Supplementary Information (SI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2024

# **Supporting information**

Hydrogen Sulfite Ion Functionalized Cationic Covalent Organic Framework Nanosheet as Separator Boosted the Energy Storage Performance of Li-S Batteries

Bingxin Jia, Bo Sun, Hongmin Yu, Chan Yao, Wei Xie, Yanhong Xu\*

Key Laboratory of Preparation and Applications of Environmental Friendly Materials, Key Laboratory of Functional Materials Physics and Chemistry of the Ministry of Education, Jilin Normal University, Changchun, 130103, China.

Email: xuyh198@163.com

### Contents

Section A. Material and methods	S2
Section B. Synthetic procedures	S3
Section C. FT-IR	S5
Section D. <sup>13</sup> C HMR	S5
Section E. SEM	S6
Section F. TGA	S6
Section G. N <sub>2</sub> adsorption	S6
Section H. Mechanical stability test	S7
Section I CV	S7
Section J. UV-vis	S8
Section K. Charging and discharging curve	S8
Section L. Cycling at high sulfur	S9

#### Section A. Material and methods

All commercially available reagents and solvents were used as received without further purification, unless otherwise noted. All solvents used, pure sulfur, conductive carbon black, and polyvinylidene fluoride (PVDF) were purchased from Aladdin.

Fourier transforms Infrared (FT-IR) spectra were recorded on a Perkin-Elmer model FT-IRfrontier infrared spectrometer. For all FT-IR tests, a small amount of sample can be directly mixed with potassium bromide and ground into a powder, compressed, and the pressed product can be directly tested. The solid-state UV-visible analyzer was used for Jasco V-770 spectrometer Solidstate. <sup>13</sup>C cross-polarization/magic angle spinning nuclear magnetic resonance (CP/MAS NMR) analysis was conducted using AVANCEIII/WB-400. Field-emission scanning electron microscopy (FE-SEM) images were performed on a JEOL model JSM-6700 operating at an accelerating voltage of 5.0 kV. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from  $2\theta = 1.5^{\circ}$  up to  $40^{\circ}$  with 0.02° increment. TGA analysis was carried out by using a Q5000IR analyzer (TA Instruments) with an automated vertical overhead thermobalance. Before measurement, the samples were heated at a rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere. X-ray photoelectron spectra (XPS) were recorded on an ESCALAB250Xielectron spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA). Nitrogen sorption isotherms were measured at 77 K with Bel Japan Inc. Model BELSORP-max analyzer. Before measurement, the samples were degassed in vacuum at 120 °C for more than 10 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume. The nonlocal density functional theory (NLDFT) method was applied for the estimation of pore size and pore size distribution. Before measurement, the samples were also degassed in vacuum at 120 °C for more than 10 h. Evaluate the wettability of the membrane by measuring the contact angle between the electrolyte and the membrane at room temperature using a contact angle measurement system (SL200 KB, Kino Industry, USA).

#### Section B. Synthetic procedures

#### 1.1 Synthesis of EB-COF

Synthesis of EB-COF was accomplished by reacting ethidium bromide (EB, 0.15 mmol) and 2,4,6-tri (4-aldehyde phenyl)-1,3,5-triazine (TFPT, 0.1 mmol), 1 mL (1:1, v/v) solvent mixture of n-butanol and o-dichlorobenzene with acetic acid (9 M, 0.1 mL). After sonication for 10 mins, the tube was flash frozen at 77 K using liquid nitrogen bath and degassed by three freeze-pump-freeze cycles, sealed under vacuum, and then heated at 120 °C for 72 h, which was isolated by filtration, washed with anhydrous acetone for 3 times, and vacuum drying at 100 °C for 12 h to afford EB-COF. The isolated yield of red powder is 76%.

#### 1.2 Synthesis of EB-COF: HSO<sub>3</sub>

First, 100 mg of EB-COF was dispersed in 0.1 mol<sup>-1</sup> sodium bisulfite solution, the mixture was continuously swept, the solution was renewed every day until the exchange was sufficient, washed with deionized water, and then dried at 80 degrees celsius for 12 h to obtain EB-COF: HSO<sub>3</sub>.

#### 1.3 Complexes of carbon sulfur (C/S) complex and cathode electrode sheet

Carbon and sulfur complexes were prepared by the melt-diffusion method, in which Super-p and sublimated sulfur were mixed in the ratio of 2.5:7.5, transferred to a reaction kettle lined with polytetrafluoroethylene, and heated at 155 °C for 20 h under argon protection, to obtain carbonsulfur (C/S) composites as the cathode materials. The carbon-sulfur complex C/S, Super P and the binder polyvinylidene fluoride (PVDF) were fully mixed in N-methylpyrrolidone (NMP) according to *w* (carbon-sulfur complex C/S) : *w* (Super P) : *w* (PVDF) = 8:1:1. Then it was coated on the carbon coated aluminum foil collector, dried in the oven at 50 °C for 2 h, and moved to the vacuum drying oven at 50 °C for 10 h. After drying, they were cut into 12 mm diameter discs to prepare positive electrode sheets. (Sulfur content  $1 \sim 1.5$  mg cm<sup>-2</sup>).

#### 1.4 Preparation of modified separators

EB-COF and EB-COF: HSO<sub>3</sub> were mixed with PVDF and Super-P in the weight ratio of 7:1:2, respectively, and ball-milled for 30 mins. Then NMP solution was added to the milled mixture and ball-milled for 1 h to obtain the slurry. The uniformly mixed slurry was evenly coated on the PP surface with a 40 mm four-sided sampler, and then dried in a vacuum oven at 60 °C for 12 h. After drying, the modified separator was cut into discs with a diameter of 16 mm.

#### **1.5 Preparation of electrolytes**

1 mol L<sup>-1</sup> LiTFSI and 1 wt% LiNO<sub>3</sub> additive in DME and DOL (1:1, *v*:*v*) as electrolytes. The DOL/DME electrolyte commonly used in Li-S battery was prepared by magnetic stirring for 24 h.

#### **1.6 Preparation of Li-S battery**

All Li-S batteries are assembled in a glove box filled with argon gas (H<sub>2</sub>O and O<sub>2</sub> content is less than (0.01 mL m<sup>-3</sup>)), using CR2032 button battery assembly, and put the positive electrode plate (diameter 12 mm), separator (diameter 16 mm), electrolyte and lithium sheet (diameter 16 mm) in turn. The amount of electrolyte used in this experiment was 40  $\mu$ L. The cathode/electrolyte mass ratios for the EB-COF and EB-COF: HSO<sub>3</sub>-modified batteries are 24 and 26  $\mu$ L mg<sup>-1</sup>, respectively.

#### 1.7 Electrochemical testing

The battery test system (LANHE CT2001A) was employed to evaluate the cycling performance with a voltage range from 1.7 to 2.8 V. CV (1.7 - 2.8V,  $0.1 \text{ mV s}^{-1}$ ), electrochemical impedance spectra (EIS) ( $10^{-1}-10^5$  Hz) and I-t curves were measured on CHI 660E, Chenhua.

The conductivity of Li<sup>+</sup> in the separator can be calculated using the EIS of a stainless steel symmetrical battery and formula (1-1):

$$\sigma = \frac{L}{RA} \# (-1)_{1.}$$

In equation (1-1), Land A represent the thickness and area of the separator, respectively, and R is the bulk ohmic resistance of the electrolyte.

Using the constant potential polarization method, the I-t curve of Li/separator/Li battery structure was tested, with a polarization voltage of 0.02 V and a polarization time of 1000 s. The Li<sup>+</sup> migration number was calculated using formula (1-2):

$$t_{Li^{+}} = \frac{I_{S}(\Delta V - I_{0}R_{0})}{I_{0}(\Delta V - I_{S}R_{S})} \# (1 - 2)$$

In equation (1-2),  $\Delta V$  represents the constant voltage applied,  $R_0$  and  $R_s$  represent the initial resistance and polarization resistance, respectively, and  $I_0$  and  $I_s$  represent the initial and steady-state current, respectively.

Section C. FT-IR



Fig. S1. FT-IR spectra of TFPT, EB, EB-COF and EB-COF: HSO<sub>3</sub>.

Section D. <sup>13</sup>C HMR



Fig. S2. <sup>13</sup>C NMR spectrum of EB-COF.



Fig. S3. EDS analysis of EB-COF.

Section F. TGA



Fig. S4. TGA curves of EB-COF and EB-COF: HSO<sub>3</sub>.

Section G. N<sub>2</sub> adsorption



Fig. S5. (a)  $N_2$  adsorption isotherms and (b) pore size distributions of EB-COF and EB-COF: HSO<sub>3</sub>.

## Section H. Mechanical stability test



(a) Initial appearance

(c) Shape after folding 3 times

Fig. S6. Mechanical properties testing chart of EB-COF: HSO<sub>3</sub> composite separator.

Section I CV



Fig. S7. CV plots of the Li-S batteries with EB-COF (scan rate: 0.1 mV s<sup>-1</sup>).





**Fig. S8.** The full UV/Vis absorption spectra for EB-COF (a) EB-COF: HSO<sub>3</sub> (b) in the range of 300 to 800 nm wavelength, Tauc's plot of EB-COF (c) EB-COF: HSO<sub>3</sub> (d) obtained from the optical absorbance spectra using a solid UV/Vis/NIR spectrophotometer.



Section K. Charging and discharging curve

**Fig. S9.** Discharge-Charge curves at various current densities of 0.1, 0.2, 0.5, 1, and 2 C of (a) EB-COF (b) EB-COF: HSO<sub>3</sub> battery and (c) EB-COF and EB-COF: HSO<sub>3</sub> batteries.



**Fig. S10.** Charge-discharge curves of (a) EB-COF: HSO<sub>3</sub> and (b) EB-COF at 5 th, 100 th, 200 th, 300 th, 400 th, and 500 th laps, respectively.

Section L. Cycling at high sulfur



Fig. S11. Cycling performance of EB-COF: HSO<sub>3</sub> at high sulfur loads.