Supporting Information

Sulfur gradient-distributed CNF composite: a self-inhibiting cathode for binder-free lithium-sulfur batteries

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Experimental

Material Synthesis & Electrode Preparation

CNF webs were prepared by electrospinning polyacrylonitrile (PAN) (Mw: 150,000 g mol^{-1}), followed with carbonization. Details of the CNF preparation process was reported in our earlier work.(Fu et al., 2013) CNF webs have a density of 1.4-1.5 mg cm^{-2} with a thickness of ~ 0.15 mm. To produce the CNF-S composites, sulfur was deposited onto CNF webs directly by a physical vapor deposition system operating at different temperatures (250, 300, and 350 ^{o}C). The schematic of the sulfur deposition process is shown in Figure 1a. Elemental sulfur (99.5-100.5% Sigma-Aldrich) of 100 mg was placed at the center of the tube furnace, with the CNF substrates loaded downstream at a distance of 20 cm away from the center of the chamber. During the deposition process, the chamber was heated up at a rate of 30 ^{o}C/min under a 20 sccm flow of Ar gas, held at the set point temperature for 15 min, and then cooled down to room temperature naturally. In this work, the actual sulfur loading density of CNF-S (250 ^{o}C), CNF-S (300 ^{o}C), and CNF-S (350 ^{o}C) composites were 0.5, 1.7, and 2.6 mg cm^{-2}, respectively. The sulfur loading density was calculated by directly measuring the mass difference of CNF cloth and CNF-S composite before and after sulfur vapor deposition.

For comparison, conventional sulfur cathode was fabricated by mixing 70 wt% of elemental sulfur, 20 wt% of carbon black, and 10 wt% of polyvinylidene fluoride binder in an N-methylpyrrolidinone (Sigma-Aldrich) solution. The slurry was casted onto an aluminum foil and dried in a vacuum oven overnight at 60 ^{o}C, followed by cutting into circular electrodes. The electrode loading was controlled at 2.1 mg cm^{-2}. Dual-layer cathode with an interlayer was also prepared by covering the conventional sulfur cathode with a piece of CNF cloth of the same size.

Characterization

The morphology of the CNF-S composites was investigated using a field emission scanning electron microscope (FE-SEM, JEOL 6400F). The crystallographic and chemical structures were studied using wide angle X-ray diffraction (WAXD, Rigaku Smartlab) and a Renishaw Raman microscope (514 nm).

Electrochemical evaluation

CNF-S composites were used directly as the cathode electrode for lithium-sulfur batteries. All the cathode disks and CNF interlayer were dried in a vacuum oven overnight at 60 ^{o}C before assembling the cell. Lithium ribbon (99.9%, Aldrich) was used as the counter electrode and Celgard 2400 membrane as the separator. The electrolyte was prepared by dissolving 1.0 M lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) and 0.1 M lithium nitrate in a 1:1 volume ratio of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME). The amount of electrolyte was added according to the actual mass of sulfur in the cathode electrode, with an electrolyte/sulfur ratio of around 10 mL g^{-1}. In each cell, the mass of sulfur in CNF-S (250 ^{o}C), CNF-S (300 ^{o}C), and CNF-S (350 ^{o}C) was around 0.6 mg, 2.2 mg, and 3.3 mg, respectively. The 2032 coin cells were assembled in an argon-filled

glove box. The coin cell assembly sequence is as follows: plastic-ring bottom case, stainless steel spring, stainless steel spacer, lithium foil, separator, cathode, and top cover. All cells were allowed to rest for 3 hours at room temperature before electrochemical measurements. A current density of 100 mA per gram of sulfur (0.06 C) was applied to cathode for battery testing. Cyclic voltammetry (CV) measurements were performed by using a Gamry reference 600 Potentiostat/Galvanostat/ZRA device at a scan rate of 0.05 mV s^{-1} in a potential range of 1.5-3.0 V. The discharge-charge voltage curves and cycling tests were carried out on a LAND-CT 2001A battery test system with cut-off potentials between 1.5 and 3.0 V. The electrochemical impedance spectra (EIS) were obtained on Gamry reference 600 by scanning cells between 1 MHz and 100 MHz at room temperature.

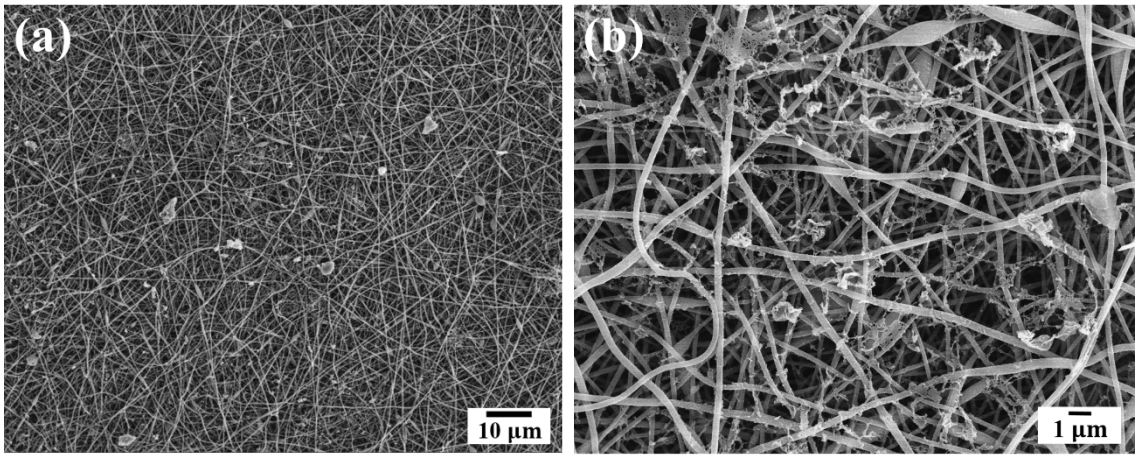

Figure S1. SEM images of CNF-S (250°C).

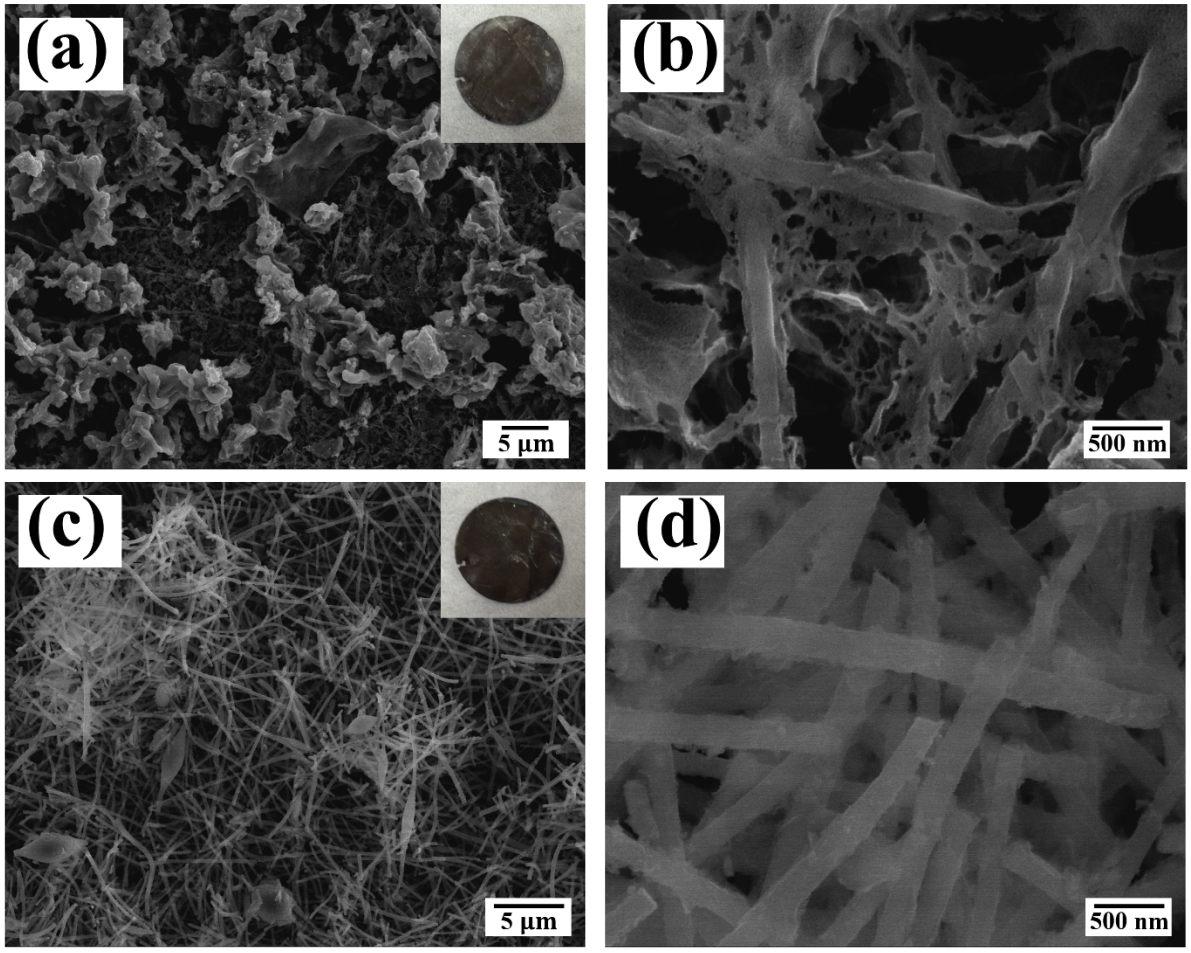

Figure S2. (a-b) SEM images of high-sulfur side of cycled CNF-S (350℃) electrode. (c-d) SEM images of non-sulfur side of cycled CNF-S (350℃) electrode. The insets are photo images of high-sulfur side and non-sulfur side of cycled CNF-S (350℃) electrode.