

In-situ atomic force microscopy study of surface microstructure stability on  $\text{LiMn}_2\text{O}_4$  thin films

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$\text{LiMn}_2\text{O}_4$  is one of the most promising cathode materials for Li ion batteries. However, it suffers from capacity fade due to surface reactions that occur during cycling, consuming the active material and forming a surface layer that inhibits charge transport. (1-6) A detailed understanding of the factors contributing to interfacial layer formation during cycling is needed in order to optimize battery performance and mitigate capacity fade. One of the factors that can influence reactions with the electrolyte are surface defects, where their type and density may be controlled by local microstructure. In-situ, small length scale probes of  $\text{LiMn}_2\text{O}_4$  surfaces with well-defined microstructure would allow the importance of specific microstructural features to be determined. The role of microstructural defects on surface reactions would be very difficult to investigate in typical battery cathodes, containing polycrystalline active material powder mixed with conductive carbon and binder.

In order to address these questions we have used pulsed layer deposited thin films of  $\text{LiMn}_2\text{O}_4$  with specific microstructural features as a model system to study surface stability and degradation. The oriented thin films offer a unique geometry for in-situ, small length scale measurements. In-situ atomic force microscopy (AFM) is used to investigate surface layer morphology during potential cycling in  $\text{LiPF}_6/\text{EC}/\text{DMC}$  on pulsed laser deposited films consisting of (111) oriented terraces and faceted grains protruding from the smooth background. Our initial results show the clear formation of nanoscale reaction products that can form near (111) step edges, but with higher concentrations near off-(111) axis faceted grains. Our results show that surface layer formation depends upon the initial microstructure, where (111) planes are the most stable, Figure 1 (a), while off-(111) axis facets are the most reactive, Figure.1b. These results indicate that the initial surface morphology is critical in formation of the interfacial layer, where reactions with the electrolyte occur at preferential sites.

This work is supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Science and Engineering. Sandia National Laboratories is a multi-program laboratory, managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U. S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

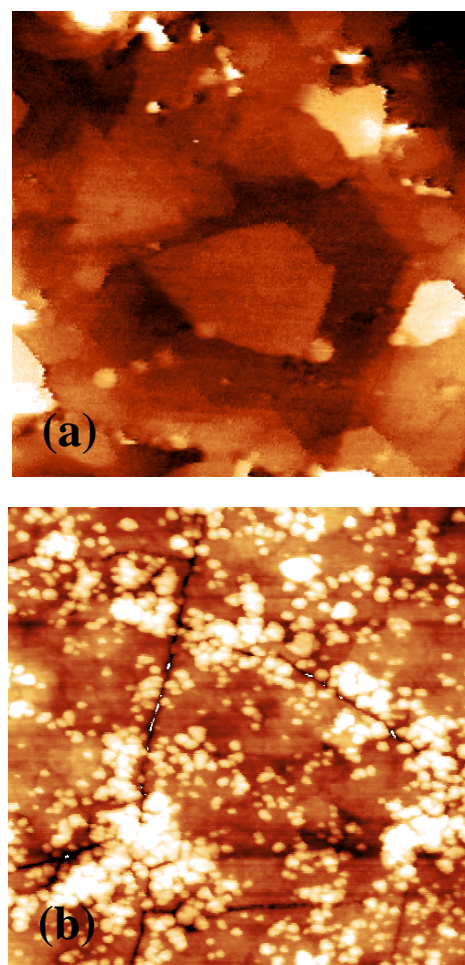


Figure 1: 500 x 500 nm AFM images of (a) (111) oriented  $\text{LiMn}_2\text{O}_4$  showing the formation of localized surface reaction products during potential cycling (b) film with high off-(111) axis facet density showing extensive surface reaction products following potential cycling.

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