An *in situ* chemically and physically confined sulfur-polymer composite for lithium sulfur battery with carbonate ester electrolyte

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Experimental section:

Preparation of SPANI samples. Sublimed sulfur (99.99%, Adamas-beta) and polyaniline (PANI, 99%, Macklin) with a mass ratio of 6:1 were thoroughly mixed by ball-milling for 1 h to yield a blackish green mixture. Then the mixture was heated at 280, 320 or 350 °C for 10 h with heating rate of 5 °C/min in a tube furnace under Ar atmosphere, and the obtained samples were noted as SPANI-280, SPANI-320 and SPANI-350.

Materials characterization. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were recorded on a field emission SEM (Nova NanoSEM 450, FEI company, USA) and TEM (JEM-2100, JEOL Ltd., Japan) respectively. The powder X-ray diffraction (XRD) patterns were recorded on X-ray diffractometer (D8 Advance, Bruker Corp., Germany) using Cu-Kα radiation (λ = 0.15418 nm) at 40 kV. Thermogravimetric analysis (TGA) curves were conducted in a thermogravimetric analyzer (TGA 7, Perkin Elmer, Inc., USA), where the temperature rose from 50 °C to 800 °C at a heating rate of 10 °C min^{-1} in the flow of argon at a flow rate of 30 mL min^{-1}. X-ray photo electron spectroscopy (XPS) was measured by a X-ray photoelectron spectrometer (AXIS ULTRA DLD, Kratos Analytical Ltd., UK) with monochromatic Al Kα source (1486.6 eV). Raman spectra were measured on a Raman microscope (DXR, Thermo Fisher Scientific Inc., USA) with a laser wavelength of 532 nm at room temperature. FTIR was recorded on a Spectrum 100 spectrometer in the frequency range of 4000-500 cm^{-1}. Elemental analysis of C, N, S and H was conducted using a Vario EL Cube elemental analyzer.

Electrochemical characterization. Electrochemical experiments were carried out using CR2016 coin cells. To fabricate working electrodes, SPANI, Super-P, and NaCMC with a weight ratio of 80:10:10 were mixed to homogeneous slurry in water. The resulting slurry was coated on aluminum foil and then dried in a vacuum oven at 60 °C overnight. The typical sulfur loading was about 1.2 mg cm^{-2}. Coin cells were assembled in an argon-filled glove box (H_2O, O_2 < 0.1 ppm, Mbraun) with Celgard 2400 (Celgard, USA) separator and pure Li foil (Alfa Aesar, 99.9%) anode. The standard electrolyte 1 M $LiPF_6$ in EC/DMC (1:1, v/v) were provided by BASF. Controlled amount of electrolytes (18 μl, 15 μl mg^{-1}_{sulfur}) were added in the coin cells by pipette. Galvanostatic charge/discharge was conducted using a Land CT2001A multi-channel battery testing system in the fixed voltage range of 1.0-3.0 V (*vs*. Li/Li^+) at room temperature. The cells were tested with different C-rates at 0.1, 0.2, 0.5, 1, 1.5 and 2 C for each 10 cycles and then back to 0.1 C. The durability test was conducted at 0.3 C and 1 C. The current density was calculated based on the theoretical capacity of S (1 C = 1672 mA g^{-1}) and the specific capacity was calculation based on the sulfur content obtained from elemental analysis. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were obtained on a PARSTAT 4000

electrochemical workstation. CV was recorded at a scan rate of 0.1 mV s^{-1} while EIS was determined in the frequency range from 100 kHz to 0.1 Hz.

Table S1. The element analysis results of SPANI samples prepared under different degrees

Sample	C	S	N	H
SPANI-280	46.70	38.09	8.04	7.18
SPANI-320	41.34	47.68	7.13	3.87
SPANI-350	43.89	45.53	7.50	3.08

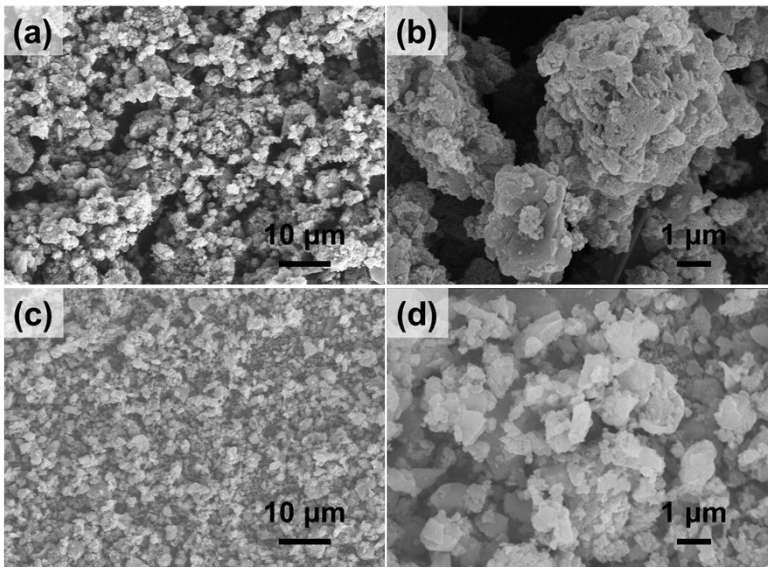

Fig. S1 SEM images of raw PANI (a, b) and SPANI (c, d) samples.

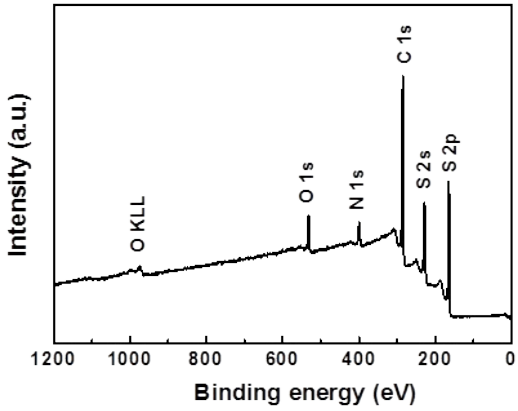

Fig. S2 Overall XPS spectrum of the SPANI sample, which shows the elements of carbon, oxygen, nitrogen and sulfur.

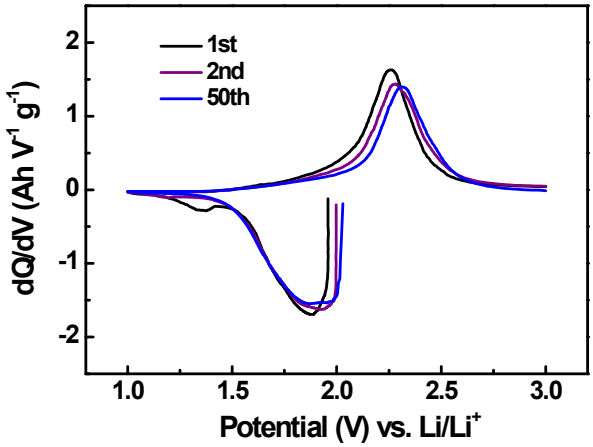

Fig. S3 Differential capacity plots of the discharge/charge curves in Fig. 4c.

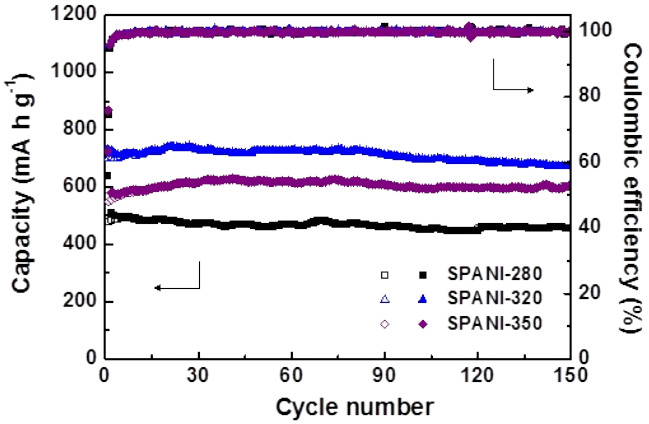

Fig. S4 Cycling test of SPANI samples prepared at different temperatures at 0.25 C (0.1 C for the 1st cycle).

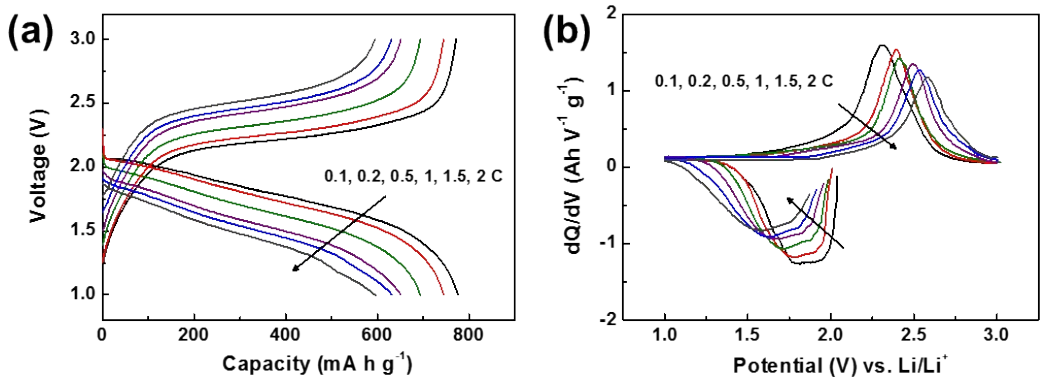

Fig. S5 Discharge/charge curves of SPANI cathode at different rates and the corresponding differential capacity plots.

Table S2. Comparison of relevant parameters in previous literatures with this work

Composite	SPANI-NT/S	PANI@C/S-280	SPANI
Raw materials	aniline, $(NH_4)_2S_2O_8$, DL-tartaric acid and sulfur	aniline, $(NH_4)_2S_2O_8$, super P, HCl and sulfur	commercial PANI and sulfur
Synthetic processes	1. polymerization of PANI-NT; 2. heat treatment of PANI-NT and sulfur at 155 °C for 12 h and then 280 °C for 12 h in Ar	1. preparation of polymerized PANI/C/S composite; 2. heat treatment at 280 °C for 12 h in Ar	one step heat treatment at 320 °C for 10 h in Ar
Electrolyte	1 M LiTFSI/DOL-DME	PEO-MIL-53(Al)-LiTFSI solid polymer electrolyte	1 M $LiPF_6$/EC-DMC
Reduction/ oxidation peaks	2.0 and 2.3/2.6 V at 25 °C	2.03 and 2.38/2.29 V at 80 °C	1.8/2.3 V at 25 °C
S content	62 wt%	43 wt%	47.7 wt%
Ref.	1	2	This work

References:

1. L. Xiao, Y. Cao, J. Xiao, B. Schwenzer, M. H. Engelhard, L. V. Saraf, Z. Nie, G. J. Exarhos and J. Liu, *Adv. Mater.*, 2012, 24, 1176-1181.
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Table S3. Comparison of representative small sulfur molecules (S_{2-4}) composite cathodes with this work in carbonate-based electrolytes

Cathode	Precursor for supporter	S content (wt%)	Current density /final discharge capacity* (mAh g^{-1})/cycle number	Current density /discharge capacity* (mAh g^{-1})	Ref.
S/C	MOF	27	0.2 C/936.5/100	3 C/632	1
S/C	phenolic resin	40	0.24 C/600/500	1.5 C/~420	2
S/C	PVDF	37.7	1 C/510/1000	2 C/486.9	3
SGDY	Graphdiyne	30.2	1 C/713.7/100	2 C/503.1	4
S@pPAN	PAN	43	0.1 C/1037/150	2 C/~1100	5
SPANI	PANI	47.7	0.5 C/692/100 1 C/571/500	2 C/570	This work

*: All the capacities are calculated based on the weight of sulfur.

References:

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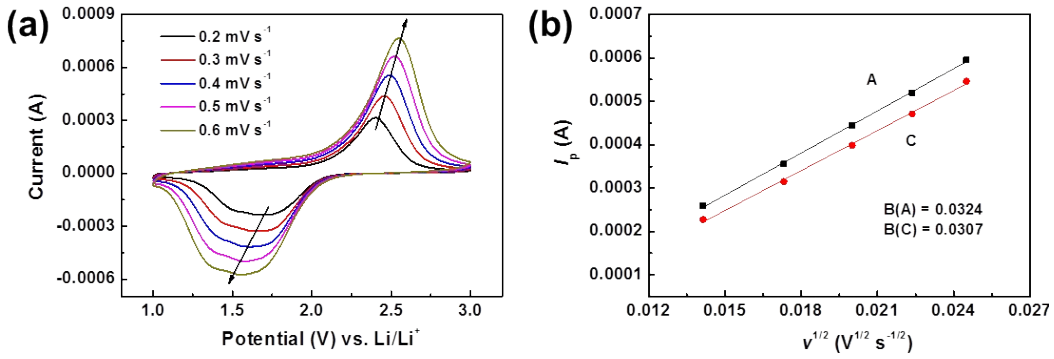

Fig. S6 (a) CV curves at various scan rates and (b) their linear fits.

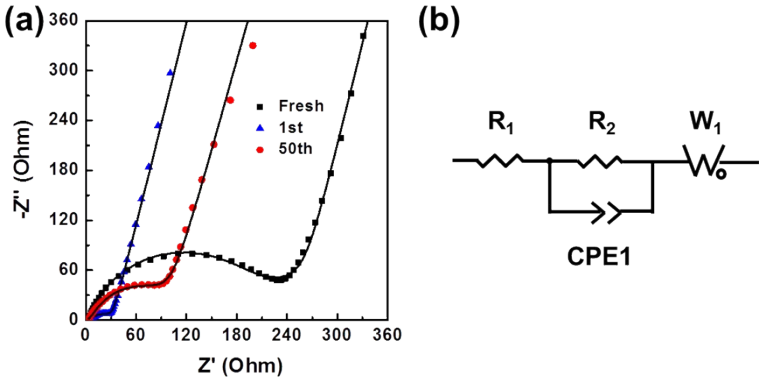

Fig. S7 (a) EIS plots of SPANI cathode after different cycles at 1 C. Solid lines in (a) are fitted to the equivalent circuit (b).