Supporting Information

Observation of partial reduction of manganese in the lithium rich layered oxides, $0.4Li_2MnO_3$-$0.6LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ during the first charge

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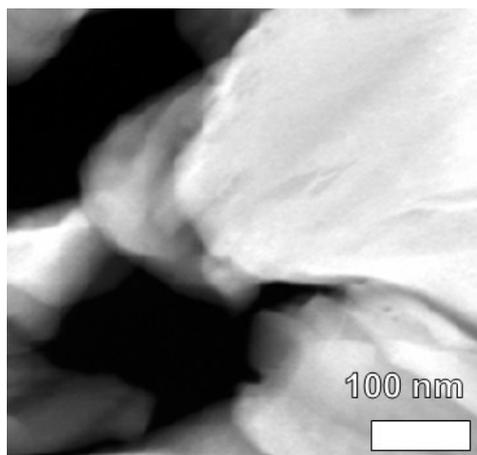
Fig. S1 STEM image of NCM samples with discharging to 2.5 V after charging up to 4.7 V.
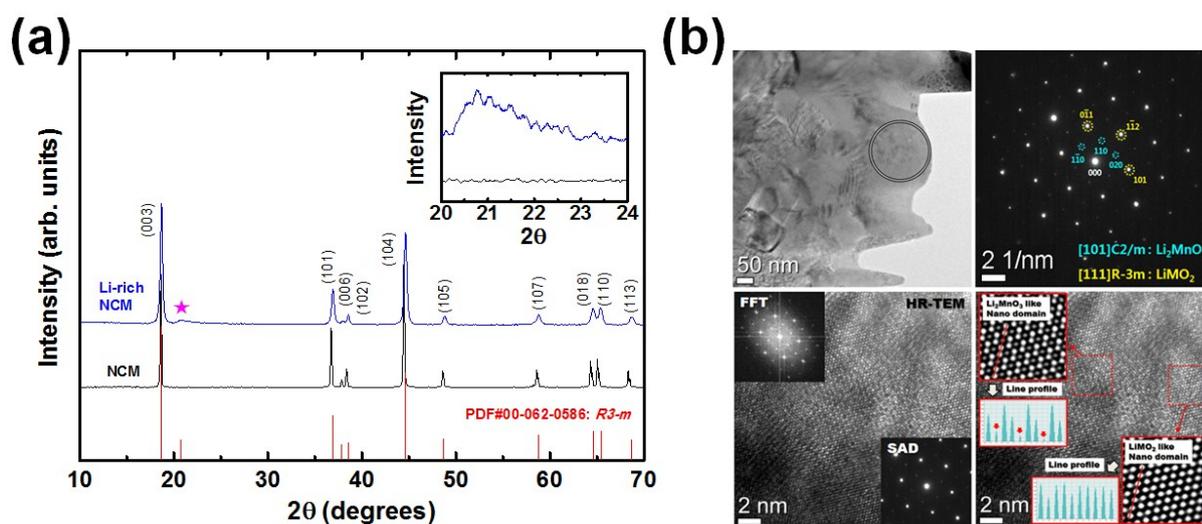
Fig. S2 (a) XRD patterns of Li-rich NCM (blue line) and NCM (black line). The inset XRD patterns corresponding the cation-ordering peak originating from Li2MnO3 phase, which are not observed in NCM sample. (b) TEM analysis of Li-rich NCM. The SAED pattern from Li-rich NCM shows refection showing cation-ordering (indicated by blue dotted circles).
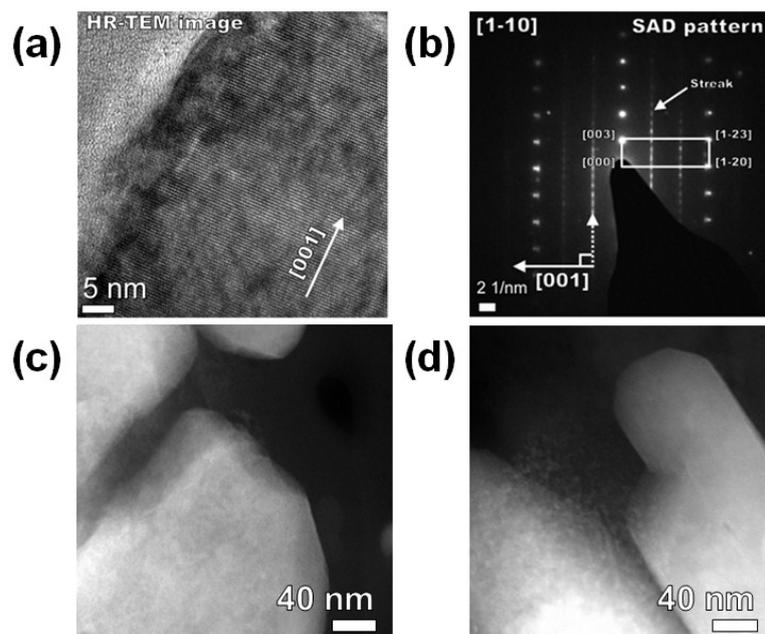
Fig. S3 (a) High resolution TEM image (b) [1-10] zone-axis SAED patterns (c) and (d) STEM images of as-synthesized Li-rich NCM samples.
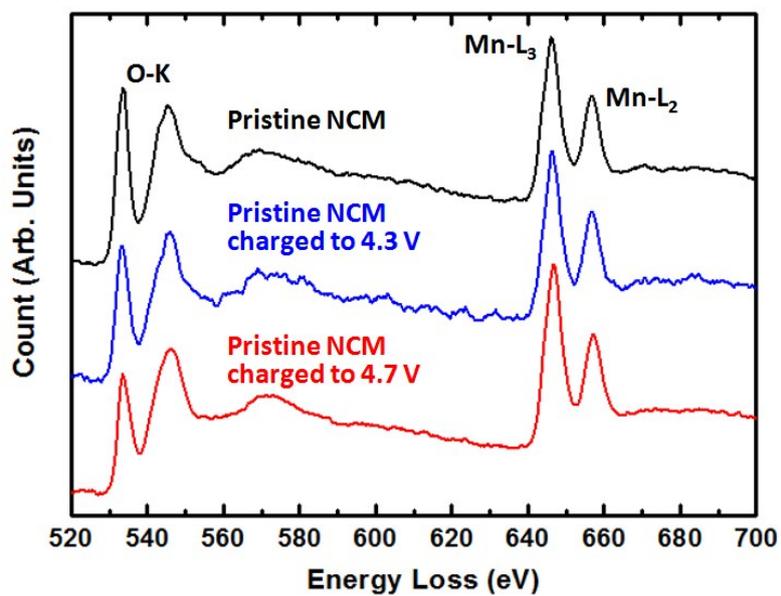
Fig. S4 The EELS spectra of Mn L-edges and O K-edges from the as-prepared NCM (black line), NCM charged to 4.3 V (blue line) and NCM charged to 4.7 V (red line).
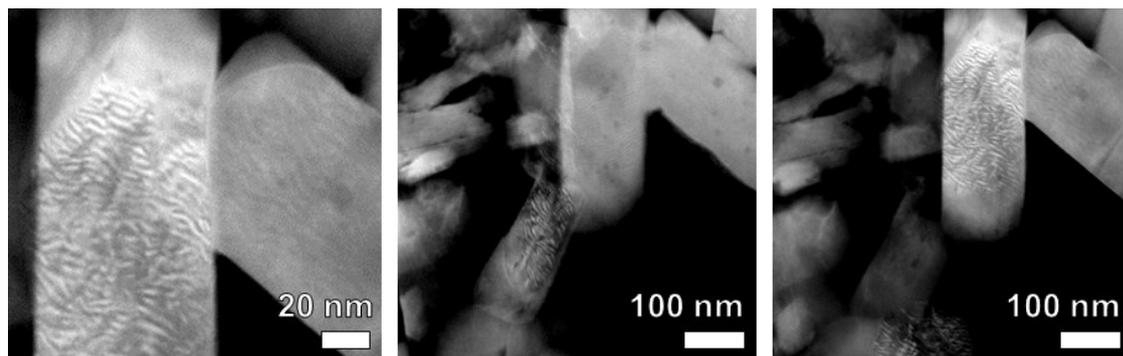
Fig. S5 STEM images of Li-rich NCM sample with discharging to 2.5 V after charging to 4.7 V.
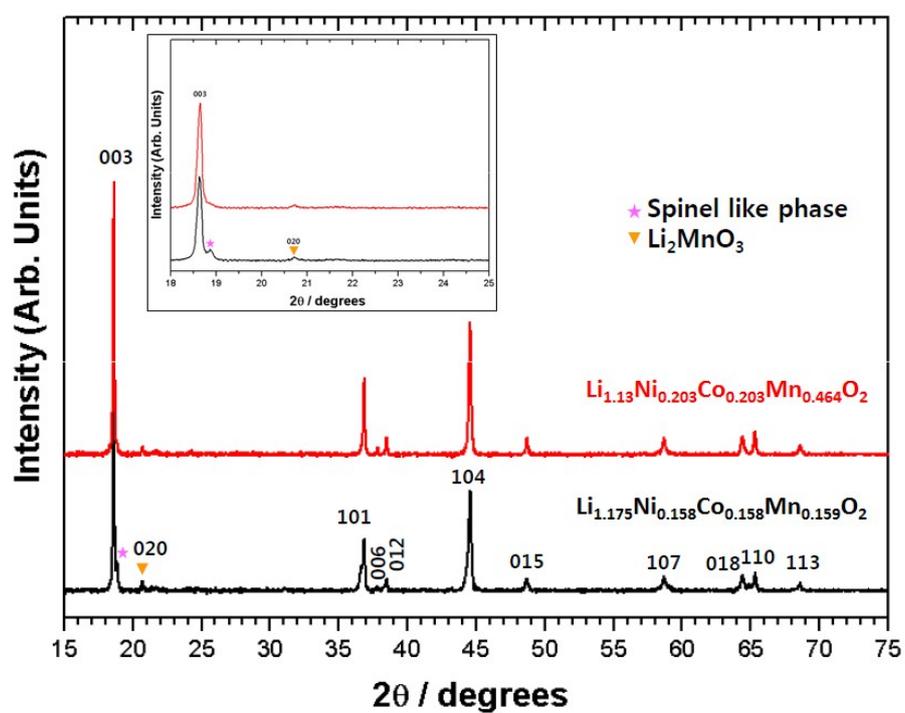
Fig. S6 The XRD patterns of $xLi_2MnO_3+(1-x)Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ (x=0.3; red line, x=0.425; black line).
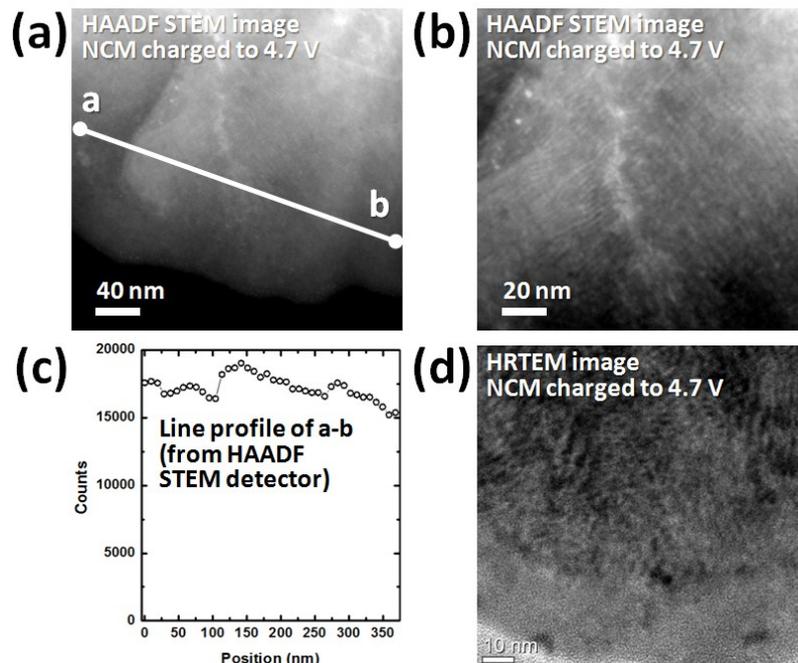
Fig. S7 (a), (b) The HAADF-STEM images of NCM charged to 4.7 V. (c) The line profiling data from *Z*-contrast between a and b at Fig. S7(a). (d) HRTEM image of NCM charged to 4.7 V.
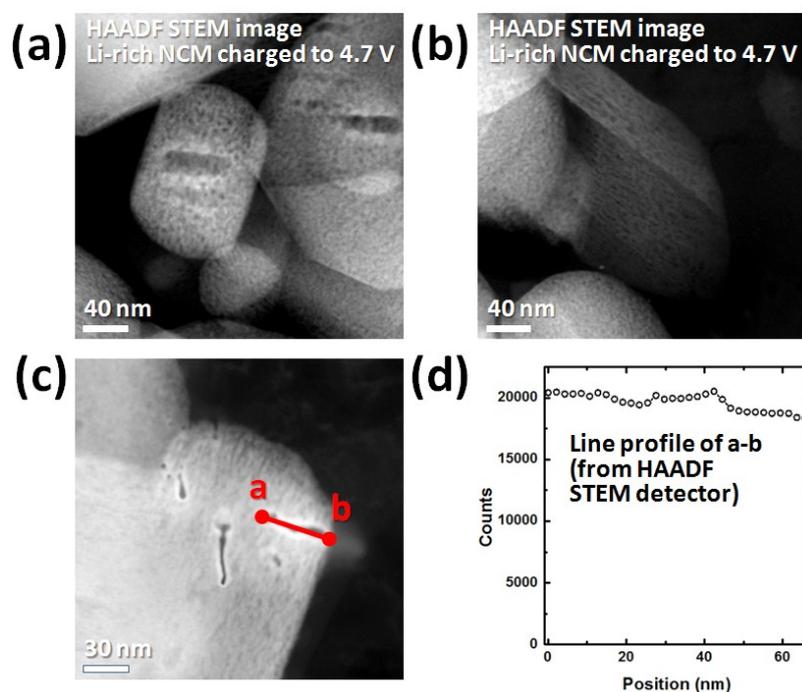
Fig. S8 (a)-(c) The HAADF-STEM images of Li-rich NCM charged to 4.7 V. (d) The line profiling data from *Z*-contrast between a and b at Fig. S7(c).
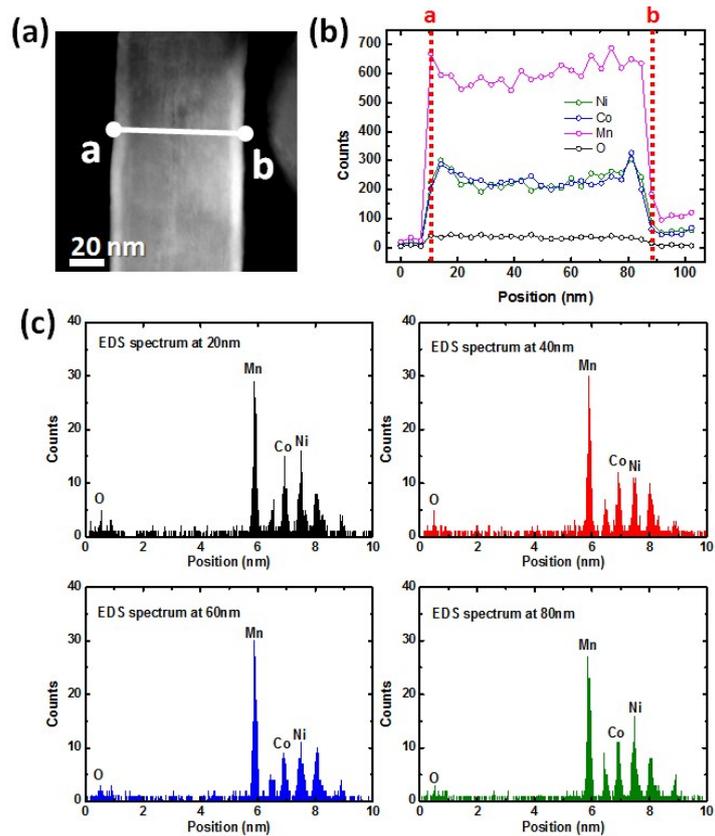
Fig. S9 (a) HAADF-STEM image of Li-rich NCM charged to 4.7 V. (b) EDS elemental concentration profiles along the scan line a-b in the Fig. S9(a). (c) EDS spectra were extracted from the scan line a-b (20, 40, 60 and 80 nm).
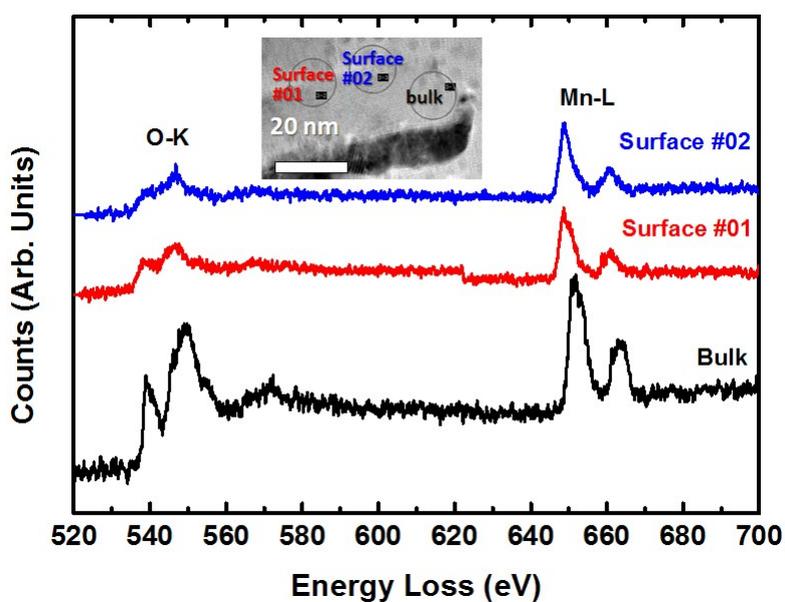
Fig. S10 Various EELS spectra from the Li-rich NCM samples charged to 4.7 V.
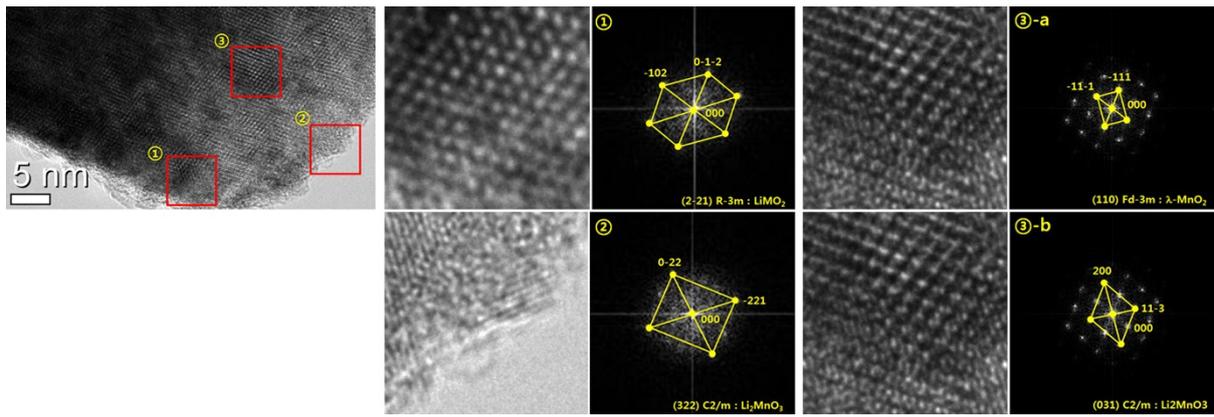
Fig. S11 The TEM analysis of Li-rich NCM sample charged to 4.7 V