Electronic supplementary information

Nano-cellular carbon current collectors with stable cyclability for Li-S batteries

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Experimental details

Elemental sulfur employed as the pure sulfur cathodes was synthesized by the precipitation method without any heat treatment. The sulfur deposition process was carried out by mixing 0.02 mole of sodium thiosulfate ($Na_2S_2O_3$; Fisher scientific) and 2 mL of hydrochloric acid (HCl; Fisher Scientific) in 750 mL of deionized-water for 24 h. The precipitated sulfur was filtered and washed with 100 mL deionized-water, ethanol, and acetone three times, and was then dried for 24 h at 50 °C in an air oven.

In this communication, the active material mixture contains 70 wt. % precipitated sulfur, 20 wt. % Super P, and 10 wt. % polyvinylidene fluoride (PVDF, Kureha) in an N-methyl-2-pyrolidone (NMP) solution. The mixture was continuously stirred for 2 days to form a viscous paste. Then, the well-mixed active material paste was simply loaded into the NC electrodes with a diameter of 1/4 inch by the porous cathode preparation process. Complex and complicated heat, surface, or acid/alkali treatments are no konger necessary for high quality sulfur cathode preparation. After the active material loading, the S-NC cathodes were dried in a convection oven at 50 °C for 24 h. For a comparison, conventional sulfur cathodes using Al foil as current collectors were prepared with the same paste by a slurry casting method. Although the resulting

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conventional cathodes also have high sulfur content of 70 wt. %, the sulfur loading is only 1.1 mg cm^{-2} due to the 2D flat morphology of the Al foil. However, the S-NC cathodes have a high sulfur loading of 2.2 mg cm^{-2} with the same sulfur content.

The microstructural investigations of the NC cathodes and the fresh S-NC cathodes were collected with a JEOL JSM 5610 scanning electron microscope (SEM), a FEI Quanta 650 SEM, and a JEOL 2010F transmission electron microscope (TEM) with scanning transmission electron microscope (STEM). The energy dispersive spectrometer (EDS) microanalysis and element mapping were performed with the FEI Quanta 650 SEM and the JEOL 2010F TEM. Physical nitrogen adsorption-desorption isotherms were carried out by the Brunanuer-Emmett-Teller (BET) method with a volumetric sorption analyzer (NOVA 2000, Quantachrome). The surface area, pore volume, and pore-size distributions of the carbon electrode and pure sulfur cathodes were calculated by the t-plot method and the Barrett-Joyer-Halenda (BJH) method. The electrolyte absorption tests of fresh S-NC cathodes and fresh conventional cathodes were performed by immersing the cathodes into 5 mL of electrolyte for 5min, and then measuring the decrease in the amount of the electrolyte.

The cell assembly was conducted in an argon-filled glove box with a controlled atmosphere (0.6 – 1.7 ppm O_2 and < 0.1 ppm H_2O). The S-NC cathodes were dried in a vacuum oven for one hour at 50 °C prior to cell assembly. The Li-S cells were assembled with the S-NC cathodes, polypropylene separator (Celgard), lithium foil anode, and nickel foam spacers in sequence in CR2032-type coin cells with an electrolyte of 1.85 M $LiCF_3SO_3$ salt (Acros Organics) and 0.1 M $LiNO_3$ salt (Acros Organics) in a 1:1 volume ratio of 1,2-Dimethoxyethane (DME; Acros Organics) and 1,3-Dioxolane (DOL; Acros Organics). The assembled Li-S cells were rested for 30 minutes at 25 °C before collecting the electrochemical data. The cyclic voltammetry (CV)

measurements were performed with VoltaLab PGZ 402 Potentiostat at a scan rate of 0.1 mV s^{-1} in a potential range of 2.8 – 1.8 V. The charge/discharge voltage profiles and cyclability tests were assessed with a battery cycler (Arbin Instruments). The cells were first discharged to 1.8 V and then charged to 2.8 V for one full cycle. The cycling rates are based on the mass and theoretical capacity of sulfur (1C = 1675 mA g^{-1}). The electrochemical impedance spectroscopy (EIS) data were recorded with a Solartron SI 1260/SI 1287 impedance analyzer between 1 MHz and 100 mHz with an AC voltage amplitude of 5 mV at room temperature. The microstructural changes and EDS microanalysis of the cycled S-NC cathodes were examined with a FEI Quanta 650 SEM and JEOL 2010F TEM. The cycled cathodes were retrieved in the argon-filled glove box and stored in an argon-filled sealed vessel.

Supporting figures

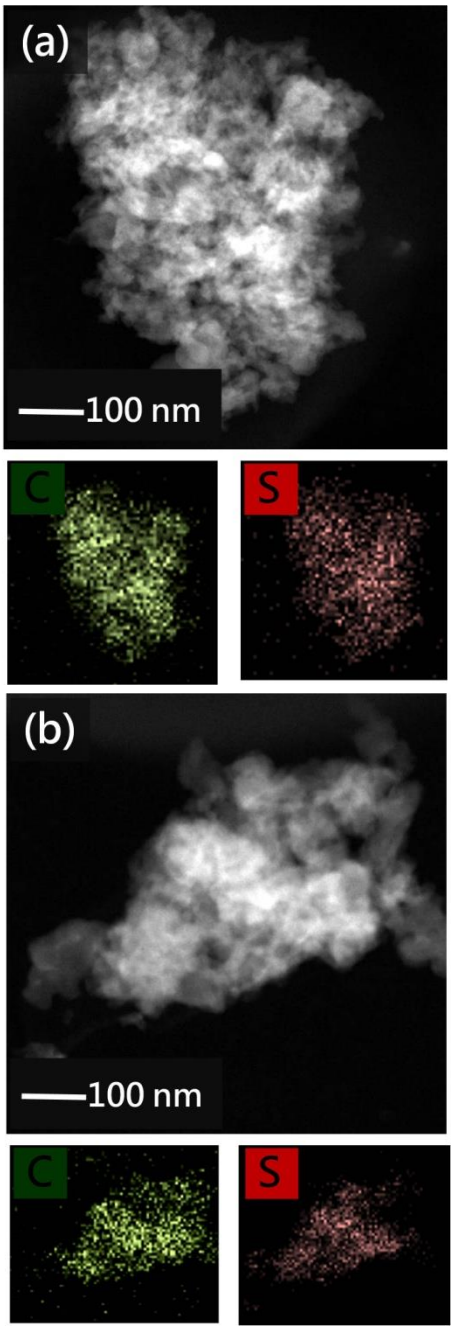

Fig. S1 STEM with elemental mapping of the (a) fresh S-NC cathodes and (b) cycled S-NC cathodes. The uniform and undiminished sulfur signal indicates a deep active material infiltration and homogeneous sulfur coverage on the nanofoam plates of the NC current collector.

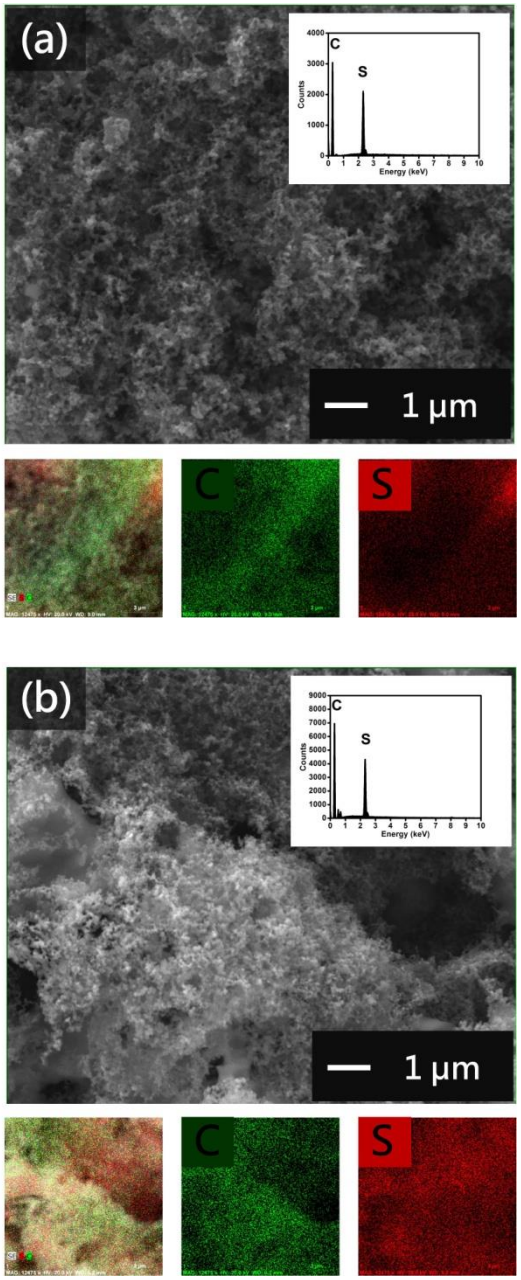

Fig. S2 Surface SEM images and EDS microanalysis: (a) fresh S-NC cathodes with elemental mapping and (b) cycled S-NC cathodes with elemental mapping. The S-NC cathodes maintain a uniform sulfur distribution and a complete sulfur coverage on the porous current collectors before and after cycling, suggesting no severe loss of active material.

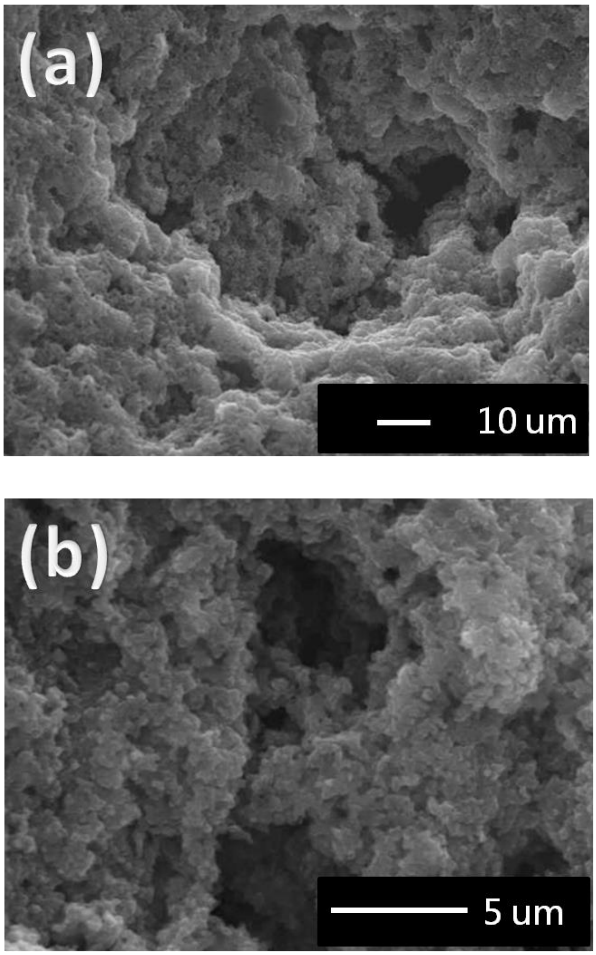

Fig. S3 (a) Surface SEM image of the S-NC cathodes after the initial discharge process and (b) high magnification SEM image of the S-NC cathodes. The surface of the S-NC cathodes retained a constant porous structure.

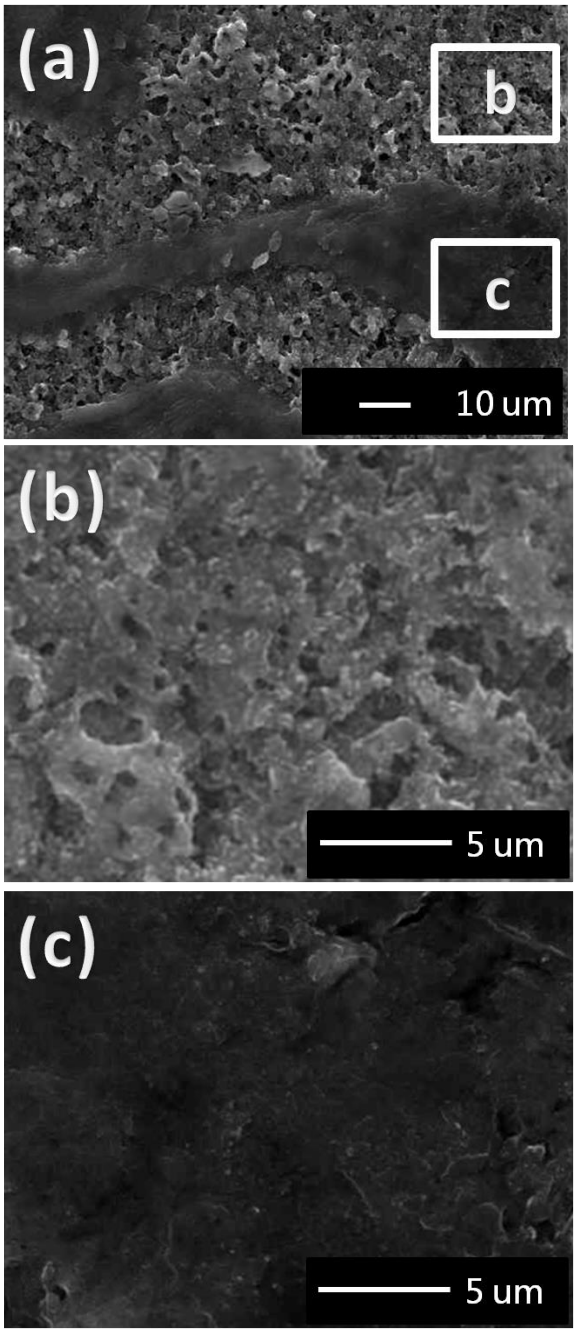

Fig. S4 (a) Surface SEM image of the conventional 2D cathodes after the initial discharge process, (b) high magnification SEM image of the light area, and (c) high magnification SEM image of the dark area. The surface of the conventional cathodes was shielded by the dark and smooth precipitates, which are the insulating discharge products, Li_2S_2/Li_2S mixtures.

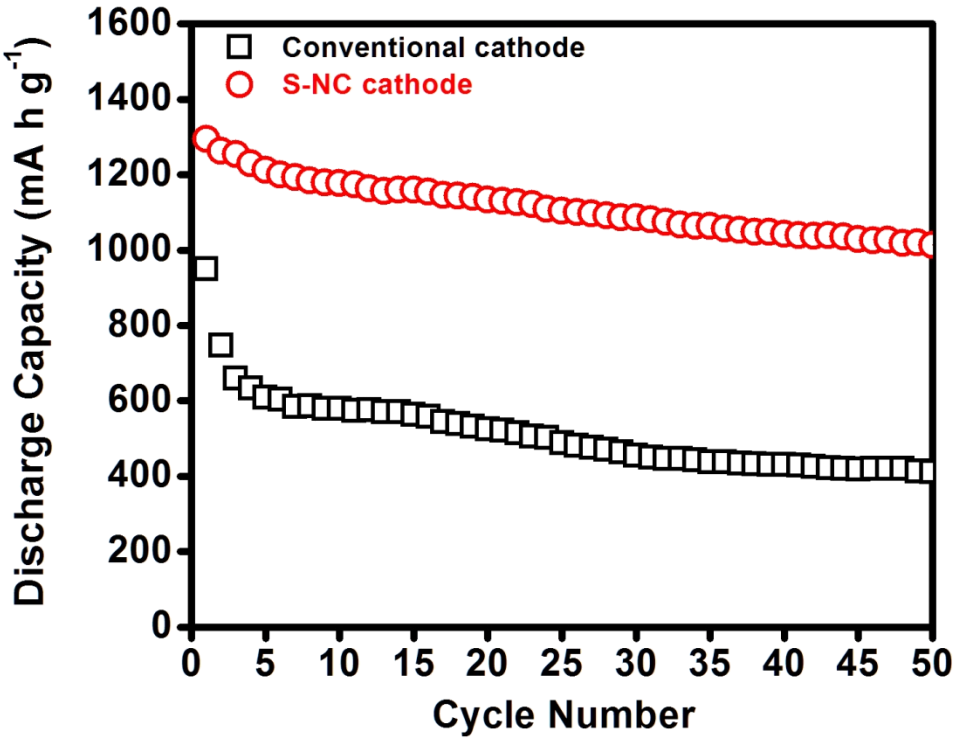

Fig. S5 Cycling profiles of the Li-S cells: comparison between the S-NC cathodes and the conventional cathodes with 60 wt. % sulfur at C/5 rate. The porous carbon electrodes offer a high discharge capacity of 1294 mA h g^{-1} with good cycle stability. The 50^{th} cycle capacity retention rate increased from 43 to 80 %.

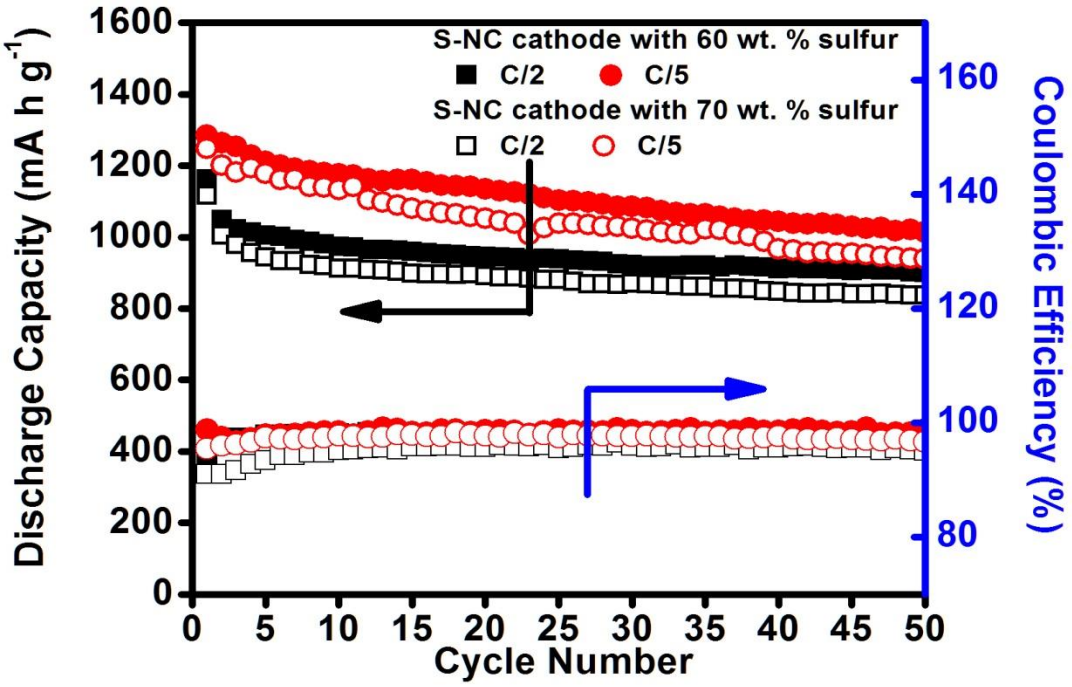

Fig. S6 Electrochemical data of the Li-S cells: S-NC cathodes with 60 and 70 wt. % sulfur cycled at different cycling rates, indicating that the S-NC cathodes not only have good cycling performance, but also tolerate a higher sulfur loading of 2.2 mg cm^{-2}.