



Graphene-supported highly crosslinked organosulfur nanoparticles as cathode materials for high-rate, long-life lithium-sulfur battery



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ABSTRACT

Lithium-sulfur batteries represent one of the next-generation Li-ion batteries; yet rapid performance degradation is a major challenge. Herein, a highly crosslinked copolymer is synthesized through thermally activated polymerization of sulfur and trithiocyanuric acid onto the surface of reduced graphene oxide nanosheets. Of the thus-synthesized composites, the sample with a high sulfur content of 81.79 wt.% shows a remarkable rate performance of 1341 mAh g⁻¹ at 0.1 C and 861 mAh g⁻¹ at 1 C with an almost 100% coulombic efficiency. The composite electrode also effectively impedes the dissolution of polysulfides and their shuttle diffusion because of the abundant and robust chemical bonding between sulfur and trithiocyanuric acid and spatial confinement of polysulfides by the reduced graphene oxide sheets, which leads to 81.72% retention of the initial capacity even after 500 deep charge-discharge cycles at 1 C, corresponding to a decay rate of only 0.0404% per cycle. This performance is markedly better than those of comparative materials prepared in a similar fashion but at either higher or lower S loading, and among the highest in sulfur copolymer cathodes to date. The results provide an effective paradigm in the preparation and engineering of polymer cathode materials for high-performance lithium-sulfur batteries.

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1. Introduction

Lithium-sulfur (Li-S) batteries are regarded as one of the most promising candidates for next-generation rechargeable batteries due to various unique advantages: (a) the energy density of Li-S batteries (2567 Wh Kg⁻¹) is about five times higher than that of conventional Li-ion batteries due to the high specific capacity of sulfur (1672 mAh g⁻¹), such that Li-S batteries can meet the ever-increasing power demands in portable electronics and electric vehicles [1–3]; (b) sulfur is among the most earth-abundant elements

and may sustain massive commercialization of Li-S batteries [4,5]; and (c) Li-S batteries are easy to fabricate, cost-effective and environmentally friendly [6–8]. However, to realize large-scale commercialization of Li-S batteries, several critical issues need to be resolved, such as the low coulombic efficiency and rate capacity resulting from the low electrical conductivity of sulfur and polysulfides ($\sim 5 \times 10^{-30}$ S cm⁻¹ at 25 °C) [9,10], rapid capacity attenuation caused by mechanical degradation of the cathode due to the large volume expansion (up to 80%) of sulfur lithiation, and the so-called “shuttle” effect of lithium polysulfides (Li₂S_n with 4 ≤ n ≤ 8) due to the dissolution and diffusion of polysulfides in organic electrolytes [11–14]. Moreover, lithium dendrites can be easily formed in the lithium metal anode during charge-discharge processes, which may short the circuit by penetration into the thin membrane, resulting in a short life-span and serious safety concerns [15].

To mitigate these issues, extensive research efforts have been devoted to the design and engineering of novel cathode materials

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[16,17], membrane separators [18–20], and anode protections [21] to prevent the dissolution and diffusion of polysulfides in the electrolyte and the formation of lithium dendrites [22–24]. As for cathode materials, a variety of carbon-based materials, such as hollow carbon spheres [25–27], carbon nanotubes [20,28,29], porous carbon [3,30–32], layered carbon matrices [33], and carbon nanofibers [34,35], have been widely used as conductive substrates for sulfur to increase the rate performance and coulombic efficiency. However, sulfur is mostly physically adsorbed on these carbon substrates, hence the issues of dissolution and diffusion of polysulfides in organic electrolytes remain unresolved [36–38]. This may be further mitigated by chemical confinement of the carbon-sulfur composites. An emerging judicious method is based on copolymerization of elemental sulfur with small organic molecules such as vinylic monomers [4], styrene [39], polyacrylonitrile [40] and dicyanobenzene [41] through inverse vulcanization. However, the insulating nature of these copolymers greatly restricts the loading of active sulfur to only 1 mg cm^{-2} or lower (shown in Table S1) and hence compromises the capacitive performance. Therefore, deliberate engineering of the sulfur copolymer-based cathodes is strongly desired to increase the loading of active sulfur for further improvement of the battery performance. This is the primary motivation of the present work.

Herein, we report the preparation of graphene-supported highly crosslinked sulfur copolymer nanoparticles as a cathode material for Li-S battery. Experimentally, trithiocyanuric acid (TTCA) was pre-deposited on the surface of highly conductive graphene oxide nanosheets as tiny nanoparticles, and then crosslinked with sulfur via radical polymerization. The resulting cp(S-TTCA)@rGO hybrids exhibited much enhanced electrical conductivity, as compared to the nanocomposites without graphene support, and the dissolution and diffusion of polysulfides was effectively suppressed by the combined contributions of chemical confinement resulting from the extensive bonding between sulfur and TTCA as well as physical confinement by the graphene crosslinked networks. Within the present experimental context, the sample with a high sulfur content of 81.79 wt.% (2.0 mg cm^{-2}) was found to exhibit the best performance as the cathode for Li-S battery, with a reversible capacity of 1341 mAh g^{-1} at 0.1 C, and a discharge capacity of 671 mAh g^{-1} even after 500 deep charge-discharge cycles at 1 C with a high capacity-retention of 81.72%.

2. Experimental section

2.1. Synthesis of cp(S-TTCA)@rGO nanocomposites

Graphene oxide was obtained by a modified Hummers' method [42]. As illustrated in Fig. 1, cp(S-TTCA)@rGO was synthesized as follows: (1) TTCA was dissolved in dimethyl formamide (DMF, 99%, Alfa Aesar) to form a solution (1.13 M), followed by the addition of graphene oxide (50 mL, 8 g L^{-1}). After magnetic stirring of the mixed solution for 2 h, a calculated amount of sodium borohydride was slowly added to the solution also under magnetic stirring for another 2 h. The obtained TTCA@rGO composites were collected by filtering, washed with distilled water and then dried. (2) The obtained TTCA@rGO was mixed with sulfur at a TTCA@rGO:sulfur weight ratio of 2:4, 1:4 and 1:7; and the mixtures were heated at $150 \text{ }^\circ\text{C}$ for 3 h to impregnate the molten sulfur into the pores between rGO sheets under an argon atmosphere, and then further heated at $170 \text{ }^\circ\text{C}$ for 8 h to initiate ring-opening polymerization of sulfur and TTCA, leading to the formation of highly crosslinked nanoparticles between S and TTCA that were supported on rGO nanosheets. The resulting composites were denoted as cp(S-TTCA)@rGO-70, cp(S-TTCA)-80 and cp(S-TTCA)-90, respectively. Simple cp(S-TTCA) was also prepared in a similar fashion but without the

addition of graphene or carbon black.

The cp(S-TTCA)@rGO-80/C composite was prepared with a mixture of cp(S-TTCA)@rGO-80, carbon black and PVDF at a mass ratio of 80: 10: 10.

2.2. Material characterization

SEM and TEM measurements were conducted on a Hitachi S-4800 field emission scanning electron microscope (FESEM) and a JEOL JEM-2100 transmission electron microscope at an acceleration voltage of 200 KV, respectively. X-ray diffraction (XRD) measurements were performed with a Bruker D8 instrument using $\text{Cu K}\alpha$ radiation. FTIR spectra were recorded on Nicolet 6700 FTIR spectrometer using a KBr pellet in the transmission mode. Raman spectra were recorded on a RENISHAW in Via instrument with an Ar laser source of 488 nm in a macroscopic configuration. XPS measurements were carried out with a Phi X-tool XPS instrument. TGA/DSC curves were acquired with a METTLER instrument under a N_2 atmosphere at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$.

2.3. Device preparation and characterization

In a typical measurement, the polyvinylidene fluoride (PVDF) binder was completely dissolved in *N*-methyl-2-pyrrolidone (NMP) under magnetic stirring. A calculated amount of the cp(S-TTCA)@rGO samples prepared above and conductive carbon black were then added into the solution to form a homogenous slurry at a cp(S-TTCA)@rGO: carbon black: PVDF mass ratio of 80: 10: 10. The slurry was then deposited on an aluminium current collector using the doctor blade method and then dried at $60 \text{ }^\circ\text{C}$ for 18 h in a vacuum oven. The obtained cathode foil was compressed and cut into circular sheets of 12 mm in diameter. The typical mass loading of active sulfur was calculated to be 2.0 mg cm^{-2} . The CR2032-type experiment cells were assembled in an argon-filled glove box. The cell comprised of a positive electrode, polypropylene (PP diaphragm Celgard 2400) as the separator, a lithium foil as the reference/counter electrode, and the mixed solution of 1,3-dioxolane and 1,2-dimethoxyethane (volume ratio 1:1) containing 1 M lithium bis(trifluoromethanesulfonyl) imide (LiTFSI), and 0.1 M LiNO_3 as the electrolyte. For comparison, coin-cells with cp(S-TTCA) and S cathodes were prepared in the same manner, at the same active substance content and mass loading of active sulfur.

Galvanostatic discharge-charge tests of the as-fabricated cells were performed by potential cycling between +1.5 and +3.0 V (vs. Li/Li^+) at different current rates using a button cell test system (LANHE CT2001A 5 V 20 mA). Cyclic voltammetry (CV) studies were performed in the potential range of +1.5 to +3.0 V at varied scan rates. EIS studies were conducted at the charged state in the frequency range of 100 KHz to 10 mHz at an AC amplitude of 5 mV.

3. Results and discussion

The synthesis of cp(S-TTCA)@rGO was illustrated in Fig. 1, where TTCA and graphene oxide (GO) nanosheets were firstly co-dissolved in *N,N*-dimethyl formamide, followed by the addition of an aqueous solution of NaBH_4 that produced reduced GO (rGO) and concurrently precipitated and deposited crystalline TTCA nanoparticles onto the rGO surface to form TTCA@rGO composites (shown in Fig. S1). The mixture of sulfur and TTCA@rGO was then heated at $170 \text{ }^\circ\text{C}$ where ring-opening radical polymerization of sulfur and TTCA yielded cp(S-TTCA)@rGO as the final product. The formation of crosslinked cp(S-TTCA) was evidenced by the color change from light yellow (TTCA) to dark-brown (shown in Fig. S2) [43].

Three samples were prepared at various S loadings.

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