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Electronic Supplementary Information

$LiNi_{0.90}Co_{0.07}Mg_{0.03}O_2$ Cathode Materials with Mg-Concentration Gradient for Rechargeable Lithium-Ion Batteries

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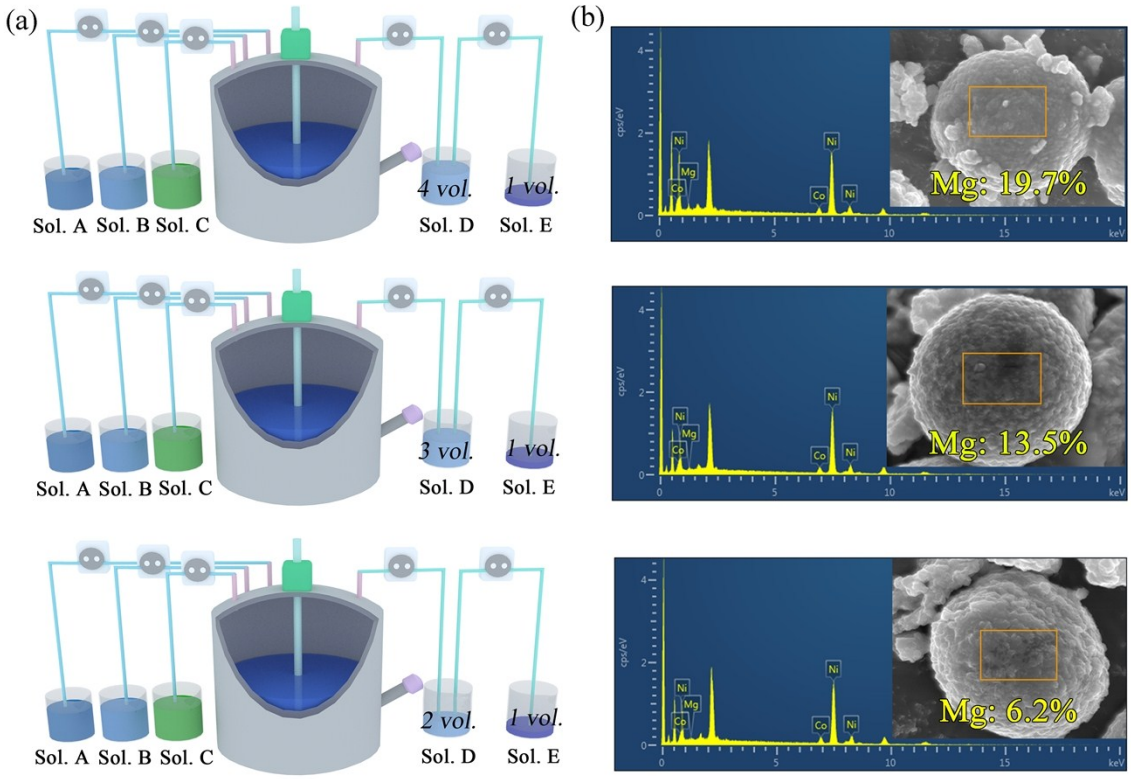

Figure S1. (a) Schematic illustration of the synthesis of hydroxide precursors by employing different volume ratios of deionized water (solution D) and $MgSO_4$ solution (solution E). (b) The corresponding EDS spectra and determined Mg content near surface region of synthesized oxide samples.

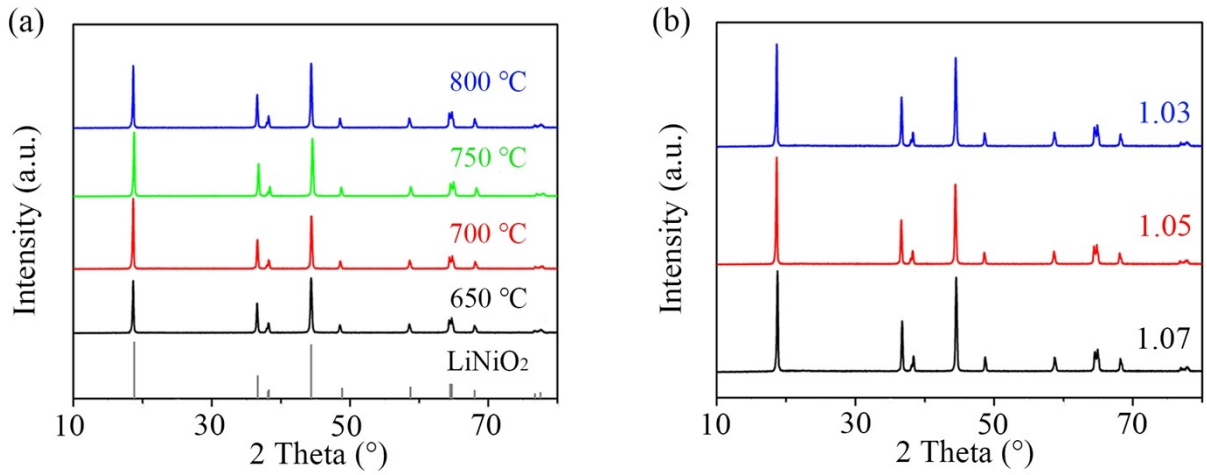

Figure S2. XRD patterns of (a) CG-NCMg samples prepared at 650, 700, 750 and 800 ℃ and (b) CG-NCMg samples calcined at Li/M molar ratio of 1.03, 1.05, and 1.07 at 700 ℃.

Table 1. Chemical composition analysis of homogeneous and concentration-gradient hydroxide precursor and lithiated oxides determined by ICP-AES.

Chemical formula of the designated samples	Mole ratio of main elements for the feeding of materials	Mole ratio of main elements for the prepared samples as analyzed
Homogeneous $(Ni_{0.9}Co_{0.07}Mg_{0.03})(OH)_2$	Ni:Co:Mg = 0.90:0.07:0.03	Ni:Co:Mg = 0.900:0.071:0.030
Concentration gradient $(Ni_{0.9}Co_{0.07}Mg_{0.03})(OH)_2$	Ni:Co:Mg = 0.90:0.07:0.03	Ni:Co:Mg = 0.899:0.070:0.031
Homogeneous $Li(Ni_{0.9}Co_{0.07}Mg_{0.03})O_2$	Ni:Co:Mg = 0.90:0.07:0.03	Ni:Co:Mg = 0.901:0.070:0.029
Concentration gradient $Li(Ni_{0.9}Co_{0.07}Mg_{0.03})O_2$	Ni:Co:Mg = 0.90:0.07:0.03	Ni:Co:Mg = 0.904:0.072:0.024

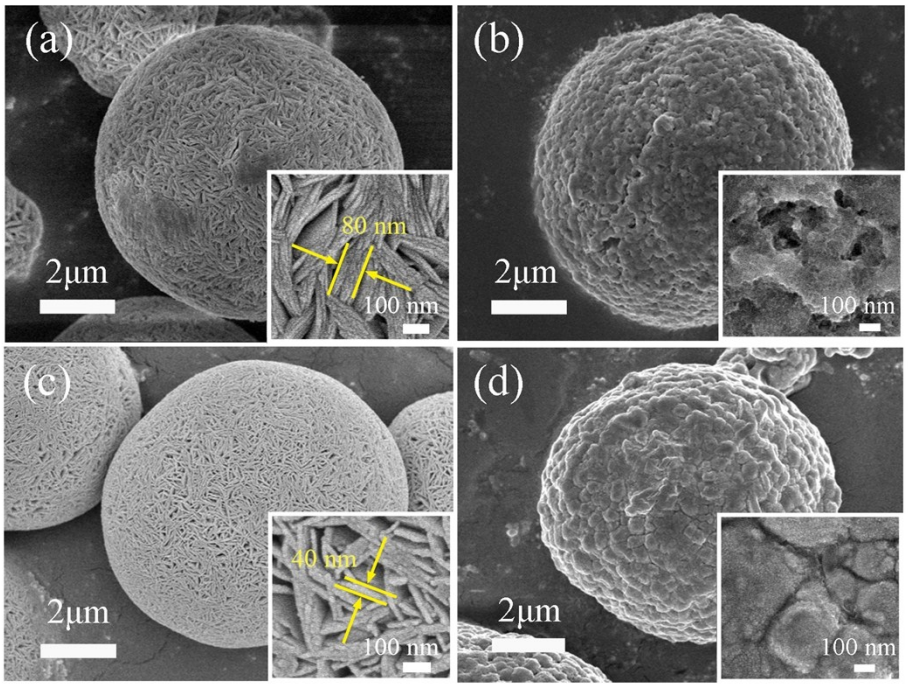

Figure S3. SEM images of (a) CG-NCMg precursor, (b) CG-NCMg, (c) CC-NCMg precursor, and (d) CC-NCMg samples. The insets show magnified images.

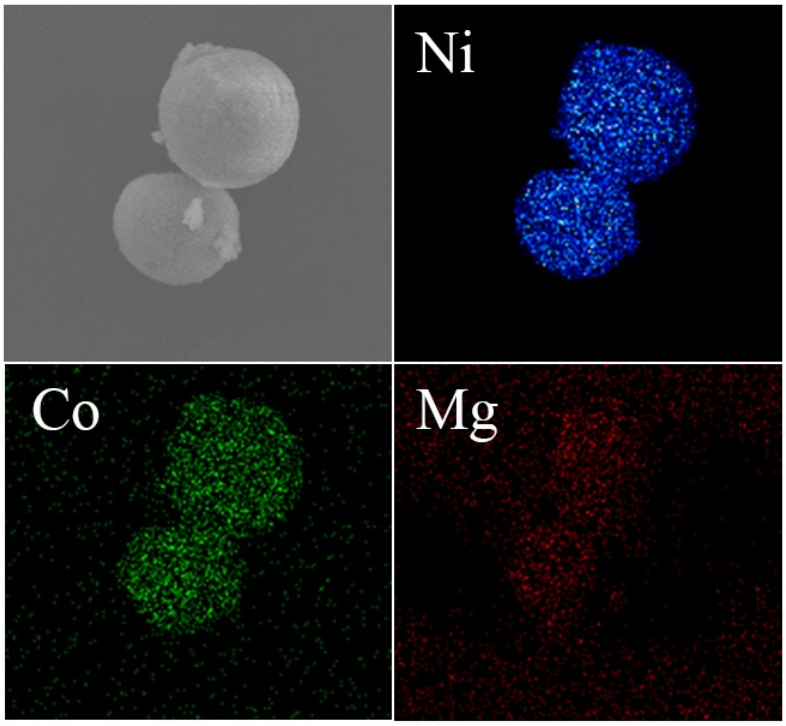

Figure S4. Elemental mapping of Ni, Co, and Mg of CG-NCMg particles.

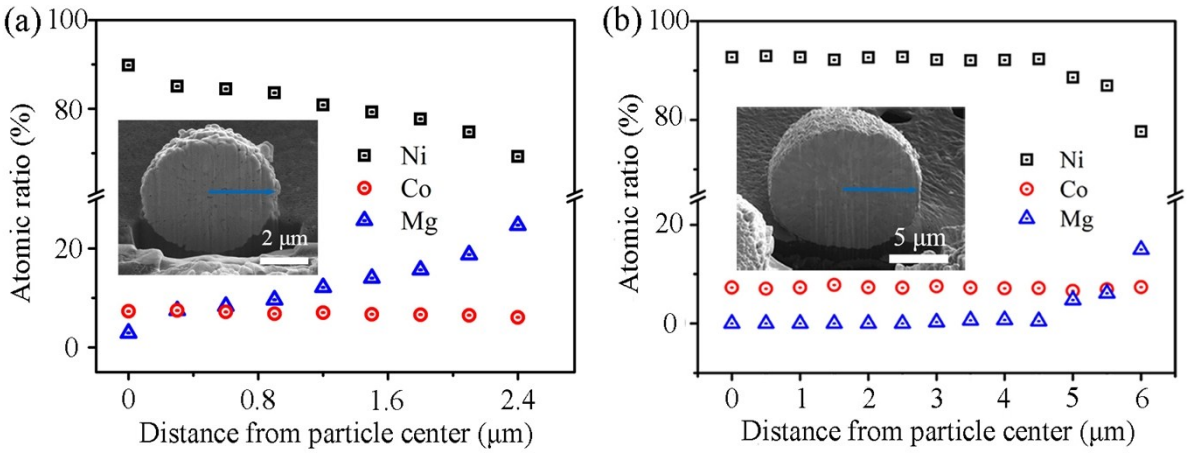

Figure S5. EDS compositional analysis of CG-NCMg particles with different diameters of (a) 5.5 μm and (b) 12.3 μm.

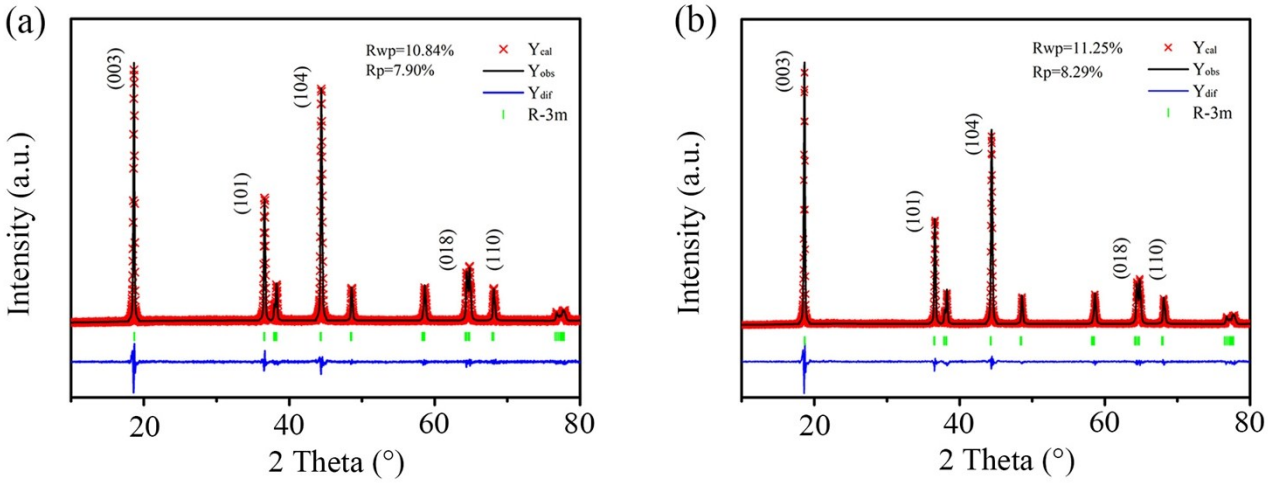

Figure S6. Rietveld refinements of XRD data of (a) CG-NCMg and (b) CC-NCMg with GSAS/EXPGUI. Y_{cal}, Y_{obs} and Y_{dif} are calculated diffraction intensity, observed diffraction intensity and intensity difference between the observed and calculated patterns, respectively. R_{wp} and R_p are reliability factors. The achieved values of *a*, *c* are 2.8846(1)Å, 14.2530(5) Å (CG-NCMg) and 2.8825(3) Å, 14.2434(8) Å (CC-NCMg).

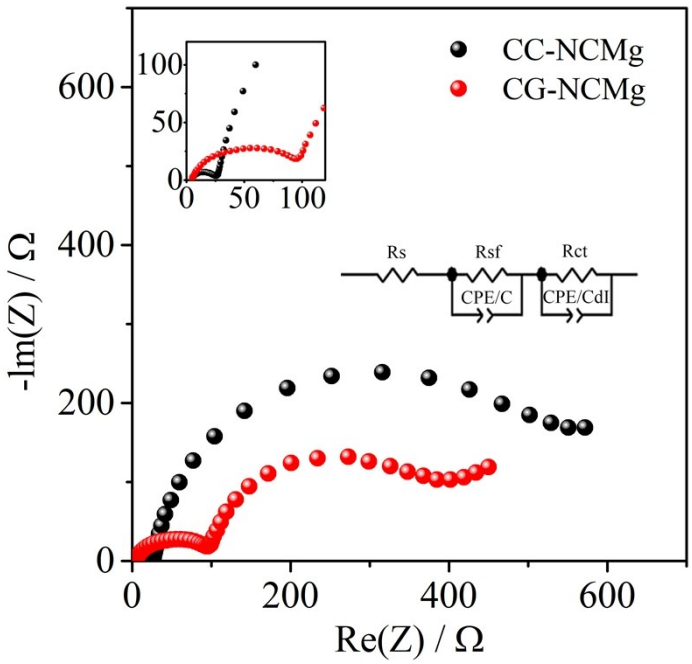

Figure S7. EIS spectra of CG-NCMg and CC-NCMg at first charged state. The insets shows magnified section at high frequency and equivalent circuit diagram.

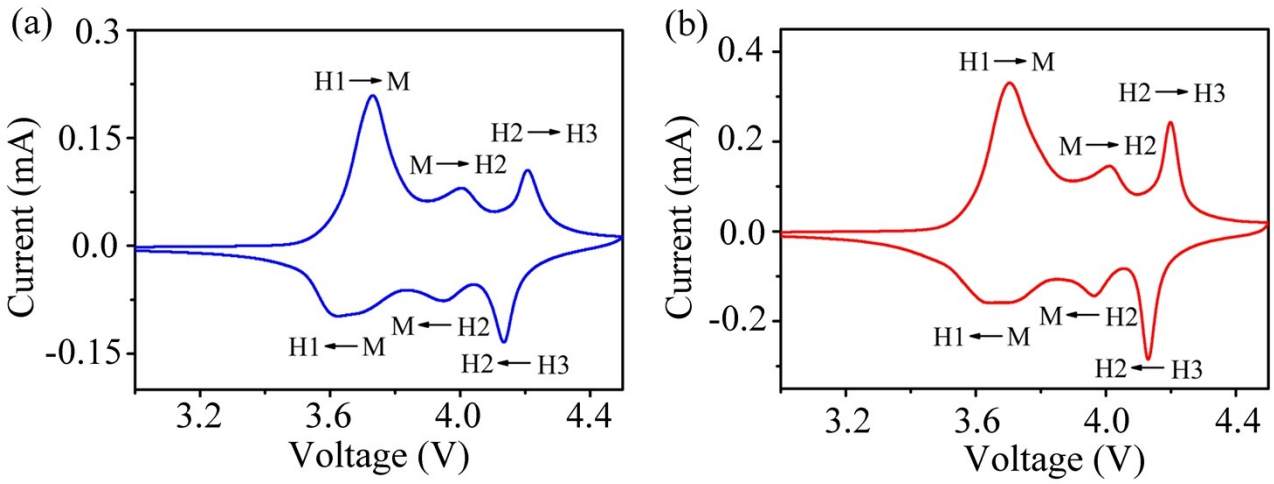

Figure S8. Cyclic voltammograms of (a) CC-NCMg and (b) CG-NCMg at the second cycle at scanning rate of 0.1 mV s^{-1}.

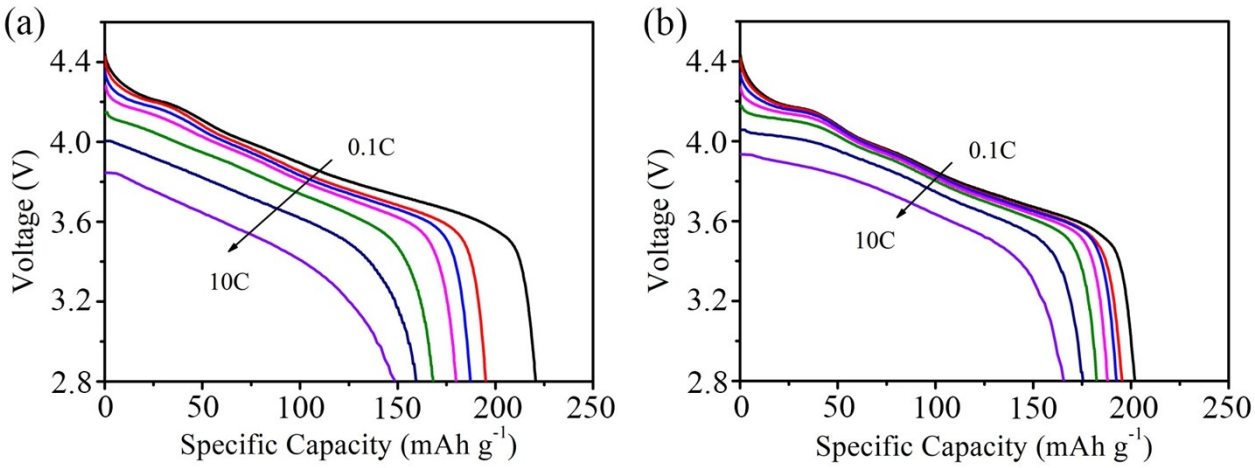

Figure S9. Discharge curves of (a) CC-NCMg and (b) CG-NCMg at various rates.

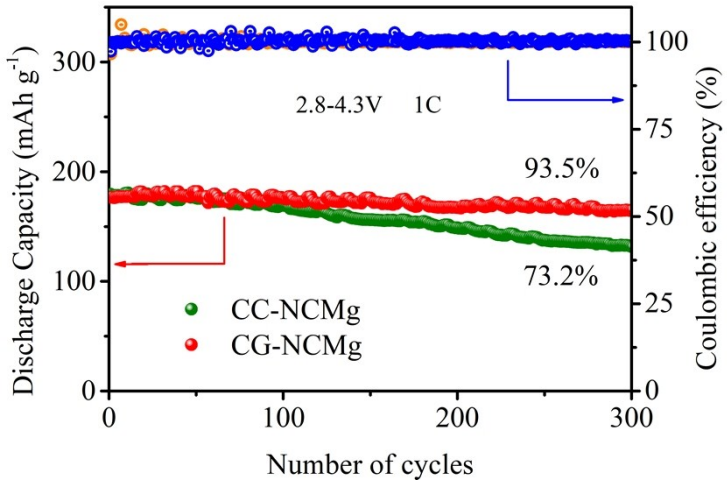

Figure S10. Cycling performance of CC-NCMg/MCMB and CG-NCMg/MCMB full cells at a rate of 1C.

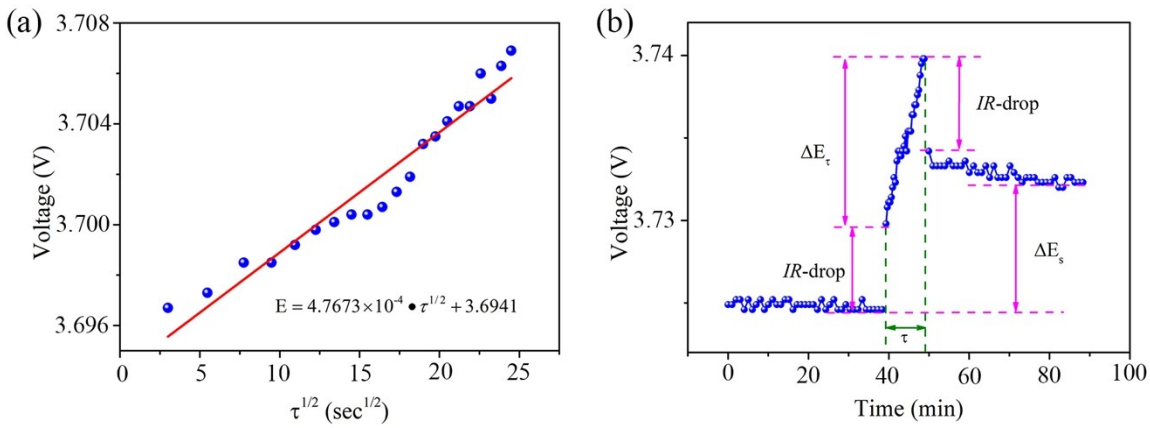

Figure S11. (a) The plot of voltage against $\tau^{1/2}$ shows the linear fit. (b) The diagram for the voltage response of a charge pulse in the GITT experiment with the labelling of parameters.

The D_{Li^+} can be calculated by the following formula:[1,2]

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

In the formula, m_B (g), M_B (g mol^{-1}) and V_M (cm^3 mol^{-1}) are mass, molar mass and molar volume of cathode material, respectively; A (cm^2) is the active surface area of the electrode; and L (cm) is the diffusion length.

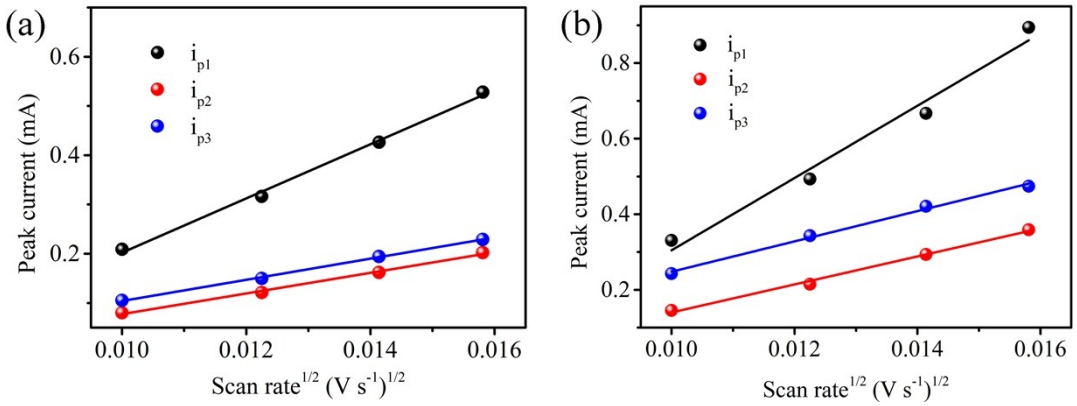

Figure S12. Linear relationship between the peak currents and square root of scan rates for (a) CC-NCMg and (b) CG-NCMg. Data are derived from cyclic voltammograms shown in Fig. 4b and c.

D_{Li^+} is calculated by the following formula:[3,4]

$$i_p = (2.69 \times 10^5) n^{3/2} A D_{Li+}{}^{1/2} C_{Li}^{*} v^{1/2}$$

In this equation, i_p, n and C_{Li}^{*} are peak current, charge transfer number and Li^+ concentration in the cathode, respectively. For CG-NCMg, the determined D_{Li^+} near 3.7, 4.0 and 4.2 V is 4.857×10^{-10}, 7.288×10^{-11} and 8.543×10^{-11} cm^2 s^{-1}, respectively. The corresponding values for CC-NCMg are 1.607×10^{-10}, 2.329×10^{-11} and 2.450×10^{-11} cm^2 s^{-1}, respectively. Clearly, CG-NCMg shows higher lithium diffusivity at close voltages.

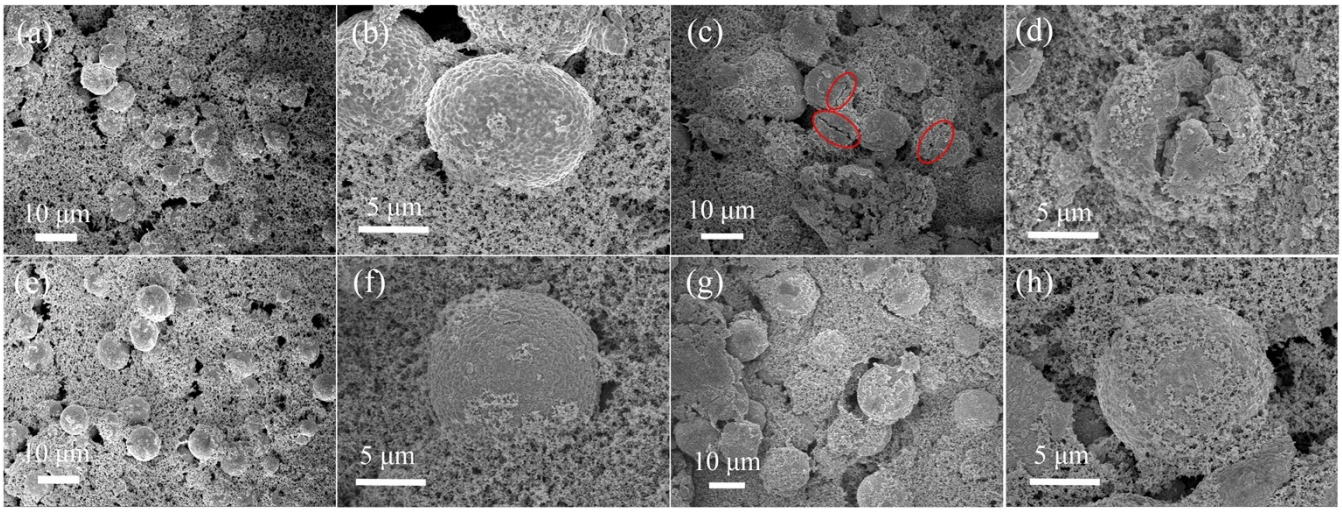

Figure S13. SEM images of (a, b) pristine CC-NCMg, (c, d) cycled CC-NCMg, (e, f) pristine CG-NCMg, and (g, h) cycled CG-NCMg.

References

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