Revealing High Na-Content P2-Type Layered Oxides as Advanced Sodium-Ion Cathodes

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DOI 10.1021/jacs.9b13572

Publication date 2020

Document Version Final published version

Published in Journal of the American Chemical Society

Citation (APA) Zhao, C., Yao, Z., Wang, Q., Li, H., Wang, J., Liu, M., ... More Authors (2020). Revealing High Na-Content P2-Type Layered Oxides as Advanced Sodium-Ion Cathodes. Journal of the American Chemical Society, 142(12), 5742-5750. https://doi.org/10.1021/jacs.9b13572

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1. INTRODUCTION

Sodium (Na)-ion batteries (NIBs) have been gaining much attention in the battery field, both academic and industrial, owing to their potential application in large-scale electrical energy storage systems (EESs).1−3 Significant efforts have been made in finding suitable electrode materials with desired properties and the determination of structure−property relationships. Because of the large compositional diversity of the structural chemistry, layered oxides are considered as one of the most important electrodes families for NIBs, where the electrochemical performance can be tailored via the introduction of different elements in the hosts.

Na-based layered oxides with the general formula of Na_xTMO_2 (TM: transition metal) can be categorized into two main structures, O3- and P2-type phases, unlike the layered electrodes of Li-ion batteries (LIBs), which mostly crystallize in the O3-type structure. O represents that Na ions at trigonal prismatic (P) sites; the number 2 or 3 represents the number of edge-sharing TMO_2 octahedra with the oxygen stacking in ABBAB or ABCABC packing (Figure S1), respectively.4 It is noteworthy that these layered oxides often experience detrimental phase transitions between O- and P-type structures during the charge−discharge process, making it a challenge to realize good cycling performance. Compared to the O3-type framework, the P2 structure enables the fast Na^+ diffusion owing to the open prismatic diffusion pathways between the TMO_2 slabs shown in Figure S1.5,6 This provides the opportunity to achieve high cycle/rate capabilities. However, it is established that P2-type electrodes usually deliver a low initial charge capacity of ~80 mAh g^-1 below 4.0 V^-1 below, or a low average voltage 125,17 (Figure S2a). Additionally, they suffer from the detrimental phase transition from P2 to O2 or OP4/2 Z phases upon charging (desodiation) in Figure 1a, which compromises the cycling stability.7,9,12,15,18

In order to enhance the properties of P2-type materials, ion-substitution and/or doping, with Li^+, Mg^2+, Al^3+, Ti^4+, and Zn^2+, having no or fully occupied d orbitals and Cu^2+ inducing the Jahn−Teller effect,13 are widely used to alleviate the structural instability. For example, it has been demon...
stratized that using 0.05 mol Mg substituting Ni in Na2/3Ni1/3Mn2/3O2 can inhibit the global O2 phase transition to some extent, but instead a local OP4/Z′ phase transition is induced.13 On the other hand, to obtain an increased charge capacity of >100 mAh g−1 below 4.0 V, the TM2+x-based P2-type oxides with TMs, such as Mn3+,12 Fe3+,9 and Co3+,23 have been studied. However, the redox potential of these P2-type cathodes is generally lower than 3.0 V, compromising the overall energy density of the battery, and they often suffer from structural transitions in both the high-voltage (P2 to O2, OP4/X′) and low-voltage (P2 to P2′) regions. Another disadvantage is that these materials are often sensitive to water and moisture in air.24 From the above, it is clear that it is challenging to realize all demands simultaneously, for which more fundamental understanding is crucial.

A key factor in structural stability of the P2 host is the Na content. Na+ shields the electrostatic repulsions between the TMO2 slabs, in which during the desodiation in the charge process, the decreased shielding of Na+ will drive the gliding of the TMO2 slabs, resulting in the structural transition between the P- to O-type stackings. Therefore, if more Na can be retained in the NaO2 slabs to prevent the structure transition, while reaching or exceeding the capacity of low Na-content P2 materials (x = 2/3).

To achieve high Na-content P2 materials, we pursue the following rational design strategy. Based on our understanding of Na-ion intercalation chemistry,25 the ratio between the interlayer distances of d(O–Na–O) and d(TM–O) can be used as an indicator to distinguish structural competition between P2- and O3-type layered Na-ion oxides. The interlayer distance d(O–Na–O) is the average perpendicular distance between the two oxygen sheets enclosing Na ions, and the interlayer distance d(TM–O) is the perpendicular distance of two parallel sheets containing transition metal (TM). This interlayer distance is a result of the interactions of electrostatic cohesion forces and electrostatic repulsive forces between the NaO2 layers and TMO2 slabs. As for the high-Na P2-type oxides, the interlayer distance d(TM–O) is the determining descriptor, a potential strategy is to substitute TMs in NaTMO2 with cations having a smaller ion-size and higher oxidation state to reduce its value. Following this strategy, we used P2-type Na2/3Ni1/3Mn2/3O2 as a starting model, which features a large fraction of Mn4+ in the host, having a small ion radius of R(Mn4+) = 0.64 Å. It represents a typical low Na content (x = 2/3) electrode, exhibiting a low initial charge capacity of ~80 mAh g−1 below 4.1 V accompanied by the detrimental P2 to O2 phase transition.25 In this work, the Na content in the P2 material was systematically varied from 2/3 to 1 mol per unit by introducing different elements into the pristine structure, such as Li+, Mg2+, Cu++, Mn2+, Fe3+, and Ti4+, to substitute the Mn4+/Ni2+. Through this approach, several high Na-content materials were obtained with a Na content between 42/54 to 45/54 mol per unit.

2. RESULTS

2.1. Structural Analysis. In this work, Na45/54Li4/54Ni16/54Mn34/54O2 was prepared based on the known P2-type Na2/3Ni1/3Mn2/3O2 through the same synthesis method (see Methods in the Supporting Information). In this as-prepared material, 34/54 mol Mn ions and 16/54 mol Ni ions exist in the tetravalent state and divalent state, as in the Na2/3Ni1/3Mn2/3O2 material. Ni2+ is used as a redox center due to the relatively high redox potential and promising two-electron transfer reaction of Ni2+/Ni4+. A large amount of Mn4+ is used as the structure former for its high abundance. The small fraction of Li+ allows an increase in Na composition to balance the charge. Inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis confirms the composition of Na0.85Li0.15Ni0.33Mn0.62O2 (Table S1). The morphology of this as-prepared material is characterized by scanning electron microscopy (SEM) (Figure S3), displaying platelike particles with a distribution of sizes in the range of 8–12 μm. The crystal structure and phase purity were evaluated by Rietveld refinement analysis of the X-ray diffraction (XRD) pattern presented in Figure 2a. All the diffraction peaks can be indexed by the hexagonal structure with the space group of P63/mmc, reflecting the disordered Ni/Mn distribution. Crystallographic data, atomic coordinates, occupancies, and anisotropic displacement parameters of this structure are listed in Tables S2 and S3. Compared to the lattice parameters of Na2/3Ni1/3Mn2/3O2 (a = 2.885 Å, c = 11.155 Å), those of
measured to be \( \sim 0.558 \) nm, which corresponds to the interlayer distance from the XRD refinement. Atomic-scale STEM image and electron energy loss spectroscopy (EELS) mappings of this P2-type material were carried out to confirm the elemental distribution, and the corresponding elemental mappings of Na, Mn, Ni, and O are exhibited in Figure 2c. TM sites are occupied by Mn and Ni in a disordered arrangement, while Na locates in the sites between the TMO2 layers.

### 2.2. Prediction of the Stability of the High Na-Content P2-Type Oxide

First-principles density functional theory (DFT) calculations are used to explore the range of Na content in P2-type Na\(_{12}\)LiNi\(_3\)Mn\(_8\)O\(_{24}\) oxide. We first study the Li/Mn/Ni ordering in the TM layer with a fully occupied Na layer (composition NaLi\(_{1/12}\)Ni\(_{1/4}\)Mn\(_{2/3}\)O\(_2\)). A P2-NaTMO2 supercell with 12 metal sites was built, resulting in 910 symmetrically inequivalent configurations for the Li:Ni:Mn ratio in 1:3:8. The total energies of these configurations were evaluated, and the one with the lowest energy is selected as the ground state of Na\(_{12}\)LiNi\(_3\)Mn\(_8\)O\(_{24}\) as shown in Figure 3a. Using the as-identified Na\(_{12}\)LiNi\(_3\)Mn\(_8\)O\(_{24}\) structure, we then explored symmetrically inequivalent Na/vacancy configurations at Na sites in the Na\(_{12}\)LiNi\(_3\)Mn\(_8\)O\(_{24}\) configuration for different compositions (Na/vacancy ratios).

Figure 2. Structural characterization of the high Na-content P2 type oxide. (a) Rietveld refinement of X-ray diffraction (XRD) pattern of Na\(_{45/54}\)Li\(_{4/54}\)Ni\(_{16/54}\)Mn\(_{34/54}\)O\(_2\) \( (a = 2.89058(7) \) Å, \( c = 11.07541(18) \) Å), with the inset showing the enlarged pattern of the (002) peak. (b) Atomic-resolution high-angle annular dark field (HAADF) and annular bright field (ABF)-scanning transmission electron microscopy (STEM) images at the [010] zone axis. The scale bar is 1 nm. (c) Electron energy loss spectroscopy (EELS) mappings of Na, Mn, Ni, and O elements.

### References

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Na–Li–Ni–Mn–O phase diagram (in Figure S5), which demonstrates an energy of ~1.68 eV/atom lower than the combination of stable phases: NaMnO$_2$ + Li$_2$MnO$_3$ + Na$_2$Mn$_3$O$_7$. Na$_2$O$_2$ + NaNiO$_2$. The predicted stability of the P2-type phase indicates the feasibility of preparing this material.

2.3. Electrochemical Performance. As shown in Figure 4a and b, this high Na-content P2-type cathode delivers a highly reversible capacity of ~102.5 mAh g$^{-1}$ in the voltage range of 2.0–4.0 V, exceeding that of ~82 mAh g$^{-1}$ for P2-type Na$_{2/3}$Ni$_1/3$Mn$_{2/3}$O$_2$. In Na$_{2/3}$Ni$_1/3$Mn$_{2/3}$O$_2$, the initial charge capacity has been demonstrated to originate from the single combination of stable phases: NaMnO$_2$ + Li$_2$MnO$_3$ + Na$_2$Mn$_3$O$_7$ + Na$_2$O$_2$ + NaNiO$_2$. The capacity is normalized by that of 3.0 C. Above 70% capacity is retained up to 2500 cycles with approximate 99.9% Coulombic efficiency (CE), but the CE is found to be unstable in the following cycles; after 3000 cycles, ~68% capacity is remained.

Figure 4. Electrochemical performance of this high Na-content P2-type cathode. Galvanostatic charge–discharge curves of (a) Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ and (b) Na$_{45/54}$Li$_{4/54}$Ni$_{16/54}$Mn$_{34/54}$O$_2$ electrodes at a rate of 0.15C (corresponding to ~22 mA g$^{-1}$) in the voltage range of 2.0–4.0 V vs Na$^+$/Na. (c) Rate capability of Na$_{45/54}$Li$_{4/54}$Ni$_{16/54}$Mn$_{34/54}$O$_2$ from 0.1C (16 mA g$^{-1}$) to 20C (3200 mA g$^{-1}$). (d) Discharge capacity retention of Na$_{45/54}$Li$_{4/54}$Ni$_{16/54}$Mn$_{34/54}$O$_2$ with the first three cycles at 0.1C (18 mA g$^{-1}$) and following cycle at 3.0C (540 mA g$^{-1}$). The capacity is normalized by that of 3.0C. Above 70% capacity is retained up to 2500 cycles with approximate 99.9% Coulombic efficiency (CE), but the CE is found to be unstable in the following cycles; after 3000 cycles, ~68% capacity is remained.

Figure 5. Desodiation process and redox sequence during the first charging process. (a) Galvanostatic charge–discharge curves of Na$_{45/54}$Li$_{4/54}$Ni$_{16/54}$Mn$_{34/54}$O$_2$ at a rate of 0.15C in the voltage range of 2.0–4.60 V. (b,c) Calculated formation energy of desodiation structures of the Na$_{10}$Li$_{3}$Ni$_{3}$Mn$_{8}$O$_{24}$ (0 ≤ x ≤ 7) convex hull and the corresponding voltage profile during the desodiation process in Na$_{45/54}$Li$_{4/54}$Ni$_{16/54}$Mn$_{34/54}$O$_2$. (d,e) Magnetization and oxidation state evolution during the desodiation process of Ni and O ions in intermediate phases from Na$_{10}$Li$_{3}$Ni$_{3}$Mn$_{8}$O$_{24}$ to Na$_{10}$Li$_{3}$Ni$_{3}$Mn$_{8}$O$_{24}$. Electronic structure evolution on partial density of states (pDOS) of the Ni 3d $e_g^*$, Mn 3d $t_{2g}$, and O 2p orbitals of $x = 0$ (f), 5 (g), and 7 (h) in Na$_{10}$Li$_{3}$Ni$_{3}$Mn$_{8}$O$_{24}$. The Fermi energy is set to 0 eV. Insets show the isosurface of the charge density for the lowest unoccupied states of different desodiated states.

it is worth noting that ~0.58 mol Na$^+$ is still lower than the maximum capacity from the two-electron transfer of 16/54 (~0.296) mol Ni$^{2+}$ to Ni$^{4+}$ per unit of Na$_{45/54}$Li$_{4/54}$Ni$_{16/54}$Mn$_{34/54}$O$_2$. To examine the origin of the charge compensation during the electrochemical desodiation, the formation energy during the charge process is evaluated as plotted in Figure 5b and c. Based on the calculated formation energies, the obtained voltage is in good agreement with the experimental observations. To obtain more insights into the redox activity, the magnetization of Ni and O ions is determined from DFT calculations, shown in Figure 5d and e, in which the number of unpaired electrons denote the
oxidation states of the ions. Two intermediate phases are highlighted, \( x = 5 \) and 7 in Na\(_{x}\)-LiNi\(_3\)Mn\(_8\)O\(_{24}\) where \( x = 5 \) corresponds to the cutoff voltage at 4.0 V, and \( x = 7 \) at 4.60 V. Further Na deintercalation at higher potentials is not investigated due to the limited oxidation stability of the electrolyte. The calculated magnetization of Mn ions (Figure S8) indicates that Mn\(^{4+}\) does not participate in the redox reaction. It has recently been reported that Mn\(^{4+}\) can be oxidized to Mn\(^{5+}\) with the migration of Mn from octahedral sites to tetrahedral sites during the charge process, although no evidence of this was found in the current system.

Upon desodiation of Na\(_{x}\)-\(0.5\) LiNi\(_3\)Mn\(_8\)O\(_{24}\) (\( 0 \leq x \leq 5 \)), Ni magnetization first decreases from 1.78 \( \mu_B \) (bohr magneton) to 1.077 \( \mu_B \) at \( x = 3 \), corresponding to the oxidation from Ni\(^{2+}\) to Ni\(^{3+}\). Meanwhile, the O magnetization maintains a value between 0.028 and 0.112 \( \mu_B \) which indicates a relative constant redox state of the O\(^{2-}\) anion. This is also reflected by the partial density of states (pDOS) of the O 2p and Ni 3d orbitals shown in Figure S5f, in which Ni 3de\(_{g}\) orbitals have a much larger contribution to the valence band below the Fermi level (\( E_F \)) than the Mn 3d and O 2p states. Further desodiation to Na\(_{x}\)LiNi\(_3\)Mn\(_8\)O\(_{24}\) (\( x = 5 \)), the decreased Ni magnetization indicates that all Ni\(^{2+}\) ions are oxidized to Ni\(^{3+}\) and 1/6 Ni\(^{3+}\) is further oxidized to Ni\(^{4+}\). Meanwhile, the O ions remain in the O\(^{2-}\) state where O magnetization retains a value between 0.002 and 0.158 \( \mu_B \). Based on the above results, the desodiation results in partial oxidation of Ni\(^{2+}\) to Ni\(^{4+}\) below charging to 4.0 V.

Upon further desodiation from Na\(_{x}\)LiNi\(_3\)Mn\(_8\)O\(_{24}\) (\( x = 5 \)) to Na\(_{x}\)Li\(_{1-x}\)Ni\(_3\)Mn\(_8\)O\(_{24}\) (\( x = 7 \)), about 1/12 of O ions display an increase in the magnetic moment to 0.35 \( \mu_B \). However, the Ni magnetization shows the opposite trend, indicating that Ni\(^{4+}\) is increased while O\(^{2-}\) is oxidized. This suggests that there is a small amount of electron transfer from O\(^{2-}\) to Ni\(^{4+}\) at higher voltages (>4.2 V).\(^{34,35}\) This internal interaction between O\(^{2-}\) and Ni\(^{4+}\) limits additional charge compensation and thus a higher capacity. Comparing the contributions of the O 2p and Ni 3de\(_{g}\) orbitals, it is observed that the latter still dominates the valence band immediately below the Fermi level (\( E_F \)).\(^{34,35}\) This implies preferential electron extraction from Ni during charge (Na\(_{x}\)-\(0.5\) LiNi\(_3\)Mn\(_8\)O\(_{24}\); 5 \( \leq x \leq 7 \)). On the other hand, during further desodiation, the Ni 3d states and O 2p states increasingly overlap near the \( E_F \) level in the valence band, as shown in Figure S5h.

Soft X-ray absorption spectroscopy (XAS), which can probe the bulk material up to a depth of 1–100 nm,\(^{36}\) has been widely used to investigate charge compensation mechanisms in electrode materials. Ni L-edge spectra of partial fluorescence yield (PFY) mode measurements were carried out at different states of charge (SOCs) shown in Figure S9. The split high-energy (\( L_3\)-high) and low-energy (\( L_2\)-low) features of the pristine spectrum demonstrate that Ni ions are in the divalent state, consistent with previous reports.\(^{37}\) During the desodiation process, both Ni \( L_3\) and \( L_2\)-edge sXAS spectra shift toward higher energies, which indicates that the Ni oxidation states increases. When increasing the potential from 3.5 to 4.0 V, the \( L_3\)-high and \( L_2\)-high features increase further, which indicates a mixture of Ni\(^{3+}\) and Ni\(^{4+}\) states.\(^{37,38}\) Furthermore, at the SOC corresponding to 4.60 V, a delocalized hole density is found near the O orbitals surrounding Ni\(^{3+}\) and Ni\(^{4+}\), which suggests the existence of the itinerant bands with a mixed O/Ni orbital symmetry. This agrees with the decreased Ni magnetization upon desodiation from Na\(_{x}\)LiNi\(_3\)Mn\(_8\)O\(_{24}\) (\( x = 5 \)) to Na\(_{x}\)LiNi\(_3\)Mn\(_8\)O\(_{24}\) (\( x = 7 \)) in Figure 5d. The features of the pre-edge peak in the ligand O K-edge spectra can expose important information on the chemical bonding between ligand and TM atomic species. Generally, the pre-edge peaks in the range of 527–535 eV are due to the electronic transitions from the O 1s state to the O(2p)-TM(3d) hybridized states, which can be further divided into a lower energy peak of the band and a higher peak of the O(2p)-TM(3d-\( \epsilon_p\)) hybridized states. The increase of the O(2p)-TM(3d-\( \epsilon_p\)) hybridized state (in Figure S10a) shows that oxidation of Ni creates more holes in the antibonding \( \epsilon_p\) orbital, leading to the increase of the O K-edge in PFY mode measurements. This is further supported by the increasing overlap of Ni 3d states and O 2p states near the \( E_F \) level during desodiation, as shown in Figure S5h. The small amount of valence electrons in the desodiated sample promotes charge transfer from O to Ni via ligand-to-metal charge transfer in the local bonding configuration.\(^{39}\) Furthermore, O K-edge spectra from surface-sensitive total electron yield measurements (TEY) demonstrate the presence of oxygen-containing decomposition products of the electrolyte and surface densification at 4.60 V. This can suppress the O(2p)-TM(3d) hybridization features for the electrodes resulting in a relative lower average valence state of Ni/Mn ions as shown in Figures S10b and S11.\(^{39}\) Meanwhile, the Mn L-edge PFY results show negligible changes upon cycling, as demonstrated in Figure S12, suggesting that the Mn\(^{4+}\) ions do not participate in the charge compensation,\(^{39}\) which is further confirmed by X-ray absorption near edge spectroscopy (XANES) spectra of the Mn K-edge at different states of charge as shown in Figure S13.

### 2.5. Structural Evolution.

To explore the structural evolution of the high Na content cathode, in situ XRD experiments were carried out during the charge–discharge process as shown in Figure 6a. From the onset of desodiation up to \( \sim 5 \) mAh g\(^{-1}\), the (002) and (004) diffraction reflections slightly shift to a lower angle, while (100), (102), and (103) reflections move toward a higher angle. Subsequently, the (002) and (004) reflections become asymmetric and broader, and two new P2 phases (phase 2 and 3) appear upon further charging. The (002) reflection of the pristine P2 phase (phase 1) continuously shifts to lower angles, while the (002) reflections of the new P2 phases grow gradually without shifting, even up to the end of charge at 4.60 V. The main difference between these P2 phases is the Na content of the unit cell.\(^{38–45}\) The material charged to 4.60 V can be fitted with three P2–Na\(_x\) Li\(_{1/54}\)Ni\(_{16/54}\)Mn\(_{34/54}\)O\(_{2}\) phases having very similar cell parameters (as presented in Figure S14 and Table S4). These three P2 phases can all be indexed by the hexagonal \( P6_3/mmc \) symmetry with phase fractions of 5.1(2)\%, 32.3(2)\%, and 62.6(2)\% and lattice parameters of \( a = 2.878(33) \) Å and \( c = 11.21(13) \) Å, \( a = 2.8668(4) \) Å and \( c = 11.2335(15) \) Å, and \( a = 2.8135(13) \) Å and \( c = 11.2763(14) \) Å, respectively. The average Na content obtained from the refinement is \( \sim 0.24 \) mol, in good agreement with ICP results (\( \sim 0.245 \) mol based on the normalized value of Mn). During the refinement, a relatively large 2\( b \) Na\(^+\) occupation is found in the Na-poor phases. This indicates that Na\(^+\) at the 2\( d \) sites is preferentially deintercalated from the structure, which should be expected based on the larger energy associated with occupying this site.\(^{43,44}\) Another difference is the \( \sim 3.5\% \) difference in volume between the Na-poor P2 phase (phase 3) and pristine phase (phase 1). In addition, the Na-poor phases 2 and 3 exhibit a larger interlayer distance compared to phase 1.
3. DISCUSSION

The P2-type layered structure ensures facile Na⁺ diffusion; however, the lower Na content (∼2/3 mol per unit) usually compromises initial charge capacity and structural stability during the long-term cycling. The present exploration of high Na-content P2-type materials shows several advantageous properties.

3.1. Promoting Oxidization of the Low-Valent Cations (e.g., Ni²⁺) to Their High-Valent States Even at a Relatively Low Cutoff Charge Voltage. For the as-prepared high Na-content cathode, the Ni²⁺/Ni⁴⁺ redox couple is successfully activated to provide additional capacity below 4.0 V, which is an essential ingredient for the design of high-performance Ni-based P2-type cathodes. Generally, the redox reaction of Ni²⁺/Ni⁴⁺ occurs at voltages around or exceeding 4.2 V. Such a higher redox potential introduces three issues, including structural transitions, electrolyte decomposition, and activation of the oxygen redox causing oxygen loss, which will degrade the performance of the cathode material in terms of capacity and structural stability. Introducing a large amount of Na (0.75–0.83 mol per unit) into the P2-type material will make the average oxidation state of the TM ions lower than that in low Na-content (∼0.67 mol) P2 materials. In high Na-content P2 oxides, the lower average oxidation state of TMs can induce a larger contribution of low-valent pathways.

Given the large Na⁺ mobility for the P2-type structure, excellent electrode performance can be expected for the present high Na-content P2-type material. The Na⁺ kinetics is studied by first-principle molecular dynamics (FPMD) simulations. Figure 6c exhibits the results of the FPMD simulations. The diffusion coefficients are determined from the Na⁺ mean square displacements (MSDs) from simulations ranging from 600 to 1800 K (Figure S17). In Figure 6c, the Na⁺ trajectories are displayed to illustrate the migration pathways. As expected, Na⁺ migrates through the two-dimensional planes of the NaO₂ layers. As compared to the low Na-content material (0.667 mol), for the present high Na-content material the trajectories are more interconnected, showing many more jumps within the same simulation time. Figure 6d shows the Arrhenius plot of the calculated diffusion coefficient, resulting in a very low activation energy for diffusion (∼0.28 eV) and a very large room temperature diffusion coefficient (∼0.55 × 10⁻¹⁰ cm² s⁻¹) as compared to those of layered Na cathodes, signifying the excellent Na⁺ mobility of the present high Na content in P2-type material.

2.6. Accelerated Aging Measurement and Full Cells.

To further study the chemical stability, the P2-type material was stored in air for half a year, after which it was soaked in deionized water for 2 h. The XRD patterns and the electrochemical results, shown in Figures S19 and S20, indicate that the material is stable against water and air. NIBs utilizing a hard carbon anode were assembled to investigate the full cell long-term cyclability of the high Na-content P2-type cathode, having a relatively high active mass loading of approximately 8 mg cm⁻², as shown in Figures S21–S23. The electrochemical results show that the reversible capacity between 1.5 and 4.0 V is above 100 mAh g⁻¹, based on the mass of the cathode at a current rate of 0.1C at a high average operation voltage of ∼3.3 V. The full cells display excellent capacity retention, exceeding >90% over 400 cycles at 2.5C current rate.
and P2-type Na\text{0.67}Li\text{1/12}Ni\text{1/4}Mn\text{2/3}O\text{2} results in an average oxidation state of the TM ions of +3.167 and +3.333, respectively, where the former displays a larger contribution near the Fermi level. This implies easier participation of Ni\textsuperscript{2+} in the charge compensation upon desodiation. The disadvantage of the high Na-content P2 phase is that it is thermodynamically less stable compared to the low Na-content P2 materials. The consequence is that the low-valent cations can be oxidized to their high state more easily.

3.2. Stabilizing P2-Type Structure to Prevent Degradation from Structural Instability

The large amount of Na in a P2-type host structure can ensure a high structural stability in a large compositional range during the desodiation process, as demonstrated in Figure 7. For low Na-content P2-type materials, structural transitions from P2 to O2 or OP4/\textsuperscript{Z} occur for voltages below \(~4.2\) V when the Na content in the structural host drops below 1/3 mol. The higher Na content allows the structure to maintain more Na\textsuperscript{+} in the interlayers when the same amount of Na is deintercalated. A smaller amount of Na in Na\textsubscript{2}O\textsubscript{2} slabs will lower TM\textsuperscript{||} – TM\textsuperscript{\prime}\textsuperscript{||} and Na\textsuperscript{+} – TM\textsuperscript{\prime}\textsuperscript{||} electrostatic repulsions, resulting in gliding of the TMO\textsubscript{2} slabs. This induces the undesired phase transitions with large volumetric changes and rapid capacity decay. Our results demonstrate that, during desodiation of Na\textsubscript{45/54}Li\textsubscript{4/54}Ni\textsubscript{16/54}Mn\textsubscript{34/54}O\textsubscript{2}, Na-poor phases have a similar structure as the pristine material. These newly formed phases have a larger interlayer distance compared to that of the pristine structure, which is expected to be beneficial for Na\textsuperscript{+} migration. The phase fractions of these desodiated phases increase upon charging and reversible transform back to the pristine structure upon discharging (sodiation).

4. SUMMARY

In this work, we have explored the peculiar structural chemistry of a high Na-content P2-type. As a proof of concept, a high Na-content layered material, Na\textsubscript{45/54}Li\textsubscript{4/54}Ni\textsubscript{16/54}Mn\textsubscript{34/54}O\textsubscript{2}, has been successfully prepared. It is revealed that the high Na-content promotes the oxidation of the low-valent cation (Ni\textsuperscript{2+}) to its high oxidation state at a low cutoff voltage upon desodiation (charge) and that this stabilizes the P2-type structure, which generally promotes Na-ion conductivity. For the application as an electrode for NIBs, this results in several advantages compared to known low Na-content P2 materials. Na\textsubscript{45/54}Li\textsubscript{4/54}Ni\textsubscript{16/54}Mn\textsubscript{34/54}O\textsubscript{2} is demonstrated to have a higher reversible capacity of >100 mAh g\textsuperscript{-1} accompanied by the favorable multielectron reaction of the Ni\textsuperscript{2+}/Ni\textsuperscript{4+} redox couple within the stability window of typical electrolytes of 2.0 – 4.0 V. Additionally, stabilizing the P2-type structure leads to an ultralong cycle life of up to 3000 cycles in combination with good rate performance. The advantages of the presently developed high Na-content P2-type material motivate further exploration of high Na-content electrode materials for NIBs. Possible doping/substituting elements that may enable alternative high N-content P2-type materials are multivalent elements (e.g., Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Y\textsuperscript{3+}, La\textsuperscript{3+}), which, when located at the Na sites, will also promote the oxidation of TM ions and stabilize the structure upon (dis)charging. The present study also reveals a promising strategy to realize multielectron transfer toward a high oxidation state, potentially relevant for other research, e.g., catalysts.\textsuperscript{48}

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.9b13572.

Detailed synthesis, characterization and calculation methods; electrochemical cycling, SEM and TEM images; stability evaluation; X-ray absorption spectra; XRD patterns; structural parameters from Rietveld refinement (PDF)

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Qidi Wang – Division of Energy and Environment, Engineering Laboratory for the Next Generation Power and Energy Storage
Netherlands Organization for Scientific Research (NWO) under the VICI Grant Nr. 16122. C.Z. is also thankful for the State Scholarship Fund of China Scholarship Council (CSC).

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