Supporting Information for

Reentrant Lithium Local Environments and Defect Driven Electrochemistry of Li- and Mn-rich Li-ion Battery Cathodes

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I. Electrochemistry

A. Methodology

All samples were subjected to a first cycle activation by charging to 4.7 V and discharging to 2.0 V at 5 mA/g. First-cycle charge capacities showed minor deviations (± 15 mAh/g) attributable to side reactions and passivation of the freshly cut ^6Li metal anode. The subsequent discharge capacities were highly reproducible averaging 273 ± 4 mAh/g. Table S1 lists sample numbers, voltages to which each cell was charged/discharged (and subsequently disassembled), the charge capacity of each cell, and the resultant SOC (state of charge). The voltage profile in Fig.S1 (and dQ/dV , Fig. S3) shows that the ^6Li -enriched system behaves identically to its non-enriched counterpart and reveals three main electrochemical processes; standard intercalation, hysteresis, and voltage fade as described in refs¹⁻³.

Table S1 Sample descriptions with corresponding SOC, capacity and charge, discharge voltages. *273 mAh/g = 100%

Sample #	Charge (V)	Discharge (V)	Capacity	SOC*
1	---	2.0	0	0
2	3.6	---	55	20
3	4.38	---	213	78
4	4.7	---	269	98
5	4.7	3.986	215	79
6	4.7	3.6	148	54
7	4.7	3.22	59	22
8	4.7	2.0	6	0
9	3.7	3.6	60	22
10	4.1	3.986	147	54
11	4.1	3.6	84	31
12	4.1	2.0	2	0

Figure S1 (left) Second cycle voltage profile with sample numbers at which NMR spectra were acquired and (right) dQ/dV plot of cycle 2 and 11.

II. NMR Characterization

A. Methodology

High resolution ^6Li MAS-NMR experiments were used to study the changes in Li local structure and correlate these changes to the electrochemical hysteresis. In order to quantify and compare the Li environments that exist within the electrode at various SOC's, all experiments were performed with fully ^6Li -enriched systems as described in the experimental section. The results presented are all mass normalized for comparison unless otherwise stated. The deconvolutions of the ^6Li NMR data presented in Fig.4, Fig. S2.a (top), and Fig. S4 have been performed based on a simple strategy; using a single Lorentzian peak for each distinct local order for pristine and cycled samples to correlate directly with well-established assignments summarized in Table S2 and 3. Cycled samples required a very broad Gaussian peak (FWHM $\sim 800\text{ppm}$), indicating multiple Li local ordering and/or distorted Li sites, in addition to the Lorentzian peaks which are already assigned to distinct Li-TM coordinations. Evolution of Lorentzian peaks with cycle number is constrained within shift ranges given in Table S2 and 3 to eliminate unrealistic Li sites that cannot be assigned using literature values. +99% is obtained for each deconvolution. Lorentzian peak widths were also kept consistent between pristine and cycled materials. One key parameter determining resonance shifts is the effect of temperature in which MAS data is acquired⁴ and can lead to inconsistencies in case of lack of precise control over spinning speeds and temperature^{5,6}. This careful control over measurement conditions has been consistently utilized here and in studies by Grey et al.^{4,7-14}

B. Supporting Discussions

Pristine and cycled material ^6Li NMR discussions

Figure S2. Deconvoluted ^6Li MAS-NMR of; pristine $0.5^6\text{Li}_2\text{MnO}_3 \cdot 0.5^6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ (top) and pristine, after the first-cycle (2.0 V), and charged to 4.7V on the second cycle (bottom).

^6Li MAS-NMR of the pristine sample in Fig. S2 (top) shows two groups of resonances for the lithium species present in the lattice. The resonances at 724/765 (1:2

ratio observed identical to reference ¹⁵) and 1470/1500 ppm are similar to those seen for the Li_{Li} and Li_{TM}, respectively, of Li₂MnO₃ while the resonance at 1309 ppm is assigned to Li-ions surrounded by 5 Mn⁺⁴ and 1 Ni⁺² (see Table S2). The peaks around 542 and 895 ppm are assigned to octahedral Li (Li_{Oct}) of the Li layers, Li_{Li}, and result from a variety of first- and second-shell correlations involving Ni⁺², Mn⁺⁴, and Li⁺ (895ppm resonance involving at least one Li-O-Ni⁺² via 180°). Fig.S2 shows ⁶Li MAS-NMR of 0.5⁶Li₂MnO₃•0.5⁶LiMn_{0.5}Ni_{0.5}O₂ electrodes as-prepared (black), after the first-cycle (2.0 V, red) and charged to 4.7 V on the second cycle (blue). Although the two sets of resonances assigned to Li_{Li} and Li_{TM} in the pristine materials are still present at the end of 1st cycle, a profound loss of order and/or reordering in the material is observed as indicated by severe broadening and damping of the overall spectrum. Significant decreases of the spinning sideband intensities for the cycled material (not shown) also suggests loss of order as well as the possible formation of Li_{tet} environments. This is mainly due to a more symmetric arrangement of ions around tetrahedral sites, reducing dipolar coupling and hence the spinning sideband intensities. The sharp peaks at 0 ppm observed for the cycled materials are due to the presence of diamagnetic electrolyte and SEI environments whereas the minor 0 ppm peak observed for the pristine sample is due to the presence of unreacted precursors or impurities from the synthesis. The loss of intensity for the ⁶Li peaks in the TM layers indicates that a limited number of Li-ions, with respect to those initially present, were reintercalated into the formal octahedral sites of the TM layers after the first cycle. When the material is subsequently charged to 4.7 V on the next cycle, all Li-ions in the Li₂MnO₃-like environments (1309-1500 ppm) are removed and a single, symmetric ⁶Li peak, with a center of mass around 575 ppm with no spinning sidebands. This peak has been assigned to a mixture of Li_{Oct} and Li_{tet}, dumbbell-type Li_{Li} atoms adjacent to Li vacancies in the TM layers (See Li dumbbell in Table S2). Alternatively, Ni⁺⁴-rich Li sites that are diamagnetic could also contribute to intensities in this region (See Table S2). In agreement with the electrochemistry, the intensity of the ~575 ppm resonance reveals that not all the Li was removed from the Li layers at the end of charge and ~25% of the total, initial Li remained in the structure.

LiMn₆-Mn_{tet} and LiMn₆-Ni_{Oct} Assignment Discussions

As briefly discussed in the main text, the 1600 ppm region involves two distinct, small peaks at ~ 1550 and 1688 ppm. The former (1550 ppm) likely indicates the presence of tetrahedral Mn (Mn_{tet} added shift of +80 ppm), but could also been attributed to the presence of octahedral Ni⁺³ in the lithium layers (added shift of +110 ppm). Li-Ni exchange and Ni occupancy in lithium layers have been shown, in pristine materials, in earlier studies. However, lithium-ions are assumed to be removed from the vicinity (1st and 2nd coordination shell) of oxidized Ni (+3 and +4), corresponding to electrochemical activity. Furthermore, the distinct loss of ordering observed for the Li₂MnO₃-like coordinations (724 and 765 ppm) post activation indicate Mn activity/migration. In addition to this, spectra collected along the 1st cycle at similar data points presented herein, for a system where nickel is substituted with cobalt (Fig.S4), have produced very similar shifts suggesting that the TM activity observed arises predominantly from Mn_{tet}. Therefore, 1550 ppm resonance has been assigned to LiMn₆-Mn_{tet}. Two possible assignment for 1688 ppm resonance can be, presence of a Mn_{Oct} in the layer above or

below the TM layer [added shift of +250ppm ($=2 \times 125$) via two 90° Li-O-Mn_{oct} interactions^{9,16}], or an unreacted Ni⁺² in an octahedral site in the lithium layers (added shift of +140 to +170ppm¹⁷). The latter is chosen as the primary assignment for 1688 ppm resonance since the absence of this component in Li₂MnO₃:LiCoO₂ sample (Fig.S4 inset) confirms the presence of LiMn₆-Ni_{oct}. Lastly, presence of a Mn_{oct} in the layer above or below of a LiMn₅Ni unit could also be a minor contributor to the intensity of the 1550 ppm resonance due to the minor spectral contribution remaining for LiMn₅Ni units post activation.

Table S2. Summary of experimental ⁶Li NMR shifts observed for different lithium local environments for layered LiTMO₂

Configuration	Observed NMR shift (ppm)	Reference
Li _{Li} in Li ₂ MnO ₃	700-780	7,9,10,14,15
Li _{Li} in Li ₂ MnO ₃ -like-Ni1 st	590,587, 567	7,9,10,12,14
Li(OMn)6-TM layers	1560-1498-1511	7,9-11,13-15
Li(OMn)5(ONi)1-TM layers	1365-1324-1341	7,9-11,13,14
Li(OMn)4(ONi)2-TM layers	1150	11,13
Li _{tet} dumbbell	570	12
Li _{tet} in Li _{Li}	690-710	11
Li _{tet} in Li _{Li} in vicinity of Ni ⁴⁺	<690	11

Table S3. Sign and magnitude of ${}^6\text{Li}$ NMR Hyperfine shifts (in ppm) observed for a single Li-O-TM contribution^{4,9,10,17}. * estimated by linear interpolation

Li-O-TM bond angle	Mn ⁴⁺	Ni ²⁺	Ni ³⁺
90°	+122 to +125	-15	-7.5
122°	+76 to +80	+45*	+34*
180°	-60	+140 to +170	+110

Figure S3. Deconvolution of the NMR spectra for samples charged to 3.6V at cycles (a) 2, (b) 11 and (c) 20.

Figure S3 shows the deconvoluted Lithium-6 NMR data for samples charged to 3.6V at varying cycle numbers. As discussed in the main text, the center of mass of the Gaussian component shifts to lower frequencies by 112 ppm within 20 cycles. Comparison of these deconvolutions with the deconvolution of pristine material suggests that there is a significant contribution of lithiums from the former Li_2MnO_3 -like component within the Gaussian resonance. This is captured clearly in the loss of Li_2MnO_3 -like resonances in the pristine sample (Fig. S2, 724-765 and 1470-1500 ppm) after the first cycle. 1550ppm resonance due to $\text{LiMn}_6\text{-Mn}_{\text{tet}}$ is clearly captured for charged $0.5^6\text{Li}_2\text{MnO}_3 \cdot 0.5^6\text{LiMn}_{0.5}\text{Co}_{0.5}\text{O}_2$ electrodes in Fig. S4 where Co (unlike Ni) does not significantly contribute to the Li NMR shifts¹⁶⁻¹⁸.

Figure S4. ^6Li MAS-NMR of $0.5 \text{Li}_2\text{MnO}_3 \cdot 0.5 \text{LiCoO}_2$, pristine (black) spinning at 67kHz, charged to 4.3V, 1st cycle spinning at 67kHz (red), and charged to 4.35V, 1st cycle spinning at 64kHz (blue). Red arrow highlights ~1550ppm resonance due to $\text{LiMn}_6\text{-Mn}_{\text{tet}}$. The inset shows the deconvolution of 4.35V sample (blue) showing TM lithiums only.

T_2 (spin-spin) relaxation effect on relative site intensities

Figure S5. The signal intensity change on ^6Li rotor synchronized spin echo experiments for sample #2 (3.6V, second charge). Numbers indicate rotor period times, corresponding to the echo delay durations of 12.68, 57.45, 117.15, 355.96 μs and 1.43 ms, respectively. The inset shows the comparison of 1, 4 and 8 rotor period experiments normalized to highest intensity peak.

As the comparison in Figure S5 shows, the relative intensities for different lithium peaks within TM and Li layer do not change up to 8 rotor periods. The effect of T_2 relaxation variations for different lithium environments are more pronounced after $\sim 118 \mu\text{s}$ echo delays. Relaxation measurements have shown that the paramagnetic lithium environment T_2 (spin-spin) times are in the order of 2ms whereas the T_1 (spin-lattice) relaxation times are in the order of 20ms.

Theoretical Calculations

A. Methodology

The first principles spin-polarized calculations performed in this work were based on density functional theory, with orbitals expressed in the PAW representation, as implemented in the VASP code^{19,20} at the GGA+U level of approximation²¹, with an effective Coulomb parameter $U_{\text{eff}}(\text{Mn}) = 4.0 \text{ eV}$ ²². The PAW potentials used in this work include three, thirteen, and six valence electrons for Li (1s2s2p), Mn (3p4s3d), and O (2s2p), respectively. The PBE exchange correlation functional²³ was used. Supercells with composition Li_2MnO_3 based on the R-3m space group are used. We use supercells (6x8x8) with $n_z=8$ sublayers (4O, 2LiMn2, and 2Li layers). In-layer dimensions of (6x8), which correspond to 96 atom (16 formula unit) and a total of 384 atoms in the cell. The supercell vectors $[A1 = (6a, 0, 0), A2 = (0, 4\sqrt{3}a, 0), A3 = (a, \sqrt{3}a/3, 2c/3)]$, where a and c are the lattice parameters of the standard hexagonal cell ($a = 2.9 \text{ \AA}$, $c = 14.25 \text{ \AA}$). The presented results correspond to Γ point sampling owing to the large supercell used here.

B. Supporting Discussions

Figure 3 in the main text shows a partially delithiated lattice post DFT relaxation for an Li_2MnO_3 type supercell described above. Three Li ions were removed from the lithium layer, as well as an oxygen ion coordinated to the migrating Mn, but away from the tetrahedral site to maintain the full four-fold coordination of the resultant tetrahedral site intact. This configuration highlights the tetrahedral Mn in the 2nd coordination shell of a Li_{TM} that will have a predicted NMR shift of 1550 ppm according to Table S3. Note that 0.7 eV energy barrier was found for Mn migration to the tetrahedral site in this case (3 Li, 1 O) vacancies [The details will be published elsewhere – manuscript in preparation].

The total frequency shift at each Li site in a composite system $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$, with ($M = \text{Mn, Ni}$) configurations (R-3m) can be estimated by the sum of all Li-O-M individual contributions using heuristic rules developed by Grey et al.⁹. Each unique Li-O-M bond pathway can be mapped onto an angle (here either 90° or 180°), where bond lengths Li-O and O-M are less than $2.5 \text{ \AA}$. The total shift for each Li cite i , can then be written as:

$$\omega_i = N_1 g_1 + N_2 g_2. \quad (1)$$

N_1 , N_2 , are the total number of Li-O-M ($M=\text{Mn, Ni}$) paths at 90° , and 180° , respectively. Where g_1 and g_2 are the corresponding assigned shifts, respectively. The following contributing assignments are used: Li-O-Mn (+122 ppm for 90° and -60 ppm for 180°), Li-O-Ni (-15 ppm for 90° and +170 ppm for 180°). For example, these assignments will give 736 ppm and 1464 ppm for Li in the Li layer, and Li in the transition metal Layer of bulk Li_2MnO_3 , respectively.

We performed an exhaustive combinatorial analysis to predict all possible shifts using a simplified site model (first and second shell neighbors). The site model for a Li center in the transition metal layer is shown in Figure SI 6. In this model, we identify five unique second nearest neighbor sites which form Li-O-M bond pathways, which we identify as 180° top, 90° top, 180° bottom, 90° bottom, and ring sites. The top and bottom sites are symmetric with respect to the transition metal layer. There are three 180° positions generating three Li-O-M pathways, and there are three 90° positions, generating six Li-O-M bond pathways. Likewise, the ring site is located in the transition metal layer with six degenerate positions which generate 12 Li-O-M bond pathways at 90°. We can fill each position with an element (Li, Mn, or Ni), and cycle through every possible combination of elements and predict a total shift per lithium.

Constraints used to narrow down combinations for assignment of new Li resonances

There are 30,000 possible combinations, if M = Mn, Ni or Li, but many of these systems are not realistic. By using chemically intuitive constraints, we can narrow our predictions down to the most likely systems and more plausible local compositions. We applied the constraint that a total of two metal (Mn or Ni) substitutions may occur in either lithium layer. In addition, the ring sites may have a Ni substitution in the transition metal layer. A subset of our results is shown in Table SI 4, where we focus on high shifts above 1500 ppm. The shifts at 1634 and 1708 ppm correspond to the most likely substitutions with one transition metal (Mn or Ni) in the lithium layer corresponding to the $\text{LiMn}_6\text{-Ni}_{\text{oct}}^{+2}/\text{LiMn}_6\text{-Mn}_{\text{oct}}$ assignment at 1688ppm. No plausible combination was found corresponding to the 1550 ppm resonance other than $\text{LiMn}_6\text{-Mn}_{\text{tet}}$ described in the main text. The other high shift combinations require double substitution, which is statistically less likely to occur, consistent with the suggested configurations in the text.

Table S4. Results of combinatorial analysis predicting NMR shifts for single and double metal substitutions in the lithium layer. Shifts are predicted based on the following rules: Li-O-Mn (+122ppm for 90° and -60ppm for 180°), Li-O-Ni (-15ppm for 90° and +140ppm for 180°)

Shift	at 180°	at 90°	TM (ring)
1460	6Li	-	6Mn
1470	4Li+2Ni	6Li	5Mn+1Ni
1544	4Li+1Mn+1Ni	6Li	6Mn
1574	5Li+1Ni	5Li+1Mn	5Mn+1Ni
1574	5Li+1Ni	5Li+1Ni	6Mn
1604	5Li+1Ni	6Li	6Mn
1648	5Li+1Mn	5Li+1Mn	6Mn
1678	6Li	4Li+1Mn+1Ni	6Mn
1678	6Li	4Li+2Mn	5Mn+1Ni
1708	6Li	5Li+1Mn	6Mn
1744	4Li+2Ni	6Li	6Mn

Table S5. Results of combinatorial analysis predicting NMR shifts for single and double metal substitutions in the lithium layer. Shifts are predicted based on the following rules: Li-O-Mn (+122ppm for 90° and -60ppm for 180°), Li-O-Ni (-15ppm for 90° and +170ppm for 180°)

Shift	at 180°	at 90°	TM (ring)
1460	6Li	-	
1530	4Li+2Ni	6Li	5Mn+1Ni
1574	4Li+1Mn+1Ni	6Li	6Mn
1604	5Li+1Ni	5Li+1Mn	5Mn+1Ni
1604	5Li+1Ni	5Li+1Ni	6Mn
1634	5Li+1Ni	6Li	6Mn
1648	5Li+1Mn	5Li+1Mn	6Mn
1678	6Li	4Li+1Mn+1Ni	6Mn
1678	6Li	4Li+2Mn	5Mn+1Ni
1708	6Li	5Li+1Mn	6Mn
1804	4Li+2Ni	6Li	6Mn

Table S6. Results of combinatorial analysis predicting NMR shifts for single and double metal substitutions (for Ni⁺³) in the lithium layer. Shifts are predicted based on the following rules: Li-O-Mn (+122ppm for 90° and -60ppm for 180°), Li-O-Ni (-15ppm for 90° and +170ppm for 180°)

Shift	at 180°	at 90°	TM (ring)
1460	6Li	-	
1410	4Li+2Ni	6Li	5Mn+1Ni
1514	4Li+1Mn+1Ni	6Li	6Mn
1544	5Li+1Ni	5Li+1Mn	5Mn+1Ni
1536.5	5Li+1Ni	5Li+1Ni	6Mn
1574	5Li+1Ni	6Li	6Mn
1648	5Li+1Mn	5Li+1Mn	6Mn
1670.5	6Li	4Li+1Mn+1Ni	6Mn
1678	6Li	4Li+2Mn	5Mn+1Ni
1708	6Li	5Li+1Mn	6Mn
1684	4Li+2Ni	6Li	6Mn

Figure S6 (a) Site model for a Li center in the transition metal layer, highlighted at center. Mn is shown with large spheres (green), O is shown with medium spheres (red), and Li is shown with small spheres (pink). (b) The top view showing the ring site in the transition metal layer.

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