



Gelatin-polyethylenimine composite as a functional binder for highly stable lithium-sulfur batteries

Naseem Akhtar^a, Hongyuan Shao^a, Fei Ai^a, Yuepeng Guan^a, Qifan Peng^a, Hao Zhang^b, Weikun Wang^b, Anbang Wang^b, Bingyin Jiang^{c, **}, Yaqin Huang^{a, *}

^a State Key Laboratory of Chemical Resource Engineering, Beijing Laboratory of Biomedical Materials, Beijing University of Chemical Technology, Beijing, 100029, China

^b Research Institute of Chemical Defense, Beijing, 100191, China

^c State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, 100190, Beijing, China



ARTICLE INFO

Article history:

Received 25 April 2018

Received in revised form

12 June 2018

Accepted 13 June 2018

Available online 15 June 2018

Keywords:

Binder

Gelatin-polyethylenimine composite

Sulfur cathode

Lithium-sulfur battery

Electrochemical performance

ABSTRACT

Lithium-sulfur (Li-S) batteries with high specific capacity are expected to be a new generation of energy storage devices. However, the shuttle effect of lithium polysulfide makes it difficult to commercialize stable Li-S batteries. In this work, we designed a gelatin-polyethylenimine composite (GPC) as functional binder for Li-S batteries to improve the stability of electrode during discharge-charge process. GPC binder combines the dispersion and adhesion ability of gelatin, which keeps cathode homogeneous and stable during electrochemical reaction, and adsorption capability of PEI for polysulfide, which suppresses the “shuttling effect”. The result shows that GPC used as a binder remarkably enhanced cyclic performance of Li-S battery with good capacity retention of about 100% at current density of 1C (sulfur loading 1.5 mg cm^{-2}) after 100 cycles. We believe that GPC would be a promising binder for highly stable Li-S batteries.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Lithium-sulfur (Li-S) batteries with high energy density (2567 Wh kg^{-1}) have received great attention of researchers to fulfill the complete requirements of energy storage devices [1–4]. However, several drawbacks hinder its commercial application such as: insulating nature of sulfur and sulfides, dissolution and shuttling of polysulfide, and volume fluctuations of sulfur [5–8]. Up to now, enormous efforts have been done to resolve the above complications through the construction of advanced composite electrode materials [9–13]. One of the most important factor in advanced electrodes is to increase the interaction of insulated sulfur with conductive agents, and many methods have been reported [14–16] to improve the conductivity of sulfur electrode. Generally, a binding agent is used to create a link between conductive materials and active materials for high conductivity. Sulfur cathode's inner-surfaces are enclosed with a binder and the

surface amendment of these binders has a large influence on sulfur cathodes. Thus, binder plays an important role to resolve these complexes in Li-S batteries. Polyvinylidene fluoride (PVDF) was used as a conventional binder to create a link between conductive materials and active materials in metallic batteries. However, commercial PVDF binder has some drawbacks such as serious volume expansion and less affinity with polysulfide. Moreover, presence of N-methyl-2-pyrrolidone (NMP) results in high toxicity on industrial scale and considered as a serious hazard for environmental protection [17–20].

Previous studies revealed that an advanced binder significantly affects the battery performance. An ideal binder for Li-S batteries should have the following properties: (i) good adhesion ability; (ii) suitable swelling capacity; (iii) high conductivity and (iv) effective adsorption of polysulfide [21–25]. Some improvements on binders have already been reported, for Li-S batteries. For instance, LA132 has been used to provide robust network structure for sulfur cathode [26]. Gelatin, which has good adhesion and dispersion abilities, can keep electrode stable during discharge-charge process [27]. And Polyethylenimine (PEI), which have hyper-branched network structures with abundant amine groups, can provides strong affinity to adsorb polysulfide (Li_2S_x) [28–31]. Therefore,

* Corresponding author.

** Corresponding author.

E-mail addresses: jiangby@iccas.ac.cn (B. Jiang), huangyq@mail.buct.edu.cn (Y. Huang).

binder is often considered as the dynamic constituent of the Li-S battery, and functional binders attract more and more attention of researchers.

In current work, we designed a gelatin-PEI composite (GPC) as a functional binder for Li-S batteries. Water soluble GPC binder contains ionizable groups, like COOH and NH₂ which shows hydrophilic properties and is substantially insoluble in commonly used organic electrolyte solvents, like carbonic acid, ester and ether, which keep electrode stable and environment friendly. Abundant amino groups and branched network structure of GPC, provides strong affinity to adsorb polysulfide intermediates during discharge-charge process through electrostatic interaction and thus lead to suppressed shuttle effect. As a consequence, when GPC was used as a binder in Li-S battery, it remarkably enhanced cyclic performance with 100% capacity retention after 100 cycles at 1C (sulfur loading 1.5 mg cm⁻²) which is 27%–35% higher than PEI and gelatin binder-based batteries. The GPC binder could be helpful to achieve the commercialization of stable Li-S batteries.

2. Experimental section

2.1. Synthesis of composite binder

GPC binder was synthesized by reaction of PEI (Branched, M.W 600,99%, Aladdin) with gelatin (160 bloom g, type B, derived from bovine bones) in the presence of solvent H₂O at 50 °C for 5 h with 1:2 ratio. A gel type material was obtained after evaporation of solvent which was further used for preparation of cathodes. Different cathodes were fabricated using three different slurries, all the slurries have 63 wt% of sulfur (99.5% analytically grade, Beijing Yili. Corp., China) as active material, 30 wt% of acetylene black (AB, Jinpu. Corp., China) as conductive material and 7 wt% of binder. Gelatin, PEI and GPC were used as binder in first, second and third slurry respectively. Homogeneous and well-defined slurries were prepared by using 4 h Ball-mill machine. The obtained slurries were thick and had a high resistance to flow. Doctor-blade with 250 μm thickness was used to paste these slurries on current collector aluminum foil and were put into vacuum oven for 15 h at 60 °C to dry and then cut into circular cathode shape. Coin type (CR2025) cells were assembled in an argon filled glovebox+x (ULTRA S1). The electrolyte consisted of 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and 0.4 M lithium nitrate (LiNO₃) as additive in solvent 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1 v/v ratio) (Beijing Chemical Reagent Research Institute).

2.2. Characterization

Fourier transform infrared spectroscopy (FT-IR, Nicolet 6700) spectrum was used to determine the bond formation and functional groups of GPC binder. The nuclear magnetic resonance (¹H NMR) spectra of GPC, gelatin and PEI were recorded by Bruker AV-600 for further support of FT-IR findings. Polysulfide absorption test was carried out using UV–vis spectroscopy (TU-1810). Scanning electron microscope (SEM, HITACHI S-4800) and energy dispersive spectroscopy (EDS, FEI Quanta 650) help us to analyze the surface morphologies of the cathodes. Solartron 1280Z was used to study the cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) with scanning rate of 0.1 mV s⁻¹ and open-circuit voltage (OCV) from 100 mHz to 10 kHz respectively.

3. Result and discussion

Polysulfide-trapping 3D mechanism of Li-S batteries with and without GPC binder and composite structure are shown in Fig. 1a.

FT-IR spectra explain the formation of GPC (Fig. 1b and c), gelatin spectrum shows amide stretching peak at 1632 cm⁻¹ but in composite two amide peaks appeared, one at 1635 cm⁻¹ and other at 1654 cm⁻¹ which confirmed the new type of amide linkage in composite. Furthermore, two clear N-H bending peaks were also observed at 1540 cm⁻¹ and 1557 cm⁻¹ in the composite spectrum but gelatin spectrum has only one peak at 1539 cm⁻¹. GPC has two different types of C-N stretching band at 1220 cm⁻¹ and 1340 cm⁻¹, but the only single peak was obtained at 1250 cm⁻¹ and 1305 cm⁻¹ in gelatin and PEI spectrum respectively. In 3300–3500 cm⁻¹ region, N-H and O-H combine broad peak appeared and slightly shifted towards low-frequency region due to the increment of amine group in GPC binder. For more detailed confirmation of GPC formation, ¹H NMR spectrum of gelatin, PEI and GPC binders are shown in Fig. S1 (Supporting Information). In the GPC ¹H NMR spectrum three types new signal appeared which confirm the formation of GPC. One signal appeared at 3.07 ppm which attribute to ethylene proton next to amide linkage. These ethylene protons of PEI portion in GPC shows chemical shift towards higher ppm values due to the presence of carbonyl group in amide linkage which deshielded the electron density on ethylene proton. PEI and gelatin spectrum have no proton signal in this area because PEI has no amide linkage and ethylene proton of gelatin portion has different environment than GPC. Other ethylene protons of GPC show collectively more intense peak (C-H at 2.5–2.8 ppm) due to presence of ethylene protons of PEI and gelatin in this region. 3rd type of proton signals in GPC spectrum appeared at 7.56 ppm and 7.59 ppm which confirmed the formation of GPC. These signals belong to newly created amide linkage protons. In this region gelatin have not amide protons. The presence of these stretching and bending signals in FT-IR spectrum and several kinds of proton signals in NMR spectrum confirmed the formation of GPC.

The predominant content of nitrogen functional groups in GPC binders with better affinity to interact polar lithium polysulfide species, can be very useful to promote chemisorption of polysulfide intermediates. To determine the effect of different binders on polysulfide absorption ability, gelatin, PEI, and GPC binders were dispersed in a 0.1 M Li₂S₆ solution (Tetrahydrofuran solvent) for 40 h and analyzed by UV–visible spectroscopy (Fig. 1e). The result demonstrate that all samples have UV absorption band at 400–450 cm⁻¹ region which is attributed to Li₂S₆ [32], while the absorption peak of sample GPC decrease sharply compared to gelatin and PEI samples. Because GPC have strong affinity to attract the polysulfide intermediates. The digital image (Fig. 1d) shows a visible discoloration of the Li₂S₆ solution, due to strong power of GPC binder to limit the dissolution of polysulfide. This discovery encouraged us to use GPC as a binder to improve the contact of N-containing species with sulfur-related substances, for highly stable Li-S batteries.

To examine the surface texture evaluation of gelatin, PEI and GPC binder-based cathodes were observed under SEM and EDS images before and after 5 cycles at a current rate of 0.5C (shown in Fig. 2). (Jeon et al. [33,34]) proposed that the rapid capacity fading causes by the non-homogeneous sulfur distribution in the cathode, which could degrade the distribution of sulfur along with cycles. High porosity and uniformly distribution of sulfur and carbon particles were clearly observed in GPC binder-based cathode before cycle are shown in Fig. 2 (c, f, i). After 5 cycles, the morphology of GPC binder still remained homogeneous and porous, no delamination was detected (Fig. 2j) due to the enhancement of adhesion and adsorption properties by copolymerization, which is a favorable feature to control the volume fluctuation of cathode during discharge-charge process because GPC binder covers the active materials which could significantly suppress the dissolution of lithium polysulfides in the organic electrolyte and restrain the

Download English Version:

<https://daneshyari.com/en/article/6602279>

Download Persian Version:

<https://daneshyari.com/article/6602279>

[Daneshyari.com](https://daneshyari.com)