Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

Overall Structural Modification of Layered Ni-Rich Cathode for Enhanced Cycling Stability and Rate Capability at High Voltage

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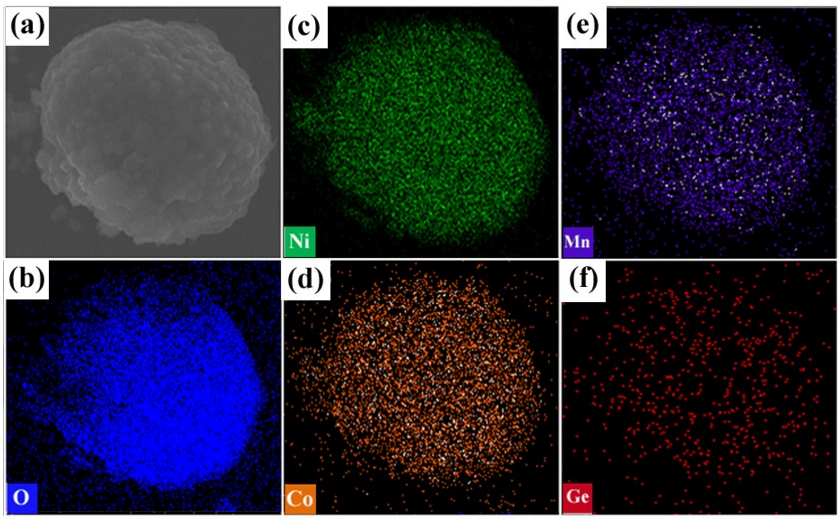

Figure S1. EDS mapping of NCM811@LGO: (a) SEM images, (b~f) O, Ni, Co, Mn, Ge element.

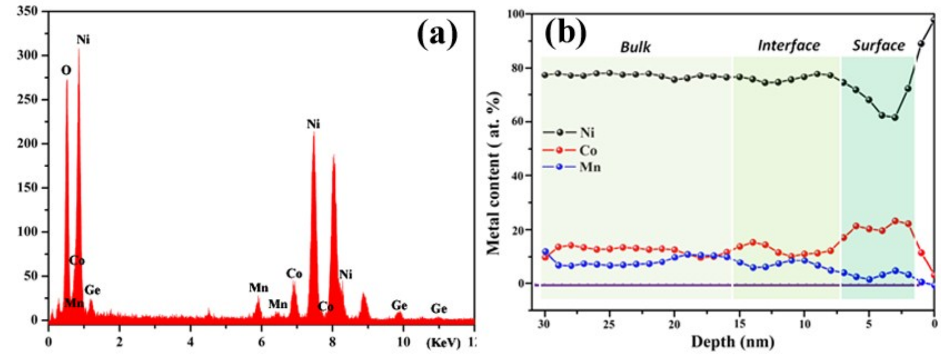

Figure S2. (a) EDS spectrum and (b) line scan from surface to bulk of NCM 811@LGO particle.

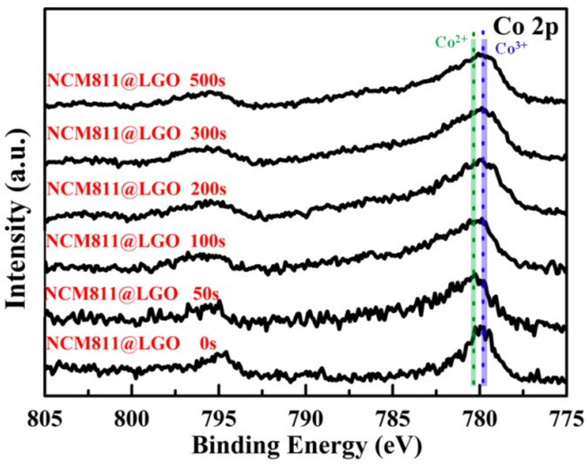

Figure S3. XPS spectra of Co 2p for NCM811@LGO with different etching time.

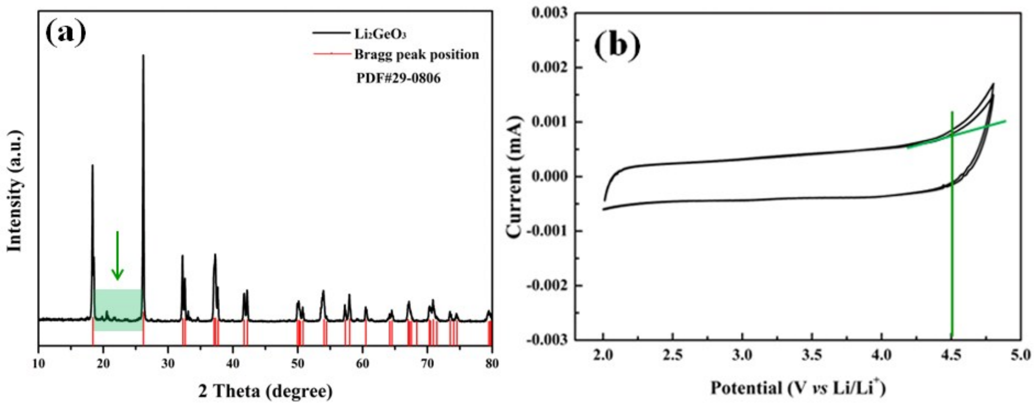

Figure S4. (a) XRD pattern and (b) CVs of the as-prepared Li_2GeO_3 powders from high-temperature solid-state method.

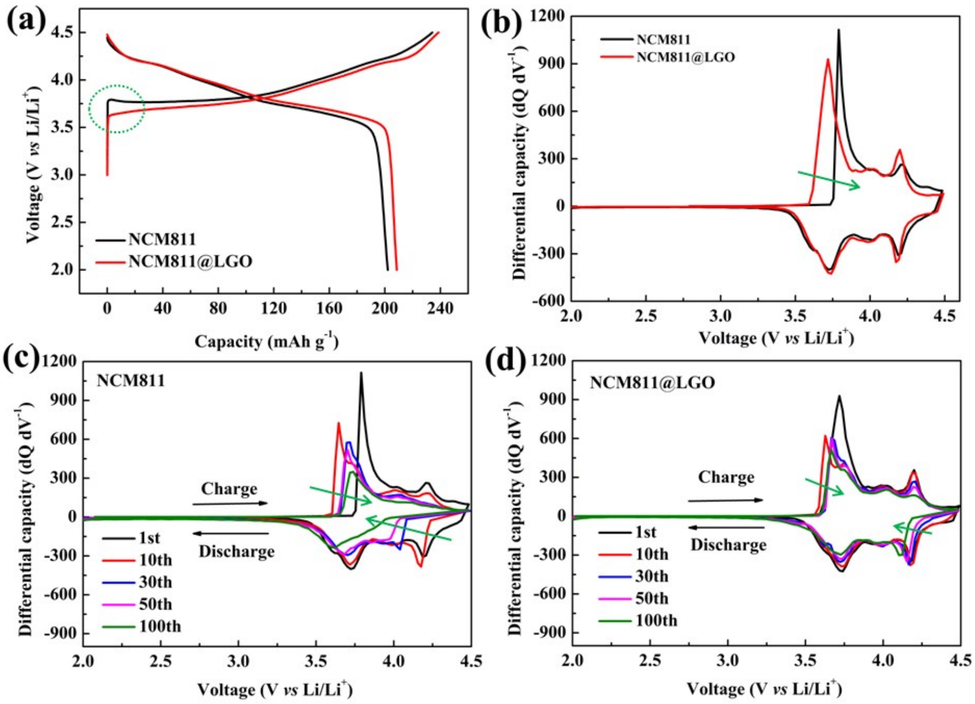

Figure S5. (a) The initial charge/discharge profiles and (b) corresponding differential capacity curves of the cathodes between 2.0 and 4.5 V *vs* Li/Li^+ at 0.1 C; Evolutions of differential capacity curves of (c) NCM811 and (d) NCM811@LGO during high-voltage cycling.

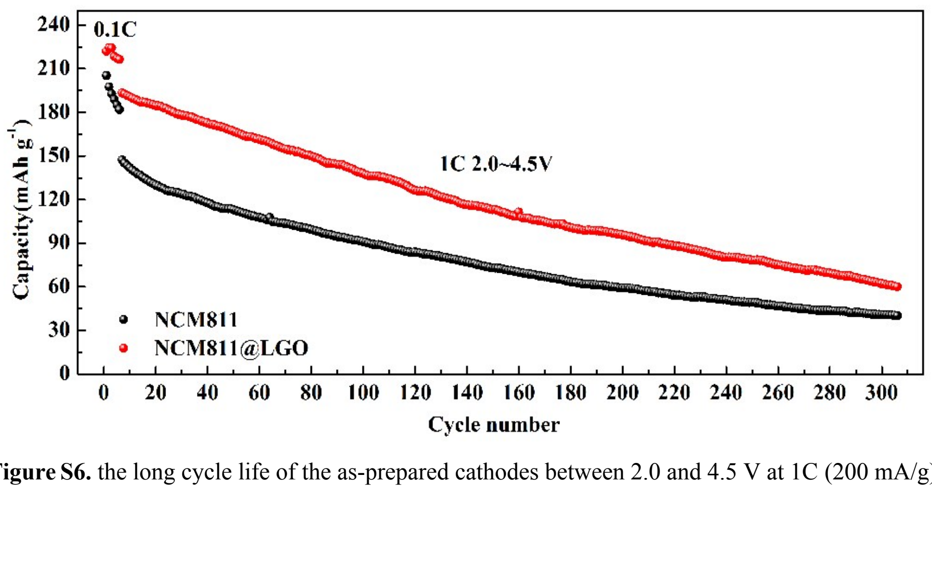

Figure S6. the long cycle life of the as-prepared cathodes between 2.0 and 4.5 V at 1C (200 mA/g).

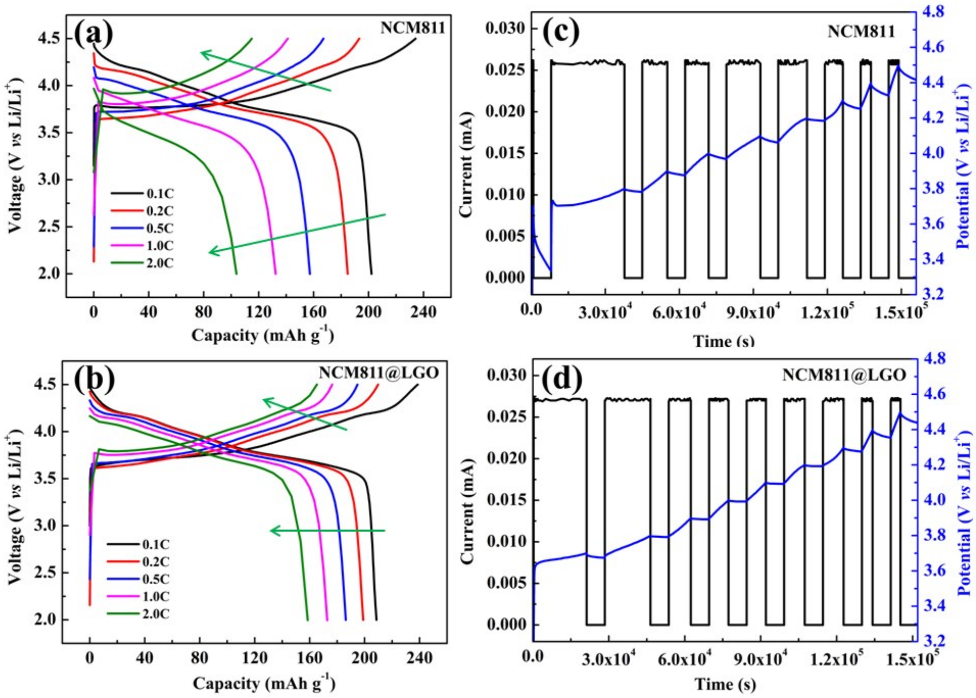

Figure S7. Evolution of the charge-discharge curves for (a) NCM811 and (b) NCM811@LGO between 2.0 and 4.5 V at different rates; Relationship of the transition current depending on the titration time at different charge potentials for (c) NCM811 and (d) NCM811@LGO.

The Li$^+$ diffusion coefficient (D_{Li+}) can be calculated with the following equation:

Equation S1 ——————

$$D_{Li^+} = \frac{4}{\pi\tau}\left(\frac{m_B V_m}{M_B S}\right)^2\left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2 \quad \left(\tau \ll \frac{L^2}{D_{Li^+}}\right)$$

Where m_B is the mass of the active material (g), V_m and M_B are the molar volume and molecular weight of the samples, respectively. S is the area of the electrode, τ is the time duration during the current pulse, ΔE_s is the difference in the steady-state voltage at a single-step GITT experiment, L is the length of Li$^+$ ions diffusion. (*Z. Huang, Z. Wang, Q. Jing, H. Guo, X. Li, Z. Yang, Investigation on the effect of Na doping on structure and Li-ion kinetics of layered $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cathode material. Electrochimica Acta, 2016, 192, 120-126*)

The reaction rate constant *k* can be calculated with the Arrhenius equation:

$$k = A\ \exp(-E/RT)$$

A is constant factor, **R** is gas constant, **T** is room temperature, and **E** is energy for one mole electron. According to this equation $k_a/k_b = \exp((E_b-E_a)/RT)$, the ratio value of k_a/k_b is varied by the exponential rise.

Taking the Li diffusion in the $LiNiO_2$ as example, the Li diffusion barrier in the Ge-doped $LiNiO_2$ is 0.49 eV while the pristine is 0.52 eV, the k_a/k_b value is 3.21 (k_a is the rate constant of Ge-doping $LiNiO_2$, k_b is for the pristine) when temperature is 298K, meaning that the Li diffusion rate in the Ge-doped $LiNiO_2$ would be 3.21 times faster than that of the pristine. Likewise, the k_a/k_b value can be calculated in the different delithiated states, the k_a/k_b value for $Li_{0.5}NiO_2$ and NiO_2 are 33.1 and 6.99 respectively.