

Supporting Information

Natural Wood as Lithium Metal Hosts

Wei-Jing Chen^{a,}, Shang-Jie Yu^a, Qian Sun^b, Xin Shen^c, Peng Shi^d, Tong-Qi Yuan^{b,*},
and Zhaoqing Lu^{a,*}*

1. Experimental section

1.1. Materials

The eucalyptus wood samples were collected from Guangxi, China. The fir, pine, paulownia, and balsa wood samples were bought from the Internet. Toluene, ethanol, sulfur (S), carbon nanotube (CNT), *N*-methyl-2-pyrrolidinone (NMP), poly(vinylidene fluoride) (PVDF, HSV-300), ethylene carbonate (EC), diethyl carbonate (DEC), 1,2-dimethoxyethane (DOL), 1,2-diamethoxyethane (DME), lithium hexafluorophosphate (LiPF₆), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), lithium nitrate (LiNO₃), polypropylene (PP) separator (Celgard 2400), copper (Cu) foil, and aluminum (Al) foil were purchased from commercial sources and used without further purification in this contribution. Lithium (Li) metal foils (50, 75, 100 and 600 μm in thickness) were purchased from China Energy Lithium Co., Ltd and were used as received.

1.2. Synthesis of Wood/Li Composite Anode

The wood samples were first extracted with toluene–ethanol ((v/v=2:1)) in a Soxhlet extractor until the liquid was colorless. The dewaxed wood samples were cut into slices with different thickness along the cross section with Semi-automated Rotary

Microtome (Zhejiang Jinhua Kedi Instrumental Equipment Co., Ltd). The wood slices were dried in the oven with 105 °C to remove water and then transferred into Ar-filled glove-box with O₂ and H₂O content below 0.1 ppm. The dried wood slices and ultrathin Li foils were stacked and rolled on the Cu foil (9 μm) in a roller press (Shenzhen Kejing Star Technology Co., Ltd). Then the wood/Li composite anode was punched into 15.0 mm diameter electrodes for coin cells. The rolling and stamping process were carried out in the dry room with a dew-point temperature of −40°C. The blank Li was fabricated with same rolling process without wood slices.

1.3. Synthesis of LiFePO₄ (LFP) and sulfur (S) cathode

To prepare the LFP cathodes, the LFP powders were mixed with carbon black and PVDF at a weight ratio of 8:1:1 with NMP as the solvent to form homogeneous slurry. Then the slurry was cast onto Al foils by a doctor blade and dried at 60°C for 24 h. To prepare the S cathodes for Li | S full cell, sulfur/carbon (S/C) composite was first prepared via ball-milling. 2.8 g sulfur powder and 1.2 g CNT were mixed in a batch. The obtained mixture was then ball-milled with PVDF binder with a mass ratio of 9:1 in NMP for 2.0 h to form a homogeneous S/C slurry. After that, the obtained slurry was directly cast onto Al foils by a doctor blade and dried at 60°C for 24 h. The LFP and S electrodes were punched into discs with 13.0 mm in diameter to be further assembled in coin cells.

1.4. Material Characterization

An automatic mercury porosimeter (AutoPore IV 9520, Micromeritics, USA) was conducted to characterized the pore structure of wood samples. A scanning electron microscope (JSM 7401F, JEOL, Japan) operated at 3.0 kV was employed to characterize the morphology of wood slices, Li, and wood/Li electrodes. Three-dimensional imaging of wood/Li was collected from 3D X-ray Microscopy (Xradia 620, Zeiss, Germany).

1.5. Electrochemical Measurements

All coin cells were assembled with standard CR2025 coin-type cells in an Ar-filled glove-box with O₂ and H₂O content below 0.1 ppm. The diameter of Li metal anode was 15.0 mm for thin Li (50 μm in thickness) and 16.0 mm for thick Li (600 μm in thickness), respectively. PP membranes with diameter of 19.0 mm served as the separators.

For Li | Cu half cell, the wood slice-covered Cu foils with diameter of 13.0 mm were employed as the working electrodes and the thick Li foils as counter electrodes. For Li | Li symmetrical cell, wood/Li electrodes were employed as both the working and counter electrodes. 1.0 M LiPF₆ in EC/DEC (v/v=1:1) was used as electrolyte with volume of 40 μL in a single Li | Cu or Li | Li cell.

Wood/Li (both of wood slices and Li foils are 50 μm in thickness) were employed as anodes for assembling Li | LFP and Li | S full cells. For Li | LFP full cell, the fabricated LFP electrodes with capacity of *c.a.* 1.6 mAh were used as cathodes. 40 μL of electrolyte (1.0 M LiPF₆ in EC/DEC (v/v=1:1)) was added. In Li | S full cell, the

sulfur loading of S/C cathodes was 1.7 for routine measurements and 5.5 mg cm⁻² for harsh conditions, 1.0 M LiTFSI in DOL/DME (v/v = 1:1) with 2.0 wt.% LiNO₃ was employed as the electrolyte in Li|S full cells. The volume of the electrolyte was 5 μL for anode and 20 or 40 μL for cathode with low or high S areal loading, respectively.

To assemble all-wood-based Li|S full cell, the wood-based S cathode was first fabricated. The dried eucalyptus wood was cut into 500 μm slice along cross section and punched into 13.0 mm diameter. Then the wood slices were calcinated in tube furnace at 400°C for 2 h and 900 °C for 6 h with 5 °C min⁻¹. After that, the as-fabricated S/C slurry was directly dropped onto the carbonaceous wood slices and then transferred into vacuum drying oven at 60 °C for 6 h. The dried wood slice (100 μm in thickness) along radial section was employed as separator without any other treatment. The Wood/Li electrodes with 50 μm in thickness (both of wood slices and Li foils) were used as anodes. 1.0 M LiTFSI in DOL/DME (v/v = 1:1) with 5.0 wt.% LiNO₃ was employed as the electrolyte.

These cells were monitored in galvanostatic mode in a Land CT2001 multichannel battery tester.

1.6. Computational methods

The distribution of electric field in a Li|Li symmetric cell is simulated using a finite element method on the platform of COMSOL Multiphysics 5.5. The transport of the charged species (Li⁺ and anions) in the electrolyte is given by the Nernst–Planck equation with the assumption of electric neutrality:

$$N_i = -D_i \nabla c_i - z_i c_i F \frac{D_i}{RT} \nabla \phi_l, \quad (1)$$

$$\sum_i z_i c_i = 0, \quad (2)$$

where D_i , c_i , and z_i denote the diffusion coefficient, the concentration, and the valence of species i , respectively. F , R , and T represent Faraday constant, ideal gas constant, and temperature, respectively. ϕ_l is the potential of the electrolyte. Besides, all the species follow mass conservation:

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot N_i. \quad (3)$$

The electrochemical reaction on the electrode surface is described by the Butler–Volmer equation:

$$i_{loc} = i_0 \left[\exp\left(\frac{\alpha F \eta_{ct}}{RT}\right) - \exp\left(-\frac{\beta F \eta_{ct}}{RT}\right) \right], \quad (4)$$

where i_0 is the exchange current density, α is the anodic charge transfer coefficient, β is the cathodic charge transfer coefficient, η_{ct} is the charge transfer overpotential.

The geometry and boundary conditions of the simulated Li | Li symmetric cell are described in Fig. S15. The PP separator was simplified as a sieve plate, which consists of narrow rectangular channels with a pore size of 200 nm. Triangular mesh is chosen with a minimum element size of 6.63 nm. A summary of the parameters for the simulations is included in Table S1. The data are taken from the simulation results at 10 s, when the electric field distribution has reached stability.

2. Supporting Figures

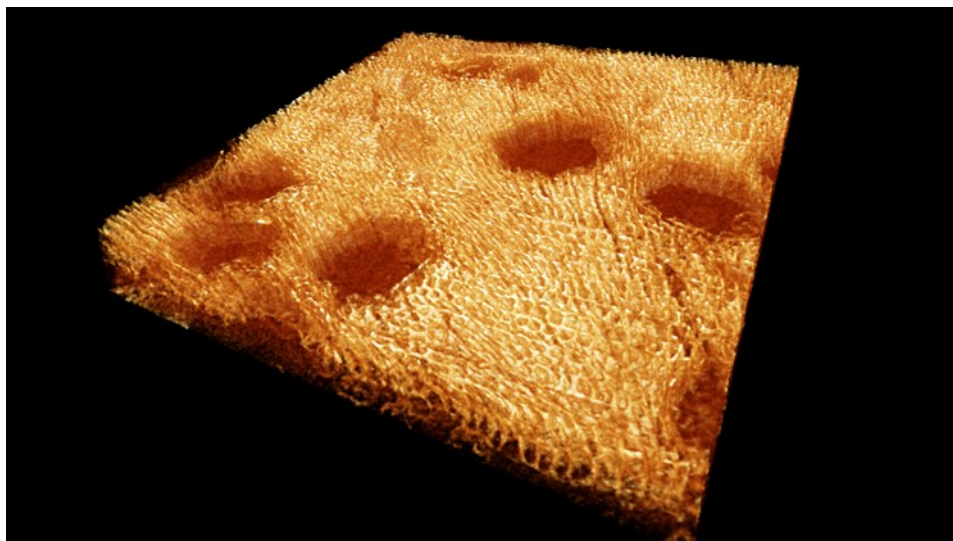


Fig. S1. The 3D morphology of the wood/Li composite anode by X-ray microscopy

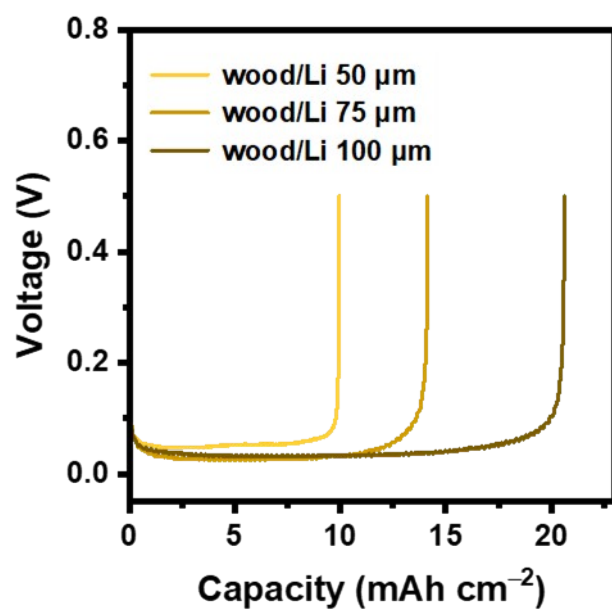


Fig. S2. Typical Li stripping curves of wood/Li composite anodes with different Li foil thicknesses.

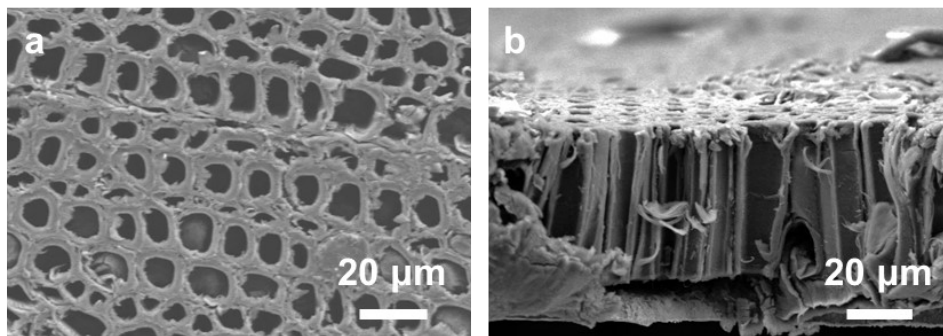


Fig. S3. SEM images of wood/Li composite anode after stripping Li with a capacity of 9.0 mAh cm^{-2} at a current density of 1.0 mA cm^{-2} .

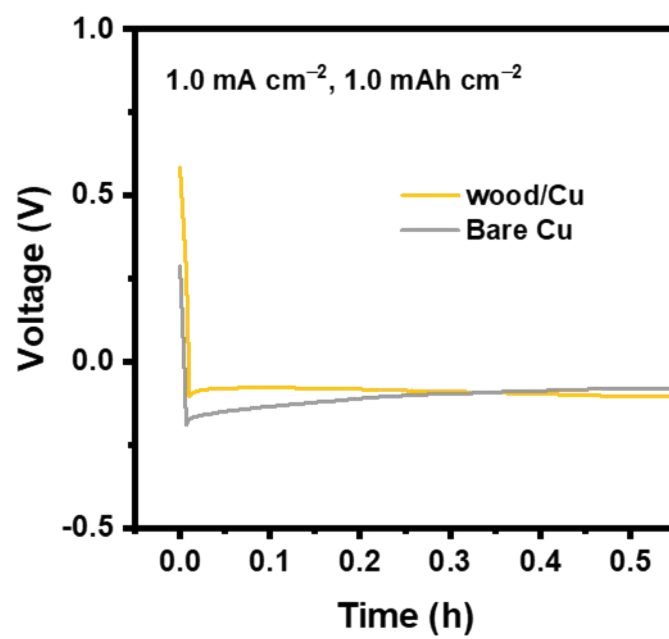


Fig. S4. The voltage–time curves during Li nucleation on Cu foil.

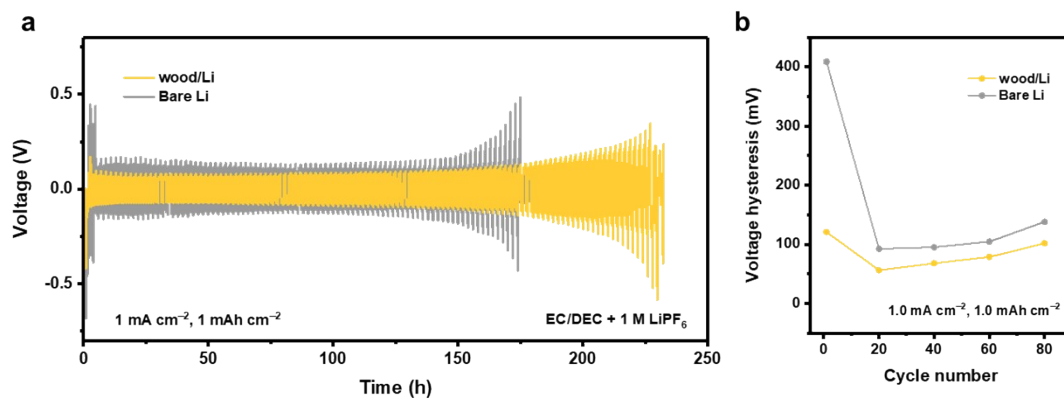


Fig. S5. Electrochemical performances of Li | Li symmetrical cells at 1.0 mA cm^{-2} , 1.0 mAh cm^{-2} : (a) long-term cycling and (b) corresponding voltage hysteresis at different cycles.

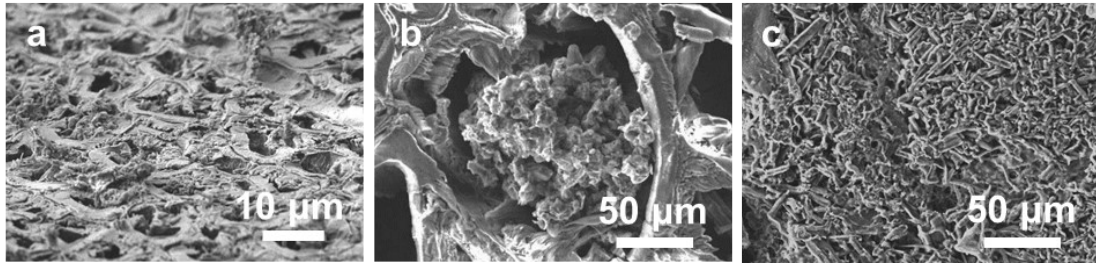


Fig. S6. SEM images of (a–b) wood/Li electrode and (c) bare Li after 5 cycles in symmetrical cells (1.0 mA cm^{-2} , 1.0 mAh cm^{-2}).

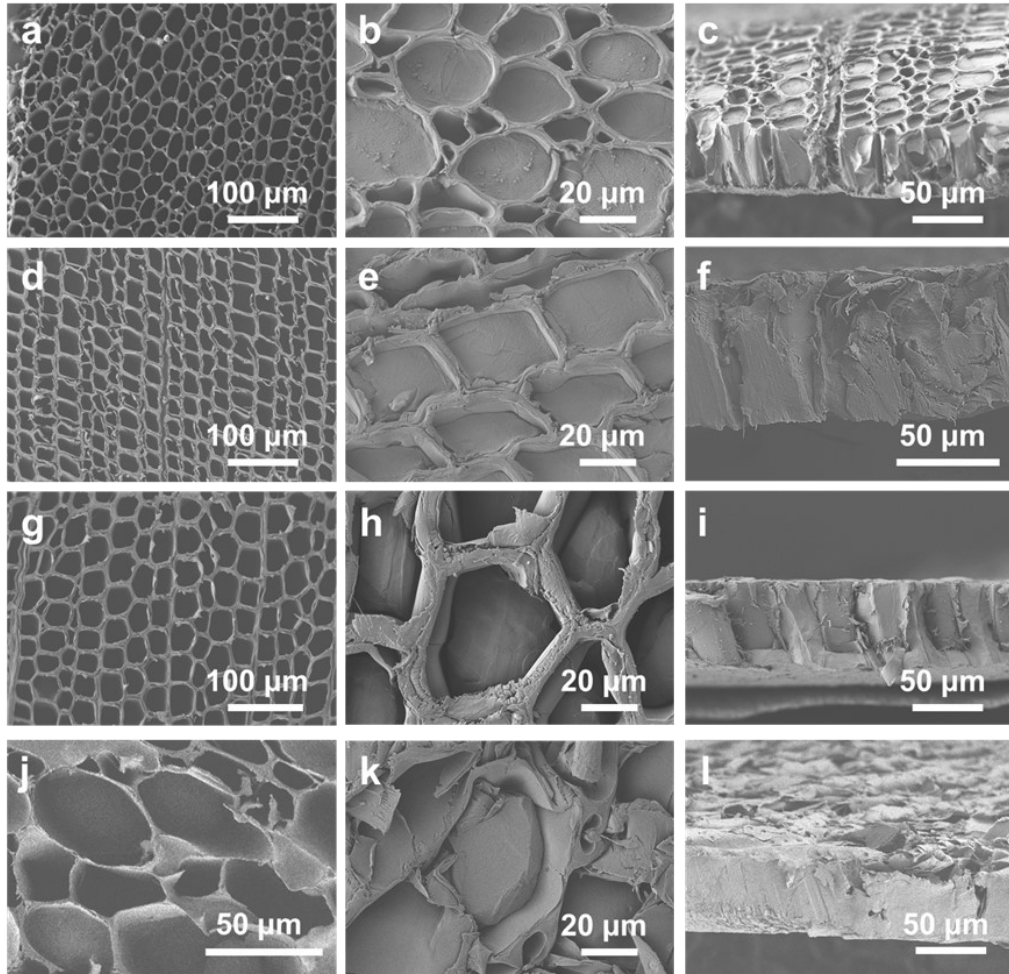


Fig. S7. SEM images of the raw wood and the corresponding composite Li anodes of (a–c) paulownia, (d–f) fir, (g–i) pine, and (j–l) balsa wood, respectively.

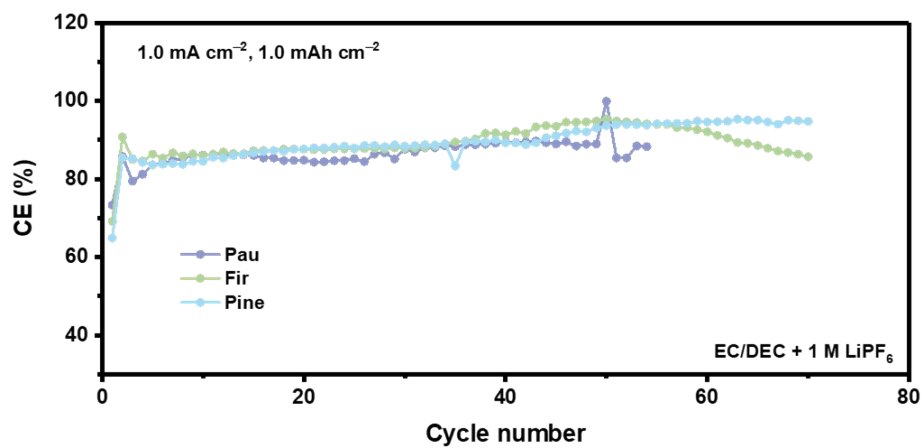


Fig. S8. Electrochemical performances of Li | Cu half cells with paulownia, fir, and pine wood host at 1.0 mA cm^{-2} , 1.0 mAh cm^{-2} , respectively.

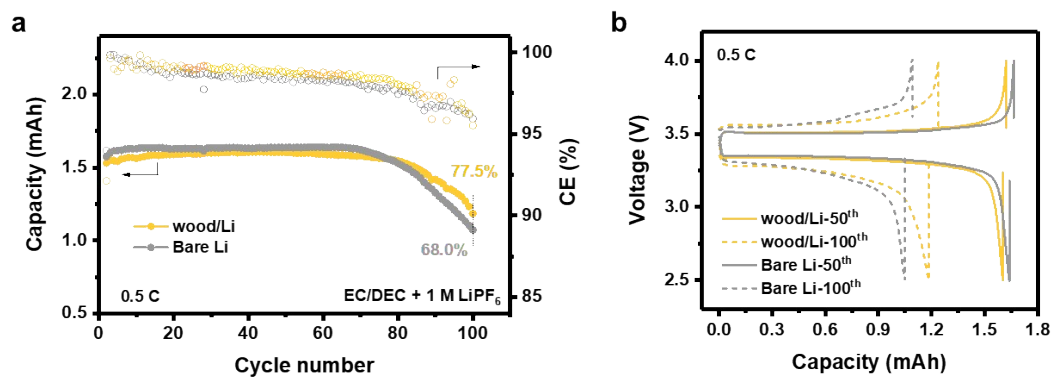


Fig. S9. Electrochemical performances of Li | LFP full cells: (a) long-term cycling performances at 0.5 C and (b) charging-discharging curves at the 50th and 100th cycle, respectively.

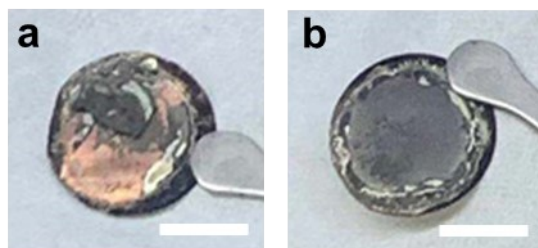


Fig. S10. Digital pictures of the anodes in Li | LFP full cells after cycling at 1.0 C: (a) bare Li anode and (b) wood/Li composite anode (the scale bar is 1 cm).

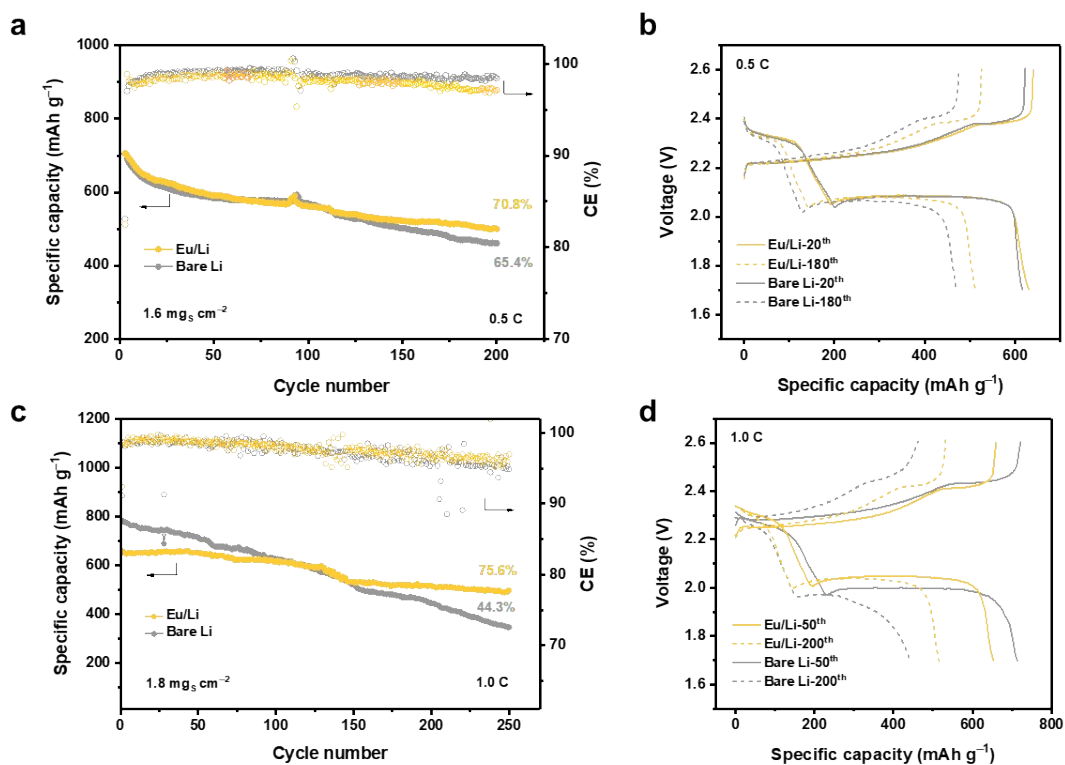


Fig. S11. Electrochemical performances of Li | S full cells with low sulfur areal loading: long-term cycling performances at (a) 0.5 C and (c) 1.0 C, (b) 0.5 C charging-discharging curves at the 20th and 180th cycle, respectively and (d) 1.0 C charging-discharging curves at the 50th and 200th cycle, respectively.

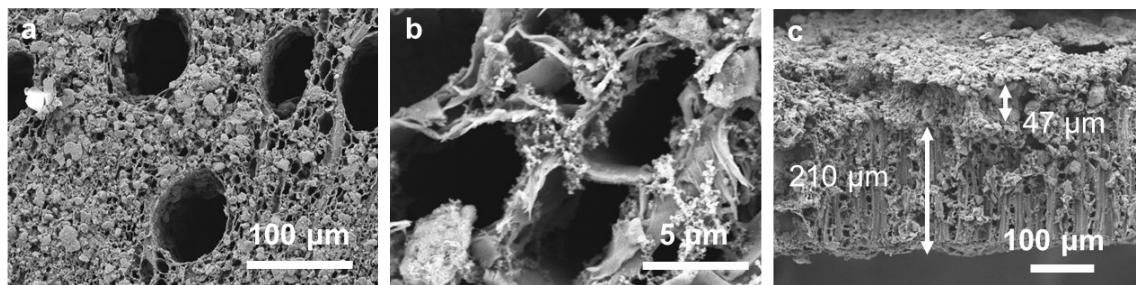


Fig. S12. (a, b) The morphology and (c) cross sectional SEM images of wood/S cathode with S/C slurry loading of 3.0 mg.

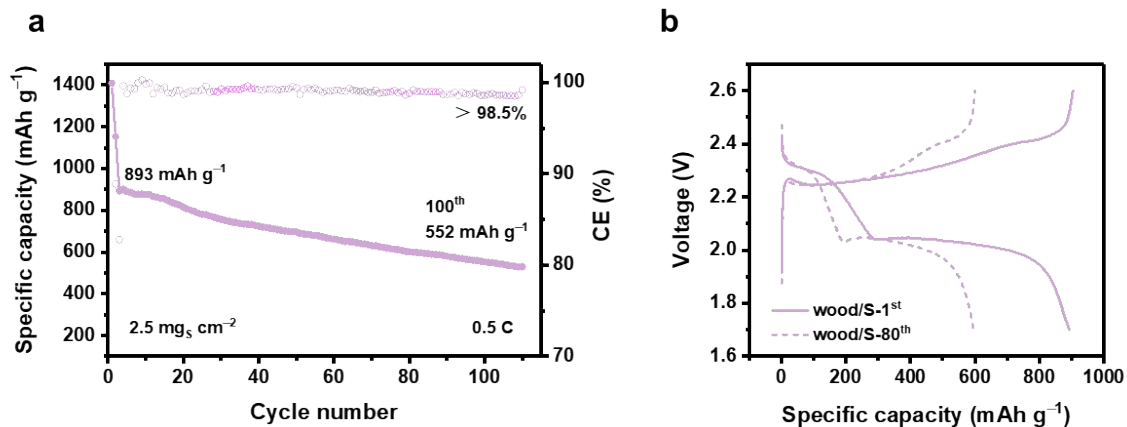


Fig. S13. Electrochemical performances of Li | S full cells with wood/S cathode and 600 μm Li anode: (a) long-term cycling performance, (b) charging-discharging curves at the 1st and 80th cycle, respectively.

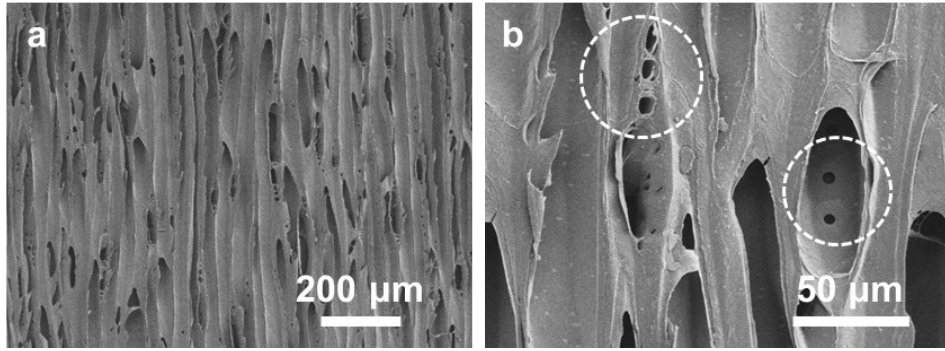


Fig. S14. SEM images of the wood separator.

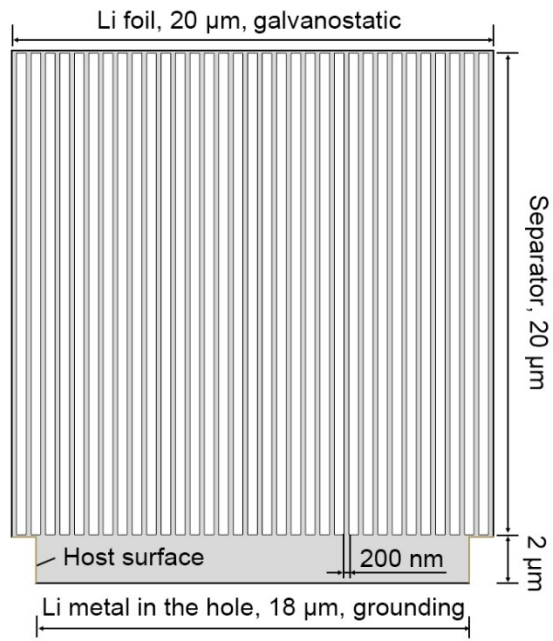


Fig. S15. The schematic of the simulated Li | Li symmetric cell.

3. Supporting Table

Table S1. Physical and electrochemical parameters used in the model.

Name	Symbol	Value	Unit
Temperature	T_0	298	K
Initial electrolyte concentration	C_{init}	1000	mol m ⁻³
Exchange current density	i_0	10	A m ⁻²
Li ⁺ diffusion coefficient	D_{Li}	1×10 ⁻⁹	m ² s ⁻¹
Charge transfer coefficient	α, β	0.5	
Applied current density	i_{app}	10	A m ⁻²