



ELSEVIER

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

A simple method to prepare a polydopamine modified core-shell structure composite separator for application in high-safety lithium-ion batteries

Chuan Shi^{a,1}, Jianhui Dai^{b,1}, Shaohua Huang^c, Chao Li^a, Xiu Shen^a, Peng Zhang^{b,*},
Dezhi Wu^c, Daoheng Sun^c, Jinbao Zhao^{a,b,*}

^a College of Chemistry and Chemical Engineering, State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovative Center of Chemistry for Energy Materials, Xiamen University, Xiamen 361005, China

^b College of Energy Research & School of Energy Research, Xiamen University, Xiamen 361102, China

^c School of Aerospace Engineering, Xiamen University, Xiamen 361005, China

ARTICLE INFO

Article history:

Received 14 March 2016

Received in revised form

6 June 2016

Accepted 30 June 2016

Available online 5 July 2016

Keywords:

Composite membrane

Lithium-ion battery

Polydopamine

Safety

ABSTRACT

In this work, we report a simple dip coating method to grow a thin polydopamine (PDA) layer on the surface of polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) nano-fibers as the composite separator for application in high-safety lithium-ion batteries. A thin adherent PDA film uniformly distributed on the surface of PVDF-HFP nano-fibers, formed a unique core-shell structure. Compared with pure PVDF-HFP nonwoven membrane, the PDA coating PVDF-HFP composite membrane (PVDF-HFP-PDA) not only exhibits much higher thermal stability, but also shows enhanced mechanical strength and tensile strength, which are very important for the assemble and long-term performance of the batteries. The ionic conductivity of the PVDF-HFP-PDA composite membrane is 1.40 mS cm^{-1} which is much higher than 0.80 mS cm^{-1} of the polypropylene (PP) separator. The lithium-ion batteries with PVDF-HFP-PDA composite membrane show excellent cyclic stability and good rate performance. The PVDF-HFP-PDA composite membrane is suitable for applications in secondary lithium-ion batteries due to its advantages mentioned above.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Large-scale lithium-ion batteries are developed to meet the requirement of energy storage systems and hybrid electric vehicles (HEVs) [1,2]. The potential safety hazard of the batteries was exacerbated with the increase of the battery capacity. Separators as one main parts of the batteries were designed to avoid the direct contact of the cathode and anode, meanwhile sustains the free transport of the lithium-ions when absorbed liquid electrolyte [3]. Polypropylene (PP), polyethylene (PE) separator with excellent mechanical strength and chemical stability were applied as

* Corresponding author at: College of Energy Research & School of Energy Research, Xiamen University, Xiamen 361102, China.

** Corresponding author at: College of Chemistry and Chemical Engineering, State key laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovative Center of Chemistry for Energy Materials, Xiamen University, Xiamen 361005, China.

E-mail addresses: pengzhang@xmu.edu.cn (P. Zhang),

jbzhao@xmu.edu.cn (J. Zhao).

¹ Both authors contribute equally to this work.

lithium-ion batteries separator. However, they also lead to serious concerns such as weak thermal stability and poor wettability in liquid electrolytes [3,4]. Compared with the conventional PE and PP separators, the nonwoven membranes [5,6] have been widely studied in the past decades since they exhibit better wettability for the polar electrolytes, lower resistance and the batteries assembled with the nonwoven separator show higher retention capacity and rate performance. Also, the thermal stability of the nonwoven membrane could be well controlled by the selection of manufacture materials.

Among these polymers used for preparing nonwoven membranes, polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) [6–9], polyvinylidene fluoride (PVDF) [10–14], polyacrylonitrile (PAN) [15–19] have drawn considerable attention due to their good process ability, good chemical stability, lightweight, high ionic conductivity (dielectric constant), excellently wettability with electrolyte and easy swelling or gelation in liquid electrolyte. It must be noted that the gel polymer electrolytes are consisted of a polymer matrix and a liquid electrolyte. Therefore, the gel polymer electrolytes can use such advantages as the safety of the

polymer matrix and high ionic conductivity of the liquid electrolyte. However, the polymer matrix of the gel polymer electrolytes will be softened by the liquid electrolyte uptake which will lead to poor mechanical properties of the membrane and further result in winding and internal shorts of the cells prepared with this membrane during the assembly processes. The weak thermo-stability and mechanical strength of nonwoven membrane limit their further application as separator for lithium-ion batteries.

Poly-dopamine (PDA) [20–28], as a small-molecule compound, contains catechol (DPA) and amine (lysine) groups. The two groups, mimic of *Mytilus edulis* foot protein 5 (Mefp-5), can establish covalent and non-covalent interactions with surfaces of organic and inorganic materials, makes it possible for PDA to deposit a thin layer with a wide variety of functional uses on the surfaces of virtually any bulk material [21,29]. Based on this finding, lots of works were carried out in the field of surface modification. Ryou et al. [20,25] have reported surface modification method for PE separators using PDA. The PDA-coated separators showed good electrochemical properties, and performed well in Lithium-ion batteries (LIBs). Works on the PDA coating nonwoven membrane were carried out for the improvement of interface and electrochemical properties [24]. From the above researches, we know that PDA has a melting temperature of about 230 °C. The PDA coating method should be beneficial, not only to the electrochemical performance improvement, but also to the thermo-stability and mechanical strength enhancement of the nonwoven membrane. However, there still lack of detailed research on the improvements of nonwoven membrane after PDA modified.

In this work, PVDF-HFP nonwoven membrane were coated with a thin adherent PDA film (PVDF-HFP-PDA) formed a core-shell structure. The thermo-stability, mechanical strength and electrochemical performance of the PVDF-HFP-PDA were carefully studied. Compared with pure PVDF-HFP nonwoven membrane, the PDA coating PVDF-HFP composite membrane (PVDF-HFP-PDA) not only exhibits much higher thermal stability, but also shows enhanced mechanical strength and tensile strength, which are very important for the assemble and long-term performance of the batteries. The ionic conductivity of PVDF-HFP-PDA composite membrane is 1.40 mS cm^{-1} which is much higher than 0.80 mS cm^{-1} of the PP separator. The lithium-ion batteries with PVDF-HFP-PDA composite membrane show excellent cyclic stability and good rate performance. Moreover, the whole react process is induced in an aqueous solution which is environmental friendly. The PVDF-HFP-PDA composite membrane could meet the safety requirements of large-scale lithium-ion batteries due to its advantages mentioned above.

2. Experiment

2.1. Fabrication of PVDF-HFP-PDA composite membrane

PVDF-HFP ($M_w \sim 3000,000$, Aldrich, Shanghai) was dissolved into a binary solvent system with acetone and N, N-dimethylformamide (DMF) at equal volume ratio to get the solution of 16 wt% concentration, and the solution was vigorously mixed by magnetic stirring for 10 h resulting in a slurry. PVDF-HFP nonwoven membrane was fabricated by the electrospinning process with the slurry. The setup for preparing the PVDF-HFP nonwoven membrane included a high voltage source (Gamma, USA), copper collector, a pump (Harvard, USA) and syringe. The ground collector placed on top of an X-Y motion stage (Googletech, Shenzhen, China) was connected to the cathode of the high voltage source while the conductive spinneret was connected to anode. The electrospinning process of PVDF-HFP was conducted under an applied bias of 10 kV with a flow rate of $125 \mu\text{l h}^{-1}$. The spinneret-to-collector distance is 10 cm. The collector moved forth and back in the X-axial direction at a speed of 40 cm min^{-1} with a moving displacement of 12 cm while moved intermittently in the Y-axial direction with a moving displacement of $40 \mu\text{m}$ after a loop movement in the X-axial direction for better distribution and uniformity of nano-fibers. Then as-prepared PVDF-HFP nonwoven membrane was dried at 110 °C overnight for the further modification.

The manufacture procedure of PVDF-HFP-PDA composite membrane is shown in Fig. 1. Simple immersion of the PVDF-HFP nonwoven membrane in a aqueous/ethanol (equal volume) solution for 48 h, per milliliter consists 2 mg dopamine hydrochloride and 10 mM tris(hydroxymethyl)aminomethane with a pH of 8.5, results in spontaneous deposition of a thin PDA layer on the surface of PVDF-HFP nonwoven membrane. As-prepared PVDF-HFP-PDA composite membrane was flushed off by deionized water and then dried overnight at 80 °C in a vacuum drying oven. Characterization of the PVDF-HFP-PDA composite membrane was investigated with PP separator (Nantong Tianfeng New Electronic Materials Co., Ltd.) and PVDF-HFP nonwoven membrane as references.

2.2. Electrode preparation and cell assembly

The 2016-type coin cells assembled with PP separator, PVDF-HFP nonwoven membrane and PVDF-HFP-PDA composite membrane were used for the measurement of batteries performance. The cathode included 5 wt% of PVDF, 90 wt% of LiMn_2O_4 (Qingdao Xinzheng Material Co., Ltd, China), 5 wt% of super-P was coated on

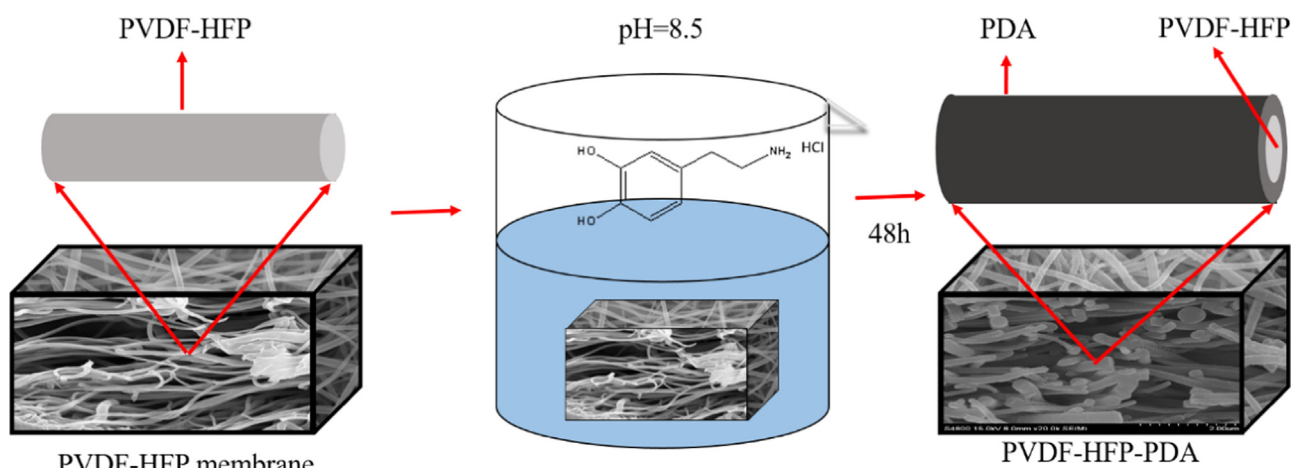


Fig. 1. The manufacture procedure scheme-demonstration figure of PVDF-HFP-PDA composite membrane.

Download English Version:

<https://daneshyari.com/en/article/632211>

Download Persian Version:

<https://daneshyari.com/article/632211>

[Daneshyari.com](https://daneshyari.com)