Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary Information for Effect of composition on the structure of lithium- and manganese-rich transition metal oxides.

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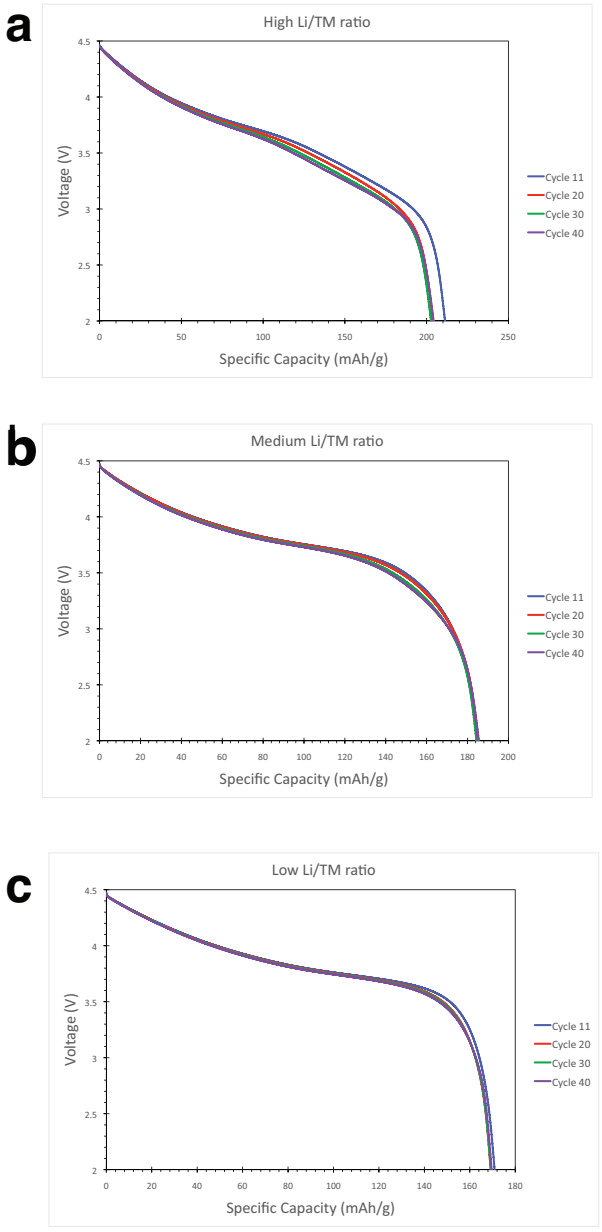
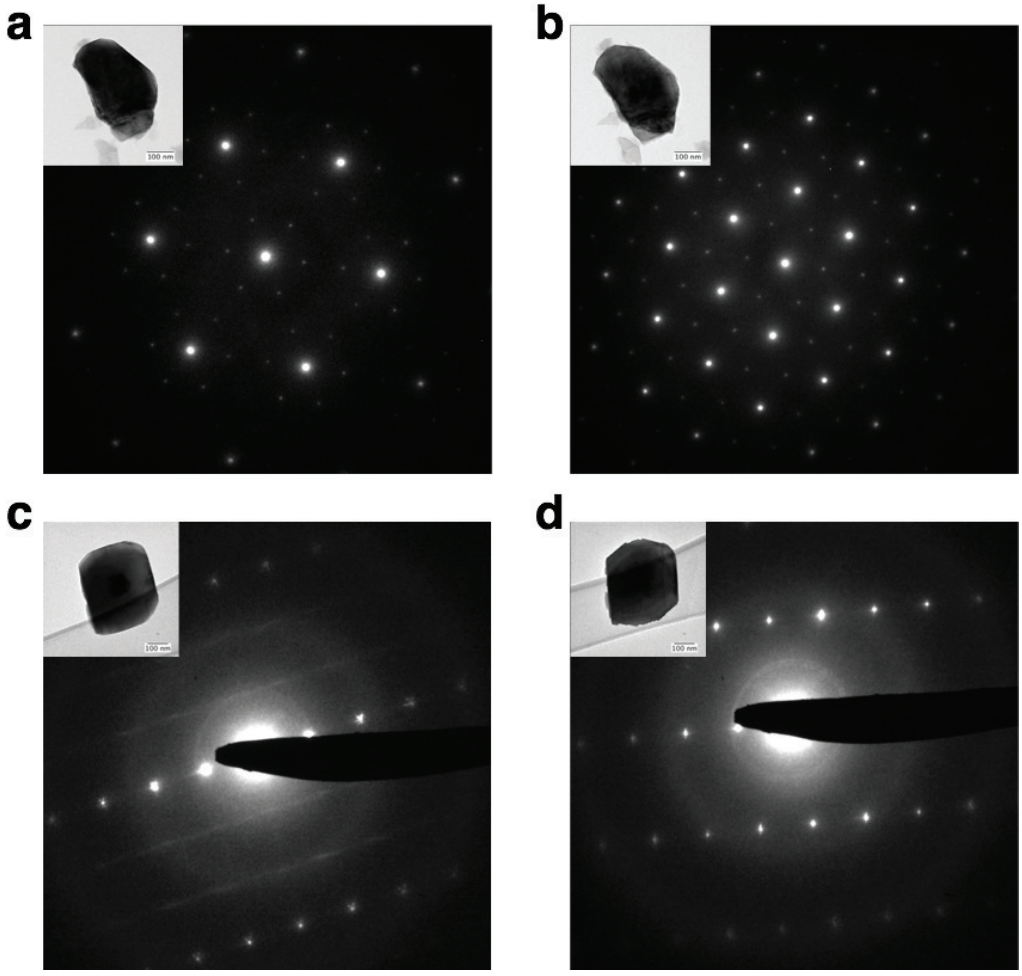
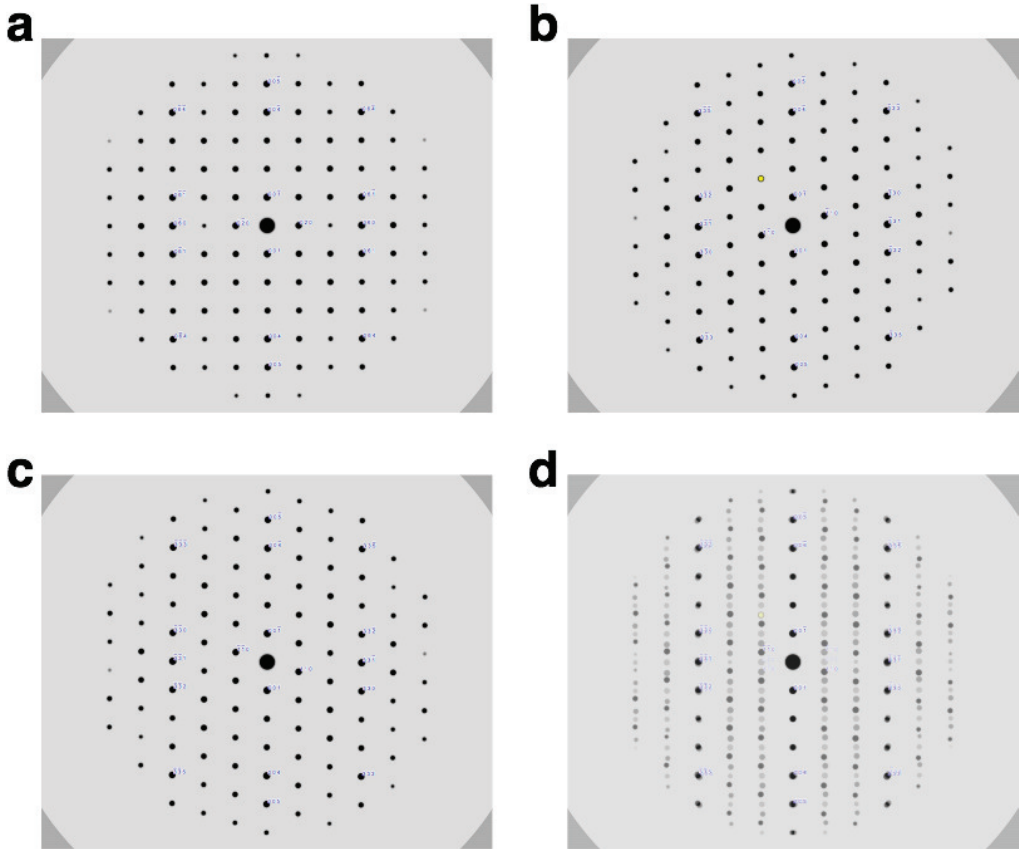


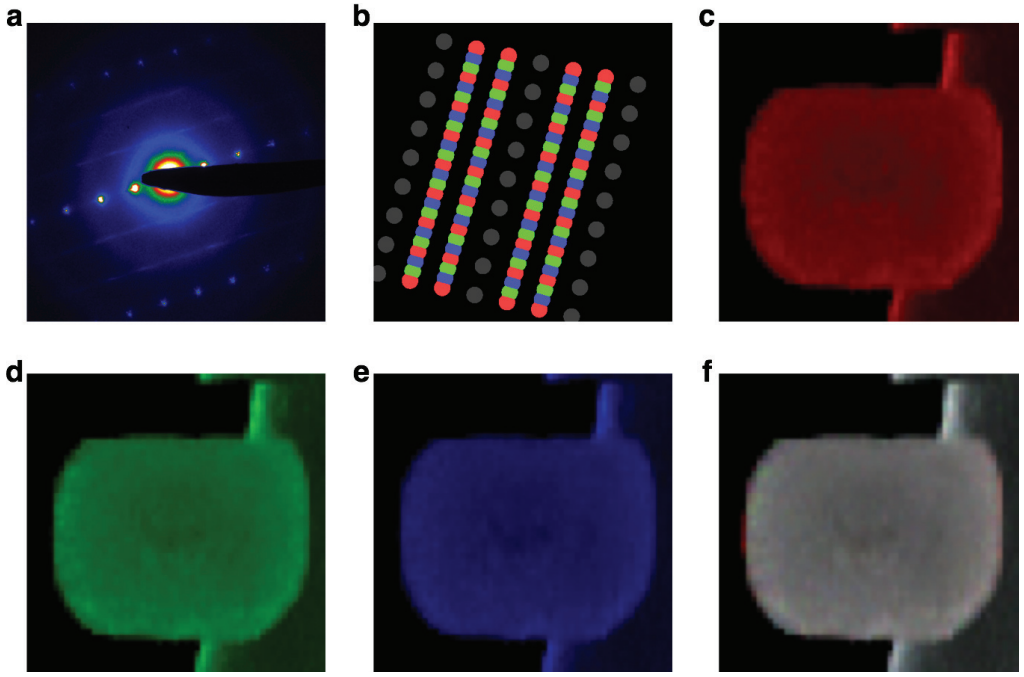
Supplementary Figure 1: Voltage profiles for LMRTMO with a) high Li/TM ratio, b) medium Li/TM ratio and c) low Li/TM ratio



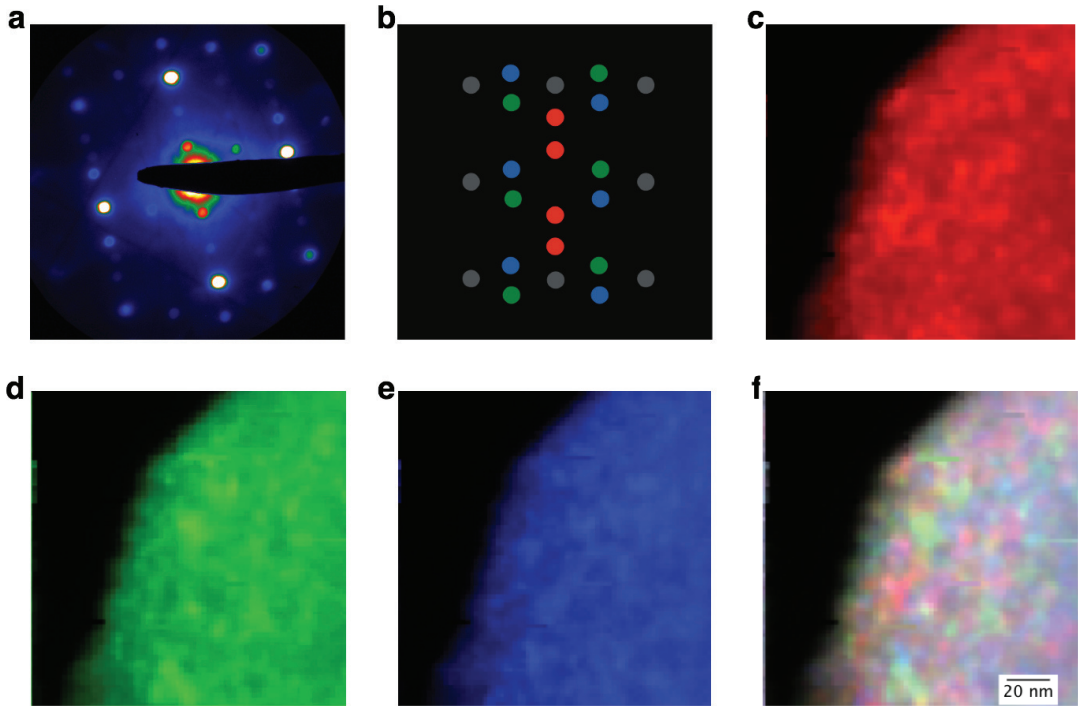
Supplementary Figure 2: Selected area electron diffraction patterns taken on LMR NMC with lowest Li/TM ratio using a) $[1\,0\,3]_{\text{monoclinic}}$, b) $[0\,0\,1]_{\text{monoclinic}}$, $[1\,0\,0]/[1\,1\,0]/[1\,\bar{1}\,0]_{\text{monoclinic}}$ and d) $[\bar{3}\,1\,0]_{\text{monoclinic}}$ zone axes. Note that $[\bar{3}\,1\,0]_{\text{monoclinic}}$ is equivalent to direction $[0\,1\,0]_{\text{monoclinic}}$. The faint reflections in a) and b) and streaks in c) arise due to the presence of three variants of monoclinic phase.



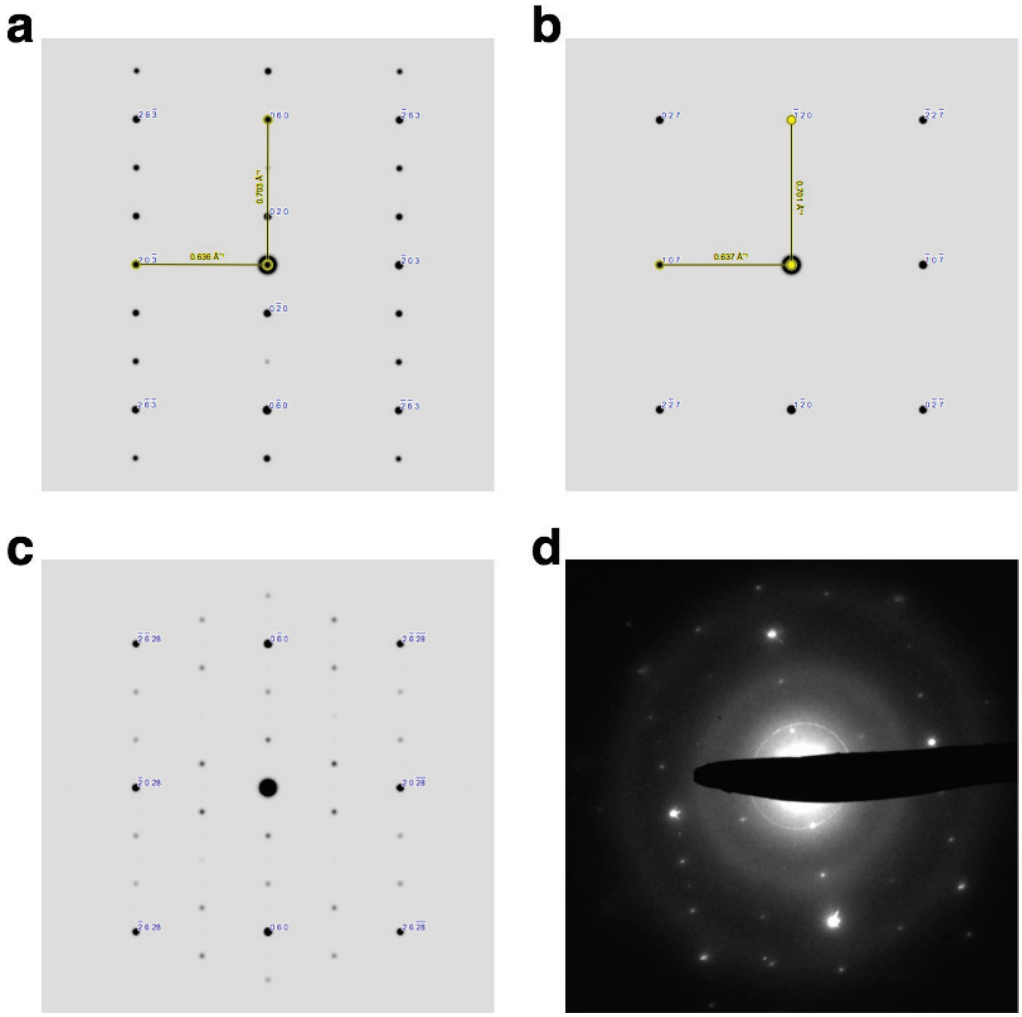
Supplementary Figure 3: Formation of streaks in a $[1\,0\,0]_{\text{supercell}}$ electron diffraction pattern: a) $[1\,0\,0]_{\text{monoclinic}}$, b) $[1\,1\,0]_{\text{monoclinic}}$, c) $[1\,\bar{1}\,0]_{\text{monoclinic}}$ and d) $[1\,0\,0]_{\text{supercell}}$ obtained by overlapping electron diffraction patterns from a, b and c.



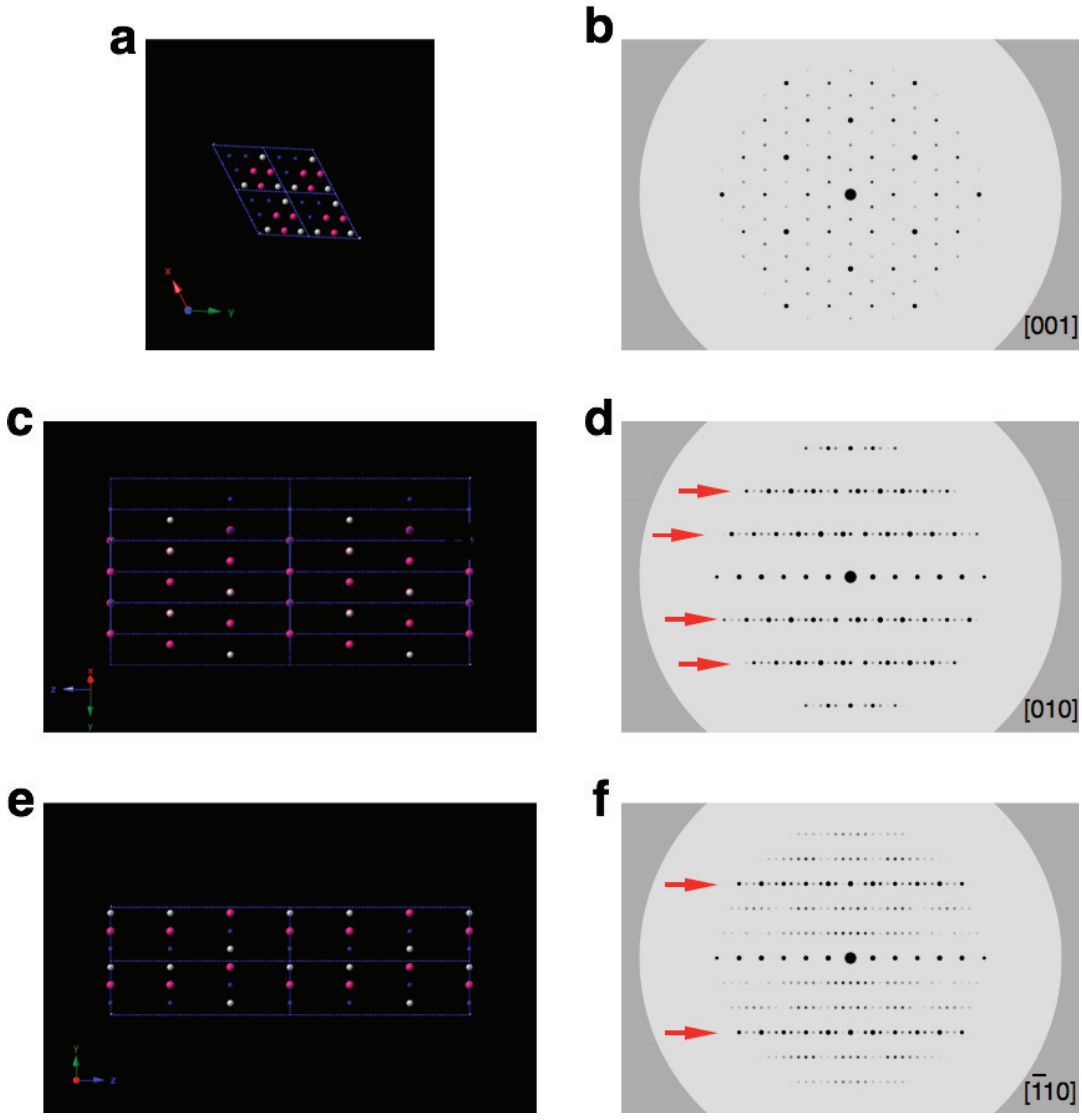
Supplementary Figure 4: 4D STEM diffraction map taken on LMR NMC with the lowest Li/TM ratio using $[100]_{\text{supercell}}$ zone axis. A probe size of approximately 2 nm and step size of 5 nm was used to obtain the data.



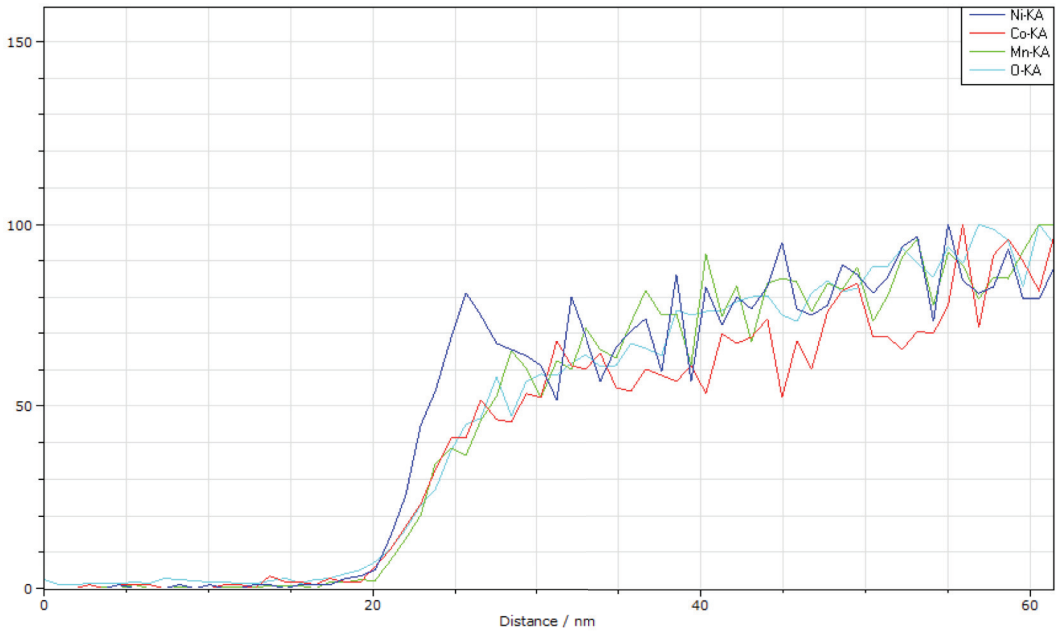
Supplementary Figure 5: 4D STEM diffraction map taken on LMR NMC with the lowest Li/TM ratio using $[3\,0\,2]_{\text{monoclinic}}$ zone axis. A probe size of approximately 2 nm and step size of 2 nm was used to obtain the data.



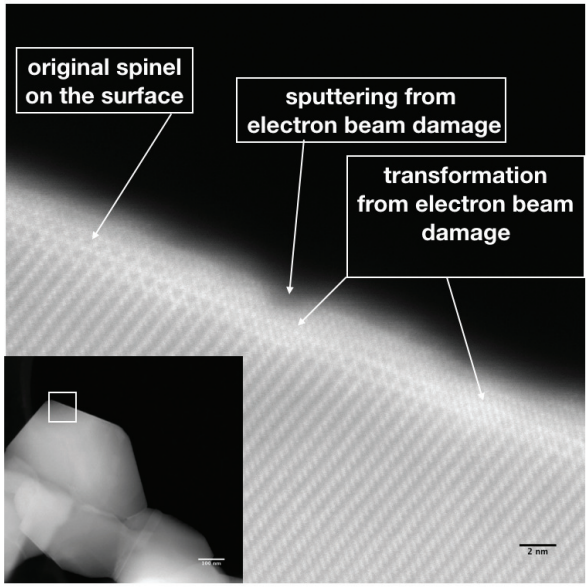
Supplementary Figure 6: a) Simulated electron diffraction pattern for $[3\,0\,2]_{\text{monoclinic}}$ zone axis, b) Simulated electron diffraction for the equivalent zone axis $[7\,\overline{7}\,2]$ for trigonal unit cell, c) Simulated electron diffraction for the equivalent zone axis for a supercell made by stacking variants of monoclinic phase and d) Experimental selected area diffraction pattern taken over an entire particle.



Supplementary Figure 7: Crystal structure (showing transition metals only for clarity) and simulated electron diffraction patterns for a $LiNiMnCoO_2$ unit cell with transition metal ordering made using Reference 10 . Note that the zone axes labeled in the image are those of conventional trigonal unit cell and are different from those used in Reference 10.



Supplementary Figure 8: XEDS line scan taken across the spinel surface layer in the high Li/TM ratio sample shown in Figure 4.



Supplementary Figure 9: HAADF STEM image showing electron beam damage on the spinel surface in LM-RTMO.