Supplementary Information

Recycled Rubber in Li-S Batteries

Byeong-Chul Yu, a Ji-Won Jung, a Kyusung Park, a John B. Goodenough* a

a Texas Materials Institute, The University of Texas at Austin, Austin, TX 78712, USA

Corresponding authors:

J. B. Goodenough (jgoodenough@mail.utexas.edu)

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Methods

Carbon-nanofiber (CNF) preparation

Polyacrylonitrile (PAN) nanofibers were synthesized by electrospinning a solution of 1 g PAN dissolved in 6 g of N,N-dimethylformamide (DMF) with conventional electrospinning equipment (NanoNC,ESR200RD); the PAN nanofiber webs had no defects or beads. Freestanding CNF paper was stabilized by calcining at 250°C for 1 h in air before carbonization at 1000°C in flowing Ar for 2 h after heating at 10°C/hour. The CNF paper was used as the cathode current collector.

Electrode Preparation

A small piece cut from a used MICHELIN tire received from a repair shop in Austin was washed in ethanol several times and dropped into a 100 ml CS₂ solution (Fisher Chemical, 500ml); this liquid, which was changed overnight to a yellow color, was filtered. To prepare a sulfur cathode, 3.4 ml CS₂ was added to 1.6 ml of the rubber solution; and to this solution was added various weights of sulfur powder (0 g, 0.1 g, 0.3 g, 0.5 g). The rubber sulfur solution was then added drop-wise onto a 3/8-inch-diameter CNF paper; the CS₂ evaporated in a few seconds and the resulting cathodes were labeled CNF/R/xS with x = 0.1 g, 0.3 g, 0.5 g. The entire process was carried out at room temperature. The CNF to rubber/sulfur ratio was 1:1 by weight, and the rubber/sulfur loading on the CNF paper was 0.7-0.8 mg/cm². Commercially available carbon paper (SIGRACET CDL 10 BA, Ion Power, Inc.) was also used as a current collector to compare with the freestanding CNF. A rubber stopper (Fisher Scientific) for an Erlenmeyer laboratory flask was also used in place of the piece of used tire to make CFF/R/S electrodes by the same procedure.
Materials Characterization

After filtering, the vulcanized rubber was examined by FT-infrared Spectroscopy (FTIR, Thermo Scientific Nicolet iS5). All cathode samples were examined by X-ray diffraction (XRD, Rigaku Miniflex 600 I). X-ray photoelectron spectroscopy (XPS, Kratos Axis X-ray photoelectron spectrometer) was used to analyze the elements in each structure and to probe chemical interactions between vulcanized rubber and lithium polysulfide. The morphologies of the pristine CNF, CNF/S and CNF/R/5S electrodes were observed by field-emission scanning electron microscopy (FESEM, Hitachi S5500) with elemental mapping. A time-of-flight secondary ion mass spectrometer (TOF.SIMS 5 by ION-TOF GmbH, 2010) was conducted to analyze the distribution of rubber and sulfur in the CNF/R/5S electrode. Data were acquired with ion-beam analysis (Bi⁺, 30 keV ion energy) in the high-current (HC) mode (≈3 pA measured sample current) for depth profiling or in the burst-alignment (BA) mode (≈0.4 pA measured sample current) for high-resolution mapping (<50 nm) of the species of interest at the surface. The analyzed area, typically 100 × 100 μm², was scanned at 256 × 256 pixels. A sputtering ion beam (Cs⁺ with 2 keV ion energy and ≈70 nA measured sample current) was used for depth profiling (250 × 250 μm² sputtered area, centered on the analysis area). The sputtering rate of the CNF/R/S electrode by the Cs⁺ beam was estimated to be ≈0.01 nm s⁻¹. The experiments were performed in ultrahigh vacuum (UHV) at a base pressure of <10⁻⁹ mbar. A thermogravimetric Analyzer (TGA) was employed to check the amount of sulfur in R/xS (x=1,3,5; 1=0.1 g, 3=0.3 g, 5=0.5 g).

Electrochemical Characterization

Coin-type cells were assembled with Li foil as the counter and reference electrodes, CNF/R/xS as cathode electrode and 1 M LiCF₃SO₃ and 0.5 M lithium nitrate (LiNO₃) in
dimethoxyethane/1,3-dioxolane (DME/DOL, 1:1 by volume) as electrolyte. Additional binders and conducting material were not needed. The electrochemical cells were tested galvanostatically between 1.8 V and 2.8 V vs. Li/Li⁺ at various rates. During the discharge step, Li was inserted into the S electrode; Li was extracted from the electrode during the charge. The capacities of the cathode were calculated by total weight of rubber and sulfur. For the ex-situ XPS after cycling, the coin-cells were disassembled in an Ar-filled glove box and the samples were washed with DME and dried under vacuum.
Figure S1 | XRD of rubber solution obtained from waste tire before (black) and after (blue) filtering. The crystalline Al$_2$Si$_2$O$_5$(OH)$_4$ (PDF# 00-058-2028) impurity was removed after filtering.

Figure S2 | FT-IR results of rubber polymer with three wavenumber regions. (a) 4000~2500 cm$^{-1}$ (b) 1800~1200 cm$^{-1}$ (c) 1000~400 cm$^{-1}$. 
Figure S3 | TGA analyses of R (black), R/1S (red), R/3S (blue) and R/5S (green) powder. The experiments were conducted from 25 °C to 600 °C at 5 °C/min rate.

Figure S4 | Optical images of freestanding CNF films for cathode electrode. (a) pristine CNF film (b) folded CNF film (c) 3/8 inch CNF electrode (d) CNF/R/5S cathode electrode. All electrode that electrochemical properties were tested were prepared by same drop method with different solution.
Figure S5 | XRDs of (a) Sulfur powder (black), (b) pristine CNF (red), (c) CNF /5S (blue), (d) CNF/R (purple) and (e) CNF/R/5S (green).

Figure S6 | XPS analyses with C 1s and S 2p of (a,d) CNF electrode, (b,e) CNF/R electrode, (c,f) CNF/R/5S electrode.
**Figure S7** | SEM images with magnified images (inset) (a) pristine CNF, (b) CNF/5S, (c) CNF/R/5S. After loading active materials, the pores between nanofibers were well maintained. This 3D network can be effective to facilitate Li ion diffusion from electrolyte through all direction.

**Figure S8** | High resolution STEM images of CNF/R/5S electrode with elemental mapping. (a) BF and (b) DF images of one nanofiber, elemental mapping with (c) carbon and (d) sulfur.
**Figure S9** | Voltage profiles of (a) CNF/5S, (b) CNF/R, (d) CNF/R/1S, (e) CNF/R/3S and (f) CNF/R/5S electrodes at first and second cycles. (c) DCP (inset) and magnified DCP of CNF/R electrode; this plot was obtained by differential of capacity by voltage. The reaction peaks of DCP were come from flat regions in voltage profile.

**Figure S10** | SEM images with magnified image (inset) of (a) commercial carbon paper (CP), (b) CP/R/5S electrode. The thickness of carbon fibers was around 10 μm. The active R/S was loaded by drop method on CP electrode. Although the surface of pristine CP was not smooth, after loading solution, thin R/S layer was formed on surface of carbon fiber.
**Figure S11** | Voltage profiles of CNF/R/5S electrode at different current rate.

**Figure S12** | Application of another rubber product for Li-S battery. Optical images of (a) rubber stopper, (b) rubber solution extracted from it. Electrochemical tests; (c) voltage profiles of different cycle and (d) cycle performance over 200 cycles at first 0.2C and 0.5C. The stopper is also consisted of vulcanized rubber which can be used as bifunctional coating layer.