Supporting Information

Micro versus Nano Channels: Carbon Micro Sieve Tubes from Biological Phloem Tissues for Lithium-Oxygen Batteries

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Abstract: Photosynthetic products and salts transport occurs continuously in the phloem tissues of the vascular hydrophyte, Typha. Multiphase transport of oxygen, electrons and ions also plays an essential role in the lithium-oxygen batteries (LOBs) cathode. The similarity in transport behavior is the inspiration for the development of advanced cathode design from natural phloem tissues. Using a top-down process, the special tissues are converted into micron scale sieve tubes. The designed structure has high ratio of tube diameter to the size of the discharged product (6:1), which ensures the uniform coverage of Li_2O_2 on micro-channel surfaces avoiding pore clogging on typical nanoscale carbons, and exhibits high specific capacity of 9100 mAh g⁻¹. Besides, the biologically enhanced structure also plays a pivotal role in the extraordinary cycle stability of 270 cycles with a cutoff capacity of 1000 mAh g⁻¹ due to the robust structure and thick tube walls. In addition, iodomethane, a bio-waste volatilized from plants, is utilized as an electrolyte additive and improves the round-trip efficiency to 86 %. The integration of phloem tissue carbon and iodomethane paves the way for the ready conversion of abundant biomass into high-value engineering products for energy-related applications.

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Figure S1. Photographs of the (a) cross-view of a Typha leaf and (b) stripped/unstripped leaf skin. SEM images of the (c) top-view, (d) cross-view of the leaf and (e) stripped leaf skin.



Figure S2. (a) Schematic of a treated leaf skin and the dimensions along different directions. (b) Electrical conductivities of the treated skin along parallel and horizontal directions.

The electrical conductivity of the treated skin was calculated by:

$$\sigma = L/(R \times S) \tag{1}$$

where σ , L, R and S are the electrical conductivity, length, electrical resistance and crosssection area of the treated Typha leaf skin, respectively. The electrical conductivities of the treated skin (3.8 ×0.5 ×0.014 cm) are 1611 S m⁻¹ and 347 S m⁻¹ from parallel and horizontal directions, respecitively.



Figure S3. The transfer velocities of DMSO electrolyte tested in (a) PTCT, (b) fresh stripped Typha skin and (c) glass fibre separator by dipping the samples into a dyed solution (1ml DMSO, dyed with Sudan III).



Figure S4. SEM image of a broken PTCT tube, showing the channels are open-end.



Figure S5. (a) Wide scan, (b) N1s and (c) F1s XPS spectra of the obtained PTCT powders.



Figure S6. HRTEM and SAED pattern of PTCT, indicating a higher gratification degree.



Figure S7. (a) BET N₂ adsoption/desorption isotherms and (b) pore size of CNTs. For porous carbon materials, according to the Young-Laplace equation, ¹ $h_0 = 2\sigma \cos \theta / \rho g R$ (2)

Where σ is the surface tension, θ the contact angle, ρ the liquid density and g the gravity acceleration constant. Equation S2 suggests that the capillary rise is larger as the pore radius Rdecrease. Thus, large quantities of micro pores (~1.5 nm) and meso pores (~3.1 nm) facilitate the capillary action in PTCT and accelerate the penetration of electrolyte, which may be the reason why the average transfer velocity of the electrolyte in PTCT is much higher than the fresh stripped Typha skin and glass fibre separator in Figure S2.



Figure S8. Full discharge curves of the Ketjen black and carbon nanofibers based LOBs under 100 mA g^{-1} .



Figure S9. SEM images of the PTCT-cathode after discharging@1500 mAh g⁻¹ with different magnifications.

Both images show that the discharge products are deposited on the outer and inner surfaces of

the micro channels of PTCT. The diameter of the discharge product is \sim 240 nm.



Figure S10. SEM images of PTCT-cathode (a, b) before and (c, d) after discharge @1500 mAh g^{-1} with different magnifications.



Figure S11. SEM images of the CNTs-cathode (a) before and (b,c) after fully discharge with different magnifications.

Discharge products are formed on the CNTs surface and the diameter of the Li_2O_2 is ~300 nm.



Figure S12. The overall voltage vs. time plots of PTCT and CNTs based LOBs.



Figure S13. TEM image of the CNTs after 50 cycles.

After cycles, as shown in the Figure S11, breakages at the CNTs surfaces can be observed clearly.



Figure S14. EIS analysis with (a) equivalent circuit model and fitting parameters, Nyquist plots of fitted results of (b) CNTs-LOB and (C) PTCT-LOB.

R₁: equivalent series resistance for the electrolyte, current collectors and electrode materials.

R₂: the total resistance combining the surface film resistance (R_{SEI}) and the charge transfer

resistance (R_{CT}) of the above LOBs.²



Figure S15. SEM images of PTCT-cathode after discharge and the corresponding elemental mapping images of one channel.



Figure S16. RDE curves of (a) PTCT in O₂-saturated 0.1 M KOH solution with various rotation speeds and a sweep rate of 10 mV s⁻¹; (b) the corresponding K-L plots (J⁻¹ versus $\omega^{-1/2}$) at different potentials. (c) OER polarization curve in KOH solution and (d) OER curve of PTCT in DMSO electrolyte at 0.2 mV s⁻¹.

A typical three-electrode cell setup involving a rotating disk electrode (RDE) was used to investigate both the ORR and OER catalytic activities of the PTCT samples. The working electrode was fabricated by casting Nafion®-impregnated catalyst ink onto a glassy carbon disk electrode (5 mm in diameter). In the preparation of catalyst ink, 5 mg of the PTCT was ultrasonically dispersed into a 1.980 mL ethanol and 20 μ L 5 wt% Nafion®solution to form a uniform carbon ink. Then, 8 μ L of the ink was deposited onto the disk. Electrochemical activity of the samples was studied using a linear sweep voltammetry. In the measurements, the PTCT-coated working electrode was immersed in a half-cell containing 0.1 M KOH aqueous electrolyte, in which a platinum foil and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The as-prepared electrodes were dried at room temperature overnight prior to the electrochemical tests. The detailed kinetic analysis was conducted according to Koutecky-Levich plots

$$\frac{1}{J} = \frac{1}{J^k} + \frac{1}{Bw^{0.5}}$$
(3)

Where J is the current density, J^k is the kinetic current, and B is the levich slpe, which is given by

$$B = 0.2nF(D_{0_2})^{\frac{2}{3}}v^{-\frac{1}{6}}C_{0_2}$$
(4)

Here, n is the number of electrons transferred in the reduction of one O₂ molecule, F is the Faraday constant (F = 96485 C mol⁻¹), ${}^{D_0}{}^{2}$ is the diffusion coefficient of O₂ (${}^{D_0}{}^{2}$ = 1.9 × 10⁻⁵ cm² s⁻¹), v is the kinematic viscosity for KOH (v = 0.01 cm² s⁻¹), and ${}^{C_0}{}^{2}$ is the concentration of O₂ in the solution (${}^{C_0}{}^{2}$ = 1.2 × 10⁻⁶ mol cm⁻³). The constant 0.2 is adopted when the rotation speed is expressed in rpm. According to Equations (3) and (4), the number of electrons transferred (n) can be obtained from the slope of the Koutecky-Levich plot of J^{-1} versus $\omega^{-1/2}$.



Figure S17. The weights of PTCT samples at different steps of the formation process.

By weighing the PTCT samples at each formation step, the yield of the carbonized PTCT to the starting biomass is 17.8 wt. %. It is well known that biological phloem tissues are mainly composed of celluloses, which can be dehydrated to form carbon during the carbonization process. The overall reaction is:

$$(C_6 H_{10} O_5) n \to 6nC + 5nH_2 O \tag{5}$$

Ideally, the remaining carbon is 44 wt. % of the original biomass, but aquatic plants also contain lots of water, which will be evaporated at high temperatures and make the carbonized PTCT lower than 20 wt. %. However, after purification, activation and grinding processes, the yield of the final product PTCT to the carbonized sample is as high as 85.8 wt. %.



Figure S18. Cyclic voltammetry (CV) curves and 1st discharge/charge plots of the PTCT-LiI and PTCT-MI LOBs.

Element (%)	PTCT
Al	0.006
Ва	0.0008
Са	0.003
Cu	0.0008
Fe	0.005
К	0.016
La	0.0037
Mg	0.012
Mn	0.028
Na	0.022
Р	0.085
S	0.017
Si	0.015
Sr	0.0027
Zn	0.0018
Zr	0.0015

Table S1. ICP-MS result of the PTCT after chemical purification process.

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