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Hierarchical three-dimensional micro/nano-architecture of polyaniline nanowires wrapped-on polyimide nanofibers for high performance lithium-ion battery separators

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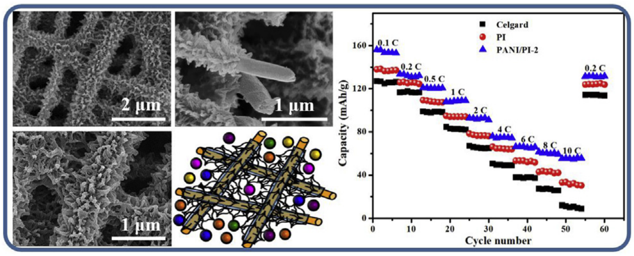
HIGHLIGHTS

- PANI-nanowires-coated PI-nanofiber separator.
- Hierarchical 3D micro/nano-structure.
- PANI/PI separator showed a superior thermal stability and a good tensile strength.
- PANI/PI composites exhibited high electrolyte uptake and ionic conductivity.
- LIB with PANI/PI separator presented a higher electrochemical performance.

GRAPHICAL ABSTRACT



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ABSTRACT

Polyaniline/polyimide (PANI/PI) composites with hierarchical 3D micro/nano-architecture have been prepared via electrospinning and *in-situ* polymerization. The PANI/PI composite prepared from 0.2 M aniline (PANI/PI-2) exhibited a small average pore size (1.730 μm) and a narrow pore size distribution (1.552–1.882 μm). Compared to the commercial polyolefin separators, the PANI/PI composite separator possesses a much better thermal stability up to 180 °C, a higher porosity (84%), a larger liquid electrolyte uptake (619%) and a higher ionic conductivity (2.33 mS cm^{-1}). The cell with PANI/PI-2 composite separator showed a low interfacial resistance, an enhanced capacity (133 mAh g^{-1} at 0.2C), a better rate capability (41.4% at 10C) and cyclability (89.3% retention after 500 charge/discharge cycles at 0.2C). The PANI/PI composite with a superior thermal stability and high electrochemical performances is a promising candidate for uses in high perform LIBs.

1. Introduction

Li-ion battery (LIB) has attracted more and more attentions as efficient energy storage system for a wide variety of new energy vehicles due to its proper operating voltage, high energy density and power density, low self-discharge rate and long cycle life [1]. In a LIB, the separator plays an essential role in preventing the physical electronic contact between electrodes and serves as a liquid electrolyte reservoir to transport ions [2]. Due to their good mechanical properties, chemical stability and acceptable cost, the commercially available polyolefin microporous membranes have

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been widely used as the LIB separators. However, the intrinsic characteristics such as a poor affinity with electrolyte, a poor thermal stability and a low porosity of the polyolefin separator, seriously affect the electrochemical performances of LIB. In the last decade, many efforts had been made to overcome these disadvantages by modifying the polyolefin separators with a thin coating layer of a polarized polymer or of inorganic nanoparticles to improve the electrolyte wettability and uptake [3–5], or to improve the thermal and dimensional stabilities of separators [6–8]; or by blending a block polymer, such as poly(ethylene-block-ethylene glycol) (PE-b-PEG) into a high density polyethylene (HDPE) to prepare the separator for improving its affinity with electrolyte [9].

For more improvements in the LIB separators, conventional nonwoven mats [10–12] and electrospun nanofiber nonwoven mats [13,14] both were tried to be used as the separators so as to make the LIB with a high performance. Compared to the conventional nonwovens, electrospun nanofiber mats possess a high porosity, a high liquid electrolyte uptake and a high ionic conductivity due to their smaller fiber diameters, interconnected open pore structures and larger surface areas [10,15–17]. These advantages make the electrospun nonwovens be an attractive separator candidate for high performance LIBs. Many electrospun polymer nonwovens, such as electrospun PVDF and their copolymers [17–22], polyethylene terephthalate (PET) [23], polyacrylonitrile (PAN) [24–26], poly (phthalazinone ether sulfone ketone) (PPESK) [27], polysulfonamide (PSA) [28] nanofiber nonwovens were used as LIB separators to enhance the LIB performances, such as cycle life, capacity and high rate capability. However, the poor thermal stability and poor mechanical strength of the above-mentioned electrospun nonvowens adversely affected the electrochemical performances of LIBs. Fortunately, polyimide (PI) is a type of high performance materials, which have been widely investigated and applied in many high technology areas [29–31]. The electrospun PI nanofiber mats possessed excellent mechanical properties [32–35], thermal stabilities [36], chemical resistance [37] and low dielectric constant [38–40]. Miao first explored the thermal stability and electrochemical properties of an electrospun PI nanofiber nonwoven as LIB separator with different thickness [16]; while Wang first reported the polymer electrolyte battery performance based on an electrospun PI nanofiber separator and found that the electrospun PI nanofiber nonwoven separator exhibited a higher porosity and higher electrolyte uptake [41]; and Jiang used electrospun PI nanofiber nonwoven as LIB separator for enhancing the safety of LIB [42]. However, as LIB separators, the pure electrospun PI nanofiber nonwovens still have many problems to be resolved, such as a larger average pore size (resulting in self-discharge), a poorer affinity with the electrolyte (leading to a higher internal resistance), and a much higher porosity (leading to a relatively poorer mechanical performance) and so on.

Compared to the single component PI nanofiber nonwoven separators, the composite nonwoven separators would have a better performance due to combining with the unique properties of each component. Shi [43] and Wang [44] developed PI nonwoven/gel composite separators to enhance the ion conductivity and thermal stability; Lee [45] coated Al_2O_3 on both side of a PI nanofiber separator via a dip-coating process to improve the cyclability and capacity of LIBs; and Liu [46] combined the thermal stability of PI and the good affinity of PVDF-co-HFP with electrolyte by coaxial electrospinning to make the PI/PVDF-co-HFP composite nonwoven separator for improving the thermal stability and high rate capability of LIBs.

Recently, nanostructured polyaniline (PANI) has been widely investigated in supercapacitors and batteries due to its easy processability, low cost, environmental stability, reversible electrical properties, excellent ion affinity, large surface area and highly porous structures [47–51]. Kumar et al. revealed that the incorporation of dedoped-PANI (insulation) nanowires could greatly improve the electrolyte ion transport in a gel electrolyte held in a dedoped-PANI nanowire network due to the good affinity of PANI nanowires with the electrolyte ions [52–57].

In this work, PANI nanowires were used to modify the electrospun PI nanofibers by *in-situ* polymerization to form a 3D hierarchical micro/nano-architecture for the LIB separator. The skeletal PI nanofiber membrane endows the separator a high thermal stability and good mechanical properties while the thin coating layer of PANI nanowires improves the electrolyte wettability, ion affinity and ionic conductivity of the separator. As a result, electrochemical performances including the battery capacity, cycling stability, and rate capability were greatly improved compared to those of the pure PI nanofiber separators and the traditional polyolefin separators.

2. Experimental

2.1. Materials

4, 4′-oxydianiline (ODA, Quzhou Kaiyuan Fine Chem Co), 4, 4′-diaminobiphenyl (BPA, Quzhou Kaiyuan Fine Chem. Co) and 1, 4-bis (3′, 4′-dicarboxyphenoxy) benzene dianhydride (HQDA, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences) were sublimated in prior to use. Aniline (AN, Shanghai Chem. Co) was distilled under reduced pressure and stored in a brown bottle prior to use. N, N-dimethylacetamide (DMAc) (99%, Tianjin Fu Chen Chemical Reagent Factory), Celgard membrane (Celgard, China) with a thickness of 25 μm and all other chemicals were used as received.

2.2. Preparation of PANI/PI nanofiber nonwovens

The polyimide precursor, polyamic acid (PAA) was synthesized from HQDA/ODA/BPA with molar ratio of 10/4/6 in DMAc with an intense mechanical stirring at 0 °C for 24 h, yielding a 25 wt% PAA solution. The obtained PAA solution was diluted into 10 wt% by using DMAc for electrospinning. The electrospinning process was carried out by applying 20 kV electrical potential to a 20 cm gap from a spinning nozzle to a fiber collector. The electrospun nanofiber nonwoven was collected on a rotating drum (diameter of 0.24 m) with rotating speed of 20 rpm. The as-spun nonwoven was dried in vacuum oven at 80 °C for 24 h and then imidized in a high temperature tubular furnace by heating the nonwoven to 150 °C (at a heating speed of 5 °C/min, N_2) and then to 320 °C (at a heating speed of 1 °C/min, N_2), respectively annealing for 1 h at the two temperature.

The PANI/PI composite membranes were prepared by an *in-situ* polymerization of AN. Firstly, the PI nonwovens were activated in a solution containing 1 wt% sodium dodecyl-benzenesulfonate by using ultrasonic for 30 min and then washed 5 times with distilled water. The activated PI nonwovens were immersed in a solution of 200 ml containing H_2SO_4 (1 M) and AN for 30 min under a N_2 atmosphere, followed by the addition of another 200 ml H_2SO_4 solution (1 M) containing 0.01 M (0.2282 g) ammonium persulfate (APS). The concentration of the AN aqueous solution (*C*AN) was 0.005, 0.01, 0.02, 0.03 and 0.04 M, respectively. The molar ratio of aniline to APS was 4/1. The polymerization was carried out in an ice-water bath (−2–0 °C) under a N_2 atmosphere for 4 h. After that, the composite membranes were washed with 200 ml aqueous ammonia (0.1 M) for 30 min and then washed with distilled water until acid neutral. Finally, the PANI/PI composite membranes were dried in vacuum oven at 60 °C for 6 h and denoted PANI/PI-0, PANI/PI-1, PANI/PI-2, PANI/PI-3 and PANI/PI-4, respectively