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Spontaneous Lithiation of Binary Oxides during Epitaxial Growth on LiCoO₂

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ABSTRACT: Epitaxial growth is a powerful tool for synthesizing heterostructures and

integrating multiple functionalities. However, interfacial mixing can readily occur and

significantly modify the properties of layered structures, particularly for those containing

energy storage materials with smaller cations. Here we show a two-step sequence involving

the growth of an epitaxial LiCoO₂ cathode layer followed by the deposition of a binary

transition metal oxide. Orientation-controlled epitaxial synthesis of the model solid-state-

electrolyte Li₂WO₄ and anode material Li₄Ti₅O₁₂ occurs as WO₃ and TiO₂ nucleate their

respective host lattices and react with Li ions from the underlying cathode. We demonstrate

that this lithiation-assisted epitaxy approach can be used for energy materials discovery and

exploring different combinations of epitaxial interfaces that can serve as well-defined model systems for mechanistic studies of energy storage and conversion processes.

Epitaxial growth is a powerful method for fabricating well-defined heterostructures of various kinds with tailored functionalities.¹ Successful implementation of heteroepitaxy for the preparation of multi-layer structures such as superlattices usually relies on the ability to suppress the mixing of layers and thus fabricate abrupt interfaces,²⁻³ as illustrated in Figure 1a. However, in many cases intermixing is unavoidable due to both thermodynamic and kinetic drivers and impacts the properties of interest.⁴⁻⁷ Figure 1a can be also envisioned as a route to the vertical integration of a cathode material (film 1) with another electrolyte (film 2) in a prototypical solid-state lithium-ion battery (LIB), which is increasingly regarded as one of the most promising next-generation energy storage solutions. In this case, the interface is expected to be less abrupt due to the abundance and high mobility of Li ions. Studying atomic species exchange at the solid-solid interface has become one of the major topics for making progress in the development of solid-state LIBs.⁸ However, it is still a big challenge in fundamental understanding how Li ions transport in different materials, because of the illdefined interfaces. Therefore, exploring the epitaxial integration of energy materials becomes very important, as well-defined interfaces offer an ideal testbed for fundamental studies of the performance and degradation mechanisms in solid-state LIBs.

It is well known that LiCoO₂ with a layered structure is one of the most widely studied and employed cathode materials in LIBs.⁹ It has been reported that the Li-ion diffusion energy barrier along the Li-containing planes is only 0.3 eV, while the Li-ion diffusion energy barrier along a vertical direction directly through the CoO₂ sheets is around 6.8 eV.¹⁰ Thus, the Li-ion diffusion is usually two-dimensionally (2D) confined by the adjacent CoO₂ planes. Previous studies have shown that LiCoO₂ thin films can be epitaxially grown on SrTiO₃ (STO) by pulsed laser deposition (PLD), and the crystallographic orientation of LiCoO₂ strongly

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depends on that of STO.¹¹⁻¹⁴ Growing LiCoO₂ on (001)-oriented STO leads to LiCoO₂(104) and the Li-containing planes intersect the STO(001) surface by an angle of 54.7° .¹⁴⁻¹⁵ Due to the 54.7° tilt of the Li-containing planes on the 4-fold symmetric substrate, twin boundaries (TBs) are observed in LiCoO₂/STO(001),¹⁴⁻¹⁵ as depicted in Figure S1 and Figure 1c. Previous first principle calculations have shown that the Li-ion diffusion energy barrier (~0.2 eV) along/across TBs is only ~ 0.2 eV,¹⁶⁻¹⁷ indicating that TBs could provide faster Li-ion diffusion channels.¹⁸⁻¹⁹ Growing LiCoO₂ on (111)-oriented STO substrate leads to LiCoO₂(001) and the Li-containing planes are parallel to the interface.¹⁴ In this case, the dominant defects are antiphase boundaries (APBs), as illustrated in Figure S1 and Figure 1d. It has been proposed that APBs can function as viable mass-transfer channels that couple inplane Li ion diffusion pathways.²⁰

We show here that out-diffused Li ions from well-defined epitaxial LiCoO₂ cathode layers can be harnessed for the controlled synthesis of model energy-material heterostructures. The deposition process involves the reaction of Li ions from LiCoO₂ with the transition metal oxide (TMO) species WO₃ and TiO₂ as they nucleate. Highly oriented films of Li₂WO₄ and Li₄Ti₅O₁₂ spontaneously form in the process of lithiation-assisted epitaxy, as illustrated in Figure 1b. Our combined diffraction, microscopy, and spectroscopy studies correlate the resulting structures and morphologies with the presence of defects in the LiCoO₂ layers, the roles of which have previously been hypothesized, but not yet firmly established.

LiCoO₂ thin films of thickness 90 to 200 nm were grown on STO (001) and STO (111) single crystal substrates by PLD. During deposition, the substrates were heated to 600 °C and the growth oxygen pressure (PO₂) was 10 mTorr. After the growth of the LiCoO₂ cathode seed layer, the substrate temperature was held at 600 °C while PO₂ was raised to 100 mTorr for the deposition of the WO₃ or TiO₂ film. For comparison, one single layer of the WO₃ or TiO₂ film was directly grown on STO substrates under the same growth conditions.

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A high-resolution X-ray diffraction (XRD) out-of-plane θ -2 θ scan of a WO₃/STO(001) sample synthesized by PLD (black curve in Figure 2a) displays a single set of (001) film peaks along with the STO substrate peaks, consistent with the nucleation of pseudocubic WO₃.²¹⁻²² The vacant interstitial sites in the cubic WO₃ lattice allow for reversible intercalation and removal of small ions (e.g., H⁺, Li⁺, Na⁺, and Ca²⁺),²³⁻²⁴ rendering this material useful in sensing and electrochromic devices. It is thus of interest to deposit WO_3 on LiCoO₂ to see if Li out-diffusion readily occurs. If Li diffusion can be completely suppressed, it is conceivable that $WO_3(001)$ would grow epitaxially on $LiCoO_2(104)$ as there is a structural match between the two materials. However, due to the high diffusivity of Li at elevated deposition temperature (e.g. 600 °C) and the high likelihood of reaction between WO₃ and Li, various reaction intermediates or final products may form. For example, substoichiometric Li ion insertion into the WO₃ lattice can produce lithium tungsten bronze Li_xWO_3 (0<x<1),²⁵ whereas a higher degree of lithiation could lead to cation-intercalated lithium tungstates (Li_xWO_{3+x/2}).²⁶⁻²⁸ XRD out-of-plane θ -2 θ scan (blue curve in Figure 2a) taken after the sequential deposition of ~ 120 nm LiCoO₂ and 30 nm of WO₃ at 600°C on STO(001) displays a single Bragg peak that is clearly at a different angle than that of the WO₃ film, and is located at a lower angle than that of the $LiCoO_2(104)$ diffraction peak. The XRD scan together with scanning transmission electron microscopy (STEM) data (Figures 2b-2d) reveal that this material is phase pure Li_2WO_4 with the epitaxial orientations $Li_2WO_4(004) \parallel$ $LiCoO_2(104) \parallel STO(001)$ and $Li_2WO_4[010] \parallel LiCoO_2[010] \parallel STO[110]$. The apparent reaction that occurs during WO₃ deposition at elevated temperatures is

$$2Li+1/2O_2+WO_3 \rightarrow Li_2WO_4 \tag{1}$$

We note that a control experiment consisting of WO₃ deposition on $LiCoO_2/STO(001)$ at room temperature results only in a $LiCoO_2$ (104) diffraction peak (Figure S2), revealing that thermal energy is required to promote out-diffusion of Li to form crystalline Li_2WO_4 .

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 Li_2WO_4 has a tetragonal structure (a = b = 11.94 Å, c = 8.41 Å)²⁹ in which Li atoms are distributed around the edge-sharing WO₆ octahedral network, as shown in Figure 2d. This oxide has been of interest for its use as a solid-state electrolyte.³⁰ Although its crystal structure has been readily elucidated by XRD, previous attempts to directly image the Li_2WO_4 lattice by TEM have been largely unsuccessful as Li_2WO_4 is electron beam sensitive due to the high mobility of Li under irradiation.³¹ In Figure 2d, we show an atomically resolved high-angle annular dark-field STEM (HAADF-STEM) image of Li_2WO_4 viewed along the [010] direction with the corresponding structural model superimposed on top. The four adjacent bright features are columns of (high-Z) W. Epitaxial strain is likely to provide enhanced structural stability, allowing us to obtain atomically resolved images.

We also performed atomic force microscopy (AFM) for each film surface. As shown in the insets of Figure 2a, both LiCoO₂ and WO₃ thin films display flat surfaces with a rootmean square roughness of <1 nm over an area of 20 μ m \times 20 μ m. In contrast, Li₂WO₄ predominately nucleates as elongated nanorods when deposited on LiCoO₂(104)/STO(001) whereas a small number of pyramid-shaped islands are also observed. A large-scale STEM image of Li₂WO₄/LiCoO₂/STO(001) shown in Figure 2b is consistent with our AFM studies. Thickness-dependent AFM studies (Figure 2e) reveal that Li₂WO₄ initially nucleates as nano islands and that these subsequently align to form the elongated nanorods. We propose a model to correlate the preferred nucleation sites with the TBs of LiCoO₂. The large distance between the intersection of CoO_2 planes with the surface in $LiCoO_2(104)$ makes the diffusion of surface adatoms anisotropic. The TBs thus interrupt the diffusion path, rendering these defects as likely nucleation sites. The initial nuclei are highly localized nanodots and continued deposition leads to the merging of individual nanodots to form elongated nanorods on top of TBs. Pyramid-shaped islands are presumably formed because of random nucleation on terraces sufficiently large that adatoms cannot reach the preferred TBs sites before condensing.

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> The Li-containing planes in LiCoO₂ can be oriented parallel to the surface by depositing on STO(111), as shown in Figure 1d. In contrast to LiCoO₂/STO(001), the dominant defects for LiCoO₂/STO(111) are APBs. Therefore, deposition of WO₃ on LiCoO₂/STO(111) may allow us to determine if Li can participate in the subsequent reactions by diffusing through the APBs.²⁰ As shown in Figure 2a, XRD θ -2 θ scan for WO₃ on LiCoO₂/STO(111) deposited at 600 °C (green curve) confirms that phase-pure Li₂WO₄(201) forms. Moreover, AFM measurements indicate that the film morphology consists of isolated islands with an isosceles triangular base. The longest edges of the base triangles are oriented along the <110> directions of STO as labeled in the inset of Figure 2a, indicating six-fold symmetry. The formation of quasi randomly distributed Li₂WO₄ islands across the surface strongly suggests that the APBs are viable pathways for Li out-diffusion.

> We have shown that Li_2WO_4 nucleation and growth is strongly mediated by defects in both LiCoO₂ orientations, but the roles these defects play are different for the two orientations. The TBs in LiCoO₂/STO(001) act as anchoring sites for nucleation, whereas the APBs in LiCoO₂/STO(111) serve as channels for Li diffusion. LiCoO₂ layers go through a delithiation process in both cases, but the impact on their crystal structures is different. For the case of LiCoO₂/STO(001), our data suggest that highly localized delithiation occurs directly beneath the Li₂WO₄ islands, as illustrated in Figure 3a. Part of the LiCoO₂ beneath the Li₂WO₄ islands shows a clear phase transition from the layered LiCoO₂ structure to a spinel LiCo₂O₄ structure (Figure 2c and Figure 3c), indicative of significant lithium loss.^{14, 32-33} APBs in LiCoO₂/STO(111) allow for redistribution of the remaining Li among different layers (as indicated by arrows in Figure 3b), effectively mitigating highly localized delithiation. As a result, the layered structure of LiCoO₂/STO(111) could be largely preserved after the growth of Li₂WO₄ islands (Figure 3d and Figure S3).

As only part of the LiCoO₂ seed layer is covered by Li₂WO₄ islands, Co signal can be still detected by X-ray photoelectron spectroscopy (XPS) measurements. At 6.6 keV, hard X-

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ray photoelectron spectroscopy (HAXPES) has an effective probing depth of ~ 20 nm. Figure 3e compares HAXPES Co 2p spectra before and after the formation of Li₂WO₄ islands to probe the changes in Co valence. Li₂WO₄ islands can effectively block Co signals underneath, thus the contributions of Co signals are from LiCoO₂ regions not covered by Li₂WO₄. After the formation of Li₂WO₄ islands, Co 2p core levels are broader than that of LiCoO₂ and have contributions from both higher and lower binding energy sides, reflecting the co-existence of multiple valence states. In the reversible range, the delithiation of $LiCoO_2$ to form Li_xCoO_2 $(0.5 \le x \le 1)$ is expected to oxidize Co above 3+. However, it is widely known that Li_xCoO₂ becomes increasingly unstable as x decreases, and releases oxygen at elevated temperatures, leading to reduce Co below 3+.34-35 In addition, over delithiation can lead to the reduction of Co³⁺ as a result of spinel Co₃O₄ or rock-salt CoO formation.^{14, 35} LiCoO₂ regions not covered by Li₂WO₄ islands grown on STO(001) experience less Li loss as illustrated in Figure 3a, and thus are expected to have better thermal stability. On the other hand, LiCoO₂ regions not covered by Li₂WO₄ islands readily contribute Li during the formation of Li₂WO₄ when growing on STO(111) (Figure 3b), which is more susceptible to reduce Co due to oxygen release at high temperature. As a result, the Co 2p spectrum of the Li₂WO₄/LiCoO₂/STO(111) sample shows a more pronounced change.

To visualize the lithium concentration change in different regions, three-dimensional (3D) time-of-flight secondary ion mass spectrometry (ToF-SIMS) imaging was conducted, and 2D images obtained at different depths can be used to analyze compositional change. Figures 3f and 3g show representative images for three positive ions (6 Li⁺, Co⁺, and WO⁺) taken from the Li₂WO₄/LiCoO₂/STO(001) sample, displayed for scans 1-8 and 21-28. These 2D images reveal that the sample surface is not flat, and the specific features are consistent with AFM results (Figure 2a). Co⁺ and WO⁺ originate from the LiCoO₂ layer and Li₂WO₄ islands, respectively. As shown in Figure 3f, a WO⁺ signal can be clearly seen in the region marked by the white dashed circle at scans 1-8. No Co+ signal was detected in this region,

indicating that this island is Li₂WO₄. The WO⁺ signal is gone in scans 21-28 (Figure 3g) whereas the Co⁺ signal appears, suggesting that the Li₂WO₄ island has been sputtered away and the underlying LiCoO₂ layer is being imaged. Based on this analysis, the regions marked by the red square in Figure 3f and the purple circle in Figure 3g were chosen as region I and region II/region III in the inset in Figure 3h, respectively. Figure 3h summarizes the ⁶Li⁺/Co⁺ counts ratio as a function of the sputter region. When moving from region I (not covered by an Li₂WO₄ island) to region II (covered by an Li₂WO₄ island), the ⁶Li⁺/Co⁺ counts ratio drops, consistent with the fact of more Li loss occurs in region II because of the delithiation process occurred in the cathode layer. The ⁶Li⁺/Co⁺ counts ratio increases when moving from region II to region III (same lateral location as region II but at a greater sputter depth), indicating that there was less Li loss in region III (close to the bottom interface) compared to region II. Furthermore, the ⁶Li⁺/Co⁺ counts ratio in region III is higher than that in region I, suggesting that some Li ions in region I also diffused away to form Li₂WO₄ due to surface diffusion at elevated temperature during the growth process.

The lithiation-assisted epitaxy approach described in Figure 1b can be readily extended to other materials systems, as seen in Figure 4 and Figure S4. Here we describe another archetypal example - $\text{Li}_4\text{Ti}_5\text{O}_{12}$, a known anode material used in LIBs,³⁶⁻³⁹ formed by depositing TiO₂ onto LiCoO₂/STO(001) (Figure 4). The overall chemical reaction describing the interaction of Li with TiO₂ in the presence of excess oxygen is

$$4\text{Li}+\text{O}_2+5\text{Ti}\text{O}_2\rightarrow\text{Li}_4\text{Ti}_5\text{O}_{12} \tag{2}$$

Out-diffused Li from LiCoO₂ reacts with arriving TiO₂ species to form Li₄Ti₅O₁₂. XRD θ -2 θ scan for a pure TiO₂ thin film grown directly on STO (001) (Figure 4a) shows two diffraction peaks, assigned as anatase TiO₂ (*a*-TiO₂) (004) and (008), consistent with previous reports.⁴⁰⁻⁴² In comparison, deposition of TiO₂ on top of LiCoO₂ leads to different peaks assigned to the (104) reflection of LiCoO₂ and the (004) reflection of Li₄Ti₅O₁₂. Bulk Li₄Ti₅O₁₂ exhibits a spinel structure with the lattice parameter of 8.357 Å (Figure 4c),

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matching what is estimated from our XRD measurement (8.445 Å). Figure 4b shows a HAADF STEM image of the Li₄Ti₅O₁₂/LiCoO₂ interface with the Li₄Ti₅O₁₂ lattice model overlaid on the image. The different contrast for Ti atoms results from different packing densities in the two kinds of Ti-containing columns in this structure.³⁶ Moreover, due to overdelithiation in the cathode layer, LiCoO₂ changes from the layered structure to the spinel Co₃O₄ structure. The Ti valence was analyzed using XPS and x-ray absorption spectroscopy (XAS). Figure 4d and Figure S5a show Ti 3s and Ti 2p XPS core-level spectra for a-TiO₂ and Li₄Ti₅O₁₂, respectively. No changes in peak shape and peak position are observed for Ti 3s and Ti 2p, confirming that the oxidation state for Ti is 4+ for both a-TiO₂ and Li₄Ti₅O₁₂. An additional peak appears at ~54.4 eV in the Li₄Ti₅O₁₂ spectrum and is assigned to Li 1s.⁴³⁻⁴⁴ Figure S5b displays the normalized Ti L edge XAS spectra of these two samples collected at room temperature. These spectra are in good agreement with that reported in the literature, ⁴⁵⁻⁴⁶ further confirming the chemical composition of *a*-TiO₂ and Li₄Ti₅O₁₂. In contrast to $Li_2WO_4/Li_{1-\delta}CoO_2$ (Figure 3e), no Co 2p signal was observed in the conventional XPS survey scan for $Li_4Ti_5O_{12}/Li_{1-\delta}CoO_2$ (Figure S6), indicating that the $Li_{1-\delta}CoO_2$ cathode seed layer was entirely covered by Li₄Ti₅O₁₂. This result is consistent with the flat surface revealed by AFM measurement (inset of Figure 4a). We note that many factors (such as the defects in the cathode seed layer, the binary transition metal oxide, and the growth temperature) affect the morphology of the resultant films. When fixed the defect type in the cathode layer and the growth temperature for depositing the binary oxide layer, the difference in the morphology of the resultant films is governed by the diffusion kinetics of different species during the nucleation and growth process. It has been reported that when WO₃ is evaporated, the majority species in the gas phase are stoichiometric W_3O_9 (or $(WO_3)_3$) clusters, also known as van der Waals complexes.⁴⁷⁻⁴⁸ In contrast to other transition-metal oxides (such as TiO₂ and Fe_2O_3), these stoichiometric neutral (WO₃)₃ clusters have been shown to exhibit extremely weak interactions with O₂ and oxide support,⁴⁹ leading to a low diffusion barrier and long

diffusion length that are favorable for Li_2WO_4 island growth. Thus, Li_2WO_4 and Li_2MoO_4 on $LiCoO_2/STO(001)$ have rod-like shape surface (Figure 2a and Figure S4a), while $Li_4Ti_5O_{12}$ and $Li_{0.5}Fe_{1.5}O_{4-\delta}$ on $LiCoO_2/STO(001)$ show smooth film-like surface (Figure 4a and Figure S4a).

In summary, our study shows that the out-diffused Li ions from the cathode seed layers can react with the arriving species on the surface to form novel solid state energy materials during epitaxial growth. The examples we present are $WO_3/LiCoO_2 \rightarrow Li_2WO_4$ (a solid-state electrolyte) and $TiO_2/LiCoO_2 \rightarrow Li_4Ti_5O_{12}$ (an anode) with controlled structures and orientations. Additionally, we argue that this approach can be extended to other TMOs such as MoO₃ and Fe₂O₃ (as shown in Figure S4). We note that the phenomena we observed here can be compared to reactive solid-phase and solid-liquid phase epitaxy,⁵⁰⁻⁵⁴ where small ions (e.g., Li⁺ and Na⁺) can be introduced to epitaxial films after the growth. Our work/approach involves the growth of epitaxial, reactive cathode layers first, which allows us to evaluate the critical roles of defects in regulating the subsequent epilayer composition, structure, orientation, and morphology, all of which are of vital importance in the design of functional materials and energy storage devices. And this novel form of heteroepitaxy can mitigate challenges in synthesizing electrochemically active materials and rationally designed interfaces. First, the upper limit of available Li for the overlayer is determined by the thickness of the Li-containing cathode seed layer, and the degree of Li out-diffusion can be controlled by adjusting the growth temperature for the binary TMOs, thereby yielding access to useful reaction intermediates and/or metastable phases hidden in uncharted territory. Second, the structure and phase evolution as a function of lithiation in the overlayer yields a high-throughput testbed for energy materials discovery. Furthermore, the insights gained here should provide a better understanding of how Li-ions transport in different materials and may

assist in designing structures, interfaces, and devices (such as $Au/Li_2WO_4/LiCoO_2$ and

Li₄Ti₅O₁₂/Li₂WO₄/LiCoO₂) that are of pertinent interest to Solid-State Ionics and LIBs.

ASSOCIATED CONTENT

Supporting Information

This supporting information is available free of charge via the internet at http://pubs.acs.org.

Methods; HAADF-STEM images; XRD and AFM for a WO3 film grown on

LiCoO₂/STO(001) at room temperature; Cross-sectional STEM images of the

Li₂WO₄/LiCoO₂ interface grown on STO(111); Generality of the lithiation-assisted epitaxy

approach to other materials systems; Ti 2p XPS and Ti L-edge XAS; Survey XPS scans.

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FIGURES AND FIGURE CAPTIONS



Figure 1. Conceptual illustration. (a) Schematic illustration of multi-step epitaxial thin film growth with negligible interdiffusion. (b) Schematic illustration of the formation of a novel Li-containing phase resulting from Li out-diffusion when a low-density binary oxide is deposited on a cathode epitaxial base layer. Lattice models for (c) $LiCoO_2$ on STO(001) and (d) $LiCoO_2$ on STO(111), highlighting a twin boundary (TB) and an antiphase boundary (APB) in epitaxial $LiCoO_2$ thin films, respectively. The grey arrows denote the Li ion diffusion pathways in the two structures.



Figure 2. One archetypal example - Li_2WO_4 (from deposition of WO₃ on LiCoO₂). (a) X-ray diffraction θ -2 θ scans of LiCoO₂ on STO(001), WO₃ on STO(001), WO₃ on LiCoO₂/STO(001) and WO₃ on LiCoO₂/STO(111). The asterisks indicate the substrate Bragg peaks. The corresponding AFM images are shown in the insets. The lateral scale bar is 5 µm and the unit in all vertical scale bars is nm. (b) Cross-sectional STEM image of Li₂WO₄/LiCoO₂/STO(001) viewed along [110] direction in the STO substrate. The dashed lines indicate the interfaces. (c) High-resolution HAADF STEM image of the top $Li_2WO_4/LiCoO_2$ interface grown on STO(001), where the layered LiCoO₂ portion has transformed to spinel structure due to Li loss to the WO₃ layer. The spinel structure of $LiCo_2O_4$ (green spheres: Co, blue spheres: Li) is also overlaid for comparison. (d) HAADF STEM image of the Li₂WO₄ film overlapped with the crystal structure (top) and the bulk Li₂WO₄ structure viewed along [010] (bottom). (e) Surface morphological evolution of PLDgrown WO₃ on LiCoO₂/STO(001) at a substrate temperature of 600°C. All AFM images have the same scale bar (5 µm). The number of WO₃ moieties incident on the surfaces is linearly proportional to deposition time in our PLD setup at fixed growth conditions. The deposition time was varied from 20 seconds to 5 minutes from left to right.



Figure 3. Impact on the structures of the cathode seed layer due to Li out-diffusion. (a) and (b) Schematic illustration of the connectivity between the nanostructures of Li₂WO₄/LiCoO₂ on STO(001) (a) and STO(111) (b). Yellow boxes denote Li₂WO₄ islands. (c) and (d) Crosssectional STEM images of the Li₂WO₄/LiCoO₂ interface grown on STO(001) (c) and STO(111) (d) viewed along the [110] substrate orientation. The white dashed lines denote the interfaces. (e) Co 2p HAXPES of LiCoO₂ films before (bare LiCoO₂) and after covered by Li₂WO₄ islands. The black dash line is the guideline for peak position. For comparison, we overlay the Co 2p spectrum of bare LiCoO₂/STO(001) (dashed grey) on the Co 2p spectra of Li₂WO₄/LiCoO₂ samples. (f) and (g) ToF-SIMS images of ⁶Li⁺, Co⁺, and WO⁺ for Li₂WO₄/LiCoO₂ on STO(001) summing over scans 1-8 (f) and 21-28 (g). The area marked by the red square in (f) corresponds to region I in the inset in (h), and this region was not covered by a Li₂WO₄ island. The island marked by the purple circle in (g) corresponds to region II (and region III at scans 29-37, not shown here) in the inset in (h). White dashed circles clearly show that a WO⁺ signal was detected in scans 1-8 (f), but not in scans 21-28 (g), suggesting that the labeled Li_2WO_4 island has been sputtered away by the time scans 21-28 were collected. (h) ⁶Li⁺/Co⁺ counts ratio for Li₂WO₄/LiCoO₂ on STO(001) as a function of the

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sputter region. The error bars are based on the statistical analysis for multiple Li_2WO_4 islands. Schematic illustrations of the corresponding sputter region are shown on the top as the insets.



Figure 4. Deposition of TiO₂ on LiCoO₂/STO(001) leads to the formation of epitaxial $Li_4Ti_5O_{12}$. (a) X-ray diffraction θ -2 θ scan for epitaxial TiO₂ on STO(001) and TiO₂ on LiCoO₂/STO(001). The AFM image for the latter is shown in the inset. The scale bar is 5 µm. (b) HAADF STEM image for the Li₄Ti₅O₁₂/LiCoO₂ interface with the Li₄Ti₅O₁₂ crystal structure overlapped with the image. The white dashed line denotes the interface. It should be noted that the LiCoO₂ region has clearly transformed to spinel structure after overdelithiation. The spinel structure of Co₃O₄ (green spheres: Co) is also overlaid for comparison. (c) The bulk Li₄Ti₅O₁₂ structure viewed along [110]. (d) Ti 3*s* XPS for the TiO₂ and Li₄Ti₅O₁₂ films. The Li 1*s* peak is clearly seen in the Li₄Ti₅O₁₂ spectrum.

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