Olivines for Sodium-Ion Batteries

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ABSTRACT: New metastable olivine phases of sodium metal phosphates, Na[Mn1−xMx]PO4 (M = Fe, Ca, Mg), are synthesized by a simple solid-state reaction at low temperature (≤100 °C) by means of a topotactic molten salt reaction that converts NH4[Mn1−xMx]PO4·H2O (M = Fe, Ca, Mg) to Na[Mn1−xMx]PO4. Their crystal structures are characterized via XRD refinement and electron diffraction. A full range of solid solution behavior was observed for olivine Na1−xMnxFe0.5PO4 in contrast to that of LiMPO4 (M = Fe, Mn) olivine materials, and is ascribed to ion size effects. The solid solution behavior of NaMn0.5Fe0.5PO4 was confirmed by electrochemical characterization.

INTRODUCTION

Lithium-ion batteries play a vital role as the prominent power sources for cell phones, laptop computers, digital cameras, power tools, electrical assist bicycles, and many consumer products. They are now also attracting tremendous interest as energy storage devices for automotive applications. In upcoming years, many electric vehicles and extended range electric vehicles will be powered by large-scale lithium-ion storage batteries. At the present time, lithium resources are confirmed to be unevenly distributed, located primarily in South America. The cost of lithium-based raw materials has roughly doubled from the first practical application in 1991 to now, and it may drastically increase when the demand for lithium increases as a result of commercialization of large-scale lithium-ion batteries in the future. However, sodium resources are inexhaustible and unlimited everywhere around the world. Furthermore, the electro-chemical equivalent and standard potential of sodium are the most advantageous for aprotic battery applications after lithium. However, only a limited number of successful reports are found concerning sodium insertion electrode materials. Regarding oxide-based positive electrodes, Dahn et al.1 and Braconier et al.2 reported the reversible de-intercalation of Na from Na0.44MnO2 and Na2MO2 (M = Co, Cr, Ni), respectively, at high potential, and the Bruce group3 has recently reported the same for Na0.44MnO2 using a sodium polymer electrolyte. Tarascon et al. demonstrated it is possible to de-intercalate Na ions in Li-MnO2.5 and Na2MnO2.6 Regarding low potential materials capable of Na-insertion necessary for the negative electrode, Dahn et al.7 and Dahn et al.8 demonstrated that Na ions can be electrochemically de-inserted in hard carbons; and recently, Alcantara et al.9 and Komaba et al.10 introduced the concept of using metal oxide materials. In the case of phosphate-based cathodes, similarly, only a handful of materials have been developed, namely, NaVPO4F11 (reported to have a tavorite structure), Na3V2(PO4)3F.12 and Na2FePO4F.13–15 The latter has numerous advantages over the first, including a layered structure that is particularly suitable for ion mobility and an inexpensive nontoxic metal. However, it suffers a little from the viewpoint of gravimetric capacity and energy density owing to the 3.4 V redox couple. Direct formation of a sodium metal phosphate with an olivine structure would be very desirable, especially for a low-cost nontoxic metal such as iron or especially manganese, which has a higher voltage redox couple and hence a theoretically higher energy density. Mixed Li[Fe,Mn]PO4 olivines have been shown to be especially promising. However, both NaFePO4 and NaMnPO4 form as an electrochemically inactive marcite phase under conventional synthetic conditions at high temperature, not the olivine phase.16 Very recently, olivine-type Na2FePO4 has been electrochemically accessed using a positive electrode containing a mixture of 70% FePO4 obtained by delithiation of olivine LiFePO4 and 30% carbon.17 Here, we introduce new metastable mixed metal olivine-type phases of Na[Mn1−xMx]PO4 (M = Fe, Ca, Mg), where 0 ≤ x ≤ 0.5, directly synthesized by a low-temperature solid-state method using a topotactic reaction and report their unusual solid solution behavior.

EXPERIMENTAL SECTION

Synthesis of Na[Mn1−xMx]PO4. Ammonium metal phosphates NH4MPO4·H2O (M = Mn, Mn0.5Fe0.5, Mn0.8Ca0.2, Mn0.8Mg0.2) were synthesized according to previously reported methods38–41 with modification. The materials were ground together with excess sodium acetate

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KEYWORDS: olivine, Na-ion battery, topotactic, low-temperature synthesis, cathode material
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trihydrate (CH₃CO₂Na•3H₂O), and heated between 65–100 °C to form Na[Mn₁₋ₓMₓ]PO₄ (M = Fe, Ca, Mg), where 0 ≤ x ≤ 0.5. Unreacted sodium acetate trihydrate was removed by washing with ethanol. The oxidation of NaMPO₄ (M = Fe₀.₃Mn₀.₇) was accomplished using a slight excess of NOBF₄ or NO₂BF₄ in acetonitrile to obtain Na₀.₅MPO₄ and Na₀.₂MPO₄, respectively.

Synthesis of NaFePO₄. LiFePO₄ was oxidized with a slight excess of NOBF₄ in acetonitrile for 5 h to obtain FePO₄, which was reduced with excess NaI in acetonitrile for two days to obtain NaₓFePO₄ (0 < x ≤ 1).

Materials Characterization. Powder X-ray diffraction (XRD) data was collected on a Bruker D8-Advance powder diffractometer using Cu Kα radiation (λ = 1.5405 Å) operating from 2θ = 10–80°. Lattice parameters were determined using full pattern matching on the basis of an initial olivine-type Pnma unit cell in the GSAS platform employing the EXPGUI interface, followed by Rietveld refinement. Scale factor, zero point, lattice parameters, atomic positions, and atomic displacement parameters were iteratively refined. For refinement of the NaMPO₄ cells (M = Mn and M = Fe₀.₅Mn₀.₅), antisite mixing on the M1 and M2 sites was permitted, with the constraint that the total occupation on either of the M1 and M2 sites was equal to one. For M = Fe₀.₃Mn₀.₇, the Fe²⁺ and Mn³⁺ occupation was additionally constrained to be equal on the basis of the ICP results that indicated the ratio of the two metals was the predicted 1:1 because XRD cannot distinguish between the scattering from Fe and Mn. Refinement of Na[Mn₀.₈Ca₀.₂]PO₄ also permitted antisite mixing on the M1 and M2 sites, with the constraint that the total occupation on either of the M1 and M2 sites was equal to one. The occupation on the M1 site included both Na⁺ and Mn³⁺, but Mg²⁺ occupation was not refined owing to the lack of distinction between scattering from Na⁺ and Mg²⁺. In this case, the Mn³⁺ occupation on the M1 site defines the degree of antisite mixing; a reasonable assumption because the total Mn²⁺ occupation on both M1 and M2 sites independently refined to 0.807 (close to the expected value of 0.8). Similarly, only Mn²⁺ and Mg²⁺ were refined on the M2 site (not Na⁺), with a total occupation on that site constrained to be one. Refinement of the XRD pattern Na₀.₅[Mn₀.₅Fe₀.₅]PO₄ was complicated by X-ray line broadening. Therefore, the occupancies of the Mn and Fe were fixed at 0.5, and only the Na occupation was refined.

The SEM samples were examined in a LEO 1530 field-emission scanning electron microscope (FE-SEM) instrument equipped with an energy dispersive X-ray spectroscopy (EDX) attachment. TEM investigations were performed using a Philips CM120 at 120 kV or a JEOL-2010F electron microscope at an accelerating voltage of 200 kV with a field-emission gun (FEG).

Electrochemistry. Samples of electrochemically active materials were mechanically mixed for 1 h with carbon black and polyvinylidene fluoride in a 60:20:20 weight ratio. The electrochemical performance was evaluated using 2220 coin cells, using a Na metal anode, and 1 M NaClO₄ in a propylene carbonate electrolyte solution. Room temperature galvanostatic experiments were performed at a current density of 3.87 mA/g (C/40).

RESULTS AND DISCUSSION

Synthesis of Na[Mn₁₋ₓMₓ]PO₄. The thermodynamically stable form of NaFePO₄ is the mineral maricite. It is similar to the well-known LiFePO₄ olivine structure in terms of its phosphate framework, but the M1 and M2 sites are occupied by Fe³⁺ and Na⁺, respectively, which is exactly the reverse of LiFePO₄ (Figure 1). This gives rise to a different connectivity of the Fe and Na octahedra, which blocks Na-ion migration pathways and, hence, results in a structure that is not amenable to Na⁺ (de)insertion. NaMnPPO₄ adopts the maricite structure in its thermodynamically stable form and has also been reported as the mineral natrophilite, where the M1 and M2 sites are both half occupied by Mn²⁺ and Na⁺. It is similarly electrochemically inactive.

The crystallization of Na[Fe,Mn]PO₄ as a metastable olivine phase thus entails the use of low-temperature synthesis methods. Our approach is to employ a low-temperature molten salt synthesis on the basis of our previous work detailing the topotactic transformation of NH₄FePO₄•H₂O to LiFePO₄ in hydrothermal media, which was also recently adopted for the synthesis of LiMnPPO₄ using NH₄MnPO₄•H₂O as a precursor. We reasoned that the transformation of NH₄MPO₄•H₂O to NaMPO₄ could follow a topotactic pathway by direct ion exchange between NH₄⁺ and Na⁺ using molten CH₃CO₂Na•3H₂O. As anticipated, the reaction of ammonium metal phosphates NH₄₁₋ₓMPO₄•H₂O (M = Mn, Mn₀.₃Fe₀.₇, Mn₀.₅Ca₀.₅, Mn₀.₃Mg₀.₂) with sodium acetate trihydrate (CH₃CO₂Na•3H₂O) between 65–100 °C readily formed the desired olivine Na[Mn₁₋ₓMₓ]PO₄ (M = Fe, Ca, Mg) phases, where 0 ≤ x ≤ 0.5. The Ca³⁺- or Mg²⁺-substituted NaMnPPO₄ olivine phases were prepared with ~20% substitution of the alkaline earth ion targeted on the Mn²⁺ site, in order to allow for the possibility of adjusting the framework slightly to favor Na⁺ mobility. However, the olivine phase of the pure iron compound NaFePO₄ could not be prepared by this direct method. Maricite was produced instead because NH₄FePO₄•H₂O decomposes about 100 degrees lower than the temperature at which ion exchange occurs. The NaFePO₄ olivine phase was prepared by a chime douce method as described earlier: olivine LiFePO₄ was delithiated at room temperature with NOBF₄ to form the orthorhombic phase of FePO₄, which was then sodiated with excess NaI.

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The corresponding X-ray diffraction (XRD) patterns of the materials shown in Figure 2 are in good accord with the predicted patterns on the basis of crystallization of the target olivine phases. Rietveld refinement of the XRD patterns was carried out for the selected materials, NaMnPO₄, NaFePO₄, Na[Mg₀.₈Mn₀.₂]PO₄ and NaFe₀.₇Mn₀.₃PO₄, to confirm their structures (Figure 3). The Ca-substituted phase, Na[Mg₀.₂Ca₀.₈]PO₄, was not readily amenable to Rietveld methods owing to its lower crystallinity, and therefore, its XRD pattern was indexed using CRYSFIRE. The lattice parameters are summarized in Table 1. Those of NaFePO₄ synthesized by chemical insertion of Na are in good agreement with a NaFePO₄ phase that was just recently reported, derived by employing FePO₄ as a cathode in a Na-ion battery.¹⁷ No evidence for any antisite mixing (exchange of Na⁺/Fe²⁺ on their respective M₁ and M₂ sites) was found when this was an allowed parameter freed in the refinement.

The new mixed metal phases prepared by molten salt synthesis have lattice parameters between their end members, showing they are solid solution phases with respect to metal occupation on the M₂ site. The unit cell volume of NaFe₀.₅Mn₀.₅PO₄ lies halfway between that of NaFePO₄ and NaMnPO₄, for example. Similarly, Mg²⁺ substitution on the Mn²⁺ site decreases the unit cell volume in accord with its smaller cation size (72 pm compared to 83 pm, whereas Ca²⁺ substitution on the M₂ site results in an increase as expected from its cationic dimensions (100 pm compared to 83 pm). EDX analysis also confirmed that the targeted levels of Mg and Ca substitution in the lattice were achieved (vide infra). Larger values for the b and c axes and cell volume for NaMnPO₄ (V = 334 Å³) and Na[Fe₀.₅Mn₀.₅]PO₄ (V = 329 Å³) compared to their lithium congeners (V = 302.2 Å³ and 296.1 Å³ for LiMnPO₄ and Li[Fe₀.₅Mn₀.₅]PO₄, respectively)⁵¹ reflect the larger size of Na (102 pm) compared to that of lithium (76 pm). Importantly, the occupancies of both M₁ and M₂ sites were allowed to vary during the final stages of the refinements to allow for antisite mixing, and we found that these materials have little cation disorder on the order of 2–3% (Table 1 and Supporting Information). The antisite disorder was negligible in Na[Mg₀.₂Mn₀.₈]PO₄ on the basis of the refined occupancy (0.004) of Mn²⁺ on the M₁ site (although the corresponding refinement of Na⁺ on the M₂ site was thwarted by the similarity in scattering between Na⁺ and Mg²⁺).

The overall low degree of cation disorder is an advantage of the proposed topotactic reaction sequence, which is illustrated in Figure 4. Comparison of the structures of olivine NaMPO₄ and NH₄MPO₄•H₂O (M = Fe, Mn, Mg) indicates how they could be related by a simple transformation. The connectivity of the iron and phosphate polyhedra in the (100) plane of NaMPO₄ in the Pnma space group is identical to that in the corresponding (101) plane of NH₄MPO₄•H₂O in the Pmn₂₁ space group; note the difference in their space groups simply switches the a and b axes. Thus, repeating polyhedral motif is the same in the two cases as shown in Figure 4. Upon ion exchange of NH₄⁺ for Na⁺, the adjacent sheets are knitted together by condensation of the NaO₆ octahedra to crystallize the olivine NaMPO₄. The structure of the NH₄MPO₄•H₂O precursors is perfectly ordered because of the bulky NH₄ ions, and thus, this order is faithfully replicated in the structure of the resulting products. The temperature is too low to

Figure 2. XRD patterns of NaMPO₄ (M = Mn₀.₅Fe₀.₅, Mn, Fe, Mn₀.₈Ca₀.₂, Mn₀.₈Mg₀.₂).

Figure 3. Rietveld refinements of NaMPO₄ for M as indicated: (a) Mn, (b) Fe, (c) Fe₀.₅Mn₀.₅ and (d) Mg₀.₂Mn₀.₈. Experimental points are in black. The fit is shown in red. Calculated reflections are in magenta. The difference map is shown in blue.
induce significant atomic position rearrangements such as switching of the $M^{2+}/Na^{+}$ ions.

SEM images (Figure 5) reveal the transformation of the flat plate morphology of the layered NH$_4$MPO$_4$·H$_2$O crystals to the nanorod morphology of the NaMPO$_4$ olivine structure. The formation of nanorods is caused by a high interface strain at the grain boundaries between NH$_4$MPO$_4$·H$_2$O and NaMPO$_4$. The $d$-spacing corresponding to the (010) reflection in NH$_4$MPO$_4$·H$_2$O is quite different from the equivalent (100) reflection for NaMPO$_4$ owing to the size of the bulk NH$_4^{+}$ ion in the interlayer space; for example, in the case of $M = Mn$, $d_{010} = 8.8$ Å (NH$_4$MnPO$_4$·H$_2$O) and $d_{100} = 4.7$ Å (NaMnPO$_4$). Although the replacement of NH$_4^{+}$ for Na$^{+}$ is topotactic, it is not instantaneous within the interlayer gallery, and hence, this large mismatch induces cleavage during the ion exchange process that creates nanorods (Figure 4). On the basis of the topotactic transformation of NH$_4$MPO$_4$·H$_2$O to NaMPO$_4$ (vide supra), the long axis of the NaMPO$_4$ nanorod must be either the $b$ or $c$ axis. Our TEM and electron diffraction studies (Figure 6a) reveal that the long axis of all the NaMPO$_4$ nanorods is the $b$ axis, which is the facile direction of ion transport for olivine materials.

However, the nanorod morphology can be altered by ball-milling the material, ideally with carbon, to enhance the conductivity of the material for use as a sodium-ion electrode. Elemental analysis carried out in the TEM using EDS confirmed that Mg and Ca were substituted into their respective Na$_{Mg0.2Mn0.8}$PO$_4$ and Na$_{Ca0.2Mn0.8}$PO$_4$ lattices (Figure 6b,c) in the targeted levels (see Figures 1S and 2S of the Supporting Information for expanded versions of the EDS spectra).

Table 1. Lattice Parameters of Na$_{1-x}$MPO$_4$ ($M = Fe$, Mn, Fe$_{0.5}$Mn$_{0.5}$, Mg$_{0.2}$Mn$_{0.8}$, Ca$_{0.2}$Mn$_{0.8}$) Compounds Obtained from Rietveld Refinement

<table>
<thead>
<tr>
<th>olivine</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>volume (Å$^3$)</th>
<th>$R_p$ (%)</th>
<th>$R_{wp}$ (%)</th>
<th>$R_F$ (%)</th>
<th>antisite mixing (%)</th>
</tr>
</thead>
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<tr>
<td>NaFePO$_4$</td>
<td>10.4207(5)</td>
<td>6.2167(2)</td>
<td>4.9529(2)</td>
<td>320.86(3)</td>
<td>4.91</td>
<td>7.42</td>
<td>9.08</td>
<td>–</td>
</tr>
<tr>
<td>NaMnPO$_4$</td>
<td>10.5578(3)</td>
<td>6.3359(2)</td>
<td>4.9966(2)</td>
<td>344.24(2)</td>
<td>5.32</td>
<td>6.99</td>
<td>5.62</td>
<td>1.9</td>
</tr>
<tr>
<td>NaFe$<em>{0.5}$Mn$</em>{0.5}$PO$_4$</td>
<td>10.4933(3)</td>
<td>6.2980(2)</td>
<td>4.9803(2)</td>
<td>329.03(3)</td>
<td>5.07</td>
<td>6.83</td>
<td>3.59</td>
<td>0.5</td>
</tr>
<tr>
<td>Na$<em>{0.3}$Fe$</em>{0.7}$Mn$_{0.7}$PO$_4$</td>
<td>10.2675(5)</td>
<td>6.0905(2)</td>
<td>4.9610(3)</td>
<td>310.24(2)</td>
<td>5.90</td>
<td>6.22</td>
<td>9.02</td>
<td>–</td>
</tr>
<tr>
<td>NaMg$<em>{0.2}$Mn$</em>{0.8}$PO$_4$</td>
<td>10.5183(3)</td>
<td>6.3083(1)</td>
<td>4.9841(1)</td>
<td>330.63(2)</td>
<td>6.00</td>
<td>7.60</td>
<td>5.03</td>
<td>0.9</td>
</tr>
<tr>
<td>NaCa$<em>{0.2}$Mn$</em>{0.8}$PO$_4$</td>
<td>10.62</td>
<td>6.38</td>
<td>5.02</td>
<td>340</td>
<td>6.80</td>
<td>7.60</td>
<td>5.03</td>
<td>–</td>
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$^a$ Cell parameters indexed using CRYSTAL.

Figure 4. Schematic diagram for the topochemical synthesis of crystalline NaMPO$_4$ nanorods.

Of significance is that although NaFePO$_4$ cannot be prepared directly by the molten salt method, this is easily accomplished for all of the NaMnPO$_4$ compounds (including substitution with 1/2 Fe and/or Mg). The olivine phase does convert to the more stable maricite phases at about 450 °C for NaFePO$_4$ at a higher temperature, about 500 °C for Na$_{[Fe0.5Mn0.5]}$PO$_4$, and at the highest temperature, about 550 °C for NaMnPO$_4$, as shown by XRD patterns (Figure 7). Thus, the olivine NaMPO$_4$ materials are metastable phases but are perfectly stable under normal operating conditions of an electrochemical cell containing a nonaqueous electrolyte.

Solid-State Chemistry of Na$_{[Mn1-xMg0.2]}$PO$_4$. Desodiation of olivine Na$_{[Fe0.5Mn0.5]}$PO$_4$ to form Na$_{0.5}$(Fe$_{0.5}$Mn$_{0.5}$)PO$_4$ and Na$_{0.3}$(Fe$_{0.5}$Mn$_{0.5}$)PO$_4$ surprisingly forms a single-phase composition as shown by XRD (Figure 8). The XRD peaks gradually shift to higher 2$\theta$ angles as the degree of Na extraction increases, and no evidence for a two-phase mixture of the end member phases is observed. The amount of desodiation was independently measured by EDS analysis (Figure 3S of the Supporting Information), confirming the expected decrease in Na content with increasing $x$ in Na$_{1-x}$(Fe$_{0.5}$Mn$_{0.5}$)PO$_4$. Formation of the single phase of Na$_{0.5}$(Fe$_{0.5}$Mn$_{0.5}$)PO$_4$ was confirmed by Rietveld refinement and gave good agreement factors as shown in Figure 9. The occupancy of Na was refined to be 0.509, very close to the target value. The Na$_{0.5}$(Fe$_{0.5}$Mn$_{0.5}$)PO$_4$ phase was stable under air at room temperature for more than at least two months, as shown by XRD (Figure 10).

The above is in strong contrast to the distinct two-phase behavior on delithiation observed for LiFePO$_4$ but similar to that...
observed for delithiation of Li(Fe$_x$Mn$_y$)PO$_4$ (i.e., $x = 0.6$, $y = 0.4$) to form Li$_{0.35}$(Fe$_{0.6}$Mn$_{0.4}$)PO$_4$ originally reported by Yamada et al.\textsuperscript{26} This has been studied theoretically by Ceder et al.,\textsuperscript{27} and experimentally confirmed by Molenda et al.\textsuperscript{28} for a composition very close to Li$_{0.35}$(Fe$_{0.6}$Mn$_{0.4}$)PO$_4$. However, the latter shows limited solid solution behavior, but Na(Fe$_{0.5}$Mn$_{0.5}$)PO$_4$ exhibits solid solution behavior over the full region. The volume difference between two phases is a critical factor to determine whether a solid solution is formed. On the basis of the Hume–Rothery rules for metals, the formation of a solid solution is unfavorable when the atomic radii of the solute and solvent atoms differ by more than 15%. In case of Na(Fe$_{0.5}$Mn$_{0.5}$)PO$_4$, the volume difference is 21%, which is much larger than the corresponding volume difference for LiFePO$_4$ (6.7%). Therefore, this phenomenon is not explained by the previous simple model. It seems that the driving force to make the solid solution is the interface stress caused by significant strain at the grain boundaries between Na-rich and Na-poor phases of Na$_{1-x}$(Fe$_{0.5}$Mn$_{0.5}$)PO$_4$. The interface effect on the formation of solid solutions in intercalation compounds has been suggested by Wagemaker et al.\textsuperscript{29} They showed the miscibility gap decreases as the size of Li$_2$TiO$_2$ nanoparticles decreases. It can be attributed to the energy penalty due to interface energy:

$$\Delta G_{\text{mix}}(X) = \frac{(x_2 - x)G_1 - (x - x_1)G_2}{x_2 - x_1} - \Delta G(X) + \frac{A(x)\gamma}{V_{Li}V}$$

where $A(x)$, $\gamma$, $V_{Li}$, $V$ are the area of the interface between the two phases 1 and 2, the interface energy, the (inserted) Li-ion molar volume, and the volume of the particle, respectively. The last term is related to the interface energy, and its effect becomes more dominant as particle size decreases, because $A(x)$ and $V$ scale with $r^2$ and $r^3$, respectively (where $r$ is the particle radius). Therefore, the energy gain due to phase separation, represented by the free energy of mixing $\Delta G_{\text{mix}}$ decreases for smaller particle sizes, resulting in the decrease in miscibility gap for Li$_2$TiO$_2$ nanoparticles. In the case of Na(Fe$_{0.5}$Mn$_{0.5}$)PO$_4$, the particle size is small. Conversely,
the interface energy, $\gamma$, is very high due to the high interface strain owing to the large size of the Na ion. Therefore, a single-phase regime is formed. The electrochemical data is in complete accord with a single-phase reaction (Figure 11), although kinetic limitations may induce a sloping voltage profile. This is currently under investigation in our laboratory.

Finally, as FePO$_4$ is partially sodiated, the XRD reflections for Na$_{1-x}$FePO$_4$ are noticeably shifted compared to NaFePO$_4$ but not continuously. We observe formation of a single phase on partial desodiation of NaFePO$_4$ to Na$_{1-x}$FePO$_4$ ($x \sim 0.4$) (Figure 12), although the substantial peak broadening, and appearance of a second phase (FePO$_4$) precluded Rietveld refinement of the structure. The new phase has very similar lattice parameters to that of recently reported Na$_{0.7}$FePO$_4$, whose refinement suggests is a very interesting single line phase. Our finding that it forms in equilibrium with the FePO$_4$ end member at intermediate values of $x$ fully supports that conclusion. Its formation may be attributed to subtle factors that drive interface strain between NaFePO$_4$ and FePO$_4$ and force cation ordering, forces that are clearly different than those that dictate single-phase formation in Na$_{1-x}$Mn$_{0.5}$Fe$_{0.5}$PO$_4$.

Figure 7. Olivine-to-marecite transition temperatures of NaMPO$_4$. XRD patterns of NaMPO$_4$ for M as indicated: (a) Fe, (b) Mn$_{0.5}$Fe$_{0.5}$, and (c) Mn) at various temperatures.

Figure 8. XRD patterns of Na$_{x}$Fe$_{0.5}$Mn$_{0.5}$PO$_4$ for varying degrees of $x$.

Figure 9. Rietveld refinement of Na$_{0.7}$FePO$_4$. Experimental points are in black. The fit is shown in red. Calculated reflections are in magenta. The difference map is shown in blue.
CONCLUSIONS

In summary, metastable olivine phases of crystalline Na-[Mn₁₋ₓMₓ]PO₄ (M = Fe, Ca, Mg) are formed by topotactic reactions using simple solid-state synthesis in molten salts at low (≤100 °C) temperatures. This is in contrast to the high-temperature synthesis of NaMnP₀₄, for example, which forms the electrochemically inactive maricite phase. Na₀.xFeₐₓM₀₋ₓP₀₄ exhibits a single-phase reaction on desodiation, not a two-phase reaction as in the case of LiFePO₄. Both nanorod formation and the solid solution behavior of Na₁₋ₓMₓP₀₄ are closely related to the large interface strain between the Na-rich and Na-poor phases due to the large size of the Na ion. Na₁₋ₓMₓP₀₄ exhibited reversible electrochemical de/intercalation, making these materials potentially interesting as cathode materials in sodium ion batteries. The detailed electrochemistry of the carbon-coated materials in the NaMPO₄ (M = Mn, Fe, Mg, Ca) family will be reported in a forthcoming publication with in situ and ex situ XRD analysis.

ASSOCIATED CONTENT

Supporting Information. EDS profile of Na₀.xM₀₋ₓM₀₋ₓPO₄, Na如下ₐₓM₀₋ₓP₀₄, and NaₓFeₓM₀₋ₓP₀₄; CIF files in tabular form; lattice constants and atomic parameters of NaFePO₄, NaMnP₀₄, Na₁₋ₓMₓPO₄, Na₁₋ₓ[Feₓ₋ₓM₀₋ₓ]PO₄, and Naₓ[Feₓ₋ₓM₀₋ₓ]PO₄ refined from powder XRD data. This material is available free of charge via the Internet at http://pubs.acs.org.

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