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Supporting Information

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High Surface Area N-Doped Carbon Fibers with Accessible Reaction Sites for All-Solid-State Lithium-Sulfur Batteries

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Experimental Section

Li_6PS_5Cl Preparation

Argyrodite Li_6PS_5Cl was synthesized by mechanical ball milling and then annealing treatment. A stoichiometric mixture of P_2S_5 (Sigma-Aldrich, 99%), Li_2S (Sigma-Aldrich, 99.98%), and LiCl (Sigma-Aldrich, 99%) was milled in an argon-filled stainless steel jar (50 mL) with 14 zirconia balls (10 mm in diameter) and 40 zirconia balls (5 mm in diameter) for 10 hours at 500 rpm. Then the as-mixed precursors were sealed in a glass tube in a vacuum and annealed in a quartz tube furnace at 550°C for 6h.

Preparation of PPCF

Electrospinning

PAN (MW 15K g/mol, Sigma-Aldrich, USA) was ground into powders, which were dissolved in *N*, *N*-dimethylformamide (DMF) (Fisher Scientific, 99.9%) at a concentration of 15 w%. As prepared PAN (Sigma-Aldrich, USA) solution was then loaded into a 10 mL syringe with a 22 gauge needle (i.d. 0.55 mm, length 38 mm). Electrospinning was carried out in a nanofiber electrospinning unit with the followed conditions: Solution feed rate, 2.0 mL/hour; applied voltage, 15 kV; the distance between the syringe needle and the Al collector, 20 cm. The formed nanofiber mesh was picked off from the Al foil and then kept in a desiccator for further processing.

Thermotreatment of PAN precursor nanofibers

The electrospun PAN precursor nanofibers were thermotreated by stabilization, carbonization, and activation in sequence. First, the as-electrospun nanofibers were stabilized in an air atmosphere in a muffle furnace (GSL 1200X, MTI Corporation, Richmond, CA). The heating was from room temperature to 250 ^{o}C with a heating rate of 1 ^{o}C min^{-1}. After heating to 250 ^{o}C, the samples were held at this temperature for one hour, which was followed by automatically cooling down to room temperature. After thermostabilization, the nanofibers underwent a carbonization process for carbon nanofibers. The carbonization process was conducted in a tubular furnace (GSL 1600X, MTI Corporation, Richmond, CA). The heating was controlled at 5 ^{o}C min^{-1}, which was from room temperature to 1000 ^{o}C. The holding time at 1000 ^{o}C was one hour, which was followed by automatically cooling down to room temperature again. Before the heating, the air in the tube furnace was exchanged with N_2 gas three times after vacuuming with the pump to 10^{-2} torr. The N_2 flow during the whole heating and cooling process was kept constant at 100 cm^3 min^{-1}.

As the last step of thermotreatment, the carbonized carbon nanofibers were chemically activated to prepare the activated carbon nanofibers. Solid KOH was used as the activation agent. Both carbon nanofibers and KOH were ground into finer powders. After that, carbon nanofibers were mixed with KOH with a weight ratio of 1:3. The heating process for activation treatment was the same as the carbonization as abovementioned. After the activation, the samples were dialyzed against deionized water until the pH value of the water was around seven. The dialyzed activated carbon nanofibers were then lyophilized. The obtained dry powders were kept in a glove box until use.

Electrochemical Characterization of ASSLSBs

Fabrication of All-Solid-State Li Sulfur Batteries

To prepare the cathode, carbon additives (PCF, PPCF, and VGCF), sulfur, and Li_6PS_5Cl were manually mixed at the weight ratio of 10/40/50 in a stainless-steel jar by mechanically milling at a rotating speed of 400 rpm for 10 hours. Then put this mixture into a sealed glass tube. The heating was controlled at 1 ^{o}C min^{-1}, which was from room temperature to 155 °C. Then maintained at 155 ^{o}C for 12 hours and cool down to room temperature with a ramp of 1 ^{o}C min^{-1}. Two hundred milligrams of Li_6PS_5Cl were first pressed into a pellet with a diameter of 12.7 mm under 300 MPa.

Then 10 mg of the as-prepared cathode was cast onto the pellet. A piece of In-Li was utilized as the anode and pressed on the other side of the pellet. Finally, the cell pellets were cold-pressed at 300 MPa with aluminum and Copper disks as cathode and anode current collectors individually.

Electrochemical performance characterization

All the ASSLSBs are tested with an electrochemical station (Biologic SP150) at room temperature. The rate and cycling performance were measured with galvanostatic cycling with a potential limitation protocol between the cutoff voltages of 0.7 and 2.7 V (vs. Li-In). The current was based on the area of SE pellet (12.7 mm in diameter). Electrochemical impedance spectroscopy (EIS) was conducted with an amplitude of 10 mV in the frequency range of one MHz to 10 mHz. The rate and cycling measurement were conducted in a protocol that the cell was charged at constant current to 2.7 V, and following discharged to 0.7 V at constant current. The current was calculated based on the mass and capacity of cathode active material.

Materials Characterization

The X-ray diffraction (XRD) was conducted on PANalytical/Philips X'Pert Pro with Cu Kα radiation. The scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were characterized by SEM (JEPL JSM 7000F). Sulfur loading in the PPCF composites was determined from the thermal gravimetric analysis (TGA) measurement (TA Q50, Inc) at the N_2 atmosphere. The chemical structure comparisons of the samples were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha). The Brunauer–Emmett–Teller (BET, Micrometrics 3 Flex surface characterization tool) was employed to detect the specific surface area. Raman spectra were measured on a Thermo Scientific DXR with 532 nm laser excitation.

Mechanism discussion of KOH activation

The activation process by KOH was explained by the combination of chemical activation, physical activation, and lattice expansion. At high temperature, the redox reactions (equations S1~S5) between C with KOH and derivations could etch the carbon through a chemical activation. Meanwhile, the generated CO and CO_2 could increase the pores through the gasification of carbon, named physical activation. In addition, the metallic K could intercalate into carbon to expand the carbon lattices. After the removal of these reaction products, the micropores are generated. Because the activation is started from the solid-solid reaction, the formation of the pores is from outside to inside. Herein, the unique core-shell structure was successfully generated by controlling the activation process.

$$6KOH + 2C \rightarrow 2K + 3H_2 + 2K_2CO_3 \tag{1}$$

$$K_2CO_3 \rightarrow K_2O + CO_2 \tag{2}$$

$$CO_2 + C \rightarrow 2CO \tag{3}$$

$$K_2CO_3 + 2C \rightarrow 2K + 3CO \tag{4}$$

$$C + K_2O \rightarrow 2K + CO \tag{5}$$

Supporting Figures

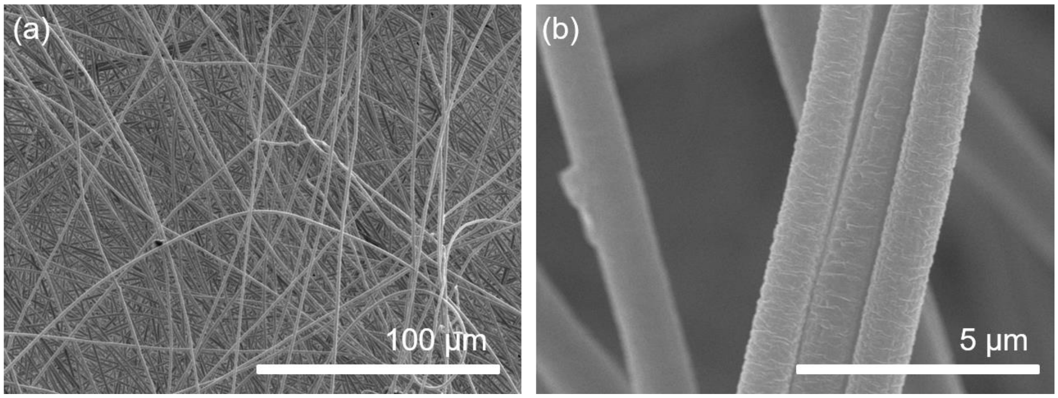

Figure S1. SEM images of as-spun PAN fibers before carbonization in (a) low and (b) high magnification.

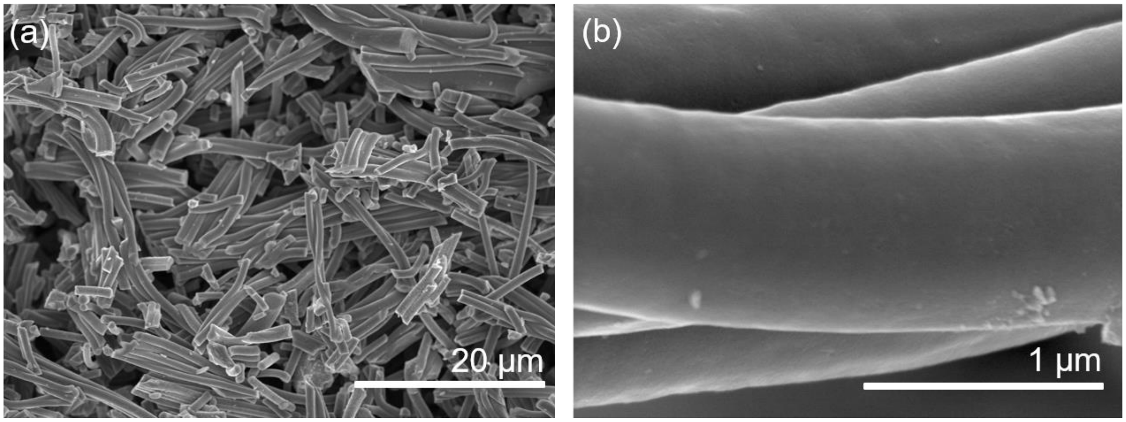

Figure S2. SEM images of PCF fibers after carbonization but before activation by KOH in (a) low and (b) high magnification.

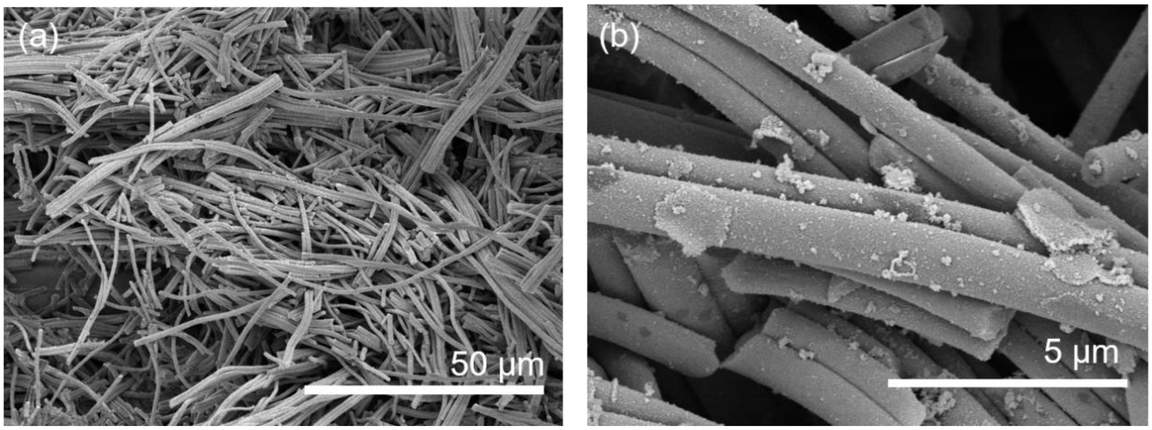

Figure S3. SEM images of PPCF after activation by KOH but before washing in (a) low and (b) high magnification.

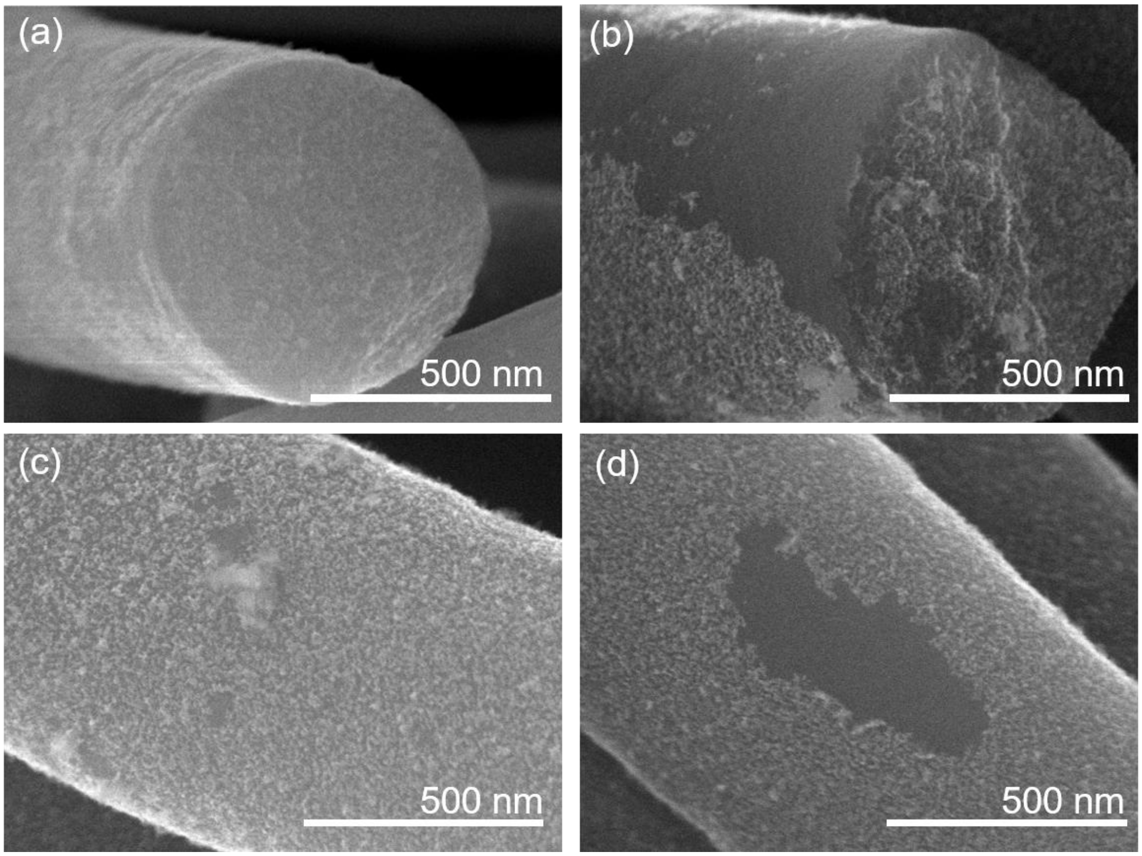

Figure S4. SEM images of PPCF after washing to show the core-shell structure where the porous layer covered on the surface. Representative cross-section images of PPCF that the porous layer (a) fully and (b) partially covered on dense carbon fiber. Representative surface images of PPCF that the porous layer (c) entirely and (d) partially covered on dense carbon fiber.

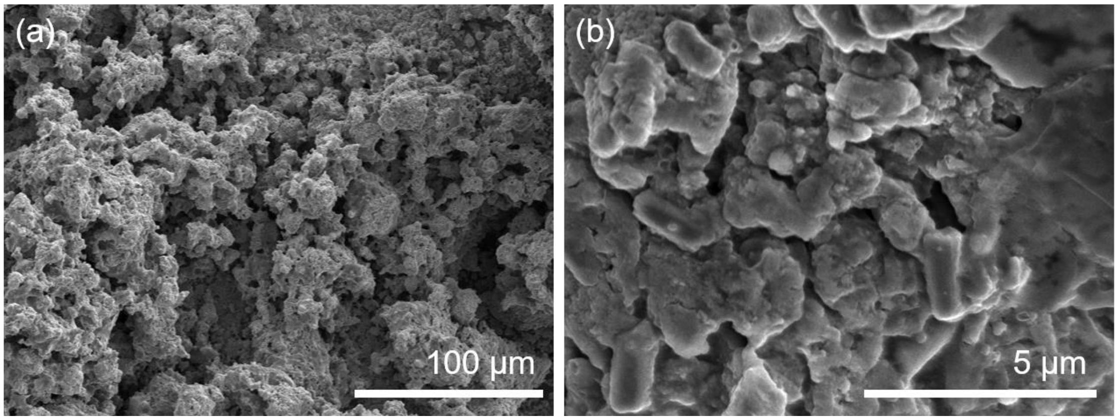

Figure S5. SEM images of S-PPCF-SE cathode before annealing in (a) low and (b) high magnification.

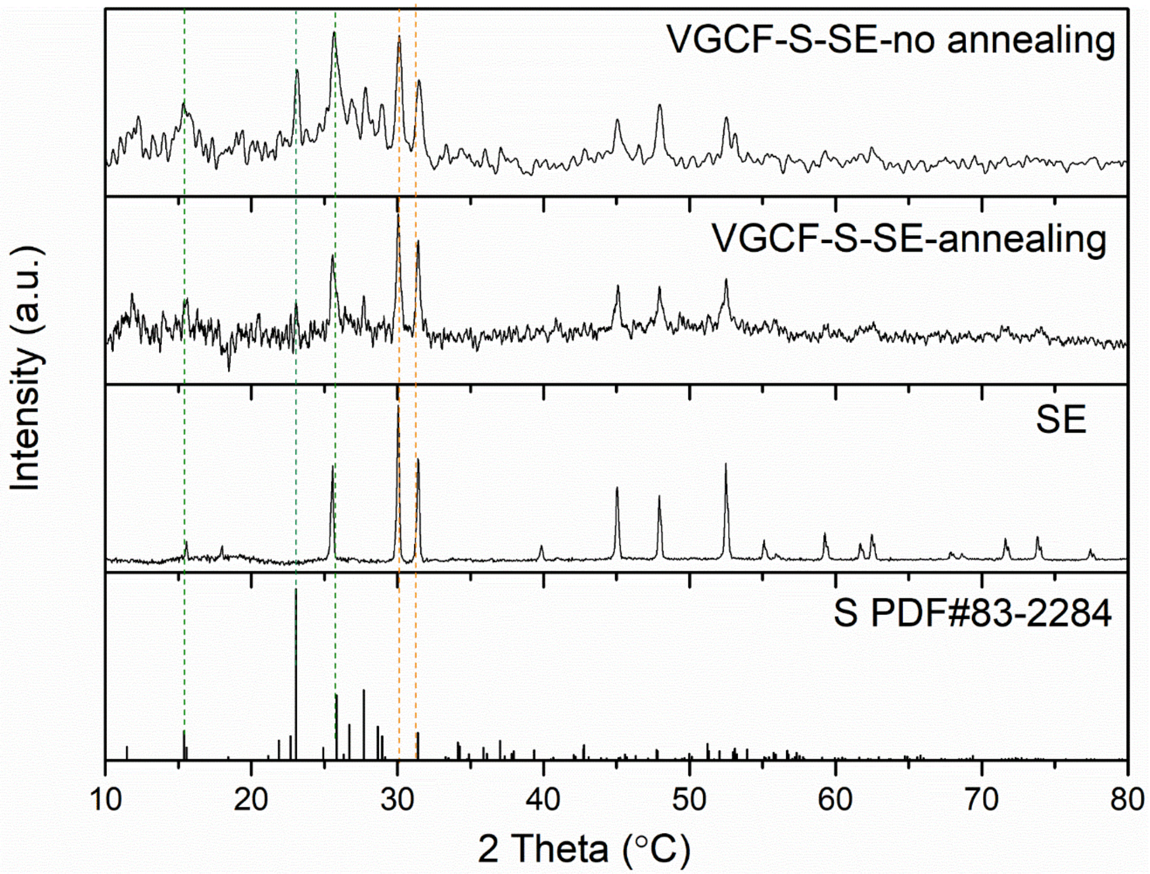

Figure S6. XRD patterns of S-VGCF-SE before and after annealing, Li_6PS_5Cl and sulfur

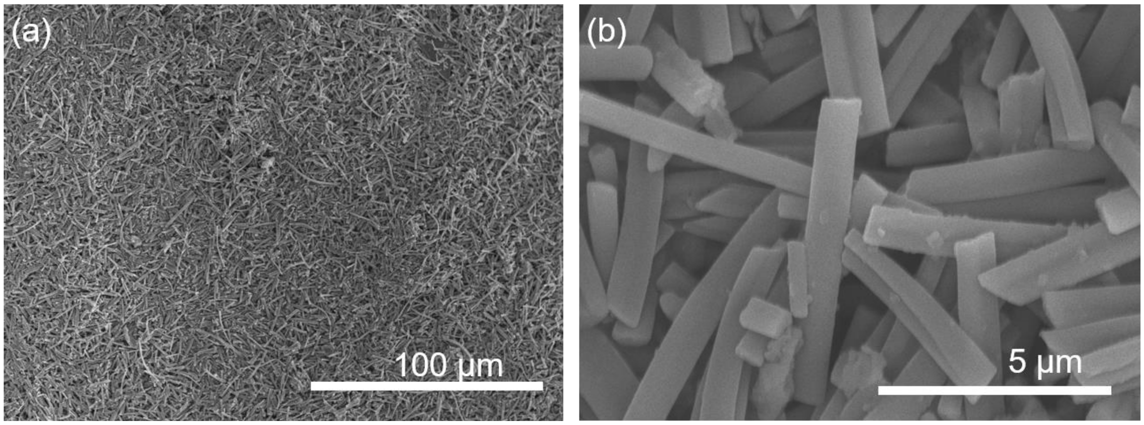

Figure S7. SEM images of PPCF after thermal infiltration with sulfur in (a) low and (b) high magnification.

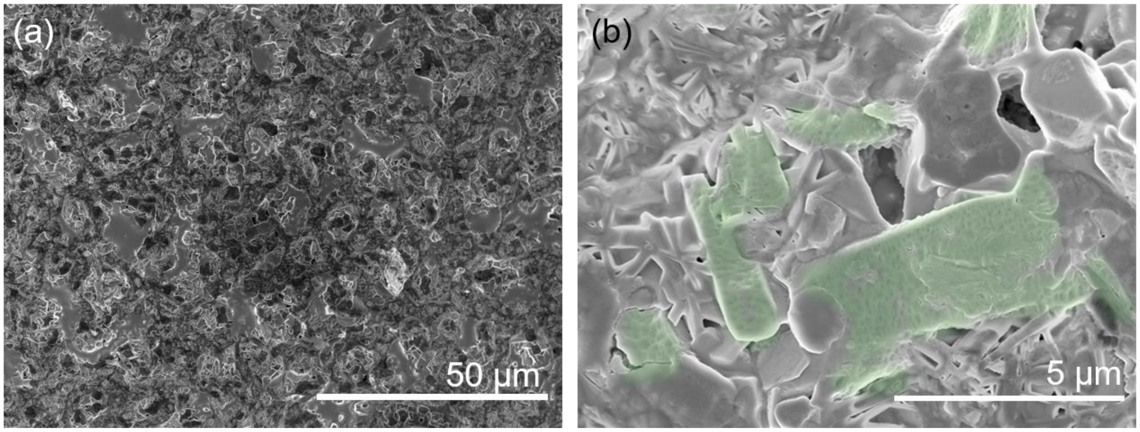

Figure S8. SEM images of S-PPCF-SE after cycling in (a) low and (b) high magnification. The green highlight is the PPCF-S.