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Harvesting polysulfides by sealing the sulfur electrode in a composite ion-selective net

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HIGHLIGHTS

- Electrostatic repulsion together with an overall sealed electrode configuration.
- Ionic conductivity of the single ion polymer electrolyte is 0.57 mS cm^{-1}.
- The polyether backbone is more compatible with ether based electrolyte.
- Capacity retention of 800 mAh g^{-1} at 2 C after 500 cycles.

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ABSTRACT

A cathode was prepared by sealing a carbon supported sulfur electrode inside a composite ion-selective net made of carbon, binder and lithiated ionomer to restrict shuttling of polysulfide anionic species. As a result, the soluble polysulfide anions become unable to escape from the composite ion-selective films due to the electrostatic repulsion between the immobilized single ion conducting ionomers and the polysulfides with no dead angles. Experimentally, lithiated 4,4′-difluoro bis(benzene sulfonyl)imide and PEG200 were copolymerized to form a polyether based single ion conducting polymer. The ionic conductivity of the blend film made of ionomer and poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP) at a mass ratio of 1:1 is 0.57 mS cm^{-1} at room temperature. The battery capacity with the sealed sulfur electrode is 1412 mAh g^{-1} at 0.5 C, 1041 mAh g^{-1} at 1.0 C, 873 mAh g^{-1} at 2.0 C and 614 mAh g^{-1} at 5.0 C, significantly better than the results with lithiated Nafion especially at high C rates. In addition, a long cycling test at 2 C for 500 cycles gives rise to a stable capacity of 800 mAh g^{-1}. The intrinsic electrostatic repulsion between polysulfide anions and the negatively charged electrolyte film, together with the overall sealed electrode configuration, is responsible for blocking the shuttling of polysulfides effectively.

1. Introduction

Lithium-sulfur batteries have attracted a great attention in recent years because of the high specific capacity (1675 mAh g^{-1}) of sulfur and the large theoretical energy density (2600 Wh kg^{-1}) of the cell. Therefore, they are promising for powering mobile electric devices such as electric vehicles and portable electric devices and for utilization in stationary energy storage [1,2]. However, sulfur has an intrinsically low electric conductivity of 5.0×10^{-30} S m^{-1}, which makes the electrochemical processes difficult to proceed [3,4]. Furthermore, polysulfides generated from step-wise electrochemical reactions are soluble in the liquid electrolyte in the battery cells. The soluble polysulfides are able to diffuse to the anode and subsequently reduced by lithium metal chemically, leading to reduction of electrochemical energy output and coulombic efficiency [5–8].

To date, great efforts have been devoted to embedding sulfur in carefully selected conductive matrices [9–23]. The abundant porous structure may prevent polysulfides from diffusion to a

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certain extent and a large surface area may facilitate adsorption of polysulfides. Both effects help extend the cycle life. Nevertheless, shuttling of polysulfides continues taking place once exceeding the intake capability of the matrix. It is worth noting that the metastable sulfur, $S_{2\text{-}4}$, confined in conductive microporous carbon may successfully avoid the generation of soluble polysulfides because the pore size is too small to allow entrance of carbonate molecules [24–27]. The effort to chemically embedding sulfur in a carbon matrix has also achieved notable progress. A typical example is that calcination of a mixture of polyacrylonitrile (PAN) and sulfur powder to prepare the sulfur cathode (PAN/S for short) resulting with improved electronic conduction and cycling stability [19,28–34]. Aside from the innovation on conductive matrices, adding polysulfides or lithium salt into an electrolyte may effectively prevent dissolution of polysulfides from a sulfur electrode based on the Le Chatelier's principle [35,36]. Hassoun et al. successfully demonstrated the effect with an advanced tin-sulfur lithium ion battery with a Sn/C composite anode, Li_2S/C cathode and PEO based gel polymer electrolyte. The composite polymer electrolyte is supplemented with lithium sulfides up to saturation, which takes effect of a combined physical and chemical barrier to prevent dissolution of polysulfides [37–39]. A subsequent study demonstrated that an addition of excessive lithium salt in an ether based electrolyte may result in the same effect since the solvated lithium ions from LiTFSI are able to retard further dissolution of polysulfides [5].

The ether based liquid electrolyte, i.e., LiTFSI dissolved in DOL and DME with $LiNO_3$ as an additive, has been extensively used in lithium sulfur batteries. In comparison to the traditional carbonate based electrolyte, the ether solvent has higher polysulfides solubility and chemical stability, which could provide fast charge transfer kinetics but, unfortunately, accompany with a serious loss of active materials in the form of polysulfide anions [36,40]. In principle, the undesirable transport of polysulfide anions can be prohibited physically. Zhou et al. demonstrated a MOF-based separator which selectively prevents penetration of large sized polysulfides [41]. But the small-sized channels limit the ion transport, resulting in a low rate ability. In addition, physically prohibition of polysulfide anions via electrostatic repulsion by the ion-selective polymer electrolyte [42,43], a kind of cation exchange membrane ($t_+ \approx 1$), has also been studied. Cao et al. demonstrated that a lithiated Nafion film as a barrier is capable of blocking polysulfide anions in a lithium sulfur battery for the first time [44]. Subsequently, lithiated Nafion as a shield against polysulfide anions has been used for lithium sulfur batteries in a variety of methods, such as casting a Nafion ionomer solution or Nafion/γ-Al_2O_3 solution on a sulfur cathode to form a barrier layer in-situ [45], filling the pores of the Celgard PP separator with Nafion ionomers [46], combining lithiated Nafion with a carbon film as the separator between lithium metal and a sulfur electrode [47], stacking a Nafion film, graphene oxide and a PP film to form a ternary PP/GO/Nafion separator [48]. Unlike the case in fuel cells in which a cathode and an anode are separated by a dense Nafion film, the cathode, separator and anode are immersed in a commercial liquid electrolyte in lithium ion batteries. Polysulfides are able to diffuse through the periphery or other gaps to the anode even if the sulfur electrode was “enveloped” [49] or “coated” [50] by the lithiated Nafion. Moreover, considering that the ionic conductivity of the lithiated Nafion is as low as ~10^{-5} S cm^{-1} in non-aqueous solvents [51], the conduction of lithium ion becomes inevitably the rate determine step once the sulfur and lithium are separated/sealed by the lithiated Nafion, which results in a large ohm polarization [52]. Therefore, single ion conductors that conduct lithium ion only ($t_+ \approx 1$) with high ionic conductivity are preferred.

Recently, Manthiram et al. reported a core-shell configuration in which the polysulfides are physically sealed inside the shell made of carbon and with an additional trapper laminated on the separator opposite to the sulfur electrode [53]. We studied the effect of surface coverage percentage of the sulfur electrode on battery performance by sealing S/C in between two pieces of films made of nano Al_2O_3, carbon (BP2000) and PTFE, in which Al_2O_3 serves as a filler to form narrow interstitials to suppress mobility of polysulfides physically [54]. In this paper, we propose to replace the non-conductive Al_2O_3 nanoparticles with single ion conducting ionomers to form a composite ion-selective net to host polysulfides via an electrostatic repulsive force, as schematically illustrated in Fig. 1. The composite ion-selective net is composed of carbon black (BP2000), a polyether based single ion conducting polymer electrolyte ($t_+ \approx 1$) and polytetrafluoroethylene (PTFE) with the mass ratio of 3:4:3. In comparison to the lithiated Nafion, the as-synthesized single ion conducting ionomers could provide faster ion conduction and better compatibility with the commercial electrolyte, resulting with long-term stability at high C rates.

2. Experimental

2.1. Chemicals

4-fluorobenzene sulfonyl chloride (97%) and 4-fluorobenzene sulfonamide (97%) were purchased from Chem Greatwall Co. Ltd. Lithium hydride (LiH, AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. and washed with petroleum ether three times before use. Poly(ethylene glycol) (PEG200) and poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP) were purchased from Aldrich. N,N′-Dimethylacetamide (DMAC) was purchased from Sinopharm Chemical Reagent Co. Ltd. and predried with phosphorous pentoxide (P_2O_5) for 24 h followed by distillation under reduced pressure protected by argon atmosphere. Acetylene black and BP2000 were bought from Shenzhen Kejingstar Technology Co. Ltd. Carbon disulfide (CS_2), sublimed sulfur, 1-methyl-2-pyrrolidinone (NMP) and 60 wt% polytetrafluoroethylene (PTFE) emulsion were bought from Sino Pharm Co. Ltd. A Nafion solution (5 wt%) was purchased from Dupont Company. A commercial electrolyte made of 1.0 M LiTFSI dissolved in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) at a volume ratio of 1:1 with 1 wt% $LiNO_3$ was used as an additive.

2.2. Polymer synthesis and characterization

2.2.1. Synthesis of lithiated poly(4,4′-difluoro bis(benzene sulfonyl) imide-alt-poly(ethylene glycol) 200)

The schematic of the polymer synthesis is given in Fig. 2a. The building block, lithiated 4,4′-difluoro bis(benzene sulfonyl) imide (LiFBSI), was synthesized following the procedures as reported [55]. To synthesize the block copolymer, 12 mmol of LiH and 5 mL of

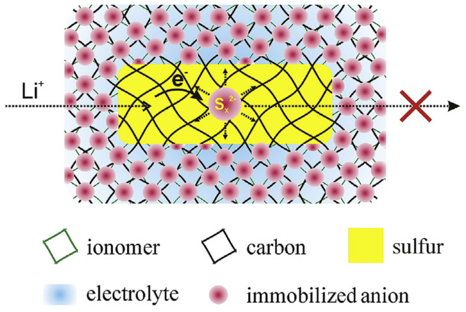

Fig. 1. Scheme of harvesting polysulfide species by restricting cathodic materials inside a composite ion-selective net via electrostatic repulsion.