Supporting Information for

Core-Shell Structured Sulfur-Polypyrrole Composite Cathodes for Lithium-Sulfur Batteries

Yongzhu Fu and Arumugam Manthiram
Materials Science and Engineering Program
The University of Texas at Austin
Austin, TX 78712, USA

Materials and Methods

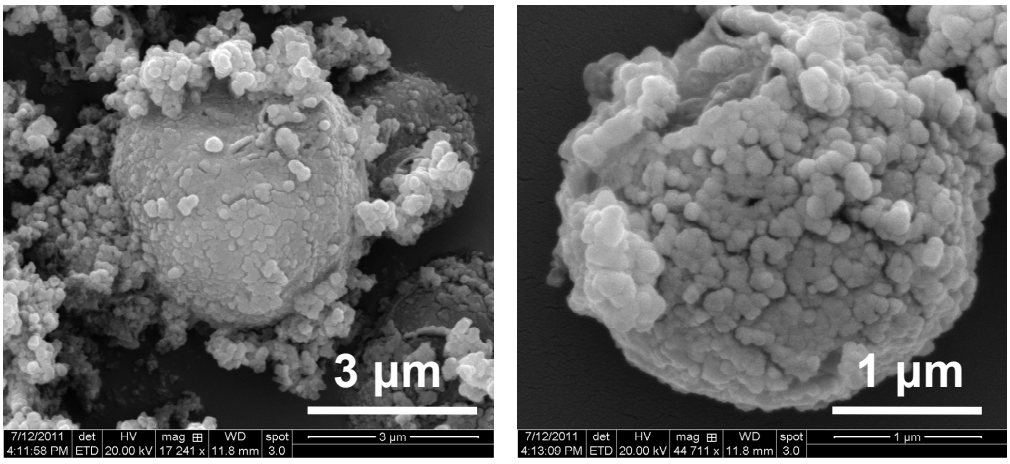
Experimental

All chemical were purchased from Sigma Aldrich and used as received. The spherical sulfur was synthesized first as follows. In a typical reaction, sodium thiosulfate pentahydrate (4.963 g, 20 mmol) was dissolved in 800 mL of de-ionized water with magnetic stirring. *p*-Toluenesulfonic acid monohydrate (*p*TSA) (7.609 g, 40 mmol) was then added and the reaction was allowed to proceed at room temperature overnight. The product sulfur formed was filtered, washed, and dried in an air oven at 50 °C for 24 h. For the synthesis of sulfur-polypyrrole (S-PPy) composites, the synthesized sulfur (0.64 g) was dispersed in decyltrimethylammonium bromide (DeTAB) aqueous solution (0.05 M, 160 mL) with magnetic stirring. The resulting dispersion was sonicated for 10 min. After adding an amount of concentrated hydrochloric acid (4 mL), an appropriate amount of pyrrole was added while the reaction mixture was cooled to 0 – 5 °C in an ice bath, followed by an addition of ammonium peroxydisulfate (1.1 equiv mole of pyrrole). The reaction was allowed to proceed at 0 – 5 °C for 4 h, during which the color of the reaction solution slowly turned into black. The product was filtered, rinsed thoroughly with de-ionized water, and dried in an air oven at 50 °C overnight to obtain a black powder. Pristine polypyrrole was also synthesized using ammonium peroxydisulfate and used in the thermogravimetric analysis for determining the compositions of the S-PPy composites.

Characterization: Morphological and particle size characterizations were carried out with a FEI Quanta 650 scanning electron microscope (SEM). The XRD data were collected on a Philips X-ray diffractometer equipped with CuKα radiation in steps of 0.04°. Thermogravimetric analysis (TGA) data were collected with a Perkin Elmer Series 7 Thermal Analysis System under flowing air from room temperature to 600 ^{o}C at a heating rate of 5 ^{o}C/min to assess the sulfur contents in the S-PPy composites. X-ray photoelectron spectroscopy (XPS) data were collected at room temperature with a Kratos Analytical spectrometer and monochromatic Al Kα (1486.6 eV) X-ray source. Depth profiling analysis with XPS was carried out by rastering an Ar^{+} ion beam on an area of 2 × 2 mm. The Ar^{+} ion gun was operated at 4 kV and the extractor current was maintained at 75 μA during the sputtering process, resulting in an average sputtering rate of 4 Å/s during these experiments.

Electrode fabrication and battery test: The cathodes were prepared by mixing the S-PPy composite (60 wt. %) with Super P carbon (20 wt. %), and poly(vinylidene fluoride) (PVdF) binder (20 wt. %) and dispersing the mixture in N-methylpyrrolidone (NMP) overnight to prepare a slurry. The slurry was then coated onto an aluminum foil, followed by evaporating the NMP at 50 °C under a flowing air oven for 24 h. The electrode was cut into circular disks of 0.64 cm^2 area. CR2032 coin cells were then assembled with the S-PPy composite electrodes thus fabricated, lithium foil anode, 1.85 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in dimethoxy ethane (DME) and 1,3-dioxolane (DOL) (55:40 v/v) electrolyte, and Celgard polypropylene separator. Cyclic voltammetry data were collected with cells between 1.5 and 3.0 V at a scanning rate of 0.2 mV/s. Electrochemical performances of the half cells were evaluated between 1.5 and 2.8 V at various C rates. Electrochemical impedance spectroscopy (EIS) data were collected with a computer interfaced HP 4192A LF Impedance Analyzer in the frequency

range of 1M Hz – 0.1 Hz with an applied voltage of 5 mV and Li foil as both counter and reference electrodes.



(a) (b)

Figure S1. SEM images of the core-shell structured sulfur-polypyrrole (S-PPy) composites, showing the polypyrrole coating on the surface of sulfur particles.

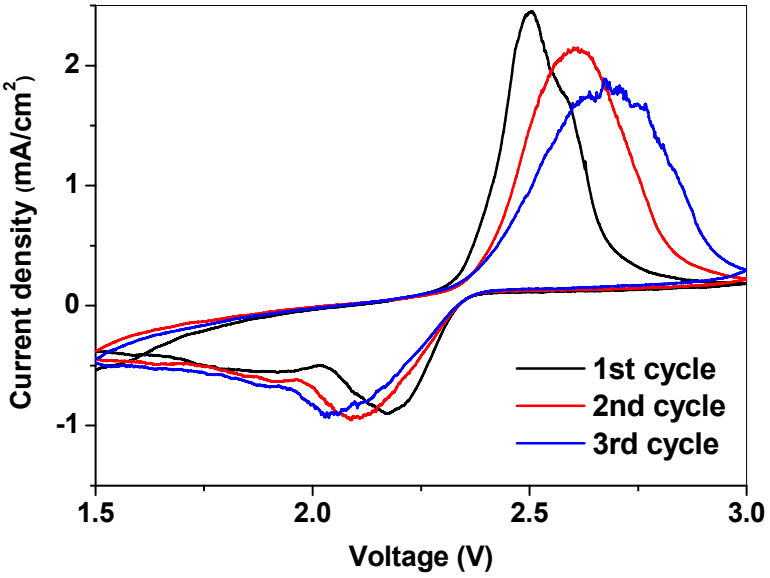


Figure S2. Cyclic voltammograms at a sweep rate of 0.2 mV/s of the pristine sulfur electrode.

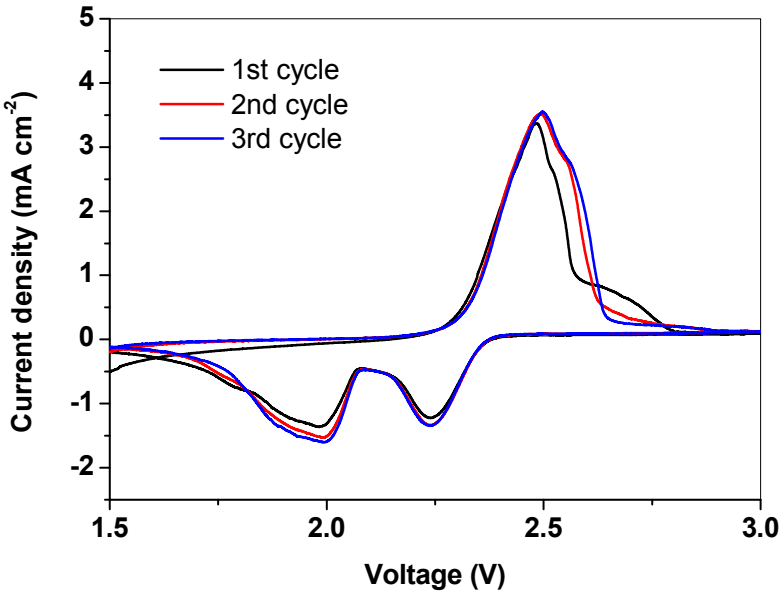


Figure S3. Cyclic voltammograms at a sweep rate of 0.2 mV/s of the S-PPy-77 composite.

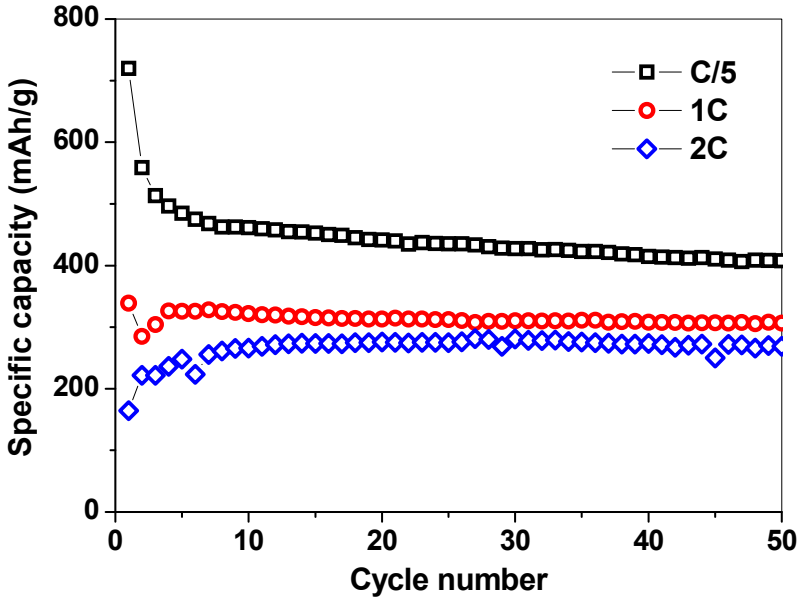


Figure S4. Cyclability of the S-PPy-77 composite at various C rates (C/5, 1C, and 2C); the capacity values are in terms of the sulfur active mass.

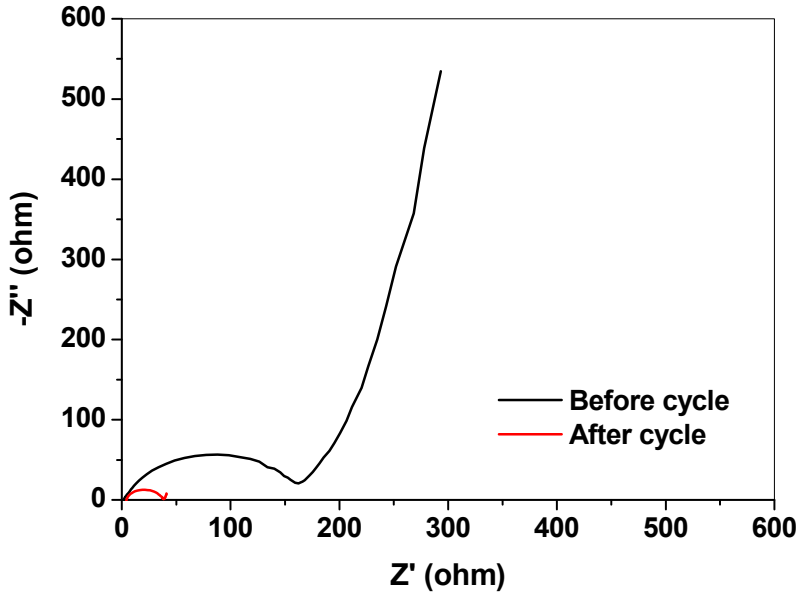


Figure S5. Impedance analysis of the half cell containing the S-PPy-77 composite electrode before (black) and after (red) 50 cycles.