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TEM Analysis of MBE Grown Model Li-Ion Cathodes

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Rechargeable batteries, especially Li-ion batteries, are at the frontline of energy storage technologies. The application of these batteries ranges from portable electronics to electric vehicles to grid scale energy storage. Lithium transition metal oxides, such as $LiMn_2O_4$ (LMO) has been an active area of research because of their cost efficacy, higher thermal stability, and environmental safety [1,2]. Nevertheless, all LMO still suffers from significant capacity fading during charge/discharge which has hindered its commercial exploitation. Thus, it is critical to identify mechanisms behind such capacity fading and implement preventive measures.

While examine both pristine and cycled cathodes, most of the analysis are done primarily in polycrystalline or nonpowered form. Due to mixture of crystallographic orientations as well as conductive carbonaceous materials used in such studies, the interpretation of surfaces and interfaces becomes complicated. Several experiments have shown that shown that crystallinity, crystallographic orientation, compositional homogeneity, point defects, and grain boundaries influence Li ion transport inside the host lattice as well as at the interface [3,4]. As such, epitaxial thin films with high crystallinity and well defined orientation are preferred. A novel method to grow such films is molecular beam epitaxy (MBE). The unique features of MBE grown thin films allow for precise control of stoichiometry, compositional homogeneity, defect concentrations surface terminations, and crystal orientation which are fundamental while analyzing surface reactions and structural changes. Previously, we reported the growth of MBE thin films of LMO cathodes on $SrTiO_3$ (STO) substrates [5]. Our single-crystal model system provides access to each of these properties, and can be optimized for atomic-scale characterization, x-ray measurements and transmission electron microscopy (TEM) observations.

100 nm thick LMO (001) and LMO(111) films were grown on STO(001) and STO(111) respectively. For electrochemical measurements, 10 nm conductive buffer layer of $SrRuO_3$ (SRO) were deposited on STO before the depositing the films. Half-cells were constructed using lithium as counter electrode, glass fiber separator, and 1M lithium hexafluorophosphate in 1:1 ethylene carbonate: dimethyl carbonate (1 M $LiPF_6$ in 1:1 EC: DC) electrolyte. All assemblies were done inside an argon filled glove box with <1 ppm H_2O and <1 ppm O_2. Cyclic voltammetry (CV) was conducted using scan rates from 1 mV/s to 20 mV/s, and potential window from 3.5V to 4.5V to ensure complete charge/discharge of the films. Figure 1(a) and 1(b) shows the HAADF images of LMO (001) films taken along STO[001] and STO[110] zone axis respectively confirming the epitaxial growth at the interface as well as in bulk areas. Figure 1(c-d) show EELS measurements for pristine and charged films. The absence of lithium peak in charged film shows lithium deintercalation during charge. This agrees with the slight position shift in Mn *M*- edge towards slightly higher energy value indicating average Mn valence increase. Figure 1(e) shows the cyclic measurement of films at different scan rate. A couple of paired redox peaks are clearly visible indicating good cyclability of the LMO (001) films. Surface reconstruction as well as loss of thickness via corrosion of active materials were observed in the cycled films (not shown). Similar behaviors were also observed for the grown LMO (111) films. These experiments show, for the first

time, the growth and cyclability of LMO epitaxial thin films using MBE. This model growth system provides opportunities for thin film cathodes examination of surfaces/interfaces along a particular crystal orientation and avoid complicating of using nano-particles/ polycrystalline materials.[6]

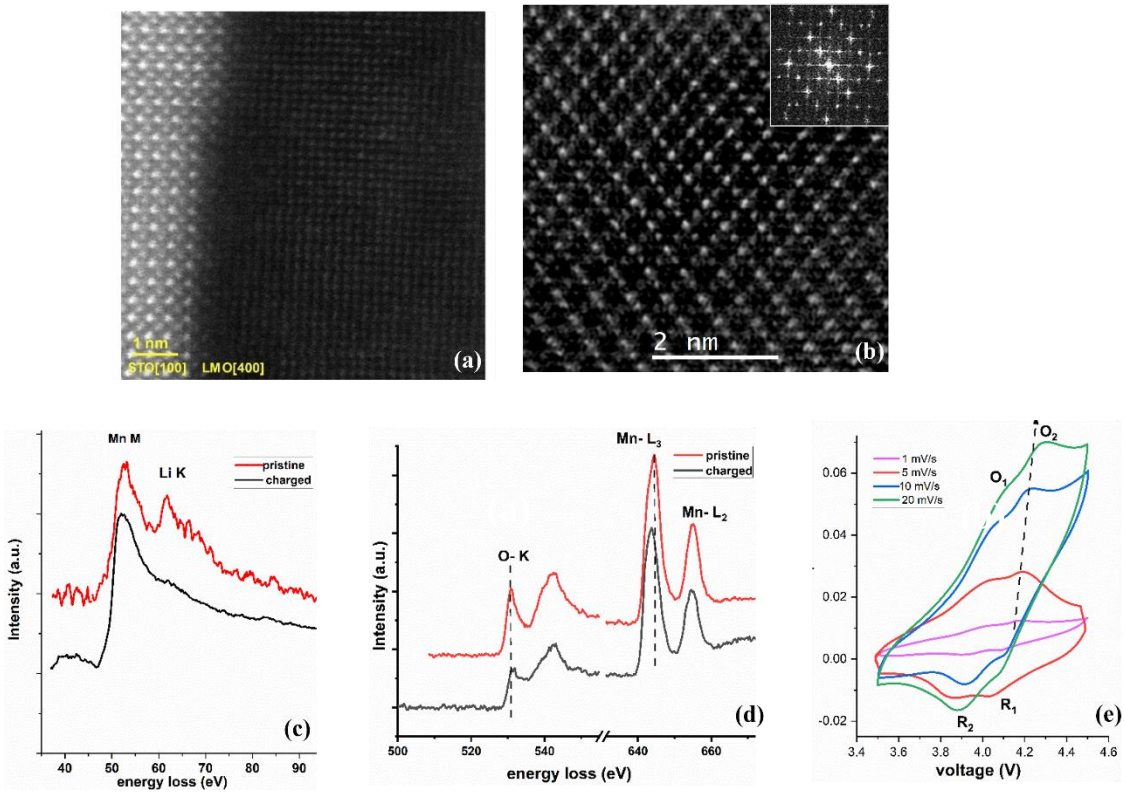

Figure 1 : (a) HAADF image of STO/LMO interface along STO[001], (b) HAADF image from bulk LMO region along STO[110], (c-d) EELS measurements showing Li *K*-edge, O *K*-edge, and Mn *M*-edges of pristine and cycled LMO(001) film, (e) CV curves of LMO(001) at different scan rates

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