Sulfur Encapsulated in Porous Hollow CNTs@CNFs for High-Performance Lithium-Sulfur Batteries

Yuming Chen,§‡ Xiaoyan Li,§† Kyusung Park,‡ Jianhe Hong,‡ Jie Song,‡ Limin Zhou,*§ Yiu-Wing Mai,§‖ Haitao Huang,† and John B. Goodenough*⊥

§Department of Mechanical Engineering and †Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, China.
‖Centre for Advanced Materials Technology (CAMT), School of Aerospace, Mechanical and Mechatronics Engineering J07, The University of Sydney, NSW 2006, Australia.
⊥Texas Materials Institute and Materials Science and Engineering Program, The University of Texas at Austin, Austin, Texas 78712, United State.
*E-mail: mmlmzhou@polyu.edu.hk; jgoodenough@mail.utexas.edu
‡These authors contributed equally.

Experimental:

Materials

Polyacrylonitrile (PAN, Mw=150 000, Aldrich), polymethylmethacrylate (PMMA, Tokyo Chemical Industry Co., Ltd), nickel acetate (Ni(Ac)_2·4H_2O, Advtechind), dimethylformamide (DMF, Aldrich).

Encapsulation of sulfur in porous hollow CNTs@CNFs

First, PAN/PMMA/Ni(Ac)_2 composite nanofibers were prepared by coaxial electrospinning, where the inner and outer solution was PMMA solution (0.5 g) in DMF (10 mL) and a mixture of Ni(Ac)_2·4H_2O (1 g) and PAN (1 g) in DMF (20 mL), respectively. The tip-collector distance, flow rate for the coaxial solutions, and high voltage were fixed at 20 cm, 0.03 mm min^{-1}, and 21 kV, respectively (KATO Tech...
PMMA could be distributed in the PAN matrix during the electrospinning process because of the use of the same DMF; thus PAN/Ni(Ac)$_2$/PMMA composite nanofibers were prepared. Second, the prepared nanofibers were pyrolyzed at 700 °C in H$_2$(5 vol %)/N$_2$(95 vol %) for 6 h and then heated in vacuum for 6 h to produce CNTs@CNFs@Ni. A mixture of CNTs@CNFs@Ni and KOH (CNTs@CNFs@Ni:KOH=1/4, weight ratio) was heated at 750 °C for 1 h in a tube furnace under a nitrogen atmosphere. The resultant mixture was further treated with HNO$_3$ to remove the Ni particles to achieve porous hollow CNTs@CNFs. Third, the porous hollow CNTs@CNFs (60 mg) and sulfur (160 mg) were mixed together and treated in quartz tubes that were sealed under vacuum at 400 °C for 24 h to facilitate sulfur diffusion into the resulting carbon matrix. Finally, the composite materials were treated at 200 °C to vaporize the sulfur on the surface of the porous hollow CNTs@CNFs, denoted as CNTs@CNFs-S.

**Characterization**

The obtained materials were characterized by X-ray diffraction (XRD, Philips, X'Pert Pro MPD), transmission electron microscopy (TEM), high-resolution TEM (HRTEM, JEOL 2010F, Japan), energy-dispersive X-ray spectroscopy (EDS, Oxford), electron energy loss spectroscopy (EELS, Gatan, Enfina), and X-ray photoelectron spectroscopy (XPS, Kratos Axis 165, Manchester), respectively. The N$_2$ adsorption and desorption isotherms at 77 K were determined (Quantachrome, Autosorb-iQ) and the pore-size distribution was calculated by the Barrett-Joyner-Halenda (BJH) method. Thermogravimetric analysis (TGA, Perkin-Elmer) was performed in a flow of N$_2$ with a heating rate of 5 °C min$^{-1}$.

**Electrochemical testing**

The cathode electrode was fabricated by mixing the prepared materials (80 wt.%), carbon black (10 wt.%) and poly(vinyl difluoride) (10 wt.%, PVDF) binder. Carbon-black (CB)/sulfur composites were also prepared for comparison. Two-electrode coin cells with activate materials as cathode and lithium foil as anode were assembled for electrochemical testing. The electrolyte was a mixture of 1.5 M
LiCF$_3$SO$_3$ and 0.1 M LiNO$_3$ salts into a 1:1 vol/vol mixture of 1,2-dimethoxyethane and 1,3-dioxolane. Charge and discharge were conducted by using an Arbin automatic battery cycler at various current densities within a voltage range of 1.5-3 V. The cyclic voltammetry (CV) measurement was performed on a Solartron SI 1287 electrochemical workstation at a scan rate of 0.1 mV s$^{-1}$. The specific capacity was calculated based on the mass of sulfur.

Figure S1. EDS line-scan profiles of the CNT@CNF@Ni.
Figure S2. Nitrogen adsorption-desorption isotherms of the porous hollow CNTs@CNFs and CNTs@CNFs-S.
Figure S3. XPS spectra of porous hollow CNTs@CNFs-S. (a) C1s spectra and (b) S2p spectra.
Figure S4. Cycling stability of CB-S electrode at 1 C