

## Supplementary Information

### Spatially Resolved Surface Valence Gradient and Structural Transformation of Lithium Transition Metal Oxides in Lithium-Ion Batteries

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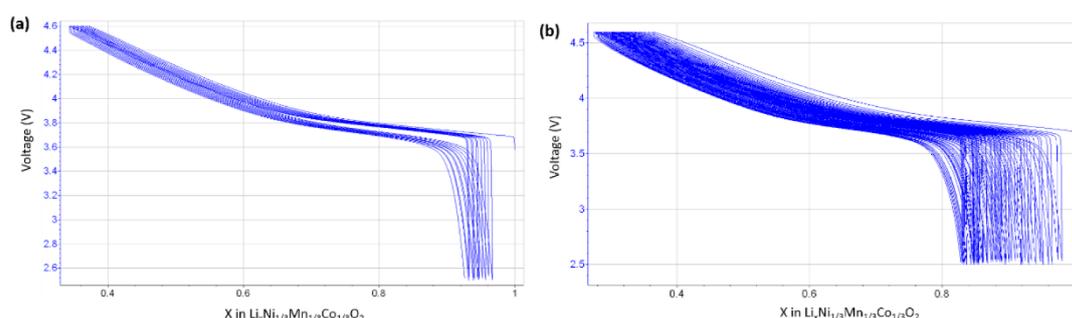


Fig. S1 Galvanostatic charge-discharge curves of NMC electrode of (a) 20 cycles, (b) 50 cycles.

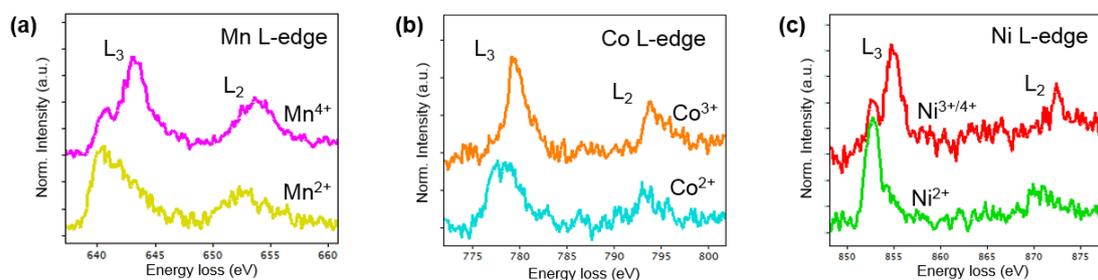


Fig. S2 Reference spectra of (a) Mn, (b) Co and (c) Ni L-edges used for the multiple linear least square (MLLS) analysis. All the reference spectra were obtained from the experimental data at the surface region and bulk region.

#### MLLS fitting for EELS spectrum

The multiple linear least square method (MLLS) fits the reference spectra and/or models to a specified energy range of the selected spectrum. A model function consisting linear combination of the specified reference spectra will be formed and used to fit the spectrum acquired from the experiment, a general model equation as shown below:

$$S(E) = \beta_1 AE^{-r} + \beta_2 S(E)_I + \beta_3 S(E)_{II} + \epsilon$$

$\beta_1$ : fitting coefficient for background function with preset  $AE^{-r}$

$\beta_2$ : fitting coefficient for reference spectrum 1 ( $Mn^{2+}$ ,  $Co^{2+}$  and  $Ni^{2+}$ , respectively)

$\beta_3$ : fitting coefficient for reference spectrum 2 ( $Mn^{4+}$ ,  $Co^{3+}$ , and  $Ni^{3+/4+}$ , respectively)

$\varepsilon$ : the sum of squared residuals.

The fitting coefficient “ $\beta$ ” will be adjusted to minimize the squared residuals “ $\varepsilon$ ” between the linear fitted model and the selected spectrum. If correctly performed, the fit coefficient can be interpreted as the relative contribution of each reference spectrum or the contribution maps with the same dimensionality of the input spectrum image.

In our case, the reference spectra of Ni, Mn and Co used for the fitting were directly extracted from the experimental EELS spectrum image (SI). The fit coefficient maps represent the relative contribution of the two reference spectra (which representing the two valence states of the transition metal element) at each pixel from the entire SI and reflect the valence distribution in the sample. Therefore, fitting coefficient maps are named as valence maps.

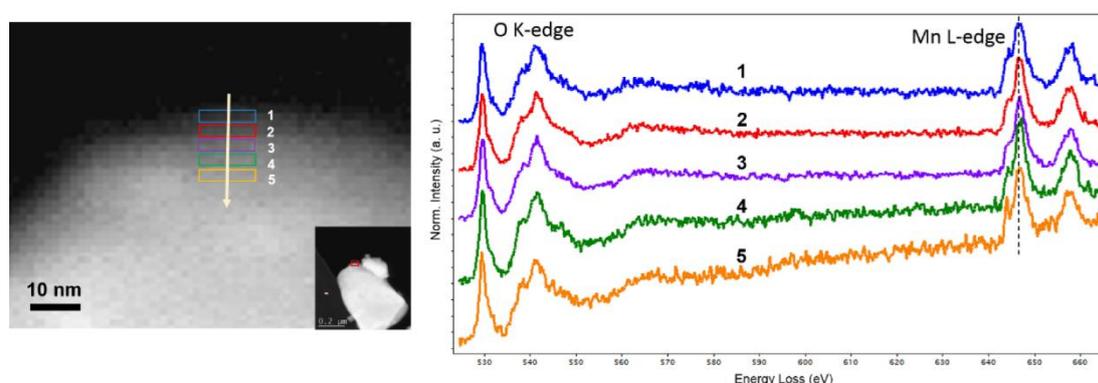


Fig. S3 EELS spectra profile of pristine NMC. The O K-edge and Mn L-edge are shown here to demonstrate the consistency of the electronic structure of NMC. It can be clearly seen that there is no intensity decrease in O K-edge from the surface to the bulk, indicating no reduction of the transition metal ions. Moreover, there is almost no change observed in the Mn  $L_{2,3}$ -edge features, suggesting there is no surface reduction in the pristine sample.

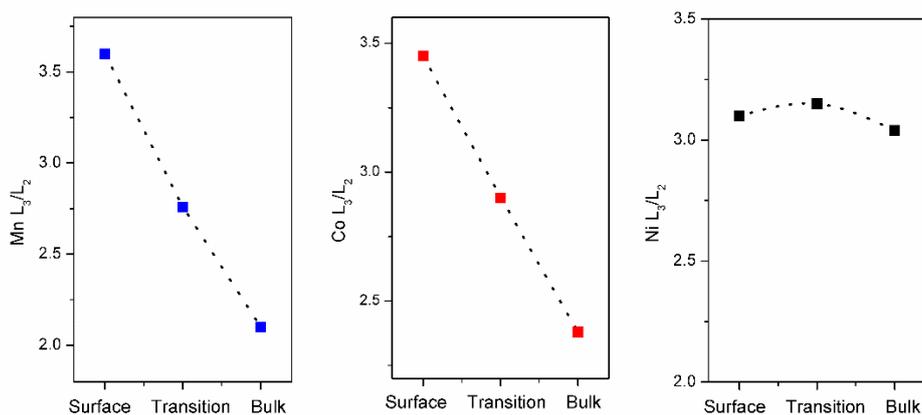


Fig. S4 L<sub>3</sub>/L<sub>2</sub> ratio of Mn, Co and Ni for NMC after 50 cycles. The three ratios were calculated from the corresponding EELS spectra (Fig. 7d) acquired from the surface layer (Surface), transition zone (Transition) and bulk region (Bulk).

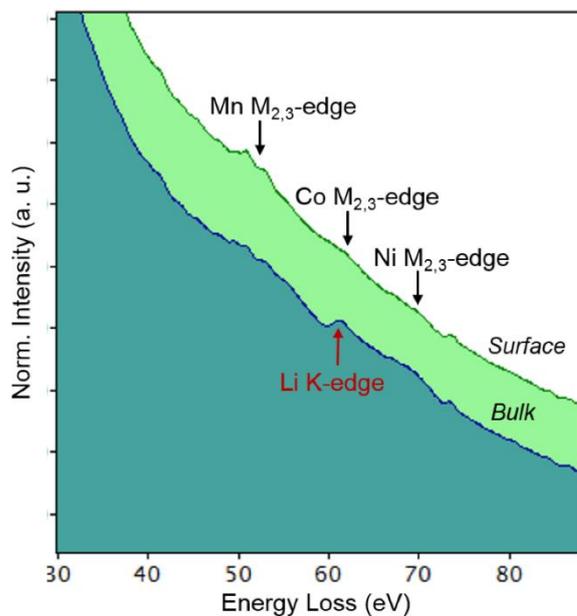


Fig. S5 Li K-edge spectra acquired at the surface reduction layer and the bulk region from the NMC cathode after 50 cycles. A significant drop in the Li K-edge intensity can be observed from the bulk to surface, indicating the drastic decrease of the Li content from the layered bulk region ( $R\bar{3}m$ ) to the surface rock-salt layer ( $Fm\bar{3}m$ ). The background subtraction is not applied to the Li K-edge due to the complexity of spectrum arising from the existence of the adjacent Mn M<sub>2,3</sub>-edge and Co M<sub>2,3</sub>-edge, as labelled in the spectrum.

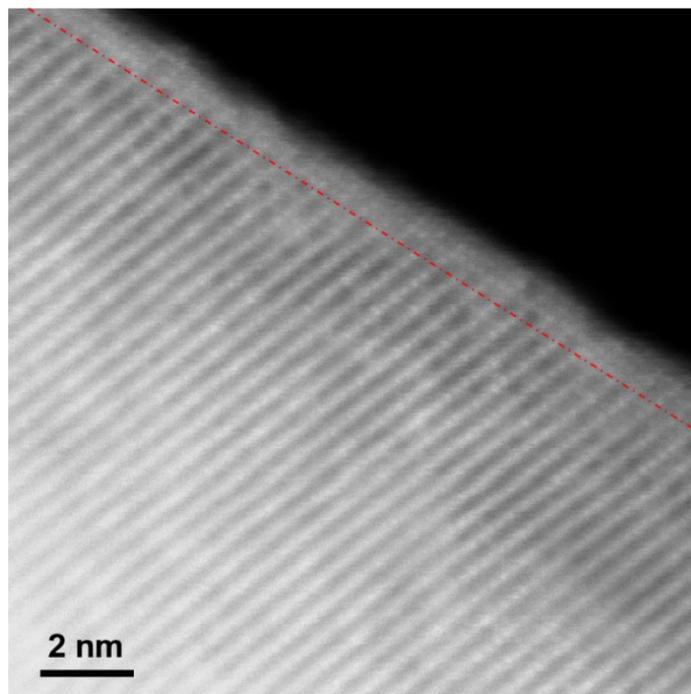


Fig. S6 Atomic-resolution HAADF-STEM image of a NMC particle after electrolyte exposure for one week. The transition metal migration into Li layer is readily observed near the particle surface.