Supporting Information

Self-Assembled Tent-Like Nanocavities for Space-Confined Stable Lithium Metal Anode

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**Experimental Details**

***Preparation of Zn/CC samples***: Zn was plating on the carbon cloth (CC) with CHI 605 electrochemical workstation. Prior to electrodeposition, the CC (WS 1009, fabric mass: 11.46 mg cm-2, thickness: 300 μm) was pre-treated with hydrochloric acid, acetone, and ethanol for 15 min, respectively. Then the electrolyte was prepared by mixed 25 g zinc sulfate heptahydrate (ZnSO4·7H2O), 25 g sodium sulfate (Na2SO4), and boric acid (H3BO3) in 200 mL DI water. Typically, the Pt sheet was employed as the counter electrode, and the AgCl electrode was used as the reference electrode.[1] The electrodeposition parameters were set to the constant density of 0.16 mA for 10 min and obtained samples were dried in a 50℃ vacuum drying oven.

***Preparation of TLI-GO/Zn/CC samples***: The GO suspension was synthesized with the Hummer method with a PH of 6.[2] The prepared Zn/CC samples were immersed into GO suspension for 1 min, then the samples were dried in a vacuum oven for 5min and repeated 5 times of the same process, the TLI-GO/Zn/CC sample was prepared.[3]

***Structure Characterizations***: The microstructure and morphology of the samples were analyzed by scanning electron microscope (SEM, JEOL JSM-7100F) with an accelerating voltage of 20 kV. Powder X-ray diffraction (XRD) patterns were acquired through the D8 Discover X-ray diffractometer (Cu Kα radiation, λ=1.054056 Å). Raman spectra were recorded using DXR, Thermo-Fisher Scientific, with 532 nm excitation from an argon-ion laser. X-ray photoelectron spectroscopy (XPS) spectra were tested on the Thermo-Fisher Scientific- ESCALAB 250Xi. Fourier transform infrared spectrometer (FT-IR) was tested by Thermo Nicolet Corporation. Transmission electron microscope (TEM) and High-resolution transmission electron microscope (HRTEM) patterns were all performed by Talos F200 S. Mechanical properties of samples were measured using Atomic Force Microscope (AFM, Dimension Icon). Force-displacement curves were performed on the surface of samples using the force-distance spectroscopy mode, and Young’s modulus was calculated.

***Electrochemical Measurements***: CR2016-type coin cells were assembled to investigate the electrochemical performance in an Argon atmosphere glove box. Polypropylene (Celgard 2500) membrane was employed as the separator and the electrolyte was 1 M Li bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1,3-dioxolane (DOL)/1,2 dimethoxyethane (DME) (v/v = 1:1) binary mixture with 1 wt % LiNO3. The electrolyte dosage was fixed at an excess of 26 µL cm-2. Bare CC, Zn/CC, and TLI-GO/Zn/CC disks (12 mm) were pre-deposited 3 mAh cm-2 of Li, then the prepared electrodes were assembled into symmetric batteries. For the coulombic efficiency test, a fixed capacity of Li (1 mAh cm-2) was deposited by discharging at 1 mA cm-2 and then charged to 1 V. The symmetric battery tests and coulombic efficiency tests were carried out on Neware electrochemical testing system. Electrochemical impedance spectroscopy (EIS) were tested using Nova with scanning frequency range from 105 to 0.1 Hz. Full cells were assembled to characterize the feasible of the Li@TLI-GO/Zn/CC anode and the LiFePO4 (LFP) was chosen as cathode. LFP, acetylene black, and polyvinylidene fluoride (PVDF) were added to N-methyl-2-pyrrolidone (NMP) in a ratio of 7:2:1, and the loading of the active material is about 2.54 mg cm-2. The mixture solution was scraped evenly onto the carbon coated aluminum foil. Then the mixture was dried in a vacuum oven at 70 °C for 12 hours. The full cells were cycled at 2.6-4 V at different current densities on LAND electrochemical testing system.

***Computational details:*** All spin-polarized density functional theory (DFT) calculations within the generalized gradient approximation (GGA) were employed in the Vienna Ab Initio Package (VASP) using the Perdew-Burke-Ernzerhof (PBE) formulation.[4] The projected augmented wave (PAW) potentials were chosen to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 450 eV.[5] Partial occupancies of the Kohn−Sham orbitals were allowed using the Methfessel-Paxton smearing method and a width of 0.2 eV. The electronic energy was considered self-consistent when the energy change was smaller than 10−5 eV. A geometry optimization was considered convergent when the energy change was smaller than 0.02 eV Å−1. The vacuum spacing in a direction perpendicular to the plane of the structure is 15 Å. The adsorption energy of Li atoms was defined as Eb = Etotal - Eslab - ELi, where Eslab represents the energy of the studied system, Etotal is the energy of the corresponding system with Li atom adsorbed, and ELi is the energy of one isolated Li atom.[6] The interface binding energy (EI) between GO and Zn was calculated as EI = EZn + EGO - Etot, where Etot represents the energy of the studied system, EZn and EGO are the energy of Zn and GO of the system.

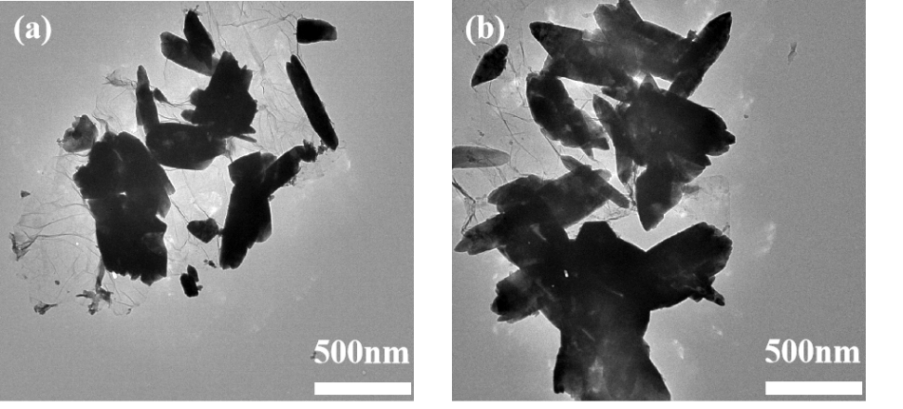


Figure S1. TEM images of TLI-GO/Zn/CC.

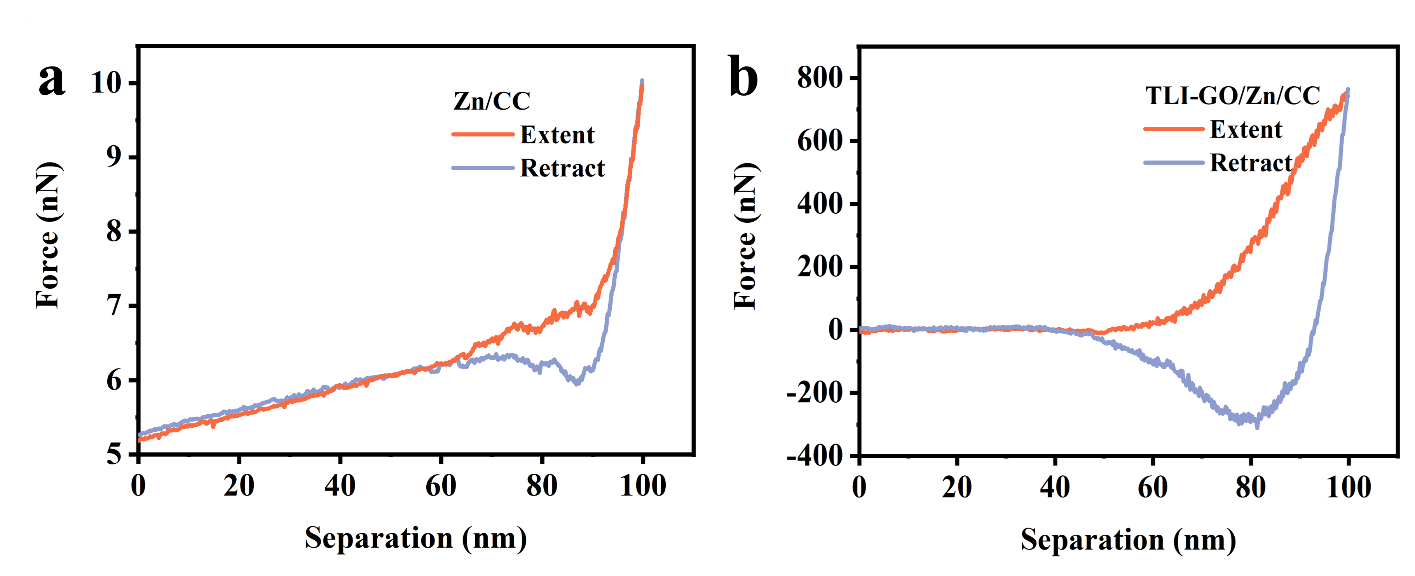
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Figure S2. Representative force-displacement curves for both Zn/CC (a) and TLI-GO/Zn/CC (b).

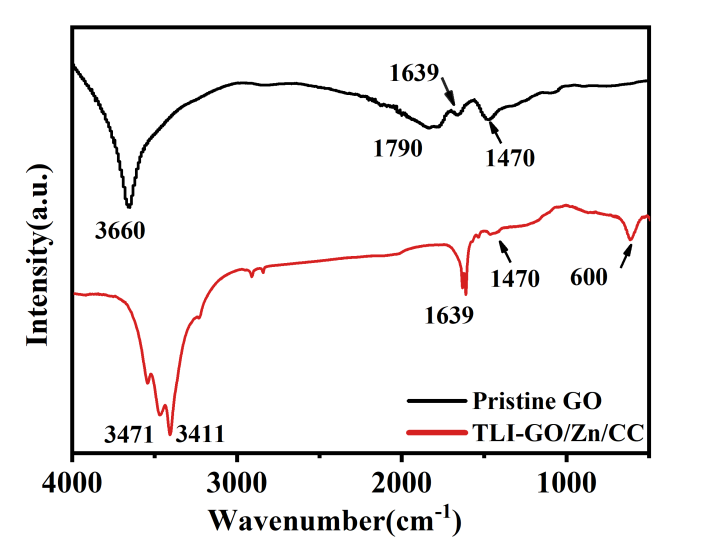


Figure S3. FTIR spectra of pristine GO and TLI-GO/Zn/CC.

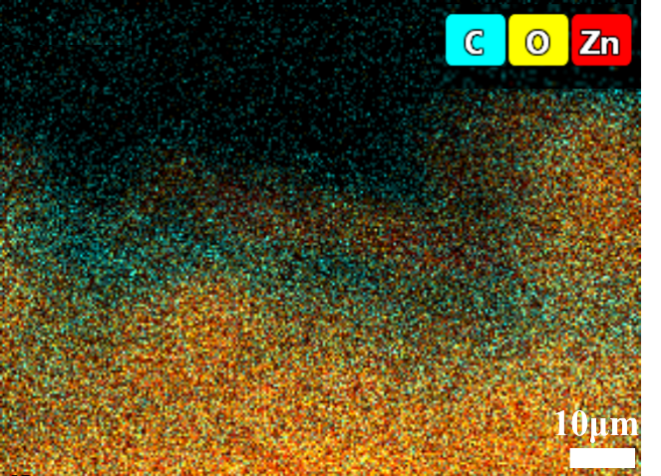


Figure S4. High magnification image with the SAED pattern of TLI-GO/Zn/CC.

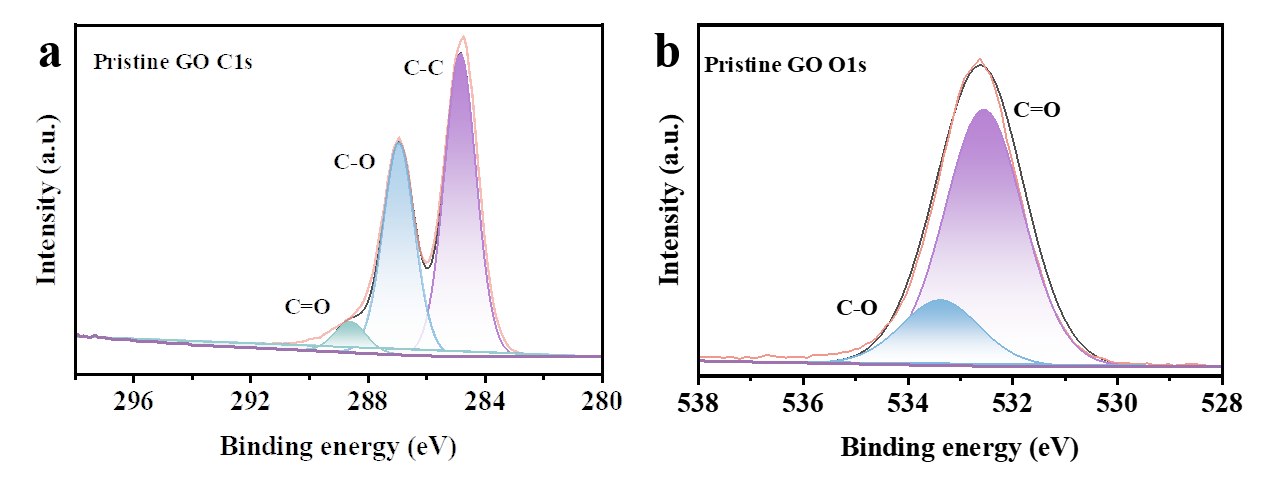


Figure S5. XPS spectra of C 1s (a) and O 1s (b) in pristine GO.

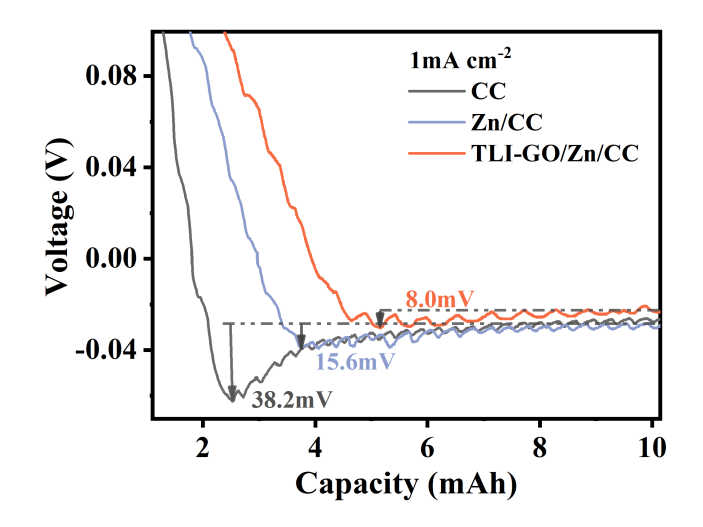


Figure S6. Voltage-capacity curves of Li plating/stripping at a current density of 1.0 mA cm-2 on varied electrodes.

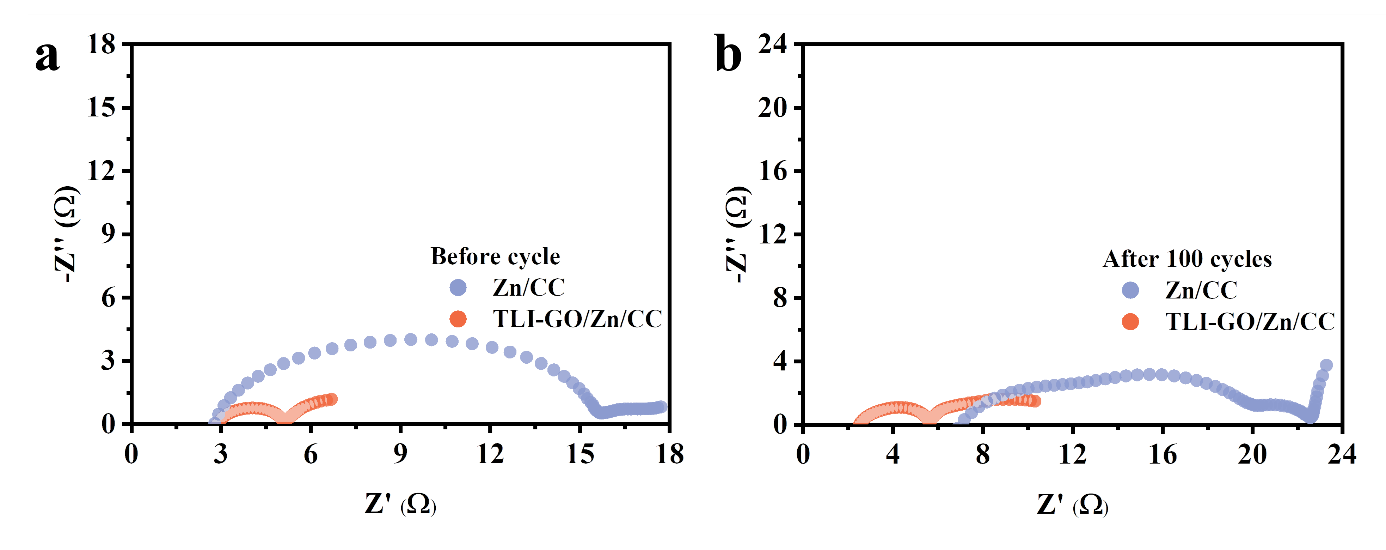


Figure S7. EIS spectra of Li-Zn/CC, and Li-TLI-GO/Zn/CC electrodes before (a) and after 100 cycles (b) at 1 mA cm-2.

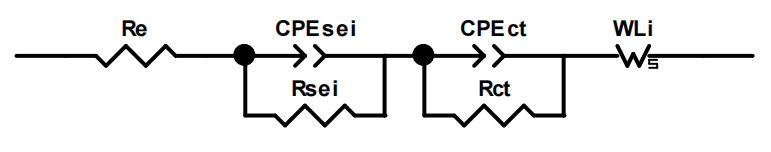


Figure S8. The equivalent circuit model for fitting the Nyquist diagrams.

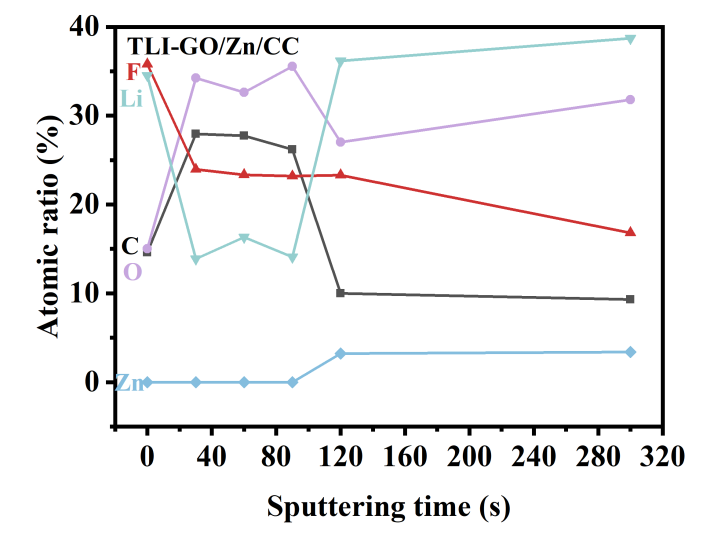


Figure S9. The corresponding depth profiles of the atomic concentration of Li, F, C, O and Zn elements of TLI-GO/Zn/CC.

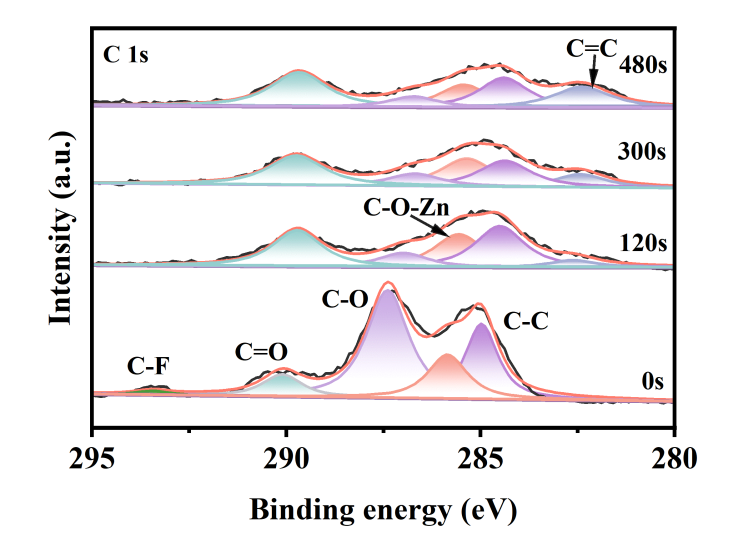


Figure S10. XPS depth profiling of C 1s at different sputtering times after 10th cycle.

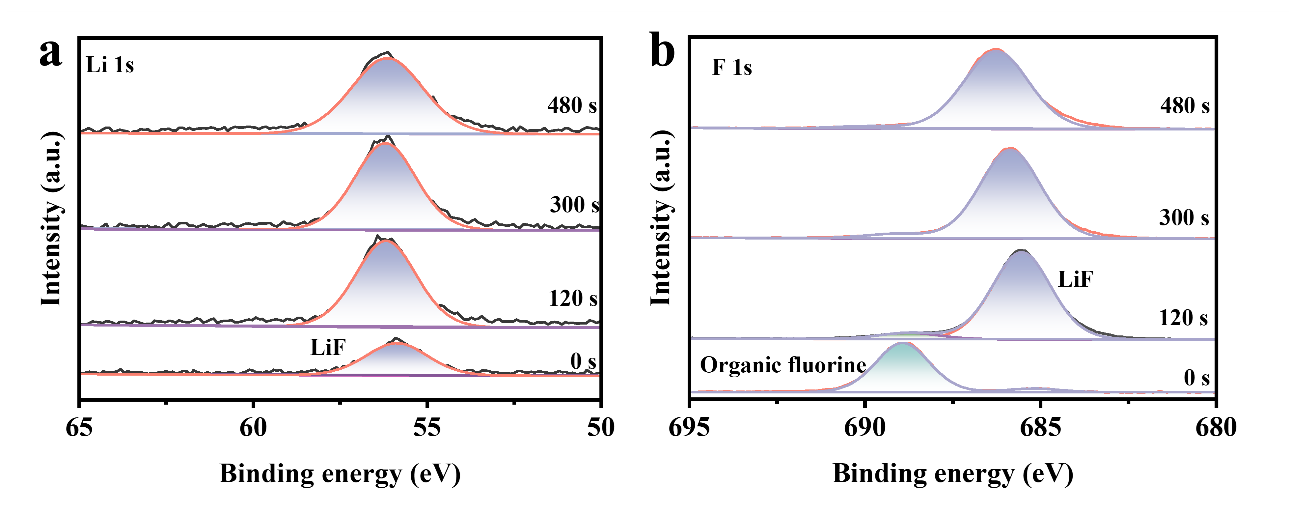


Figure S11. XPS depth profiling of Li 1s (a) and F 1s (b) at different sputtering times after the Zn/CC electrodes cycling 10 times.

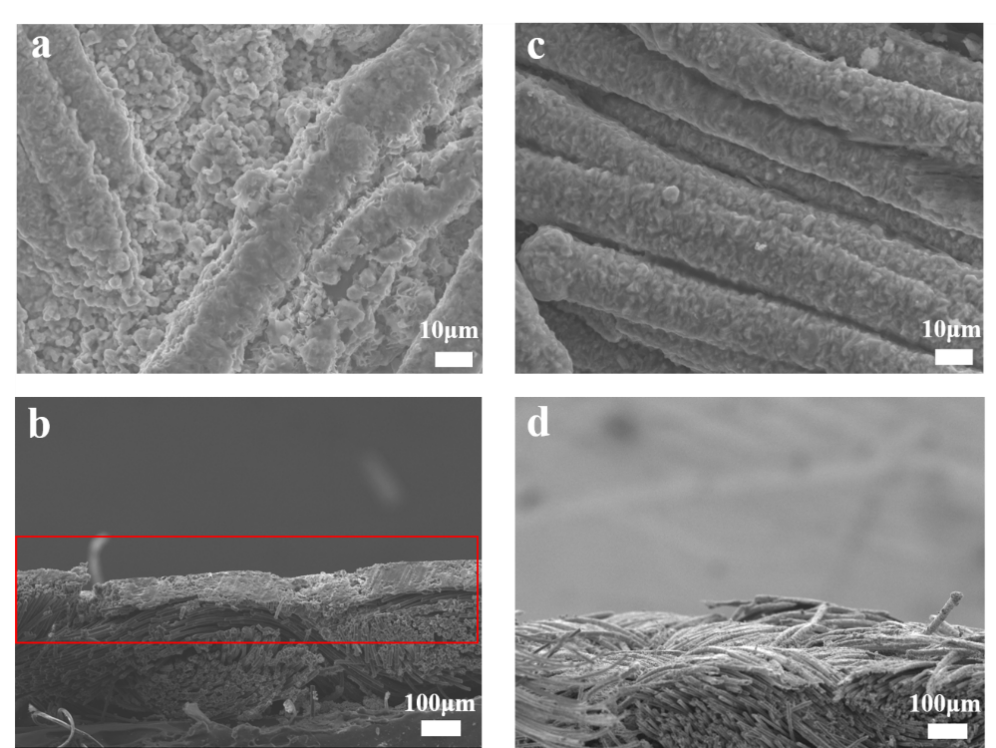


Figure S12. Morphology of plating with 1 mAh cm-2 and corresponding cross section images of Zn/CC (a, b) and TLI-GO/Zn/CC (c, d).

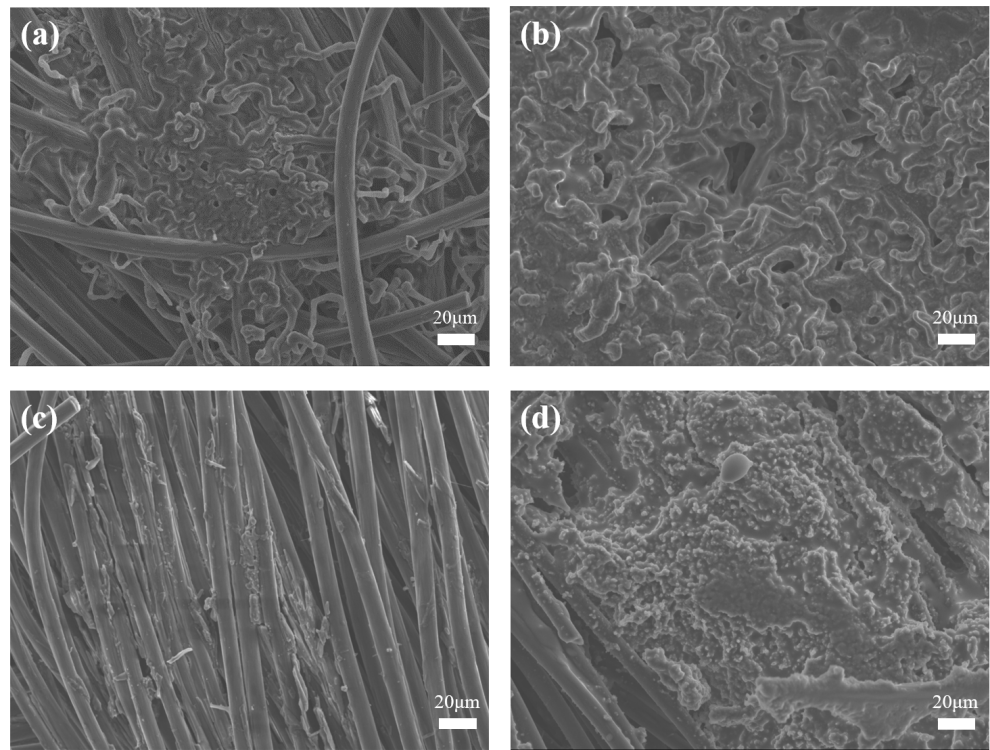


Figure S13. Morphology of CC at different states. SEM images of plating with 1 mAh cm-2 (a), 5 mAh cm-2 (b) and after 1st (c), 10th (d) cycle.

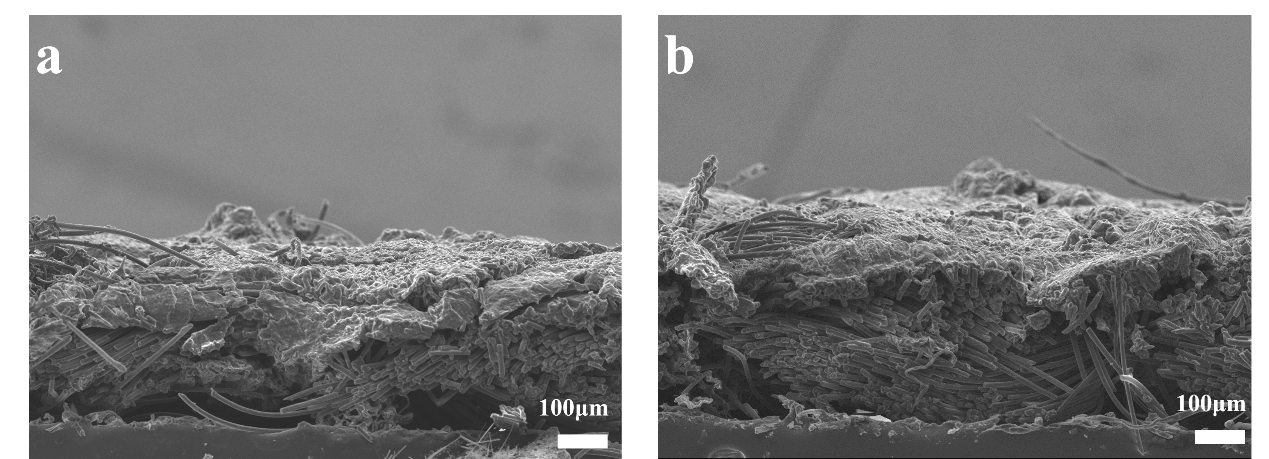


Figure S14. Morphology of cross section images after plating with 1 mAh cm-2 (a) and 5 mAh cm-2 (b) of CC.

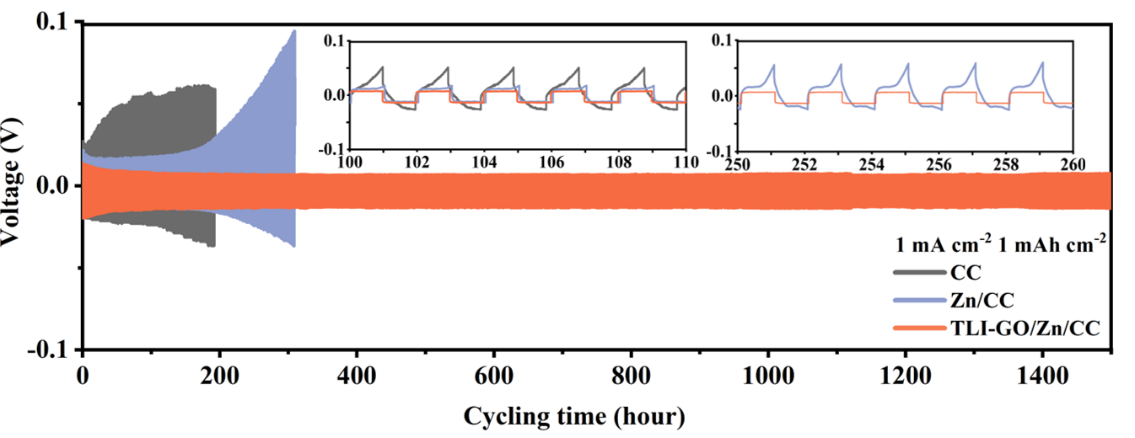


Figure S15. The Li/Li symmetrical battery performance and corresponding local magnified images at 1 mA cm-2.

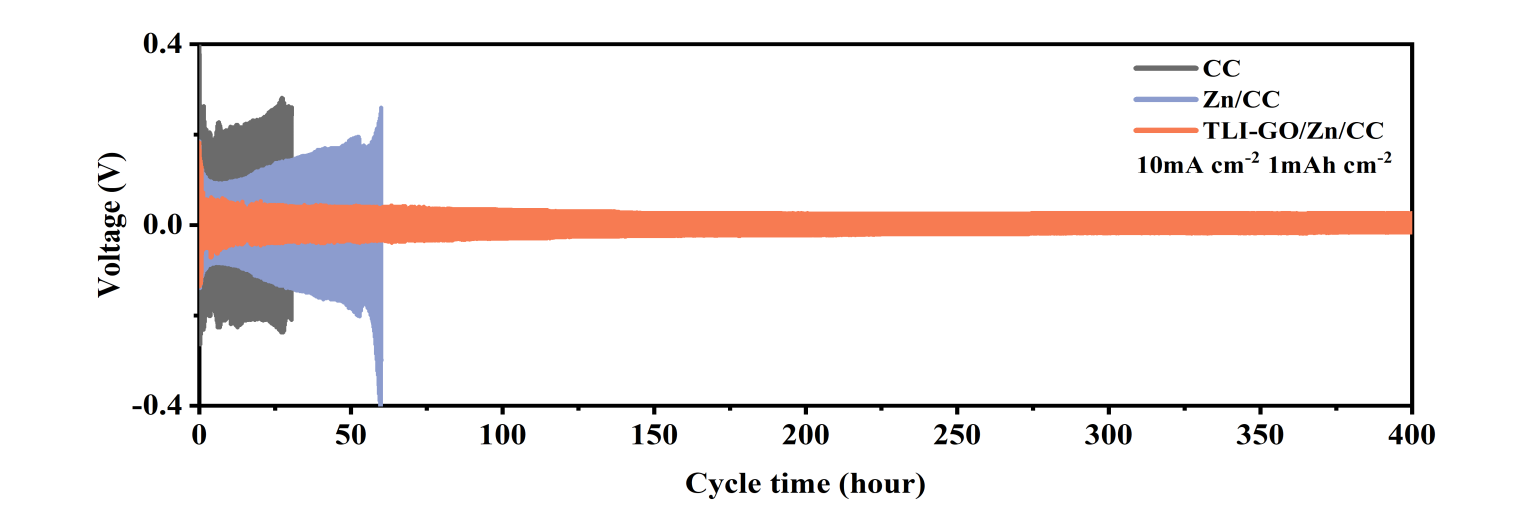


Figure S16. Cycling performance of Li/Li symmetric batteries with different electrodes at 10 mA cm-2, 1 mAh cm-2.

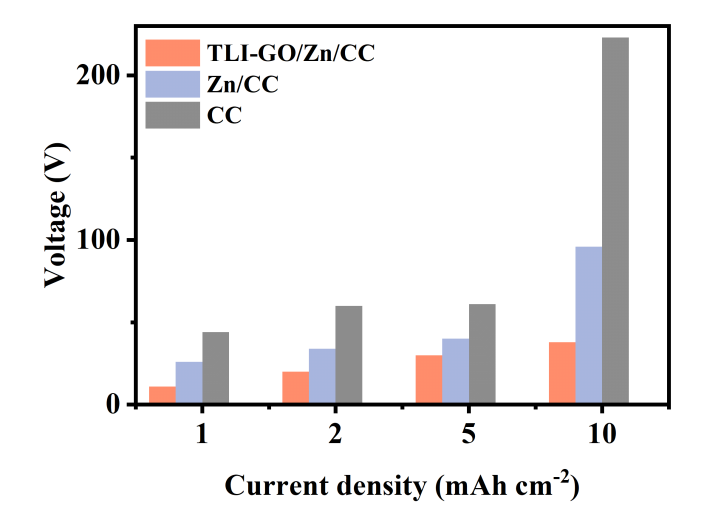


Figure S17. Voltage polarization histogram at different current conditions.

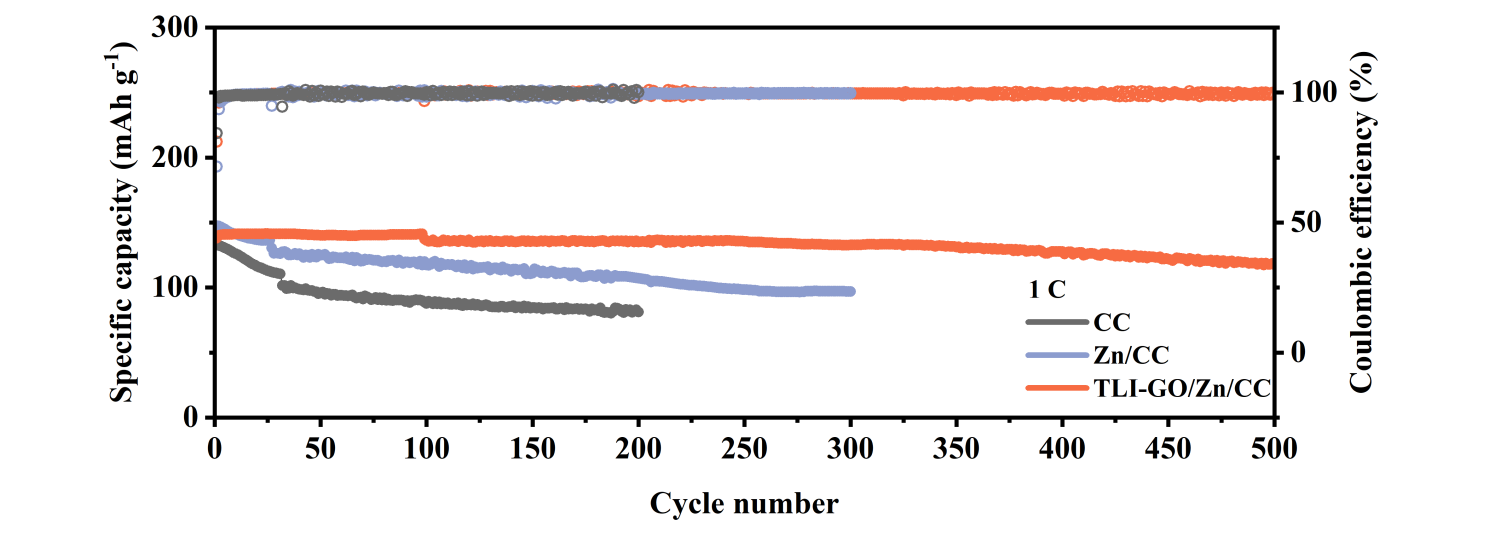


Figure S18. Voltage profiles for full cells with different anodes under 1 C.

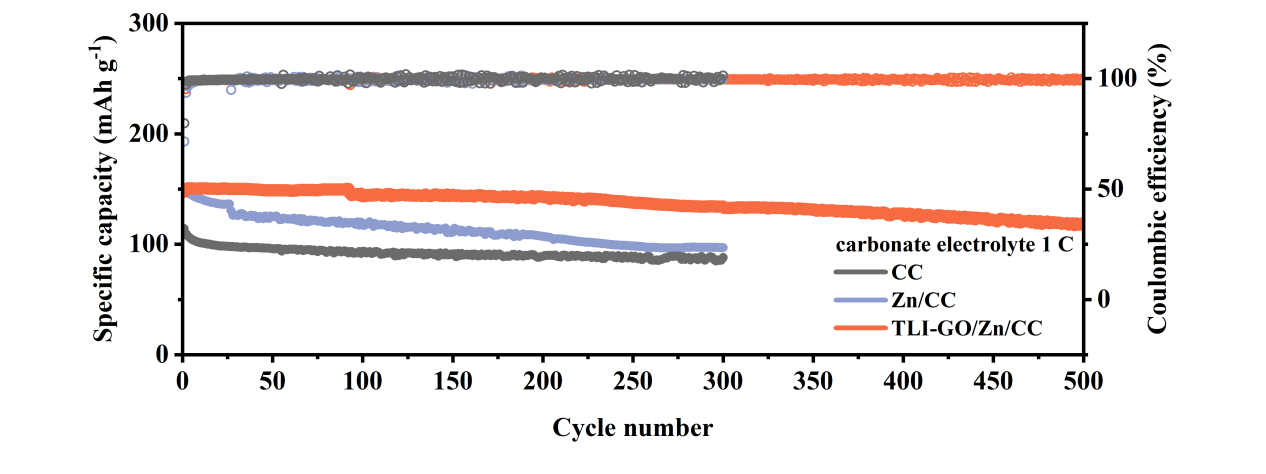


Figure S19. The cycling performances at 1 C in carbonate electrolytes.

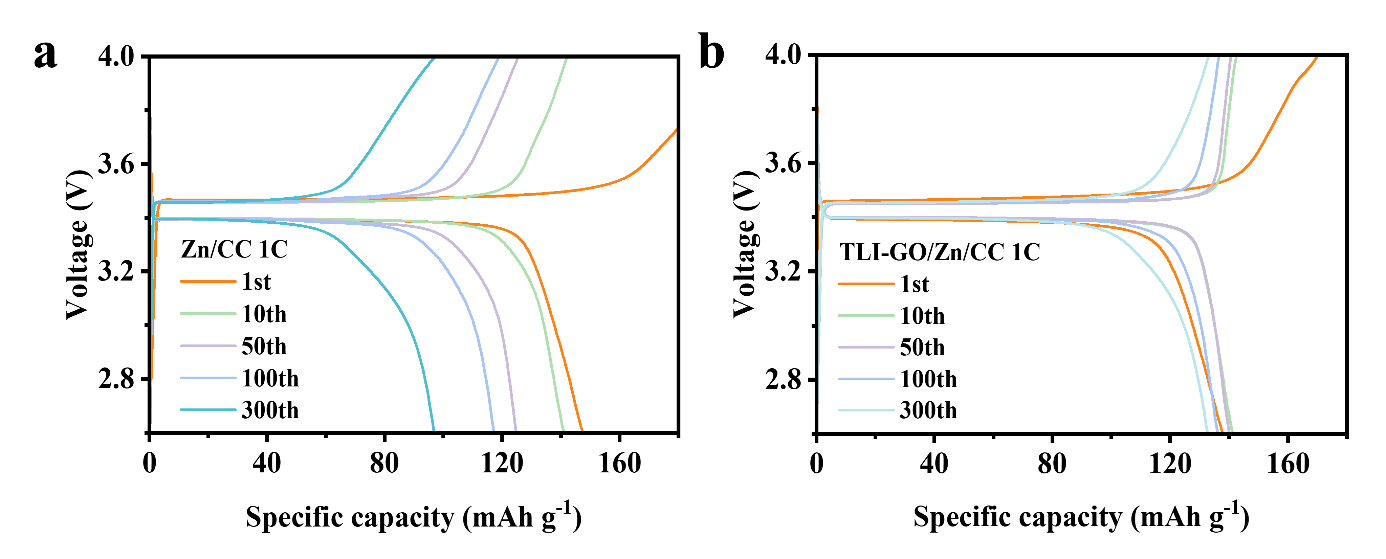


Figure S20. Charge/discharge profiles with different anodes at 1 C.

Table S1. The interface binding energy between GO and Zn layer of tent-like interface.

|  |  |  |  |
| --- | --- | --- | --- |
| **Etot/eV** | **EZn/eV** | **EGO/eV** | **EI/eV** |
| -407.57898 | -75.116355 | -305.26114 | 27.201485 |

Table S2. Absorption energy calculation of isolated Li atom to different substrates.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | **Etotal/eV** | **Eslab/eV** | **Eb/eV** | **ELi/eV** |
| Li to Zn slab | -82.497 | -80.663 | -1.792 | -0.042 |
| Li to Zn–O–C | -407.579 | -410.676 | -3.097 |

Table S3. The resistances of fitting results in Zn/CC@Li and TLI-GO/Zn/CC@Li symmetric cells.

|  |  |  |  |
| --- | --- | --- | --- |
| **Sample** | **Re (ohm)** | **Rsei(ohm)** | **Rct (ohm)** |
| Zn/CC | 2.6924 | 13.388 | 3.9805 |
| Zn/CC after 100th | 6.9438 | 14.370 | 3.284 |
| TLI-GO/Zn/CC | 2.8944 | 2.2795 | 3.8096 |
| TLI-GO/Zn/CC after 100th | 2.569 | 3.1753 | 4.6094 |

Table S4. Comparison of cycling life of symmetrical batteries with Li@TLI-GO/Zn/CC composite anodes and various reportes interface-modified anodes under different current densities.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Refer** | **Current**  **(mA cm-2)** | **Capacity**  **(mAh cm-2)** | **Cycle time (hour)** | **Overpotential (mV)** | **Samples** |
| [7] | 2 | 1 | 800 | 20 | Co@C@CC |
| [8] | 1 | 1 | 1000 | 25 | LiC6@C |
| [9] | 1 | 1 | 1000 | 30 | Li@CFeltCu |
| [10] | 1 | 1 | 400 | 60 | Li@CF/Ag |
| [11] | 1 | 1 | 600 | 40 | SRC-Zein@CS |
| [12] | 1 | 1 | 600 | 15 | (CNT)/NiO |
| [13] | 1 | 1 | 1200 | 25 | NCH-CFs |
| [14] | 1 | 1 | 400 | 24 | Cu3P/CoP@C/CNT |
| [15] | 3 | 1 | 800 | 120.8 | Li@GaLi |
| [16] | 1 | 1 | 1600 | 50 | Li@DPL |
| [17] | 0.5 | 1 | 1000 | 10 | Li@MMT |
| [18] | 1 | 1 | 1500 | 17 | Li@MCI |
| [19] | 1 | 1 | 1200 | 40 | Li@PTCDI |
| [20] | 1 | 1 | 1200 | 15.2 | Zn-MXENE |
| [21] | 0.5 | 0.5 | 1050 | 12 | Ti3C2Tx/g-C3N4 |
| [22] | 1 | 1 | 1000 | 14 | LTO/PVDF |
| [23] | 1 | 2 | 1100 | 36 | Li@N-organic/Li3N |
| This work | 1 | 1 | 1600 | 11 | Li@TLI-GO/Zn/CC |

Remarks: all the electrolytes are LiTFSI in DOL/DME (v/v = 1:1) with x mol% LiNO3 in the table.

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