Electronic Supplementary Information for

Dual-mode sulfur-based cathode materials for rechargeable Li-S batteries

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Experimental Section

1. Preparations of composite materials

1.1. pPAN-S composite preparation

The PAN was firstly mixed with S powder by ball milling in a given weight ratio, and then the mixture was heated at 300 °C for 7 h in flowing N_2 atmosphere. After the system was naturally cooled to room temperature, the black powder product was finally obtained with sulfur content of ca. 45 wt.%.

1.2. mGO-S composite preparation

Graphite Oxide (GO) was synthesised from fine natural graphite fine powder by a modified Hummers method. In our experiment, the GO was suspended in ultrapure water and then sonicated to form a stable GO dispersion. The sodium polysulfide (Na_2S_x) solution was obtained by dissolving S into a Na_2S aqueous solution. Then, the Na_2S_x solution was added to the above-prepared GO dispersion and the as-prepared GO/Na_2S_x blended solution was stirred for 24 h. The precipitate was filtered and washed with acetone and distilled water for several times to eliminate salts and impurities. After filtration, the precipitate was dried at 50 ℃ in a drying oven for 48 hours. The as-synthesized mGO-S composite was heat-treated in a sealed vessel under folwing argon at 150 ℃ for 12 h to obtained mGO-S composite.

1.3. pPAN-S/mGO-S composite preparation

Firstly, the pPAN-S composite was prepared as the above-mentioned method and then added into the GO dispersions to form a pPAN-S/GO dispersion. Followed the Na_2S_x solution was added and the subsequent steps are the same as described in 1.2.

2. Structural and morphological characterizations

X-ray powder diffraction (XRD) analysis was conducted on a Rigaku diffractometer D/MAX-2200/PC equipped with Cu Kα radiation (λ=0.15406 nm) to characterize the structure of the composite materials. The Sulfur content of the composite was determined by elemental analysis (Vario EL III elemental analyzer, Elementar, Germany). The electronic conductivities of the composites were measured by a four-point probe method (RTS-8 Four-Point probe meter). BET specific surface areas of the samples were obtained on a Brunauer-Emmett-Teller surface area analyzer (BET, ASAP 2010 M+C, Micromeritics Inc.). The particle morphology was observed using scanning electron microscopy (SEM) on a JEOL field-emission microscope (JSM-7401F), and transmission electron microscopy (TEM) on a JEOL high-resolution electron microscope (JEM-2010).

3. Electrochemical Measurements

Electrode slurry was prepared by mixing 80 wt.% active material, 10 wt.% super-P carbon powder and 10 wt.% poly(vinylidene fluoride) (PVDF) dissolved in N-methyl-2-pyrrolidinone. The electrodes in diameter of 12 mm were formed by coating the slurry onto aluminium foil current collector and drying at 80 °C for 4h under vacuum. The weight of active composite material in electrodes is 1-2 mg cm^{-2}. Electrochemical behaviour of the composite materials was investigated via CR 2016 coin cells with lithium metal anode, ENTEK ET20-26 PE membrane separator and 1M LiTFSI/DOL+DME (v/v, 1:1) electrolyte with or without $LiNO_3$ additive. The cells were assembled in the argon-filled glove box. Galvanostatic charge-discharge measurements were conducted at ambient temperature on a Land battery measurement system (Wuhan, China) with the cut-off voltage of 3/1 V vs. Li/Li^+

at 0.1 C (1C means the current rate for charging or discharging the theoretical capacity of S in

1 h, 1675 mA g^{-1}).

Table S1 Component distributions of the final products in mass

Samples	pPAN	mGO	S (pPAN)	S (mGO)
pPAN-S (wt.%)	54.7	---	45.3	---
mGO-S (wt.%)	---	18.3	---	81.7
pPAN-S/mGO-S (wt.%)	26	9	23	42

Table S2 Physical properties parameters of final composites

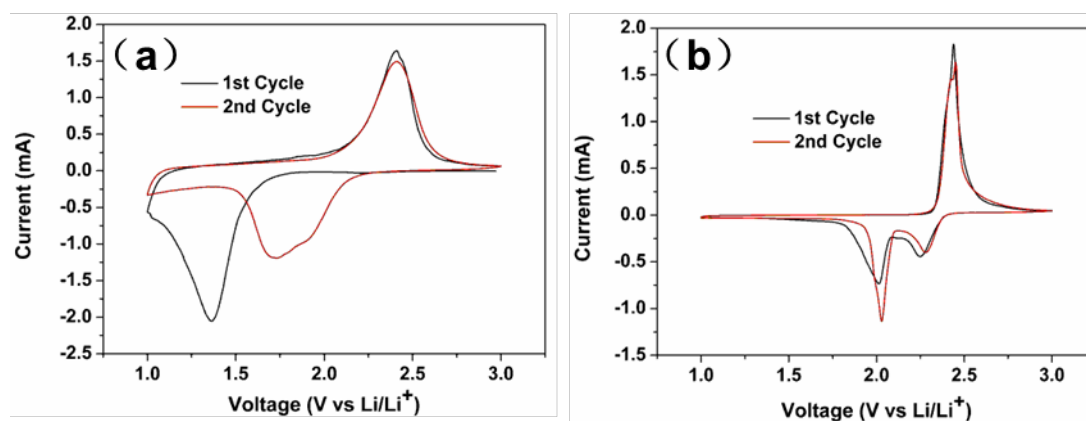| Samples	pPAN-S	mGO-S	pPAN-S/mGO-S
Specific Surface area ($m^2 g^{-1}$)	16.5	183.4	53.2
Conductivity (S cm^{-1})	0.00041	0.152	0.0027

Fig. S1 Cyclic voltammogram curves of (a) pPAN-S and (b) mGO-S composite

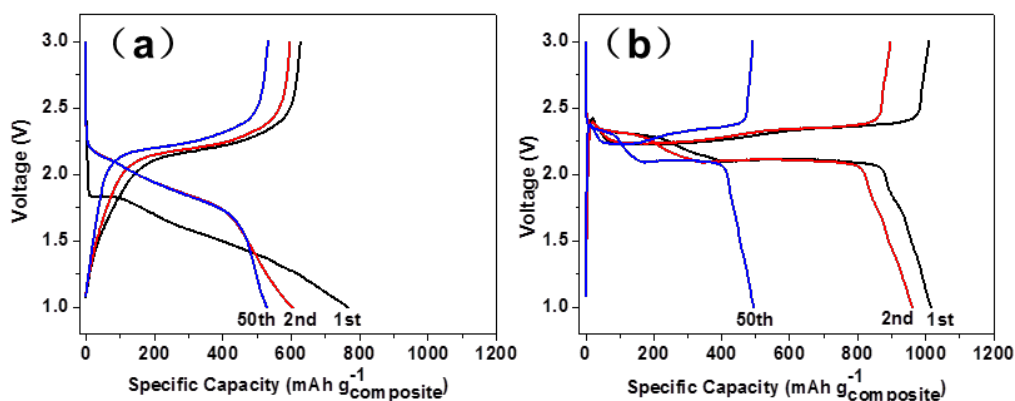cathodes in the electrolyte with LiNO$_3$ at 0.05mV s^{-1} scanning rate.

Fig. S2 Galvanostatic charge/discharge profiles of (a) pPAN-S and (b) mGO-S
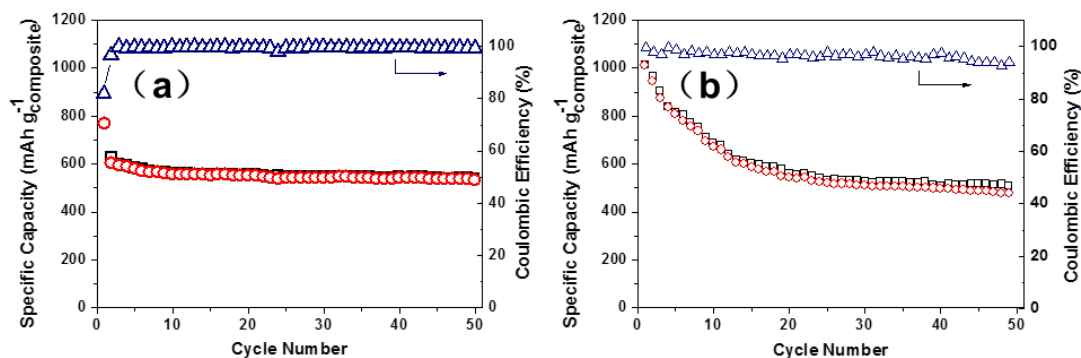
composite cathodes at 0.1C rate.

Fig. S3 Cycling stability of (a) pPAN-S and (b) mGO-S composite cathodes in the

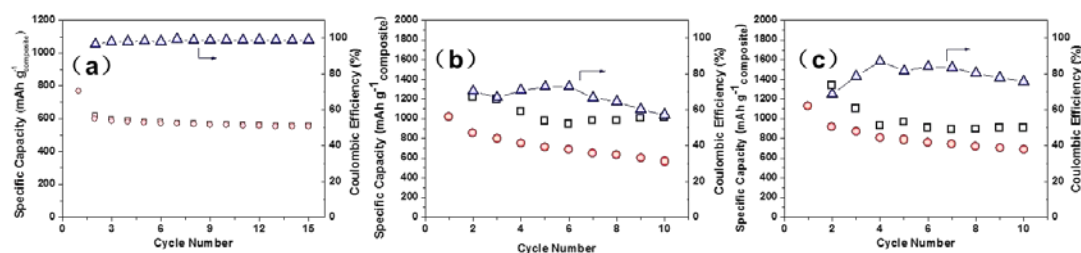electrolyte with $LiNO_3$ at 0.1C. The coulombic efficiencies are also demonstrated.

Fig. S4 Cycling stability of (a) pPAN-S, (b) mGO-S and (c) pPAN-S/mGO-S

composite cathodes in the electrolyte without $LiNO_3$ at 0.1C. The coulombic

efficiencies are also demonstrated.