

Electronic Supplementary Information

Steering the liquid-solid redox conversion of lithium-selenium batteries through ultrafine MoC catalyst

Xin Ma,^a Cheng Yuan,^a Genlin Liu,^a Lei Wang,^a Tianran Yan,^a Pan Zeng,^b and Liang Zhang^{ac,*}

^aInstitute of Functional Nano & Soft Materials (FUNSOM), Soochow University, 199 Ren'ai Road, Suzhou 215123, China

^bInstitute for Advanced Study, Chengdu University, Chengdu 610106, China

^cJiangsu Key Laboratory of Advanced Negative Carbon Technologies, Soochow University, Suzhou 215123, Jiangsu, China

Email: liangzhang2019@suda.edu.cn

Methods

Preparation of MoC@FC

First, 1.441 g urea and 0.120 g NaMoO₄ were completely dissolved in 7.5 mL deionized water (DIW) and stirred for 0.5 h to form solution A. Then, 0.75 g polyethylene oxide-polypropylene oxide-polyethylene (P123) was completely dissolved in 7.5 mL DIW, 1 mL commercial acidic silica was added, and then the solution was stirred for 0.5 h to form solution B. After that, solution B was added to solution A and stirred for 0.5 h at room temperature. The obtained mixture solutions were then freeze-dried into a fluffy block. After that, the dry block was subjected to consecutive pyrolysis, which was calcined at 550 °C for 4 h and further calcined at 900 °C for 2 h under inert atmosphere. The obtained black powders were soaked into dilute hydrofluoric acid solutions for 12 h to remove the nano-silica. After repeated filtering with ethyl alcohol and deionized water, the solid powders were then dried in a vacuum oven at 80 °C for 12 h to obtain the final product, which was denoted as MoC@foam carbon (MoC@FC). For comparison, the FC were prepared without adding sodium molybdate.

Polysulfide absorption experiments

Se power and metal lithium in a 3:1 molar ratio was dissolved in 1,2-dimethoxyethane (DME) solvent with stirring at 60 °C for 48 h to produce Li₂Se_x solution. Then 10 mg of MoC@FC and FC powders were placed in 1 mL Li₂Se_x solution, respectively. After the solution was left standing for a designated time, the supernatant was absorbed for UV-vis spectroscopy, and the adsorbed powder was dried for X-ray photoelectron spectroscopy (XPS).

Assembly and Electrochemistry Testing of the Symmetric Cell

MoC@FC and FC were mixed with polyvinylidene fluoride (PVDF) in N-methyl pyrrolidinone (NMP) solvent with a mass ratio of 4:1, respectively. The mixed material was coated on the carbon coated aluminum foil, and then dried under vacuum at 60 °C for 12 h. The obtained electrodes were cut into disks with a diameter of 12 mm. Li₂Se_x solution containing 1 M lithium bis (trifluoromethane sulfonyl) imide (LiTFSI) and 2.0 wt% LiNO₃ in DME and 1,3-dioxolane (DOL) (1:1, v/v) solvent (conventional electrolyte) was used as electrolyte. Two identical electrodes were used to assemble a symmetrical battery with 30 μL electrolyte. The voltage range for cyclic voltammetry (CV) tests of symmetric cells was conducted between -1 and 1 V.

Preparation of MoC@FC functional separators

MoC@FC functional separators were prepared by a slurry casting method. MoC@FC, acetylene black, and PVDF were mixed in NMP solvent with a mass ratio of 7:2:1, and the mixed precursor was coated on the polypropylene separator (PP, Celgard-2500). After drying, functional separators were cut into disks with a diameter of 19 mm. The areal loading of the material was controlled at 0.4 mg cm⁻².

Electrochemical Measurements

The Li-Se batteries were assembled under Ar in a glove box with the oxygen and water content below 0.1 ppm. The amount of electrolyte was maintained at an electrolyte to selenium (E/S) ratio of 30 μL mg⁻¹. The selenium cathode consists of 40 wt% selenium powder, 50 wt% acetylene black, and 10 wt% PVDF. Selenium loading was approximately 1 mg cm⁻² for routine testing and high temperature and low temperature testing (E/S = 30 μL mg⁻¹) and 5 mg cm⁻² for high loading testing (E/S = 30 μL mg⁻¹). Note that the high selenium loading cathode was obtained by mixing 90 wt% selenium and 10 wt% conductive carbon with carbon cloth as the current collector, and the weight of carbon cloth was not taken into consideration in general. The batteries were assembled with lithium metal as the anode and selenium as the cathode with modified separators to form the standard 2032 coin-type batteries. The galvanostatic charge-discharge test was measured by the Landt CT2001A battery test system. A CHI660E electrochemical workstation was used for CV tests, and the scan rate was from 0.1 to 0.5 mV s⁻¹ in the voltage range of 1.65 to 2.8 V. Electrochemical impedance spectroscopy (EIS) was measured in the frequency range of 10 mHz to 100 kHz. The Li⁺ diffusion coefficient (D_{Li}^+) was calculated via the Randles-Sevcik equation, as shown below.

$$I_p = (2.69 \times 10^5) \times C_{Li}^+ \times D_{Li}^{0.5} \times A \times v^{0.5} \times n^{1.5}$$

Where I_p is the peak current, C_{Li}^+ (mol mL⁻¹) represents the concentration of Li⁺ in the electrolyte, D_{Li}^+ indicates the Li⁺ diffusion coefficient, A (cm²) is the area of the active electrode, v (V s⁻¹) is the scan rate and n ($n = 2$) represents the charge transfer number.

Table S1. ICP for Mo element of MoC@FC

Element	Mo
Mass ratio (wt%)	3.2464 wt%

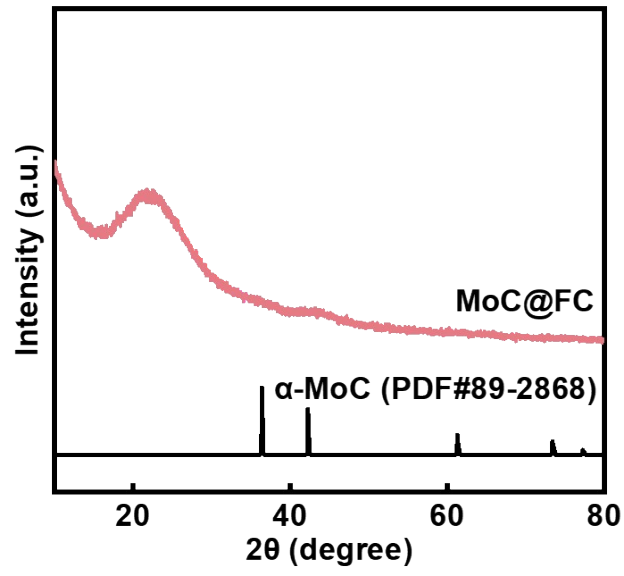


Fig. S1. XRD pattern of MoC@FC.

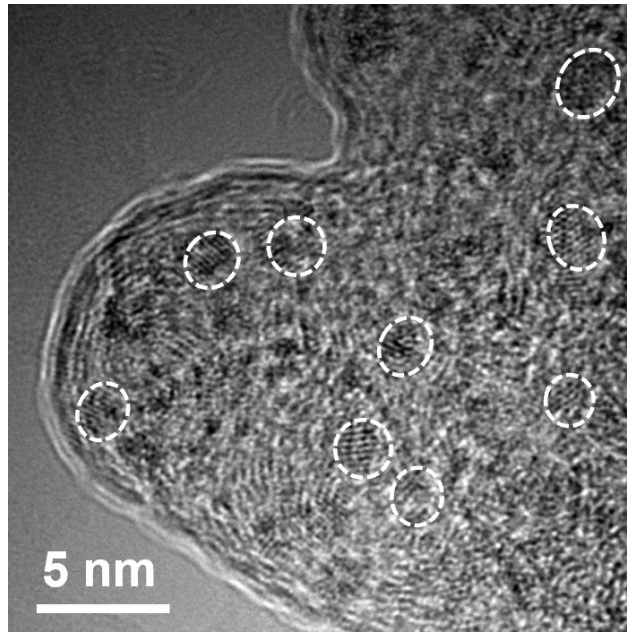


Fig. S2. HRTEM of MoC@FC.

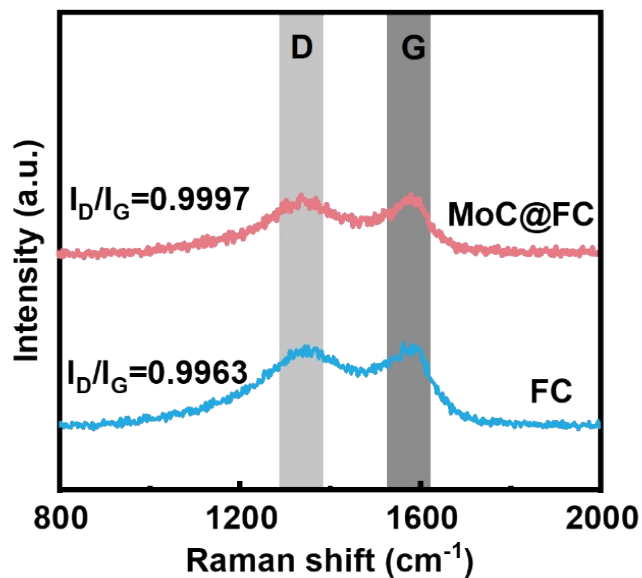


Fig. S3. Raman spectra of MoC@FC and FC.

There are two peaks located at 1590 and 1330 cm⁻¹ in the Raman spectra of MoC@FC and FC (Fig. S3), which are attributed to the in-plane stretching vibration of sp² carbon (G band) and disorder-induced asymmetric vibration mode (D band) respectively. The similar intensity ratio of G band to D band (I_G/I_D) for MoC@FC and FC indicates that the presence of ultra-fine and highly dispersed MoC nanoparticles did not affect the structure of as-formed FC.

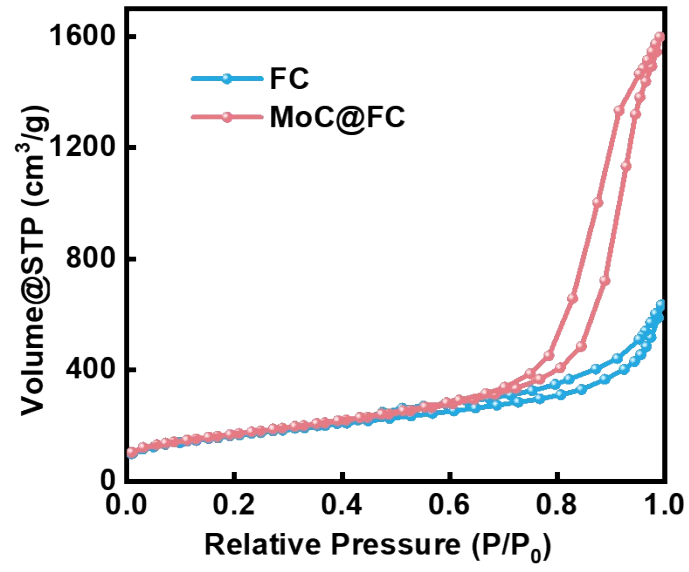


Fig. S4. N₂ adsorption/desorption isotherms of MoC@FC and FC.

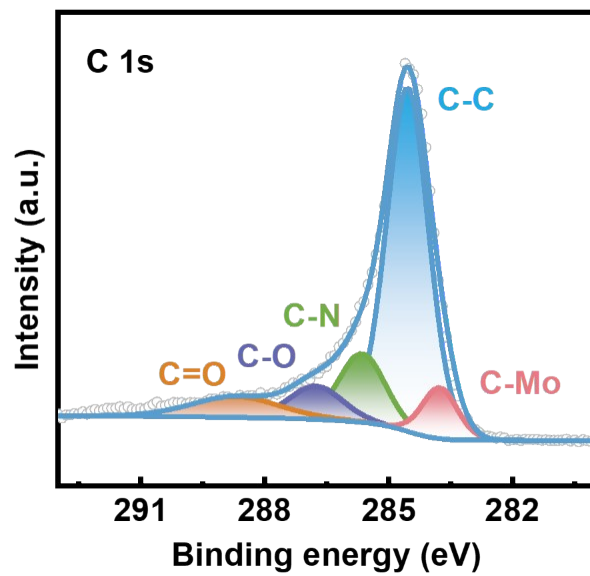


Fig.S5. C 1s XPS spectrum of MoC@FC.

Table S2. BET for MoC@FC and FC.

	BET surface area (m ² /g)	Volume of pores (cm ³ /g)	Average pore diameter (nm)
MoC@FC	573.52	2.45	15.26
FC	557.84	0.94	7.07

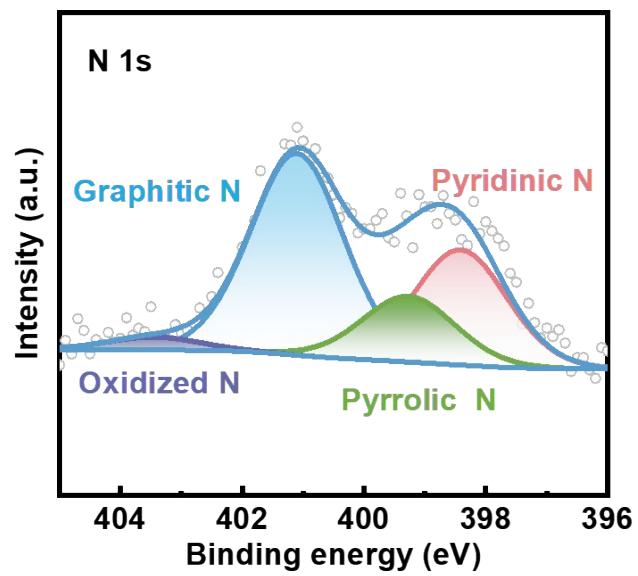


Fig. S6. N 1s XPS spectrum of MoC@FC.

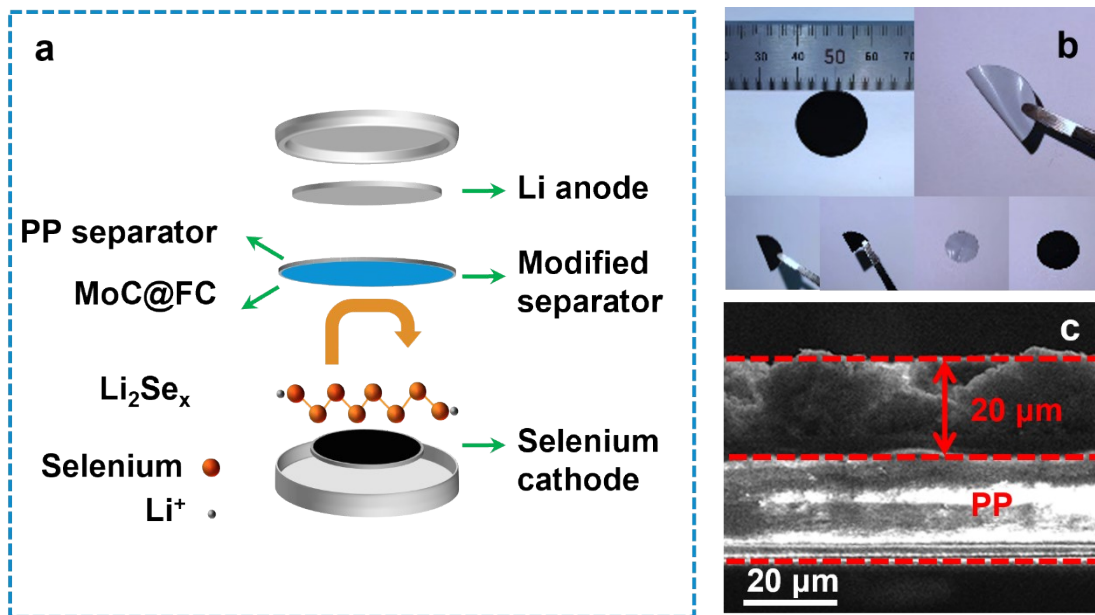


Fig. S7. (a) Assembly diagram for Li-Se battery. (b) Physical properties tests for MoC@FC functional separator. (c) SEM diagram of MoC@FC separator.

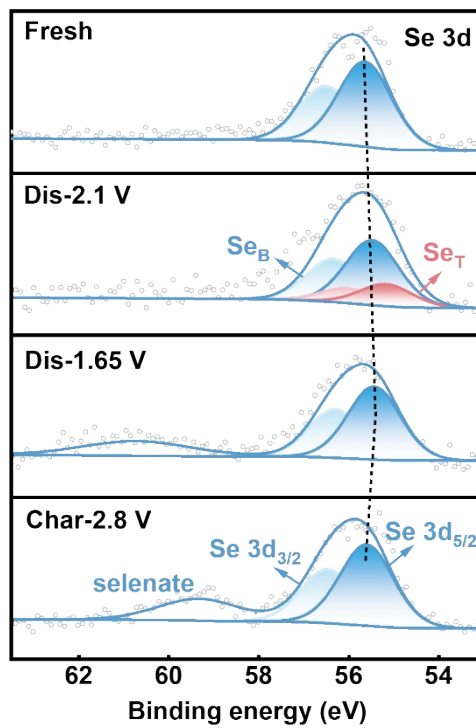


Fig. S8. Ex situ XPS analysis of MoC@FC at different states of charge.

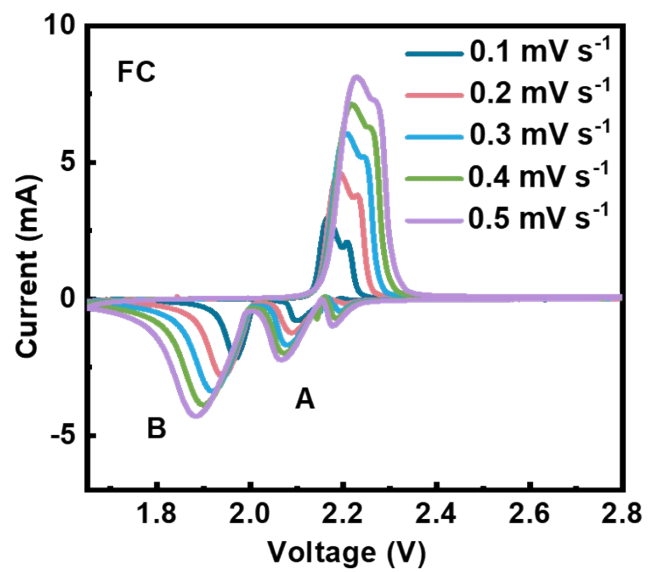


Fig. S9. CV curves at different scan rates from 0.1 to 0.5 mV s⁻¹ with FC.

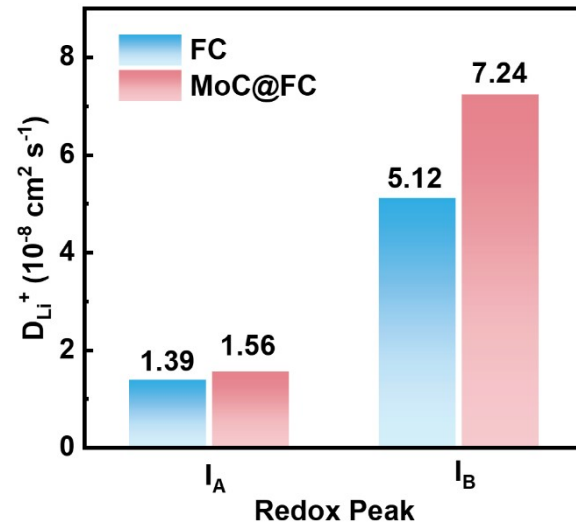


Fig. S10. Li⁺ diffusion coefficient fits of redox peak current of I_A and I_B for MoC@FC and FC.

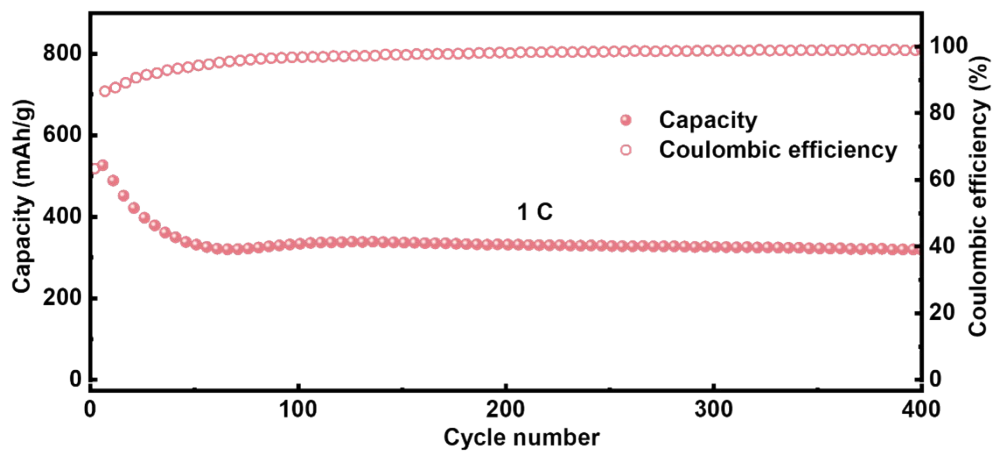


Fig. S11. Long-term cycling performance with MoC@FC at 1 C.

Table S3. Summary of the reported materials in Li-Se batteries

Samples	Current rate	Capacity (mAh/g)	Ref.
Se NPs@CTAB-MWCNTs	0.5 C	171.8 (500 cycles)	1
GPNFs	0.5 C	159 (100 cycles)	2
WO ₃	0.1 C	494 (100 cycles)	3
PCN	0.2 C	423 (100 cycles)	4
MoO ₃	0.5 C	446.7 (100 cycles)	5
OHPC-100	0.2 C	360 (200 cycles)	6
MoC	0.2 C	482.1 (100 cycles)	Our work
	1 C	320.1 (400 cycles)	

Notes and references

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