Improving Energy Density and Structural Stability of Manganese Oxide Cathodes for Na-Ion Batteries by Structural Lithium Substitution

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ABSTRACT: We report excellent cycling performance for P2−Na0.6Li0.2Mn0.8O2, an auspicious cathode material for sodium-ion batteries. This material, which contains mainly Mn4+, exhibits a long voltage plateau on the first charge, similar to that of high-capacity lithium and manganese-rich metal oxides. Electrochemical measurements, X-ray diffraction, and elemental analysis of the cycled electrodes suggest an activation process that includes the extraction of lithium from the material. The “activated” material delivers a stable, high specific capacity up to ∼190 mAh/g after 100 cycles in the voltage window between 4.6−2.0 V versus Na/Na+. DFT calculations locate the energy states of oxygen atoms near the Fermi level, suggesting the possible contribution of oxide ions to the redox process. The addition of Li to the lattice improves structural stability compared to many previously reported sodiated transition-metal oxide electrode materials, by inhibiting the detrimental structural transformation ubiquitously observed with sodium manganese oxides during cycling. This research demonstrates the prospect of intercalation materials for Na-ion battery technology that are active based on both cationic and anionic redox moieties.

INTRODUCTION

Sodium and lithium layered metal oxides provide rich opportunities for electrochemical energy storage applications. In particular, lithium- and manganese-rich oxides, denoted as xLi2MnO3·(1−x)LiMO2 (M = Ni, Mn, Co), have attracted much interest as alternative high energy batteries owing to their high capacities (≥240 mAh/g) when charged to high cutoff voltages (≥4.5 V). They are related to Li[Li1/3Mn2/3]O2, which crystallizes in a layered structure with a slightly distorted O3 scheme (space group C2/m).1 Li2MnO3 was initially considered electrochemically inactive owing to the existence of Mn4+, until it was proved that the material is in fact active when charged to ≥4.5 V, and it can deliver a high capacity up to 200 mAh/g. A long plateau at 4.5 V over the first charge is a characteristic feature of Li2MnO3 and Li2MnO3-based composites. Extensive efforts have been made to understand the nature of the redox reactions involved in the charge/discharge of these materials. The initial charge process has been explained by simultaneous extraction of lithium and oxygen, which results in a partial reduction of Mn4+ to Mn3+, partial oxidation of oxygen ions, and Li+−H+ exchange as a consequence of electrolyte decomposition.2−5

In spite of the great promise of Li2MnO3-based oxides, these materials suffer from voltage fading over cycling, which eventually results in battery failure. Extensive research has been devoted to understanding the driving force of this phenomenon. Various characterization techniques have detected a layered to spinel structural rearrangement, which is believed to be responsible for voltage fading. A neutron diffraction study6 elucidated a layered to spinel structural evolution pathway in Li1.2[Mn0.55Ni0.15Co0.1]O2 after long-term cycling as follows: Li ions migrate from the octahedral sites in the Li layers and transition-metal (TM) layers to the tetrahedral sites of the Li layers. Following this process, manganese ions migrate from the octahedral sites of the TM layers to the tetrahedral sites of the Li layers and finally to the octahedral sites of Li layers, resulting in the formation of a spinel-like structure.
structure. Based on these findings, two strategies were proposed to mitigate the layered to spinel structural evolution (and thus the voltage fading problems). The first is the incorporation of alkali metal ions such as Na and K in the lithium layers because they are believed to be too large to be accommodated in the tetrahedral sites of a cubic-closed packed oxygen array, thus making spinel formation unfavorable. The second is decreasing the Mn ion content in the composition to hinder its migration into the Li layer, which leads to the layered-to-spinel transition.

Many Na-ion battery cathode materials have an analogy with their Li counterparts. However, there is no report of the synthesis of Na0.80Li0.12Ni0.22Mn0.66O2, to the best of our knowledge, which is not surprising considering the large size mismatch between the ionic radii of Mn4+ (0.53 Å) and Na+ (1.02 Å) ions. With the same structure, Na3RuO2, was reported to be electrochemically active based on the Ru4+/Ru5+ redox reaction, delivering ~140 mAh/g specific capacity with excellent retention over 20 cycles. Tarascon et al.9 reported a high capacity for Na3Ru2−xSnxO3 arising from both cationic (Ru4+/Ru5+ and anionic (O2−/O−) redox reactions. Komaba et al.10,11 have reported capacities exceeding the theoretical limit based on the Mn3+/4+ redox reaction in two materials. The first charge of P2−Na2/3Mg0.28Mn0.72O2 and Na0.6Li0.2Mn0.8O2 exhibit a voltage plateau at 4.2 and 4.1 V (vs Na+/Na), respectively. The former delivers an initial reversible specific capacity of 220 mAh/g and preserves over 150 mAh/g capacity after 30 cycles. Na0.6Li0.2Mn0.8O2 delivers a reversible specific capacity of ~200 mAh/g and retains ~175 mAh/g after 20 cycles. Superlattice diffraction lines, corresponding to in-plane cation ordering in Na0.6Li0.2Mn0.8O2, disappear after charge above the voltage plateau, similar to the case of Li2MnO3, suggesting a very significant rearrangement of cations after extraction of oxygen. On the contrary, superlattice lines in the Na2/3Mg0.28Mn0.72O2-O2 diffusion pattern are still evident after five cycles, suggesting the different nature of structural changes in those two compositions. The contribution of oxide ions to the redox reaction and/or in activating manganese ions were suggested as mechanisms responsible for anomalous high capacities in both materials, analogous to Li2MnO3-based oxides. In a recent study, Yamada et al.12 clearly demonstrated the participation of oxygen orbitals in redox reactions by X-ray absorption spectroscopy (XAS) and electronic structure calculations.

Examination of mixed Li–Na and Mn-rich sodium layered oxides has yielded particularly interesting results. P2−Na0.6Li0.2Mn0.8O2 was studied by Xu et al.13 The Na0.6Li0.2Mn0.8O2/Na cell delivers an initial specific capacity of 133 mAh/g when cycled between 2 to 4.4 V and retains about 115 mAh/g after 30 cycles. Additional capacity above that of the Ni2+/4+ redox reaction over the first discharge was attributed to electrolyte decomposition. Operando synchrotron X-ray diffraction (XRD) analysis showed that the P2 structure is preserved over the full range of sodium content, explaining the good capacity retention of the material. Ex situ nuclear magnetic resonance (NMR) analysis revealed the mobility of Li-ions during charge/discharge: Li+ ions are mostly accommodated in the transition-metal oxide layer in the pristine material but migrate to the Na layer when charged to 4.4 V and reversibly move back to their initial sites upon discharge.

Even though a few reports have clearly demonstrated high capacity beyond cationic redox reactions for sodium host positive electrode materials, there are many open questions regarding the fundamental understanding of these systems at present. These include electrochemical performance, structural evolution over long cycling, and charge compensation mechanisms. Here, we report our exploration of Mn-based sodium host positive electrode materials, analogous to Li2MnO3. We investigated compositions in which the Mn atoms are in an oxidation state of 4+: P2−Na0.6Li0.2Mn0.8O2 and Na0.6Li0.2Mn0.8O2. These have a very similar structure (as demonstrated by XRD) and electrochemical response. We show that these materials exhibit outstanding capacity retention of over ~190 mAh/g over 100 cycles, outperforming previously reported sodium (lithium) metal oxide materials. We also compare the lithiated positive electrode material, Na0.6Li0.2Mn0.8O2, with its nonlithiated analogue (Na0.6MnO2). The improvement in the electrochemical performance by lithium substitution is clearly demonstrated. While capacity fading of cells over more prolonged cycling is compromised by the sodium electrode, our long-term experience shows that major performance aspects of positive electrode materials (for many different metal-ion batteries) can be demonstrated and understood in cells that undergo up to a hundred cycles. XRD and density functional theory (DFT) studies were employed to investigate the crystal structure and electronic structure of the materials, revealing complex structural changes—albeit with overall stability—and indeed suggesting the participation of anion redox processes.

**METHODS**

**Experimental Section.** Na0.6MnO2 and Na0.6Li0.2Mn0.8O2 were synthesized by self-combustion reactions (SCR), as reported earlier.14 In a typical synthesis of Na0.6Li0.2Mn0.8O2, 5.020 g of Mn(NO3)2, 0.362 g of LiNO3, and 1.340 g of NaNO3 were dissolved in 80 mL of doubly distilled water, and 5 wt % of Li and Na nitrates were used in excess in order to compensate for Li and Na loss upon annealing at high temperature. Sucrose (13.7 g) was then added to the solution with continuous stirring. The solution was evaporated by heating at about 100 °C for a few hours to obtain a syrupy mass, which on further heating at 350 °C resulted in the self-ignition of the reactants giving an amorphous compound. This product was ground to a fine powder, annealed at 500 °C for 3 h, and cooled to room temperature. The obtained powder was then ground and finally annealed at 900 °C for 15 h to obtain the desired oxide. Na0.6MnO2 was synthesized following a similar procedure.

Elemental analysis of the synthesized materials was carried out using an inductively coupled plasma technique (ICP-AES, spectrometer Ultima-2 from JobinYvon Horiba). Scanning electron microscopy (SEM) imaging, using a JEOL-JSM 700F instrument, was performed to investigate the morphology of the positive electrode materials. The XRD patterns of the materials were obtained by X-ray diffraction with a Bruker D8 Advance X-ray diffractometer using Cu Kα (λ = 1.5418 Å) as the source, operated at 40 mA and 40 kV. Diffraction data for the Rietveld refinement were collected in the angular range of 10° < 2θ < 140°, step size 0.02°, step time 6 s/step. The data were analyzed by the Rietveld structure refinement program, FULLPROF.15 The Thompson-Cox-Hastings pseudo-Voigt function was used for the peak-shape approximation. The background was fitted manually by linear interpolation. Operando X-ray powder diffraction (XRPD) data was collected on a PANalytical Empyrean instrument using Cu Kα radiation equipped with a PIXcel bidimensional detector with a Ni Kβ filter using θ/θ Bragg–Brentano geometry. Operando XRD was performed by the use of a homemade cell. During the acquisition, the cell was cycled at a rate of C/20 with a pattern collection time of ~20 min (Δθ ≈ 0.02° in Na2MnO4). The lattice parameter evolution during charge/discharge was determined using the Le Bail method16 within the FullProf software suite.
X-ray photoelectron spectroscopy (XPS) data was collected using a Thermo VG Scientific ESCALab 250 Imaging Microprobe. All spectra were fitted by Gaussian–Lorentzian functions and a Shirley-type background using CasaXPS software. The binding energy values were all calibrated using the C 1s peak at 285.0 eV.

The positive electrodes were fabricated by mixing 80 wt % of Na0.6MnO2 or Na0.6Li0.2Mn0.8O2 with 10 wt % of carbon black and 10 wt % of PVdF binder. A planetary centrifugal vacuum mixer was used to shake the vials at 2000 rpm for 10 min under vacuum. The obtained slurry was cast onto aluminum foils using a doctor blade. The electrodes were dried overnight at 60 °C in air and then at 110 °C overnight under vacuum. The resulting foil was cut into disks of 14 mm in diameter, which were weighed and dried at 110 °C overnight in vacuum to remove the moisture adsorbed during the preparation process. Composite electrodes were assembled with polyethylene separators using 2325 coin-type cells. All cell fabrication was performed in a pure argon atmosphere in glove boxes.

Electrochemical measurements were carried out using a multi-channel galvanostat/potentiostat (Arbin). Electrochemical impedance spectroscopy (EIS) experiments were measured using a VMP BioLogic potentiostat with a 1260 FRA system from Solartron. The electrolyte solution was either 0.5 M NaPF6 or 1.0 M NaClO4 in propylene carbonate (PC).

Residual gas analysis was performed by online electrochemical mass spectroscopy (OEMS) using a commercial electrochemical flow cell (EL-Cell, ECC-DEMS) attached in-line to a gas flow controller (Bronkhorst, F-200CV) and quadrupole mass spectrometer (Stanford Research Systems, RGA 200). The evolved gases upon cycling were swept from the cell to the quadrupole mass spectrometer detector through a fused silica capillary (50 μm ID). The pressure inside the chamber was 2 × 10−6 Torr during the experiment. The electrode preparation and cycling were performed similarly to the procedure described above, except that P50 porous carbon paper was used as the current collector instead of aluminum foil for gas collection.

**RESULTS AND DISCUSSION**

**Structural Characterization.** SEM images of Na0.6Li0.2Mn0.8O2 (Figure 2a,b) show well-defined crystallites of ~4–5 μm in dimension. Figure 2c shows their XRD pattern. Rietveld analysis (Figure S3) reveals a major phase with a hexagonal P2 structure (space group P63/mmc, a = 2.854 Å, c = 11.128 Å), similar to previously reported lithiated sodium manganese oxides. ICP measurements yielded a stoichiometric ratio of 1.00 Na: 0.37 Li: 1.30 Mn for the pristine Na0.6Li0.2Mn0.8O2 material, confirming the theoretical compo-
sition. It should be noted that this material is quite air-sensitive, similar to many other layered sodium metal oxides.24,25

The electronic structure of the materials was computed by DFT calculations. Based on the chemical composition of Na$_{0.6}$MnO$_2$, the average oxidation state of Mn is expected to be +3.4. We note that due to the presence of Na-vacancies, the local coordination of O ions bound to Mn ions are different. This is clearly reflected in the different Mn–O interatomic distances observed in the crystal structure, as shown in Table S1. The projected density of states (PDOS) of Na$_{0.6}$MnO$_2$ (Figure 3a and Figure S4) and the calculated magnetic moments suggest that in the unsubstituted material, 50% of the Mn ions are in a +3 formal oxidation state (magnetic moment ~4.0 μB); 40% of the ions have an oxidation state between +3 and +4 (denoted as Mn$^{(3+4)}$, magnetic moment ~3.7 μB); and 10% of the Mn ions have +4 formal oxidation state (magnetic moment ~3.3 μB). On the other hand, in Na$_{0.6}$Mn$_{0.8}$Li$_{0.2}$O$_2$, the spin-singly occupied Mn-t$_2g$ states and spin-doubly unoccupied e$_g$ states (Figure 3b, Figure S4) with a magnetic moment of ~3.2 μB, suggest a t$_{2g}$(↑↑↑↑) e$_g^0$(↑↑↑↑) electronic configuration with a +4 valence state for all Mn ions, as expected. The significant decrease in the average Mn–O distances, $R_{\text{Mn–O}}$ on Li substitution (unsubstituted $R_{\text{Mn–O}}$ = 2.03 Å and Li-substituted $R_{\text{Mn–O}}$ = 1.94 Å, Table S1) also indicates that the charge state of Mn in the substituted material is Mn$^{4+}$. These results show that partial Li substitution for Mn results in oxidation of the Jahn–Teller active Mn$^{3+}$ ions to inactive Mn$^{4+}$ ions to compensate for the charge. The computed electronic structure also suggests that the unsubstituted material is metallic. This is in agreement with a previous theoretical study on hexagonal NaMnO$_2$.23 However, on Li substitution, the material becomes insulating due to the fully unoccupied e$_g$ states. These changes in the electronic structure can effectively mitigate the detrimental cooperative effect of the Jahn–Teller ions. XPS analysis also confirmed that the majority of manganese ions (∼96%) in this material are tetravalent (Figure S5).

Interestingly, inspection of the PDOS shows that in the Li-substituted material the states of Mn are located significantly below the Fermi level, suggesting that Mn is inactive. However, oxygen states are located near the Fermi level; therefore, deintercalation could be achieved at the expense of oxygen oxidation, which could possibly result in oxygen release and reduction of Mn$^{4+}$ ions to Mn$^{3+}$ during electrochemical cycling. We note that the contribution of oxygen atoms near the Fermi level is mainly from the oxygen atoms bound to lithium atoms (Figure S6).

**Improved Electrochemical Performance of the Li-Substituted Composition.** The electrochemical properties of the hexagonal P2-structure Na$_{0.6}$Li$_{0.4}$Mn$_{0.8}$O$_2$ as a positive electrode material for Li-ion batteries have been reported.11 In this work, we examined for the first time the electrochemical behavior of this material as a positive electrode material for Na-ion batteries. Figure 4 presents the voltage profiles of

![Figure 3. Schematic of the projected density of states of (a) Na$_{0.6}$MnO$_2$, (b) Na$_{0.6}$Mn$_{0.8}$Li$_{0.2}$O$_2$.](image)

![Figure 4. Charge/discharge curves (galvanostatic cycling) of Na$_{0.6}$MnO$_2$ (a) and Na$_{0.6}$Li$_{0.4}$Mn$_{0.8}$O$_2$ (b) electrodes in sodium half-cells, measured at 30 °C and a C/15 rate in 0.5 M NaPF$_6$ PC electrolyte.](image)


The discharge/charge profiles of Na$_{0.6}$MnO$_2$ are typical of Na$_{x}$MnO$_2$ layered positive electrode materials, showing several sloping steps, which reflect a combination of phase transitions and solid solutions during the sodiation/desodiation processes. The multitransition processes that these materials undergo during charge/discharge cycles underline the complexity of the intercalation mechanism and have been assigned to structural transformations between single-phase domains with different Na$^+$ ion/vacancy arrangements. The main drawback of such transitions is that they induce capacity fading due to strain effects which the large sodium ions produce upon insertion into the lattice during cycling. This is also true for the material analyzed here. The Na$_{0.6}$MnO$_2$ positive electrode delivers an initial discharge capacity of 162 mAh/g, which is stable for around five cycles, as shown in Figure 4a. The following charge/discharge cycles showed constant fading, presenting a total capacity retention of 87% and 75% of the initial capacity after 60 and 100 charge/discharge cycles, respectively (Figure 5). The evolution of the voltage profiles of the Na$_{0.6}$MnO$_2$ electrode exhibits a stable average voltage around 2.7 V, whereas the average voltage of the Na$_{0.6}$Li$_{0.2}$Mn$_{0.8}$O$_2$ electrodes stabilizes after the activation process at a value around 2.8 V. Our ongoing studies (beyond the scope of this paper) suggest that the initial changes in the average voltage during cycling (inset of Figure 5) may relate to the redox activity of oxide ions, as proposed for lithium and manganese-rich high capacity cathode materials for Li-ion batteries. Considering the maximum capacity reached for each material (~160 mAh/g for Na$_{0.6}$MnO$_2$ and ~190 mAh/g for Na$_{0.6}$Li$_{0.2}$Mn$_{0.8}$O$_2$), and the average discharge voltage, the deliverable specific energy values of the electrode material are 437 Wh/kg and 532 Wh/kg for Na$_{0.6}$MnO$_2$ and Na$_{0.6}$Li$_{0.2}$Mn$_{0.8}$O$_2$, respectively. Thus, the incorporation of lithium into the structure improves the specific capacity of the resultant Na-ion intercalation cathodes by >15% along with stabilizing the capacity on cycling.

The differential capacity (dQ/dV versus V) curves of the studied electrode materials were examined to better understand the electrochemical properties (Figure 6). The profiles related to the Na$_{0.6}$MnO$_2$ electrode show several sharp peaks (upper half of figure), whose position and intensity remain nearly stable during the first five cycles (Figure 6a). These features are direct responses to the intercalation processes and the phase transitions that the material undergoes during galvanostatic cycling. Beyond five cycles, these peaks change position and intensity as noted for the 10th cycle, however. These changes in the most intense peaks below 2.6 V vs Na are seen clearly over 100 cycles (Figure 6b), indicating that during cycling the main charge transfer step becomes progressively more hindered. This finding agrees with the capacity fading described in Figure 4 and Figure 5.

The differential capacity curves of Na$_{0.6}$Li$_{0.2}$Mn$_{0.8}$O$_2$ are rather different (Figure 6c, d). Upon initial cycling, the derivative curves show a strong anodic feature around 4.4 V, which dominates the electrochemical response and disappears within a few cycles. These processes are accompanied by a slight change in both the position and intensity of the cathodic peak around 4.1 V (Figure 6c). This feature is related to the long voltage plateau observed at 4.4 V during the initial charging step (Figure 4b). We note this activation process during the first cycles allows a 20% increase of the initial capacity delivered by the Li-substituted electrode material (Figure 5).

After 10 cycles, the derivative curves of the Na$_{0.6}$Li$_{0.2}$Mn$_{0.8}$O$_2$ positive electrodes show broader peaks, which do not change their position upon cycling, and exhibit an intensity that remains nearly stable up to 100 cycles. These results are in close agreement with the smooth sloping behavior of the voltage profiles observed in Figure 4b. Also, they confirm that the incorporation of the lithium ion into the structure of sodium manganese oxide increases the stability of the material due to the changes of the sodium insertion/extraction mechanism.

The effect of Li-substitution on the stability of the electrode material was further studied by electrochemical impedance spectroscopy (EIS) measurements. Figure 7 presents the Nyquist plots of Na$_{0.6}$MnO$_2$ (a) and Na$_{0.6}$Li$_{0.2}$Mn$_{0.8}$O$_2$ (b) electrodes in Na cells after different cycling steps. These curves comprise the typical components observed in the impedance spectra of composite sodium insertion positive electrodes. The high-medium frequency semicircle is usually attributed to both surface films ($R_{\text{film}}$) and interfacial charge-transfer resistances ($R_{\text{ct}}$) and the relevant capacitances. It should be
emphasized that in the case of such composite ion insertion cathodes, it is hard to distinguish among the contribution of the various time constants and to assign spectral features to them. A Warburg-type element in the low-frequency region is also observed (Figure 7) and can be related to the diffusion of Na$^+$ ions in the bulk of the cathode material. Even though the composite nature of the electrodes renders a rigorous analysis of the impedance response difficult, such spectroscopic studies are valuable on the qualitative level because they reflect all the time constants related to the electrode processes, indicating whether or not the systems reach steady-state stability.

In the case of the nonlithiated cathode (Na$_{0.6}$MnO$_2$) material, the high-medium frequency impedance resistance increases with cycling by $\sim$100% and $\sim$200% after 50 and 100 cycles, respectively.

Figure 6. Differential capacity curves ($dQ/dV$ vs $V$, or voltage profile derivatives) for Na$_{0.6}$MnO$_2$ over 10 and 100 cycles (a and b, respectively) and Na$_{0.6}$Li$_{0.2}$Mn$_{0.8}$O$_2$ over 10 and 100 cycles (c and d, respectively). Electrodes were cycled in sodium half-cells at 30 °C and at a C/15 rate in 0.5 M NaPF$_6$ PC electrolyte.

Figure 7. Electrochemical impedance spectroscopy (EIS) of electrodes in sodium half-cells. Nyquist plot of Na$_{0.6}$MnO$_2$ (a) and Na$_{0.6}$Li$_{0.2}$Mn$_{0.8}$O$_2$ (b) in 0.5 M NaPF$_6$ in PC at different cycling steps.
cycles, respectively (Figure 7a). This pronounced impedance change upon cycling is in line with the aforementioned capacity fading and the structural instability of the Na0.6MnO2 electrode during cycling. A completely different picture emerges for the Nyquist plots of the Li-substituted electrode (Figure 7b). The relevant impedance spectrum of the Na0.6Li0.2Mn0.8O2 electrode shows the same general features as the Na0.6MnO2 electrode, but in the former case, the electrode’s impedance decreases from the 10th cycle to the 50th cycle. Between these cycles, the impedance of the Li-substituted electrode decreases by roughly 50%. These changes may be linked to the initial activation mechanism of this electrode material (see below). The Nyquist plot after 50 cycles remains nearly unchanged, thereafter, revealing that the incorporation of the lithium improves the stability.

**Study of Evolved Gases over the First Cycle by Online Electrochemical Mass Spectrometry.** The evolved gases from the cell during the first cycle were monitored by online electrochemical mass spectrometry (OEMS). A Na0.67Li0.22Mn0.78O2 electrode was galvanostatically cycled between 4.5 to 1.5 V versus sodium metal as the negative electrode. Two broad peaks corresponding to the release of CO2 gas are observed over the first charge (Figure 8); the first peak emerges as charge commences, and the second peak appears at a higher voltage. However, no oxygen release was detected, unlike the case of overlithiated transition-metal oxides (in 1 M LiPF6 solution in a mixture of ethylene carbonate, propylene carbonate, and dimethyl carbonate,335 where O2 evolution was observed at high voltages).

In our materials, the source of CO2 evolution appears complex. O2 release has been shown to cause decomposition of alkyl carbonates in the electrolyte solutions, resulting in carbonate species as proven by detection of CO2 gas via OEMS.35 In our study, although O2 gas was not detected, immediate reaction of oxygen species evolved from the activation process with the electrolyte solution at the electrode surface could similarly be responsible for solution decomposition (see discussion below). We note that OEMS on a blank electrode (without active material) showed traces of CO2 release starting at the same potential, 4 V (Figure S7), suggesting that some electrolyte could also be simply decomposed at the electrode surface between 4−4.6 V versus Na. CO2 release from carbonates on the metal oxide surface arising from air contamination36 are likely responsible for the sharp CO2 release peak at around 3.0 V in Figure 8, since this feature is not present in the “blank” electrode.

**Study of the Evolution of Crystal Structure upon Cycling by Operando and Ex Situ X-ray Diffraction.**

**Operando XRD Analysis.** The evolution of the XRD pattern of Na0.6Li0.22Mn0.78O2 induced by extraction and insertion of sodium ions over the first cycle was monitored by operando XRD. Figure 9 shows that the P2 structure is preserved all over the cycling range (4.5−1.5 V). The peak positions are shifted as a function of sodium content and the peak intensities are decreased compared to the initial structure. However, all the reflections corresponding to the P2 structure are present in the XRD pattern of the Na0.6Li0.22Mn0.78O2 electrode charged up to 4.5 V, contrary to the Fe-substituted material.37 Moreover, many Mn-containing sodium metal oxide electrodes convert to an orthorhombic P’2 phase at low voltage due to the cooperative effect of Jahn−Teller active Mn3+ ions. Although the peaks in the XRD pattern of the discharged Na0.6Li0.22Mn0.78O2 are broadened, no distinct split in the (10l) peaks is observed over discharge implying that an orthorhombic in-plane distortion does not occur in this material.

Figure 10a represents a map of the evolution of (002) and (100) reflections in the XRD pattern of Na0.6Li0.22Mn0.78O2 over
In Li$_2$MnO$_3$-based oxides, simultaneous lithium and oxygen removal, proven by mass spectroscopy and neutron diffraction analysis, is known to be the main mechanism responsible for the anomalously large capacity at the first charge.

Figure 10 shows the evolution of voltage and the lattice parameters of Na$_{x}$Li$_{1-x}$Mn$_{0.78}$O$_2$ as a function of sodium content (or as a function of time in galvanostatic charge/discharge). Over the first charge, the $a$ parameter decreases slowly, whereas the fourth charge, it decreases twice as quickly. The $a$ parameter increased from 2.83 Å in the pristine electrode material to 2.89 Å at about the same sodium content ($x$) and voltage in the fourth charge. The larger in-plane lattice parameter is consistent with the lowering of the mean oxidation state, due to a higher concentration of Mn$^{3+}$ ions due to the activation process in the first charge. The increase of the $c$ parameter over the first and the fourth charge is in agreement with the extraction of sodium from the structure and, therefore, the repulsive interaction of oxygen ions in the adjacent layers. However, at the end of charge ($x \sim 0.1$ over the first charge and $x \sim 0.2$ over the fourth charge), the $c$ parameter (which is related to the interlayer distance) does not change and even shrinks. In other layered lithium/sodium metal oxides, contraction of the $c$ parameter at the end of charge was also observed. For example, an abrupt decrease in the $c$ parameter of Li$_{1.2}$Mn$_{0.78}$O$_2$ upon the 1st and 4th cycles, along with the cell voltage. (b) Evolution of lattice parameters of Na$_{x}$Li$_{1-x}$Mn$_{0.78}$O$_2$ as a function of sodium content.

Ex Situ XRD Studies of Cycled Electrodes. The structural evolution of the electrode materials over long-term cycling was further investigated by ex situ XRD. Figure 11a shows changes in the XRD pattern of the Na$_{0.67}$MnO$_2$ electrode material before cycling and after 10 cycles; the 00l reflections are shifted to higher angles, and a small shoulder and a new small peak appear at the higher angle side of the 002 and 004 peaks,
Na$_{0.6}$MnO$_2$ Electrodes and Those after 10 and 100 Cycles, Measured from Ex Situ X-ray Diffraction Analysis

Table 1. Lattice Parameters of Pristine Na$_{0.6}$Li$_{0.2}$Mn$_{0.8}$O$_2$ and Na$_{0.6}$MnO$_2$ Electrodes and Those after 10 and 100 Cycles, Measured from Ex Situ X-ray Diffraction Analysis

<table>
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<th>composition</th>
<th>cathode</th>
<th>phase</th>
<th>lattice parameters, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$<em>{0.6}$Li$</em>{0.2}$Mn$_{0.8}$O$_2$</td>
<td>pristine</td>
<td>I</td>
<td>a: 2.854(2), c: 11.098(3)</td>
</tr>
<tr>
<td></td>
<td>after 10 cycles</td>
<td>II</td>
<td>a: 2.889(2), c: 11.085(3)</td>
</tr>
<tr>
<td></td>
<td>between 2 and 4.3 V</td>
<td>II</td>
<td>a: 2.929(2), c: 11.089(3)</td>
</tr>
<tr>
<td></td>
<td>after 100 cycles</td>
<td>II</td>
<td>a: 2.889(4), c: 11.131(6)</td>
</tr>
<tr>
<td>Na$_{0.6}$MnO$_2$</td>
<td>pristine</td>
<td>I</td>
<td>a: 2.905(3), c: 11.070(4)</td>
</tr>
<tr>
<td></td>
<td>after 10 cycles</td>
<td>II</td>
<td>a: 2.905(3), c: 11.070(4)</td>
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</tbody>
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The Li-substituted composition (Na$_{0.6}$Li$_{0.2}$Mn$_{0.8}$O$_2$) exhibits related yet different structural changes, as presented in the XRD patterns before and after 100 galvanostatic cycles of the electrode (Figure 11b). After cycling, the “in-plane” reflections (100, 102, 103, 104, 106) broaden and shift to lower angles, similar to the trend observed for the unsubstituted electrode after 10 cycles. However, the evolution of the (00l) reflections is different: namely, virtually no shift is observed in the (00l) reflections for the Li-substituted composition even after 100 cycles. Table 1 presents a quantitative comparison of the lattice parameters of pristine Na$_{0.6}$MnO$_2$ and Na$_{0.6}$Li$_{0.2}$Mn$_{0.8}$O$_2$ electrodes after cycling (the voltage profile and the XRD pattern of the Na$_{0.6}$Li$_{0.2}$Mn$_{0.8}$O$_2$ electrode after 10 cycles to 4.3 and 4.6 V are shown below in Figures 12 and 13, respectively). The magnitude of the slight increase in the a parameter of both compositions is similar after 10 cycles. While the c parameter of the Li-substituted composition does not significantly change and in fact appears to slightly increase over cycling, that of Na$_{0.6}$MnO$_2$ contracts by 0.6%. Such a contraction would be expected to give rise to poorer sodium transport and hence can explain the significant capacity fading observed for the unsubstituted phase. In contrast, Na$_{0.6}$Li$_{0.2}$Mn$_{0.8}$O$_2$ shows mainly in-plane structural changes during long-term cycling. In-plane cation rearrangements were also observed for P2$_1$−Na$_{0.6}$Mg$_{0.2}$Mn$_{0.2}$O$_2$ after charging to high voltage. In accord with what has been reported for lithium-rich electrode materials for Li-ion batteries, this behavior is presumably induced by partial oxygen loss and lithium extraction from the crystal lattice.

To confirm this hypothesis, ICP measurements were carried out on the cathode materials after cycling. Cells were run either in the window of 2.0−3.8 V or 2.0−4.6 V. After 10 galvanostatic cycles, the cells at their full discharge state were opened inside a glovebox, and the electrodes were washed with pure PC. The elemental compositions of the dried electrodes were analyzed by ICP measurements, and the Li/Mn ratio was calculated. The Li/Mn ratio was 0.254 and 0.126 for the electrodes cycled up to 3.8 and 4.6 V, respectively. These results confirm that if the activation process is avoided (i.e., stopping at 3.8 V), all the lithium remains in the cathode structure, because the Li/Mn ratio remains identical to that of the pristine powder. However, when these electrodes are cycled in the full voltage window, there is depletion of lithium upon cycling. This extraction of Li will be explored more quantitatively in a follow-up study.

The electrochemical behavior of Na$_{0.6}$Li$_{0.2}$Mn$_{0.8}$O$_2$/Na cells (Figure 12) charged to different voltages after 10 cycles was accompanied by ex situ XRD investigation of the cycled electrodes (Figure 13). After cycling, the cells were opened inside an argon-filled glovebox, and the electrodes were thoroughly washed with PC and extracted. In order to avoid any reaction with the atmosphere, they were transferred to the X-ray diffractometer in hermetically sealed holders. Regarding the electrochemistry, limiting the upper cutoff voltage partially suppresses the activation process observed at the first charge. Figure 12 shows the electrochemical behavior of
Na0.6Li0.2Mn0.8O2 electrodes in NaPF6 PC electrolyte solution when charged to different voltages and then discharged to 2.0 V (vs Na) at 12 mA/g current in a conventional coin cell. Prior to the first charge, all cells were discharged to 2.0 V. In each case, the obtained discharge capacity was roughly 10 mAh/g, confirming that the cathode material is practically inactive before undergoing the activation process. The absence of the voltage plateau on the voltage profiles of the cell charge up to 3.8 V (Figure 12a) confirms that the activation process of the first charge is avoided when the potential range is limited. At the same time, the XRD pattern of the electrode after cycling remains identical to that of the pristine electrode (Figure 13), showing that no structural changes occur during cycling. Even though a small plateau was observed when the cell was charged up to 4.1 V—delivering a capacity ∼30 mAh/g (Figure 12b)—no significant changes in the XRD pattern were observed when the cells were cycled up to this voltage (Figure 13).

Clear structural changes along with a gradual increase of the capacity, were observed when the cells were charged above 4.1 V, however. The discharge capacity increases from 50 to 80 to 100 mAh/g, when cells are charged up to 4.2, 4.3, or 4.4 V, respectively (Figures 12c–e). This gradual activation process is accompanied by the broadening and the splitting of the in-plane reflections, which is not observed for the 00l reflections (Figure 13). Moreover, when the cell is charged to 4.6 V, where the activation process is fully unleashed, the splitting of the in-plane peaks disappears, and the XRD pattern is identical to the pattern for the cathode after 100 cycles (compare Figure 11 and Figure 13). These results provide further confirmation of the structural stability of the Na0.6Li0.2Mn0.8O2 electrodes after the first activation process for more than 100 cycles (compare Figure 11 and Figure 13).

Figure 12. Charge/discharge curves (galvanostatic cycling) of Na0.6Li0.2Mn0.8O2 cathodes charged up to different voltages, recorded over 10 cycles. Experiments were conducted at 30 °C and at a current density of 12 mA/g in 0.5 M NaPF6 PC electrolyte in standard sodium coin-cells.

Figure 13. Ex situ XRD patterns of Na0.6Li0.2Mn0.8O2 electrodes before (pristine) and after 10 galvanostatic cycles of cathodes charged up to different voltages. Blue asterisks denote the signals related to the aluminum current collector.
pristine electrode, while the lattice parameters of the second phase are the same as in the electrode cycled between 2 and 4.6 V.

Similarly, a two-phase region over a narrow range of composition was reported over the second charge of Na$_{0.6}$Li$_{0.2}$Mn$_{0.8}$O$_2$ by operando XRD analysis. This two-phase region emerges at lower voltage and higher sodium content onsets in P$_2$-Na$_{0.5}$Mg$_{0.5}$MnO$_2$ compared to P$_2$-Na$_{0.6}$Li$_{0.4}$Mn$_{0.8}$O$_2$. Two P$_2$-type phases with slightly different lattice parameters and sodium contents were uncovered by the Rietveld refinement of Na$_{0.6}$Mg$_{0.4}$MnO$_2$. This two-phase region was suggested to be due to the sodium redistribution between the two available crystal sites. We propose a similar mechanism occurs in Na$_{0.6}$Li$_{0.4}$MnO$_2$. Note that the two-phase region detected by ex situ XRD of Na$_{0.6}$Li$_{0.4}$MnO$_2$ electrodes charged up to 4.2–4.5 V for 10 cycles was not detected by the operando XRD analysis over the first four cycles. This might be because this phase segregation occurs after some number of cycles (not observed for the first few cycles). Another reason to explain these two observations could be the fact that an ex situ experiment characterizes the electrode material upon relaxation, whereas an operando experiment provides information about the real-time state of the material, which could be affected by kinetics of the transformations.

No evidence of a classic layered to spinel structural transition was observed over the long-range cycling of Na$_{0.6}$Li$_{0.4}$MnO$_2$. Such an irreversible process that occurs upon activation of Li- and Mn-rich lithium insertion positive electrode materials has an adverse effect on their average discharge voltage over cycling. Recently, it was postulated by means of theoretical calculations that the formation of spinel phases in Na$_x$MnO$_2$ cathodes is thermodynamically unstable and highly kinetically hindered. These claims were later confirmed experimentally by Komaba et al. and more recently by Liu et al. However, as the material charged to 4.6 V is highly disordered, identification of its structure is not possible with direct XRD analysis. Pair-distribution function analysis, which is beyond the scope of this work, is currently underway to attempt to elucidate the structural details.

## CONCLUSIONS

The advantages of using lithium as a structural substituent for sodium manganese oxide cathodes for sodium ion batteries are clear, as shown by the stable electrochemical behavior of Na$_{0.6}$Li$_{0.4}$MnO$_2$. Comparison of this cathode material to unsubstituted Na$_{0.6}$MnO$_2$ shows that incorporation of the lithium substituent improves the specific capacity by 20%, resulting in a stable capacity of 190 mAh/g for more than 100 cycles. The addition of lithium appears to partially suppress the detrimental phase transition observed upon operating Na-ion insertion cathodes up to high potentials and reduces cooperative Jahn–Teller distortions. Detailed analysis by ex situ and in situ XRD, and operando OEMS measurements suggest that the material undergoes an activation process during the first cycles, which involves lithium extraction from the crystal lattice and potentially partial oxygen loss. DFT calculations suggest that it is highly possible that oxide anions play an important role in the charge compensation of these materials during redox reactions. Even though the role of oxide anions in the redox reactions of Li- and Mn-rich oxide electrode materials is still subject to debate, it has been proposed that they play an important role in charge compensation through a solid-state type reaction without any oxygen loss. It is likely that similar mechanisms are relevant to sodium-ion battery electrode materials as the one described and discussed here. Further work on resolving this issue is in progress, but nonetheless, the authors believe that it is possible to develop optimized cathodes for Na-ion batteries based on manganese oxides with targeted lattice substituents.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.6b04078.

Details of powder diffraction results, XRD patterns, relative potential energies of Na-vacancy orderings, density-of-states diagrams, XPS spectrum, and online mass spectrum for a blank electrode containing no active material (PDF).

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### Notes

The authors declare no competing financial interest.

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