Recent Progress on Germanene and Functionalized Germanene: Preparation, Characterizations, Applications, and Challenges

Nana Liu  
*University of Wollongong, nl709@uowmail.edu.au*

Guyue Bo  
*University of Wollongong, gb029@uowmail.edu.au*

Yani Liu  
*University of Wollongong, Beihang University*

Xun Xu  
*University of Wollongong, Beihang University, xun@uow.edu.au*

Yi Du  
*University of Wollongong, Beihang University, ydu@uow.edu.au*

See next page for additional authors

Publication Details

Recent Progress on Germanene and Functionalized Germanene: Preparation, Characterizations, Applications, and Challenges

Abstract
2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim A new family of single-atom-thick 2D germanium-based materials with graphene-like atomic arrangement, germanene and functionalized germanene, has attracted intensive attention due to their large bandgap and easily tailored electronic properties. Unlike carbon atoms in graphene, germanium atoms tend to adopt mixed sp2/sp3 hybridization in germanene, which makes it chemically active on the surface and allows its electronic states to be easily tuned by chemical functionalization. Impressive achievements in terms of the applications in energy storage and catalysis have been reported by using germanene and functionalized germanene. Herein, the fabrication of epitaxial germanene on different metallic substrates and its unique electronic properties are summarized. Then, the preparation strategies and the fundamental properties of hydrogen-functionalized germanene (germanane or GeH) and other ligand-terminated forms of germanene are presented. Finally, the progress of their applications in energy storage and catalysis, including both experimental results and theoretical predictions, is analyzed.

Disciplines
Engineering | Physical Sciences and Mathematics

Publication Details

Authors
Nana Liu, Guyue Bo, Yani Liu, Xun Xu, Yi Du, and Shi Xue Dou

This journal article is available at Research Online: https://ro.uow.edu.au/aiimpapers/3757
Recent Progress of Layered Transition Metal Oxide Cathodes for Sodium-Ion Batteries

Qiannan Liu, Zhe Hu, Mingzhe Chen, Chao Zou,* Huile Jin, Shun Wang, Shu-Lei Chou*

Dr. Q. Liu, A/Prof. C. Zou, Dr. H. Jin, Prof. S. Wang
College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou, Zhejiang 325027, China
E-mail: zouchao@wzu.edu.cn

Dr. Q. Liu, Z. Hu, M. Chen, Prof. S.-L. Chou, Prof. S.-X. Dou
Institute for Superconducting and Electronic Materials, Australian Institute for Innovative Materials, University of Wollongong, Innovation Campus, Squires Way, North Wollongong NSW 2522, Australia
E-mail: shulei@uow.edu.au

Keywords: layered transition metal oxides, cathodes, sodium ion batteries, full cells

Sodium-ion batteries (SIBs) are attracting increasing attention and considered to be a low-cost complement or an alternative to lithium-ion batteries (LIBs), especially for large-scale energy storage. Their application, however, is limited because of the lack of suitable host materials to reversibly intercalate Na\(^+\) ions. Layered transition metal oxides (Na\(_x\)MO\(_2\), M = Fe, Mn, Ni, Co, Cr, Ti, V, and their combinations) appear to be promising cathode candidates for SIBs due to their simple structure, ease of synthesis, high operating potential, and feasibility for commercial production. In the present work, the structural evolution, electrochemical performance, and recent progress of Na\(_x\)MO\(_2\) as cathode materials for SIBs are reviewed and summarized. Moreover, the existing drawbacks are discussed and several strategies are proposed to help alleviate these issues. In addition, the exploration of full cells based on Na\(_x\)MO\(_2\) cathodes and future perspectives are discussed to provide guidance for the future commercialization of such systems.

1. Introduction

With the ever-increasing energy consumption and demands on energy sources, renewable energy storage systems with low cost, high efficiency, long lifespan, and adequate safety are especially needed. Among all the energy storage techniques, rechargeable batteries serve as
one of the most efficient technologies to store electricity and provide power for electronic devices. Lithium-ion batteries (LIBs) have been commercially applied and would definitely be the best choice for portable electric vehicles due to their high energy density, high energy conversion efficiency, and simple maintenance. When considering large-scale energy storage such as electric cars or stationary storage system where the energy density is less critical, however, the low abundance, high cost and non-uniform distribution of lithium in the Earth’s crust make it a necessity to find another low-cost candidate.\textsuperscript{[1-6]} In this regard, sodium-ion batteries (SIBs) are attracting increasing attention as a complement or an alternative because of the abundance, easy accessibility and low cost of sodium as well as the similar “rocking-chair” sodium storage mechanism to that of LIBs, especially for large-grid applications.\textsuperscript{[7-14]} In addition, SIBs show suitable redox potential (\(E_{\text{Na}/\text{Na}^+}\) = 2.71 V vs. standard hydrogen electrode (SHE), 0.3 V higher than that of \(\text{Li}^+/\text{Li}\)) as rechargeable batteries. Structures that do not suitable for LIBs may perform well with SIBs. For example, sodium does not alloy with aluminium, and therefore Al foil can be used as the current collector for both the cathode and anode materials, which may replace the use of the more expensive and heavier copper as the current collector and is beneficial for realizing low-cost and high gravimetric energy density.\textsuperscript{[15-21]} The good possibility of finding new materials and exploring new chemistry for SIBs in the future further increases its potential.

Critical battery characteristics such as specific capacity, cycling stability, and operation voltage are primarily determined by the intrinsic electrochemical properties of the electrode materials. Therefore, the main concern in the SIB system is to find suitable electrode materials, especially cathode materials, which, to a great extent, determine the energy density of a battery. Several different groups of cathode materials for SIBs have been investigated,\textsuperscript{[22-25]} including polyanionic compounds,\textsuperscript{[26-29]} metal hexacyanometalates,\textsuperscript{[30]} metal oxides,\textsuperscript{[31]} and organic compounds.\textsuperscript{[32]} Among the candidates, transition metal oxide cathodes (\(\text{M} = \text{Fe}, \text{Mn}, \text{Ni}, \text{Co}, \text{Mg}, \text{Cu} \))
Cr, Ti, V, and their combinations) are particularly promising and have been extensively exploited due to their simple structure, ease of synthesis, high operating potential, and feasibility for commercial production. Unlike their Li analogues, where only LiCoO$_2$ and LiNiO$_2$ show the ability to intercalate Li$^+$ ions, almost all Na$_x$MO$_2$ compounds can reversibly intercalate Na$^+$ ions.$^{[33]}$ The larger size of Na$^+$ (1.02 Å) helps to minimize the cation disorder between Na$^+$ ions and the transition metal ions compared to that of Li$^+$ (0.76 Å). Moreover, different transition metal elements can be mixed together in the transition metal layers to form Na$_x$MO$_2$ compounds with tuneable properties. For example, Ni-Fe-based Na$_x$MO$_2$ normally exhibits high specific capacity and high redox potential coming from the Ni$^{2+}$/Ni$^{4+}$ and Fe$^{3+}$/Fe$^{4+}$ redox couples. The full cell performance using Na$_x$MO$_2$ cathodes for SIBs has been investigated by many researchers and demonstrates their potential for future practical application. There are several published review papers on electrode materials for SIBs to shed lights on their development, among them some important works about layered metal oxide cathodes are mentioned.$^{[17, 24]}$ To the best of our knowledge, there is no special review on the full cell progress of layered metal oxide cathodes, and strategies to alleviate their existing drawbacks also need to be taken care and kept in mind.

In this work, recent research progress on layered Na$_x$MO$_2$ cathodes for SIBs is summarized, focusing especially on their structural evolution, electrochemical performance and existing drawbacks, and several strategies are proposed to help alleviate these issues. In addition, the exploration of full cells is discussed to provide guidance for the future commercialisation of layered Na$_x$MO$_2$ compounds. Further work to improve their overall performance, reduce their irreversible phase transition, and enhance their air stability is needed through materials design (metal substitution, mixed phase preparation and morphology modification), sacrificial salt compensation, and protective coating layer. The attractive properties of Na$_x$MO$_2$ cathodes make it a powerful candidate for SIBs.
2. Overview of transition metal oxide cathodes for sodium ion storage

2.1. Structural classification

The initial reports on layered oxide materials for SIBs can be traced back to 1980s, which was to investigate substitutes for LIBs with low cost and high energy density. Similar to their lithium counterparts, the Na$_x$MO$_2$ compounds are made up of sheets of MO$_6$ octahedra, which provide two-dimensional transport channels for the extraction/insertion of Na$^+$ ions between them, as illustrated in the Figure 1.$^{[24]}$ Typical Na$_x$MO$_2$ can be classified into P2- and O3-phases based on the Na environment and the number of oxygen stacking sequences.$^{[34]}$ The letter indicates the chemical environment where Na$^+$ ions are located, and the number indicates the quantity of repeated transition metal layers within a unit cell. Normally, Na is located at trigonal prismatic sites (edge-sharing or face-sharing) with an AB BA oxygen sequence and octahedral sites (edge-sharing) with an AB CA BC oxygen arrangement for the P2- and O3-phase, respectively.

The different structures of P2- and O3-type materials result in their different electrochemical characteristics. In the pristine P2-phase, Na$^+$ ions are energetically stabilized and occupy large prismatic sites (typically $0.6 < x < 0.7$ in Na$_x$MO$_2$). When certain amounts of Na$^+$ are extracted from the P2-Na$_x$MO$_2$ framework, the sheets of MO$_6$ octahedra tend to glide with vacancies left in the octahedral sites. A new O2 phase with an AB AC oxygen stacking arrangement is thus formed, along with big contraction and a decreased interlayer distance compared to the P2 crystal structure, leading to poor cycling performance. A prime symbol (′) is used to indicate in-plane distortion of the hexagonal lattice in the crystal structure, such as for P′2-type Na$_x$MnO$_2$ with an orthorhombic lattice.$^{[35]}$ Different phases maybe formed at different temperatures. For example, as P2-type Na$_x$MnO$_{2+y}$, $\alpha$-Na$_{0.7}$MnO$_{2+z}$ and $\beta$-Na$_{0.7}$MnO$_{2+y}$ are known to be stable at low temperature ($<600$ °C) and high temperature ($>600$ °C), respectively.$^{[36]}$
In the O3-type structure, Na\(^+\) ions are originally located at the edge-sharing octahedral sites associated with MO\(_6\) octahedra. When partly extracted from the framework, Na\(^+\) ions at prismatic sites become energetically stable, together with the formation of vacancies, resulting in the formation of a structure similar to P2-phase. More prismatic sites are subsequently formed by the gliding of MO\(_2\) sheets with no need for breaking M-O bonds. As a result, the oxygen stacking changes from the “AB CA BC” sequence in O3 phase to the “AB BC CA” sequence, forming a new phase defined as P3. In fact, the P3-type structure is thermodynamically stable and can be obtained directly if the synthesis temperature is lower than 800°C. For example, P3-type Na\(_{0.6}\)Mn\(_{0.5}\)Ni\(_{0.25}\)Co\(_{0.10}\)O\(_2\) is obtained after calcining at 700°C, while P2-type structures are prepared at 800, 900, and 1000°C.\(^{[37]}\) The phase transformation from P3 or O3 to P2 is impossible through electrochemical de-sodiation because a high temperature heat-treatment is required to break the M-O bonds to form P2 phase.\(^{[38]}\)

### 2.2. Issues and strategies for transition metal oxides for SIBs

As mentioned above, both P2 and O3 layered phases commonly suffer from a series of phase transitions induced by the extraction of Na ions during electrochemical cycling. The irreversible P2-O2 phase transition of P2-type materials at high voltage causes structural collapse and rapid capacity degradation. O3-type materials undergo more complex phase transitions than the P2-type structures, such as the structural change of O3 \(\rightarrow\) (O3+O’3) \(\rightarrow\) P3 \(\rightarrow\) (P’3+P3’’) \(\rightarrow\) P3’’ for NaNi\(_{0.5}\)Mn\(_{0.5}\)O\(_2\) during the charging process.\(^{[39]}\) All O3-type Na\(_x\)MO\(_2\) compounds experience a O3-P3 transition after ~25% Na-ion extraction.\(^{[40]}\) It should be noted that the P2–O2 and O3–P3 phase transitions could alter the in-plane Na-ion diffusion mechanism. For example, the activation energy of Na-ion diffusion in P2-Na\(_x\)[Ni\(_{1/3}\)Mn\(_{2/3}\)]O\(_2\) (1/3 < x < 2/3) is calculated to significantly increase in O2-Na\(_x\)[Ni\(_{1/3}\)Mn\(_{2/3}\)]O\(_2\) (0 < x < 1/3).\(^{[41]}\) Two strategies have been applied to alleviate the phase transformation problems. The first one is to limit the high cut-off voltage to avoid the
occurrence of phase change at high voltage, nevertheless it may result in insufficient specific capacity.\cite{49} The second strategy is to introduce different transition metals, such as Fe, into the structure to improve the cycling stability by suppressing the Na\textsuperscript{+} ordering process, or electrochemically inactive elements, such as Mg, Al, or Zn, to delay structural transitions at higher voltages.\cite{31, 43-47} The addition of different metals has different impacts. For Fe/Mn based materials, the problems of Fe migration, Jahn-Teller effect and Mn dissolution, etc. maybe big issues limiting their battery performance. Instead of eliminating the Na\textsuperscript{+} ordering process, Ni-substitution is proven to enhance structural stability by decreasing the Jahn-Teller distortion of Na\textsubscript{2/3-z}[Mn\textsubscript{1/2}Fe\textsubscript{1/2}]O\textsubscript{2} and delaying the phase transitions between 2.1 and 1.5 V.\cite{48}

Second, it is acknowledged that the Na storage performance of Na\textsubscript{x}Fe\textsubscript{1−y}Mn\textsubscript{y}O\textsubscript{2} with the earth abundant elements Fe and Mn is not always satisfactory.\cite{49-51} It is often necessary to introduce Ni or Co into the transition metal layers to help achieve better performance, which would definitely increase the cost of battery preparation. It is important to find a balance between the performance and the cost for final practical application. Regarding the different Na\textsubscript{x}MO\textsubscript{2} structures, for P2 phase materials, Na ions can theoretically diffuse for direct transport between two face-sharing trigonal prismatic sites with a low diffusion barrier in the MO\textsubscript{2} layers, leading to their better rate performance than that of O3 phase.\cite{52} The expected good rate performance for P2-type Na\textsubscript{x}MO\textsubscript{2} is often degraded, however, by the Na\textsuperscript{+}-vacancies and charge ordering, which lead to limited Na\textsuperscript{+} ion transport kinetics.\cite{53} In addition, the P2-phase contains vacancies in the Na layers and is only stable at low Na concentrations (sodium deficiency) in the pristine state, which limits its charge capacity. As a result, a first cycle coulombic efficiency higher than 100% is observed when cycling in a half cell SIB system. The large fraction of unoccupied vacancy sites also leads to problems when designing electrode balancing in a full cell. Sacrificial salts, such as NaN\textsubscript{3} or Na\textsubscript{3}P, are used as an additional source of sodium ions to partially alleviate this issue. Although O3-phase materials normally deliver higher capacities
due to their higher initial Na content than P2-type materials, their structures are less reversible when cycled above 4.0 V. As in the case of O3-type Li$_{x}$CoO$_2$, since directly moving from one octahedral site to another adjacent site needs a large activation energy to overcome diffusion barriers, transport of Na$^+$ ions in O3-type materials tends to take place through interstitial tetrahedral sites (faced-shared sites with MO$_6$ octahedra in the MO$_2$ layer), resulting in lower rate performance of O3-type structures than of P2-type materials.

Furthermore, due to their unique crystallographic nature, layered Na$_x$MO$_2$ are rather sensitive to the ambient environment and prone to take up water and CO$_2$ molecules into the alkali metal layers to form electrochemically inactive NaOH or Na$_2$CO$_3$ on the surface of the active materials when exposed to air.$^{[54-55]}$ Moreover, some Na-ions are extracted from Na layers due to the oxidation reaction between them and water or H$^+$/Na$^+$ exchange, which would lead to structural variation. The thus-decreased shielding effect of Na$^+$ ions would cause larger interlayer spacing, resulting from increased repulsion forces between adjacent oxide layers.$^{[56-57]}$ The insertion of CO$_3^{2-}$ into the transition metal layers need to be balanced by the oxidation of transition metal to higher valence in the lattice.$^{[58]}$ All these consequences will definitely result in deterioration in the battery performance and increase the costs of material storage, transportation, and battery production. It is indispensable to explore layered transition metal oxides with sufficient air stability for practical applications.$^{[55, 58-61]}$

3. Transition metal oxide cathodes for sodium ion storage

The electrode potentials of redox couples for different transition metals versus Li or Na are illustrated in Figure 2. It can be seen that Ni$^{2+}$/Ni$^{3+}$/Ni$^{4+}$ redox couples exhibit the largest potential in both Li and Na battery systems. Other redox couples (Mn$^{4+}$/Mn$^{3+}$, Co$^{4+}$/Co$^{3+}$, Fe$^{3+}$/Fe$^{2+}$ etc.) also provide acceptable potential vs. Na$^+$/Na. Almost all Na$_x$MO$_2$ can reversibly store sodium in the MO$_2$ layer, which is different from their Li analogues, where limited types of materials, such as LiCoO$_2$, LiMnPO$_4$, LiFePO$_4$, and LiNi$_{0.5}$Mn$_{0.5}$O$_2$, are capable of
reversibly intercalating and deintercalating Li ions.\[62\] Besides studies on Na\textsubscript{x}CoO\textsubscript{2} due to the successful commercialization of LiCoO\textsubscript{2}, many investigations have focused on Na\textsubscript{x}MnO\textsubscript{2} and Na\textsubscript{x}FeO\textsubscript{2} due to the abundant resources of Mn and Fe.\[63-66\] V- or Ti-based Na\textsubscript{x}MO\textsubscript{2} act as low voltage sodium insertion compounds.\[67\] NaTiO\textsubscript{2} is even used as an anode material due to its low voltage Ti\textsuperscript{4+}/Ti\textsuperscript{3+} redox couple.\[68\]

3.1. Materials classification

Metal doping or substitution strategies and the preparation of novel multi-metal oxides are proven to be important and reliable approaches to stabilize the interslab spaces, reduce multiple phase transitions, and lead to enhancements in the long-term cycling and output voltage of Na\textsubscript{x}MO\textsubscript{2}. Research has been extended from Na\textsubscript{x}MO\textsubscript{2} with a single transition metal to compounds with two, three, and even four or more metal ions by introducing different metals into Na\textsubscript{x}MO\textsubscript{2} framework, taking advantage of the unique characteristics and synergetic contributions of various metal elements, such as the high redox potential of Na\textsubscript{x}FeO\textsubscript{2} and the high specific capacity of Na\textsubscript{x}MnO\textsubscript{2}. For instance, it was pointed out that the intrinsic structural instability of NaFeO\textsubscript{2} caused by Fe-ion migration can be addressed by partially replacing the Fe atoms in MO\textsubscript{2} slabs to form binary or ternary compounds such as NaFe\textsubscript{0.5}Co\textsubscript{0.5}O\textsubscript{2},\[69\] Na[Ni\textsubscript{1/3}Fe\textsubscript{1/3}Mn\textsubscript{1/3}]O\textsubscript{2},\[70\] and Na\textsubscript{0.6}Li\textsubscript{0.2}Mn\textsubscript{0.5}Ti\textsubscript{0.5}O\textsubscript{2}.\[71\] In the following part, the Na\textsubscript{x}MO\textsubscript{2} compounds are introduced based on the number of transition metals in the structure. With different and suitable amounts of elements added, the specific capacities, cycling stability, average operating voltage, and air stability of Na\textsubscript{x}MO\textsubscript{2} can be tuned to some extent.

3.1.1. Single metal oxides

Na\textsubscript{x}CoO\textsubscript{2} has been widely investigated due to its commercially applied Li-analogue LiCoO\textsubscript{2}.\[72-76\] In 1981, a reversible phase transition of O3↔O'3↔P'3 was proposed for the O3-Na\textsubscript{x}CoO\textsubscript{2} during its electrochemical process.\[74\] Ceder’s group constructed a phase diagram of Na\textsubscript{x}CoO\textsubscript{2} with \( x \) ranging from 0.60 to 1.05 between 450 and 750°C, as shown in Figure 3a.\[72\] They
concluded that pure O3, O’3, and P’3 phases can only be formed with $x$ fixed at 1.00, 0.83, and 0.67, respectively, while the P2 phase exists in the composition range with $0.68 \leq x \leq 0.76$.

The structural evolution of P2-Na$_x$CoO$_2$ was also demonstrated by an in-situ X-ray diffraction (XRD) experiment (Figure 3b), and it exhibits various single- or two-phase domains with different voltage vs. Na content patterns.$^{[73]}$

Another widely studied Na$_x$MO$_2$ subclass is the Na$_x$MnO$_2$ system, in which the crystal structure changes from three-dimensional (3D) at $0 < x \leq 0.44$ to two-dimensional (2D) at $0.44 < x \leq 1$, as summarized in Figure 4.$^{[77]}$ The layered P2-Na$_x$MnO$_2$ is stable when $x$ is between 0.6 and 0.7. Introducing small quantities of elements (e.g. Ni, Co, Fe, Li) into the Na$_x$MnO$_2$ structure has been used to enlarge the range of P2 phase stability.$^{[78]}$ By doping with different metals, the upper limit of Na content for P2 phase stability can reach up to $x = 0.9$, arising from unfavorable occupation of nearest neighbor sites. The Jahn-Teller effect of Mn$^{3+}$is illustrated in Figure 5.$^{[79-80]}$ P2-Na$_{0.6}$MnO$_2$ was reported to deliver a capacity of 140 Ah kg$^{-1}$ in the initial few cycles, but rapid capacity decay was observed, resulting from the structural collapse caused by continuous extraction and insertion of Na$^+$ ions.$^{[81]}$ The electrochemical mechanisms of distorted and undistorted P2-type Na$_{2/3}$MnO$_2$ were studied by Komaba’s group. It was found that the distorted (P’2-type) Na$_{2/3}$MnO$_2$ delivered a high capacity of 216 mAh g$^{-1}$ as a 3 V class cathode material, with excellent cycling stability and better electrochemical behaviour compared to the undistorted Na$_{2/3}$MnO$_2$, as presented in Figure 6(a and b).$^{[82]}$

Monoclinic $\alpha$-NaMnO$_2$ (C2/m) shows an initial capacity of 185 mAh g$^{-1}$ when cycling between 3.8 and 2.0 V. It also experiences fast capacity decay, however, in subsequent cycles.$^{[83]}$

NaFeO$_2$ was demonstrated to show good capacity retention with a reversible capacity of 80 mAh g$^{-1}$ at 3.3 V associated with Fe$^{3+}$/Fe$^{4+}$ redox couple when the charge voltage was set to 3.4 V (Figure 6c).$^{[84]}$ This reversibility, however, significantly deteriorated when the electrodes were charged to higher voltage above 3.5 V, where losses of Na conduction paths in
the host structures occurred because of the irreversible structural change. Unlike its Li-analogue LiCrO$_2$, which is electrochemically inactive, NaCrO$_2$ can deliver a highly reversible capacity of \(~ 120\) mAh g$^{-1}$ (Figure 6d) supported by the Cr$^{3+}$/Cr$^{4+}$ redox couple due to the faster diffusion of Na$^+$ ions than Li$^+$ ions and less decomposition of electrolyte solution, resulting from the longer alkali-oxygen bonding and larger interslab spaces of NaCrO$_2$ compared with those of LiCrO$_2$.\cite{85} Na$_x$VO$_2$ was reported to have more than 50\% of its capacity centred near 1.6 to 1.7 V for both P2-Na$_{0.7}$VO$_2$ and O3-NaVO$_2$, as shown in Figure 6(e and f).\cite{86} The charge–discharge polarization of Na$_{0.7}$VO$_2$ is amazingly small (< 50 mV) compared to that (200 mV) for the NaVO$_2$ phase, since NaVO$_2$ is an insulator, while Na$_{0.7}$VO$_2$ is a semiconductor presenting much higher electronic conductivity.

3.1.2. Binary metal oxides

Although Na$_x$MO$_2$ compounds with single metal have their own advantages as cathode materials, they normally suffer from problems of either low capacity or fast capacity decay due to the structural change and phase transformation during the sodium extraction-insertion processes. The study of binary metals in transition metal oxide layers is based on the synergetic effects of different transition metals and mainly focuses on low-cost Fe or Mn in combination with Ni or Co. It was reported that an increased Ni content could result in an increased capacity but it may be accompanied by progressively lower capacity retention. The addition of Co can play an important role in stabilizing the structure of the Na$_x$MO$_2$ framework.\cite{87} In addition, other metal elements, such as Mg, Cu, Ti, or Li, are also incorporated to induce cation rearrangements in the Na$_x$MO$_2$ framework for enhanced electrochemical performance.\cite{88-93}

P2-Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ was reported to deliver a high capacity of 160 mAh g$^{-1}$, with nearly all Na removed from and reversibly inserted into the metal oxide layers.\cite{94} During the Na extraction process, the structure of Na$_x$Ni$_{1/3}$Mn$_{2/3}$O$_2$ changes from P2 ($x > 1/3$) to (P2 + O3) ($x = 1/3$), and then to (P2 + minor O2 + Ni$_{1/3}$Mn$_{2/3}$O$_2$) for $x < 1/3$.\cite{94-96} Rapid capacity fading
occurred due to the P2 to O2 phase transformation at and above 4.2 V. O3-type NaNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> exhibited capacities of 105-125 mAh g<sup>-1</sup> in the voltage range of 2.2 - 3.8 V (Figure 7a). When it was charged to 4.5 V, a large capacity of 185 mAh g<sup>-1</sup> was even obtained but with poor reversibility, which was caused by the significant expansion of interslab space due to the complex phase change of O3-P3-P′3-P″3 during the sodium ion extraction process.

Partial Co replacement of Fe in O3 phase NaFeO<sub>2</sub>-based materials was proved to suppress its irreversible phase transition. NaFe<sub>0.5</sub>Co<sub>0.5</sub>O<sub>2</sub> was reported to deliver a reversible capacity of ~160 mAh g<sup>-1</sup> with good capacity retention and excellent rate performance between 2.5 and 4.0 V, resulting from the reversible formation of Na<sub>0.3</sub>Fe<sub>0.5</sub>Co<sub>0.5</sub>O<sub>2</sub> (Figure 7b). A combined Co-doping and morphology optimization strategy was applied to modify P2-NaxMnO<sub>2</sub> to endow it increased capacity and cycling stability. Both P2-type Na<sub>x</sub>MnO<sub>2</sub> and Na<sub>x</sub>Co<sub>0.1</sub>Mn<sub>0.9</sub>O<sub>2</sub> with hexagonal flake and hollow sphere morphologies were successfully synthesized, respectively. The Na<sub>x</sub>MnO<sub>2</sub> flakes undergo a Jahn-Teller induced phase transition to orthorhombic structure upon Na<sup>+</sup> insertion, while 10% Co-doping suppresses this structural transformation in Na<sub>x</sub>Co<sub>0.1</sub>Mn<sub>0.9</sub>O<sub>2</sub>. The less phase transformation, along with the suppression of Na<sup>+</sup> ordering and enhanced Na<sup>+</sup> kinetics, enables higher capacity retention of the doped Na<sub>x</sub>Co<sub>0.1</sub>Mn<sub>0.9</sub>O<sub>2</sub> than the un-doped Na<sub>x</sub>MnO<sub>2</sub>. The superior cycling stability of materials with the hollow sphere morphology is attributed to the reduced volume changes and structural stress compared to the flake-like materials. As a result, the Co-doped Na<sub>x</sub>Co<sub>0.1</sub>Mn<sub>0.9</sub>O<sub>2</sub> spheres exhibited the best battery performance by combining the advantages of these two strategies.

Delmas et al. studied four different Na<sub>x</sub>(Mn, Fe)O<sub>2</sub> phases, namely, P2-NaxMn<sub>2/3</sub>Fe<sub>1/3</sub>O<sub>2</sub>, P2-NaxMn<sub>1/2</sub>Fe<sub>1/2</sub>O<sub>2</sub>, O3-NaxMn<sub>1/2</sub>Fe<sub>1/2</sub>O<sub>2</sub>, and O3-NaxMn<sub>1/3</sub>Fe<sub>2/3</sub>O<sub>2</sub>, and concluded that they delivered discharge capacities of 135-155 mAh g<sup>-1</sup> between 1.5 and 3.8 V (Figure 7c). The discharge capacities of the O3 materials are lower than those observed for the P2 phases because of the higher energy requirement to remove Na<sup>+</sup> ions from the interlayer in the O3
oxygen stacking. P2-Na0.67Fe0.5Mn0.5O2 was also reported to deliver a capacity of 190 mAh g−1 from a reversible Fe4+/Fe3+ conversion.[101] When the cell was charged above 4.1 V, it was found that a low crystallinity OP4 phase was formed, arising from the configurational disorder on transition metal sites, which efficiently prevented the long-range Na+/vacancies ordering and prevented the detrimental structural transitions. As a result, reversible extraction and insertion of Na+ was realized over a wide range (0.15 < x < 0.9 in NaₓFe0.5Mn0.5O2) corresponding to capacity of approximately 200 mAh g−1 with a 65% capacity retention after 50 cycles.[95] Similarly, P2-Na2/3Fe2/3Mn1/3O2 also undergoes a phase transformation from P2 to highly disordered Z or OP4 phase when charged above 4.0 V.[102] This phase change can be prevented in P2-Na2/3Fe0.4Mn0.6O2 with higher Mn content, for which the P2 phase can be retained to the discharged state, but another distorted P′2 phase and more than two other phases are formed.[103]

The effects of Mg doping on the structural stability and electrochemical performance of P2-Na2/3MnO2 were systematically investigated through comparison among three compositions: Na2/3Mn1−yMgyO2 (y = 0.0, 0.05, and 0.1), as shown in Figure 8. The Mg addition reduced the amount of Mn3+ Jahn–Teller centres and delayed the occurrence of the phase transition at high voltage, leading to a stabilized P2 phase with fewer distinct electrochemical variations, resulting in higher capacity retention and improved rate performance.[105] The sample with 5% Mg retained a reversible capacity of 140 mAh g−1 after 50 cycles at 1 A g−1, and 106 mAh g−1 at 5 A g−1. More Mg addition can further improve the cycling stability, but at the expense of the discharge capacity.[104, 106]

Li-excess manganese oxide, Na5/6[Li1/4Mn3/4]O2 was synthesized and delivered enhanced electrochemical performance compared to Mn-based NaₓMnO2 electrodes.[107] In this structure, Li is expected to be incorporated into the Mn sites in the transition metal layers, since the prismatic sites in the alkaline metal layers are intensively unfavourable for Li+. Its large
reversible capacity of ~200 mAh g⁻¹ (Figure 9a) comes from the in-plane cation rearrangements induced by oxygen loss that occurs after charging to a high-voltage region, a similar structural activation process to that in O3-type Li₂MnO₃-based electrode materials. Similarly, Na(Li₁/₃Mn₂/₃)O₂ shows high redox potentials (~ 4.2 V) with capacity of 190 mAh g⁻¹ induced by the anionic redox reaction (O²⁻/O⁻) to compensate charges during the intercalation process (Figure 9b). The excellent capacity retention can be attributed to the stabilized phase over a wide potential range of electrochemical cycling. P3-Na₀.₆Li₀.₂Mn₀.₈O₂ and β-Na₀.₇[Mn₁-xLiₓ]O₂+y are also reported to be able to deliver improved electrochemical performances through anionic redox reaction.

3.1.3. Ternary metal oxides

Besides Ni and Co, other dopant elements (Cu, Ti, Mg, Zn, Al, and Li) have been introduced into binary transition metal oxides to achieve better performance in ternary metal oxides. Only small quantities are added, however, because they would decrease the electroactive species. Moreover, some NaₓMO₂ compounds with ternary metals are reported to be air stable.

Cu or Zn doping is used for P2-Naₓ(Ni, Mn)O₂ to reduce the occurrence of the P2-O₂ transformation at high voltage. In the case of Na₂/₃Ni₁/₃Mn₂/₃O₂ electrode, the Ni²⁺/Ni³⁺/Ni⁴⁺ redox reactions endow it with high specific capacity and high operating voltage. Rapid capacity decay occurs, however, due to the P2-O₂ phase change and Na⁺/vacancy ordering as mentioned above. The as-synthesized Cu-doped P2-type Na₀.₆₇Ni₀.₁Cu₀.₂Mn₀.₇O₂ shows improved battery performance with greatly alleviated structural degradation compared to Na₀.₆₇Ni₀.₃Mn₀.₇O₂ (Figure 10a). The presence of Cu(II) can stabilize the P2 phase, and at the same time contribute to capacity due to the high potential of the Cu²⁺/Cu³⁺ redox couple. Similarly, the Zn²⁺ doping reduces the degree of distortion of Ni-O octahedra during the charge/discharge processes of Na₀.₆₆Ni₀.₃₃Mn₀.₆₆O₂ while improving the reversibility of the distortion, endowing it with better voltage and capacity retention than Na₀.₆₆Ni₀.₃₃Mn₀.₆₆O₂.
Li substitution is also confirmed to delay the P2-O2 phase transformation that takes place in Na$_{x}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ and even greatly improves its air stability.\cite{118} Na$_{x}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ is extremely moisture sensitive once charged to 3.7 V, where water molecules can be readily intercalated into the P2 layers. By contrast, the lithiated Na$_{x}$Li$_{0.12}$Ni$_{0.22}$Mn$_{0.66}$O$_2$ shows no hydration until charged up to 4.4 V, demonstrating its enhanced air stability.

For Na$_x$(Co, Mn, Ni)O$_2$ materials, the effects of composition on the electrochemical performance and the stability of the solid solution compounds P2-[(1−y)Na$_x$CoO$_2$−yNa$_x$Mn$_{2/3}$Ni$_{1/3}$O$_2$] (y = 0, 1/3, 1/2, 2/3 and 1), namely Na$_x$Co$_{1−y}$[Mn$_{2/3}$Ni$_{1/3}$]$_y$O$_2$, were investigated, as shown in Figure 11a.\cite{119} When cycled between 2.0 and 4.2 V, the Na$_x$Co$_{1/2}$Mn$_{1/3}$Ni$_{1/6}$O$_2$ (y=1/2) delivered the highest discharge capacity of 101.04 mAh g$^{-1}$ with 97% capacity retention at the 100th cycle and a coulombic efficiency of > 99.2%. It was assumed that the Mn in the composition is at the +4 valence, thereby avoiding the Mn$^{3+}$ Jahn-Teller distortion. Furthermore, Ni plays the role of enhancing the energy density and the average discharge potential arising from its high redox potential. Likewise, P2-Na$_{0.45}$Ni$_{0.22}$Co$_{0.11}$Mn$_{0.66}$O$_2$ was reported to exhibit a capacity of ~140 mAh g$^{-1}$ with good cycling and moderate rate performance.\cite{122} O3-Na$_{x}$Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ was reported to reversibly intercalate 0.5 Na, exhibiting a capacity of 120 mAh g$^{-1}$ in the voltage range of 2.0–3.75 V with good cycling performance. Its instability in air, however, still limits its application.\cite{123} Na$_{x}$Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ with a mixed P2/O3/O1 structure exhibits better electrochemical performance and thermal stability than the one with P2/O3 phase integration or with a single P2 phase.\cite{120} This P-/O-type intergrowth inhibits the irreversible P2–O2 phase transformation during cycling and improves the structural stability of the O3 and O1 phases, which was demonstrated by an in-operando high energy XRD study (Figure 11b).

The layered Na$_x$Li$_y$Ni$_{0.25}$Mn$_{0.75}$O$_6$ oxides (0.7 ≤ x ≤ 1.2 and 0 < y ≤ 0.5) were found to be able to reversibly intercalate sodium with negligible structural change at high rates.
Na$_{1.0}$Li$_{0.2}$Ni$_{0.25}$Mn$_{0.75}$O$_5$ was prepared via a solid-state method and normalized to be a layered mixed Na/Li compound with the formula Na$_{0.85}$Li$_{0.17}$Ni$_{0.21}$Mn$_{0.64}$O$_2$. The cell shows an average potential of 3.4 V with stable capacities of 95–100 mAh g$^{-1}$ over 50 cycles. Li, Ni, and Mn are located in the transition metal layer in octahedral coordination, where Li acts as a component to stabilize the charge ordering between Ni and Mn. Only Na in trigonal prismatic coordination occupies the adjacent layer, and the commonly observed cation disorder in materials containing only Li is negated. The air-protected P2-Na$_{0.67}$Mn$_{0.5}$Fe$_{0.5}$O$_2$ was reported to exhibit much lower polarization and higher capacity than that exposed to air, for which the carbonate ions inserted in the layered structure are balanced by the oxidation of Mn$^{3+}$ to Mn$^{4+}$ in the lattice. With Ni substitution, Na$_{0.67}$Mn$_{0.6}$Ni$_{0.1}$Fe$_{0.3}$O$_2$ and Na$_{0.67}$Mn$_{0.63}$Ni$_{0.15}$Fe$_{0.2}$O$_2$ demonstrated better electrochemical performance, as shown in Figure 11c. The average potential of P2-Na$_{2/3}$Mn$_{1/2}$Fe$_{1/2}$O$_2$ is increased, and its reactivity towards ambient atmosphere is to some extent suppressed. Another promising material, O3-Na$_{0.9}$[Cu$_{0.22}$Fe$_{0.3}$Mn$_{0.48}$]O$_2$, was also reported to be air-stable and able to deliver an energy density of 210 Wh kg$^{-1}$.

Ti substitution is also a useful way to enhance the electrochemical performance of Na$_x$MO$_2$ cathodes. P2-Na$_{2/3}$Mn$_{0.8}$Fe$_{0.1}$Ti$_{0.1}$O$_2$ with small quantities of Ti and Fe was synthesized by a ceramic method. Na solid-state nuclear magnetic resonance (NMR) confirms the fast Na$^+$ mobility in the interlayer space and co-substitution of Ti and Fe at the Ti$^{4+}$ sites in the transition metal layer, which leads to structural stability and thus stable electrochemical performance. The electrode delivers a second discharge capacity of 144.16 mAh g$^{-1}$ with 95.1% capacity retention after 50 cycles at C/10 within the voltage range of 4.0–2.0 V. In addition, the moisture-exposed electrode delivers reversible capacities larger than 130 mAh g$^{-1}$ with superior capacity retention. O3-type Na$_{0.8}$Ni$_{0.4-x}$Co$_{x}$Ti$_{0.6}$O$_2$ ($x$=0, 0.05, 0.1, and 0.15) samples were investigated. Among them, Na$_{0.8}$Ni$_{0.3}$Co$_{0.2}$Ti$_{0.3}$O$_2$ exhibits excellent cycling stability with about 95% of the capacity retained after 90 cycles.
3.1.4. Multi-metal oxides

Besides the most commonly used Mn, Fe, Ni, and Co, minor quantities of Li, Mg, Ti, and/or Cu are introduced into the layered Na_xMO_2 framework to promote improved battery performance for Na_xMO_2 with four or more transition metal elements compared with those with fewer transition metals. Materials with novel mixed O- and P-type phases with unique properties may be obtained.

A quaternary material with the composition Na(Mn_{0.25}Fe_{0.25}Co_{0.25}Ni_{0.25})O_2 (MFCN) for SIBs showed an initial discharge capacity of 180 mAh g\(^{-1}\) and energy density of 578 Wh kg\(^{-1}\). Examining the in-suit evolution of MFCN (Figure 12a) indicated that no monoclinic distortion occurred during the charging process, resulting from anisotropic Na ordering. O3 and P3 coexists with 20-26% Na de-intercalation, followed by a single P3 area beyond 26% Na de-intercalation. New hexagonal O3 phases, O3' and O3'' phases, are formed at 66% and 80% Na de-intercalation respectively. Moreover, the amount of Jahn–Teller ions in MFCN in the metal layer is less than that in Na(Fe_{0.5}Co_{0.5})O_2 (FC) and Na(Ni_{0.5}Mn_{0.5})O_2 (NM). At a high cut-off voltage, its cycling performance is noticeably better than those of FC and NM, as shown in Figure 12b.[126] Cu/Ti co-substitution was reported to effectively improve the air stability of O3-type NaNi_{0.45}Cu_{0.05}Mn_{0.4}Ti_{0.1}O_2 (NaNCMT) cathode by reducing the interlayer spacing of Na layers caused by enhanced suppression of oxidization and spontaneous Na extraction (Figure 12c). Unlike NaNi_{0.5}Mn_{0.5}O_2 (NaNM), no monoclinic O’3 or P’3 phases are observed during the charge/discharge process of NaNCMT (Figure 12d). The as-obtained NaNCMT can stay a 20 times longer stable period than NaNM, and even maintains its original structure and capacity after being deliberately soaked in water.[61]

Li-containing or Li-substituted of transition metal oxides are extensive in multi-metal oxide cathodes with a relatively stable structure. O3-type Na[Li_{0.05}(Ni_{0.25}Fe_{0.25}Mn_{0.5})_{0.95}]O_2 was synthesized via a co-precipitation method.[127] The Na[Li_{0.05}(Ni_{0.25}Fe_{0.25}Mn_{0.5})_{0.95}]O_2
electrode delivered a high capacity of 180.1 mAh g\(^{-1}\) at the 0.1 C rate due to the Li supporting structural stabilization of the transition metal layer. A layered composite with P2 and O3 integration, Na\(_{0.66}\)Li\(_{0.18}\)Mn\(_{0.71}\)Ni\(_{0.21}\)Co\(_{0.08}\)O\(_{2+δ}\), was reported by integrating a minor O3 component into Li-substituted P2-majority materials.\(^{[128]}\) This mixed P2+O3 phase show excellent electrochemical performance with a discharge capacity of 200 mAh g\(^{-1}\) at the rate of 0.1 C, and a high energy density of 640 Wh kg\(^{-1}\). It is easier to achieve mixed phase in Na\(_3\)MO\(_2\) compounds with multi-metal elements. Other layered quaternary materials, Na\(_{x}\)Mn\(_y\)Ni\(_z\)Fe\(_{0.1}\)Mg\(_{0.1}\)O\(_2\) (0.67 ≤ \(x\) ≤ 1.0; 0.5 ≤ \(y\) ≤ 0.7; 0.1 ≤ \(z\) ≤ 0.3) consisting of single P2-, or O3-, or a mixture of P3/P2/O3-type structures, were prepared under different conditions. This unique composite with P3/P2/O3 phase demonstrated superior performance compared to the P2- and O3-type samples, delivering specific discharge capacities of up to 155 mAh g\(^{-1}\) at a current density of 18 mA g\(^{-1}\) in the potential range of 2.0–4.3 V.\(^{[129]}\) The synthesis methods and electrochemical properties of different types of layered Na\(_3\)MO\(_2\) cathodes are summarized in Table 1. Comparison among capacity and average voltage of selected materials are made and plotted in Figure 13. It can be found that metal oxides with several elements are more likely to exhibit higher energy densities, especially Mn-based materials, than those with single element. Some energy densities, such as that of mixed P3/P2/O3-type Na\(_{0.76}\)Mn\(_{0.5}\)Ni\(_{0.3}\)Fe\(_{0.1}\)Mg\(_{0.1}\)O\(_2\),\(^{[129]}\) are even comparable to that of commercial LiCoO\(_2\) cathode (~ 532 Wh kg\(^{-1}\) vs. Li\(^+\)/Li) for LIBs.

### 3.2. Full cells

The exploration of full cell systems is essential for the practical application and commercialisation of SIBs. It is well acknowledged that the battery performance in a half-cell can be largely different from that in a full cell, and Na metal is not favourable as electrode for rechargeable batteries due to its potential safety issue.\(^{[162-164]}\) Several reports in the literature have considered full cells based on layered Na\(_3\)MO\(_2\) cathodes, normally those with more than
one transition metal element, and their electrochemical characterisations are summarized in Table 2. Pre-sodiation treatment is sometimes performed to compensate the sodium deficiency, but this approach may be not very suitable for commercial production due to the complicated process and much increased cost. Sacrificial salt compensation and surface modification methods are also used to improve the battery performance of electrode materials.

A full-cell SIB based on a presodiated carbon-coated $\text{Fe}_3\text{O}_4$ anode and a layered $\text{NaNi}_{0.25}\text{Fe}_{0.5}\text{Mn}_{0.25}\text{O}_2$ (NFM) cathode in high-voltage electrolyte solution ($\text{NaClO}_4$ in FEC and ethyl methanesulfonate (EMS)) was investigated (Figure 14).\(^{[165]}\) The as-synthesized NFM was air stable and formed as a solid solution between $\text{NaFeO}_2$ and $\text{Na[Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2$. The high electric conductivity and structural stability of the conversion anode and intercalation cathode, as well as the wide electrochemical window of the novel EMS-based electrolyte, endowed the cell with high capacity, high rate capability, much improved cycle life and good thermal stability. The full cell battery could be operated reversibly at around 2.4 V, delivering a capacity of around 130 mAh g\(^{-1}\) with 82.8% capacity retention after 100 cycles.

Hard carbon is a commonly accepted anode and considered to be the most promising and suitable negative material for SIBs when studying full cell performance.\(^{[197]}\) Coin-type full cells consisting with $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cathode and hard carbon anode were tested in PC solutions containing 1 mol L\(^{-1}\) $\text{NaClO}_4$, $\text{NaPF}_6$, and sodium $\text{NaN(SO}_2\text{CF}_3)_2$, respectively.\(^{[172]}\) Superior cycling performance with capacity retention of more than 70% after 50 cycles was obtained with the $\text{NaPF}_6$ and $\text{NaN(SO}_2\text{CF}_3)_2$ solutions compared with the decreasing reversible capacity observed in the $\text{NaClO}_4$ system. The hard-carbon//$\text{NaN(SO}_2\text{CF}_3)_2$//$\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cell exhibited a high capacity (above 200 mAh g\(^{-1}\)) and an average operating voltage of ~ 3 V, achieving ~ 60% of the energy density of the conventional LIBs (Figure 15a). In addition, no significant capacity decay was observed when the full cell was tested at a rate of 300 mA g\(^{-1}\),
demonstrating a remarkable rate capability. A similar cycling performance at 60°C to that at room temperature was observed over 50 cycles with negligible degradation.

A sacrificial salt, NaN₃, was added into the Na₀.₆₇[Fe₀.₅Mn₀.₅]O₂ cathode to compensate the irreversible capacity of the hard carbon anode for the Na₀.₆₇[Fe₀.₅Mn₀.₅]O₂/hard carbon full cell system. As shown in Figure 15b, the addition of 10 wt% NaN₃ led to an additional charge capacity of ~25 mAh g⁻¹ compared to bare Na₀.₆₇[Fe₀.₅Mn₀.₅]O₂, since the accessibility of the active material to the electrolyte was improved by the activation of NaN₃. Further reduction of Fe⁴⁺ was achieved by further increasing the NaN₃ content to 20 wt%, resulting in an increase in the first charge capacity to ~148 mAh g⁻¹. More sodium ions were intercalated into the negative electrode with the increased amount of NaN₃ addition, and the reversible capacity changed from 50 mAh g⁻¹ for 0 wt% NaN₃ addition to ~130 mAh g⁻¹ for 20 wt% NaN₃ addition. The addition of higher amounts of NaN₃ may have negative impact on the cycling stability, however.

O₃-type Na[Li₀.₀₅Mn₀.₅₀Ni₀.₃₀Cu₀.₁₀Mg₀.₀₅]O₂ (NLMNMC) cathode material with high tap density was successfully synthesized via a co-precipitation method and subsequent annealing. The final product was aggregated from numerous NLMNMC nanoplate crystals and maintained the microsphere structure of the precursor. This morphology not only efficiently facilitates the transport of Na⁺ ions in the secondary-aggregated particles due to the short diffusion distance among the primary nanocrystals, but also is favourable to future scaling-up of production and for high volumetric energy density. Meanwhile, the full cell system consisting of hard carbon anode and NLMNMC cathode showed a first cycle reversible efficiency of up to 80.6%, exhibited excellent rate performance, and had a high energy density up to 215 Wh kg⁻¹ (Figure 15c). Another air-stable O₃-Na₀.₉[Cu₀.₂₂Fe₀.₃₀Mn₀.₄₈]O₂ cathode was configured with hard carbon anode to constitute a prototype 3.2 V class SIB with high efficiency. The full cell showed an energy density of 210 Wh kg⁻¹ with excellent cycling
stability and high round-trip energy efficiency of 90%. Surprisingly, the battery delivered 74% of its initial capacity at a high current rate of 6 C.

Surface modification is also performed by coating a protective layer on the surface to endow Na₅MO₂ with enhanced surface stabilization for long-term cyclability. The surface of layered Na₂/3[Ni₁/₃Mn₂/₃]O₂ was modified with ionic and conducting NaPO₃ nanolayers with 10 nm in thickness via melt-impregnation at 300°C. The NaPO₃ nanolayers on the surface had a positive impact on the battery performance by scavenging HF and H₂O in the electrolyte, which lowers the cell resistance and leads to less by-products formation on the surface of the cathode. As a result, the full cell based on NaPO₃-coated Na₂/3Ni₁/₃Mn₂/₃O₂ cathode and hard carbon anode exhibited high capacity retention of 73% over 300 cycles (Figure 15d). An in-suit high-temperature XRD study revealed that the coated NaPO₃ layer can suppress oxygen release in highly desodiated state, thus delaying exothermic decomposition.[195] Similarly, Al₂O₃-coated O3-type Na[Ni₀.₆Co₀.₂Mn₀.₂]O₂ was synthesized through Al₂O₃ modification using a facile ball-milling method. The pouch-type full cell, consisting of hard carbon anode and Al₂O₃-coated Na[Ni₀.₆Co₀.₂Mn₀.₂]O₂ cathode, exhibited good rate capability and 75% capacity retention after 300 cycles with an energy density of 130 Wh kg⁻¹. The densely coated nanoscale Al₂O₃ layer on the surface of the cathode effectively minimized side reactions between the active material and the electrolyte solution while simultaneously assisting Na⁺ migration. In addition, the Al₂O₃ coating layer played an important role in resolving the degradation pathways of the Na[Ni₀.₆Co₀.₂Mn₀.₂]O₂ surface and protecting it from hydrogen fluoride attack.[196] More and more researches on layered Na₅MO₂ synthesized by industrially feasible methods (solid-state or co-precipitation) with favourable properties and commercial availability is on the way, and their successful report indicates that the group of layered transition metal oxides can be employed in future practical SIBs for large-scale electrical energy storage.

3.3. Battery manufacture
Very recently, Faradion Limited reported the scale-up and commercialisation of a high energy and structurally stabilized sodium nickel oxide $\text{Na}_a\text{Ni}_{(1-x-y-z)}\text{Mn}_x\text{Mg}_y\text{Ti}_z\text{O}_2$ as a cathode material targeting stationary energy storage.$^{[198]}$ In the prototype pouch cells, double-sided electrodes are utilized to maximize the energy density and packaging efficiency. Carbon-coated Al current collectors are employed and used for both electrodes to minimize the cell impedance and to enhance the adhesion between electrode and current collector. The anode used is commercial hard carbon and the separator is commercial polyolefin material. The electrolyte is a 0.5 M solution of $\text{NaPF}_6$ in a combination of several carbonates, including EC, DMC, DEC, and PC. The theoretical specific capacity of this material is over 165 mAh g$^{-1}$ based on the Ni$^{2+}$/Ni$^{4+}$ redox couple. Under low-rate testing conditions, the cathode delivered a high reversible capacity of 157 mAh g$^{-1}$ with an average operating voltage of ~ 3.2 V.

When designing a full cell, it is important to implement a suitable mass balance to guarantee a capacity match between the anode and the cathode, and make the best of their intrinsic chemistry.$^{[164]}$ Based on the current achievements and increasing requirements, some issues for the full-cell SIB system still need to be addressed. It is important to perform a rational material design to ensure overall electrochemical performance and control the phase transformation and hygroscopic characteristic of layered cathodes.$^{[199-201]}$ Also, efforts need to be devoted to increasing the initial coulombic efficiency and decreasing the sodium dendrites formation on the surface of the anode at low voltage. Besides a suitable configuration of the positive and negative electrode materials, the commercial full-cell design also needs to take into consideration the choices for a stable electrolyte solution (salts and solvents), and the choices of additives, binders, and separators, as well as the material costs and the fabrication, equipment, operational, maintenance, and transportation costs and safety of the battery system.$^{[202-206]}$ For example, a $\text{NaClO}_4$-based electrolyte solution could not be used in the commercial battery industry due to its explosion hazard,$^{[19]}$ and using glass fiber as separator...
could lower the energy density of SIBs considering the whole weight or volume of all the constituents in the system. The ratios of the price to performance of different cathode materials are particularly needed to be taken into consideration.\cite{204} For example, Ni and Co-containing Na\(_{x}\)MO\(_2\) cathodes are more expensive per unit energy density than those composed of Mn, Fe, and Cu. There is still a long way to overcome the persistent obstacles to realize the practical application of Na\(_{x}\)MO\(_2\) at the industrial level. Coordinated efforts between fundamental research and advanced techniques for scaling up to mass production are needed to balance the requirements of material choice, electrode manufacture, and industry demands to effectively promote the use of layered Na\(_{x}\)MO\(_2\) in the rechargeable battery market in the near future. From Faradion’s successful use of sodium nickel oxide in stationary and automotive energy applications, it is anticipated that optimized versions of layered Na\(_{x}\)MO\(_2\) targeted for higher energy/power applications and large scale production are on the way.

4. Summary and perspectives

Remarkable achievements and great progress have been made on layered transition metal oxide electrodes for SIBs in the last 10 years. In-depth investigations of the structure-property relationship, electrochemical mechanism, and suitable material design need to be further identified to push these cathode materials onto the battery market. Several strategies have been demonstrated to effectively endow Na\(_{x}\)MO\(_2\) with enhanced cyclibility, rate performance, and air stability, including morphology modification,\cite{66, 99, 207-209} cationic substitution,\cite{106, 164, 210-211} sacrificial slat compensation using NaN\(_3\) or Na\(_3\)P,\cite{193-194} surface modification by coating a protective (carbon, Al\(_2\)O\(_3\), NaPO\(_3\), or TiO\(_2\)) layer on the surface,\cite{133, 195, 212-215} and mixed P-/O-type structure/composition design.\cite{128-129, 160, 216} Among all those approaches, cationic substitution is mostly effective and proven to be capable of providing a significant improvement in the overall electrochemical performance. A reasonable balance between the average operating voltage, specific capacity, and capacity retention needs to be carefully
considered, however, when designing specific systems. Rational sacrificial salt compensation and surface modification could effectively endow the NaₓMO₂ materials with enhanced structure stability and improved electrochemical performance. The new class of mixed P-/O-type phases introduces new perspectives for the progress of layered NaₓMO₂ cathodes for SIBs.

When it comes to practical application of a battery, there are many factors that need to be considered, including the energy density, power density, energy efficiency, charging rate, cycle life, life span, safety, and cost. Substantive efforts are needed to design stable anodes, cathodes, and electrolytes that can provide batteries with high energy density, high power, long lifetimes, and adequate safety at competitive production costs. Investigation of the full cell SIB system is of great importance, as it acts as the bridge between the half-cell and practical batteries. Both academic and industrial organizations need to stay in close cooperation and devote extensive efforts to making full-cell SIBs ready for practical industrialisation. Although there are still various challenges to overcome, we believe that greater application of layered NaₓMO₂ cathodes for rechargeable SIBs will take place at the industrial level and is potentially promising to promote the substantial use of low-cost SIBs for energy storage systems in the near future.

Acknowledgements

This work was financially supported by an Australian Renewable Energy Agency (ARENA) (S⁴ project) grant. The authors are grateful to Dr. Tania Silver for her critical revision of the manuscript. All the authors have given approval to the final version of the manuscript.

References


Figure 1. Schematic illustration of Na migration paths in different layered structures. A, B, and C represent different oxygen packing patterns in Na$_x$MO$_2$ frameworks. Reproduced with permission.[24] Copyright 2014, American Chemical Society.

Figure 2. Schematic diagram of electrode potentials for various transition metal redox couples. Reproduced with permission.[17] Copyright 2013, Royal Society of Chemistry.
Figure 3. (a) Synthesis phase diagram of Na$_x$CoO$_2$ as a function of the Na:Co ratio of the precursor. Reproduced with permission.\cite{72} Copyright 2014, American Chemical Society. (b) Cycling curve of a P2–Na$_x$CoO$_2$ battery with the crystal structure shown in the lower left inset. The upper right inset is an enlargement of the indicated range. Reproduced with permission.\cite{73} Copyright 2011, Nature Publishing Group.

Figure 4. (a) Domain of stability for different structures observed for Na$_x$MnO$_2$ compounds; and (b) extended range of Na content in which the P2–Na$_x$MnO$_2$ structure is stable through doping on the Mn lattice. Reproduced with permission.\cite{77} Copyright 2015, The Electrochemical Society.
Figure 5. (a) Schematic of a Jahn–Teller distortion (JTD) involving the elongation of the axial Mn–O bonds to lift the orbital degeneracy of the Mn$^{3+}$ configuration. Reproduced with permission.$^{[79]}$ Copyright 2013, American Chemical Society. (b) Pathway for layered to spinel structural transition observed for deintercalated layered oxides. Reproduced with permission.$^{[80]}$ Copyright 2015, American Chemical Society.
Figure 6. Charge-discharge profiles of different single metal oxide cathodes for SIBs: (a) P2-Na$_{2/3}$MnO$_2$ and (b) P'2-Na$_{2/3}$MnO$_2$. Reproduced with permission.\cite{ref1} Copyright 2016, Wiley-VCH. (c) LiCrO$_2$ and (d) NaCrO$_2$. Reproduced with permission.\cite{ref2} Copyright 2010, Elsevier. (e) Na$_{0.7}$VO$_2$ (P2) and (f) NaVO$_2$ (O3). Reproduced with permission.\cite{ref3} Copyright 2011, Elsevier.
Figure 7. (a) Initial charge/discharge profiles of the Na/NaNi_{0.5}Mn_{0.5}O_{2} cell at a current density of 4.8 mA g^{-1} in the voltage ranges of 2.2−4.5 and 2.2−3.8 V. Reproduced with permission.\textsuperscript{[39]} Copyright 2012, American Chemical Society. (b) Charge/discharge curves of NaFe_{0.5}Co_{0.5}O_{2} with a cycling performance comparison (inset) of NaFeO_{2}, NaCoO_{2}, and NaFe_{0.5}Co_{0.5}O_{2} at a rate of 12 mA g^{-1}. Reproduced with permission.\textsuperscript{[69]} Copyright 2013, Elsevier. (c) Comparison among the cycling performances (left), initial charge profiles (middle), and initial discharge profiles (right) of four different Na/N_a(Mn, Fe)O_{2} cells. Reproduced with permission.\textsuperscript{[97]} Copyright 2013, The Electrochemical Society.
Figure 8. (a) Ranges of P2, P2’, and OP4 phase stability upon Na removal and reinsertion; (b) charge-discharge profiles of second cycle; and (c) cycling stability of Na2/3Mn1-yMg2O2 (y = 0.0, 0.05, 0.1). Reproduced with permission. Copyright 2016, Royal Society of Chemistry.

Figure 9. (a) Rate-capability of Na/Na5/6Li1/4Mn3/4O2 cells charged at 10 mA g⁻¹ to 4.4 V, and discharged at different current densities. Reproduced with permission. Copyright 2014, Wiley-VCH. (b) A combined graph of the charge profile of Na(Li1/3Mn2/3)O2 up to 4.3 V at 10 mA g⁻¹ and the theoretically calculated desodiation potentials for Na1-x(Li1/3Mn2/3)O2 (0.0 ≤ x ≤ 1.0). Reproduced with permission. Copyright 2017, Wiley-VCH.

Figure 10. (a) In situ XRD patterns of Na0.67Ni0.3Mn0.7O2 (top) and Na0.67Ni0.1Cu0.2Mn0.7O2 (bottom). Reproduced with permission. Copyright 2017, Royal Society of Chemistry. (b) In situ XRD patterns of Na0.66Ni0.33Mn0.67O2 (top) and Na0.66Ni0.26Zn0.07Mn0.67O2 (bottom). Reproduced with permission. Copyright 2016, American Chemical Society.
Figure 11. (a) $dQ/dV$ vs. potential curves (left) and cycling performance (right) of P2-Na$_{x}$Co$_{(1-y)}$Mn$_{2y/3}$Ni$_{1/3}$O$_2$ ($y = 0, 1/3, 2/3, 2/3$ and $1$) within the voltage range of 2.0-4.2 V. Reproduced with permission.\cite{119} Copyright 2017, American Chemical Society. (b) In situ XRD patterns of Na$_{x}$Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ with P2/O3/O1 structure during the first cycle between 2.0 and 4.4 V. Reproduced with permission.\cite{120} Copyright 2017, Royal Society of Chemistry. (c) Charge/discharge profiles of air exposed Na$_{0.67}$Mn$_{0.5+y}$Ni$_{y}$Fe$_{0.5-2y}$O$_2$ ($y = 0, 0.1$, and $0.15$), with profiles for the air-protected electrodes shown in grey curves for comparison. Reproduced with permission.\cite{58} Copyright 2015, American Chemical Society.
Figure 12. (a) In-situ XRD patterns and corresponding charge/discharge profiles of Na(Mn<sub>0.25</sub>Fe<sub>0.25</sub>Co<sub>0.25</sub>Ni<sub>0.25</sub>)O<sub>2</sub> at the C/50 rate; and (b) cycling performances of Na(Mn<sub>0.25</sub>Fe<sub>0.25</sub>Co<sub>0.25</sub>Ni<sub>0.25</sub>)O<sub>2</sub>, Na(Fe<sub>0.5</sub>Co<sub>0.5</sub>)O<sub>2</sub>, and Na(Ni<sub>0.5</sub>Mn<sub>0.5</sub>)O<sub>2</sub> at the C/10 rate. Reproduced with permission.© 2014, Elsevier. (c) Comparison of calculated configuration of NaNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> and NaNi<sub>0.45</sub>Cu<sub>0.05</sub>Mn<sub>0.4</sub>Ti<sub>0.1</sub>O<sub>2</sub> and (d) in-situ XRD patterns of NaNi<sub>0.45</sub>Cu<sub>0.05</sub>Mn<sub>0.4</sub>Ti<sub>0.1</sub>O<sub>2</sub> collected during the first charge/discharge process. Reproduced with permission.© 2017, American Chemical Society.

Figure 13. Comparison among capacity and average voltage of selected metal oxide cathodes for SIBs with energy density curves superimposed.
Data based on 0.2 C; data based on 0.5 C; and all others are based on 0.1 C as reported in references.

Figure 14. (a) Schematic illustration and (b) charge–discharge profiles for the 1\textsuperscript{st} and 2\textsuperscript{nd} cycles of the Na[\(\text{Ni}_{0.25}\text{Fe}_{0.5}\text{Mn}_{0.25}\)]O\(_2\)//C-Fe\(_3\)O\(_4\) full-cell sodium-ion battery. Reproduced with permission.\textsuperscript{[165]} Copyright 2014, American Chemical Society.
Summary of synthesis methods, phases and electrochemical performances of different transition metal oxides as cathodes for sodium ion batteries.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Synthesis method</th>
<th>Phase</th>
<th>Electrolyte</th>
<th>Voltage range (V)</th>
<th>Discharge capacity (mAh g(^{-1}))/current density (mA g(^{-1}))</th>
<th>Rate capacity (mAh g(^{-1}))/C rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCrO(_2)</td>
<td>Solid-state</td>
<td>O3</td>
<td>1 M NaClO(_4) in PC</td>
<td>2.0-3.5</td>
<td>-</td>
<td>-</td>
<td>[74]</td>
</tr>
<tr>
<td>Na(_{0.7})Co(_2)</td>
<td>Solvothermal</td>
<td>P2</td>
<td>1 M NaClO(_4) in EC:DEC (1:1, v/v)</td>
<td>2.0-3.8</td>
<td>125/5 (0.04C)</td>
<td>98/4C</td>
<td>[130]</td>
</tr>
<tr>
<td>NaMnO(_2)</td>
<td>Solid-state</td>
<td>O3</td>
<td>1 M NaPF(_6) in EC:DMC (1:1, v/v)</td>
<td>2.0-3.8</td>
<td>197/24 (0.1C)</td>
<td>-</td>
<td>[83]</td>
</tr>
<tr>
<td>Na(_{0.8})MnO(_2)</td>
<td>Sol-gel</td>
<td>P2</td>
<td>1 M NaClO(_4) in PC</td>
<td>2.0-3.8</td>
<td>140/0.21 mA cm(^{-2})</td>
<td>-</td>
<td>[81]</td>
</tr>
<tr>
<td>Na(_{0.6})MnO(_2)</td>
<td>Ultrasonic spray pyrolysis and</td>
<td>P2</td>
<td>1 M NaClO(_4) in FEC:DMC (1:1, v/v)</td>
<td>2.0-3.8; 1.5-4.3</td>
<td>(155; 205)/24.4 (0.1C)</td>
<td>115/2C; -</td>
<td>[131]</td>
</tr>
<tr>
<td>Na(<em>{0.6})Ni(</em>{0.3})Mn(_{0.6})O(_2)</td>
<td>high temperature annealing</td>
<td></td>
<td></td>
<td></td>
<td>(105; 155)/0.1C</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Na(<em>{0.6})Fe(</em>{0.2})Ni(<em>{0.15})Mn(</em>{0.65})O(_2)</td>
<td>Solid-state</td>
<td>O3</td>
<td>1 M NaPF(_6) in EC:DMC (1:1, v/v)</td>
<td>1.25-3.75</td>
<td>123/23.5 (0.1C)</td>
<td>-</td>
<td>[132]</td>
</tr>
<tr>
<td>NaFeO(_2)</td>
<td>Solid-state</td>
<td>O3</td>
<td>1 M NaClO(_4) in PC + 2 vol.% FEC</td>
<td>2.5-3.4</td>
<td>80/12</td>
<td>-</td>
<td>[84]</td>
</tr>
<tr>
<td>NaCrO(_2)</td>
<td>Emulsion-drying</td>
<td>O3</td>
<td>0.5 M NaPF(_6) in PC + 2 vol.% FEC</td>
<td>2.0-3.6</td>
<td>112/20</td>
<td>3/5.5 A g(^{-1})</td>
<td>[133]</td>
</tr>
<tr>
<td>Carbon-coated NaCrO(_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>121/20</td>
<td>106/5.5 A g(^{-1})</td>
<td></td>
</tr>
<tr>
<td>NaV(_2)O(_5)</td>
<td>Solid-state</td>
<td>O3</td>
<td>1 M NaClO(_4) in EC</td>
<td>1.2-2.4</td>
<td>120/0.05C</td>
<td>-</td>
<td>[96]</td>
</tr>
<tr>
<td>Na(_{0.8})V(_2)O(_5)</td>
<td></td>
<td>P2</td>
<td>1 M NaClO(_4) in EC</td>
<td></td>
<td>100/0.05C</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>NaNi(<em>{0.5})Mn(</em>{0.5})O(_2)</td>
<td>Solid-gel</td>
<td>O3</td>
<td>1 M NaClO(_4) in EC:PC (1:1, v/v) + 3% FEC</td>
<td>2.0-4.0</td>
<td>141/12 (0.05C)</td>
<td>80/2C</td>
<td>[134]</td>
</tr>
<tr>
<td>NaFe(<em>{0.2})Mn(</em>{0.8})O(_2)</td>
<td>Solid-state</td>
<td>O3</td>
<td>1 M NaClO(_4) in PC</td>
<td>1.5-4.3</td>
<td>(100-110)/12</td>
<td>-</td>
<td>[101]</td>
</tr>
<tr>
<td>Na(<em>{2})Fe(</em>{0.2})Mn(_{0.8})O(_2)</td>
<td>Solid-state</td>
<td>P2</td>
<td>1 M NaClO(_4) in PC</td>
<td>1.5-4.3</td>
<td>190/12</td>
<td>130/260 mA g(^{-1})</td>
<td></td>
</tr>
<tr>
<td>NaFe(<em>{0.2})Cu(</em>{0.2})O(_2)</td>
<td>Solid-state</td>
<td>O3</td>
<td>1 M NaClO(_4) in PC + 2 vol.% FEC</td>
<td>2.5-4.0</td>
<td>160/12 (0.05C)</td>
<td>&gt; 100/30C</td>
<td>[39]</td>
</tr>
<tr>
<td>Material</td>
<td>Synthesis Method</td>
<td>Product</td>
<td>Solvent</td>
<td>Current</td>
<td>Current Density</td>
<td>Reference</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>------------------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>----------------</td>
<td>-----------</td>
<td></td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>Solid-state</td>
<td>P2</td>
<td>1.2 M NaClO$_3$ in PC + 5 vol.% FEC</td>
<td>2.5-4.3</td>
<td>~160/86.5 (0.5C)</td>
<td>[135]</td>
<td></td>
</tr>
<tr>
<td>Na$<em>2$O-coated Na$<em>2$Ni$</em>{10/3}$Mn$</em>{2/3}$O$_2$</td>
<td>Solid-state and wet-chemistry</td>
<td>P2</td>
<td>1 M NaPF$_6$ in PC</td>
<td>2.0-4.5</td>
<td>138/12 (0.1C)</td>
<td>[136]</td>
<td></td>
</tr>
<tr>
<td>Na$<em>8$Na$</em>{0.2}$Mn$_{0.6}$O$_2$</td>
<td>Hydrothermal</td>
<td>P2</td>
<td>1 M NaClO$_3$ in PC:EC (1:1, v/v)</td>
<td>1.5-3.8</td>
<td>(147 for flakes; 188 for spheres)/2/0</td>
<td>[99]</td>
<td></td>
</tr>
<tr>
<td>Na$<em>8$Co$</em>{0.1}$Mn$<em>{0.9}$O$</em>{2+x}$ flakes/spheres</td>
<td>Combustion</td>
<td>P2</td>
<td>1 M NaClO$_3$ in PC:EC (1:1, w/w)</td>
<td>1.5-3.8</td>
<td>(153 for flakes; 183 for spheres)/2/0</td>
<td>[99]</td>
<td></td>
</tr>
<tr>
<td>Na$<em>8$[Mg$</em>{0.2}$Mn$_{0.72}$]O$_2$</td>
<td>Solid-state</td>
<td>P2</td>
<td>1 M NaClO$_3$ in PC:DMC (1:1, v/v) + 2 vol.% FEC</td>
<td>1.5-4.4</td>
<td>&gt;200/10</td>
<td>[137]</td>
<td></td>
</tr>
<tr>
<td>Na$<em>8$Mn$</em>{1.8}$Mg$_{0.2}$O$_2$</td>
<td>Solid-state or co-precipitation</td>
<td>P2</td>
<td>1 M NaClO$_3$ in EC:PC (1:1, w/w)</td>
<td>1.5-4.0</td>
<td>~175/12</td>
<td>[106]</td>
<td></td>
</tr>
<tr>
<td>Na$<em>8$Ni$</em>{0.4}$Ti$_{0.6}$O$_2$</td>
<td>Solid-state</td>
<td>O3</td>
<td>1 M NaClO$_3$ in PC + 2 vol.% FEC</td>
<td>2.0-4.0</td>
<td>83/0.2 C</td>
<td>[138]</td>
<td></td>
</tr>
<tr>
<td>Na$<em>8$Ni$</em>{1.3}$Ti$_{2.7}$O$_2$</td>
<td>Ball-milling and subsequent annealing</td>
<td>P2</td>
<td>0.5 M NaPF$_6$ in EC:DEC (1:1, v/v)</td>
<td>2.0-4.2</td>
<td>90/1.8 (0.02C)</td>
<td>~45/1C</td>
<td>[139]</td>
</tr>
<tr>
<td>Na$<em>8$[Li$</em>{0.9}$Mn$<em>{0.1}$]O$</em>{2+y}$</td>
<td>Solid-state</td>
<td>P2</td>
<td>1 M NaClO$_3$ in EC:DEC (1:1, v/v)</td>
<td>2.0-3.8</td>
<td>~180/19</td>
<td>-</td>
<td>[111]</td>
</tr>
<tr>
<td>Na$<em>8$[Li$</em>{1.4}$Mn$_{3.6}$]O$_2$</td>
<td>Solid-state</td>
<td>P2</td>
<td>1 M NaClO$_3$ in PC + 2 vol.% FEC</td>
<td>1.5-4.4</td>
<td>200/10</td>
<td>150/236 mA g$^{-1}$</td>
<td>[107]</td>
</tr>
<tr>
<td>Na$<em>8$[Cr$</em>{0.6}$Ti$_{0.4}$]O$_2$</td>
<td>Solid-state</td>
<td>P2</td>
<td>0.8 M NaPF$_6$ in EC:DEC (4:6, v/v)</td>
<td>2.5-3.84</td>
<td>75/7.6 (0.1C)</td>
<td>64/1C</td>
<td>[140]</td>
</tr>
<tr>
<td>Na$<em>{10}$Li$</em>{0.1}$Ni$<em>{0.35}$Mn$</em>{0.55}$O$_2$</td>
<td>Co-precipitation</td>
<td>O3</td>
<td>1 M NaClO$_3$ in PC + 2 vol.% FEC</td>
<td>2.0-4.2</td>
<td>128/12</td>
<td>-</td>
<td>[141]</td>
</tr>
<tr>
<td>Na$<em>{10}$Li$</em>{0.2}$Ni$<em>{0.25}$Mn$</em>{0.55}$O$<em>6$ (Na$</em>{0.85}$Li$<em>{0.17}$Ni$</em>{0.21}$Mn$_{0.6}$O$_2$)</td>
<td>Solid-state</td>
<td>P2</td>
<td>1 M NaClO$_3$ in PC</td>
<td>2.0-4.2</td>
<td>~100/15</td>
<td>65/1.8 A g$^{-1}$ (25C)</td>
<td>[124]</td>
</tr>
<tr>
<td>Na$<em>{10}$Li$</em>{0.2}$Ni$<em>{0.2}$Mn$</em>{0.6}$O$_2$</td>
<td>Self-combustion reaction</td>
<td>P2</td>
<td>0.5 M NaPF$_6$ in PC</td>
<td>2.0-4.6</td>
<td>120/12 (C/15)</td>
<td>92/2C</td>
<td>[142]</td>
</tr>
<tr>
<td>Na$<em>{10}$Li$</em>{0.2}$Ni$<em>{0.2}$Mn$</em>{0.6}$O$_2$</td>
<td>Co-precipitation</td>
<td>P2</td>
<td>1 M NaClO$_3$ in PC:EC (1:2)</td>
<td>2.0-4.4</td>
<td>115/11.8 (0.1C)</td>
<td>101.5/1 C</td>
<td>[143]</td>
</tr>
<tr>
<td>Na$<em>{10}$Ni$</em>{0.1}$Fe$<em>{0.1}$Mn$</em>{0.8}$O$_2$</td>
<td>Solid-state</td>
<td>O3</td>
<td>1 M NaClO$_3$ in PC</td>
<td>2.0-4.0</td>
<td>~120/13</td>
<td>-</td>
<td>[79]</td>
</tr>
<tr>
<td>Na$<em>{10}$[Ni$</em>{0.2}$Fe$<em>{0.13}$Mn$</em>{0.63}$]O$_2$</td>
<td>Co-precipitation and solid-state</td>
<td>P2</td>
<td>1 M NaPF$_6$ in PC</td>
<td>1.5-4.6</td>
<td>150/100 (0.5C)</td>
<td>60/715 mA g$^{-1}$</td>
<td>[144]</td>
</tr>
<tr>
<td>Na$<em>{10}$Cu$</em>{0.2}$Fe$<em>{0.3}$Mn$</em>{0.4}$O$_2$</td>
<td>Solid-state</td>
<td>O3</td>
<td>0.8 M NaPF$_6$ in PC + 2 vol.% FEC</td>
<td>2.5-4.05</td>
<td>100/10</td>
<td>72/2C</td>
<td>[60]</td>
</tr>
<tr>
<td>NaFe0.4Ni0.6Mn1/2O2</td>
<td>Solid-state</td>
<td>O3</td>
<td>1 M NaClO3 in PC + 2 vol.% FEC</td>
<td>2.0-3.8</td>
<td>130/12 (0.05C)</td>
<td>110/4C</td>
<td>[143] 1</td>
</tr>
<tr>
<td>Na0.7Cu0.3Fe0.9Mn1/2O2</td>
<td>Solid-state</td>
<td>P2</td>
<td>0.8 M NaPFs in EC</td>
<td>2.5-4.2</td>
<td>89/10 (0.1C)</td>
<td>64/1C</td>
<td>[59] 1</td>
</tr>
<tr>
<td>Na0.66Ni0.26Zn0.07Mn0.67O2</td>
<td>Solid-state</td>
<td>P2</td>
<td>1 M NaClO3 in PC + 2 vol.% FEC</td>
<td>2.2-4.4</td>
<td>143/12</td>
<td>79/768 mA g⁻¹</td>
<td>[146] 1</td>
</tr>
<tr>
<td>Na1.2Ni0.8Mn0.2Ru0.8O2</td>
<td>Solid-state</td>
<td>O3</td>
<td>1 M NaClO3 in EC:PC (1:1, v/v) + 5 vol.% FEC</td>
<td>1.5-3.8</td>
<td>128/52.4 (0.2C)</td>
<td>111/2C</td>
<td>[147] 1</td>
</tr>
<tr>
<td>Na0.85Mn0.5Ti0.2O2</td>
<td>Solid-state</td>
<td>O3</td>
<td>1 M NaClO3 in PC</td>
<td>2.0-4.0</td>
<td>138/13 (0.1C)</td>
<td>111/1C</td>
<td>[148] 1</td>
</tr>
<tr>
<td>Na20.6Ni1/3Mn1/2Ti0.8O2</td>
<td>Ball milling and subsequent annealing</td>
<td>P2</td>
<td>1 M NaPFs in PC</td>
<td>2.5-4.5</td>
<td>127/12.1 (0.05C)</td>
<td>101.6/1C</td>
<td>[149] 1</td>
</tr>
<tr>
<td>Na0.66Ni0.26Mg0.1Mn0.67O2</td>
<td>Sol-gel</td>
<td>P2</td>
<td>1 M NaClO3 in EC:DEC (4:6, v/v)</td>
<td>2.0-4.5</td>
<td>105/48</td>
<td>74/384 mA g⁻¹</td>
<td>[150] 1</td>
</tr>
<tr>
<td>Na20.6Ni0.8Mn0.2Al0.8O2</td>
<td>Liquid-state and high-temperature annealing</td>
<td>P2</td>
<td>1 M NaClO3 in EC:PC (1:1, v/v)</td>
<td>1.6-4.0</td>
<td>118/0.1C</td>
<td>84.4/1C</td>
<td>[151] 1</td>
</tr>
<tr>
<td>Na0.66Mn0.36Fe0.2Ni0.15O2</td>
<td>Sol-gel</td>
<td>P2</td>
<td>1 M NaPFs in EC:DEC (1:1, v/v)</td>
<td>1.5-4.3</td>
<td>208/13 (0.05C)</td>
<td>128/4C</td>
<td>[47] 1</td>
</tr>
<tr>
<td>NaNi1/3Co1/3Fe1/3O2</td>
<td>Solid-state</td>
<td>O3</td>
<td>1 M NaPFs in EC:DEC (1:1, v/v)</td>
<td>2.0-4.2</td>
<td>165/11.85 (0.05C)</td>
<td>80/30C</td>
<td>[152] 1</td>
</tr>
<tr>
<td>NaNi0.22Co0.11Mn0.66O2</td>
<td>Co-precipitation and solid-state</td>
<td>P2/P3</td>
<td>1 M NaPFs in PC</td>
<td>1.5-4.6</td>
<td>-</td>
<td>-</td>
<td>[55] 1</td>
</tr>
<tr>
<td>Na20.6Mn0.4Ni0.36Co0.1O2</td>
<td>Co-precipitation</td>
<td>P2</td>
<td>1 M NaPFs in PC + 2 wt.% FEC</td>
<td>1.7-4.0</td>
<td>125/0.05C</td>
<td>80/1C</td>
<td>[153] 1</td>
</tr>
<tr>
<td>Na20.6Ni0.4Co0.2Ti0.5O2</td>
<td>Solid-state</td>
<td>O3</td>
<td>1 M NaClO3 in EC:DEC (4:6, v/v)</td>
<td>2.5-4.2</td>
<td>84/0.1C</td>
<td>65/1C</td>
<td>[125] 1</td>
</tr>
<tr>
<td>AlOx coated-Na20.6Mn0.4Ni0.1Co0.1O2</td>
<td>Sol-gel and atomic layer deposition</td>
<td>P2</td>
<td>1 M NaClO3 in EC:DEC (1:1, v/v)</td>
<td>2.0-4.5</td>
<td>123/160 (0.1C)</td>
<td>~110/5C</td>
<td>[154] 1</td>
</tr>
<tr>
<td>NaNi1/3Co1/3O2</td>
<td>Sol-gel</td>
<td>O3</td>
<td>1 M NaClO3 in EC:DMC (1:1, v/v)</td>
<td>2 - 3.75</td>
<td>120/0.24 mA cm⁻² (0.1C)</td>
<td>80/1C</td>
<td>[123] 1</td>
</tr>
<tr>
<td>NaNi0.22Mn0.7Co0.1O2</td>
<td>Solvothemal</td>
<td>P2/O3/O 1</td>
<td>1 M NaPFs in PC + 2 vol.% FEC</td>
<td>2.0-4.4</td>
<td>142.8/15 (0.1C)</td>
<td>68.8/5C</td>
<td>[120] 1</td>
</tr>
<tr>
<td>Na0.65[Mn0.65Co0.2Ni0.15]O2</td>
<td>Sol-gel</td>
<td>P2</td>
<td>1 M NaPFs in EC:DEC (1:1, v/v)</td>
<td>2.0-4.4</td>
<td>125/20</td>
<td>-</td>
<td>[155] 1</td>
</tr>
<tr>
<td>Na0.65[Mn0.65Ni0.3Co0.15Al0.05]O2</td>
<td>Sol-gel</td>
<td>P2</td>
<td>1 M NaPFs in EC:DEC (1:1, v/v)</td>
<td>2.0-4.4</td>
<td>129/20</td>
<td>~60/400 mA g⁻¹</td>
<td>[156] 1</td>
</tr>
<tr>
<td>Na20Co20Mn20Ni10O2</td>
<td>Sol-gel</td>
<td>P2</td>
<td>0.5 M NaPFs in PC</td>
<td>2.0-4.2</td>
<td>80/12.6 (0.05C)</td>
<td>77/1C</td>
<td>[156] 1</td>
</tr>
<tr>
<td>Na3Ni1.3Mg0.5Sb5O6</td>
<td>Solid-state</td>
<td>honeycomb-layered</td>
<td>1 M NaClO3 in EC:PC (1:1, v/v) + 2 vol.% FEC</td>
<td>2.0-4.0</td>
<td>99/13.3 (0.1C)</td>
<td>-</td>
<td>[157] 1</td>
</tr>
<tr>
<td>Na0.66Ni0.13Co0.17Ti0.66O2</td>
<td>Solid-state</td>
<td>P2</td>
<td>1 M NaClO3 in PC + 2 vol.% FEC</td>
<td>2.0-4.0</td>
<td>55/0.2C</td>
<td>-</td>
<td>[158] 1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Materials (Cathode//Anode)</th>
<th>Anode presodiated (Yes/No)</th>
<th>Average open circuit voltage (V vs Na+/Na)</th>
<th>Voltage range (V vs Na+/Na)</th>
<th>Electrolyte</th>
<th>Initial coulombic efficiency</th>
<th>Capacity (mAh g⁻¹/current density)</th>
<th>Capacity retention/number of cycles</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNi0.67Li0.13Mn0.71Ni0.25Co0.08O2</td>
<td>-</td>
<td>1 M NaPF₆ in EC:DEC (1:1, v/v)</td>
<td>1.5-4.5</td>
<td>200/10 (0.1C)</td>
<td>-</td>
<td>100/2C</td>
<td>[128 1]</td>
<td></td>
</tr>
<tr>
<td>Na(NiCoFeTi)11O2</td>
<td>Solid-state</td>
<td>O3</td>
<td>1 M NaClO₄ in EC:PC (1:1, v/v) + 5 wt.% FEC</td>
<td>2.0-3.9</td>
<td>116/12 (0.1C)</td>
<td>101.9/5 C</td>
<td>-</td>
<td>[159 1]</td>
</tr>
<tr>
<td>NaNi0.45Cu0.05Mn0.4Ti0.1O2</td>
<td>Solid-state</td>
<td>O3</td>
<td>1 M NaClO₄ in PC + 5% FEC</td>
<td>2.0-4.0</td>
<td>124/0.1C</td>
<td>81/10C</td>
<td>-</td>
<td>[61]</td>
</tr>
<tr>
<td>NaNi0.25Fe0.25Co0.25Ni0.25O2</td>
<td>Solid-state</td>
<td>O3</td>
<td>1 M NaPF₆ in EC:DEC (1:1, v/v)</td>
<td>1.9-4.3</td>
<td>180/0.1C</td>
<td>-</td>
<td>-</td>
<td>[126 1]</td>
</tr>
<tr>
<td>NaNi0.65Mn0.35Ti0.2-Li0.2</td>
<td>Solid-gel</td>
<td>P2/O3</td>
<td>1 M NaClO₄ in PC</td>
<td>1.5-4.2</td>
<td>(147, 150, 158)/12 (0.05C) (x=0, 0.1, 0.2)</td>
<td>(240, 99, 109)/1C</td>
<td>-</td>
<td>[160 1]</td>
</tr>
<tr>
<td>NaNi0.35Ni0.15Fe0.15Mg0.10O2</td>
<td>Solid-state</td>
<td>P3/P2/O3</td>
<td>1 M NaPF₆ in PC</td>
<td>2.0-4.3</td>
<td>155/18</td>
<td>134/180 mA g⁻¹</td>
<td>-</td>
<td>[129 1]</td>
</tr>
<tr>
<td>NaNi0.32Fe0.13Co0.15Mn0.40O2</td>
<td>Solid-state</td>
<td>O3</td>
<td>0.5 M NaPF₆ in PC + 2 vol.% FEC</td>
<td>1.5-4.3</td>
<td>182/30 (0.2C)</td>
<td>137.4/5 C</td>
<td>-</td>
<td>[161]</td>
</tr>
<tr>
<td>NaNi0.25Fe0.5Mn0.25O2/C-Fe₂O₃</td>
<td>Yes</td>
<td>~ 2.4</td>
<td>0.5-3.6</td>
<td>1 M NaClO₄-EMS + 2 vol.% FEC</td>
<td>-</td>
<td>130/0.1C</td>
<td>82.8%/10 0</td>
<td>-</td>
</tr>
<tr>
<td>NaCrO₂/hard carbon</td>
<td>No</td>
<td>3.0</td>
<td>1.8-3.4</td>
<td>0.5 M NaPF₆ in PC + 2 vol.% FEC</td>
<td>-</td>
<td>97/25 mA g⁻¹</td>
<td>70%/100</td>
<td>-</td>
</tr>
<tr>
<td>Carbon-coated NaCrO₂/hard carbon</td>
<td>No</td>
<td>2.9</td>
<td>1.8-3.4</td>
<td>0.5 M NaPF₆ in PC + 2 vol.% FEC</td>
<td>-</td>
<td>102/25 mA g⁻¹</td>
<td>90%/300</td>
<td>-</td>
</tr>
<tr>
<td>(NaCrO₂ + 10% Na₂NiO₃)//Sb/C</td>
<td>No</td>
<td>2.2</td>
<td>0.5-3.15</td>
<td>1 M NaClO₄ in EC:DEC: FEC 4.5/4.5/1 v/v/v</td>
<td>-</td>
<td>92.1/0.5C</td>
<td>63.3%/50</td>
<td>-</td>
</tr>
<tr>
<td>NaNi0.35Mn0.65O₂//Sn-C</td>
<td>Yes</td>
<td>2.5</td>
<td>1.5-4.0</td>
<td>1 M NaClO₄ in PC + 2 vol. % FEC</td>
<td>-</td>
<td>120/0.2C</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na₂Ni₁₀Mn₂O₁₄//hard carbon</td>
<td>-</td>
<td>3.5</td>
<td>0-3.9</td>
<td>1 M NaClO₄ in EC:DEC (1:1 v/v)</td>
<td>76%</td>
<td>&gt;300/0.1C</td>
<td>73%/150</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2. Characteristics of reported full cells in the sodium-ion system based on transition metal oxide cathodes.
<table>
<thead>
<tr>
<th>Material</th>
<th>Reaction</th>
<th>Current Density</th>
<th>Voltage</th>
<th>Capacity</th>
<th>Cycles</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaLix5Mnx5Ni30Cu0.10Mgo.05O2/hard carbon b)</td>
<td>NaClO4 in EC:DEC (1:1 v/v) + 2 vol.% FEC</td>
<td>~2.9</td>
<td>1.01-4.19</td>
<td>80.6%</td>
<td>~50/0.5C</td>
<td>-</td>
</tr>
<tr>
<td>NaLix5Fe20Mnx5O2/hard carbon a)</td>
<td>NaClO4 in PC + 2 vol.% FEC</td>
<td>-</td>
<td>3.2</td>
<td>1.75-4.3</td>
<td>-</td>
<td>149.1/0.5C</td>
</tr>
<tr>
<td>NaNi0.5Fe10Mnx3O2/hard carbon a)</td>
<td>NaNiO in PC</td>
<td>-</td>
<td>~2.75</td>
<td>1.5-4.1</td>
<td>72%</td>
<td>100/75 mA g⁻¹</td>
</tr>
<tr>
<td>NaNi0.5Cu2Fe10Mnx3O2/hard carbon b)</td>
<td>NaNiO in EC:DEC (1:1)</td>
<td>-</td>
<td>3.5</td>
<td>1.0-4.2</td>
<td>79%</td>
<td>313/0.2C</td>
</tr>
<tr>
<td>NaNi0.5Cu2Fe10Mnx3O2/hard carbon b)</td>
<td>NaNiO in EC:DEC (1:1)</td>
<td>-</td>
<td>3.2</td>
<td>1-4.05</td>
<td>85%</td>
<td>300/0.5C</td>
</tr>
<tr>
<td>NaNi0.5Mnx3O2/hard carbon b)</td>
<td>NaNiO in PC + 2 vol.% FEC</td>
<td>-</td>
<td>&lt;2.4</td>
<td>1.2-4.2</td>
<td>1 M NaPF6 in EC:DMC (1:1 v/v) + 2 vol.% FEC</td>
<td>-</td>
</tr>
<tr>
<td>NaNi0.5Co0.02Mnx3O2//hard carbon</td>
<td>NaNiO in EMS + 2 vol.% FEC</td>
<td>Yes</td>
<td>2.84</td>
<td>1.5-3.9</td>
<td>0.5 M NaPF6 in EMS + 2 vol.% FEC</td>
<td>-</td>
</tr>
<tr>
<td>NaNi0.5Co0.02Mnx3O2//hard carbon</td>
<td>NaNiO in EMS + 2 vol.% FEC</td>
<td>Yes</td>
<td>~3.0</td>
<td>-</td>
<td>1 M NaPF6 in PC</td>
<td>-</td>
</tr>
<tr>
<td>NaNi0.5Co0.02Mnx3O2//hard carbon</td>
<td>NaNiO in EMS + 2 vol.% FEC</td>
<td>-</td>
<td>~3.4</td>
<td>2.5-4.0</td>
<td>1 M NaPF6 in EC:DEC</td>
<td>-</td>
</tr>
<tr>
<td>NaNi0.5Co0.02Mnx3O2//hard carbon</td>
<td>NaNiO in EMS + 2 vol.% FEC</td>
<td>-</td>
<td>1.8</td>
<td>1.0-2.6</td>
<td>1 M NaClO4 in PC</td>
<td>-</td>
</tr>
<tr>
<td>NaNi0.5Mnx3O2//hard carbon a)</td>
<td>NaNiO in PC + 2 wt.% FEC</td>
<td>Yes</td>
<td>-</td>
<td>-</td>
<td>0.5 M NaPF6 in PC + 2 wt.% FEC</td>
<td>-</td>
</tr>
<tr>
<td>NaNi0.5Mnx3O2//hard carbon a)</td>
<td>NaNiO in PC + 2 wt.% FEC</td>
<td>-</td>
<td>~2.7</td>
<td>0.7-4.1</td>
<td>NaNiO in PC + 2 wt.% FEC</td>
<td>-</td>
</tr>
<tr>
<td>Na37CoO3/graphite</td>
<td>NaNiO in TEGDME</td>
<td>Yes</td>
<td>~2.2</td>
<td>0.5-3.7</td>
<td>1 M NaClO4 in NaClO4 in PC</td>
<td>-</td>
</tr>
<tr>
<td>Na84Mnx0.4CoO.4O2//NiSb</td>
<td>NaNiO in PC</td>
<td>Yes</td>
<td>2.6</td>
<td>1.0-4.2</td>
<td>1 M NaClO4 in PC</td>
<td>66.7%</td>
</tr>
<tr>
<td>Na20Ni10Mnx0.5O2//Sb b)</td>
<td>NaNiO in PC + 2 wt.% FEC</td>
<td>Yes</td>
<td>2.9</td>
<td>1.4-4.0</td>
<td>1 M NaClO4 in EC:PC/1:1 v/v + 5 wt.% FEC</td>
<td>-</td>
</tr>
<tr>
<td>Na20Ni10Mnx0.5O2//SbS3</td>
<td>NaNiO in PC</td>
<td>No</td>
<td>2.18</td>
<td>0.5-3.5</td>
<td>1 M NaNiO in 1 M NaClO4 in PC</td>
<td>55%</td>
</tr>
<tr>
<td>System</td>
<td>Charge</td>
<td>Discharge</td>
<td>Capacity</td>
<td>Rate</td>
<td>Energy Efficiency</td>
<td>Ref.</td>
</tr>
<tr>
<td>--------</td>
<td>--------</td>
<td>-----------</td>
<td>----------</td>
<td>------</td>
<td>------------------</td>
<td>------</td>
</tr>
<tr>
<td>NaNi0.66Fe0.16Mn0.66O2//hard carbon</td>
<td>No</td>
<td>3.0</td>
<td>1.5-3.8</td>
<td>1 M NaClO4 in PC:EMC: FEC (50:48:2, v/v/v)</td>
<td>-</td>
<td>10 Ah/1A 85%/100</td>
</tr>
<tr>
<td>NaNi0.66Ti0.5O2//hard carbon a)</td>
<td>No</td>
<td>3.05</td>
<td>1.5-4.0</td>
<td>1 M NaClO4 in PC</td>
<td>73%</td>
<td>93/10mA g⁻¹ 72%/100</td>
</tr>
<tr>
<td>NaNi0.66Co0.16Mn0.66O2//hard carbon b)</td>
<td>Yes</td>
<td>~2.4</td>
<td>0.5-3.9</td>
<td>1 M NaClO4 in EC:PC (1:1)</td>
<td>-</td>
<td>250/20 81%/100</td>
</tr>
<tr>
<td>NaNi0.66Li0.16Ni0.22Mn0.66O2//Sn S2-rGO b)</td>
<td>No</td>
<td>2.3</td>
<td>1.0-4.2</td>
<td>1 M NaPF6 in EC:DEC (1:1, v/v) + 5 vol.% FEC</td>
<td>64%</td>
<td>0.708mA/0.334mA 74%/50</td>
</tr>
<tr>
<td>NaNi0.51Ni0.51Mn0.51O2//Sb b)</td>
<td>-</td>
<td>2.75</td>
<td>-</td>
<td>1 M NaClO4 in EC:PC (1:1 v/v)</td>
<td>-</td>
<td>462/0.5 A g⁻¹ 70%/100</td>
</tr>
<tr>
<td>NaNi0.66Co0.16Mn0.66O2//Fe1.5S@CNTs a)</td>
<td>-</td>
<td>2.0</td>
<td>0.5-3.9</td>
<td>1 M NaClO4 in EC:PC (1:1 v/v) + 5 wt.% FEC</td>
<td>-</td>
<td>123/0.5C 85%/80</td>
</tr>
<tr>
<td>NaNi0.66SbO6//Sb/C b)</td>
<td>-</td>
<td>2.4</td>
<td>1.5-3.6</td>
<td>1 M NaPF6 in EC:DEC (1:1, v/v)</td>
<td>-</td>
<td>105/20 mA g⁻¹ 70%/50</td>
</tr>
<tr>
<td>NaNi0.66Ti0.5O2// NaNi0.3MoO2 a)</td>
<td>Yes</td>
<td>~2.4</td>
<td>0.6-3.6</td>
<td>1 M NaPF6 in EC:DEC (1:1, v/v)</td>
<td>-</td>
<td>80/20 mA g⁻¹ 94.8%/100</td>
</tr>
<tr>
<td>NaNi0.35Mn0.35Ti0.10//hard carbon a)</td>
<td>Yes</td>
<td>2.9</td>
<td>1.5-4.0</td>
<td>1 M NaClO4 in PC + 5 vol.% FEC</td>
<td>92%</td>
<td>131/12 mA g⁻¹ 85%/50</td>
</tr>
<tr>
<td>NaNi0.35Mn0.35Ti0.10//hard carbon a)</td>
<td>No</td>
<td>3.2</td>
<td>1.5-4.0</td>
<td>1 M NaClO4 in PC + 5 vol.% FEC</td>
<td>73%</td>
<td>106/12 mA g⁻¹ 76%/50</td>
</tr>
<tr>
<td>NaNi0.66Ni0.16Ti0.10O2//NaHBD C b)</td>
<td>No</td>
<td>3.6</td>
<td>-</td>
<td>1M NaPF6 in EC:DMC (3:7 w/w)</td>
<td>43%</td>
<td>257/20 mA g⁻¹ 93%/50</td>
</tr>
<tr>
<td>NaNi0.35Ti0.5O2//NaNi0.35Ti0.5O2 @S-TiO2 b)</td>
<td>Yes</td>
<td>2.7</td>
<td>1.0-4.0</td>
<td>1 M NaClO4 in EC:DMC (1:1 v/v) + 2% FEC</td>
<td>-</td>
<td>210/0.2C -</td>
</tr>
<tr>
<td>NaNi1.25V3O8//carbon nanofiber a)</td>
<td>No</td>
<td>2.3</td>
<td>-</td>
<td>1 M NaClO4 in EC:DMC (1.2 w/w)</td>
<td>-</td>
<td>143.8/200 mA g⁻¹ 77%/200</td>
</tr>
<tr>
<td>NaNi0.66Ni0.17Co0.17Ti0.66O2//NaNi0.66Ni0.17Co0.17Ti0.66O2</td>
<td>No</td>
<td>3.1</td>
<td>2.0-3.5</td>
<td>1 M NaClO4 in PC + 2</td>
<td>-</td>
<td>84/20 mA g⁻¹ 75.9%/100</td>
</tr>
<tr>
<td>Positive Material</td>
<td>Charge Depth</td>
<td>Electrolyte</td>
<td>Vol. % FEC</td>
<td>Capacity</td>
<td>Temperature</td>
<td>References</td>
</tr>
<tr>
<td>-----------------------------------------</td>
<td>--------------</td>
<td>-----------------------------------</td>
<td>------------</td>
<td>----------</td>
<td>-------------</td>
<td>------------</td>
</tr>
<tr>
<td>Na$<em>{0.6}$[Cr$</em>{0.6}$Ti$<em>{0.4}$]O$<em>2$/Na$</em>{0.6}$[Cr$</em>{0.6}$Ti$_{0.4}$]O$_2$</td>
<td>No</td>
<td>~2.53 1.5-3.0 0.8 M NaPF$_6$ in EC/DEC (4:6, v/v)</td>
<td>-</td>
<td>~80/1C</td>
<td>-</td>
<td>[140]</td>
</tr>
<tr>
<td>(NaFe$<em>{0.5}$Mn$</em>{0.5}$O$_2$ + 10%Na$_3$P)/C $^a$</td>
<td>No</td>
<td>~2.6 0-4.3 1 M NaClO$_3$ in EC:DMC (1:1, v/v)</td>
<td>63%</td>
<td>155/0.1C</td>
<td>84.5%/20</td>
<td>[193]</td>
</tr>
<tr>
<td>(Na$<em>{0.67}$[Fe$</em>{0.5}$Mn$_{0.5}$]O$_2$ + Na:N)/hard carbon $^a$</td>
<td>No</td>
<td>~3.1 1.0-4.1 1 M NaPF$_6$ in EC:DEC (1:1, w/w)</td>
<td>-</td>
<td>75/15 mA g$^{-1}$</td>
<td>100%/40</td>
<td>[194]</td>
</tr>
<tr>
<td>NaPO$<em>3$-coated Na$</em>{2/3}$[Ni$<em>{1/3}$Mn$</em>{2/3}$]O$_2$/hard carbon $^a$</td>
<td>Yes</td>
<td>~3.2 1.2-4.2 0.8 M NaPF$_6$ in PC + 2 vol.% FEC</td>
<td>-</td>
<td>189/40 mA g$^{-1}$</td>
<td>73%/300</td>
<td>[195]</td>
</tr>
<tr>
<td>Al$<em>2$O$<em>3$-coated Na$</em>{[Ni$</em>{0.6}$Co$<em>{0.2}$Mn$</em>{0.2}$]O$_2$/hard carbon}</td>
<td>No</td>
<td>~2.9 1.0-4.1 0.5 M NaPF$_6$ in PC + 2 vol.% FEC</td>
<td>75.3%</td>
<td>~100/75 mA g$^{-1}$</td>
<td>75%/300</td>
<td>[196]</td>
</tr>
</tbody>
</table>

$^a$) The capacity was calculated based on the mass of the positive material; $^b$) The capacity was calculated based on the mass of the negative material; TEGDME: tetraethylene glycol dimethyl ether; rGO: reduced graphene oxide; CNT: carbon nanotube; NaHBDC: monosodium terephthalate; NaTFSA: sodium bis(trifluoromethylsulfonyle)amide.