Supporting Information

Controllable Long-term Lithium Replenishment for Enhancing

Energy Density and Cycle Life of Lithium-ion Batteries

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1. Calculation methodology

Electrolyte uptake: The electrolyte uptake (Δ M) of the separator was measured by weighing the mass of the separator before and after immersing in electrolyte (1 M LiPF₆ in EC:DMC=3:7 vol% with 2 wt% VC) for 12 h, and then calculated according to the following equation:

$$\Delta M = \frac{m_e - m_0}{m_0} \times 100\%$$

where m_0 , m_e are the weight of the separator before and after immersing in liquid electrolytes, respectively.

Ionic conductivity: The ionic conductivity (σ) of the separator after electrolyte filling was calculated by measuring the bulk resistance of SS/separator/SS cells through electrochemical impedance spectroscopy (EIS). To eliminate the impact of the coating's electronic conductivity on the ion conductivity test, we symmetrically placed two pieces of LRS, with the coating layer sandwiched between PP substrate. The electron-insulating PP prevented direct contact between the coating layer and the stainless steel. The ion conductivity is calculated according to the following equation:

$$\sigma = \frac{1}{s \times R} \times 100\%$$

where l is the thickness of the separator, s is the contact area between SS and the separator, and R is the measured resistance.

2. Supporting figures



Fig. S1. SEM image of Li₂C₄O₄ obtained by vacuum drying at 80 °C



Fig. S2. Electronic conductivity of Li₂C₄O₄-CNT composite with different concentrations of CNT.



Fig. S3. FTIR spectra of Li₂C₄O₄.



Fig. S4. Thermogravimetric (TG) curves of the freshly-prepared Li₂C₄O₄ and Li₂C₄O₄ exposed in moist air for 7 days.



Fig. S5. Air stability tests of Li₂C₄O₄. (a) XRD pattern of freshly-prepared Li₂C₄O₄ and Li₂C₄O₄ stored in air for 180 days. (b) FTIR spectra of Li₂C₄O₄ before and after stored in air for one year. (c) ¹³C NMR spectra of Li₂C₄O₄ before and after stored in air for one year. (d) Galvanostatic charge profiles of freshly-prepared Li₂C₄O₄-3CNT and air-exposed Li₂C₄O₄-3CNT at 0.02 C.



Fig. S6. CV curves of Li₂C₄O₄-3CNT half cell.



Fig. S7. The top-view SEM and optical images of the prepared LRS. (a) The blank side of the LRS. (b) The Li₂C₄O₄-3CNT coated side of the LRS.



Fig. S8. The folding/recovery test of as-prepared LRS.



Fig. S9. Schematic diagram of the CLR strategy and SLR strategy.



Fig. S10 DEMS test with a 5-µm-thick CNT film interlayer between LRS and LFP.



Fig. S11. The SEM images of the LFP cathode with CLR strategy (a and b) and SLR strategy (c and d) after the initial cycle.



Fig. S12. Electrochemical Impedance Spectroscopy (EIS) for the LFP||Gr full cells with SLR and CLR strategies before cycling.



Fig. S13. Effects of LRS on resistance. Resistance of a cell (a) without lithium replenishment (b) with CLR strategy (c) with SLR strategy.



Fig. S14. Electrochemical Impedance Spectroscopy (EIS) for the LFP||Gr full cells with SLR and CLR strategies after 1st cycle.



Fig. S15. Overview and magnified SEM image of the LRS after the decomposition of $Li_2C_4O_4$ -3CNT.



Fig. S16. Initial charge-discharge profiles of the LRS||Li half cells.



Fig. S17. EIS spectra for the LFP||Gr full cells with SLR and CLR strategies when an extra amount of Li₂C₄O₄-3CNT is preloaded. (a) EIS spectra of full cells before cycling. (b) EIS spectra of full cells after 1st cycle, the Li₂C₄O₄-3CNT is partly decomposed.



Fig. S18. Thermal shrinkage behavior of PP separator and LRS-15 after thermal treatment for 10 min at 150 °C.



Fig. S19. The long-term lithium replenishment strategy validated by Li₂C₄O₄-3CNT||Li half cells. (a) Magnified charge-discharge profiles of one of the lithium replenishment processes.
(b) Charge profiles and allocation strategy of Li₂C₄O₄-3CNT at each lithium replenishment point (LRP).



Fig. S20. Charge/discharge curves of the full cells without lithium replenishment (a) and with long-term lithium replenishment (b) at different cycles.



Fig. S21. Charge-discharge profiles of LFP|LRS-15|Gr full cell at 2nd, 8th, 14th LRP (0.1 C charge, 0.05 C discharge).



Fig. S22. Electrochemical performance of LFP||Gr and LFP|LRS-15|Gr full cells. (a) Cycle performance of full cells at 0.5 C. (b-c) Charge-discharge profiles of full cells at 1st and 4th LRP.



Fig. S23. Long-term lithium replenishment strategy with LRP set after every 100 cycles.



Fig. S24 Initial charge-discharge curves and cycling performance of LFP||Gr full cells with different N/P ratios.