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Covalent-Organic Frameworks: Potential Host Materials for Sulfur Impregnation in Lithium-Sulfur Batteries

Huaping Liao, Huimin Ding, Bijian Li, Xinping Ai and Cheng Wang**

Key Laboratory of Biomedical Polymers (Ministry of Education), College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China

Email: chengwang@whu.edu.cn, xpai@whu.edu.cn

1. General Methods

1,4-Dicyanobenzene (99.0%) and sublimed sulfur powder (99.5%) were purchased from Aldrich. The electrolyte was purchased from Guotai-Huarong New Chemical Materials Co., Ltd. (Zhang Jiagang, China). All the reagents and starting materials were used without further purification. The nitrogen adsorption and desorption isotherms were measured at 77 K using a NOVA 4200e surface area size analyzer. Powder X-ray diffraction (PXRD) data was collected on PANalytical EMPYREA with CuKα1 (λ = 1.54056 Å) radiation operated at 40 kV and 40 mA. Samples were mounted on glass substrates by dropping powders from a wide-blade spatula and then leveling the sample with a razor blade. The best counting statistics were achieved by collecting samples using a 0.02° 2θ step scan from 1–50°. The morphologies of the samples were studied by scanning electron microscopy (Sirion 2000, FEI). EDX elemental mapping (Genesis 7000) was employed to visualize elemental compositions. The samples were prepared by putting a small a of powder on a conductive adhesive tape and then transferring to a vacuum sputtering chamber for coating with gold. XPS analysis was conducted on an ESCALab220i-XL electron spectrometer (VG Scientific) using 300W Al Kα radiation. TGA analyses were performed on a thermo-gravimetric analyzer (Setsys Evolution 16 apparatus) with samples held in a Al_2O_3 pan from room temperature to 750 °C under N_2 atmosphere, with a heating rate of 10 °C/min. The galvanostatic charge and discharge tests were performed on a programmable computer-controlled battery charger (CT2001A Land Battery Testing System, Wuhan, China).

2. Powder X-ray Diffraction Analysis

In order to confirm the crystalline structure of CTF-1 still remains in CTF-

1/S@155°C composite, we soaked the CTF-1/S@155°C in CS_2 for 3 hours to remove sulfur, followed by being dried in vacuum at 120 °C. Fig. S1 clearly shows the XRD signal of CTF-1 could be restored. As such, we can conclude that the crystalline structure of CTF-1 is still intact in CTF-1/S@155°C composite.

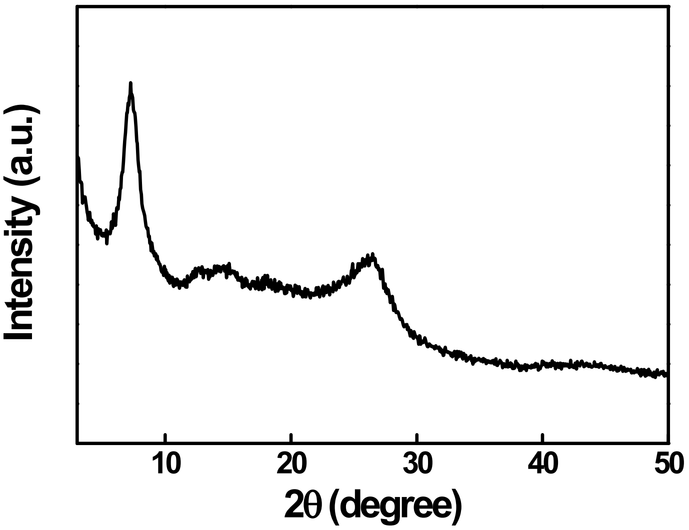

Fig. S1 The XRD spectrum of CTF-1/S@155°C composite after removing the sulfur (λ = 1.54056 Å).

2. Nitrogen Adsorption Isotherms

For nitrogen adsorption isotherms, CTF-1 was degassed at 150 °C and a vacuum below 10^{-3} Torr for 10 h prior to the measurements, whereas CTF-1/S@155°C composite was degassed at 60 °C. For CTF-1/S@155°C composite, since the BET surface is really low, we used about 1 gram composite for this experiment. The specific surface areas were calculated from the adsorption data by using Brunauer-Emmett-Teller (BET) methods. Pore size distributions were obtained from the adsorption branches using non-local density functional theory (NLDFT) method.

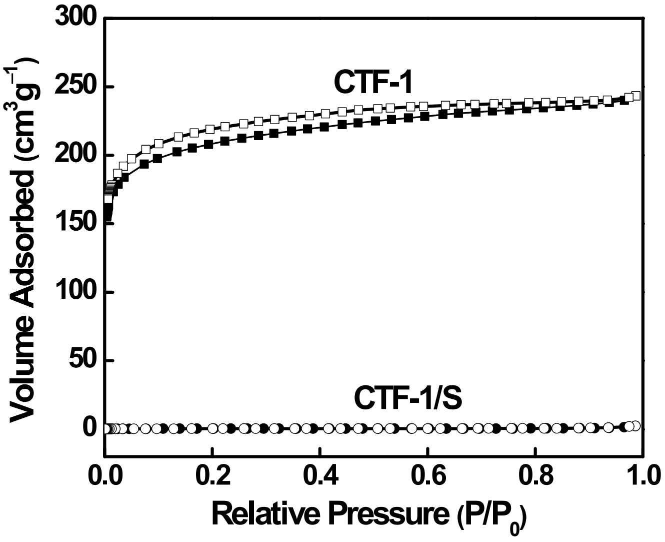

Fig. S2 N_2 absorption/desorption isotherms before and after impregnation with sulfur.

3. X-ray photoelectron spectroscopy

The XPS spectra of CTF-1/S@155°C and sulfur powder were shown as followed. We can see the starting sulfur has a peak with different binding energy (167-171.5 ev), which should be assigned to sulfur atoms in a sulfate like environment.

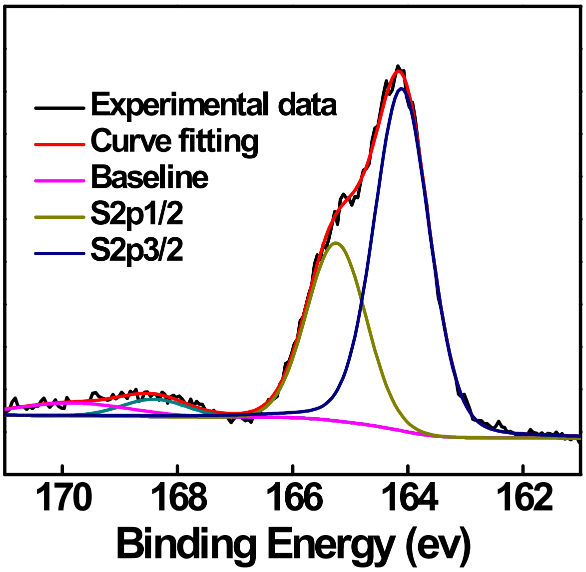

Fig. S3 XPS S2p spectra of CTF-1/S@155°C.

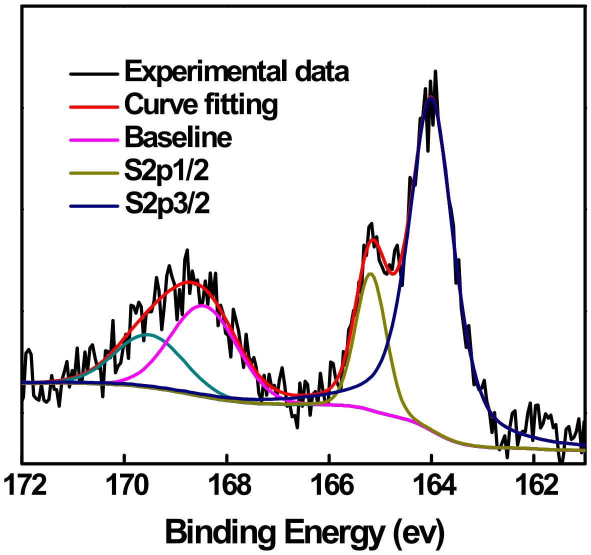

Fig. S4 XPS S2p spectra of sulfur powder.

4. Thermal Gravimetric Analysis

Fig. S4 shows the TGA profiles of CTF-1/S@155°C composite and CTF-1 under a N_2 atmosphere. From these data, we can calculate the weight loss between 200 °C and 450 °C is about 34%, which represents the amount of sulfur and is well consistent with the weighing result.

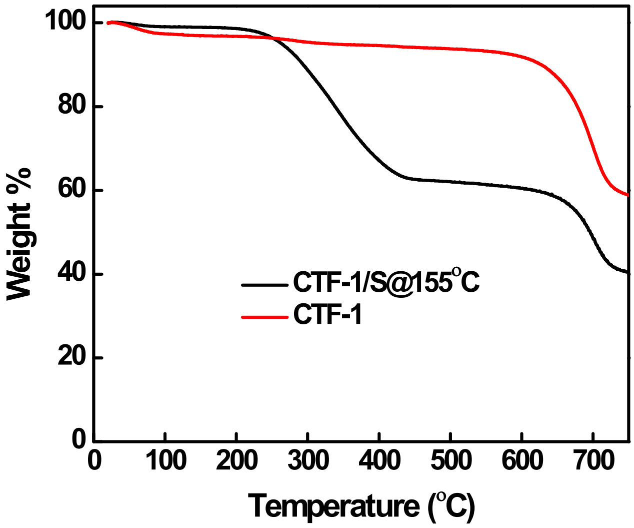

Fig. S5 TGA curves of CTF-1 and CTF-1/S@155°C composite recorded in N_2 atmosphere.

7. Electrochemical Measurement

The sulfur cathode was prepared by mixing 60 wt.% CTF-1/S, 30 wt.% acetylene black and 10 wt.% PTFE (poly tetrafluoroethylene) into a paste and roll-pressing the paste into a film, finally, pressing the electrode film onto an aluminum grid. The obtained film was cut into a disk with about 5.5 mg in weight. The film disks were dried at 60 °C for 24 h before use. All electrochemical tests for the sulfur electrode were carried out by using coin cells with lithium sheet as counter electrode and reference electrode. The organic carbonate electrolyte used in this study was 1 M lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) dissolved in dimethoxyethane (DME) and 1,3-dioxolane (DOL) (1:1, v:v). A microporous membrane (Celgard 2300) was used as the separator. The coin cells were assembled in an argon-filled glove box. The adding amount of the electrolyte in a single coin cell is ~ 20 uL. The galvanostatic discharge-charge experiments were performed at a voltage interval of 1.1-3.0 V (vs Li^+/Li) on a programmable computer-controlled battery charger. The specific capacity was calculated on the basis of the active sulfur material. Cyclic voltammetry (CV) measurement was conducted on a CHI 600A electrochemical workstation with a scan rate of 0.1 mV s^{-1} in the potential range of 1.1-3.0 V (vs Li^+/Li).

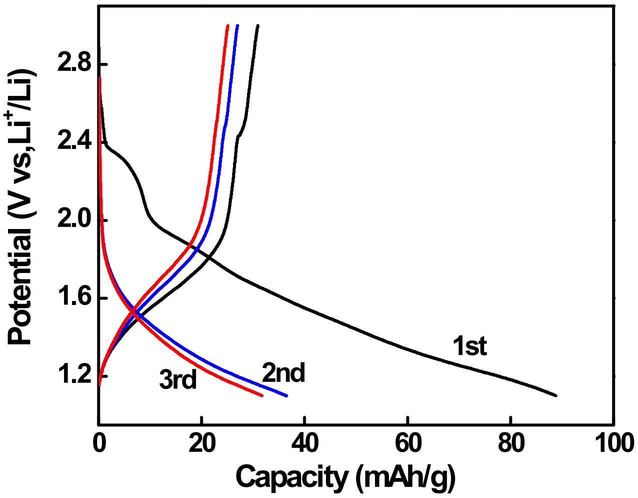

Fig. S6 The discharge and charge curves of the CTF-1 substrate at a current density of 30 mA/g in 1 M LiTFSI/DOL-DME electrolyte.

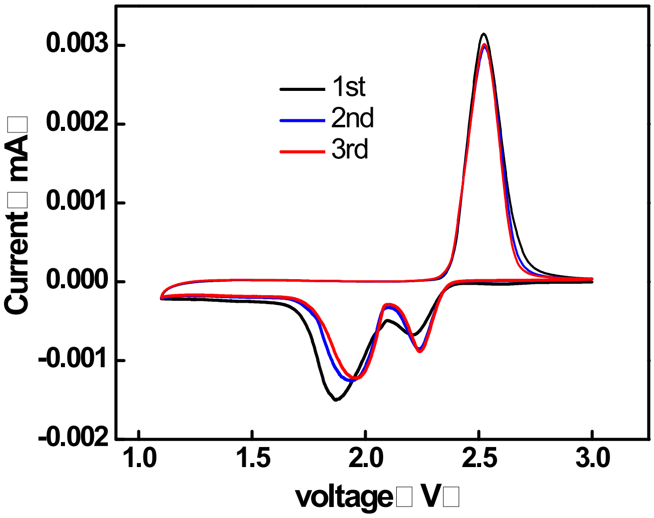

Fig. S7 The first three CV curves of CTF-1/S@155°C composite electrode.

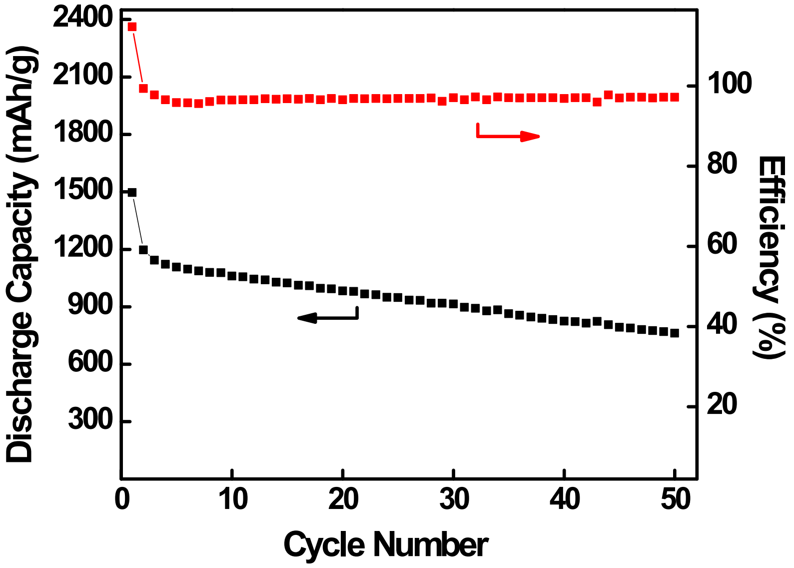

Fig. S8 Cycling performance of the CTF-1/S@155 °C composites at a rate of 0.1 C current density in 1 M LiTFSI/DOL-DME electrolyte.