Electronic Supplementary Information for Hollow Polyaniline sphere@Sulfur Composites for Prolonged cycling Stability of Lithium Sulfur batteries

Guoqiang Ma, Zhaoyin Wen*, Jun Jin, Yan Lu, Xiangwei Wu, Meifen Wu and Chunhua Chen
CAS Key Laboratory of Materials for Energy Conversion,
Shanghai Institute of Ceramics, Chinese Academy of Sciences,
Shanghai, China, 200050
Fax: +86-21-52413903; Tel: +86-21-52411704;
E-mail: zywen@mail.sic.ac.cn

1. Experimental

1.1. Preparation of PANI hollow sphere

The polystyrene particles were prepared by emulsifier-free emulsion polymerization[1]. Water (140 mL) was added to a 200 mL four-necked round flask and heated to 70 °C. It was purged with nitrogen to eliminate the inhibiting effect of oxygen before the addition of styrene monomer under mechanical stirring. Following the attainment of a uniform dispersion, Potassium persulphate dissolved in water (0.23 g/10 mL) was added. The polymerization was allowed to proceed under a N_2 atmosphere for 24 h before cooling to room temperature.

After purification and drying, polystyrene fine powder and concentrated sulfuric acid (98%,) were introduced to a conical flask[2]. After ultrasonic dispersion, the sulfonation was allowed to take place at 40 ◦C under magnetic stirring for 12h. When cooled to the room temperature, the product was separated by repeated centrifugation (8000 rpm) and washed with a large excess of ethanol.

Sulfonated polystyrene powder (6 g) was dispersed in 200 ml of water. Subsequently, 1.4g aniline monomer in 20ml 2M HCL aqueous was added to the above mixture. The monomer/sulfonated polystyrene reaction mixture was stirred in an ice bath for 5 h, then added 3.5 g $[NH_4]_2S_2O_8$ (in 20ml deionized water). The polymerization was proceeded for 24 h by stirring slowly at 0 ◦C. After the resulting PANI-coated polystyrene particles were purified by repeated centrifugation/ redispersion cycles and dried in vacuum drying oven at 50 ◦C, then polystyrene-PANI core-shell microspheres were obtained. After dissolved in Chloroform, polystyrene cores were removed from

core-shell particles and uniform hollow PANI microspheres were obtained.

1.2. Preparation of PANI-S composite

Mixtures of sulfur and the PANI hollow spheres in the weight ratio of 2:1 were co-heated at 155 ◦C for 12 h and 280℃ for 6h. During the heating process, the sulfur was molten and filled to the holes of the PANI hollow sphere. The pure sulfur cathode is prepared by heating the mixture of acetylene black(AB) and sulfur (weight ratio of 2:1) at 300◦C for 6 h.

1.3. Preparation of the sulfur cathode and coin-type cell

To prepare a cathode, the slurry was prepared by ball milling 80wt% sulfur based composite, 10wt% acetylene black (AB) as conductive agent, both 5wt% CMC, 5wt% SBR as binders and deionized water as the solvent. The slurry was then casted onto an aluminum foil substrate. After the solvent evaporated, the coated electrode was cut into circles with 14 mm in diameter and then dried at 60 °C under vacuum for 12 h. There is approximately 1.5 $mg.cm^{-2}$ sulfur loading on the electrode. CR2025 type coin cells were assembled in a glove box with oxygen and water contents less than 1 ppm. The electrolyte consisted of 0.1 M anhydrous lithium nitrate (analytical grade) and 1 M $LiN(CF_3SO_2)_2$ (LiTFSI) in a mixed solvent of 1,3-dioxolane (DOL) and dimethyl ether (DME) at a volume ratio of 1:1. Celgard 2400 was used as the separator and lithium foil as both the counter and reference electrodes.

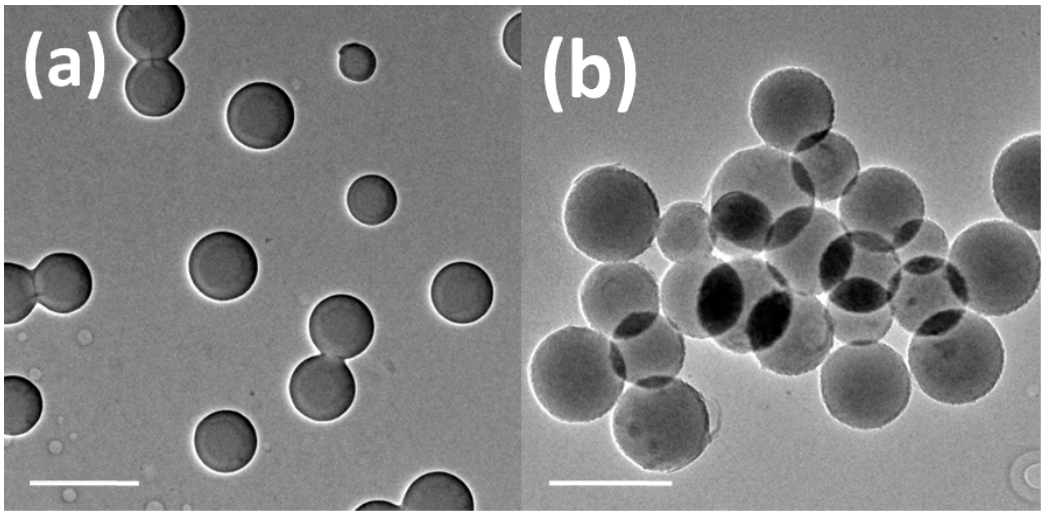
1.4. Characterization

Thermogravimetry (TG) (NETZSCH 409 PC) was applied under N_2 atmosphere to determine the components of the composite. FTIR spectra were carried out on a Thermo Nicolet 7000-C Fourier Transform Spectrometer with $\pm 2cm^{-1}$ resolution between 4000 and $400cm^{-1}$ using KBr disk method. Specific surface area was tested using the Brunauer-Emmett-Telley (BET) method on a Micromeritics Tristar 3000. SEM images were measured with field emission scanning electron microscope (FESEM JSM-6700) and scanning electron microscope (Hitachi S-3400N). Transmission electron microscopy (TEM) images were measured on a JEOL JEM-2010 transmission electron microscope.

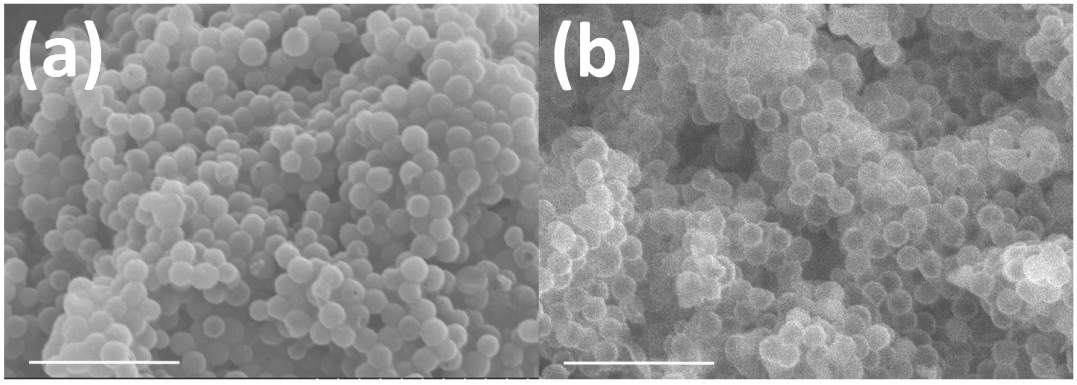
AC impedance measurements were carried out by a Frequency Response Analyzer (FRA)

technique on an Autolab Electrochemical Workstation over the frequency range from 0.01Hz to 10 MHz with the amplitude of 10 mV. Cyclic-voltammetry (CV) measurement was also conducted using the Autolab Electrochemical Workstation. The galvanostatic charge and discharge tests were conducted on a LAND CT2001A battery test system in the voltage range of 1.5-2.8 V (vs. Li/Li^+).

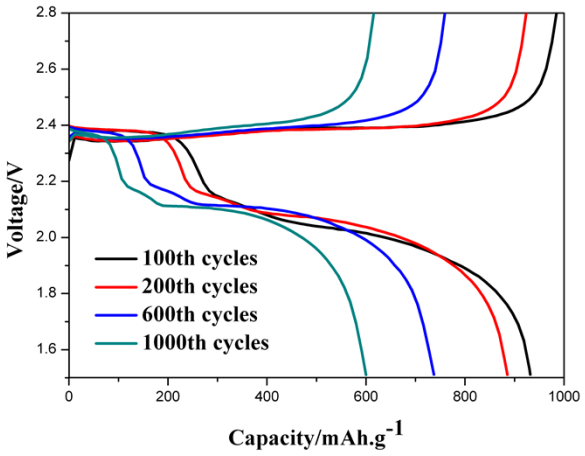
2. Lists of Figures



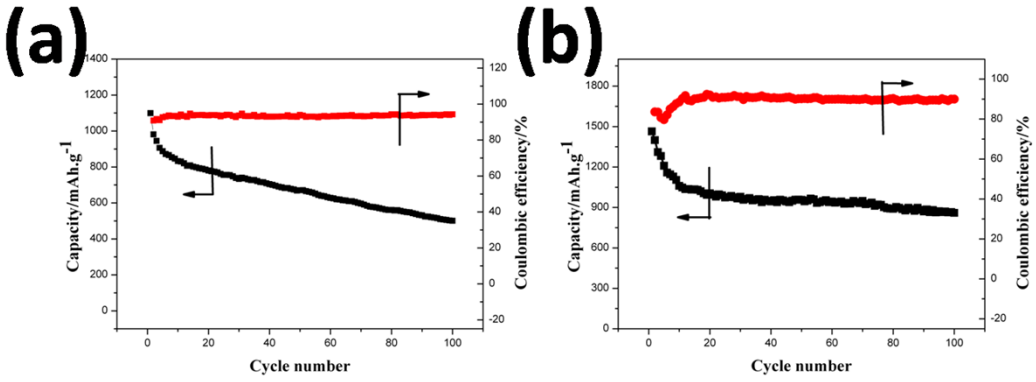
Supplementary Fig. S1 TEM images of sulfonated polystyrene spheres (a) and PANI wrapped sulfonated polystyrene(b). Both scale bars: 1μm. The diameter of PANI wrapped sulfonated polystyrene is larger than that of sulonated polystyrene, showing a core-shell microstructure is obtained.



Supplementary Fig. S2 SEM images of PANI hollow spheres (a) and PANI-S composite (b). Both scale bars: 5 μ m. The diameters of PANI hollow spheres are uniform, and which don't show evident difference from those of PANI-S particles. And PANI-S particles aren't damaged during heating treatment.

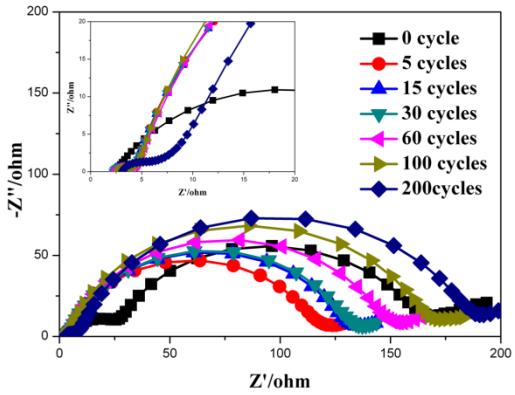


Supplementary Fig. S3 The charge/discharge profiles of PANI-S sulfur cathode at different cycles. Two voltage plateaus at about 2.38V and 2.08V are observed at 0.2C. The high voltage plateau corresponds to the reduction from elemental sulfur to PS. The low voltage plateau is attributed to the reduction of PS to Li_2S_2 and Li_2S. and the slope during the two plateau may be attributed to the S-C bond. There is no evident evolution of the curves during prolonged cycles, indicating the electrochemical reaction during the charge/discharge process is reversible.

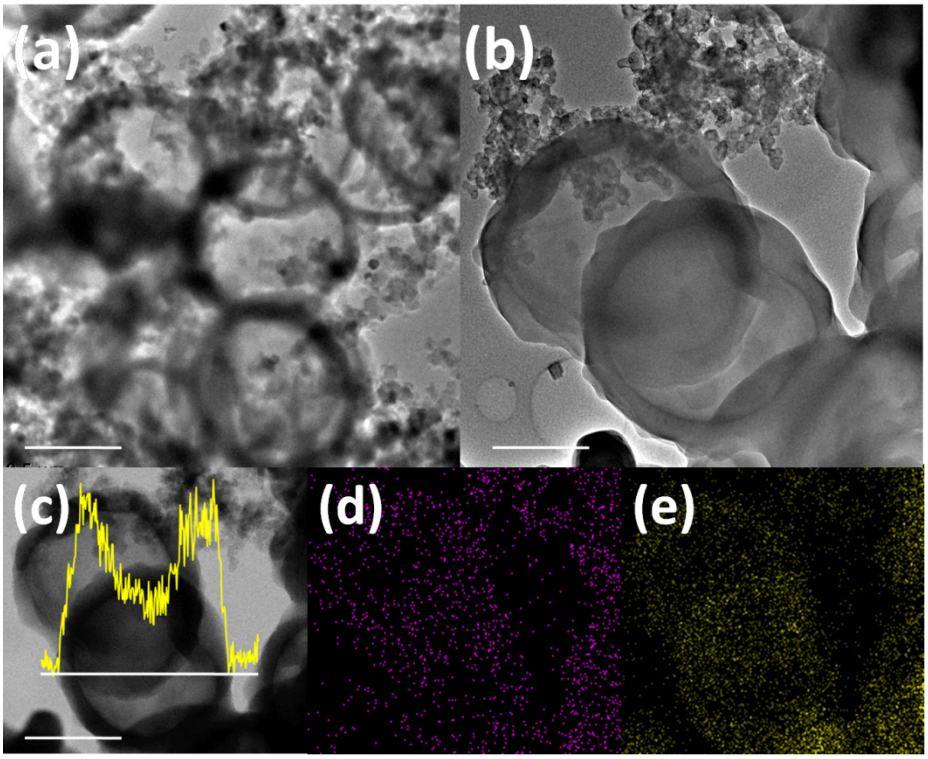


Supplementary Fig. S4 The cycling performance of the pure sulfur cathode in the 0.1M $LiNO_3$ modified electrolyte (a) and the PANI-S sulfur cathode in the electrolyte without $LiNO_3$. As shown, the cycling performance for sulfur@PANi cathode in the electrolyte without LiNO3 is not as excellent as that of the cathode in the electrolyte with 0.1M $LiNO_3$, but it is still attractive for Li-S battery. Furthermore, the cycling performance of the pure sulfur cathode in the electrolyte with 0.1M $LiNO_3$ is bad compared with that of sulfur@PANi cathode in the same electrolyte.

Therefore, the enhanced cycling performance can be mainly attributed to the designed cathode other than the modified electrolyte.



Supplementary Fig. S5 Electrochemical impedance spectroscopy plots of PANI-S cathode in different cycles after fully charged to 2.8V at 0.2C. The resistance of the cell decreases to the lowest value (119Ω) after 5 cycles, indicating the electrochemical activation and the dissolution of sulfur on the outer surface of PANI hollow spheres. Consequently, the resistance increases slowly to 193Ω after 200cycles, indicating the deposition and aggregation of sulfur on the surface of electrode are not serious and a stable cathode structure is obtained.



Supplementary Fig. S6 TEM images of PANI-S cathode after 100cycles at 0.5C (a) and (b), STEM image in (b) (c), and corresponding EDX elemental mappings of carbon(d) and sulfur (e). Scan bar: 500nm (a), 300nm (b) and (c). The volume expansion during charge/discharge process is buffered by the void space in the PANI-S spheres. Thus no obvious structural change of the cathode appears even after such a long cycling, indicating sufficient mechanical strength of the shell building the hollow PANI spheres. Furthermore, the elemental analysis results also show the remaining of the uniform distribution of sulfur in PANI hollow sphere after long cycling.

3. **Calculation of the pore volume inside each PANI hollow sphere.**

Density of S: $\rho_S = 2\ g/cm^3$.

Density of PANI: $\rho_{PANI} = 1\ g/cm^3$.

The thickness of PANI shell (based on Fig. 2 and S-Fig.2):

60 nm.

The average diameter of the PANI-S nanoparticles:

D =700 nm.

Therefore, the hollow core volume in the PANI hollow sphere:

$$\frac{580nm^3}{700nm^3 - 580nm^3} \times \frac{1}{1g/cm^3} = 1.31cm^3/g$$

And we know that the sulfur content in the PANI-S composite is 62wt.%, and specific capacity of the PANI-S cathode reached 920 $mAh.g^{-1}$ after 40cycles at 0.2C, indicating that the utilization rate of sulfur in the cathode attains: $\frac{920mAh/g}{1675mAh/g} = 54.9\%$. It is supposed that the sulfur on the outer surface of PANI hollow sphere will be dissolved in the electrolyte, and the sulfur on the inner surface of PANI hollow sphere will be used completely. So the volume of the sulfur in the inner surface of the PANI hollow sphere for 1g PANI is:

$$54.9\% \times (\frac{1}{1 - 65\%} - 1) / 2 = 0.51cm^3$$

And it is reported that the volume expansion of sulfur during the charge/discharge process reaches 80%, so the volume of the activity material after lithiated is:

$0.51 \times (1+80\%) = 0.91cm^3$,

which is smaller than that of the porous volume in the PANI hollow spheres, so the PANI hollow sphere can buffer the volume expansion of sulfur during charge/discharge process effectively.

Reference

1. Y. Yang, Y. Chu, F. Yang and Y. Zhang, *Mater Chem Phys*, 2005, **92**, 164-171.
2. Q. Wu, Z. Wang and G. Xue, *Adv Funct Mater*, 2007, **17**, 1784-1789.