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TiO_2 ceramic-grafted polyethylene separators for enhanced thermostability and electrochemical performance of lithium-ion batteries

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ABSTRACT

The separator is one of the most critically important components of lithium-ion battery to ensure battery safety. Herein, we introduce a novel TiO_2 ceramic-grafted polyethylene (TiO_2-grafted PE) separator prepared by electron beam radiation. The TiO_2-grafted PE separator displays similar thickness and pore structure to the bare PE separator. Moreover, The TiO_2-grafted PE separator exhibits not only stronger dimensional thermal stability (a shrinkage ratio of only 36% even at 150 °C), but also better electrochemical performance than the bare PE separator. Therefore, the TiO_2-grafted PE separator is greatly beneficial for constructing safer lithium-ion batteries.

1. Introduction

Lithium-ion batteries (LIBs) have demonstrated successful applications in a variety of portable electronic devices and are considered as one of the most promising candidates for electric vehicles and renewable power stations, due to their high energy and power density, minimal memory effects, and environmental friendliness [1,2]. However, the safety concern arising from the low thermal tolerance of the electrodes and electrolyte prevented the market acceptance of the LIBs in transportation applications. Once LIBs are subjected to extreme conditions, such as external or internal short-circuiting, overcharging, high-temperature thermal impacting, etc, these side-reactions may be triggered and subsequently accelerated with the temperature increasing through a dangerous positive feedback mechanism, producing excessive heat within a very short time, melting the separator and thus leading to thermal runaway, cell cracking, fire or even explosion [3]. In this regard, the separator plays an important role in determining not only the battery performance but also the safety [4,5].

Currently, most commercially employed separators for LIBs are based on polyolefin membranes, specifically microporous polyethylene (PE) or/and polypropylene (PP) separators. However, they may cause the safety issues because of their low thermal stability [6,7]. Especially for applications of these separators in LIBs for electric vehicles, excessive heating should cause enormous dimensional shrinkage of the separator due to its melting, leading to an internal short circuit between the electrodes and consequently triggering thermal runaway reactions. To conquer these drawbacks of polymer-based separators, an effective strategy is to coat them with ceramic particles by using polymer as the binder [8,9]. Ceramic-coated separators display excellent thermal stability, negligible shrinkage at high temperatures and excellent electrolyte wettability due to the high thermostability and hydrophilicity of ceramic materials [4,10]. A small amount of ceramic particles such as SiO_2 [11–13], Al_2O_3 [14,15] and TiO_2 [16] have been introduced to coat onto the surface of the polymer to obtain the ceramic-coated separators. For instance, Yang et al. evaluated that a core–shell structured SiO_2–PMMA sub-microspheres coated PE separator exhibited better thermal stability and improved cycle performance [13]. Lee et al. developed a PDA/Al_2O_3-coated PE separator which demonstrated superior thermal stability and cell performance [17]. Though the resultant separators exhibit good thermal stability and excellent wettability to liquid electrolytes, their increased thickness and partially blocked pores by modification of the ceramic nanoparticles impede their applications especially in high-energy and high-power systems. On the other hand, the insufficient binding between the nanoparticles and separator should cause particle shedding to lead to the alleviation of the thermal stability [8,18].

Induced graft polymerization of monomers by electron beam

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radiation is a simple and effective method to modify the structure and properties of polymer materials, because the high intensity of electron beams can produce free radicals to uniformly initiate grafting in fast rate [19–22]. In this work, we report a novel TiO_2 ceramic-grafted PE (TiO_2-grafted PE) separator prepared by electron beam radiation technique. The TiO_2-grafted PE separator exhibits not only similar thickness and pore structure to the bare separator, but also stronger dimensional thermal stability. In addition, the $LiFePO_4$ cathode and graphite anode using TiO_2-grafted PE separators show better electrochemical performance than those with bare PE separators.

2. Experimental

2.1. Preparation of the TiO_2-grafted PE separator

The PE separator (SKLiBS, SK Energy) with 8 μm thickness was washed with ethanol and dried at 60 °C prior to use. The PE separator was immersed in isopropyl trioleyl titanate (IPTT, supplied by Nanjing Upchemical Co. Ltd, Nanjing, China) and then radiated by an electron beam with doses of 80 kGy (1 Gy=1 J kg^{-1}) at the dose rate of 20 kGy/pass at room temperature by a 1 MeV electron accelerator (Wasik Associates, USA). After grafting, the IPTT-grafted separator was immersed in the ethanol solution containing 0.12 mol/L tetrabutyl titanate, 0.05 mol/L hydrochloric acid, 0.5 mol/L water and 0.03 mol/L acetylacetone at 70 °C for 4 h to obtain the TiO_2-grafted PE separator. Finally, the TiO_2-grafted PE separator was cleaned with ethanol and dried at 60 °C before use.

2.2. Characterizations

The surface functionalities of the separators were analyzed by FT-IR spectroscopy (Nicolet 6700) at room temperature in the wavenumber range of 4000–400 cm^{-1}. Contact angles were determined by the sessile drop method with distilled water (2 μL) as a probe liquid on a Dataphysics OCA20 CA system at room temperature. The morphology and microstructure were characterized by a field emission scanning electron microscope (FE-SEM, ZEISS Merlin Compact VP, Germany). Surface element analysis was conducted using energy dispersive X-ray spectroscopy (EDS, Oxford Instruments Link ISIS).The mechanical intensity was measured at room temperature at a speed of 5 mm min^{-1} on a universal testing machine (CMT 6503, Shenzhen SANS Test Machine, Shenzhen, China) according to ISO 527-3, 1995 (E). Thermal analysis of the separators was carried out on a DSC Q200 system of TA Instrument in a temperature range of 60–180 °C at a heating rate of 10 °C/min under a N_2 atmosphere. The thermal shrinkage of the separators was determined by measuring the dimensional changes after storage at 150 °C for 0.5 h. The degree of thermal shrinkage was calculated by using Eq. (1):

$$\text{Shrinkage }(\%) = \frac{W_i - W_f}{W_i} \times 100 \qquad (1)$$

where W_i is the initial area and W_f is the final area of the separator after the storage test.

2.3. Electrochemical measurements

The batteries for ionic conductivities tests of the separators were measured by electrochemical impedance spectroscopy (IM6, Zahner-elektrik, Kronach, Germany). A typical 2016 coin-type test cell was assembled by sandwiching the separator between two stainless steel (SS) electrodes and soaking it into the liquid electrolyte (1 M $LiPF_6$ in EC/DEC/DMC 1:1:1 by volume) for AC impedance measurements. Impedance data were obtained in the frequency range of 10 Hz–100 kHz with an amplitude of 10 mV at room temperature. The ionic conductivity (σ) was calculated using the following Eq. (2):

$$\sigma = \frac{d}{RA} \qquad (2)$$

where d is the thickness of the separator, A is the area of the stainless steel electrode, and R is the bulk electrolyte resistance measured by one AC impedance test.

The electrochemical stability window of the separators was measured by the linear sweep voltammetry (LSV) using a CHI600a electrochemical workstation (Shanghai Chenhua Inc., China). The separator was sandwiched between a steel working electrode and lithium metal counter electrode. The LSV test was carried out at a scan rate of 10 mV s^{-1} over a voltage range 3.0–5.0 V vs. Li^+/Li to check oxidative decomposition.

The battery performance of the separators was examined using 2016 coin-type half-cells. The positive electrode consisted of 80 wt% $LiFePO_4$, 10 wt% of PTFE and 10 wt% of acetylene black and the graphite electrode was composed of 90 wt% graphite, 2 wt% acetylene black and 8 wt/% PTFE. The electrolyte was 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) (1:1:1 v/v/v). The cells were assembled in a high-purity argon-filled glove box with water/oxygen content lower than 1 ppm. The coin cells were cycled galvanostatically on a LAND cycler (Wuhan, China) at room temperature between 3.0 and 4.0 V at 40 mA g^{-1} for $LiFePO_4$ cathode, and 0.01–3.0 V at 100 mA g^{-1} for graphite anode, respectively.

3. Results and discussion

3.1. Surface functionalization process of PE separator

The preparation process of TiO_2-grafted PE separator consists of two steps, including electron beam induced grafting and hydrolysis, as illustrated in Fig. 1. In the electron beam radiation process,

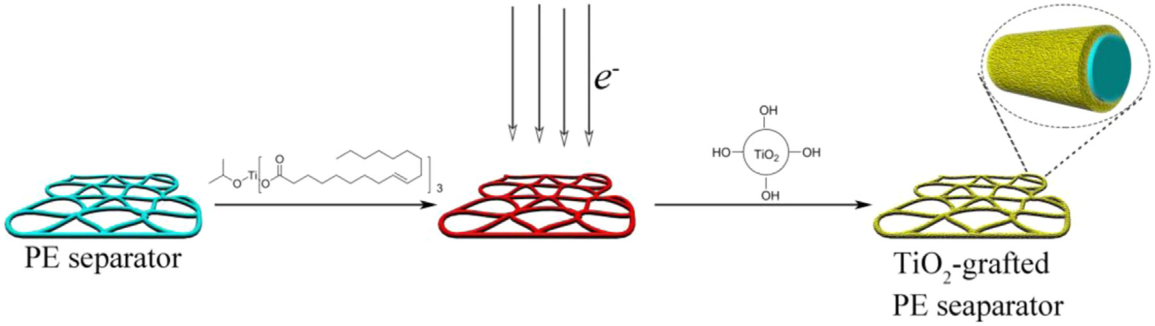

Fig. 1. The preparation process of the TiO_2-grafted PE separator.