Supporting information for

Structural and Chemical Evolution of Li- and Mn-rich Layered Cathode Material

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Supporting Figures

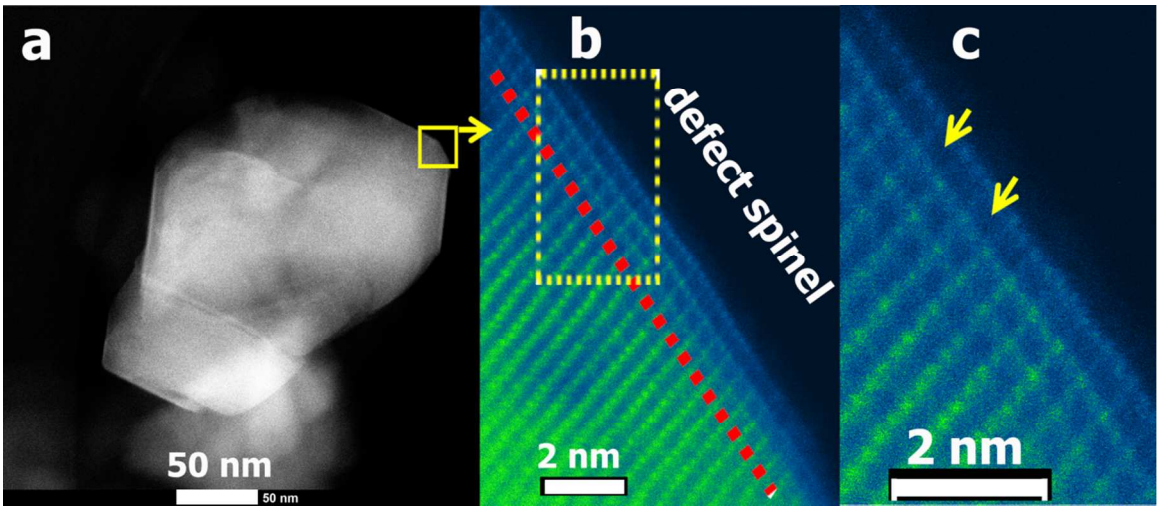

Figure S1. (a) Overview Z-contrast image of LMR cathode particles after 1 cycle. (b) Z-contrast image viewed from the [100] zone axis of R-3m structure (magnified from the region labelled with yellow square in (a)) showing the LT-$LiCoO_2$ type defect spinel formation at the outmost particle surface. (c) Z-contrast image enlarged from the yellow dashed square in (b) showing that the 16c octahedral sites of evolved LT-$LiCoO_2$ type defect spinel are not occupied.

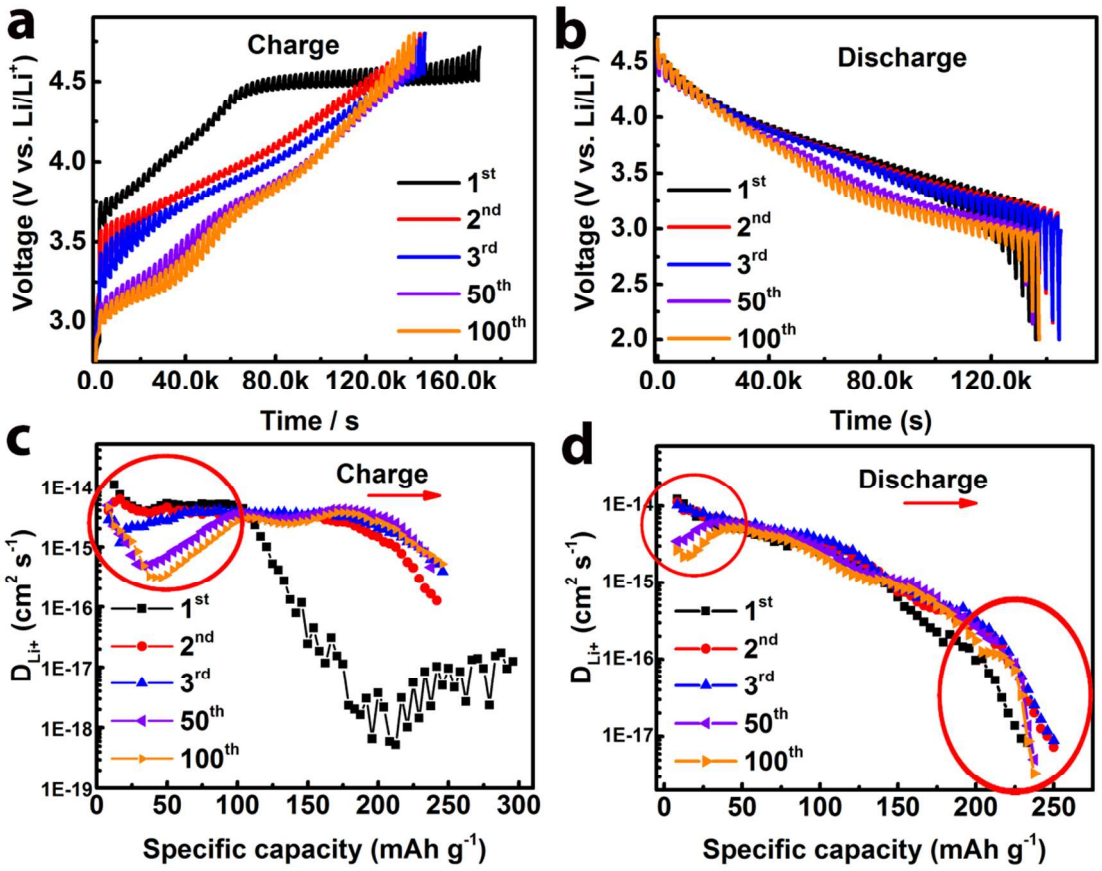

Figure S2. Electrochemical kinetics of LMR cathode $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ during cycling at C/10 rate. Galvanostatic intermittent titration technique (GITT) measurement curves during (a) charge and (b) discharge processes in the initial three cycles and at 50^{th} and 100^{th} cycles. Lithium ion diffusion coefficients as a function of specific capacity during (c) charge and (d) discharge processes. GITT was carried out on the Solartron 1287 electrochemical interface coupled with 1255B Frequency Response Analyser. The cell was charged or discharged for 10 min at 25 mA g^{-1} followed by a relaxation time interval of 30 min. This procedure was repeated in the voltage window of 2.0 - 4.8 V with varying state of charge (SOC) and for the desired number of charge-discharge cycles.[1]

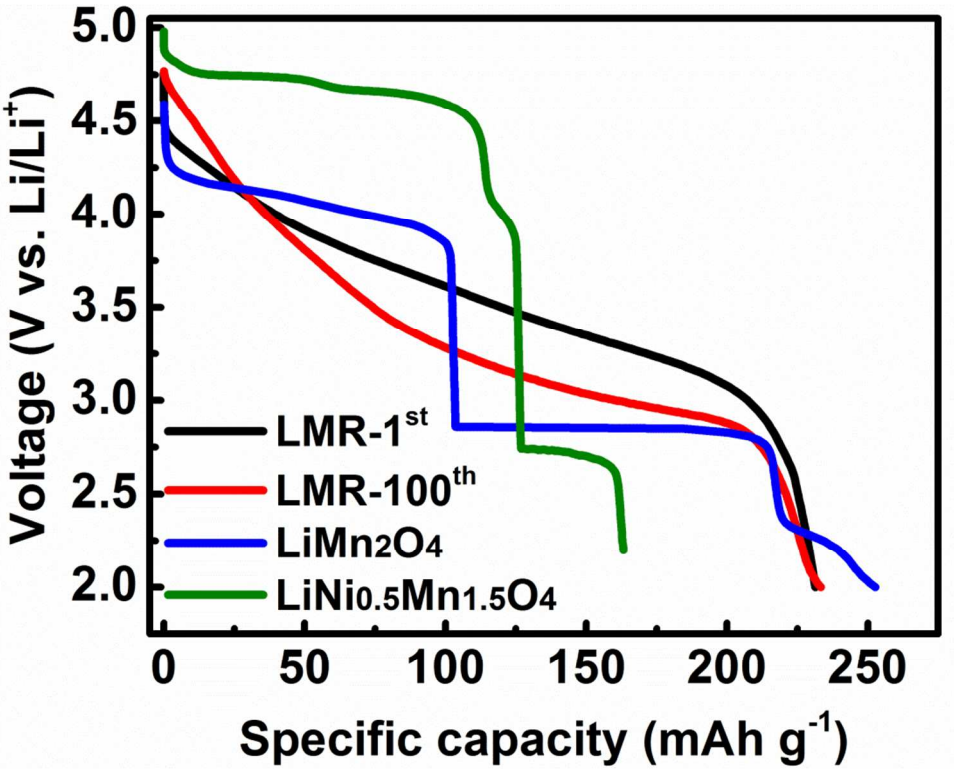

Figure S3. Comparison on the discharge profiles of LMR cathode $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ and spinel cathodes ($LiMn_2O_4$ and $LiNi_{0.5}Mn_{1.5}O_4$) at C/10 rate. The discharge profiles of LMR cathode $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ exhibit a solid solution reaction pathway even after 100 cycles, which is very different from the two-phase reaction pathway for spinel cathodes.

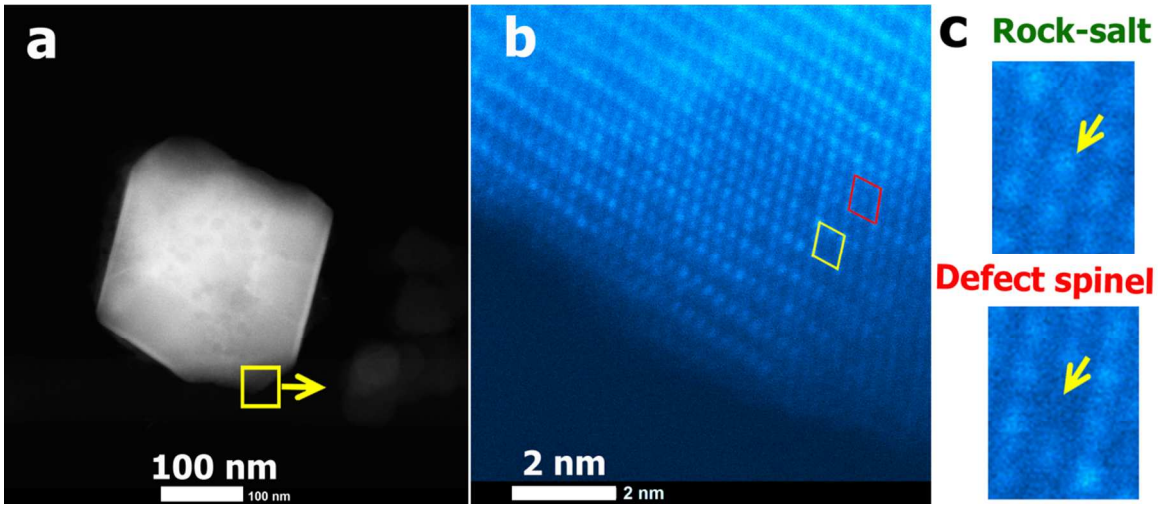

Figure S4. (a) Overview Z-contrast image of LMR cathode particles after 10 cycles. (b) Z-contrast image (magnified from the region labelled with yellow square in (a)) showing formation of the LT-$LiCoO_2$ type defect spinel and disordered rock-salt structure at the particle surface. (c) Z-contrast image enlarged from the red and yellow rhombuses in (b) showing that the difference of cation arrangements in rock-salt structure and defect spinel structure.

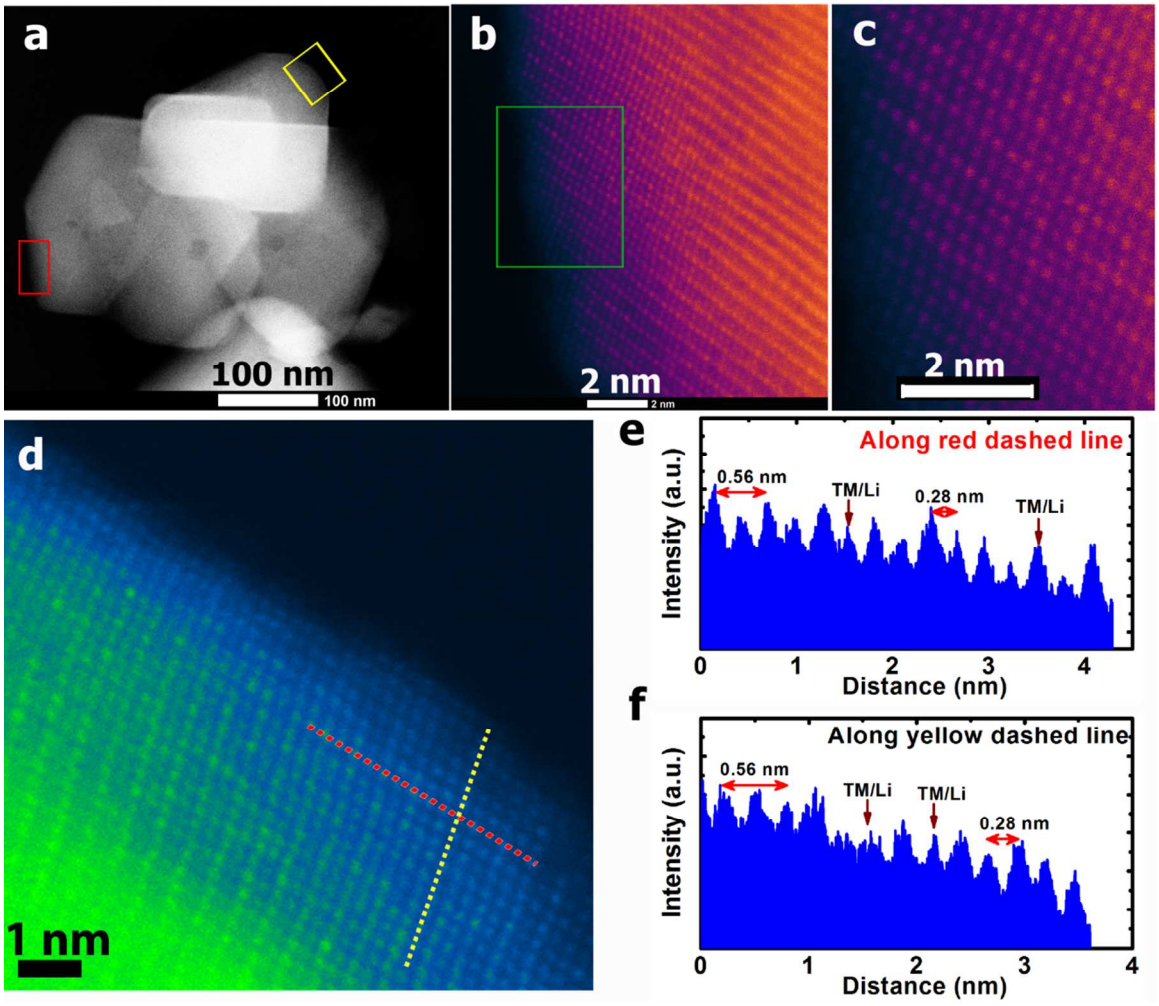

Figure S5. (a) Overview Z-contrast image of LMR cathode particles after 100 cycles. (b) Z-contrast image (magnified from the region labelled with red square in (a)) showing formation of the disordered rock-salt structure at the particle surface region. (c) Z-contrast image enlarged from the green square in (b). (d) Z-contrast image (magnified from the region labelled with yellow square in (a)) showing formation of the disordered rock-salt structure at the particle surface region. (e) Intensity plot along the red dashed line shown in (d). (f) Intensity plot along the yellow dashed line shown in (d).

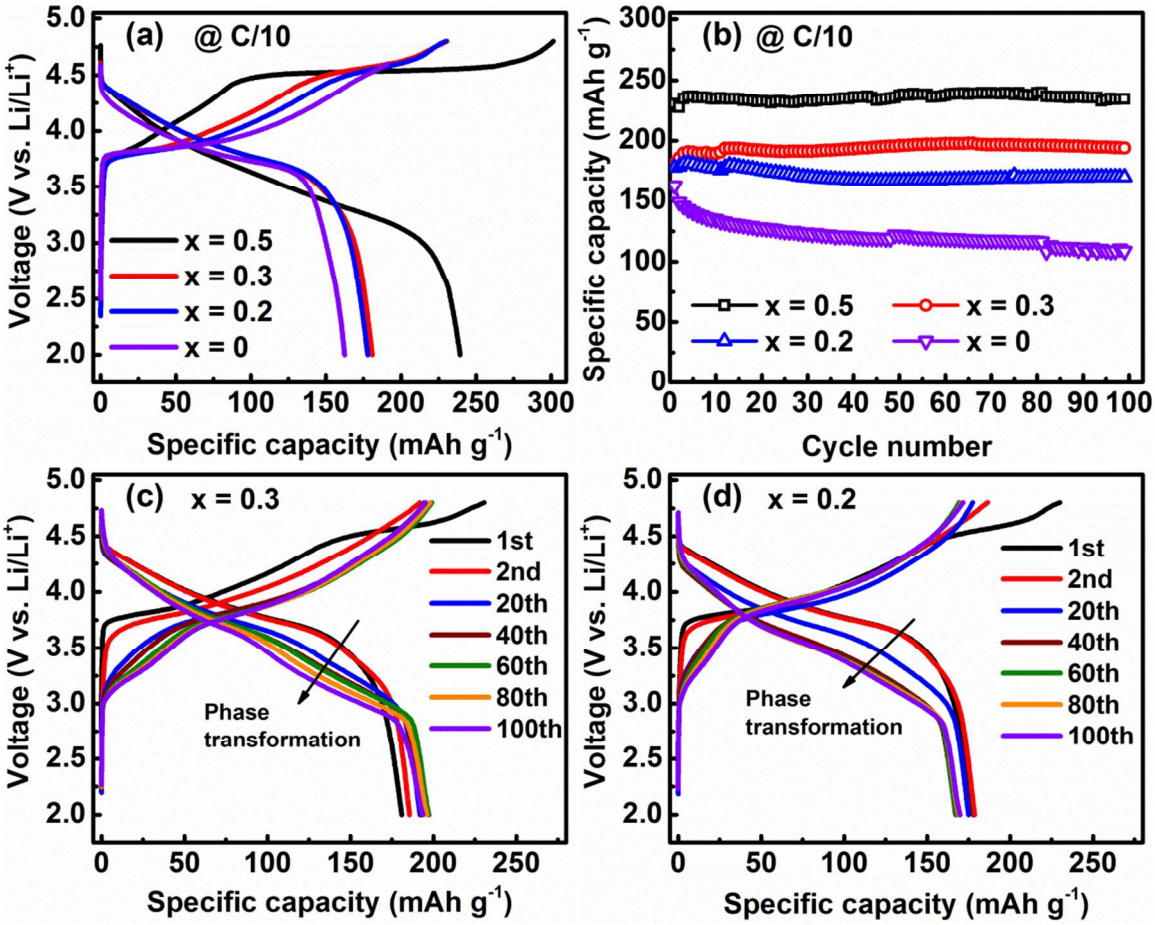

Figure S6. Electrochemical performance of LMR cathode materials x Li_2MnO_3 · (1-x) $LiNi_{0.5}Mn_{0.5}O_2$ at C/10 in the voltage range of 2.0 - 4.8 V. The material $LiNi_{0.5}Mn_{0.5}O_2$ (x = 0) was cycled between 2.0 - 4.6 V, which exhibits the fast capacity degradation. (a) Initial charge/discharge profiles; (b) cycling performance; (c) charge/discharge profile evolution of material x = 0.3 ($Li[Ni_{0.304}Li_{0.131}Mn_{0.565}]O_2$) during cycling; (d) charge/discharge profile evolution of material x = 0.2 ($Li[Ni_{0.364}Li_{0.091}Mn_{0.545}]O_2$) during cycling.

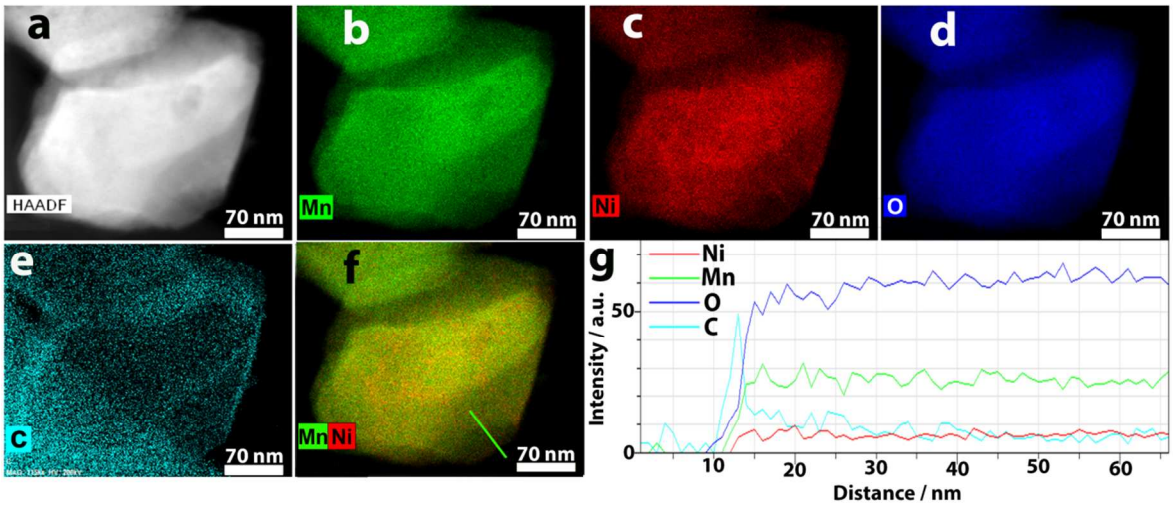

Figure S7. Z-contrast imaging and EDS mapping of material after 100 cycles at C/10 rate. (a) HAADF Z-contrast image; EDS maps of (b) Mn, (c) Ni, (d) O, (e) C, (f) overlaid Mn/Ni maps; (g) EDS signals (Ni/Mn/O/C) from the line scan indicated by the green line in (f).

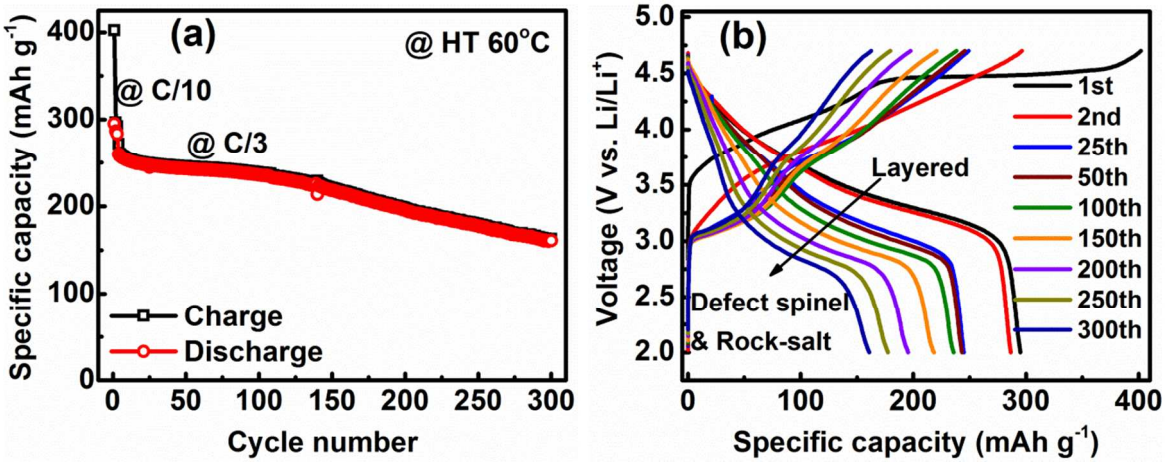

Figure S8. High temperature (60°C) electrochemical performance of LMR cathode $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ at C/3 after 3 formation cycles at C/10 in the voltage range of 2.0 ~ 4.7 V. (a) Cycling performance; (b) charge/discharge profile evolution during cycling.

REFERENCES

(1) Zheng, J.; Shi, W.; Gu, M.; Xiao, J.; Zuo, P.; Wang, C.; Zhang, J.-G. *J. Electrochem. Soc.* **2013,** 160, A2212–A2219.