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Enhanced wettability and thermal stability of nano-SiO₂/poly(vinyl alcohol)-coated polypropylene composite separators for lithium-ion batteries

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ABSTRACT

To improve the electrolyte wettability and thermal stability of polypropylene (PP) separators, nano-SiO₂/poly(vinyl alcohol)-coated PP composite separators were prepared using a simple but efficient sol-gel and dip-coating method. The effects of the tetraethoxysilane (TEOS) dosage on the morphology, wettability, and thermal stability of the composite separators were investigated using Fourier-transform infrared spectroscopy, scanning electron microscopy, and contact-angle measurements. All the composite separators gave a smaller contact angle, higher electrolyte uptake, and lower thermal shrinkage compared with the PP separator, indicating enhanced wettability and thermal stability. Unlike the case for a traditional physical mixture, Si—O—C covalent bonds were formed in the coating layer. The composite separator with a TEOS dosage of 7.5 wt% had a unique porous structure combining hierarchical pores with interstitial voids, and gave the best wettability and thermal stability. The ionic conductivity of the composite separator containing 7.5 wt% TEOS was 1.26 mS/cm, which is much higher than that of the PP separator (0.74 mS/cm). The C-rate and cycling performances of batteries assembled with the composite separator containing 7.5 wt% TEOS were better than those of batteries containing PP separators.

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Introduction

With the rapid development of the electronic industry, lithium-ion batteries (LIBs) have been increasingly used in electronic devices such as laptops, mobile phones, and digital cameras because of their high energy densities and power densities, and long cycling lifetimes (Tan, Yan, Xu, Chen, & Yang, 2017; Liao, Sun, Hu, & Li, 2013; Choi, Kim, & Kim, 2010). Separators, one of the most critical components in LIBs, play an important role in physically separating the anode and cathode to avoid internal short circuit and providing a path for free transport of lithium ions during absorption of a liquid electrolyte, and charging or discharging (Li et al., 2015; Zhang, 2007).

Currently, commercial separators are typically manufactured from polyolefins, predominantly polypropylene (PP) and polyethylene (PE). These are widely used in LIBs because of their good chemical stability, mechanical properties, and low manufactur-

ing costs (Wang & Gao, 2016; Chen et al., 2016). However, their inherently low surface energies make polyolefin-based separators hydrophobic. This results in poor wettability with polar liquid electrolytes and insufficient electrolyte absorption, greatly restricting the cell performance. The melting temperatures of PE and PP separators are only about 135 and 165 °C, respectively, which can lead to serious thermal shrinkage and cause direct contact between the anode and cathode. This can lead to internal short circuit, fire outbreaks, or even explosions when LIBs are exposed to abnormal conditions such as overcharging or overheating (Song et al., 2012).

Considerable efforts based on nanotechnology have been made to overcome these drawbacks by improving the wettability and thermal stability of separators. One method involves preparation of nanofiber separators with alternative materials such as polyimide (PI), poly(vinylidene fluoride) (PVDF) and poly(acrylonitrile) by electrospinning. Shayapat, Chung, and Park (2015) used electrospinning to prepare PI-SiO₂-nanoparticle composite nanofibers and PI-Al₂O₃-nanoparticle composite nanofibers for separators. No shrinkage and no melting were observed at 200 °C. Contact-angle and electrolyte uptake tests showed that the composite nanofibers had excellent wettability. Zhang, Ma, Cao, Li, and Zhu

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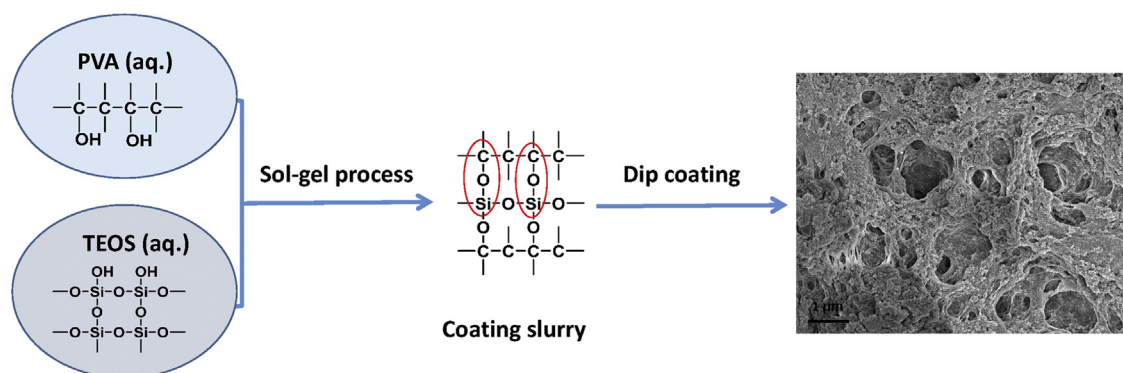


Fig. 1. Preparation of nano-SiO₂/PVA-coated PP composite separator.

(2014) prepared PVdF/SiO₂ composite nanofiber membranes by synchronously electrospinning a PVdF homopolymer and SiO₂ sol. LIBs prepared with these membranes as separators showed good thermal stability, high ionic conductivities, and excellent electrochemical performances. However, the low production efficiency and high manufacturing cost of electrospinning restrict its large-scale use. Another method involves introducing nanoparticles on the surface of a polyolefin-based separator. Wang et al. (2015) developed a new Al₂O₃-coated composite PP separator with phenolphthalein poly(ether ketone) as the binder; this separator had good thermal stability and gave a good charge/discharge performance. Kim et al. (2014) prepared a ceramic composite separator by coating moisturized ZrO₂ nanoparticles with a poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) copolymer on a PE separator. Because of the abundant micropores formed in the ceramic layers, both the electrolyte uptake and thermal stability of the ceramic composite separator were improved. The introduction of composite layers on the surfaces of polyolefin-based separators is an effective strategy for enhancing their wettability and thermal stability, but many of the organic solvents such as acetone, *N,N*-dimethylacetamide, and *N*-methylpyrrolidone that are used as solvents for polymer binders are harmful to the environment and human health. A physical mixture does not provide sufficient adhesion between inorganic particles and polymer binders, therefore coated ceramic particles are easily detached from the coating layer during cell assembly (Huang & Hitt, 2013).

In this study, using a simple but efficient sol-gel and dip-coating method, we prepared a nano-SiO₂/poly(vinyl alcohol) (PVA)-coated PP composite separator. The nano-SiO₂ was synthesized by an alkali-catalyzed reaction of a silica precursor, i.e., tetraethoxysilane (TEOS), and the composite separator was obtained by dip-coating. Unlike the case for traditional physical mixtures, Si–O–C covalent bonds were formed between the ceramic particles (SiO₂) and polymer binder (PVA) during the sol-gel process. The effects of the TEOS dosage on the physical properties, i.e., the morphology, wettability, and thermal stability, of the composite separators were investigated. The cell performance indicators, i.e., the C-rate capability and cyclability, of the composite separators were also investigated. A commercial PP separator was examined for comparison.

Experimental

Materials

PVA (saponification degree 96.0%–98.0%, molecular weight 72,000 g/mol), TEOS (purity ≥ 98.0%, density 0.931–0.934 g/mL at 20 °C), and ethanol (purity 100%, density 0.789–0.791 g/mL at 20 °C) were purchased from the Guangzhou Yushao Trade Co.

(Guangzhou, China). A liquid electrolyte consisting of LiPF₆ (1 mol) in a mixture of ethylene carbonate, dimethyl carbonate, and diethyl carbonate (1/1/1, v/v/v) was purchased from the Zhengzhou Jinghong New Energy Technology Co., Ltd. (Zhengzhou, China). A PP separator (thickness 25 μm, porosity 41.0%) was supplied by the Zhuhai Smoothway Electronic Materials Co., Ltd. (Zhuhai, China).

Preparation of composite separators

Composite separators were prepared using a process based on previously reported methods (Jiang et al., 2016; Pirzada, Arvidson, Saquing, Shah, & Khan, 2012); the process is shown in Fig. 1. PVA (7 g) was dissolved in deionized water (93 g) at 85 °C. The mixture was vigorously stirred for 5 h to give a 7 wt% PVA viscous solution. TEOS solutions (100 g) containing 0, 5, 10, or 15 wt% TEOS were prepared by dissolving TEOS in ethanol and deionized water (1/1, wt/wt). The TEOS solutions were gradually added to the PVA solution (100 g) and the mixture was stirred at 40 °C for 0.5 h to give a homogeneous mixture. Ammonia (0.1 mol) was added dropwise and the mixture was continuously stirred for 12 h to give a coating slurry.

The slurry was coated on both sides of a commercial PP separator pretreated with ethanol via a dip-coating method. The as-prepared separator was dried at ambient temperature for 2 h to evaporate the solvent, followed by drying in a vacuum oven at 60 °C for 24 h.

For convenience, the composite separators containing 0, 2.5, 5.0, and 7.5 wt% TEOS are denoted by CS1, CS2, CS3, and CS4, respectively.

Characterization

The surface functional groups of the separators were identified using Fourier-transform infrared (FTIR) spectroscopy (VERTEX 70, Bruker, Germany). Spectra were recorded at room temperature across the wavenumber range 4000–400 cm⁻¹.

The separator morphology was examined using scanning electron microscopy (SEM; JSM-6700F, JEOL, Japan).

The porosity of the separator was investigated using the *n*-butanol uptake method, and calculated using Eq. (1):

$$\varepsilon = \frac{W_1 - W_0}{\rho V} \times 100\%, \quad (1)$$

where ε is the separator porosity, W_0 and W_1 are the weights of the separator before and after soaking in *n*-butanol for 1 h, respectively, ρ is the density of *n*-butanol, and V is the separator volume.

Contact angles were measured by the sessile drop method, with deionized water as the probe liquid, using a Dataphysics OCA20CA

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