

## **Identifying the Nanostructure of Residual Li in High-Ni Cathodes for Lithium-ion Batteries**

|            | LiOH<br>(ppm) | Li <sub>2</sub> CO <sub>3</sub><br>(ppm) | Total residual Li<br>(ppm) |
|------------|---------------|--|----------------------------|
| Bare NCM   | 3,950         | 2,880                                    | 1,680                      |
| Washed NCM | 950           | 2190                                     | 687                        |
| Dried NCM  | 3,120         | 3,165                                    | 1,503                      |

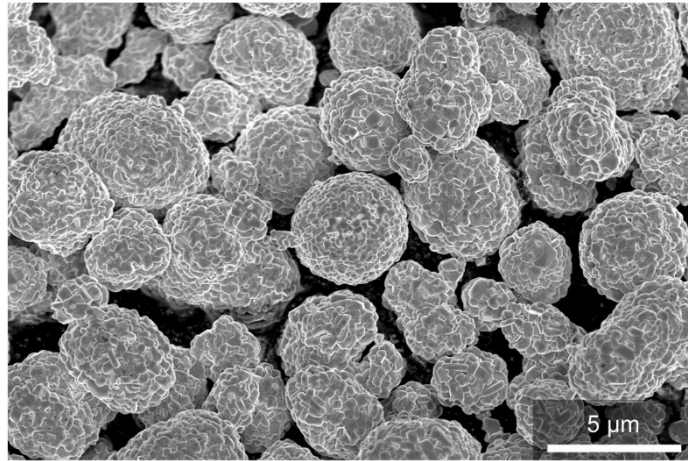
**Table S1.** Amount of residual Li of bare, washed, and dried NCM powder

| Sample     | Relative molar ratio |      |      |      |
|------------|----------------------|------|------|------|
|            | Li                   | Ni   | Co   | Mn   |
| Bare NCM   | 10.36                | 7.97 | 1.00 | 1.01 |
| Washed NCM | 10.06                | 8.00 | 1.00 | 1.02 |

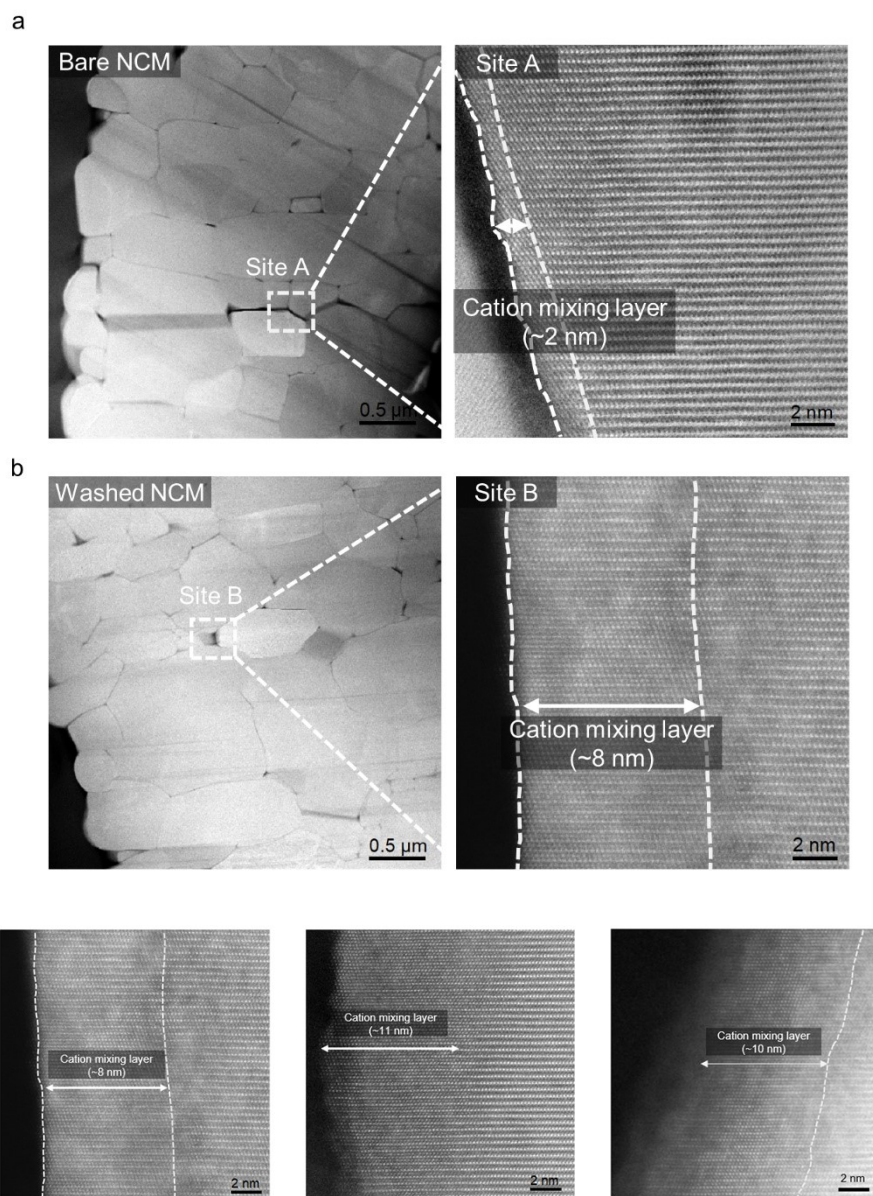
**Table S2.** ICP-OES results for bare and washed NCM powder

**Table S3.** Rietveld results for bare and washed NCM powder

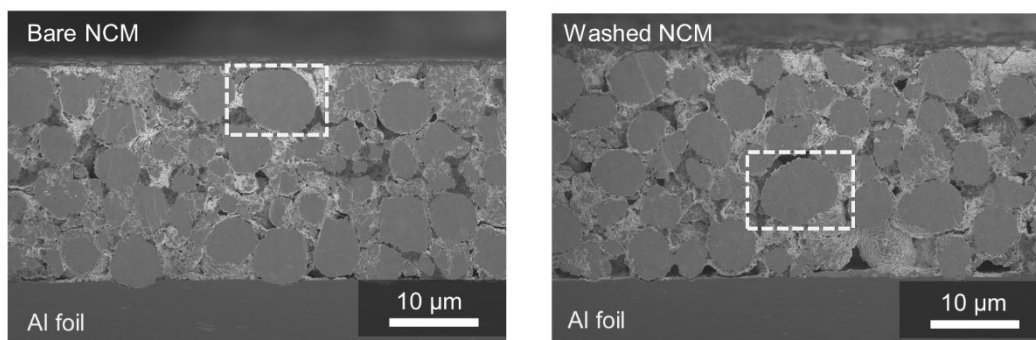
| Compound   | $a_{\text{hex}}$ [Å] | $c_{\text{hex}}$ [Å] | Ni <sup>2+</sup> in Li layer [%] |
|------------|----------------------|----------------------|----------------------------------|
| Bare NCM   | 2.87250(4)           | 14.2192(3)           | 1.90                             |
| Washed NCM | 2.87183(6)           | 14.2281(5)           | 3.70                             |



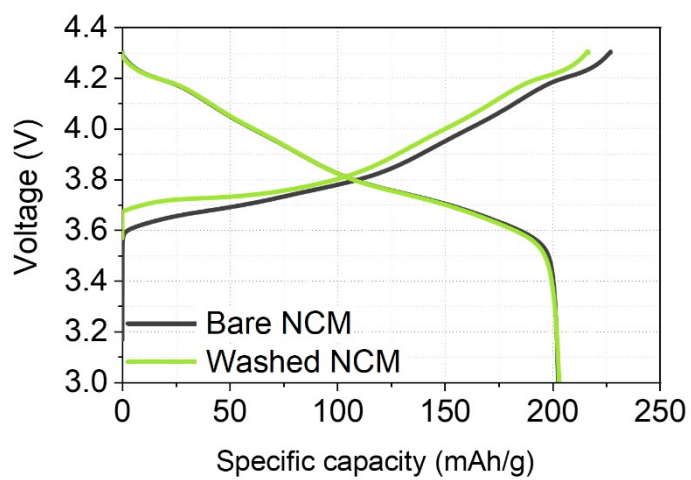
**Figure S1** SEM image of bare NCM powder.



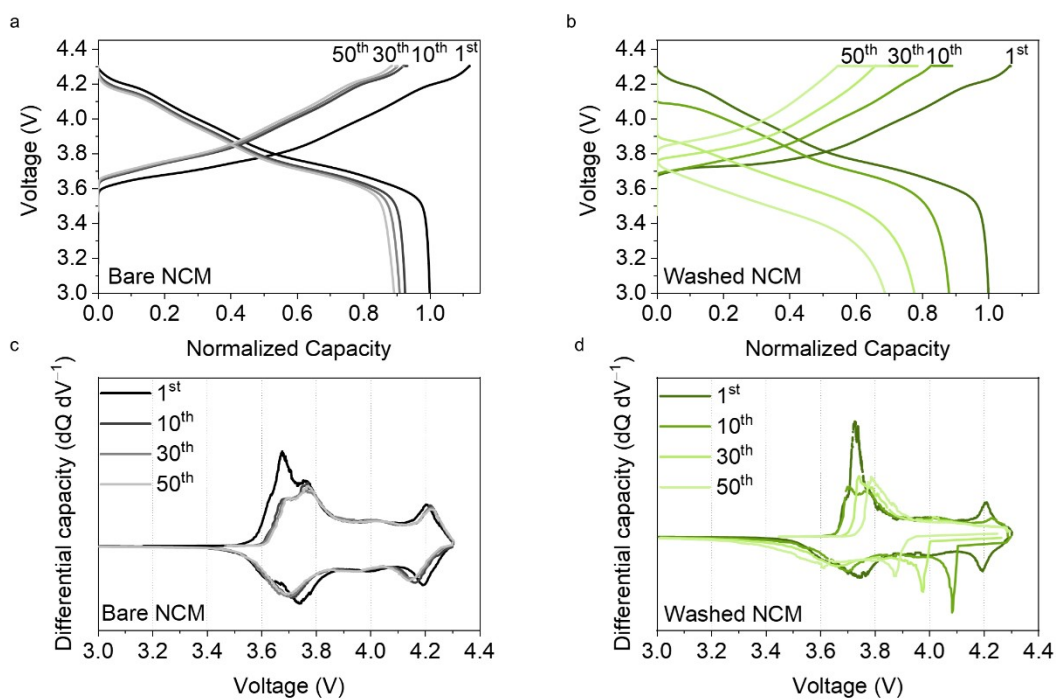
**Figure S2** HR-TEM images of (a) bare NCM and (b) washed NCM.



**Figure S3** SEM images of cross-sectioned bare NCM and washed NCM electrode.

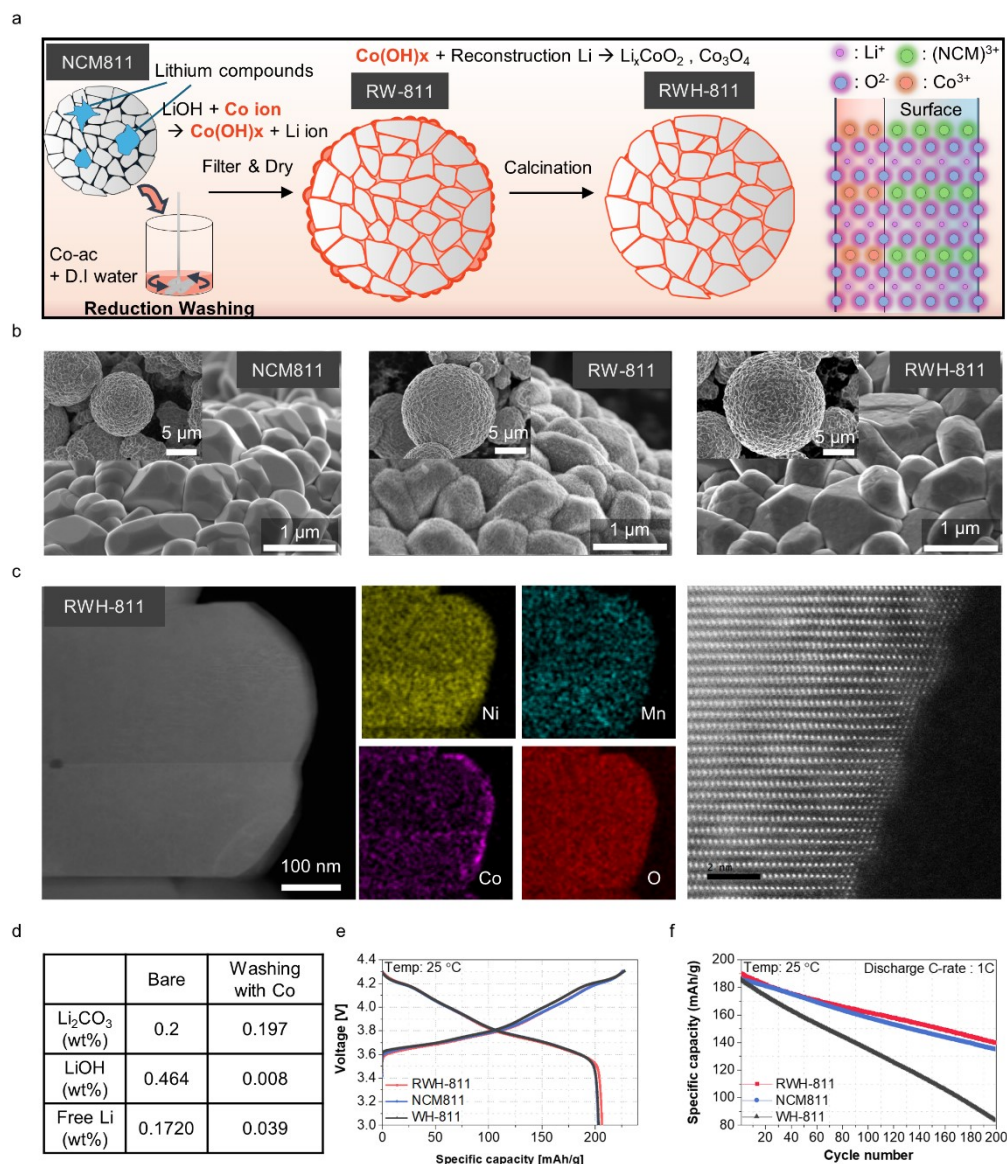


**Figure S4** Voltage profiles for the formation cycle of bare NCM and washed NCM in a half-cell configuration in the voltage range of 3.0–4.3 V with a 0.1 C rate.

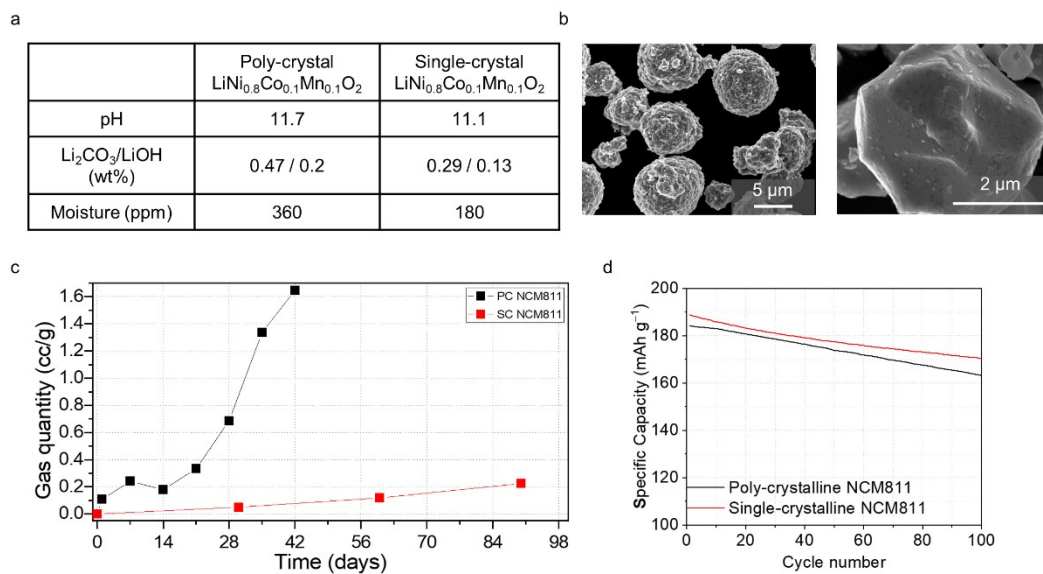


**Figure S5** Voltage profiles of the 1<sup>st</sup>, 10<sup>th</sup>, 30<sup>th</sup>, and 50<sup>th</sup> cycles during cycling with a 0.1 C rate in the voltage range of 3.0–4.3 V for (a) bare NCM and (b) washed NCM in a half-cell configuration and corresponding dQ/dV plots of (c) bare NCM and (d) washed NCM.





**Figure S6** (a) Illustration of Co-dissolved washing process; (b) SEM images of bare NCM, NCM after Co-dissolved washing, and NCM after annealing with 500 °C followed by Co-dissolved washing; (c) HR-TEM image and EDS mapping of NCM after annealing with 500 °C followed by Co-dissolved washing; (d) amounts of residual Li compounds before and after Co-dissolved washing; (e) voltage profiles for the formation cycle in a half-cell configuration in the voltage range of 3.0–4.3 V with a 0.1 C rate; (f) cycle performance with a 1 C rate in the voltage range of 3.0–4.3 V.



**Figure S7** (a) Chemical properties and (b) SEM images of polycrystalline and single-crystalline NCM; (c) gas evolution results for poly-crystalline and single-crystalline full cells in the fully charged state at 4.2 V; (d) cycle performance of each cathode at a 1 C rate in the voltage range of 3.0–4.3 V.