Addressing voltage decay in Li-rich cathodes by broadening the gap between metallic and anionic bands

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Oxygen release and irreversible cation migration are the main causes of voltage fade in Li-rich transition metal oxide cathode. But their correlation is not very clear and voltage decay is still a bottleneck. Herein, we modulate the oxygen anionic redox chemistry by constructing Li2ZrO3 slabs into Li2MnO3 domain in Li1.21Ni0.28Mn0.51O2, which induces the lattice strain, tunes the chemical environment for redox-active oxygen and enlarges the gap between metallic and anionic bands. This modulation expands the region in which lattice oxygen contributes capacity by oxidation to oxygen holes and relieves the charge transfer from anionic band to antibonding metal–oxygen band under a deep delithiation. This restrains cation reduction, metal–oxygen bond fracture, and the formation of localized O2 molecule, which fundamentally inhibits lattice oxygen escape and cation migration. The modulated cathode demonstrates a low voltage decay rate (0.45 millivolt per cycle) and a long cyclic stability.
ncreasing dependence of electric vehicles and energy-storage systems on high-energy Li-ion batteries pressing calls for continual developments in the performance of cathode materials. The improvement space for traditional cathode materials based on transition metal (M) cationic redox is limited to the gradually approached energy-density ceiling. Such limitation is foreseen to be transcended by Li-rich Mn-based oxides, which exhibit both M and O redox activities and a high reversible capacity (>250 mAh g⁻¹). But Li-rich Mn-based oxides universally manifest a daunting challenge of voltage fade with electrochemical cycling, seriously obstructing its practical applications. Although a variety of methods, including bulk doping, surface modification, and adjusting element compositions, have been adopted to restrain voltage fade, none can fundamentally solve it. Recently, scientists have achieved remarkable results in suppressing voltage fade using some other strategies. For example, Li et al. prepared Li-gradient Li-rich single crystals by extracting LiO from molten salt, showing a voltage attenuation rate of 1.17 mV per cycle. Kang’s group synthesized a Li₃O₂-type Li-rich oxide by ion-exchanging, exhibiting a voltage decay rate of about 1.1 mV per cycle. However, the voltage fade issue for Li-rich oxides has still not been fundamentally solved, and its underlying mechanism remains unclear. Both experiments and calculations demonstrate that the direct cause of voltage fade is the irreversible migration of M cations into an empty Li site and the subsequent structural collapse. Recent research manifests that M migration is intrinsically linked with oxygen anionic redox (OAR). For thoroughly studying the voltage decay mechanism, and better suppressing voltage attenuation, a substantial key should lie in regulating OAR chemistry. But this is slowed down by two difficulties.

First, accurate regulation of specific LiₓMnOᵧ lattice should be achieved. The OAR activities are originated from O 2⁻ doping, surface modification, and adjusting element compositions, have been adopted to restrain voltage fade, none can fundamentally solve it. Recently, scientists have achieved remarkable results in suppressing voltage fade using some other strategies. For example, Li et al. prepared Li-gradient Li-rich single crystals by extracting LiO from molten salt, showing a voltage attenuation rate of 1.17 mV per cycle. Kang’s group synthesized a Li₃O₂-type Li-rich oxide by ion-exchanging, exhibiting a voltage decay rate of about 1.1 mV per cycle. However, the voltage fade issue for Li-rich oxides has still not been fundamentally solved, and its underlying mechanism remains unclear. Both experiments and calculations demonstrate that the direct cause of voltage fade is the irreversible migration of M cations into an empty Li site and the subsequent structural collapse. Recent research manifests that M migration is intrinsically linked with oxygen anionic redox (OAR). For thoroughly studying the voltage decay mechanism, and better suppressing voltage attenuation, a substantial key should lie in regulating OAR chemistry. But this is slowed down by two difficulties.

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respectively. This is also verified by the line-intensity profiles (Supplementary Fig. 6) and extended X-ray absorption fine-structure (EXAFS) spectra (Fig. 1e and Supplementary Fig. 7). As declared by the crystal structures of Li$_2$MnO$_3$ and Li$_2$ZrO$_3$ in Supplementary Fig. 8, the metal cations in Li$_2$MnO$_3$ are arranged alternately by Li/Mn layer and Li layer, while in Li$_2$ZrO$_3$, only Li/Zr layer is stacked.

Here in our samples, it is worth noting that the stacking sequence of Mn$_2$Li plate is largely affected. Compared with the perfect Li$_2$MnO$_3$ lattice (Supplementary Fig. 9), the Mn$_2$Li layer of LSLR has a relative slip of $\sim$3°. This change is attributed to the presence of Li$_2$ZrO$_3$ slab distributed in the Mn$_2$Li plate of Li$_2$MnO$_3$, and the resulted lattice strain between Li$_2$ZrO$_3$ and Li$_2$MnO$_3$. To confirm this, AC-STEM was also performed on LR (Supplementary Fig. 10). The result showed that the Li$_2$MnO$_3$ lattice in LR matched perfectly the lattice arrangement of Li$_2$MnO$_3$. The chemical environments of Li are characterized by $^7$Li magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectra. Compared with LR, MAS-NMR results declare that the chemical environment of 30.7% Li in LSLR is changed. These data are far greater than the added Zr content (2%), which should be caused by Mn$_2$Li plate stacking sequence changing, evidenced by STEM image in Fig. 1f. Based on the above analysis, the crystal structure of Li$_2$MnO$_3$ domain in LSLR is confirmed to be slightly distorted as shown in Fig. 1g.

Electrochemical performances of LSLR. The initial charging plots in Fig. 2a declare that the oxygen activation plateau of LR is lower than that of LSLR. The dQ/dV plots clearly show a reduction of 0.07 V for the lattice oxygen activation threshold potential in LSLR than LR. The Li$^{+}$ diffusion performance of LSLR is also different from that of LR. Galvanostatic intermittent titration technique (GITT, Fig. 2b and Supplementary Fig. 11)
shows, at TM redox stage, the diffusion coefficient of Li\(^+\) (\(D_{\text{Li}}\)) for LR and LSLR is almost at the same level. While at oxygen-activating plateau, the \(D_{\text{Li}}\) in LSLR is one order of magnitude higher than that in LR. These results confirm the structural differences in Li\(_2\)MnO\(_3\) domain between LR and LSLR above revealed by structural characterizations. Because of the special structure, voltage and capacity attenuation of LSLR is significantly restrained. The almost unchanged shape of the charging–discharging plots (Fig. 2c) and the corresponding \(dQ/dV\) curves (Fig. 2d) of LSLR manifest a stable redox reaction and low-voltage decay rate. The voltage maintenance and galvanostatic charge/discharge performances of LR and LSLR at 1 C are presented in Fig. 2e. After 300 cycles, LSLR yields a high capacity and voltage retention (91.8% and 96.3%), while LR maintains much less (58.2% and 88.4%). The average voltage attenuation rate per cycle of LSLR is only 0.012% (0.45 mV per cycle). As far as we know, the voltage decay rate is the lowest value among all the previous reports (Supplementary Table 3). Coulomb efficiency indicates that the redox reaction in LSLR is more stable than that in LR. Moreover, LSLR also has a significant effect in suppressing voltage attenuation at a low current rate (Supplementary Fig. 12). In addition, the discharge curves of LR and LSLR are also slightly different (Supplementary Fig. 13). The above results imply different lattice oxygen redox behaviors in LR and LSLR.

Restrained cation migration in LSLR. The migration and redox behaviors of metal cations are largely influenced. Ex situ XRD plots for electrodes at different states of charge indicate that, after one cycle, LR has undergone a certain degree of structural damage, while the structure of LSLR is well maintained, which is evidenced by the coincidence degree of (003) peaks at 18.5° and superlattice peaks at 20.5° for pristine and discharge 2.0-V electrodes (Fig. 3a). Raman results in Fig. 3b demonstrate that a substance similar to rutile MnO\(_2\) (the crystal structure is declared in Supplementary Fig. 14) is produced on the 4.6-V charged LR electrode and does not completely disappear after full discharge, while this phenomenon is not found in the LSLR electrodes. According to the structural characteristics of Li\(_2\)MnO\(_3\) and rutile MnO\(_2\), this MnO\(_2\)-like product should be the result of the superlattice degradation and cation migration. XRD and Raman together demonstrate the good performance of LSLR in maintaining the superlattice.
Considering that the redox behaviors of lattice oxygen will directly affect the coordinated metal, we speculate that the above ex situ XRD and Raman distinctions are caused by the different redox evolution of Mn coordinated with active lattice oxygen during (dis)charging for LR and LSLR. To verify this, both hard and soft X-ray absorption spectra (XAS) are adopted to accurately detect the coordination and valence information of Mn cations in LR and LSLR at different electrochemical states. Two information can be obtained from Mn K-edge spectra (Fig. 3c). Compared with LR, the variations in the chemical environment and valence state of Mn in LSLR with (dis)charging are inhibited, which are evidenced by the reduced changes in the shape of the absorption edge and the white line peak intensity. The comparisons between normalized XAS spectra of the Mn K pre-edge of pristine and 4.6-V charged electrodes for LR and LSLR also support the above discussions. A faint peak, which may come from a reduced Mn–O compound, appears near the Mn K pre-edge region for the 4.6-V charged LR electrode, while LSLR does not have this new peak.

The Mn L2-edge spectra obtained in total electron yield (TEY) mode (Fig. 3d) reveal that, prior to charging, Mn element in LR and LSLR shows a typical lineshape for Mn$^{4+}$, including a major peak at 642.8 eV and a weak shoulder at 640.4 eV. However, significant differences are produced after (dis)charging for Mn cations in LR and LSLR. From pristine to charged and discharged states, Mn cations in LR are increasingly reduced, declared by the appearance of peaks located at 639.6 and 641.0 eV, which are attributed to Mn$^{2+}$ and Mn$^{3+}$, respectively. While for Mn cations in LSLR, it is only slightly reduced at the discharged state. It indicates a different redox behavior for Mn cations in LSLR from that in LR. The restrained formation of Mn$^{2+}$ and Mn$^{3+}$ is favorable for inhibiting cation dissolution and maintaining structural stability. In addition, the same changing trend of Ni L$_3$-edge spectra with (dis)charging for LR and LSLR (Supplementary Fig. 15) rules out the possibility of the influence of Ni cations on the redox behaviors of Mn cations in two materials. Therefore, the different redox evolution of Mn cations shown by LR and LSLR is due to different oxygen redox mechanisms.

AC-STEM images of charged LSLR to 4.6 V along [100] and [103] axis of Li$_2$MnO$_3$ domain are provided in Fig. 3e, f. Different from the phenomenon of OAR accompanied by cation migration in Li-rich oxides reported in literature, no obvious cation migration is detected in charged LSLR. It can be seen from the AC-STEM and the corresponding fast Fourier transform (FFT) images that the charged LSLR still maintains the original superlattice structure. However, for LR at the same electrochemical state, we could not find a suitable crystal direction and take clear STEM pictures, which may be due to the deteriorated structure, or generated organic decompositions on the particle surface (Supplementary Fig. 16), or great structural changes. Whatever the reason it is, the corresponding FFT image of the STEM picture for charged LR does illustrate that LR has undergone a significant structural change after charging (Supplementary Fig. 17).
Modulated O redox chemistry of LSLR. To study the mechanisms of oxygen redox in LR and LSLR, synchrotron radiation soft X-ray techniques are adopted. The OAR properties of LR and LSLR at different states of charge are characterized by soft XAS, and the electrochemical state selection for the collecting spectrum is shown in Fig. 4a. Point A declares the open-circuit voltage (OCV) state. The voltages at Points B and C are 4.35 V and 4.6 V (vs Li$^+$/Li), respectively, for separating the cationic and anionic redox reactions. D and E are the states of discharging to 2.0 V after charging to the upper limit of 4.6 and 4.35 V, respectively. Figure 4b, c exhibits the differentials between the (dis)charged and pristine state for the normalized O–K-edge spectra for LR and LSLR, so as to capture the distinction on OAR reactions between LR and LSLR. The C–A curves corresponding to LR and LSLR show similar fluctuations, indicating that OAR reaction occurs in both LR and LSLR at 4.6-V charged state. After the initial cycle with a voltage range of 4.6–2.0 V, the electronic structure of lattice oxygen for LR changed irreversibly, which is manifested by the spectra changes related with M 3d–O 2p and M 4sp–O 2p. While LSLR suppresses it well. When the voltage interval does not include OAR, the irreversible change of the electronic structure of lattice oxygen shown by cycled LR disappears, as displayed in curve E–A, indicating that the obvious fluctuations for the D–A line of LR are indeed caused by OAR, and it also proves the significant effect of LSLR in stabilizing OAR.

Figure 4d reflects the normalized pre-K-edge peaks of lattice oxygen in LR and LSLR. The spectra are normalized based on the $t_{2g}$ peak at about 529 eV$^{31}$. The peak at 530.5 eV is generally recognized as a characteristic peak of OAR$^{32}$. At 4.35 V, the oxygen redox occurs in LSLR but not in LR, indicating a lower threshold potential and a different mechanism for OAR. The lower threshold potential of OAR is due to the more ionic O environments in LSLR$^{33}$, which derives from the varied interactions of coordinated cations to lattice oxygen$^{34,35}$. Studies show that the oxygen redox degree can be reflected by the integrating areas of pre-K-edge peaks of lattice oxygen$^{32,36}$. It manifests that the lattice oxygen redox degree of LR and LSLR is very close (Supplementary Fig. 18). But the oxidation products of the lattice oxygen and the interactions between the oxidized oxygen and Mn in bulk lattice for the two samples are obviously different. Resonant inelastic X-ray scattering (RIXS) has a high-energy resolution and can keenly detect oxygen redox behaviors. All the RIXS spectra were tested at the excitation energy of 531 eV. For the convenience of quantitative comparison, the RIXS spectra are normalized based on the inelastic peak $\alpha$ at energy loss.
of about 5 eV (absolute energy: 526 eV). Peak α reflects the electronic structure of the metallic band of the oxides, while peak β is the RIXS characteristic of OAR in Li-rich oxides. Compared with LR, α and β in LSLR show different degrees of shifts toward low-energy loss (Fig. 4e). Both metallic and anionic bands have undergone energy elevating, but the metallic band elevates more. This phenomenon has an important relationship with the effect of LSLR on the inhibition of cation migration and OAR modulation, which will be explained in detail in the following section.

By comparing the relative integral area of the elastic peak, the difference of the lattice oxygen oxidation state in two samples can be captured (Fig. 4e). Specifically, the oxidation products of the lattice oxygen in LSLR project more oxygen anions with an electron hole than LR. In a latest study, this effect was also achieved in a cathode material for sodium-ion batteries\(^{37}\). The underlying fine structure could be revealed by the vibration near the elastic peak at 0.1–0.9 eV (Fig. 4f)\(^{36,38}\). It is reported that the vibration frequency is closely related to the species of O–O dimer\(^{26}\). For charged LR, a progression of small energy-loss peaks related to the O–O vibrations with a frequency of 1600 cm\(^{-1}\) rightly matches that of molecular O\(_2\). In this case, it can be interpreted as localized O\(_2\) molecule with Mn–O bond fracture in the lattice, which is consistent with Bruce’s work\(^{39}\). While for charged LSLR, the vibrational frequency is reduced to 1500 cm\(^{-1}\), indicating a lattice-bonded O–O dimer with a strengthened interaction between O–O dimer and Mn in the lattice for charged LSLR compared with charged LR\(^{39}\). Therefore, a deduction can be obtained that redox-active O–Mn bond in LSLR is more stable than LR. More evidence will be provided in the following. Moreover, the production of O–O species is also obviously inhibited for LSLR, which is demonstrated by the intensity of the elastic peak (Fig. 4h). The behaviors of OAR will directly affect cation migration and OAR escape. This result has also been observed in other studies\(^{41,42,44}\). While for LSLR, localized O\(_2\) molecule is changed to lattice-bonded O–O dimer or lattice oxygen with an electron hole, and the destruction of Mn–O bonds is largely reduced, with maintaining MnO\(_6\) octahedron and the superlattice well during the (dis)charging process. Therefore, cation mixing and O\(_2\) generation, which are caused by Mn migration to the Li site, formation of unstable localized O\(_2\) molecule, and irreversible charge transfer from Mn to O, are obviously inhibited. Thus, LSLR shows a good structural resilience during cycling.

### First-principle calculations of LR and LSLR

First-principle calculations declare that the introduction of Zr into the lattice of LR has obvious effects on the characteristics of subtle crystal structure and the energy bands related with lattice O and Mn. First, compared with Li\(_2\)MnO\(_3\) without Zr, the average Mn–O bond length in Li\(_2\)MnO\(_3\) with Zr introduced was elongated (Supplementary Fig. 20). This has also been demonstrated by neutron diffraction refinement of LR and LSLR. The elongated Mn–O bond would increase the ionicity of the material, thus to increase the bandgap between the metallic and anionic states. In the dynamics aspect, this bandgap could also be called the charge-transfer gap (\(\Delta_{\text{CT}}\)). This signifies the energy that electrons have to overcome to transfer from the metallic band to the oxygen lone-pair band. Mathematically, \(\Delta_{\text{CT}}\) shows the difference value between the band centers for antibonding (M–O\(^*\)) band and O\(_{2p}\) band. Here, M stands for Ni and Mn. Declared by Fig. 5a, b, at energy range of 0–5 eV in the densities of states (DOS) of M 3d orbitals, according to the crystal orbital overlap population (COOP), M–O is at antibonding state. For the energy range of 0 to ~9 eV, the DOS of O 2p orbitals depict the M–O band and O 2p lone-pair state. Through calculating the band centers of (M–O\(^*\)) and O\(_{2p}\), \(\Delta_{\text{CT}}\) could be obtained. Supplementary Fig. 21 declares, within 0 to ~1.83 (or ~1.74) eV in the DOS of O 2p for LR (or LSLR), roughly 1.36 electrons per LR (or LSLR) formula can be extracted. In all, 1.36 is exactly the number of electrons in O\(_{2p}\) band for active O. Based on this, the band centers of O\(_{2p}\) band for active O in LR and LSLR are calculated to be 1.24 and 1.18 eV, respectively. By stacking up the DOS of Ni 3d orbitals and Mn 3d orbitals, the energy band center of (M–O\(^*\)) can be obtained after calculating (Supplementary Fig. 22). Compared with LR, both O\(_{2p}\) and (M–O\(^*\))\(^+\) bands shift to higher energy locations in LSLR, and the (M–O\(^*\))\(^+\) band elevates more, which accords with the RIXS results. It declares the expansion of \(\Delta_{\text{CT}}\) after introducing Zr for LSLR, verifying the above deduction. Comparing with the calculated DOS diagrams for O 2p and Mn 3d orbitals of LR and LSLR before and after charge, the change of LSLR is less than that of LR (Supplementary Figs. 23 and 24). Furthermore, a signal caused by the O 2p splitting appears at the (M–O\(^*\))\(^+\) band range in the O 2p DOS diagram for charged LR, but it is not present for charged LRLS (Supplementary Fig. 23). This is consistent with the experimental results mentioned above.

### Discussion

On the basis of a previous study\(^{45}\), and our experimental and calculated results, we summarize a universal law to improve the reversibility and stability of OAR (Fig. 5c). With delithiating, the oxygen lone-pair band will split into two bonding states (\(\sigma^*\) and \(\pi^*\)) and two antibonding states (\(\sigma^+\) and \(\pi^+\)), and the metallic band will move down. When the metallic band overlaps \(\sigma^*\) state, the oxidation product of lattice oxygen will transform from oxygen holes to peroxides. When the metallic band shifts further and reaches \(\pi^*\) band, charge transfers will occur between \(\pi^*\) and metallic bands, resulting in O\(_2\) formation and Mn cation reduction. While for LSLR, this situation is obviously suppressed by widening the bandgap and delaying the overlap of the metallic
and anionic bands, which stabilizes redox-active O–M bond, anchors M cations and oxidized O anions simultaneously, thus fundamentally solving the issues of irreversible cation migration and O release.

Here, we appeal to researchers to concentrate on modulating OAR chemistry and paying more attention to the correlations between the metallic and anionic bands, with aiming at fundamentally addressing the critical issues of cathode materials with oxygen redox, such as lattice oxygen escape, voltage decay, irreversible cation reduction, and other daunting challenges.

In this work, we propose a strategy of modulating OAR chemistry to fundamentally address voltage fade by precisely constructing Li$_2$ZrO$_3$ slabs into Li$_2$MnO$_3$ domains in Li-rich Mn-based oxides through a simple and economical precipitation–calcination route. The introduction of Li$_2$ZrO$_3$ slab into Li$_2$MnO$_3$ domain, owing to the lattice strain, slips the Mn$_2$Li slabs of Li$_2$MnO$_3$ ~3°, elongates Mn–O bond from 1.918 to 1.946 Å, resulting in the chemical environment changing of the active lattice oxygen and the bandgap widening between the metallic and anionic states. Experimental and calculated results reveal that the modulated band structure of Li-rich oxide expands the region in which lattice oxygen contributes capacity by oxidation to oxygen holes, delays the surpassing of the capacity limit, and explains the divergence on the correlation between OAR and cation migration.

This study provides a universal theory concerned with OAR and fundamentally addressing the structural recession and voltage fade.

**Methods**

**Synthesis.** To synthesize LR (Li$_{1.21}$Ni$_{0.28}$Mn$_{0.51}$O$_2$), stoichiometric amounts of NiSO$_4$·6H$_2$O (99.9%, MACKLIN), MnSO$_4$·5H$_2$O (99%, MACKLIN) were dissolved in distilled water and coprecipitated by H$_2$C$_2$O$_4$·2H$_2$O (99.5%, MACKLIN). The precipitated oxalate precursor was collected and washed with distilled water three times and with ethanol twice. After drying the precursor, it was mixed with 5% excess stoichiometric amount of LiOH·H$_2$O (99%, MACKLIN) and calcined at 900 °C for 12 h in air.

To synthesize LSLR (Li$_{1.21}$Ni$_{0.28}$Mn$_{0.49}$Zr$_{0.02}$O$_2$), stoichiometric amounts of NiSO$_4$·6H$_2$O (99.9%, MACKLIN), MnSO$_4$·5H$_2$O (99%, MACKLIN), and Zr (CH$_3$COO)$_4$ (Zr, 15.0–16.0%, MACKLIN) were dissolved in distilled water and coprecipitated by H$_2$C$_2$O$_4$·2H$_2$O (99.5%, MACKLIN). Refer to the synthesis of LR for the remaining steps.

**Characterization.** The crystal structure of the as-prepared materials was characterized using an X-ray diffractometer (XRD, Ultima IV, Cu Kα) in 2θ range of 10°–80°. Data were recorded at a step width of 0.02° and a scan rate of 10° per minute. Neutron powder diffraction measurements were performed on the powder diffractometer GPPD at China Spallation Neutron Source. The patterns were analyzed by the Rietveld refinement method using the software of FullProf. NMR data were collected on a 400-MHz Bruker Avance III spectrometer at the $^7$Li Larmor frequency of 155.13 MHz. The $^7$Li spectra were externally referenced with LiCl aqueous solution at 0.0 ppm. An aberration-corrected scanning transmission electron microscope JEM ARM200F (JEOL, Tokyo, Japan) equipped with two CEOS (CEOS, Heidelberg, Germany) probe aberration correctors was used to probe the structure at the atomic scale. The surface composition analysis was performed by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI) and Raman spectra (Renishaw inVia, 532 nm). Morphology of the samples was observed with a scanning electron microscope (SEM, HITACHI SU8010). Chemical compositions of the materials were measured by inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent 730). Hard XAS was performed at BL14W1 beamline at Shanghai Synchrotron Radiation Facility (SSRF). Wavelet transform of XAS spectra is performed based on script (http://perso.u-pem.fr/fargues/wav/).

**Electrochemical measurements.** The cathode materials (80 wt%), such as carbon black (10 wt%) and polyvinylidene fluoride (10 wt%) were mixed uniformly with N-methyl pyrrolidnone. The obtained slurry was spread uniformly on an Al foil current collector and dried under vacuum at 110 °C for 12 h. The active material loading of the cathode electrode is 2–3 mg cm$^{-2}$. LiPF$_6$ (1 M) dissolved in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) (1:2:2 by volume) was used as electrolyte. A polypropylene membrane with micropores (Celgard 2500) was used as the separator. The 2025-

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**Fig. 5 First-principle calculations of LR and LSLR.**

(a, b) Calculated partial DOS for O/Mn/Ni and COOP analysis of Mn–O/Ni–O in LR (a) and LSLR (b). c Sketch of the oxidation process in charge transfer on metallic and anionic bands for LR and LSLR. Source data are provided as a Source Data file.
type coin cells were assembled in an Ar-filled glove box. Galvanostatic charge–discharge cycling was performed on a computer-controlled battery testing system (Neware, CT-4000FT) at room temperature. The galvanostatic intermittent titration technique (GITT) measurement was programmed to supply a constant current of 0.1 C for 15 min and a subsequent relaxation for 60 min on an activated cell. Unless otherwise stated, all the cells were tested at an electrochemical window of 2.0–4.8 V (vs. Li/Li$^+$).

**Ex situ and operando electrode analysis**

*Ex situ hard XAS.* Mn K-edges of electrodes at different states of charge were conducted at BL14W1 beamline at SSRF. A double-crystal monochromator was used. Metal foil was measured before the XAS measurements to make sure the data can be calibrated in case of any drift of the monochromator position. The electrodes were measured in a transmission mode. The XAS data were processed using the Athena software.

*Ex situ soft XAS.* O K-edges, Mn L$_3$-edges, and Ni L$_2$-edges of electrodes were conducted at beamline 20 A at NSRRC and beamline 02B02 at SSRF. The L-edge of Mn, Ni, and the K-edge of O XAS were collected using surface-sensitive total electron yield (TEY) and bulk-sensitive total fluorescence yield (TFY) modes simultaneously at room temperature in an ultrahigh vacuum chamber with a base pressure of ~5×10$^{-10}$ Torr. The photon energy was calibrated with the spectra of the reference samples (MnO, NiO, and SrTiO$_3$), which were measured simultaneously.

*Ex situ RIXS.* Ex situ RIXS data were collected at the PEAXIS beamline of synchrotron BESSY II at Helmholtz-Zentrum Berlin (HZB). The O K-edge RIXS spectra of the electrodes were collected at an excitation energy of 351.0 eV.

*Ex situ Raman.* Ex situ Raman experiment was performed on a Raman spectrometer. The prepared electrodes were sealed in a closed die with a quartz window.

*Ex situ XRD.* Ex situ XRD experiment was performed on a X-ray diffractometer. The electrodes were prepared through a linear voltammetry route on an electrochemical workstation 0.1 mV s$^{-1}$.

*Ex situ AC-STEM.* The material was scraped off the prepared electrodes and ground gently in a mortar. Ethanol was added to disperse the sample, followed by ultrasonic treatment. The sample was then dropped onto the microgrid for TEM experiment. During sample preparation, the sample is strictly isolated from air.

*In situ DEMS.* In situ DEMS data were carried out using a cell with a gas inlet and outlet ports. Ar carrier gas was flown at a constant rate (0.2 ml min$^{-1}$) through the cell and into a quadrupole mass spectrometer (Omnistar GSD 320) equipped with a turbomolecular cular pump (Pfeiffer Vacuum).

**First-principles calculations.** The density functional theory (DFT) calculations were performed using the Vienna Ab-initio Simulation Package (VASP)$^{45}$. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE)$^{45}$ functional was used. Uniform G-centered k-point meshes with 2×2×0.04 Å$^{-1}$ resolution and Methfessel-Paxton electronic smearing were used on the conformation in the Brillouin zone for geometric optimization. A cutoff energy of 500 eV was adopted for the simulation. Structure relaxation proceeded until all forces on atoms were less than 1 meV Å$^{-1}$ and the total stress tensor was within 0.01 GPa of the target value, as in a previous study$^{30}$. In order to accurately describe the electronic structure of the transition metal, the DFT + U approach was used, assuming U values for Mn-3d, Ni-3d, and Zr-4d of 6.0, 7.4, and 4.0 eV, respectively. For crystal orbital overlap population (COOP) calculations, the LOBSTER program$^{22}$ was adopted.

**Data availability**

The data that support the findings of this study have been deposited at https://figshare.com/s/557bec380f9385131438. All other relevant data are available from the corresponding author on reasonable request. Source data are provided with this paper.

**Code availability**

The authors declare that all the relevant codes are available within the paper and its Supplementary Information file or from the corresponding author upon reasonable request.

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**Author contributions**

X.F.L. directed the research. X.F.L. and J.C.Z. designed the experiments. J.C.Z. performed the synthesis, electrochemical tests, and hard XAS experiments. J.C.Z. and X.F.L. cowrote the paper. Q.H.Z. and L.G. performed the AS-STEM experiment. N.Z. and G.X.R. contributed to the measurement of soft XAS. D.W. and C.S. performed the RIXS experiment. L.H.H. conducted the ND experiment. Y.Y. contributed to the ND Rietveld refinement. All authors discussed the results and the paper.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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