Metal-to-metal charge transfer driven by electropositive species for stable anionic redox

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Abstract

Apart from conventional redox chemistries, exploring high-voltage redox processes, such as high-valent redox of a transition metal (TM) or novel anionic redox, is challenging due to unstable energy states correlated with destructive structural disorder in intercalation-type cathode materials. Here, we show a new strategy to design high-energy-density 4d-based Li-excess oxides with strong structural reversibility by substituting electropositive species. It is known that TMs in 4d-based Li-excess oxides, in contrast to 3d-based oxides, actively interact with neighboring oxygen ligands, inducing b_1/b_1^* energy levels. Metal-to-metal charge transfer, driven by covalency competition within the asymmetric $\text{TM}_{3d}\text{-O-TM}_{4d}$ backbone, induces a larger overlap between electronegative species and oxygen ligands, leading to stable high-voltage redox. Furthermore, we reveal that redox-inactive dopants control the reversibility of cation migration, thereby extending the battery lifetime. These insights open new perspectives for the control of intrinsic redox chemistry and enable rational designs for high-energy-density Li-excess cathodes.

Full Text

With the sustained growth of the electric vehicle and electric power industries, the global energy storage market has entered a new phase where the innovative design of cathode materials is inevitably desired beyond commercial energy materials¹. As the oxidation number of redox-active transition metals (TMs) limits the theoretical specific capacity in a conventional charge compensation system^{2–6}, the possibility of incorporating novel anionic redox chemistry into the conventional charge compensation system has been extensively explored. The cumulative cationic and anionic redox processes enable discharge capacities exceeding 250 mAh g^{-1} with a high upper cut-off potential of 4.6 V, delivering high-energy densities of up to $1,000 \text{ Wh kg}^{-1}$.^{2,7} However, such a high-voltage redox (hereafter denoted as HV-redox), commonly known as oxygen-redox (hereafter denoted as O-redox), triggers remarkable voltage hysteresis, voltage fading, and sluggish kinetics accompanied by irreversible structural transformations such as oxygen evolution and phase transition^{8–10}. Previous studies have addressed these issues by (1) involving 4d-TM Ru and 5d-TM Ir to stabilize the oxygen state via stronger M-O bonding than that in 3d-TM Mn^{11,12} and (2) doping inactive TMs to enhance the anionic redox reversibility^{13–15}. Despite the positive outcomes, the interpretation of the origin of O-redox still remains challenging in these new types of cathode materials for high-energy Li-ion batteries.

Typical Li-excess layered oxides ($x\text{Li}_2\text{TMO}_3 \cdot (1-x)\text{LiTMO}_2$) possess honeycomb-type atomic arrangements of $\text{Li}_{1/3}\text{TM}_{2/3}$, where four Li-ions and two TM ions coordinate oxygen to form an OTM_2Li_4 octahedron (**Fig. 1a**). Considering the orbital orientation of $\text{TM}t_{2g}$ and one of the O_{2p} orbitals along the direction where oxygen ions linearly bond to two Li-ions (Li-O-Li configuration), they do not hybridize with each other via sigma bonding, as shown in the inset in **Fig. 1a**, thus retaining nonbonding electrons around the oxygen anions². From a quantitative molecular orbital perspective (**Fig. 1b**), the O_{2p} nonbonding (denoted as O_{NB}) energy states are located close to the original energy levels of oxygen and higher than the energy

levels of bonding states from the hybridized bond. The general perception is that these O_{NB} states enable anionic oxidation, O^{2-}/O^- , prior to the depopulation of the M–O bonding state, causing a permanent occurrence of highly reactive oxygen radicals¹⁶. We previously defined this type of oxidation as the oxidation of the orphaned oxygen O_{2p} state along the Li–O–Li configurations³. First-principles calculations demonstrated that the hole density around the O anions resided along with the Li–O–Li local configuration after extracting labile electrons from O_{NB} states in the highly charged state. However, this theoretical modeling should be discussed assuming that the O_{NB} orbital does not overlap with adjacent TM orbitals such as Ni–O, Co–O, Mn–O, etc. Considering this, in the case of Ru (4d) and Ir (5d) with more spatially expanded orbitals than Mn (3d)^{11,17}, the t_{2g} orbitals of TM are more likely to interact with O_{NB} orbitals via π -type interactions¹⁵. Therefore, a deeper study of the “O-redox” process is necessary for 4d- and 5d-based Li-excess materials. The orbital hybridizations between the t_{2g} and O_{NB} orbitals lead to energy splitting into the b_1^* antibonding state and b_1 bonding state; the splitting degree is affected by the covalence of the TM–O bond (**Fig. 1c**)¹⁸. Li-excess oxides with hybridization than one without hybridization facilitate the oxidation of hybridized t_{2g} and O_{NB} orbitals, allowing further oxidation beyond conventional TM oxidation. However, oxidation of the O-dominant b_1^* state causes structural distortion followed by the formation of peroxo-like O–O species by unstable HV-redox^{19,20}. Although highly covalent Ru and Ir can sustain peroxo-like O–O species via ligand-to-metal charge transfer (LMCT), the so-called reductive coupling mechanism, such structural distortion induces O–O bond shortening from approximately 2.5 Å in peroxo-like O–O species to 1.5 Å in O–O dimers, eventually resulting in the decoordination of dioxygen from TMs. Several studies have demonstrated that Sn-substituted materials ($Li_2Ru_{1-y}Sn_yO_3$ ²¹ and $Li_2Ir_{1-y}Sn_yO_3$ ¹⁵) serve as reversible redox hosts in the form of $M_{Li}-V_M$ antisite-cation-vacancies even at a high voltage, inducing stable 1.8 Å TM=O oxo species and short 1.4 Å O–O dimers, but the underlying redox chemistry remains elusive.

Here, we propose a metal-to-metal charge transfer (MMCT) process driven by substituting species (TM_{3d}), where internal charge transfer is activated from electropositive (TM_{3d}) to electronegative species (TM_{4d}), as shown in **Fig. 1d**. Such charge transfer induces a significant difference in TM–O covalency within the asymmetric TM_{3d} –O– TM_{4d} backbone, rectifying orbital overlap between TM_{4d} and O_{NB} with a shifted redox potential of b_1^* (**Fig. 1e**). Independent of its oxidation number, denoted by the integer number according to the octet rule, TM with a large charge density affords metallic characteristics to the b_1^* antibonding states, thereby enabling reversible HV-redox (**Fig. 1f**). We explore the intrinsic HV-redox chemistry in $Li_{1.22}Ni_{0.17}Ru_{0.61}O_2$ (denoted as LNRO) in contrast to that in Li_2RuO_3 (denoted as LRO) using bulk-sensitive *operando* X-ray absorption spectroscopy and first-principles calculations. The redox chemistry of LRO consists of a stable TM-dominant $Ru^{4+/5+}$ state and an unstable O-dominant $Ru^{5+/6+}$ state^{11,22}. We demonstrate that Ni substitution induces polarized electrons toward electronegative Ru away from electropositive Ni, such that Ru ions pull the partial electron density away from Ni ions, leading to a stable TM-dominant $Ru^{5+/6+}$ redox state. In particular, it is well known that bond breaking is much more likely to occur with weak covalent TM–O bonds under bias voltage²³, leaving highly reactive

dangling oxygen. We reveal that the reactive Ru-O part is stabilized via π back-bonding between O (Lewis base) and Ru (Lewis acid), preferentially over the formation of O-O peroxides, whereas Ni species partially reversibly migrate to tetrahedral sites, and then part of them further migrate toward octahedral sites in the Li layer. It is known that such migration often induces irreversible phase transformation from layered to spinel, which is a primary cause of voltage hysteresis and capacity fading^{10,24,25}. We confirm how additional Al doping thermodynamically suppresses Ni migration through electrochemical tests, advanced analytical tools (synchrotron XRD, HR-TEM, TOF-SIMS, and *operando* XAFS), and first-principles calculations. The results of this paper shed new light on ternary Li-excess oxides as potential candidates for ultrahigh-energy-density batteries.

Electrochemical evaluation and phase transition in L(N)RO

LRO and LNRO were synthesized by a conventional solid-state reaction²⁶ described in the Methods section. The structures were confirmed by synchrotron XRD combined with Rietveld refinement analysis of LRO and LNRO (**Supplementary Fig. 1**), confirming that both are well fitted to the C2/c space group with a slight peak broadening due to defects, which are similar to already reported Ru-based Li-excess layered oxides^{22,27}.

The effects of Ni substitution on the redox chemistry in Ru-based Li-excess oxides were investigated using galvanostatic electrochemical testing at a current density of 0.1 C (20 mA g⁻¹) between 2.0 and 4.6 V. The voltage profiles exhibit remarkable gravimetric capacity beyond its theoretical capacity for both LRO and LNRO, as shown in **Fig. 2a,d**. Theoretically, it is well-known that the stable redox couple of Ru is Ru^{4+/5+}, which corresponds to 164.5 mAh g⁻¹ for LRO.²² **Fig. 2a** demonstrates that LRO delivers 299.6 mAh g⁻¹ reversible capacity, which corresponds to 1.82 Li⁺ per formula unit, indicating that Ru⁴⁺ is overoxidized to Ru^{>5.5+}. The following cycle supplies 1.71 Li⁺, i.e., 94.4% of reversible Li⁺ is supplied on the first cycle. As differential electrochemical mass spectrometry (DEMS) analysis (bar chart in **Fig. 2a,d**) runs simultaneously to detect gas evolution, a significant amount of oxygen evolution was detected beyond Ru⁵⁺, attributed to lattice-oxygen dimerization. Meanwhile, in **Fig. 2d**, LNRO exhibits high reversible capacities (228.1 mAh g⁻¹, corresponding to 0.96 Li⁺) beyond the theoretical capacities (226.7 mAh g⁻¹, corresponding to 0.95 Li⁺), calculated from Ni^{2+/4+} and Ru^{4+/5+} redox (**Fig. 2e**). Moreover, LNRO exhibits 226.2 mAh g⁻¹ reversible capacity (corresponding to 0.95 Li⁺) on the second cycle with 99.2% capacity loss after the formation process. Noticeably, the DEMS result for LNRO contrasted with that for LRO, showing almost no oxygen evolution. The comparison of synchrotron XRD patterns also supports the results before and after the formation process (**Supplementary Fig. 2**). The superstructure peaks ranging from 19° to 34° represent the typical Li_{1/3}TM_{2/3} honeycomb-type ordering mentioned earlier^{8,9,15}. LRO shows overall peak broadening and dissipation, as estimated by a 36.8% peak area decrease, whereas LNRO maintains its original peak shapes with only a 10.8% peak area decrease. The results apparently show that Ni substitution effectively relieves the structural disorder.

In the same context, galvanostatic intermittent titration technique (GITT) analysis was performed to compare the voltage hysteresis of LRO and LNRO for the 2nd cycle (**Fig. 2b,e**). GITT measurements show that the overpotential of each relaxation step gradually increases in the early stage of charging but rapidly increases during HV-redox. Relaxation behaviour at a high voltage shows that both samples are kinetically hindered by different parameters (insets in **Fig. 2b,e**). The relaxation step of LRO proceeds during the steady-state voltage change, whereas that of LNRO is largely contributed by the IR drop, which corresponds to the ohmic resistance and charge transfer. Recently, it was reported that the steady-state voltage change is affected by phase transition or local atomic rearrangement²⁸. Despite similar voltage relaxation, our results show that HV-redox species would be structurally stabilized due to Ni substitution, consistent with significantly reduced voltage hysteresis as confirmed by equilibrium voltage curves (dashed curves in **Fig. 2b,e**). **Fig. 2c,f** shows the comparison of voltage profiles at 25 and 60 °C, demonstrating that the kinetic hindrance during HV-redox is temperature-dependent, and that reduced delivery capacities are sufficiently compensated for the addition of the CV step.

Redox mechanism during the first cycle

To understand the underlying redox mechanism, we employed *operando* synchrotron transmission X-ray absorption near edge structure (XANES) at the Ru and Ni K-edges during the formation cycle, as shown in **Fig. 3a–c**. Ru K-edge XANES spectra consist of three representative peaks: i) pre-edge: 1s → hybridized 4d-5p transition, whose peak intensity stands out as the TMO₆ symmetry is more distorted, ii) whiteline (WL) edge: 1s → 5p transition, and iii) back peak: 1s → 5p transition by single scattering, following the dipole transition rules^{29–31}. At the voltage increase to 3.9 V, as shown in **Fig. 3a**, the Ru WL energy in LRO shifts from 22140.0 to 22141.5 eV ($\Delta = 1.5$ eV corresponding to 1.0 e[−] per f.u. of Ru), with the corresponding WL intensity decrease and back peak intensity increase, taking the typical shape of the Li₁Ru⁵⁺O₃ plot³¹. However, as the cell potential remains beyond 4 V, where oxygen dimerization evolves, the pre-edge peak protrudes due to structural distortion, and the back peak weakens due to the loss of the O neighbor to scatter. The results consistently imply that the HV-redox of LRO involves progressive structural degradation with fluctuating lattice oxygen. In contrast, LNRO shows different redox behavior, as confirmed by the differential crossline intensity ($\Delta I: I_{nth} - I_{1st}$) in the inset of **Fig. 3b** (dotted circle), showing no definite propensity related to the structural distortion and oxygen loss in the vicinity of 22120 eV. Remarkably, the Ru WL energy in LNRO increases from 22139 eV, which is lower than that in LRO (22140 eV), indicating that Ru⁴⁺ in LNRO holds a higher charge density than Ru⁴⁺ in LRO. After charging, a peak shift of 2 eV (corresponding to 1.3 e[−] per f.u. of Ru) occurs in LNRO. In the meantime, a shift in the WL energy of Ni K-edge spectra from 8350 to 8353.6 eV proceeds until charging up to 4.6 V (**Fig. 3c,f**). Considering that the Ni K-edge XANES spectra of LNRO are shifted to larger energy with respect to the Ni²⁺O reference²⁵, Ni²⁺ in pristine LNRO seems to have a lower charge density than that in NiO. As mentioned earlier, the results show that MMCT occurs from electropositive Ni to electronegative Ru via the O-bridge. The phenomena were also identified through computed average Bader charge, indicating that the more Ni is located near Ru, the higher charge value Ru has (**Supplementary Fig. 10**). Notably, Ni is oxidized up to approximately 3+ during charging as the redox potential of Ni increases with decreasing

charge density^{32–34}, in contrast to the perception that Ni can be oxidized to 4+ on typical NCM cathode materials^{6,30}. The same is identified through first-principles calculations in **Supplementary Table 2**, indicating that full oxidation ($\text{Ni}^{2+/4+}$) of partial Ni is thermodynamically hindered depending on the TM sites. Thus, we emphasize that the $\text{Ru}^{4+/5+}$ and $\text{Ru}^{5+/6+}$ redox reactions via MMCT are the main charge-compensating factors, whereas Ni species play a role in auxiliary electron donors for charge redistribution in LNRO. The following section investigates how such electrochemistry is coupled with structural changes.

High-voltage redox stability coupled with local structural change

To monitor the local structural change caused by HV-redox, we measured the *operando* extended X-ray absorption fine structure (EXAFS) at the Ru and Ni K-edges. Radial distribution functions of Fourier-transformed (FT) k^3 -weighted EXAFS provide local structure information on specific TM species and interatomic distances, corresponding to TM-O bonding (~ 2.05 Å, denoted as O) and TM-TM bonding (~ 3.55 Å, denoted as T)²⁵. As shown in **Fig. 4a**, EXAFS contour maps demonstrate a drastic contrast between LRO and LNRO, especially in the TM-O peak range corresponding to the first coordination shell. In the charged state, the FT intensity of the O peak in the LRO-Ru spectra, which is an indicator of atomic disordering (Debye–Waller factor, σ) and coordination number³¹, decreases abruptly with no complete recovery at the end of the formation cycle, which is direct evidence for irreversible oxygen evolution. In contrast, the FT intensity of the O peak in the LNRO-Ru spectra remains constant during the 1st cycle, providing convincing proof that Ni aids the local structural stability of Ru, which is the main redox species. At the same time, Ni spectra exhibit highly fluctuating but reversible spectral changes. Empirically, we determined that Ni ceaselessly migrates along its thermodynamically preferential routes, as verified through *operando* EXAFS results and calculations of relative site energies. The 2D contour map tracking migrated Ni species relative to fixed Ru species shows that the T-peak at ~ 3.4 Å splits into two peaks, ~ 3.2 Å peak for the Li layer, and ~ 3.4 Å peak for the TM layer, as shown in **Fig. 4a, right panel** and **Supplementary Fig. 13**. Considering that Ru is fixed at its original sites, such a peak split represents Ni migration toward its thermodynamically preferential neighboring site depending on the stoichiometry of delithiated LNRO. Additionally, the FT intensity of the O peak in the Ni spectra initially decreases, followed by a reciprocal tendency at the end of the charging process (marked by the white arrow in **Fig. 4a**), indicating that Ni undergoes out-of-plane migration from Oh_{TM} to Td_{Li} sites and further to Oh_{Li} sites, simultaneously changing its coordination number ($6 \rightarrow 4 \rightarrow 6$) (**Supplementary Fig. 14**). The energy landscapes also provide consistent proof of whether Ni is the most stable at the Td_{Li} sites or Oh_{Li} sites, depending on the state of charge (SOC) (**Supplementary Fig. 16**). This is in agreement with a previous report that TM tends to trap the Li layer with a thermodynamic preference⁸. These results highlight the importance of the research addressing such an irreversible cationic migration, which will be discussed in the next section.

We compared the O peak in the EXAFS spectra depending on the cell voltage (**Fig. 4b,c**) to specify the oxygen stability during HV-redox. The O peaks in the LRO-Ru spectra can be distinguished into three

regions corresponding to the short TM-O peak (~ 1.14 Å, denoted as S), main TM-O peak (~ 1.61 Å, denoted as M), and long TM-O peak (~ 2.05 Å, denoted as L). In particular, the interatomic distance of the S peak is similar to that of double bonds¹⁵. Two remarkable changes are observed in the EXAFS spectra of LRO upon charging: 1) as the cell voltage increases, the M peak generally contracts with L peak splitting, which is attributed to the distorted Ru octahedron due to the increased interaction between Ru and O originating from the higher oxidation states³¹. The extended TM-O bond weakens and ultimately gives rise to decoordinated oxygen²⁰. 2) The decrease in S peak intensity and peak broadening also represent a disordered phase, which correlates with an unstable oxygen state upon charging. On the other hand, the O peaks of LNRO-Ru remain unchanged during delithiation, except for the S peak. The S peak gradually evolves while the cell is charged, indicating Ru-O bonds approaching double bonds through additional π -bonds. This terminal oxo species, which is double bound to Ru, can be stably maintained compared with single bound oxyl species^{35,36}, finally leading to a highly reversible HV redox.

We performed first-principles calculations to unveil the energetic effect of Ni on the redox system in the Ru-based Li-excess layered oxides (**Fig. 4d,e**). First, we visualized the electronic structures calculated on the basis of the Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional³⁷, enabling us to predict the partial density of states (pDOS) of the O 2p and Ru 4d states around the Fermi level (E_F) for LRO and LNRO. For both pristine LRO and LNRO, hybridized orbitals consisting of Ru 4d and O 2p located just below the Fermi level indicate the most preferential redox of $\text{Ru}^{4+/5+}$ at a low voltage (top of **Fig. 4d,e**). However, after all, Ru converts to the 5+ oxidation state, and the behaviour of the redox-contributing energy states of LRO and LNRO is quite different (bottom of **Fig. 4d,e**). The charge compensation of LRO at a relatively high voltage stems from the unstable $\text{Ru}^{5+/6+}$, which is caused by O-dominant states. In stark contrast, pDOS of LNRO exhibits much more TM-dominant features near E_F . The corresponding hybridized orbital states can be identified by visualizing the charge density for the energy range between 0 and -1.64 eV. The labile electrons of delithiated LNRO are contributed from TM-dominant b_1^* states, whereas those of delithiated LRO are from O-dominant b_1^* states (inset in the bottom of **Fig. 4d,e**). Computational analyses such as electron localization function (ELF) and integrated crystal orbital overlap population (ICOOP) also demonstrate a strong covalency between Ru 4d orbitals and O 2p orbitals in LNRO compared with that in LRO (**Supplementary Fig. 18**). As expected from the XANES analysis, the MMCT process induced by Ni substitution enriches the charge density around Ru, making the redox system more reversible even at a high voltage, where the σ -bonding between p orbitals on neighboring oxygen ligands is inhibited by the competitive π -type interaction between Ru and O³⁸.

Our suggestions regarding oxygen states coupled with the coordinated environment are summarized in **Fig. 4f,g**. According to crystal field theory³⁹, the orbital energy state of Ru splits into upper e_g^* states and lower t_{2g} states. In particular, partially filled t_{2g} states, which are affected by O_{2p} neighbors via π -type interactions, split into b_1^* antibonding states and b_1 bonding states. As mentioned earlier, the b_1^* states of Ru in LRO in **Fig. 4f** consist of a highly reversible redox of $\text{Ru}^{4+/5+}$ (blue line) and unstable redox of $\text{Ru}^{5+/6+}$ (red line). When the energy states reach unstable b_1^* states of $\text{Ru}^{5+/6+}$ during HV-redox, the

crystal structure suffers from severe distortion, followed by the formation of peroxo-like O-O species. On the other hand, the d states of Ru in LNRO hold higher charge densities by taking the negative charge from the Ni species via the MMCT process, where stronger Ru-O covalency induces larger splitting of b_1/b_1^* states (black dotted line). This shifted energy state of b_1^* makes both redox couples ($\text{Ru}^{4+/5+}$ and $\text{Ru}^{5+/6+}$) TM-dominant (blue line in **Fig. 4g**). Additionally, Ru-O bonding can be stabilized by pulling the O ligands close to Ru accompanied by the spontaneous breaking of the Ni-O bond. Here, we conclude that the most critical chemistry inherent in stable HV-redox is the stabilization of high valent redox couples³⁵ along with terminal oxo species through double bonding before RuO_6 distortion, which leads to the formation of O-O peroxide.

Improving structural reversibility during extended cycling

Thus far, we have revealed how Ni species affect the redox chemistry of Ru-based Li-excess layered oxides. However, various Ni-related issues have already been considered the primary degradation mechanism, such as Ni trapping and irreversible phase transitions^{8,10,40}. To prevent such irreversible Ni migration, we propose the aluminum doping of stoichiometric $\text{Li}_{1.22}\text{Al}_{0.05}\text{Ni}_{0.12}\text{Ru}_{0.61}\text{O}_2$ (denoted as LANRO), one of the most effective methods to suppress structural issues in NCM and NCA cathode materials^{41,42}.

Fig. 5a compares the voltage profiles of the first and 50th cycles versus the normalized capacity of LRO, LNRO, and LANRO. The voltage profile of LANRO is similar to that of LNRO, which delivers 286.9 mAh g^{-1} with Coulombic efficiency (C.E.) of 81.0 % on charging. The low first-cycle C.E. might be attributed to the synergistic effect of the slightly increased O-dominant HV-redox due to the reduced Ni/Ru atomic ratio and irreversible Al migration. Meanwhile, the capacity retention and voltage decay are significantly enhanced starting from the second cycle. LANRO shows a superior stability of 97.5% over LRO (86.5%) and LNRO (89.2%) over 50 cycles at 0.5 C between 4.6 and 2.0 V versus Li^0/Li^+ at 25 °C (**Fig. 5b**). To better understand the structural stability, we checked the average potential on each cycle. LRO with irreversible O-dominant HV-redox shows a remarkable voltage decay from 3.29 V for the second cycle to 2.96 V for the 50th cycle ($\Delta = 0.33 \text{ V}$). LNRO shows a relatively stable average voltage drop of 3.48 V to 3.28 V ($\Delta = 0.20 \text{ V}$), manifesting less severe Ni-induced structural degradation caused by oxygen evolution. As expected, the LANRO exhibits superior stability with a slight voltage drop from 3.40 to 3.32 V ($\Delta = 0.08 \text{ V}$), proving that the harmony between Ni and Al brings outstanding redox stability in Ru-based Li-excess materials. These advantages are also observed through ex-situ synchrotron XRD of pristine, 4.6 V charged, 2.0 V discharged materials, and those after 50 cycles (**Supplementary Fig. 22**). All XRD patterns exhibit well-defined representative peaks of the honeycomb-phase superstructure (shaded region). In particular, these peaks are still clearly seen even at 4.6 V charging and after 50 cycles, which means a well-maintained cationic arrangement with almost no migration within TM layers during HV-redox and subsequent cycling.

Interestingly, HR-TEM data of each Li-excess oxide after cycling reveal how severely the cells are aggravated during cycling and how much Al doping enhances the structural integrity at the atomic level. (**Fig. 5c** and **Supplementary Fig. 25**) After prolonged cycles under the 0.5 C-rate, severe vacancies and microcracking were observed in LRO, as shown in **Fig. 5c (left)**, which originate from severe lattice-oxygen-evolution. In addition, atomic arrangements are not recognized on high magnification (high-MAG) HR-images with random cationic disordering and numerous defects and vacancies. In contrast, low magnification (low-MAG) HR-images of LNRO do not reveal microcracking, but numerous voids are still clearly seen, especially near the surface (**Fig. 5c, middle**). We attributed these voids to Ni dissolution into electrolytes, eventually toward the opposite side, which catalyzes electrolytic decomposition on the anode side and increases the cell resistance^{43,44}. This phenomenon is clearly identified through TOF-SIMS mapping on anode surfaces after cycling, as shown in **Supplementary Fig. 26**. For the sake of convenience, we conducted full-cell tests with a graphite anode under identical conditions. Heavier Ni dissolution, compared with Ru dissolution, is observed in LNRO, where Ru dissolution might be attributed to the destructive impact of lattice-oxygen-evolution⁴⁵ and Ni dissolution might be attributed to its intrinsically unstable repetitive out-of-plane migration⁴⁶. In particular, these migrated Ni atoms are presumably trapped into tetrahedral sites in the Li layer (see high-MAG TEM images in **Fig. 5c, middle**), in agreement with a previous report indicating that the Ni species are thermodynamically stable on the intermediate Td site of the O3 structure⁸. In stark contrast with both previous samples, the cycled LANRO shows almost flawless low-MAG TEM images and well-defined TM layers with slight cationic fluctuations in the high-MAG TEM images in **Fig. 5c (right)**. In addition, TOF-SIMS data also confirm that Al doping is notably effective in suppressing Ni dissolution (see **Supplementary Fig. 26**).

To reveal local structural changes in LANROs during cycling, we analyzed the migration behavior of each atom with 2D contour maps. In contrast to LRO and by analogy to LNRO (**Fig. 4a-c**), EXAFS at the Ru K-edge of LANRO demonstrates an entirely static propensity on the formation, the second cycle, and the 50th cycle (**Supplementary Fig. 27**). However, a remarkable feature arises at the end of the charging where the Ru-TM₂ peak irreversibly splits into those corresponding to the TM layer (~3.6 Å) and Li layer (~3.2 Å), which is attributed to Al migration. Such irreversible peak splitting does not occur in the next cycle; instead, a new peak reversibly appears at a similar interatomic distance. Therefore, the irreversible out-of-layer migration of Al atoms on the formation step induces a reversible atomic rearrangement within the structural network after the 2nd cycle, suggesting the positive interplay of Ni and Al in Ru-based materials.

A thermodynamic penalty of Ni migration by Al dopants

A previous report proposed that Al atoms located in the tetrahedral sites in Al-doped LiNiO₂ may mitigate the phase transformation upon increasing the temperature by disrupting Ni out-of-plane migration⁴². This statement is also experimentally verified in this work by the change in Ni coordination number during charging from (6→4→6) to (6→4) with Al doping, blocking the final migration toward octahedral sites (**Supplementary Fig. 27**).

To clarify how Al thermodynamically hinders Ni migration, we conducted a computational study on the site preferences of Ni and Al (tetrahedral or octahedral sites) in Li slabs. Beforehand, we statistically examined the distribution of Ni ions neighboring Al among the 15 most stable LANRO structures based on Ewald summation followed by GGA+U relaxation (**Supplementary Fig. 28**). In 9 of 15 structures, all Ni ions (3Ni) are located on TM sites adjacent to Al within the second nearest neighboring Oh sites in the TM layer. Five of 15 structures hold two-thirds of Ni in the identical range. Statistically, Al is surrounded mainly by Ni in approximately 93% of modeled structures, i.e., most Ni migration can be controlled by Al ions within the crystal structure, in agreement with a previous paper reporting the same phenomenon through NMR spectroscopy⁴⁷. The intriguing point is that Al migration to Td sites is thermodynamically and kinetically preferential for Ni migration nearby. The nudged elastic band (NEB) calculation in **Fig. 5e** shows that the migration barrier for Ni (1.54 eV) is higher than that for Al (1.16 eV), implying sluggish Ni migration around Al dopants.

Furthermore, it is noteworthy that Al_{Td} significantly increases the site energy of both Td and Oh sites in Li slabs (**Fig. 5f**). Fundamentally, all Ni ions tend to migrate to adjacent Td sites on delithiated LNRO. Among them, the relative site energy of the Oh site near Ni (i) is estimated to be -0.92 eV, which indicates further migration toward the Oh site. As the rest of the Ni ions also have a minor thermodynamic barrier for nearby Oh sites, their further migration is also feasible. In contrast to delithiated LNRO, however, Al prevents Ni migration toward Td sites, changing the site energy from negative to positive, except for Ni (i). Although Ni (i) can move toward the Td site (-0.29 eV), Ni (i) migration is entirely suppressed in comparison with LNRO (-0.88 eV), and it is hard to migrate toward the Oh site (+0.10 eV) further. Thus, it is concluded that Al doping can support the structural integrity not only by physically preoccupying the empty sites toward which Ni tends to migrate but also by raising the relative thermodynamic free energy of neighboring sites.

Discussion

Resonant inelastic X-ray scattering (RIXS) has been considered one of the most powerful tools to understand Li-excess cathode materials due to its high resolution to detect oxygen oxidation. In this regard, it has been known that the O-redox of $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Ru}_{0.6}\text{O}_2$ is inactivated so far because the RIXS spectra do not show fingerprinting features of the O_{NB} hole at 530.8 eV excitation and 523.7 eV emission energies, meaning that its delivery capacities might be compensated for both $\text{Ni}^{2+/4+}$ and $\text{Ru}^{4+/5+}$.^{27,48} Recently, however, it was reported that $\text{Na}_{2-x}\text{Mn}_3\text{O}_7$ does not show a characteristic RIXS signature despite its O-redox activity⁴⁹. Based on the fact that $\text{Na}_{2-x}\text{Mn}_3\text{O}_7$ does not form O-O peroxide (<1.5 Å), they proposed a new interpretation for the origin of RIXS signatures; such a sharp RIXS feature originates from the excitation of $1s \rightarrow \sigma^*$ in the short O-O peroxides, not the hole of O_{NB} states.

Currently, RIXS analyses have been carried out in many pieces of research related to Li-excess materials, regardless of 3d, 4d, and 5d TM. Taking into account that 4d and 5d TM with stronger TM-O covalency induce additional hybridization of t_{2g} states and O_{NB} states, as mentioned earlier, interpretations of RIXS

results for “O-redox” should be differentiated, depending on whether the origin of HV-redox is the oxidation of O_{NB} states or high-valent redox of TM. Considering that thermodynamic energies associated with unstable highly oxidized states cause O-O pairing induced by structural distortion, their new approach for sharp RIXS signatures at 530.8 eV excitation is sufficiently acceptable.

We spectroscopically identified the coexistence of LMCT ($O \rightarrow Ru$) and MLCT ($Ni \rightarrow O$) in Fig. 3, even at a pristine state, supported by Bader charge analysis (**Supplementary Fig. 10**), which is similar to the inductive effect⁵⁰. This interplay of LMCT and MLCT, that is, MMCT ($Ni \nabla Ru$), shifts the energy states of $Ru^{5+/6+}$ toward higher energy levels, enabling reversible TM-dominant HV-redox. In particular, accompanying out-of-plane Ni migration can be enough to mitigate the energetic penalty associated with local distortion such that short O-O pairing is suppressed, as verified through reduced voltage hysteresis in experimental GITT results. That is why $Li_{1.2}Ni_{0.2}Ru_{0.6}O_2$ does not show RIXS features for conventional O-redox, in contrast to Li_2RuO_3 and $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ (see **Supplementary Fig. 29**).

Furthermore, we also reveal that large voltage hysteresis is not entirely due to cationic migration but due to local structural distortion of the main redox species because $Li_{1.22}Ni_{0.17}Ru_{0.61}O_2$ exhibits infinitesimal voltage hysteresis, despite its ceaseless Ni migration during cycling, which is similar to $Li_{1.17}Ti_{0.33}Fe_{0.5}O_2$ ²⁸. Such behaviour is in accordance with the ultimate design goal for Li-excess materials. Thus, our discovery provides not only new perspectives on a general understanding of the nature of anionic redox but also guidance for the design of cathode materials.

Conclusion

Our work is based on the following hypothesis that more spatially expanded TM, such as Ru and Ir, can strongly hybridize the neighboring O via π -type interactions, consequently leading to stronger covalence of TM-O bonds followed by additional splitting of t_{2g} and O_{NB} energy levels into b_1 and b_1^* states. In particular, we believe that a higher charge density near Ru via MMCT induces more significant splitting of b_1/b_1^* , making the b_1^* state more reversible during HV-redox. This proves that electropositive species play critical roles in stabilizing the HV-redox of electronegative species coupled with double-bonded O ligands. Therefore, we propose that strategies to improve the performance of Li-excess cathode materials should be differentiated based on the energy structure of their intrinsic molecular orbitals, namely, whether HV-redox utilizes the O_{NB} or b_1^* energy level. Such observations guide us to find a structural stabilizer to control cationic migration, such as redox-inactive Al dopants, and provide new insights into the design strategy to tune the relative energy states and control irreversible cationic migration for stable anionic redox.

Methods

Sample preparation. LRO, LNRO, and LANRO were prepared by using stoichiometric amounts of $Li(CH_3COO)$, RuO_2 , $Ni(CH_3COO)_2 \cdot 4H_2O$, and $Al(NO)_3 \cdot 9H_2O$ as precursors using a planetary ball mill with

a small amount of acetone. A 5 wt% excess of $\text{Li}(\text{CH}_3\text{COO})$ was used to compensate for lithium evaporation during high-temperature synthesis. The mixed powder was heat-treated at 650 °C for 6 h and at 1000 °C for 12 h at a ramp rate of 2 °C/min in ambient atmosphere, followed by an intermediate grinding process and further heating at 900 °C for 12 h. Subsequently, the furnace was cooled to room temperature.

Electrochemical characterizations. All electrochemical evaluations in this work were performed by using 2032 coin-type cells under the same conditions on each material. Electrodes were prepared by mixing 80 wt% active material, 10 wt% carbon black, and 10 wt% polytetrafluoroethylene binder dissolved in N-methyl-2-pyrrolidone. The obtained slurry was cast using a doctor blade and then dried under vacuum at 120 °C for 2 h. Electrochemical cells were assembled in an argon-filled glove box. The electrolytes were used with a composition of 1 M LiPF₆ in ethylene carbonate (EC)/ethyl methyl carbonate (EMC)/dimethyl carbonate (DMC) in a volume ratio of 3:4:3. Electrochemical evaluations were carried out between 2.0 and 4.6 V at 0.1 C-rate during the formation process, followed by cycling at 0.5 C-rate at room temperature and high temperature (60 °C). At room temperature, constant voltage steps (CV step) at 4.6 V charged state was added to every cycle until the current decreased to 0.05 C-rate. The galvanostatic intermittent titration technique was conducted under constant current pulses (C/10-rate) for 1 h, followed by relaxation for 4 h.

Operando X-ray absorption spectroscopy (XAS) analysis. *Operando* XAS data were collected on the BL10C beamline (WEXAFS) at the Pohang light source (PLS-II) with top-up mode operation under a ring current of 250 mA at 3.0 GeV. Monochromatic X-ray beams were obtained with a liquid-nitrogen-cooled double-crystal monochromator (Bruker ASC) with available *in situ* exchange in a vacuum between a Si (111) and Si (311) crystal pair. The Si (111) crystal pair was used for TM K-edge XAS measurements. For *operando* XAS measurements, pouch-type half-cells were assembled with a counter electrode of Li-metal foil in a dry room in transmittance mode using N₂ gas-filled ionization chambers (IC-SPEC, FMB Oxford) for the incident and transmitted X-ray photons. To eliminate higher-order harmonic contamination, we detuned the incident X-ray intensity by ~30%. With reference to TM foils placed in front of the third ion chamber, energy calibration processes were conducted for each XAS measurement. The XAS spectra for all TMs were obtained with a scanning time of 20-30 minutes for one spectrum. Using 0.2 C-rate of charging and discharging, 25-35 scans of XAS spectra for each TM were conducted to acquire reliable electronic/crystalline structures. Based on the standard XAS analysis procedure, the reduction of spectral data was performed into normalized XANES and Fourier transformed radial distribution functions (RDFs). AUTOBK and FEFFIT modules in the UWXAFS package were used to obtain the k^3 -weighted TM K-edge EXAFS spectra, $k^3\chi(k)$, with the removal of background and the normalization processes on the edge jump. The $k^3\chi(k)$ spectra were Fourier transformed (FT) in the k range between 2.5 and 12.0 Å⁻¹. A difference of 0.3-0.5 Å between actual interatomic distances and observation values of radial distribution functions exists because phase correction was not conducted.

Transmission electron microscopy (TEM) analysis. Aberration-corrected ARM300 (JEOL) electron microscopes were used to obtain HR-TEM and HAADF-STEM images, operating at 160 Kv using a convergence semiangle of 22 mrad for direct observations of atomic behaviors. The inner and outer collection semiangles for HAADF were 54 and 220 mrad, respectively. We used GMS 3 and CrysTbox programs to analyze the obtained atomic images, structure, and FFT patterns. For TEM analysis, samples were prepared by focused ion beam (FIB, Helios 450HP, FEI) using a 2-30 kV Ga ion beam. Prior to the analysis in the FIB workstation, epoxy and carbon deposition were conducted to avoid damage to the Ga ion beam. The prepared TEM samples were polished to remove surface contamination using an Ar-ion milling system (Model 1040 Nanomill, Fischione). The energy-dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS) results were attained using the same HR-TEM.

Synchrotron X-ray diffraction (XRD) analysis. Synchrotron XRD for each electrode with different states of charge (SOCs) during the 1st cycle and after 50 cycles were measured from 10° to 120° at $0.02^\circ \text{ step}^{-1}$ (10 s for one step) using a 9B beamline from the Pohang Accelerator Laboratory (PAL) to observe the phase transition.

Material characterization. The chemical compositions of the cathode material were determined by ICP-OES (Varian 700-ES, Varian, Inc.). *Operando* differential electrochemical mass spectrometry (DEMS) analysis was conducted on Swagelok-type cells between 2.0 and 4.6 V (versus Li/Li⁺). TOF-SIMS mapping (Model TOF-SIMS 5, ION-TOF GmbH) was conducted for cycled graphite electrodes paired with our samples to detect the dissolved transition metals toward the anode side. The analysis chamber was maintained in an ultrahigh vacuum at a pressure below 5.0×10^{-10} torr. All detected secondary ions of interest had a mass resolution $>10,000$.

Computational details. Spin-polarized density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP). The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functionals was used to describe the exchange-correlation potentials. Additionally, the projector-augmented wave (PAW) method was used. For a correction of the self-interaction error in the d orbital states of transition metal ions, Hubbard U correlations were adopted ($U = 4.0$ and 6.2 for Ru and Ni, respectively). All DFT calculations employed a plane-wave basis set with an energy cutoff of 520 eV. The atomic position, cell shape, and volume of the structures are fully relaxed (ISIF=3) until the residual forces on the cell are smaller than $0.05 \text{ e } \text{\AA}^{-3}$ for all cases. The method to prepare the structures of Li_2RuO_3 (LRO), $\text{Li}_{1.22}\text{Ni}_{0.17}\text{Ru}_{0.61}\text{O}_2$ (LNRO), and $\text{Li}_{1.22}\text{Al}_{0.05}\text{Ni}_{0.12}\text{Ru}_{0.61}\text{O}_2$ (LANRO) and further computational details are provided in Supplementary Note 1.

Declarations

Data availability

The authors declare that the data supporting the findings of this study are available from the corresponding author upon request.

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Author Contributions

M.-H.K., H.J., and E.R.L. contributed to equally this work. M.-H.K., D.-H.S., and H.-W.L. conceived and designed the experiments. M.-H.K. performed overall experiments and interpreted the experimental results. J.S. assists experiments and characterization. H.J. and M.G.K. carried out XAS measurements. E.R.L. and D.-H.S. performed 1st principle calculations. T.K. and Y.H.J. analyzed synchrotron XRD and Rietveld refinements. J.P., and S.J.K. assisted with DEMS analysis. M.-H.K. wrote the initial draft. M.-H.K., H.J., E.R.L., D.-H.S. and H.-W.L. discussed the results and revised the manuscript.

Competing Interests

The authors declare no competing financial interest.

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Figures

Figure 1

Band structure of Li-excess oxides and their anionic redox chemistry. **a**, In-plane cationic ordering of Li/TM within the TM layer; gray, yellow, and red spheres represent ruthenium, lithium, and oxygen, respectively. The inset shows a schematic illustration of the orbital orientation of M t_{2g} and O_{NB} . **b**, Molecular orbital energy diagram of the MO_6 octahedron of Li-excess oxides. The σ -type interactions split hybridized energy states into an M-dominant band (M band) and an O-dominant band (O band), remaining unhybridized M t_{2g} and O_{NB} . **c**, Additional π -type interaction between M t_{2g} and O_{NB} orbitals depending on TM-O covalency. Beyond the stable M band, low covalency in M_{3d} (Mn) leads to electron extraction from O_{NB} states (i.e., Li-O-Li configuration). In contrast, high covalency in M_{4d} (Ru) and M_{5d} (Ir)

induces π -type hybridized states with discrete b_1^* antibonding and b_1 bonding states. Here, anionic redox chemistry changes from the oxidation of the Li-O-Li configuration to deep b_1^* states at a high voltage. (Also known as high-valent redox) **d**, Comparison of classical ligand-to-metal charge transfer (LMCT) and proposed metal-to-metal charge transfer (MMCT) where the direction of charge transfer is determined by relative covalency between both sides on oxygen centre. **e**, Schematic illustration of the band structure affected by π -type interactions and metal-to-metal charge transfer, inducing energy splitting between the b_1 and b_1^* states. During HV-redox, as shown in **f**, classical oxidation of O_{NB} states or the LMCT model suggests O-O pairing between unstable oxygen ligands, triggering oxygen evolution. In contrast, the asymmetric M_{3d} -O- M_{4d} configuration induces internal charge transfer from M_{3d} with low electronegativity to M_{4d} with high electronegativity, followed by an energy shift of its conduction band to a higher value; that is, it enables highly reversible HV-redox at a relatively lower voltage, instead of oxygen evolution.

Figure 2

Electrochemistry of LRO and LNRO. Electrochemical profiles of Li_2RuO_3 (a–c) and $\text{Li}_{1.22}\text{Ni}_{0.15}\text{Ru}_{0.61}\text{O}_2$ (d–f). a, d, Galvanostatic charge-discharge profiles in the 2.0–4.6 V range during the two initial cycles. The bar graph indicates the amounts of oxygen evolution characterized by operando differential electrochemical mass spectrometry (DEMS) analysis. LRO exhibits significant amounts of oxygen evolution during unstable $\text{Ru}^{5+/6+}$ redox, but LNRO does not, demonstrating that HV-redox of LNRO is stabilized. b, e, GITT measurements for the second cycle at room temperature. The tests were performed with a 1 h pulse at C/10-rate followed by a 4 h relaxation step. Black dashed curves indicate equilibrium voltage profiles that show reduced voltage hysteresis of LNRO (e) compared to LRO (b). Both relaxation

steps at a high voltage are dominated by different parameters, as described by the black dotted line width in the insets. c, f, Comparison of electrochemical profiles for the 2nd cycle at 25 (blue) and 60 (red) °C. Increased delivery capacities at 60 °C show that the kinetic hindrance during HV-redox is temperature-dependent, and such hindrance can be compensated for by the addition of the CV step. (inset)

Figure 3

Operando XANES characterization during the first cycle. a–c, Ru K-edge XANES spectra of LRO (a) and LNRO (b) and Ni K-edge XANES spectra of LNRO (c) at 25 °C. The insets in a, b indicate crossline intensity ($I_{\text{nth}} - I_{\text{1st}}$), reflecting the peak evolution of nth spectra relative to initial spectra. The dotted circle indicates the degree of the pre-edge peak evolution, manifesting the suppression of severe distortion of the RuO_6 octahedron owing to Ni substitution. The inset in c indicates magnified images of the pre-edge region of the Ni XANES spectra, which can be used as fingerprints to identify its local structure. Variation of the corresponding WL energies is plotted in d–f, the yellow line indicates WL energy of $\text{Li}_2\text{Ru}^{4+}\text{O}_3$, while green, blue, and red lines indicate those of Ni^{2+}O , $\text{LiNi}^{3+}\text{O}_2$, and Ni^{4+}O_2 reference lines, respectively. Ru^{4+} in LNRO has lower electronic energy than that in LRO (e), meaning that partial charge is transferred from the neighboring O ligands. In contrast, Ni K-edge WL energy in LNRO (f) is higher than that in the Ni^{2+}O reference, certifying that the partial charge is transferred toward the neighboring O ligands; internal charge transfer occurs from Ni to Ru via O ligands.

Figure 4

Atomic structural evolution during HV-redox and its correlating electronic structure. **a**, 3D contour maps obtained from *operando* EXAFS oscillations; the Fourier transformed peak positions of TM-O (denoted as O) and TM-TM (denoted as T) are ~ 2.1 Å and ~ 3.5 Å, respectively. The 2D contour map shows out-of-plane cationic migration during the first cycle, where a peak evolution of ~ 3.2 Å indicates migration toward the Li layer. **b**, **c**, Ru K-edge EXAFS spectra of LRO (**b**) and LNRO (**c**); the O peak is subdivided into the three peaks of short TM-O bonding (~ 1.14 Å, denoted as S), main TM-O bonding (~ 1.61 Å, denoted as

M), and long TM-O bonding ($\sim 2.05 \text{ \AA}$, denoted as L); spectral variation is observed due to severe structural distortion in Ru K-edge spectra of LRO. On the other hand, the Ru K-edge spectra of LNRO remain unchanged except for the short peak, which corresponds to the TM=O double bond length. **d, e**, Projected density of states (pDOS) of the Ru d orbitals (cyan line), O p orbitals (red line), and Ni d orbitals (yellow line). Upper panels are energy states in the pristine state, and lower panels are those when all of Ru has 5+ oxidation state. The isosurface of the charge density (yellow) around the Fermi level indicates where the electrons extracted during HV-redox originate. **f, g**, Schematic illustrations of the energy diagram and its corresponding M-O local configurations in LRO (above) and LNRO (below). The O-dominant b_1^* state is preferable in LRO, whereas the M-dominant b_1^* state is preferable in LNRO, meaning that HV-redox is more reversible in LNRO than in LRO.

Figure 5

The role of Al doping on Ni-substituted lithium ruthenate. **a**, Voltage profiles of LRO, LNRO, and LANRO during the first cycle. The black dotted line indicates the relative reduction in the average potential after 50 cycles. **b**, Capacity retention during 50 cycles, including specific capacities, Coulombic efficiencies, and average potentials. **c**, Evolution of atomic structure after 50 cycles in LRO, LNRO, and LANRO. **d**, 2D contour maps of Ru K-edge EXAFS spectra of LANROs during the first cycle (upper) and second cycle

(below). White dotted lines inside the third white box (Ru-TM₂) indicate long TM-TM peak splitting; irreversible migration toward the Li layer during the first cycle, and reversible migration toward the Li layer during the 50th cycle is identified. **e**, Energy landscape for atomic migration from the Oh_{TM} to Td_{Li} sites calculated along the migration paths indicating the thermodynamic prevalence of Al migration over Ni. **f**, Relative site energies of neighboring Td and Oh sites in the Li layer for Ni of LNRO (cyan) and LANRO (red). The inset shows the original sites of each Ni (i, ii, iii); red triangles indicate atomic sites where migration is hindered due to Al doping, whereas blue triangles indicate the sites where Ni migration into neighboring Td sites is possible but further migration into Oh sites is impossible. In schematic drawings, yellow boxes indicate the most feasible migration **sites**, but red dotted boxes indicate thermodynamically prohibited migration sites.

Supplementary Files

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