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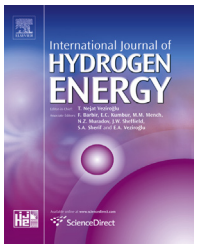

Composite melt-blown nonwoven fabrics with large pore size as Li-ion battery separator

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ABSTRACT

A kind of composite melt-blown nonwoven fabric with larger pore size compared to commercial microporous polyolefin-based separators was prepared in order to improve the cell performance and safety of Li-ion batteries at high C-rate. Heavy-weight melt-blown nonwoven fabrics were directly assembled into coin-type Li-ion batteries. Then light-weight melt-blown nonwoven fabrics were chosen as the substrate and the coating process with a series of concentrations of nano-SiO_2 and polyvinylidene fluoride (PVDF) was studied. The pore size and distribution, porosity, electrolyte absorption capacity, wettability and thermal dimensional stability of the composite melt-blown nonwoven fabrics were measured. Finally, the cell performances of Li-ion batteries assembled with composite nonwoven fabrics were tested in comparison with the microporous polyolefin-based separator. It is found that the composite nonwoven fabrics had higher electrolyte absorption capacity, better wettability and thermal dimensional stability than the polyolefin separator. The composite nonwoven fabrics demonstrated higher discharging capacities and better cycling performance. In addition, Li-ion batteries assembled with composite nonwoven fabrics showed better C-rate performance than that of the polyolefin separator.

Introduction

Secondary rechargeable Li-ion batteries appeal to many users because they can offer high specific energy, high energy density, long cycle lifetime and high operational voltage, etc. [1]. A basic Li-ion battery consists of three components including the positive and negative electrodes sandwiching a separator, all of which are saturated with a liquid electrolyte [2]. The separator is a kind of porous materials placed between positive and negative electrodes. Its primary function is to keep the electrodes apart to prevent electrical short circuits and at the same time allow rapid transport of ion [3]. The separator is one of the main factors affecting the charge and discharge process and safety of Li-ion batteries. The microporous polyolefin membranes are the most widely used Li-ion battery separators, which attributes to their thin thickness, small pore size and good electrochemical stability [4]. But the heat-resistant properties of polyolefin are not good enough which limits its use in motive power batteries because of

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safety problems. In addition, the small pore size, relatively low porosity and poor wettability with polar liquid electrolyte restrict the cell performance [5].

Among numerous approaches to overcome these shortcomings of microporous polyolefin-based separators, the use of nonwoven fabrics has drawn great attention owing to their superior thermal properties, large pore size, high porosity, and cost competitiveness [6–8]. Nonwoven fabrics have more choices in the compositions and structure so that the characteristics of separators can be designed to satisfy the needs [9]. Several methods can be used to prepare nonwoven fabrics. Among them, the wet-laid process is the most commonly used method because of its good homogeneity and sufficient mechanical strength [10,11]. Nonwoven separators made of sub-micron sized fibers by wet-laid nonwoven process have been developed and tested in Li-ion batteries. They exhibited good dimensional stability at elevated temperature as well as high effective ionic conductivities [1,11]. In addition, electrospinning is widely used to prepare Li-ion battery separators in laboratories [12,13]. But it currently has several limitations, especially its low output and weak fiber strength.

Besides wet-laid process and electrospinning, melt-blown nonwoven fabrics are produced by melting polymers and extruding the melt through spinning nozzles. Ultrafine fibers with diameter less than 5 μm are achieved [14], allowing to produce thinner fabrics with lighter basic weight.

As we know, one of the most important parameters to be improved is the possible (dis)charge current rate in order to push Li-ion batteries towards large-scale applications, especially plug-in hybrid electric vehicles [15]. In principle, the cell capacity mainly relies on the type and structure of the electrodes. However, many researchers have found that the structure of separators also plays an important role in determining the measured cell performance since the separator structure affects the ion transportation between the electrodes, which is critically important in determining the cell kinetics [16]. Pore size is a key factor of Li-ion battery separator. Undersize pore will decrease Li-ion transmission rate. A relatively large pore size is necessary for low ionic resistance, which can result in good charge/discharge acceptance at high C-rate [17]. However, in order to suppress the self-discharge and internal short circuits of batteries, separators must have sufficiently small pore size and narrow pore size distribution [18]. The average pore size of traditional polyolefin-based membranes is normally in the range of 0.03 μm–0.1 μm. Most of the pore size of reported modified Li-ion battery separators are less than 1 μm [19,20]. It is questioned that if separators with larger pore size than 1 μm can be used as Li-ion battery separator and exhibit better cell performance.

In this study, heavy-weight melt-blown nonwoven fabrics were directly assembled into Li-ion batteries in order to testify that separator with larger pore size than 1 μm can be used as Li-ion battery separator. Then light-weight melt-blown nonwoven fabric was chosen as the substrate in order to decrease the thickness and increase the energy density of Li-ion batteries. The substrate was further coated with nanoparticles in order to further decrease its pore size. Finally, the cell performances of composite nonwoven fabrics were measured in comparison with the microporous polyolefin-based separator.

Experimental

Preparation of nano-SiO_2 coated melt-blown nonwoven fabrics

Silica nanoparticles (nano-SiO_2, with average particle size of 100 nm, Jing Rui New Materials Co., Ltd) was mixed with acetone (analytical reagent, Shanghai Ling Feng Chemical Reagents Co., Ltd.) with a series of contents of 4%, 6%, and 8%, respectively. The mixture was stirred for 2 h by using a JB50-S motor stirrer in a venting cupboard. A kind of melt-blown nonwoven fabric with size of 20 cm × 30 cm was soaked into the slurry for 1 min. Then it was taken out and stayed in the venting cupboard for 9 min. The process was repeated four times. Finally, the nonwoven fabric was dipped into polyvinylidene fluoride (PVDF)/acetone solution (PVDF 21216, Solvay Co.), followed by drying in a hot-oven at 60 °C for 6 h. Finally, the nano-SiO_2 coated composite nonwoven fabrics with different contents of SiO_2 and PVDF were obtained.

Electrodes preparation and coin-type cell assembly

CR 2025-type Li-ion cells were prepared in order to evaluate the electrochemical performance of different types of separators. The cells were assembled with $LiCoO_2$ as the cathode, lithium metal foil as the anode, and 1 M $LiPF_6$ in EC/DMC/EMC 1:1:1 (v/v) (Zhangjiagang Guotai Huarong Chemical New Materials Co. Ltd.) as the electrolyte. The $LiCoO_2$ type cathode was prepared by blending $LiCoO_2$ as active material with black carbon as electronic conductor and poly(vinylidene fluoride) as binder in the ratio of 93.5: 4: 2.5 *wt.%*.

Characterization

Pore size and pore size distribution of samples were tested by using a capillary flow porometer (Porometer 3G, Quantachrome Instruments). SwiftED3000 scanning electronic microscopy (SEM) (Hitachi Ltd.) was used to observe the surface of composite nonwoven fabrics. Contact angle was measured by using OCA15EC video-based contact angle measuring device (Dataphysics, Germany).

Porosity

Thickness and weight of a sample with size of 50 mm × 50 mm was measured. Then it was kept in methyl silicone oil for 3 min. Extra methyl silicone oil on the surface of the sample was wiped with a piece of filter paper and then it was weighed again. The porosity of the sample is calculated according to equation (1).

$$\varepsilon = \frac{V_1}{V} \times 100\% \quad (1)$$

Where ε is the porosity of the sample, 100%; V_1 is the volume of methyl silicone oil (the density is 0.96 g/cm^3), mm^3; V is the volume of the sample, mm^3.

Electrolyte absorption

A sample with diameter of 19 mm was weighed and then soaked in the electrolyte (1 M $LiPF_6$ in EC/DMC/EMC 1:1:1) for