Determining the Criticality of Li-Excess for Disordered-Rocksalt Li-Ion Battery Cathodes

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The development of Li-excess disordered-rocksalt (DRX) cathodes for Li-ion batteries and interpretation through the framework of percolation theory of Li diffusion have steered researchers to consider “Li-excess” (x > 1.1 in Li_xTM_{2-x}O_2; TM = transition metal) as being critical to achieving high performance. It is shown that this is not necessary for Mn-rich DRX-cathodes demonstrated by Li_{1.05}Mn_{0.90}Nb_{0.05}O_2 and Li_{1.20}Mn_{0.60}Nb_{0.20}O_2, which both deliver high capacity (>250 mAh g⁻¹) regardless of their Li-excess level. By contextualizing this finding within the broader space of DRX chemistries and confirming with first-principles calculations, it is revealed that the percolation effect is not crucial at the nanoparticle scale. Instead, Li-excess is necessary to lower the charging voltage (through the formation of condensed oxygen species upon oxygen oxidation) of certain DRX cathodes, which otherwise would experience difficulties in charging due to their very high TM-redox potential. The findings reveal the dual roles of Li-excess – modifying the cathode voltage in addition to promoting Li diffusion through percolation – that must be simultaneously considered to determine the criticality of Li-excess for high-capacity DRX cathodes.

1. Introduction

While there remains an urgent need for low-cost and high-energy-density cathode materials for Li-ion batteries, the chemical and structural space to design from is increasingly restrictive.[1,2] The recent discovery and development of cathode materials with hybrid anionic and cationic redox (HACR) enabled through Li-excess composition revealed a new approach to achieve high capacity and energy density.[3-5] In particular, Mn-rich HACR cathodes are attractive due to the low cost and earth abundance of Mn compared to Ni or Co, which are the primary transition metals (TM) in conventional cathode materials (e.g., LiCoO_2).[6,7] The best known Mn-rich HACR cathodes have been the layered Li- and Mn-rich oxides (e.g., Li_{1.2}Ni_{0.13}Mn_{0.54}O_2).[8,9] Meanwhile, recent discoveries of high-capacity disordered-rocksalt (DRX)-type cathodes also raised substantial interest in developing the DRX-type Mn-rich HACR cathodes, such as Li_{3}Mn_{2/3}Nb_{1/3}O_2, as well as compositions with other TMs (e.g., Li_{2}Fe_{0.4}Ti_{0.4}O_2).[10-30] These materials can be made with a wide variety of cations (e.g., Li, Na, Ti, V, Cr, Mn, Fe, Ni, Co, Nb, Zr, Mo, W, Ta) and anions (e.g., O, F, S), which considerably broadens the chemical space of possible high-energy cathodes.[10-30] Also, many DRX-cathodes do not experience the issue of low first-cycle coulombic efficiency.[10,12,21,22,28] which is a critical drawback of the layered Li- and Mn-rich cathodes.[8,9]

The recent interest in DRX-cathodes grew from observations that DRX Li-TM oxides with Li-excess compositions (e.g., x = 1.2 in Li_{1.2}TM_{2-x}O_2) could deliver superior capacities (>250 mAh g⁻¹), while those without Li-excess (e.g., x = 1.0 in Li_xTM_{2-x}O_2) typically showed limited performance (<100 mA h g⁻¹).[10,15,16,31-33] Theoretical studies attribute the difference in performance to percolation of the so-called “0-TM channels” (0-TM percolation), which promotes Li diffusion in the DRX-cathodes, only possible if the degree of Li-excess exceeds a critical threshold (e.g., x > 1.1 in Li_{1.1}TM_{2-x}O_2; note that this percolation threshold can vary with the short-range ordering).[10,12,23] In the DRX structure, there are tetrahedral sites that share faces with zero TM (0-TM), one TM (1-TM), or two TM-cations (2-TM), which can connect two neighboring octahedral Li-sites (Figure 1a). Because TMs in the cathodes are in a high-valent state (e.g., TM^{3+},4+) thus repulsive to Li⁺-ions, the absence of a face-sharing TM-cation leads to a lower migration barrier for Li⁺ when it
diffuses through the 0-TM tetrahedral site (0-TM channel), compared with 1-TM or 2-TM channels that are considered nearly inactive due to their high Li-migration barriers.[10,11] Thus, improved Li-transport kinetics due to percolation of the 0-TM channels enabled by Li-excess has been considered critical to achieving high capacity in DRX cathodes. Indeed, DRX Li-Ni-Ti-Mo-oxides and Li-Fe-Ti-oxides were designed on this basis and showed significant improvement in their reversible capacity as the Li-excess level was increased.[15,16] Moreover, besides oxides, various Li-excess DRX oxyfluorides and sulfides were developed (e.g., Li3NbS4, Li2VO2F), achieving ultrahigh capacity (≈300 mAh g⁻¹).[12,18,19,21,28] Based on these findings, the Li-excess strategy for 0-TM percolation has become a de facto design principle of the DRX cathodes.

While introducing Li-excess facilitates 0-TM percolation, it raises the initial average TM valence and thus may trade the theoretical TM cation-redox capacity for O anion-redox capacity, as demonstrated in many Li-rich cathodes shown to operate on oxygen redox as an additional electron reservoir.[5,8,9,20,36,37] Indeed, Li-excess DRX cathodes have shown poor capacity retention upon extended cycling.[13,14,16,21,22] Consequently, recent efforts reported in the DRX cathode literature have concentrated on minimizing the GOM-triggered structural damage that is coupled with improving the Li-transport through a high-level of Li-excess.[20,21,28,39] For instance, F-substitution for O could enhance the capacity retention of the Li-excess DRX oxides (e.g., Li1.2Mn0.7Nb0.1O1.8F0.2) by increasing the TM-redox capacity at a given Li-excess level.[20,39] Also, Nb-doping and LiNbO3-surface modification have been shown to enhance the performance of the DRX Li-excess Ni-Ti/Mo oxides.[40,41]

In this work, we demonstrate in a case study of Li1.05Mn0.90Nb0.05O2 (M90) and Li1.2Mn0.60Nb0.20O2 (M60) that once the particle size is sufficiently reduced, the Mn-rich DRX cathodes cycle well regardless of the Li-excess level, effectively removing the Li-excess "constraint" without sacrificing capacity.

Figure 1. a) The schematic of the disordered-rocksalt cathode structure and explanation of the percolation theory, illustrating types of Li-diffusion channels (0-/1-/2-TM), migration barriers, and percolation thresholds under different assumptions.[10,11] b) X-ray diffraction patterns of Li1.05Mn0.90Nb0.05O2 (M90) before and after ball-milling. c) Scanning electron microscopy images of the as-made and ball-milled M90. d) The elemental mapping (Mn, Nb, and O) on an as-made M90-particle via energy-dispersive-X-ray spectroscopy. Scale bar: 2 µm.
and also mitigating the O-redox-triggered side reactions. Both M90 and M60 were first synthesized into DRX cathodes using a solid-state method and were then mechanically pulverized to have a small particle size below \( \approx 150 \text{ nm} \). Although the low Li-excess level (5%) in M90 is well below the calculated 0-TM percolation threshold,\[^{10,11}\] M90 can deliver similarly high capacity (\( \approx 250 \text{ mAh g}^{-1} \)) and rate capability (\( \approx 185 \text{ mAh g}^{-1} \) at 400 mA g\(^{-1}\)) as M60 with a Li-excess level (20%) above the percolation threshold. Furthermore, capacity-voltage retention is substantially better for M90 than M60.

Our finding that Li-excess is not critical for cycling Mn-rich DRX-cathodes with small particles motivates addressing why other DRX cathodes with different chemistries, such as Li-Ni-Ti-Mo oxides or Li-Fe-Ti oxides, do require a high level of Li-excess to achieve high capacity, even with nano-sized active particles. By contextualizing our results with other reports from the DRX literature and confirming with density functional theory (DFT) calculations, we elucidate that the 0-TM percolation is not critical at the nanoparticle scale. Instead, Li-excess is necessary to decrease the thermodynamic anion-redox voltages of certain DRX cathodes (Ni/Ca/Fe-based DRX), which otherwise would face difficulties in charging due to their higher and more spread-out redox potentials (see Section 2.5). Overall, introducing Li-excess in DRX cathodes modifies the thermodynamic cathode voltage in addition to facilitating Li diffusion through 0-TM percolation, and both effects must be carefully considered together to design for high capacity.

### 2. Results and Discussion

#### 2.1. Synthesis and Characterization of Mn-Rich DRX Compounds

Li\(_{1.05}\)Mn\(_{0.90}\)Nb\(_{0.05}\)O\(_2\) (M90: 5%-Li-excess) and Li\(_{1.20}\)Mn\(_{0.60}\)Nb\(_{0.20}\)O\(_2\) (M60: 20%-Li-excess) were selected as representative Mn-rich DRX compounds with insufficient (M90) and sufficient (M60) Li-excess for 0-TM percolation (percolation threshold \( \approx 10 \%) \).\[^{10,11}\] These materials were made with a solid-state method (see the Method section) and can be considered as solid-solution compounds between Li\(_{1-x}\)Mn\(_x\)\(^{2+}\)O\(_2\) and Li\(_{1-x}\)Nb\(_{5}\)\(^{5+}\)O\(_2\).\(_4\)\([x = 5 (M90) or 20 (M60) in Li\(_{1-x}\)Mn\(_{1-x/10}\)Mn\(_{20}\)\(_{1-x/10}\)Mn\(_{5}\)\(_{1-x/10}\)O\(_2\).\(_4\)\)\] as discussed in earlier papers.\[^{13,14}\] Nb\(^{5+}\) is already in its highest oxidation state in these compounds, thus cannot contribute to the charging capacity. As a result, Li-Mn-Nb-O cathodes are known to operate on Mn\(^{3+}\)/Mn\(^{4+}\) and O-redox.\[^{13,14}\] In principle, pure cationic Mn\(^{3+}\)/Mn\(^{4+}\) redox would lead to a theoretical Mn-capacity of 258.33 mAh g\(^{-1}\) for M90 and 175.04 mAh g\(^{-1}\) for M60 to use before O-redox. We chose M90 to represent the Mn-rich compounds without the 0-TM percolation instead of the ones with even less Li-excess (i.e., Li\(_{1.02}\)Mn\(_{0.98}\)Nb\(_{0.02}\)O\(_2\); 2%-Li-excess) because it was the least Li-excess Mn–Nb DRX oxide that we could synthesize successfully using the conventional solid-state synthesis method. The elemental analysis via inductively coupled plasma optical emission spectrometry (ICP-OES) shows that the actual Li: Mn: Nb atomic ratio is 1.071: 0.883: 0.046 for M90 and 1.233: 0.583: 0.184 for M60.

Figure 1b shows the X-ray diffraction (XRD) patterns of the as-made and ball-milled Mn-rich samples. We observe well-defined peaks of a disordered-rocksalt phase from the XRD pattern of the as-made M90 powder. LiMnO\(_2\) is known to form into either an orthorhombic (space group: \( \text{Pnmm} \)) or monoclinic (\( \text{C2/m} \)) phase,\[^{29,33}\] and its DRX-polymorph (\( \text{Pn-3m} \)) could be made only through the mechanochemical synthesis route due to its metastable nature.\[^{29,33}\] Considering that M90 has a similar composition as LiMnO\(_2\), it is remarkable that it can directly form into the DRX structure via a solid-state method, indicating the effectiveness of the Li\(_3\)NbO\(_4\) as a cation-disordering agent.\[^{13,43}\] After the solid-state synthesis, we ball-milled the powder to reduce the particle size, and the XRD peaks become broader, representative of the particle-size reduction. The XRD refinement suggests that the lattice parameter of M90 slightly decreases from 4.1656 (7) to 4.1569 (2) Å after ball milling (Figure S1, Supporting Information). Scanning electron microscopy (SEM) images show that the as-made M90 forms into big particles (3 \( \mu \text{m} < d < 10 \mu \text{m} \)), yet ball-milling pulverizes them into polycrystalline nanoparticles (50 nm \( < d < 150 \text{ nm} \)) that form loosely packed secondary particles (Figure 1c and Figure S2: Supporting Information). Such nanostructured particles have been repeatedly utilized in the literature as it improves the capacity of the DRX cathodes.\[^{10–10}\] Energy-dispersive-spectroscopy (EDS) mapping shows uniform distribution of Mn, Nb, and O within an M90 particle (Figure 1d), confirming that Nb is soluble in the Mn-rich DRX-oxide lattice. M60 also crystallizes into the DRX structure, and nanoparticles (80 nm \( < d < 150 \text{ nm} \)) were formed after ball milling (Figures S3 and S4, Supporting Information). The electronic conductivities of the as-made M90 and M60 were measured to be \( \approx 1.8 \times 10^{-4} \) and \( \approx 8.6 \times 10^{-5} \text{ S cm}^{-1} \), respectively.

#### 2.2. Electrochemical Properties of M90 and M60

Figure 2a,b shows the voltage profiles of M90 and M60 when they are cycled between 1.5 and 4.8 V at 40 mA g\(^{-1}\) and room temperature. We also show their 100 mA g\(^{-1}\)-rate voltage profiles in Figure S5 (Supporting Information). We tested the ball-milled samples because the as-made particles (3 \( \mu \text{m} < d < 20 \mu \text{m} \)) are too big for the materials to achieve high capacity.\[^{11,27}\] To the best of our knowledge, no micrometer-size DRX-cathode particles have ever been successfully cycled. While 5%-Li-excess is below the 0-TM percolation threshold (\( \approx 10 \%) \) Li-excess in the DRX structure, M90 can still deliver an impressively high capacity of \( \approx 250 \text{ mAh g}^{-1} \) (\( \approx 0.87 \text{ Li/f.u.} \approx 730 \text{ Wh kg}^{-1} \)) with a high 1st-cycle coulombic efficiency of 98.5% through the Li-intercalation reaction (Figure 2a and Figure S6: Supporting Information). Note that although 5%-Li-excess is insufficient for the 0-TM percolation, it is well above the threshold (\( x > 0.75 \) in Li\(_{1-x}\)TM\(_3\)\(_2\)O\(_4\)) for percolation of mixed 0-TM and 1-TM channels (Figure 1a).\[^{13}\] suggesting that Li diffusion through mixed 0/1-TM channels could be sufficient to cycle M90. Meanwhile, M60 delivers a slightly higher first-discharge capacity of 277 mAh g\(^{-1}\) (\( \approx 0.95 \text{ Li/f.u.; } 860 \text{ Wh kg}^{-1} \)); yet, its capacity fades below 250 mAh g\(^{-1}\) after the initial three cycles (Figure 2b). Note that the measured 277 mAh g\(^{-1}\) is quite higher than the theoretical Mn-contribution of 175.04 mAh g\(^{-1}\) (even if all 0.6 Mn are fully utilized), assuring significant oxygen anion-redox \( O^{2−} \leftrightarrow O^{3−} \) contribution in M60. The discharge capacity delivered above 3 V is higher for M60 than M90. This is likely due to more O-redox contribution in M60 than M90 since \( O^{2−}/O^{3−} \) is
intrinsically a higher voltage redox process than Mn$^{3+}$/Mn$^{4+}$ redox. Over 40 cycles, there is $\approx$15% and $\approx$31% capacity loss for M90 and M60, respectively, indicating better capacity retention for M90 (Figure 2c). Also, the average discharge voltage decreases by 170 meV (145 meV) for M90 and by 400 meV (366 meV) for M60 after 40 cycles at 40 mA g$^{-1}$ (100 mA g$^{-1}$). Thus, voltage retention is also better for M90 (Figure 2d). It has been shown in the literature that the cycling stability of DRX cathodes declines with an increasing degree of O-redox, as it triggers GOM-related side reactions (e.g., O loss, electrolyte decomposition).[17,20,23,27] Therefore, the improved capacity- and voltage-retention of M90 is likely due to its higher Mn-content than M60, leading to higher Mn-redox capacity contribution relative to O-redox for M90, compared to M60. Note we also tested Li$_{1.10}$Mn$_{0.80}$Nb$_{0.10}$O$_2$ (M80). It delivers a similar capacity ($\approx$255 mA h g$^{-1}$ at 40 mA g$^{-1}$) as M90 (Figure S7, Supporting Information).

We find that the rate capability of M90 compares well with M60. Figure 2e,f shows the voltage profiles of M90 and M60, respectively, when they are charged at 20 mA g$^{-1}$ and discharged at different rates (10, 50, 100, 200, 400, 1000, and 2000 mA g$^{-1}$). Although M60 delivers a higher discharge capacity (287 mA h g$^{-1}$) than M90 (261 mA h g$^{-1}$) at 10 mA g$^{-1}$, their capacities become similar to each other as the discharge rate increases. For instance, M90 and M60 deliver 185 and 189 mA h g$^{-1}$, respectively, at 400 mA g$^{-1}$.

For a more quantitative comparison of the kinetic properties of M90 and M60, we performed the galvanostatic intermittent titration technique (GITT) measurement with a 5 h relaxation step after every charging or discharging increment of 10 mAh g$^{-1}$ (at 20 mA g$^{-1}$). Figure 2g shows the 1st discharge portion of the GITT profile with the characteristic vertical voltage shifts corresponding to the voltage relaxation (overpotential).[44] Slightly reduced overpotential is observed from M60 compared to M90, indicating improved kinetics in M60. For instance, after the first discharging to 150 mA h g$^{-1}$, voltage relaxation is $\approx$44 meV for M60, while it is $\approx$166 meV for M90. The estimation of the chemical Li diffusion coefficient based on the GITT profiles suggests about 1.2–5.0 times higher apparent diffusivity for M60 than M90 during discharge.

Figure 2. The initial five-cycle voltage profiles of a) M90 and b) M60 when they are cycled at 40 mA g$^{-1}$ between 1.5 and 4.8 V. c) The capacity retention of M90 and M60 during the 40 and 100 mA g$^{-1}$ cycling tests. d) The average discharge voltage of M90 and M60 upon cycling (40 or 100 mA g$^{-1}$, 1.5–4.8 V). The discharge profiles of e) M90 and f) M60, when they are charged at 20 mA g$^{-1}$ and then discharged at different rates (10, 50, 100, 200, 400, 1000, and 2000 mA g$^{-1}$). g) The discharge portion of the galvanostatic intermittent titration technique (GITT) profiles of M90 and M60, shown as a function of discharge capacity. The inset zooms in the portion of the M90’s GITT profile shown as a function of time (hours). h) The calculated Li-diffusivities of M90 and M60 based on the GITT results and i) their ratio.
while the absolute magnitudes for both compounds are at the low range of 10^{-10} to 10^{-15} cm² s^{-1} (Figure 2h,i and Figure S8: Supporting Information). As a comparative reference, the chemical Li diffusion coefficient of layered LiCoO₂ is between 10^{-13}–10^{-18} cm² s^{-1}.[45] Note that diffusivity calculation on pulverized cathode particles tends not to be precise because of the irregular particle morphology, while the mathematical model used to fit the GITT profile requires certain assumptions about the geometry of the electrode or electrode particles (Figure S8, Supporting Information). However, considering that both M90 and M60 were synthesized and processed to have similar morphology, the diffusivity ratio between the two materials would still be meaningful (Figure 2i). Considering all, we confirm that Li-excess indeed improves Li-transport in the DRX structure. However, the degree of improvement from 0/1-TM percolation to 0-TM percolation is by less than one order of magnitude, and the Li-diffusivity remains low for both compounds.

Note that the 0-TM percolation concept relates to the intrinsic Li diffusivity rather than the chemical diffusion coefficient that contains the thermodynamic factor.[10,11,23] However, knowing that chemical diffusion is the process that occurs in the presence of concentration (or chemical potential) gradient, resulting in a net transport of mass (thus reflecting the net Li transport in and out of the cathode), we believe that the estimation of the chemical Li diffusivity is useful to evaluate the practical impact of 0-TM percolation. At this point, we have no clear explanation about why the improvement in the chemical diffusivity is not significant after 20% Li-excess. It might be due to the formation of short-range order (SRO) in M60, which can degrade the quality of 0-TM percolation compared to when the cation distribution is completely random.[23] Or, M90, as a highly Mn-rich oxide, may experience local DRX-to-spinel transformation during cycling, which could improve its Li-transport property compared to when M90’s structure remains fully cation-disordered.[10,29] Hidden structural parameters such as these can make the diffusivity improvement via Li-excess less evident in the Mn-DRX. Meanwhile, our XRD refinement indicates that the degree of spinel transformation in the first-cycled M90 should not be significant enough (<14% spinel-character developed at maximum) for it to modify the percolation property meaningfully (Figure S9, Supporting Information).[19] Thus, we believe the good performance of M90 achievable from the beginning of cycling should be discussed in the context of conventional DRX materials, although the positive influence on Li transport by the spinel formation cannot be neglected completely.

On the other hand, while the Li-diffusivity may be low for both M90 and M60, the materials’ reversible capacity and rate performance are still quite good, indicating that Li-diffusion is not the major bottleneck when the particle size is sufficiently small. This observation is not surprising considering that in a spherical nanoparticle, for example, with \( d = 100 \) nm, only 20 nm diffusion length is necessary to access \( \approx 80\% \) of the capacity. This translates to a minimum of only \( 2 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1} \) \( (5 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}) \) for a 30 min (20 h) charge or discharge (according to the relationship of \( \Delta x \sim \Delta t \) (Figure S10, Supporting Information)). Furthermore, we observe that for this reduced particle size, a pseudocapacitive rather than diffusion-limited signature emerges in the cyclic voltammetry profiles of M90 or M60 (Figure S11, Supporting Information).

### 2.3. Chemistry-Dependent Effects of Li-Excess on the DRX-Capacity

Turning to the DRX-cathode literature, we note that nearly all previous studies utilized \( d < 200 \) nm nanoparticles either directly (e.g., sol–gel, mechanochemistry) or by “post-synthesis” pulverization (as we did for M90 and M60). As motivated above, the difference between 0-TM percolation and mixed 0-TM/1-TM percolation with respect to the characteristic diffusion time should not be significant at small particle length scales. Nevertheless, for certain DRX-cathode chemistries, there is a clear positive correlation between the degree of Li-excess and achieving high capacity. As shown in Figure 3a, nominally stoichiometric DRX-LiFeO₂, LiCoO₂, and LiNiO₂ (compounds 1, 9, and 10 in Figure 3a) can discharge \( \ll 50 \) mAh g⁻¹ even when heavily pulverized,[15,31] but the highly Li-excess versions, such as Li₁₋ₓNi₁₋ₓTiₓMo₂O₇ and Li₁₋ₓFe₀.₉₆M₀.₄₈O₂ (compounds 15, 19, respectively) can deliver a high capacity of over 200 mAh g⁻¹, due to reduced voltage of oxygen-redox as well as being assisted by 0-TM percolation (see later discussion).[16,25] To provide additional context to our results, included in Figure 3a are also discharge capacities of several other DRX-cathodes reported in the literature obtained under a slow rate (e.g., 20 mA g⁻¹) (Figure 3a).

To reconcile the inconsistency that Li-excess strongly correlates with the achieved capacity in some cases but not in others (depicted in Figure 3a), we consider two factors that can curtail the reversible capacity. One possibility (case 1) is the slow kinetics contribute excessive over-potential during charge preceding discharge, and the voltage cut-off is prematurely reached before appreciable capacity can be accrued. This explanation is consistent with the percolation theory framework of Li-excess, which is a kinetic argument that 0-TM percolation is a prerequisite for high capacity.[10,11]

Another possibility (case 2) is limited charging capability due to the high thermodynamic redox potential of a cathode. For instance, Li₂MnP₂O₇ shows limited capacity because the equilibrium redox potential to cycle the second Li is too high (5.3 V).[46] Moreover, materials with high redox potential have disadvantages regarding charging; because, for them, there will be less room to apply overpotential before the predetermined charge cut-off (e.g., 4.8 V, which is often limited by the electrolyte electrochemical stability) is reached, rendering slow kinetics less acceptable. In principle, the charging capacity could continuously increase to its maximum by applying higher and higher voltage, but this would require the development of electrolytes with ultra-high stability. Also, Li-TM-oxides typically have poor structural stability at high voltage, experiencing irreversible cation migration and O loss. Thus, there is a practical upper-voltage limit to which a cathode can accumulate the charge capacity \( \approx 4.8 \) V in lab tests) to ensure enough room for discharge. These explanations then suggest that the cathode’s redox potential (a thermodynamic property), which extends to the choice of TM and crystal structure, can further influence the accessible capacity of the cathode.

Investigating case 2 further as a limiting factor for DRX-materials, we plot the reported capacities of DRX-cathodes for a fixed degree of Li-excess (0%) organized by TM in Figure 3b and remark that “not all” 0%-Li-excess DRX cathodes perform...
poorly. For instance, while DRX-LiFeO$_2$, LiCoO$_2$, and LiNiO$_2$ showed limited capacity (<50 mAh g$^{-1}$)[31,32] DRX-LiVO$_2$, LiV$_0.5$Co$_0.5$O$_2$, LiMnO$_2$, and LiMoO$_3$ could still deliver high capacity (~200 mAh g$^{-1}$)[29,30,47,48]. This suggests that the achievable capacity indeed does not depend entirely on the cycling kinetics, which is expected to be slow in all 0% Li-excess DRXs. To identify a possible correlation between the discharge capacity values with TM-redox voltage, we also plot in Figure 3c the calculated average voltage of various Li-TM oxides utilizing different TM-redox couples as extracted from the Materials Project database.[49] While the voltages depicted in Figure 3c do not correspond to DRX structures (rather ordered structures such as R-3m LiCoO$_2$ and Imma-LiCoO$_2$), the plot clearly reveals broad trends that exist within oxides. For example, some TM-redox couples (e.g., Ni$^{3+}$/Ni$^{4+}$, Fe$^{3+}$/Fe$^{4+}$) have categorically higher operating potentials than others (e.g., Mo$^{3+}$/Mo$^{4+}$, V$^{3+}$/V$^{4+}$, Mn$^{3+}$/Mn$^{4+}$). Taking Figure 3b,c together, 0%-Li-excess DRX cathodes with low reversible capacity occur with high-voltage TM-redox couples (e.g., Ni$^{4+}$/Ni$^{3+}$), while high capacity is achievable using low-voltage TM-redox couples (e.g., Mo$^{4+}$/Mo$^{3+}$). It is therefore critical to take the redox potential into account to understand the achievable capacity of DRX-cathodes.

The combination of high-voltage TM-redox and DRX cathodes presents a multifaceted challenge. As discussed above, materials with high redox potential are more susceptible to overpotential-induced premature-reach of upper cut-off voltage upon charging, so slow kinetics tends to curtail the accumulated charge capacity preceding discharge to greater effect. Moreover, there are inherent, non-diffusion-related problems of the DRX-structure, which aggravate voltage swing and penalize TM oxidation, making charging through high-voltage TM-oxidation challenging. For instance, it was shown that Ni$^{3+}$/Ni$^{4+}$-oxidation barely occurs in the DRX oxides (e.g., Li$_{1.2}$Ni$_{1.2}$Ti$_{0.8}$Mo$_{2.15}$O$_{2}$, even Ni$^{3+}$/Ni$^{4+}$-reservoir is not fully utilized) when it readily occurs in Ni-based layered cathodes (e.g., LiNi$_{1/3}$Mn$_{1/3}$O$_{2}$).[9,16,20,50] To pinpoint the mechanistic origin, we compare critical differences in the electronic structure and intercalation thermodynamics of DRX and layered cathode materials.

2.4. Promoted TM-Oxidation in Layered Structure Facilitates Charging of Layered Cathodes

In layered structure,[5] the band center positions ($\mathbf{\varepsilon}$) have the following order: $\mathbf{\varepsilon}$ (Mn$^{3+}$/Mn$^{4+}$) $> \mathbf{\varepsilon}$ (Ni$^{3+}$/Ni$^{4+}$) $> \mathbf{\varepsilon}$ (Co$^{3+}$/Co$^{4+}$) $> \mathbf{\varepsilon}$ (O$^{2-}$), and Li-extraction using TM-oxidation (e.g., Ni/Co-oxidation) occurs within a narrow voltage window without much overlap with the O-2p band. For example, nearly ~80% of Li ($\sim$220 mAh g$^{-1}$-charge) can be extracted from layered LiNiO$_2$ within 3.5–4.3 V (only 0.8 V voltage swing) via Ni$^{3+}$/Ni$^{4+}$ oxidation.[31] To explain, we recall that the equilibrium cathode potential ($U$) is negatively proportional to the chemical potential of Li in the cathode structure ($\mu_{Li^{+}}$) and an electron ($\mu_{e^{-}}$) in a layered structure with limited numbers of distinct sites for Li$^{+}$ ions (e.g., for perfectly layered R-3m LiCoO$_2$, there is only one crystallographically unique site for Li), the Li$^{-}$site energy (proportional to $\mu_{Li^{+}}$) varies little upon charging.

Also, in the layered structure, TM's form a distinct TM–O slab (TM-layer, Figure 4a), and the TM's can collectively...
reduce their TM–O bond-length upon charge. For instance, it was shown experimentally that the TM–O bond distance of LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2 decreases from 1.961 to 1.896 Å when charged to 4.3 V.[52] This trend is also observed in our DFT calculations. Figure 4b shows the change in the average TM–O bond distance in layered Li_{1−x}TM_{0.2}O_2 (TM = V, Mn, Fe, Co, Ni) before (x = 0) and after delithiation (x = 1), predicted by the calculations. The details of this modeling are shown in the Method section. There is a significant decrease in the average TM–O bond length after delithiation in all cases. For instance, the average Ni–O distance is calculated as 1.989 Å (standard deviation, STD: 0.118 Å) in layered LiNiO_2, and it decreases to 1.875 Å (STD: 0.001 Å) after Li-removal. This shortened bond length increases the covalency of the TM–O bond through the greater overlap between TM–d and O–2p orbitals in the layered structure, which in turn raises the energy level of the anti-bonding TM–d-states (e.g., Ni–e_g*), as demonstrated by Aydinol et al.[51,53] This “upshifted” TM-redox-band (i.e., nonrigid-band effect) facilitates further TM-oxidation upon charging, as it makes further electron-extraction from the band require less energy compared to a rigid band. Moreover, this nonrigid-band effect partially opposes the downshift of the Fermi level upon electron depletion, overall minimizing the variation of μ_{Li}^{+}\text{-cathode} and μ_{e}^{-}\text{-cathode} with state of charge in the DRX structure, which leads to a more sloped voltage profile as widely seen experimentally[13,16,21] and supported theoretically by Abdellahi et al.[54] A large voltage slope pushes the extraction of some electrons to an exceedingly high voltage and thus penalizes achieving high charging capacity.

Furthermore, our DFT calculations find a longer average TM–O bond length in DRX Li_{1−x}TM_{0.2}O_2 (TM = V, Mn, Fe, Co, Ni) than in layered Li_{1−x}TM_{0.2}O_2 before and after Li-removal, except for (lithiated, x = 0) LiMnO_2 (Figure 4b). This trend can be explained by the “pillar effect” of large-size Li^{+} ions (r = 0.76 Å) sharing the same cation-slab with smaller-size TM ions (e.g., Co^{3+}: r = 0.545 Å) in the DRX structure, resulting in distortion and expansion of the TM–O octahedron. For instance, the average Co–O bond length in DRX LiCoO_2 is calculated to be 2.001 Å (STD: 0.1 Å), which is longer than the value (1.933 Å, STD: 0 Å) in layered LiCoO_2. This bond elongation makes the bond more ionic, lowering the energy level of TM–d states with an anti-bonding characteristic (e.g., Ni–e_g*).[51] Also,
we find a smaller reduction in the TM–O bond length after Li-removal in the DRX structure, showing that the relaxation of the TM–O bond is more limited, rendering the TM-redox band more rigid in the DRX structure than in the layered structure. All these effects would widen the TM cationic-redox bandwidth and make deep TM-oxidation harder in the DRX structure. As a result, our calculations find increased average redox potential for DRX LiMnO2, LiFeO2, LiCoO2, and LiNiO2 than for their layered counterparts (Figure 4c). In particular, consistent with the prediction made by Abdellahi et al. as high as 4.4 V-average redox potential is predicted for DRX LiNiO2 (vs 3.9 V for layered LiNiO2), rendering a large portion of Li in the structure barely accessible with a practical upper cut-off voltage. Indeed, it was seen experimentally that the first-charge capacity of DRX-LiNiO2 is limited to \( \approx 80 \, \text{mAh g}^{-1} \) (4.3 V-charge), whereas the capacity can reach \( \approx 220 \, \text{mAh g}^{-1} \) for layered LiNiO2 (4.3 V-charge). Also, it is known that Ni is hard to oxidize past Ni\(^{3+}\) in the DRX structure. Along with slower Li diffusion in DRX structure imposing large overpotential, these added difficulties related to TM-oxidation explain why charging is harder in the DRX cathodes, especially when they are made with high-voltage TMs with deep d-electrons (e.g., Fe, Co, Ni) whose redox potential is high even in the layered structure.

2.6. Resolving the Redox-Potential Issue in the DRX Structure with Li Excess

We find that this redox-potential issue in high-voltage-TM-containing DRX cathodes can be resolved with Li-excess. Along with introducing 0-TM percolation, Li-excess increases the number of local environments for oxygen where some O-2p-orbitals are left unhybridized with TM-orbitals, the so-called Li–O–Li states. The lack of hybridization with TMs makes these O-2p states higher in energy than the bonding O-2p states so that oxygen can more easily participate in a redox process. However, it should be noted that according to the rigid band model of Li-TM oxides, O-oxidation (unaccompanied by structure relaxation) occurring after or mixed with problematic high-voltage TM-oxidation will have little impact on improving the DRX’s charging performance. This is because the electron level (negatively proportional to the cathode voltage) of the Li–O–Li states will be just as low as the problematically deep TM-d state, although the Li–O–Li states are higher in energy than the bonding O-2p states.

Nevertheless, as we will show below, what makes charging highly Li-excess materials different is the ability for oxidized oxygen in the lattice to form condensed oxygen species (e.g., \( \text{O}_2^– \)) by forming O-redox bonds, leading to the average overpotential of \( \approx 4.38 \, \text{V} \) (Figure 5c). For DRX Li\(_{1.22}\)Ni\(_{0.17}\)Ti\(_{0.61}\)O\(_2\) (Figure 5d), Li-extraction voltage can decrease from the average of \( \approx 4.50 \, \text{V} \) (Path 1, without O–O bonds) to \( \approx 4.28 \, \text{V} \) (Path 2, an arbitrary path with O–O bonds) and \( \approx 3.94 \, \text{V} \) (Path 3, the lowest voltage path with O–O bonds) by forming O–O bonds, revealing that high Li-excess triggering O-oxidation and O–O bond formation can substantially facilitate the charging of Ni-DRXs. This result, in turn, suggests that DRX materials with barely oxidizable TMs (e.g., Ni\(^{3+}\), Fe\(^{3+}\), Co\(^{3+}\)) can resolve their charging issue via Li-excess, resulting in high charging capacity and room for high discharge capacity (e.g., compounds 1–7 and 11–15 in Figure 3a).

Meanwhile, the charging voltage is predicted to be reasonable for both DRX LiMnO2 (\( \approx 3.71 \, \text{V} \) average, O–O bonds are not favored) and Li\(_{1.22}\)Mn\(_{0.5}\)Nb\(_{0.23}\)O\(_2\) (\( \approx 3.86 \, \text{V} \) average without O–O bond; \( \approx 3.65 \, \text{V} \) with O–O bond) (Figure 5e,f and Figure S13: Supporting Information), explaining how DRX-cathodes with low-voltage TMs (e.g., V, Mn, Nb) could achieve high charging (reversible) capacity regardless of Li-excess (Figure 3b).

In this case, the benefit of Li-excess would remain at the diffusivity-improvement-level (0-TM percolation), which becomes less important once the particle size is sufficiently reduced.
2.7. Dual Roles of Li-Excess in DRX Cathodes

To summarize, Li-excess (x > 0 in Li\(_{1+x}\)TM\(_{-x}\)O\(_2\)) plays at least two roles in DRX cathodes. Increasing x enhances Li bulk diffusion via 0-TM percolation,[10,11,23] but this should become less critical with reduced transport length in small particles. Our finding that Li\(_{1.05}\)Mn\(_{0.90}\)Nb\(_{0.05}\)O\(_2\) (M90) with sufficiently small particle size demonstrates high capacity comparable with a much higher Li-excess version (M60) serves as confirmation. The notion of Mn-based DRX materials being able to operate without a high degree of Li-excess is interesting because nearly all previous reports on Mn-DRXs describe synthesis with both high degrees of Li-excess (to ensure 0-TM percolation) and pulverization into small polycrystalline nanoparticles (d < 200 nm).[13,14,21,24,28] Moreover, mechanochemically synthesized Mn-based DRX cathodes (e.g., Li\(_2\)Mn\(_{2/3}\)Nb\(_{1/3}\)O\(_2\)F) typically have 10–20 nm nano-grains in each primary particle,[21,22] which should further render high Li-diffusivity non-critical given such a short diffusion length.

While apparently uncritical for certain chemistries, introducing significant Li-excess is necessary to enable high capacity in DRX cathodes comprised of high-voltage TMs (e.g., Fe\(^{3+}\), Co\(^{3+}\), Ni\(^{2+}\)). It is important to note that Ni\(^{2+}/Ni^{3+}/Ni^{4+}\) and Co\(^{3+}/Co^{4+}\) redox are accessible at a reasonable voltage in layered materials but not in the DRX materials. In this case, introducing Li-excess offsets TM-oxidation with O-oxidation accompanied by short O–O bond formation, which enables significant Li-extraction at a lower, more reasonable voltage (4.3–4.6 V), leaving room for discharge. On the other hand, low-voltage TMs (e.g., Mn\(^{3+}\), Mo\(^{3+}\), V\(^{3+}\)) are readily oxidizable in the DRX structure. Thus, the low-voltage TM-DRXs do not require a high degree of Li-excess to operate once their particle size is sufficiently reduced, as shown in Figure 3b. So while DRX cathodes with high-voltage TMs and low-voltage TMs are both capable of high capacity, the former must rely on O-redox with Li-excess, and the latter can utilize TM-redox without significant Li-excess. In other words, in order to achieve >200 mAh g\(^{-1}\), Ni/Co/Fe-DRX has to be more HACR, relying more heavily on Li-excess, whereas Mn/Mo/V-DRX can work well with more conventional TM-redox with light (or without) Li-excess as long as the particle size is nanoscale.

Ultimately, capacity from TM-redox can be regarded as a "safe asset" compared to O-redox (a "risky asset"), which triggers O-loss and permanent structural damage by promoting global oxygen mobility (GOM).[5] Fortunately, the Li-excess constraint is effectively removed in low-voltage-TM (V/Mn/Mo)-based DRXs to increase the TM-redox reservoir, minimizing the risk of detrimental O-redox-related side-reactions.[30,36,37,39] As a further downstream consequence, with more Mn or other TMs replacing Li, the electronic conductivity could reasonably increase, allowing for higher active material content and reduced
carbon content in the cathode film, leading to higher cell-level energy density. Overall, great attention must be devoted to identifying “Goldilocks” Li-excess levels, such that the improved beginning-of-life capacity via Li-excess does not rapidly fade upon extended cycling due to excessive GOM-side reactions.

It is worth noting that the near entirety of the DRX literature, including this work, has focused primarily on small particle sizes so that low intrinsic Li diffusivity can be acceptable. However, regardless of the particle size, high Li diffusivity is beneficial for both capacity and rate performance. Moreover, in practice, large particles are desirable for improved cathode packing density, reduced side reactions with the electrolyte, less TM-dissolution (e.g., Mn-dissolution from Mn-DRX), and surface treatments for enhanced cycling stability.[58,59] To cycle large particles, intrinsic Li-diffusivity must be sufficiently high to support long-range Li-diffusion at a reasonable rate. Therefore, we believe that 0-TM percolation enabled by Li-excess will continue to play an important role in the design of the DRX cathodes, and detailed studies on the SRO effect on the percolation or the role of the thermodynamic factor on the chemical Li diffusivity must be conducted to optimize the 0-TM percolation for the fastest Li-transport.[23,60,61]

Finally, most DRX researches, including this work, have used a large amount of conductive carbon (usually 20–30 wt%) in the electrode film to minimize the impact of DRX’s electronic conductivity on their performance.[10–30] However, a practical electrode should contain a minimum amount of carbon (<5 wt%) for high energy density,[58] for which the electronic conductivity of the DRX particles itself should be sufficiently high. In this context, we believe the systematic study of the electronic conductivity, likely influenced by both the Li-excess level and TM chemistry, must be followed in future DRX research.

3. Conclusion

In this work, based on the experimental results of high capacity (>250 mAh g⁻¹) in both Li₁₀.₅Mn₀.₉Nb₀.₅O₂ and Li₁₂₀Mn₀.₆₀Nb₂₀.₂₂O₂, exhaustive literature examination, and supporting DFT calculations, we demonstrated that “Li-excess” – widely considered essential to unlock the capacity of the DRX cathodes by enabling bulk Li diffusion – is non-critical for low-voltage TM-based DRXs at the nanoparticle scale. Meanwhile, regardless of the particle size, Li-excess is crucial for DRXs made with high-voltage TMs (e.g., Ni), as it lowers the charging voltage of those cathodes (through the formation of condensed oxygen species upon oxygen oxidation), which otherwise would face difficulties in charging due to their excessively high redox potential. This understanding, in turn, suggests that the Li-excess can be cut back to maximize the TM-redox capacity and reduce the O-redox activity for the low-voltage TM DRXs to improve their cycling stability, which has been a significant bottleneck for their practical use in Li-ion batteries.

4. Experimental Section

Material Synthesis: To synthesize Li₁₀.₅Mn₀.₉Nb₀.₅O₂ (M90) and Li₁₂₀Mn₀.₆₀Nb₂₀.₂₂O₂ (M60), Li₂CO₃ (Alfa Aesar, ACS, 99% min), MnO₂ (Alfa Aesar, 98%), and Nb₂O₅ (Alfa Aesar, 99.5%) were used as precursors. The stoichiometric amount of MnO₂ and Nb₂O₅ needed to form the compounds were mixed with a 10% excess amount of Li₂CO₃ precursors through the planetary ball-mill (PQ-N2, Across International) for 6 h at 400 rpm: the excess amount of Li₂CO₃ was to compensate for the possible loss of lithium during the calcination. Then, the precursor mixture was pelletized and calcined for 1 h in Argon at 1300 °C for M90 and 1100 °C for M60, followed by furnace cooling to room temperature: the ramping rate was 5 °C min⁻¹ (~4 h to reach 1300 or 1100 °C). After the calcination, the pellets were manually ground into fine powders. Then, the as-made M90 and M60 powders were planetary-ball-milled (MSK-PCV-300, MTI) into nanoparticles under the vacuum condition. The 3 g of powders were put in a 30 mL C2H2MnV steel container with 25 g of zirconia balls. Then, two-rounds of 1000 rpm (for 3 min)—600 rpm (for 3 min)—1000 rpm (for 3 min) ball mill was conducted, and there was a 20 min rest between the rounds to prevent overheating. After the ball mill, the pulverized powders were manually collected and stored in an Argon-filled glovebox.

Electrochemical Tests: To prepare a cathode film, first 350 mg of the pulverized M90/M60 and 100 mg of carbon black (TIMCAL, Super C65) was mixed by ball-milling (MSK-PCV-300, MTI) for 3 h at 600 rpm. Then, 180 mg of the mixture powder and 20 mg of polytetrafluoroethylene (PTFE, DuPont, Teflon 8 A) were manually mixed using a mortar and pestle and rolled into a thin film in an Ar-filled glovebox, such that the weight ratio between the active material, carbon black, and PTFE becomes 70:20:10 in the film. Coin cells (CR2032) were assembled with the cathode, the Li-counter electrode, a glass-fiber separator (Whatman), and a 1 M solution of LiPF₆ in a mixture of ethyl carbonate/dimethyl carbonate (EC/DMC, 1:1 v/v) in an Ar-filled glove box. The active material’s loading on the cathode film was ~4 mg cm⁻². The galvanostatic charge/discharge, intermittent titration tests, and rate-capability tests were performed using a potentiostat (LAND CT2001, China) at room temperature otherwise specified. The specific capacity was calculated based on the amount of the active material in the cathode film. The cyclic voltammetry test was conducted using the Gamry reference 3000. The scan-rate was sequentially increased from 0.1 to 0.2 mV s⁻¹, 0.5 mV s⁻¹, 0.7 to 1 mV s⁻¹, upon the anodic sweep to 4.8 V and cathodic sweep to 1.5 V.

Material Characterization: The X-ray diffraction (XRD) patterns were collected on a PANalytical multipurpose diffractometer (Cu source) in the 2θ range of 15°–85°. To perform XRD on the cyclized electrodes, coin cells were disassembled in an Ar-filled glovebox and washed with dimethyl carbonate (DMC). Then, the cathode film was sealed with Prolene thin-film (Cemplex Spectromembrane 3018) and vacuum grease and was placed on a zero-background silicon holder. The Rietveld refinement on the collected XRD patterns was completed using the PANalytical X’ pert HighScore Plus software. Scanning electron microscopy (SEM) and energy-dispersive-X-ray spectroscopy were performed with the Zeiss Merlin High-resolution SEM. Elemental analysis of the compounds was performed with ICP-OES, Agilent 725 ICP-OES) for lithium, manganese, and niobium. To measure the electrical conductivity, first the as-made M90 or M60 powder was pressed into a pellet under a pressure of 12 tons for 5 min. The pellet diameter was 11 mm. Both M90 and M60 pellets had a thickness of ~0.05 mm, measured by a Vernier caliper. The electrical conductivities of the samples were measured by a Four Point Probe Resistive machine (RST-9 from 4 Probes Tech).

DFT Calculations: All calculations were performed using density functional theory (DFT) as implemented in the Vienna ab initio simulation package.[82] The Perdew–Burke–Ernzerhof functional[35] was adopted for spin-polarized generalized gradient approximation (GGA) calculations. Hubbard U correction (GGA+U) was introduced for all TM atoms except Ti and Nb to compensate for the self-interaction error of GGA.[64] U values were 3.2, 3.9, 5.3, 3.3, and 6.2 eV for V, Mn, Fe, Co, and Ni, respectively.[49] Projector augmented wave potentials were employed with kinetic energy cut-off of 520 eV and k-point meshes with their densities of at least 1000 per number of atoms in the supercell. All structures were fully relaxed until the forces on atom converged within 0.05 eV. The method to prepare the structures by AIMD is provided in the Supporting Information.
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

Keywords

disordered-rocksalt cathodes, Li-excess, Li-ion batteries, Mn-rich cathodes, oxygen redox, percolation

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