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Surface stability of oxygen deficient $LiMn_2O_4$ thin films

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Although $LiMn_2O_4$ is a promising cathode material for Li ion batteries, the capacity fade observed during cycling limits its ability to meet reliability requirements for applications such as electric vehicles. Capacity fade has been attributed to Mn dissolution and surface reactions with the electrolyte that consume the active cathode material and inhibit charge transport (1-6). The extent of Mn dissolution depends on the disproportionation reaction of Mn^{3+} (7-11). The average oxidation state of Mn in $LiMn_2O_4$ is 3.5, where the oxidation state of surface Mn may be lower due to reduced coordination, resulting in a surface that is more susceptible to dissolution. Oxygen deficiency can also lower the Mn oxidation state and reduce surface stability. High spatial resolution imaging of oxygen deficient $LiMn_2O_{4-\delta}$ surfaces with well-defined microstructure following potential cycling would allow a better understanding of surface Mn dissolution.

We have used pulsed layer deposited thin films of (111) oriented $LiMn_2O_4$ as a model system to study the effect of oxygen stoichiometry on surface stability and degradation during potential cycling. Oxygen deficient surfaces are created by annealing the films after growth in an argon atmosphere for short times at temperatures between 450°C and 500°C. Atomic force microscope (AFM) images show that the initial surface morphology does not change after annealing in either air or argon. Furthermore, the surface of the films annealed in both air and argon remains stable while cycling the potential in EC:DMC:$LiPF_6$ between 3.8 V and 4.3 V vs Li/Li^+ up to 40 times. However, after 50 potential cycles, the films annealed in argon show clear signs of dissolution and reaction product formation as shown in Figure 1. The mechanisms responsible for the loss in surface stability due to oxygen deficiency will be discussed based on studies of surface constituents and charge transport using x-ray photoelectron and impedance spectroscopy measurements.

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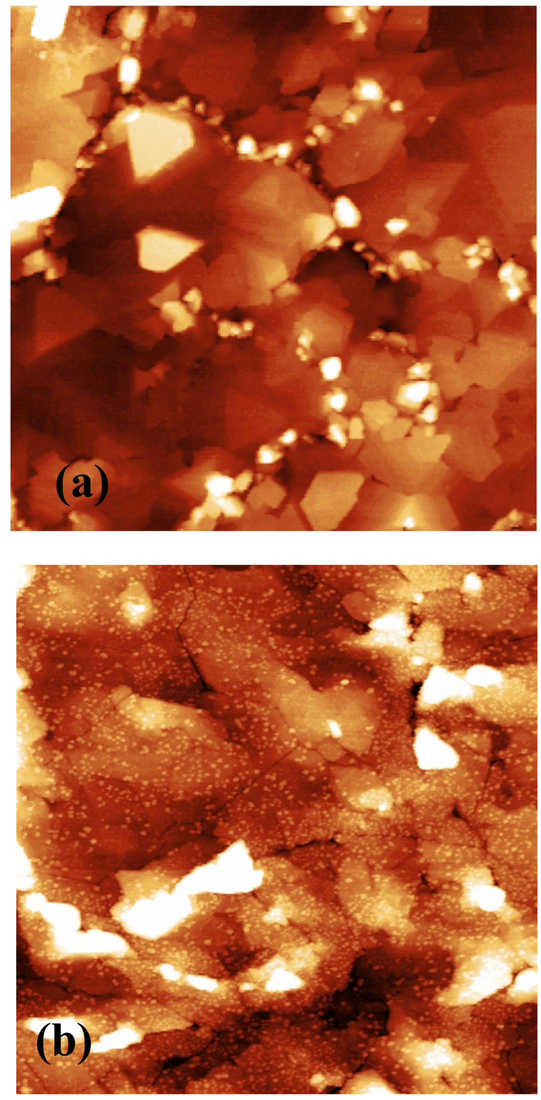

Figure 1: 1 x 1 µm AFM images comparing surface stability following 50 potential cycles of (a) $LiMn_2O_4$ thin film annealed in air and (b) an oxygen deficient film showing surface dissolution and reaction products.

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