

One-pot approach to synthesize PPy@S core-shell nanocomposite cathode for Li/S batteries

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Abstract A polypyrrole-coated sulfur composite (PPy@S) was synthesized by in situ polymerization of pyrrole monomers on the surface of nano-sulfur particles. High resolution transmission electron microscopy and energy dispersive spectroscopy mapping showed the formation of a highly developed core-shell structure with uniform PPy coating on the surface of sulfur particles. The electrochemical properties of the resulting PPy@S composite cathode have been evaluated by cyclic voltammograms and galvanostatic discharge-charge cycling. The results show that the PPy@S composite exhibits a reversible capacity of 1,200 mAh g⁻¹ at the initial cycle, with 913 mAh g⁻¹ remaining after 50 cycles. Even up to 2.5 C, a reversible capacity of 437 mAh g⁻¹ is obtained. The excellent electrochemical performance can be attributed to the conductive PPy-coating nanolayer, which provides both an effective electron conduction path and a strong physical and chemical confinement setting for elemental sulfur and resident polysulfides, minimizing the loss of active material during cycling.

Keywords Core-shell structure · Lithium/sulfur battery · Nanostructured sulfur cathode · Sulfur/polypyrrole composite · Energy storage

Introduction

Due to their relatively high energy density, stable and long cycle life lithium-ion batteries are leading the path as the power sources for various portable applications, such as laptops and cellular phones (Aricò et al. 2005). However, cost, safety, toxicity, and limited capacity issues related to anode, cathode, and electrolyte materials restrict the wider usage of early generations of lithium-ion batteries, especially in large scale applications, such as for hybrid electric vehicles and electric vehicles (Bakenov et al. 2008). Sulfur, largely abundant in nature and of low cost, is promising candidate for the next generation of cathode materials for lithium rechargeable batteries. Elemental sulfur cathode has a theoretical-specific capacity of 1,672 mAh g⁻¹, which is higher than that of any other known cathode material for lithium batteries (Zhao et al. 2012b; Armand and Tarascon 2008). Despite these advantages, several challenges compromise the suitability of sulfur for use as cathode in lithium batteries, namely: (i) the low conductivity of sulfur leads to low utilization and poor rate capability of the cathode; (ii) multistep electrochemical reduction processes during charge-discharge generate various

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forms of soluble intermediate lithium polysulfides that dissolve in the electrolyte and undergo the so-called shuttle effect, causing irreversible loss of sulfur active material over repeated cycling; (iii) volume changes of sulfur upon cycling leads to particle breakage and, consequently, rapid degradation of the cathode electrochemical performance (Zhang et al. 2011).

A variety of strategies have been employed to improve the discharge capacity, cyclability, and coulombic efficiency of the sulfur cathode in Li/S batteries. Among these, preparation of sulfur/carbon and sulfur/conductive polymer composites has received considerable attention (Ding et al. 2013; Fu and Manthiram 2012a, b; Ji et al. 2009; Li et al. 2012; Wang et al. 2013a, b; Wu et al. 2010; Zhang et al. 2012, 2013b, c, d, e; Zhao et al. 2012a, 2013). In particular, the use of conductive polymers surface coatings shows good potential in tackling the drawbacks of sulfur cathodes (Wu et al. 2010; Fu and Manthiram 2012a, b; Shao et al. 2013). Conductive polymer layer can act both as an electronic conductivity enhancer and as a sulfur vault. Nevertheless, attempts using those strategies on preparation of core-shell type particles always yield a large agglomerate, usually of hundreds of microns in size, which still remains insufficient for practical application. Moreover, the multi-step synthetic procedures are complicated, time and energy consuming, and sulfur is evaporated and lost during the required heat treatment steps. Hence, the development of simple techniques to prepare sulfur composites without heat treatment is of technological and economical interest. To the best of our knowledge, there are no reports on the synthesis of nanoscopic conductive polymer-coated nano-sulfur particles without heat treatment and/or their use in Li/S battery.

Herein, we describe a simple one pot method to synthesize a core-shell-structured sulfur/polypyrrole (PPy@S) composite by in situ chemical oxidative polymerization of pyrrole on the surface of spherical nano-sulfur particles. The physical and electrochemical properties of the composite as a cathode material for lithium secondary batteries are also reported.

Experimental

Polypyrrole was synthesized from pyrrole monomer (Aldrich, 98 %) by chemical oxidative procedure, using FeCl_3 (Sigma-Aldrich, 97 %) as oxidant.

Polypyrrole-coated sulfur (PPy@S composite) was obtained by in situ polymerization of pyrrole on the surface of nano-sulfur particles. 0.2 g pyrrole was added into 4 g aqueous suspension of nano-sulfur (US Research Nanomaterials Inc., 10 wt%) and stirred for 0.5 h. 15 mL of 0.5 M FeCl_3 aqueous solution was added dropwise with constant sonication at ambient temperature. After sonication for 2 h, the precipitate was filtered, thoroughly washed with deionized water and methanol, and then vacuum-dried overnight at 70 °C.

Fourier transformed infrared (FTIR) spectra of PPy and PPy@S were obtained between 750 and 2,000 cm^{-1} using a Bruker Vertex 80. The crystalline nature of the samples were analysed by powder X-ray diffraction (XRD) using a Bruker D8 Discover equipped with $\text{Cu K}\alpha$ radiation. The composite surface morphology was examined by field emission scanning electron microscopy (FESEM, Leo-1530, Zeiss). The interior structure of PPy@S composite was observed using high resolution transmission electron microscopy (HRTEM, FEI TITAN 80-300) equipped with energy dispersive spectroscopy (EDS). The diameter distribution of PPy@S composite, the calculation of the geometric mean diameter $d_{g,p}$ and the geometric standard deviation σ_g was calculated by random sampling of the nanoparticles from the SEM images. The sulfur content in the PPy@S composite was determined using chemical analysis (CHNS, Vario Micro Cube, Elementar).

The electrochemical performance of PPy@S composite sample was evaluated using coin-type cells (CR2032). The cell was composed of lithium metal anode and PPy@S cathode separated by a microporous polypropylene separator soaked in 1 mol L^{-1} solution of lithium bistrifluoromethanesulfonamide (Aldrich, 96 % purity) in tetraethylene glycol dimethyl ether (Aldrich, 99 % purity). The composite cathode was prepared by mixing 80 wt% PPy@S composite, 10 wt% polyvinylidene fluoride (PVdF) (Kynar, HSV900) as a binder and 10 wt% acetylene black (AB) (MTI, 99.5 % purity) conducting agent in 1-methyl-2-pyrrolidinone (NMP, Sigma-Aldrich, ≥ 99.5 % purity). The resultant slurry was cast onto an Al foil and dried in a vacuum oven for 12 h at 60 °C, after which disk of 1-cm diameter was cut out to be used as cathode. The cathodes with the composition PPy:AB:PVdF = 6:3:1 and S:AB:PVdF = 6:3:1 were also prepared in the same way as the PPy@S composite

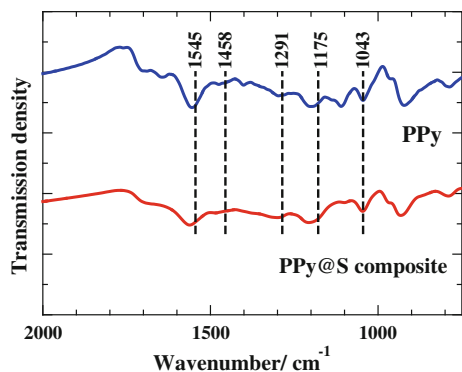


Fig. 1 FTIR spectrums of PPy and PPy@S composite

cathode, and tested for comparison. The coin cells were assembled in a MBraun glovebox filled with high purity argon (99.9995 % purity). The cells were cycled galvanostatically on a multichannel battery tester (BT-2000, Arbin Instruments) between 1 and 3 V versus Li/Li⁺ electrode. Applied currents and specific capacities were calculated on the basis of the weight of S in the cathode. Cyclic voltammetry (CV) was performed with a potentiostat (VMP3, Biologic) between 1 and 3 V versus Li/Li⁺ at a scanning rate of 0.1 mV s⁻¹. All electrochemical measurements were performed at room temperature.

Results and discussion

The FTIR spectrum of PPy (Fig. 1) displays the characteristic bands of the PPy: the pyrrole ring fundamental vibrations at 1,545 and 1,458 cm⁻¹, the =C–H in-plane vibrations at 1,291 and 1,043 cm⁻¹, and the C–N stretching vibration at 1,175 cm⁻¹. This signifies that the PPy structure was successfully obtained via the chemical polymerization method. The aforementioned characteristic peaks of PPy are also observed in the PPy@S composites, albeit with reduced intensity due to the lower content of PPy.

The XRD patterns of as prepared PPy, elemental S and PPy@S composite samples are shown in Fig. 2. The broad feature at 26° is characteristic of PPy and indicates a low degree of crystallinity of this phase. In contrast, the XRD patterns of S exhibit the characteristics features of orthorhombic sulfur in the *Fddd* space group. These sharp peaks are also present in the PPy@S composite showed but with reduced intensity. This is most likely consequence of the well-dispersed

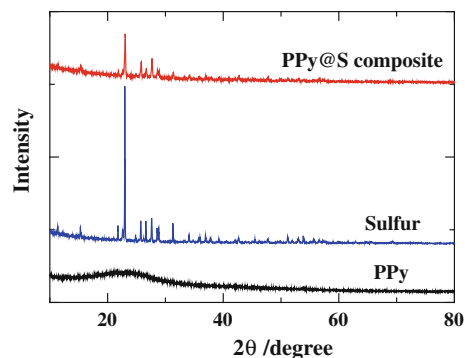


Fig. 2 XRD patterns of Sulfur, PPy, and PPy@S composite

character of nanoscopic sulfur in the core–shell structure, as evidenced by electron microscopy analysis.

The SEM image of the PPy@S composite is shown in Fig. 3a. Most particles are discrete, nearly spherical, and of uniform size, although a small amount of larger aggregates is also observed. And at higher magnification, the SEM images reveal that the PPy coating is rough as shown in the inset of Fig. 3a2. The HRTEM (Fig. 3b) clearly depicts sulfur particles coated with a PPy layer (also as indicated by the arrows): well-defined particles of PPy shells and dense sulfur cores are readily observed. The inset of Fig. 3b presents the particle-size distribution of PPy@S composite powders obtained from the SEM data. The particles have geometric mean diameter of $d_{g,p} = 313.8$ nm and a geometric standard deviation of $\sigma_g = 1.2$. The well-developed core–shell structure was also confirmed by the EDS mapping results shown in Fig. 3c, d. The core–shell structure of the PPy@S composite may effectively prevent sulfur dissolution into the electrolyte. In addition, the PPy matrix is thought to enhance the composite electrical conductivity, by reducing the particle-to-particle contact resistance, and to increase the contact area between the electrode and the electrolyte facilitating lithium diffusion.

The curves for the first, second, and fifth CV cycles of Li/S cell with PPy@S composite cathode are shown in Fig. 4. Two major redox processes are observed and can be attributed to the transition of S to polysulfides (Li₂S_n, $n \geq 4$), and their further transformation to lithium sulfide Li₂S (Zhang et al. 2013a). During the first cycle, the activation process associated with the penetration and transport of the electrolyte and

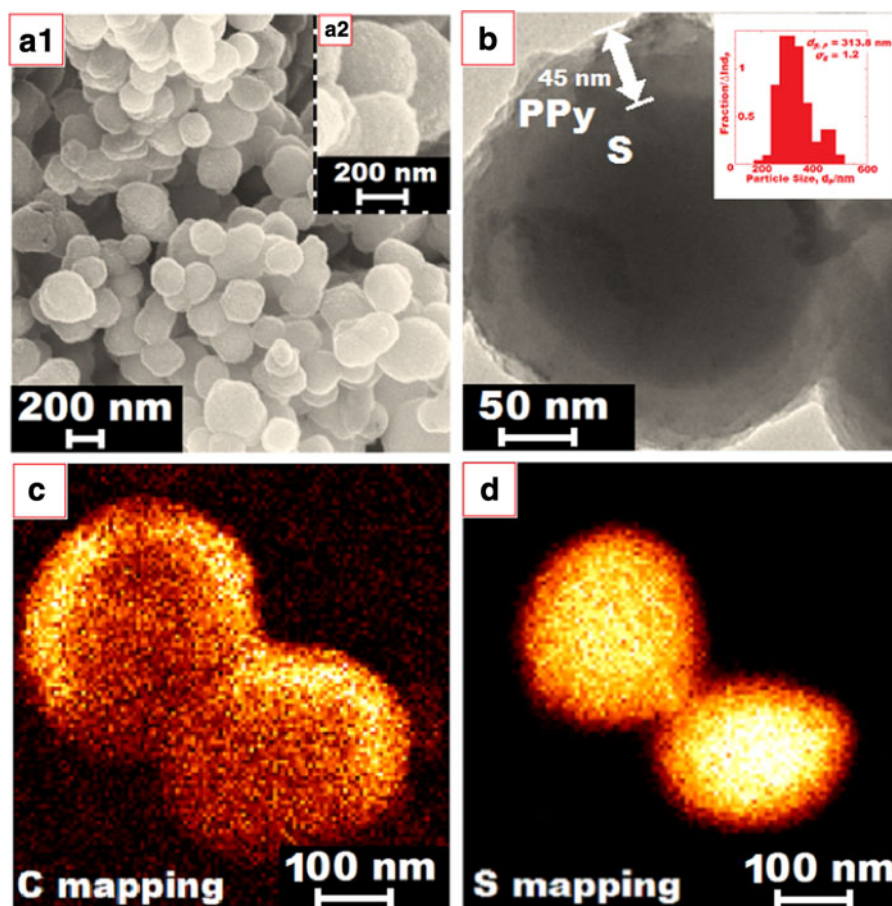


Fig. 3 **a** SEM image of PPy@S composite at different magnifications. **b** HRTEM images of PPy@S composite and particle-size distribution of PPy@S composite. **c, d** EDS mapping showing distribution of carbon (C) and sulfur (S) in composite of PPy@S

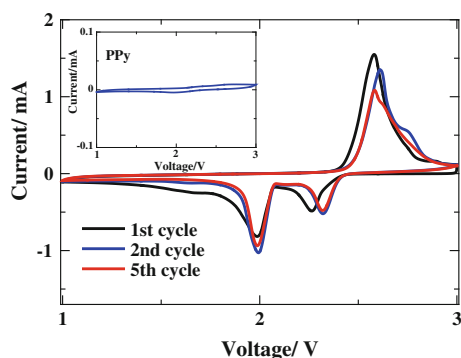


Fig. 4 CV profiles of lithium cells with PPy and PPy@S composite cathodes (the potential sweep rate is 0.1 mV s^{-1})

lithium-ions through the PPy layer on the PPy@S composite lead to an anodic peak at slightly lower potential (2.3 V vs. Li/Li^+). The intensity of the main

peaks slightly decreases from the second to fifth cycle, suggesting good reversibility of the redox processes. The inset of Fig. 4 confirms that the PPy is not electrochemically active in the selected voltage region.

The electrochemical performance of the PPy@S composite and pure S cathode in galvanostatic charge/discharge tests are shown in Fig. 5a. At 0.2 C, the PPy@S composite shows much better cycling stability with 913 mAh g^{-1} reversible capacity after 50 cycles. In contrast, the discharge capacity of pure sulfur cathode drops to 380 mAh g^{-1} by the 50th cycle, which is almost a half of the value of the PPy@S composite. This is likely due to the ability of the core-shell structure of the PPy@S composite to minimize losses of active material during cycling and enhance electronic conductivity of the cathode material. Figure 5a shows a better coulombic efficiency for the

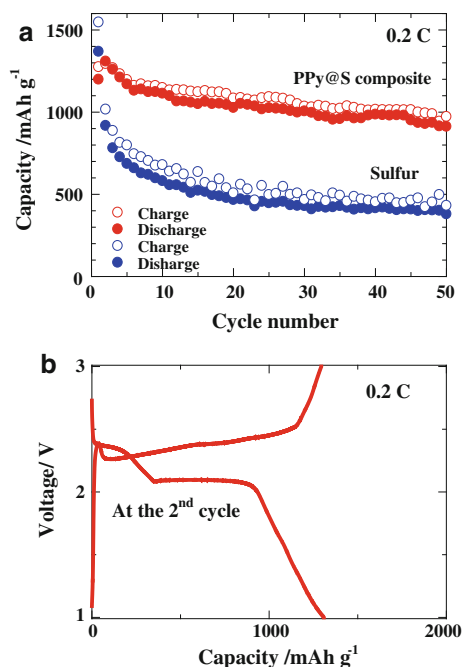


Fig. 5 **a** Cycle performance of lithium cells with sulfur and PPy@S composite cathodes at 0.2 C. **b** Charge/discharge profiles of lithium cells with PPy@S composite cathode at the second cycle

PPy@S composite in the range of 93.5–101.1 %, suggesting that the PPy-coating layer effectively blocks the severe shuttle effect of soluble lithium polysulfides (Li et al. 2012). The voltage profile for the second cycle of the PPy@S composite (Fig. 5b) shows two main discharge plateaus at 2.4 and 2.0 V versus Li/Li⁺, in good agreement with the CV data. Up to 1,309 mAh g⁻¹ discharge capacity is attained by the PPy@S composite at 0.2 C on the second cycle.

The rate capability results, as depicted in Fig. 6a, reveal excellent performance for the PPy@S composite. After the two initial activation cycles at 0.2 C, the composite achieves a discharge capacity of 1,023 mAh g⁻¹ at 0.5 C. There is a gradual capacity reduction with the increasing current rate, although 437 mAh g⁻¹ reversible capacity was sustained even at 2.5 C. More importantly, the composite regains most of its reversible capacity (773 mAh g⁻¹) when the discharge rate is modulated back to 0.5 C, showing the high abuse tolerance of the PPy@S. This superb rate performance can be attributed to the electronic conductivity enhancement by the introduction of

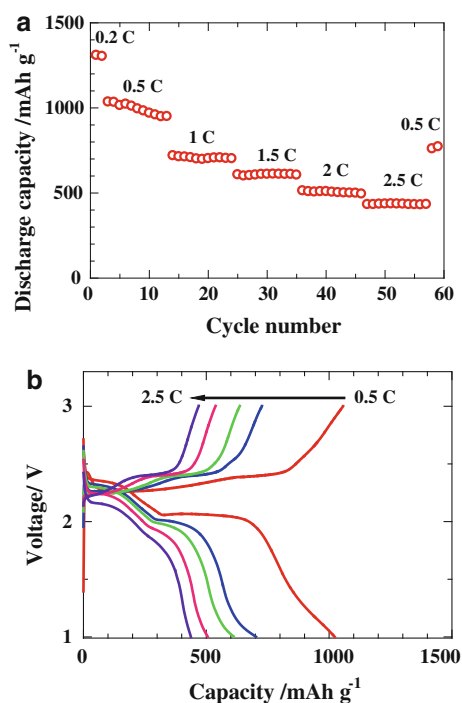


Fig. 6 **a** Rate capability of lithium cells with PPy@S composite cathodes. **b** Charge/discharge profiles of lithium cells with PPy@S composite cathodes at various rates

conductive PPy layer coating on the nano-sulfur particles. The charge/discharge profiles for the PPy@S composite at various discharge rates, presented in Fig. 6b, reveal that the polarization augments upon increasing current rate. Noteworthy, the capacity corresponding to the higher plateaus on the discharge curves does not decrease appreciably with the increasing current rate, whereas that corresponding to the formation of lower polysulfides and Li₂S is notably reduced (Zhao et al. 2012a).

To demonstrate the integrity of the pure S and PPy@S composite electrodes, fresh and after 20 charge/discharge cycles at 0.2 C, their structures are characterized by SEM. It can be seen from Fig. 7 that pure sulfur cathode morphology drastically changes upon cycling, and the sulfur particles severely agglomerate and merge into a large solid bulk, negatively affecting the cathode conductivity and sulfur utilization. In contrast, the morphology of the PPy@S composite does not change remarkably after 20 cycles (see Fig. 7d), due to the PPy protective layer coating the surface of the nanosulfur particles.

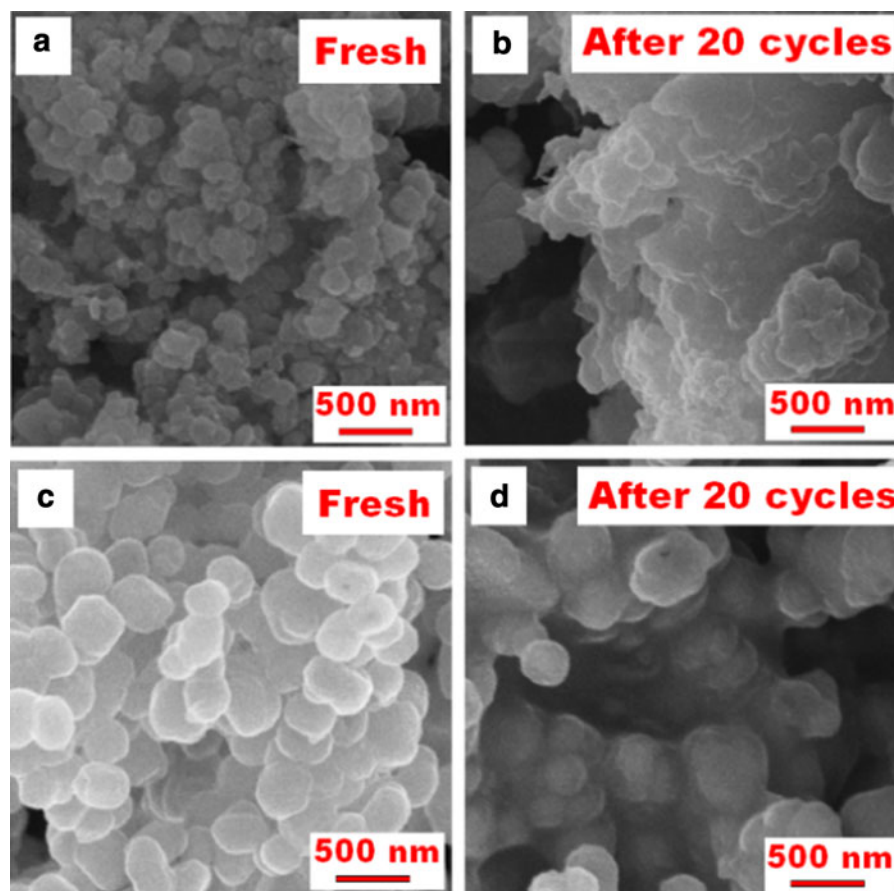


Fig. 7 SEM of **a, b** sulfur and **c, d** PPy@S composite before and after 20 charge/discharge cycles at 0.2 C

Conclusions

A polypyrrole-coated sulfur composite was synthesized by the in situ polymerization of pyrrole on the surface of nano-sulfur particles. The composite showed good capacity and cycling stability in Li/S rechargeable batteries. The initial discharge capacity was $1,200 \text{ mAh g}^{-1}$ at 0.2 C, with 913 mAh g^{-1} remaining after 50 cycles, and 437 mAh g^{-1} at 2.5 C. The electrochemical performance of the composite shows that the conductive PPy nanolayer coating provides both an effective electron conduction path and a strong physical and chemical confinement setting for elemental sulfur and resident polysulfides, minimizing the loss of active material during cycling.

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