



Polymeric binders for the sulfur electrode compatible with ionic liquid containing electrolytes

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ABSTRACT

A novel ionic liquid-containing electrolyte has been demonstrated to improve charging efficiency, lifetime and safety of Li/S cells. However, the high viscosity of the ionic liquid can reduce the kinetics of the electrochemical process and degrade the wettability of the S electrode by the electrolyte, which limits electrochemical utilization of the active S. To realize the advantages of the ionic liquid in the electrolyte, while maintaining good cell performances, we have investigated the critical properties of polymeric binders such as polyvinylidene fluoride (PVDF), styrene-butadiene rubber (SBR), carboxymethyl cellulose (CMC), polyacrylic acid (PAA) and lithium polyacrylate (LiPAA) for the S electrode operated in ionic liquid-containing electrolytes. The PAA binder electrode showed the most promising cell performance which is attributed to its good physical stability and wettability. Moreover, the cell performance of the PAA binder electrode was further improved by combining the PAA binder with the PVDF binder, which enhances the specific capacity up to 1.3 times higher than that of the PAA binder electrode.

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1. Introduction

Since the lithium/sulfur (Li/S) cell has been brought into the spotlight with its high theoretical specific energy of 2600 Wh/kg (vs. ~ 600 Wh/kg for conventional Li-ion cells) and the low cost of S (<\$200/ton), a lot of researchers have dedicated their efforts to realize practical Li/S cells for high specific energy (Wh/kg) applications such as electrical vehicles, electrical aircraft and drones. Great progress has been made in advancing the design of S active materials by addressing three main issues of S electrodes: poor electrical conductivity of S and Li₂S; polysulfide dissolution into liquid organic electrolyte and its shuttle; the volume change of S particles during cycling, which demonstrated promising cell performances with the long cyclability and excellent rate performance [1–8]. However, the low level of S mass loading (generally ~ 1.0 mgS/cm²) on the S electrode and the high percentage of “dead weight” of the cell components that do not contribute to capacity such as carbon additives, binder and especially electrolyte have been raised as important issues for development of high specific

energy Li/S cells.

More recently, significant attempts to address the practical issues of Li/S cells have been made, where the high S areal mass loading (<6 mgS/cm²) and the low electrolyte to S weight ratio (E/S ratio) (>5) have been reported, while maintaining good cell performance [9–17]. Those results were achieved by optimizing the S electrode configurations that provide active S with tailored electrochemical environments such as electronic conduction pathways, Li ion accessibility from the bulk electrolyte, physical/chemical stability so that good electrochemical performance can be maintained, while increasing the S mass loading and decreasing the dead weight of the cells.

Previously, we demonstrated that the effect of the ionic liquid is to improve the cyclability and the charge efficiency as well as the morphological stability of the Li metal electrode of Li/S-GO cells [5,9]. It has been demonstrated that ionic liquid can restrain the polysulfide dissolution from the S electrode by limiting the solubility of polysulfides and reducing the polysulfide shuttle effect due to its high viscosity [8,18,19]. In addition, ionic liquid forms a protective solid electrolyte interphase on the Li metal electrode, so that the morphology of the Li metal is stabilized during cycling [9,20]. One issue relating to employing ionic liquid in the electrolyte that needs to be addressed is its high viscosity along with poor wetting of the S electrode, which can interfere with the electrochemical

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reaction of the Li/S cell by increasing the Li ion mass transport resistance of the electrolyte. For this reason, relatively larger discharge and charge overpotentials along with lower S utilization can be caused by the presence of ionic liquid in the electrolyte compared to the conventional electrolyte [9].

To secure the benefit of the ionic liquid-containing electrolyte for Li/S cells, we have investigated the properties of the S electrode prepared using several polymeric binders and their influence in the cell performance with the ionic liquid-containing electrolyte. Among the S electrode components, the polymeric binder plays a very important role, where it physically holds a mixture of active S particles and conductive carbon particles onto the current collector to maintain the electronic conduction pathway between active S particles and current collector. Architectures and physical/chemical properties of S electrodes along with their electrochemical cell performance are strongly influenced by the distribution and structure of the binder network as well as binders' own properties [21–28]. In this work, the physical/chemical properties of the conventional polymeric binders for the S electrodes such as polyvinylidene fluoride (PVDF), styrene-butadiene rubber (SBR), carboxymethyl cellulose (CMC), polyacrylic acid (PAA) and lithiated PAA (LiPAA) are demonstrated and the compatibility of the S electrodes prepared with those binders with the ionic liquid-containing electrolyte are investigated.

2. Experimental section

2.1. Synthesis of cetyltrimethyl ammonium bromide modified sulfur-graphene oxide (S-GO-CTA) nano-composite

The S-GO-CTA nano-composite was prepared *via* a published method [5]. Briefly, 0.58 g of sodium sulfide powder (Alfa Aesar, Na₂S, anhydrous) was dissolved in 25 mL of ultrapure water to form a Na₂S solution. A sample of 0.72 g of elemental sulfur powder (Alfa Aesar, S, ~325 mesh, 99.5%) was added to the Na₂S solution and stirred with a magnetic stirrer at 60 °C until the solution became a transparent orange color (a sodium polysulfide (Na₂S_x) solution). 18 mL of single layer graphene oxide dispersion (GO, ACS materials, 10 mg/mL) in water was diluted to form a GO suspension (180 mg of GO in 180 mL of ultrapure water). 2.5 mM of cetyltrimethyl ammonium bromide (Sigma Aldrich, CTAB) was added to the GO suspension and stirred for 2 h with a magnetic stirrer. Then the prepared Na₂S_x solution was added to the GO-CTAB composite solution and stirred overnight. The as-prepared Na₂S_x-GO-CTAB composite solution was slowly added to 100 mL of 2.0 M formic acid (Aqua Solutions) and stirred for 2 h to precipitate elemental S onto the GO. Finally, the S-GO-CTA nano-composite was filtered and washed with acetone and ultrapure water several times to remove salts and impurities. The obtained powder sample was dried at 50 °C in a vacuum oven overnight. The dried powder sample was ground using mortar and pestle and heat-treated in a tube furnace at 155 °C for 18 h under an Ar atmosphere.

2.2. Material characterization

The morphology of the powdered samples was observed using a scanning electron microscope (SEM, ZEISS Gemini Ultra 55) at an accelerating voltage of 5 kV. Thermogravimetric analysis (TGA, TA Instruments Q5000) was used to determine the content of S in the S-GO-CTA nano-composite up to 600 °C under nitrogen atmosphere. Contact angle measurements were performed using a Kruss EasyDrop. The PVDF, SBR, CMC, PAA and LiPAA films were casted onto the silicon wafer. 2 μL of N-methyl-N-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR₁₄TFSI), mixture of dioxolane (DOL)/dimethoxyethane (DME) (1:1, v/v) or the electrolyte

composed of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 1.0 M) and lithium nitrate (LiNO₃, 0.50 M) in PYR₁₄TFSI/DOL/DME (1:1:1, v/v/v) was dropped onto the binder films. For peel force measurement, composite S electrodes identical to those tested in coin cells were prepared with PVDF, SBR, CMC, PAA and LiPAA binders. The prepared samples were cut into strips 10-mm-wide and 40-mm-long and attached to 3 M adhesive tape. The peel force measurement was conducted with a TCD225 digital force tester (Ametek). The applied load was measured, while the 3 M adhesive tape was removed by peeling at an angle of 180° at a constant displacement rate of 100 μm/s. Photographs of the samples were taken after the experiments.

2.3. Electrochemical tests

The S electrode was prepared by mixing the S-GO-CTA nano-composite, carbon black (Timcal, Super P) and a binder at a weight ratio of 70:20:10. Water was used for PAA, LiPAA and CMC binders and N-methyl-2-pyrrolidone (NMP) was used for PVDF, SBR and PAA-PVDF composite binders. In order to prepare the LiPAA binder, a stoichiometric amount of LiOH was first dissolved in water and the binder was added into the LiOH solution [29]. The PAA-PVDF composite binder was prepared with the weight ratio of 8:2 between the PAA and the PVDF binders. The slurries were stirred using a magnetic stirrer overnight and casted onto aluminum (Al) foil, then pre-dried at room temperature followed by vacuum drying in an oven at 50 °C overnight. The average S mass loading of the electrodes was 2.7 mg/cm². The conventional electrolyte was composed of 1.0 M LiTFSI and 0.50 M LiNO₃ in DOL:DME (1:1, v/v) and the ionic liquid-containing electrolyte was composed of 1.0 M LiTFSI and 0.50 M LiNO₃ in PYR₁₄TFSI:DOL:DME (1:1:1, v/v/v). Type CR2032 coin cells were prepared with a lithium foil as counter/reference electrode, a polypropylene separator (2400, Celgard), and 35 μL of electrolyte in a glove box filled with argon (Ar) gas. A galvanostatic cycling test was conducted using a battery cycler (Maccor) between 1.70 and 2.70 V at 0.3 mA/cm². The open circuit voltage (OCV) of the cells was measured immediately after the cells were assembled. Every 15 h during the OCV measurement, the electrochemical impedance was measured from 10 mHz to 1 MHz using a potentiostat. Rate capability tests were also performed at various discharge current densities from 0.2 mA/cm² to 0.8 mA/cm² and then back to 0.1 mA/cm².

3. Results and discussion

In order to demonstrate the influence of the polymeric binder properties on the electrochemical behavior of the S electrodes, the S-GO-CTA nano-composite was prepared (SEM image, Fig. S1) as the active material. The S content of 80% in the S-GO-CTA nano-composite was confirmed by TGA (Fig. S2). Electrodes were fabricated using the five representative polymeric binders (PVDF, SBR, CMC, PAA and LiPAA) with an Al foil current collector (Average S mass loading: 2.7 mgS/cm²). The morphology of the prepared electrodes was observed under the SEM and the results are shown in Fig. 1 (top view and cross-section view). There is no significant difference between the morphologies of the S-GO-CTA electrodes in the top-view SEM images, however, significant cracks and aggregations were observed in the cross-section view of the CMC binder electrode, whereas the electrode materials of the other electrodes were more homogeneously distributed throughout the electrodes.

Since the physical stability of the S electrode is very important in tolerating the volume change of the S particles during the discharge/charge process, the binders should provide good mechanical stability so that electronic disconnection between active S

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