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The functional separator coated with core–shell structured silica–poly (methyl methacrylate) sub-microspheres for lithium-ion batteries

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ABSTRACT

To improve the safety of lithium-ion batteries (LIBs), a functional ceramic-coated separator (FCC separator) is developed by coating core–shell structured silica–poly(methyl methacrylate) (SiO_2–PMMA) sub-microspheres on one side of a conventional porous polyethylene (PE) separator. The FCC separator possesses multi-functional properties of better separator thermostability and higher electrolyte stability by combining the advantages of both the ceramic-coated separator and the gel polymer electrolyte (GPE). The heat-resistant SiO_2 core particles effectively protect the FCC separator from thermal shrinkage. Meanwhile, the PMMA shells form a gel after swelling and activation by the liquid electrolyte, which endows the FCC separator with the functional properties of the GPE to stabilize the electrolyte. As a result, the FCC separator shows considerable wettability for the liquid electrolyte and outstanding electrolyte retention ability at elevated temperature. Moreover, the FCC separator with the coating layer improves the safety performance of cells by preventing cells from experiencing internal short circuits at high temperature. Meanwhile, the cells assembled with such separators demonstrate superior cycle performance and C-rate capability. Therefore, the FCC separator provides LIBs with greater security and better electrochemical performance.

1. Introduction

Lithium-ion batteries (LIBs) have been widely used in portable electronic devices and are considered to be the most competitive power source for hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs), pure electric vehicles (PEVs) and the storage of wind, solar and tidal energy in smart grids [1,2]. However, despite providing high-energy-density storage, LIBs have been seriously plagued by safety issues [3]. The safety performance of LIBs, closely related to both the thermal behavior of the separators and the stability of the electrolytes, is considered one of the most important factors in these application fields [3–5].

In LIBs, the separator plays the key role of maintaining electrical isolation between electrodes of opposite polarity while allowing free ionic transport [4,6–8]. Currently, micro-porous membranes based on polyethylene (PE), polypropylene (PP), and various combinations of the two materials are mainly used as separators for commercial LIBs due to their suitable pore size, excellent mechanical strength and chemical stability. Nevertheless, their low thermostability at high temperature, which induces internal short circuits between electrodes, results in the thermal runaway of the batteries and eventually leads to safety issues, such as risk of fire or explosion. Furthermore, the large difference in polarity between the non-polar polyolefin separators and the polar organic liquid electrolytes leads to poor wettability [4,8,9].

Many studies have attempted to overcome the abovementioned problems by modifying commercial micro-porous separators using such approaches as radiation-induced graft polymerization [10,11], surface-initiated atom transfer radical polymerization (ATRP) [12], polymer-coating [13,14] and ceramic-coating [9,15–17]. Among these approaches, the application of ceramic-coated separators has been proved to be a particularly promising method. Ceramic powders, such as Al_2O_3, SiO_2 and TiO_2, are usually coated on one or both sides of the separators due to their effectiveness in preventing the thermal shrinkage and mechanical breakdown of the separators [15–17]. However, the safety of LIBs relates to not only the thermal behavior of separators but also the stability of the electrolytes, as the organic liquid electrolytes may leak, produce combustible gases and then catch fire or explode under abnormal abuse conditions [3–5]. Therefore, a safer and more reliable electrolyte system is urgently needed.

Solid polymer electrolytes (SPEs), despite providing enhanced safety, are far from being ready for application due to their poor

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ambient-temperature conductivity. Midway between SPEs and liquid electrolytes are the conceptual “hybrid polymer” electrolytes, leading to so-called GPEs [4]. Gel is a particular state of matter that simultaneously possesses both the cohesive properties of solids and the diffusive transport properties of liquids [18]. This unique characteristic allows GPEs to exhibit such virtues as high ionic conductivity, a wide electrochemical window, good compatibility with electrodes and superior electrolyte retention ability [12,18–22]. Most importantly, the GPEs have such advantages as the elimination of leakage problems and the reduction of combustible reactions of electrolytes. However, the most prominent drawback of GPEs is their poor mechanical strength [4,12,20].

Extensive efforts have been made to improve the safety of LIBs by either modifying separators or stabilizing electrolytes [9–17,19,21,22]. To overcome the safety issue of LIBs in the context of separators and electrolytes, we focused on modified separators combining the functional properties of ceramic-coated separators and GPEs. In the present work, a core–shell structured SiO_2–PMMA sub-microsphere was designed, prepared and coated on one side of a conventional porous PE separator to form a functional ceramic-coated separator (FCC separator). In the separator produced, the porous PE separator acted as a skeleton, providing mechanical strength, and the heat-resistant SiO_2 core particles retained the dimensional stability and markedly suppressed the thermal shrinkage. Meanwhile, the PMMA shells displayed the following three merits: (i) the polymer, PMMA, exhibited considerable wettability for organic liquid electrolyte due to the higher affinity of the carbonyl group toward carbonate solvents, such as ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) [12]; (ii) after swelling and activation by the liquid electrolyte, the PMMA shells became a gel and then exhibited some characteristics of GPEs; and (iii) the PMMA gel-shells absorbed and retained the liquid electrolyte effectively, preventing the leakage of the liquid electrolyte and slowing the emission of combustible solvents at high temperature. The effect of the coating layer on the safety performance of the cells was discussed, and the cycle performance and C-rate capability of the cells with the FCC separator were investigated.

2. Experimental

2.1. Synthesis of core–shell structured SiO_2–PMMA sub-microspheres

The SiO_2 core particles were prepared in ethanol according to the Stöber method [23] and then grafted with the silane coupling agent, methacryloxypropyltrimethoxysilane (KH-570, Qufu Huarong Chemical New Materials Co., Ltd.) in the solution over 8 h under vigorous machine stirring at 25 °C. After centrifuging and washing with deionized water, the grafted SiO_2 core particles were obtained by drying under vacuum at 50 °C for 12 h.

The core–shell structured SiO_2–PMMA sub-microspheres were synthesized by soap-free emulsion polymerization [24] via the synthetic scheme shown in Fig. 1. In a typical experiment, 1.00 g of grafted SiO_2 core particles were dispersed in 100 mL of deionized water by ultrasonication in a four-neck flask, and 0.05 g of potassium persulfate (KPS) as the initiator and 3.00 g of MMA as the monomer were also added to the flask with mechanical stirring. The polymerization was carried out in an atmosphere of argon for 6 h at 80 °C. The core–shell structured SiO_2–PMMA sub-microspheres were then dried under vacuum at 50 °C for 12 h after several cycles of centrifugation and dispersion with deionized water.

2.2. Preparation of the FCC separator

The slurry was prepared by mixing core–shell structured SiO_2–PMMA sub-microspheres, styrene–butadiene rubber (SBR) and carboxymethyl cellulose (CMC) into water/ethanol (5 ml/5 ml) mixed solvent, where the weight of SiO_2–PMMA sub-microspheres/SBR/CMC was fixed at 0.95 g/0.03 g/0.02 g. After 30 min of ultrasonic dispersion, the slurry was uniformly mixed by magnetic stirring for 5 h. A PE separator (thickness = 20 μm, Asahi Kasei Corp.) manufactured by a wet process was chosen as the coating substrate. The as-prepared slurry was coated on one side of the PE separator by an automatic film coating machine (Shanghai Environmental Engineering Technology Co., Ltd.). The prepared separator was then dried in a vacuum oven at 60 °C for 12 h to obtain the FCC separator.

2.3. Electrodes preparation and coin cells assembly

The cathode was prepared by coating the N-methylpyrrolidine (NMP)-based slurry containing 90 wt% Li_2MnO_4, 1 wt% graphite, 4 wt% super-P and 5 wt% PVDF on aluminum foil and drying at 80 °C for 12 h in a vacuum oven. A cell was assembled in a 2016 coin cell by sandwiching a separator between a Li_2MnO_4 cathode and a lithium-metal anode and then injecting a certain amount of the liquid electrolyte, 1 M $LiPF_6$ in EC/DEC/DMC (1:1:1 by volume, Zhangjiagang Guotaihuarong New Chemical Materials Co., Ltd.). All cells were assembled in a glove box (M. Braun GmbH) filled with argon gas.

2.4. Characterization of the separators

The morphologies of the SiO_2 core particles and core–shell structured SiO_2–PMMA sub-microspheres were examined using a field emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Ltd.) and a field emission transmission electron microscope (FE-TEM, JEM-1400, JEOL, Ltd.). The surface and cross-sectional morphologies of the PE separator and the FCC separator were examined by FE-SEM. All samples were sputtered with platinum prior to FE-SEM measurement. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet IS5 spectrometer (Thermo Fisher Scientific Inc.) in the range of 400–4000 cm^{-1} with KBr powder-pressed pellets. The thermal shrinkage of the separator was determined by measuring the dimensional change (area-based, 4 cm × 4 cm) after heat treatment at 130 °C for 0.5 h, and the shrinkage was computed based on

$$\text{Thermal shrinkage} \quad (\%) = (S_0 - S)/S_0 \times 100\% \tag{1}$$

where S_0 and S are the areas of the separator before and after heat treatment, respectively. The wetting behavior was measured using photographs obtained immediately after dropping the liquid

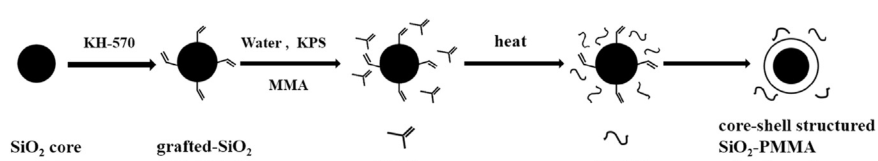

Fig. 1. Synthetic scheme of the core–shell structured SiO_2–PMMA sub-microspheres.