Molecular Beam Epitaxy (MBE) Growth of Model Cathodes to Study Interfacial Ion Diffusion

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1. Introduction

Lithium-ion batteries (LIBs) have been the focus of research for decades owing to their superior energy storage potential and wide range of applications. However, long-term stability issues still persist in LIB cathodes as the result of the formation of a solid electrolyte interface (SEI), structural transformations, or the loss of active cathode materials. In nanoscale cathodes, it is often impossible to isolate, let alone mitigate the causes of the observed capacity loss. Herein, a novel approach is presented to synthesizing LIB cathode model systems using thin-film molecular beam epitaxy (MBE). Specifically, 100 nm thick LiMn₂O₄ (LMO) thin-film cathodes are grown on SrRuO₃/SrTiO₃ (100) single-crystal substrates and characterized in their pristine and cycled states. The pristine thin films exhibit the electro-chemical cycling behavior and structural evolution previously seen in bulk LMO cathodes. The formation of surface-layer rocksalt MnO and spinel Mn₃O₄ along with the mass-loss associated with the corrosion of active Mn ions is also reported. It is, therefore, demonstrated that these MBE-grown model systems can be used for detailed studies of their surface structures and the electrode/electrolyte interfacial evolution in LIB cathodes, leading to the development of materials for rechargeable batteries with higher capacity and better stability.

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However, systematic studies of the role that specific surface orientations or terminations play in these structural or chemical effects in LIB powder cathodes remains challenging, if not impossible, since the size distribution of active cathode materials can vary significantly. Moreover, LIB cathode materials, including LMO, usually consist of a highly heterogenous mixture of active particles and carbonaceous materials to provide good electrical conductivity, and establishing direct correlations between the observed microstructural effects and the overall battery performance is very difficult. Therefore, it is necessary to develop and study model systems that provide facile control of bulk crystallographic orientation and surface termination of the spinel LMO cathodes and also provide the electrochemical cycling performance expected for LMO particle cathodes.

Epitaxial thin films, especially in single-crystal form, can provide a material with well-defined bulk orientations, limited defect concentrations and targeted surface terminations, allowing various properties to be tailored to address specific scientific questions, including cycling stability, thermal stability, and increased power density. Although thin films of LMO have been grown using deposition techniques, such as atomic layer deposition (ALD) or pulsed laser deposition (PLD), the growth mechanism is susceptible to lithium deficiency, local inhomogeneities, and surface roughness. Here, we demonstrate, for the first time, the molecular beam (MBE) growth of epitaxial single-crystal thin films on SrTiO$_3$ substrates. Our single-crystal model systems provide access to controlling the defect concentrations, compositional homogeneity, surface terminations, stoichiometry as well as crystal orientation in macroscopic samples, which can be optimized for a large variety of structural and chemical characterization, including transmission electron microscopy (TEM) and X-ray scattering or spectroscopies. Since we are unaware of any published results on Li-transition metal oxide thin film synthesis, we document our growth parameters, including temperature, flux ratio, and oxygen partial pressure. We also report high-resolution scanning transmission electron microscopy (STEM), electron energy-loss (EELS), and energy-dispersive X-ray spectroscopy (XEDS) of LMO films grown in two different orientations and demonstrate how their different electro-chemical cycling properties are related to the films’ microstructure.

2. Experimental Section

A commercial Veeco Gen II oxide MBE chamber was modified allowing for lithium transition metal oxide thin film synthesis (see Figure 1). Specifically, a portable Ar-filled inflatable polyethylene glove bag was used to load lithium effusion cell onto the MBE chamber, avoiding any potential contamination, air exposure, and related hazard issues. The MBE system was baked at 200 °C for 24 h to remove hydrocarbons and other residual gas and maintained at UHV (<10$^{-8}$ Torr) to minimize outgassing during film deposition. High purity lithium pellets (99.9% from Sigma-Aldrich), and high purity manganese (99.95% from Kurt J. Lesker) were evaporated in a 5 cc conical pyrolytic boron nitride (PBN) and a 5 cc conical alumina crucibles, respectively, to generate stable molecular beam fluxes. An oxygen plasma was generated using a RF generator, breaking the high purity (99.999%) molecular oxygen using a forward power of 300 W. Oxygen plasma been shown to be more oxidizing than molecular oxygen for MBE thin films. The Li and Mn effusion cell temperatures were constantly monitored electronically, while the oxygen plasma pressure was monitored and maintained at constant flow rate of 4 sccm using a solenoid valve. The Li, Mn, and plasma valves were controlled by pneumatic shutters.

Single-crystal SrTiO$_3$ substrates, 10 × 10 mm$^2$ in size with ± 0.5° miscut were acquired from MTI Corp. As received substrates were sonicated in acetone, followed by isopropanol alcohol, and DI water sonication for 10 minutes each and subsequently dried using argon gas (99.999% purity). The substrates were then etched in HF and annealed at 1000 °C for 2 h in a tube furnace with oxygen flow. Conductive SrRuO$_3$ (SRO) buffer layers were deposited using a separate PLD system at Northwestern University (Supporting Information). The STO and STO/SRO substrates were loaded and degassed at 600 °C for 2 h prior to growth, in an effort to eliminate any contamination. The MBE chamber is also equipped with an
Ar-filled glove box (see Figure 1b) to store and manipulate the LMO thin films after deposition.

X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were conducted to examine average bulk composition of the synthesized films. XRD measurements were performed using a Bruker D8 Discover with a Lynxeye detector. The accelerating voltage and tube current were 40 kV and 40 mA respectively, with Cu as target anode (λ = 1.5418 Å), and out of plane coupled θ-2θ was performed from 2θ = 10° to 80°. Kratos AXIS-165 Surface Analysis System with Monochromatic Al X-ray source and fitted with a charge neutralization coil was used for (XPS).

Cross-sectional TEM samples were prepared by mechanical polishing using a Allied Multiprep polishing system, as well as a ThermoFisher Helios focused ion beam (FIB)/SEM system for TEM lamella preparation. Prior to any FIB liftout, a platinum layer was deposited on top of the sample for damage protection.

TEM data was acquired using a JEOL JEM-3010 at 300 kV with LaB₆ electron source equipped with an ultra-high-resolution pole piece (Cₜ = 0.6 mm) that provides 0.14 nm lattice resolution and 0.17 nm point-to-point resolution. High-angle annular dark field (HAADF) images, energy dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS) in STEM mode were acquired using a JEOL JEM-ARM 200CF located at UIC. This TEM/STEM instrument is equipped with a cold-field emission electron source and a CEOS probe aberration corrector, providing a probe-size of 0.73 Å, and an energy resolution of 0.35 eV. It is also equipped with an Oxford X-Max 100TLE windowless silicon drift detector as well as post-column Gatan Continuum imaging filter for atomic resolution XEDS and EELS measurement. The high-angle annular dark field (HAADF) measurements were taken with a convergence angle of 25 mrad and a collection angle of 90−174.5 mrad, while the EELS data was acquired using probe semi-convergence angle of 178 mrad and collection angle of 53.4 mrad.

Cyclic voltammetry (CV) was conducted in a coin cell setting using a Bio-Logic VMP3 potentiostat/galvanostat. Half-cells were constructed using lithium as counter electrode, a glass fiber separator, and 1 M LiPF₆ in 1:1 EC:DC electrolyte in an inert Ar-filled glove box with <1 ppm H₂O and O₂. Scan rates from 1 to 20 mV s⁻¹, and potential window from 3.5 to 4.5 V were used to ensure complete charge/discharge of the films.

3. Results and Discussion

Due to the lack or prior reports on MBE-grown LiMn₂O₄ thin films, several permutations of substrate temperatures, Li:Mn flux ratio, and background O₂ plasma pressure were tried to optimize the thin film composition and crystallinity (see the Supporting Information). Although three types of substrates were used here, bare STO, Nb-doped STO and STO with a thin SRO buffer layer, the MBE growth recipe was developed using bare STO. STO has a cubic perovskite structure with lattice parameter of 3.905Å, which is a well-established substrate for growth of oxide films.[17] We found that it works best to use the conditions where a stable flux of Mn is established to determine the growth rate of the thin films. Li, on the other hand, is very mobile and volatile, and the flux changes rapidly even with slight temperature fluctuations (see growth parameters in Table S1 and Figure S2, Supporting Information).

Figure 2a shows the XRD patterns for three LMO thin-film samples grown on STO(100) substrates at different temperatures with a Mn:Li flux ratio of 1:4 and 4 sccm of oxygen flow. All films exhibit predominant out-of-plane orientation of LMO(100) on STO(100). At a growth temperature of 460 °C, impurity phases are present in the films, indicated by the broad peaks close to the LMO(004) peak, as well as an extra LMO(111) peak at =2θ = 18.6°. At 500 °C, impurity phases are absent and a sharp LMO(004) reflection is observed at 2θ = 43.88°. At higher temperature, e.g., 540 °C, the film intensity peak decreases, and shifts slightly towards the left, indicating a Li deficient film, LiₓMn₁₋ₓ[LiₓMn₂O₄] with larger lattice parameter. The XRD pattern for the films grown at 540 °C also show a small peak at 2θ = 41.7°, possibly due to the presence of a thin layer of non-stoichiometric Liₓ₋ₓMn₂O₄₋ₓ at the top surface.

XPS measurements were performed for the samples grown at 500 °C. Figure 2b shows the peaks for Li, O, Mn, and adventitious carbon. The carbon peak (C 1s) was calibrated at 284.8 eV, and all peaks are measured relative to this signal. The peaks used from the broad survey of binding energies can be used to estimate the atomic percentage composition of thin films. By using the relative sensitivity factor (RSF) and area under the peaks, the atomic percentage of Li, Mn, and O were calculated to be approximately 13%, 27%, and 60%, with Li: Mn ratio of 1:2.07 being very close to stoichiometric. Figure 2c shows a

![Figure 2](image-url)
magnified view of the Mn 2p_{3/2} and 2p_{1/2} peaks taken also from the samples grown at 500 °C. The two Mn peaks are separated by 11.7 eV. Further deconvolution of Mn 2p_{3/2} peak was carried using a Voight profile composed of Gaussian (70%) and Lorentzian (30%) and Shirley-type background subtraction. Fitting was satisfactory with 2 peaks, where the relative contribution from Mn^{3+} and Mn^{4+} are approximately 48% and 52%, respectively, which gives an average Mn valence of nearly 3.5+, as expected for LiMn_{2}O_{4}.

TEM images and selected area diffraction (SAED) patterns (Figure 3a–d) were acquired for the samples shown in Figure 2a. The lattice parameter difference between STO(100) and LMO (100) of ≈5.5% clearly shows up in electron diffraction patterns, where the STO(002) and LMO(004) have close but distinguishable spots, as labeled in Figure 3a-c. In addition to multiple overlapping diffraction spots, implying the presence misoriented grains, the films grown at 460 and 540 °C also show extra diffraction spots not associated with LMO (100), suggesting that impurity phases are present. The high-resolution TEM images and electron diffraction patterns of the films grown at 500 °C (Figure 3c,d) show clear epitaxial relationship and high crystallinity of the LMO film. Based on XRD, XPS, and TEM analysis, the films at 500 °C yielded the best composition ratio and film crystallinity and will be used for the remainder of this report.

Atomic-resolution HAADF images for samples along the substrate STO[100] orientation are shown in Figure 4. Here, an atomically sharp interface between the substrate and the LMO film is seen in Figure 4a. A one unit-cell thick step in the TiO_{2}-terminated STO surface is indicated by the rectangular box in Figure 4a and the inset shows the FFT pattern of the entire image. Figure 4b shows the inverse FFT image when contribution from only the LMO(400), STO(200) type spots are allowed. Now, two edge dislocation are clearly visible as highlighted by the symbol “T” in Figure 4b. There are two reasons for these dislocation to occur, the step in the substrate surface and the lattice mismatch between the STO substrate and the LMO film. For a substrate miscut of 0.5°, TiO_{2} terminated one-unit cell steps and terraces structure with height of 3.9 Å are routinely observed on the STO surface.[18,19] These surface steps often nucleate edge dislocations in epitaxial films, where the lattice parameters between the substrate and film do not match. For the STO/LMO interface, the lattice mismatch is 5.5% and the strain in the film is released by the formation of misfit dislocations. Such misfit-induced edge dislocations are visible in Figure 4b at the locations of the steps in the STO surface. Geometric phase analysis (GPA)[20] can be used to measure the strain in the epitaxial thin film, as shown in Figure 4c for the in-plane strain $\varepsilon_{\text{xx}}$ and the out of plane strain $\varepsilon_{\text{yy}}$. The masks were taken from $g = 110$ and $g = 1-10$ spots with lateral spatial resolution of 1 nm. The STO substrate at the interface was used as a reference to calculate relative strain throughout the LMO film. Figure 4c shows that the LMO is strained for first 4–5 nm near the interface and then relaxes as expected.

Figure 5a shows the STO/LMO interface along the STO[110] zone axis, and the inset shows the FFT pattern of the image, while Figure 5b shows an atomic-resolution STEM image of the relaxed film further away from the interface. A common way to visualize the LMO lattice is along the [110] orientation where the spinel structure is seen by the diamond- shaped Mn sublattice. In this configuration, the Mn, Li, and O atoms reside at separate columns giving distinct contrast for STEM images, as shown in the schematic in Figure 5c. Figure 5d shows the HAADF image intensity of a line profile drawn in dashed red line in Figure 5b.
showing the position of Mn, O atoms along the column. In the (110) projection, the m:n ratio, where m is the length between shorter diagonal and n is the distance between longer diagonal (Figure 5c), can be used to measure tetragonal distortion in the film. For a perfect cubic spinel, the ratio is 0.7071. Near the interface, an average m:n ratio of 0.733 is measured for the first five layers where the film is highly strained, followed by 0.7214 for the next five layers, and then 0.711 further away from the interface where the film approaches its unstrained state. Similar distortions near the substrate/film interface have previously been reported in the literature for epitaxial thin films with similar lattice mismatch, suggesting that oxygen vacancies are present at the interface. [21]

Compositional homogeneity of Mn and O throughout the film thickness was evaluated using XEDS. Figure 6a shows that the distribution of Mn and O appears uniform through the film. Lithium could not be measured using EDX. However, the Li K-edge was measured using EELS, as shown in Figure 6b, where the Mn M- and Li K-edges taken from the LMO films are displayed. The compositional homogeneity of Li throughout the film thickness was also measured (Figure S5, Supporting Information), which shows uniformity throughout the 100 nm thick films. In addition, the Mn M-edge shows a pre-peak intensity, indicated by the arrow in Figure 6b, that has been reported as a fingerprint for spinel LMO, arising from the Mn atoms in the octahedral 16d sites. [22,23] Figure 6c shows that O K- and Mn L-edges of the LMO films. The O K-edge shows a clear pre-peak intensity at 530.5 eV (indicated by the dashed line), which stems from transition of O 1s electrons into the unoccupied O 2p-Mn 3d hybridized orbitals and is reported as characteristic feature of 3d transition metal oxide materials. [24,25] The Mn valence state can be determined using the L-edge energy or...
branching ratio ($L_3/L_2$) of the EELS signal. \cite{25,26} Figure 6c shows that the Mn $L_3$ edge is located at 641.7 eV, the Mn $L_1$ and $L_2$ edges are separated by 10.6 eV and the branching ratio of $L_1/L_2$ is 2.05. These values agree with the presence of a mixed Mn$^{3+}$ and Mn$^{4+}$ valence state in the LMO films, \cite{24-27} thus confirming our prior XPS measurements.

The cycling behavior of thin films was examined using a coin cell setup for three different kinds of samples, STO(100)/LMO, Nb:STO(100)/LMO, and STO(100)/SRO(100)/LMO. For LMO films deposited on pure STO (100) substrates, a conductive aluminum contact grid layer was deposited (Figure S6, Supporting Information). Contact points were established at the perimeter of the LMO film, but we were not able to detect any current signal. This was attributed to the insulating nature of the STO substrates. Yet, films deposited on STO (100) doped with 0.1% Nb (Nb:STO) also did not show any current associated with the electrochemical cycling. It was previously demonstrated that the ultra-high vacuum annealing of the Nb:STO substrates prior to LMO film deposition could result in creation of oxygen vacancies at the top surface, resulting in an insulating layer at the interface between Nb:STO and LMO films. \cite{28} Therefore, we deposited a thin conductive layer of epitaxial SRO (≈10 nm) using PLD on STO to serve as current collector. The resulting CV curves for the STO(100)/SRO/LMO films are shown in Figure 7a for scan rates ranging from 1 to 20 mV s$^{-1}$. The redox peaks are clearly visible and cathodic peak potentials are labeled O$_1$, O$_2$ while the anodic peak potentials are labeled R$_1$ and R$_2$. This pair of coupled anodic and cathodic peaks (O$_1$, O$_2$, R$_1$, R$_2$) are seen for the Mn$^{3+}$/Mn$^{4+}$ redox couple during charge/discharge corresponding to (de)intercalation of Li from LiMn$_2$O$_4$. The cathodic peak O$_1$ is found at a voltage range from 3.98 to 4.09 V, while O$_2$ is found at 4.18–4.26 V with peak separation of $\Delta V = 125–140$ mV depending on the scan rate. The anodic peak R$_1$ is located at a range of 3.91–3.98 V, while R$_2$ is found between 4.03 and 4.10 V with peak separation $\Delta V = 135–170$ mV depending on the scan rate. Anodic and cathodic peak potentials agree with previous measurements of the Li intercalation behavior of LMO. \cite{29,30} The peak current increases for higher scan rate as a faster rate is imposed on the reaction. The peak potential positions and the separation between the anodic/cathodic peak increase slightly at higher scan rates, suggesting quasi-reversibility of the thin films at higher scan rates. The Randles–Ševčík equation, which describes the effect
of scan rate on the peak current, suggests that for reversible and diffusion-controlled processes, the peak current is proportional to the square root of the scan rate: \( I_{\text{peak}} \propto (\text{scan rate})^{1/2} \). In Figure 7b, the peak current \( I_{\text{peak}} \) from our cyclic voltammetry is plotted as a function of the square root of the scan rate, and the linear behavior according to the Randles–Ševčík equation is shown by the solid line. It can be seen that the peak current is linearly dependent on the square root of the scan rate, suggesting that the lithium (de) intercalation is governed by diffusion.

The structural evolution of the STO (100)/SRO/LMO films during electrochemical cycling was characterized using STEM analysis. Atomic-resolution high-angle annular dark field imaging and EELS measurements were performed to study changes in the film’s surface morphology and chemistry. Figure 8a shows images along the along STO[110] direction of pristine and cycled films charged to 4.5 V. HAADF images were taken from the surface and sub-surface areas to assess any structural transformation, while EELS was used to determine the change in Li concentration and Mn valence state. The low magnification images in Figure 8a show formation of MnO rocksalt like (blue solid circles) and Mn_3O_4 spinel like structure (red solid circles). There is also an ≈5–6 nm loss in thickness of charged film after cycling, which is attributed to corrosion of the Mn-O after coming in contact with the electrolyte. Corrosion of active cathode surfaces is commonly reported, particularly in Mn-rich oxides. The accepted mechanism for Mn loss is the disproportionation reaction \( 2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+} \), creating \( \text{Mn}^{2+} \) that dissolves in electrolyte and gets deposited at the anode. On the other hand, the metastability of surface \( \lambda\text{-MnO}_2 \) suggests that surface structure stabilizes by transforming into final products of spinel \( \text{Mn}_3\text{O}_4 \) and rocksalt like MnO structure during electro-chemical cycling (as seen in Figure 8a).

Figure 8b shows EELS measurements for pristine and charged films. Extraction of lithium from the film is confirmed by the absence of Li K-edge in charged film. This agrees with the slight shift in the Mn M-edge towards slightly higher energy value for the bulk film (as \( \text{Mn}^{3.5+} \rightarrow \text{Mn}^{4+} \)). Similarly, the Mn M-edge of surface region shifts towards slightly lower energy value indicating decrease in average Mn valence (\( <\text{Mn}^{3.5+} \) due to presence of \( \text{Mn}^{2+} \), \( \text{Mn}^{3+} \) ions). The position shift of O K- and
Mn $L$-edges have been marked by dashed lines in the core loss regime. The changes in these positions are directly correlated to the Mn valence in the lattice structure during lithium insertion/extraction and structural transformation. For the bulk of charged film, O $K$-edge pre-peak shifts towards lower energy loss of 529.7 eV, while Mn $L_3$ simultaneously shifts towards higher value of 642.6 eV, and $L_3$-$L_2$ peak separation decrease to 10.1 eV, indicating the increase in valence state of Mn. However, for the surface area, the O $K$-edge prepeak shifts higher and Mn $L_3$ shifts lower indicating a decrease in Mn valence compared to pristine film. This is attributed to the formation of MnO/Mn$_3$O$_4$ structures as seen in Figure 8a, which contain Mn$^{2+}$ and Mn$^{3+}$ ions, thus decreasing the overall valence of Mn. The concentration of oxygen at the charged surface is also lower than that of pristine and charged bulk area corresponding to the formation of new surface phases with lower O content.

Finally, we followed the same protocols as described above to grow LMO(111) films on SRO/STO (111) substrates. It has been shown in literature that crystal orientation dependent behavior for thin films affects both the pristine and cycled states of the film. Density functional theory (DFT) calculations have shown that depending upon the termination layers of LMO films, i.e., Li terminated, O-terminated, different orientations, such as (100), (110), (111) have different energy. Thus, it is important to understand the role of surface orientation for efficient cycling and corrosion control of active electrode material. To date, there have been very few mentions of such surface dependent behavior of LMO cathodes.

Cross-sectional specimen were prepared along STO [100] to evaluate film morphology using TEM. Figure 9a shows the epitaxial deposition of SRO on STO, Figure 9b,c shows raw and Radial Wiener (RW) filtered images of epitaxial growth of LMO(111) on SRO/STO(111), where the strain induced by the lattice mismatch is clearly visible at the interface. XEDS and EELS measurements were performed on the pristine LMO (111) films (Figures 10 and 11).

Electrochemical measurements were performed with same settings as those described for the LMO(100) samples.
Figure 12a,b shows the CV curves of LMO(111) performed at scan rate of 5 mV s$^{-1}$ and compared to the previously described CV curves of LMO (100) films. While the structural analysis confirms the presence of LiMn$_2$O$_4$ (111) thin film, the peaks separation and the peak position shifts are in general larger for LMO(111) films as compared to the LMO(100) films (see Supporting Online Materials). In addition, the polarization is generally higher for the LMO(111) films compared to the LMO(100) films. Similar observations in cycling behavior have been made in films grown with (111) truncated orientations$^{[32,33]}$ indicating larger polarization at the LMO(111) surface. Such behavior has been attributed to stable SEI formation on the LMO(111) planes while the LMO(100) surface is better suited for Li diffusion at the expense of corrosion of active Mn materials$^{[6,34]}$.

4. Conclusions

We have successfully demonstrated that model cathode systems, consisting of single-crystal LiMn$_2$O$_4$ thin films on conductive SRO/STO can be synthesized with control over the crystal orientation. Specifically, we have grown LiMn$_2$O$_4$ along (100) and (111) orientations for the first time using an oxide-MBE approach. The quality of films during growth was highly sensitive to substrate temperature, Li:Mn ratio, and oxygen plasma background pressure. Our structural and electro-chemical characterization shows that the MBE-grown films exhibit many of the same properties seen in conventional cathode nano-particles and can, therefore, be seen as model systems for isolating interfacial effects in Li$^+$ and potentially even multi-valent ion cathode systems. We found a loss of active materials and the formation of secondary phases near the film surface, especially in LMO grown along the (100) orientation, which have been previously identified as causes of capacity fade.

The observed orientation-dependent properties of the MBE-grown LMO films in their pristine and cycled states demonstrate that it will now be possible to isolate specific interfacial properties and assess the role of structural and or kinetic barriers on the cathode behavior. In particular, future studies focusing on varying the number cycles, cycling rate, cycling temperature and storage time can directly address fundamental issues in the LMO nano-particle cathode system.

A significant advantage of thin film model systems over traditional powder electrodes for materials characterization is that multiple experiments can be conducted on the same materials, including in situ or atomic-resolution STEM, XPS, XRD and as well as X-ray microscopy. Many of these experiments can even be performed operando due to the large area of the available thin films surface. Furthermore, the efficacy of epitaxial surface layers designed to prevent the corrosion of Mn-oxide from the cathode surface, can now be directly evaluated on the thin film model systems.

Finally, for battery chemistries, where extrinsic factors such as the low conductivity and high viscosity of electrolytes, or the poor connectivity of the cathodes with the electrode constitute bottlenecks in evaluating cell performance, the MBE-grown thin film cathodes provide the ideal platform to assess the intrinsic effects of the cathode/electrolyte interface. This is of particular relevance in multi-valent ion systems, where ionic-liquid electrolytes are often used. Initial experiments have shown that the LMO thin films can also be used for multivalent ion intercalation, when charged against a Li anode, which is then replaced by a multivalent, e.g. Mg, anode.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.
Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

cyclic voltammetry, electron microscopy, Li-ion cathode, molecular beam epitaxy, thin films

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[1] J. W. Fergus, J. Power Sources 2010, 195, 939.
[2] Y. Huang, Y. Dong, S. Li, J. Lee, C. Wang, Z. Zhu, W. Xue, Y. Li, J. Li, Adv. Energy Mater. 2021, 11, 2000997.
[3] J. Li, Y. Zhu, L. Wang, C. Cao, ACS Appl. Mater. Interfaces 2014, 6, 18742.
[4] J. Zhao, Y. Wang, J. Phys. Chem. C 2012, 116, 11867.
[5] P. Arora, R. E. White, M. Doyle, J. Electrochem. Soc. 1998, 145, 3647.
[6] R. Hendriks, D. M. Cunha, D. P. Singh, M. Huijben, ACS Appl. Energy Mater. 2018, 1, 7046.
[7] J.-S. Kim, K. Kim, W. Cho, W. H. Shin, R. Kanno, J. W. Choi, Nano Lett. 2012, 12, 6358.
[8] Nanomaterials for Lithium-Ion Batteries: Fundamentals and Applications (Ed: R. Yazami), CRC Press, Boca Raton, FL 2013.
[9] A. Rougier, K. A. Striebel, S. J. Wen, T. J. Richardson, R. P. Reade, E. J. Cairns, Appl. Surf. Sci. 1998, 134, 107.
[10] C. Julien, E. Haro-Poniatowski, M. A. Camacho-Lopez, L. Escobar-Alarcon, J. Jimenez-Jarquin, Mater. Sci. Eng., B 2000, 72, 36.
[11] S. B. Tang, M. O. Lai, L. Lu, S. Tripathy, J. Solid State Chem. 2006, 179, 3831.
[12] V. Miikkulainen, A. Ruud, E. Østreng, O. Nilsen, M. Laitinen, T. Sajavaara, H. Fjellvåg, J. Phys. Chem. C 2014, 118, 12558.
[13] X. Chen, M. Vörös, J. C. Garcia, T. T. Fister, D. B. Buchholz, J. Franklin, Y. Du, T. C. Droubay, Z. Feng, H. Iddir, L. A. Curtiss, M. J. Bedzyk, P. Fenter, ACS Appl. Energy Mater. 2018, 1, 2526.
[14] R. E. Warburton, H. Iddir, L. A. Curtiss, J. Greeley, ACS Appl. Mater. Interfaces 2016, 8, 11108.
[15] M. Brahlek, A. S. Gupta, J. Lapano, J. Roth, H.-T. Zhang, L. Zhang, R. Haislmaier, R. Engel-Herbert, Adv. Funct. Mater. 2018, 28, 1702772.
[16] R. F. Klie, A. Gulec, Z. Guo, T. Paulauskas, Q. Qiao, R. Tao, C. Wang, K. B. Low, A. W. Nicholls, P. J. Phillips, Cryst. Res. Technol. 2014, 49, 653.
[17] R.amesh, D. G. Schlimo, Nat. Rev. Mater. 2019, 4, 257.
[18] A. Biswas, C.-H. Yang, R. Ramesh, Y. H. Jeong, Prog. Surf. Sci. 2017, 92, 117.
[19] T. Ohnishi, K. Shibuya, M. Lippmaa, D. Kobayashi, H. Kumigashira, M. Oshima, H. Koinuma, Appl. Phys. Lett. 2004, 85, 272.
[20] M. J. Hýtch, T. Pfammann, Ultramicroscopy 2001, 87, 199.
[21] Y. H. Ikuhara, X. Gao, R. Huang, C. A. J. Fisher, A. Kuwabara, H. Moriwake, K. Kohama, J. Phys. Chem. C 2014, 118, 19540.
[22] P. Gao, R. Ishikawa, E. Tochigi, A. Kumamoto, N. Shibata, Y. Ikuhara, Chem. Mater. 2017, 29, 1006.
[23] P. Parajuli, H. Park, B. J. Kwon, J. L. Guo, B. Key, J. T. Vaughrey, P. Zapol, R. F. Klie, Chem. Mater. 2020, 32, 10456.
[24] L. A. Grunes, R. D. Leapman, C. N. Wilker, R. Hoffmann, A. B. Kunz, Phys. Rev. B 1982, 25, 7157.
[25] F. M. de Groot, M. Grioni, J. C. Fuggle, J. Ghijsen, G. A. Sawatzky, H. Petersen, Phys. Rev. B 1989, 40, 5715.
[26] H. Tan, J. Verbeeck, A. Abakumov, G. Van Tendeloo, Ultramicroscopy 2012, 116, 24.
[27] H. K. Schmid, W. Mader, Micron 2006, 37, 426.
[28] K. Fukushima, S. Shibagaki, Thin Solid Films 1998, 315, 238.
[29] D. Albrecht, H. Wulfmeier, H. Fritze, Energy Technol. 2016, 4, 1558.
[30] T. Aoshima, K. Okahara, C. Kiyohara, K. Shizuka, Y. Ikuhara, H. Koinuma, J. Phys. Chem. C 2014, 118, 19540.
[31] S. Kim, M. Aykol, C. Wolverton, Phys. Rev. B 2015, 92, 115411.
[32] Y. Tao, Y. Lu, Y. Guo, J. Guo, M. Xiang, W. Bai, X. Liu, H. Bai, J. Alloys Compd. 2022, 904, 164027.
[33] C. Jiang, Z. Tang, S. Wang, Z. Zhang, J. Power Sources 2017, 357, 144.
[34] W. Sun, F. Cao, Y. Liu, X. Zhao, X. Liu, J. Yuan, J. Mater. Chem. 2012, 22, 20952.