## Supporting Information

## Probing the Origin of Voltage Decay in Li-Rich Layered Cathode Materials at Atomic Scale

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**Figure S1.** Voltage profiles of the  $1^{st}$  and  $60^{th}$  cycles between 2 and 4.8 V at C/100. The charge and discharge from the  $2^{nd}$  to 59<sup>th</sup> cycle were performed at C/10.



**Figure S2.** dQ/dV plots of the  $1^{st}$  and  $60^{th}$  cycle between 2 and 4.8 V at C/100. The charge and discharge from the  $2^{nd}$  to 59<sup>th</sup> cycle were performed at C/10.



**Figure S3.** (a) BF-STEM image of a particle after 18 cycles between 2 and 4.8 V. (b) FFT pattern from region A. (c) FFT pattern from region B.



**Figure S4.** dQ/dV plots of the 2-4.4 V cycled specimen after charging to 4.8 V in the initial cycle. The cycling was performed at C/10. The  $Co^{4+/3+}/Ni^{4+/3+/2+}$  and  $Mn^{4+/3+}$  reduction peaks of the layered phase are marked in the discharge curve with  $\checkmark$  and  $\blacklozenge$ , respectively.