A High-Energy NASICON-Type Cathode Material for Na-Ion Batteries

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Over the last decade, Na-ion batteries have been extensively studied as low-cost alternatives to Li-ion batteries for large-scale grid storage applications; however, the development of high-energy positive electrodes remains a major challenge. Materials with a polyanionic framework, such as Na superionic conductor (NASICON)-structured cathodes with formula Na$_x$M$_2$(PO$_4$)$_3$, have attracted considerable attention because of their stable 3D crystal structure and high operating potential. Herein, a novel NASICON-type compound, Na$_4$MnCr(PO$_4$)$_3$, is reported as a promising cathode material for Na-ion batteries that deliver a high specific capacity of 130 mAh g$^{-1}$ during discharge utilizing high-voltage Mn$^{2+/3+}$ ($3.5$ V), Mn$^{3+/4+}$ ($4.0$ V), and Cr$^{3+/4+}$ ($4.35$ V) transition metal redox. In addition, Na$_4$MnCr(PO$_4$)$_3$ exhibits a high rate capability (97 mAh g$^{-1}$ at $5$ C) and excellent all-temperature performance. In situ X-ray diffraction and synchrotron X-ray diffraction analyses reveal reversible structural evolution for both charge and discharge.

1. Introduction

The abundance and widespread distribution of sodium make Na-ion batteries a significantly less expensive alternative to Li-ion batteries, which is particularly attractive for large-scale grid storage applications.[1] Nevertheless, to make Na-ion batteries competitive, the development of high-energy cathode materials is crucial.[2] Extensive efforts have thus been devoted to the investigation of Na-ion cathode materials, especially sodium-layered oxides and polyanionic compounds.[3] Despite the high specific capacity of layered compounds,[4] they often lack structural stability in the highly charged state and require a low discharge cutoff voltage to achieve enough capacity.[5] In contrast, polyanionic compounds usually have a 3D robust framework that provides better cycling stability and a flatter voltage profile compared with those of layered oxides. In addition, owing to the inductive effect of the polyanion group (e.g., (PO$_4$)$_3$$^{-}$, (P$_2$O$_7$)$_4$$^{-}$, and (SO$_4$)$_2$$^{-}$), a higher operating voltage can be achieved,[6] making these compounds interesting candidates for stable, high-energy-density cathode materials for Na-ion batteries.

The most studied polyanionic Na-ion cathode materials are the vanadium-containing phosphate Na$_3$V$_2$(PO$_4$)$_2$F$_3$ (NVP)[7,8] and the fluorophosphate Na$_3$V$_2$(PO$_4$)$_2$F$_3$ (NVPF).[9] NVPF has a theoretical capacity of 128 mAh g$^{-1}$ (two electrons per formula unit) at $3.9$ V, with specific energy reaching $500$ Wh kg$^{-1}$. Moreover, the electrochemical properties of NVPF can be tuned by substituting F anions by O, forming the complete solid solution Na$_3$V$_2$(PO$_4$)$_2$O$_2$F$_{1-y}$ (0 ≤ y ≤ 1).[10] For example, Bianchini et al. showed that at the low-voltage end, an additional Na can be inserted in Na$_3$V$_2$(PO$_4$)$_2$O$_2$F to produce Na$_4$V$_2$(PO$_4$)$_2$O$_2$F upon discharge, which enables three-electron cycling between Na$_3$V$_2$(PO$_4$)$_2$O$_2$F and Na$_3$V$_2$(PO$_4$)$_2$O$_2$F.[11] However, the extraction of the third Na from Na$_3$V$_2$(PO$_4$)$_2$O$_2$F to V$_2$(PO$_4$)$_2$F has not yet been demonstrated to be practical because of the high Na extraction potential (predicted to be ≈4.9 V), which is beyond the stability window of organic Na-ion electrolytes.[12] Cation substitution has been considered in an effort to lower this high Na extraction voltage; however, only a few metal cations, such as Al, can substitute for V in the NVPF structure, with their solubility limited to 0.2.[11,13]

NVP has a Na superionic conductor (NASICON)-type structure. Na-ion cathode materials with the NASICON structure tend to have high multielectron capacity, a stable framework, and fast Na diffusion.[14] NVP has the general chemical formula Na$_x$MM$'$(PO$_4$)$_3$, where M and M$'$ represent transition metals and x can vary between 1 and 4.[15,16] The 3D host framework of NVP is built up by interlinking [MO$_6$] octahedra and [PO$_4$] tetrahedra via corner-shared oxygen; the strong covalent bonding results in good thermal stability and long cycle life. This open framework also provides 3D channels for fast Na-ion diffusion, yielding excellent rate performance.[17,18] Numerous...
NASICON-type compounds with different metal cation combinations (V\textsubscript{2+}, Mn\textsuperscript{2+}, Mn\textsuperscript{3+}, Mn\textsuperscript{4+}, V\textsuperscript{3+}, V\textsuperscript{4+}, Cr\textsuperscript{3+}, Cr\textsuperscript{4+}, Ti\textsuperscript{3+}, Zr\textsuperscript{4+}, etc.) have been synthesized and studied,\textsuperscript{[15,16,19–24]} giving rise to a much more diverse chemical space and tunable electrochemical properties in contrast to NVPF. Though NASICON-type compounds have a large Na reservoir with potentially up to four extractable Na (i.e., a theoretical capacity of \( \approx 220 \) mAh g\textsuperscript{−1}), reversible extraction/insertion of more than 2Na can rarely be achieved. NVP delivers a discharge capacity of 110 mAh g\textsuperscript{−1} with an average voltage of 3.4 V based on the V\textsuperscript{3+/4+} redox. Partially substituting Al, Ga, or Cr for V can slightly increase the energy density by activating the high-voltage V\textsuperscript{4+/5+} redox;\textsuperscript{[8,21,22]} nevertheless, the capacity remains limited to a 2Na capacity. Replacing one V with Mn leads to another well-known NASICON-type compound, Na\textsubscript{4}Mn\textsubscript{V}(PO\textsubscript{4})\textsubscript{3} (NMCP), from which 3Na can be electrochemically extracted when charged to 4.3 V versus Na metal.\textsuperscript{[25,26]} However, a recent in situ X-ray diffraction (XRD) study performed by Chen et al. revealed that NMCP undergoes an irreversible structural change after 3Na deintercalation and that only \( \approx 2Na \) can be intercalated back, with poor cycling stability observed for the second and subsequent cycles.\textsuperscript{[25]} Other Mn-based NASICONs such as Na\textsubscript{3}MnZr(PO\textsubscript{4})\textsubscript{3} (NMZP) and Na\textsubscript{3}MnTi(PO\textsubscript{4})\textsubscript{3} (NMTU)\textsuperscript{[19,27]} exhibit stable cycling based on Mn\textsuperscript{2+/3+} and Mn\textsuperscript{3+/4+} redox; however, the theoretical capacities are also limited to 2Na because Zr and Ti are not electrochemically active at a useful cathode potential. Recently, Zhu et al. reported that NMTU can be initially discharged to 1.5 V, uptaking one more Na from the electrolyte/Na metal anode, with 3Na cycling achieved between the theoretically allowed voltages of Na\textsubscript{4}Mn\textsubscript{3+}Ti\textsuperscript{3+/4+} redox;\textsuperscript{[8,21,22]} therefore, the capacity remains limited to a 2Na capacity.

In this work, we computationally designed and experimentally synthesized a novel NASICON-type compound Na\textsubscript{4}MnCr(PO\textsubscript{4})\textsubscript{3} (NMCP), achieving for the first time reversible 2.35Na (de)intercalation at the highest average voltage (3.59 V) among NASICON-type cathode materials. Reversible transition metal redox (Mn\textsuperscript{2+/3+}, Mn\textsuperscript{3+/4+}, and Cr\textsuperscript{3+/4+}) is confirmed by X-ray absorption spectroscopy. Moreover, in situ XRD and synchrotron XRD analyses reveal a combined single-phase, two-phase, and single-phase reversible Na (de)intercalation mechanism during cycling of this novel NASICON-type compound.

**2. Results**

The feasibility of synthesizing the Mn/Cr-based NMCP was evaluated and compared with that of Na\textsubscript{3}MnM(PO\textsubscript{4})\textsubscript{3} (M = Ti and Zr) with the same NASICON structure using density functional theory (DFT) calculations. Ground-state phase diagram was computed by generating the respective quaternary convex hulls constrained with all the competing phases present in the Materials Project.\textsuperscript{[29]} The calculated phase stabilities are summarized in Table S1 (Supporting Information). The Mn/Cr-based NMCP compound has a relatively low energy above the hull (\( \leq 25 \) meV atom\textsuperscript{−1}) across the full Na\textsubscript{1}–Na\textsubscript{4} region, suggesting synthetic accessibility and good structural stability upon Na extraction/reinsertion. Figure 1 presents the DFT-calculated voltage profiles of Na\textsubscript{3}MnM(PO\textsubscript{4})\textsubscript{3} (M = Cr, Ti, Zr; \( x = 0, 1, 2, 3, \text{and } 4 \)) obtained using DFT calculations. The dashed lines are considered inaccessible voltages according to the phase stability analysis (Supporting Information).

The NMCP compounds were synthesized by mixing the precursors through a sol–gel method followed by preheating the product at 400 °C and annealing at 650 °C in an argon atmosphere (Experimental Section). The synchrotron XRD data for NMCP is presented in Figure 2a with no obvious impurity phases observed. The as-synthesized NMCP has the typical NASICON structure (Figure 2b) with rhombohedral space group R-3c and lattice parameters \( a = 1480.4(1) \) Å, \( b = 8.9228(5) \) Å, \( c = 21.471(1) \) Å as obtained from Rietveld refinement, yielding a volume \( V = 1480.4(1) \text{ Å}^3 \) per unit cell. The values of \( a \) and \( c \) are slightly smaller than those reported for NVMF,\textsuperscript{[16]} consistent with the smaller ionic radius of Cr\textsuperscript{3+} (0.615 Å) relative to that of V\textsuperscript{3+} (0.64 Å). There are two distinct sodium sites in the structure as shown in Figure 2b, the 6b site with sixfold coordination (Na\textsubscript{A}) and the 18e site with eightfold coordination (Na\textsubscript{B}). The Na occupancies obtained from the Rietveld refinement are 1 for Na\textsubscript{A} and 0.999 for Na\textsubscript{B} (Table S2, Supporting Information). The Na\textsubscript{A} vacancies obtained from the Rietveld refinement are 1 for Na\textsubscript{A} and 0.999 for Na\textsubscript{B} (Table S2, Supporting Information).})
The cycling performance of NMCP in different voltage windows is summarized in Figure 3c. When cycled between 1.5 and 4.5 V, the discharge capacity of NMCP fades to 90 mAh g\(^{-1}\) after 20 cycles, whereas the Coulombic efficiency gradually increases from 91% to 97%. The capacity retention can be improved by decreasing the high-voltage cutoff to 4.35 V (88% retention after 20 cycles), although the initial discharge capacity is reduced to 96 mAh g\(^{-1}\). These results indicate that the capacity fading of NMCP may originate from the capacity loss in the high-voltage region. At this point, we do not know if this capacity loss at high voltage is due to electrolyte failure or an intrinsic degradation of the material.

The Na diffusion kinetics of NMCP was investigated by means of the galvanostatic intermittent titration (GITT) and rate testing. Figure 3d presents the GITT curve for the second cycle. A small overpotential (20–30 mV) is observed during most of the charge and discharge, demonstrating good kinetics for Na diffusion, especially at high voltage when the composition has low Na content (red). A larger overpotential is present in the lower-voltage regions, marked by the orange and blue regions in the time versus voltage plot (inset) respectively. At the end of discharge, the overpotential for Na insertion is 324 mV, and 200 mV for Na extraction when the charge is started. The rate performance of NMCP was tested in a half-cell cycled between 1.5 and 4.5 V. As shown in Figure 3e, NMCP exhibits excellent rate capability with discharge capacities of 105 and 97 mAh g\(^{-1}\) at 2 and 5 °C, respectively, corresponding to 81% and 75% of the discharge capacity at C/20. Interestingly, the capacity loss at increased rate is mainly associated with the low-voltage region, and the high-voltage plateaus are better maintained upon increasing the current (Figure 3f). This rate test confirms the finding in the GITT experiment that Na diffusion kinetics is very good in the Na-deficient phase. Even though the cathode particles are microsized, this rate performance is comparable to that of other reported nanosized NASICONs.\(^{19,28,31}\)

The electrochemical performance of the NMCP|Na metal half-cell was then investigated at temperatures well above and below room temperature (RT). A capacity cutoff (100 mAh g\(^{-1}\), \(\approx\)2Na) was applied during charge to ensure that the samples at different temperatures were deintercalated to the same Na content, and a 1.5 V voltage cutoff was applied during discharge. The charge and discharge curves at \(-10, 20,\) and 50 °C in Figure 4a can be divided into a low-voltage region (\(\approx\)3.6 V) and a high-voltage region (\(\approx\)4.2 V). The capacity of the low-voltage region increases substantially with increasing temperature, whereas the trend for the high-voltage region is clearly reversed: from \(-10\) to \(20\) °C and then to \(50\) °C the charge capacity of the low-voltage region is extended, whereas the discharge capacity of high-voltage region is decreased. This observation suggests that at low temperature, during discharge, more capacity is delivered at high voltage. This finding is unusual as improved electrochemical performance is expected at high temperature because of the improved Na kinetics; however, the performance of NMCP at \(-10\) °C is as good as that at high temperature and even better in terms of energy density. The inset of Figure 4a clearly shows that the high-voltage discharge capacity at \(-10\) °C is almost twice that at \(50\) °C. Same behavior is observed using a 4.5 V voltage cutoff (Figure S5, Supporting Information). The cycling performance at \(-10, 20,\)
and 50 °C is summarized in Figure 4b. NMCP exhibits negligible capacity loss with nearly 100% Coulombic efficiency at all the temperatures after ten cycles, indicating its stable all-temperature electrochemical performance.

Because of the poor electrical conductivity of NMCP, the electrochemical performance is greatly affected by the carbon content. Cathode films with different carbon contents were prepared and tested under identical conditions (Figure S2, Supporting Information). As the active material:carbon:polytetrafluoroethylene (PTFE) ratio changes from 70:30:0 to 70:30:5 and then to 70:20:10, the discharge capacity first remains relatively constant from 131 to 130 mAh g⁻¹ and finally drops to 112 mAh g⁻¹, indicating that the electrical conductivity of the cathode composite is a limiting factor. Moreover, the largest discharge capacity, 131 mAh g⁻¹ (1.5–4.5 V) was achieved using a 70:30 active material to carbon ratio without any PTFE binder (Experimental Section), which is electronically insulating, yielding a high energy density of ≈470 Wh kg⁻¹.

X-ray absorption spectroscopy (XAS) analysis was conducted to investigate the redox mechanism of NMCP. Several ex situ samples were prepared at different charge and discharge states as shown in Figure S3 (Supporting Information). Figure 5a and Figure 5b show the X-ray absorption near-edge structure (XANES) for the Mn K-edge and Cr K-edge, respectively. Both the Mn and Cr K-edges shift to higher energy during charge and return almost to their initial positions when discharged.
back to 1.5 V, indicating that both Mn and Cr are electrochemically active and reversible during cycling. Specifically, Mn redox and Cr redox occur in sequence: Mn is only active from the open-circuit voltage (OCV) to somewhere between 3.9 and 4.3 V, as the Mn K-edge spectra at 4.3 and 4.5 V are almost identical. Cr is active from somewhere between 3.9 and 4.3 V to 4.5 V but not at lower voltage. While it is possible that within a small voltage region near 4.3 V, Mn and Cr redox could be both active, as the calculated voltages of Mn $^{3+/4+}$ and Cr $^{3+/4+}$ redox are extremely similar (Figure 1), it has been experimentally verified.

Figure 4. a) NMCP|Na metal half-cell cycled at −10, 20, and 50 °C at C/10. The charge capacity is limited to 100 mAh g$^{-1}$. The inset shows the discharge capacities of the high-voltage plateau cycled at different temperatures. b) Capacity retention of NMCP during first ten cycles at C/10. The charge capacity is limited to 100 mAh g$^{-1}$, and the voltage cutoff for discharge is 1.5 V.

Figure 5. XAS spectra of NMCP at different charge/discharge states: a) Mn K-edge shift and b) Cr K-edge shift. c) $k^2$-weighted Fourier transform magnitudes of Mn K-edge EXAFS spectra. d) Pre-edge feature of Cr K-edge.
reported that Cr redox in NASICON framework tends to be higher than Mn redox.\[20\] Therefore, it is likely that the Mn redox contributes to the first two plateaus in the charge profile (Figure 3a) of NMCP, whereas the Cr redox mainly contributes to the third. The capacities of the first two plateaus are almost equal to two electrons per formula unit, so it is plausible to assume that double redox Mn\(^{2+}/3^+\) and Mn\(^{3+}/4^+\) are active. This observation is also consistent with the computational predictions in Table S3 (Supporting Information), which indicate that Mn\(^{2+}/3^+\) and Mn\(^{3+}/4^+\) redox are active from Na\(^4\) to Na\(^2\) and that the Cr\(^{3+/4+}\) redox is active from Na\(^2\) to Na\(^1\).

The extended X-ray absorption fine structure (EXAFS) of Mn for samples at various charge states is presented in Figure 5c, where the first peak reflects the Mn–O bond length variation. As the pristine material is charged to 3.9 V, the first peak (Mn–O bond) shifts to the left and its intensity decreases. The reduced Mn–O bond length is consistent with the oxidation of Mn\(^{2+}\) to Mn\(^{3+}\), and the decrease in peak intensity can be attributed to the Jahn–Teller distortion of Mn\(^{3+}\) that reduces the octahedral symmetry. Upon charging from 3.9 to 4.3 V, the Mn–O peak intensity increases again, indicating restored octahedral symmetry and Mn\(^{3+}\) ion is oxidized to Mn\(^{4+}\). Note that the Mn–O peak position does not show obvious change between Mn\(^{3+}\) and Mn\(^{4+}\), which is consistent with several previous studies.\[21,32\] When the sample is further oxidized to 4.5 V, both the intensity and position of the first peak barely change, consistent with the conclusion from the XAS data in Figure 5a that Mn is not active at higher voltage (>4.3 V). The EXAFS spectrum of the sample after one cycle does not perfectly overlap with that of the pristine sample, indicating a slight change of the Mn local structure as not all the Na extracted during charge is intercalated back when the material is discharged to 1.5 V.

Figure 5d shows the variation of the Cr pre-edge feature, providing insight into the Cr oxidation state. The spectrum taken in the pristine state remains unchanged upon charge to 3.9 V with only a single peak at \(5590.05\) eV. Upon further charge to 4.3 V, another peak at higher energy appears and continues to grow before returning to the pristine spectrum after one cycle. This prominent pre-edge peak results from the 1s–3d quadrupole transition, indicating the existence of Cr\(^{6+}\).\[20\] As Cr\(^{6+}\) with the \(d^2\) electron configuration usually has a distorted octahedral symmetry, the probability of Cr–3d and O–2p orbital mixing increases, thus increasing the probability of a 1s–3d transition; this transition is forbidden when Cr is present as Cr\(^{3+}\) which has a symmetric octahedral coordination.\[33\] In addition, the intensity of this pre-edge peak is less than 10% of the edge height, as shown in Figure 5b, thereby excluding the existence of Cr\(^{6+}\), as tetrahedrally coordinated Cr\(^{6+}\) increases the pre-edge peak intensity dramatically (≈80% of the edge height). This pre-edge feature confirms that Cr is indeed oxidized to Cr\(^{6+}\) during charge.

To investigate the structural evolution during charge/discharge, in situ XRD analysis was performed and the results are plotted in Figure 6. The four observed peaks for the uncharged sample at \(x = 4\) can be assigned as the (024), (211), (116), and (300) Bragg peaks of the pristine NMCP. Between \(x = 4\) and \(x \approx 3.5\), all four peaks shift slightly toward higher angle with no additional peak emerging, indicating that in this composition range NMCP forms a solid solution. Between \(x = 3.5\) and \(x \approx 3.2\), Na is further extracted by a two-phase mechanism as evidenced by the discrete position change of the (024) and (116) peaks and the disappearance of the (211) and (300) peaks. In addition, a new peak appears at 16.2°. From \(x \approx 3.2\) to the top of charge, NMCP undergoes further single-phase desodiation since the (116) and (300) peaks continuously shift to higher angle, reaching a composition of Na\(^{1.75}\)MnCr(PO\(_4\))\(_3\) at 4.5 V. The discharge of NMCP follows the same but inverse sequence: single phase, two phases, and single phase. This reversible structural evolution is also observed for the subsequent cycle, as confirmed by the in situ diffraction data of two full cycles in Figure S4 (Supporting Information).

The structural evolution of NMCP was further studied using ex situ synchrotron XRD. Figure 7a presents the diffraction patterns of samples at different states of charge with the extracted lattice parameters summarized in Figure 7b. The patterns for the pristine sample and sample after one cycle are almost identical, except for a slightly lower intensity for the cycled sample. In the single-phase region, between \(x = 4\) and \(x \approx 3.5\), the lattice parameters \(a = b\) and \(c\) both decrease negligibly (\(|\Delta a/a| = 0.17\%, |\Delta c/c| = 0.37\%\), resulting in a small overall decrease in the unit cell volume (\(|\Delta V/V| = 0.7\%)\). The second phase appears at 3.9 V, of which the (2–10), (113), and (300) diffraction peaks are marked by the dashed line. They continue to shift to higher angle to the top of charge. Note that at 3.9 V, (2–10) and (104) peaks are so close to each other that they are not clearly distinguished. Upon further Na removal, (2–10) peak shifts to higher angle faster than (104) peak. As a consequence, two peaks are observed separately at 4.5 V. In this region, NMCP endures a slightly larger lattice change, with the \(a\) and \(b\) lattice parameters decreasing (\(|\Delta a/a| = 1.18\%\)) and the \(c\) lattice parameter increasing (\(|\Delta c/c| = 1.85\%\)). The increase in \(c\) lattice parameter is prominent between \(x = 2\) and \(x = 1\) (Figure 7b), indicating that the third Na is likely extracted from the Na\(^1\) site (Figure 2b) where the absence of Na leads to large electrostatic repulsion between adjacent \([\text{Mn/Cr}]\text{O}_6\]
3. Discussion

The NASICON structure is able to accommodate different transition metal cations and is synthetically accessible with various Na contents, leading to a rich chemical space and tunable electrochemical performance.[16,18,22,23,34] Among all the redox-active metals, V and Mn have been favored because they can provide double redox at high voltage (V^{3+}/V^{4+} and M^{2+}/M^{3+}). However, reversible 3Na (de)intercalation has not been possible in NMTP, Ti^{3+}/Ti^{4+} the reduction potential of the active metals, V and Mn have been favored because they can utilize Mn^{2+/3+} redox, have also been considered; however, they also require an additional Na source in a full cell to use Mn^{3+/4+}. In addition, it is relatively difficult to synthesize NASICON compounds with Mn^{3+} rather than with Mn^{2+} in the pristine material because of the reducing environment from the carbon source used during the synthesis created. 3) Finally, Na_{4}Mn_{2}(PO_{4})_{3} can be considered; this compound type can use M_{n}^{2+/3+}, M_{n}^{1+/2+}, and M^{3+/4+} redox, and the pristine material contains 4Na, which is optimal for achieving electrode balance in the full cell. Therefore, a NASICON-type compound with the composition Na_{4}Mn_{2}(PO_{4})_{3}, in principle, has three-electron redox at high voltage, and the trivalent metal can be Cr^{3+/4+}, Fe^{3+/4+}, Co^{3+/4+}, or Ni^{3+/4+}. The redox potentials of Co^{3+/4+} and Ni^{3+/4+} might be too high to access in the poly-anionic framework[35] and the Fe^{3+/4+} redox potential is around 3 V which is less attractive.[36] Cr^{3+/4+} redox has been demonstrated to occur ~4.5 V in NASICON-type Na_{2}Cr_{2}(PO_{4})_{3}, which is within the electrolyte stability window, though significant capacity decay is observed in this compound.[28] However, in this work we demonstrate that based on the synergetic effect of Mn and Cr, Na_{2}MnCr(PO_{4})_{3} achieves a reasonable cyclability at a high operating voltage, and the highest energy density among all reported NASICON-type Na-ion cathodes (Figure 8).

It is instructive to compare NMCP with another Mn^{2+}, M^{3+} compound in this category, NMVP. Although NMVP also has enough redox-active transition metal, it experiences an irreversible phase transformation when the third Na is extracted,[25] evidenced by the asymmetry behavior in the charge and discharge. A single-phase as well as two-phase structural transformation occurs in sequence in the charge of NMVP, whereas the discharge follows a single solid-solution mechanism with no two-phase region being observed. This structural irreversibility results in a low Coulombic efficiency of ~74%, and the subsequent charge and discharge of NMVP occur via a single solid-solution mechanism with significant capacity fade.[25] In contrast, we observe in the present work that NMCP has a symmetric voltage profile, i.e., the charge and discharge curves both have three distinct plateaus, with the solid-solution and

![Figure 7](image-url)
two-phase reactions reversibly taking place during charge and discharge. This reversible structural evolution leads to a larger discharge capacity (130 mAh g\(^{-1}\)) at high voltage and higher Coulombic efficiency (\(-91.5\%\)) compared with NMVP. Our ex situ synchrotron XRD results also suggest that NMCP undergoes less volume change from Na\(_2\) to Na\(_1\) than NMVP (NMCP: \(\Delta a/a = 1.18\%; \Delta c/c = 1.8\%;\) NMVP: \(\Delta a/a = 6.1\%; \Delta c/c = 2.4\%\)).

Because capacity fading is observed for both NMCP and NMVP after the extraction of 3Na, we computationally investigate the structural stability of the NASICON framework in the highly desodiated state by calculating the energy penalty of transition metal (TM) migration at a Na content of \(x = 1\). As shown in Table S4 (Supporting Information), the calculated energy penalty associated with the migration of a Cr\(^{4+}\) (V\(^{3+}\)) cation to the adjacent unoccupied Na\(_2\) site (Figure 2b) is 2.47 eV per defect (3.01 eV per defect), which is much higher than the M defect formation energy in layered Na\(_x\)MO\(_2\) materials, which are known to suffer from structure instability at high voltage due to TM migration.\(^{[17]}\) In addition, having Na reoccupied the TM site (TM/Na antisite) does not necessarily reduce the energy penalty. Our calculation suggests that TM migration is unlikely in the NASICON structure even at Na content \(x = 1\); therefore, the origin of capacity fading at high voltage requires further investigation.

The electrochemical tests at various temperatures indicate that NMCP has a higher energy density at \(-10^\circ\)C than at RT and 50 °C if a capacity cutoff of 100 mAh g\(^{-1}\) is applied. This difference is observed because the temperature affects the capacity from the low-voltage and high-voltage regions differently, i.e., during discharge, low temperature increases the high-voltage capacity but decreases the low-voltage capacity. Figure 9a presents the voltage profile of the first two cycles of NMCP at 50 °C followed by a third cycle at 9 °C. Although the high-voltage discharge region is shortened at 50 °C, the capacity is regained during the following cycle at 9 °C, indicating that the high-voltage capacity reduction occurring at 50 °C is not an irreversible process. Ex situ XRD patterns of NMCP cycled at 50 and 9 °C are presented in Figure 9b, with no obvious difference observed at the top of charge, i.e., the charged crystal structures at 50 and 9 °C are the same. This observation indicates that the different voltage profiles may result from the different Na (de) intercalation pathways at various temperatures rather than to any structural aspect at the top of charge. As revealed by the in situ diffraction results, the Na (de)intercalation mechanism differs at the two plateaus: for the low-voltage plateau, NMCP is desodiated via a two-phase reaction, whereas a solid-solution mechanism is observed for the high-voltage one (Figure 6) so that it should probably be referred to as a “pseudoplateau” consistent with the fact that the GITT-relaxed voltages in this region are not constant (Figure 3d). As a two-phase reaction occurs through the nucleation and motion of an interface, extra kinetic barriers need to be overcome. High temperature will accelerate the nucleation and growth as these processes have a higher activation energy than diffusion, resulting in the elongation of the two-phase region (low-voltage region). Figure 9a clearly shows that the voltages in the low-voltage region at 50 °C are constant (two-phase reaction), while they do not become constant (solid solution) at 9 °C. Malik et al.\(^{[38]}\) report a similar behavior of LiFePO\(_4\) cathode, of which a nonequilibrium single-phase delithiation pathway is triggered by high rate to bypass...
the equilibrium two-phase reaction. However, in our case, direct evidence such as in situ XRD at various temperatures is needed to confirm this speculation. We also plot in Figure S5 (Supporting Information) the voltage profile of NMCP cycled at low temperature (9 °C) and high temperature (50 °C) using a voltage cutoff (1.5–4.5 V). Though the charge capacity at high temperature is substantially larger than that at low temperature, the discharge capacities are similar because high temperature introduces more capacity degradation at high voltage.

In conclusion, we computationally predicted the phase stability and voltage profile of a novel NASICON-type compound, Na4MnCr(PO4)3, which is synthesized via a sol-gel-assisted solid-state method. Electrochemically, NMCP delivers a capacity of 130 mAh g\(^{-1}\) when cycled between 1.5 and 4.5 V, with a high energy density of 470 Wh kg\(^{-1}\). XAS analysis revealed a reversible redox mechanism based on Mn\(^{2+/3+}\), Mn\(^{3+/4+}\), and Cr\(^{3+/4+}\) redox. Reversible and symmetric structural evolution during cycling was confirmed using in situ XRD and ex situ synchrotron XRD. The compound also has the remarkable property that it delivers higher energy density at low temperature than at high temperature.

4. Experimental Section

First-principles calculations were performed using DFT as implemented in the Vienna ab initio simulation package.\cite{Si2010} A kinetic energy cutoff of 520 eV was selected for the plane-wave basis set, and a \(2 \times 2 \times 1\) k-point grid was used in all the calculations. The Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) exchange-correlation functional with the rotationally invariant scheme of Hubbard-U correction\cite{PBE1996} was applied to calculate the voltages. The values of \(U_{\text{eff}}\) = 5.09 and 3.7 eV were employed for Mn and Cr, respectively, consistent with previous ab initio studies of the intercalation voltage of MnZr NASICONs and Mn phosphates.\cite{MnNASICON1999,MnPO42006} Desodiated structures with Na/vacancy ordering were prescreened using an electrostatic energy criterion followed by DFT geometry optimizations. Na ions were extracted in the sequence from three Na ions at the Na2 sites to one Na ion at the Na1 site, which was consistent with previous findings in other NASICON structures.\cite{Li2019,MnNASICON1999}

**Material Synthesis:** \(\text{Na}_4\text{MnCr(PO}_4\text{)}_3\) was synthesized via a sol-gel-assisted solid-state method. First, manganese(II) acetate tetrahydrate (Aldrich, 99%) and chromium(III) nitrate nonahydrate (Sigma-Aldrich, 99%) in a 1:1 ratio were dissolved in deionized water. Then, citric acid (Sigma-Aldrich, 99.5%) was added using a 3:2 (transition metal) ratio. The solution was heated at 60 °C for 2 h with magnetic stirring before stoichiometric amounts of sodium phosphate monobasic (Sigma-Aldrich, ≥99%) and sodium acetate (Sigma-Aldrich, ≥99%) were added sequentially to the solution, which was then thoroughly stirred at 90 °C overnight to evaporate the solvent. The resulting gel-like mixture was collected, ground, and fired at 400 °C for 6 h in argon and then re-ground and fired at 650 °C for 8 h in argon.

**Structural Characterization:** High-energy X-ray powder diffraction data were collected at beamline 6-ID-D at the Advanced Photon Source, Argonne National Laboratory with a wavelength of \(\lambda = 0.1236\ \text{Å}\). The samples were sealed in Kapton capillaries with the measurements performed using a 0.1 s exposure time for 30 s. Ex situ synchrotron XRD samples were prepared using a 70:30 ratio of active material:Csp:PTFE and cycled to various states of charge at C/20 before the powder was recovered, washed, centrifuged, and collected. Lab XRD data were collected using a Rigaku MiniFlex 600 diffractometer. Data analysis was performed using Rietveld refinement\cite{Tamura1998} (as-synthesized material) and the Le Bail method\cite{Kumagai2007} (ex situ samples) using FullProf software.\cite{Kumagai2007} Structure visualization was performed with VESTA.\cite{Momma2011}

**SEM images were captured using a Zeiss Gemini Ultra-55 analytical field-emission microscope at the Molecular Foundry at Lawrence Berkeley National Laboratory.**

**High-angle annular dark-field scanning transmission electron microscopy and EDX mapping were performed using an FEI TitanX 60–300 at the Molecular Foundry at Lawrence Berkeley National Laboratory.**

**XAS data were collected at beamline 20 BM at the Advanced Photon Source, Argonne National Laboratory. Samples were prepared with a 70:30:5 active material:Csp:PTFE ratio and cycled to various states of charge at C/20 before the powder was recovered, rinsed, and collected. All the samples were sealed with Kapton tape for XAS measurements. Data reduction, normalization, and analysis were performed using the Demeter package.\cite{Kumagai2007}**

In situ electrochemical tests were performed with a customized cell with a beryllium window allowing X-ray penetration. The experiments were conducted on a Bruker D8 diffractometer using Bragg–Brentano geometry with Mo K\(\alpha\) radiation. Each scan was performed for 1 h while the cell was cycled at C/24 for two full cycles.

**Electrochemical Methods:** To prepare the cathode film, the \(\text{Na}_4\text{MnCr(PO}_4\text{)}_3\) powder and carbon black (Timcal, Super P) were mixed using a Fritsch Pulverisette ball mill (with one steel sphere) for 20 min at 20 s\(^{-1}\). The powder was then recovered and PTFE (Dupont, Teflon SC) was added and mixed using a mortar and pestle before the sample was rolled into a thin film inside an argon-filled glove box. The weight ratio of active material:Csp:PTFE was 70:30:5. To assemble a coin cell for electrochemical tests, 1 m \(\text{NaPF}_6\) in a 1:1 solution of ethylene carbonate (Sigma-Aldrich, 99%, anhydrous) and diethyl carbonate (Sigma-Aldrich, ≥99%, anhydrous) was used as the electrolyte, and Na metal was used as the negative electrode. The CR2032 coin cells were assembled inside an argon-filled glove box and tested on an Arbin instrument at room temperature in galvanostatic mode.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

Na-ion batteries, Na-ion cathode materials, NASICON