

Surface modification of polyolefin separators for lithium ion batteries to reduce thermal shrinkage without thickness increase

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Abstract

Surface chemical modification of polyolefin separators for lithium ion batteries is attempted to reduce the thermal shrinkage, which is important for the battery energy density. In this study, we grafted organic/inorganic hybrid crosslinked networks on the separators, simply by grafting polymerization and condensation reaction. The considerable silicon-oxygen crosslinked heat-resistance networks are responsible for the reduced thermal shrinkage. The strong chemical bonds between networks and separators promise enough mechanical support even at high temperature. The shrinkage at 150 °C for 30 min in the mechanical direction was 38.6% and 4.6% for the pristine and present graft-modified separators, respectively. Meanwhile, the grafting organic-inorganic hybrid crosslink networks mainly occupied part of void in the internal pores of the separators, so the thicknesses of the graft-modified separators were similar with the pristine one. The half cells prepared with the modified separators exhibited almost identical electrochemical properties to those with the commercial separators, thus proving that, in order to enhance the thermal stability of lithium ion battery, this kind of grafting-modified separators may be a better alternative to conventional silica nanoparticle layers-coated polyolefin separators.

Key words

thermal shrinkage; organic/inorganic hybrid crosslinked network; chemical grafting; separator; lithium ion battery

1. Introduction

Due to the advantages in high-energy capability, high-power density, cost competitiveness, long life cycle and little memory effect, lithium-ion batteries (LIBs) are widely used for various portable electric vehicles and energy storage systems [1–5]. However, the safety issues have become more critical in preventing widespread use of LIBs as power battery [6–8].

Internal short-circuit is believed to be the most critical threat in securing battery safety, while the separator, which should maintain electronic isolation between cathode and anode, is now responsible for the internal short circuits during thermal evolution [9–11]. Most of the separators currently used in LIBs are commonly manufactured from series of polyolefin, such as polyethylene (PE) or polypropylene

(PP), which could offer excellent mechanical strength, proper porosity, easy processing and chemical/electrochemical stability to cells. However, they exhibit large shrinkage at high temperature (140 or 150 °C) [12–14], which causes internal shorting and thermal runaway when cells are exposed to abnormal conditions such as overcharge or overheating. This problem is fatal for large-scale application of LIBs as power battery. To overcome this drawback, in general, lots of efforts have been invested to improve the thermal stability of polyolefin separators focusing on silica nanoparticle coating [15–18], which still suffers from generating spatially inhomogeneous Li ion fluxes caused by nanoparticle aggregation [19], thus increasing several micrometers thickness and pulverization phenomenon due to weak physical interaction between particles and separators [19,20].

In this study, we try to improve the thermal stability of

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commercial polyolefin separators by organic/inorganic hybrid crosslinked network via chemical grafted. Due to the presence of the robust heat-resistant silicon-oxygen crosslinked networks grafted on the surface, the modified separators exhibit good thermal stability and sufficient adhesion, which could avoid the conventional silica nanoparticle detaching from separators during cells assembling processes. It is noteworthy that hybrid crosslinked network is spatial homogeneous system, which could avoid the inhomogeneous ionic fluxes during cell charging/discharging processes.

Meanwhile, the grafting organic-inorganic hybrid crosslink networks here mainly occupied part of space in the internal pores of the separators, so the thicknesses of the graft-modified separators were similar with the pristine one. However, previous ceramic nanoparticle coating method would bring an increasement of thickness. Saving several micrometers thickness could avoid a very serious issue for high capacity cell. The thinner separators take up less space, permit the use of longer electrodes and decrease internal resistance [21]. Therefore, this kind of modified separators could overcome the large shortcoming of previous approaches with ceramic particles coating. Using these organic/inorganic hybrid separators, we assembled half cells, and their rate capacities and charge-discharge cycling data were evaluated in details.

2. Experimental

2.1. Chemicals and materials

Celgard-2300 separators were purchased from Celgard Company. 3-(triethoxysilyl)propyl methacrylate (TEPM) was dried over calcium hydride for 24 h at room temperature and distilled before use. Tetraethylorthosilicate (TEOS), hydrochloric acid (HCl), toluene, benzoyl peroxide (BPO) and other reagents were used as received without further purification.

2.2. Preparation of Celgard-PTEPM

Celgard-2300 microporous separators were first immersed into the acetone solution of BPO (2.5 wt%) for 1 h. Then, the separators were taken out and left to evaporate the solvent slowly at room temperature. After impregnating with the aqueous solution of TEPM (1 vol%) for 2 h at 90 °C, the microporous separators were washed by acetone in an ultrasonic bath for three times. The final product (Celgard-PTEPM) was dried under vacuum over night.

2.3. Preparation of Celgard-SiO₂

The as-obtained product, Celgard-PTEPM, was exposed to HCl atmosphere for about 24 h and then dried under vacuum at 60 °C for 12 h. Finally, the organic/inorganic hybrid separators (Celgard-SiO₂) were obtained.

2.4. Preparation of Celgard-SiO₂-TEOS

The as-obtained product, Celgard-PTEPM, was immersed into the toluene solution of TEOS (10 wt%, 20 wt% and 30 wt%) for 1 h. Then, the separators were taken out and left to evaporate the solvent slowly at room temperature. After being exposed to HCl atmosphere for about 24 h, the separators obtained above were washed by distilled water and acetone in an ultrasonic bath for three times. The final products (Celgard-SiO₂-TEOS-10%, Celgard-SiO₂-TEOS-20% and Celgard-SiO₂-TEOS-30%) were dried under vacuum over night.

2.5. Thermal shrinkage measurement

The thermal shrinkage of separators was evaluated by measuring one-dimensional length changes in the axial and transverse directions after being kept at different temperature for 30 min. The degree of thermal shrinkage was calculated according to the following equation: Thermal shrinkage (%) = $(L_b - L_a)/L_b \times 100\%$ (L_b and L_a represent the side lengths of the squares before and after being kept in high temperature storage, respectively). Experiments were done in triplicate under each condition.

2.6. Electrical measurement

85 wt% of LiCoO₂ materials were mixed uniformly with 5 wt% acetylene black, 5 wt% conductive graphite and 5 wt% polyvinylidene fluoride (PVdF), using N-methyl-2-pyrrolidone (NMP) as the dispersant, and then the mixture was coated onto aluminum foil, dried and compressed, finally resulting into cathode electrodes. The cells (lithium sheets as the anode and ethylene carbonate (EC)/diethyl carbonate (DEC) (1 : 1, v/v) with 1.0 mol/L lithium hexafluorophosphate (LiPF₆) as electrolyte) were assembled in a glove box with water and oxygen content below 20 ppm. The cyclability of charge and discharge performances of the cells was tested with LAND cyler at 0.2 C between 2.75 V and 4.2 V at room temperature. The C-rate capabilities were evaluated by varying different current densities (from 0.1 C to 8 C) between 2.75 V and 4.2 V at room temperature.

Ionic conductivities of separators were measured by preparing cells, where separators immersing with electrolyte were sandwiched between stainless steel blocking electrodes. The ionic conductivities were calculated according to the following equation, $\sigma = l/(R \times S)$, where l was the thickness of the separator, S was the area of stainless steel blocking electrodes and bulk resistance (R) was measured by AC impedance technique. AC impedance measurements were conducted at room temperature using the electrochemical workstation. The frequency range and voltage amplitude were set from 100 kHz to 1 Hz and at 10 mV, respectively.

3. Results and discussion

In order to get well-defined separator grafting with or-

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