

Significantly Raising the Cell Performance of Lithium Sulfur Battery via the Multifunctional Polyaniline Binder



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ABSTRACT

Binder is critical component to maintain the cathode integrity in lithium-sulfur battery, but it is generally non-conductive. Here sulfuric acid doped polyaniline was successfully developed as conductive binder, which showed multifunctionality when used in Li-S battery cathode, *i.e.*, in addition to necessary adhesion function, it could trap polysulfide species to abate shuttling affect while provide good electrical conductivity. The unique adhesive behavior of conductive polyaniline was attributed to the sufficiently long polar chains consisting of amine salt, iminium and aromatic ring. Based on theoretical analysis, all the electrode components could be bound together by Van der Waals and electrostatic interactions even under very low polyaniline loading. Such low loading could form conductive polyaniline cobweb which helped the polyaniline binder to resist sulfur swelling while provide adequate channels for ion transportation. In an optimal condition, the polyaniline binder loading in cathode could be reduced to *Ca.* 2.0 wt%, and the sulfur loading in cathode increased by 11.0 wt% compared with that using common non-conductive binder. Compared with cathode employing common PVDF binder, the specific capacity using polyaniline binder increased by *Ca.* 104% and 74% at current density of 122 mA g⁻¹-sulfur and 610 mA g⁻¹-sulfur, respectively, which was mainly attributed to the stable conducting feature of polyaniline binder during the charging-discharging process, as reflected from low charge transfer resistance of 37 ohm for the cathode.

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1. Introduction

Lithium-sulfur battery (Li-S battery) has been the focus of academic concern for many years because of its attractive theoretical energy density of 2576 Wh kg⁻¹ based on the high capacity of sulfur cathode (1675 mAh g⁻¹) [1–3]. For the purpose of practical application, effectively confining active material within the cathode while improving the sulfur content in total cathode is required [4–6]. Solid-phase sulfur undergoes so-called reversible solid-liquid transition which is gradually converted into soluble polysulfide intermediates (Li₂S_x, x = 3–7) during discharging, and vice versa during charging [7–9]. A complex evolution has been proposed during the whole charge-discharge process, from aggregation to diffusion, and then shuttling between the cathode and electrolyte solution. Once the electron transport with conductive matrix is interrupted, the insulating sulfur species

immediately lose the ability of electron gain or loss leading to obvious capacity fading. It is rarely noticed that during the charging process, sulfur precipitates not only on the surface of original sulfur matrix, but also on the surface of conductive additive (*e.g.*, acetylene black) as well as insulating binder. Such phenomenon should not be neglected since the conductive additive and insulating binder constitute *Ca.* 25 wt% of the total cathode material. Unfortunately, acetylene black has poor restraint capacity on sulfur because of its low binding energy, therefore the predominant surface for sulfur precipitating is the insulating binder. It is interesting if the binder becomes conductive which can conduct electron transfer between sulfur species and conductive matrix.

Commonly used poly-(vinylidene fluoride) (PVDF) adhesive can maintain the mechanical integrity of the whole electrode as well as bonding the mixture on the current collector [10,11], however, it is insulating. Since polar materials such as TiO₂, Ti₄O₇, and MnO₂ could bind with lithium polysulfides to keep them within the cathode region [12–16], Wang et al. developed new high polar adhesive, *e.g.*, poly(vinylidene difluoride-trifluoroethylene) (P

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(VDF-TRFE)), and obtained a 80% higher capacity compared with that using PVDF binder [17], whereas it was still insulating. Conducting polymer may act as ideal functional binder since its high molecular polarity could restrict polysulfides diffusion while facilitate electron transfer, in fact, Cui et al. proved that the chemical bonding between the heteroatoms (oxygen, nitrogen) in the conducting polymers and Li_xS ($0 < x \leq 2$) played essential roles in improving the cycling stability [18,19]. However, most conjugated conducting polymers are brittle due to their rigid backbone, and cannot adapt to the serious volume swelling of sulfur (~80%) during discharge process, resulting in large sulfur loss and poor binding performance, which severely limit their use as binder [20]. Milroy et al. designed a nanocomposite material composed of polypyrrole and polyurethane (PPyPU) as electrochemically active binder for sulfur cathode [21], while Pan et al. developed a binder based on the mixture of polyacrylic acid (PAA) and conductive poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) [22], both with significantly improvement of the specific capacity as well as cycling stability of Li-S battery. But the matrix polymer like PU or PAA was insulating, which inevitably reduced the electrical conductivity of binders. In this article, we explored the possibility of directly utilizing conducting polyaniline (PANI) as multifunctional binder for the cathode of Li-S battery. It is encouraging that this novel polyaniline binder showed an effective adhesion property, and meanwhile provided a manifest increase in capacity of Li-S battery due to its conductive feature.

2. Experimental

2.1. Materials preparation

Polyaniline was prepared as follows: aniline (1 mL) and ammonium peroxydisulfate (APS) (2.27 g) were dispersed in sulfuric acid aqueous solution (50 mL, 1 M), respectively. They were put in an ice bath (0–5 °C) for 60 min, then the APS solution was dropped into the aniline suspension slowly with violent stirring. The mixture was stirred for 24 h in an ice bath (0–5 °C). The product was harvested by filtration, washed with large quantity of ethyl alcohol and DI water in several turns until the pH value of the filtration liquid reached 7. Finally, the filter cake was dried in vacuum at 50 °C for about 12 h.

To prepare the conducting polyaniline binder, polyaniline powder (0.25 g) was added into *m*-cresol (39.43 mL). This dispersion was stirred for 1 h, following by ultrasonic dispersion (300 W) for 2 h. After 2 days of violent stirring, trichloromethane solvent (39.43 mL) was added into the above solution with violent stirring to produce the conducting binder.

Sulfur-wrapped activated carbon (C-S) composite with sulfur loading of 81% was prepared as follows: concentrated sulfuric acid (25.79 g) and sodium thiosulfate (62.04 g) were dissolved in DI water (80 mL), respectively. They were dropped to 200 mL of 10 g L^{-1} activated carbon (super P) water/ethanol dispersion (water/ethanol = 10/1, v/v) at the same time under violent stirring with the speed of 40 drops per minute. Keeping stirring for another 24 h, the product was filtered, washed, and dried at 60 °C in vacuum till constant weight to obtain C-S composite with sulfur loading of 81 wt%. C-S composite with sulfur loading of 68 wt% was prepared similar to the above process with suitable adjustment in reactant ratio.

S-C composite was mixed together with activated carbon (mass ratio C-S: C = 4:1) in 500 ml of water/ethanol dispersion (water/ethanol = 10/1, v/v). The dispersion was stirred for 3 h. Then, the solvent was removed by reduced pressure distillation and the product was dried at 50 °C in vacuum till constant weight.

2.2. Materials characterization

Measurements of scanning electron microscope (SEM), wide-angle X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA) and electrochemical measurement were carried out according to our previous work [23]. Zetasizer Nano ZS90 was used to test the zeta potential of doped polyaniline. The molecular weight of polyaniline was obtained by gel permeation chromatography (GPC) (Waters 1515) method using *N*-methyl 2-pyrrolidone as eluent in polystyrene standard.

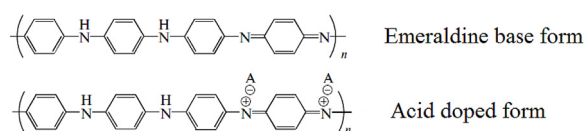
2.3. Electrochemical tests

The as-prepared mixture of C-S composite and activated carbon was mixed with polyaniline binder prepared as described above at the weight ratio of 50:1. The slurry was formed by grinding for 3 min, and uniformly cast onto carbon-coated aluminum foil. The weight ratio of the as-prepared mixture to binder was 5:1 when binders were polyvinylidene fluoride (PVDF, Solvay), polytetrafluoroethylene (PTFE, aladdin) or acrylonitrile copolymer (LA132, Chengdu Indigo Power Sources Co., Ltd.). The solvent for PVDF binder was *N*-methyl-2-pyrrolidone (NMP, Alfa Aesa), while DI water was used for the other two. All of the slurry cast onto aluminum foil prepared above was dried at 60 °C in vacuum for 24 h. The mass content of the electrode was 1.0–1.4 mg per cm^2 . The electrolyte was 1 M bis(trifluoromethane)sulfonylimide lithium (LiTFSI) in a mixed solvent of 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) (v/v = 1:1) with 0.2 M of LiNO_3 . The CR2016-type coin cells were assembled by sandwiching the polypropylene separator (Celgard 2500) between Li foil (Materials Technology Co., Ltd., China) and the as-prepared cathodes. All the assembling processes were carried out in high-purity Ar-filled glove box. The cells were electrochemically cycled between 1.65 and 2.85 V (vs. Li^+/Li) at various current density. The potential value of Li^+/Li reference electrode was -3.040 V vs. SHE.

3. Results and discussion

Polyaniline in emeraldine base form consists of phenylenediamine and quinondiimine structure, while its acid doped form consists of polar groups like amine salt, iminium and aromatic ring, or so-called positively charged conjugated backbone balanced by counter anion (Scheme 1).

The conducting polyaniline has Van der Waals and electrostatic interactions with sulfur and conductive particles leading to the integrated electrode, displaying unique adhesive behavior. Moreover, the positively charged conductive matrix and heteroatoms may help to electrostatically adsorb negatively charged polysulfides and lithium sulfides in the charging-discharging process. However, the brittle polyaniline chain is hardly adapt to the serious volume swelling of sulfur during discharge process once it covered on the whole surface of sulfur particles, resulting in large sulfur loss, moreover, the compact polyaniline layer would hinder ion transportation. An effective strategy is providing enough space for sulfur swelling and adequate channels for ion transportation. The extended conducting polyaniline chains with good electrical



Scheme 1. Molecular structures of polyaniline in emeraldine base and acid doped form [24].

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