Anomalous metal segregation in lithium-rich material provides design rules for stable cathode in lithium-ion battery

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Despite the importance of studying the instability of delithiated cathode materials, it remains difficult to underpin the degradation mechanism of lithium-rich cathode materials due to the complication of combined chemical and structural evolutions. Herein, we use state-of-the-art electron microscopy tools, in conjunction with synchrotron X-ray techniques and first-principle calculations to study a 4d-element-containing compound, Li2Ru0.5Mn0.5O3. We find surprisingly, after cycling, ruthenium segregates out as metallic nanoclusters on the reconstructed surface. Our calculations show that the unexpected ruthenium metal segregation is due to its thermodynamic insolubility in the oxygen deprived surface. This insolubility can disrupt the reconstructed surface, which explains the formation of a porous structure in this material. This work reveals the importance of studying the thermodynamic stability of the reconstructed film on the cathode materials and offers a theoretical guidance for choosing manganese substituting elements in lithium-rich as well as stoichiometric layer-layer compounds for stabilizing the cathode surface.
Designing layered cathode materials with high reversible lithium storage capacity, as well as structural and chemical stabilities, is essential for developing new generations of lithium-ion batteries with long cycle life. Lithium-rich layered oxides, in particular, are a class of high-capacity layered cathode materials that can meet the high energy density demand of battery electric vehicles. These oxides, however, are prone to significant oxygen loss during charge/discharge cycles, which in turn leads to notable voltage and capacity fading. The cathode degradation problem can be improved by surface treatment or introducing a content concentration gradient. The cathode degradation problem can be improved by surface treatment or introducing a concentration gradient. The cathode degradation problem can be improved by surface treatment or introducing a concentration gradient. The cathode degradation problem can be improved by surface treatment or introducing a concentration gradient. The cathode degradation problem can be improved by surface treatment or introducing a concentration gradient. The cathode degradation problem can be improved by surface treatment or introducing a concentration gradient. The cathode degradation problem can be improved by surface treatment or introducing a concentration gradient. The cathode degradation problem can be improved by surface treatment or introducing a concentration gradient. The cathode degradation problem can be improved by surface treatment or introducing a concentration gradient. The cathode degradation problem can be improved by surface treatment or introducing a concentration gradient. The cathode degradation problem can be improved by surface treatment or introducing a concentration gradient.

Results

Electrochemical measurement. The electrochemical performance of LRMO materials was tested using lithium half-cells in standard 2032 coin-cells. The cycled electrodes were collected for the subsequent chemical sensitive electron tomography, aberration-corrected electron microscopy, and X-ray spectroscopy. The half-cell was discharged between 2.0 V and 4.6 V. Figure 1a shows the electrochemistry behavior of LRMO material at a charge/discharge rate of C/10 (see the method section for details). It shows a high voltage plateau at around 4.2 V in the first charging process and a large first-charge capacity of 290 mAh/g. It has been widely accepted that the high voltage plateau is associated with the anionic redox activation. With continued cycling, capacity and voltage fading were observed for this high voltage charge limit cycling (Fig. 1a, b).

Bulk structure and chemistry. The lithium-rich layered structure proposed for LRMO shown in the inset of Fig. 1c is verified by an X-ray powder diffraction measurement (Fig. 1). Because pair distribution function (PDF) measurement is sensitive to both short-range and long-range ordering of structures, we investigated the ensemble structural change of the oxide lattice by X-ray pair distribution function (PDF) measurement of a pristine electrode and an electrode after the twentieth cycle (Fig. 1d and Supplementary Fig. S15). By comparing with the PDF of a Li2RuO3 reference, it shows that the pristine LRMO material retains the structure of Li2RuO3 with reduced lattice parameter values due to the inclusion of the smaller manganese ions. After 20 cycles, however, all peaks in the LRMO PDF become weaker and broader (also see Supplementary Fig. 15). This is indicative of the increased disorder in the structure, which suggests that the long-range ordered oxide lattice has been broken into smaller domains.

This finding agrees with our electron microscopy results that will be shown next. In addition, the transition metal-oxygen (TM-O) peak shifts to a larger distance, indicating the reduction of transition metal and the loss of oxygen. Apart from structural measurement, hard and soft X-ray absorption spectroscopy are employed to study the change of local bonding environment of Ru and Mn. Figure 1e shows the X-ray absorption near-edge structure (XANES) of Ru K edge before and after cycling. The change in the XANES spectra, although small, is noticeable showing that there is a very slight reduction Ru at the reconstructed oxide surface and forms metallic clusters at the nanoscale. In conjunction with ab initio calculations, this study reveals the intricate connection between the instability of the reconstructed layer at the surface and the degradation of the layered cathode materials in bulk. At the first glance, the metallic Ru segregation effect seems to contradict Shin et al.’s computational prediction that Ru is a high-ranking oxygen retention dopant on the surface of Li2MnO3. On the contrary, the two studies investigate surface stability of lithium-rich oxides in different regimes of oxygen release. In this study the consideration of the surface reconstruction phase, when severe oxygen release takes place in deep charging states, adds an additional constraint to guide the screening of surface dopants. Our DFT calculations identify that 3d element dopants, Sc, Ti, V, Cr, and 4d element dopants, Y, Zr, Nb, Mo can be added to the surface to conceal capacity contributing but less stable elements in the bulk. Based on the theoretical calculation, we synthesize a lithium-rich nickel-titanium-niobium oxide material, expecting that titanium and niobium can stabilize the surface. Imaging results of this material show no hint of elemental segregation even after 50 charge/discharge cycles, which experimentally validates our theoretical prediction.
the bulk level; however, the change of Ru oxidation state is too little to be quantified with statistical significance. On the other hand, soft X-ray absorption spectra of Mn L3 edge measured in the partial-fluorescence-yield (PFY) mode and the total-electron-yield (TEY) mode show a more noticeable reduction of the valence state. By fitting the PFY Mn L3 edge with a linear combination of Mn2+,3+,4+ reference spectra, Mn’s bonding environments are decomposed as Mn2+:Mn3+:Mn4+ = 0.024:0.138:0.838 for the pristine material and Mn2+:Mn3+:Mn4+ = 0.039:0.402:0.559 after 15 cycles. The considerable reduction of Mn suggests that oxygen loss likely occurred. The decomposition of TEY Mn L3 edge shows more prominent valence reduction, i.e., Mn3+:Mn4+ = 0.220:0.441:0.339 after 10 cycles and Mn2+:Mn3+:Mn4+ = 0.320:0.517:0.163 after 17 cycles (It is worth noting that s-XAS has a probe depth of ~100 nm in the PFY mode and a probe depth of ~10 nm in the TEY mode. Therefore the TEY spectral information reflects Mn reduction on the surface, which typically is more degraded than the bulk; whereas, the Mn valence quantification of the PFY spectra here is considered qualitative for the bulk information). All these synchrotron X-ray measurements suggest although the overall oxide structure is maintained, irreversible crystal and microstructural degradation occurred in the LRMO materials during cycling.

**Morphological and chemical change at the particle and the atomic scales.** To obtain a direct visualization of the structural changes, electron tomography and atomic-resolution transmission electron microscopy study were performed. Using energy dispersive X-ray spectroscopic (EDX) mapping in the scanning transmission electron microscopy (STEM) mode, in conjunction with electron tomography, we obtained the chemical distribution of ruthenium and manganese in the LRMO primary particles in three dimensions. Figure 2a shows that the as-prepared sample has a manganese-rich surface and a ruthenium-rich core (also see Supplementary Movie 1). Apart from some minor...
content inhomogeneity, the as-prepared primary particles are generally in uniform solid solution structure without observable internal defects or pores (see Supplementary Figures 1 and 21 and Movie 2 for the visualization of the internal structures of a pristine particle). It is worth noting that the LRMO primary particles are terminated with rounded surface with sparseness of well-defined facets (Supplementary Figs. 1, 23, and 26). This “potato-like” crystal habit is different from those of the materials made using co-precipitation or molten-salt methods, which typically provide primary particles with well-defined facets. After 97 charge/discharge cycles, however, the chemical distribution of manganese and ruthenium in a fraction of the particles was significantly different from the pristine sample as shown in the reconstructed STEM-EDX tomography images in Fig. 2b and Supplementary Movie 3. A significant chemical segregation is observed at the scale of tens of nanometers.

To investigate the atomic structure evolution, an extensive number of aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were recorded. Only some of the representative ones are shown here in Fig. 3 and Supplementary Figures 20, 26 and 27. Because HAADF-STEM uses high-angle scattered electrons to form images, the contrast of the resulting image is sensitive to the projected atomic mass of the underlying atomic columns. This contrast is commonly referred to as Z-contrast. Therefore, when the layered oxide is oriented such that the c-axis basal planes are parallel to the electron beam, the atomic-resolution Z-contrast image would show an alternation of transition metal (higher intensity) and lithium (lower intensity) layers with a period of ~4.8 angstroms.

**Fig. 2** Three-dimensional visualization of the chemical and structural change of Li$_2$Ru$_{0.5}$Mn$_{0.5}$O$_3$ (LRMO) before and after extended charge/discharge cycling. Three-dimensional distribution of Ru and Mn of **a** pristine LRMO and **b** LRMO after 97 charge/discharge cycles reconstructed by STEM-EDX tomography. **c** annular dark-field STEM tomographic (ADF-STEM) reconstruction of a LRMO primary particle after 97 cycles. Two cross-sectional images of the three-dimensional reconstruction are presented to demonstrate that a porous structure had developed throughout the particle (also see Supplementary Figs. 2 and 16 and Supplementary Movie 2). (Scale bar: 100 nm)
Figures 20, 26 and 27 show that the projected structure of the pristine oxide follows this layered pattern, and the lattice maintains coherence from the surface to the interior/bulk as expected from previous PDF results. It is worth noting that in the pristine sample, all lithium channels remain dark with nearly no observable surface reconstruction layer. To support this claim, a wide field image of the surface is shown in Fig. 3a(iv) and images of other surfaces/facets are shown in Supplementary Figures 20, 26, 27. However, upon cycling, drastic structural changes occurred in the material as shown in Fig. 3b and Supplementary Figure 3. The oxide backbones are significantly disrupted and small 1–2 nm clusters are segregated out onto the surfaces. In addition, based on the Z-contrast STEM image, the near-surface portion of the lithium channels are filled with transition metals (Fig. 3b(ii) and for details see Supplementary Fig. 4). Furthermore, we analyzed the segregated nanoparticles on the surface. The higher intensity of the segregated nanoparticles on the surface indicates that they likely contain ruthenium atoms. This is further confirmed by STEM-EDX mapping showing that the high-intensity particles are clearly rich in ruthenium (Supplementary Fig. 5). Interestingly, we found that the atomic structure of the segregated nanoparticles agrees well with the hexagonal close packed ruthenium metal, as shown in the inset picture in Fig. 3b. Such metallic segregation phenomenon at the
atomic scale has never been reported before in lithium-ion battery cathode materials. To eliminate the possibility that the formation of clusters is caused by a reaction that happens at the lower voltage region during electrochemical cycling, we raised the lower cutoff voltage to 3.5 V. Supplementary Figure 6 shows that in this condition, after one charge/discharge cycle, high-intensity clusters are still observed in the near-surface region of the LRMO particles, confirming that the formation of these clusters is not driven by an electrochemical conversion reaction.

**Surface chemistry.** To confirm the segregated particles are ruthenium metal clusters, we further investigated the chemistry of the segregated particles using spatially-resolved electron energy loss spectroscopy (STEM-EELS) and X-ray photoelectron spectroscopy (XPS) with around 5 nm probe depth. The STEM-EELS chemical maps, shown in Fig. 4a, indicate three different regions: the first region has all three elements, Ru, Mn, and O (marked as region 1 in Fig. 4a); the second region has Ru only (marked as region 2); and the third region has Mn and O and little Ru (marked as region 3). Figure 4b shows the spectra integrated from the three marked areas in Fig. 4a. It is interesting to note that in region 2, both ruthenium $M_{4,5}$ and $M_{3,4}$ edges are prominent, but no signal representing oxygen K-edge and Mn $L_{2,3}$ can be detected. In region 3, both manganese $L_{2,3}$ and oxygen K edges are present with very little observable signal representing ruthenium $M_{4,5}$ and $M_{3,4}$ edges. These results show that the ruthenium is segregated from manganese oxide framework and fully reduced to a metallic state.

To understand the chemical environment of Mn and its spatial variance, we performed a near-edge fine structure mapping of the O-K edge and the Mn $L_{2,3}$ edges in the near-surface region of a cycled primary particle (Supplementary Fig. 7). The results show that there is a clear down-shift of the Mn $L_3$ white line and a reduction of $L_3/L_2$ ratio as the probed area moves closer to the surface, which indicate that the valence of Mn decreases when approaching oxide surface. At the very surface, the Mn spectral shape has a close reproduction of the near-edge fine structures of Mn$^{2+}$, which is consistent with our XPS results (Supplementary Fig. 24); whereas the area that is 6 nm away from the surface, a Mn$^{3+}$ fingerprint and $L_3/L_2$ ratio are shown, which is in agreement with the soft-XAS TEY results (Supplementary Fig. 7e). The pre-peak of the O-K edge, that probes the unfilled $O 2p$-TM 3$d$ hybridized states, shows the same trend; the
pre-peak intensity is reduced close to the surface area, which indicates a reduction of the transition metals in the oxide. The Mn$^{2+}$ surface layer becomes much thicker in the electrode after the 120 cycles (Supplementary Fig. 25). All these results suggest that there is a Mn-O rock-salt or a Li$_{1-x}$Mn$_{1+x}$O$_2$ lithium-containing disordered rock-salt reconstruction layer formed on the surface due to oxygen loss.

To be cautious about the potential artifacts induced by radiation damage of the electron beam, the EELS map was collected with limited dosage. To fully eliminate this concern, we also performed X-ray photoelectron spectroscopy (XPS) study on the cathode surface to confirm the EELS results, since the radiation damage caused by a broad X-ray beam in this type of material is negligible. The XPS results of ruthenium 3p$_{1/2}$ and 2p$_{3/2}$ core-level spectroscopy, plotted in Fig. 4c and Supplementary Figure S22, clearly show that the reduction of ruthenium from Ru$^{4+}$ to Ru$^{0}$ took place on the surface through cycling. This does not only confirm our atomic-resolution imaging and EELS results, but also indicates that the reduction of Ru$^{4+}$ and formation of metallic Ru, occurred not only in limited regions, but also over most parts of the LRMO cathode surfaces, since XPS probe a large area of the sample surface. The XPS spectra of Mn 2p, as shown in Supplementary Figure 24, shows that after 120 charge/discharge cycles, manganese is reduced from 4$^+$ to 2$^+$ valence state, which is in agreement with our STEM-EELS results shown in Supplementary Figure 25.

Theoretical understanding and prediction. The formation of metallic ruthenium on the surface of the cathode is unexpected and surprising, but it aligns with the observed segregation of ruthenium and manganese at the submicron-scale by the chemical sensitive tomography technique. Our PDF results suggest that the layered oxide backbone in the bulk is still preserved after charge/discharge cycling, which is in good agreement with our atomic-resolution images. However, the STEM-EELS and XPS results suggest that a rock-salt/lithium-containing disordered rock-salt surface reconstruction occurred on the cathode surface. Since ruthenium and manganese are intermixable in the pristine layered oxide structure, we highly suspect that the segregation of metallic ruthenium is due to its incompatibility with the surface-reconstructed rock-salt/lithium-containing disordered rock-salt environment.

To explore this hypothesis, we performed a full convex-hull calculation for the Ru-Mn-O system. It is worthwhile to mention that transition metal segregation and surface reconstruction, from layered structure to spinel structure and finally to rock-salt/lithium-containing disordered rock-salt structure, are gradual degradation processes upon electrochemical cycling. Figure 5a shows the calculated ternary phase diagram and Fig. 5b presents the stable phases along the bisecting line of the phase diagram for Ru:Mn = 1:1 with changing oxygen chemical potential. It shows that under equilibrium conditions, for the full range of manganese being 2$^+$ valence state, ruthenium is only stable in its metallic form. It means it is thermodynamically favorable for ruthenium to reduce to metallic state, which then subsequently segregate out as pure ruthenium clusters in the degraded rock-salt environment.

Our full convex-hull calculation explains why ruthenium spontaneously segregate out on the surface of LRMO and form metal clusters. More importantly, it illustrates that even if ruthenium and manganese are intermixable in their respective parent layered compounds, oxygen loss and surface reconstruction can induce reduction and subsequent segregation/dealloying effects. In comparison, in 3$d$ layered oxides, such as LMR-NMC, the loss of oxygen and collapse of the lithium channels similarly occurs at the surface. The surface reconstruction layer is typically an NMC spinel/rock-salt oxide. Even though it impedes lithium diffusion, it acts as a relatively stable passivation film because NIO, MnO, and CoO are intermixable at any ratios. However, in our LRMO case, the reconstructed surface is thermodynamically unstable and can spontaneously decompose at room temperature (see Supplementary Fig. 8 for ab initio MD calculation revealing the fast kinetics of this decomposition reaction at room temperature). It is disrupted into patches due to the segregation exposes new LRMO surface. This process may repeat itself until the LRMO bulk is fully degraded and hence such a recursive surface disruption directly impacts the bulk structure (see Supplementary Fig. 17). In our LRMO case, the porous morphology is likely a direct consequence of the recursive disruption pathway—i.e., the domino effect or chain reaction—and such phenomenon has also been observed in LRM0 at the secondary particle level.

By combining experiments and ab initio calculations, we have studied the relationship between the stability of the surface reconstruction film and the bulk degradation pathway. When choosing transition metal cations for the surface of layered cathode, rather than only looking at the stability of the layered oxides in their pristine structure, it is equally important to look at the stability and intermixibility of the elements in the reconstructed metal-oxygen (MO) rock-salt/lithium-containing Li$_{1-x}$Mn$_{1+x}$O$_2$ disordered rock-salt phase. To guide future synthesis, we calculated the formation energy of MO for 3$d$ and 4$d$ transition elements and their intermixability with MnO, NiO, and CoO because Mn, Ni, Co are the most widely used elements that can form/stabilize stoichiometric and lithium-rich layered oxide. The trend in Fig. 5c is very clear such that Ru and Rh exhibit positive formation energies and hence possess a thermodynamic driving force for segregation. By further requiring an intermixability with Mn, Ni, and Co, our calculation can narrow the selection to a handful candidates (Fig. 5d and Supplementary Fig. 9), specifically 3$d$ elements, Sc, Ti, V, Cr, and 4$d$ elements, Y, Zr, Nb, Mo (Molybdenum is a borderline candidate, which mix well with Co and Ni but not Mn. It is also worth noting that even though the CaO are SrO are stable in MO, they are not intermixible with MnO/NiO/CoO). These elements can be added to the surface to conceal other active elements, Ru for example, in the bulk. We prospect that only a few atomic layers of doping with these recommended elements can greatly improve the surface stability of the material without sacrificing the energy density and rate capability.

Discussion
Based on our aforementioned theoretical calculations, we synthesized a lithium-rich nickel-titanium-niobium oxide material, expecting that titanium and niobium can stabilize the surface (see supplementary methods for details). Additional, niobium is chosen for it higher intensity in Z-contrast imaging—any segregation of niobium can be easily observed in Z-contrast STEM without ambiguity. The electrochemical performance of lithium-rich nickel-titanium-niobium oxide material is shown in Supplementary Figure 10. This material was imaged in its pristine state, after 15, and 50 cycles, respectively (Supplementary Figs. 11, 12, and 13). The atomic-resolution images of the near-surface area of the oxide material show no hint of elemental segregation even after 50 charge/discharge cycles. This result experimentally validates our theoretical calculation. Here, we only consider using lithium nickel-manganese-cobalt oxide or Li$_2$MnO$_3$ as the backbone structure as these are widely studied by the lithium-ion battery community for their potential
application in next generation batteries for electric vehicles. For other cathode chemistry, for example Sn-, Ti-, Mo-, Nb-based lithium-rich oxide, additional intermixibility diagrams need to be calculated. Additionally, we want to point out that designing a cathode material requires much more consideration than reconstructed surface stability, and our study provides new concepts and an additional design rule for increasing the long-term cyclability of layered oxides. Of course, surface chemistry and uniformity are only two of the important factors for novel lithium-rich cathode material surface coating design. Many other factors, including electronic/ionic conductivity, energy density, side reaction with electrolyte, and manufactural cost should also be taken into consideration.

Additionally, we would like to point out that the ruthenium-manganese system has high thermal stability as long as the delithiation level is not too high. This is also indicative that the Ru segregation, metallic Ru formation, and the resulting porous morphology could be avoided if the battery cell is not charged to

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**Fig. 5** Ab initio calculation for ruthenium segregation and prediction for Mn/Co/Ni substitution that can stabilize the surface. 

**a** Ternary phase diagram showing the complete convex hull for the system.

**b** Presentation of stable phases as a function of oxygen chemical potential phases along the bisecting line of the phase diagram.

**c** Ab initio DFT calculation of the formation energy of metal-oxygen (MO) rock-salt structure.

**d** Ab initio DFT calculation of the solubility of 3d/4d transition metals in MnO, NiO, and CoO. (See Supplementary Figure 9 for the full solubility calculation)
high voltage or the surface of the material is well protected (e.g., concentration gradient, surface coating, electrolyte additives). On the other hand, in this paper, we provide an interesting study to show what would happen when oxygen loss occurs in cells that are deep charged or overcharged.

A multi-dimensional study on the anomalous structural and chemical evolution in Li$_2$Ru$_0.5$Mn$_0.5$O$_3$ is presented in this paper, which combines synchrotron-based X-ray techniques, atomic-scale imaging and spectroscopy, and three-dimensional tomography. Our observations indicate that this oxide undergoes a chemical segregation/dealloying process triggered by high level of delithiation in the bulk and the oxygen loss at the surface. More importantly, the metallic ruthenium clusters are formed and are randomly distributed on the surfaces, which may in turn facilitate a recursive degradation process similar to the domino effect. Our findings provide a new and experimentally validated concept in guiding the selections of proper transition metal elements for the surface of cathode materials in lithium-ion batteries.

Methods

Synthesis of lithium-rich ruthenium-manganese oxide. The Li$_2$Ru$_0.5$Mn$_0.5$O$_3$ samples were prepared by a solid state reaction method. Li$_2$CO$_3$ (Alfa Aesar, 99%), MnCO$_3$ (Alfa Aesar, 99.9%), and RuO$_2$ (Alfa Aesar, 99.9%) (5 wt. % excess of Li$_2$CO$_3$ was used in order to compensate for the loss of Li) were mixed by hand grinding for 1 h. The resulting mixture was heated at 900 °C for 15 h and then 950 °C for 15 h. The heating and cooling rates were maintained at 2 °C min$^{-1}$. Figure S23 shows the morphology and the three-dimensional reconstruction of the as-synthesized Li$_2$Ru$_0.5$Mn$_0.5$O$_3$ material.

Electrochemical measurement. The composite cathode was prepared by slurring the active material (Li$_2$Ru$_0.5$Mn$_0.5$O$_3$), carbon black, and polyvinylidene fluoride (PVDF) with a weight ratio of 8:1:1 in a N-methylpyrrolidone solvent. The slurry mixture was then coated onto an aluminum current collector. High-purity lithium foil was used as the anode.

Synchrotron X-ray pair distribution function (PDF) measurement. Total scattering pair distribution function (PDF) experiments were carried out at beamline 28-ID-2 in NSLS-II of BNL using an X-ray energy of 66.7 keV ($\lambda = 0.186 \, \text{Å}$) and an amorphous silicon area detector (Perkin-Elmer) to obtain data to large momentum transfer values. Data were integrated using the program FIT2D47. PDFgetX348 was used to correct the data for background contributions, Compton scattering and detector effects, and to Fourier transform ($Q_{\text{max}} = 23.5 \, \text{Å}$) the data to generate the pair distribution function, $G(r)$.

TEM imaging and spectroscopy. The atomic-resolution scanning transmission electron microscopy (STEM) imaging of the LRMO cathode material was performed on Hitachi HD2700 (200 keV), JEOL Grand Arm (300 keV), and FEI Talos F200X (200 keV) in a high-angle annular dark-field mode. The electron energy loss spectra were collected by Gatan Enfina and Efinium spectrometers.

X-ray photoemission spectroscopy. Our X-ray photoelectron spectroscopy (XPS) experiments were carried out in an ultrahigh vacuum (UHV) system with base pressures $<2 \times 10^{-9}$ Pa. A monochromatic X-ray source (Al Kα, Mg Kα) was used at 1253.6 eV. The photoelectron signal was collected by a hemispherical electron energy analyzer (PERL). The data were normalized using the Au 4f$_{7/2}$ peak at 84.0 eV. The binding energies were calibrated with respect to the Ag 3d$_{5/2}$ peak at 368.2 eV.

Electron tomography. The annular dark-field STEM (ADF-STEM) tomography tilt series were acquired on an uncorrected scanning/transmission electron microscope with a X-FEG field emission source (FEI Talos F200X). Projection images were acquired from $-70$ degrees to $+70$ degrees with two-degree tilt intervals. The chemical sensitive tilt series were acquired on the same instrument using the spectroscopic signals collected by a Bruker Super-X energy dispersive X-ray spectroscopy (EDX) detector. Projection STEM-EDX maps of ruthenium and manganese were acquired from $-70$ degrees to $+70$ degrees with ten-degree tilt intervals. The tomograms were reconstructed using a custom-written Matlab script implementing the multiplicative simultaneous iterative reconstruction technique. The three-dimensional reconstructions are visualized by Avizo.

Full convex-hull phase diagram calculation. The phase diagram of Ru-Mn-O was calculated using the Phase Diagram app of the Materials Project45. In this project, the total energy of compounds is calculated using the density-functional theory as implemented in the Vienna Ab Initio Simulation Package (VASP) software. For the exchange-correlation functional, a mixture of Generalized Gradient Approximation (GGA) and GGA + U are used and U values for many transition metals of interest have been calibrated using the approach outlined in Wang et al.’s work50.

Ab initio molecular dynamics simulation. The Ab Initio molecular dynamics (AIMD) simulation was carried out by Vienna ab Initio Simulation Package (VASP). The Perdew, Burke and Ernzerhof functional3 is functionalized to describe the electron–electron exchange-correlation interaction with a plane-wave basis set. The cutoff was 2 × 2 × 2 supercell of RuMnO$_3$ with rock-salt structure is modeled as the starting structure. The canonical ensemble is used with Nose-thermostat and the temperature in AIMD is 300 K. The time step is 0.5 fs with the total 1.3 ps. Spin polarization was not included in AIMD and formation energy calculations.

Formation energy calculation. Self-consistent field, first-principles plane-wave calculations within density-functional theory (DFT) were performed for total energy and optimized structure calculations, as implemented in Quantum Espresso simulation package. The calculations made use of the spin-dependent generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE)52, including Hubbard-U corrections following the formalism developed by Dudarev et al.53. The wave function was expanded in a plane-wave basis set with an energy cutoff of 650 eV, and the unit cell and atomic positions of all structures in the delithiation were optimized until the atomic forces were less than 0.026 eV/Ångstrom. The electron states were sampled using a k-point mesh of 4 × 4 × 2 centered at the origin. For details, please see Supplementary Materials.

Code availability

The custom-written code used in this study is available upon request.

Data availability

The data supporting the findings of this study are available within the article and its Supplementary Information files, or from the corresponding authors on reasonable request.

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H.L.X., X.Y., and X.Q.Y. conceived the idea. All authors designed the experiments. R.L. performed the electrochemical experiments with supervision from X.Q.Y. R.L. performed electron microscopy studies and analyzed the results with supervision from H.L.X. E.H., H.L.X., X.Y., and X.Q.Y. conceived the idea. All authors designed the experiments. R.L. performed measurements and analysis. M.L., Q.W., H.C., J.Z., and K.A.P. performed the ab initio calculations. R.L. performed the synthesis, thermal, and morphological characterization of Li2CoO3 cathodes for Li-ion cell. J. Electrochem. Soc. 151, A1899–A1904 (2004).

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Author contributions

H.L.X., X.Y., and X.Q.Y. conceived the idea. All authors designed the experiments. R.L. performed the electrochemical experiments with supervision from X.Q.Y. R.L. performed electron microscopy studies and analyzed the results with supervision from H.L.X. E.H., X.Q.Y., S.B., Y.W., J.N., and W.Y. performed the X-ray scattering and absorption measurements and analysis. M.L., Q.W., H.C., J.Z., and K.A.P. performed the ab initio calculations. R.L., J.T., J.Z., and X.Q.Y. performed XPS studies and analysis. All authors discussed the implication of the results. R.L. wrote the manuscript with help from all authors.
