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TEM Analysis of Model Li-Ion Battery Cathodes Grown by Molecular Beam Epitaxy

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The search for new cathode materials that can intercalate Li-ions more efficiently and at higher reversible concentrations is still a highly active research area, with considerable interest on lithium transition metal oxides, such as $LiMn_2O_4$. Studies have shown that thin layer of simple oxide/complex oxide coating of spinel $LiMn_2O_4$ allows improved electrochemical performance such as capacity and cyclability. [1,2] However, these materials are generally only available as coarse powders, making detailed study of surfaces and interfaces difficult. Single crystals provide well-defined orientations, defect concentrations, and surface terminations that allow isolation of specific chemical and structural aspects of intercalation to be examined. These features make single crystals highly desirable for characterization of pristine and cycled cathodes, compared to polycrystals/particles.

Here, we show that single-crystal $LiMn_2O_4$ films can be grown on $SrTiO_3$ substrates molecular beam epitaxy (MBE) and will function as model cathodes for Li-ion batteries. MBE thin film synthesis allows for atomically flat layers to be grown with well-defined surface terminations, orientations, defect concentrations and a homogenous distribution of compositional elements, which provides a good opportunity to characterize the cathodes in pristine and cycled states. The simplicity of single crystals, compared to polycrystalline particulate cathode materials allows specific structural and chemical aspects of intercalation to be isolated and examined using nanoscale characterization techniques such as transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and electron energy-loss spectroscopy (EELS), as well as X-ray diffraction (XRD), or X-ray photoemission spectroscopy (XPS).

A considerable body of experimental evidence has shown that crystallinity, compositional homogeneity, crystallographic orientation, point defects, and grain boundaries influence Li ion transport [3,4]. Single-crystal model systems give access to each of these properties, and can be optimized for atomic-scale characterization, such as thinning to full electron transparency for STEM. Furthermore, these experiments will be essential for careful study of SEI layer, Li-ion diffusivity, and understanding structural framework changes in cycled cathodes to improve cyclability and capacity retention.

Several ~100 nm thick films were grown in via MBE in an ultra-high vacuum (UHV) environment. Elemental flux rate, oxygen partial pressure, and growth temperature were adjusted to obtain higher crystalline films. STEM, EDS, EELS measurements were performed in a JEOL ARM200CF at UIC, while XRD and XPS are used for structural and chemical characterization. Figure 1a-e) shows the XRD pattern of film, XPS spectrum of Mn L-edge, EDS quantitative analysis, and Li *K*-edge EEL spectrum for one of the samples. Figure 2a-d) shows the thickness, crystallinity, defects, and diffraction spots from the same film obtained using a JEOL JEM3010 TEM. The images confirm that we have successfully synthesized MBE thin films of lithium manganate suitable both for electrochemical testing and for high-resolution STEM/EDS/EELS characterization. Electrochemical tests were performed to study structural changes in the film and interfaces during (de)intercalation [5].

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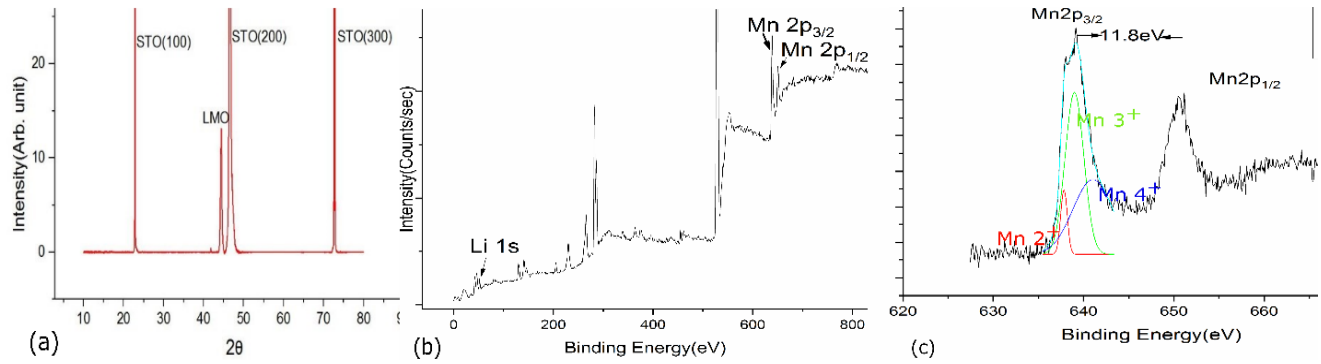
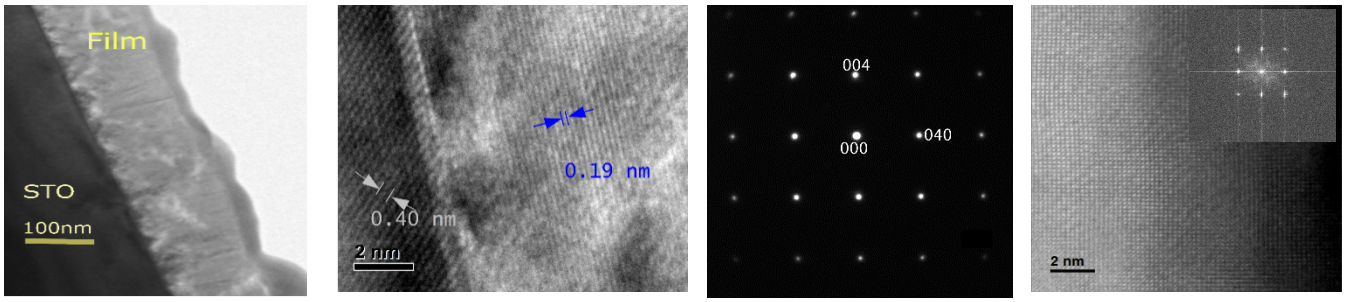


Figure 1. (a) XRD pattern, (b) XPS spectrum of Li k-edge, Mn L-edge, (c) Mn L-edge



(a) (b) (c) (d)

Figure 2. (a) TEM image of film, (b) STO/LMO interface and lattice fringes (c) Selected area diffraction (SAED) along [001] zone axis, and (d) FFT filtered HAADF- STEM image, inset showing FT of the image

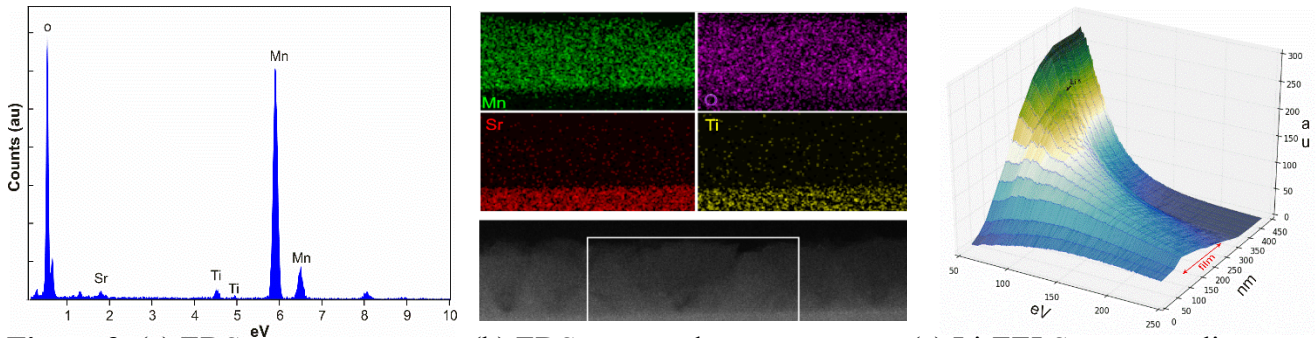


Figure 3. (a) EDS spectrum (b) EDS map, and (c) Li-EELS spectrum line scan

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