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Functionalized polyimide separators enable high performance lithium sulfur batteries at elevated temperature

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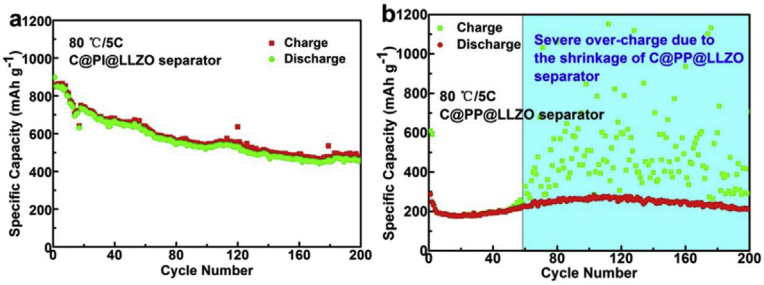
HIGHLIGHTS

- Sandwich-type polyimide separator was prepared by facile slurry-coating methods.
- Sandwich-type polyimide separator can suppress polysulfide shuttle.
- Sandwich-type polyimide separator can prevent lithium-metal dendrite growth.
- Li-S cells with as-prepared separator can operate well at 80 °C and even 100 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

High temperature lithium-sulfur batteries are seldom investigated due in part to the lack of mechanical robust separators and the more serious parasitic polysulfide shuttle effects at elevated temperature. Here, we for the first time present high performance lithium-sulfur cells that can be cycled at elevated temperature of 100 °C via designing asymmetric functionalized polyimide-based separators using a facile and scalable blade-casting method. In this sandwich configuration, polyimide nonwovens act as electrochemically and mechanically robust skeleton while Super-P nanoparticles coating and poly (ethylene oxide)-integrated-lithium lanthanum zirconium oxide coating render additional functions of immobilizing polysulfides and inhibiting lithium dendrite growth, respectively. By virtue of the multifarious functions of the modified polyimide-based separator, a high specific capacity of 1474.3 mAh g^{-1} without severe over-charge behavior is also firstly demonstrated at a higher temperature of 100 °C. Additionally, Li-S cells using the modified polyimide -based separator deliver excellent cycling stability (only 0.2% capacity decay $cycle^{-1}$ on average exceeding 200 cycles at 80 °C) at a relatively high rate of 5C. The experimental results validate the pivotal role of newly designed separators for high performance lithium-sulfur chemistry especially at elevated temperature.

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1. Introduction

Developing high energy density electrode materials is of primary importance for the future secondary battery technology [1,2]. Sulfur, characterized by low cost and environmental benignity, is believed to be such a promising material which theoretically delivers a high specific capacity of 1675 mAh g^{-1} at ~2.0 V, yielding 10-folds higher energy density than that of classical Li insertion/desertion compounds [2–4]. In the past decades, explosive growth in the development of sulfur-containing cathodes [5,6], functional interlayers and/or separators [7], and lithium anode protection techniques [8,9] has been developed towards alleviating the insulating issues of sulfur and its discharged counterparts of Li_2S, the so-called "polysulfides' shuttling effects", and the lithium dendrites-derived safety problems respectively. Despite these great progresses, lithium-sulfur (Li-S) batteries still suffer from severe capacity fades and low Couloumbic efficiency, especially at higher operating temperature [10].

Rational design of cathode structures, including various unique sulfur-inorganic [11], sulfur-carbon [12] and sulfur-polymer structures [13], free-standing sulfur-composite electrodes [14,15], liquid-phase cathode [10] and so on, have been demonstrated to effectively improve the cycle life of Li-S batteries by the inhibition of polysulfide shuttle processes and/or the increasing the electronic conductivity of cathodes.

Modifying Li-S battery configuration using novel multi-functional separators/interlayers is a very useful strategy for improving their sulfur utilization and capacity retention. The introduction of functional interlayers between cathode and separator can not only effectively trap polysulfides without freely-diffusing out from the cathode, but also react with the entrapped sulfur for further improvement of the cyclic stability of Li-S cells [16–18]. Functional interlayer systems, although beneficial for the performance improvement, are electrochemically-inert components, which inevitably compromise the overall energy density of Li-S batteries [7,18]. Meanwhile, the fabrication of the functional interlayers needs extra material manipulating processes. In contrast, modifying separators via facile slurry-coating process is more cost-effective and adaptable for scaling up than prepared segregated interlayers. Especially, Manthiram and co-workers proposed that employing light-weight Super-P-coated commercial PP separator could accomplish both dynamic and static cycle stability of Li-S cells, resulting in a relatively low cycling decay rate of 0.20% per cycle at 2.0 C[19]. Janus separator comprising of mesoporous cellular graphene and PP separator was presented by Zhang's group, which further reduced the cycle degradation rate to 0.081% per cycle even at relatively low current density of 0.5 C[20]. Moreover, graphene oxide (GO)-coated PP separators [17], multi-walled CNT (MWCNT)-modified PP separators [21] and various oxide (such as Al_2O_3, V_2O_5 and so on)-modified PP and/or PE separators were demonstrated to be effective in improving Li-ion storage properties of Li-S batteries. Nevertheless, modified separators generally hinder the transfer of solvated Li-ions and consume extra amount of electrolyte. In addition, the degradation of lithium metal anode cannot be resolved by merely modifying single face of the separator. Stiff metal oxide coated onto separators of the anode side may effectively prevent the dendrite growth [9,22]. In this regard, dual faces-modified separator via simple slurry-coating processes may be promising routes towards trapping polysulfides and simultaneously suppressing lithium dendrite penetration, which is seldom concerned in previous reports.

Choosing mechanically-robust, cost-effective and thermal stable polymer membranes as separators is also highly required for the development of high performance Li-S batteries. PP-based separator is widely used in Li-ion and Li-S batteries. However, its poor thermal stability retards its utilization at elevated temperatures [23–25]. Furthermore, its low permeability and wettability towards the liquid electrolyte is unsuitable for efficient ion transport. Polyimides (PIs), intrinsically-featured by high thermal stability, high mechanical strength, and good electrochemical stability, were used as high performance separators for Li-ion batteries [24–28]. Electro-spun PI nonwovens exhibit a high affinity toward the non-aqueous electrolyte and show no visible shrinkage and deformation when heated to 150 °C [23, 29, 30]. It was demonstrated that Li-ion batteries using PI nonwovens deliver higher specific capacity and better rate capability compared to batteries with polyolefin separators [24,26]. So far, there are fewer reports relating to electro-spun PI nonwovens applied in Li-S batteries, which is probably due to its large pore size (typically > 1 μm) increasing the risk of electrolyte leakage and batteries' overcharge behaviors.

Herein, an asymmetric PI-based nonwoven separator is devised via facile slurry-coating, which composes of super-P nanoparticles coating towards sulfur-composite cathode and poly (ethylene oxide)-integrated-lithium lanthanum zirconium oxide (PEO-integrated-LLZO) coating towards the Li metal anode, respectively. In this configuration, PI nonwovens act as an electrochemically and mechanically robust skeleton, while super-P nanoparticles coating and PEO-integrated-LLZO coating renders additional functions of immobilizing polysulfides and inhibiting lithium dendrite growth, respectively. These two coatings are beneficial for achieving high Coulombic efficiency and capacity retention. By virtue of the high thermal stability of PI separator, high capacity Li-S batteries operating at elevated temperature of 80 °C and 100 °C are firstly demonstrated. The findings convincingly validate the pivotal role of newly designed separators for high performance Li-S chemistry.

2. Experimental section

Preparation of the PI nonwovens: Firstly, a certain concentration of polyamic acid spinning solutions were prepared in N,N-dimethylformamide (DMF, 99.9%, Aladdin) according to previous literature [22]. Electro-spinning of polyamic acid solutions was conduct at the supply rate of 0.8 mL h^{-1} by applying 15–25 kV on the spinneret. The distance between the spinneret and the collector was 30 cm. The electro-spinning polyamic acid films with a thickness of 15 μm were collected within 2 h. As-spun polyamic acid fibers were stepping wisely imidized in a tubular furnace (250 °C for 30 min and 370 °C for 30 min) under a nitrogen atmosphere.

Preparation of the super-P coated PI nonwovens (C@PI): Super-P nanoparticles (Wedafr Ltd. (Shenzhen)) were mixed with PVDF binders (Wedafr Ltd. (Shenzhen)) with a weight ratio of 4:1 within N-methylpyrrolidone (NMP, 99.9%, Aladdin) solvent to for the coating slurry. The C@PI separator was fabricated via facile blade-casting method.

Preparation of the super-P coated PI nonwovens with PEO-integrated LLZO coatings (C@PI@LLZO): Polyethylene oxide (M_p = 300000, Aladdin) and LLZO particles (Shanghai Institute of Ceramics, Chinese Academy of Sciences) with a weight ratio of 10:1 were dispersed into acetonitrile (Sinopharm Chemical Reagent Co.,Ltd) to form a homogeneous milk-like solution. The C@PI@LLZO separator was fabricated via facile blade-casting on the pre-prepared C@PI separator. The solids loads used for the preparation of the coatings were about 0.11 g mL^{-1}.

Preparation of the sulfur-carbon nanotubes (S@CNTs) cathode: S@CNTs composites were prepared via a melt-diffusion process. In a typical process, 0.8 g S powder (Aladdin) and 0.2 g carbon nanotube (Xianfeng Nano; The carbon nanotubes were used as received.) were mixed and ground using a mortar, and then transferred into a sealed stainless steel autoclave filled with Ar. It was calcined at 160 °C for one day to obtain the S@CNTs composites.

Scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis: The surface and cross-section morphology of the C@PI@LLZO separator and S@CNTs composites were characterized by a field-emission scanning electron microscopy (FE-SEM, JSM 6700 F). The microstructure of S@CNTs composites was characterized by transmission electron microscopy (TEM, FEI Tecnai G20). The phase compositions of sulfur powder, carbon nanotubes, and