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Black phosphorus-modified sulfurized polyacrylonitrile with high C-rate and cycling performance in ether-based electrolyte for lithium sulfur batteries

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Experimental Section

The BP-SPAN composite was synthesized by co-heating of sublimed sulfur, polyacrylonitrile monomer and prepared black phosphorus at Argon/ 300 ^{o}C/ 10 h. Gram-scale of BP was synthesized using a recyclable liquid phase method at low temperature of 120-200 ^{o}C, as our previous reported method.[1] Typically, 1.568 g of nano sublimed sulfur (~50 nm), 0.4 g of polyacrylonitrile monomer (M_w 150000, Aldrich) and 0.032 g BP were dispersed in 10 mL ethanol medium, followed by continuous ball-milling at a speed of 500 rpm min^{-1} for 8 h. After centrifuged and washed with ethanol, the mixture was dried at a vacuum oven at 60 ^{o}C for 12 h.

Subsequently, the sample was calcined in a tube furnace at 300 °C for 10 h under argon atmosphere. After disposed with grinding and sieving (200 mesh), the BP-SPAN-2 (mass (BP): mass (BP + Sulfur) = 0.02) was successfully synthesized, giving a black powder. The BP-SPAN-5 (mass (BP): mass (BP + Sulfur) = 0.05) was synthesized by adjusting the mass of raw materials (1.52 g sublimed sulfur, 0.4 g of polyacrylonitrile monomer, 0.08 g BP). The SPAN was synthesized by the same method, except the mass of sublimed sulfur and polyacrylonitrile monomer were adjusted to 1.6 g and 0.4 g, respectively.

Electrochemical Measurements

The electrochemical performances of the materials were evaluated using CR2025 coin-type half cells assembled in an argon-filled glove box (O_2, H_2O< 0.1 ppm). The working electrode was prepared by casting the slurry with active materials (80wt%), super P (10wt%) and polyvinylidene fluride (PVDF, 10wt%) on the carbon-coated aluminum current collector, followed by drying in vacuum oven for 12 h at 80 °C. The diameter of electrode film was 14 mm and the sulfur aera loading on the electrode was around 1 mg cm^{-2}. The electrolyte/sulfur ratio is controlled at ~50 μL/mg. The electrolyte was composed of 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Aldrich) and 0.4 M $LiNO_3$ (Aldrich) as additive in a mixture of 1,2-dimethoxyethane/ 1,3-dioxolane (DME: DOL, volume ratio=1:1), and the separator was Celgard$^{@}$ 2400 polypropylene membrane. The galvanostatic (dis-)charge tests were conducted with Neware battery testing system operated at 28 °C. Cyclic voltammetry (CV) measurements were carried on an AUTOLABPGSTAT302N electrochemical workstation under a scan rate of 0.1 mV s^{-1} between 1.0 and 3.0 V. Electrochemical impendence spectroscopy (EIS) was evaluated on a PARSTAT 2273 workstation in the frequency range of 10^5 to 10^{-2} Hz with an amplitude (sinusoidal voltage) of 5 mV.

The lithium diffusion coefficient of cathodes can be calculated using the following equation:[2]

$$D_{Li^+} = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2} \qquad \text{(S1)}$$

where, D_{Li+} is the lithium ion diffusion coefficient, R is the gas constant, T is the absolute temperature, A is the aera of cathode/electrolyte interface, n is the number of electrons transfer per molecule, F is the Faraday's constant, C is the concentration of lithium ion, and Warburg coefficient (σ) is the slope of the line $Z' \sim \omega^{-1/2}$, respectively.

Materials Characterization

The morphology and structure of the materials were investigated by transmission electron microscopy (TEM, FEI Talos F200X). The X-ray diffraction (XRD) spectra were collected using a Netherlands' PANalytical X'pert power diffractometer equipped with Cu Kα radiation (λ=1.54 Å). The TurboFlash™ Combustion Technology (CHNS, EA 3000, Elementar) elemental analyzer was operated to test the accurate sulfur content. The X-ray photoelectron spectroscopy (XPS) analysis of materials was conducted with a Thermo Fisher Scientific ESCALAB 250XI spectrometer using a monochromic Al Kα source (1486.6 eV), and the binding energy values were calibrated based on the C1s peak at 284.6 eV. The Raman spectra were measured using a Horiba Jobin Yvon Labram-HR800 micro-Raman system with a 532 nm YAG laser excitation.

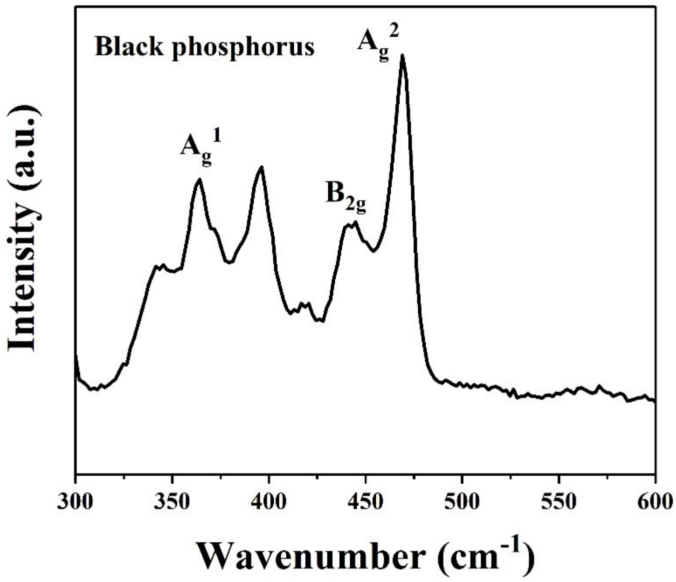

Fig. S1 Raman spectrum of black phosphorous.

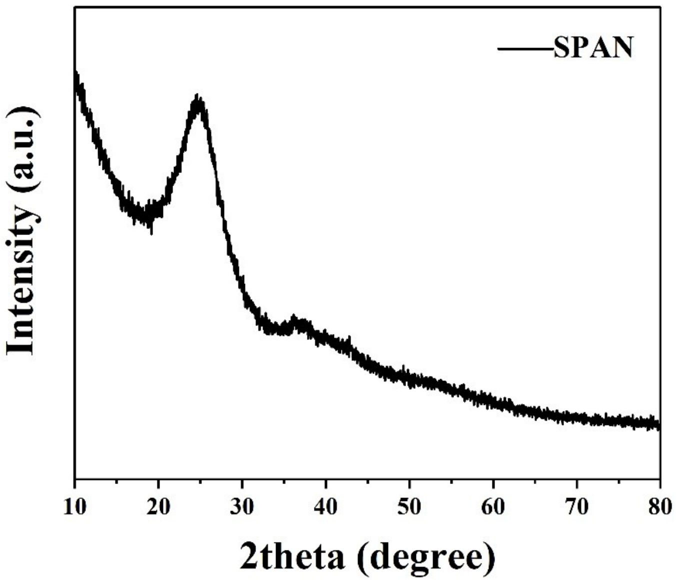

Fig. S2 XRD pattern of SPAN.

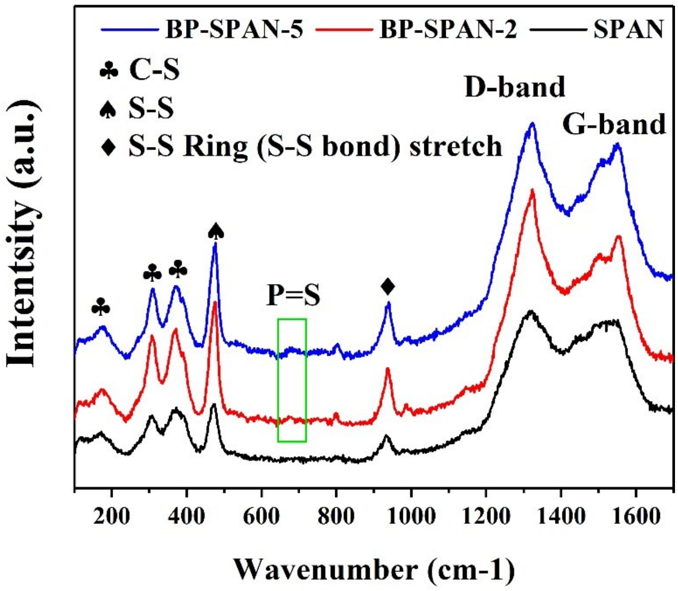

Fig. S3 Raman spectrum of SPAN, BP-SPAN-2 and BP-SPAN-5.

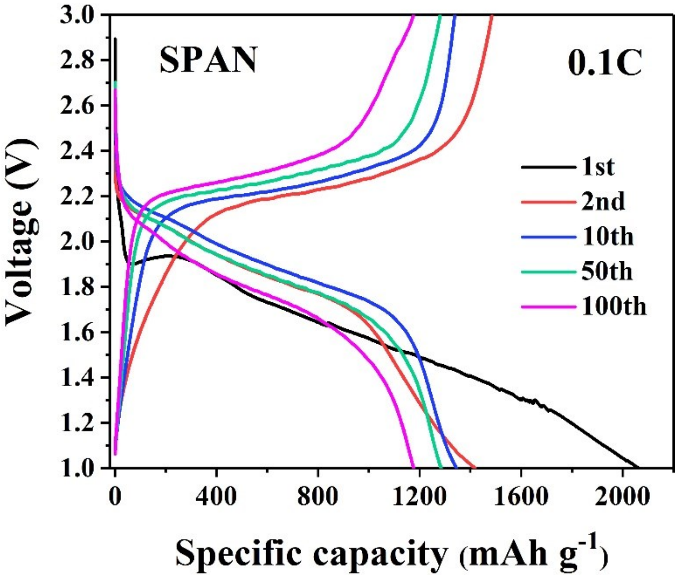

Fig. S4 (Dis-)Charge curves of SPAN at 0.1C.

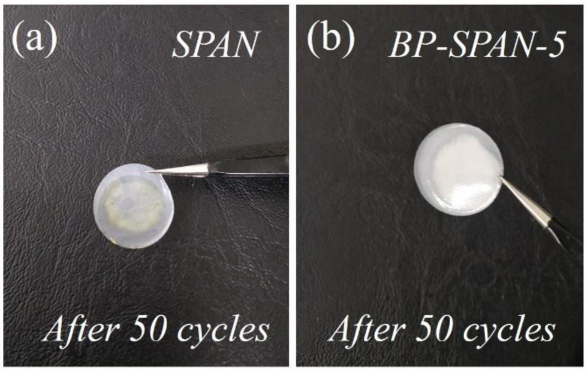

Fig. S5 The separator of disassembled cells after 50 cycles, (a) SPAN, (b) BP-SPAN-5.

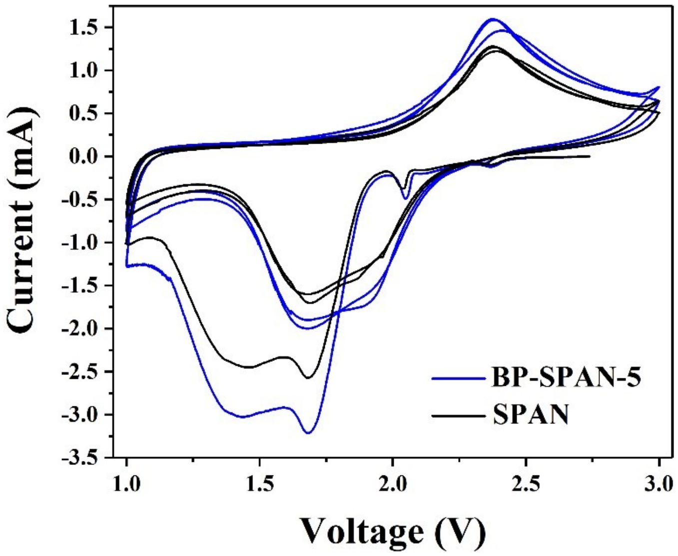

Fig. S6 CV curves of SPAN and BP-SPAN-5.

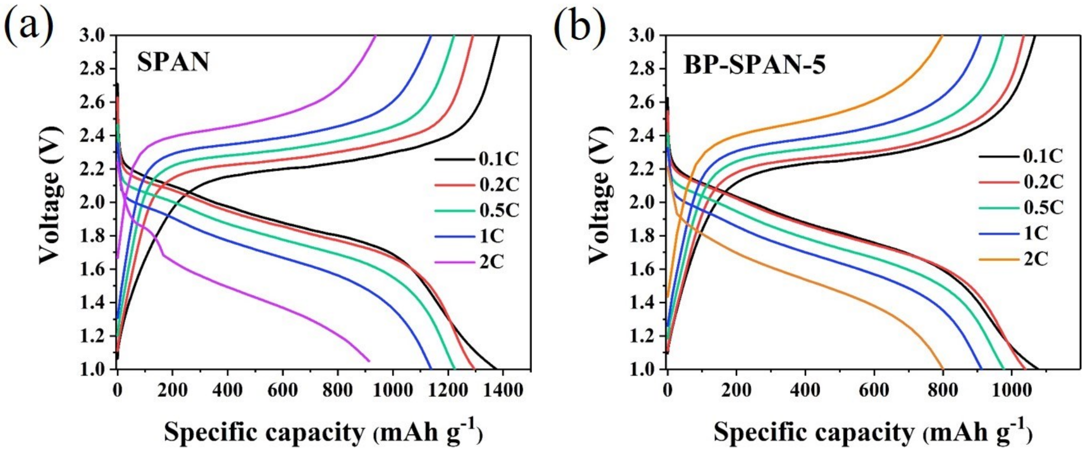

Fig. S7 (Dis-)Charge curves of cathodes at various C-rate, (a) SPAN, (b)BP-SPAN-5.

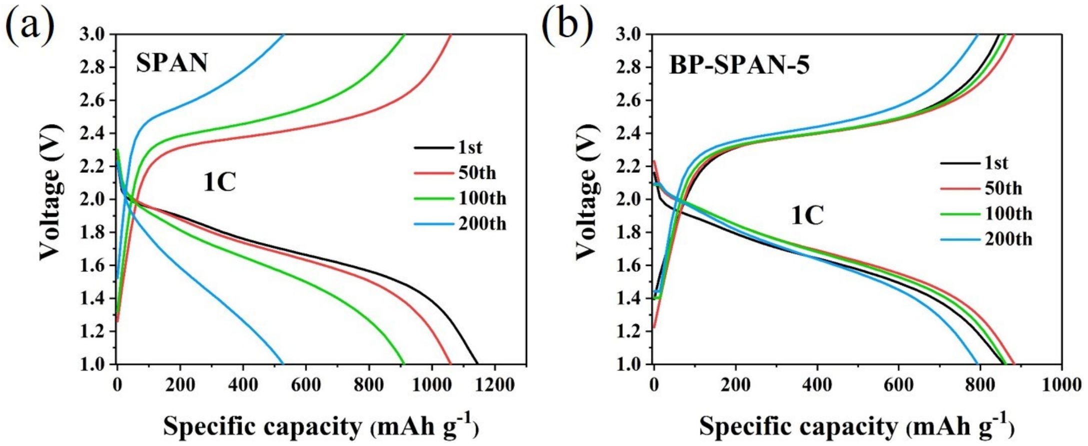

Fig. S8 Discharge/charge curves of cathodes for long cycling at 1C, (a) SPAN, (b)BP-SPAN-5.

Table. S1 Accurate values of cathodes at various states, including R_0, R_f and R_{ct}, calculated by modeling the impedance spectra.

Samples	**Initial**			**After 1 cycle (2nd)**			**After 10 cycles (10th)**		
	R_0	R_f	R_{ct}	R_0	R_f	R_{ct}	R_0	R_f	R_{ct}
SPAN	5.435	**-**	120.1	5.65	17.27	41.65	6.104	19.17	37.85
BP-SPAN-2	5.314	**-**	74.86	5.219	5.811	27.59	5.785	8.458	25.56

Reference

1. Y. Wang, M. He, S. Ma, C. Yang, M. Yu, G. Yin and P. Zuo, *J Phys. Chem. Lett.*, 2020, **11**, 2708-2716.
2. M. Levi and D. Aurbach, *Electrochimica. Acta*, 1999, **45**, 167-185.