

Electronic Supplementary Information

Selenium-confined microporous carbon cathode for ultrastable lithium-selenium batteries

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Experimental section

Preparation of microporous carbon polyhedrons (MICP): MICP was synthesized according to a reported method with some modification.^{1,2} In a typical synthesis, 7.34 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($\geq 99.0\%$, Sigma-Aldrich) was dissolved in 500 mL of anhydrous methanol (MeOH, $\geq 99.5\%$, Sinopharm Chemical Reagent Co., Ltd.) under magnetic stirring. Another solution was prepared by dissolving 8.10 g of 2-methylimidazole (99%, Sigma-Aldrich) and 4.05 g of 1-methylimidazole (99%, Alfa Aesar) in 500 mL of MeOH. Then, the later solution was poured into the former one under vigorous stirring. The resultant solution was stirred for 5 min and then kept static for 24 h at room temperature. The produced white precipitate (ZIF-8) was collected by centrifuging, washing with ethanol and drying under vacuum at 70 °C for 12 h. Afterward, the carbonization of ZIF-8 was carried out at 1000 °C for 8h under argon atmosphere. After carbonization, the as-formed black powder was washed with 1M hydrochloric acid, deionized water, ethanol, and then dried under vacuum at 70 °C for 12 h. Finally, the resulting product was activated at 600 °C for 2h under argon atmosphere to get MICP.

Preparation of selenium@microporous carbon polyhedrons (Se@MICP): 100 mg of Se powder (99.99%, Sigma-Aldrich) and 100 mg of the as-prepared MICP were mixed by grinding for 1 h. Subsequently, the mixture was sealed in a glass tube under vacuum and heated at 260 °C for 12 h to achieve Se@MICP. As a control sample, a physical mixture of Se and MICP (Se-MICP) was prepared by directly grinding Se and MICP with a weight ratio of 50:50 for 1 h.

Materials characterization: Scanning electron microscopy (SEM) measurements were conducted on a JEOL JSM-7600F scanning electron microscope operated at 10 kV. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) characterizations were carried out on a JEOL JEM-2100F transmission electron microscope operated at 200 kV. Energy dispersive X-ray spectroscopy (EDX) analysis and scanning transmission electron

microscopy (STEM) measurements as well as elemental mapping characterizations were performed on a Tecnai G2 F20 U-TWIN field emission transmission electron microscope equipped with an EDAX system. Nitrogen adsorption and desorption isotherms at 77.3 K were determined with an ASAP 2050 surface area-pore size analyzer. X-ray photoelectron spectroscopy (XPS) measurement was recorded on an ESCALab250Xi electron spectrometer from VG Scientific using 300W Al K α radiation. X-ray diffraction (XRD) pattern was measured on a Rigaku D/max 2500/PC diffractometer using Cu K α radiation. Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 449 F3 under nitrogen flow with a heating rate of 10 °C min⁻¹. Raman measurements were performed using a Labram HR800 with a laser wavelength of 514.5 nm.

Electrochemical measurements: Electrochemical experiments were carried out using CR2032 coin cells. To fabricate working electrodes, Se@MICP, Super-P carbon black, and sodium alginate with a weight ratio of 80:10:10 were mixed into homogeneous slurry in water using mortar and pestle. The resulting slurry was pasted onto pure aluminum foil (99.0 %, Goodfellow) and then dried in a vacuum oven at 40 °C overnight. The electrolyte for all tests was 1 M LiPF₆ in ethylene carbonate/diethyl carbonate (1:1 v/v). Glass fibers (GF/D) from Whatman were used as separators and pure lithium metal foil (Aldrich) was utilized as the counter electrode. The coin cells were assembled in an argon-filled glove box (H₂O, O₂ < 0.1 ppm, Mbraun). The charge and discharge measurements of the batteries were conducted on a Land CT2001A multi-channel battery testing system in the fixed voltage range of 1.0–3.0 V vs. Li⁺/Li at room temperature. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed on a PARSTAT 4000 electrochemical workstation. CV was recorded at a scan rate of 0.1 mV s⁻¹ while EIS was determined in the frequency range from 100 kHz to 100 mHz.

References

- 1 H. B. Wu, S. Wei, L. Zhang, R. Xu, H. H. Hng and X. W. Lou, *Chem. Eur. J.*, 2013, **19**, 10804–10808.
- 2 J. Cravillon, R. Nayuk, S. Springer, A. Feldhoff, K. Huber and M. Wiebcke, *Chem. Mater.*, 2011, **23**, 2130–2141.

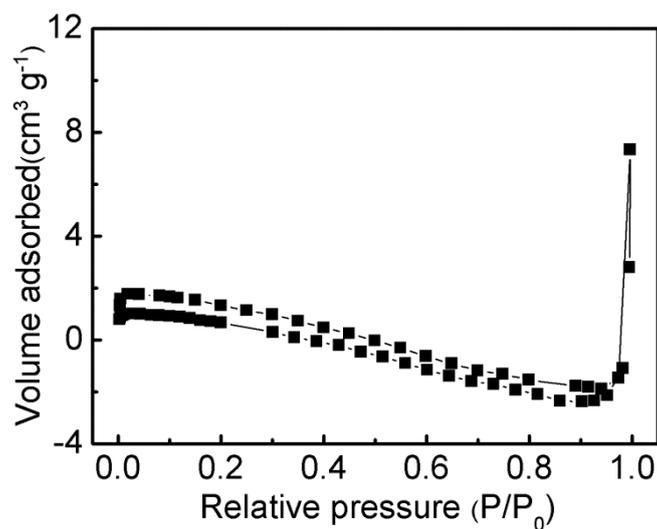


Figure S1. Nitrogen adsorption/desorption isotherms of Se@MICP (Brunauer–Emmett–Teller surface area = 0.98 m² g⁻¹).

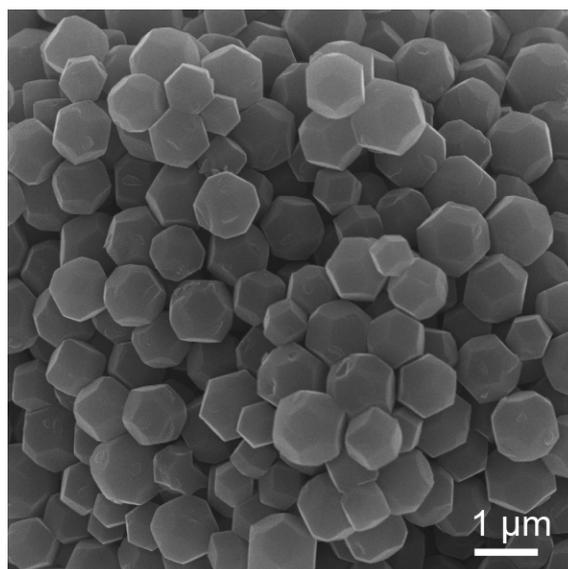


Figure S2. SEM image of MICP.

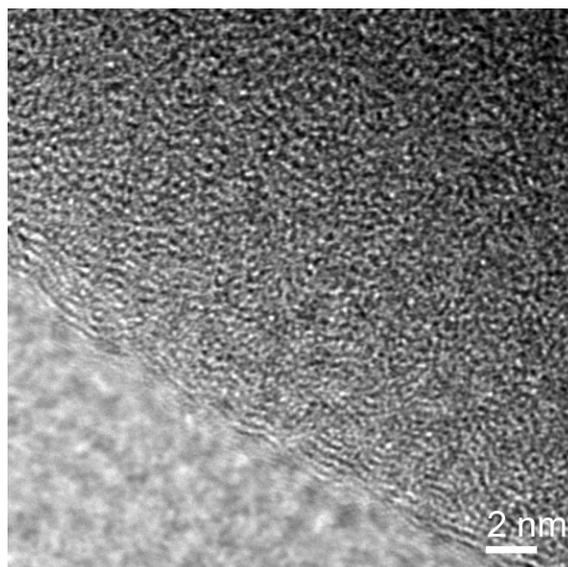


Figure S3. HRTEM image of Se@MICP.

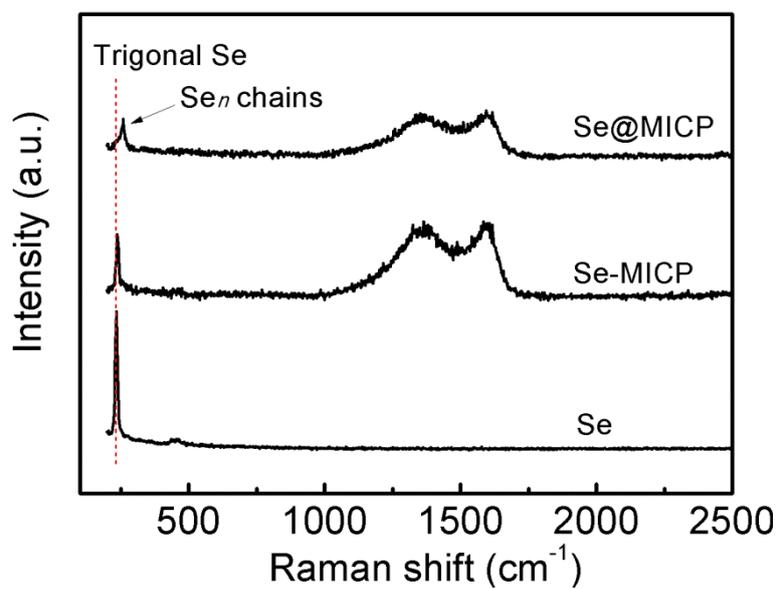


Figure S4. Raman spectra of Se, Se-MICP, and Se@MICP.

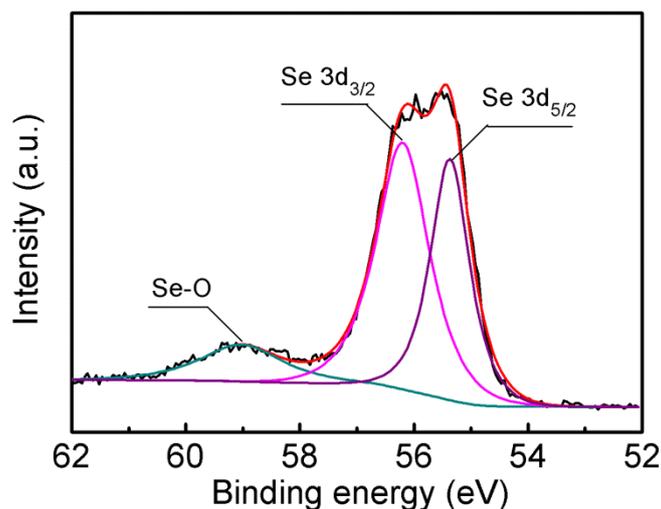


Figure S5. Se 3d XPS spectrum of Se@MICP. It could be splitted into three peaks at 55.4, 56.2, and 59.0 eV, respectively. The peaks at 55.4 and 56.2 eV are ascribed to Se 3d_{5/2} and Se 3d_{3/2}, respectively. The third peak at 59.0 eV is attributed to Se–O bonding, confirming the generation of SeO₂.

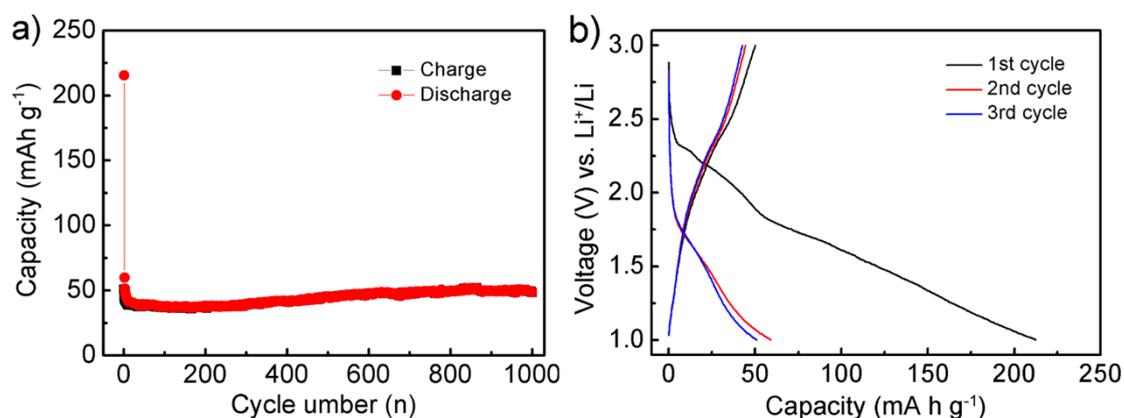


Figure S6. (a) Cycling performance and (b) galvanostatic charge-discharge profiles for the initial three cycles of Se-MICP at 0.1 C (67.8 mA g⁻¹) in the voltage range of 1.0–3.0 V vs. Li⁺/Li.

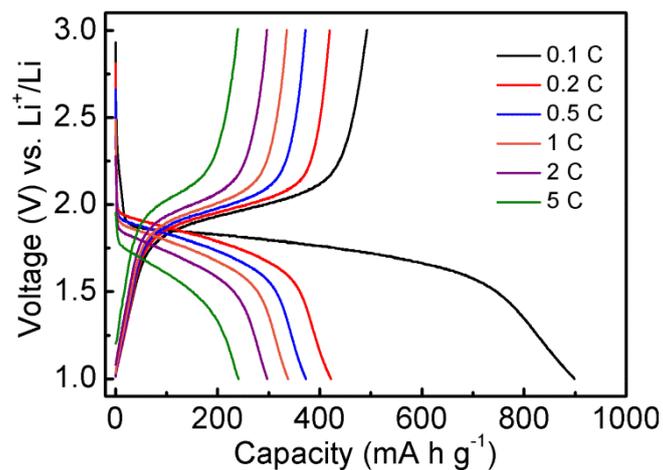


Figure S7. Galvanostatic charge-discharge profiles of Se@MICP at various current densities in the voltage range of 1–3 V vs. Li⁺/Li.

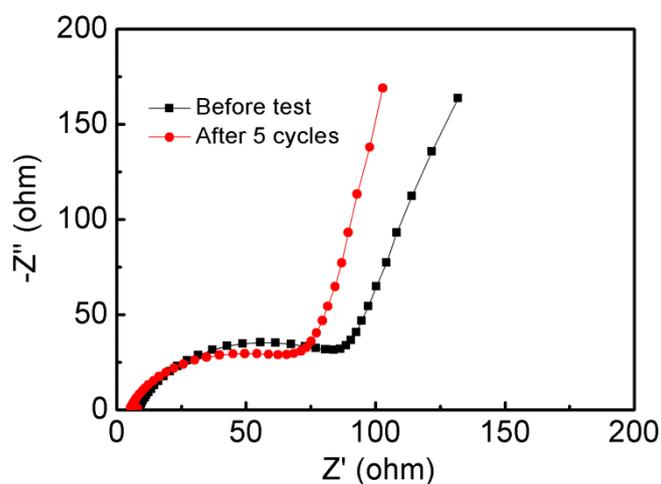


Figure S8. Nyquist plots of Se@MICP before test and after 5 cycles achieved by applying a sine wave with amplitude of 10.0 mV over the frequency range of 100 kHz–100 mHz.