



ELSEVIER

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Nanoparticle-on-nanofiber hybrid membrane separators for lithium-ion batteries via combining electrospinning and electrospinning techniques

Meltem Yanilmaz, Yao Lu, Mahmut Dirican, Kun Fu, Xiangwu Zhang*

Fiber and Polymer Science Program, Department of Textile Engineering, Chemistry and Science, North Carolina State University, Raleigh, NC 27695-8301, USA

ARTICLE INFO

Article history:

Received 21 November 2013

Received in revised form

8 January 2014

Accepted 9 January 2014

Available online 19 January 2014

Keywords:

Electrospinning

Electrospinning

Polyvinylidene fluoride

SiO₂ nanoparticle

Battery separator

ABSTRACT

Nanoparticle-on-nanofiber hybrid membranes were prepared by electrospinning of SiO₂ dispersions and electrospinning of polyvinylidene fluoride (PVDF) solution *simultaneously*. The aim of this study was to design new high-performance separator membranes with superior electrochemical properties such as high C-rate performance and good thermal stability compared to polyolefin based membranes. Uniform, bead-free fibrous structure with high amount of SiO₂ nanoparticles exposed on PVDF nanofiber surfaces was observed. It was found that wettability and ionic conductivity were improved by dispersing SiO₂ nanoparticles onto PVDF nanofiber surfaces. Electrochemical properties were enhanced due to the increased surface area caused by the unique hybrid structure of SiO₂ nanoparticles and PVDF nanofibers. Compared with commercial microporous polyolefin membranes, SiO₂/PVDF hybrid membranes had larger liquid electrolyte uptake, higher electrochemical oxidation limit, and lower interfacial resistance with lithium. SiO₂/PVDF hybrid membrane separators were assembled into lithium/lithium iron phosphate cells and demonstrated high cell capacities and good cycling performance at room temperature. In addition, cells using SiO₂/PVDF hybrid membrane separators showed superior C-rate performance compared to those using commercial microporous PP membrane.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Li-ion batteries are important power sources with high energy density, high operational voltage, long cycle life, and low self-discharge rate, and hence they have been widely used to power many portable devices such as cellular phone, laptops, digital cameras, etc. Although current Li-ion batteries have the highest energy density compared to other commercial rechargeable batteries, significant improvements are still needed in energy density, safety, durability and cost to meet the long-term performance targets for plug-in hybrid electric vehicles and all electric vehicles [1–3].

Presently available Li-ion batteries utilize liquid electrolyte which makes them prone to catching fire and explosion. There are two ways to overcome this problem: firstly, by using solid state electrolytes [4,5], and secondly, by using thermally-stable separators [6]. Separators are placed between the positive and negative electrodes in Li-ion batteries. They must be electronic insulators to prevent electron transfer between two electrodes and, at the same time, they must be highly porous to allow Li-ions to travel. Although they do not participate in electrochemical reactions, separators play a vital role in preventing short circuit, allowing Li ion transfer, and regulating cell kinetics. As a result, the physical properties of separators can

affect the cell capacity, cell resistance, rate performance, and long-term cycling capability of Li-ion batteries [7–10]. There are many requirements for separator materials such as good mechanical, dimensional, chemical stabilities, low ionic resistance, high wettability, and excellent structural uniformity to obtain good safe batteries with high performance. Among them, low resistance, low shrinkage, and uniform pore structure are essential for separators. Currently, microporous membranes are the most commonly used separator types and they are polyolefin-based materials with good mechanical properties and chemical stability [11–14]. However, their wettability and thermal stabilities are not sufficient for applications that require high operating temperature and high performance such as higher charge/discharge rate. Low affinity of these membrane to liquid electrolyte also leads to high cell resistance that affects the cycling performance and rate performance negatively [15].

Due to the superior properties such as large specific surface area, small pore size and high porosity, electrospun nanofiber membranes can be good separator candidates for high-performance lithium-ion batteries [8]. Polyvinylidene fluoride (PVDF) and its copolymers are the most studied materials for nanofiber separators due to their high polarity, good thermal and mechanical properties, high affinity to electrolyte solutions, good chemical stability, and excellent compatibility with electrodes [16].

Moreover, the performance of nanofiber membranes can be further improved by introducing ceramic fillers which form Lewis acid/base interactions with the ionic species in the liquid electrolyte [17–19].

* Corresponding author. Tel.: +1 919 515 6547; fax: +1 919 515 6532.
E-mail address: xiangwu_zhang@ncsu.edu (X. Zhang).

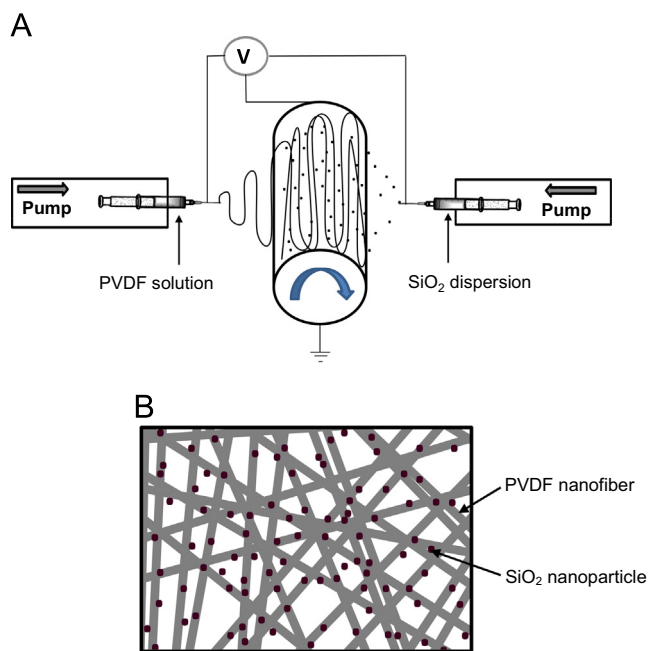


Fig. 1. (A) Preparation and (B) schematic view of SiO₂/PVDF nanoparticle/nanofiber hybrid separators.

Although ceramic/polymer composites can be prepared by encapsulating ceramic particles directly into polymer nanofibers, the performance of the resultant composite membranes are restricted because these nanoparticles are not exposed to liquid electrolytes and have limited effect on improving the cell performance.

Here, we introduce new nanoparticle-on-nanofiber hybrid membrane separators by combining electrospinning with electro-spraying. Both techniques utilize electric forces to draw jets from charged liquids and deposit them onto grounded collector. In electro-spraying, when the electric force is higher than surface tension of the liquid, the jets are atomized into fine droplets. In electrospinning, the electric repulsion force cannot overcome the intermolecular forces in the liquid, and hence the jets are not broken and they extend, bend and eventually reach the collector forming a nonwoven mat of nanofibers [20–22]. In this study, SiO₂/PVDF nanoparticle/nanofiber hybrid membranes were prepared by *simultaneously* electro-spraying of SiO₂ dispersion and electrospinning of PVDF solution (Fig. 1A). By using this electro-spraying–electrospinning combined process, SiO₂ nanoparticles were attached on the nanofiber surfaces (Fig. 1B) and are more effective to improve the separator properties since they are not encapsulated and separated from liquid electrolytes. Experimental results showed that these novel hybrid membranes had higher conductivities, lower interfacial resistances and better C-rate performance compared to pure PVDF nanofiber membrane and microporous PP membrane. It is, therefore, demonstrated that SiO₂/PVDF nanoparticle/nanofiber hybrid membranes prepared by the electro-spraying–electrospinning combined process are promising separator candidate for high-performance Li-ion batteries.

2. Experimental

2.1. Chemicals

Hydrophilic pyrogenic SiO₂ (Aerosil 380, particle size=7 nm, surface area=380 m²/g) was supplied from Evonic industries. Polyvinylidene fluoride (PVDF, $M_w=30 \times 10^4$ – 50×10^4) was obtained from Shanghai Ofluorine Chemical Technology. N,N-dimethylformamide (DMF), acetone, methanol and n-butanol were purchased from

Sigma Aldrich. Liquid electrolyte, 1 M lithium hexafluorophosphate (LiPF₆) in ethylene carbonate and ethyl methyl carbonate (EC+EMC, 1:1 by volume), was supplied from Ferro Corp. Celgard 2400 microporous polypropylene was used for comparison. LiFePO₄ was obtained from Hydro-Qubec. All chemicals were used as received without further purification.

2.2. Separator preparation

SiO₂/PVDF nanoparticle/nanofiber hybrid membranes were prepared by electro-spraying of SiO₂ dispersions and electrospinning of PVDF solution *simultaneously*. SiO₂ dispersions were prepared by dispersing different amounts of SiO₂ nanoparticles (0, 1, 3 and 5 wt%) into methanol. The dispersions were stirred at room temperature overnight and ultrasonicated before electro-spraying to ensure the uniformity. PVDF solution was prepared by dissolving 10 wt% PVDF in DMF/acetone (7:3 by volume), which was stirred at 60 °C for at least 8 h to ensure dissolution of the polymer.

During the preparation of SiO₂/PVDF hybrid membranes, a variable high voltage power supply (Gamma) was used to provide a high voltage of 20 kV. For both SiO₂ dispersions and PVDF solution, the feeding rate used was 1.5 ml/h and the tip-to-collector-distance was 17 cm. Electro-sprayed nanoparticles and electrospun PVDF nanofibers were accumulated on the collector *simultaneously* to form nanoparticle/nanofiber hybrid membranes. The resultant membranes were dried at 80 °C for at least 24 h to remove residual solvents.

2.3. Structure characterization

The morphology of SiO₂/PVDF hybrid membranes was studied using a JEOL JSM-6400F field-emission scanning electron microscope (FESEM). The SiO₂ contents in SiO₂/PVDF hybrid membranes were analyzed on a Perkin Elmer 2000 DV ICP-Optical emission spectrometer after acid digestion.

The porosities of the membranes were determined by using n-butanol uptake tests. In a uptake test, the porosity was calculated using the following equation:

$$\text{Porosity (\%)} = \frac{w_w - w_d}{\rho_b V} \quad (1)$$

where w_w and w_d are the weights of wet and dry membranes, respectively, ρ_b the density of n-butanol, and V the geometric volume of the membrane.

2.4. Performance evaluation

The dimensional stability of the membranes were determined by thermal shrinkage tests at 150 °C for 30 min. The mechanical properties of the membranes were determined by using a universal tensile tester (Instron 5544) with 100 N capacity load cell. The dimensions of test specimens were 10 mm wide, 60 μm thick, and 60 mm long.

Liquid electrolyte uptakes were measured by soaking weighed membranes in the liquid electrolyte of 1M LiPF₆ in EC+EMC (1:1 in volume) for 2 h at room temperature. The electrolyte uptake (EU) was calculated by

$$\text{EU (\%)} = \frac{w_1 - w_0}{w_0} \times 100 \quad (2)$$

where w_0 and w_1 are the weights of dry and wet membranes, respectively.

The ionic conductivities of liquid electrolyte-soaked membranes were measured by electrochemical impedance spectroscopy (EIS) using Reference 600 Potentiostat/Galvanostat/ZRA (GAMRY). The impedance measurements were performed on liquid electrolyte-soaked membranes sandwiched between two

Download English Version:

<https://daneshyari.com/en/article/633742>

Download Persian Version:

<https://daneshyari.com/article/633742>

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