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Correlations between Transition Metal Chemistry, Local Structure and Global Structure in $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ Investigated in a Wide Voltage Window

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ABSTRACT: $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$, a high capacity lithium rich layered cathode material for lithium-ion batteries, was subject to comprehensive diagnostic studies including *in situ/ex situ* X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), pair distribution function (PDF) and high resolution scanning transmission electron microscopy (STEM) analysis, to understand the correlations between transition metal chemistry, structure and lithium storage electrochemical behavior. Ru-Ru dimers have been identified in the as-prepared sample and found to be preserved upon prolonged cycling. Presence of these dimers, which are likely caused by the delocalized nature of 4d electrons, is found to favor the stabilization of the structure in a layered phase. The *in situ* XAS results confirm the participation of oxygen redox into the charge compensation at high charge voltage, and the great flexibility of the covalent bond between Ru and O may provide great reversibility of the global structure despite of the significant local distortion around Ru. In contrast, the local distortion around Mn occurs at low discharge voltage and is accompanied by a “layered to 1T” phase transformation, which is found to be detrimental to the cycle performances. It is clear that the changes of local structure around individual transition metal cations respond separately and differently to lithium intercalation/deintercalation. Cations with the capability to tolerate the lattice distortion will benefit for maintaining the integrality of the crystal structure and therefore is able to enhance the long-term cycling performance of the electrode materials.

■ INTRODUCTION

Lithium rich layered oxides have attracted a great deal of interests as cathode materials for high energy density lithium ion batteries.¹⁻¹⁵ These materials can be described in average structure of $\alpha\text{-NaFeO}_2$ ($R\bar{3}m$) where excess lithium ions exist in transition metal layers, exhibiting high reversible lithium storage capacity of 250-300 mAh g⁻¹, twice that of commercialized LiCoO₂. Among them, lithium rich manganese based layered oxides (LMLO) are intensively explored.¹⁻¹¹ Consensus has been reached that oxygen release⁵⁻⁶ and redox reaction on oxygen anions^{13, 16-20} partially contributes to the large irreversible capacity observed on first charge and abnormally high reversible capacity on the subsequent cycles. The anionic redox process also triggers migration of transition metal ions, creation of oxygen vacancies and release of oxygen gas, resulting in capacity decay and voltage fade which are major problems that need to be solved for practical applications.^{1-3, 21-23} Attempts have been made to suppress or avoid evolution of oxygen by introducing other cations into LMLO, in particular 3d or 4d transition metals (e.g. Cr, Mo, Nb, Ru) having the capability to realize multiple electron transfer.²⁴⁻³³ The different chemical nature of these elements also affect the bonding nature (e.g. covalency) with oxygen and thus affect the anionic redox process as well as the associated structural degradation.^{12-13, 19, 34} Therefore, it will be interesting to investigate lithium rich layered oxides with variant combination of transition metal cations so as to understand the interplay

between chemical nature of transition metal elements and the lithium storage behavior.

In addition, the lithium rich layered materials present complex short-range structures, as some are described in a composite form with integration of trigonal LiMO₂ phase ($R\bar{3}m$) and monoclinic Li₂MO₃ phase ($C2/m$), while others are claimed to preserve a single solid-solution structure with long-range ordering.^{9-10, 35-39} These differences may arise from not only the different synthetic protocols but also the physical and chemical nature (size, charge etc.) of different elements constituting these materials. It has been argued that different short-range structures will result in differences in overall de/intercalation kinetics for lithium rich oxides.⁴⁰ Moreover, the changes of local structure upon electrochemical cycling are closely related to the overall crystal structural stability associated with cycle performances. Therefore, it will be of great importance to investigate the short-range structure in a variety of lithium rich oxide compounds composed of different transition metal cations, as well as the structural evolution along with lithium insertion and extraction.

In this manuscript, the lithium rich layered cathode $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$, with the combination of 3d and 4d transition metal cations in transition metal layer, is being focused on. The 4d Ru based lithium rich oxides have attracted intensive interests recently, because Ru is able to realize multiple electron transfer and thus has the capability to achieve high lithium storage capacity. Numerous research work indicates that Ru based lithium rich oxides

show fairly good capacity retention (cycle performances) as well as good structural stability (suppress voltage fade).^{12, 15, 21, 41} However, the detailed mechanisms need further in-depth exploration. There are two major reasons to choose the specific composition of $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$: (1) From a structural point of view, the similar crystal structure of Li_2RuO_3 to that of Li_2MnO_3 enables their integration into a solid solution phase at atomic scale,^{15, 28} and thus might potentially simplify the structural analysis and make it an ideal model material to demonstrate. (2) $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ exhibits the best electrochemical performances among the series of $\text{Li}_2\text{Ru}_x\text{Mn}_{1-x}\text{O}_3$ compounds ($x=0, 0.2, 0.4, 0.5, 0.6, 0.8, 1$) as reported by Sathiya and coworkers.¹⁵

The lithium storage behavior in $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ will be discussed in detail in the present work and the discussion is divided into two parts. Firstly, the structural evolution of $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ on multi-length scales over the first charge-discharge process are studied by using a combination of characterization techniques, such as X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), pair distribution function (PDF) and scanning transmission electron microscopy (STEM). On the basis of these experimental observations, the origins of the highly reversible lithium storage capacity for $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ and the factors that affect its cycle stability in the wide range of lithium extraction and insertion are discussed in the second half of the manuscript. Comparisons between $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ and lithium rich oxide composed of other transition metal cations are made, to highlight the uniqueness of the chemical nature of Ru to the different electrochemical behaviors.

RESULTS

Structure of pristine $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$. The average crystal structure of $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ was characterized by XRD with the result shown in **Figure 1**. The overall pattern indicates a well layered structure (e.g. the splitting of two peaks (108) and (110) between 63° and 65°). In addition to the peaks belonging to conventional layered structure, there are superlattice peaks between 20° and 35° that arise from lithium/transition metal ordering. Such ordering reduces the symmetry of the crystal structure from original $R\bar{3}m$ to $C2/m$. A closer look at these superlattice peaks indicates that they are asymmetric, broadened, and different from those observed in the well crystallized Li_2MnO_3 which also has the $C2/m$ symmetry. Such differences have previously been attributed to stacking faults present in the material.⁴²⁻⁴³ In order to obtain more detailed information of the crystal structure, Rietveld refinement⁴⁴ was carried out with TOPAS software using a model structure with $C2/m$ symmetry. In this structure, there are two kinds of stacking planes: the lithium/transition metal plane where lithium occupies the 2b site and transition metal occupies 4g site and the lithium only plane where lithium occupies the 2c and 4h sites. The detailed refinement results are shown in **Table 1**. As can be seen from the table, intraplanar cation mixing (between 2b and 4g sites within the lithium/transition metal plane) instead of interplanar cation mixing (between lithium/transition metal plane and lithium only plane) can well reproduce the XRD pattern. This agrees well with previous synchrotron XRD and neutron powder diffraction results of similar systems.¹⁵

However, it has been demonstrated by Miura and Kimber *et al.* that for pure Li_2RuO_3 the structure should be described by the $P2_1/m$ space group instead of the $C2/m$ space group used for Li_2MnO_3 , due to the prevalence of Ru-Ru dimers caused by metal-metal bonding.⁴⁵⁻⁴⁶ In $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$, it is very likely that Ru-Ru dimers still exist but the confirmation of its existence is challenging. A good fitting of the XRD pattern using the $C2/m$ space group does not rule out the possibility of such existence because Ru-Ru dimers

may distribute randomly and the whole symmetry is not lowered. To address this issue, pair distribution function (PDF) analysis, which provides both short-range and long-range structural information, was carried out and the results are shown in **Figure 2**. The peaks in PDF correspond to various atom-atom distances in the structure. Clearly, even though the $C2/m$ space group can well describe the long-range ($3.3\text{-}20\text{ \AA}$) structure, it fails to describe the short-range structure ($1.7\text{-}3.3\text{ \AA}$). The peak at around $2.5\text{ \AA}$ can only be fitted well using the $P2_1/m$ space group. Therefore, it is unambiguously shown that Ru-Ru dimers still exist in $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$.

Figure 1. Rietveld refinement on the XRD data of the pristine $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$. The black circles and red lines correspond to the observed and calculated intensities respectively. The differences between the observed and calculated patterns (cyan line) and the referenced peak positions of $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ corresponding to space group $C2/m$ are also shown. The inset shows the structure of the pristine $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ material with the O3 stacking. Lithium atoms are yellow, transition metal are blue (Mn and Ru) and oxygen atoms are red.

Figure 2. (a) Results of fitting the short-range ($1.7\text{-}3.3\text{ \AA}$) PDF data using $C2/m$ and $P2_1/m$ space group (blue circles: experimental data; red line: calculated intensities; dark cyan line: the difference). The arrow indicates that the short Ru-Ru bond can only be described well by the $P2_1/m$ space group. The honeycomb clusters in $P2_1/m$ and $C2/m$ space group. Lithium atoms are yellow, transition metal are magenta (Ru) or blue (Mn) and oxygen atoms are red. (c) Results of fitting the long range ($3.3 < r < 20\text{ \AA}$) PDF using model with $C2/m$ space group.

Table 1. Results of the Rietveld refinement in $C2/m$ space group.

Space group $C2/m$			Bragg R-factor= 5.4		
a= 4.994(1) Å, b= 8.6626(9) Å, c= 5.0743(8) Å and β= 109.11(1)					
Atom	Wyckoff site	X	Y	Z	Occ
Li1	2b	0	0.5	0	0.814(7)
TM on Li1					0.186(7)
Li2	2c	0	0	0.5	1
Li3	4h	0	0.286(5)	0.5	1
TM on TM	4g	0	0.1649(4)	0	0.907(4)
Li on TM					0.093(4)
O1	4i	0.187(3)	0	0.216(2)	1
O2	8j	0.258(3)	0.3081(9)	0.235(2)	1

To further understand the local structure of the pristine material, HAADF-STEM was employed to obtain a direct vision of the atomic structure. The STEM image of pristine $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ recorded along the $[100]$ direction is shown in **Figure 3**. Since the image intensity of each atomic column reflects the average atomic number of each atomic column (approximately $Z^{1.7}$),⁴⁷ the bright dots in Figure 3a result from the heavy atomic columns (Ru and Mn) in $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$, while light atoms (O and Li) are nearly invisible in the image. It can be seen that there are no bright dots (representing Ru and Mn columns) in lithium layers, which is consistent with the Rietveld refinement results that there is no cation mixing between the lithium only plane and the lithium/transition metal plane. In the lithium/transition metal plane, most areas mainly have a pattern with a pair of two bright dots followed by one dark dot, indicating a regular intraplanar arrangement of “-Li-TM-TM-Li-” (TM= transition metal) in the lithium/transition metal plane as often seen in Li_2MnO_3 .⁴⁸ In addition, the dark column still exhibits some intensities, indicating the existence of transition metal ions in lithium column. These results agree well with the conclusion of intraplanar cation mixing determined by XRD. However, the lithium/transition metal plane appears a bit corrugated, which cannot be described by Li_2MnO_3 with $C2/m$ space group (Mn, 4g site: 0, y, 0) but perfectly match Li_2RuO_3 with $P2_1/m$ space group (Ru, 4f site: x, y, z) as shown in Figure 3b. Therefore, it further confirms the existence of Ru-Ru dimers in $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$.

Figure 3. (a) The HAADF-STEM image of pristine $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ along $[100]$ zone axis. (b) The structures of

Li_2MnO_3 (space group: $C2/m$) and Li_2RuO_3 (space group: $P2_1/m$)⁴⁵ respectively. Only transition metal ions are presented (Mn atom in blue and Ru atom in magenta). The lithium/transition metal plane become corrugated instead of flat in the presence of Ru-Ru dimers in Li_2RuO_3 .

Electrochemical behaviors of $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$. To evaluate the structure stability of $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ in a wide range of lithium intercalation/deintercalation, the $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3/\text{Li}$ half cells were assembled and cycled in the voltage range between 1 and 4.6 V at a rate of 0.1 C. The voltage profile of the $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ sample shown in **Figure 4a** looks similar to that of LMLO composites.^{4-5, 15} The first charge curve displays a first plateau located near 3.6 V (stage I) followed by a second plateau at 4.3 V (stage II). 1.79 mole lithium ions are estimated to be extracted from $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ on first charge, reaching a chemical composition of $\text{Li}_{0.21}\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ at the end of the charge (corresponding to a charge capacity of 342 mAh g⁻¹). The following discharge profile is different as it shows two distinct slopes above and below 2 V respectively. A discharge capacity of 231 mAh g⁻¹ is achieved on the first slope (stage III), similar to that observed in earlier reports.^{12, 28} Further discharge causes an abrupt voltage drop followed by a voltage slope located at around 1.2 V. A remarkably high discharge capacity of 402 mAh g⁻¹ is obtained for the entire discharge process. The charge-discharge profiles for subsequent cycles look the same. Hysteresis behavior are observed for each charge-discharge cycle and the charge-discharge profile looks asymmetric, that is the voltage profile displays a longer low voltage slope for discharge than that for the corresponding charge process. This phenomenon has also been observed in other layered cathode materials, such as $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, $\text{Li}_2\text{Ru}_{0.9}\text{Zr}_{0.1}\text{O}_3$ and $\text{Li}_{1.2}\text{Cr}_{0.4}\text{Mn}_{0.4}\text{O}_2$, cycled in a wide voltage range.^{29, 49-50}

Galvanostatic intermittent titration technique (GITT) measurements were performed to study the thermodynamic and kinetic features of the material. The open circuit voltage (OCV) curves are showed in Figure 4b. The OCV profile for the first charge process is totally different from that for first discharge process, implying a different reaction mechanism as often seen in other LMLO materials between lithium extraction/insertion on first cycle.^{14, 51-53} A voltage drop, concomitant with large reaction polarization, occurs at the value of around $x=1.4$ in $\text{Li}_x\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ on discharge. The onset of voltage drop takes place at a relatively higher lithium content than that in $\text{Li}_{1.2}\text{Cr}_{0.4}\text{Mn}_{0.4}\text{O}_2$,²⁹ as reported in our previous

work, suggesting a larger capacity can be obtained in cathode region (above 2 V) for $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$. These differences arise from a different phase transition pathway between $\text{Li}_{1.2}\text{Cr}_{0.4}\text{Mn}_{0.4}\text{O}_2$ and $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ upon lithium insertion/extraction, and will be discussed in the later section. In addition, the large overpotential occurs at the end of stage III and similar to that occurs at the end of stage II, representing a slow kinetic process due to the reversible/partially reversible transition metal migration, which changes the site energy of lithium and causes large reaction hysteresis as proposed by Croy *et al.*⁵⁴

Figure 4c shows the cycle performance of $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ in the voltage range of 1–4.6 V. Strikingly, it can cycle very well with a large amount of lithium intercalation/deintercalation. The coulombic efficiency after the first cycle is around 95%, and the discharge capacity retains about 250 mAh g^{-1} after 70 cycles. The decomposition of the electrolyte and side reaction at high charge voltage is partially contributed to the irreversible capacity.^{15, 41} Rate performance was also examined and the results are shown in **Figure S1**. At 1 C rate, the discharge capacity remains 60% of the capacity under 0.1 C discharge. Such a high capacity and reversibility is unusual when compared with other layered compounds.⁴ The presence of Ru may increase electronic conductivity and account for the enhanced rate capability. The electrochemical performance of $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ in the voltage range of 2.0–4.6 V was also tested for cathode use (**Figure S2**). The coulomb efficiency of the first cycle is about 73.8% and reaches 98% for the subsequent cycles. A sustained capacity retention of 207 mAh g^{-1} can be obtained for 50 cycles, similar to that reported by M. Sathiyaraj *et al.*¹⁵ In addition, it displays a suppressed voltage fade than that in Li rich NMC typed $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ reported previously, as shown in **Figure S3**.

Figure 4. (a) Composition vs. voltage profiles of $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3/\text{Li}$ cell cycled at 0.1 C (1 C = 383 mAh g^{-1}) rate between 1.0 and 4.6 V at room temperature. The curve divided into two regions on charge (I–II) and two regions on discharge (III–IV). (b) The GITT profile and open-circuit voltage curves of the $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3/\text{Li}$ cell during charge and discharge as a function

of the Li content or capacity. (c) The cycle performance and coulombic efficiency of the cell for the first 70 cycles.

Redox mechanism investigated by *in situ* X-ray absorption near edge structure (XANES). The redox reaction and the local structure change of $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ during the first cycle and the second charge process were investigated by *in situ* XAS. **Figure 5** shows the normalized XANES spectra for Mn and Ru K-edges, respectively. For easy interpretation, the entire electrochemical process was divided into several stages as marked on the charge-discharge curve. The spectra collected at the beginning and end of the each stage are highlighted with a thicker solid line and color encoded with the cycle labelled on the charge-discharge curve. In general, the threshold energy position of the K-edge XANES spectra of the transition metals is sensitive to their oxidation states, while the shape of the peaks is sensitive to the local structural environment of the absorbing element. The half-height energy position of the XANES spectra can be used to semi-quantitatively determine the valence state of the probing element,⁴ which we use to track the oxidation state changes of the Mn and Ru during electrochemical cycling as shown in **Figure 6**.

The valence states of Mn and Ru are estimated to be Mn^{4+} and Ru^{4+} for the pristine material by comparing the XANES spectra with those of Li_2MnO_3 (Mn^{4+}) and RuO_2 (Ru^{4+}). On the initial charge process in stage I, Ru K-edge XANES spectra clearly show an entire shift towards higher energy, while Mn K-edge XANES spectra only present a slight shape change. It indicates that oxidation of Ru^{4+} compensates for the charge neutrality during lithium extraction. The evolution of the Ru half-energy position shown in Figure 6 reveals that the Ru^{4+} has been oxidized to Ru^{5+} at the end of the stage I, in good agreement with the deintercalation of 0.5 Li^+ in this region. Upon further charging in stage II, both the Mn and Ru XANES spectra do not show rigid edge shift but only display shape changes, suggesting that the charge compensation is not taken place solely on Mn or Ru atoms but also on oxygen atoms as a result of the covalence feature of Mn–O and Ru–O. This has also been proved by Sathiyaraj *et al.*^{15, 41} through the XPS studies that oxygen functions as an electron donor for this charging process. It is noteworthy that a much sharper increase in the pre-edge intensity for Ru (22121 eV) is observed than that for Mn (6540 eV). The pre-edge peak corresponds to the electronic transition from 1s core levels to the 5p(4p) components of 4d(3d)–5p(4p) hybridized states when the Ru(Mn) O_6 octahedral distortion occurs, and the more distorted the octahedron is, the stronger the peak intensity of the pre-edge is.⁵⁵ These imply that the RuO_6 octahedrons in the $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ electrode become more distorted than MnO_6 . Therefore, it is most likely that O atoms around Ru participate more in the oxidation process with the deintercalation of Li^+ , either through removal of some oxygen from the lattice with the formation of oxygen vacancies or creation of holes in oxygen (O[•]). During discharge in stage III, only the XANES spectra for Ru display continuous shift to lower energy, indicating the reduction of Ru^{5+} . The Ru^{5+} ions have been reduced to Ru^{4+} at the end of this stage, where the edge position of Ru XANES spectrum is close to that for pristine $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ as shown in Figure 6. From simple electron counting, the reduction of Ru^{5+} to Ru^{4+} can only account for the reversible intercalation of 0.5 Li^+ per unit formulas and not 1.15 as estimated from the discharge capacity (220 mAh g^{-1} , $\text{Li}_{0.21}\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ to $\text{Li}_{1.42}\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$). Reduction of $\text{O}^{\cdot-}$ to O^{2-} must take place for the charge compensation. Upon further discharge in stage IV, XANES spectra for both Ru and Mn show a rigid shift to lower energy, indicative of simultaneous reduction of Ru and Mn. Compared with standard oxides with known valence state, Ru ions have been found to reduce to slightly lower than Ru^{3+}

at the end of discharge (1.0 V, $\text{Li}_{2.31}\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$), while higher than Mn^{3+} for Mn as shown in Figure 6 and **Figure S4**. The Mn ions become more actively involved in the redox reaction on subsequent cycling and a portion of Mn ions are reduced to Mn^{2+} after 10 cycles (**Figure S5**). It has also been suggested by Zhang *et al.* that Mn^{2+} species formed during the discharge process of LMLO, and could be stored in the cathode.⁵⁶ This may contribute to the voltage and capacity fade in Li-rich materials. During the second

charge (stage V and VI), although the voltage profile is distinct from that of the first discharge, the charge compensation process shows a very similar behavior as the first discharge process but in a reversed direction. This implies that the kinetic issues are more likely to be responsible for the asymmetric charge-discharge profile observed for most layered cathode materials cycling in a wide voltage range.

Figure 5. *In situ* XANES measurement of $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ during charge-discharge process. The normalized Mn and Ru K-edge XANES spectra of $\text{Li}_x\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ during the first cycle and the second charge between 4.6 and 1.0 V vs. Li^+/Li at a rate of 1/8 C. The entire electrochemical process was divided into several stages as marked on the charge-discharge curve. The spectra collected at the beginning and end of the each stage are highlighted with a thicker solid line and color-encoded with the cycle labelled on the charge-discharge curve. The green arrow indicates a rigid edge shift of XANES spectra, therefore representing an oxidation/reduction process taking place on the probing element. The red arrow indicates the shape and intensity change, representing the distortion of the local structure.

Figure 6. Variation of valence state of Ru and Mn estimated from the half-edge position of XANES spectra.

Evolution of structure over the charge-discharge process.

(1) Average crystal structure evolution investigated by *in situ* XRD. *In situ* XRD measurements were carried out to study the average structure change during the first cycle and the second charge. **Figure 7a** shows the selected regions of the *in situ* XRD patterns with the charge-discharge curve given in the right panel. (The full XRD patterns are displayed in **Figure S6**). The invariant peaks are caused by the inactive components of the cell (e.g. PTFE and BeO). All other peaks except those superlattice peaks are indexed using the $R\bar{3}m$ space group for easy interpretation with layered structure. In stage I, it can be seen either from the shifting of the (003) peak in Figure 5a or the fitted lattice parameters in Figure 5c that the lattice parameter “*c*” increases. This is in accordance with previous observations in the conventional layered material (e.g. LiCoO_2) in

which the repulsion between two adjacent oxygen layers increases as lithium is deintercalated, leading to an increase in “*c*”. Interestingly, unlike the case of conventional layered material where lattice parameter “*a*” decreases as a result of delithiation, here an increase of “*a*” is observed. This unconventional increase of “*a*” has also been observed in previous studies by Sathiyar *et al.*¹⁵ The origin of such unconventional behavior has recently been explained by Zhou *et al.*²⁶ and is attributed to the presence of metal-metal bonding. Overall, the “*a*” and “*c*” lattice parameters both increase during the beginning and decrease during the final of the charge, and increase during the discharge, which is the so-called unit cell breathing in layer-structured cathode materials.^{26, 57} The structural evolution of $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ is quite different from that observed in Li_2RuO_3 and Li_2MnO_3 . A significant peak broadening concomitant with the disappearance of the superlattice peaks is observed in stage II, suggesting either the loss of long range stacking order as suggested by recent DFT calculations⁵⁸ or the loss of lithium/transition metal ordering resulting from cation rearrangement. It is worthwhile to note that peaks of (018)/(110), (006)/(012) move towards each other during stage II, indicating the phase transformation from layered to disordered rock-salt or spinel structure.

During discharge on stage III, the peaks shift back to lower angles and the peak intensities increase. The clear split of the peaks of (018)/(110), (006)/(012) during discharge reveal that the layered structure reformed. Superlattice peaks, originally seen in pristine material, are barely observable, indicating that lithium re-insertion cannot bring the system fully back to its original state. Overall, the structural evolution of $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ is quite different from that observed in Li_2RuO_3 and Li_2MnO_3 . For Li_2MnO_3 , the “*c*” lattice parameter increases during the entire charge process.⁵⁹ The structure changes of Li_2RuO_3 associated with lithium extraction and insertion are more complicated. In the process of lithium deintercalation, Li_2RuO_3 is transformed to different phases as monoclinic $\text{Li}_{1.4}\text{RuO}_3$ and rhombohedral $\text{Li}_{0.9}\text{RuO}_3$.⁶⁰ This phase transformation does not happen in $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$.

Figure 7. *In situ* XRD measurement of $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_2$ during charge-discharge process. (a) The selected regions of *in situ* XRD patterns of $\text{Li}_x\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ between 1.0 and 4.6 V vs. Li^+/Li during first cycle and the second charge. (b) The patterns collected at different charge and discharge states. (c) Evolution of the unit cell parameters as a function of time and the Li content. The values were derived from *in situ* XRD data by profile fitting using the $R\bar{3}m$ space group. The shadow mask highlights the region where abnormal lattice expansion occurs, which is only observed during the first charge process.

(2) Local structure evolution investigated by *in situ* extended X-ray absorption fine structure (EXAFS). The EXAFS experiment is a powerful technique to determine the changes of the local structure of the selected absorbers Ru and Mn for $\text{Li}_x\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$. The selected k^3 weighted Fourier transformed (FT) spectra with the uncorrected phase at the Ru and Mn K-edge for as prepared $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ are shown in **Figure S7** and Least-squares fits were performed (**Table S1**). The peak position on the FT-EXAFS plot is typically 0.3-0.4 Å shorter than the actual interatomic distance because of phase shift. A pronounced peak, located at around 2.1 Å of Ru K-edge FT-EXAFS, can be assigned to short Ru-Ru dimer as previously revealed by PDF observation. The major FT peaks in $R < 3$ Å are influenced by single Metal-Metal scattering. The selected FT spectra during first charge and discharge process were presented in **Figure 8**. (More EXAFS spectra are shown in **Figure S8**). In order to collect enough XAS spectra to track the dynamic process during *in situ* experiment, a relatively short k

range data was collected and thus the quantitative fitting of the spectra was not performed. The EXAFS spectra display several unique features when compared with other LMLO materials (e.g. $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Co}_{0.13}\text{Ni}_{0.13}\text{O}_2$,⁶¹ $\text{Li}_{1.2}\text{Cr}_{0.4}\text{Mn}_{0.4}\text{O}_2$,^{29, 62} etc.): (a) A sharp decrease in peak intensities is observed solely on Ru at fully charged state ($\text{Li}_{0.21}\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$), which suggests a significant change of the local environment around Ru. As there is little coordination number change for the first coordination environment due to the minimal scale of oxygen loss,⁶³ the main factor that contributes to first peak intensity reduction might be the local structural distortion. The phenomenon of a significant increase in disorder around a specific transition metal elements is not observed in NMC type lithium rich layered cathodes at charged state,^{29, 64-65} (b) The lithium intercalation/deintercalation process causes local changes around Ru and Mn individually. The local environment around Ru and Mn changes significantly at a deeply delithiated (charged) and lithiated (discharged) state respectively, as schematically shown in **Figure 8b**.

Figure 8. (a) The k^3 -weighted Fourier transform magnitudes of the Mn (left) and Ru (right) K-edge EXAFS spectra of $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ at different charge and discharge states. The suppressed peak intensity of Metal-Oxygen interaction represents the distortion of the metal-oxygen octahedral, which occurs at Ru site during the charge process and Mn site during the discharge process. (b) Schematics of the distorted local environment around Ru and Mn at a deeply delithiated (charged) and lithiated (discharged) state respectively.

(3) Local structure evolution probed by X-ray PDF. Unlike the EXAFS technique which can only provide very local structural information of the first several coordination shells, the PDF method is able to probe a local structure with a longer distance scale ($> 30 \text{ \AA}$). *Ex situ* PDF measurements were performed at the 1st and 5th cycle and the results are displayed in **Figure 9**. The peak position and relative intensity remain similar in both pristine and cycled (1st and 5th) samples, showing the overall conservation of the layered structure. The slight decrease in peak intensity of the PDF curves for cycled samples is indicative of the loss of crystallinity of sample

particles after the first charge and discharge process. The peak around $2.5 \text{ \AA}$, due to the Ru-Ru metal-metal interaction, is observable in all PDF curves of $\text{Li}_x\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ samples. Based on the theoretic calculation of Johannes *et al.* in Li_2RuO_3 ,⁶⁶ the Ru-Ru dimers will be destroyed along with a phase transition from monoclinic to rhombohedra symmetry upon deep delithiation, as can be seen in Figure 9b. This has not happened in $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ and the Ru-Ru dimerization preserves upon the entire charge-discharge process.

Figure 9. (a) *Ex situ* PDF of $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ collected at different charge and discharge states. The dash lines correspond to the first and second coordination shell around transition metals. The peak located at $\sim 2.5 \text{ \AA}$ corresponds to the Ru-Ru bonding, which exists during the entire charge-discharge process. For comparison, PDF of $\text{Li}_{1.2}\text{Cr}_{0.4}\text{Mn}_{0.4}\text{O}_2$ is displayed, which shows no sign of short Metal-Metal bond located at $\sim 2.5 \text{ \AA}$. (b) Comparison of PDF results for $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ and Li_2RuO_3 systems. Ru-Ru dimer interaction disappears for charged Li_2RuO_3 ($\text{Li}_{0.5}\text{RuO}_3$) due to the phase transformation upon extraction of lithium.

(4) Atomic structure evolution probed by HAADF-STEM. HAADF-STEM experiments were further performed to understand the structural change of $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ during charge and discharge at atomic level. The HAADF-STEM images of

$\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ at fully charged state ($\text{Li}_{0.21}\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$), 2 V discharged state ($\text{Li}_{1.42}\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$) and 1 V discharged state ($\text{Li}_{2.31}\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$) are presented in **Figure 10** and **Figure 11**.

For the fully charged sample, the "TM-TM-Li" cation ordering in the lithium/transition metal plane disappears after deep delithiation as evidenced by continuous bright dots, in good agreement with the

in situ XRD results. Moreover, bright dots appear in the Li layers, suggesting the existence of transition metal atoms in lithium layers on the surface of the sample particle. It is likely that a portion of transition metal atoms in the lithium/transition metal plane migrates to the Li layers, resulting in the formation of a disordered structure. Migration of transition metal ions into the lithium layer to fill out the Li vacancies (or tetrahedral site) has also been observed in many other LMLO cathode materials and reported to be one of the causes for the capacity decay and voltage fading.^{9-10, 67-69} In addition, clear atomic images of the well crystallized layered

(or rock-salt) structure cannot be seen in most area of Figure 10b. This is distinct from that observed in many other lithium rich layered materials that layered or spinel framework can still be seen when lithium ions are extracted to a similar extent as in this study. The local structure in $\text{Li}_x\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ turns highly disordered at the fully charged state, likely with microstructural defects (strain and/or size) and inhomogeneity (loss of oxygen, shear of planes, stacking faults, spinel nanodomains formation, transition metal migration, etc.).¹⁵

Figure 10. The HAADF-STEM images of $\text{LiRu}_{0.5}\text{Mn}_{0.5}\text{O}_3$ sample at (a) pristine, (b) charged state (4.6 V, $\text{Li}_{0.21}\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$) and (c) discharge state (2 V, $\text{Li}_{1.42}\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$). The images were recorded along $[100]_{\text{monoclinic}} ([\bar{1}\bar{1}2]_{\text{cubic}})$ directions.

The HAADF-STEM image of the discharged sample at 2.0 V is shown in Figure 10c. The layered structure is recovered after reinsertion of lithium ions, which is supported by *in situ* XRD results showing that the peaks of (018)/(110), (006)/(012) become separate during the discharge process. Pairs of two bright columns can be clearly seen from the transition metal layers in the image, suggesting that most of the migrated transition metal ions have moved back to the original sites as in the pristine material. Bright columns can still be seen but become much less in the Li layers. Even though the local structure experienced highly distortion and cation migration took place upon charging, the "TM-TM-Li" ordering in lithium/transition metal plane is able to be partially recovered.

The local discrepancies between 1 V discharged ($\text{Li}_{2.31}\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$) and the pristine sample are remarkable as shown from the HAADF-STEM images (Figure 11a). (a) The "TM-TM-Li" atomic arrangement in transition metal layers becomes much clearer as compared to that in sample at both pristine and 2.0 V discharged state. Furthermore, the stacking faults are barely seen, as also indicated by Fell *et al.* in their study of $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$.⁷⁰ They suggested that the oxygen framework intends to adopt a different stacking after oxygen vacancy formation and cation migration during the first charge, and such stacking changes may be responsible for the disappearance of the superstructure peaks in the XRD pattern; (b) the anti-phase domain boundary, referred to a shift of cation layers in half distance related

to each other, can be observed as highlighted by the green dash rectangular box shown in Figure 11b. The formation of the anti-phase domain boundaries is often accompanied by the occurrence of a secondary phase. Because all octahedral sites are fully occupied in $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$, further lithiation necessitates the formation of another structure so as to accommodate additional lithium ions until the formation of $\text{Li}_{2.31}\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ at 1 V. The new phase, determined by the high resolution synchrotron XRD, is the so called "1T" phase (space group $P\bar{3}m1$) which was initially observed by Dahn *et al.* when lithiating LiNiO_2 to yield Li_2NiO_2 .⁷¹ The distance between the transition metal layers measured directly from the STEM image is also consistent with that estimated from the structure determined from the Rietveld refinement (Figure 11c and 11d).

Anti-phase domain boundaries have been found to affect the overall lithium diffusivity in these materials.⁷² Zheng *et al.* found that anti-phase domain boundaries exist in LiCoO_2 thin films deposited on single-crystal sapphire substrates.⁷³ They concluded that the domain boundaries disconnect Li-ion diffusion pathways between domains and thus are expected to have a detrimental effect on Li-ion conductivity. The DFT calculation performed by Meng *et al.* also suggests that the formation of anti-phase boundaries in layered Li_2MnO_3 is energetically unfavorable.⁷⁴ Therefore, the anti-phase domain boundaries observed here in deeply lithiated $\text{Li}_x\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ might account for the relatively large overpotential observed in the lower discharge plateau as shown in Figure 4.

Figure 11. Phase evolution of $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ upon discharge to 1 V. Comparison of the HAADF-STEM images of $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ along [100] direction between (a) the pristine and (b) 1 V discharged state ($\text{Li}_{2.31}\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$). (c) Synchrotron XRD pattern of $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ at 1 V discharged state, diffraction peaks belonging to 1T phase can be observed. (d) Schematic representations of the crystal structure changes associated with layered ($R\bar{3}m$) to 1T ($P\bar{3}m1$) phase transition. Lithium atoms are presented in yellow, transition metal are purple and oxygen atoms are red. The rearrangement of oxygen framework from *ccp* to *hcp* stacking is involved.

■ DISCUSSION

(1) Charge compensation mechanism.

The *in situ* hard X-ray Mn and Ru K-edge XANES results indicate that Ru^{4+} is only oxidized to Ru^{5+} and remains unchanged or undergoes a reductive coupling process as claimed by Sathiyar *et al.* (oxidized and self-reduced to promote the oxidation of O^{2-}),¹⁵ which cannot fully explain the large capacity observed on first charge. It is therefore unequivocally demonstrated that the lattice oxygen participates in a redox reaction to compensate the charge neutrality upon extraction of lithium at high voltage (>4 V vs. Li^+/Li). This also agrees well with their findings that the creation of oxygen hole occurs on first charge and O^{2-}/O^- redox process contributes to the reversible capacity on subsequent cycles.^{15, 41} It is interesting to note that the oxygen anions do not universally (or in different forms) participate in the charge compensation as indicated by the Ru K-edge EXAFS spectra. The Ru EXAFS spectra display remarkable peak suppression upon lithium extraction over the initial charge process, implying that the oxygen dimers are more likely to locate around ruthenium cations. The capacity below 2 V can be well explained by the reversible redox reaction occurred on both Ru and Mn, though the charge-discharge curve in this region looks asymmetric. This phenomenon, being explained by Dahn and in our recent work, has been observed in other layered oxides during lithium insertion/extraction in the low voltage range.^{29, 49-50}

(2) Ru-Ru dimer effect and its relevance to structural stability.

The d electron of ruthenium (4d transition metal) is relatively more delocalized than that of 3d transition metal,⁷⁵ enabling the Ru-Ru

dimerization in such a specific layered structure.⁷⁶ Although the Ru-Ru dimers are locally formed, they have global impact on the average crystal structure as well as the overall electrochemical performances. (a) The existence of Ru-Ru bonding restrains the contraction of the “*a-b*” plane during lithium extraction as usually seen in LMLO, and the overall lattice shows abnormal lattice expansion;⁷⁶ (b) Unlike the disappearance of Ru-Ru dimer in delithiated Li_2RuO_3 ($\text{Li}_{0.5}\text{RuO}_3$), Ru-Ru dimer interaction exists over the entire charge-discharge process for $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$. The Mn cations act as “structural stabilizer” to tolerate the local structural changes occurring around Ru upon lithium extraction, without incurring phase transformations as happened in Li_2RuO_3 .⁶⁰ Meanwhile, the relatively flexible Ru-O framework (a wide variation of Ru-O bond distance) might favor the stabilization of oxygen holes and dimers as demonstrated by Chen and Wang, enabling the reversible utilization of oxygen related redox reactions;^{77,78} (c) In addition, the Ru-Ru dimer interaction seems to favor stabilization of the phase in a perfect layered structure. Even though deep lithium extraction causes significant distortion of local structure as well as interplanar cation mixing upon charging, the entire crystal structure is able to convert back to its pristine state with the **partially recovery** of in-plane ordering upon discharging (2 V state, $\text{Li}_{1.42}\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$), as supported by *in situ* XRD, and *ex situ* STEM. Therefore the $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ exhibits fairly good cycling performances in the cathode operating voltage range (2-4.6 V) in comparison to those of Li_2MnO_3 and Li_2RuO_3 .^{48, 79-80}

(3) Phase transformation associated with overlithiation.

The atomic resolution STEM image of discharged sample ($\text{Li}_{2.31}\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$: nominal composition of $\text{Li}_{1.21}[\text{Li}_{0.33}\text{Ru}_{0.335}\text{Mn}_{0.335}]\text{O}_2$ in the layered oxide form) clearly shows a region with antiphase grain boundary. This kind of dislocation can act as nucleation center for growth of a new phase, as proposed and directly observed by A. Ulvestad *et al.* based on their *in situ* Bragg coherent diffraction imaging researches on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.⁷⁴ Indeed, the formation of a secondary phase is unavoidable when lithiation exceeds the lithium content than that in pristine $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$. The overlithiation usually leads to growth of the 1T Li_2NiO_2 phase and accounts for the low voltage plateau on the discharge curve for most layered cathode oxides.⁸¹ The phase transformation from originally O3 layered structure ($\alpha\text{-NaFeO}_2$ layered structure) to 1T Li_2NiO_2 structure involves the change of the oxygen framework from *ccp* stacking to *hcp* stacking and causes a large increase in the unit cell volume of around 38%. Such phase transformation with large unit cell volume changes is kinetically not favorable for cycle and rate capability.⁸² However, the “layered to 1T” phase transformation has not been observed in $\text{Li}_{1.2}\text{Cr}_{0.4}\text{Mn}_{0.4}\text{O}_2$ upon overlithiation until $\text{Li}_{1.5}\text{Cr}_{0.4}\text{Mn}_{0.4}\text{O}_2$ (nominal composition of $\text{Li}_{1.3}[\text{Li}_{0.2}\text{Cr}_{0.4}\text{Mn}_{0.4}]\text{O}_2$ in the layered oxide form). Because the Cr cation is mobile during charge and discharge, the structure is able to be stabilized in a disordered spinel phase,⁶² which is able to accommodate additional lithium without causing a structural change involving rearrangement of the oxygen sublattice upon overlithiation as illustrated in **Figure 12**. As a consequence, the $\text{Li}_{1.2}\text{Cr}_{0.4}\text{Mn}_{0.4}\text{O}_2$ displays better cycle performances than $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ when cycling in a wide voltage range of 1–4.6 V.

Figure 12. Phase transition at low discharge voltage (1 V) and its impact on electrochemical cycling performance. (a) Comparison of capacity retention between $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ and $\text{Li}_{1.2}\text{Cr}_{0.4}\text{Mn}_{0.4}\text{O}_2$, cycled at a rate of 0.1 C. (b) Significant cation mixing occurs in $\text{Li}_{1.2}\text{Cr}_{0.4}\text{Mn}_{0.4}\text{O}_2$ after first charge-discharge process (OCV=4.8 V–1 V), due to the migration of Cr. The cation mixing favors the stabilization of the oxygen sublattice in *ccp* stacking, other than transformation to *hcp* stacking as observed in $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ during deep discharge to 1 V. Lithium atoms are presented in yellow, transition metal are light purple (Cr) or blue (Ru) and oxygen atoms are red in the schematic figure.

It is noteworthy that for practical use, cathode materials are not discharged to a voltage as low as 1 V (vs. Li^+/Li) to allow overlithiation, and as a result it is unlikely to happen under normal operating conditions. However, due to chances of the inhomogeneity of the electrochemical reaction, it is reasonable to expect some areas are more deeply lithiated than other areas, especially upon discharging at a high rate. These areas may be regarded as “locally overlithiated”

and might be detrimental to the battery performances. Therefore, the investigation of the layered oxide in a wide range of lithium extraction and insertion is of vital importance for designing cathode materials with better cycle life.

CONCLUSIONS

To sum up, a multi-faceted investigation has been carried out to study the lithium storage mechanism in $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ and several conclusions have been achieved.

(1) The $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ has a similar average crystal structure of Li_2MnO_3 , which can be described by a monoclinic phase with $C2/m$ space group. Due to the formation of Ru-Ru dimers, its local symmetry is lowered to $P2_1/m$.

(2) The Ru-Ru dimer interaction favors the stabilization of $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$ in a perfect layered structure without interplanar cation mixing, and preserves upon prolong cycling as indicated by the PDF measurements.

(3) The charge compensation mechanism has been determined. The *in situ* XANES experiment confirms the oxidation of Ru^{4+} to Ru^{5+} during the charge process (4.6 V) and reduction of Ru^{5+} to Ru^{3+} , Mn^{4+} to Mn^{3+} during the discharge process (1 V). The residual capacity, which cannot be explained by redox reaction on Ru and Mn, is most likely due to the redox reaction on oxygen anions.

(4) The change of the local environment around Ru and Mn respond differently upon charge and discharge, and significantly affect the cycle performances associated. Ru-O and Mn-O octahedral become highly distorted at deeply delithiated and lithiated state respectively. The distortion of Mn-O octahedral triggers a phase transformation from layered to orthorhombic 1T phase, associated with changes of the oxygen sublattice from *ccp* stacking to *hcp* stacking. Such a “layered to 1T” phase transformation is not observed in $\text{Li}_{1.2}\text{Cr}_{0.4}\text{Mn}_{0.4}\text{O}_2$ due to the migration of Cr during charge and discharge. The migration of Cr allows the structure to be stabilized in a disordered spinel form, which is able to accommodate additional lithium without causing a structural change involving rearrangement of the oxygen sublattice. Therefore, $\text{Li}_{1.2}\text{Cr}_{0.4}\text{Mn}_{0.4}\text{O}_2$ shows better cycle performance than that of $\text{Li}_2\text{Ru}_{0.5}\text{Mn}_{0.5}\text{O}_3$. However, the lithium diffusion kinetics is affected due to the disordered nature of the structure.

It is obvious that different transition metal elements behave differently upon electrochemical cycling and thus affects the overall electrochemical performances of the materials in different aspects. In order to achieve high reversible lithium storage capability with reasonable lithium diffusion kinetics for layered oxide cathode materials, multi-functional elemental doping or substitution is necessary. As for Ru, the increase of the covalence with oxygen favors the reversible redox reaction on oxygen anions. The lattice with Ru also seems to be more tolerant with local distortion, and therefore it is good for maintaining structural stability during long-term cycling. Although Ru is a precious metal, a low concentration doping is still considerable to be implemented, to enhance the structural stability of the layered oxide cathode materials for high energy density applications.

ASSOCIATED CONTENT

Supporting Information

Experimental section, electrochemical properties, *in situ* XRD patterns, *in situ* and *ex situ* XAS. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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