



# Effect of a thin ceramic-coating layer on thermal and electrochemical properties of polyethylene separator for lithium-ion batteries



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## HIGHLIGHTS

- CMC–SBR is used as mixed binder to prepare ceramic-coating separator.
- Only 5% in weight of CMC–SBR is needed to form the coating slurry.
- The solvent water is environment friendly.
- Punch cells with ceramic-coating separator present excellent properties.

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## ABSTRACT

In this paper, a new kind of ceramic-coating separator for lithium-ion batteries is successfully prepared by forming a ceramic layer consisted of Al<sub>2</sub>O<sub>3</sub> powder, carboxymethyl cellulose (CMC) and styrene-butadiene rubber (SBR) mix binder onto one side of pristine PE separator. During the preparation of the separator, water is used as solvent and a very small amount of SBR–CMC mixture is applied as binder to obtain better thermal stability. The effect of thickness of the ceramic-coating layer on its thermal stability, physical properties and electrochemical performance is also investigated. The results clearly showed that the ceramic-coating separator with SBR–CMC binder has wonderful thermal stability, good wettability and high uptake of liquid electrolyte. Pouch cell tests with the ceramic-coating separator also show excellent stable cycle performance.

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## 1. Introduction

Lithium-ion batteries have been widely used in portable consumer electronics due to the high energy density and particularly good cycle life [1]. Furthermore, lithium-ion batteries are also regarded as one of the most promising power sources for electric vehicles (EVs) and storage of new energy in a smart grid [2]. In most commercialized lithium-ion batteries, polyolefin porous membranes, specifically polyethylene (PE) and polypropylene (PP), have been used as separators which prevent physical contact of the positive and negative electrodes while permitting free ionic transport within the cell. Although such membranes offer some

advantages as excellent mechanical strength and chemical stability, they exhibit large thermal shrinkage at high temperature [3], which could cause a short circuit between electrodes in cases of some inevitable occurrence of hazardous behaviors, such as electrical overcharging and high thermal impact. This shrinkage and resulted short circuit usually induces the thermal runaway of LIBs, which could eventually lead to fire or explosion of the cells. A shutdown separator composed by multilayer polyolefin as PP/PE/PP is commonly used as a fail-safe device in commercial cells to prevent this problem [4]. Multilayer separators offer advantages by combining the lower melting temperature of PE with the high-temperature strength of PP. As the temperature approaches the melting point of PE (~130 °C), the porosity in the separator collapses, so that cells fail as the ion conduction is cut off. But if the temperature continues to increasing above the melting point of PP (~160 °C), the separator could fail in separating the electrodes, thereby result in internal shorting of the cell potentially [5].

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Therefore, a separator that does not shrink or melt at elevated temperatures becomes desirable.

The application of composite separators, which are prepared by using binders to coating the organic materials, inorganic materials or organic-inorganic mix materials on the surface of the polyolefin separators, is an effective method for improving the safe performance of the LIBs [6–10]. Among them, the ceramic-coating separator draws considerable attention as it combined characteristics of polymeric separator and heat resistant inorganic powder.  $\text{Al}_2\text{O}_3$  [9,11,12] and  $\text{SiO}_2$  [13,14] were usually used as the inorganic powder, while polymethyl methacrylate (PMMA) [6], polyvinylidene fluoride (PVDF) [12], polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) [13,14] and other polymers [11] were used as the binder in ceramic-coating separator. However, such binders cannot meet the requirement for safety of the battery due to their high shrinkage. In addition, most binders are readily swollen, gelled, or even dissolved in non-aqueous liquid electrolytes to form viscous fluid or gel polymer electrolyte, which results in desquamation of coating layer from the separator [15]. Furthermore, those binders were usually consumed more than 20% in weight to form the coating layer [9,11].

In this paper, a kind of ceramic-coating separator (CCS) for lithium-ion battery was developed.  $\text{Al}_2\text{O}_3$  and PE separator and a water-soluble binder composed of carboxymethyl cellulose (CMC), styrene-butadiene rubber (SBR) were applied as the coating substrate, inorganic powder and binder respectively. SBR–CMC mixture binder is not only a high adhesion agent but also a strong dispersion medium [16,17], which favors the uniform distribution of  $\text{Al}_2\text{O}_3$  particle. Compared to other polymer binders such as PVDF, only 5% in weight of SBR–CMC is needed to form the coating slurry and as the solvent, water is friendly for environment. The effect of thickness of the ceramic-coating layer was also carefully studied. The CCS membrane with SBR–CMC binder shows wonderful thermal stability, better wettability and higher uptake of liquid electrolyte. Pouch cell tests with CCS membrane also show better stable cycle performance.

## 2. Experiments

### 2.1. Preparation of the ceramic coating separators

The slurry for ceramic-coating layer was prepared by mixing  $\text{Al}_2\text{O}_3$  particle (Average particle size = 400 nm, Taimei Chemicals, Japan), SBR and CMC (Guangzhou Songbai Chemical, China) into water/ethanol (5 ml: 5 ml) mixed solvent, where the weight of  $\text{Al}_2\text{O}_3$ /SBR/CMC was fixed at 0.95 g/0.03 g/0.02 g. After ultrasonically dispersed for 10 min, the slurry was further subjected to vigorous mixing by bead-milling with a speed of 400 r min<sup>-1</sup> for 2 h. A PE separator (thickness = 20  $\mu\text{m}$ , Asahi Kasei, Japan) manufactured by a wet process was chosen as the coating substrate while the coating slurry was applied onto one side of the pristine PE separator by automatic film coating machine (Shanghai Environmental Engineering Technology Co., Ltd, China). The thickness of the coating layer can be accurately controlled by the slit of the applicator. After the coating process, the prepared separator was dried under vacuum line at 60 °C for 6 h to remove the solvent in the coating slurry. The CCS membrane with the coating layer controlled in 3  $\mu\text{m}$ , 6  $\mu\text{m}$ , 9  $\mu\text{m}$  were respectively prepared and referred to as CCS-3, CCS-6 and CCS-9 membrane.

### 2.2. Electrode preparation and cell assembly

The battery performance of the material was tested using pouch cells (7.5 cm × 3 cm × 0.3 cm, 280 mAh). The cathode had a composition of 90wt. %  $\text{LiCoO}_2$  (Hunan Shanshan New Material Co.,

China); 5 wt. % Super-P, 5 wt. % PVDF and anode had a composition of 95 wt. % synthetic graphite (Shanghai Shanshan New Material Co., China) and 5 wt. % PVDF. The *N*-methyl pyrrolidine (NMP)-based cathode slurry was coated on a 15  $\mu\text{m}$  thickness aluminum foil and anode slurry was coated on a 10  $\mu\text{m}$  thickness copper foil then dried at 80 °C overnight in a vacuum drying oven. The prepared CCS membrane and pristine PE separator used as pouch cell's separator, the pristine separator used as reference. The pouch cell was injected the same weight of electrolyte. All cells were assembled in a glove box (Mbraun, Germany) filled with argon gas.

### 2.3. Characterization of the ceramic coating separators

The surface and cross-sectional morphologies of the pristine PE separator and CCS membranes were investigated by using a field emissions scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan), while the membranes were cooled in liquid nitrogen and broken into two parts mechanically, and then the SEM micrographs of the cross-sections were taken. The thermal shrinkage of the ceramic-coating separators was determined by measuring the dimensional change (area based, 4 cm square) after being subjected to heat treatment at various temperatures for 0.5 h and the shrinkage can be computed as the following equation:

$$\text{Shrinkage}(\%) = \frac{S_0 - S}{S_0} \times 100\%$$

where  $S_0$  and  $S$  stand for the area of separator before and after heat treated. The hot punch test was measured by putting the separator 3 mm below the automatic temperature control metal bar (200 °C and 2 mm in diameter) for 1 min. The contact angle measurement of the PE separator and CCS membranes was carried out by using a commercial drop shape analysis system (Powereach JC2000C1, Shanghai Zhongchen Digital Technique Equipment Co. Ltd., China) to ascertain the effect of the coating layer on the wettability of the electrolyte. The electrolyte uptake was computed as following equation:

$$\text{Uptake}(\%) = \frac{W - W_0}{W_0} \times 100\%$$

where  $W_0$  is the net weight of membrane, and  $W$  is the weight of the membrane after absorbing the liquid electrolyte. The ionic conductivity of the CCS membrane with electrolyte was measured by sandwiching the membranes between two stainless steel electrodes. Impedance data were obtained with electrochemical workstation (Solartron, SI-1260, England) over a frequency range of 1 Hz–100 kHz.

Punch cells were assembled by sandwiching the separator between graphite anode and  $\text{LiCoO}_2$  cathode, and then the liquid electrolyte was added. Before the electrochemical tests, the cell was activated by cycling it at 0.1 C rate in a voltage range of 3 V–4.2 V. The charge and discharge cycling tests of the cell were measured at 0.5 C with battery test equipment (LAND-V34, Land Electronic, China). The heating test of the  $\text{LiCoO}_2$ /graphite punch cell which was fully charged to 4.2 V at room temperature was carried out by storing the cells in a drying oven of 130 °C to monitor its OCV changes with electrochemical workstation. To analyze the change of cell and electrode structure during the above mentioned tests, the punch cells were opened in glove box.

## 3. Results and discussion

The top surface scanning electron micrographs of the pristine PE and a series of CCS membranes are shown in Fig. 1. The pristine PE

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