Glass fiber separator coated by porous carbon nanofiber derived from immiscible PAN/PMMA for high-performance lithium-sulfur batteries

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ABSTRACT

Lithium-sulfur (Li-S) batteries with high energy density are promising candidates for next-generation rechargeable energy storage. However, the shuttle effect of intermediate polysulfides hinders the practical application of today's Li-S batteries. Here, immiscible polyacrylonitrile (PAN)/poly(methyl methacrylate) (PMMA) blends were used to prepare porous carbon nanofibers (PCNFs) as coating layers on a glass fiber (GF) separator to block polysulfide diffusion in Li-S batteries. The resultant PCNF coated GF (PCNF@GF) separators exhibited multifunctional advantages: (1) thermally stable GF separator as the substrate helped avoid destructive effects of Li dendrites grown from the lithium anode; (2) the porous conductive PCNF coating functioned as an upper current collector to increase the electrical conductivity and provided an efficient reservoir for absorbing the migrating polysulfides; and (3) the rough GF surface improved the adhesion of additives on the separator and formed efficient electronic contact with S. An enhanced Li-S battery with PCNF@GF-7:3 separator delivered an initial capacity of $1499\,\mathrm{mA\,h\,g^{-1}}$ and a high reversible capacity of $808\,\mathrm{mA\,h\,g^{-1}}$ after 200 cycles at 0.2 C. Additionally, the Li-S cell with PCNF@GF separator also presented outstanding anti-self-discharge capacity even after 24 h resting. Therefore, this study demonstrates that PCNF@GF is an excellent separator candidate for the construction of dynamically and statically stable high-performance Li-S batteries.

1. Introduction

To meet ever-growing requirements of large-scale energy storage and electric vehicles, the development of high-energy-density battery systems is highly attractive. A considerable number of efforts have been focused on lithium-sulfur (Li-S) batteries due to their extremely high theoretical specific capacity and energy density of $1675\,\mathrm{mA\,h\,g^{-1}}$ and $2600\,\mathrm{W\,h\,kg^{-1}}$, respectively [1]. As an appealing cathode active material, S also has indisputable convenience, such as low cost, environmental benignity, and earth abundance [2]. However, the obstacles to realize the commercialization of Li-S batteries include low electrochemical utilization, high internal resistance, rapid capacity fading on cycling, and severe self-discharge [3]. Indeed, it is difficult to achieve high utilization of active materials in Li-S batteries because of the insulating nature of S and the limited charge transfer caused by discharge end products (Li_2S_2/Li_2S) during a battery operation. Besides, in a typical charging and discharging process, S is converted to highly soluble

polysulfides (Li_2S_x, $4 \leq x \leq 8$), which diffuse through the separator and shuttle between the anode and cathode repeatedly, resulting in losing active materials. Meanwhile, the shuttle phenomenon of polysulfides leads to "dynamic" capacity fading and low Coulombic efficiency, causing corrosion of the Li anode and increased internal cell resistance [1,4–6]. Even when the Li-S cell is resting, S gradually reacts with the Li ions in the electrolyte and transforms to polysulfides, which is recognized as a "static" decrease in the cell capacity called self-discharge. Rapid diffusion of polysulfides or dissolved S species through the separator would cause a prompt redox shuttle process and fast self-discharge rate [5–8]. Besides, A large volume change (80%) of S and Li_2S during cycling brings about the structural collapse of the cathode and fast capacity decay, e.g., the metallic Li anode forms mossy metal deposits and dendrites, resulting in poor cycling life and serious safety concerns [4].

Various attempts have been carried out by researchers to address these challenging issues in Li-S batteries. For example, extensive

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approaches have been devoted on the design of cathode materials, which either improve the electrical conductivity of the composite S cathodes and/or localize the active materials within the cathode regions [9–11]. For example, S-porous carbon composites [12], S-metal oxide/chalcogenide composites [13], S-graphene composites [14], S-conductive polymer composites [15], binder additives [16], and biomimetic architectures [17] have been extensively studied in Li-S batteries, which not only enhance the conductivity of the cathodes but also accommodate the electrode volume expansion of active materials during the cell operation to suppress polysulfide dissolution. Unfortunately, these frequently used approaches often result in side effects. For instance, the introduction of nanocomposite cathodes or polymer additives involves laborious multistep synthetic processes and reduces the S content complicating the practicality of Li-S battery production as well.

Separator, a basic and key component of the Li-S battery, is a porous membrane that plays a critical role of providing transport channels for Li^+ while serving as an electronic insulator [18]. Microporous polyolefin membranes made of polyethylene (PE) and/or polypropylene (PP), such as Celgard 2730 (PE, with 43% porosity), Celgard 2400 (PP, with 40% porosity), Celgard 2320 (PP/PE/PP, with 42% porosity), etc., are the most widely used Li-S battery separators because of their excellent chemical stability and mechanical strength [19]. However, they have critical drawbacks such as weak thermal stability, low porosity and extremely poor wettability, which lead to large thermal shrinkage at high temperatures, increased internal resistance, reduced electrochemical kinetics and low rate capability of the batteries. On the other hand, glass fiber (GF) separators with excellent thermal stability create a network with holes in the macro scale range by randomly arranged fibers, and this unique highly porous structure (e.g. Whatman GF, GF/A) leads to high electrolyte intake, consequently facilitating rapid ionic transportation [20,21]. GF separators also act as decent reservoir for liquid polysulfides to slow down their diffusion, providing Li-S cells with more stable capacity retention and better rate capability as compared to the cells with PP/PE separators, which is demonstrated as a new route to further enhance the practical application of Li-S batteries [22].

Recently, modifications of the separators have been reported for Li-S batteries to enhance their electrochemical performance. Those modified separators are typically prepared by coating Al_2O_3 [23], Nafion [24], Super P [7,25], multiwall carbon nanotubes [26] and graphene [27] on the surface of commercial polyolefin separators to act as the physical obstacle to retard polysulfide migrations. But this separator design often results in a long diffusion distance and a high ion-transport resistance leading to a severe electrode potential drop and a small accessible surface area [20,28]. Even though the cycling stability of the batteries can be improved, those systems still cannot simultaneously satisfy safety, low cost and high rate performance for large-scale energy storage applications. Recently, significant improvements in the capacity and cyclability have been achieved by using various 1-dimensional carbon nanofibers (CNFs) as separator coating materials in Li-S batteries. CNFs not only have small diameter, excellent conductivity, and good thermal dimensional stability, but also can shorten pathways for electron transportation, provide high ion-accessible surface sites, and facilitate the electrolyte penetration [29,30]. The benefits that CNF-coated separators could be significantly enhanced by introducing mesopores to the fibrous structure since they can physically trap Li polysulfides, accommodate the large volume change of S during lithiation, and promote the electrolyte penetration to guarantee fast transport of Li ions during discharge/charge process [31–33]. However, to date, the Li-S cell configuration with GF separator coated with porous and fibrous carbon materials in order to have the structure features of high porosity and good electrolyte wettability has not been reported.

Based on the above mentioned considerations, here, we prepared and evaluated porous carbon nanofibers (PCNFs) as coating layers on a glass fiber (GF) separator for blocking polysulfide diffusion in Li-S batteries. This unique separator design not only avoided the side effects on the electrochemical performance but also accommodated a large amount of polysulfides by their porous structure during cell operation. PCNFs were fabricated from immiscible polyacrylonitrile (PAN)/polymethyl methacrylate (PMMA) blends with different weight ratios by electrospinning and followed by thermal treatment, during which PAN was converted to carbon while PMMA was decomposed to generate small open pores in the carbon nanofiber matrix [34]. By adjusting the relative content of PMMA, i.e., the pore generator, the influence of PCNF@GF on the performance of the resultant Li-S battery was investigated. Results showed that this simple approach provided multiple potential functions in the Li-S battery. Firstly, while ensuring the primary function of a separator for preventing electrical shorts and allowing ionic transport between the electrodes, incorporation of thermally stable GF separator helped avoid destructive effects by Li dendrites formed on the lithium anode. Secondly, the porous conductive PCNF coating not only functioned as an upper current collector to provide more active sites for transferring electrons and ions, but also served as an efficient reservoir for absorbing the migrating polysulfides, which further enhanced active materials utilization, thereby lowering the impedance and polarization of the Li-S battery. Thirdly, the surface roughness of the GF substrate improved the adhesion of additives on the separator and enhanced electronic contacts with the S. In consequence, enhanced cyclability of Li-S batteries with PCNF@GF coated separators can be achieved, with an initial capacity of 1499 mA h g^{-1} and a high reversible capacity of 808 mA h g^{-1} after 200 cycles at 0.2 C. This study implies that introduced separator design is feasible to develop a cost-effective and straightforward strategy that can not only improve the cyclic performance of Li-S batteries but also result in stable rate performance and eventually enhances anti-self-discharge capability.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN, Sigma-Aldrich, 150,000 g mol^{-1}), polymethyl methacrylate (PMMA, Sigma-Aldrich, 120,000 g mol^{-1}), N,N-dimethylformamide (DMF, 99.8%, Sigma-Aldrich), Sulfur (S, 99.5–100.5%, Sigma-Aldrich), bis(trifluoromethane) sulfonamide lithium (LiTFSI, 99.95% trace metals basis, Sigma-Aldrich), lithium nitrite (99.99% trace metals basis, Sigma-Aldrich), n-butyl alcohol (99%, Sigma-Aldrich), N-methyl-2-pyrrolidone (NMP, 99%, Sigma-Aldrich), 1,3-dioxolane (DOL, 99%, Sigma-Aldrich), 1,2-dimethoxyethane (DME, 99.5%, Sigma-Aldrich), super P carbon black (C-65, TIMCAL Graphite & Carbon Ltd.) and polyvinylidene fluoride (PVDF- 5130, Solvay) were used as received. GF membrane (Whatman, 260 μm thickness, 53 g m^{-2} areal density) made from borosilicate microfibers was used as the separator in this study.

2.2. Coating layer fabrication

Schematic illustration of the fabrication process of PCNFs is shown in Fig. 1. To fabricate PCNFs, three precursor solutions were prepared by blending PAN with PMMA at different weight ratios of 9/1, 7/3 and 5/5 into DMF while the total polymer concentration was fixed at 8 wt%. The blend solutions were mechanically stirred for 12 h. The precursor solutions were set on an electrospinning setup (New Era Pump Systems, Inc. USA) and a voltage of 16 kV was applied by using a high voltage power supply (Gamma ES50P-20W/DAM) for nanofiber formation. The nanofibers were collected on an aluminum plate with a flow rate of 0.75 mL h^{-1} and a tip-to-collector distance of 15 cm. The as-prepared nanofiber mats were stabilized in air at 250 °C for 2.5 h with a heating rate of 5 °C min^{-1}, and then treated in nitrogen at 800 °C for 2 h with a heating rate of 2 °C min^{-1} to obtain three different PCNFs, which were denoted as PCNFs-9:1, 7:3, and 5:5, respectively, based on the PAN/PMMA ratios used in the precursor solutions.