

Modulating Redox Pathways in Manganese-Based Disordered Rocksalt Cathodes via Molybdenum Incorporation

Marcela Calpa,* Randy Jalem, Taiga Ozawa, Minako Nishioka, Anna Myojin, Gen Hasegawa, Naoaki Kuwata, Shoichi Matsuda, Kei Kubota, and Kazunori Takada



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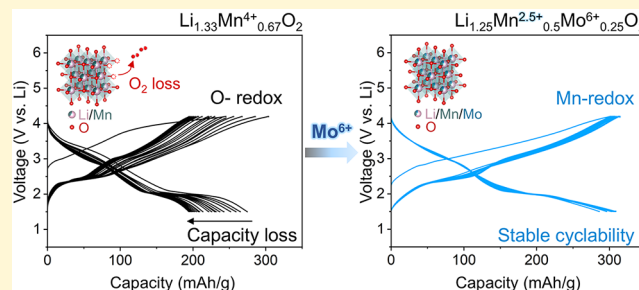
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ABSTRACT: Cation-disordered rocksalt oxides offer broad compositional flexibility and high theoretical capacities, but their electrochemical performance is often limited by uncontrolled competition between transition metal and oxygen redox processes. In particular, controlling the balance between Mn and O redox activities remains a key challenge in Mn-based disordered oxides. Here, a previously unexplored compositional space in the Li–Mn–Mo–O system is investigated, revealing that Mo incorporation systematically alters the electronic structure and redox behavior of Mn-based disordered rocksalt oxides. Mo doping lowers the average Mn oxidation state, thereby stabilizing a Mn-dominated charge-compensation mechanism. Combined spectroscopic characterization and first-principles calculations reveal a shift in charge compensation from oxygen-centered to Mn-centered redox processes with Mo doping. As a result, $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$ delivers a reversible capacity exceeding 300 mAh g^{−1} with enhanced electrochemical stability. These findings demonstrate that targeted compositional and electronic structure modulation enables effective control of redox pathways in cation-disordered oxides and offers design principles for stable, high-capacity Mn-based cathode materials.



INTRODUCTION

Cation-disordered rocksalt oxides represent a chemically versatile class of transition metal oxides that expand the compositional landscape for designing high-capacity electrode materials beyond conventional layered structures. Their compositional flexibility and high lithium contents enable theoretical capacities exceeding those of traditional layered oxides.¹ However, their electrochemical behavior emerges from an intricate interplay between local structure, electronic configuration, and redox chemistry, making the rational design of stable high-capacity compositions a fundamental challenge in materials chemistry.^{2,3}

Among disordered rocksalt oxides, Mn-based compounds are particularly attractive because of the natural abundance, low cost, and environmental compatibility of manganese. Nevertheless, Mn-rich disordered oxides frequently exhibit pronounced oxygen redox activity, which is often accompanied by structural degradation and irreversible oxygen loss, resulting in limited electrochemical stability.⁴ Recent studies have shown that the balance between Mn-centered and oxygen-centered redox processes is influenced by local coordination environments, lithium excess levels, and the electronic structure of transition metal cations.^{1,2} Despite these advancements, achieving controlled and stable Mn-dominated redox behavior in disordered rocksalt systems remains an unresolved challenge, limiting their practical application.⁵

In this work, Li-rich Mn–Mo disordered rocksalt oxides derived from the solid-solution system $3/2\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2$ – $x\text{LiMoO}_2$ are investigated as a platform for modulating redox chemistry through compositional and electronic structure tuning. By combining electrochemical measurements with spectroscopic characterization and first-principles calculations, the relationship between composition, electronic structure, and charge-compensation mechanisms is elucidated.

EXPERIMENTAL SECTION

Synthesis and Characterization

Disordered rocksalt-type lithium metal oxides consisting of solid solutions of $3/2\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2$ – $x\text{LiMoO}_2$ are synthesized for x having a value of 0, 0.1, 0.25, and 0.5. To synthesize $3/2\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2$ – $x\text{LiMoO}_2$ compounds, $\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2$ and LiMoO_2 in stoichiometric amounts are ball milled in a planetary Mono mill (Fritsch, Pulverisette 6) and subject to a rotation of 350 rpm for a total milling time of 90 h, under Ar atmosphere. The ball-milling process is carried out in alternating cycles of 30 min of milling followed by 30 min of rest.

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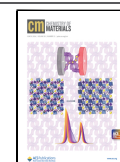


Figure S1 shows the evolution of the XRD pattern during the ball-milling process. To synthesize $\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2$, Li_2CO_3 (99.9%, Kojundo Chemical Co., Ltd.) and Mn_2O_3 (99.9%, Kojundo Chemical Co., Ltd.) are used as precursors. Li_2CO_3 with 10 wt % excess and Mn_2O_3 are mixed using a mortar and pestle for 15 min. The reagent mixture is placed on an alumina crucible and heated at 800 °C for 10 h. Heating is carried out using a tube furnace under N_2 (80 vol %) and O_2 (20 vol %) flowing, with a heating rate of 5 °C/min. To synthesize LiMoO_2 , Li_2CO_3 (99.9%, Kojundo Chemical Co., Ltd.), MoO_3 (99.5%, Kanto Chemical Co., Inc.), and C (Acetylene black, HS100, Denka Co., Ltd.) are used as precursors in a 1:2:1.5 molar ratio. Li_2CO_3 , MoO_3 , and C are mixed using a mortar and pestle for 15 min. The reagent mixture is placed on an alumina crucible and heated at 800 °C for 10 h. Heating is carried out using a tube furnace under Ar flowing, with a heating rate of 5 °C/min.

X-ray diffraction (XRD) patterns are collected using a Rigaku SmartLab diffractometer with $\text{Cu-K}\alpha$ radiation over a 2θ range of 10–90° and a step size of 0.01°. Morphology is observed by scanning electron microscopy (SEM) performed with a JEOL JSM-7800F. Transmission electron microscopy (TEM) images and electron energy loss spectroscopy (EELS) are performed on a JEOL JEM-ARM200F microscope. ^7Li magic-angle spinning (MAS) NMR spectra are recorded on a JEOL 400 spectrometer operating at a ^7Li resonance frequency of 155.4 MHz. Samples are spun at 20 kHz using a 3.2 mm MAS probe, and spectra are acquired with a spin-echo pulse sequence at room temperature. The $\pi/2$ pulse length was 2.8 μs , the recycle delay was 1.0 s, and 512 scans were accumulated. The ^7Li chemical shifts are referenced to 1 mol L^{-1} LiCl aqueous solution at 0 ppm.

All-solid-state batteries are constructed as follows. $3/2\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2$ - $x\text{LiMoO}_2$ compound powders, argyrodite-type solid electrolyte (Mitsui Kinzoku), and acetylene black (HS100, Denka Co., Ltd.) are mixed in a 5:5:2 weight ratio, respectively, using a mortar and pestle for 15 min, to prepare the positive composite electrode. To construct all-solid-state batteries, a bilayer pellet ($\varphi = 10$ mm) consisting of the positive composite electrode (5 mg, 6.4 mg/cm^2) and argyrodite-type solid electrolyte (Mitsui Kinzoku, 100 mg) is obtained by pressing under 185 MPa at room temperature. Indium (Nilaco Corp.) and lithium (Honjo Metal Co., Ltd.) foils are attached to the opposite side of the solid electrolytes by pressing under 260 MPa. The resulting solid-state battery is sandwiched between two stainless steel rods, which serve as current collectors for both positive and negative electrodes, and the assembly is secured with screws tightened to 6 N·m each (Figure S2).

Charge–discharge measurements are carried out in an environment of 50 °C using a constant current (CC) mode at 10 mA g^{-1} , within a voltage window of 1.5 V–4.2 V vs Li. All electrochemical tests are performed using a charge–discharge test system (BCS-805, Biologic).

Gas evolution is monitored using a Canon Anelva Quadrupole Mass Spectrometer (M-401GA-DM) as previously described.⁶ For this analysis, all-solid-state batteries are assembled according to the procedure outlined above but employing a customized cell equipped with a gas inlet and outlet. To ensure sufficient detection of gas evolution above background levels, 20 mg of the positive composite electrode was used. The charge–discharge tests were carried out at room temperature.

Computational Methods

Density functional theory (DFT) calculations are carried out using the Vienna Ab Initio Simulation Package (VASP). It employs the generalized gradient approximation (GGA) approach with the projector-augmented-wave (PAW) basis set.⁷ The structure coordinate data for the $Fm\bar{3}m$ disordered rocksalt $\text{Li}_{1-x}\text{M}_x\text{O}$, where M represents the transition metal species and x denotes its fraction occupying the cation sublattice, is taken from an experimental report.⁸ Two compositions are considered: $\text{Li}_{1.25}\text{Mn}_{0.6875}\text{O}_2$ and $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$. The unit cell is expanded into a $2 \times 2 \times 2$ supercell, which is then used as a template for generating 500 random configurations of Li–Mn–Mo–vacancy arrangements. Next, a total of 10 structures with the lowest electrostatic Ewald energies are

subjected to DFT geometry optimization. The lowest DFT total-energy structure is then chosen as the representative for further analyses. Structure geometry optimization is performed with spin polarization switched on. The kinetic energy cutoff is set to 520 eV, and the k -point is fixed to at least 1000 with a γ -point centered mesh. The following pseudopotentials are used: Li with s shell treated as valence states, standard Mn, Mo with p shell treated as valence states, and standard O. The strong on-site Coulomb interaction is accounted by employing the GGA + U scheme.⁹ The effective Hubbard U parameters for Mn-3d and Mo-4d are set to 4.9 and 6.3 eV, respectively.¹⁰ The optB88-vdW functional is used to describe the van der Waals interaction in the structures.¹¹ Convergence criteria for energy and force are fixed to <1 meV/atom and <0.01 eV/Å, respectively.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of $3/2\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2$ - $x\text{LiMoO}_2$ compounds with x having a value of 0, 0.1, 0.25, 0.5.

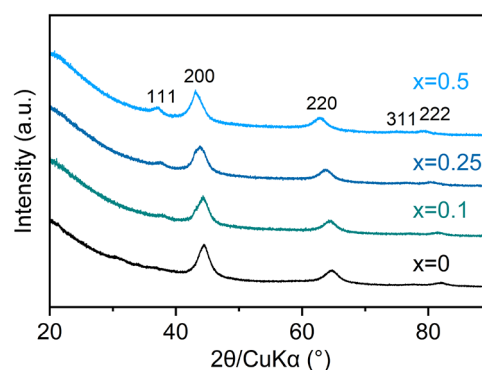


Figure 1. XRD patterns of $3/2\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2$ - $x\text{LiMoO}_2$ compounds with $x = 0, 0.1, 0.25$ and 0.5 .

and 0.5 ($\text{Li}_{1.33}\text{Mn}_{0.67}\text{O}_2$, $\text{Li}_{1.31}\text{Mn}_{0.63}\text{Mo}_{0.06}\text{O}_2$, $\text{Li}_{1.29}\text{Mn}_{0.57}\text{Mo}_{0.14}\text{O}_2$, and $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$, respectively). All samples exhibit characteristic XRD patterns of a disordered rocksalt-type structure, in which reflections can be indexed as 111, 200, 220, 311, and 222 in the cubic rocksalt lattice. The lattice constant increases with increasing Mo content, calculated as 4.07 Å, 4.09 Å, 4.13 Å, and 4.18 Å for $x = 0, 0.1, 0.25$, and 0.5 , respectively (Table S1 and Figures S3–S6). Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) analyses are performed on $\text{Li}_{1.34}\text{Mn}_{0.66}\text{O}_2$ and $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$, as representative compositions (Figure 2). Elemental mapping reveals a

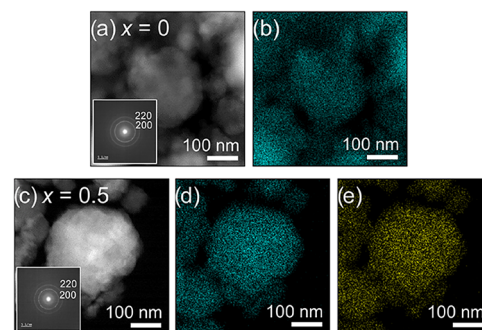


Figure 2. TEM images of (a) $\text{Li}_{1.33}\text{Mn}_{0.67}\text{O}_2$ ($x = 0$) and (c) $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$ ($x = 0.5$), with corresponding elemental mappings for (b) Mn in $\text{Li}_{1.33}\text{Mn}_{0.67}\text{O}_2$ and (d–e) Mn and Mo in $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$.

homogeneous distribution of Mn and Mo, confirming the formation of solid-solution disordered rocksalt oxides. All samples consist of irregularly shaped particles with sizes ranging between 200 nm and 1 μm (Figure S7).

Figure 3 shows the O K-edge, Mn L-edge, and Mo L-edge EELS spectra for $3/2\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2\text{-}x\text{LiMoO}_2$ compounds with

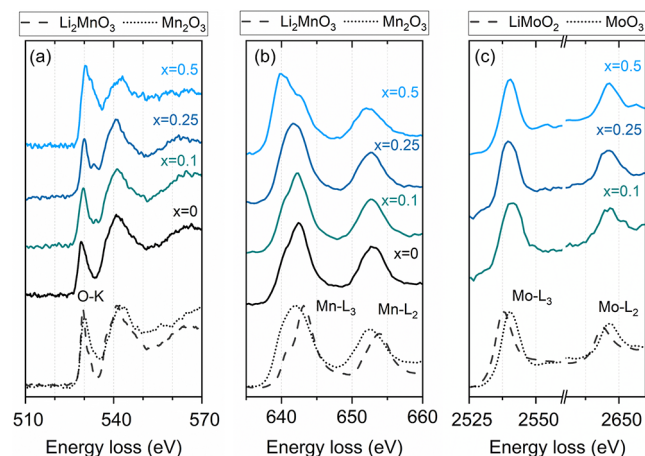


Figure 3. (a) O K-edge, (b) Mn L-edge, and (c) Mo L-edge EELS spectra for $3/2\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2\text{-}x\text{LiMoO}_2$ compounds with $x = 0, 0.1, 0.25$, and 0.5 ($\text{Li}_{1.33}\text{Mn}_{0.67}\text{O}_2$, $\text{Li}_{1.31}\text{Mn}_{0.63}\text{Mo}_{0.06}\text{O}_2$, $\text{Li}_{1.29}\text{Mn}_{0.57}\text{Mo}_{0.14}\text{O}_2$, and $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$, respectively). EELS spectra of Li_2MnO_3 , LiMoO_2 , Mn_2O_3 , and MoO_3 precursors are shown for comparison.

$x = 0, 0.1, 0.25$, and 0.5 . Figure 3b shows that the increasing value of x shifts the Mn L-edge peak to lower energies. This shift indicates that manganese is reduced with higher levels of Mo doping. On the other hand, the Mo-L-edge spectra for all compositions in Figure 3c resemble that of MoO_3 , indicating that Mo in the $3/2\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2\text{-}x\text{LiMoO}_2$ compounds is hexavalent. These findings reveal that during the synthesis process molybdenum is oxidized from the trivalent state in LiMoO_2 to a hexavalent state, while manganese is reduced from the tetravalent state in Li_2MnO_3 to a lower oxidation state according to the Mo content in the compound. Considering a three-electron transfer per Mo atom ($\text{Mo}^{3+} \rightarrow \text{Mo}^{6+} + 3\text{e}^-$), the expected average oxidation states in $3/2\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2\text{-}x\text{LiMoO}_2$ compounds with $x = 0, 0.1, 0.25$, and 0.5 are estimated to be $\text{Li}_{1.33}\text{Mn}_{0.67}^{4+}\text{O}_2$, $\text{Li}_{1.31}\text{Mn}_{0.63}^{3.7+}\text{Mo}_{0.06}^{6+}\text{O}_2$, $\text{Li}_{1.29}\text{Mn}_{0.57}^{3.3+}\text{Mo}_{0.14}^{6+}\text{O}_2$, and $\text{Li}_{1.25}\text{Mn}_{0.5}^{2.5+}\text{Mo}_{0.25}^{6+}\text{O}_2$.

Figure 4 shows the ^7Li NMR spectra for $3/2\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2\text{-}x\text{LiMoO}_2$ compounds with $x = 0, 0.1, 0.25$, and 0.5 , providing insight into the evolution of the local lithium environments upon Mo incorporation. The spectrum of $\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2$ ($x = 0$) exhibits a very broad and significantly shifted ^7Li resonance, which is a characteristic of Mn-based cation-disordered rocksalt structures. The large spectral width reflects the broad distribution of Li environments inherent to the disordered cation lattice, where Li nuclei experience a range of hyperfine interactions with neighboring paramagnetic Mn ions, together with fast relaxation typical of paramagnetic systems.^{12,13} Upon Mo incorporation, the center of this broad resonance progressively shifts toward lower ppm values, moving from approximately 520.3 ppm in $x = 0$ to about 291 ppm in $x = 0.5$ (Figure S8e). This shift reflects a change in the average magnetic environment surrounding Li and is

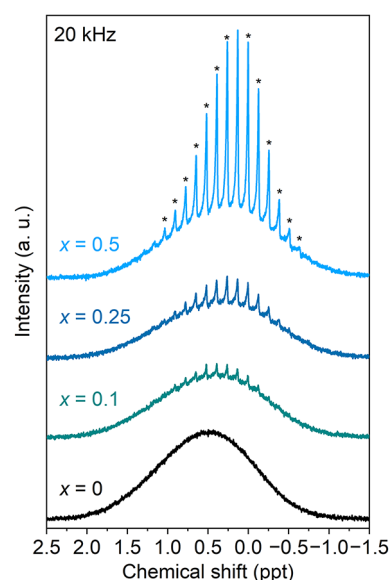


Figure 4. ^7Li MAS NMR spectra of $3/2\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2\text{-}x\text{LiMoO}_2$ compounds with $x = 0, 0.1, 0.25$, and 0.5 . Asterisks (*) indicate spinning sidebands.

consistent with the reduction of the average Mn oxidation state. In addition to this systematic shift, a much narrower resonance centered at 130.5 ppm emerges, with its intensity increasing with higher Mo content (Figures 4 and S8f). The appearance of this signal indicates the formation of a distinct local Li environment associated with the Mo incorporation. The narrower line width of this peak is consistent with Li sites located near diamagnetic Mo^{6+} centers and suggests the formation of preferred Mo-containing local configurations. HRTEM observations in $\text{Li}_{1.29}\text{Mn}_{0.57}\text{Mo}_{0.14}\text{O}_2$ ($x = 0.25$) as a representative composition (Figure S9) reveal a continuous crystalline lattice, with no indication of secondary phase formation. These results suggest that such Mo-containing local configurations correspond to locally favored cation arrangements embedded within the disordered rocksalt lattice.

To further examine the effects of Mo^{6+} incorporation on Li^+ migration, the migration energy barrier for a single-vacancy mechanism is estimated by the DFT nudged elastic band (NEB) method for representative local pathways in $\text{Li}_{1.31}\text{Mn}_{0.63}\text{Mo}_{0.06}\text{O}_2$ and $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$ (Figure S10). The calculated forward (backward) migration barriers are 0.76 (0.20) and 0.87 (0.70) eV, respectively. These values are comparable in magnitude, suggesting that representative local Li^+ migration barriers remain broadly similar to Mo incorporation.

To elucidate how the Mo-induced modification of Mn oxidation states influences electrochemical behavior, the electrochemical performance of $3/2\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2\text{-}x\text{LiMoO}_2$ compounds ($x = 0, 0.1, 0.25$, and 0.5) is investigated in solid-state batteries. Solid-state cells are employed to suppress transition metal dissolution commonly observed in liquid electrolytes,¹⁴ which could otherwise obscure the intrinsic redox chemistry of Mn-based disordered oxides. Figure 5a–d compares the charge–discharge voltage profiles over 20 cycles of $3/2\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2\text{-}x\text{LiMoO}_2$ compounds with $x = 0, 0.1, 0.25$, and 0.5 , respectively. Figure 5e depicts the discharge capacity of all compounds as a function of cycle number, elucidating a trend of higher capacity retention with increasing Mo content. Although the average operating voltage varies

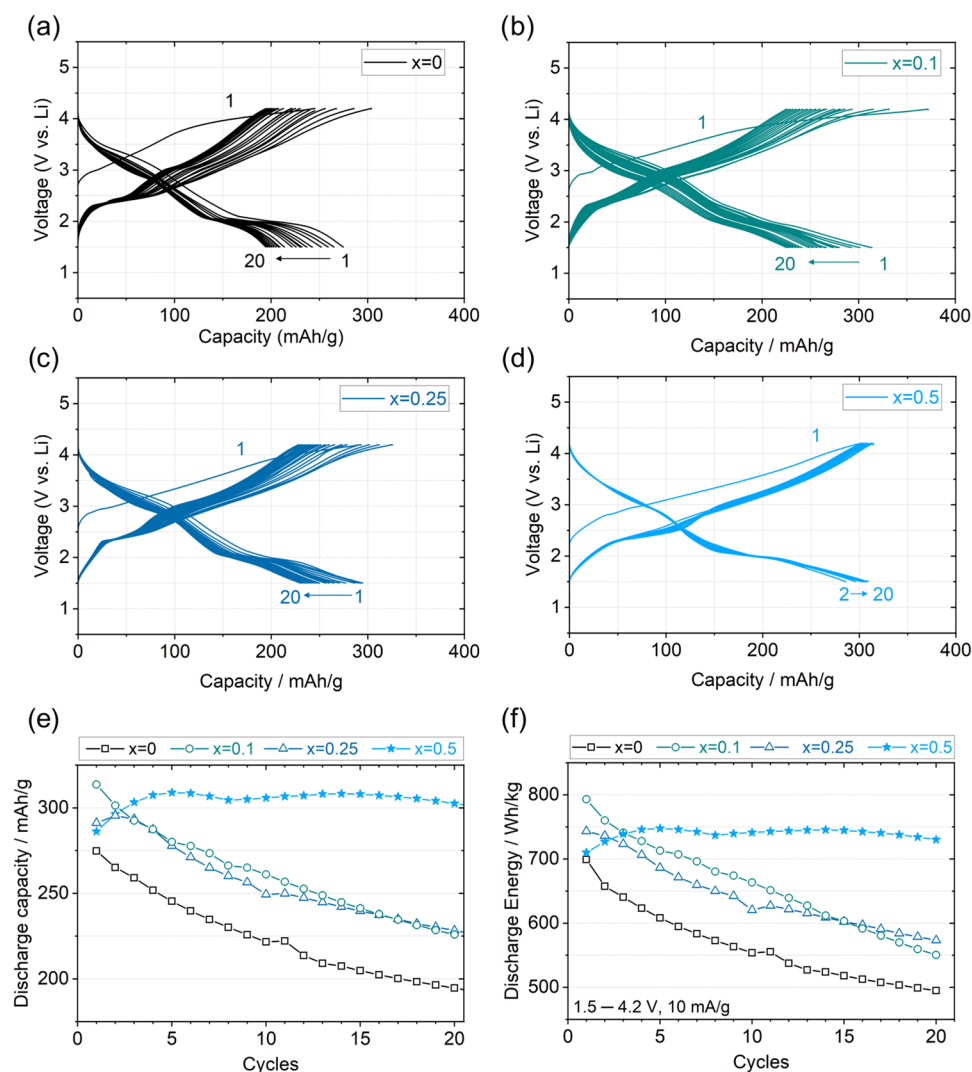


Figure 5. (a–d) Charge and discharge curves of $3/2\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2-x\text{LiMoO}_2$ compounds with $x = 0, 0.1, 0.25$, and 0.5 ($\text{Li}_{1.33}\text{Mn}_{0.67}\text{O}_2$, $\text{Li}_{1.31}\text{Mn}_{0.63}\text{Mo}_{0.06}\text{O}_2$, $\text{Li}_{1.29}\text{Mn}_{0.57}\text{Mo}_{0.14}\text{O}_2$ and $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$, respectively). (e) Discharge capacity and (f) discharge energy as a function of cycle number. Measurements are performed in solid-state cells employing an argyrodite-type solid electrolyte and a Li–In counter electrode at 50°C .

slightly among the compounds (Figure S11), the improved capacity retention leads to superior energy density during cycling, as shown in Figure 5f.

To gain deeper insight into the Mo-induced changes in the electronic structure and their impact on redox behavior, first-principles DFT calculations are performed to analyze the electronic density of states (DOS) and oxidation state evolution (by Bader charge analysis) in $\text{Li}_{1.33}\text{Mn}_{0.67}\text{O}_2$ ($x = 0$) and $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$ ($x = 0.5$) as representative compositions. Figure 6 presents the Bader charge (Q_{Bader}) distributions of transition metal and oxygen atoms in $\text{Li}_{1.33}\text{Mn}_{0.67}\text{O}_2$ and $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$, using $\text{Li}_{20}\text{Mn}_{11}\text{O}_{32}$ and $\text{Li}_{20}\text{Mn}_8\text{Mo}_4\text{O}_{32}$ supercells with random configurations of Li–Mn–Mo–vacancy arrangements, as model structures, respectively. In $\text{Li}_{20}\text{Mn}_{11}\text{O}_{32}$, the $Q_{\text{Bader,Mn}}$ distribution, lower and upper bounds ($l_{\text{Bader,Mn}}$, $u_{\text{Bader,Mn}}$), are determined to be $+1.83\text{e}$ and $+1.97\text{e}$, respectively (Figure 6a, $n = 20$), these values are close to that in $\text{P4}_2/\text{mmn}$ MnO_2 (average $Q_{\text{Bader,Mn}} = +2.00\text{e}$, see Table S2 for the reference compounds and suggest a dominantly oxidized state in the form of Mn^{4+} . The corresponding O Bader charge parameters $l_{\text{Bader,O}}$ and $u_{\text{Bader,O}}$

values are -1.26e and -1.11e , respectively (Figure 6c, $n = 20$). In contrast, Mo incorporation in $\text{Li}_{20}\text{Mn}_8\text{Mo}_4\text{O}_{32}$ leads to a pronounced downshift of Mn Bader charges, with $l_{\text{Bader,Mn}}$ and $u_{\text{Bader,Mn}}$ values decreased to $+1.69\text{e}$ and $+1.70\text{e}$, respectively (Figure 6b, $n = 0$), comparable to that in Pcab Mn_2O_3 (average $Q_{\text{Bader,Mn}} = +1.78\text{e}$), which indicates a reduced oxidation state close to Mn^{3+} . $l_{\text{Bader,Mo}}$ and $u_{\text{Bader,Mo}}$ values are both $+2.51\text{e}$ (Figure 6e, $n = 0$), approaching that of Pnma MoO_3 (average $Q_{\text{Bader,Mo}} = +2.84\text{e}$) and hinting at a Mo oxidation state closer to $6+$. The corresponding $l_{\text{Bader,O}}$ and $u_{\text{Bader,O}}$ values are -1.35e and -1.25e , respectively (Figure 6d, $n = 0$). Here, the overall downshift in $Q_{\text{Bader,Mn}}$ and $Q_{\text{Bader,O}}$ values in $\text{Li}_{20}\text{Mn}_8\text{Mo}_4\text{O}_{32}$ relative to $\text{Li}_{20}\text{Mn}_{11}\text{O}_{32}$ demonstrates that Mo incorporation redistributes electronic charge from Mo to Mn and O, consistent with the experimentally observed redox tendency (Figure 3). The experimentally inferred average Mn oxidation state of $+2.5$, which indicates the presence of Mn^{2+} in $\text{Li}_n\text{Mn}_8\text{Mo}_4\text{O}_{32}$, is, however, not apparent in the present calculation result. Small quantitative differences may arise because the present supercell model assumes a random Li–Mn–Mo distribution and therefore does not fully capture

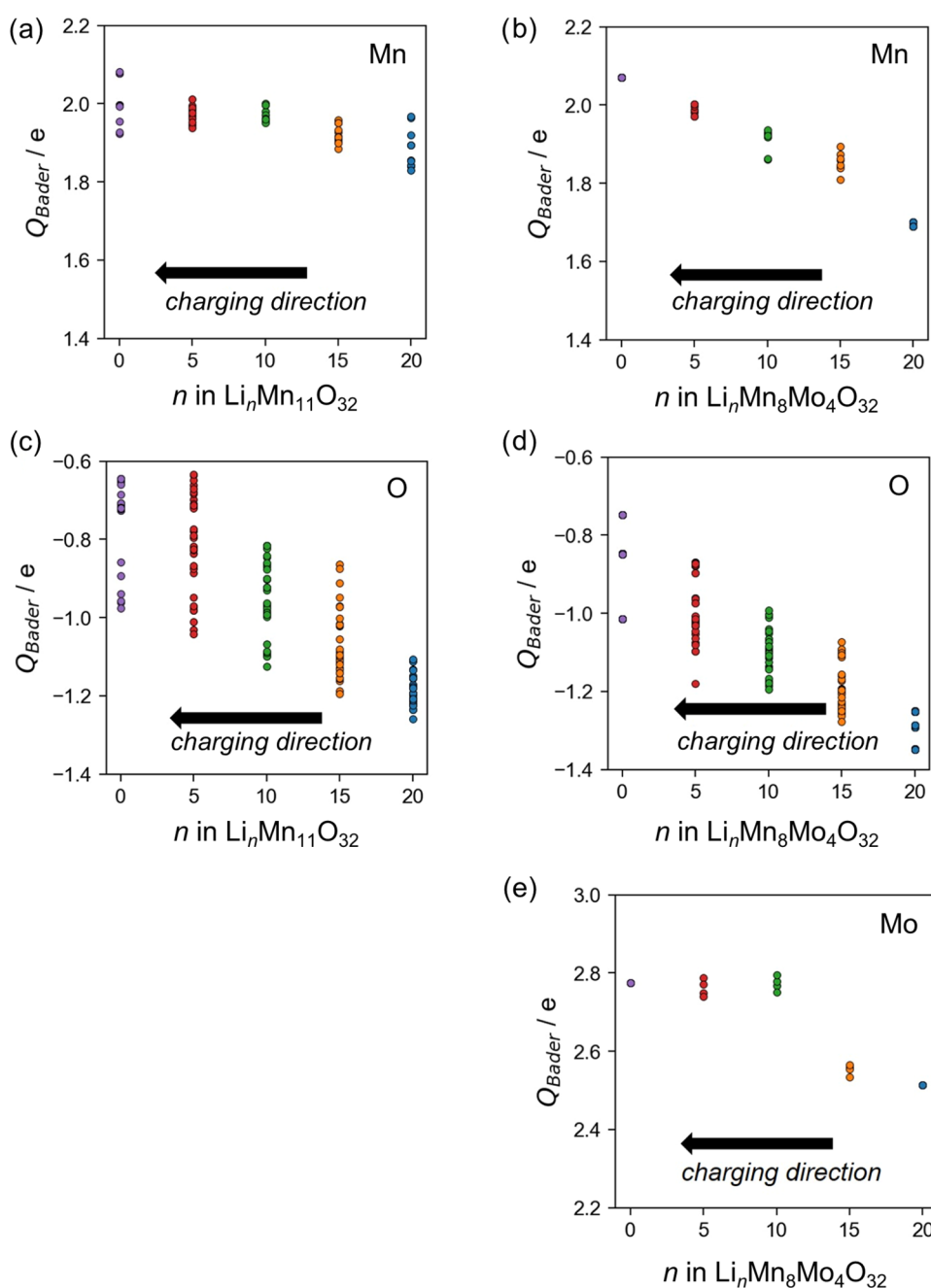


Figure 6. DFT-based Bader charge (Q_{Bader}) distributions of transition metal and oxygen atoms in $\text{Li}_n\text{Mn}_{11}\text{O}_{32}$ and $\text{Li}_n\text{Mn}_8\text{Mo}_4\text{O}_{32}$ supercell model structures, respectively, with $n = 20$ as the precharged state. (a, c) Q_{Bader} distributions for Mn and O, respectively, in $\text{Li}_n\text{Mn}_{11}\text{O}_{32}$. (b, d, e) Q_{Bader} distributions for Mn, O, and Mo, respectively, in $\text{Li}_n\text{Mn}_8\text{Mo}_4\text{O}_{32}$.

the preferred local cation configurations indicated experimentally (Figure 4). In addition, inherent limitations of Bader charge analysis, such as the tendency to overestimate the ionic nature of bonds, should also be considered. Figures S12a and S13a show the electronic DOS profiles of $\text{Li}_{1.33}\text{Mn}_{0.67}\text{O}_2$ and $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$ structures, respectively. In the precharge state, nonbonding O 2p states contribute significantly to the highest occupied states in $\text{Li}_{1.33}\text{Mn}_{0.67}\text{O}_2$ (Figure S12a), implying potential oxygen redox activity upon cycling. In contrast, the contribution of the O 2p states to the highest occupied states is considerably reduced in $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$ (Figure S13a).

The evolution of Bader charges upon delithiation further reveals a qualitative change in the charge-compensation mechanism. For $\text{Li}_n\text{Mn}_{11}\text{O}_{32}$, the main contribution to the capacity is shown to be coming from oxygen oxidation, as evidenced by the $Q_{\text{Bader},\text{O}}$ distribution, which becomes progressively less negative as n decreases (Figure 6c). The concurrent increase in the distribution width of $Q_{\text{Bader},\text{O}}$ also reflects the pronounced oxygen oxidation activity in the structure. In contrast, there is only minimal change vs n for Mn atoms (Figure 6a), with $Q_{\text{Bader},\text{Mn}}$ values remaining largely unchanged even up to full-Li deintercalation ($n = 20$). These trends are consistent with the electronic DOS profiles (Figure S12), in which as n decreases, the O 2p states are increasingly

up-shifted in energy, while the Mn electronic structure hardly changes. On the other hand, for the $\text{Li}_n\text{Mn}_8\text{Mo}_4\text{O}_{32}$ structure, the capacity is contributed by the initially reduced Mn^{3+} , as shown by $Q_{\text{Bader,Mn}}$ values becoming more positive as n increases (Figure 6b). Meanwhile, the extent of the $Q_{\text{Bader,O}}$ change vs n (Figure 6d) is shown to be significantly less than that in $\text{Li}_n\text{Mn}_{11}\text{O}_{32}$ (Figure 6c), indicating suppressed O redox activity. It is pointed out that the Mo atoms have $Q_{\text{Bader,Mo}}$ values that are relatively invariant and remain close to an oxidation state of 6+ as n decreases. The corresponding electronic DOS profiles for Mn, O, and Mo support the aforementioned Bader charge analysis results (Figure S13). In particular, up to $n = 10$, the Mn DOS profiles reveal a trend in which Mn-3d states below the Fermi level become increasingly lifted up in energy with decreasing n , while the O and Mo DOS profiles only show a relatively minimal change. For low values of n ($n < 10$), the charge-compensation mechanism also involves the participation of O oxidation (Figure S13). Complementary analyses of Mn/Mo–O bond lengths and Mn/Mo magnetic moments (Table S3) further support the Bader charge analysis, indicating that Mn is in a more reduced state in $\text{Li}_n\text{Mn}_8\text{Mo}_4\text{O}_{32}$ and becomes strongly involved in charge compensation during delithiation, while Mo remains in a relatively highly oxidized state.

To experimentally validate the DFT-predicted charge-compensation mechanism, O K-edge, Mn L-edge, and Mo L-edge EELS spectra are collected for $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$ at different states of charge (SOC) during the first cycle (Figure 7a–c). Figure 7d shows the first cycle voltage profile of $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$, indicating the SOC points (i–v) at which

EELS measurements are performed. Upon the first charge to 4.2 V vs Li, the Mn L-edge peak (Figure 7b) shifts from an energy lower than that of Mn_2O_3 , which is used as a standard for Mn^{3+} , to a higher energy similar to that of Mn^{4+} in layered Li_2MnO_3 . After discharge to 1.5 V vs Li, the Mn L-edge peak returns almost to the original position. This indicates that $\text{Mn}^{2.5+}$ (oxidation state estimated from the electron transfer from Mo to Mn) is oxidized to Mn^{4+} during the initial charge and subsequently reduced back to an oxidation state near $\text{Mn}^{2.5+}$ during the discharge. Consistent behavior is also observed in the Mn L-edge XANES (X-ray near-edge structure, Figure S14), confirming the reversibility of the Mn redox process. In contrast, the Mo L-edge energy remains similar to that in MoO_3 throughout the charge and discharge (Figure 7c), indicating that molybdenum does not participate in the redox reaction through the charge and discharge. These results are in good agreement with results from the Bader charge analysis (Figure 6) and demonstrate that the charge compensation in the $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$ compound is predominantly governed by the oxidation and reduction of manganese, with no contribution from molybdenum.

In contrast to $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$, the Mn L EELS spectra of $\text{Li}_{1.33}\text{Mn}_{0.67}\text{O}_2$ collected at different states of charge (Figure S15) do not show a clear shift toward higher energy, indicating that Mn is not the dominant charge-compensation species during charge. A similar behavior in the Mn EELS spectra has been reported for layered $\text{Li}_{1.33}\text{Mn}_{0.67}\text{O}_2$ ¹⁵ and has been associated with oxygen charge compensation and oxygen loss. Consistently, online mass spectroscopy (Figure S16) shows that oxygen gas evolution begins at an early state of charge (~ 168 mAh/g). These results suggest that charge compensation in $\text{Li}_{1.33}\text{Mn}_{0.67}\text{O}_2$ has a major oxygen contribution, in agreement with the Bader charge analysis and is accompanied by oxygen loss. This oxygen-deficient charged state may also contribute to the excess lithium insertion observed during discharge (Figure S15c), possibly through defect environments generated by oxygen loss.

Table 1 summarizes the nominal composition of $3/2\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2 \cdot x\text{LiMoO}_2$ compounds, together with the estimated oxidation states of the transition metals, the theoretical capacities based on the Li reservoir and Mn redox, the experimental first charge capacities, the calculated Mn redox contribution, and the capacity retentions relative to the third cycle. Increasing x progressively shifts the charge compensation from oxygen redox to Mn redox. However, for all compositions, the practical charge capacity exceeds the theoretical value expected from the Mn redox alone. Bader charge analysis suggests that this extra capacity arises from the oxygen redox activity. Although the oxygen redox contribution progressively diminishes with increasing Mo content, capacity retentions remain similar for $x = 0$, $x = 0.1$, and $x = 0.25$ (75.1%, 77.2%, and 77.7%, respectively), while a marked improvement is observed for $x = 0.5$ (99.7%). These results suggest that, among the compositions studied, the reduction in oxygen redox becomes sufficient only at $x = 0.5$ to substantially mitigate the degradation process, resulting in a distinct and more stable cycling regime. Figure 8 shows the online mass spectroscopy (MS) analysis conducted on a solid-state cell using $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$ ($x = 0.5$) during the first cycle at room temperature. No gas evolution is detected for $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$, even as the charge progressed up to 250 mAh/g (with the diminishing oxygen background coming from the carrier gas). These results further confirm that

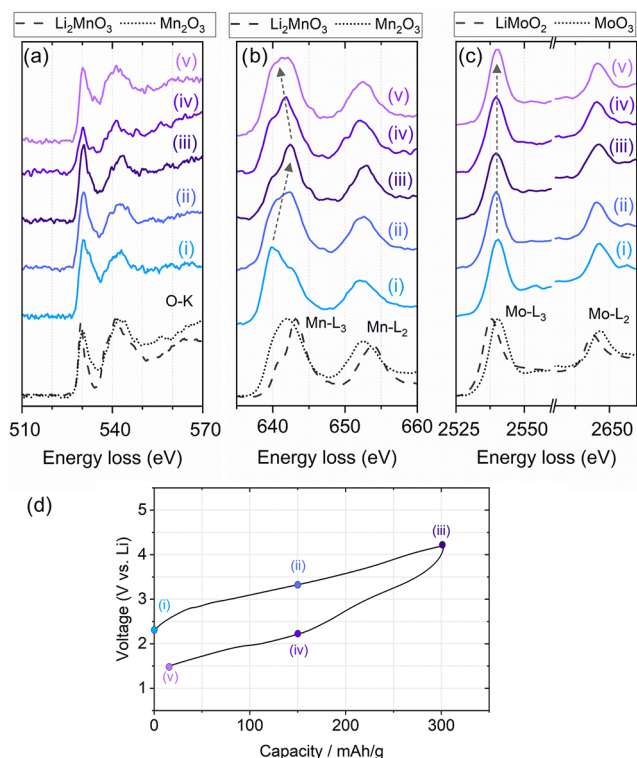


Figure 7. (a) O K-edge, (b) Mn L-edge, and (c) Mo L-edge EELS spectra of samples obtained from cells using $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$ ($x = 0.5$) cycled at different states of charge (SOC) over the first cycle. (d) First-cycle voltage charge–discharge curves indicating the selected SOC points i, ii, iii, iv, and v.

Table 1. Nominal Compositions of $3/2\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_{2-x}\text{LiMoO}_2$ Compounds, Together with the Estimated Transition Metal Oxidation State, Theoretical Capacities Based on Available Li, and Mn Redox, First Charge Capacities, Calculated Mn Redox Contribution, and Capacity Retentions Relative to the Third Cycle

x	nominal composition	theoretical capacity based on Li / mAh/g	theoretical capacity based on Mn redox / mAh/g	first-charge capacity / mAh/g	Mn redox contribution / %	capacity retention / %
0	$\text{Li}_{1.34}\text{Mn}_{0.66}^{4+}\text{O}_2$	458.9	0	245.4	0	75.1
0.1	$\text{Li}_{1.31}\text{Mn}_{0.625}^{3.7+}\text{Mo}_{0.0625}^{6+}\text{O}_2$	431.9	61.7	371.7	17	77.2
0.25	$\text{Li}_{1.29}\text{Mn}_{0.57}^{3.3+}\text{Mo}_{0.14}^{6+}\text{O}_2$	400.6	131.3	292.6	45	77.7
0.5	$\text{Li}_{1.25}\text{Mn}_{0.5}^{2.5+}\text{Mo}_{0.25}^{6+}\text{O}_2$	363.6	218.2	301.9	72	99.7

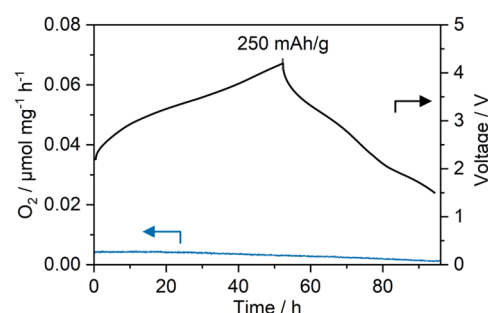


Figure 8. Gas analysis of a $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$ ($x = 0.5$) solid-state cell performed at room temperature ($\sim 20^\circ\text{C}$). The cell employed an argyrodite-type solid electrolyte and a Li–In counter electrode.

molybdenum incorporation shifts the charge-compensation mechanism toward manganese-centered redox processes by stabilizing Mn at lower oxidation states. As a consequence, the contribution of oxygen redox is minimized, leading to the effective suppression of gas evolution for $x = 0.5$ (Figure 8). Molybdenum incorporation, therefore, emerges as an effective strategy for simultaneously modulating the electronic structure and lithium stoichiometry in Mn-based disordered rocksalt oxides. By lowering the average Mn oxidation state to trivalent or lower while maintaining a high lithium content in the structure, Mo doping enables a predominantly Mn-based charge-compensation mechanism without sacrificing the lithium excess. According to the lithium percolation theory,¹⁶ increased lithium excess enhances lithium-ion percolation, thereby enabling higher capacities. This combination of high lithium excess and a low oxidation state in manganese thus underpins both high capacity (exceeding that of previously reported Mn-based disordered rocksalt materials such as LiMnO_2 and $\text{Li}_{1.05}\text{Mn}_{0.85}\text{Ti}_{0.1}\text{O}_2$, Figures S17–S19) and improved cyclability, owing to minimized contribution of oxygen redox in the electrode reaction.

The electrochemical performance of $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$ is further investigated under increased cathode mass-loading conditions in the solid-state battery. Figure 9 shows the charge–discharge voltage profiles and cycling performance of solid-state cells with composite cathode mass loadings of 10.2 mg/cm^2 and 20.4 mg/cm^2 , cycled at a C-rate of C/20 (corresponding to current densities of 0.06 mA/cm^2 and 0.13 mA/cm^2 , respectively). Even at elevated mass loading, $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$ demonstrates a high discharge capacity exceeding 300 mAh/g and relatively high-capacity retention after 50 cycles of 91.4% and 85.8% (relative to the 10th cycle) for mass loadings of 10.2 mg/cm^2 and 20.4 mg/cm^2 , respectively. While a promising cathode material for solid-state batteries, the applicability of $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$ to conventional liquid-electrolyte cells is also demonstrated (Figure S20). In liquid-electrolyte Li-ion cells using LiFSI in DMC, $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$ delivers a discharge capacity approaching its theoretical value (363.6 mAh/g), an initial discharge energy density of 955 Wh/kg , and an energy density retention of 96% after 50 cycles.

CONCLUSIONS

Mn-based cation-disordered rocksalt oxides in the solid-solution system $3/2\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_{2-x}\text{LiMoO}_2$ ($x = 0, 0.1, 0.25$, and 0.5) have been synthesized and systematically investigated to elucidate the role of Mo incorporation in governing the redox chemistry and electrochemical performance. Combined

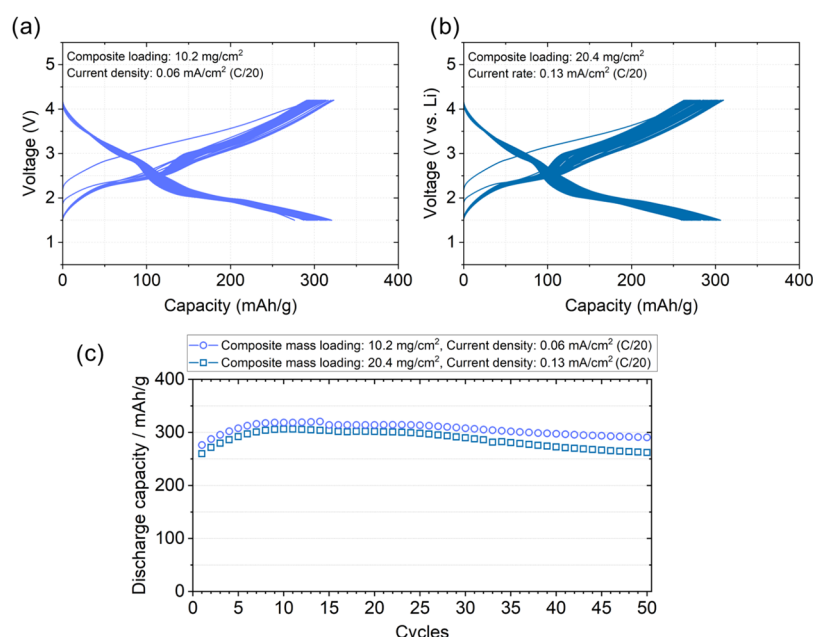


Figure 9. (a, b) Charge and discharge curves of $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$ solid-state cells with composite cathode mass loadings of (a) 10.2 mg/cm^2 and (b) 20.4 mg/cm^2 , and (c) the corresponding discharge capacity as a function of cycle number. Measurements are performed in all-solid-state cells employing an argyrodite-type solid electrolyte and a Li–In counter electrode at 50°C .

spectroscopic characterization and first-principles calculations reveal that Mo incorporation lowers the average Mn oxidation state and shifts the charge-compensation mechanism from oxygen-centered to predominantly Mn-centered redox processes. These results establish Mo incorporation as an effective strategy for simultaneously controlling transition metal oxidation states, lithium stoichiometry, and redox pathways in Mn-based disordered oxides. More broadly, the present study highlights compositional and electronic structure engineering as a powerful design principle for tuning redox chemistry in cation-disordered oxides and advancing the development of high-capacity Mn-based cathode materials with superior cyclability.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.6c00304>.

XRD patterns of Li_2MnO_3 ($\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2$), and LiMoO_2 precursors, and of $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$ sample after 30, 60, and 90 h of ball-milling (Figure S1). Schematic illustration of the battery prototype (Figure S2). Le Bail refinement results for the XRD pattern of $3/2\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2 \cdot x\text{LiMoO}_2$ compounds (Table S1 and Figures S3–S6). SEM images of $3/2\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2 \cdot x\text{LiMoO}_2$ compounds (Figure S7). Gaussian fit of the ^7Li MAS NMR spectra of $3/2\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2 \cdot x\text{LiMoO}_2$ compounds (Figure S8). HRTEM image of $\text{Li}_{1.29}\text{Mn}_{0.57}\text{Mo}_{0.14}\text{O}_2$ ($x = 0.25$, Figure S9). Li^+ migration energy profile for single-vacancy mechanism by the DFT nudged elastic band (NEB) method for $\text{Li}_{1.33}\text{Mn}_{0.67}\text{O}_2$ and $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$ (Figure S10). Discharge weighted average voltage energy as a function of cycle number of $3/2\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2 \cdot x\text{LiMoO}_2$ compounds (Figure S11). DFT-calculated average Bader charges and corresponding assigned oxidation states of transition

metal and oxygen atoms in selected reference Mn- and Mo-based oxides (Table S2). DFT-calculated electronic density of states (DOS) at different stages of charge (n) for the $\text{Li}_n\text{Mn}_{11}\text{O}_{32}$ and $\text{Li}_n\text{Mn}_8\text{Mo}_4\text{O}_{32}$ supercell model structures (Figures S12 and S13). DFT-calculated bond lengths and magnetic moments at different state-of-charge levels n in $\text{Li}_n\text{Mn}_{11}\text{O}_{32}$ and $\text{Li}_n\text{Mn}_8\text{Mo}_4\text{O}_{32}$, together with reference compounds (Table S3). Mn L-edge XANES spectra of $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$ (Figure S14). O K-edge, and Mn L-edge EELS spectra of samples obtained from $\text{Li}_{1.33}\text{Mn}_{0.67}\text{O}_2$ ($x = 0$) cycled at different states of charge (SOC) over the first cycle (Figure S15). Gas analysis of a solid-state cell using $\text{Li}_{1.33}\text{Mn}_{0.67}\text{O}_2$ ($x = 0$, Figure S16). XRD pattern and SEM image of LiMnO_2 (Figure S17). XRD patterns and SEM images of $\text{Li}_{1.05}\text{Mn}_{0.85}\text{Ti}_{0.1}\text{O}_2$ (Figure S18). Electrochemical performance of $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$ compared to LiMnO_2 , and $\text{Li}_{1.05}\text{Mn}_{0.85}\text{Ti}_{0.1}\text{O}_2$ (Figure S19). Electrochemical performance of $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Mo}_{0.25}\text{O}_2$ in liquid-electrolyte cells (Figure S20) (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Marcela Calpa – Center for Green Research on Energy and Environmental Science, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan; orcid.org/0000-0003-4934-4595; Email: calpa.marcela@nims.go.jp

Authors

Randy Jalem – Center for Green Research on Energy and Environmental Science, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan; orcid.org/0000-0001-9505-771X

Taiga Ozawa – Center for Green Research on Energy and Environmental Science, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan

Minako Nishioka – Center for Green Research on Energy and Environmental Science, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan

Anna Myojin – Center for Green Research on Energy and Environmental Science, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan

Gen Hasegawa – Center for Green Research on Energy and Environmental Science, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan; orcid.org/0000-0002-9297-6902

Naoaki Kuwata – Center for Green Research on Energy and Environmental Science, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan; orcid.org/0000-0002-0736-6967

Shoichi Matsuda – Center for Green Research on Energy and Environmental Science, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan; NIMS-SoftBank Advanced Technologies Development Center, National Institute for Material Science, Tsukuba, Ibaraki 305-0044, Japan; orcid.org/0000-0002-0640-3404

Kei Kubota – Center for Green Research on Energy and Environmental Science, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan; orcid.org/0000-0001-8941-3650

Kazunori Takada – Center for Green Research on Energy and Environmental Science, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan; NIMS-SoftBank Advanced Technologies Development Center, National Institute for Material Science, Tsukuba, Ibaraki 305-0044, Japan; orcid.org/0000-0001-7568-1806

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acs.chemmater.6c00304>

Notes

The authors declare no competing financial interest.

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