Supporting Information

Suppressing Intergranular Cracking with Near-Surface Layer Regulation for Electrochemical-Thermal Stabilization of LiCoO$_2$

Kangwei Song[a,&], Yu Shen[b,&], Tongmin Xu[a,&], Yushuang Lin[a], Zheming Chen[a], Weicheng Zhang[a], Congyu He[a], Zhenzhong Yang[b,*], Ke Qu[b,*], Zheyuan Liu[a, *], Yan Yu[a], Chengkai Yang[a,*]

[a] College of Materials Science and Engineering, Fuzhou University, Fuzhou, Fujian, 350108, China
[b] Key Laboratory of Polar Materials and Devices (MOE), Shanghai Center of Brain-inspired Intelligent Materials and Devices, Department of Electronics, and Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai, 200241, China
[&] Authors contributed equally to this work
* Corresponding mails: kqu@chem.ecnu.edu.cn (K.Qu), zzyang@phy.ecnu.edu.cn (Z.Z Yang), zheyuan.liu@fzu.edu.cn (Z.Y Liu), chengkai_yang@fzu.edu.cn (C.K. Yang)

synthetic materials

Synthesis of $LiCoO_2$ Material: First, Li_2CO_3 and Co_3O_4 are mixed in a molar ratio of Li=1.03:1, ball milled at 400 rpm/min for 4 hours with a ball-to-powder ratio of 5:1, then calcined in a muffle furnace at 900°C for 15 hours, and finally ground and sieved (200 mesh) to obtain $LiCoO_2$ (Bare-LCO).

Synthesis of $Mg_2B_2O_5$ Coated $LiCoO_2$ Material: First, Li_2CO_3 and Co_3O_4 are mixed in a molar ratio of Li=1.03:1, ball milled at 400 rpm/min for 4 hours with a ball-to-powder ratio of 5:1, then calcined in a muffle furnace at 900°C for 15 hours. The calcined $LiCoO_2$ and $Mg_2B_2O_5$ are transferred to a beaker with an appropriate amount of ethanol, stirred and heated until the ethanol is completely evaporated, and finally calcined in a muffle furnace at 850°C for 5 hours, then ground and sieved (200 mesh) to obtain $Mg_2B_2O_5$ coated $LiCoO_2$ (referred to as MB-LCO).

Characterization

The crystal structure of the samples was analyzed using X-ray diffraction（XRD MiniFlex600 Japan） with Cu Kα radiation (λ = 1.546 Å) at a scan rate of 5°C/min. Field emission scanning electron microscopy (SEM Nova Nano SEM 230 America) and aberration-corrected transmission electron microscopy (AC-TEM JEM-ARM300 Japan) were used to observe the microstructure and morphology of the cycled cathodes. X-ray photoelectron spectroscopy (XPS ESCALAB 250 America) was employed to analyze the chemical composition, elemental content, and depth distribution on the surface of the cycled cathodes.

Battery Performance Testing

The battery performance tests were conducted using coin cells (type 2032). The working electrodes were prepared by dispersing the active material, conductive carbon black (acetylene black), and polyvinylidene fluoride (PVDF) in a mass ratio of 90:5:5 in N-methyl-2-pyrrolidone (NMP). The slurry was coated onto a 16μm thick aluminum foil using a 400μm doctor blade and dried in a vacuum oven at 120°C for 12 hours. The aluminum foil was then cut into 12mm diameter disks, and the mass was measured with a balance, subtracting the mass of a blank 12mm aluminum foil to determine the active

material load on the aluminum foil (approximately 10mg).The coin cells were assembled in an argon-filled glove box (with water and oxygen levels below 0.1ppm) using the prepared working electrodes, a porous separator (polypropylene, Celgard 2400), and a lithium metal disc (0.55mm thick, 12mm diameter).The electrolyte composition was 1M lithium hexafluorophosphate (LiPF$_6$) in a solvent mixture of dimethyl carbonate, ethylene carbonate, and ethyl methyl carbonate (DMC:EC=1:1:1 by volume), with 5% fluoroethylene carbonate (FEC).

Cycling performance was tested with constant current cycling in the voltage range of 3 ~ 4.5 V (vs Li/Li$^+$). The cycling rate was gradually increased from 0.1C to 5C and then returned to 1C to test the cycling performance. Electrochemical impedance spectroscopy (EIS) measurements were performed by recording Nyquist plots in the frequency range of 0.01 Hz to 1 MHz with an AC amplitude of 10 mV. Galvanostatic intermittent titration technique (GITT) tests were conducted with a charge/discharge time of 20 minutes at a rate of 0.1C, followed by a relaxation time of 2 hours.

Theoretical Calculations

All calculations mentioned in this paper were performed under the spin-polarized density functional theory (DFT) within the generalized gradient approximation (GGA),[1] using the Perdew-Burke-Ernzerhof (PBE) functional.[2] The Vienna Ab initio Simulation Package (VASP) was used,[3] with the Brillouin zone processed using the Monkhorst-Pack schem,[4] and a k-point mesh of (1×2×1) for both preliminary optimization and charge calculations. The convergence criterion for electronic self-consistency was set to 0.04. AI-MD simulations were conducted using the MD software CP2K. The initial box size was set to 11.25×11.25×22.43 Å with periodic boundary conditions applied in all three directions. The integration time step was set to 1 fs. The temperature was maintained at 298 K using the NPT ensemble. The radial distribution functions were analyzed using the VMD software package.
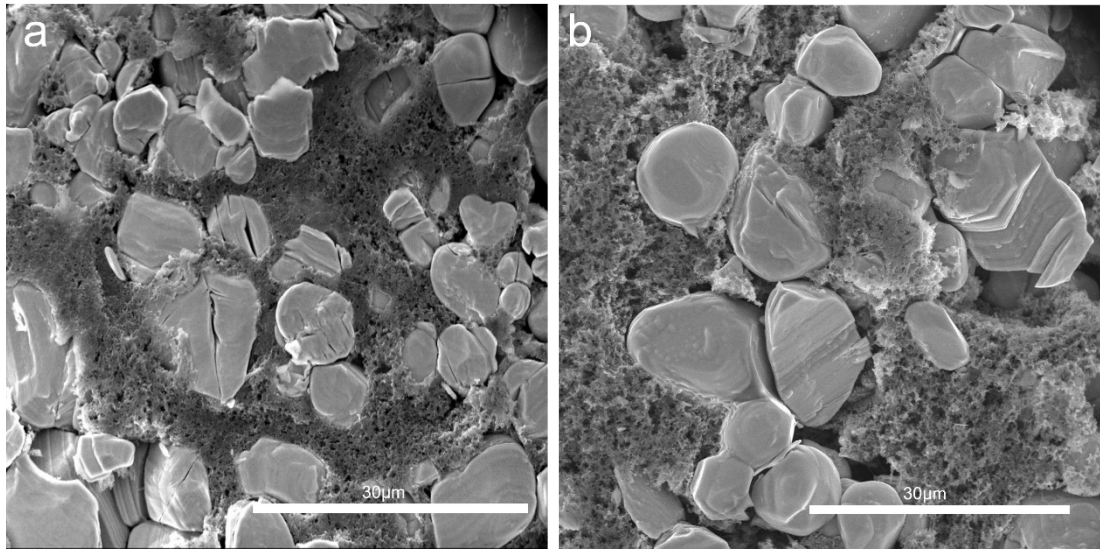
Supporting Figures

Figure S1 (a) SEM image of Bare-LCO at 5000x magnification; (b) SEM image of MB-LCO at 5000x magnification.
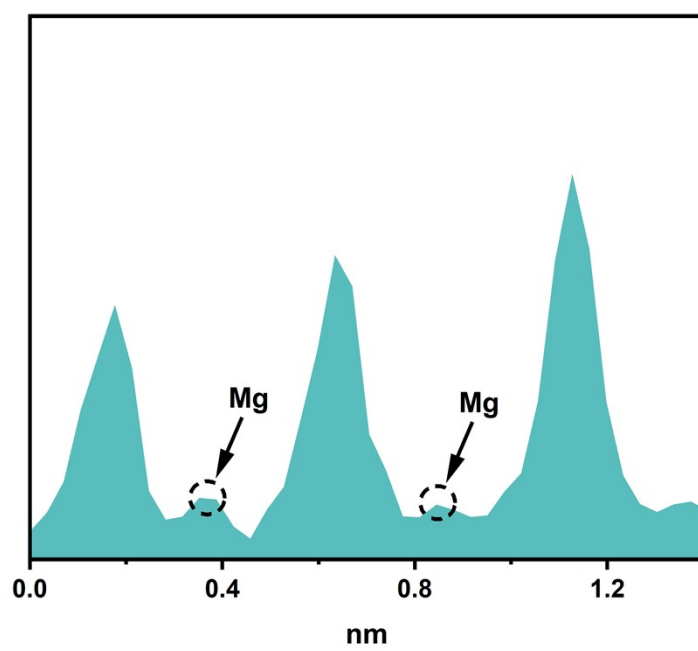
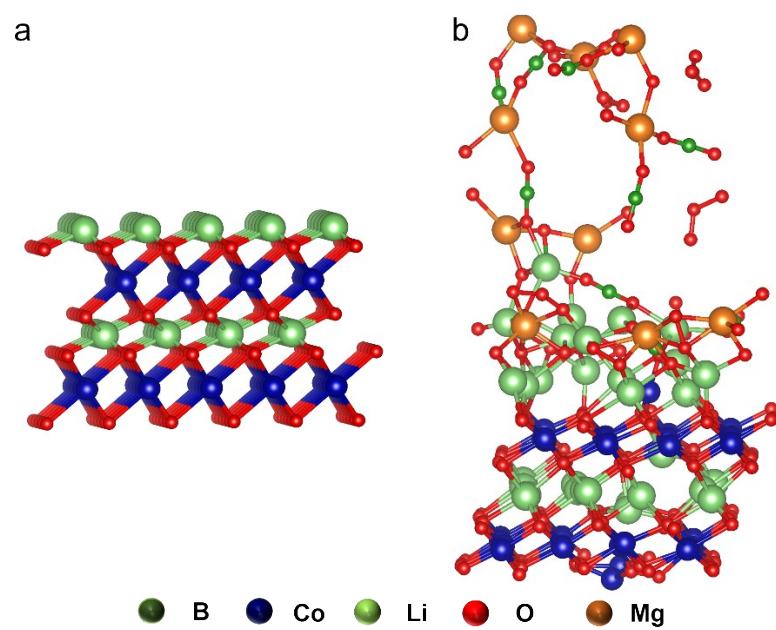**Figure S2** Lattice intensity map corresponding to Figure 2g

a   b

  ● B ● Co ● Li ● O ● Mg

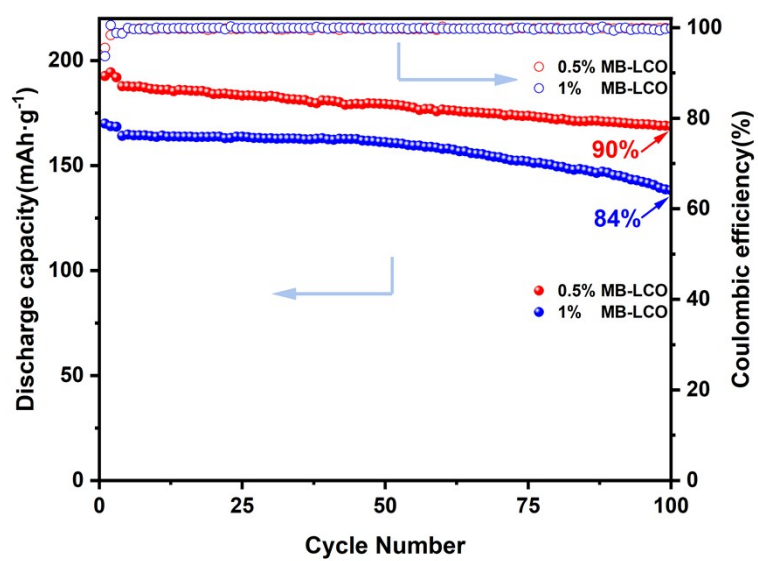**Figure S3** (a) Optimized structure of Bare-LCO; (b) Optimized structure of MB-LCO

Figure S4 Cycling performance of 0.5% MB-LCO and 1% MB-LCO at 1C
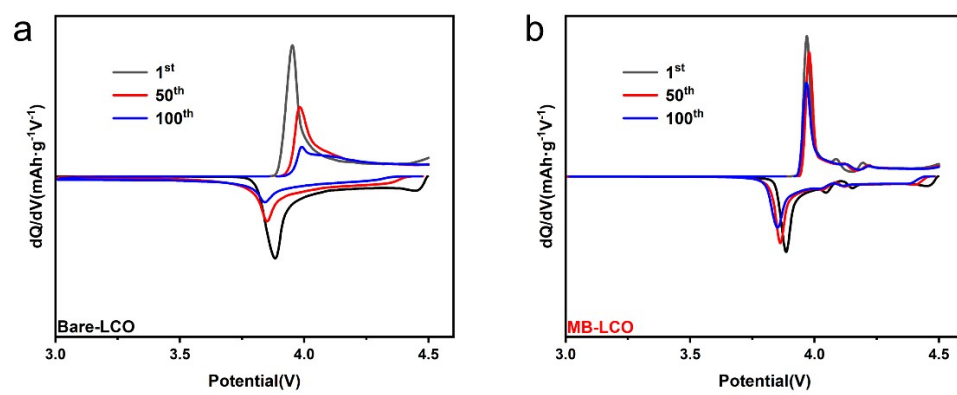
Figure S5 (a)dQ/dV curves of Bare-LCO (b) dQ/dV curves of MB-LCO

References

[1] P. E. Blöchl, *Phys. Rev. B* **1994**, *50*, 17953.

[2] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.

[3] D. Alfè, G. D. Price, M. J. Gillan, *Physics of the Earth and Planetary Interiors* **1999**, *110*, 191.

[4] H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* **1976**, *13*, 5188.