

## Effect of Chemical Treatment on the Surface Structure of $\text{Li}_{1-x}[\text{Mn}_2]\text{O}_4$

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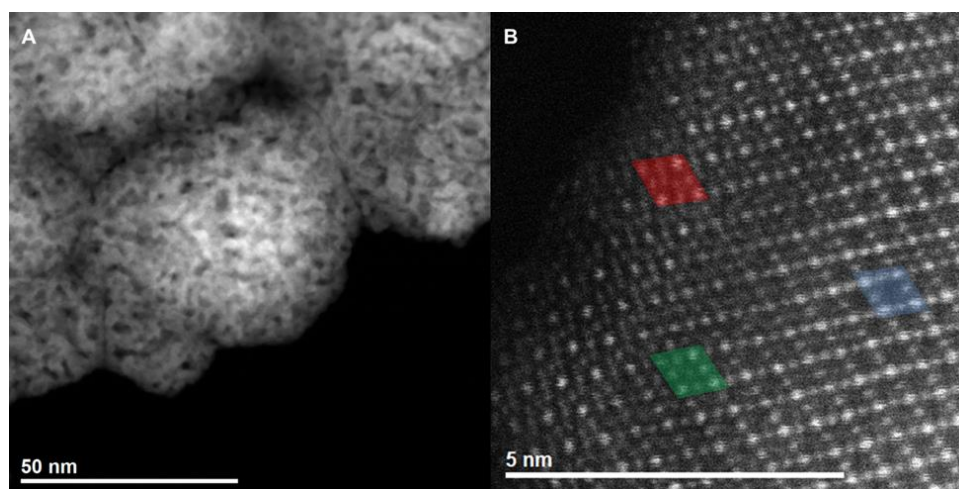
The rising need for portable energy storage has led to the creation of a formidable Li-ion battery industry, which is poised to grow strongly in the near future [1]. Of the many cathode chemistries for Li-ion batteries,  $\text{Li}[\text{Mn}_2]\text{O}_4$  (LMO) stands out as a particularly appealing cathode due to its moderate capacity, use of environmentally-friendly and cost-effective Mn, and high rate capabilities associated with its cubic spinel framework, which allows three dimensional  $\text{Li}^+$  diffusion. These attributes are attractive, but in order to realize these benefits and significantly contribute to the Li-ion battery industry, its cyclability must be improved. The cyclability issues of LMO are associated with the loss of  $\text{Mn}^{2+}$  from its surface to the organic liquid electrolyte during electrochemical cycling. The surface disproportionation of Mn ( $2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$ ) creates the  $\text{Mn}^{2+}$  and leads to a stabilization of the surface of LMO through a surface reconstruction that creates a thin surface layer of  $\text{Mn}_3\text{O}_4$  and a Li-rich subsurface layer of  $\text{Li}_{1+x}[\text{Mn}_2]\text{O}_4$  [2].

In this work, to further understand the sensitivity of the surface reconstruction of LMO and therefore the surface disproportionation of Mn to Li content and chemical environment, we have applied an aqueous acid treatment, a non-aqueous chemical delithiation, and an oxygen plasma treatment to LMO. The acid treatment removes  $\text{Li}^+$ ,  $\text{Mn}^{2+}$ , and oxygen in the form of water from LMO in a strong acid solution, just as Hunter described previously [3]. Chemical delithiation only removes  $\text{Li}^+$  from LMO through a direct chemical reaction in a non-aqueous solvent, similar to what occurs in a battery [4]. The oxygen plasma treatment creates a highly reactive, oxidative atmosphere that reacts with LMO, which can decrease the content of  $\text{Li}^+$  and oxygen relative to the amount of Mn. In order to study the effects of the various chemical treatments, we use a combination of high-angle annular dark-field (HAADF) aberration-corrected scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) to identify the atomic surface structure and chemistry of  $\text{Li}_{1-x}[\text{Mn}_2]\text{O}_4$ .

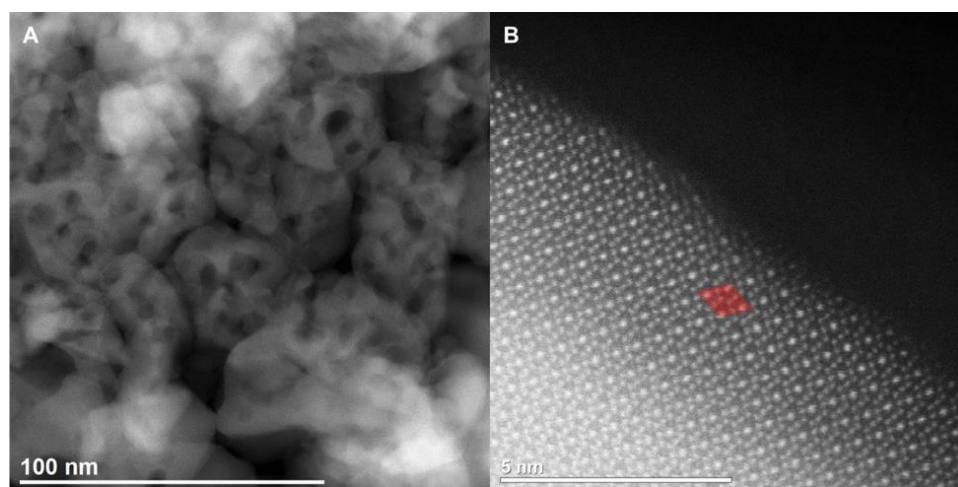
We find that  $\text{Mn}_3\text{O}_4$  is a robust surface phase in the  $\text{Li}_{1-x}[\text{Mn}_2]\text{O}_4$  system regardless of the chemical treatment that is applied and the level of lithiation. The surface of  $\text{Li}_{1-x}[\text{Mn}_2]\text{O}_4$  will contain at least a thin layer of  $\text{Mn}_3\text{O}_4$  that is cubic due to a lack of Jahn-Teller cooperativity, but when the layer becomes thicker, it gains sufficient cooperativity to undergo a thermodynamically-favorable tetragonal distortion. Surface reconstruction to  $\text{Mn}_3\text{O}_4$  occurs in untreated LMO and all of the chemically-treated samples indicating the unavoidable surface disproportionation of Mn ( $\text{Mn}_b^{3+} + \text{Mn}_s^{3+} \rightarrow \text{Mn}_b^{4+} + \text{Mn}_s^{2+}$ , where b is bulk, and s is surface) [5]. Our work shows the surface structure of LMO with and without Li, representing the discharged and charged states, respectively, which are encountered in a fully-assembled battery. Our fundamental understanding of this system is providing new insights into mitigating the non-faradaic surface reactions that occur in LMO and thus contributing to the development of this promising cathode material.

## References:

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**Figure 1.** (A) Low-resolution HAADF STEM image of chemically-delithiated LMO powder indicating significant porosity (Titan, Dose Rate:  $1.3 \times 10^9 \text{ e}^-/\text{\AA}^2\cdot\text{s}$ , Dose:  $4.9 \times 10^4 \text{ e}^-/\text{\AA}^2$ , Geometric Factor (GF): 1). (B) High-resolution HAADF STEM image of chemically delithiated LMO that confirms the bulk spinel structure (blue) as well as the surface  $\text{Mn}_3\text{O}_4$  phase (red) (ARM200F, Dose Rate:  $1.0 \times 10^8 \text{ e}^-/\text{\AA}^2\cdot\text{s}$ , Dose:  $1.3 \times 10^5 \text{ e}^-/\text{\AA}^2$ , GF:40). An additional rock-salt phase (green) is observed subsurface.



**Figure 2.** (A) Low-resolution HAADF STEM image of oxygen-plasma-treated LMO powder indicating a substantially modified morphology with large cavities, indicating a significant loss of powder material. (Titan, Dose Rate:  $4.0 \times 10^8 \text{ e}^-/\text{\AA}^2\cdot\text{s}$ , Dose:  $8.7 \times 10^3 \text{ e}^-/\text{\AA}^2$ , GF: 1). (B) High-resolution HAADF STEM image of oxygen-plasma-treated LMO showing a thick  $\text{Mn}_3\text{O}_4$  surface phase (red), thicker than the one that occurs in untreated LMO (ARM200F, Dose Rate:  $1.0 \times 10^8 \text{ e}^-/\text{\AA}^2\cdot\text{s}$ , Dose:  $2.5 \times 10^5 \text{ e}^-/\text{\AA}^2$ , GF: 79).