

## Electronic Supplementary Information

### Highly dispersed Sulfur in porous aromatic framework as cathode for Lithium-Sulfur batteries

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#### Experimental

A porous aromatic framework (PAF) was prepared via Yamamoto-type Ullmann reaction.<sup>1</sup> PAF-S composite was prepared by grounding PAF powder (0.1 g) and sulfur (0.5 g) together in a mortar, followed by heating at 155 °C for 6h. The composite was then heated at 300 °C under argon for 1h to evaporate the surface sulfur. Methyl isopropyl sulfone (MiPS) was obtained from TCI America and was distilled three times over CaH<sub>2</sub> to reduce the water content below 50 ppm as detected from Karl-Fisher titration. Methyl propylpyrrolidiniumbis(trifluoromethanesulfonyl)imide (MPPY.TFSI) was synthesized and dried as described before<sup>32</sup>. LiPF<sub>6</sub> was obtained from Novolyte Technologies Inc. and was directly used without further treatment. LiTFSI was obtained from Aldrich and was dried at 150 °C under vacuum for 24 hours before use. The electrolyte solutions, 1.0 M LiPF<sub>6</sub>/MiPS, and 0.5M LiTFSI/MPPY.TFSI, were made inside an Argon filled glovebox with both oxygen and moisture level below 0.5ppm.

Nitrogen adsorption isotherms were measured at -196°C using TriStar 3000 volumetric adsorption analyzer manufactured by Micromeritics Instrument Corp. (Norcross, GA). Before adsorption measurements the samples were degassed in flowing nitrogen at 100°C for two hours. The specific surface area of the samples was calculated using the Brunauer-Emmett-Teller (BET) method within the relative pressure range of 0.05 to 0.20.<sup>2</sup> Pore size distributions were calculated using the BJH algorithm for cylindrical pores according to the KJS method calibrated for pores up to 10 nm.<sup>3</sup> A statistical film thickness for a reference carbon adsorbent<sup>4</sup> was also used for the  $\alpha_S$ -plot analysis.<sup>5</sup> Wide angle X-ray diffraction (WAXS) patterns were recorded on a Siemens D5005 diffractometer operating at 40 kV and 40 mA. The thermal gravimetric analysis (TGA) profile was recorded on a TGA thermogravimetric analyser (TA Instruments, Inc.). X-ray photoelectron spectroscopy (XPS) data were collected using a PHI 3056 spectrometer with an Al anode source operated at 15KV and an applied power of 350 W.

Electrochemical experiments were carried out using coin cells. The sulfur composite electrode was prepared by casting a well-homogenized slurry of PAF-S composite (65 wt %), carbon black (20 wt %), and PVdF (15 wt %) in NMP on aluminum foil using a doctor blade. The dried electrodes were pressed under a hydraulic load of 1 ton for 1 min before cutting into discs of 1.3 cm diameter. The discs were further dried at 60 °C under vacuum for 24 h before transferring into the glovebox for battery assembly. The sulfur loading within the PAF-S cathode is in the range of

0.35 and 0.5 mg. The batteries were assembled as 2032-type coin cells inside an argon-filled glovebox by using the PAF-S composite as the cathode electrode, lithium metal as the anode electrode, Celgard 3401 as the separator, and either 0.5 M LiTFSI/MPPY.TFSI or 1.0 M LiPF<sub>6</sub>/MiPS as the electrolyte. Galvanostatic discharge-charge experiments were tested in the voltage range of 1.0-3.0 V on an Arbin battery test system at different temperatures.

The capacities are calculated based on the mass of sulphur.

References:

1. T. Ben, K. Shi, Y. Cui, C. Y. Pei, Y. Zuo, H. Guo, D. L. Zhang, J. Xu, F. Deng, Z. Q. Tian and S. L. Qiu, *J. Mater. Chem.*, 2011, **21**, 18208-18214.
2. M. Kruk and M. Jaroniec, *Chem. Mater.*, 2001, **13**, 3169-3183.
3. M. Jaroniec and L. A. Solovyov, *Langmuir*, 2006, **22**, 6757-6760.
4. J. Choma, J. Gorka and M. Jaroniec, *Microporous and Mesoporous Materials*, 2008, **112**, 573-579.
5. M. Kruk, M. Jaroniec and K. P. Gadkaree, *Journal of Colloid and Interface Science*, 1997, **192**, 250-256.

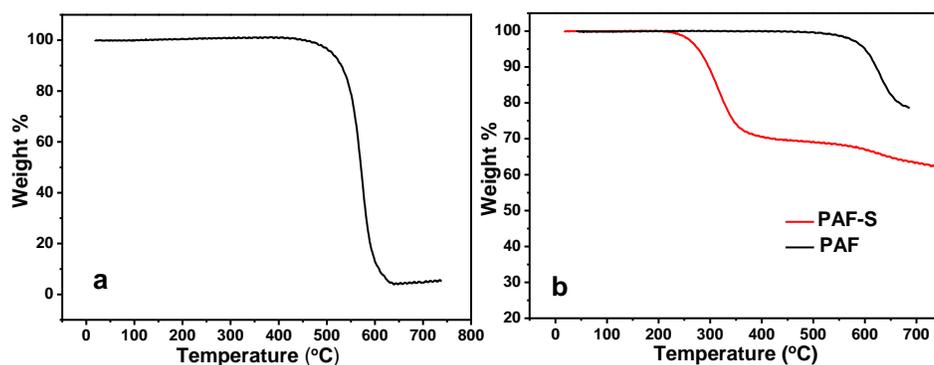


Fig. S1 (a) TGA curve of PAF recorded in air; (b) TGA curves of PAF and PAF-S recorded in N<sub>2</sub>.

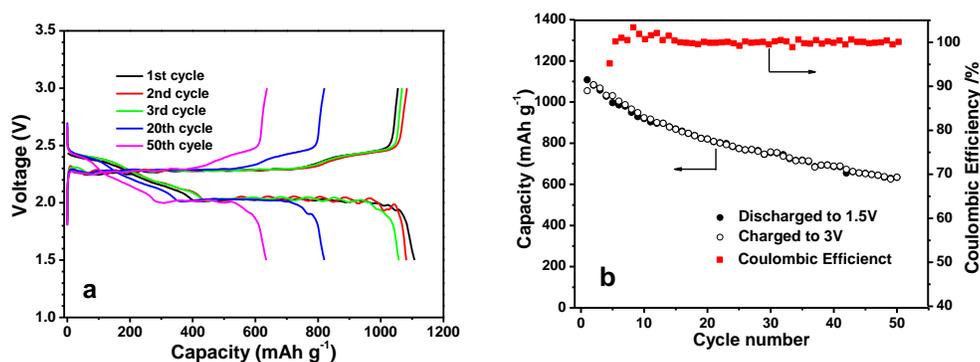


Fig. S2 Galvanostatic discharge/charge curves (a) and cycling performance (b) of the Li||PAF-S cell under a current rate of 0.05C in 1 M LiPF<sub>6</sub>/MiPS at 25 °C

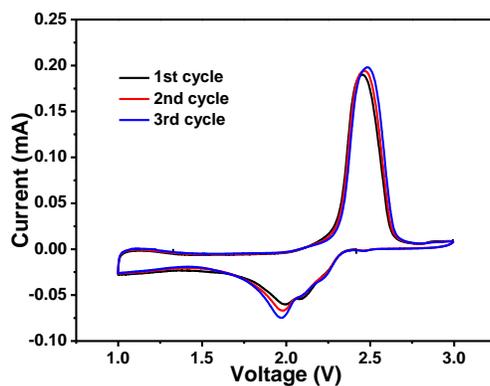


Fig. S3 CV curves of the Li||PAF-S cell at a scan rate of  $0.1 \text{ mV s}^{-1}$  in  $1 \text{ M LiPF}_6/\text{MiPS}$  at  $25 \text{ }^\circ\text{C}$

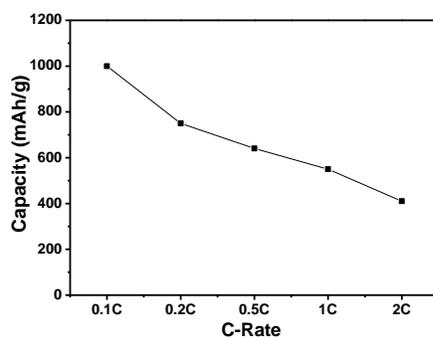


Fig. S4 Discharge capacity for the PAF-S composite at different rates in  $1 \text{ M LiPF}_6/\text{MiPS}$  at  $25 \text{ }^\circ\text{C}$ .

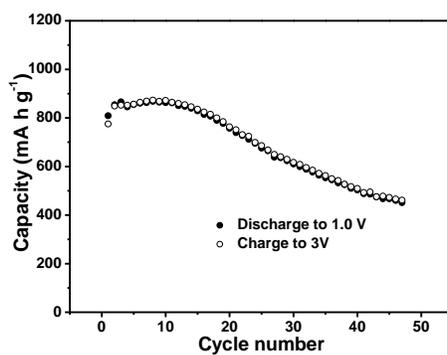


Fig. S5 cycling performance of the Li||PAF-50%S cell under a rate of  $0.05 \text{ C}$  in  $0.5 \text{ M LiTFSI/MPPY.TFSI}$  at  $50 \text{ }^\circ\text{C}$