Deciphering Structural Origins of Highly Reversible Lithium Storage in High Entropy Oxides with In Situ Transmission Electron Microscopy

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1. Introduction

In recognition of their contribution to the development of advanced electrode materials in lithium-ion batteries (LIBs), the 2019 Nobel Prize in Chemistry was awarded jointly to John B. Goodenough, M. Stanley Whittingham, and Akira Yoshino who enabled the naissance of “a rechargeable world.”[1] So far, the lithium-intercalated anode and cathode materials are still utilized in the majority of commercial LIBs, such as carbons[2–5] and metal oxides,[6–8] characterized by high structural and cycling stability but moderate specific capacity. Unfortunately, the ever-increasing popularity of high-end portable electronic devices and the rapidly evolving electric vehicle industry have spurred the innovations of LIBs toward higher energy and power densities, which are hardly satisfied by the current intercalation-type electrodes. This issue has been addressed through the development of conversion- and alloying-type metal oxide electrodes with quite high theoretical specific capacities.[9–13]
Nonetheless, such electrodes often suffer from rapid capacity fading and disappointing cycling stability due to severe structural degradation with cycling. To reconcile these sharp contradictions, revolutionary design concepts in materials science are desired imminently to expand the library of almighty electrode materials.

Very recently, on the basis of a novel concept of entropy stabilization effect to fabricate single-phase crystal structures of solid solutions, an emerging category of high entropy oxides (HEOs) with multi-component (generally ≥ 5) metallic cations in equimolar or near-equimolar ratios has been prevailing.\(^{[14-22]}\) These cations randomly occupy the same Wyckoff positions of the same crystal structure to maximize configurational entropy \((S_{\text{config}})\). The rocksalt-structured \((\text{Mg}_2\text{Co}_3\text{Ni}_6\text{Cu}_2\text{Zn}_3)_2\text{O}\) compound is the first studied HEO, belonging to an equimolar solid solution of \(\text{MgO}, \text{CoO}, \text{NiO}, \text{CuO}, \text{and ZnO}.\(^{[34]}\) As reported, working as a LIB anode, the HEO materials exhibited high cycling stability (>900 cycles) and specific capacity of nearly 700 mA h g\(^{-1}\) at 0.2 C with Coulombic efficiency very close to unity.\(^{[23-26]}\) By comparison to conventional LIB electrodes, this kind of HEOs also shows superior rate capability with full recovery even after cycling at higher specific currents. Moreover, the relevant electrochemical performances are closely dependent on each of the existing metallic cations, and removing any cation would cause significant battery failure. It is obvious that strong interactions among distinct cations that can be compositionally tailored, and thus the tunable crystallographic structures and unexpected properties are prospectively achieved. Based on the composition engineering, the spinel-type HEO anodes, such as \((\text{Mg}_2\text{Ti}_3\text{Zn}_3\text{Cu}_2\text{Fe}_2)_2\text{O}_4\) and \((\text{Ni}_3\text{Co}_3\text{Mn}_3\text{Fe}_2\text{Ti}_3)_2\text{O}_4\) have also been already designed, leading to the highest charge-discharge capacity of 1235 mA h g\(^{-1}\) among all known HEOs, with 90% capacity retention after 200 cycles.\(^{[27-29]}\) In addition, the entropy stabilization effect is also adopted to create new cathode materials of HEOs with even up to twelve metal cations,\(^{[30]}\) further manifesting the advantage of the large compositional flexibility.

Different from nonmetallic oxides, such as \(\text{SnO}_2, \text{ZnO}, \text{and MoO}_3\),\(^{[31-33]}\) the entropy-stabilized single-phase crystal structure of HEOs could be preserved to act as a host matrix for redox reactions with cycling, which ensures highly reversible energy storage. For instance, Sarkar et al. speculate that although the conversion reactions upon lithiation occurs in \((\text{Cu}_2\text{Co}_3\text{Mg}_2\text{Ni}_3\text{Zn}_2)_2\text{O}\), the formed tiny nuclei still remain “trapped” inside the rocksalt host structure.\(^{[23,24]}\) Therefore, the participating cations can readily re-occupy lattice sites after delithiation and the parent crystal structure can be completely or partially recovered. Apparently, this recovery over the redox process has been regarded to be a key cause for the observed stable cycling behavior. Additionally, it is considered that electrochemically inert Mg\(^{2+}\) may exert a “spectator effect” to restrain the agglomeration of active substances and to maintain as far as possible the HEO structure intact,\(^{[34]}\) which also contributes to the cycling stability. Remarkably, in operando X-ray absorption spectroscopy (XAS) study on this HEO system further points outs that the conversion reactions are irreversible due to the collapse of the rocksalt structure, and this phenomenon of the highly reversible specific capacity should be attributed to the reversible alloying-dealloying reactions involving Mg and Zn.\(^{[35]}\)

The controversy in lithium storage mechanisms also appear in spinel-structured HEOs. The in operando XAS investigation on \((\text{Ni}_0\text{Co}_0\text{Mn}_0\text{Fe}_0\text{Ti}_0)_2\text{O}_4\) conducted by Chen et al. proposed that Ti cations cannot participate in the conversion reaction during lithiation, but instead the spinel \(\text{LiTi}_2\text{O}_4\) was generated to stabilize the parent HEO spinel structure.\(^{[29]}\) This enables most of lithiated products from the conversion reactions of \(\text{M}_2\text{O}_4\) \((\text{M} = \text{Ni}, \text{Co}, \text{Mn}, \text{Fe})\) to easily oxidize back to the original spinel structure. By contrast, it has been proved that even if the inactive Ti cations exclusively present in this HEO system were replaced by electrochemically active Cr cations, high electrode cycling stability can still be achieved.\(^{[27]}\) This suggests that all the cations were subjected to the conversion reactions upon lithiation, resulting in various valence states of the cations; while during delithiation, the spinel structure can be partially recovered, thus ensuring such a good electrode cycling stability. However, for this same HEO electrode, Wang et al. believe that the preservation of the spinel structure is not obligatory.\(^{[36]}\) Despite the irreversible amorphous phase formed during lithiation, the excellent electrode cycling stability and electrochemical performance can be achieved as well. The above-mentioned divergent debates indicate that although the burgeoning HEOs have exhibited congenital potentials as the LIB electrodes, a comprehensive and precise understanding of lithium storage mechanisms of HEOs is still in chaos.

In this work, in situ transmission electron microscopy (TEM) approach\(^{[37,38]}\) including electron diffraction (ED), imaging and spectroscopy is employed to directly observe the lithiation and delithiation behaviors of a new rocksalt \((\text{Co}_0.2\text{Ni}_0.2\text{Zn}_0.2\text{Fe}_0.2)_2\text{O}_4\) HEO material at atomic scale. The in situ approach allows us to track the real-time phase transformations induced by electrochemical reactions as well as the morphological evolution of individual HEO nanoparticles (NPs). Through analyses of the in situ ED results coupled with the spatiotemporal variations of valence states of metal species, the formation sequences of distinct phases are well identified, which is directly correlated with the conversion and alloying reaction kinetics for better understanding of lithiation mechanisms. Furthermore, the polypeptide state after lithiation can be reversibly recovered to the original single-phase structure via the symmetrical deconversion and dealloying reactions upon full delithiation. This reliable structural recovery of HEOs ensures both the superior reversibility and high capacity in lithium storage. In addition, these in situ TEM observations are supported by ex situ measurements and rigorous electrochemical tests to further validate the structural recovery in HEOs responsible for the reversible high-capacity Li-storage even after long-term cycling. Besides, we have also developed one-step high-energy ball-milling (HEBM) method\(^{[39]}\) at room temperature (RT) to prepare such HEOs that can maintain the stable single phase and avoid the occurrence of phase segregations induced by high-temperature solid-state synthesis.\(^{[14,40]}\) It is anticipated that our work can provide valuable guidelines for designing the compositionally engineered HEOs toward almighty electrode materials with long-life energy storage.
2. Results and Discussion

2.1. Structural Identification

The crystallinity and phase purity of (Co\(_{0.2}\)Ni\(_{0.2}\)Mn\(_{0.2}\)Zn\(_{0.2}\)Fe\(_{0.2}\))\(_3\)O\(_{3.2}\) prepared by HEBM have been examined by means of powder X-ray diffraction (XRD), followed by Rietveld refinement analysis.\(^{[41]}\) Figure 1a. For convenience, (Co\(_{0.2}\)Ni\(_{0.2}\)Mn\(_{0.2}\)Zn\(_{0.2}\)Fe\(_{0.2}\))\(_3\)O\(_{3.2}\) is abbreviated as M\(_3\)O\(_{3.2}\) (M = Co, Ni, Mn, Zn, and Fe). The diffraction peaks observed at 36.5°, 42.3°, 61.4°, 73.6°, and 77.5° can be well indexed to (111), (200), (220), (311), and (222) planes of the rocksalt structure (ICDD PDF #01-078-0431, space group \(\text{Fm} \text{3} \text{m}\) #225, \(a = 4.262\ \text{Å}, \alpha = 90°\)), respectively. Apart from the above diffraction peaks, no additional XRD peaks arising from impurities can be detected, indicating a pure single-phase crystal structure of this M\(_3\)O\(_{3.2}\) HEO. The refinement analysis of the sample shows that Chi\(^2\) (≈1.06) is almost 1 and Rwp (≈0.56%) is far below under 5%, indicating that the result of the Rietveld refinement is highly reliable. More parameters about the Rietveld refinement are provided in Table S1, Supporting Information. Furthermore, the ball-and-stick model of the rocksalt structure is used to vividly illustrate the atomic-level occupation of this five-cation HEO material, Figure 1b. Green balls represent oxygen anions that occupy the vertex positions of the octahedron, whereas red balls denote cationic sites occupied randomly by five metal cations with an equal probability, resulting in a high configurational entropy (\(S_{\text{config}}\)) of 1.61R calculated by the following formula:\(^{[23]}\)

![Figure 1. Structural and compositional characterizations of as-synthesized M\(_3\)O\(_{3.2}\) HEO materials. a) XRD pattern of M\(_3\)O\(_{3.2}\). Rietveld refinement shows data points (red circle), the calculated intensity (black line), the positions of reflection peaks (green vertical bar) and the difference profile (blue line). b) Crystal structure model of the rocksalt-structured M\(_3\)O\(_{3.2}\). Green balls represent oxygen anions that occupy the vertex positions of the octahedron, whereas red balls denote cationic sites occupied randomly by five metal cations with an equal probability. c) The ED patterns show the polycrystalline feature of M\(_3\)O\(_{3.2}\). Scale bar, 5 1/nm. d) SEM image of M\(_3\)O\(_{3.2}\) shows the morphology of agglomeration consisting of M\(_3\)O\(_{3.2}\) NPs. Scale bar, 0.5 μm. e) TEM image of a single M\(_3\)O\(_{3.2}\) NP exhibits the diffraction contrast-induced speckle-like morphology, implying that the NP consist of smaller secondary crystallites with random orientations. Scale bar, 50 nm. f) HRTEM image of M\(_3\)O\(_{3.2}\). Scale bar, 2 nm. g) HAADF-STEM image and h–m) STEM-EELS elemental mappings at single-nanoparticle level. Scale bar, 50 nm.](https://www.advancedsciencenews.com/doi/10.1002/adma.202205751)
where $R$ is the ideal gas constant, $x_i$ and $x_j$ stand for the molar fractions of ions in cationic and anionic sites, and $N$ represents the number of anions and cations existing in HEOs. More detailed entropy calculation can be found in Supporting Information. In addition, selected area ED has been performed to identify crystal phase of $M_3O_{3.2}$, Figure 1c. The polycrystalline characteristics of this HEO are reflected by eight sharp diffraction rings attributable to (111), (200), (220), (311), (222), (400), (331), and (422) planes of the rocksalt structure (ICDD PDF #01-078-0431), respectively. It should be emphasized that compared with the XRD analysis, the ED identification can gain abundant information of more crystal planes due to its more sensitive detection threshold.

The morphology of $M_3O_{3.2}$ sample has been further characterized by scanning electron microscope (SEM) and TEM imaging. The overview SEM image shows the morphology of agglomeration comprising $M_3O_{3.2}$ NPs with 50–200 nm in size, Figure 1d. The low-magnification TEM image of a single $M_3O_{3.2}$ NP exhibits the diffraction contrast-induced speckle-like morphology, Figure 1e, implying that the NP consists of smaller crystallites with random orientations. As shown by high-resolution TEM (HRTEM) imaging in Figure 1f, the lattice spacings are measured to be 1.32 Å, 2.50 Å, 2.17 Å, and 1.52 Å, corresponding to the rocksalt-structured (311), (111), (200), and (220) planes (ICDD PDF #01-078-0431), respectively. Besides, the $M_3O_{3.2}$ NPs were also analyzed using scanning transmission electron microscopy (STEM) coupled with electron energy loss spectroscopy (EELS) to scrutinize chemical homogeneity of the multi-cationic compound at single-NP level. The high-angle annular dark-field (HAADF)-STEM (namely Z-contrast) imaging combined with the STEM-EELS elemental mappings show that Mn, Co, Ni, Fe, Zn, and O elements exhibit uniform spatial distributions on the atomic scale without any visible segregation, Figure 1g. All the above analyses demonstrate that the as-synthesized $M_3O_{3.2}$ sample should be the chemically and structurally homogeneous solid solution with single-phase rocksalt structure, despite the utilization of Fe$_3$O$_4$ with mixed 2+/3+ valence states as one of the starting raw materials. This suggests a large replaceability between similar metal species used for HEO synthesis due to the strong entropy-stabilized effect, although Fe$^{3+}$ has larger dissimilarity than Fe$^{2+}$ with the other 2+ metal species used here, which may introduce different electronegativity and atomic coordination and thus become a hindering factor to form a homogeneous HEO. The recent report published in Science pointed out that although HEOs could be synthesized above 1150 K followed by indispensable fast quenching, they were kinetically metastable and tended to separate into several constituents at RT. However, the high temperature and fast quenching procedures are not required for our HEO materials prepared only by one-step HEBM method at RT, which can naturally avoid the structural and chemical instabilities caused by the drastic temperature variation. Furthermore, we have confirmed that even if the $M_3O_{3.2}$ sample has been stored for a relatively long time (around twenty months) at RT, it can still maintain the single-phase rocksalt structure with unchanged chemical homogeneity, as validated by additional analyses of XRD, ED, and STEM-EELS elemental mapping in Figures S1–S3, Supporting Information. All these characterizations have verified the success of one-step HEBM method in preparing the stable single-phase HEO materials.

2.2. Real-Time Observation of Lithiation Dynamics at Single-NP Level

In situ TEM investigation has been carried out to explore the lithiation process of $M_3O_{3.2}$ at single-NP level and unravel the underlying lithium storage mechanisms. The nanosized LIB consisting of $M_3O_{3.2}$ NPs was first constructed inside a TEM using a Nanofactory TEM-scanning tunneling microscopy (STM) holder for real-time observation of electrochemical lithiation reactions, as schematically illustrated in Figure 2a. Figure 2b presents the chronological TEM snapshots of three lithiating NPs (labeled I–III), in which only NP I directly contacted Li source (see also Movie S1, Supporting Information). Upon applying a bias to the NPs, the lithiation of NP I was immediately triggered from the point of contact with the Li source, accompanied by an obvious volume expansion. We also notice that NP II exhibited a weaker contrast and its original dark speckles gradually vanished upon lithiation. By further focusing on the area marked by orange frames in Figure 2b, numerous ≈3 nm fine crystallites uniformly dispersed in the expanded NP matrix can be observed after lithiation for 93 s, as highlighted in Figure 2c. In addition, the emergence of diffused but continuous diffraction rings (insets in Figure 2c) after lithiation also suggests the formation of nanoscale crystallites. This finding is in sharp contrast to the previous in situ TEM observations on the conversion or alloying-type electrodes that undergo serious amorphization process. It should be noticed that although NP II cannot directly contact Li source, it was also lithiated by NP I due to the unimpeded inter-NP lithium transport, exhibiting the similar volume and contrast changes to NP I. These two lithiation scenarios, namely, volume-diffusion-dominated lithium transport within single NPs and interface-related inter-NP lithium transport for closely connected NP networks, would be expected to coexist in real electrodes. The inter-NP lithium transport pathway enables thorough energy storage even to such NPs that are not reached by electrolyte in a real cell. However, under the same field of view, there was no any perceptible changes in morphology and contrast in NP III even after more than 30 min. Obviously, it was not lithiated possibly due to its unforeseen separation from NPs I and II. This contrast also implies that the observed morphological changes were attributed to electrochemical lithiation reactions rather than beam-induced phase decomposition, as corroborated by further beam-blank experiments shown in Figure S4, Supporting Information. Therefore, the beam effect on lithiation behaviors of this HEO material can be nearly ignored and the current in situ observations are fully credible.

After confirming the occurrence of lithiation using the in situ TEM observation, the lithiation dynamics of $M_3O_{3.2}$ NPs were further studied by tracking the propagation of lithiation...
reaction front (RF) within individual NPs in real time. It can be found from Figure 2d and Movie S2, Supporting Information, that upon lithiation, a moving RF with a sharp boundary (as marked by red dotted line) began to emerge on NP A that was divided into two kinds of distinct contrasts highly correlated with degrees of lithiation. The lithiated region behind RF showed a weaker contrast and moderate volume expansion compared with the pristine region ahead of RF. As the lithiation proceeded, the RF seemed to be pushed forward by the generation of lithiated region and gradually swept across the entire NP from left to right (as indicated by red arrows), finally completing the full lithiation within around 100 s. By measuring the ratio ($R$) of the projection area of lithiated region on the entire NP as a function of the lithiation time ($t$), the intra-NP lithiation kinetics can be roughly evaluated. To ensure the measurement accuracy, the dynamic lithiation processes of five individual NPs were collected for analysis, as shown by the plots in Figure 2e. All the tested NPs exhibited similar lithiation kinetics regardless of their various original sizes, namely, the percentage of the lithiation area of each NP was rapidly increased at the early stage and then gradually reduced. The sluggish kinetics was likely derived from the reduced lithium concentration and the altered reaction driving force near the RF as lithium was depleted, implying that the lithiation process was mainly controlled by intrinsic volume diffusion of lithium. Further, the plots of the $R$ versus $t$ can be fitted to a temporal power function,[44] namely, $R \propto t^n$ with $n = 0.41$, which obeys the classic volume-diffusion-controlled kinetics behavior. Moreover, the lithiation reaction homogeneity at single-NP level was also examined by HAADF-STEM imaging and STEM-EELS element mapping, Figure 2f. After lithiation shown in Movie S3, Supporting Information, the lithium element was uniformly distributed on the entire particle. Meanwhile, Mn, Co, Ni, Fe, Zn, and O elements were still distributed uniformly without any obvious atomic segregation. The analysis demonstrates that the lithiated NP still maintained the chemical homogeneity, implying that the entire NP underwent the same degree of lithiation. Notably, no cracks and fracture formation appeared in the NPs after lithiation, in sharp contrast to monometallic oxide electrodes that undergo serious materials degradation due to drastic volume change.[45,46] The in situ TEM observation confirmed the reliable mechanical toughness during lithiation of this $\text{M}_3\text{O}_{3.2}\text{HEO}$ material.
2.3. Tracking Phase Transformations during Lithiation by In Situ ED

In concept, the entropy-stabilized HEO still belongs to the category of oxides that universally store lithium by conversion and/or alloying reactions. However, different from traditional monometallic oxides, the multi-cationic HEOs can incorporate various metallic cations into single-phase crystal structures, and their interactions within HEOs could possibly cause more complicated lithiation reaction pathways. Therefore, we have utilized in situ ED to identify phase changes “operando” throughout the entire lithiation process of M$_3$O$_{3.2}$, Figure 3a–f. To ensure the measurement accuracy of each individual phase, at least twenty groups of ED patterns were adopted to determine the interplanar spacing, and then a typical paradigm is provided in Table S2, Supporting Information. Figure 3a shows the pristine ED pattern with eight sharp diffraction rings indexed as the rocksalt phase (ICDD PDF #01-078-0431). Upon an initial lithiation, the grain of Fe phase was first reduced, as detected by an emerging diffraction ring of Fe (111) plane (ICDD PDF #04-002-7431). Meanwhile, Li$_2$O phase was also generated as a featured lithiation product with a diffraction ring of Li$_2$O (220) plane (ICDD PDF #04-004-4918). These indicate the beginning of conversion reaction. At this lithiation stage, the intensity of diffraction rings of M$_3$O$_{3.2}$ became lower and even its (311) plane cannot be distinguished any more. As lithiation proceeded, new diffraction rings of Ni (002) and (011) planes (ICDD PDF #00-045-1027) appeared as well, accompanied by the formation of another Li$_2$O (111) plane, Figure 3c. Further lithiation led to the appearance of Co (220) plane (ICDD PDF #01-073-6906), indicating the reduction of Co phase. Note that the diffraction intensity of M$_3$O$_{3.2}$ was greatly weakened and some diffraction rings, such as its (422) and (400) planes, completely vanished, Figure 3d. Meanwhile, Mn phase with the observable (221) plane (ICDD PDF #04-007-2059) was also detected, Figure 3e. Interplanar spacing values for \{hkl\} planes of various lithiated products are summarized in Table S5, Supporting Information.

Figure 3. Phase transformations tracked by in situ ED and HRTEM imaging during lithiation. a–f) ED patterns used for identifying the phase evolution during the first electrochemical lithiation. After a full lithiation, the rocksalt structure of M$_3$O$_{3.2}$ disappeared; instead, metallic or alloying phases including Fe, Ni, Co, Mn, and Li$_2$Zn$_{0.8}$ were formed. Scale bar, 2.1 nm. g) The radially integrated intensity profiles from time-sequenced ED patterns were plotted as a function of lithiation time. The peaks corresponding to M$_3$O$_{3.2}$ gradually fade away along with simultaneous appearance and gradual increase of a broad peak including Fe, Ni, Co, Mn, and Li$_2$Zn$_{0.8}$ phases. h–l) Ex situ HRTEM images and corresponding FFT patterns of lithiated M$_3$O$_{3.2}$ that was disassembled from the half-cells discharged to 0.01 V. The ex situ observations confirm the presence of Fe, Ni, Co, Mn, and Li$_2$Zn$_{0.8}$ nano-crystallites. Scale bar, 2 nm.
At this stage, the conversion reactions forming Fe, Ni, Co, and Mn phases occurred. However, it is interesting to notice that no Zn phase was detected by the ED patterns. By prolonging lithiation time to full lithiation, the rocksalt structure of M₃O₃.₂ nearly disappeared; instead, apart from Fe, Ni, Co, and Mn phases, the intermetallic phase of Li₀₂Zn₀.₈ with the detectable (100) and (101) planes (ICDD PDF #04-011-9312) was identified, Figure 3f. The indexing of Li₀₂Zn₀.₈ is also provided Figure S5 and Table S3, Supporting Information. The alloying of Zn with Li indicates that before this alloying reaction, Zn phase should have been precipitated via the conversion reaction. But, it cannot be detected by the ED possibly owing to transient existence of Zn phase. To better visualize the overall phase transformations during lithiation, the radially integrated intensity profiles from time-sequenced ED patterns are quantitatively plotted in Figure 3g and the detailed procedures are described in Figure S6, Supporting Information. By comparing the variation of ED intensity upon lithiation, one can see that the peaks attributable to M₃O₃.₂ gradually fade away, along with simultaneous appearance and gradual increase of broad peaks including Fe, Ni, Co, Mn, and Li₀₂Zn₀.₈ phases. The majority of lithiation was completed within around 80 s for the observed NP (shown in Figure S7, Supporting Information). To further validate the in situ ED results, the M₃O₃.₂-based half-cells discharged to 0.01 V were disassembled and the related lithiation products were analyzed by ex situ TEM observations. As shown in Figure 3h–i, the HRTEM imaging and corresponding fast Fourier transformation (FFT) also verify the presence of fine Fe, Ni, Co, Mn, and Li₀₂Zn₀.₈ crystallites. Therefore, through the aforesaid in situ and ex situ TEM analyses, we can deeply understand that M₃O₃.₂ HEO underwent the conversion and alloying reactions during lithiation, resulting in a polyphase state containing Fe, Ni, Co, Mn, Li₀₂Zn₀.₈, and Li₂O phases.

2.4. Visualization of Valence State Distribution by In Situ EELS

In addition to revealing the structure of materials by the real-time imaging and ED, information about their bonding state and band-structure can also be acquired and quantified on a highly spatially resolved scale, via spectroscopic methods provided by the collation of advanced in situ TEM techniques, for example, EELS. Correspondingly, the spectroscopic information can be deciphered to further unravel atomic-level electron state and valence state in materials. Therefore, such capabilities make the EELS become a powerful tool for studying multi-component electrode materials with complicated multi-reaction systems. Here, the valence mappings extracted from STEM-EELS spectra were used to directly visualize the element valence state evolution of lithiating M₃O₃.₂ NPs, which can help further probe lithiation kinetics and pathways, Figure 4. To ensure the accuracy of valence states, 40 (length) × 25 (width) data points in each EELS mapping were selected to analyze for each element, as indicated by horizontal and longitudinal coordinates. The chemical shift and white-line ratio methods were adopted to determine the valence state of each data point. A typical example of describing the detailed process about how the spatial valence mappings of Fe element were obtained from the STEM-EELS mapping is provided in Figures S8–S11, Supporting Information. Figure 4a displays the colored height profile reflecting 3D valence state distribution of Fe species on a partially lithiated NP. For an intuitive observation at single-NP level, the 3D height profile can be converted into 2D contour mapping by projection to show the overall trend of valence state evolution through color scale bars, Figure 4b. We find that on the whole NP, the lower right region of NP in contact with the lithium source (Figure S12, Supporting Information) exhibited a lower Fe valence state as compared to that of the upper left region, due to a longer lithiation time of the former. However, the change trend of Fe valence state was not monotonous. As
shown by Figure 4b, the purple and blue regions on behalf of low Fe valence states even appeared in front of the yellow and green regions representing high Fe valence states. In addition, the 2D distribution contours of Fe valence states also exhibit discrete horizontal stripes. These findings indicate that the lithiation pathways at single-NP level are variable, showing the multi-pathway characteristics.

Moreover, the 2D distribution contours of Ni, Co, and Mn valence states were also obtained in the same way as Fe, Figure 4c–e. At first glance, their valence state distributions have similar trends with Fe, such as the discontinuous gradient and the discrete stripe contours. However, in sharp contrast to Fe, less metallic Ni, Co, and Mn were reduced by comparing their purple areas (near zero valence state) at the same lithiation time. This implies that Fe component had faster reaction kinetics than Ni, Co, and Mn components. Particularly, the purple area with the lowest proportion can be observed for the reduced Mn phase, Figure 4e, indicating the slowest reaction kinetics among them. Further comparisons reveal that the whole piece of unreacted red region appeared on the same location (the upper left part) for Fe, Ni, Co, and Mn components, Figure 4c–e. Nevertheless, this phenomenon is not seen for the distribution of Zn component (Figure 4f), which indirectly implies different reaction mechanisms (i.e., the conversion and alloying reactions) involving with Fe, Ni, Co, Mn, and Zn components. According to the EELS-based valence mappings, one can deduce that the kinetics rate of the conversion reactions can be ranked in sequence forming metallic Fe → Ni → Co → Mn phases. Notably, this sequence is closely related to redox potentials of these cations except for Zn. As listed in Table S4, Supporting Information, Fe$^{3+}$, Fe$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Zn$^{2+}$, and Mn$^{2+}$ cations have different standard electrode potentials ranging from −0.036 V to high −1.180 V, respectively. While for the Zn component, the lowest reaction kinetics could possibly result from its additional alloying process with lithium after its reduction, as proved by the aforesaid in situ ED results shown in Figure 3a–g.

2.5. Structural Recovery Proven by In Situ and Ex Situ Measurements

The highly reversible insertion and extraction of lithium ions in electrode materials are prerequisite for rechargeable LIBs. Furthermore, if the original crystal structure of a certain electrode material can be reversibly recovered upon discharge–charge cycling, it would be regarded as an ideal candidate. However, this structural recovery is difficult to fulfil by current conversion and/or alloying-type electrodes. To evaluate this property of our HEO material, a reversed bias was applied to the already lithiated M$_2$O$_3.2$ NPs to extract lithium ions, imitating a delithiation scenario. The direct comparisons between the pristine, the fully lithiated, and the fully delithiated states from a same individual NP are demonstrated. With the complete outflow of lithium from the lithiated NP, the NP can recover to its initial morphology with the nearly same size and imaging contrast, as observed in Figure S13a, Supporting Information, and Figure 5a,b (see also Movies S4 and S5, Supporting Information). The ED patterns corresponding to the pristine and fully delithiated states are almost the same in the intensity and number of the reflection rings, Figure S13b, Supporting Information. In addition, the FFT patterns from localized HRTEM imaging on the same region (marked by green square frames in Figure S13a, Supporting Information) are also used to show the structural reversibility after full delithiation, Figure S13c,d, Supporting Information. Except for the reflection intensity, the same number of reflection rings in the FFT patterns is observed for the pristine and post-delithiation states, Figure S13d, Supporting Information. These direct comparisons on the same NP should be able to confirm the recovery of the original rocksalt phase after delithiation. It must be noted that the claimed structural recovery does not mean the duplication of original microstructure layouts, including sizes, locations, and defects of the newly formed crystallites within a same NP. So, it is reasonable that the FFT patterns after delithiation exhibit a little different reflection intensity from that before lithiation. More in situ lithiation and delithiation comparisons on the same NPs are provided in Figure S14, Supporting Information (see also Movies S6 and S7, Supporting Information).

The detailed structural evolutions from another NP during delithiation were also tracked in real time by the in situ ED, and the phase transformation pathways were identified, as displayed in Figure 5c–h. Upon delithiation, Li$_{0.2}$Zn$_{0.8}$ phase first vanished from the ED pattern, Figure 5d. It is evident that the dealloying reaction of Li$_{0.2}$Zn$_{0.8}$ phase happened. Meanwhile, the diffraction ring of M$_2$O$_{3.2}$ (200) plane re-appeared again, indicating that the original rocksalt phase began to recover. As the delithiation proceeded, the diffraction rings of Co (114) and Mn (221) planes cannot be clearly discerned any more, accompanied by the emergence of M$_2$O$_{3.2}$ (220) and (111) planes, Figure 5e. Further delithiation led to the disappearance of Mn (442), Ni (103), and Co (220) planes along with the emergence of M$_2$O$_{3.2}$ (420), (311), and (222) planes, Figure 5f. Afterward, Fe (222) and (111), Ni (002) and (011), and Li$_2$O (311) planes also became invisible in succession, Figure 5g. The disappearance of these metallic phases was derived from their re-oxidation induced by the reversible deconversion reactions. At this stage, eight sharp diffraction rings occurred and can match well with the ED patterns of pristine M$_2$O$_{3.2}$ sample shown in Figure 1. With the final disappearance of Fe (111) and Li$_2$O (111) planes in Figure 5h, the entire delithiation process came to the end and the rocksalt-structured M$_2$O$_{3.2}$ can be almost fully recovered, except for a small amount of residual lithium in the form of Li$_2$O. Of course, the residual lithium can be completely by prolonging the delithiation time, as proved by Figures S13 and S14, Supporting Information. Correspondingly, this process of structural recovery can be intuitively reflected by the radially integrated intensity profiles from the above-mentioned ED patterns, Figure S15, Supporting Information. In addition, by comparing the formation sequences of phases through the in situ ED patterns in Figures 3 and 5, we notice an unexpectedly symmetrical phase transformation during lithiation/delithiation involving with the reversible conversion/alloying reactions, as schematically illustrated in Figure 5i. It is supposedly posed that this symmetry can ensure the reversible recovery of the rocksalt structure of M$_2$O$_{3.2}$, thus enabling the highly reversible lithium storage. This finding is absolutely amazing, because most of the conversion- or alloying-type monometallic
oxide electrode materials, such as ZnO, SnO$_2$, MnO$_2$, CuO, Fe$_2$O$_3$, and MoO$_3$,

are typically not reversible to transform back to their original crystal structure after the first lithiation/delithiation cycle. Obviously, the recovery capability of the original rocksalt structure of five-cation M$_3$O$_{3.2}$ HEO after the first cycle should be attributed to its entropy-stabilization effect.

To directly visualize the structural recovery capability, the in situ HRTEM was utilized to compare the pristine state with the states during lithiation and delithiation on a same localized region of an individual M$_3$O$_{3.2}$ NP, Figures S16–S18, Supporting Information (see also Movies S8 and S9, Supporting Information). Before lithiation, HRTEM image clearly showed

Figure 5. Structural recovery capability of the rocksalt structure upon delithiation. a,b) TEM snapshots of morphology evolution of a fully delithiated NP from Movies S4 and S5, Supporting Information, showing the obvious morphological recovery with the outflow of lithium. Scale bars, 50 nm. c–h) ED patterns used for identifying phase evolutions during delithiation. The ED patterns attributable to Li$_2$ZnO$_{0.8}$, Mn, Co, Ni, Fe, and Li$_2$O phases gradually vanished, while the ED patterns of the original rocksalt structured M$_3$O$_{3.2}$ gradually appeared and finally was recovered. Scale bar, 2 nm. i) Schematic diagram of the ED pattern evolutions during the first lithiation and delithiation cycle, vividly demonstrating shows the visualization process of phase evolutions and structural recovery capability in HEO materials.
the polycrystal nature with small secondary HEO crystallites with different crystal orientations, as indicated by blue square frames in Figure S16, Supporting Information. As lithiation reactions progressed, clear lattice fringes of secondary crystallites gradually disappeared, Figure S17, Supporting Information. While upon delithiation, the secondary HEO crystallites with clear lattice fringes re-appeared, Figure S18, Supporting Information. This direct HRTEM comparison on the same region confirms the same structural feature before lithiation and after delithiation. If the single-phase rock-salt HEO cannot be recovered and instead randomly mixed but spatially separated MO (M = Fe, Ni, Co, Mn) phases are formed after delithiation, such secondary HEO crystallites with large-scale lattice fringes would not be re-formed, Figure S18, Supporting Information. In addition, the bulk-level XRD analysis was also used to verify the recovered rocksalt structure, Figure S19, Supporting Information. As expected, the diffraction peaks attributable to the rocksalt structure of HEO anodes vanished after multiple discharges at 0.2 A g\(^{-1}\) instead, a new broadening diffraction peak from metallic (or alloying) nano-crystallites occurred due to the lithiation-induced conversion (or alloying) reactions, as also identified by the in situ ED analysis in Figure 3. It must be emphasized that even after full conversion and alloying reactions, the disappeared rocksalt structure can recover again after delithiation, as proved by the XRD patterns after the 1st, 2nd, and 100th charge at 200 mA g\(^{-1}\), Figure S19, Supporting Information. The bulk-level hard evidence combined with the localized in situ HRTEM observations should be able to support the structural recovery statement.

2.6. Highly Reversible Li Storage Originating from Structural Reversibility

According to the above-mentioned in situ observations, it can be predicted that such an HEO material is fully competent for LIB electrodes with highly reversible Li storage properties. To probe its electrochemical performance, the half-cells based on the as-prepared M\(_2\)O\(_3\).2 and Li metal counter electrode were assembled and tested, Figure 6. The initial three cyclic voltammetry (CV) curves are shown in Figure 6a. Evidently, the area of the first CV curve is larger than those of the other two cycles, probably due to additional contributions from side reactions such as solid electrolyte interphase (SEI) formation.\(^{[55]}\) We have used the ex situ TEM observation to compare the morphology of anode NPs before and after the 1st discharge and charge cycle and found a layer of film formed on the surface of NPs, Figure S20, Supporting Information. This layer of film is around 2–5 nm in thickness, which fits the description of SEI in the previous reports.\(^{[56-60]}\) X-ray photoelectron spectroscopy (XPS) analysis was carried out to further verify the SEI formation after the 1st cycle. As shown in Figure S21, Supporting Information, all the chemical compositions typically attributable to the SEI can be detected by XPS.\(^{[56-60]}\) Note that the nearly full overlap of the second and third CV curves provides strong evidences for the highly reversible Li storage reactions of this HEO anode. The discharge/charge curves of the M\(_2\)O\(_3\).2 anode at a current density of 100 mA g\(^{-1}\) are shown in Figure 6b. The first discharge process shows a typical voltage profile of metal oxide anode in LIBs. There is a clear voltage plateau at around 0.75 V for the first discharge, which is associated with the reduction of M\(_2\)O\(_3\).2 to Co\(_6\), Ni\(_6\), Mn\(_8\), and Zn\(_4\) and the formation of SEI layer and agrees well with the CV result. The initial discharge and charge capacities are 1000 and 717 mAh g\(^{-1}\), corresponding to an initial Coulombic efficiency of \(\approx71\%\), which can be possibly improved by further optimization of electrode binders and electrolytes. In addition, the rate performance of M\(_2\)O\(_3\).2 at various current densities is also examined and is shown in Figure 6c. In previous reports, such conversion and alloying-type oxide electrodes often exhibit substantial capacity degradation at high currents due to limited ionic diffusion kinetics during (de)lithiation. Despite the fact that the M\(_2\)O\(_3\).2 HEO still belongs to the category of oxides, it can deliver high specific capacities of 1076, 780, 746, 686, 608, and 506 mAh g\(^{-1}\) at 0.05, 0.1, 0.2, 0.5, 1, and 3 A g\(^{-1}\), respectively. Even at the high current density of 1 A g\(^{-1}\), it can still maintain \(\approx78\%\) of the capacity delivered at 0.1 A g\(^{-1}\), indicating an effective rate capability. Furthermore, after enhancing the current density to 3 A g\(^{-1}\) for five cycles, the capacity could still be recovered to its original value once the current density was returned to 0.1 A g\(^{-1}\), demonstrating an excellent recovery performance.

Figure 6d further shows cycling performance and coulombic efficiency of M\(_2\)O\(_3\).2 anode over 200 cycles at 0.1 A g\(^{-1}\) with two initial formation cycles at 0.05 A g\(^{-1}\). The initial discharge capacity reaches up to 1000 mAh g\(^{-1}\), and after stabilization at the third cycle, the cell can deliver a stable capacity of 770 mAh g\(^{-1}\) and even 835 mAh g\(^{-1}\) at the 45th cycle. The capacity increase is commonly described as “negative fading” induced by more active sites from as-formed tiny crystallites in conversion-type electrodes.\(^{[61]}\) However, the decrease trend in capacity is also observed after around 70 cycles. This phenomenon could be ascribed to the lacking of optimization for other factors (e.g., binders, electrolytes, and electrode compositions) in the cell. After all, this M\(_2\)O\(_3\).2 HEO is a newly designed electrode material. But even so, the long-term high capacity of above 600 mAh g\(^{-1}\) can still be achieved after 200 cycles and the coulombic efficiency is found to be close to 98.6%. Regarding the rate capability and cycling stability, this HEO possesses better electrochemical performances than monometallic oxides containing five elements of M\(_2\)O\(_3\).2. Figure 6e shows low-magnification TEM image of an M\(_2\)O\(_3\).2 NP disassembled from the half-cell after 200 cycles. Although the NP is entangled with amorphous carbon from additives, it can still remain integrated in shape and no cracks and fracture are visible. The preservation of the original rocksalt phase of the delithiated NP after 200 cycles can be manifested by the corresponding ED pattern and HRTEM image in Figure 6f, g. in sharp contrast to the observations of its lithiated state in Figure S22, Supporting Information, in which the ED, HRTEM, and EELS analyses witness its polyphase state with vanished long-range order in rocksalt M\(_2\)O\(_3\).2. Further XPS comparison show that both the pristine and the delithiated anodes exhibit the mixed valence states of Fe\(^{2+}\) and Fe\(^{3+}\), Figure S23, Supporting Information. This result preliminarily reflects the electrochemical reversibility and structural reversibility, although it does not show how much Fe\(^{2+}\) and Fe\(^{3+}\) can be recovered after delithiation. Certainly, a reasonable proportion should be 1/3 and 2/3, respectively. All these evidences confirm that the HEO mate-
can possess both the highly reversible lithium storage and the structural recovery capability upon cycling. Further in-depth fundamental studies on the electrochemical reversibility will still be necessary in subsequent works, including but not limited to this rocksalt-structured $\text{M}_3\text{O}_3.2\text{H}_2\text{O}$ material.

A comprehensive understanding of Li storage mechanisms of HEOs through the in situ TEM observation reaps positive influences, which can be divided into three aspects. The first aspect is in the RT synthesis of HEOs, which breaks the shackles of high-temperature solid-state synthesis of HEOs.
and eliminates the risk of phase segregations of HEOs stored at RT.[69] Obviously, it is prerequisite for the reversible energy storage and structural recovery of single-phase HEOs. Especially once phase segregations are generated, lithium or sodium superionic conductivity in HEOs would be greatly degraded and the corresponding rate capability would also deteriorate.[17] The second aspect is related to the optimization of reaction kinetics in multi-cationic HEOs. The number of conversion and alloying reactions can be controlled by adopting distinct metal species. For the as-prepared five-cation M$_2$O$_3.2$ HEO, the Fe, Co, Ni, and Mn components only take part in the conversion reaction while Zn species participates in both the conversion and alloying reactions. This can further enhance the electrode capacity but a longer reaction time is required. Thus, it is very necessary to make an effective design of HEOs with rational formulations for desired electrochemical discharge–charge properties. In addition, engineering multiple reaction kinetics can relieve build-up of internal strains induced by large volume changes of NPs, preventing from the pulverization of HEOs upon cycling. Eventually, it is proposed that more attentions should be paid to the optimization of battery system, including conductive additives, organic binders, and working electrolytes suitable for newborn HEOs.

3. Conclusion
In summary, we have proposed a successful one-step HEBM method to fabricate the configurational entropy-stabilized single-phase HEOs at RT, and thus occurrence of phase segregations in HEOs prepared by high-temperature solid-state method can be effectively avoided. Furthermore, the advanced in situ TEM methodology was employed to directly visualize distinct reaction dynamics and phase transformations during (de)lithiation of rocksalt-type M$_2$O$_3.2$ HEO, revealing the novel composition-dependent conversion/alloying reaction kinetics and spatiotemporal variations of valence states. More importantly, we demonstrate the first experimental proof that the polyphase state after lithiation can be recovered to the original single-phase structure of HEO materials via the symmetrical deconversion/dealloying reactions upon delithiation. The unexpected structural recovery can be maintained even after hundreds of discharge-charge cycles, which would undoubtedly ensure the highly reversible lithium storage, as corroborated by the rigorous electrochemical tests and postmortem TEM analysis. The precise understanding of overall lithium storage mechanisms is expected to afford valuable guidelines to compositionally engineer new almighty HEO electrodes for advanced next-generation long-life secondary batteries.

4. Experimental Section

Raw Materials and HEO Synthesis: Manganese oxide (MnO, 99.5%), cobalt oxide (CoO, 99.5%), nickel oxide (NiO, 99.5%), zinc oxide (ZnO, 99.5%), and iron oxide (Fe$_2$O$_3$, 99.5%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. and used without any further purification. The explanation for selection rationale of candidate binary metal oxides can be found in Supporting Information. For two purposes, the Fe$_3$O$_4$ with mixed +2/+3 valence states was used here. One purpose was to verify whether a same metal with different valence states can be replaced with each other or not during HEO synthesis, considering that Fe$^{3+}$ had larger dissimilarity than Fe$^{2+}$ with the other 2+ metal species, which may induce different atomic coordination and become a hindering factor to form a homogeneous HEO. The other purpose was to evaluate the possible but unproven electrochemical reversibility by comparing the evolution of Fe$^{2+}$ and Fe$^{3+}$ species in the cycled HEO anodes. HEO samples were prepared through a facile one-step HEBM method. In a typical procedure, MnO (0.2 mol, 0.9355 g), CoO (0.2 mol, 0.9881 g), NiO (0.2 mol, 0.9850 g), ZnO (0.2 mol, 1.0736 g), and Fe$_2$O$_3$ (0.067 mol, 1.078 g) were weighed and mixed with an equimolar amount of metal species. Then, this mixture was poured into a 100 mL cemented carbide vial with a 20:1 ball-to-powder weight ratio. Specifically, the high-hardness WC/TiC vials and balls (5 mm, 8 mm, and 10 mm in diameter) were used to ensure the required synthesis energy. The HEBM process was carried out at a speed of 500 rpm for 60 h using a planetary ball mill (MITR-YXQM-0.4L, Changsha Miqi Instrument Equipment Co., Ltd.). Finally, the as-synthesized HEOs, termed (Co$_{0.2}$Mn$_{0.2}$Zn$_{0.2}$Fe$_{0.3}$)$_2$O$_3$ for keeping charge neutral, were sieved with a 60-mesh filter for subsequent characterization and testing.

Sample Characterization: Powder XRD analysis of HEO samples were performed by a Bruker D8 Advance X-ray diffractometer equipped with a Cu Ka radiation source operated at 40 kV and 50 mA. An aberration-corrected transmission electron microscope (Cs-TEM, FEI Titan 80–300 kV) was used to identify structural information of the samples by ED and HRTEM imaging. A SEM (FEI Helios 600) was used to observe the morphology of the samples. HAADF-STEM imaging and EELS mapping were conducted to analyze compositional distribution and valence state. The crystal phase of the cycled HEO anodes is identified using a Rigaku MiniFlex600/600-C X-ray diffractometer.

Cell Assembly and Electrochemical Testing: The electrochemical performance testing was carried out with CR2016 coin cells. The as-obtained HEO powder (70 wt%) together with super-P carbon black (20 wt%) were ground evenly, then mixed with aqueous solution of carboxymethylcellulose (CMC, 10 wt%) to form a slurry. Then the slurry was cast onto Cu foil and dried under vacuum at 60 °C for 12 h, and punched to match the required dimensions of the CR2016 coin cell. The active material loading was 0.5–1.0 mg cm$^{-2}$, measured by an electronic balance (Mettler Toledo XPE analytical balance, 0.01 mg resolution). The electrolyte used was 1.0 M LiPF$_6$ in EC/DMC (1:1) with 5 vol% FEC. Lithium foils were adopted as the counter electrode and the reference electrode, respectively. Whatman GF-D glass fiber filters were used as the separator. The coin cells were assembled in a glove box filled with argon gas. The discharge–charge properties, including specific capacity, rate capability, and cycling stability, of the cells were performed in the potential range of 0.01–3.00 V (vs Li+/Li) and the scan rate was 0.1 mV s$^{-1}$. The CV tests were conducted in the potential window of 0.01–3.00 V (vs Li+/Li) at a scan rate of 0.5 mV s$^{-1}$ on an electrochemical workstation (BioLogic VMP3, Dalian Huayang Analytical Instrument Co., Ltd.). The postmortem analyses on the electrode materials were also carried out. The cycled electrodes were taken out of the cells inside the glove box, washed with ethyl alcohol, and then vacuum dried. Afterward, the samples were subjected to TEM characterization.

In situ TEM Electrochemical (De)Lithiation Experiments: The in situ electrochemical lithiation experiments were carried out using a Nanofactory TEM-STM holder in the Cs-TEM (FEI Titan 80–300 kV). In a typical process, the electrochemical setup consisted of the HEO sample as the working electrode, a layer of LiO$_2$ as the solid electrolyte, and bulk Li metal as the counter electrode. The HEO sample was glued to a gold rod by conductive silver paste. A 0.25 mm-thick tungsten (W) wire was cut to produce a fresh tip to scratch Li metal in a glove box filled with argon gas and then was mounted onto the STM-STEM holder. The holder was transferred into the TEM column within several seconds and a native LiO$_2$ layer formed on the surface of Li metal due to its exposure to air. The LiO$_2$/Li electrode on the mobile STM probe could be piezoelectrically driven to contact the HEO with 3D high-precision.
Electrochemical lithiation (or delithiation) occurred when a negative (or positive) bias was applied to the HEO with respect to the Li metal. This drove the transport of Li ions through the LiO₂ layer and enabled lithiation (or delithiation) reactions that could be recorded in real time for subsequent analysis. During the whole process, the joint utilization of ED, EELS, and HRTEM was performed to track phase transformations of HEO and concomitant valence variations of distinct metal species.

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.

Author Contributions
L.S., J.R., and T.L. contributed equally to this work. F.X. and T.L. synthesized the bulk HEO material using a high-energy ball-milling method. F.X. and L.S. conducted all the in situ TEM experiments: W.L., J.R., and L.M. performed electrochemical test of HEO electrodes. F.X. and L.S. prepared the figures and wrote the manuscript with the help of all other coauthors. F.X., L.M., L.S., and Q. Z. supervised the whole work and analyzed energy storage mechanisms. All authors participated in the discussion of the results.

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

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High-entropy oxides, in situ transmission electron microscopy, lithium-ion batteries, reversible lithium storage, structural recovery

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