Revealing the Reconstructed Surface of Li[\text{Mn}_2\text{O}_4]

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ABSTRACT: The spinel Li[\text{Mn}_3\text{O}_4] is a candidate cathode for a Li-ion battery, but its capacity fades over a charge/discharge cycle of Li_{1-x}[\text{Mn}_2\text{O}_4] (0 < x < 1) that is associated with a loss of Mn to the organic-liquid electrolyte. It is known that the disproportionation reaction 2Mn^{3+} = Mn^{2+} + Mn^{4+} occurs at the surface of a Mn spinel, and it is important to understand the atomic structure and composition of the surface of Li[\text{Mn}_3\text{O}_4] in order to understand how Mn loss occurs. We report a study of the surface reconstruction of Li[\text{Mn}_3\text{O}_4] by aberration-corrected scanning transmission electron microscopy. The atomic structure coupled with Mn valence and the distribution of the atomic ratio of oxygen obtained by electron energy loss spectroscopy reveals a thin, stable surface layer of Mn$_3$O$_4$, a subsurface region of Li$_{1+x}$[\text{Mn}_2\text{O}_4] with retention of bulk Li[\text{Mn}_2\text{O}_4]. This observation is compatible with the disproportionation reaction coupled with oxygen deficiency and a displacement of surface Li$^+$ from the Mn$_3$O$_4$ surface phase. These results provide a critical step toward understanding how Mn is lost from Li[\text{Mn}_3\text{O}_4] once inside a battery.

KEYWORDS: HAADF STEM, EELS, LiMn$_2$O$_4$, Mn-disproportionation, surface reconstruction

The spinel Li[\text{Mn}_3\text{O}_4] (LMO), a candidate cathode for lithium-ion batteries, is known to undergo the disproportionation reaction 2Mn$^{3+}$ = Mn$^{2+}$ + Mn$^{4+}$ at its surface (for convenience, we use the notation Mn$^{n+}$ to indicate the valence state with the knowledge that there is a significant electron transfer from the oxygen ligands to the Mn$^{n+}$ cations). In addition, Li[\text{Mn}_3\text{O}_4] has been shown by Hunter to convert to \lambda-MnO by the extraction of Li$^+$ and Mn$^{4+}$ in a strong acid to leave Mn$^{3+}$ in the spinel octahedral-site framework [\text{Mn}_2\text{O}_4].

Electrochemical extraction of Li from Li_{1-x}[\text{Mn}_2\text{O}_4] is reversible over 0 < x < 1 at ~4.0 V versus a metallic–lithium (Li$^0$) anode, which is well-matched to the highest occupied molecular orbital (HOMO) of the conventional organic liquid-carbonate electrolytes used in a Li-ion battery. This match makes the Li$_{1-x}$[\text{Mn}_2\text{O}_4] spinel system of interest for a low-cost cathode of a Li-ion battery. However, problems with loss of Mn$^{4+}$ from the surface on cycling causes a capacity fade. Additionally, the spinel Li[\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4] provides a high-voltage cathode having a Ni$^{4+}$/Ni$^{3+}$ redox energy pinned at the top of the O-2p bands at about 4.7–4.8 V versus Li$^0$; the electrolyte is oxidized at a V > 4.3 V. This latter spinel is also of fundamental interest because there is a loss of oxygen above 700 °C that induces a segregation of a Ni-rich rock-salt phase that is reabsorbed into the spinel phase on cooling through 700 °C. Moreover, Li$_{1+x}$[\text{Mn}_2\text{O}_4] (0 ≤ x < 1) also retains the spinel framework [\text{Mn}_2\text{O}_4] with the Li being cooperatively displaced from the spinel tetrahedral sites to interstitial octahedral sites of the [\text{Mn}_2\text{O}_4] framework. These observations show that Mn$^{2+}$[\text{Mn}_2$^{3+}$\text{O}_4], Li$_{1+x}$[\text{Mn}_2\text{O}_4] and rock-salt MnO have in common a close-packed-cubic oxide-ion array with the possibility of a facile redistribution of their cations to promote the disproportionation reaction in a surface reconstruction. We have investigated the surface structure of as-prepared Li[\text{Mn}_2\text{O}_4] and show the existence of a thin Mn$^{2+}$[\text{Mn}_2$^{3+}$\text{O}_4] surface phase and a subsurface Li$_{1+x}$[\text{Mn}_2\text{O}_4] phase with bulk Li[\text{Mn}_2\text{O}_4] retained; all three phases have the spinel [\text{Mn}_2\text{O}_4] framework with a redistribution of the interstitial cations.

Materials and Methods. Materials Synthesis. Li[\text{Mn}_3\text{O}_4] (LMO) samples were prepared from lithium and manganese nitrate precursors mixed in solution with citric acid in a molar ratio of 1:1.05 cation to citric acid. The solution was then heated isothermally at 90 °C for 24 h with intermediate calcination twice at 200 °C and then cooled at a rate of 3 °C/min. X-ray powder diffraction (XRD) spectra of the final products were obtained with a Philips XPERT theta–theta diffractometer and Cu Kα radiation with a step size of 0.02° over the 2θ range 10 to 90°.

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Electrochemical Cycling. LMO electrodes were prepared by mixing 78.0 wt % active material in a mortar and pestle with 10.4 wt % carbon and 11.6 wt % polyvinylidene fluoride (PVDF) that was dissolved to 5 wt % in N-methyl-2-pyrrolidone (NMP) and added from solution. The resulting slurry was cast on aluminum foil and heated at 110 °C overnight to dry it. The dried electrode composite was passed through a rolling press to condense it; 5/8”-diameter discs were cut from the sheets. These discs included both electrodes and bare aluminum discs. The final weight of the electrodes was determined by subtracting the average weight of the bare aluminum discs, 0.0117g, from the disc-electrode weight. Typical active material masses were ~4 mg. CR2032 coin cells of LMO cathodes were assembled in an argon-filled glovebox with metallic lithium (Li0) as the anode, 1 M LiPF6 in 1:1 ethylene carbonate—diethyl carbonate as the electrolyte and Celgard polypropylene separators. The cells rested for 6 h before they were galvanostatically cycled at room temperature and a C/10 rate for both charge and discharge between 3.2 and 4.4 V versus Li0, charging first.

STEM/EELS. Low-dose (2.6 × 10⁶ e⁻/Å²) and medium-dose (1.3 × 10⁷ e⁻/Å²) HAADF STEM images (Table 1 for dose conditions) were taken on a JEOL ARM200F with a 200 kV acceleration voltage and a probe diameter of ~1.0 Å. In the gun-lens system an A1 anode voltage of 3.14 kV and an A2 anode voltage of 7.05 kV were used. Probe currents were measured with a picoammeter at the large phosphorus viewing screen, the small phosphorus viewing screen, and at the sample with a faraday cup holder. The currents measured at the Faraday cup were the currents used for dose calculations. For low-dose STEM imaging, the probe current was 4.3 pA with a pixel dwell time of 10 μs. For medium-dose STEM imaging, the probe current was 12.7 pA with a pixel dwell time of 31.8 μs.

Table 1. Dose Conditions for the Various Techniques Used in This Study

<table>
<thead>
<tr>
<th>Condition</th>
<th>Probe current (pA)</th>
<th>Probe diameter (Å)</th>
<th>Dose rate (10⁷ e⁻/Å²)</th>
<th>Pixel dwell time (μs)</th>
<th>Geometric factor</th>
<th>Dose (10⁷ e⁻/Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-Dose STEM Conditions</td>
<td>4.3</td>
<td>~1.0</td>
<td>(3.4 × 10⁶)</td>
<td>10.0</td>
<td>7.8</td>
<td>(2.6 × 10⁶)</td>
</tr>
<tr>
<td>Medium-Dose STEM Conditions</td>
<td>12.7</td>
<td>~1.0</td>
<td>(1.0 × 10⁷)</td>
<td>38.8</td>
<td>40</td>
<td>(1.3 × 10⁷)</td>
</tr>
<tr>
<td>High-Dose EELS Conditions</td>
<td>30</td>
<td>~1.0</td>
<td>(2.4 × 10⁸)</td>
<td>200</td>
<td>1</td>
<td>(4.8 × 10⁹)</td>
</tr>
</tbody>
</table>

The geometric factor is an approximation of electron probe overlap when scanning at high magnifications. It is included as a multiple in the dose calculation. A geometric factor of one indicates no electron probe overlap.

High-dose (4.8 × 10⁹ e⁻/Å²) EELS collection (Table 1) was performed on a NION UltraSTEM100 at 100 kV with a collection angle of 48 mrad, a probe current of 30 pA, a probe diameter of ~1.0 Å, and a pixel dwell time of 200 ms. Low-dose, medium-dose, and high-dose are relative terms used to express increasingly higher doses, each term separated by many orders of magnitude. The low-dose STEM imaging in this work is within an order of magnitude of the low-dose STEM imaging conditions established by Buban et al.⁵ and represents the lowest dose practicable. All STEM images and EELS data were collected under high vacuum conditions (<1 × 10⁻⁷ Torr) on as-prepared, uncycled LMO particles.

STEM Simulations. Atomic models for STEM simulations were created in VESTA⁶ and exported to the HREM Simulation Suite having a TEM/STEM simulation software package based on the FFT multislice technique.⁷ The HREM Simulation Suite evaluates, based on the approximation of Weickenmeier and Kohl,⁸ both the wave function and its Fourier transform at each slice to calculate the elastic scattering amplitude. This approximation is appropriate for electrons scattered at high angles, which is the geometry for recording HAADF images.⁹,¹⁰ The HAADF intensity is then calculated by adding the thermal diffuse scattering factor to the elastic scattering amplitude. This term is important as atomic vibrations dampen the intensity of the electron waves as they pass through the specimen. The microscopy parameters used for the simulations include an acceleration voltage of 200 kV, a condenser aperture of 20 μm, a convergence angle of 16–18 mrad, HAADF collection angles between 50 and 180 mrad, a sample thickness of 50 nm, and a probe diameter of 0.8 Å. These parameters correspond to the settings used in the operation of the JEOL ARM200F. For each structure, the multislice simulations were carried out by assuming a step scanning size of 0.2 Å (less than the distance to be resolved) and a minimum slice thickness of 1.0 Å.

Results. The Li:Mn ratio of our LMO sample was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) to be 1.05:2.00 compared to the ideal 1.00:2.00. Electrochemical cycling (Figure 1) gave the characteristic voltage profile and capacity of LMO in good agreement with previously published results.⁴ First galvanostatic cycle of LMO, charging first (black line) to 4.4 V and then discharging (red line) to 3.2 V. Observed in the profile are the two intrinsic plateaus characteristic of LiMn₂O₄.
agreement with literature data.\textsuperscript{11} XRD of the as-prepared LMO powder confirmed the spinel structure (space group $Fd\bar{3}m$) without any visible impurities (Figure 2). The lattice parameter was 8.222 Å.

For STEM imaging, the sample was tilted to be viewed along the [110] cubic axis of the spinel structure where like-atom columns are parallel to the electron beam. In order to facilitate interpretation of the HAADF STEM images, a structural model of LMO was built and rotated along the [110] cubic-spinel axis, as shown in Figure 3A. A diamond unit (shaded-blue area) is characteristic of the spinel structure and is referred to as the LMO diamond. The periphery of the diamond consists of octahedral-site Mn atoms (shown in purple); the tetrahedral sites occupied by Li in LMO are shown in green, and the oxygen atoms are shown in red. Due to the mass-thickness contrast of the atomic columns in the HAADF STEM images of Figure 3B, only the Mn atoms of the diamond periphery are visible.

Figure 4 shows a medium-dose ($1.3 \times 10^5 \text{ e}^-/\text{Å}^2$) STEM image of an LMO sample where both the bulk and the surface are visible. The bulk of the sample shows the LMO diamonds indicative of the $[\text{Mn}_2]\text{O}_4$ spinel framework; however, the surface shows quite clearly LMO diamonds containing Mn in the tetrahedral sites, which is indicative of a surface reconstruction where Mn ions displace the surface Li to a subsurface $\text{Li}_{1+x}[\text{Mn}_2]\text{O}_4$ phase. The surface phase (Figure 5) can be characterized by two columns of Mn occupying the Li tetrahedral sites within the LMO diamond, or equivalently, as a hexagonal ring of Mn columns with a brighter column of Mn in the center; we refer to this surface-phase as the “ring-phase”. There is no room for the Li in the ring phase, and only oxygen can be displaced to the vacuum. The stable $\text{Li}_{1+x}[\text{Mn}_2]\text{O}_4$ phase is known to have an $x > 0.8$ with the Li displaced to the octahedral sites of the interstitial space of the $[\text{Mn}_2]\text{O}_4$ framework.\textsuperscript{4} However, the contrast of a HAADF STEM image of the $\text{Li}_{1+x}[\text{Mn}_2]\text{O}_4$ phase is indistinguishable from the LMO diamond image. Instead, due to the occupancy of excess Li in the $\text{Li}_{1+x}[\text{Mn}_2]\text{O}_4$ phase, the LMO and $\text{Li}_{1+x}[\text{Mn}_2]\text{O}_4$ can be distinguished by their unique Mn oxidation states.

In order to determine the distribution of Mn valence states in LMO, the tip of a particle was analyzed along the cubic spinel [110] axis with a 100 keV NION UltraSTEM in high-dose ($4.8 \times 10^7 \text{ e}^-/\text{Å}^2$) EELS mode; the images were taken after the bulk LMO diamonds and surface ring phases had been confirmed. The results are presented in Figure 6. Three distinct compositional ranges were identified by their unique EELS signatures.\textsuperscript{12} The surface layer of the particle to a depth equal to that of the observed ring-phase layer was found to contain a mixture of Mn$^{3+}$ and Mn$^{2+}$ ions as in Mn$^{2+}[\text{Mn}_2^{3+}]\text{O}_4$; the bulk contained a mixture of Mn$^{4+}$ and Mn$^{3+}$ as expected for Li$[\text{Mn}^{4+}\text{Mn}^{3+}]\text{O}_4$; and a region intermediate to the bulk and surface phases consisted almost exclusively of Mn$^{3+}$ ions as expected for Li$_{1+x}[\text{Mn}_2]\text{O}_4$ ($x > 0.8$). Further analysis of the EELS data of Figure 6 shows an oxygen deficiency near the surface. Although there may be some loss of surface oxygen during the high-dose EELS experiments, the shift in Mn valence from Mn$^{3+}$ and Mn$^{2+}$ at the surface to an all-Mn$^{3+}$ subsurface to Mn$^{4+}$ and Mn$^{3+}$ in the bulk is qualitatively indicative of the shift observed during low-dose and medium-dose STEM imaging. Upon further refinement of the electron energy loss spectra in Figure 6, the atomic percent oxygen is found to be approximately 57% for the near-surface region and 66% for both the intermediate and bulk regions; these values are very close to the ideal full oxygen-coordination values of 57.1% for...
Figure 4. HAADF STEM image of LMO viewed along the [110] zone axis (top). LMO diamonds (blue) are found in the bulk, while a new phase (red diamond) is visible at the surface. A fast Fourier transform (FFT) of the original full image is included to indicate the crystal orientation (top inset). Magnified images of the new phase and the LMO diamond are included on the bottom left and right, respectively.

Figure 5. (A) Atomic structural model of the Mn₃O₄ along the [110] zone axis. Mn atoms (purple) occupy both octahedral and tetrahedral sites. The oxygen atoms are depicted in red. The orange-colored hexagon is an alternative unit to recognize the formation of Mn₃O₄. In this case the periphery contains Mn columns of similar mass, forming a ring-type structure, while the center is composed of a higher density Mn column. This is the origin of the name “ring phase.” (B) Corresponding simulated HAADF STEM image.
Mn\textsuperscript{2+}[Mn\textsuperscript{3+}]O\textsubscript{4} and 66.7\% for Li\{Mn\textsuperscript{4+}Mn\textsuperscript{3+}\}O\textsubscript{4} and Li\textsubscript{1+x}[Mn\textsubscript{2}]O\textsubscript{4} (x > 0.8).

**Discussion.** Benedek and Thackeray\textsuperscript{13} have argued that all three \{100\}, \{110\}, and \{111\} spinel surface planes of LMO are unstable and would undergo a reconstruction. They also indicated that all surfaces of LMO contain, on average, a lower Mn oxidation state than their bulk counterparts, which would necessitate a deficiency of oxygen in order to balance charge. However, it has been unknown what surface reconstruction should take place and what phases should form at the surface of LMO. Richard et al.\textsuperscript{14} investigated with XRD the reduction of LMO under a flow of ammonia and proposed the following reaction:

\[
18\text{LiMn}_2\text{O}_4 + 8\text{NH}_3 = 9\text{Li}_2\text{Mn}_2\text{O}_4 + 6\text{Mn}_3\text{O}_4 + 12\text{H}_2\text{O} + 4\text{N}_2
\]

which corresponds to the creation of both a Li-rich (Li\textsubscript{2}Mn\textsubscript{2}O\textsubscript{4}) and a Mn-rich (Mn\textsubscript{3}O\textsubscript{4}) spinel phase upon the loss of oxygen from the surface of LMO.

Figure 6. HAADF STEM image of an LMO particle (top). The green rectangle in the STEM image shows the area from where an EEL spectrum image was acquired. The colored maps (red, yellow, and green) and corresponding colored spectra below each image represent the location of different Mn valence states within the nanoparticle. The atomic ratio of oxygen extracted from the O–K and Mn L\textsubscript{2,3} edges is shown (middle right). The black arrow shows where the atomic ratio of oxygen (bottom right) was extracted. The ratio is determined by the number of oxygen atoms to the total number of atoms in the sample.
In our experiments, a surface layer of the spinel ring phase \( \text{Mn}_3\text{O}_4 \) is stabilized on every surface including the low index surfaces mentioned specifically by Benedek and Thackeray. There is also a Li-rich subsurface layer as indicated with the spectra acquired with EELS. These observations are consistent with the mechanism shown by Richard et al. and with the assertions proposed by Benedek and Thackeray.

\( \text{Li}_x\text{Mn}_2\text{O}_4 \) contains 50:50 \( \text{Mn}^{4+} : \text{Mn}^{3+} \), so its surface can undergo the Mn disproportionation reaction \( 2\text{Mn}^{3+} = \text{Mn}^{2+} + \text{Mn}^{4+} \) with corresponding oxygen deficiency to create a stable surface layer of \( \text{Mn}^{2+}[\text{Mn}^{3+}]\text{O}_4 \). Mn\(^{2+}\) can be expected to induce a surface restructuring in which the Mn\(^{3+}\) displace Li\(^+\) from the tetrahedral sites to a subsurface phase to maintain stoichiometry. Mn\(^{2+}\) has a strong tetrahedral-site preference and \( \text{Li}_x\text{Mn}_2\text{O}_4 \) with \( x > 0.8 \) is a stable phase with all the Li in the interstitial octahedral sites of the spinel framework; the surface \( \text{Mn}_3\text{O}_4 \) spinel phase is essentially 2D. This surface reconstruction creates a more stable, cation-dense surface layer that is oxygen-deficient as compared to stoichiometric LMO in order to achieve local charge neutrality.

Benedek and Thackeray suggest that pristine LMO surfaces are unstable and therefore have to undergo a reconstruction. Either the surface will always reconstruct in the manner discussed above and is stable during STEM observation or the act of STEM observation causes the reconstruction of LMO’s pristine yet unstable surfaces. Both scenarios would result in the surface reconstruction shown in this work. The only way to determine if the surface reconstruction of LMO is electron-beam-induced and not native is to minimize the effect of the electron beam and observe an unreconstructed LMO surface.

An effort was made to minimize the electron dose delivered during HAADF STEM imaging in accordance with established low-dose STEM conditions. Figure 7B shows a Fourier-filtered image of LMO in which the surface \( \text{Mn}_3\text{O}_4 \) phase is observed, even under low-dose STEM conditions \((2.6 \times 10^3 \text{ e}^-/\text{Å}^2)\). Figure 7C shows a higher magnification image of the same surface in Figure 7A, which illustrates the stability of the surface even under higher-dose conditions \((5.3 \times 10^4 \text{ e}^-/\text{Å}^2)\). When LMO is damaged purposefully with a very high electron dose \((1.5 \times 10^9 \text{ e}^-/\text{Å}^2)\) from an EELS probe, the LMO spinel structure converts into a completely different structure—the rock-salt structure (Figure 8)—which is not otherwise observed. From this result, we conclude that if the \( \text{Mn}_3\text{O}_4 \) ring phase was indeed caused by the electron beam, it would be expected that LMO would convert into the ring phase under very-high-dose conditions rather than the rock-salt phase that is observed.

The atomic structure of LMO, revealed during low-dose and medium-dose STEM imaging, and the Mn-valence and the distribution of the atomic ratio of oxygen obtained by high-dose EELS correlate well with a \( \text{Mn}_3\text{O}_4 \) surface phase, a \( \text{Li}_{1+x}\text{Mn}_2\text{O}_4 \) subsurface region and bulk \( \text{Li}_x\text{Mn}_2\text{O}_4 \). These results, coupled with the deliberate damaging of LMO, which led to a rock-salt phase, suggest that the \( \text{Mn}_3\text{O}_4 \) and \( \text{Li}_{1+x}\text{Mn}_2\text{O}_4 \) phases observed are a result of stabilized LMO surfaces and not a forced reconstruction due to an effect of the electron beam.

Research on surface structural changes in cathodes using advanced electron microscopy techniques has been performed previously\(^{5,16}\) but that work was focused on the restructuring of layered cathodes after cycling. In fact, a surface \( \text{Mn}_3\text{O}_4 \) phase...
has been reported in LMO, but those works also indicate phase formation after cycling. In those cases the cathodes were cycled to above 4.1 V to as high as 5.1 V versus Li. Overcharging of LMO induces the evolution of O₂ from the particle’s surface. Since oxidation of Mn⁴⁺ in an oxide does not occur, holes are introduced into the O-2p bands. These surface peroxide ions condense, and O₂ is evolved from the material. By electrochemically evolving oxygen, the amount of Mn₃O₄ phase observed at the surface of LMO would be much thicker than the surface observed in our uncycled material. Indeed, Tang et al. observed thick regions of Mn₃O₄ in their electrochemically cycled material.

Although both Mn²⁺[Mn₃⁺]O₄ and Li₂[Mn₃⁺]O₄ have a sufficient concentration of Mn³⁺ to give a cooperative Jahn–Teller distortion to tetragonal c/a > 1 in the bulk phases, our images provide no evidence of a distortion from cubic symmetry for either phase. We presume the 2D character of these phases bonded to a cubic bulk phase prevents a room-temperature cooperative Jahn–Teller distortion.

There is an interesting and significant implication that arises given this surface reconstruction in LMO. The Mn₃O₄ surface phase contains Mn in tetrahedral and octahedral sites, but the cathode is able to shuttle Li⁺ into and out of the bulk during cycling despite the apparent Mn blockage. Perhaps Li is inserted into and out of Mn₃O₄ by a rocksalt conversion that should increase the activation energy for Li transport between the bulk and the electrolyte.

**Figure 8.** HAADF STEM image of LMO after irradiating the near surface with a very high electron dose (1.5 × 10⁸ e⁻/Å²) from an EELS line scan. The red circle demarcates the area of the sample damaged by the electron beam. Both the Mn₃O₄ ring phase and the LMO phase are transformed into a previously unobserved rock-salt phase (green). This result suggests that the Mn₃O₄ and Li₁−x[Mn₃⁺]O₄ phases observed are a result of stabilized LMO surfaces and not forced reconstruction due to an effect of the electron beam.
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NOTE ADDED AFTER ASAP PUBLICATION

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