Insights into the High Voltage Layered Oxide Cathode Materials in Sodium-ion Batteries: Structural Evolution and Anion Redox

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Abstract
The phase evolution and anion redox behaviours under electrochemical cycling of sodium transition metal layered oxides have both been intensively studied. In this review, we focus on the relationship between them at high voltage states-of-charge, in the context of growing evidence that anion redox begins at an earlier state of charge than previously thought, and that the final structural change can behave in either a biphasic or a pseudo-solid solution manner, depending on the transition metal element. By systematically reviewing major breakthroughs in experimental materials discovery, characterization techniques and theoretical understanding, we tentatively propose a new way to think about the phase transition dynamics and a path to improving the theory of anion redox.

Introduction
The past decade has witnessed significant gains in the efficiency of lithium ion batteries (LIBs), and a parallel surge in the development of sodium ion batteries (SIBs) aimed at the stationary energy storage sector. Key to this has been an improved understanding of the electrochemical mechanisms at the atomic and electronic structure level. Due to the different ionic radii and ionicities of sodium and lithium, all components of SIBs – cathode and anode electrode materials, electrolytes, even separator and current collector – must be selected and optimized according to different criteria than for LIBs. The most significant shortcomings for SIBs compared with LIBs are their lower operating voltage (0.1 - 0.6 V) and inferior ionic conductivity[1]. Two types of cathode materials, namely polyanion compounds and layered oxides have shown potential for commercialization due to the high operating voltage (can operate above 4 V) and fast ionic conductivity when compared with other types of cathodes, e.g., sulfides, fluorides, metal hexacyanometalates, and organic compounds[2,3]. In general, layered oxides exhibit higher ionic and electronic conductivity, higher capacity, marginally lower voltage and greater stability than polyanion compounds. Both materials may find their vintage application fields. We will focus on a comprehensive review on the structural changes and the possibility of anion redox (or oxygen redox) in sodium layered oxides with the general formula Na_x(TM,M)O_2 (TM = transition metal, M = compatible inactive substitution) for
high-voltage SIBs cathode electrodes\cite{6-10}.

In this review, we first lay out the most comprehensive current theories of phase evolution and anion redox behavior in these materials. We then apply them as a framework to a series of important materials based on first-row transition metals suitable for use as cathode electrodes with working voltage higher than 3 V vs. Na$^+$/Na. We use the nomenclature of Claude Delmas\cite{11} for the different interlayer-ordered phases (O1, O3, P3, O2, P2, etc.) based on the presence of octahedral (O) or prismatic (P) coordination environments for sodium ions and the number of stacking repeats of the oxygen lattice in a unit cell, e.g., ABABAB (O1), ABCABC (O3), ABCCCA (P3), ABAB (O2), or ABBA (P2). A prime (’) is added if the symmetry of the structure is lowered from hexagonal or rhombohedral to orthorhombic, monoclinic or triclinic. Additional primes indicate higher states-of-charge. We note that O1 has sometimes been used to represent O3’, which we correct in this review. Furthermore, we summarize the most applicable characterization techniques/tools with commentary on their use thus far and their future potential. In the final section, we propose a new way in which to think about phase transitions in these layered oxides and proffer some suggestions to improve the current theory of anion redox.

Figure 1 (a) Face-sharing schemes in the O1, O3, and P3 structures. (b) Comparison of optimized distributions among sodium ions occupying O- and P-type layers at Na$_{1/2}$ content. (c) Comparison of anion-anion distances in O- and P-type coordinations assuming the same cation and anion radii. (a)-(c) are reprinted from reference\cite{12} with permission. Copyright American Chemical Society. (d) (e) Comparison of hybridized TM-O orbital topology in O3 and O1
structures reprinted from reference\textsuperscript{[13]} with permission. Copyright Royal Society of Chemistry. (f) Schematic electronic structure of anion redox dynamics that distinguishes three types of oxidation process: reversible, hysteretic, and irreversible. (g) Four types of cycling curves taking reduction processes into account. Both from reprinted from reference\textsuperscript{[10]}; permission pending. Copyright Springer Nature.

There are three key crystal-chemical principles behind the adoption of O vs. P types, and the transformations between them.\textsuperscript{[12]} (1) Intercalant cation face sharing with transition metals. There are two shared faces in O1, one in P3 and none in O3. (2) Intercalant cation site topology. There are twice as many intercalant sites in P-type structures compared to in O-type structures, which allows cations to be distributed further away from one another in P-type. Note, however, that this is only true for cation concentration lower than 1/2. (3) Intercalant cation coordination, as shown in Figure 1(a)-(c). Prismatic coordination shortens the anion-anion distance compared to octahedral coordination, for the same cation and anion radii. Accordingly, the structure is stabilized in structures with fewer shared faces, longer cation-cation distances and longer anion-anion distances. Density functional theory (DFT) calculations, with van der Waals dispersion interactions and without on-site Hubbard corrections, reveal different decisive factors in different cases. Intercalant cation-cation repulsion is the driving force at intermediate concentration for large cations, as is often observed in O→P transformation in Na, K, Ca system. Anion-anion repulsion dominates in smaller intercalant cation Li, Mg system where no O→P transformation is found. For low and high intercalant concentration, O-type structures are often found with the domination of face-sharing effect. The distinction between O1 from O3 is due to another factor: ionicity/covalency of the transition metal-anion bonds. More covalent transition metal-anion (TM-X) bonds stabilise the O1 structure as shown in an extreme case, Li\textsubscript{2}TiS\textsubscript{2}, where O1 prevails for all x regardless of the face-sharing effect. This is corroborated by an argument that the steric effect of anion orbitals dominates in covalent systems, vs. electrostatic force dominating in ionic systems,\textsuperscript{[13]} even in the fully deintercalated TMX\textsubscript{2} as shown in Figure 1(d)(e).

Electrochemical reactions of transition metal layered oxides at high voltage are often associated with oxygen/anion redox, a concept that can be traced back to the early stage of Li-ion technology development\textsuperscript{[9]}. An unified theory was developed recently to explain the cycling behaviour of alkali metal-rich transition metal oxides\textsuperscript{[10]}, A(Al\textsubscript{δ}TM\textsubscript{1-δ})O\textsubscript{2}. (Note that to distinguish this from the general formula of layered oxides A\textsubscript{x}TM\textsubscript{2}O\textsubscript{δ}, we use δ here instead of x in the original paper.) The A-rich oxides are characterized by a localized O 2p band in the valence band-top region, or an oxygen lone pair orbitals in real space, which is the main electron donor in the charging process as illustrated in Figure 1(f). The band gap, or the charge-transfer gap, Δ_{CT}, between O 2p and unoccupied TM d band (TM d*) in the conduction band-bottom region, determines the reversibility of the oxygen redox reaction. As the O-O distance is shortened in charging process, the O-O interaction increases as reflected in the splitting of O 2p band into O-O bonding and antibonding bands up to point (1), when O-O antibonding bands partly lie below TM d*, up to point (2), when O-O antibonding bands are fully above TM d*.

Cycling below (1) is reversible, categorized as type a. Between (1) and (2), voltage hysteresis is often observed, featuring an “S-curve” in the discharge process when electrons first fill the TM d* band followed by the O-O antibonding bands, depending on the discharge capacity available. This is type c behaviour. Some degree of irreversibility is often associated with type c cycling. TM migration, which helps accommodate O-O bond formation, is postulated to account for part of the
irreversibility. On charging above (2), $O_2$ molecules are generated and escape from the surface, leading to significant irreversibility; this is type b and type d, depending on how much TM d* is activated.

The unified theory postulates that anion redox is reversible as long as the number of holes on each oxygen, $h^0$, generated upon full charging is less than $\delta$ in $A(A_6\text{TM})O_2$, and $\delta$ is generally less than 1/3. It turns out that $\delta$ is related to the number of lone pairs on each oxygen $N_{LP} = 3 - 3(1 - \delta) = 3\delta$. In this review we will compare $h^0$ and $N_{LP}/3$ in known cases.
Enumeration of Important Materials

Na$_3$MnO$_2$

O$3'$ type $\alpha$-NaMnO$_2$ cycled between 2 - 3.8 V shows more than 0.8 Na extraction/insertion with multiple voltage plateaux$^{[14]}$. The new phase appearing at Na$_{0.7}$MnO$_2$ can be indexed in the same space group as the pristine material. Voltage profile asymmetry, or hysteresis, is observed. The fully sodiated state cannot be achieved after full discharge. Mn migration through the tetrahedral “dumbbell” configuration is claimed to be minimized by the large size of Na$^+$ ions. However, the hysteresis suggests Mn migration at low Na content. In situ XRD data show more than 6 phase changes upon charging NaMnO$_2$ to 4.2 V, at which point Na is almost fully depleted$^{[15]}$. Unfortunately, further details of this research are unavailable. Based on the shift of the first peak, a P-type phase should form as indicated by earlier research$^{[16]}$. A recent study of $\alpha$-NaMnO$_2$ using high-energy XRD suggests a phase transformation path O$3'$→O$3''$→P$3$→P$3'$→Z upon charging to 3.8 V$^{[17]}$. The O$3''$ phase Na$_{0.5}$MnO$_2$ was revealed to be sodium-ordered and Mn$^{3+}$-Mn$^{4+}$ charge-ordered, with significant lattice distortion due to cooperative Jahn-Teller (J-T) effects$^{[18]}$. The Z phase was postulated to be an O-type phase with some Mn migration to tetrahedral sites and a significant number of stacking faults. Crystal-field stabilization energy analysis suggests that Mn at the tetrahedral site might be Mn$^{2+}$.

$\beta$-NaMnO$_2$ consists of zig-zag layers of transition metal-oxygen octahedra, with sodium ions in octahedral vacancies between. Only one phase transition was observed by in situ XRD in an intergrown $\alpha$- and $\beta$-NaMnO$_2$ sample upon charging to 4.2 V vs. Na$^+$/Na$^{[19]}$. Loss of long-range structural ordering at low sodium content was confirmed by TEM; but the original structure could be recovered upon discharging to 2 V. Ex situ $^{23}$Na NMR revealed that the dominant $\beta$ phase slowly transforms into an $\alpha$ phase after prolonged cycling$^{[20]}$. The complication of the intergrown structure has so far eluded a clear understanding of its evolution under electrochemical cycling.

P2-type Na$_x$MnO$_2$ can be synthesized in two forms by carefully controlling the cooling rate$^{[21]}$. Orthorhombic P2 (o-P2) crystallizes in Cmcm due to Mn$^{3+}$/Mn$^{4+}$ ordering, while hexagonal P2 crystallizes in P6$_3$/mmc due to the introduction of Mn vacancy and thus lower Mn$^{3+}$ content. ICP and iodometry reveal that the o-P2 material has the formula Na$_{0.6}$Mn$^{3+}_{0.6}$Mn$^{4+}_{0.4}$O$_2$ and the h-P2 material Na$_{0.5}$Mn$^{3+}_{0.18}$Mn$^{4+}_{0.74}$□$_{0.12}$O$_2$ (□ stands for vacancy). Despite multiple steps in the cycling voltage profile, only one pronounced phase transition was observed for o-P2 during charging to 4.4 V vs. Na$^+$/Na. This is P2$'$→OP4, where OP4 has a much shorter c axis and sodium ions in both octahedral and prismatic sites. No phase transitions were observed for h-P2. The Mn$^{4+}$/Mn$^{3+}$ redox can account for all the initial charging capacity of o-P2 phase, which shows voltage polarization. This is not the case for h-P2 material, which shows voltage hysteresis above 4 V. Anion redox must therefore be considered. The number of oxygen holes, $h^0 = (0.59/0.255)/2 = 0.17$, is larger than $\delta = 0.1$, and the corresponding cycling curve is identified as type b. Both materials display transitions to distorted P2-type upon discharging to lower voltages around 2 V, suggesting a strong J-T effect due to Mn reduction.
Triclinic Na$_{4/7}$□$_{1/7}$Mn$_{6/7}$O$_2$ (P-1 space group) is another layered structure with ordered vacancies in the MnO$_2$ layer. Mn is ordered in a $\sqrt{7} \times \sqrt{7}$ supercell with substantially more planar faults than the O3 type phase. Sodium ions are located in highly distorted octahedral sites as well as prismatic sites. For convenience, we refer to this as the OP3’ phase (where the underline denotes that O and P coordinations are within the same layer). It can cycle in 3 - 4.7 V or 1.5 - 3 V vs Na$^+$/Na, where oxygen and Mn$^{IV}$/Mn$^{III}$ redox processes are activated separately as shown in Figure 2(b)[23]. Some polarization and irreversibility are observed in the cycling curve, typical of a type a anion redox mechanism with minor irreversibility, which might be caused by electrolyte instability. The holes on oxygen for 2/7 Na removal, $h^0 = 1/7$, is equivalent to $\delta = 1/7$. There are two types of oxygen site in the structure, O1 and O2, coordinated by two Mn and three Mn sites respectively. Projections of valence band-top electron states of Na$_{4/7}$□$_{1/7}$Mn$_{6/7}$O$_2$ and conduction band-bottom hole states of Na$_{2/7}$□$_{1/7}$Mn$_{6/7}$O$_2$ show that the redox centre is located mainly on O1 with non-bonding 2p orbitals as shown in Figure 2(c)(d). In situ synchrotron XRD reveals that a highly distorted P3-type structure is formed with negligible volume change in the first plateau above 4 V[22]. Surprisingly, the symmetry is raised from P-1 to Cm. The second plateau is associated with reversible expansion/contraction of ordered vacancies in the TM layer, again with negligible volume change as shown in Figure 2(a).

Na$_x$(LiMn)O$_2$

P2-type Na$_{0.72}$(Li$_{0.24}$Mn$_{0.76}$)O$_2$ undergoes an activation process in the first charge to 4.5 V vs. Na$^+$/Na, at which point almost all sodium is extracted, followed by voltage hysteresis in the discharge
This material falls into type c with irreversibility. The number of holes on oxygen, $h^O = 0.36$, is larger than $\delta = 0.24$ but smaller than $(1+\delta)/2 = 0.62$. Surprisingly, an anion redox plateau is observed in the second charge process and the cyclability of the material is appreciable. The structure largely remains P2-type with significant peak-broadening in the in situ X-ray Diffraction (XRD) data upon charging to 4.5 V. On the other hand, a small amount of O2 type phase and Na-TM cation mixed phase is observed as revealed by atomic-resolution scanning transmission electron microscopy (STEM) images of samples at the highest state of charge.

**P3-type Na$_{0.6}$Li$_{0.2}$Mn$_{0.8}$O$_2$** can have 0.4 Na extracted upon charging to 4.5 V vs. Na$^+/$/Na$^0$. It shows voltage polarization of 0.2 V rather than hysteresis, and more than 0.1 Na ions irreversibility in the first cycle. The plateau above 4 V is accompanied by an unidentified phase transition. A combination of in situ XRD and stacking-fault modelling indicates a mixed O-P structure with shorter interlayer distances. The redox mechanism belongs to type c with irreversibility. The number of holes on oxygen $h^O = 0.2$ is equivalent to $\delta = 0.2$. Refinement against neutron diffraction data at the highest state-of-charge reveals that the oxygen occupancy barely changes, i.e., there is almost no oxygen loss.

A comparative study using a combination of XRD, atomic resolution STEM, $^6$Li magic angle spinning nuclear magnetic resonance (MAS NMR), high-resolution resonant inelastic X-ray scattering (RIXS) spectroscopy and density functional theory (DFT) calculations identified the important factors that distinguish the voltage hysteresis of P2-type Na$_{0.6}$Li$_{0.2}$Mn$_{0.8}$O$_2$, which is comparable with its P3-type counterpart, and P2-type Na$_{0.275}$Li$_{0.25}$Mn$_{0.75}$O$_2$, which is very close in stoichiometry to the aforementioned Na$_{0.22}$Li$_{0.24}$Mn$_{0.76}$O$_2$. Both are characterized by LiMn$_6$ ordering in the TM layer, and both evolve to P-O mixed structures upon charging to 4.5 V vs. Na$^+/$/Na$^0$. The LiMn$_6$ clusters in Na$_{0.6}$Li$_{0.2}$Mn$_{0.8}$O$_2$ are sparsely distributed into a ribbon-like superstructure and are retained in the form of $\square$Mn$_6$ ($\square$ for vacancy) upon charging to 4.5 V with Li-ion migration to the Na layer. The LiMn$_6$ clusters in Na$_{0.75}$Li$_{0.25}$Mn$_{0.75}$O$_2$ are closely together and desintegrate upon removal of Na ions, via a combination of Li and Mn migration to the Na layer and Mn migration within the TM layer. In the fully charged state, molecular-like O$_2$ coordinated Mn-$\eta^1$-O moieties are formed in both compounds, with stable electron holes formed on oxygen only in Na$_{0.6}$Li$_{0.2}$Mn$_{0.8}$O$_2$. After discharging to 2 V, only Na$_{0.6}$Li$_{0.2}$Mn$_{0.8}$O$_2$ regains its original ribbon-like superstructure. A careful examination of Li content in Na$_{0.6}$Li$_{0.2}$Mn$_{0.8}$O$_2$ after prolonged cycling shows that there is continuous lithium loss during cycling.

Na$_x$(MgMn)$_2$O$_2$

Less than 10% Mg substitution on TM positions smooths the voltage curve for P2-type Na$_x$Mn$_{1-y}$Mg$_y$O$_2$ under cycling between 1.8 - 3.8 V vs. Na$^+/$/Na. The incorporation of Mg delays the onset of the phase transition to OP4 above 3.5 V and minimizes the polarization, improving the high-rate performance. Unexpectedly, the Mg “spectator” also lowers the average working voltage. The large voltage hysteresis remains at 10% Mg doping even though Mn$^{4+/3+}$ redox can account for the cycling capacity of 0.7 Na ions.

Higher Mg substitution induces anion redox. P2-type Na$_{2/3}$Mg$_{0.28}$Mn$_{0.72}$O$_2$ transforms to O2-type upon charging to 4.4 V vs. Na$^+/$/Na. Cycling between 1.5 - 4.4 V is almost perfectly reversible, although voltage hysteresis is observed. Mg-Mn ordering at ratios close to 1:2 is preserved throughout the cycling process. The formula can be written as Na$_{2/3}$Mg$_{0.28}$Mn$_{3+0.11}$ Mn$_{4+0.61}$O$_2$, to
indicate that 0.42 Na ions is accounted for by oxygen redox when considering the initial capacity of about 150 mAh/g. The oxygen redox mechanism is type c with the number of holes on oxygen hO = 0.21 less than δ = 0.28, suggesting fully reversible oxygen redox.

Atomic STEM shows that Mg does not migrate like Li in the TM layers. This explains the better stability compared with lithium substitution\cite{30}. However, the voltage curves show irreversibility in the plateau above 4 V and hysteresis upon discharge, which suggests cation migration. Operando mass spectroscopy detected trace CO2 release caused by the oxidation of electrolyte at the end of the high-voltage plateau, which contributes to the irreversibility.

Na0.5CrO2

Figure 3 (a) Cycling curve of NaCrO2, (b) corresponding unit cell parameter evolution upon charging to 4 V and (e) ex situ XANES of NaCrO2 and Cr3+/Cr6+ standards, reprinted from reference\cite{31} with permission. Copyright American Chemical Society. (c) STEM images of Cr migration at the surface region and corresponding fast Fourier transform (FFT) showing the formation of a rock-salt phase in NaCrO2 charged to 3.8 V reprinted from reference\cite{32} with permission. Copyright Elsevier.

0.5 Na ions can be reversibly extracted from O3-type NaCrO2 cycled over 2.5-3.7 V vs. Na+/Na, giving a formula Na0.5Cr2+0.5Cr4+0.5O2. Further charging to 3.8 or 4.0 V leads to significant irreversibility. In situ and ex situ XRD during the charging process reveal phase transformations from O3 to O3’ to P3’ below 3.7 V and to O3” (with substantial shrinkage in the c axis) above 3.7 V, followed by eventual transformation to a mixed-cation rock-salt phase through CrOct→Crket→CrOct migration as shown in Figure 3(a)(b)\cite{31,32}. The mixed-cation state, confirmed by electron diffraction and refinement against ex situ XRD data, turns out to be more stable and accounts for the reversibility. Tetrahedral coordination of Cr is confirmed by X-ray absorption near edge structure (XANES) and extended fine structure (EXAFS) spectroscopy. It is surmised that the Cr4+ may be
oxidised to Cr$^{6+}$ based on the pre-edge feature below the Cr K-edge as shown in Figure 3(e). HAADF-STEM images of a sample charged to 3.8 V reveal Cr migration in the surface region as shown in Figure 3(c)(d)[32].

Through aliovalent substitution and careful control of synthesis temperatures, P2-type Na$_{2/3}$Cr$_{2/3}$Ti$_{1/3}$O$_2$ can be obtained[34]. Ti$^{4+}$ as a spectator ion drastically elevates the reversible sodium insertion/extraction voltage until the composition reaches Na$_{1/3}$Cr$^{3+}$$_{1/3}$Cr$^{4+}$$_{1/3}$Ti$_{1/3}$O$_2$, corresponding to 3.8 V. However, it does not prevent the irreversibility upon further charging to 4 V, which is associated with transformation to an O-type phase with substantial stacking faults and CrO$_4$ tetrahedra, as for Li$_x$CrO$_2$[35].

NaVO$_3$ & NaCuO$_2$

**Monoclinic NaVO$_3$** was reported to show oxygen redox activity through an activated charging process at 4.9 V vs. Na$^+$/Na.[36] However, the 1$^{st}$ charge curve was very different to subsequent charge processes, suggesting that they might not be involved in the same electrochemical processes. Significant voltage hysteresis and irreversibility is observed on cycling between 1.5 - 4.9 V, typical of type d behaviour. The reversibility is greatly improved on cycling between 1.5 - 4 V. It was speculated that the subsequent charge/discharge process in NaVO$_3$ mainly involved V$^{4+/5+}$ redox chemistry[37], due to the low voltage profile and limited reversible capacity. The sodium extraction in the first charge to 4.9 V corresponds to 0.68 Na, equivalent to h$^0$ = 0.23, which is less than δ. The fact that it shows type d behaviour makes NaVO$_3$ a violation of the unified theory.

**Monoclinic NaCuO$_2$** shows the same large first-cycle irreversibility and voltage hysteresis, i.e., type d behaviour, over the voltage range 1.7 - 4.2 V vs. Na$^+$/Na[38]. CuO is detected upon charging to 4.2 V (in trace amounts) and upon discharging to 1.7 V (in large amounts) by ex situ XRD[39]. It is reasonable to believe that anion redox is activated, but with highly unstable oxygen species. NaCuO$_2$ has planar CuO$_4$ coordination due to J-T distortion of Cu$^{3+}$ (d$^8$ electronic configuration). Oxgens in NaCuO$_2$ are insufficiently bonded, which leads to δ = N$_{LP}$/3 = 1/3. An earlier X-ray photoemission spectroscopy and configuration-interaction calculation study showed that d$^9$L (L for ligand hole) is the dominant state[40], indicating that all of the capacity comes from anion redox. The first-cycle charge removes 0.6 Na ions, i.e., h$^0$ = 0.3, which is less than δ. NaCuO$_2$ is therefore another violation of the unified theory.
NaFeO$_2$

Figure 4 (a)-(d) In situ XRD patterns and corresponding charging curve of NaFeO$_2$ reprinted from reference$^{[41]}$ with permission. Copyright Royal Society of Chemistry. (e)-(f) Ex situ O K-edge XAS and corresponding charged states of NaFeO$_2$ reprinted from reference$^{[42]}$ with permission. Copyright American Chemical Society. (g) Na$_x$FeO$_2$ at fully charged state, (h) ex situ Fe K edge XAS showing variation of pre-edge peak intensity and (i) (partial) densities-of-states at different Na content, all reprinted from reference$^{[43]}$ with permission. Copyright Elsevier.

O3 type NaFeO$_2$ cycled between 2.5 - 4.5 V vs. Na$^+$/Na shows 0.67 Na ions extraction but almost no sodium reinsertion. At least two phase transformations occur in the charging process, as revealed by in situ synchrotron XRD: O3H$\rightarrow$O3’H$\rightarrow$O3’m, where H is hexagonal and m is monoclinic$^{[42]}$. When cycled over 2 - 4.4 V, 42% of NaFeO$_2$ converts back to O3 after the first discharge. A detailed study on the relative intensities of Bragg peaks suggests that O3’m could be assigned to a P3 or P3’ type phase, which quickly merges with the residual O3’H phase into an unknown phase “X” below 4 V$^{[41]}$. Upon discharging to 1.5 V, this “X” phase persists. While the final stage phase assignment remains ambiguous, a “Y” shaped (003) peak trajectory observed in 2D diffraction contour plots upon charging hints at the evolution of competing phases as shown in Figure 4(a)-(d). Acceptable reversibility is only achieved by cycling in the window 2.5 - 3.5 V, with less than 0.4 Na ions (de)intercalation.

The Fe$^{4+}$/3+ reaction below 3.5 V, proved by Mössbauer spectroscopy, no longer takes place in the second cycle$^{[44]}$. The capacity of the second and following cycles, due mainly to anion redox, degrades rapidly. X-ray absorption spectra show that the Fe K-edge positions of NaFeO$_2$ at different states-of-charge hardly change, suggesting a reductive coupling mechanism$^{[10]}$ whereby the evolution of (O$_2$)$^n$ species couples with Fe$^{4+}$/3+ reduction. This can be expressed as Fe 3d$^4$$\rightarrow$ Fe 3d$^5$.


where \( \mathbf{L} \) is the ligand hole. This is proved by the ligand hole feature manifest in the O K-edge X-ray Absorption Spectroscopy (XAS) and the large fraction of O 2p participation in the band-top states shown by systematic DFT calculations as presented in Figure 4(f)(i)\(^{[43]}\). The voltage profile over the 2.5 - 4.5 V cycle, which shows large polarization and irreversibility, can be tentatively categorized as type d with a dramatic distinction: type d process usually activate a redox couple, e.g., Mn\(^{4+/3+}\) in Li\(_2\)MnO\(_3\) while that of Na\(_x\)FeO\(_x\) deactivates a redox couple, Fe\(^{4+/3+}\). Assuming that 0.4 Na (at most) is reversibly extracted by Fe\(^{4+/3+}\) redox in the first cycle, the ligand-hole created by charging to 4.5 V is ca. \( h^0 = 0.14 \) with no oxygen lone pair available.

The cation mixing that results from Fe migration, which emerges as early as Na\(_{0.6-0.7}\)FeO\(_2\) ca. 3.3 V vs. Na\(^+\)/Na, has been elucidated by High Angle Annular Dark Field Imaging (HAADF) STEM image\(^{[43]}\) as shown in Figure 4(g) as well as by modeling the relative diffraction intensities\(^{[41]}\). The Fe migration process is spontaneous, as shown by the increased interfacial impedance and in the decrease of discharge capacity with extended storage time after charging to 3.6 V\(^{[44]}\). The tetrahedrally coordinated Fe, evidenced in the pre-edge feature of Fe K-edge XAS of a sample charged to 4.4 V, suggests a migration path Fe\(_{\text{Ox}}\) \( \rightarrow \) Fe\(_{\text{Ox}}\) \( \rightarrow \) Fe\(_{\text{Ox}}\) as shown in Figure 4(h). A simple crystal-field stabilization energy (CFSE) analysis suggest that tetrahedral vacancies favour Fe\(^{4+}\) over Fe\(^{3+}\) (assuming high-spin configurations), which corroborates the reductive coupling mechanism. The readily “mobile” Fe may play a crucial role in explaining the “Y” shape phase evolution: the formation of cation mixed phase in competition with the typical O-P phase transformation.

\[ \text{Na}_x(\text{FeMn})\text{O}_2 \]

By adjusting the sodium content and Mn/Fe ratio, O3 and P2 type Na\(_x\)(FeMn)O\(_2\) can be obtained. O3 type Na\(_x\)Mn\(_{1/2}\)Fe\(_{2/3}\)O\(_2\) cycled at 1.5-4.3 V vs. Na\(^+\)/Na shows drastically improved reversibility and less voltage hysteresis compared with NaFeO\(_2\) mentioned above. Upon charging, the initial O3 phase transforms to a P3 phase concomitantly with the appearance of a modified O3” phase (where the double-prime distinguishes it from the low voltage O3’ phase). Both of these are characterized of stacking faults and eventually merge into an unknown phase “X”\(^{[45]}\). Surprisingly, a “Y” shaped trajectory of the (003) peak during the phase evolution is observed, as for NaFeO\(_2\). The difference is that in this work, the X phase is much more reversible. In light of this, it is reasonable to expect a P3 type phase at some point during NaFeO\(_2\) phase evolution. For \( x > 2/3 \), the redox centre Mn\(^{4+/3+}\) manifests as the lower voltage plateau. Above \( x < 2/3 \), the redox center becomes Fe\(^{4+/3+}\) or/and anion redox which accounts for ca. 0.45 Na ions extraction in the first cycle. In the second cycle this reduces to 0.4 Na ions extraction, in accordance with Fe\(^{4+/3+}\) reactivity in NaFeO\(_2\). A small amount of irreversibility persists in the following cycles due to the mobile Fe issue as observed in NaFeO\(_2\). An earlier study on the similar compound Na\(_x\)Fe\(_{1/2}\)Mn\(_{1/2}\)O\(_2\) (O3 type) proposed an OP2 type structure for the high voltage phase\(^{[46]}\), as a potential solution to the “X” phase.

Fe migration has been shown to be related to cooperative Jahn-Teller (J-T) effect of high spin Fe\(^{4+}\) ions. Spectator ions are needed to dilute these Fe\(^{4+}\) ions which otherwise would initiate the migration with the help of Fe-Fe-Fe clusters\(^{[47]}\). On the other hand this very same J-T effect could also facilitate Na diffusion in highly charged state in O3-type phase through FeO\(_6\) octahedral “buckling”, which makes Fe\(^{4+}\) a benevolent component when operating in the high-voltage region.

For example, P2 type Na\(_x\)Mn\(_{1/2}\)Fe\(_{1/2}\)O\(_2\) cycled between 1.5 - 4.3 V vs. Na\(^+\)/Na shows P2’ \( \rightarrow \) P2 \( \rightarrow \) “Z” phase evolution path upon charging\(^{[48]}\). The P2’ phase is a distorted version of P2 due to the Mn\(^{3+}\)-
induced J-T effect. The “Z” phase here is an OP4 type phase according to the aforementioned early study on P2-type Na$_x$Fe$_{1/2}$Mn$_{1/2}$O$_7$.[46] From around $x = 0.5$, Mn$^{4+/3+}$ gives way to Fe$^{4+/3+}$ redox couple. The latter is responsible for less than 0.4 Na ions, making the reaction highly reversible. Pair distribution function (PDF) analysis of diffraction data from chemically oxidized “Z” phases in a series of similar P2-type materials Na$_x$Mn$_{0.5}$Fe$_{0.5}$O$_2$, Na$_x$Mn$_{0.66}$Fe$_{0.34}$O$_2$ and Na$_x$Mn$_{0.65}$Fe$_{0.35}$O$_2$ successfully identified tetrahedrally coordinated transition metal (TM) ions in the sodium layer, with decreased proportions of TM migration (12.5%, 9.4%, 3.1% respectively).[49,50] The “Z” phase is associated with anion redox on the basis of \textit{in situ} X-ray absorption spectroscopy (XAS), which shows no TM valence change after the emergence of the “Z” phase in the charging process. The ligand to metal charge transfer promotes TM migration and Ni substitution is demonstrated to counteract the effect while maintaining electrochemical activity.

NaCoO$_2$

By controlling Na:Co ratio and temperature, P3, P3’, O3, P2 phases of Na$_x$CoO$_2$ can be obtained.[51] Starting with fully sodiated O3 phase, or $\alpha$-phase, at least 0.5 Na can be reversibly extracted, with the phase transformation pathway O3$\rightarrow$O3’$\rightarrow$P3’$\rightarrow$P3$\rightarrow$P3’ upon charging. While the P2 phase, or $\gamma$-phase, remains unchanged over the range $x = 0.4 - 0.9$, it gives a much more complex voltage profile.[52] A huge amount of effort has been dedicated to studying the phases at each of the step-like voltage plateaux.

At room temperature, electron diffraction reveals different sodium ordering patterns in Na$_x$CoO$_2$ at $x = 0.75$ (incommensurate), 0.64 (incommensurate), 0.5 ($\sqrt{3}a \times 2b \times 1c$), 0.3 (incommensurate), and 0.15 ($\sqrt{3}a \times \sqrt{3}b \times 1c$).[53] X-ray diffraction shows sodium ordering in Na$_{2/3}$CoO$_2$,[54] resulting in a $2\sqrt{3}a \times 2\sqrt{3}b \times 1c$ supercell. Neutron diffraction confirms the $\sqrt{3}a \times 2b \times 1c$ supercell in Na$_{1/2}$CoO$_2$,[55] due to sodium ordering. Just below room temperature, sodium ordering corresponding to a $\sqrt{7}a \times \sqrt{7}b \times 1c$ supercell is observed in Na$_{0.58}$CoO$_2$ or Na$_{0.7}$CoO$_2$ by powder neutron diffraction.[56]. All of above mentioned refinement results incorporate more than one type of Co positions, suggesting correlation between sodium ordering and transition metal ordering, in this case, Co$^{4+}$/Co$^{3+}$ charge ordering. Experimental evidence for the charge-ordering also comes from nuclear quadrupole resonance obtained at temperatures as low as 4.2 K.[54].

In an attempt to understand the sodium ordering energetics, grand-canonical Monte Carlo simulation with cluster expansion models based on DFT in both Generalized Gradient Approximation (GGA) and GGA+U approximations have been employed to search for ground states at different sodium contents.[57,58] More ground states were found using GGA+U than in GGA, which better reproduces the many stages in the experimental cycling curve. However, GGA+U has successfully reproduced Co$^{4+}$/Co$^{3+}$ ordering[59] while GGA gives totally delocalized holes among Co. Simulations with temperature taken into consideration have shown that there are fewer phases at elevated temperatures,[58,60], i.e., less staircases in the predicated voltage/chemical potential curve compared with experimental results.

Apart from a series of simple phases, an infinite series of ground state Na-vacancy ordering phases are predicted for P3- and P2-Na$_x$CoO$_2$ above $x = 13/16$ and $x = 31/36$ respectively by Monte Carlo simulations.[61,62] These phases are comprised of triangular Na clusters/droplets separated by vacancies, or so-called antiphase boundaries. Although no experimental evidence has been obtained so far on these phases at such high sodiated states, this theoretical work suggests an
explanation for the “devil’s staircase” voltage profile. On the other hand, by neglecting the effect of sodium ordering, band structure calculation using the KKR method for oxygen-deficient Na₈CoO₂, suggest an alternative explanation[63]. The idea of relating the Fermi level directly with the open-circuit voltage potential of Na₈CoO₂ provides complementary understanding of the voltage variation when neither sodium ordering nor solid solution behaviour are observed. The kaleidoscope of phases in Na₈CoO₂, even at room temperature, thus remains to be definitively characterized and explored.

**O₃-type NaCo₁₂/₈Fe₁₂/₈O₂** follows the phase transformation path O₃→P₃→P₃’→O₃’ upon charging to 4.0 V vs. Na⁺/Na⁺, corresponding to 0.7 Na extraction. The Co⁴+/³⁺ redox couple is active before the Fe⁴+/³⁺ redox couple, as shown by ex situ XAS Co K- and Fe K-edge spectra and a systematic Bader charge analysis[64]. The charge analysis also shows that oxygen starts to lose charge at very early stage, indicating the strong covalency of Co/Fe-O bands and the difficulty in determining the number of effective holes on oxygen. The redox potentials of both Co⁴+/³⁺ and Fe⁴+/³⁺ are elevated due to the inductive effect of substitution. As each redox couple accounts for 0.35 Na ions extraction, no Fe migration is observed. Of note is that NaCoO₂ can be charged to 4.0 V. However, detailed structural changes above 3.5 V have never been reported in the literature.

**P₂ type Na₂/₃Mn₄Co₁/₃O₂.** The dQ/dV of the cycling curves of a series of isovalent substitution materials Na₂/₃Mn₄Co₁/₃O₂ show an interesting trend from 4 - 1.5 V vs. Na⁺/Na⁺: the Co⁴+/³⁺ redox couples are elevated with increasing Mn substitution, while those of Mn⁴+/³⁺ are pushed to lower voltage with increasing Co substitution[65]. The latter does not follow the general trend of inductive effects of substitution in layered oxides. An ex situ soft XAS study on Na₆Mn₁₁/₈Co₁/₂O₂ shows clear evidence of the Co³+/²⁺ redox couple for x > 2/3 in addition to the Mn⁴+/³⁺ redox couple[66]. This combination is rare and may explain the voltage shift trend mentioned above. A cooperative J-T effect is expected as there is only one occupied state in the e₈ orbitals of both Co³⁺ and Mn³⁺ ions, from a molecular-orbital perspective. However, neither in situ XRD patterns of Na₂/₃Mn₁₁/₈Co₁/₂O₂ cycled over 1.5 - 4.3 V (0.36 - 0.94 Na)[67] nor ex situ XRD results of Na₂/₃Mn₁₁/₈Co₁/₂O₂ cycled over 1.5 - 4 V (0.4 - 0.9 Na)[68] shows any phase other than P₂-type. The prevalent P₂-O₂ transformation in the high-voltage region is suppressed by the elevated voltage. The reason for the absence of a monoclinic distortion in the low-voltage region remains unclear. Of note is that Na₂/₃Mn₁₁/₈Co₁/₂O₂ show good rate performance, as also reflected by the negligible polarization of its cycling curves.

**P₂-type Na₂/₃Mn₁₂/₈Fe₁₂/₈Co₁/₂O₂** cycled in 4.5 - 1.5 V vs Na⁺/Na⁺ shows only one phase transformation at about 4.2 V, or Na₀.₃₄ upon charging: P₂→“Z” phase, as evidenced by in situ XRD[69]. The end-state of this “Z” phase was later shown to be an O₂ phase in a in situ synchrotron XRD experiment on the very similar compound Na₀.₇Fe₀.₄Mn₀.₅₄Co₀.₄O₂[70]. As for Na₂/₃Mn₁₁/₈Co₁/₂O₂, Na₂/₃Mn₁₂/₈Fe₁₂/₈Co₁/₂O₂ shows no monoclinic distortion in the highly sodiated state, where good rate performance is achieved due to the large range over which the P₂ phase is preserved by simultaneous reduction of Co³⁺ and Mn⁴⁺.

NaNiO₂

**O₃ type NaNiO₂** cycled over 4 - 1.5 V vs. Na⁺/Na⁺ passes through four stages biphasic regions: O₃→P₃→P₃”→O₃’ ”→O₃” ” (Na₀.₃₇) upon charging and O₃””→O₃”→P₃→P₃→O₃”” (Na₀.₈₃) upon discharging, which means the irreversibility is due to the material not being able to discharge to fully sodiated state[71]. The interlayer distance grows monotonically even as the structure
transforms to O3 type at the highest state-of-charge. This phenomenon is unique among layered oxides where one typically finds that the interlayer distance is reduced at the P→O transformation in the charging process. An early study indicated that O3-type NaNiO2 could be charged to 4.5 V with some irreversibility coming from the voltage plateau above 4 V[72]. Ex situ XRD on electrode materials after reaching 4.5 V raised the possibility of a phase with a much shorter interlayer distance, but this is still unclear as for NaCoO2 above 3.5 V. The structural evolution should be investigated in more detail as the Rietveld refinement of NaNiO2 shows Ni deficiency, which might be due to ion mixing of Na/Ni or Ni vacancy formation. The instability of Ni^{4+} at high temperature prevents the synthesis of P2-type Na,NiO2.

O3-type NaNi0.5Fe0.5O2 and NaNi0.5Ti0.5O2 both exhibit reversible O3→P3 phase transitions and 0.5 Na ions removal when cycled over 2 - 3.8 V vs. Na+/Na with smooth voltage curves. It is paradoxical, in conventional valence designation, that the average voltage of the Ni^{3+/2+} couple in NaNi^{2+}0.5Ti^{2+}0.5O2 is higher than that of Ni^{2+/3+} couple in NaNi^{3+}0.5Fe^{3+}0.5O2[73]. Configuration-interaction full-multiplet (CIFM) calculations show significantly increasing ligand-to-metal charge transfer from (Ni^{2+}O6)10−, (Ni^{3+}O6)9 to (Ni^{4+}O6)8 clusters, indicating different redox centers in the two systems. NaNi0.5Ti0.5O2 is more ionic and active through the Ni^{3+/2+} redox couple while NaNi0.5Fe0.5O2 is more covalent and mainly through anion redox. According to CIFM calculations, there are 57% [Ni^{3+}(O^{2−})6O] states and 36% [Ni^{2+}(O^{2−})4(O^{−})2] states in NaNi0.5Ni0.5Fe0.5O2, which amounts to h° = 1/6x57%+1/3x36%=0.2, a highly reversible anion redox of type a with delocalized electrons instead of lone pair electrons.

O3 type NaNi0.5Co0.5O2 goes through O3→O3′→P3′→P3→P3′→O3′′ (Na0.39) phase transitions with multi-stage voltage profile upon charging to 4.2 V and O3′′→P3→P3′→O3′ (Na0.93) upon discharging to 2 V vs. Na+/Na[74]. The total magnetic moment calculated by spin-polarized DFT shows that Ni^{4+/3+} is responsible for the first 0.5 Na ions removal before Co^{3+/2+} for the rest of Na ions extraction in the charging process. The multi-stage voltage profile indicates that sodium ordering structures should be considered apart from O-P stacking sequence to fully understand the phase behaviour. This implies that random Ni/Co distribution does not compromise sodium ordering, which in turn might induce charge ordering among Ni/Co regardless of Ni^{4+/3+} preceding the Co^{4+/3+} reaction, or vice versa. As pointed out earlier, the whole idea of distinguishing valence change in transition metals during electrochemical reactions might be outdated.

O3′ type NaNi2/3Sb1/3O2 or Na3Ni5SbO6 cycled between 4 - 2 V vs. Na+/Na shows three main steps of phase transitions, with 2/3 Na ions reversibly (de)intercalating: O3′→P3→P3→O1[75]. The interlayer space increases monotonically as for NaNiO2. The presence of Sb^{5+} increases the ionicity of the system and raises the redox reaction voltage as a consequence. The formation of the O1 phase, which is favoured in highly covalent systems, seems counterintuitive as the remaining sodium ions have to “share faces” with highly charged Sb and Ni. The peculiarity of NaNi2/3Sb1/3O2 is that Sb-Ni forms honeycomb-ordering in the TM layer, which might explain the formation of an O1 phase instead of an O3 phase above 3.5 V. Another honeycomb-ordered P2 type phase, Na2/3Ni2/3Te1/3O2 (or Na3Ni2TeO6), can be cycled over 4.5 - 3 V vs. Na+/Na due to inductive effect of even higher-valence Te^{6+} ions[76]. However, a mechanistic study has yet to be performed in this system.
Na$_x$(NiMn)O$_2$

Figure 5 (a) Cycling curves of P2 type Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ reprinted from reference[77]; permission pending. Copyright Electrochemical Society. (b) the oxygen layer in P2 Na$_x$Ni$_{1/3}$Mn$_{2/3}$O$_2$ structure and spin density section plot cutting at an oxygen layer for x=2/3 and x=0 reprinted from reference [78] with permission. Copyright Royal Society of Chemistry. (c) Cycling curve and in situ XRD of P2 type Na$_{2/3}$Ni$_{1/6}$Mn$_{1/2}$Fe$_{1/3}$O$_2$ reprinted from reference[79] with permission. Copyright Royal Society of Chemistry.

P2-type Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ cycled over 4.5 - 2.5 V vs. Na$^+$/Na shows P2$\rightarrow$O2 transformation at around Na$_{1/3}$ as evidenced by in situ[77] and ex situ XRD[78]. The O2 structure is shown to be the fully desodiated state as Ni$_{1/3}$Mn$_{2/3}$O$_2$ with much shorter interlayer distances. The good reversibility and small polarization in the range Na$_{2/3}$-Na$_0$ implies that TM migration might not exist in the highly charged state. Two major voltage plateaux are observed, which are assigned to Na-vacancy ordering at Na$_{2/3}$ based on synchrotron XRD data and at Na$_{1/3}$ based on DFT calculations, as shown in Figure 5(a)(b). The dramatic change in the spin-density on oxygen atoms revealed by DFT calculations suggests that oxygen redox starts after Ni$^{2+}$$\rightarrow$Ni$^{3.5+}$ in the high voltage plateau. In this case, h$^0$ = 1/12 and no lone pair is explicitly found. Nevertheless we can categorize the voltage profile of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ as type a.

P2-type Na$_{2/3}$Ni$_{1/6}$Mn$_{1/2}$Fe$_{1/3}$O$_2$ goes through P2$\rightarrow$OP4 type phase transition upon charging to 4.5 V vs. Na$^+$/Na. An OP4 phase is clearly observed by ex situ synchotron XRD data and annular dark-field STEM images[79]. However, the in situ XRD patterns seemingly show a solid solution instead of a biphasic process above 4 V, as shown in Figure 5(c). What undermines the definition of the solid solution reaction in this case is the splitting of (004) reflection, which is successfully modeled by an intergrowth of P2 and OP4 types. Mössbauer spectroscopy shows evidence for Fe$^{4+}$/3+ redox above 4 V in line with the onset of phase change. No evidence for Fe migration is found. In comparison, P2-type Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ goes through a typical biphasic process from P2 to O2 above 4 V upon Na removal. The interlayer distance of the O2 phase is refined to be 4.4 Å. This suggests that a sodium-free O-type phase can be reached from either a P2 or P3 starting structure.
It is still unclear why some P2-type materials transform into O2 directly with the involvement of neither an intermediate OP4 phase nor a P-O intergrowth.

**Lithium substituted P2-type NaNi_{0.98}Sn_{0.02}Mn_{0.86}O_{2}** does not undergo obvious phase transitions when cycled over 4.4 - 2 V vs. Na\(^+\)/Na, corresponding to 0.5 Na ions (de)intercalation with a smooth voltage curve\(^{[80]}\). A small amount of O-type stacking faults is observed above 4.05 V by **in situ** synchrotron XRD. Surprisingly, no voltage staging phenomena caused by Na-vacancy ordering are observed even though neutron diffraction revealed that the stoichiometry yields Li/Ni-Mn\(_2\) ordering, which could potentially promote Na ordering. Both the delayed phase transition and the sodium ordering could possibly be impeded by lithium ions jumping between the TM layer and the Na layer upon charging and discharging, as suggested by **ex situ** \(^7\)Li MAS NMR analysis. Assuming that the Ni\(^{4+/3+/2+}\) redox is responsible for 0.44 Na ions, there is tiny bit of anion redox involved, resulting in h\(^+\) = 0.03, which is much less than h = 0.12 in this case. The highly reversible cycling behaviour belongs to type a.

**O3-type NaNi\(_{0.5}\)Sn\(_{0.5}\)O\(_2\)** cycled over 3.8 - 2.2 V vs. Na\(^+\)/Na shows 0.6 Na ions extraction upon charging, corresponding to structural change O3→O3’→P3→P3’, which is fully reversible upon discharging\(^{[81]}\). Comparing the structural pathway and voltage curve with that of O3 type NaNiO\(_2\), one can conclude that Mn substitution elevates the voltage of the Ni\(^{3+/2+}\) redox couple. The fully sodiated phase cannot be achieved at a cutoff of 2.2 V, as for O3-type NaNiO\(_2\). When cycled in 4.5 - 2.2 V, all the Na ions can be extracted from the structure upon charging, just like the aforementioned P2 material. The structure of the final stage cannot be well characterized by **ex situ** XRD because it transforms into a water-intercalated phase almost instantaneously. This implies that there is no TM migration in the Na\(_0\) structure, or at least, the TM migration is highly reversible. **In situ** XRD studies revealed that the final stage phase can be indexed to an O3 structure with much shorter interlayer distance\(^{[82,83]}\). Recently our group employed **in situ** neutron diffraction and first principles calculation to elucidate unambiguously for the first time this final stage phase at high voltage state-of-charge to be a fully desodiated layered structure, or O3s phase as we call it\(^{[84]}\). Orbital-projected density of states shows that oxygen redox participates mainly in the final stage phase transition from O3 to O3s phase. The number of holes on oxygen is hard to define as the calculations are performed on limited number of structures.

**O3-type NaNi\(_{0.5}\)Sn\(_{0.3}\)Ti\(_{0.2}\)O\(_2\)** (y = 0.3 - 0.5) undergoes only a O3→P3 phase transition when cycled over 4.2 - 2.5 V vs. Na\(^+\)/Na\(^{[82]}\). The materials exhibit a 0.5 - 0.7 V higher discharge voltage plateau and lower polarization compared with O3-type NaNi\(_{0.5}\)Mn\(_{0.5}\)O\(_2\). Through systematical Bader charge analysis from DFT calculations, Sn substitution increases the ionicity of Ni-O bonds and consequently elevates the electrochemical reaction voltage, which eliminates the detrimental P3→O3’ transition above 4 V. The O3→P3 transition at the beginning of charge is also delayed by Sn substitution as the increased ionicity of the lattice destabilizes the P-type structure where Na ions have to “share faces” with more localized charge, compared with the case of no Sn substitution. The side effect of increased voltage is obviously due to compromised capacity while keeping the same voltage limit. The ionicity increases in other d\(^{10}/d^5\) substitutions are calculated to be in the following order: NaNi\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) > NaNi\(_{0.5}\)Sn\(_{0.5}\)O\(_2\) > NaNi\(_{0.5}\)Sn\(_{0.5}\)O\(_2\) > NaNi\(_{0.5}\)Sn\(_{0.5}\)O\(_2\). The reason for Ti having a lesser ionicity effect compared to Zr lies in the fact that Ti is in the same period as Ni, such that the d-band electrons are more delocalized due to energy match/orbital overlap. As a result, Ti substitution does not delay the O3→P3 transition but does prevent the P3→O3’ transition upon
charging, such as O3 type Na$_{0.9}$Ni$_{0.4}$Mn$_{0.4}$Ti$_{0.2}$O$_2$, making Ti substitution advantageous in terms of cyclability and rate capacity compared to Sn substitution[85].

**Ti/Cu substitution.** As mentioned above, Ti substitution mildly raises the ionicity of NaNi$_{0.5}$Mn$_{0.5}$O$_2$. Thus, O3-type NaNi$_{0.5}$Mn$_{0.4}$Ti$_{0.1}$O$_2$ still suffers from the P3→O3′→O3” transition when cycled over 4.5 V - 2 V vs. Na⁺/Na. The interlayer distance in O3” is refined to be 4.4 Å, in agreement with the aforementioned P2-type Na$_{2/3}$Ni$_{1/6}$Mn$_{1/2}$Fe$_{1/3}$O$_2$. By replacing some Ni with Cu, the P3→O3′→O3” transition with a large interlayer distance change (17%) is converted to the P3→P3′→O1 transition for NaNi$_{0.4}$Cu$_{0.1}$Mn$_{0.4}$Ti$_{0.1}$O$_2$ with a much smaller interlayer distance change (3%), evidenced by *in situ* X-ray diffraction[83]. The broadened diffraction peaks indicate an O1-P3 intergrowth. The emergence of the O1 phase at Na$_{0.15}$ content where Cu$^{3+/2+}$ starts to activate is confirmed by EPR spectrum. At the same time, HAADF-STEM images show TM migration. Jahn-Teller active Cu$^{3+}$ ions are speculated to move into the rectangle faces of prismatic site at earlier stage of charging. The O1 phase induced by Cu substitution suggests that Cu raises the covalency of the system, i.e., the opposite effect to that of Ti. Of note is that Cu solubility is no higher than 0.1 in O3-type NaNi$_{0.5}$Mn$_{0.5}$O$_2$.

**O3-type NaNi$_{1/3}$Fe$_{1/3}$Mn$_{1/3}$O$_2**

cycled between 4.3 - 2 V vs. Na⁺/Na undergoes reversible O3→P3→O3’ phase transitions[86]. Fitting Extended X-ray Absorption Fine Structure (EXAFS) of charged states of a similar compound NaFe$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ reveals an interesting correlation between redox couples and capacity[87]. The Ni$^{3+/2+}$ reaction is evidenced by a significant decrease of the Ni-O bond length upon removing the first 1/3 Na ions below 3.5 V. The Fe$^{4+/3+}$ reaction is confirmed by a decrease in the Fe-O bond length upon deintercalating the last 1/3 Na ions above 4 V. For the middle 1/3 Na ions, however, both Ni-O and Fe-O bond lengths change so mildly that it appears no significant valence change is undergone by either Ni or Fe, implies that a redox centre other than TM ions is involved.

Na$_2$RuO$_3$ & Na$_2$IrO$_3$

*Figure 6 (a) Schematic structures of ordered Na$_2$RuO$_3$, NaRuO$_3$ and Na$_{0.5}$RuO$_3$ with TM layer octahedra in grey (Ru), yellow (Na), white (vacancy), Na ions in yellow, Na ions in typical coulombic force fields as dashed circles, oxygen stacking sequence denoted as ABC and gliding vectors as t reprinted from reference [88]; permission pending.*
**O3’ type Na3RuO3** or Na[Na1/3Ru2/3]O2 with NaRu6 honey-comb ordering undergoes O3→O1→O1’ phase transitions upon charging to 4 V vs. Na+/Na, with two plateaux around 2.5 and 3.6 V\(^{[88]}\). The electrochemical reaction is almost fully reversible upon discharging to 1.5 V, with the large hysteresis at the 3.6 V plateau indicating anion redox, and the negligible polarization at the 2.5 V plateau marking Ru\(^{5+/4+}\) redox as evidenced by Ru L-edge XAS\(^{[90]}\). This falls into type a behavior with hysteresis and h\(^0\) = 1/3 less than \(\delta = 1/3\). In situ XRD shows that the O3→O1 transition is accompanied by the Ru\(^{5+/4+}\) reaction while O1→O1’ is concomitant with anion redox. Contrary to the general trends, O3→O1→O1’ leads to the interlayer distance shrinking steadily. Structural refinement shows that Na migrates out of the TM layer with the formation of O1 and O1’ phases, where Na directly shares faces with one RuO\(_6\) octahedron and one vacancy (O1) or with two vacancies (O1’) in adjacent TM layers to minimize the strong coulombic force field exerted by highly charged Ru\(^{5+}\) ions, as shown in Figure 6(a). Of note is that these phase transitions are accomplished by layer-gliding on the basis of NaRu6 ordering, which explains the completely different phase behavior and properties compared to Na-Ru disordered Na3RuO3.

**O3’ type Na3IrO3** resembles Na3RuO3 in terms of phase transitions and electrochemistry, however with no hysteresis in the high-voltage reaction. Iridium redox contributes to most of the sodium removal to NaIrO3 before anion redox to Na0.5IrO3 upon charging as evidenced in Ir 4f XPS\(^{[89]}\), which can be categorized into type a with h\(^0\) = 1/3 equivalent to \(\delta = 1/3\). In this case the unified theory applies so accurately that further Na-extraction leads to irreversible O2 formation, as evidenced by in situ mass spectrometry. The shortened O-O distance is unambiguously characterized by a combination of neutron diffraction and STEM as shown in Figure 6(b)-(d), which implies O-O bond formation stabilized as Ir-O-O, as described in the unified theory. In fact, the high-voltage phase proves to be so stable that it contributes to irreversibility in prolonged cycles. It seems that the tendency for O1 and O1’ phase formation is higher in the iridium system compared to the ruthenium system, as exemplified in a recent study on disordered O3-type Na1.2Mn0.8Ir0.2O2 materials that show O3→O1→O1’\(^{[1]}\) phase transitions upon charging to 4.4 V vs. Na+/Na\(^{[91]}\). The charge compensation is accounted by Mn\(^{4+/3+}\) for 0.4 Na ions before anion redox for 0.6 Na ions as evidenced by Mn 2p XPS and in situ Raman spectroscopy. The voltage hysteresis, irreversibility and changed voltage curve after the first cycle put the reaction into type b with h\(^0\) = 0.3 greater than \(\delta = 0.2\).

Characterization of structural evolution and anion redox

**X-ray and neutron diffraction** have been widely used to study the structural evolution of layered oxides during electrochemical cycling, taking advantage of their well-defined diffraction peaks and the relatively high-symmetry crystal structures. It is now becoming routine to perform in situ diffraction experiments, enabled by high-resolution area detectors, e.g. MYTHEN (Microstrip sYstem for Time-rEsolved experimeNts)\(^{[82]}\) for XRD and \(^3\)He based position-sensitive detectors (PSD) for neutron powder diffraction (NPD). Based on the survey in this review, in situ XRD is favoured

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1 a name sequence different from the original research article is used to keep the narrative consistent.
due to the simpler sample preparation procedure. This is usually achieved by constructing an effectively X-ray “transparent” window on a coin-cell setup as similar as possible to that used for lab-grade testing conditions. The window is made of beryllium metal or inert polymer tape, e.g. Kapton, which proves problematic in some cases because it fails to provide the same mechanical pressure on the area observed by X-ray as on the area covered by the spring-forced shells of the coin cell.\(^\text{[93]}\)

In situ NPD requires a much larger quantity of sample due to the cross sections for neutron scattering being orders of magnitude smaller than for X-rays. However, this has the advantage that the neutron beam is highly penetrating, which allows a window-free and pressurized setup that is close to industry-grade testing condition. To minimise neutron absorption and the incoherent neutron scattering from hydrogen that degrade the signal-to-noise ratio, deuterated electrolyte and minimum amounts of counter-electrode must be used.\(^\text{[94]}\) Although widely regarded as a complementary tool to XRD for structural determination due to the irregular elemental cross sections and angle-independent elastic scattering behaviour, in situ NPD characterization remains challenging. Indeed, of the compounds surveyed for this review, we failed to find any in situ NPD work on sodium layered oxides, and only a few ex situ studies.

Transmission electron microscopy has been successfully used to demonstrate anion redox by directly revealing the shortened O–O distances in the charged-state material Na$_2$IrO$_3$.\(^\text{[89]}\) This is realized in the so-called annular bright-field scanning TEM mode (ABF-STEM), which is dedicated to probe lighter atoms such as oxygen, in a modern aberration-corrected TEM. The shortened O–O distances are a consequence of electron loss from the O 2$p$ orbitals and the formation of O–O bonds as illustrated in the Introduction to this work. While not a truly quantitative measurement for anion redox, imaging the O–O lengths has been successful in materials containing 4$d$ and 5$d$ TM metals where “knock-on” damage is negligible.

However, TEM has proved to be a powerful tool for studying TM migration in the high state-of-charge and Na-depleted layered oxides, as exemplified in this review. This is realized in the so-called high-angle annular dark-field scanning TEM mode (HAADF-STEM), which provides atomic number contrast images. TM migration happens only in the near-surface area in some cases, which might result from reaction with electrolyte. The trivial amount of TM-migrated phase prevents effective detection by conventional diffraction technique. TM migration of sodium layered oxides might be different from its lithium counterpart due to the apparent ionic radii difference. It is postulated that TM migration could be negligible or largely reversible in some sodium layered oxides. TEM characterization will hopefully answer this postulation.

The most valuable feature of state-of-art TEM is exemplified by work on α-Na$_2$MnO$_3$ where atomic displacement due to cooperative Jahn-Teller effect and Mn$^{3+/4+}$ charge-ordering were unambiguously illustrated on an atom-by-atom scale. This was achieved by simultaneous STEM and EELS (electron energy loss spectroscopy).\(^\text{[18]}\) Charge-ordering and its correlation with Na-vacancy ordering is key to understanding phase transitions and remains challenging to characterize.

Solid state nuclear magnetic resonance (ssNMR) is increasingly used to provide local chemical information about layered oxides without damaging the sample. This is because the energy required to excite nuclear spin states lies in the radio-frequency range, while XAS uses high-energy X-ray radiation and TEM uses electrons of even higher energy. The key factor determining the
position and shape of NMR signals in a typical layered oxide Na₃TMO₂ is paramagnetic correlations between unpaired d-orbital electrons from TM and the probe Na₂¹⁹ nuclear spin via a bridging oxygen atom, i.e., the TM-O-Na bond pathway shift [95], which is a function of the coordination environment (prismatic, octahedral, tetrahedral, or even amorphous), TM species and valence. The ability to differentiate local structures is illustrated by the study of β-NaMnO₂ with ex situ ssNMR [19]. Three peaks corresponding to three types of Na environments were unambiguously found in the NMR spectra: those in β-NaMnO₂; in α-NaMnO₂; and in the boundary region of α,β-NaMnO₂, offering a unique insight into the structural evolution aspects.

⁷Li can also be used as a NMR probe, especially in lithium substituted materials, Na₆Li₃TM(1-x)O₂ as noted a number of times in the previous section. The most profound information obtained by determining the environment of Li is that lithium ions become extremely mobile when almost all sodium ions are removed. Originally located in the TM layer, these lithium ions can hop back and forth between the TM and Na layers upon (dis)charging at high voltage, which contributes to the stability as well as hysteresis. In theory, any nucleus with even number of proton or/and neutron can act as a NMR probe, e.g. ⁵⁵Mn, ⁵⁹Co, ⁵⁹Ni. Probing heavy nuclei could potentially disclose the more details on TM migration and the electronic states without damaging or changing the status of the samples. However, the heavier nuclei require higher magnetic fields (according to the gyromagnetic ratio) and a more complex theoretical treatment.

First principles calculations based on density functional theory (DFT) have demonstrated an capability to predict phase transitions and anion redox phenomenon in sodium layered oxides, exemplified by numerous cases reviewed in the previous section. Modern high-performance computer clusters make it practical to solve the Kohn-Sham equation for electronic density in the exact ground state. The challenge in modelling the voltage profile of layered oxides with respect to the state-of-charge lies in the almost infinite number of Na/vacancy configurations given an arbitrary sodium content. This can be addressed by employing the cluster-expansion Hamilton to enable selection of the ground state configurations with sufficient accuracy and efficiency [96,97]. Based on the cluster-expansion Hamilton, the temperature-composition phase diagram can be obtained by using the Metropolis Monte Carlo method and neglecting the lattice vibration contribution (both enthalpy and entropy), yielding a more accurate voltage profile at temperatures other than 0 K [58,98].

With DFT methods, it is often effective to start by matching the experimental voltage profile to validate the calculations, after which other calculated properties of the material can be investigated with confidence. In particular, the density of states and the direct projection of the electronic density can be readily extracted from the calculation. By analysing the electron states close to the Fermi level, one can qualitatively identify the redox centres. Other methods such as Bader charge analysis [99] and the electronic localization function (ELF) [10,100] can reveal the electron distribution quantitatively. However, the quality of DFT predictions largely depends on which exchange correlation functional is chosen, from local spin-density approximation (LDA), generalized gradient approximation (GGA) to meta-GGA, with or without on-site Coulombic interaction correction (DFT+U) [101,102]. Sometimes a Van der Waals density functional is needed to model layered structure [103]. The most precise models involve non-local Hartree-Fock exchange or hybrid functionals, which are still not applicable to large material systems due to their high computational cost. In this regard, DFT calculation results should always be considered in light of
the computational details.

**X-ray spectroscopy** techniques have become indispensable in materials science thanks to the development of synchrotron X-ray sources. These sources have enabled the study of materials using X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS). The variation of cross-section with respect to X-ray energy divides XAS techniques into: fluorescence/Auger-electron mode, i.e., soft-XAS for the low-energy K-edges of light atoms and L-edges of heavy atoms; and transmission mode, i.e., hard-XAS for the high-energy K-edges of heavy atoms. For layered oxides NaTMO₂, both the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) of the spectrum offer invaluable information about coordination environments, oxidation states and electronic structures, although EXAFS measurements in soft-XAS are often impossible due to interference from other absorption edges. The intensity of the pre-edge peak at TM K-edges follows a well-defined trend in terms of coordination: octahedral < square-pyramidal < tetrahedral \[^{[104]}\]. This is because the transition event evolves from dipole-forbidden 1s→3d to dipole-allowed 1s→3d-4p hybridization. The coordination information can be further quantified by fitting EXAFS data to a conjectured structure. These analyses complement diffraction techniques, which can be ambiguous due to ion-mixing/migration and amorphisation, as exemplified in the study of Na₃CrO₂ \[^{[31]}\]. In comparison, the pre-edge peak of at the O K-edge is more conspicuous due to hybridization in the transition 1s→2p-3d\(^{TM}\) and can be directly compared to the calculated valence-band density of states as exemplified in research on Na₃FeO₂ \[^{[42]}\]. The fine structure of the TM L-edge will be discussed in the next section.

In the case of Na₂IrO₃, XPS was employed to reveal not only the oxidation change of iridium but also a new species of oxygen \((O_2)^n\) \[^{[89]}\], supporting a proposed anion redox contribution to the total capacity. However, the X-ray source was Al Kα emission (~1.5 keV) which penetrate to less than 10 nm. The spectrum obtained was heavily masked by surface oxygen-containing species, e.g., decomposed carbonates that are hard to remove when preparing ex situ samples. Hence the deconvolution of the spectrum is challenging as the signal \((O_2)^n\) is buried between peaks of lattice oxygen and surface deposits. This issue can be addressed by using hard X-ray photoelectron spectroscopy (HAXPES) which penetrates deeper with increased X-ray energy as demonstrated in the study of a Li-rich layered oxide \[^{[105]}\]. As with hard-XAS, the radiation damage can be significant, especially for metastable samples at high states-of-charge, therefore measurements should always be taken with care.

**Perspective**

**Structural evolution**

Although the phase transformations in the high-voltage region (usually above 4 V) of sodium transition metal layered oxides have been shown to take P→O type pathways at roughly the same stage of desodiation \((Na_xMO_2, x = 0.3 – 0.4)\) in the charging process, as shown in Table 1 and Table 2, distinctive biphasic diffraction patterns are not always available even using the state of art \(in situ\) diffraction technology. The most remarkable example is the comparative study of P2-type Na₂/3Ni₂/3Mn₁/2Fe₁/2O₂ and Na₂/3Ni₂/3Mn₂/3O₂\[^{[79]}\] with corresponding intergrowth mechanisms proposed. Various theoretical studies have shown that the P→O transformation is energetically favoured as the sodium content decreases. The most comprehensive example is the theoretical
study of multiphase evolution of NaTiS$_2$, where O1, O3, P3, O1-O3 and O1-P3 intergrowth are compared in a single formation energy diagram$^{[60]}$. Other than an energy perspective, there are no studies from the point of view of kinematics and the dynamics of phase change. Hence, we intend to draw the attention of scientific community by a brief discussion on the process of P$\rightarrow$O transformation via layer gliding, which might shed light upon the understanding of ambiguous phase change in the high-voltage region and guide the discovery of new phases.

The phase change from P- to O-type often happens at room temperature under galvanostatic desodiation conditions. Hence, the only possible way to accomplished the phase transition in a single particle is via cooperative layer gliding according to the principle of least action, rather than layer rotation or TM-O covalent bonds breaking. Layer rotation would require atoms far away from the rotation centre to travel a long distance and bond breaking usually requires elevated temperatures.

Table 1 Phase stability range upon charging and cycling voltage range of O/P3 type materials. The left boundary is set according to the emergence of the marked phase.Irreversible phases are denoted in red. Solid-solution type phase transitions are indicated with a dash “-” and biphasic type with an arrow “$\rightarrow$” where the onset of the new phase is not determined. “C, D/V” column stands for charge/discharge cut off voltage.

<table>
<thead>
<tr>
<th>Materials</th>
<th>C, D/V</th>
<th>Na$_{0.8}$</th>
<th>Na$_{0.6}$</th>
<th>Na$_{0.4}$</th>
<th>Na$_{0.2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O3‘-Na$_2$MnO$_4$</td>
<td>3.8/2</td>
<td>O</td>
<td>P</td>
<td>Z</td>
<td></td>
</tr>
<tr>
<td>P3 Na$<em>2$(Li$</em>{1/3}$Mn$_{2/3}$)O$_3$</td>
<td>4.5/3.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O3 NaCoO$_2$</td>
<td>3.7/2.5</td>
<td>O</td>
<td>P</td>
<td>P$\rightarrow$O$_{(4.0 \text{ V})}$</td>
<td></td>
</tr>
<tr>
<td>O3 NaFeO$_2$</td>
<td>4.0/2.5</td>
<td>O</td>
<td>P</td>
<td>X$_{(4.5 \text{ V})}$</td>
<td></td>
</tr>
<tr>
<td>O3 Na$<em>{0.6}$Mn$</em>{0.2}$Fe$_{0.2}$O$_2$</td>
<td>4.3/1.5</td>
<td>O</td>
<td>P</td>
<td>X-OP2</td>
<td></td>
</tr>
<tr>
<td>O3 NaCoO$_2$</td>
<td>4.0/2.5</td>
<td>O</td>
<td>P</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O3 Na$<em>{0.6}$Fe$</em>{0.4}$O$_2$</td>
<td>4.0/2.5</td>
<td>O</td>
<td>P</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>O3 NaNiO$_2$</td>
<td>4.0/2.5</td>
<td>O$\rightarrow$P</td>
<td>P</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>O3 NaNi$<em>{0.8}$Fe$</em>{0.2}$O$_2$</td>
<td>3.8/2</td>
<td>O</td>
<td>P</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O3 Na$<em>{0.6}$Co$</em>{0.2}$O$_2$</td>
<td>4.2/2</td>
<td>O</td>
<td>P</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>O3 Na$<em>{0.2}$Sb$</em>{0.8}$O$_2$</td>
<td>4.2/2</td>
<td>O</td>
<td>P</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>O3 Na$<em>{0.6}$Mn$</em>{0.2}$O$_2$</td>
<td>4.5/2.2</td>
<td>O</td>
<td>P</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>P3 Na$<em>{0.8}$Ni$</em>{0.2}$Mn$_{0.2}$O$_2$</td>
<td>4.3/2.5</td>
<td>P</td>
<td>O</td>
<td>O3s</td>
<td></td>
</tr>
<tr>
<td>O3 NaNi$<em>{0.6}$Sn$</em>{0.2}$O$_2$</td>
<td>4.2/2.8</td>
<td>O</td>
<td>P</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O3 NaNi$<em>{0.2}$Mn$</em>{0.8}$O$_2$</td>
<td>4.5/2</td>
<td>O</td>
<td>P</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O3 Na$<em>{0.6}$Cu$</em>{0.4}$Mn$_{0.4}$O$_2$</td>
<td>4.5/2</td>
<td>O</td>
<td>P</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>O3 Na$<em>{0.6}$Fe$</em>{0.4}$Mn$_{0.4}$O$_2$</td>
<td>4.3/2</td>
<td>O</td>
<td>P</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>O3 Na$<em>{0.4}$Ni$</em>{0.4}$Fe$_{0.2}$O$_2$</td>
<td>4.1/1.5</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>O3 Na$<em>{0.4}$Ni$</em>{0.4}$Ti$_{0.2}$O$_2$</td>
<td>4.1/1.5</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>O3 Na$<em>{0.4}$Mn$</em>{0.4}$H$_{0.1}$O$_2$</td>
<td>4.4/1.5</td>
<td>O</td>
<td>O</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Cooperative layer gliding of P2-type structures (P6₃/mmc) involves adjacent layers moving along one of the six-fold symmetric directions by \( a/\sqrt{3} \), or along a set of vectors \( \{ \gamma \} \) shown in Figure 7(a). \( \{ \gamma \} = \{ 2/3a + 1/3b, 1/3a + 2a/3b, 2/3a + 1/3b, 1/3a + 2/3b, 2/3a + 1/3b \} \). Take for example the most comprehensible P2→O2 and P2→OP4 transitions\(^{[46,77]}\): the P2→O2 transition is achieved by one layer gliding \( \{ \gamma \} \) for every other layer (one unit cell); while the P2→OP4 transition is achieved by two adjacent layers gliding \( \{ \gamma \} \) and \( \{ \gamma' \} \) for every four layers (two unit cells), as shown in Figure 7(c), while ignoring changes in cell parameters. However, there is a 5-% chance that \( \{ \gamma \} \) and \( \{ \gamma' \} \) gliding results in the O2-type structure, which explains why stacking faults are often observed in the P2→OP4 transition. Although the same number of glides are made in both P2→O2 and P2→OP4, the driving force for P2→O2 is greater as more O2 phase is formed.

Table 2 Phase stability range upon charging and cycling voltage range of O/P2 type materials. The left boundary is set according to the emergence of the marked phase. Solid-solution type phase transitions are indicated with a dash “-. “C, D/V” column stands for charge/discharge cut off voltage.

<table>
<thead>
<tr>
<th>Materials</th>
<th>C, D/V</th>
<th>Na₀.₈</th>
<th>Na₀.₆</th>
<th>Na₀.₄</th>
<th>Na₀.₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>P₂ Na₀.₅MnO₂ (^{[26]})</td>
<td>4.4/1.5</td>
<td>P</td>
<td>P</td>
<td>OP4</td>
<td></td>
</tr>
<tr>
<td>P₂ Na₀.₅Mn₃O₆ (^{[26]})</td>
<td>4.4/1.5</td>
<td>P</td>
<td>P</td>
<td>P+O</td>
<td></td>
</tr>
<tr>
<td>P₂ Na₀.₅Li₂Mn₃O₁₂ (^{[26]})</td>
<td>4.5/1.5</td>
<td>P</td>
<td>P</td>
<td>P+O</td>
<td></td>
</tr>
<tr>
<td>P₂ Na₀.₅Li₂Mn₃O₁₂ (^{[26]})</td>
<td>4.5/2</td>
<td>P</td>
<td>Z-OP4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P₂ Na₀.₅Li₂Mn₃O₁₂ (^{[26]})</td>
<td>4.4/1.5</td>
<td>P</td>
<td>P</td>
<td>P+O</td>
<td></td>
</tr>
<tr>
<td>P₂ Na₀.₅Li₂Mn₃O₁₂ (^{[26]})</td>
<td>3.8/2.5</td>
<td>P</td>
<td>P</td>
<td>P+O</td>
<td></td>
</tr>
<tr>
<td>P₂ Na₀.₅Li₂Mn₃O₁₂ (^{[26]})</td>
<td>4.3/1.5</td>
<td>P</td>
<td>Z-OP4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P₂ Na₀.₅Li₂Mn₃O₁₂ (^{[26]})</td>
<td>4.3/1.5</td>
<td>P</td>
<td>P</td>
<td>O2</td>
<td></td>
</tr>
<tr>
<td>P₂ Na₀.₅Li₂Mn₃O₁₂ (^{[26]})</td>
<td>4.5/1.5</td>
<td>P</td>
<td>P</td>
<td>Z-OP4</td>
<td></td>
</tr>
<tr>
<td>P₂ Na₀.₅Li₂Mn₃O₁₂ (^{[26]})</td>
<td>4.2/2</td>
<td>P</td>
<td>P</td>
<td>PO</td>
<td></td>
</tr>
</tbody>
</table>

For P₃-type structures (R3m or R-3m) there are two sets of gliding vectors needed to fulfil the P→O transition, \( \{ \alpha \} = \{ 2/3a + 1/3b, -1/3a + 1/3b, -1/3a + 2/3b \} \) \( \{ \beta \} = \{ 1/3a + 2/3b, 1/3a + 2/3b, -2/3a + 1/3b \} \) as shown in Figure 7(b). The \( \{ \alpha \} \) glide leads to TM ions facing the upper adjacent TM ions (z+1/3) while the \( \{ \beta \} \) glide leads to TM ions facing the lower adjacent TM ions (z-1/3). As there is no mirror plane perpendicular to the c axis, the up vs. down orientation matters. Taking for example the comparative study of O3-type NaNi₀.₅Mn₀.₄Ti₀.₁O₂ and NaNi₀.₅Mn₀.₄Ti₀.₁O₂ with the high-voltage transition P3→O3’→O3” and P3’→P3’→O1 intergrowth\(^{[83]}\), as well as the P3→OP2 transition in O3-type NaFe₁₂Mn₁₂O₂\(^{[106]}\), one can appreciate the complexity of phase transitions in P3/O3 type structures. If two layer glides are allowed in one unit cell of the P3 structure, one can have four combinations \( \{ \alpha \}, \{ \beta \}, \{ \alpha \} \{ \beta \} \) resulting in O3, O1, OPO3, O₂OPO3 structures as shown in Figure 7(e). “O₁” denotes an O1 type layer where TM ions of adjacent layers face each other along the c
axis. If one layer glides are allowed in one unit cell of the P3 structure, one can have four combinations \{\alpha\}_{1/3}, \{\alpha\}_{2/3}, \{\beta\}_{1/3}, \{\beta\}_{2/3} resulting in P01O3, O1PO3, PO013, OO3P structures as shown in Figure 7(f). Subscripts “1/3” or “2/3” denote the gliding layer z position. One should note that OPO13, PO1O3, O1P03, POO13, OO1P3 are equivalent due to the rhombohedral symmetry. To realize P3→OPO13 or P3→O2PO3, \{\alpha\} or \{\beta\} glides instead of \{\alpha\}\{\alpha\} or \{\beta\}\{\beta\} are involved according to the principle of least action. Finally, if four layer glides are allowed in two unit cells of the P3 structure, an P3→OP2 transition is realized as shown in Figure 7(d), the driving force of which is expected to be less than that of P3→O3/O1 with the same percentage of gliding layers.

![Figure 7](image.png)

Figure 7 Illustration of possible phase transformation pathways. (a) P2 lattice with only TM metals shown in purple and displacement vectors \(\gamma\). (b) P3 lattice with only TM metals shown in purple and displacement vectors \(\alpha\) and \(\beta\). (c) phase transitions P2→O2 and P2→OP4 via shifting \(\gamma\). (d) phase transition P3→OP2 via shifting \(\alpha\) and \(\beta\). (e) phase transitions P3→O3, P3→O1, P3→OPO3 and P3→O2PO3 via shifting \(\alpha\) and \(\beta\). (f) phase transitions P3→O2O3, P3→O1OP3, P3→O1OP3 and P3→POO13 via shifting \(\alpha\) or \(\beta\). All structures viewed along [100] direction. All cell parameters changes have been ignored. All TM octahedra are shown in purple and all Na sites in yellow.

Anion redox

The unified theory has so far successfully predicted the electrochemical behavior of layered oxides whose TM layers contain vacancy or inactive atoms (Li, Na or Mg) and whose capacity is greater than that offered by nominal valence change of active atoms (Cr\(^{3+/2+}\), Mn\(^{3+/2+}\), Fe\(^{3+/2+}\), Co\(^{3+/2+}\), Ni\(^{3+/2+}\), Ru\(^{3+/4+}\)). However, as shown in Table 3, there are violations to the unified theory in late transition metal systems (Fe, Co, Ni) and in those unconventional layered oxides with no cation redox at all (V, Cu). From this we can say that: oxygen lone pair electrons or non-bonding oxygen states are not a prerequisite for anion redox; and anion redox might not be reversible even if there is a surplus of oxygen lone pairs. Thus, a few refinements should be made to the unified theory to answer the following questions.
1) How can we effectively define the number of holes, or at what stage anion redox takes over from cation redox or vice versa in electrochemical cycling?

2) How can we effectively define the number of oxygen lone pairs for non-octahedrally coordinated layered oxides, e.g., NaVO$_3$ and NaCuO$_2$, or find other criteria to use when there is no lone pair?

3) Considering that phase transitions or/and ion-migration from TM layers to Na layers are associated with anion redox in some cases but not others, what are the cause and effect relationships among them?

We will tentatively address the first question while leave the latter two open.

Table 3 A list of anion redox materials based on the unified theory. The number of holes on oxygen $h^0$ is calculated based on anion redox capacity. Generalized $\delta$ is calculated based on the nominal number of oxygen lone pair electrons. These calculations can be found in corresponding paragraphs in the second section.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$h^0$</th>
<th>$\delta$</th>
<th>Type</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$<em>{0.59}$Mn$</em>{0.9}$□$_{0.10}$O$_2$</td>
<td>0.17</td>
<td>0.1</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>Na$<em>{2/3}$Mn$</em>{1/3}$O$_2$</td>
<td>0.14</td>
<td>0.14</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>Na$<em>{0.72}$(Li$</em>{0.24}$Mn$_{0.76}$)O$_2$</td>
<td>0.36</td>
<td>0.24</td>
<td>C</td>
<td>With irreversibility</td>
</tr>
<tr>
<td>Na$<em>{0.64}$(Li$</em>{0.2}$Mn$_{0.8}$)O$_2$</td>
<td>0.2</td>
<td>0.2</td>
<td>A</td>
<td>With irreversibility</td>
</tr>
<tr>
<td>Na$<em>{0.35}$(Li$</em>{0.25}$Mn$_{0.75}$)O$_2$</td>
<td>0.27</td>
<td>0.25</td>
<td>C</td>
<td>With irreversibility</td>
</tr>
<tr>
<td>Na$<em>{2/3}$Mg$</em>{0.28}$Mn$_{0.72}$O$_2$</td>
<td>0.21</td>
<td>0.28</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>NaVO$_3$</td>
<td>0.23</td>
<td>0.56</td>
<td>D</td>
<td>Violation</td>
</tr>
<tr>
<td>NaCuO$_2$</td>
<td>0.3</td>
<td>0.33</td>
<td>D</td>
<td>Violation</td>
</tr>
<tr>
<td>NaFeO$_3$</td>
<td>0.14</td>
<td>0</td>
<td>D</td>
<td>Violation</td>
</tr>
<tr>
<td>NaNi$<em>{0.5}$Fe$</em>{0.5}$O$_4$</td>
<td>0.2</td>
<td>0</td>
<td>A</td>
<td>Violation</td>
</tr>
<tr>
<td>Na$<em>{2/3}$Ni$</em>{1/3}$Mn$_{1/3}$O$_2$</td>
<td>0.08</td>
<td>0</td>
<td>A</td>
<td>Violation</td>
</tr>
<tr>
<td>Na$<em>{0.80}$(Li$</em>{0.12}$Ni$<em>{0.52}$Mn$</em>{0.68}$)O$_2$</td>
<td>0.03</td>
<td>0.12</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>Na(Na$<em>{1/3}$Ru$</em>{2/3}$)O$_2$</td>
<td>0.17</td>
<td>0.33</td>
<td>A</td>
<td>With hysteresis</td>
</tr>
<tr>
<td>Na(Na$<em>{1/3}$Ir$</em>{2/3}$)O$_2$</td>
<td>0.33</td>
<td>0.33</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>Na$<em>{1/3}$Mn$</em>{0.4}$Ir$_{0.4}$O$_2$</td>
<td>0.3</td>
<td>0.2</td>
<td>B</td>
<td></td>
</tr>
</tbody>
</table>

As discussed above under Characterization, oxygen participation in the electrochemical reactions of layered transition metal oxides has been qualitatively revealed by DFT calculation, O K-edge XAS and angular bright field-STEM (applicable only to super stable 4-5d transition metal oxides). In contrast, quantification of electron holes on oxygen has been scarcely attempted. The difficult problem of defining the oxygen hole is exemplified by an ex situ XAS study on P2-type Na$_x$CoO$_2$, where the ligand hole is postulated to persist over the range $x = 0.46$ - 0.86 based on only one pre-edge peak in Co K-edge absorption spectroscopy$^{[107]}$. From a molecular orbital standpoint, there ought to be two pre-edge peaks corresponding to the dipole-forbidden transition from 1s to 3d $e_g$ and $t_{2g}$ orbitals of Co ions in the charged state $(t_{2g})^{5+x} (e_g)^0$. The observation of only one pre-edge feature suggests that the Co ions are more likely in the charged state $(t_{2g})^{5+x} (e_g)^0 \downarrow$, where $\downarrow$ denotes ligand holes. The persistent ligand hole is further illustrated in another ex situ XAS study at the O K-edge, where three pre-edge peaks A, A' and B are observed$^{[108]}$. These remarkable peaks indicate strong hybridization of O 2p with Co 3d orbitals. The increased intensity of A and A' peaks assigned...
to the $d^6 \rightarrow d^6$ transition, and the decreased intensity of the B peak assigned to the $d^6 \rightarrow d^7$ transition, with sodium extraction implies that the redox centre shifts from Co$^{3+}$ to anion redox over the charging process as shown in Figure 8(b).

The ligand hole $L$ can be quantitatively calculated from first principles by the configuration-interaction full-multiplet (CIFM) method, used in the aforementioned spectroscopy study of Na$_x$Ti$_0.5$Ni$_0.5$O$_2$ and Na$_x$Fe$_0.5$Ni$_0.5$O$_2$ as shown in Figure 8(a) [73]. Na$_x$(Fe/Ti)$_0.5$Ni$_0.5$O$_2$ at any state-of-charge can be modelled by a combination of three clusters [NiO$_6$]$^{10-}$, [NiO$_6$]$^{9-}$ and [NiO$_6$]$^{8-}$, each of which is made up of different proportions of ligand-to-metal charge transfer (LMCT) states $[\text{Ni}^{3+}(O^2-)_{3}]_\text{A}$, $[\text{Ni}^{3+}(O^2-)_{3}O^2\text{-}]$ and $[\text{Ni}^{3+}(O^2-)_4(O^2-)_{2}]$. The weighted total number of holes from CIFM calculations could potentially serve to indicate the reversibility of anion redox, especially for later transition metals (Fe, Co, Ni, Cu) marked by LMCT.

Figure 8 (a) Ex situ Ni L$_3$-edge in partial fluorescence yield (PFY) mode (black line), CIMF calculation (red dotted line) and corresponding fraction of each cluster [NiO$_6$]$^{10-}$ (green), [NiO$_6$]$^{9-}$ (blue), [NiO$_6$]$^{8-}$ (orange) for pristine, $x=0.5$, $x=1$ of Na$_x$TMO$_2$ materials reprinted from reference [73] with permission. Copyright American Chemical Society. (b) Isotropic O 1s XAS measured on single crystals Na$_{0.5}$CoO$_2$, Na$_{0.67}$CoO$_2$ and Na$_{0.75}$CoO$_2$ reprinted from reference [108] with permission. Copyright American Physical Society. (c) The mapping of RIXS of Na$_{2/3}$Mg$_{1/3}$Mn$_{2/3}$O$_2$ at different state-of-charge, with oxygen redox feature indicated by red arrow. (d) super PFY signals of O 1s XAS generated by integration of the intensities in the range of emission energies indicated by dotted lines in (c). Both reprinted from
A direct way to quantify oxygen redox is by mapping resonant inelastic X-ray scattering (mRIXS) at the O K-edge for ex situ samples. mRIXS can reveal features that are hidden in the fluorescence signals of conventional XAS. The X-ray emission spectrum at 523.7 eV, extracted from mRIXS, with an X-ray excitation energy of 531 eV is postulated to result from oxygen states resembling those in peroxides and oxygen gas. This spectrum is therefore a signature of oxygen redox, as shown in Figure 8(c) for a typical electrode material operating almost completely on oxygen redox, Na$_{2/3}$Mg$_{1/3}$Mn$_{2/3}$O$_2$. This signature can be totally buried by X-ray emission peaks just above 524 eV in partial or total fluorescence yield (PFY or TFY) XAS spectra. Integrating the intensities over a small range around 523.7 eV emission energy reveals a pronounced signal, the so-called super partial fluorescence yield (sPFY), that makes quantification straightforward as shown in Figure 8(d) for Na$_{2/3}$Mg$_{1/3}$Mn$_{2/3}$O$_2$ at different state-of-charge. The calculated result can be confirmed by quantifying the TM metal redox contribution. This can also be achieved using mRIXS, e.g., at the Mn L-edge in the case of Na$_{2/3}$Mg$_{1/3}$Mn$_{2/3}$O$_2$, by integrating the intensities in the O K emission regimes then inverting to give Mn L inversed partial fluorescence yield (iPFY); or in the Mn 3s→2p emission regimes, to give core-core partial fluorescence (ccPFY). Both iPFY and ccPFY signals are free from low-energy excitons (phonons, plasmons, spinons, orbitons) and can be quantified linearly, which is impossible in conventional XAS.

In light of this critical review of the literature, we are confident that a complete understanding of the phase transitions and anion redox behaviour in layered sodium transition metal oxides, under high-voltage operating conditions in sodium-ion batteries, is within reach. The key will be a deeper understanding of the structural evolution from the perspective of thermodynamics through a combination of long-range (X-ray/neutron diffraction) and local probes (ssNMR, STEM, EXAFS). We have tentatively suggested some extensions to the unified theoretical framework within which they can be placed; and identified electronic spectroscopy as the class of experimental method most likely to yield decisive insights. This complete understanding will permit the rational design of new high-voltage/high-capacity sodium-ion batteries that are competitive with state-of-art lithium-ion batteries, while also helping to advance research on other types of electrode materials.

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