Uptake of CO$_2$ in Layered P2-Na$_{0.67}$Mn$_{0.5}$Fe$_{0.5}$O$_2$: Insertion of Carbonate Anions

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ABSTRACT: Batteries based on sodium layered transition metal oxides are a promising alternative to current state-of-the-art lithium-ion systems for large-scale energy storage, resulting in recent intensive efforts to develop high-energy density, low cost, stable cathode materials. Some of the most promising degrade on exposure to ambient atmosphere; however, the process is not understood. Here, using neutron/X-ray diffraction coupled with mass spectroscopy and thermal analysis, we reveal the nature of the reactivity. We demonstrate the unprecedented insertion of carbonate ions in the vacancy-rich layered structure of P2-Na$_{0.67}$[Mn$_{0.6}$Fe$_{0.4}$]O$_2$, Mn(IV). The material exhibits much higher charge/discharge polarization and lower capacity than rigorously air-protected P2-Na$_{0.67}$[Mn$_{0.6}$Fe$_{0.4}$]O$_2$; a detailed study by online electrochemistry mass spectroscopy reveals that the inserted carbonate ions decompose during electrochemical charging, accounting for the differences observed between the first and second cycles. Furthermore, we show that Ni-substituted materials P2-Na$_{0.67}$[Ni$_{0.5}$Mn$_{0.5}$Fe$_{0.5}$]O$_2$ are less prone to such reactivity and thus are more promising candidates for scalable processing. Understanding these mechanisms provides a vital guide for future sodium metal oxide battery research.

INTRODUCTION

The growing demands of today’s societies for energy and the inevitable importance of providing it from renewable and green resources requires the development of efficient and sustainable energy storage systems. Lithium ion batteries (LIBs) are extensively used to power portable electronic devices and are expanding to transportation applications. However, resource availability and the cost of lithium, as well as the cost and environmental impact of the electrode materials, are important concerns regarding the large scale application of lithium batteries and will become more significant as the LIB powered-vehicle market grows. Despite the inevitably lower gravimetric capacity of sodium batteries, this technology offers very interesting prospects to meet the price and sustainability requirements of grid storage and even can attain energy densities comparable to Li-ion batteries. Today, sodium battery technology has emerged as an important subject of research and development as a promising alternative for lithium batteries because of its advantages in terms of cost and sustainability.

Along with the interesting possibilities offered by sodium polyanion materials, the search for new positive electrode materials for sodium ion batteries has been dominated by the research conducted on sodium layered oxides, Na$_x$MO$_2$, with M consisting of transition metals (TM) such as Fe, Co, and Mn. In all these oxides, the transition metal forms layers of edge sharing MO$_6$ octahedra, similar to the CdI$_2$ structure. The sodium atoms are located between the transition metal layers in either octahedral or prismatic environments, depending on the stacking of the MO$_6$ layers. A convenient way to refer to these oxides was introduced by Delmas et al. using a letter (O or P) to describe the sodium coordination polyhedra, followed by the number of transition metal layers required to describe the cell stacking. Layered sodium metal oxides (Na$_x$MO$_2$) adopt various polymorphs depending mainly on the sodium content, the two most common structures being O3 for $x \sim 1$ and P2 for $x \sim 2/3$.

Not only do the sodium analogues of lithium host materials show good performance, e.g., O3-Na$_x$CoO$_2$ and O3-Na$_x$[Mn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$]O$_2$, but substitution of lithium by sodium also enables access to redox couples such as O3-Na$_x$FeO$_2$ and O3-Na$_x$CrO$_2$ that are inactive in the corresponding Li metal oxides. The larger size of sodium compared to lithium prevents mixing between alkali and transition metal cations. The sodium layered oxides can tolerate higher concentrations of sodium vacancies, but strong interaction of the latter with the cations leads to multiple phase transitions between O3/P3 and P2/O2 structures as the sodium content varies on cycling.

Sodium layered oxides with the P2 structure exhibit particularly high capacities and good sodium mobility. One
of the reasons for their superior behavior resides in the disorder found in the sodium-occupied layer. Na⁺ ions are located in two sites, called Na⁰ and Na⁶, in which the NaO₆ prisms share edges or faces with MO₆ octahedra, respectively. The Na⁰ site is more stable compared to Na⁶ due to its longer Na–M distance which minimizes cation repulsion (Figure 1). Among all the P2 compositions, Na₀.₇MnO₂ has been considered a promising material due to its low cost and environmental friendliness. Attempts to increase the working voltage by substitution of manganese by nickel resulted in a decrease of the reversible capacity due to the multiple structural transitions induced by Ni/Mn ordering. Substitution of Mn by Co suppresses these transitions, smoothing the charge/discharge profile and improving the capacity retention but at the expense of lower reversible capacity. More recently, it was shown that iron substituted P2-Na₀.₆₇[Mn₁₋ₓFeₓ]O₂ phases demonstrate significantly superior performance in terms of specific capacity and cyclability. Activation of the Fe³⁺/Fe⁴⁺ couple is a promising route to design low-cost high voltage positive material due to its low cost and environmental friendliness.

**EXPERIMENTAL SECTION**

**Synthesis.** Na₀.₆₇[Mn₀.₅Fe₀.₅]O₂ phases with y = 0, 0.1, 0.15 were synthesized by solid state methods. Stoichiometric amounts of Na₂CO₃ (EMD Millipore, ≥99.5%), MnO₃ (Sigma-Aldrich, 99%), NiO (Sigma-Aldrich, 99.8%), and Fe₂O₃ (Sigma-Aldrich, ≥99%) powders were mixed using a ball mill and pressed into pellets. These were heated in air at 750 °C for 4 h followed by a final annealing at 900 °C for 6 h. Samples referred to as “air-exposed” were then cooled to room temperature in the furnace and stored under ambient conditions, whereas “air-protected” samples were obtained by heat treatment in a protective atmosphere (Ar, He, or vacuum) at 600 °C for 12 h and transferred to an argon filled glovebox (MBraun, O₂ and H₂O < 0.1 ppm).

**Material Characterization.** X-ray powder diffraction (XRPD) data were collected on a PANalytical Empyrean instrument using Cu Kα radiation outfitted with a PIXcel bidimensional detector. In order to protect samples from exposure to air, the samples were loaded in glass capillaries (Ø = 0.3 mm) in an argon filled glovebox. Rietveld quality patterns were recorded in Debye–Scherrer geometry using a parabolic X-ray mirror in the incident beam. For high temperature XRDP under a controlled atmosphere, the samples were heated in an Anton Paar HTK 1600 chamber using 0/0 Bragg–Brentano geometry.

Neutron powder diffraction (NPD) experiments were recorded on the time-of-flight (t.o.f.) spectrometer POWGEN at the Spallation Neutron Source (SNS) of the Oak Ridge National Laboratory (ORNL). The powders were loaded in 8 mm vanadium sample cans in an argon filled glovebox and sealed with a copper gasket.

The evolution of the lattice parameters during the thermodeformation experiments were extracted using the Le Bail fitting procedure. Structural models of the selected compositions were refined against the NPD and XRDP data set using the Rietveld method within FullProf. Nuclear Fourier difference maps were calculated using the GFOUR algorithm, implemented in FullProf, and the maps were plotted using the VESTA 3D visualization software.

The SEM images were recorded using a Zeiss Ultra Plus scanning electron microscope (FE-SEM) at 15 kV in secondary electron mode. The molar ratios of transition metal ions of each composition were verified by energy dispersive X-ray spectroscopy (EDS) (EDAX) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Prodigy high dispersion ICP, Teledyne Leeman Laboratories). The molar ratio of sodium to transition metal was determined to be 0.65(2) in all three compositions by ICP-AES.

Thermogravimetric analyses (TGA) were performed in platinum crucibles using a TA Instruments SDT Q600 under high purity argon, oxygen, and carbon dioxide. The evolved gas analysis was performed in a separate experiment using a quadrupole mass spectrometer (Stanford Research Systems, RGA 200).

**Electrochemistry.** To investigate electrochemical properties, each active material composition was mixed with 10 wt % carbon black and 10 wt % polyvinylidene fluoride (PVDF) (Aldrich average Mw ∼ 534 000) suspended in N-methyl-2-pyrrolidone (NMP) (Sigma-Aldrich, 99.9%) and cast on aluminum foil with a typical loading of 7–9 mg/cm². The electrodes were dried in a vacuum oven at 90 °C overnight. For air-protected electrodes, all the electrode preparation procedures were performed inside a glovebox under argon (O₂ and H₂O < 0.1 ppm). The compounds were examined as the positive electrode in 2325 coin cells with sodium metal as the negative and separators (Merck Millipore). Galvanostatic cycling was performed using a multiple channel MPG-2 galvanostat/potentiostat (Bio-Logic, Claix, France) at 24 °C between 1.5 and 4.3 V with a current density of 13 mA/g corresponding to a C/20 rate.

The residual gas analysis was performed with a modified design based on an online electrochemical mass spectrometer (OEMS) apparatus reported by Tsiovouaras et al. A commercial electrochemical mass flow cell (EL-Cell, ECC-DEMS) was attached in-line to a gas flow controller (Bronkhorst, F-200CV) and quadrupole mass spectrometer (Stanford Research Systems, RGA 200). During cell operation, a controlled flow of Ar (Praxair, 5.0 grade) swept the evolved gases from the cell to the quadrupole mass spec detector through a fused silica capillary (50 μm ID). The pressure inside the chamber was 2 × 10⁻⁵ Torr during operation. The electrodes were prepared and cycled as previously described except that they were cast
on a P50 gas diffusion layer (porous carbon paper) instead of aluminum foil in order to allow for gas collection.

RESULTS AND DISCUSSION

Air-Protected Na_{0.67}Mn_{0.5}Fe_{0.5}O_{2}. X-ray/neutron diffraction studies (Figure 2a,b and Table 1) on air-protected samples of Na_{0.67}Mn_{0.5}Fe_{0.5}O_{2} were employed to probe potential metal cation ordering within the lattice and changes in cell parameters as a function of air-exposure. All reflections could be indexed in the P6_{3}mmc space group of the ideal P2 structure type, where the refined atomic positions are consistent with an undistorted structure. Importantly, the cell parameters obtained for Na_{2/3}Mn_{1/2}Fe_{1/2}O_{2} (Figure S1, Supporting Information) are different from those previously reported,^{1,13,17} this discrepancy is explained by the evolution of the cell parameters even upon minor degrees of air exposure. Strong microstructural effects resulting in hkl-dependent peak broadening, as previously reported,^{11} are clearly visible in the NPD and XRPD patterns (insets Figure 2a,b). The peak profiles of (10l) reflections are clearly much broader than (00l) and (hk0) lines. Therefore, the peak shape could not be modeled properly even with Stephens strain correction.^{26} For these reasons, the reliability factors based on integrated peak intensity, such as R_{Bragg}, are the most meaningful and more satisfactory (Table 1) compared to $\chi^2$ which uses all the measured points. Microstructural effects have been attributed to stacking faults^{11} which could originate from a variety of reasons, such as the mismatch in size of the different cations on the metal site. In addition, the presence of Jahn–Teller active Mn^{3+} introduces strain in the lattice. It was shown that the high concentration of Mn^{3+} in the parent P2 oxide Na_{2/3}MnO_{2} results in an orthorhombic distortion of the ideal hexagonal symmetry.^{27–30} Therefore, variation of the local structure around the Mn^{3+} atoms is expected. To minimize the number of refined parameters, constraints on the stoichiometry were used; in agreement with the ICP-AES results, the sodium fraction was fixed to 0.67 and the Fe/Mn ratio was set to 1.

![Figure 2. Combined Rietveld refinement of (a) neutron and (b) X-ray powder diffraction data of Na_{2/3}Mn_{1/2}Fe_{1/2}O_{2}. For each pattern, the observed data is shown in red, and the calculated pattern is shown in black; the difference curve is shown in blue, and the calculated Bragg reflections are shown in green. (c) First two galvanostatic charge/discharge cycles and (d) capacity retention of air-protected P2-Na_{2/3}Mn_{1/2}Fe_{1/2}O_{2} cycled at 13 mAh g^{-1} (C/20).](image-url)
We find that the two prismatic NaO₆ sites in Na₂/₃[Mnₓ/₂Feₓ/₂]O₂, Na₆ and Na₈, exhibit significant configurational disorder, as observed in P2-type Na₂/₃MnO₂ and Na₂/₃CoO. This was taken into account by splitting the positions Na₆ (2d) and Na₈ (2b) into the lower symmetry 6h Wyckoff position. The occupancy of site Na₆ is twice that of the Na₈ site, in agreement with the higher stability of site Na₆. The observed disorder on the sodium position suggests a high ionic mobility of sodium cations in this structure.

The combined refinement of the neutron and X-ray data sets (Figure 2a,b) unambiguously proves that the iron and manganese atoms are statistically distributed over the transition metal site. The configurational disorder plays an important role in the excellent electrochemical performance of this oxide as a positive electrode material. Namely, the voltage profile of Naₓ[0.67Mn0.5Fe0.5]O₂ is very smooth (Figure 2c). This is uncommon, since sodium layered oxides generally undergo numerous ordering phenomena leading to multiple step charge/discharge profiles, such as those observed in the closely related oxide, NaₓMn₁/₂O₂. The irreversible structural changes associated with this ordering induce low reversible capacity, poor capacity retention, and limited rate capability.

When Naₓ[0.67Mn0.5Fe0.5]O₂ is charged at voltages higher than 4.1 V vs. Na, it was reported that the undistorted P2 phase converts into a low crystallinity O4 phase. This high voltage phase, consisting of a glide of two transition metal layers out of every four, is believed to be an intermediate step in the generally observed P2 to O2 structural transition. It appears that the configurational disorder that we demonstrate on the transition metal site efficiently prevents the long-range ordering of the sodium cations/vacancies and blocks the detrimental structural transitions. Hence, reversible insertion/extraction of Na atoms is observed over a large range of stoichiometry (0.15 < x < 0.9) corresponding to capacities of approximately 200 mAh g⁻¹ (Figure 2d). The capacity fading of Naₓ[0.67Mn0.5Fe0.5]O₂ is moderate with 65% retention after 50 cycles, showing that, despite its reversibility, the P2 to O4 phase transition impacts the cycling properties of this material.

The voltage profile of Naₓ[0.67Mn₁/₂Fe₁/₂]O₂ exhibits very small polarization in the low voltage region and higher polarization in the high voltage range, as previously reported. Different from that work, we observe separation of these two regions on charge that is signaled by a voltage jump at exactly x = 0.5. Since Mn⁴⁺ undergoes redox at a lower potential than Fe³⁺, in the ideal composition (Naₓ[0.17Mn₁/₂Fe₁/₂]O₂), this sodium stoichiometry corresponds to the theoretical mass loss calculated from eq 1 (see text).

Air Sensitivity of the Studied Materials. Sodium layered oxides are known to be reactive under ambient atmosphere. Several mechanisms have been proposed, including insertion of water molecules between the MO₂ slabs. Complex oxidation mechanisms were reported in the case of Naₓ[0.67MnO₂] involving the creation of Mn vacancies and formation of carbonate on the surface of O3 phases. The reactivity of the Naₓ[0.67Mn₀.₃Fe₀.₇]O₂ depends on the precise composition of the atmosphere, temperature, and the exposure time. The physical changes of the sample aged under air are visible to the naked eye; volume expansion causes pellets to crack, and the color evolves from black to brown.

Thermogravimetric analysis coupled with mass spectroscopy (TGA-MS), under argon of a week-old air-exposed sample of Na₂/₃[Mnₓ/₂Feₓ/₂]O₂ shows a two-step mass loss of more than 7% (reported with respect to the mass after heating) (Figure 3). Analysis of the nature of the gases released during the low temperature mass loss observed at ~100 °C reveals that an important quantity (~2% wt) of CO₂ and water is physisorbed on the surface of the grains. During the high temperature mass loss, commencing at ~300 °C, the evolved gases are CO₂ and O₂, consistent with the decomposition of carbonate ions. In situ diffraction data collected from a sample subjected to sequential temperature ramps under a helium flow (“thermodiffraction”; Figure S1, Supporting Information) shows that the 100 °C mass loss has only a very marginal effect on the cell parameters, as expected from the release of surface bound species. In contrast, the second mass loss is accompanied by elongation of the lattice parameter a and contraction of the lattice parameter c, suggesting a modification of the structure.

The formation of carbonate on the surface of sodium layered oxides is well-known. However, in the case of air-exposed P2-Naₓ[0.67Mn₁/₂Fe₁/₂]O₂, irrespective of exposure time, no diffraction peak indicative of any carbonate phase could be evidenced by XRD. This observation is of particular importance since thermonatrite (Na₄CO₃·2H₂O), a hydrated sodium carbonate phase, is easily detectable in air-exposed XRD patterns of the corresponding O3-Naₓ[Mn₁/₂Fe₁/₂]O₂ composition (Figure S2, Supporting Information).
Rietveld refinement of the neutron diffraction pattern of an air-exposed sample of P2-Na2/3[Mn1/2Fe1/2]O2 shows that, similar to the oxidation of P2-Na2/3MnO2, cationic vacancies are created in the iron substituted composition upon air exposure. More importantly, the Fourier difference map (Figure 4a) revealed that, in addition to very small imperfections in modeling the disorder present in the sodium layer, a large residual nuclear density is observed in the tetrahedral sites of the MO2 layer. This site, with effective X–O bond lengths (with X being the center of the tetrahedron) of the order of ~1.6 Å, is much too small to accommodate Fe\(^{3+}\) (see below). A smaller Mn\(^{4+}\) or H\(^+\) cation would result in a weak signal around the carbon position, both on the faces and the edges of the tetrahedral site, supporting the distribution of the nuclear density around the average position, in line with dynamic disorder (Figure 4c). In particular, the density of the edge of the tetrahedron midway between the two average sites is suggestive of mobility of the carbonate ions, which would be necessary to achieve intercalation. A consequence of the Mn/Fe vacancies generated by the expansion of the oxygen framework can be seen by the splitting of the position of the Na\(_\alpha\) site. This position is less favorable than the Na\(_\alpha\) position in the air-protected sample (Table 1) due to electrostatic repulsion with the transition metal. It becomes the most occupied in the air-exposed sample. Moreover, Na\(_\alpha\) was modeled with a 3-fold split position in the ab plane in the pristine sample, but a 2-fold split position along the c axis is observed in the air-exposed sample. These changes compared to the air-protected structure are a direct consequence of the fact that some [Fe/Mn]O6 octahedra are empty in the air-exposed structure, allowing stabilization of the Na\(_\alpha\) site and a displacement of this position along the c axis.

Table 2. Atomic Parameters and Unit Cell Constants of Na0.60Mn0.44Fe0.44C0.08O2 Calculated from Rietveld Refinement of Neutron t.o.f. Diffraction Data

<table>
<thead>
<tr>
<th>site</th>
<th>Wyck.</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>(U_{iso}) ((\text{Å}^2))</th>
<th>at./f.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(_\alpha)</td>
<td>6h</td>
<td>0.630(4)</td>
<td>0.370(4)</td>
<td>1/4</td>
<td>0.017(5)</td>
<td>0.28(1)</td>
</tr>
<tr>
<td>Na(_\beta)</td>
<td>4e</td>
<td>0</td>
<td>0</td>
<td>0.232(2)</td>
<td>0.034(3)</td>
<td>0.32(1)</td>
</tr>
<tr>
<td>Fe/Mn</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0060(4)</td>
<td>0.89</td>
</tr>
<tr>
<td>C</td>
<td>4f</td>
<td>1/3</td>
<td>2/3</td>
<td>0.9892(2)</td>
<td>0.004(2)</td>
<td>0.08</td>
</tr>
<tr>
<td>O</td>
<td>4f</td>
<td>1/3</td>
<td>2/3</td>
<td>0.0904(2)</td>
<td>0.0103(3)</td>
<td>2</td>
</tr>
</tbody>
</table>

\(^{2519}\) DOI: 10.1021/acs.chemmater.5b00097

Chem. Mater. 2015, 27, 2515–2524
The insertion of carbonate ions is accompanied by the oxidation of Mn$^{3+}$ to Mn$^{4+}$ in P2-Na$_{2/3}$[Mn$_{1/2}$Fe$_{1/2}$]O$_2$. The large quantity of CO$_2$ and H$_2$O molecules adsorbed on the surface of the material, evidenced by TG-MS (Figure 3), suggests the following two-step mechanism. Carbonate ions are formed by combination of CO$_2$ and H$_2$O to produce carbonic acid (H$_2$CO$_3$) that readily dissociates (eq 2). As the carbonate ions enter the transition metal layer, the remaining protons are transported in the surface layer of physisorbed species and the electrons travel within the oxide to the reduction site of oxygen, reforming the consumed water molecule (eq 3). Overall, this accounts for oxygen reduction in the presence of CO$_2$ (and water) to form carbonate (eq 4). The P2-oxide has a suitable redox potential to carry out this reaction. This is suggested by its OCV of 2.4 V vs Na ($-0.3$ Vs SHE, see lower) and by the oxygen reduction potentials for a variety of Mn$^{3+}$ oxides which function as oxygen reduction catalysts.$^{37,38}$ In the present case the reaction is enthalpically driven to completion, limited by the oxidation of Mn and insertion of carbonate. We note that, although carbonate ions are well-known to intercalate into layered metal double hydroxides which bear a fixed positive charge on the layers,$^{39}$ the charge compensation mechanism is completely different for the sodium layered metal oxide and without precedent.

\[
\begin{align*}
\text{CO}_2(\text{ads}) + \text{H}_2\text{O}(\text{ads}) & \rightarrow 2\text{H}^+_\text{surf} + \text{CO}_3^{2-} \text{(insert)} \quad (2) \\
+ 2\text{H}^+_\text{surf} + \frac{1}{2}\text{O}_2(\text{gas}) + 2e^- & \rightarrow \text{H}_2\text{O}(\text{ads}) \\
& \rightarrow \text{CO}_2 + \frac{1}{2}\text{O}_2 + 2e^- \rightarrow \text{CO}_3^{2-} 
\end{align*}
\]

The role of water was investigated by thermogravimetric analysis under different atmospheres: air, wet oxygen, and wet carbon dioxide. For each experiment, the sample was first heated under dry argon at 600 °C in order to obtain a reference sample free from any air contamination. After cooling down to room temperature, the atmosphere was switched to the gas of interest and the reactivity of the material was monitored at room temperature for 12 h. The temperature was then raised to 600 °C to study the kinetics at high temperature (Figure 5). As expected, the mass of the sample exposed to air increases at a steady rate during the entire isothermal analysis, showing that the reaction is not complete after 12 h. Further heating results in an almost flat curve up to 200 °C; the mass then increases again to reach the maximum value of 1.5% at 450 °C. For temperatures higher than 450 °C, the mass returns to the original.

Experiments under wet CO$_2$ show that the reactivity with carbon dioxide in the presence of water is both fast and important. The mass increase at room temperature is more than 5.5% after 12 h, and no sign of saturation is visible. Heating of the sample exposed to wet CO$_2$ results in an important mass loss around 100 °C which is attributed to the release of the previously mentioned surface species. At temperatures higher than 400 °C, the mass curve shows a second loss due to the decomposition of the carbonate species as observed for the sample under air. The unique nature of this uptake is further illustrated by an experiment carried out under water-saturated O$_2$. Despite the rapid adsorption of surface species, the saturation behavior observed in the room temperature isothermal analysis and the evolution of the mass curve upon heating clearly differs from what is observed in the reference experiment under air. A more complete study of the reactivity of P2-Na$_{2/3}$[Fe$_{1/2}$Mn$_{1/2}$]O$_2$ can be found in Figure S4, Supporting Information.

Figure 5. Reactivity of Na$_{2/3}$[Fe$_{1/2}$Mn$_{1/2}$]O$_2$ studied by TGA under different atmospheres: in each experiment, the sample was first annealed under dry Ar at 600 °C in order to obtain a reference sample free from any air contamination. After cooling down to room temperature, the atmosphere was switched to the gas of interest and the reactivity of the material with the flowing gas was inspected at 25 °C for 12 h followed by annealing to 600 °C.

Further evidence supports the insertion of carbonate within the structure. First, the structure of a sample heated at 600 °C under oxygen is perfectly modeled without carbonate insertion and shows only cationic vacancies (Figure S5, Supporting Information). Second, no evidence of the formation of an amorphous phase was found in SEM images of the P2 phase exposed to air for less than 2 weeks (Figure 6a). However, while studying the long-term reactivity of P2-Na$_{2/3}$[Fe$_{1/2}$Mn$_{1/2}$]O$_2$, we found that, after a few weeks of air exposure, particles with a ribbon-like morphology start to appear as evidenced by ex situ SEM monitoring (Figure 6b) and continue to grow for months (Figure 6c). These particles can be washed away with distilled water, and the diffraction pattern remains unchanged. Due to their degradation under the electron beam, it was not possible to record an SAED pattern. We identified these particles as amorphous carbonate based on two observations: the pH of the wash solution was $\sim 11$ (pK$_a$(HCO$_3^-$) = 10.3) and acidification of that solution produces bubbles of gaseous CO$_2$. The ribbon-like morphology is in good agreement with a formation mechanism consisting of a progressive extrusion of the carbonate and sodium ions from within the layered structure. There is no driving force that would induce a change of morphology from an amorphous layer of carbonate coating on such grains (as observed in ref 5) to these ribbon-like particles. The appearance of a small peak near 34° in the XRD pattern of a month-old sample (Figure 6d) suggest that trona (Na$_2$(CO$_3$)HCO$_3$·2H$_2$O) might be the carbonate phase grown as the consequence of exposure to air for months.

After the initial immediate slight shift of the cell parameters when the sample is exposed to air, as mentioned early on in the discussion, new peaks are spotted on the diffraction pattern of samples aged for a long time (Figure 6d). After approximately 2 weeks, two broad peaks appear to the left side of the (002) and (102) reflections, suggesting the formation of a new poorly
crystalline phase, Phase 2, with a larger interlayer spacing of \( \sim 6.3 \) Å (i.e., 12.6 Å for a doubled \( c \) axis that can be compared to 11.2 Å for the pristine material). These peaks then decrease in intensity, coincident with growth of a set of sharp reflections indicative of a new Phase 3, with an even larger interlayer spacing of \( \sim 7.1 \) Å. The formation of this phase takes about a month to initiate and then progresses slowly. We propose these phases are due to the intercalation of water between the layers, owing to the similarity of the positions of their XRD reflections, particularly for Phase 3, to the “hydrated phases” reported by Lu and Dahn\(^\text{20}\) for P2-Na\(_{2/3}\)Co\(_{1/3}\)Mn\(_{2/3}\)O\(_2\). The growth of the sodium carbonate ribbons extract the sodium from the structure, yielding a sodium-depleted P2 phase. Recently, Passerini and co-workers have shown that P2/P3-Na\(_{x}\)Ni\(_{0.22}\)Co\(_{0.11}\)Mn\(_{0.66}\)O\(_2\) was markedly more prone to absorb water once the sodium content was electrochemically decreased.\(^\text{21}\) We conclude that the same phenomenon is true for the P2-Na\(_{0.67}\)[Mn\(_{1/2}\)Fe\(_{1/2}\)]O\(_2\) composition: namely, the chemical extraction of sodium triggers the absorption of water molecules. Thermidiffraction analysis (Figure S6, Supporting Information) shows that Phase 3 disappears below 100 °C and Phase 2 is decomposed at 200 °C yielding a sodium-depleted P2 phase, P2-Na\(_{1/2}\)[Mn\(_{1/2}\)Fe\(_{1/2}\)]O\(_2\) phase (see below).

**Influence of the Reactivity of Na\(_{0.67}\)[Mn\(_{1/2}\)Fe\(_{1/2}\)]O\(_2\) on Electrochemical Properties.** Figure 7a shows that air-exposed P2-Na\(_{2/3}\)[Mn\(_{1/2}\)Fe\(_{1/2}\)]O\(_2\) materials have significantly different charge/discharge profiles compared to materials annealed under vacuum (gray curve). The air-exposed sample exhibits much lower discharge capacity (about 70% of the air-protected material) and larger polarization, especially in the low voltage region. Particularly significant is that the first (partial) charge curve does not superimpose with the second charge curve, clearly indicating a transformation after cycling. On initial charge of an air-exposed P2-Na\(_{2/3}\)[Mn\(_{1/2}\)Fe\(_{1/2}\)]O\(_2\) electrode, the voltage almost immediately rises to the potential corresponding to the Fe\(^{3+/4+}\) redox couple, indicating that almost no Mn\(^{3+}\) remains in this material owing to a predominately Mn\(^{4+}\) composition balanced by carbonate insertion as described in eq 1.

The substitution of Fe\(^{3+}\) by Mn\(^{4+}/\text{Ni}^{2+}\) has already been reported as a suitable way of increasing the average voltage of P2-Na\(_{2/3}\)[Mn\(_{1/2}\)Fe\(_{1/2}\)]O\(_2\).\(^\text{29,40}\) As shown in Figure 7b,c for P2-Na\(_{2/3}\)[Mn\(_{0.8}\)Ni\(_{0.2}\)Fe\(_{0.0}\)]O\(_2\) and P2-Na\(_{2/3}\)[Mn\(_{0.8}\)Ni\(_{0.15}\)Fe\(_{0.05}\)]O\(_2\), this substitution also has a positive effect on the perturbations induced by exposure to air. The higher the nickel content, the smaller is the discrepancy between the performance of air-protected and air-exposed electrodes. This increase in stability can be related to the increase of the mean oxidation state of Mn as the Ni content increases. It is also in agreement with a previous study on P2-Na\(_{2/3}\)MnO\(_2\), describing Mn\(^{3+}\) as the...
unstable species, and demonstrates that the insertion of carbonate in the P2 structure is not specific to the Na$_{2/3}$[Mn$_{1/2}$Fe$_{1/2}$]O$_2$ composition.

As previously mentioned, although the insertion of carbonates is the most rapid "aging" process at room temperature, it is not the only one to be considered. The influence of other contaminants or sample treatment was also studied (Figure 8). The sample annealed at 600 °C under oxygen (Figure 8b) shows a potential jump at $x = 0.57$ suggesting a formula of Na$_{0.66}$[Fe$_{0.49}$Mn$_{0.49}$]O$_2$ (i.e., Na$_{2/3}$[Fe$_{1/2}$Mn$_{1/2}$]O$_2$), in perfect agreement with the TGA data (Figure S4, Supporting Information). The voltage step exhibited by the material exposed to wet argon at room temperature and dried at 90 °C under vacuum, and (d) exposed to air for months, washed with distilled water, filtered, and dried at 200 °C under vacuum.

![Figure 8](image)

**Figure 8.** Charge/discharge profile of Na$_{2/3}$[Mn$_{1/2}$Fe$_{1/2}$]O$_2$: (a) annealed under vacuum at 600 °C (for comparison), (b) annealed under oxygen at 600 °C, (c) exposed to wet argon at room temperature and dried at 90 °C under vacuum, and (d) exposed to air for months, washed with distilled water, filtered, and dried at 200 °C under vacuum.

When the sodium content at which the potential jump is observed on the second charge implies oxygen or water exposure cannot independently reproduce the electrochemical behavior observed for the air-exposed material. Finally, a sample exposed to ambient conditions for 5 months, i.e., that is almost completely converted to Phase 3, was washed with water to remove the carbonate particles and dried at 200 °C under vacuum to produce a sodium deficient P2-Na$_{2/3}$[Mn$_{1/2}$Fe$_{1/2}$]O$_2$ phase. Its electrochemical behavior exhibits a potential jump at the very beginning of the charge, according to the expected sodium stoichiometry (Figure 8d). The superimposability of the first and second charge implies that washing the electrode material with water, as reported by others, is a good way to remove the carbonate contamination. However, in the case of Na$_{2/3}$Fe$_{1/2}$Mn$_{1/2}$O$_2$, the material annealed at 600 °C under argon clearly outperforms the material obtained by washing, possibly due to proton exchange in the latter case.

**Online Electrochemical Mass Spectroscopy Study of Na$_{2/3}$[Fe$_{1/2}$Mn$_{1/2}$]O$_2$.** A detailed study of Na$_{2/3}$[Fe$_{1/2}$Mn$_{1/2}$]O$_2$ by online electrochemical mass spectroscopy (OEMS) was undertaken to monitor the gases released during cycling (Figure 9) and gain a better understanding of the processes responsible for the difference between air-exposed and air-protected samples. Of all the monitored species (O$_2$, H$_2$O, H$_2$, and CO$_2$), only the signal corresponding to CO$_2$ exhibits meaningful changes upon cycling. During the first charge of the air-exposed sample (Figure 9a), significant CO$_2$ is evolved on the plateau at 4.1 V, i.e., in the range of 0.55 < $x$ < 0.4, as illustrated by the circled region. This feature is not observed for the air-protected sample (Figure 9b) and is consistent with the evolution of CO$_2$\(^{2-}\) inserted on air exposure as previously described. The broad peak is due to the decomposition of the carbonate ions CO$_2$\(^{2-}\) into CO$_2$ and oxygen species; since no oxygen signal is detected by OEMS, we assume the oxygen reacts with the electrolyte and/or is incorporated into the lattice as oxide ions (see below).

All of the other features presented in the OEMS in Figure 9 are related to CO$_2$ evolution as a result of electrolyte decomposition. Despite the fact that all the features occur at a slightly different sodium content, in each case, they correspond to the point at which charge compensation switches over from Mn$^{3+/4+}$ to Fe$^{3+/4+}$, concomitant with the jump in potential. Irrespective of air-exposure, small amounts of CO$_2$ are released at the voltage step on charge. The release of carbon dioxide at each potential jump, i.e., at the formation of Fe$^{4+}$, suggests that the latter catalytically decomposes the electrolyte. The small range in which these peaks are observed is probably due to the passivation of the surface by the decomposition products.

Upon discharge, large amounts of CO$_2$ are produced for $x > 0.7$ in the air-exposed sample (Figure 9c), later in the charge process than for the air-protected sample where the onset is at $x = 0.5$ (Figure 9d). In both cases, the CO$_2$ release starts at the activation of the Mn$^{4+}$/Mn$^{3+}$ couple, i.e., at the same sodium content at which the potential jump is observed on the second charge. The reason is probably due to surface disproportionation of Mn$^{3+}$, a very common issue with positive electrode materials containing manganese. Similar to what was proposed for LiMn$_2$O$_4$,\(^{42,43}\) dissolution of Mn$^{2+}$ induces decomposition of the electrolyte at the origin of the CO$_2$ signal recorded during
discharge. Thus, at the end of discharge, the surface of the grains are manganese depleted. This in turn leads to a higher iron concentration at the surface and in more CO₂ evolution during the potential jump on the subsequent charge. This would also explain the accentuated capacity fade rate during the first 5 cycles (Figure 4).

We note a shift in the CO₂ evolution with respect to "x" for the air-exposed sample (Figure 9c) between the first and second charge. As CO₂⁻⁻ decomposition is accompanied by release of active oxygen species, was the oxygen to react with the electrolyte, a composition similar to the air-protected sample should be achieved for the second charge; that is, the CO₂ emission peak due to activation of the Fe³⁺/⁴⁺ couple should be observed at x = 0.5 (Figure 9d). If the oxygen species remain in the structure as oxide ions (i.e., substitution of CO₃²⁻ by O²⁻), then no shift of the potential jump is expected. The observation of the potential jump at x = 0.62 in the second charge of the air-exposed sample implies that both mechanisms play a role, but substitution dominates as expected.

■ CONCLUSIONS

The layered P2-type Na₆.₆₇[NiₓMn₃₋ₓFeₓO₂₋ₓ]₂O₂ sodium metal oxides are highly promising cathode materials for sodium-ion batteries. They demonstrate a smooth discharge/charge profile resulting from disorder on the metal site, revealed by our neutron diffraction study on the pure Na₆.₆₇[NiₓMn₃₋ₓFeₓO₂₋ₓ]₂O₂ phase. Nonetheless, several reports have outlined the problem of stability of sodium layered transition metal oxides to ambient conditions. The present work establishes that the reactivity of the iron substituted manganese oxides has been underestimated issue, leading to discrepancies in the literature, and establishes the nature of the underlying processes.

Rigorous protection of Na₂/₃[MnₓFe₁₋ₓO₂]₂O₂ against an ambient atmosphere is critical to obtain good electrochemical performance. The material undergoes a complex aging process in air, revealed by our in-depth investigation of its reactivity by TGA-MS under a controlled atmosphere. The oxidation mechanism involves the unprecedented room temperature insertion of CO₂⁻ ions within the transition metal layer of the sodium metal oxide, which is balanced by the oxidation of Mn (III) in the lattice to Mn (IV). Online electrochemical mass spectroscopy proves that the nonsuperimposability of the first two charge curves observed in the case of air-exposed samples results from the decomposition of the inserted carbonate ions. This was confirmed by examining the influence of different mechanisms on the electrochemical behavior of Na₂/₃[MnₓFe₁₋ₓO₂]₂O₂. We show that only the presence of carbonate ions can explain the hysteresis observed in the case of air-exposed samples. Nickel substitution of Na₂/₃[MnₓFe₁₋ₓO₂]₂O₂ is an efficient way of markedly reducing the reactivity to ambient atmosphere. The complex reactivity described in this work should naturally prompt warning when studying sodium layered oxides. However, the possibility of modifying the framework could also be used to tailor new materials by post-treatment. These findings can pave the way to new materials discovery within this large class of materials.

■ ASSOCIATED CONTENT

1 Supporting Information

Detailed powder diffraction refinement results, thermogravimetric analysis, XRD patterns, structural parameters and Rietveld refinement of the t.o.f. NPD pattern of Na₂/₃FeₓMn₁₋ₓO₂ equilibrated under O₂ at 600 °C, and elevated temperature diffraction studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Natural Sciences and Engineering Council of Canada for generous financial support of this work, through their Discovery and Canada Research Chair programs. This research at ORNL’s Spallation Neutron Source was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy. V.D. warmly thanks A. Huq and M. Kirkham at the ORNL for their invaluable help during measurements on the POWGEN diffractometer.

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