Layered Oxide Material as a Highly Stable Na-ion Source and Sink for Investigation of Sodium-ion Battery Materials

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Investigating Na-ion battery (SIB) materials is complicated by the absence of a well-performing (reference) electrode material since sodium metal cannot be considered as a quasi-reference electrode. Taking advantage of the activity of both Ni and Mn, herein, the P2-type and Mn-rich Na$_{0.8}$Ni$_{0.2}$Al$_{0.1}$Mn$_{0.66}$O$_2$ (NAM) material, known to be an excellent positive electrode, is investigated as a negative electrode. To prove NAM stability as both positive and negative electrode, symmetric cells have been assembled without pre-sodiation, which showed a reversible capacity of 73 mAh g$^{-1}$ and a remarkable capacity retention of 82.6% after 500 cycles. The outstanding cycling performance is ascribed to the high stability of the active material at both the highest and lowest Na-ion storage plateaus and the rather limited electrolyte decomposition and solid-electrolyte-interphase (SEI) formation occurring. The long-term stability of NAM at both electrodes enables its use as a “reference” electrode for the investigation of other positive and negative electrode materials for SIBs, resembling the role played by lithium titanate (LTO) and lithium iron phosphate (LFP) in LIBs.

Introduction

Sodium-ion batteries (SIBs) are considered as complementary to lithium-ion batteries (LIBs) due to the high abundance and lower cost of the sodium-related raw materials,$^{[1,2]}$ coupled with the similar production technology, which reduces the development costs.$^{[3]}$ The research for highly stable, high-energy density, but low cost electrode materials is, thus, the main challenge for the SIB exploitation.$^{[4]}$ Generally, SIBs adopt asymmetric configuration consisting of a high-performance cathode material, e.g., layered oxide,$^{[5,6]}$ polyanion compounds,$^{[7]}$ or Prussian Blue Analogues (PBAs),$^{[8]}$ and a compatible anode material (mainly hard carbon$^{[9]}$ or sodium metal$^{[10]}$). Much efforts have been placed into developing high capacity and high stability positive electrode materials, which already meet levels enabling commercial configuration.$^{[10]}$ For example, the layered transition metal oxides (TMOs) have been widely investigated as cathode materials for SIBs, and much progress has been made on their improvements including energy density and cycling stability. This is especially true for P2-type layered oxides, which exhibits superior electrochemical performance compared to other type layered structures due to their relatively abundant Na$^+$ vacancies and low Na$^+$-diffusion barriers.$^{[5,11]}$

On the negative electrode (anode) side, the most promising candidate of anode material for SIBs is hard carbon, expressing a highly reversible discharge capacity of $>$ 300 mAh g$^{-1}$, i.e., rather comparable to graphite for lithium-ion batteries. Nonetheless, hard carbon encounters a safety issue resulting from a fairly low discharge plateau (close to 0 V vs. Na/Na$^+$), which possibly induces the growth of sodium dendrites.$^{[12]}$ Even worse, an unstable SEI layer is formed originating from a continuous electrolyte decomposition, leading to increasing electrode/electrolyte resistance.$^{[8,13]}$ Layered titanium-based materials attracted much attention recently in virtue of their high capacity and low voltage. For example, Na$_5$Ti$_3$O$_7$ was investigated in sodium storage system and revealed a low average potential of 0.3 V vs. Na/Na$^+$ as well as a specific capacity of ~200 mAh g$^{-1},^{[14]}$ but accompanied by a dissatisfying cycling performance due to inevitable and detrimental surface reactions and bulk structural distortion.$^{[14]}$ Sodium deficient P2-type titanium oxides, e.g., Na$_{5.66}$[Li$_{0.22}$Ti$_{0.78}$]O$_7$$^{[15]}$ Na$_2$[Ti$_{3.2}$O$_7$]O$_2$$^{[17]}$ Na$_{0.16}$[Cr$_{0.3}$Ti$_{1.7}$]O$_2$$^{[16]}$ were also investigated as anodes due to the existence of sodium vacancies within the layers allowing for additional sodium insertion at low voltage. These layered oxides show a minor volume variation and excellent cycling stability as anodes for sodium storage, but low coulombic efficiency during the initial cycles. This probably ascribed to the electrolyte’s decomposition catalysed by Ti$^{4+}$, leading to the generation of a thick SEI layer on the anodes.$^{[15]}$

Finally, metallic Na is not easily applicable in full- and, even, half-cells because of the extensive electrolyte decomposition...
occurring at the electrode/liquid electrolyte interface. This process leads to the generation of a thick and unstable SEI, adding decomposition products into the electrolyte and, thus, affecting the positive electrode performance.[19-24]

Therefore, the R&D of Na-ion batteries is lacking a stable electrode material to be used as a “reference” electrode enabling for the investigation of new positive and negative electrode materials.

Manganese-based layered oxides (Na$_2$MnO$_2$) are regarded as promising intercalation hosts due to their relatively high capacity and low cost.[5] Additionally, the adverse Jahn-Teller phase transitions can be mitigated by partial other metals substitution.[25-27] For example, the aluminium-doped and Mn-rich P2-type Na$_2$Ni$_{0.22}$Al$_{0.11}$Mn$_{0.66}$O$_2$ (NAM) is known to offer a rather limited reactivity with the electrolyte, which grants rather stable performance. Starting from this background, its performance as anode material is investigated as potentially SEI-free anode material taking advantage of the Mn$^{3+}$/Mn$^{4+}$ redox couple. In the absence of a suitably stable electrode, symmetric NAM/NAM cells have been tested to investigate the cycling stability, in particular the stability of the electrolyte/NAM electrode interphase as both positive and negative electrode.

Results and Discussion

The Na$_2$Ni$_{0.22}$Al$_{0.11}$Mn$_{0.66}$O$_2$ electrode material, synthesized as reported in previous work,[6] reveals a P2-type structure ($P6_3/mmc$, s.g. 194) with ~2/3 of the total Na content in the Na(e) site as evidenced by X-ray diffraction analysis (XRD, Figure S1). The material contains two redox active metals, i.e., Ni and Mn, offering redox couples with distinct potentials. As shown by cyclic voltammetry (CV) measurements (Figure 1), three different redox couples in the potential range of 1.5–4.6 V (vs. Na/Na$^+$) are observed, among which the one detected at 1.9 V, i.e., a relatively low potential, belongs to the Mn$^{3+}$/Mn$^{4+}$ redox couple (green rectangle). The second peak couple, associated to the Ni$^{2+}$/Ni$^{4+}$ redox, is located at 3.5–3.7 V (red rectangle), while the strong redox peak couple at ~4.3 V is due to the structural transformation from P to O (P–O) stacking.[26-27] To verify the reversibility of redox reactions, more cycles were conducted as shown in Figure S2. The CV curves fully overlap in the Ni$^{2+}$/Ni$^{4+}$ region, indicating that the sodium ions can (de-)intercalate in the TMO layers without affecting the structural stability. On the other hand, the P–O transition oxidation peak shows a large intensity decrease upon cycling while the reduction counterpart shows a moderated intensity decrease, but a clear shift towards lower voltages. These suggest the P–O phase transition to be partially irreversible in the initial stage. Regarding the Mn$^{3+}$/Mn$^{4+}$ region, a slight peak contraction is observed upon oxidation, while the reduction step remains stable without obvious intensity decay. Therefore, the material can act as both sink or source of Na$^+$ ions. In particular, the Mn$^{3+}$/Mn$^{4+}$ redox couple can store/release Na$^+$ ions at low potential, even suitable as negative electrode (anode), while the Ni$^{2+}$/Ni$^{4+}$ redox couple and the P–O stacking transition can release/store the Na$^+$ ions at high potentials, i.e., suitable as positive electrode (cathode). Thus, the NAM material exhibits the potential to act both as cathode and anode enabling the assembly of cells (including symmetric cells) for the investigation of other materials.

To further study the electrochemistry of NAM as positive and negative electrode material avoiding the effect of Na metal and hard carbon, symmetric cells were assembled with a P/N ratio of around 1:1. However, a small sodium metal auxiliary electrode was also built into the cell to monitor the positive electrode potential, according to the cell wiring displayed in Figure S3. The first charge/discharge cycle at 0.1 C (1 C rate corresponds to a specific current of 100 mA g$^{-1}$) is shown in Figure 2a. The actual cell voltage (blue trace) starts obviously from around 0 V. Three potential plateaus are clearly observed during the charge process, below 1 V, between 1.4–1.8 V and above 2 V. These plateaus can be assigned taking advantage of the Na auxiliary electrode, which allows to separate the positive and negative electrode voltages. First, all plateaus appear to be

![Figure 1. Cyclic voltammetry of NAM electrode using 1 M NaPF$_6$ in PC: EC (2:1, w/w) electrolyte.](image)

![Figure 2. Electrochemical performance of NAM positive and negative electrodes in symmetric Swagelock-type cells.](image)
bound to the positive electrode, while the negative electrode voltage changes rather smoothly. In particular, the first and second plateaus correspond to the peaks associated to the oxidation of Ni$^{3+}$ to Ni$^{4+}$ while the third plateau corresponds to the P/O stacking transition. Correspondingly, three voltage plateaus are also observed during the discharge step. However, the P/O plateau is much shortened due to the partially irreversible phase change, also resulting in the lower initial Coulombic efficiency (73.6%). To provide an insight into the phase change during the following cycles, the 2nd and 3rd charge/discharge cycle profiles are also displayed in Figure 2b. The result reveals that the plateau of the P/O phase transition is not detected in the subsequent cycles anymore. However, the discharge behaviour of the 3rd cycle is quite consistent with the 2nd cycle, suggesting the NAM structure reached a stabilized state in both the positive and negative electrodes without further structural variation. As a result, the Coulombic efficiency in the 2nd and 3rd cycles reached 94.5% and 97.2%, respectively.

To assess the rate capability of the NAM electrodes, the cell was subjected to cycling tests at various currents from 0.1 C to 2 C, as presented in Figure 2c and Figure S4. The cell, thus, both the positive and negative NAM electrodes, delivered a high specific capacity of 74 mAh g$^{-1}$ (5th cycle) at 0.1 C, 69 mAh g$^{-1}$ (10th cycle) at 0.2 C, 62 mAh g$^{-1}$ (15th cycle) at 0.5 C, 56 mAh g$^{-1}$ (20th cycle) at 1 C, 47 mAh g$^{-1}$ (25th cycle) at 2 C, respectively, suggesting that both positive and negative NAM electrodes have excellent rate capability even at a high current. Further, the cycling stability was also evaluated upon a long-term galvanostatic cycling at 1 C rate following three activation cycles at 0.1 C. The results (Figure 2d) demonstrate a remarkable cycling stability with high capacity retention (82.6% after 500 cycles at 1 C) and average Coulombic efficiency (99.8%). Compared to other reported symmetric cells based on layered TMO (Figure 2e), the superior cycling performance and reversible capacity in this study clearly demonstrates the outstanding stability of NAM used as the anode to realize Na-ion cells.

To further investigate the outstanding stability of the NAM-based electrodes in symmetric cells, the voltage evolution of the cell, the cathode and the anode upon 100 cycles are displayed separately (Figure 3). Besides the high reversibility observed for the full cell, only a slight capacity decay is determined in the profile, the charge/discharge voltage profile of the cathode is practically unaltered, confirming the excellent structural stability of NAM when employed as the cathode. A small voltage variation, however, is shown by the anode, probably associated to the minor irreversible phase transition induced by Jahn-Teller distortion effect, resulting in a slight performance fading of the full cell.

The structural changes occurring in the NAM electrodes after long-term cycling, were investigated by ex-situ XRD measurements (Figure 4a). For these experiments, the negative and the positive electrode were taken from disassembled symmetric cells after 100 cycles at 1 C. First, the XRD patterns of both electrodes show no new phases after cycling. More importantly, no significant peak shift is observed for the cathode, although a small peak shift to higher angles is detected for the anode, probably due to the above-mentioned Jahn-Teller distortion effect.[1] Overall, the XRD patterns corroborate the high structural stability of NAM when employed as either cathode or anode. Following, the structural evolution of NAM as anode upon sodium (de)intercalation was investigated via in-situ XRD measurements during the first electrochemical cycle (Figure 4b, Figure S5). The main (002) and (004) reflections show a slight shift to higher angles during the discharge step, while the (10X) reflections shift in the opposite direction, suggesting a simultaneous ab plane expansion and c axis shrinkage due to the insertion of sodium ions as well as the reduction of Mn$^{3+}$ to Mn$^{2+}$, inducing an increased distance of TMO layers.[18] No new reflections besides those of the P2 structure are detected during the entire charge/discharge process, while the reversible shift of the reflections indicate for the high structural stability of NAM anode. Additionally, the positive electrode was also investigated by in-situ XRD (Figure 4c). The reversibility of the main reflections demonstrating the stability of NAM as cathode. Apart from the new peak detected at the end of the charging process, probably associated to the P to O stacking consistently with Figure 1, the two additional peaks appearing upon charge may be related to

![Figure 3](image1.png)

**Figure 3.** Selected (a) full cell and (b) individual cathode/anode voltage profiles upon charged/discharge cycles at 1 C. The cell was initially subjected to three cycles at 0.1 C (not shown) for the activation.

![Figure 4](image2.png)

**Figure 4.** (a) XRD patterns of NAM electrodes as made and after cycling as cathode and anode for 100 cycles at 1 C. The electrodes were extracted from a cycled symmetric cell after discharge. See Figure 3 and related text for further details. (b) In situ XRD patterns of the NAM negative electrode recorded during the first charge/discharge process of a symmetric cell in the voltage range of 0.5–2.5 V. (c) Structure of NAM as made (center), oxidised (desodiated, left) and reduced (oversodiated, right).
the intercalation of water (leaking in the not perfectly sealed in situ XRD cell) causing the formation of a hydrated phase.\textsuperscript{5,29}

The structures depicted in Figure 4c show the Na ion sites in pristine, desodiated (cathode) and oversodiated (anode) NAM. When NAM is acting as the positive electrode (cathode), Na\textsuperscript{+} ions are gradually released upon oxidation, which is accompanied by the oxidation reaction of Ni\textsuperscript{2+} to Ni\textsuperscript{4+} and the P–O stacking transition. Based on the electrochemical measurements, approximately 0.25 Na ions per formula unit are still left in the fully charged structure (Figure 4c, left). For the role as the negative electrode (anode), Na\textsuperscript{+} ions are inserted in the interlayer slabs with the simultaneous reduction of Mn\textsuperscript{4+} to Mn\textsuperscript{3+}, ending with about 1 Na ion per formula unit in the oversodiated layered structure, filling the corresponding Na sites entirely (Figure 4c, right). Upon oversodiation, NAM gather a rather stable and compact structure explaining its outstanding stability.

To track the morphological changes occurring in the NAM electrodes upon cycling, scanning electron microscopy (SEM) images were collected from both the cathode and anode extracted from the symmetric cells after 100 cycles at 1 C. While distinct NAM particles can be observed in the fresh electrode (Figure 5a), the cycled electrodes appear denser most likely due to the precipitation of electrolyte components (Figure 5b and c). However, even at higher magnification, it is difficult to distinguish any difference in the surface morphology of the pristine (Figure 5d) and the cycled positive (Figure 5e) and negative (Figure 5f) electrodes. This supports for the presence of a rather thin SEI (CEI) layer on the anode (cathode) surface. Further, energy dispersive X-ray spectroscopy (EDX) was employed to determine the elemental composition on the electrode surfaces. The corresponding results are presented in Figure 5g. Only a slight increase of fluorine content is detected on the cycled anode compared to the fresh electrode, which could be ascribed to the residual NaPF\textsubscript{6} salt. This would also explain the higher content of sodium in the cycled electrodes.

With regards to nickel and aluminium, it is hard to detect the variation among the electrodes before and after cycling. In other words, the EDX results suggest for a rather low amount of decomposition products (to form SEI or CEI layer) covering the electrodes' particles. Regarding manganese, its content decreases in both cycled electrodes, indicating for a slight manganese dissolution upon long-term charge/discharge cycling, which may be associated to the structural changes observed after cycling.

The chemical composition of the CEI and the SEI was determined in more detail by X-ray photoelectron spectroscopy (XPS) on cycled positive and negative electrodes after 100 cycles at 1 C. The detail spectra in the C 1s region in Figure 6a show, besides the main peak at 284.8 eV assigned to the conductive C additive and to other C–C/C–H species, two other peaks at 286.4 and 288.3 eV, which are associated to C–O and C=O species, respectively. These are mainly electrolyte decomposition products (e.g., polyethylene oxide (PEO)-like species, sodium alkyl carbonates (ROCO\textsubscript{2}Na\textsubscript{2}), etc.). In addition, two other peaks with the same intensity can be observed for the fresh sample, which are due to the two groups of PVDF binder (CF\textsubscript{2}: 290.9 eV, CH\textsubscript{2}: 286.4 eV). Finally, for both cycled samples, a new feature due to carbonates (Na\textsubscript{2}CO\textsubscript{3}) is found at 290.5 eV (according to the F 1s spectra, a smaller contribution from PVDF to this peak also seems possible). The detail spectra in the F 1s region show two main features at 688.0 eV, assigned to PVDF and low amounts of PF\textsubscript{6} for the cycled samples, and 685.0 eV, due to NaF. When comparing the three different samples, an increase of the C–O and C=O features (in the C 1s region) and NaF (in the F 1s region) is obvious for the cycled electrodes, which is slightly more pronounced for the anode than for the cathode. This confirms the formation of an interphase layer at both the electrodes during cycling with a slightly larger extent of decomposed organic electrolyte at the anode side (i.e., a slightly thicker SEI layer). However, the Mn 2p region of both electrodes shows the Mn 2p peak doublet for both cycled samples, albeit with reduced intensity with respect to the fresh

Figure 5. SEM micrographs of (a, d) fresh electrode, cycled (b, e) positive electrodes and cycled (c, f) negative electrodes after 100 cycles at 1 C. (g) EDX analysis of a fresh electrode and the cycled positive and negative electrodes.

Figure 6. XPS detail spectra in the (a) C 1s, (b) F 1s, and (c) Mn 2p region from fresh electrode, cycled positive and negative electrode after 100 cycles at 1 C.
Conclusions

Summarising, P2-type and Mn-rich Na$_{0.6}$Ni$_{0.22}$Al$_{1.1}$Mn$_{0.66}$O$_2$ shows high promise as “reference” electrode for the investigation of materials for Na-ion batteries. The electrolyte decomposition and interphase formation is very moderate resulting in an SEI less formation on the anode side, which typically grows thicker than for both electrodes, i.e., less than 5 nm.[31]

Experimental section

Electrode preparation and characterization: The P2-type layered Na$_2$Ni$_2$Al$_{1.1}$Mn$_{0.66}$O$_2$ (NAM) material was prepared by a co-precipitation method as reported in a previous study.[31] The NAM electrodes were prepared via spreading a slurry containing active material, conductive agent Super C65 (IMERYS) and polyvinylidene fluoride (PVdF, Solef 6020, Solvay) in the 85:10:5 ratio onto aluminum foil. Disc electrodes (12 mm diameter) were punched after pre-drying in the 80 °C oven, then dried under vacuum at 120 °C for 12 h and then pressed at 8 ton cm$^{-2}$. The electrochemical performance was evaluated in three-electrode Swagelok-type cells assembled in an argon-filled glove box (MB200B ECO, MBraun; H$_2$O and O$_2$ content lower than 0.1 ppm). The NAM electrodes were used as working and counter electrodes, the positive/negative mass ratio was set to about 1.1 (the average areal loading of negative electrode is approximately 2.1 ± 0.2 mg cm$^{-2}$). Sodium metal foils served as auxiliary, quasi-reference electrode. Glass fiber disks (Whatman GF/D) were used as separator, which were soaked with the electrolyte solution (1 M NaPF$_6$ in ethyl carbonate (EC) / propylene carbonate (PC), 1:2 w/w). Galvanostatic discharge cycling tests were performed at 20 ± 2 °C utilizing a battery tester (Maccor 54300). The cells were cycled in two-electrode configuration, however, an auxiliary channel was employed to monitor the cathode potential versus the Na quasi-reference electrode. The first three galvanostatic cycles were performed within the 0.5–3.0 V voltage range at 0.1 C while the following cycles were conducted at the 1 C rate. The (dis)charge rate of 1 C corresponds to a specific current of 100 mAg$^{-1}$. Cyclic voltammetry (CV) tests were performed at a scan rate of 0.1 mV s$^{-1}$ within the 4.6–1.5 V (vs. Na/Na$_2$) potential range with a multi-channel potentiostat-galvanostat (VMP3, Biologic Science Instruments).

Materials characterization: The crystalline structure of the material (as powder or electrode coating) was characterized by X-ray powder diffraction (XRD) using a Bruker D8 Avance diffractometer (Cu Kα radiation, λ = 0.154 nm) in the 2θ range between 10° < 2θ < 90° with a step size of 0.03°. Rietveld refinement was performed using the GSAS-II software.[32] An hexagonal structure (P6/mmc, s. g. 194) proposed by Lu and Dahn[33] was considered and manually edited to consider a mixed elemental composition of Mn:Na:Mn:Al = 0.67:0.22:0.11. In a P2 structure, the Na$_2$O polyhedra share with the TM$_2$O$_3$ (TM = Mn/Na/Al) octahedra either edges (Na$_x$ site) or faces (Na$_y$ site).[34] Therefore, two different Wyckoff sites for Na ions were considered, and their total occupancy was fixed to 0.6. The instrumental parameters were obtained from a LaB$_6$ standard; accordingly, the instrumental broadening parameters, i.e., L, W, X, and Y, were kept fixed to 4.397·10$^{-4}$·deg, -5.720·10$^{-4}$·deg, 2.577·10$^{-3}$·deg, 1.855·10$^{-2}$·deg, and 2·10$^{-2}$·deg, respectively. The peak shape was refined with a uniaxial domain size model by optimizing the respective equatorial and axial size parameters. The scale, background, sample displacement, unit cell parameters, peak shape, and atomic parameters were refined in this order by applying constraints and restraints as reported in the Supplementary information.

The recorded reflections were assigned to the patterns recorded using the ICDD database implemented in the EVA software (Bruker). To investigate the materials morphology and composition, scanning electron microscopy was performed utilizing a Zeiss Crossbeam 340 field-emission electron microscope equipped with an energy dispersive X-ray (EDX) spectrometer (X-ray Instrument X-Max Xtreme, 100 mm$^2$, 1–5keV). The elemental composition and chemical state of the electrodes’ topmost surface layer (sampling depth ~3–5 nm) was investigated by X-ray photoelectron spectroscopy (XPS) using the Specs XPS system with a Phoibos 150 energy analyzer. The measurements were acquired using monochromatic Al Kα radiation (1486.6 eV), a take-off angle of 45° and pass energies of 30 and 90 eV at the analyzer for detail and survey spectra, respectively. To avoid surface contamination, the samples were prepared in an Ar filled glovebox and transferred in inert gas atmosphere to the sample load lock of the XPS system. For binding energy calibration, the C1s main peak was set to 284.8 eV. Peak fitting was accomplished using CasaXPS software with Shirley-type backgrounds and Gaussian-Lorentzian peak profiles.

In situ XRD measurements: In situ XRD experiments were performed by an in-house developed, in situ, two-electrode cell with a beryllium window on a Bruker D8 Avance diffractometer (Cu Kα radiation (λ = 0.154 nm) in the 2θ range between 10° < 2θ < 90°. The electrodes were made casting the electrode slurry (same composition as above) on a beryllium window (diameter: 19 mm). The positive/negative mass ratio of in situ cell was set to a value lower than 1. The electrodes were dried at 60 °C oven overnight, then further dried under vacuum at 80 °C for 12 hours before transfer into the glovebox. These electrodes were used as the positive or the negative electrode for the in-situ XRD measurements, being matched by counter electrodes of the same active material deposited on Al current collectors. XRD patterns were recorded every 15 minutes upon low rate charge (35 μA up to 2.5 V) and discharge (35 μA to 0.5 V).
Supporting Information

The authors have cited additional references within the Supporting Information. [18,31,34]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Keywords: Na-ion battery · P2-type Mn-rich cathode · symmetric cells · SEI-less · reference electrode

Electrodes for Na-ion batteries: A P2-type and Mn-rich Na$_{0.6}$Ni$_{0.22}$Al$_{0.11}$Mn$_{0.66}$O$_2$ material was investigated as a negative electrode, the symmetric cells without presodiation demonstrate a remarkable capacity retention of 82.6% after 500 cycles. This outstanding cycling performance is ascribed to the high stability of the active material at both the highest and lowest Na-ion storage plateaus and the rather limited electrolyte decomposition and solid-electrolyte-interphase formation occurring.