



A high-temperature stable ceramic-coated separator prepared with polyimide binder/ Al_2O_3 particles for lithium-ion batteries

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ABSTRACT

An effective and practical way to develop the lithium-ion power batteries with better safety performance is to increase the thermal shrinkage resistance of the separator at high temperature. In this work, a ceramic coating separator (CCS-PI) is manufactured by coating Al_2O_3 ultrafine powder and thermal stable polyimide binder onto the surface of the porous polyethylene (PE) membrane. CCS-PI exhibits no thermal shrinkage up to 160 °C in dry state and maintains stable when packed inner the cells up to 165 °C. Meanwhile CCS-PI hasn't been punctured during the hot metal rod piercing testing. The above results all prove that the CCS-PI has high thermo-stability. In addition, the CCS-PI presents higher electrolyte uptake, better wettability with the electrolyte and enabled high ionic conductance when it is saturated with liquid electrolyte. The cells with this CCS-PI show good cyclic performance. Therefore, as-prepared CCS-PI is a promising separator to improve thermal safety and capacity retention for lithium-ion power batteries.

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1. Introduction

Recent years, polyethylene (PE) and polypropylene (PP) porous membranes have been used as separators for preparing lithium-ion batteries [1–3]. Those separators manufactured by stretching polymer membrane through a wet or dry process can guarantee the rapid transport of the ionic charge carriers [4], meanwhile, keep the negative and the positive electrodes apart to avoid internal short of the batteries [5–7]. The nonpolar properties of polyolefin membranes prepared with such fabrication methods can offer advantages as excellent chemical stability and mechanical strength, however, they also lead to serious concerns such as weak thermal stability and extremely low wettability with liquid electrolytes [8–11]. The cells with polyolefin membranes would be safe in a normal application environment, but when used in a harsh environment such as high thermal impacting or electrical

overcharging, they could finally result in fire, even explosion of the cells [12,13]. A multilayer polyolefin membrane as PP/PE/PP is used to meet harsh application of the batteries [1]. At temperature over the melting point of porous PE, the thermal current will induce the film shrink, the pore close and the ion transportation stop, thus the PE layer will serve as a fail-safe device in cells [1,14,15]. However, the morphology change of PP at elevated temperature over 160 °C will lead to incomplete isolation between cathode and anode, which will result in internal short-circuit and catastrophic cell failure. Therefore, a separator with excellent thermal stability becomes imperative and desirable.

It has been reported that using composite membrane [9,16–33] is a useful method for enhancing the stability at high temperature of lithium-ion batteries. Among those composite separators, the ceramic-coating separator, which is prepared by coating inorganic materials onto the surface of polyolefin separators, has drawn considerable attention, since it combined the characteristics of membranes with the heat resistant of inorganic powders [34–36]. However, the ceramic-coating separators still expose several intrinsic disadvantages. Firstly, the inorganic powders (oxides as SiO_2 [19] and Al_2O_3 [8,11] etc.) and the polymer binders such as polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) [19,37], polymethyl methacrylate (PMMA) [17,26] and polyvinylidene fluoride (PVDF) have been usually employed in the preparations of ceramic-coated separators. Those ceramic-coated separators suffer

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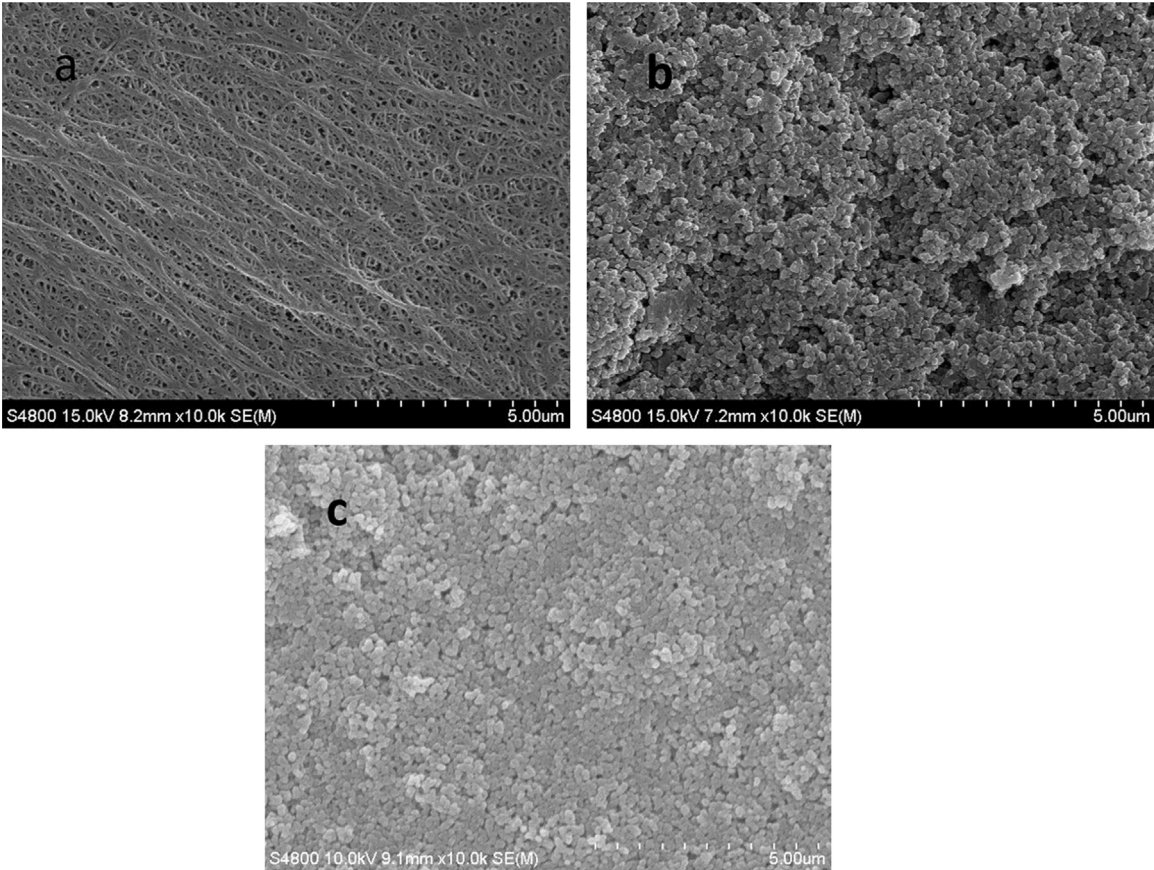


Fig. 1. Surface morphology of: (a) PE separator, (b) CCS-PVDF-HFP, (c) CCS-PI.

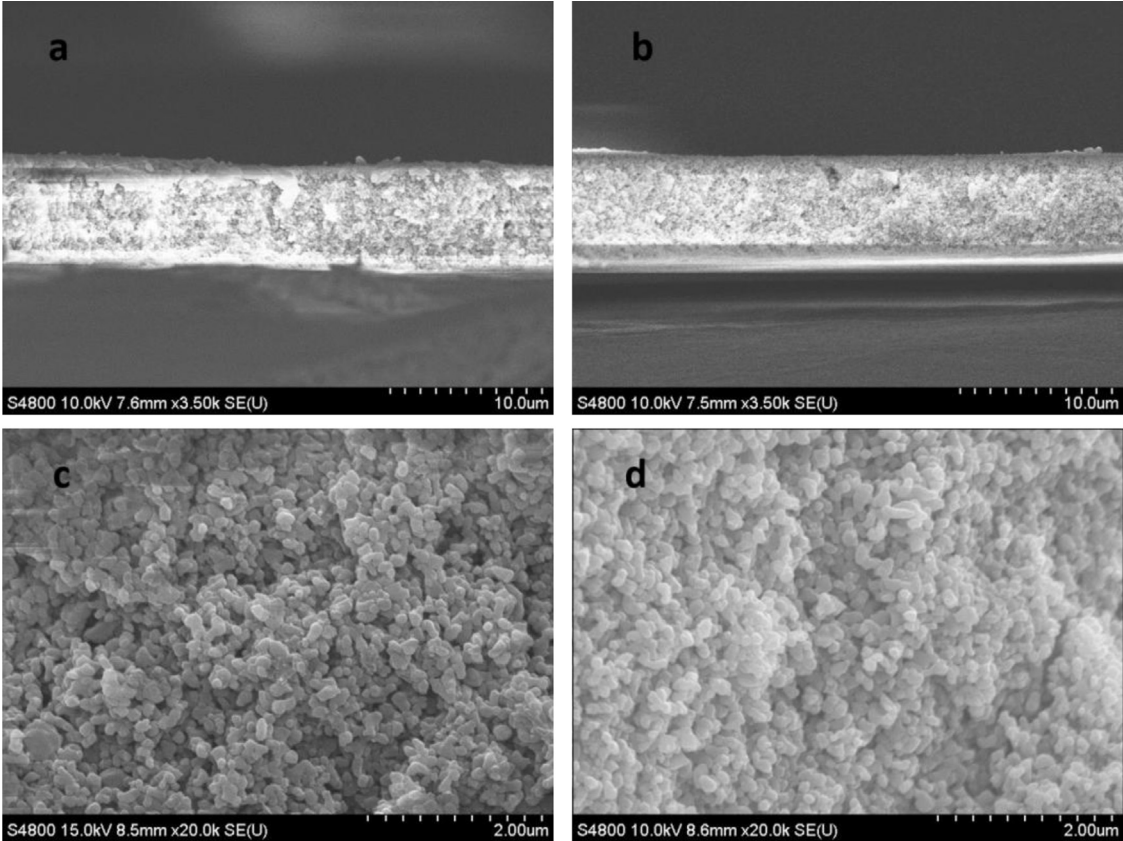


Fig. 2. Cross section morphology of: (a) (c) CCS-PVDF-HFP, (b) (d) CCS-PI.

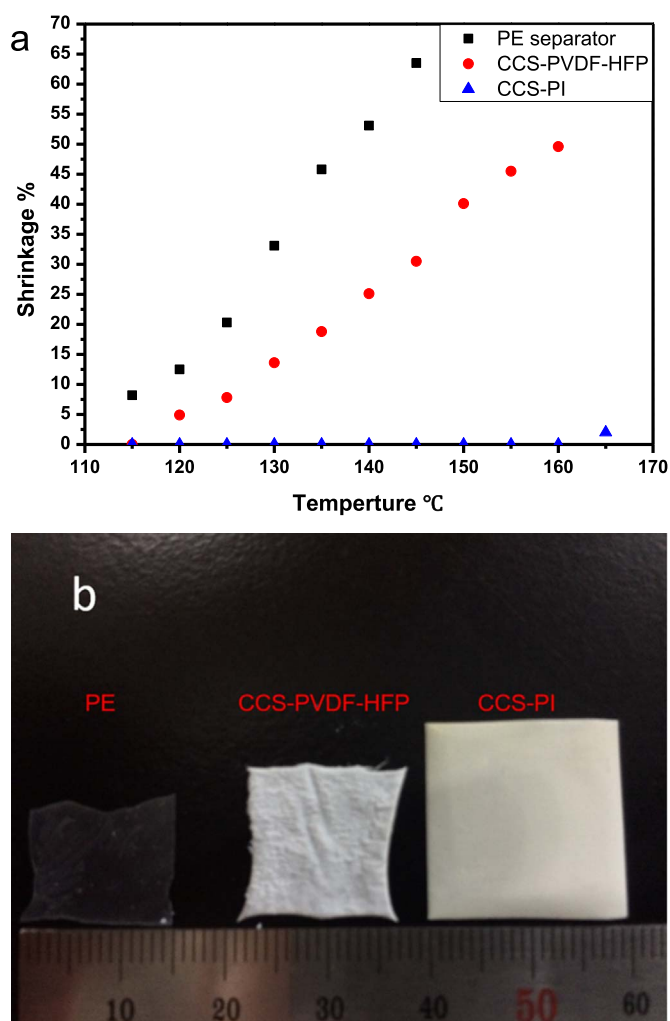


Fig. 3. (a) Thermal shrinkage (%) of PE separator, CCS-PVDF-HFP and CCS-PI. (b) Photograph of the PE separator, CCS-PVDF-HFP and CCS-PI after being held at 140 °C for 30 min.

less thermal shrinkage than the pristine separators, but they still cannot meet the requirements for the safety of batteries because of their high shrinkage at high temperature due to the low melting point of binders [19]. Secondly, the coating layers are easy to desquamate from the porous polyolefin separator because the binders used to form the coating layer are readily swollen and gelled. Thirdly, more than 20% in weight of such binders were used for preparing ceramic coating separator, resulting in high product cost of the separator [37]. Obviously, for solving above-mentioned problems, a kind of for the ceramic coating separators with high temperature thermal stability and non-swelling property in the electrolytes is needed.

In this work, a novel ceramic-coating separator with high thermo stability for lithium-ion batteries has been successfully obtained. The PE separator is used as the coating substrate, and the Al_2O_3 and the PI [14,15,38–41] are used as the inorganic power and binder, respectively. The Al_2O_3 and the PI were coated onto one side of the porous PE separator. It must be point out, in comparison to conventional double-sides coating, one-side coating is a cost efficient design for the industrial application. The practical application shows that ceramic-coating separator prepared with one-side coating also exhibits very good overall performance. Compared with the PVDF-HFP, PMMA and some other binders mentioned above, PI with excellent thermal stability, outstanding mechanical property, high radiation resistance and inertness to

solvents has been widely applied in lots of advanced technology fields. Such CCS-PI exhibits excellent thermal stability, more electrolyte uptake and better wettability with electrolyte. Meanwhile, when saturated with liquid electrolyte, the CCS-PI shows enabled high ionic conductance. The cells with this CCS-PI have showed stable repeated cyclic performance and rate capacity at room temperature.

2. Experiments

2.1. Fabrication of the ceramic coating separators

The PE separator with a thickness of 20 μm (Asahi Kasei, Japan) was used as the coating substrate and the Al_2O_3 particles (Average particle size of 400 nm, Taimei Chemicals, Japan) and PI (Hangzhou Sumengte Chemical, China) at $\text{Al}_2\text{O}_3/\text{PI}$ weight ratio of 9/1 (w/w) into N-methyl pyrrolidone (NMP)/ethanol (4/1, v/v) mixed solvent were prepared as the coating slurry. The resulted slurry, after ultrasonically dispersed for 10 min and vigorous mixed with bead-milling at a speed of 400 rpm for 2 h, was coated onto one side of the porous PE separator by automatic film coating machine (Shanghai Environmental Engineering Technology Co., Ltd, China). As-prepared separators were dried under vacuum at 60 °C [42] overnight to obtain the CCS-PI for the further tests. As contrast, the ceramic coating separator used PVDF-HFP as binder (CCS-PVDF-HFP) was prepared by the similar way of CCS-PI.

2.2. Electrode preparation and cell assembly

Coin cells (2016 type) and punch cells were used for the tests of the batteries performances. For the coin cells: cathode included 90 wt% of LiMn_2O_4 (Qingdao Xinzheng Material Co., Ltd, China), 5 wt% of super-P and 5 wt% of PVDF, and the metal Li was used as the anode. For the pouch cells (7.5 cm \times 3 cm \times 0.3 cm, 280 mgh): cathode included 90 wt% of LiCoO_2 (Hunan Shanshan New Material Co., China), 5 wt% of super-P and 5 wt% of PVDF, and anode included 95 wt% of synthetic graphite and 5 wt% of PVDF. The PE separator: CCS-PVDF-HFP and CCS-PI were used as separators for preparing the cells. Cells after injected the same weight of electrolyte were assembled in argon gas with a glove box (Mbraun, Germany).

2.3. Characterization of the separators

Field emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan) at an acceleration voltage of 15 kV was used for the measurement of the surfaces and cross-sectional morphologies of the porous PE, CCS-PVDF-HFP and CCS-PI separators. The membranes were broken mechanically after cooled in liquid nitrogen, and then the smooth cross-sectional morphologies of the separators were taken. The adhesion strength tests were conducted on a tensile testing machine (SHIMADZU, Japan), for which square membranes with a side length of 1 cm were used.

Square separators with a length of 2 cm sandwiched between two glass plates were subjected to various temperatures from 110 °C to 165 °C for 0.5 h for the heat treatment. The thermal shrinkage of the separator was calculated according to the following equation:

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

where S_0 and S are the areas of the membranes before and after heat-treating test, respectively. An automatic temperature control metal bar with a diameter of 2 mm was used for the hot punch test

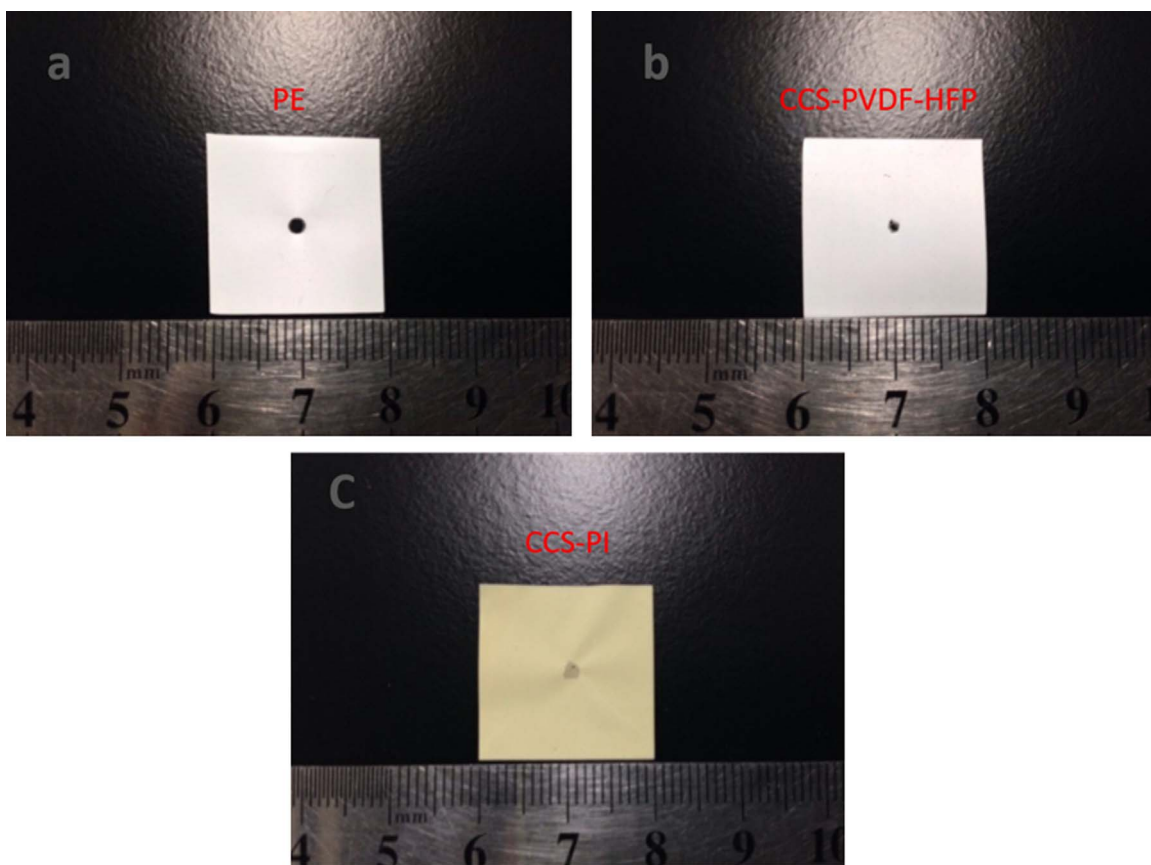


Fig. 4. Hot metal rod piercing (a) PE separator, (b) CCS-PVDF-HFP, (c) CCS-PI.

to further study the thermo stability. Static contact angle of the membranes as one of the indicators for the wettability of the separator with the electrolyte was taken by using a commercial drop shape analysis system (Powereach JC2000C1, Shanghai Zhongchen Digital Technique Equipment Co. Ltd., China). The following equation was used to calculate the electrolyte uptake of the membranes:

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

where W_0 and W are the weights of the membrane before and after absorbing the liquid electrolyte, respectively.

In order to investigate the ionic conductivity (impedance data) of the separator, a blocking-type cells were fabricated by sandwiching the liquid electrolyte-soaked membranes between two stainless steel electrodes, then the impedance data of the cells were measured by electrochemical workstation (Solartron, SI-1260, England) with a frequency range from 1 Hz to 100 kHz. The ionic conductivity can be calculated as the following equation:

$$\sigma(T) = S / (RL), \quad \sigma(T) = \sum n_i q_i \mu_i,$$

where s is the area of the separator, L is the thickness of the separator, R is the resistance of the separator and n_i stands for the number of carrier, q_i stands for the quantity of electric charge and μ_i stands for the ion migration rate.

In order to investigate the change in alternating-current (AC) impedance of cells with cycling. The AC impedance data of the LiMn_2O_4 cells prepared with PE separator and CCS-PI were measured by electrochemical workstation (Solartron, SI-1260, England) with a frequency range from 0.01 Hz to 10 kHz.

The LiCoO_2 /graphite punch cells with different separators were

stored in a drying oven with temperature program at 1°C min^{-1} after fully charged to 4.2 V at room temperature, while monitoring their open circuit voltage (OCV) changes with electrochemical workstation (Solartron, SI-1260, England) to carry out the heating tests of the separator inner the cells. The cells with different separators were prepared to investigate the influence of the separator on the cycle and rate capability with a battery test equipment (LAND-V34, Land Electronic, China). The cyclability tests of the cells under a voltage range between 3 and 4.2 V at a constant current density of 1.0 C and the C-rate performances were carried out at current rates of 0.5 C, 1.0 C, 2.0 C, 4.0 C and 0.5 C.

3. Results and discussion

As a comparison, the surface SEM of PE membrane exhibit the typical morphology of wet process and uniformly interconnected submicron pore structure as shown in Fig. 1a. The Al_2O_3 powders with polymer PVDF-HFP (Fig. 1b) or PI (Fig. 1c) binder are coated onto the PE substrate and the scanning electron micrographs of the CCS-PVDF-HFP and CCS-PI are presented in Fig. 1b and c, respectively. It can be found from Fig. 1b that the ceramic particles interconnected by PVDF-HFP binder present partly agglomeration. In comparison, the CCS-PI shows much less agglomeration on the smooth surface of the ceramic coating layer. The above difference is caused by the fact that the PVDF-HFP is more easily gelled and agglomerated in the process of drying [33,43]. It must be noted that the CCS-PVDF-HFP and CCS-PI are prepared by the same procedures.

The cross-sectional morphologies of the ceramic coating layer with uniformity thickness of about $6\ \mu\text{m}$ are shown in Fig. 2a and

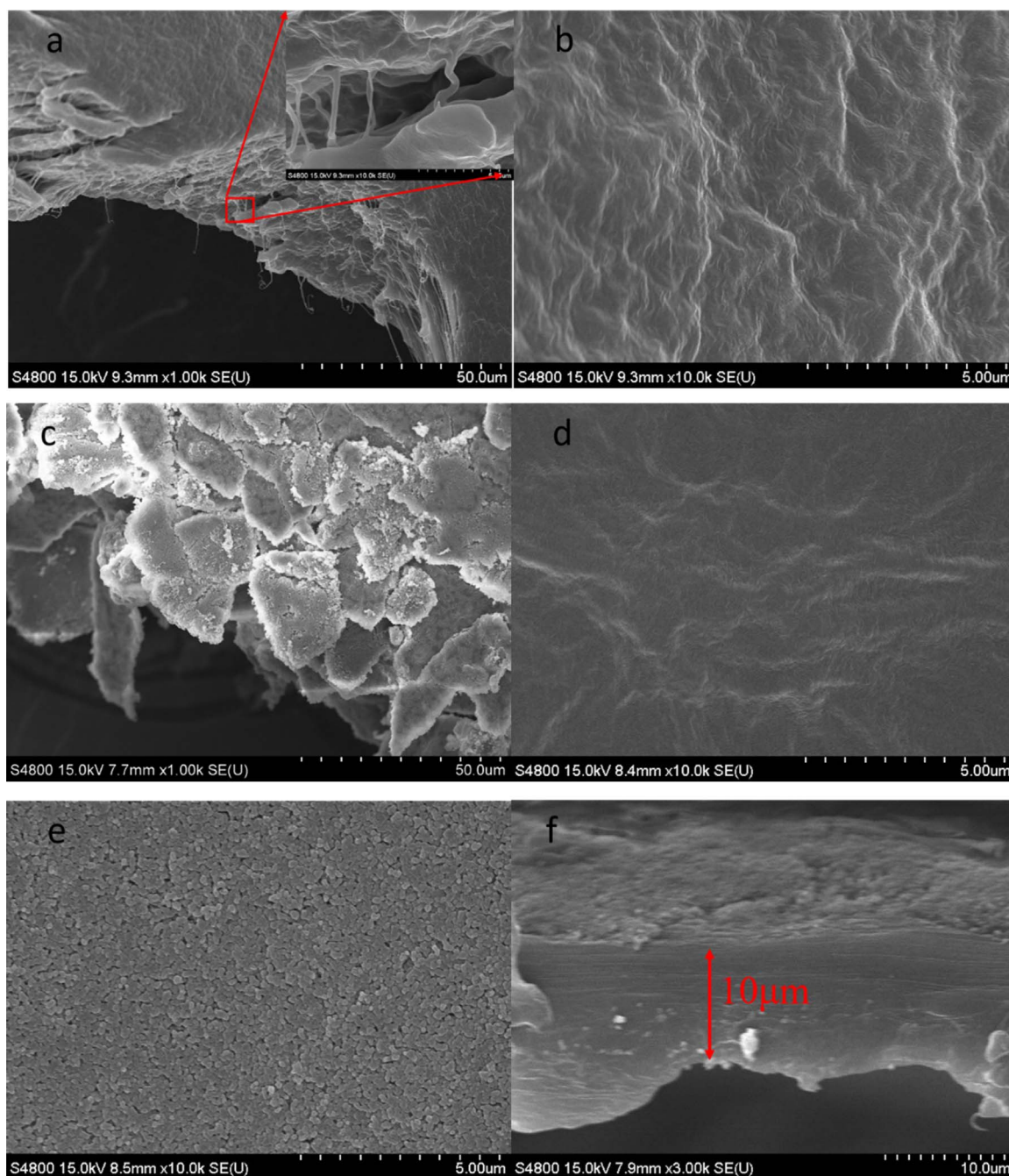


Fig. 5. Morphologies of separators after hot metal rod piercing (a) (b) PE separator, (c) the coating side of CCS-PVDF-HFP, (d) the PE side of CCS-PVDF-HFP, (e) CCS-PI, (f) Cross section of CCS-PI.

b. High magnification cross-sectional SEM images are provided as Fig. 2c and d. The figure exhibits that there are no obvious differences of the microstructure between CCS-PVDF-HFP and CCS-PI. Both smooth surface and uniformity thickness of the coating layer are important requirement and characterization for practical applications of lithium-ion batteries since the separators can form better interface with the electrodes to guarantee sufficient flow of the electrolyte. Moreover, the smooth surface and uniformity thickness of coating layer can guarantee electric current uniformly distribute inner the batteries and further suppress the growth of metal Li. Also, this coating layer with heat-resistant Al_2O_3 inorganic particles and PI binder is expected to prevent the membrane from shrinking under the environment of high temperature, which is particularly important for the large-scale lithium-ion

power batteries designed to meet the requirement of energy storage systems and electric vehicles [1,35]. The porous structures in the ceramic coating layers formed by Al_2O_3 particles are beneficial for improving the wettability with the electrolyte and the electrolyte uptake of the membranes [36].

Adhesion strength between the ceramic coating layer and PE separator was measured and shown in Fig. S1. Adhesion strength of CCS-PI is about 1.2 MPa and CCS-PVDF-HFP is about 0.5 MPa. The adhesion strength between the PE separator and ceramic coating layer with PI binder was higher than the adhesion between the PE separator and ceramic coating layer with PVDF-HFP binder. Ceramic coating layer of CCS-PI is harder to be separated from the PE support layer. The major cause for this end, among others, is the non-uniformity of force caused by the fact that PVDF-

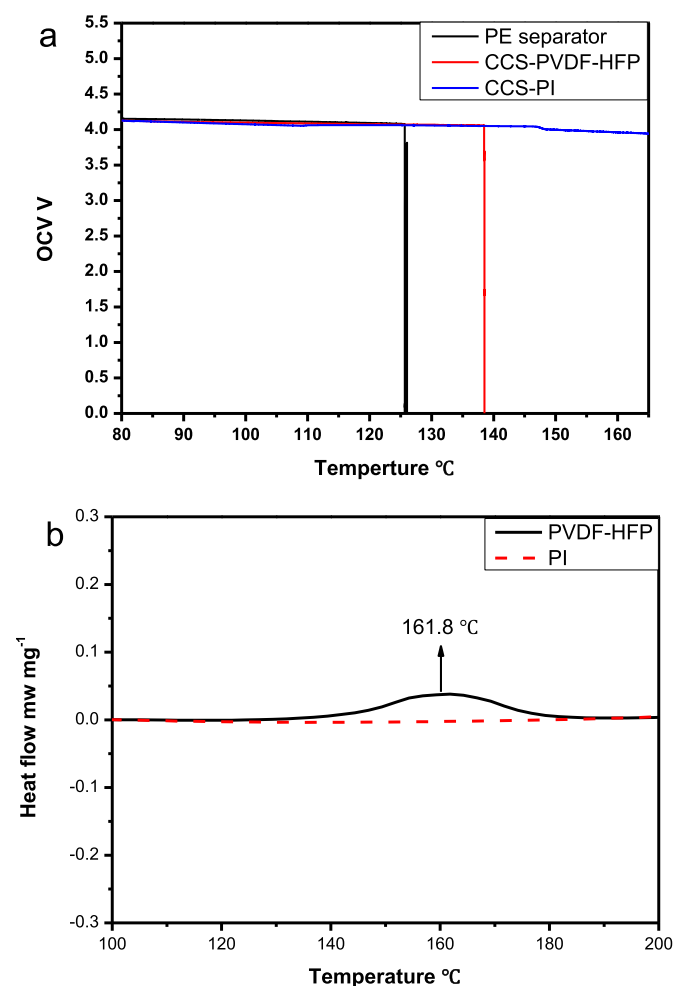


Fig. 6. (a) OCV change of LiCoO₂/graphite cells from 80 °C to 165 °C of PE separator, CCS-PVDF-HFP and CCS-PI. (b) The DSC curve of PVDF-HFP and PI.

HFP is more easily gelled and agglomerated in the process of drying.

The main functions of the separators are to prevent anode and cathode from contacting each other which will lead to electrical short circuits and, meanwhile, have the capacity conducting lithium-ions when soaking electrolyte [4]. Thus, the separators should be stable in the batteries even in cases of some battery related accidents happen. However, the conventional PE and PP membranes fabricated by multiple stretching processes are easily to suffer dimensional change under the environment of high temperatures as they only have a melting point of around 130 °C and 160 °C [1,4], which will lead to thermal run away even combust fire or explosion of the cells assembled with those separators. In order to calculate the thermal shrinkage percent of the membranes at high temperature, the separators were subjected to various temperatures from 110 °C to 165 °C for half an hour and the results are shown in Fig. 3. The separators were sandwiched between two glass plates during the hot testing. So the asymmetric curvature behavior of the separator (prepared with one side coating) during the high-temperature storage test can be suppressed effectively. The PE separator presents thermal shrinkage of more than 8% at 110 °C while there are no area changes for both CCS-PVDF-HFP and CCS-PI separators. In comparison to the PE separator, the ceramic coating separator shows less thermal shrinkage at wider range of temperatures which is due to the application of high heat resistance Al₂O₃ particles in the ceramic coating layer. The picture of PE separator, CCS-PVDF-HFP and CCS-

PI storing at temperature of 140 °C for 30 min is shown in Fig. 3b. From the picture we can find that the PE separator suffered a large percent of thermal shrinkage with the color changed from white to transparent. The CCS-PI remains intact, but as a comparison, the CCS-PVDF-HFP suffers obvious thermal shrinkage. The above difference is due to the application of the high heat resistance PI binder. It must be noted out that, the PI has been widely studied as it is thermally stable at temperatures even up to 500 °C [14,15,38].

The porous internal structure of the PE as controls before the heating tests were shown in Fig. S2a and b. Cross section SEM of PE membrane exhibit interconnected submicron pore structure before heat treatment. The structure of the CCS-PI after the tests were shown in Fig. S2. Compared with the ceramic surface of CCS-PI (shown in Fig. 2c), there is almost no obvious changes in the morphologies after heat treatment. However, on the PE side, the porous surfaces of PE separator became a smooth surface (with no holes on the surface shown in Fig. S2d). Cross section morphologies of CCS-PI after 160 °C treatment for 30 min were shown in Fig. S2e, f and g. The Figure exhibits that the parts of PE melted and flowed into the gap between the Al₂O₃ particles. Also the holes inner the PE separator were shut (the porous structure of PE membrane became non-porous structure after the heat treatment) and decreased the thickness of the PE support membrane.

Thermo stability of the separators were further studied by place the separators 3 mm below a hot metal rod with diameter of 2 mm and heated to 200 °C. The results were shown in Fig. 4. From Fig. 4a we can find that the PE separator under the hot metal rod formed a hole after a quickly melting process, which could lead to safety issue of cells prepared by PE separator. Compared with the hole of PE separator formed under the hot metal rod, the hole of the CCS-PVDF-HFP is much smaller in area (show in Fig. 4b). From Fig. 4c, it can be found that the Al₂O₃ coating layer of CCS-PI was still a complete self-supporting layer when the PE substrate was melt.

The SEM of the separator near the melt hole after hot metal rod piercing experiment was investigated in detail and shown in Fig. 5. As Fig. 5a and b shown, the holes inner the separator were shut and the PE membrane under the rod formed a hole after a quickly melting process as the PE separator was prepared through multiple stretching processes. The CCS-PVDF-HFP shown in Fig. 5c and d also suffered dimensional change and finally formed a hole when exposed at high temperature. As a comparison, the dimensional of CCS-PI (shown in Fig. 5e and f) was not changed while the thickness of the basic PE separator decreased significantly from 20 μm to 10 μm. The volume decreases caused by shut of the holes inner the basic PE layer of the ceramic coating separator will result in thickness decrease rather than dimensional change.

In order to make clear the effect of the separators with or without the ceramic coating layer inner the cells at high temperature, the OCV changes of the graphite/LiCoO₂ batteries assembled with PE separator, CCS-PVDF-HFP and CCS-PI during heat exposure was also measured. The LiCoO₂/graphite cell was stored at vacuum oven with the temperature rise at the rate of 1 °C min⁻¹ after fully charged to 4.2 V. Fig. 6a shows the OCV changes of the graphite/LiCoO₂ cell as a function of temperature. The OCV of the graphite/LiCoO₂ batteries assembled with PE separator dropped rapidly from 4.2 V to 0 V at about 125 °C. In contrast, the OCV of the graphite/LiCoO₂ cell based on CCS-PVDF-HFP was running well until 138 °C and the OCV of the LiCoO₂/graphite batteries assembled with CCS-PI was running well even over 165 °C. Clearly, the OCV drop (as well as internal short circuits in the punch cell) is caused by the dimensional change of the separator under high temperature environment. Although the thermal stability of CCS-PVDF-HFP has been improved, it still does not meet the requirement for higher temperature. The CCS-PI with better thermal stability seems to be suitable to serve as a separator

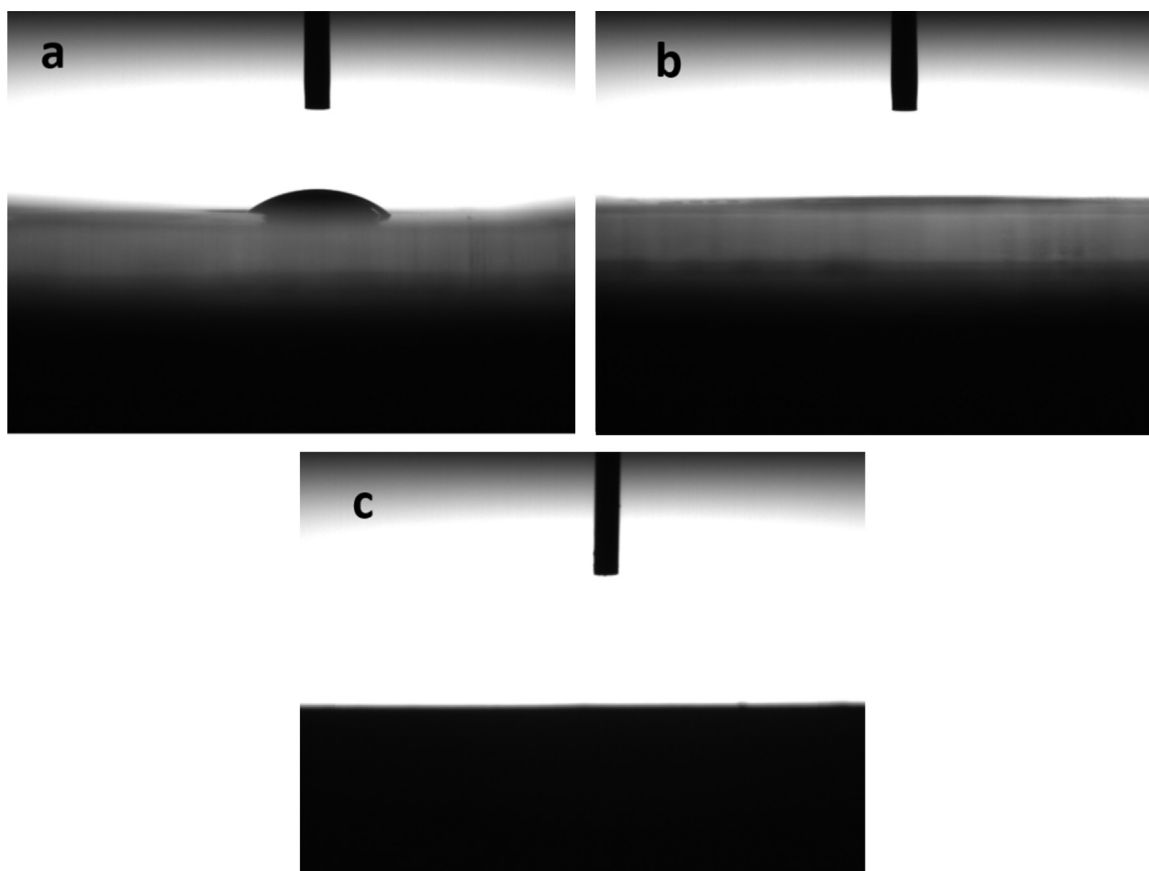


Fig. 7. Contact angle tests of: (a) PE separator, (b) CCS-PVDF-HFP and (c) CCS-PI.

Table 1

Electrolyte uptake and ionic conduction.

Separator	PE separator	CCS-PVDF-HFP	CCS-PI	PVDF-HFP	PI
Average uptake (%)	54 ± 1	85 ± 2	77 ± 1	29 ± 1	≤ 1%
Ionic conductivity (mS cm ⁻¹)	0.78 ± 0.01	0.89 ± 0.03	0.70 ± 0.03	0.025 ± 0.003	2.2 × 10 ⁻⁴

for large scale lithium ion batteries. The DSC curve of the PVDF-HFP and PI were measured and shown in Fig. 6b to make clear why the CCS-PI showed higher thermo-stability than the CCS-PVDF-HFP. From the DSC profiles shown in Fig. 6b we can find that PVDF-HFP had one clear endothermic peak at 161.8 °C which was attributed to the melting of PVDF-HFP materials. The DSC profiles of PI showed no endothermic peak even up to 200 °C, which means PI materials won't melt even up to 200 °C. The DSC result proved that the high thermo-stability of the ceramic coating separator was attributed to the high thermo-stable binder.

The wettability of the separator with electrolyte is an important character for battery manufacture and performance. Since the good wettability of the separator with electrolyte can not only reduce electrolyte filling time during the assemble process effectively, but also improve the ability of retain electrolyte solution and facilitate ion transport between electrodes during running process. The contact angle of liquid electrolyte on the surface of membranes is measured and shown in Fig. 7 to make clear the wettability of the membrane with the electrolyte is good or not. According to the usual procedure, the contact angle is immediately measured in 3 s when the interface of separator contacts with a drop of electrolyte. As shown in the Fig. 7, after the same time of the separator interface touch with the electrolyte, the PE separator showed a contact angle about 35.0° which is much higher than

that of the CCS-PVDF-HFP and CCS-PI (0°). Such low contact angle represents an excellent wettability of the ceramic coating surface with the electrolyte.

The electrolyte uptake of separators with electrolyte as an important character for the batteries performance were measured and summarized in Table 1. The electrolyte uptake of PE is 54%, in contrast, the CCS-PVDF-HFP and CCS-PI is 85% and 77%, respectively. For the PE separator, the electrolyte can only trapped in inner pores result in the lowest electrolyte uptake of the separator. While for the CCS-PVDF-HFP and CCS-PI, liquid electrolyte could not only be trapped in inner porous of the PE support membrane, but also be retained on the hydrophilic surfaces and inside the porous of coating layer formed by the hydrophilic Al₂O₃ inorganic particles and the PVDF-HFP or PI binder networks [21]. However, the electrolyte uptake of the CCS-PVDF-HFP is higher than the CCS-PI. This is caused by the fact that the PVDF-HFP is easy gelling in the electrolyte with the electrolyte uptake of 29%, but the PI is not gelling in the electrolyte.

The ionic conductivity of PE separator, CCS-PVDF-HFP and CCS-PI after soaking in electrolyte solution were measured and summarized in Table 1. The ionic conductivity of CCS-PVDF-HFP is 0.89 mS cm⁻¹ which is higher than the PE separator 0.78 mS cm⁻¹ as reported in previous works [19,35]. However, the ionic conductivity of CCS-PI 0.70 mS cm⁻¹ is a little lower than the

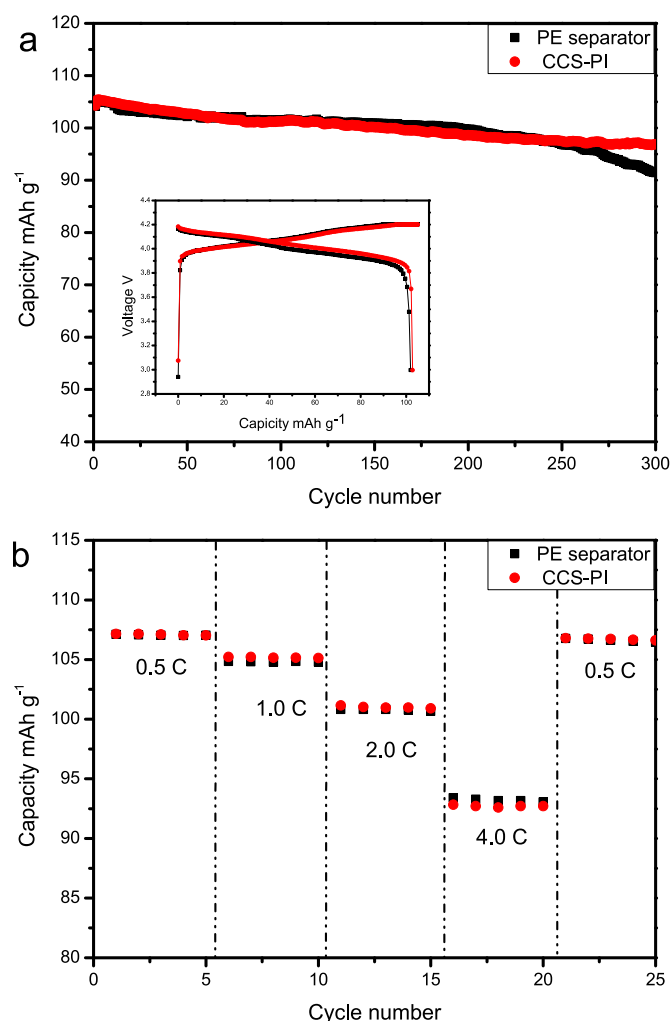


Fig. 8. (a) Cycle performance of the coin cells with PE separator and CCS-PI membrane. Insert image is the first charge/discharge profiles of LiMn_2O_4 prepared with different kinds of separator. (b) Rate performance of the batteries with PE separator and CCS-PI membrane.

PE separator. The q_i of CCS-PI is increased with the increases of the electrolyte uptake. However, the μ_i maybe decreased due to that the PI is not gelled in the electrolyte and the transmission of lithium-ions inner the PI binder is completely prevented which lead to the increase of the distance of ion migration inner the coating layer. As shown in Table 1, the ionic conductivity of PVDF-HFP is 0.025 mS cm^{-1} and the PI is $2.2 \times 10^{-4} \text{ mS cm}^{-1}$ as a result of that PI cannot take up any electrolyte. The ionic conductivity of CCS-PI does not decrease significantly when the transmission of lithium-ions in inner PI binder is prevented, which may be due to that most of lithium-ions can go through the pores of the separator and the porous coating layer comprised of the hydrophilic Al_2O_3 particles and binder networks.

The influence of Al_2O_3 and PI coated PE separators on the electrochemical performance was evaluated in the $\text{Li}/\text{LiMn}_2\text{O}_4$ coin-type half cells at the potential range from 3.0 V to 4.2 V at 1 C rate. The charge-discharge behaviors of the assembled cells with PE separator and CCS-PI are shown in Fig. 8a. As shown in the inset figure of Fig. 8a, the first charge/discharge profiles of cells prepared with PE separator and CCS-PI were almost the same. The results show clearly that the CCS-PI has no impact on the charge and discharge behavior of the batteries. The discharge capacity of coin-type cells with CCS-PI separator seems a slightly higher than the cells with the original PE separator. The discharge capacity of

the batteries may be decreased with the increase of ion migration resistance in the separator caused by the additional coating layer. However, the capacity retention is improved by coating Al_2O_3 powders and PI polymer binder onto the porous PE membrane. This result may be caused by the fact that the retaining electrolyte solution ability of the CCS-PI is improved by the ceramic coating layer. Also, trace amounts of acidic impurity and moisture in electrolyte can be captured by the Al_2O_3 powders in the coating layer, which is beneficial to the repeat cyclic performance of batteries. Change in alternating-current (AC) impedance of cells with cycling was examined and provided in Fig. S3. The figure exhibits that the charge-transfer resistance (R_{ct}) of the cells prepared with PE separator increases from 28.5 (10 cycles) to 44.8 Ω (100 cycles). The charge-transfer resistance (R_{ct}) of the cells prepared with CCS-PI increases from 28.1 (10 cycles) to 45.9 Ω (100 cycles) [44]. The Change in AC impedance of cells prepared with different separators are almost the same. The results show clearly that the AC impedance of cells won't be deeply influenced by the separator.

The rate performance of the coin cells with PE separator and CCS-PI charged to 4.2 V and discharged to 3 V at current rates of 0.5 C, 0.1 C, 2.0 C, 4.0 C and 0.5 C is evaluated and the results were shown in Fig. 8b. The Fig. 8b shows that the capacity retentions of cells with different separator at 0.5 C rate are similar and their discharge capacities decrease gradually with the increase in rate. Compared with cells assembled with PE separator, the rate capacities of cells assembled with CCS-PI appear to have a little decrease at 2 C and 4 C rate, but almost the same. The rate performance is agreed with previous results about ionic conductivity of the cells.

4. Conclusions

The CCS-PI has been successfully prepared by coating Al_2O_3 ultrafine powders and thermal stable PI binder onto one side of the porous PE membrane. The CCS-PI with the ceramic layer exhibits no thermal shrinkage up to 160 $^{\circ}\text{C}$ in dry state and maintains stable when packed inner the cells up to 165 $^{\circ}\text{C}$. There is no hole formed through the body of the CCS-PI during the hot metal rod piercing testing. In addition, compared with the PE separator, the electrolyte uptake (77%), wettability with the electrolyte (with a contact angle of 0°) of CCS-PI were improved significantly. Also, CCS-PI showed enabled high ionic conductance (0.70 mS cm^{-1}) when saturated with liquid electrolyte. The cells with this CCS-PI showed a stable voltage at high temperature and stable cyclic performance at room temperature. The CCS-PI prepared in this study is expected to improve thermal safety and capacity retention for lithium-ion batteries.

Acknowledgments

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.memsci.2016.06.035.

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