Supporting Information

# **3D** lithiophilic-lithiophobic-lithiophilic dual gradient porous skeleton for highly stable lithium metal anode

Hongfei Zheng, Qingfei Zhang, Qiulin Chen, Wanjie Xu, Qingshui Xie\*, Yuxin Cai, Yating Ma, Zhensong Qiao, Qing Luo, Jie Lin, Laisen Wang, Baihua Qu, Baisheng Sa\*, and Dong-Liang Peng\*

H. Zheng, Q. Zhang, Q. Chen, W. Xu, Y. Cai, Dr. Y. Ma, Z. Qiao, Q. Luo, Dr. J. Lin, Dr. Q. Xie, Dr. L. Wang and Prof. D.-L. Peng

Department of Materials Science and Engineering, State Key Lab of Physical Chemistry of Solid Surface, Collaborative Innovation Center of Chemistry for Energy Materials, College of Materials, Xiamen University, Xiamen 361005, China.

Dr. B. Qu

Pen-Tung Sah Institute of Micro-Nano Science and Technology, Xiamen University, Xiamen 361005, China

Dr. B. Sa

Key Laboratory of Eco-materials Advanced Technology, College of Materials Science and Engineering, Fuzhou University, Fuzhou 350108, PR China Corresponding author: xieqsh@xmu.edu.cn (Q. Xie), bssa@fzu.edu.cn (B. Sa), dlpeng@xmu.edu.cn (D.-L. Peng). Tel: 86-592-2180155; Fax: 86-592-2183515.

# **Experimental Section**

#### 1. Preparation of Cu-Au-ZnO-PAN-ZnO current collector

Cu foil was rinsed with 5% oxalic acid  $(H_2C_2O_4)$  to remove surface coatings and oxides, and then rinsed by alcohol for three times before serving as substrate. Thin Au film was directly deposited on Cu foil by magnetron sputtering. The polyacrylonitrile (PAN) fiber skeleton fabricated by electrostatic spinning was modified by zinc oxide (ZnO) on both surface by magnetron sputtering to develop porous lithiophiliclithiophobic-lithiophilic dual-gradient ZnO-PAN-ZnO skeleton. The thickness of ZnO deposited on PAN skeleton was controlled by the sputtering time. The obtained ZnO-PAN-ZnO skeleton was covered on the Au surface to prepare desired Cu-Au-ZnO-PAN-ZnO (CAZPZ) current collector.

#### 2. Preparation of Cu-Au-ZnO-PAN-ZnO-Li Hybrid Anode

After galvanostatic activation process at 0.05 mA cm<sup>-2</sup> from 0.01 V to 0.5 V for 5 cycles to remove surface contamination and stabilize the SEI layer, Li was pre-plated into the CAZPZ current collector at 0.25 mA cm<sup>-2</sup> for 5 mA h cm<sup>-2</sup> in CAZPZ || Li cells. Then the cells were disassembled and the CAZPZ-Li electrode was taken out and used as protected Li hybrid anode. The ZnO-PAN-ZnO skeleton and deposited Li were controlled to be 1.1 mg cm<sup>-2</sup> and 1.3 mg cm<sup>-2</sup>, respectively.

## 3. Preparation of LTO, LFP and MNC-411 electrodes

To prepare LTO, LFP and MNC-411 cathodes, 70wt% of active materials (commercial LTO and LFP materials and self-prepared MNC-411 Li-rich layered oxide

materials) were mixed with 20 wt% of acetylene black and 10 wt% of polyvinylidene fluoride (PVDF) using N-Methy 1-2-pyrrolidone (NMP) as the solvent. The obtained slurry was directly coated on A1 current collector and then dried in a vacuum oven at 80 °C for 10 h. The average mass loading of active materials for LTO, LFP and MNC-411 electrodes were 2 mg cm<sup>-2</sup>, 2 mg cm<sup>-2</sup> and ~1 mg cm<sup>-2</sup>.

#### 4. General characterizations

X-ray diffraction (XRD) (Rikagu Ultima IV, Cu Kα radiation source, 40 kV, 40 mA) was used to obtain structural information. The SEM images and corresponding EDX elemental mappings were recorded on an SEM (Hitachi SU-70).

### 5. Electrochemical Measurements

Coin-type cells (2025) were assembled in the Ar-filled glovebox (the content of  $O_2$  and  $H_2O < 1.0$  ppm) with the counter electrode of Li foils, the working electrodes of pure Cu, Au (Au was sputtered on Cu foil), Cu-PAN, Cu-Au-PAN and Cu-Au-ZnO-PAN-ZnO and the separator of Celgard 2300 polyethylene film. The 1 M LiTFSI in DOL/DME (V/V = 1:1) with 1.0 wt% LiNO<sub>3</sub> additive was used as the electrolyte (70 µL). The cycling and rate performances measurements were performed on Neware battery testing system. The Coulumbic ellciency was tested after galvanostatic activation process. The discharge time was fixed for limited capacity in the lithium plating process, and the charge time in the lithium stripping process was controlled by a cut-off voltage of 0.5 V. To measure the time-voltage curves, the charge/discharge capacity was fixed with desirable current densities. Electrochemical impedance

spectroscopy (EIS) (Frequency is 0.1 MHz to  $1 \times 10^{-2}$  Hz and perturbation amplitude is 5 mV) tests were carried out on an Autolab electrochemical workstation (NOVA 1.9).

The full cells, CAZPZ-Li || LTO/ LFP/ MNC-411, were assembled to measure the lithium storage properties of CAZPZ-Li anode and its compatibility property with different cathodes. In CAZPZ-Li || LFP and CAZPZ-Li || LTO full cells, the electrolyte was 1 M LiTFSI in DOL/DME (V/V = 1:1) with 1.0 wt% LiNO<sub>3</sub> additive. In CAZPZ-Li || MNC-411 full cells, the high voltage electrolyte was mainly composed of 1M LiPF<sub>6</sub> in a mixed solvent of EMC/EC/DMC (1:1:1 in volume). The electrolyte amount in LTO/ LFP/ MNC-411-based full cells was 50 µL. CAZPZ-Li || LTO full cells were tested within 1.0-3.0 V (vs. Li/Li<sup>+</sup>) at a rate of 1 C (1 C =175 mA g<sup>-1</sup>) in the initial cycle and 5 C or 10 C in subsequent cycles at ambient temperature. The CAZPZ-Li || LFP cells were tested from 2.5V to 4.0V at a rate of 0.1 C (1 C =170 mA g<sup>-1</sup>) in the initial cycle and 1 C or 5 C in subsequent cycles at ambient temperature. For CAZPZ-Li || MNC-411 cells, the voltage range was 2.0-4.6 V and the initial cycle was tested at 0.2 C (1 C =250 mA g<sup>-1</sup>) at ambient temperature.

#### 6. Simulation of the electric field distribution

The electric field distribution on the surface of Cu and CAZPZ current collectors after Li nucleation formation was simulated using the finite element method and the Comsol Multiphysics software was utilized. The length of two-dimensional electrodeposition models was set to 15 µm and the height of electrolyte, Li, Cu, and Au was set to 50, 15, 5, and 1 µm, respectively. The ZnO-PAN-ZnO skeleton was depicted according to its sectional view and the ZnO-PAN-ZnO skeleton was set with diameter of 500 nm and height of 15 µm. The interval between the neighboring two bundles in ZnO-PAN-ZnO skeleton was 1 µm. To simplify the model, the porous ZnO-PAN-ZnO skeleton structure is considered as a unified mesh structure. The dendrite nuclei is assumed to have a diameter of 200 nm and a height of 2 µm. The dielectrical coefficient of 1 M LiTFSI in 1:1 DOL: DME was set to 7.15 according to linear superposition result of volume (the dielectric coefficient of DOL is 7.1 and the dielectric coefficient of DME is 7.2). The dielectric coefficients of ZnO are set as  $\varepsilon_{11}=\varepsilon_{22}=8.55$  and  $\varepsilon_{33}=11.52$ , the dielectric coefficient of PAN is 3.1. The overpotential of 500 mV was employed as voltage excitation. The electric field distribution is acquired according to the following relationship:

$$\nabla \mathbf{D} = \rho_{v} \tag{1}$$

$$\mathbf{E} = -\nabla \mathbf{V} \tag{2}$$

where D,  $\rho_v$ , E and V are electric displacement, charge density, electric field and potential, respectively.

#### 7. Computational details

Our density functional theory (DFT) calculations were performed by using the GPU accelerated Vienna ab initio simulation package (VASP)<sup>1, 2</sup> in conjunction with the projector augmented wave (PAW) generalized gradient approximations (GGA)<sup>3</sup> of

Perdew-Burke-Ernzerhof (PBE)<sup>4</sup> pseudopotentials and the Grimme's dispersioncorrected method (D3)<sup>5</sup>. The valence electron configurations for the Li, Cu, Au, and O were  $2s^1$ ,  $4s^{13}d^{10}$ ,  $6s^{15}d^{10}$ , and  $2s^22p^4$ , respectively. The relaxation convergence for ions and electrons were  $1 \times 10^{-5}$  and  $1 \times 10^{-6}$  eV, respectively, which were achieved with the cut-off energy of 700 eV. The crystal structures and isosurfaces were visualized by using the VESTA package.<sup>6</sup> We used five-layer (111) slab with  $2 \times 2 \times 1$  supercell models to simulate the anode surfaces. We fixed the atoms in the bottom two layers as the bulk part. And all the other atoms were fully relaxed. The absorption models were set up with a vacuum space of 30 Å to avoid the coupling between periodically neighboring structures.<sup>7</sup> The  $3 \times 3 \times 1$  K-point grid with  $\Gamma$  symmetry was set for all the calculations. The Li-anode binding energy  $E_b$  was calculated as following<sup>8</sup>:

$$E_{\rm b} = E_{\rm total}^{\rm Li-anode} - E_{\rm total}^{\rm anode} - E_{\rm total}^{\rm Li-atom}, \qquad (3)$$

where  $E_{\text{total}}^{\text{Li-anode}}$ ,  $E_{\text{total}}^{\text{anode}}$  and  $E_{\text{total}}^{\text{Li-atom}}$  are the total energy of anode surface bound with one Li atom, the pristine anode surface, and single Li atom, respectively.

During the first discharging process, the adsorbed Li atoms would interact with ZnO to form Zn nanocrystals embedded into Li<sub>2</sub>O matrices according to the following reaction:

$$2\text{Li}+\text{ZnO} \rightarrow \text{Zn}+\text{Li}_{2}\text{O}$$
 (4)

And we have got the reaction energy  $E_r = -3.04$  eV from the DFT calculations by:

$$E_{\rm r} = E_{\rm total}^{\rm Zn} + E_{\rm total}^{\rm Li_2O} - 2E_{\rm total}^{\rm Li} - E_{\rm total}^{\rm ZnO}, \qquad (5)$$

where  $E_{\text{total}}^{\text{Zn}}$ ,  $E_{\text{total}}^{\text{Li}_{2}\text{O}}$ ,  $E_{\text{total}}^{\text{ZnO}}$  and  $E_{\text{total}}^{\text{Li}}$  are the calculated total energy of bulk Zn, Li<sub>2</sub>O, ZnO, and Li, respectively. The negative value of the reaction energy indicates that the

ZnO reduction process is a spontaneous exothermic reaction.



**Fig. S1.** Schematic diagram for the preparation of 3D Cu-Au-ZnO-PAN-ZnO current collector.



**Fig. S2.** (a) Cross-sectional SEM image of ZnO-PAN-ZnO skeleton, the thickness is about 80 μm (the film is fluffy and its thickness will change within slight range depend on the pressure on it). The EDX data of (b) region 1, (c) region 2 and (d) region 3 in Fig. S2a. Fig. S2a-d reveal that the content of ZnO is higher on the top and bottom parts but nearly nonexistent in the middle, which evidence the successful fabrication of 3D porous lithiophilic-lithiophobic-lithiophilic dual-gradient ZnO-PAN-ZnO skeleton.



**Fig. S3.** SEM images of surface morphology for (a) Cu foil and (b) Cu-Au substrate. The corresponding EDS-mappings of (c) Cu and (d) Au in the red rectangle in Fig. S3b.



**Fig. S4.** Optical images of (a) pure PAN (white), (b) ZnO-PAN-ZnO (faint yellow), (c) pure Cu foil (copper red), (d) Cu-Au foil (golden), (e) Cu-Au electrode and (f) Cu-Au-ZnO-PAN-ZnO current collectors.



**Fig. S5.** Voltage profiles of Cu, Au and Cu-Au-ZnO-PAN-ZnO current collectors during Li plating under current density of 0.05 mA cm<sup>-2</sup> for fixed capacity of 1 mA h cm<sup>-2</sup>.



**Fig. S6.** Cross-sectional SEM images of CAZPZ-Li after plating for (a) 0.5 mA h cm<sup>-2</sup>, (b) 1 mA h cm<sup>-2</sup>, (c) 3 mA h cm<sup>-2</sup>, (d) 5 mA h cm<sup>-2</sup> and (e) 10 mA h cm<sup>-2</sup>. (f) Crosssectional SEM image of CAZPZ after stripping for 10 mA h cm<sup>-2</sup>. Optical images of CAZPZ surface after plating for (g) 5 mA h cm<sup>-2</sup> and (h) 10 mA h cm<sup>-2</sup>. Top-view SEM images of CAZPZ surface after plating for (i) 5 mA h cm<sup>-2</sup> and (j) 10 mA h cm<sup>-2</sup>. It is easily found that when plating 5 mA h cm<sup>-2</sup> of Li, CAZPZ surface remains its original porous structure, while Li grows outside of the surface partially after 10 mA h cm<sup>-2</sup>. The plated Li would fill into the porous space of ZnO-PAN-ZnO skeleton from bottom to top, and no Li dendrite form on the surface of CAZPZ even excess Li plating.



**Fig. S7.** The voltage profiles of (a) Cu-Au-ZnO-PAN-ZnO and (b) Cu firstly cycled at 0.01-0.5 V (vs. Li/Li<sup>+</sup>) at 0.05 mA cm<sup>-2</sup> for 5 cycles for the contamination removal and interface stabilization. It needs to be mentioned that the electrochemical tests with the working electrodes of pure Cu, Au, Cu-PAN, Cu-Au-PAN and Cu-Au-ZnO-PAN-ZnO started after the galvanostatic activation process at 0.05 mA cm<sup>-2</sup> from 0.01 V to 0.5 V versus Li/Li<sup>+</sup> for 5 cycles to remove surface contamination and stabilize the SEI layer.



**Fig. S8.** Comparison of the voltage profiles of (a) Cu-Au-ZnO-PAN-ZnO || Li, (b) Cu-Au-PAN-ZnO || Li, (c) Cu-Au-ZnO-PAN || Li and (d) Cu-ZnO || Li asymmetrical cells when discharged to 0.01 V (vs. Li/Li<sup>+</sup>) at 0.05 mA cm<sup>-2</sup> in the first cycle. The conductivity of polyacrylonitrile (PAN) is ~1.0\*10<sup>-9</sup> S/m, while that of Au is as high as ~4.17\*10<sup>7</sup> S/m, the PAN-based skeleton shows much poorer electronic conductivity than Cu-Au substrate. During the initial lithiation process in CAZPZ || Li cell (Fig. S8 (a)), the voltage rapidly decreases from 1.84 V to 0.35 V and then increases to 0.43 V, finally decreases very slowly in the voltage range of 0.43-0.28 V. This inclined voltage plateau from 0.43 to 0.28 V corresponds to the conversion reaction between ZnO and Li<sup>+</sup> ions/electrons to form Zn nanocrystals and Li<sub>2</sub>O. In contrast, the conversion reaction between ZnO || Li cell (Fig. S8 (d)). Distinctly, CAZPZ || Li asymmetrical cell shows larger voltage polarization than Cu-ZnO || Li cell. The ZnO-PAN-ZnO skeleton is poor conductive, thus, the conversion reaction kinetics of upper ZnO in skeleton during

lithiation process is limited, finally leading to large voltage polarization. The voltage profiles of Cu-Au-PAN-ZnO || Li and Cu-Au-ZnO-PAN || Li asymmetrical cells (Fig. S8 (b-c)) further confirm that the ZnO (no matter on the bottom or top of the skeleton) can participate in the electrochemical reaction before Li plating during initial lithiation process, and the huge voltage polarization can also be seen in the Cu-Au-PAN-ZnO || Li asymmetrical cell due to its difficulty of obtaining the electrons for upper ZnO. To conclude, although ZnO-PAN-ZnO skeleton possesses poor electronic conductivity, the conversion reaction between ZnO (no matter on the bottom or top of the skeleton), Li<sup>+</sup> ions and electrons would take place prior to Li plating during the initial lithiation process, and the huge voltage polarization occurs during the conversion lithiation process of upper ZnO due to the limited electrochemical reaction kinetics caused by the much poorer electronic conductivity of ZnO-PAN-ZnO skeleton than Cu-Au substrate.



**Fig. S9.** The SEM images and optical images of top surface in CAZPZ (a) before and (b) after the electrochemical reactions of ZnO with Li<sup>+</sup> ions and electrons. The morphology and color changes in the top surfaces of CAZPZ prove that the upper ZnO would react with Li<sup>+</sup> ions and electrons before Li plating during initial lithiation process.



**Fig. S10.** Top-view SEM images of Cu surface after (a) 5th, (b) 50th and (c) 100th cycles at 0.5 mA cm<sup>-2</sup>. Top-view SEM images of (d) Cu-PAN, (e) Cu-Au and (f) Cu-Au-PAN surfaces after 100th cycles at 0.5 mA cm<sup>-2</sup>. Top-view SEM images of Cu-Au-ZnO-PAN-ZnO surface after (g) 5th, (h) 50th and (i) 100th cycles at 0.5 mA cm<sup>-2</sup>.



**Fig. S11**. Optical images of Cu surface after (a) 5th, (b) 25th, (c) 50th and (d) 100th cycles at 0.5mA cm<sup>-2</sup>. Optical images of Cu-Au-ZnO-PAN-ZnO surface after (e) 5th, (f) 25th, (g) 50th and (h) 100th cycles at 0.5 mA cm<sup>-2</sup>.



**Fig. S12.** Comparison of coulombic efficiencies of Cu-Au-ZnO-PAN || Li, Cu-Au-PAN-ZnO || Li and Cu-Au-ZnO-PAN-ZnO || Li asymmetrical cells during Li plating/stripping.



**Fig. S13.** Voltage profile and CE of CAZPZ || Li for 5 mA h cm<sup>-2</sup> and corresponding CEs.



**Fig. S14.** (a) The voltage-time curves at 3 mA cm<sup>-2</sup> for plating/stripping capacity of 1mA h cm<sup>-2</sup>. The Li plating overpotential on pure Li side (blue dashed rectangle in Fig. S11a) sharply increases after 95 h. (b) The voltage-time curves at 5 mA cm<sup>-2</sup> for plating/stripping capacity of 3 mA h cm<sup>-2</sup>.



**Fig. S15**. Surface SEM images of (a) CAZPZ-Li and (b) Li counter electrode part in Cu-Au-ZnO-PAN-ZnO-Li || Li cell after cycling for 120 h at 3 mA cm<sup>-2</sup>.



Fig. S16. SEM images of (a-b) LFP, (c-d) LTO and (e-f) MNC-411.



Fig. S17. X-ray di a raction (XRD) patterns of (a) LFP, (b) LTO and (c) MNC-411.



**Fig. S18.** Cycling performance of CAZPZ-Li || LTO and CAZPZ-Li || LTO cells at 10 C.

**Table S1.** The fitting results of the EIS in Fig. 4e-f. The Electrochemical impedance spectra (EIS) of CAZPZ || Li and Cu || Li cells after activation process at 50  $\mu$ A cm<sup>-2</sup> and after 50 cycles at 0.5 mA cm<sup>-2</sup>.

Fitting results		After activation	After 50 cycles
CAZPZ    Li cell	$R_{ct}(\Omega)$	42.4	18.3
Cu    Li cell	$R_{ct}(\Omega)$	118.3	150.9

# References.

- M. Hacene, A. Anciaux-Sedrakian, X. Rozanska, D. Klahr, T. Guignon and P. Fleurat-Lessard, J. Comput. Chem., 2012, 33, 2581-2589.
- 2. M. Hutchinson and M. Widom, Comput. Phys. Commun., 2011, 183, 1-7.
- 3. J. P. Perdew and Y. Wang, Phys. Rev. B, 1992, 45, 13244-13249.
- 4. J. P. Perdew, *Phys. Rev. B*, 1996, **54**, 16533-16539.
- 5. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys., 2010, 132, 154104.

- 6. K. Momma and F. Izumi, J. Appl. Crystallogr., 2011, 44, 1272-1276.
- B. Sa, Y.-L. Li, J. Qi, R. Ahuja and Z. Sun, J. Phys. Chem. C, 2014, 118, 26560-26568.
- R. Zhang, X. Chen, X. Shen, X.-Q. Zhang, X.-R. Chen, X.-B. Cheng, C. Yan, C.-Z. Zhao and Q. Zhang, *Joule*, 2018, 2, 764-777.