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Silica/polyacrylonitrile hybrid nanofiber membrane separators via sol-gel and electrospinning techniques for lithium-ion batteries

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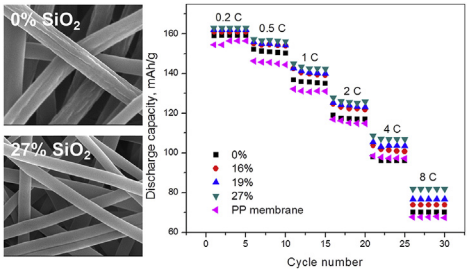
HIGHLIGHTS

- SiO_2/PAN membranes were prepared using sol-gel and electrospinning techniques.
- SiO_2 nanoparticle content up to 27 wt % was achieved by using sol-gel technique.
- High cell capacities and good cycling performance were demonstrated.
- Superior C-rate performance was obtained for cells with SiO_2/PAN membranes.

GRAPHICAL ABSTRACT



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ABSTRACT

Silica/polyacrylonitrile (SiO_2/PAN) hybrid nanofiber membranes were fabricated by using sol-gel and electrospinning techniques and their electrochemical performance was evaluated for use as separators in lithium-ion batteries. The aim of this study was to design high-performance separator membranes with enhanced electrochemical performance and good thermal stability compared to microporous polyolefin membranes. In this study, SiO_2 nanoparticle content up to 27 wt% was achieved in the membranes by using sol-gel technique. It was found that SiO_2/PAN hybrid nanofiber membranes had superior electrochemical performance with good thermal stability due to their high SiO_2 content and large porosity. Compared with commercial microporous polyolefin membranes, SiO_2/PAN hybrid nanofiber membranes had larger liquid electrolyte uptake, higher electrochemical oxidation limit, and lower interfacial resistance with lithium. SiO_2/PAN hybrid nanofiber membranes with different SiO_2 contents (0, 16, 19 and 27 wt%) were also assembled into lithium/lithium iron phosphate cells, and high cell capacities and good cycling performance were demonstrated at room temperature. In addition, cells using SiO_2/PAN hybrid nanofiber membranes with high SiO_2 contents showed superior C-rate performance compared to those with low SiO_2 contents and commercial microporous polyolefin membrane.

1. Introduction

Li-ion batteries have received great attention as promising candidates for electric and hybrid vehicles due to their high energy density, large operational voltage, long cycling life, and low self-discharge rate. However, new battery components must be developed for these applications to obtain high-performance Li-ion

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batteries with better safety and lower cost [1,2].

The thermal behavior and stability of electrolyte-soaked separators directly affect the safety feature of Li-ion batteries. The separator is placed between two electrodes to prevent electronic contact, allow ionic transport, and regulate cell kinetics in Li-ion batteries. Due to the advantages of good chemical stability and high mechanical strength, microporous polyolefin membranes are currently the most commonly-used separators for Li-ion batteries. However, these membranes have low porosity, poor wettability with polar liquid electrolyte and large thermal shrinkage at high temperatures. These drawbacks affect cell resistance, energy density, rate capability and safety of Li-ion batteries [2–6].

Electrospun nanofiber membranes have recently been presented as good separator candidate for Li-ion batteries because of their large porosity, small pore size and high specific surface area with unique pore structure. Earlier studies have reported enhanced electrochemical performance such as higher C-rate capability, better cycling performance and lower cell resistance for Li-ion cells using electrospun membranes [5]. Various polymers have been used to prepare electrospun nanofiber membranes [2,4]. Among them, polyacrylonitrile (PAN) is a commonly-studied separator material due to its superior properties such as high ionic conductivity, good thermal stability, high electrolyte uptake and good compatibility with Li metal [7].

It is also well-known that introducing ceramic nanoparticles improves thermal stability and wettability of separators, leading to enhanced electrochemical performance of the resultant Li-ion cells [8]. However, when pre-prepared nanoparticles are used directly to prepare separator membranes, the nanoparticle contents are limited (typically, <15 wt%) because the membrane formation process may be hindered by the high solution viscosities at high contents [9,10]. Moreover, ceramic nanoparticles can easily aggregate in the membranes, which in turn reduces the separator quality and performance [5]. To address these challenges, sol-gel technique can be used to obtain nanofiber membranes containing high amount of inorganic nanoparticles. The sol-gel technique improves the compatibility of inorganic nanoparticles with organic matrix by forming inorganic network in hybrid structures. As a result, when an organic polymer is mixed with a metal alkoxide, such as tetraethyl orthosilicate (TEOS, $Si(OCH_2CH_3)_4$), hydrolysis and polycondensation of TEOS occur *in-situ* with the presence of polymer matrix, which allows us to fabricate organic-inorganic composite structures with uniform dispersion of high-content inorganic nanoparticles. In this study, sol-gel technique and electrospinning were used to prepare SiO_2/polyacrylonitrile (PAN) hybrid nanofiber membranes with high thermal stability and enhanced electrochemical properties. The resultant membranes with high SiO_2 contents showed good thermal stability and superior electrochemical properties including higher ionic conductivities, lower interfacial resistances and superior C-rate performance compared to microporous polyolefin membrane owing to high amount of inorganic particles in the structure. It is, therefore, demonstrated that SiO_2/PAN hybrid nanofiber membranes with superior electrochemical and thermal properties are promising separator candidate for high-performance Li-ion batteries.

2. Experimental

2.1. Chemicals

Polyacrylonitrile (PAN, Mw = 150,000) was supplied from Pfaltz& Bauer Inc. *N*,*N*-dimethylformamide (DMF), TEOS (99%), ethanol, and hydrochloric acid (HCl, 37%) were purchased from Sigma Aldrich. Liquid electrolyte, 1 M lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate and ethyl methyl carbonate (EC+EMC, 1:1 by volume), was supplied from Ferro Corp. Celgard 2400 microporous polypropylene (PP) membrane was used for comparison. $LiFePO_4$ was obtained from Hydro-Qubec. All chemicals were used as received without further purification.

2.2. Separator preparation

SiO_2/PAN hybrid nanofiber membranes were prepared by the combination of sol-gel and electrospinning techniques. PAN solution (10 wt%) was prepared by dissolving PAN into DMF at 60 °C and mechanically stirred for 12 h. TEOS solution (20 wt% in DMF) was prepared by dissolving TEOS in DMF, followed by adding HCl solution (37 wt% in water). The molar ratio of the TEOS solution was TEOS:HCl = 1:0.04. The TEOS solution was stirred at room temperature for 3 h and was then gradually added to the PAN solution. The as-prepared TEOS/PAN solution was stirred at room temperature for 24 h, followed by ultrasonic treatment for 1 h to obtain a homogenous dispersion. During that process, TEOS was converted to well-dispersed SiO_2 nanoparticles. The as-prepared SiO_2/PAN dispersion was then electrospun into nanofibers with a flow rate of 0.75 ml/h, a voltage of 16 kV, and a tip-to-collector distance of 25 cm. SiO_2/PAN hybrid nanofibers with different SiO_2 contents (16, 19, 27 wt%) were obtained by changing PAN:TEOS ratios. For comparison, PAN nanofibers were also prepared. Electrospun PAN and SiO_2/PAN nanofibers were accumulated on the collector to form free-standing membranes. The resultant nanofiber membranes were rinsed and dried to remove residuals before use. The thicknesses of the prepared nanofiber membranes were around 65 μm.

2.3. Structure characterization

The SiO_2 contents in SiO_2/PAN hybrid nanofiber membranes were analyzed by using ICP-Optical emission spectrometer. After the digesting process, samples were diluted with DI water and run against a Si calibration curve. The resultant ICP-OES spectra were used to determine the SiO_2 contents of the hybrid membranes. The average SiO_2 contents in hybrid nanofiber membranes were measured to be 16, 19 and 27 wt%, respectively.

The morphology of PAN and SiO_2/PAN hybrid nanofiber membranes was studied by using a JEOL JSM-6400F field-emission scanning electron microscope (FESEM). The fiber diameters were calculated by measuring 50 randomly-selected nanofibers in SEM images using Revolution 1.6 software for each sample.

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

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

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.

The chemical structure of SiO_2/PAN hybrid nanofiber membranes was analyzed using FTIR (Thermo Fisher Nexus 470 FTIR with Continuum Microscope and ORBIT/OMNI ATR's) in a range of wavenumbers from 500 to 4000 cm^{-1}. X-ray diffraction analysis was conducted with Rigaku Smartlab X-ray diffraction system using Cu Kα radiation (α = 1.544 Å). The samples were scanned in a 2θ range of 10–60°, with 2θ step-scan interval of 0.1°.

The dimensional stability of the membranes was 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