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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) (SiO₂-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 SiO₂ 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.

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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.

http://dx.doi.org/10.1016/j.memsci.2014.09.047 0376-7388/© 2014 Elsevier B.V. All rights reserved. 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 Al₂O₃, SiO₂ and TiO₂, 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 SiO₂-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 SiO₂ 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 gelshells 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 SiO₂-PMMA sub-microspheres

The SiO₂ 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 SiO₂ 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 submicrospheres 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 SiO₂– PMMA sub-microspheres, styrene–butadiene rubber (SBR) and carboxymethyl cellulose (CMC) into water/ethanol (5 ml/5 ml) mixed solvent, where the weight of SiO₂–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 μ m, 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 SiO₂ core particles and core–shell structured SiO₂–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 \times 4 cm) after heat treatment at 130 °C for 0.5 h, and the shrinkage was computed based on

Thermal shrinkage
$$(\%) = (S_0 - S)/S_0 \times 100\%$$
 (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 SiO₂-PMMA sub-microspheres.

electrolyte onto the surface of the separator. The contact angle was measured by a contact angle goniometer (Powereach JC2000C1, Shanghai Zhongchen Digital Technique Equipment Co., Ltd.). As per the usual procedure, a drop of electrolyte was deposited onto the surface of the separator, and a photograph of the contact angle was taken immediately in 1 s. And then the data was got after the analysis of the photograph. The electrolyte uptake was calculated as

Electrolyte uptake
$$\% = (W - W_0)/W_0 \times 100\%$$
 (2)

where W_0 is the net weight of the separator, and W is the weight of the separator after saturation with the liquid electrolyte. The ionic conductivity was measured by electrochemical impedance spectroscopy (EIS) in a blocking-type cell fabricated by sandwiching a separator between two stainless steel electrodes. Impedance data were obtained with an electrochemical working station (AutoLab, Sino-Metrohm Technology Ltd.) in the frequency range of 1 Hz–100 kHz. The ionic conductivity was calculated using

$$\sigma = L/(R_{\rm b} \times A) \tag{3}$$

where σ is the ionic conductivity, R_b is the bulk resistance, L is the thickness of the separator and A is the area of the stainless steel electrode (because the area of the separator is larger than that of the steel electrode). The electrolyte retention ability of the separator was studied by thermogravimetry (TG) and derivative thermogravimetry (DTG) using a Model STA 449 instrument (NETZSCH Machinery and Instruments Co., Ltd.). Typically, 4.0 mg of the separator was soaked in the electrolyte and saturated with the liquid electrolyte beforehand. The electrolyte-filled separator was placed in an alumina crucible, and an empty alumina crucible was used as a reference. The TG curve and DTG curve were recorded between 50 °C and 200 °C at a heating rate of 2 K/min under argon atmosphere.

To compare the safety performance of cells assembled with the PE separator and the FCC separator, pouch cells were assembled by sandwiching the separators between Li_2MnO_4 cathodes and graphite anodes. The cells were charged to 4.2 V at room temperature and then placed in a vacuum oven for measurement of the open circuit voltage (OCV) at 130 °C using an electrochemical working station (AutoLab, Sino-Metrohm Technology Ltd.) by monitoring the OCV of the cells as a function of time. To investigate the cycle performance, the coin cells were cycled with a battery testing system (LAND-V34, Wuhan LAND Electronics Co., Ltd.) under the following regime. The cells were charged at a current density of 1.0 C up to a target voltage of 4.3 V and then charged at constant voltage until the charge current reached 10% of the initial current (called the CCCV charge). Second, the cells were discharged to

a cut-off voltage of 3.0 V at the same current density (called the CC discharge). The cells were charged to 4.3 V at current rates of 0.5 C, 1.0 C, 2.0 C and 5.0 C and discharged at current rates ranging from 0.5 C to 5.0 C to investigate the C-rate capability.

3. Results and discussion

 SiO_2 core particles and core-shell structured SiO_2 -PMMA submicrospheres were synthesized. Fig. 2a and b presents the SEM micrographs of these materials. The SiO_2 core particles are nearly monodisperse and have a uniform spherical shape with an average particle size of 260 nm. The core-shell structured SiO_2 -PMMA sub-microspheres, which were synthesized using the monodisperse SiO_2 core particles, also exhibit a monodisperse size distribution and have a uniform spherical shape with an average diameter of 340 nm.

The diameters of the SiO₂ core particles and the core-shell structured SiO₂-PMMA sub-microspheres measured from the TEM micrographs (Fig. 3) are consistent with the SEM micrographs. Every SiO₂-PMMA sub-microsphere exhibits a very uniform core-shell morphology with a PMMA shell (light area) with an average thickness of 40 nm surrounding a SiO₂ core particle (dark area), and each sub-microsphere contains only one core. Moreover, there is no color contrast in the TEM micrographs of SiO₂ core particles. This result indicates that the SiO₂ core particles are well encapsulated by the PMMA shells with a uniform thickness.

The abovementioned result is also supported by the FT-IR spectra shown in Fig. 4. The spectrum of the core–shell structured SiO_2 –PMMA sub-microspheres shows a sharp peak at 1731 cm⁻¹ corresponding to the stretching vibration of the C=O group, and the peaks at 2950 and 2998 cm⁻¹ are ascribed to the stretching vibration of the methyl and methylene groups of PMMA [24]. These peaks indicate that the SiO₂ core particles have been well doped in the PMMA shells.

The surface morphologies of the PE separator and the FCC separator were investigated, and the SEM micrographs are presented in Fig. 5a and b. The PE separator exhibits a uniform submicron porous structure. Concerning the FCC separator, the sub-microspheres are homogeneously distributed in the surface layer without agglomeration. Highly connected interstitial voids form between the ceramic powder particles, affording a well-developed porous structure, which is expected to be filled with the liquid electrolyte and provide a facile pathway for ion movement in addition to improving the wettability of the separator [9,15,25]. The cross-sectional morphology shown in Fig. 5c reveals that



Fig. 2. SEM micrographs of (a) the SiO₂ core particles and (b) the core-shell structured SiO₂-PMMA sub-microspheres.



Fig. 3. TEM micrographs of (a) the SiO₂ core particles and (c) the core-shell structured SiO₂-PMMA sub-microspheres. Magnified TEM micrographs of (b) a single SiO₂ core particle and (d) a single core-shell structured SiO₂-PMMA sub-microsphere.



Fig. 4. FT-IR spectra of SiO_2 core particles and core-shell structured SiO_2 -PMMA sub-microspheres.

core–shell structured SiO₂–PMMA sub–microspheres are deposited uniformly and that the coating layer is approximately 5- μ m thick, which is relatively thin for coatings obtained using a laboratory technique [9,14–16,19,25]. Using industry techniques, the thickness of the coating layer could be decreased to 3 μ m and even thinner. As thinner separators take up less space and permit the inclusion of a larger volume of active materials in the cells, the cell capacity can be increased by making the separators thinner [4,13].

As is well known, the thermostability of the separators plays a vital role in preventing internal short circuits between the electrodes when the batteries are exposed to high temperature, which is especially important for the large-scale LIBs being developed for electric vehicles and energy storage systems [9]. However, the PE separator has a melting point of approximately 135 °C and easily loses dimensional stability upon exposure to high temperatures above 100 °C [4,25]. Fig. 6 shows that the FCC separator (12.9%) suppressed the thermal shrinkage to a markedly greater extent than the PE separator (31.4%). This improvement could be ascribed to the introduction of the frame structure of the core-shell structured SiO₂-PMMA sub-microspheres, more specifically the heat-resistant SiO₂ core particles [9,15]. In addition, because the elastomeric SBR possesses higher flexibility, stronger binding force and higher heat resistance, the high-heat-resistance SBR-CMC mixture used as a binder also contributes to the improved properties [26,27].

The wettability of the separators is also essential for battery performance because a separator with good wettability can retain the liquid electrolytes easily and quickly while also effectively facilitating ion transport between electrodes [4,8]. However, the inherent hydrophobic property of polyolefin-based separators often leads to poor wettability and poor electrolyte retention for liquid electrolytes containing polar solvents [28]. As a result, separators cannot be wetted quickly and completely in liquid



Fig. 5. SEM micrographs of the surface of (a) the PE separator, (b) the FCC separator and (c) the cross-section of the FCC separator.



Fig. 6. Photograph of (a) the PE separator and (b) the FCC separator after being held at 130 $^\circ\text{C}$ for 30 min.

electrolytes, creating problems in the fluid injection process and limiting the performance of batteries [4]. Therefore, it is urgent to enhance the wettability of the separators.

We compared the liquid electrolyte wetting behavior by photographing the liquid electrolyte immediately after dropping it onto the separator. Fig. 7 clearly shows that the FCC separator is much more effective in wetting the liquid electrolyte than the PE separator. The wettability of the separator is also evaluated by the liquid electrolyte contact angle. Generally, a smaller contact angle corresponds to a higher affinity [12]. As shown in Fig. 8, the contact angle of the PE separator is 32.8° but only 6.1° for the FCC separator. This change shows that the affinity between the separator and the liquid electrolyte is markedly enhanced. This enhancement is attributed to two factors. The first is the porous structure of the coating layer, which allows the liquid electrolyte to infiltrate through the well-connected interstitial voids, possibly driven by the capillary force [25]. The second is that the PMMA shells have a higher affinity to the liquid electrolyte due to the similarity of the chemical structures (carbonyl group) of the PMMA and the solvents (EC, DMC and DEC) [14].

The electrolyte uptake is another indicator of the wettability of separators and is summarized in Table 1. The FCC separator leads to a higher electrolyte uptake (89.5%) than the PE separator (57.7%). For the PE separator, the liquid electrolyte is mostly located in the pores, and the electrolyte uptake is basically proportional to the porosity. For the FCC separator, the liquid electrolyte is stored in both the pores of the PE separator and the interstitial voids between the sub-microspheres and the swelled PMMA shells [12]. All of the above generally improve the uptake of the liquid electrolyte.

In our experiment, the ionic conductivity of the FCC separator $(1.08 \times 10^{-3} \, {\rm S} \, {\rm cm}^{-1})$ is higher than that of the PE separator $(7.80 \times 10^{-4} \, {\rm S} \, {\rm cm}^{-1})$. The ionic conductivity increases with the electrolyte uptake due to the availability of more Li⁺ ions for conduction in the same volume [9,29]. For the FCC separator, although a coating layer thickens the separator, the simultaneous improvement of the electrolyte uptake results in a slightly higher ionic conductivity.



Fig. 7. Photographs of the liquid electrolyte wetting behavior of (a) the PE separator and (b) the FCC separator.



Fig. 8. Contact angle photographs of (a) the PE separator and (b) the FCC separator.

Table 1	
Physical properties of the PE separator and the FCC separator.	

	PE separator	FCC separator
Thickness (µm)	20	25
Thermal shrinkage (%)	31.4	12.9
Contact angle (°)	32.8	6.1
Electrolyte uptake (%)	57.7	89.5
Ionic conductivity (S cm^{-1})	$7.80 imes 10^{-4}$	1.08×10^{-3}

The electrolyte retention ability of separators is crucial for the safety of LIBs [19]. The TG curves of the PE separator and the FCC separator saturated with the liquid electrolyte are shown in Fig. 9. When the temperature reaches 113.4 °C, the evaporable solvents in the electrolyte in the PE separator disappear completely. In the case of the FCC separator, the solvent component remains at 135.8 °C, and the evaporation rate (weight loss rate) is much slower than that in the case of the PE separator. The DTG curves show that the maximum evaporation rate of the PE separator is 2.73% min⁻¹ at 109.1 °C, whereas that of the FCC separator is 2.29% min⁻¹ at 128.3 °C. Due to their similar chemical structure (carbonyl group) to the solvents (EC, DMC and DEC), the PMMA shells enhance the interaction between the FCC separator and the liquid electrolyte [12,30]. Meanwhile, after swelling and activation by the liquid electrolyte, the PMMA shells form a gel and exhibit some characteristics of GPEs, such as enhanced stability of the



Fig. 9. TG curves and DTG curves of the PE separator and the FCC separator with the liquid electrolyte.

liquid electrolyte entrapped in the PMMA gel-shells. This enhanced stability prevents the leakage of the electrolyte and slows the emission of the solvents in the electrolyte at high temperature [12].

The solvents used in LIBs are typically volatile, which creates the serious risk of the cells catching fire or exploding due to the combustible hot electrolyte vapors [5]. This also suggests that the loss of solvent at high temperature may lead to failure in the electrode/electrolyte contact as well as reduction of the ionic conductivity [30]. As the temperature rises, the lower evaporation rate of the electrolyte in the FCC separator will slow the emission of combustible solvents. This functional property of the separator is expected to provide LIBs with greater safety and good electrochemical performance due to their outstanding electrolyte retention ability at high temperature.

To further study the safety performance of cells assembled with the PE separator and the FCC separator, the OCV of pouch cells at 130 °C was measured. As shown in Fig. 10, the OCV curve of the cell based on the PE separator drops sharply close to 0.0 V after approximately 23 min because of an internal short circuit resulting from the thermal shrinkage of the PE separator at high temperature. In contrast, the cell assembled with the FCC separator operates well even after 40 min, as the FCC separator maintains its dimensional stability and prevents the cell from experiencing an internal short circuit. Combining the features of high dimensional stability, which protects the cells from internal short circuits, and good electrolyte retention ability, which slows the emission of combustible solvents, this FCC separator is expected to be attractive for battery systems requiring high safety.

Fig. 11 compares the cycle performance of coin cells assembled with different separators as a function of the cycle number. The initial discharge capacity of the cell containing the FCC separator is slightly higher due to the improved ionic conductivity after coating with the core–shell structured SiO_2 –PMMA sub-microspheres. The discharge capacity of the coin cell containing the PE separator is 94.6% of its initial capacity after 100 cycles compared to 95.4% in the case of the FCC separator. The discharge capacity retention of the cells with different separators is almost the same, indicating that the presence of an additional coating layer has no visible negative impact on the cycle performance of cells.

The discharge capacities of the cells fabricated with different separators are compared in Fig. 12. It is notable that the discharge capacity of the cell assembled with the FCC separator is higher in all C-rate tests. The better C-rate capability of the cell with the FCC separator relative to the cell with the PE separator could be ascribed to the former's improved ionic conductivity and superior electrolyte retention ability. These results strongly suggest that the FCC separator can be used to produce LIBs with better electrochemical performance by improving the cycle performance and the C-rate capability.



Fig. 10. OCV curves of pouch cells assembled with the PE separator and the FCC separator.



Fig. 11. Cycle performance of coin cells assembled with the PE separator and the FCC separator (1.0 C CC and CV charge, 1.0 C CC discharge, cut-off of 3.0–4.3 V).



Fig. 12. C-rate capability of coin cells assembled with the PE separator and the FCC separator.

4. Conclusions

Core-shell structured SiO₂-PMMA microspheres have been successfully prepared and coated on one side of a conventional porous PE separator to form an FCC separator. The multi-functional separator, combining the advantages of both the ceramic-coated separator and the GPE, exhibits functional properties of better separator thermostability and higher electrolyte stability. In addition to substantial improvements in the thermal shrinkage, liquid electrolyte wettability, ionic conductivity and electrolyte retention ability, it significantly enhances the safety performance of the cells. The coin cells assembled with the separator exhibit improved cycle performance and C-rate capability. Thus, ceramic-coated separators with new functions and features can be obtained by introducing different polymer materials into ceramic powders and then using the ceramic powders in the design of cell components while controlling the morphology of the ceramic powders and polymer materials. These separators have the potential to provide large-scale LIBs with better electrochemical performance and higher safety for application in electric vehicles and energy storage systems.

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