



Fabrication of a novel sandwich-like composite separator with enhanced physical and electrochemical performances for lithium-ion battery



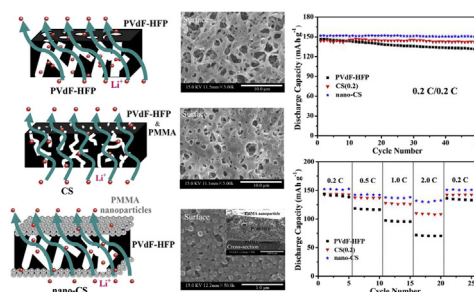
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HIGHLIGHTS

- A sandwich-like PP nonwoven/PVdF-HFP separator with the introduction of PMMA nanoparticles on the surface is constructed.
- The composite separator possesses enhanced thermal stability and electrolyte uptake.
- The coin-type half-cells display excellent C-rate capacity and cyclability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 20 December 2014

Received in revised form

7 April 2015

Accepted 30 April 2015

Available online 15 May 2015

Keywords:

Lithium-ion battery

Separator

Gel polymer electrolyte

Poly(methyl methacrylate) nanoparticle

Poly(vinylidene fluoride-co-

hexafluoropropylene)

Polypropylene nonwoven

ABSTRACT

In this work, two kinds of composite separators are prepared and used for lithium-ion batteries, which are a PP nonwoven/PVdF-HFP/PMMA blending-type composite separator (CS) and a sandwich-like PP nonwoven/PVdF-HFP composite separator with the introduction of PMMA nanoparticles on the surface (nano-CS). The morphology, electrolyte uptake, ionic conductivity and electrochemical properties of the separators are studied by SEM analysis, impedance measurements, charge–discharge cycle and C-rate tests, respectively. The nano-CS and CS(0.2) exhibit similar properties in electrolyte uptake (212% and 202%, respectively) and porosity (77.9% and 75.3%, respectively). Nonetheless, nano-CS shows enhanced thermal stability and higher ionic conductivity compared with CS(0.2) and commercial PP nonwoven/PVdF-HFP separators. Meanwhile, the LiFePO₄/Li half-cell assembled with nano-CS displays the best C-rate capacity and cyclability especially at the high discharge current rate, indicating that the nano-CS separator is a kind of promising candidate for the high-performance lithium-ion batteries.

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1. Introduction

Rechargeable lithium-ion batteries (LIBs) have been considered as one of the most promising energy storage devices for modern

portable electronics, hybrid electrical vehicles since their initial commercialization by the Sony Corporation in 1991 [1–3]. As an essential part of LIBs, separators play an important role to prevent physical contact of the anode and cathode whereas allowing the free transport of ions. Currently, microporous polyolefin (polyethylene and polypropylene) membranes are widely used in LIBs due to their suitable chemical stability, mechanical strength and low cost [4–6]. However, several intrinsic factors severely restrict

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the electrochemical performance of LIBs, such as low electrolyte uptakes, poor thermal stability, as well as the insufficient wettability and high cell resistance derived from large difference of polarity between the extremely polar liquid electrolyte and the nonpolar polyolefin separators. Therefore, the development of new separators with better properties has become significantly important for constructing high-performance rechargeable LIBs.

Gel polymer electrolytes (GPEs), which are fabricated by adsorbing a large amount of liquid electrolytes in polymer matrices, have received increasing attention because of some attractive properties, such as higher ionic conductivity than solid polymer electrolytes, better safety performance than conventional liquid electrolytes, wide electrochemical window and good thermal stability [7–9]. Moreover, compared with commercial polyolefin separators, it is easy for the separators with polar segments to attract and retain liquid electrolyte because they possess three-dimensional structures. Some typical matrices used in GPEs are poly(ethylene oxide) (PEO) [10,11], poly(methyl methacrylate) (PMMA) [12], poly(vinylidene fluoride) (PVdF) [13,14], poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) [15–17], biocompatible cellulose [18–20], as well as the glass fiber mat [21,22]. Among them, PVdF and its copolymers (PVdF-HFP and PVdF-TrFE) exhibit favorable properties including high polarity, electron-withdrawing fluorine atoms in the backbone structure, and good chemical inertness and stability [23]. PVdF-HFP has low degree of crystallinity due to the addition of hexafluoropropylene (HFP), high mechanical flexibility and good compatibility with respect to liquid electrolytes.

However, there are also some drawbacks of these GPEs to be resolved, such as non-ideal ionic conductivity, poor mechanical strength, large thermal shrinkage and unstable C-rate performance, which have prevented their wide practical applications [24–27]. Extensive efforts have been developed to overcome these limitations. For example, various kinds of composite separators were fabricated by mixing functional ingredients with the supporting matrices, such as inorganic nanoparticles (SiO_2 , TiO_2 , Al_2O_3 , and Sm_2O_3 , etc.) [26–30], and polyborate [31,32]. It has also been found that the introduction of some functional groups onto the surfaces of polyolefins or non-woven fabrics before coating modification could enhance the compatibility between substrates and support materials and finally to improve the electrolyte uptake [30,33,34]. Furthermore, researchers have reported that the addition of PMMA could greatly improve ionic conductivity by raising the electrolyte uptakes because of the similar chemical structure (carbonyl group) between PMMA and the solvents of organic liquid electrolyte (such as ethylene carbonate, dimethyl carbonate and propylene carbonate) [35–37]. Lee et al. have fabricated nanoporous composite separators by introducing PMMA nanoparticle arrays (nano-PMMA) onto a PET nonwoven or PE support [38,39]. They found that well-connected interstitial voids were formed between nanoparticles with low curvature and strong capillary action, which could greatly contribute to the improvement of C-rate performance. In addition, the rigid nano-PMMA coating could enhance the thermal stability of composite separators in some extents.

Herein, we have prepared two kinds of composite separators based on PP nonwoven and PVdF-HFP, one is a blending-type composite separator (CS) with PMMA solution, and the other is a sandwich-like composite separator (nano-CS) with the introduction of PMMA nanoparticles on the surface. We investigated the structure change before and after the addition of PMMA in PVdF-HFP membrane and its effect on the electrochemical properties of $\text{LiFePO}_4/\text{Li}$ half-cells assembled with these separators, such as ionic conductivity, C-rate capability and cycle performance. It was found that the sandwich-like structure with PMMA nanoparticles coating would obviously improve the properties of separators including

thermal stability, ionic conductivity, as well as the electrochemical performance.

2. Experimental

2.1. Materials and chemicals

MMA (Sigma–Aldrich) was purified by distillation under reduced pressure before use. PP nonwoven fabrics (Changxing Tianchuan Nonwovens, $\rho = 9 \text{ g/m}^2$), poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP, Solvay), polymethyl methacrylate (PMMA, Sigma–Aldrich, $\bar{M}_w = 120,000 \text{ g mol}^{-1}$), LiFePO_4 (Heolo Technology) and lithium tablet (China Energy Lithium) were used as received. The liquid electrolyte solution consisting of 1.0 M LiPF_6 in ethylene carbonate (EC) and diethyl carbonate (DMC) (1:1, v/v) was purchased from Zhangjiagang Guotai-Huarong New Chemical Materials. Other reagents were reagent grade and used as received from Shanghai Sinopharm Chemical Reagent.

2.2. Fabrication of the composite separators

PMMA nanoparticles ($\bar{D}_z = 190 \text{ nm}$, size PDI = 0.098) were prepared by emulsifier-free emulsion polymerization according to a previously reported method [40]. To prepare the composite separator, PP nonwoven fabrics were dip-coated in the homogeneous coating solution for 2 min. The solution was prepared by dissolving PVdF-HFP (5.0 g) and various amounts of PMMA (0.56, 1.25, 2.14, 3.33 and 5.0 g, respectively) in a mixed solvent of DMF (5.0 g) and acetone (45.0 g). The composite separator was then dried at ambient temperature for 30 min, followed by drying under vacuum at 60 °C for 12 h. For simplicity, the composite separators were abbreviated as CS(0.1), CS(0.2), CS(0.3), CS(0.4) and CS(0.5), respectively, in which the number in the bracket means the percentage of PMMA used above.

For the fabrication of PMMA nanoparticles-coated composite polymer separator (nano-CS), PP nonwoven fabrics were first dip-coated in the homogeneous solution for 2 min, which was prepared by dissolving PVdF-HFP (5.0 g) in a mixed solvent of DMF (5.0 g) and acetone (45.0 g). After drying at ambient temperature for 30 min and under vacuum at 60 °C for 12 h, PP nonwoven fabrics supported PVdF-HFP was then immersed into the PMMA colloidal solution (the solid content is 10 wt% in deionized water), followed by vacuum drying at 80 °C for 12 h to obtain nano-CS.

2.3. Physical characterizations

The surface morphologies of separators were investigated using a scanning electron microscope (SEM, S-4700, Hitachi). The stress–strain tests of dry separators were conducted at room temperature by using a universal testing instrument (WDW-100, Shenzhen QQL Test Instrument) with a crosshead speed of 1 mm min^{-1} . The samples were cut into a rectangular type (50 mm length \times 10 mm width \times 0.10 mm thickness) for testing. The specimens with a gauge length of 30 mm were carefully mounted in the instrument.

The porosities of the separators were determined by a weighing method. The weights of separators were measured before (W_0) and after (W_t) being immersed in n-butanol for 2 h, respectively. The porosity of the membrane was calculated by Eq. (1):

$$\text{Porosity (\%)} = \frac{W_t - W_0}{\rho V} \times 100 \quad (1)$$

where ρ is the density of n-butanol and V is the volume of separator.

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