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Improving the Wettability and Thermal Resistance of Polypropylene Separators with a Thin Inorganic-organic Hybrid Layer Stabilized by Polydopamine for Lithium Ion Battery

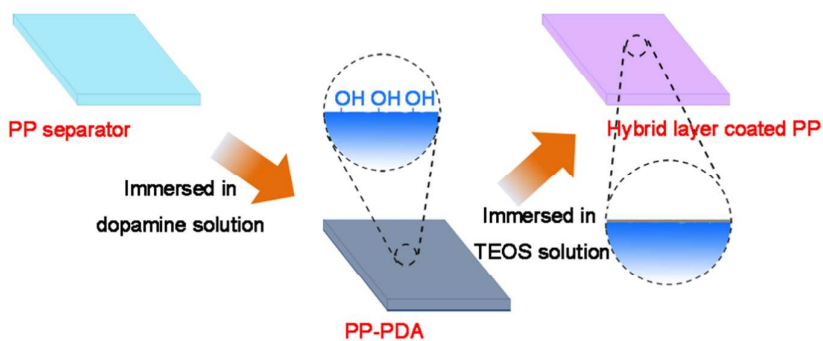
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A thin inorganic-organic hybrid layer coated polypropylene separator was prepared by a twice immersing process, with improved wettability and thermal resistance.



ARTICLE

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This study aims to improve the wettability and thermal resistance of polypropylene (PP) separators for lithium ion batteries. PP separator was first coated with polydopamine (PDA) on the basis of mussel-inspired surface chemistry. Then a thin inorganic-organic hybrid layer was immobilized onto the PDA-coated separator via a sol-gel process of tetraethoxysilane (TEOS) solutions. This method does not need any commonly-used polymeric binders because of the unique adhesion behaviour of the PDA intermediate layer, which greatly reduces the thickness of the modification layer and avoids excessive pore blocking. Owing to the incorporation of the hybrid layer, the composite separators showed better affinity with liquid electrolyte and obvious reduction in thermal shrinkage in comparison to the unmodified separator. And the battery performances, such as interfacial resistance, discharge capacity and C-capacity were all improved as well after modification. Considering the effective adhesion of PDA onto nearly all kinds of separator/membrane surfaces, this modification strategy can be widely used without causing any obvious damage to the mechanical strength of the unmodified separators/membranes.

Introduction

Lithium-ion batteries have attracted lots of interests in recent years because of their excellent cycle lives, higher energy density, environmentally friendliness, etc. The current challenges for further development of lithium ion batteries are centered on increasing the stored energy density and battery safety¹. As an important part in the battery, especially in liquid lithium-ion batteries, polyolefin separators play a key role in conducting lithium ions and isolating the contact of the cathode and the anode²⁻⁴. To achieve higher energy density, it is necessary to improve the surface energy and lithium ionic conductivity of the polyolefin separators⁵. Meanwhile, in term of battery safety, the thermal resistance property of separators is the essential factor influencing battery performances. When the separator undergoes meltdown, it would be deteriorated and shrink, causing an internal short circle and a safety hazard⁶. Furthermore, with increasing applications of lithium ion batteries, high-temperature battery is put on the agenda and becoming one of the major trends in the future.

Immobilization of inorganic layers on the polyolefin separators is deemed as a good solution for enhancing thermal resistance and wettability of the separators^{3, 4, 7}. The incorporation of the heat-resistant inorganic layers could not only reduce the thermal shrinkage of composite separators but also improve the affinity of the separators to liquid electrolyte^{8, 9}. Among the diverse

modification methods, the most widely used one for introducing an inorganic layer on polyolefin separators is coating⁸⁻¹¹. However, drawbacks of this method lie in the increase of separator thickness¹² and possible pore blocking, resulting from polymeric binders. The former would reduce the amount of active materials in the battery with a fixed size¹². This would absolutely decrease the energy density of the battery. The latter might depress the ionic conductivity, which is unfavourable for the improvement of C-capacity. To overcome above problems, Kim et al.¹² prepared an inorganic thin layer-coated porous separator by the chemical vapour deposition method. A thin and very condensed silica film was deposited on the separator surface. The resultant separator not only showed increased thermal and dimensional stability but also displayed extended cycle life.

Previous researches usually used polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP)^{8, 10, 11, 13} as a polymeric binder of the ceramic nanoparticle layer, while the weak adhesion with polyolefin separators may cause additional interfacial resistance between coating layers and separators¹⁴. To enhance the interface interaction, many investigators treated the unmodified or modified separators with gamma ray irradiation¹⁴, alkali¹⁵ or plasma^{12, 16}. However, these techniques usually cause damage to the separator matrix¹². In recent research, Ryou et al.^{17, 18} have reported a surface modification method for polyethylene (PE) separators using bioinspired polydopamine (PDA). The PDA-treated PE separator had excellent electrochemical properties and applied to high-power

lithium ion batteries. Due to the mild modification conditions, the dopamine coating process would not harm the separator matrix¹⁹. Considering the strong adhesive capability of PDA and the facile immersing process²⁰⁻²⁴, PDA was used to modify the surfaces directly or acted as intermediate layer for further functionalization. Kang et al²⁵ develop an integrative bioinspired approach to improve the rate performance and thermal stability by coating silica layer on PDA/2-dimethylaminoethanethiol hydrochloride (DMAET) surface. In this work, the PDA layer was incorporated as the intermediate layer without other reagents (such as, DMAET) to immobilize a thin inorganic layer onto the PP separator. The thin inorganic-organic hybrid layer coated PP separators were prepared via immersed the PDA-treated separator into TEOS solution during its sol-gel process. The solvents of TEOS solutions were only water and ethanol, which were environmentally friendly²⁵. And the effect of capacity of immobilization layer of inorganic-organic hybrid layer on the properties of separators was carefully studied. Moreover, the effects of hybrid layer on thermal stability and wettability, as well as electrochemical performances of the PP separators were investigated in detail.

Experimental

Materials

Commercialized PP separator (Celgard 2500, porosity 51%) was provided by Celgard Company and cleaned in ethanol before use. Tris (hydroxymethyl) aminomethane (Tris) and TEOS were bought from Sinopharm Chemical Reagent Co. (China). 3,4-Dihydroxyphenethylamine (dopamine) was purchased from Sigma-Aldrich. Dopamine was dissolved in Tris-HCl buffer solution (10.0 mM, PH 8.5)²⁶ with a concentration of 2.0 g L⁻¹.

Preparation of inorganic-organic hybrid layer coated PP separator

The modified PP separators were prepared by a twice immersing process as shown in Fig. 1. The unmodified PP separators were immersed into the dopamine solution for 8 h (The dopamine coated PP separator is coded as PP-PDA), followed with being thoroughly rinsed by de-ionized water. Then separators were immersed in the mixture of TEOS, water and ethanol (30/35/35, wt/wt/wt). Separators were taken out from the TEOS solution at regular intervals and then they were washed by water/ethanol several times to remove unstable affixed modification components and dried under ambient temperature before characterization. The inorganic-organic hybrid layer modified PP separators are coded as hybrid layer coated PP. As comparisons, an unmodified PP separator and an air plasma treated PP separator were directly transferred into the same TEOS solution (The obtained separators are coded as PP_{control} and PP_{plasma}, respectively). The air plasma treated separator was treated between an air gap of 2 mm by the power of 200 W for 60 s on plasma generator (Suman CTP-2000K, China).

Characterization of the separators

The surface chemical composition of separator surface layer was determined by Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet NEXUS 670, USA) and energy dispersive X-ray spectroscopy (EDX, Hitachi S4800, Japan). The capacity of immobilization (COI) of inorganic-organic hybrid layer on the separator skeleton was calculated by the equation: $COI (\%) = (M - M_0) / M_0 \times 100$, where M_0 and M are the

weight of the separator before and after modification, respectively. The surface

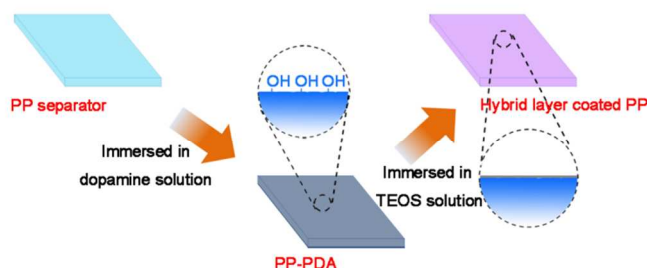


Fig. 1. Schematic description of a hybrid layer coated PP separator by a twice immersing process.

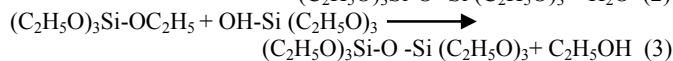
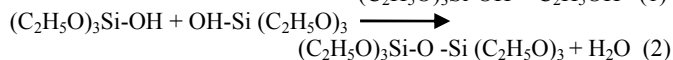
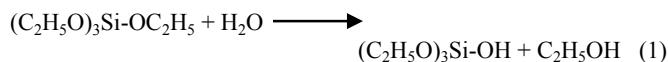
and cross-section morphologies were observed by field emission scanning electron microscopy (FESEM, Hitachi S4800, Japan) after gold coating. The mechanical properties were tested by RGWT-4002 tensile tester (Reger, China) at room temperature. The elongation rate was 20 mm min⁻¹ and the size of samples was 30 mm × 10 mm. The thermal shrinkage property of separators was measured by determining the transversal and longitudinal dimensional change after being treated at 165 °C for 1 h. The electrolyte wettability was examined by measuring liquid electrolyte contact angles on separators on a contact angle measurement system (Dataphysics, OCA20, Germany). Liquid electrolyte of 1mol L⁻¹ LiPF₆ in EC/DMC/EMC (1/1/1 by weight, Guotai Huarong Company, China) was used to evaluate the electrochemical performances. The air permeability of the separators was characterized by determining the time of nitrogen passing through a settled volume under a given pressure (0.02 MPa) and was represented by a Gurley value (sec 100 cc⁻¹).

The liquid electrolyte uptake by the separators (ΔW) was determined by immersing separators in liquid electrolyte solution for 24 h at 25 °C under the atmosphere of dry Ar gas, and was calculated by $\Delta W(\%) = (W_w - W_d) / W_d \times 100$, where W_w and W_d are the weight of the dry separator and separator after absorbing liquid electrolyte, respectively. Bulk impedance data (R_b) were measured on an electrochemical work station system (Princeton Applied Research 2273, PARC, USA) at 25°C (using frequency range of 1-10⁵ Hz at amplitude of 5 mV) between two stainless steel (SS) electrodes. The ionic conductivity (σ) was calculated based on $\sigma = d / (A \times R_b)$, where d and A are the thickness and effective area of separator, respectively. The activated separator was sandwiched between a LiFePO₄ cathode and a lithium anode and then assembled into a tightly sealed coin cell in a glove box filled with Ar. The interfacial resistance was also measured on the electrochemical work station system with the assembly of LiFePO₄/separator-liquid electrolyte/lithium at AC impedance mode. The charge/discharge cycling performance and charge C-rate capability of the cells were determined on a Land testing system (CT2001A, China) between 2.5 V and 4.2 V at 25 °C.

Results and discussion

The sol-gel process includes the precursor, i.e., TEOS, dispersed in the solvent hydrolyzing to form active monomers; silica particles being formed by the condensation reaction of the active monomers; silica particles gradually aggregating to form a network, until the gel

being obtained; gel aging process²⁷. The possible reactions in the sol-gel process of TEOS solution are as follows.



In this work, we tried to coat silica particles formed in the sol process onto the PP separator via chemical or/and physical adhesion. Different separators (unmodified PP separator, plasma treated PP separator and dopamine treated PP separator) immobilized with silica layer were compared. These separators were immersed in the TEOS solution for 24 h at 30 °C and then taken out. After treated via the drying-rinsing-drying process, the modified separators were characterized by ATR-FTIR. The spectra are shown in Fig. S1 (Electronic Supplementary Information). As can be seen, the spectrum of PP_{control} is identical with that of the unmodified PP separator, which suggests that silica particles could not be attached onto the surface of the unmodified separators. The spectrum of PP_{plasma} is also the same with that of the PP separator. A possible reason is that the insufficient polar functional groups were created on the surface when treated by plasma and could not adsorb silica particles effectively. TEOS solution treated PP-PDA is coded as PP_{dopamine-treated}. An obvious adsorption peak occurs at 1100 cm⁻¹ in the ATR-FTIR spectrum of PP_{dopamine-treated}, which corresponds to the Si-O stretching vibration²⁸ and suggests successful introduction of the hybrid layer. The effective adsorption of the silica to the PDA layer might originate from the multi hydrogen bonding between -OH/-NH₂ in PDA and Si-OH on silica or Si-O-Si at cleaved silica surface, together with the hydrolysis reaction of -OH/-NH₂ groups in PDA with TEOS^{16, 23, 29}. However, more profound exploration is still on the way. The hybrid layer was further confirmed by EDX test. Fig. 2 also gives the EDX results of the hybrid layer coated PP separator (COI 10.2%). A high proportion of silicon is observed in the EDX spectrum (Fig. 2a). The silicon distribution (marked in red) on the separator surface by the mapping mode is shown in Fig. 2c. All in all, the results suggest that PDA could effectively and uniformly immobilize silica and finally the inorganic-organic hybrid layer was formed on the PP separator. Moreover, the stability evaluation experiment is also carried out. (Several pieces of the

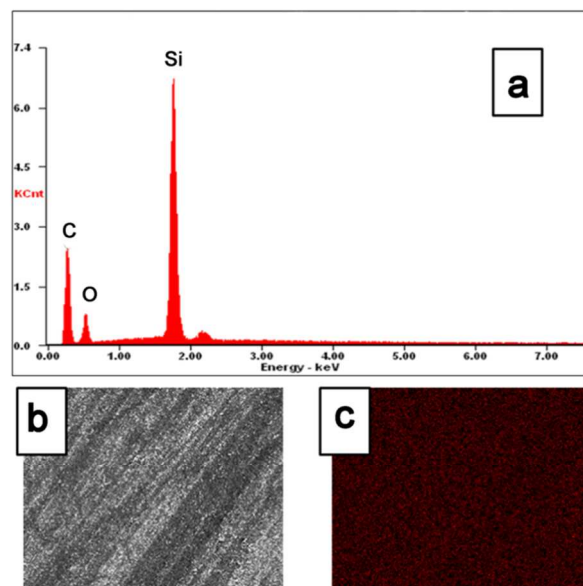


Fig. 2. EDX results (a, b, c) of hybrid layer coated PP (COI 10.2%).

hybrid layer coated PP (COI 10.2%) were shaken in liquid electrolyte solution at room temperature and taken out at regular intervals. The surface compositions of the separators were detected by ATR-FTIR after the separators were rinsed in ethanol for three times and dried.) The ATR-FTIR results are listed in Fig. S2 and Table S1. As shown in the spectra, the intensity of the peak at 1100 cm⁻¹ does not obviously weakened after being shaken for 96h. And the absorbance ratios of peak 1100 cm⁻¹ (PH1100) to peak 1460cm⁻¹ (PH1460) (representing the C-H bending vibration on PP) of all the samples are nearly the same. That means the amount of Si-O bond on the hybrid layer was relatively stable when immersed in liquid electrolyte solution, indicating that the modification layer could not be detached on the substrate during usage.

Fig. 3a gives the COI changes as a function of coating time. The treatment temperature was 30 °C. TEOS concentration was 30 wt%, and the solvent was the mixture of water and ethanol (w/w=1/1). The COI increases obviously with the extension of treatment time. It could be explained as follows. On the one hand, the silica particles in the solution were immobilized onto the separator surface to form silica layer continuously. On the other hand, the immobilized hybrid layer on the separator surface could keep on reacting with the active monomers in the solution³⁰. The increasing COI also could be characterized by ATR-FTIR (Fig. 3b). The intensity of the peak at 1100 cm⁻¹ enhances obviously when the COI increases. The results suggest that the modification process is controllable.

The surface morphologies of the unmodified PP separator and the modified separators are shown in Fig. 4 and Fig. S3. The unmodified PP separator has many open pores on the surface. Due to the extremely thin modification layer, the introduction of the PDA layer and inorganic-organic hybrid layer hardly changes the pore structures. And the pore size hardly decreases, which would be favourable for lithium ion transportation. Fig. S3 gives the cross-section SEM images of the unmodified PP separator and hybrid layer coated PP (COI: 11.9%). The thickness of the separator has no obvious changes, being about 25µm.

The mechanical properties of unmodified PP separator, hybrid layer coated PP (*COI*: 11.9%) and plasma treated PP separators were determined (Fig. 5). The corresponding tensile strength and elongation are listed in Table S2. It is observed that the elongation is greatly weakened when the PP separator is treated by plasma. The unmodified PP separator has an elongation of 76.5%, while the elongation of plasma treated PP separator decreases to 30.6%. And the tensile strength of plasma treated PP is reduced to about 85.6% of that of PP separator, which is similar with the results in Kim's work¹². In comparison, the tensile strength and elongation of hybrid layer coated PP are even larger than those of the unmodified PP separator, which might be caused by the strong intermolecular interactions such as hydrogen-bonding, π - π interactions on the surface of PP separator after PDA coating³¹. In other words, the twice immersing process is mild, and would not cause deterioration of the mechanical properties.

The thermal stability of the modified separators was also investigated. The unmodified PP separator and hybrid layer coated PP with different *COI* were cut into square samples of the same size (1.5 cm \times 1.5 cm). The initial size for the samples is presented by the dashed frame in Fig. 6 inset. The thermal shrinkage of separators was determined by the measuring the longitude and transversal shrinkage after separators being stored at 165 °C for 1 h. The unmodified PP separators are prepared by uniaxial tensile method. So the

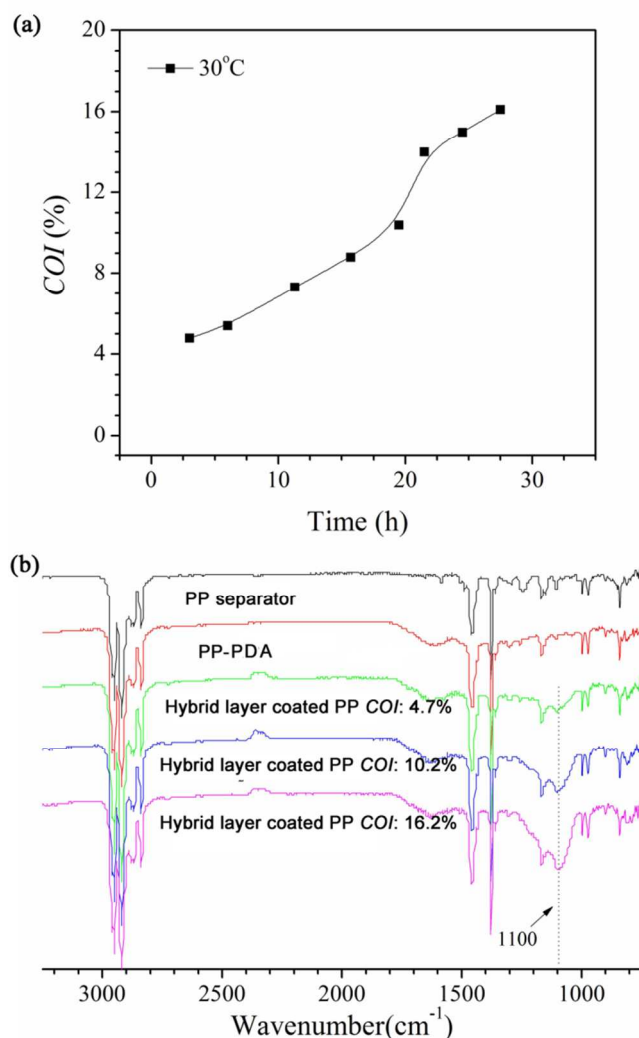


Fig. 3. (a) *COI* as a function of coating time at 30 °C, (b) The ATR-FTIR spectra of unmodified PP separator, PP-PDA and hybrid layer coated PP with different *COI*.

longitudinal direction and the transversal direction are defined to be parallel and perpendicular to the stretching direction, respectively³². The shrinkage ratio is defined as the ratio of the dimensional shrinkage value with the original value. The shrinkage ratio as a function of *COI* is shown in Fig. 6. The shrinkage in longitudinal direction is obvious, while the transversal shrinkage ratio of all the separators is 0%. The difference is mainly attributed to the preparation method of PP separators. Since PP separators are prepared by uniaxial stretching process, the polymer chains highly orient along the stretching direction (Longitudinal direction). When the treatment temperature reaches the melting point of PP (165 °C), the mobility of polymer segments is greatly enhanced, and polymer chains would tend to curl up to obtain a more stable configuration. As a result, separators easily lose dimensional stability and show significant shrinkage in the longitudinal direction.

The longitudinal shrinkage ratio decreases with increasing *COI*. The unmodified PP separator has a longitudinal shrinkage ratio of 100% (as shown in Fig. 6 inset, left). The introduction of the hybrid layer improves the thermal stability of the separators, and when *COI*

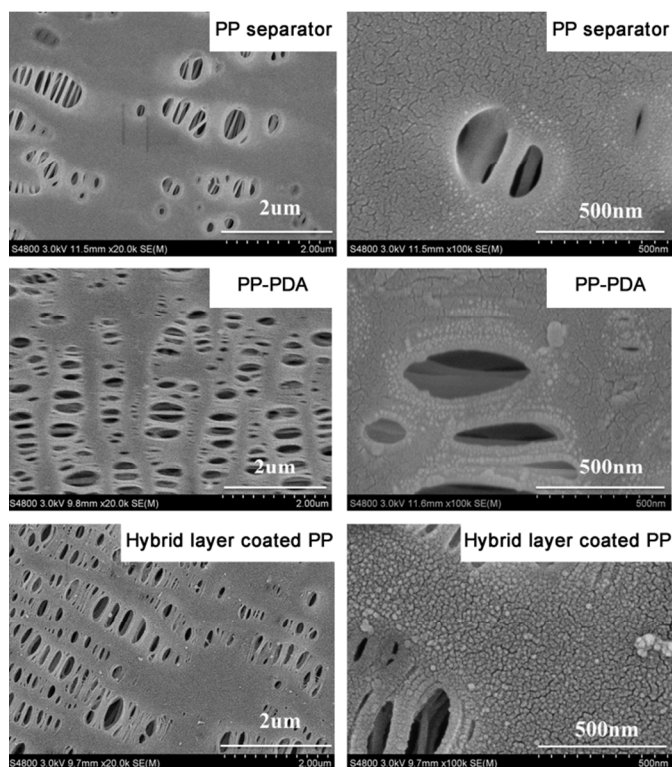


Fig. 4. The surface morphologies of unmodified PP separator, PP-PDA and hybrid layer coated PP with *COI* 11.9% at different magnification (20,000 \times and 100,000 \times).

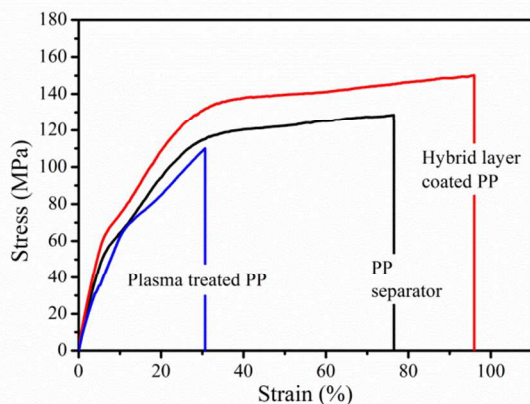


Fig. 5. The tensile curves of PP separator, hybrid layer coated PP (*COI* 11.9%) and plasma treated PP separator.

reaches 16.4% (as shown in Fig. 6 inset, right), the shrinkage ratio in the longitudinal direction is decreased to 40% (The area-based shrinkage ratio is also 40%). Fu et al.⁸ reported a kind of silica modified PP separator with PVDF-HFP as the polymeric binder. And the unmodified PP separator was the same as the one used in this work. As was reported, when the coating gain was 20%, the area-based shrinkage ratio reached 45% when separators were stored at 150 °C for 0.5 h.

Furthermore, thermal shrinkage of PP, PP-PDA and hybrid layer coated PP (*COI*: 11.9%) was also compared for further investigation of the contribution of PDA layer and hybrid layer. As

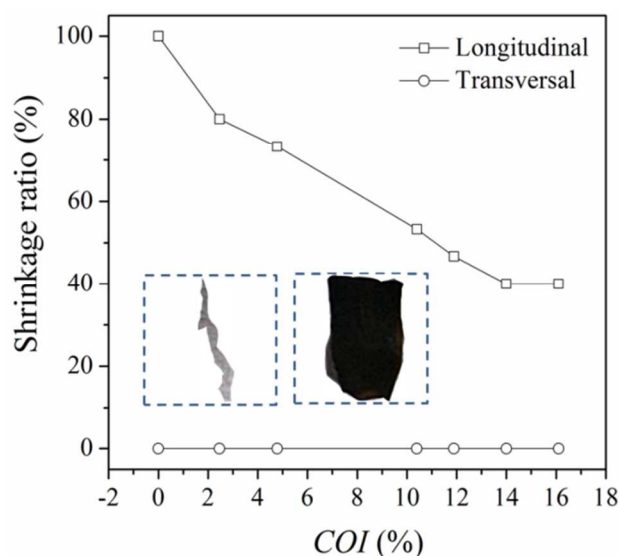


Fig. 6. The longitudinal shrinkage and transversal shrinkage of the unmodified PP separator and hybrid layer coated PP with different *COI* treated at 165 °C for 1 h.

shown in Fig. S2, PP-PDA exhibits better thermal stability than the unmodified PP separator. The thermal shrinkage of PP-PDA is 7% at 120 °C for 4h, in comparison to 17% for the unmodified PP separator. This noticeable improvement may be attributed to the thermal resistance of PDA layer, which is in accord with previous literature¹⁸. For hybrid layer coated PP, the thermal shrinkage is obviously suppressed compared to that of the unmodified PP separator and PP-PDA. At 165 °C for 1h, PP separator has totally melted down, and PP-PDA maintains 20% of the original dimension, while hybrid layer coated PP could still keep 55%. This further improvement in thermal shrinkage is attributed to the existence of the inorganic-organic hybrid layer. The heat-resistant silica coating layer effectively prevents the composite separator from thermally shrinking^{8, 11, 12}. Therefore, introduction of PDA layer, especially hybrid layer, remarkably improves the thermal stability of the separator.

The wettability of the separators was characterized by the liquid electrolyte contact angle. Generally, lower contact angle corresponds to better wettability. As shown in Fig. 7, the liquid electrolyte contact angle of unmodified PP separator is 45°. Introducing of PDA coating layer yields separators lower contact angle (24°), as reported in previous reports¹⁷. The hybrid layer further reduces the liquid electrolyte contact angle (22° for *COI*: 2.5%). That is to say, the wettability of the hybrid layer coated PP is better than that of the unmodified PP separator and PP-PDA. Furthermore, the liquid electrolyte contact angle decreases with increasing *COI*. For hybrid layer coated PP with *COI*: 16.2%, the contact angle decreases to 11°. In summary, the inorganic-organic hybrid layer improves the wettability of the separator.

The porous structure of the modified separators was quantitatively characterized by the Gurley value (sec.100cc⁻¹) (Fig. 8). A higher Gurley value corresponds to lower air permeability, smaller pore size and excessive pore blocking¹¹. As can be seen, the Gurley value slightly increases with increasing *COI*, suggesting pores are gradually blocked by the introduced hybrid layer and porosity gradually decreases. Fig. 8 also shows the liquid electrolyte uptake by the modified separators as a function of *COI*. The separators' uptake of liquid electrolyte increases at the beginning and then decreases. The liquid electrolyte uptake by unmodified PP

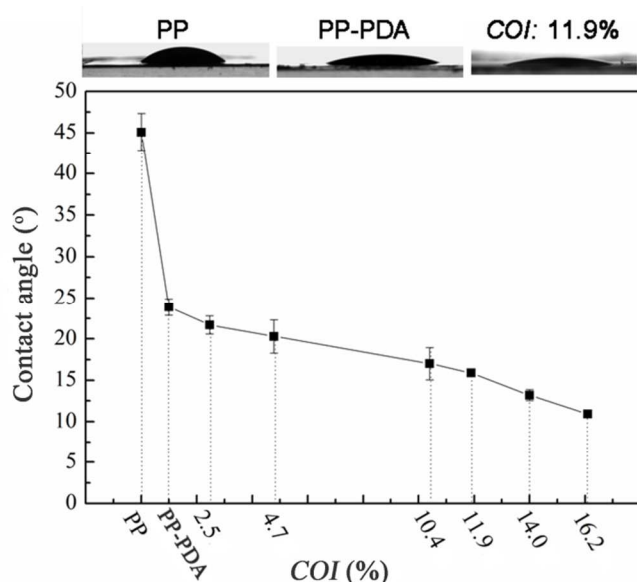


Fig. 7. The contact angles of PP separator and hybrid layer coated PP with different *COI*.

separator is about 106%, while the liquid electrolyte uptake by the hybrid layer coated PP with *COI* 11.9% reaches 122%. For unmodified PP separator, the liquid electrolyte is mainly stored in pores.⁵ When the *COI* is relatively low, the degree of pore blocking is slight, so the amount of liquid electrolyte stored in the pores hardly changes. The immobilized hybrid layer could also absorb a part of liquid electrolyte due to the existence of the polar groups in the hybrid layer, giving rise to a slightly increased uptake. When the *COI* is further elevated, the pore blocking effect becomes obvious and acts as the dominant factor affecting the uptake. As a result, a downward trend for the separators' uptake is observed due to the decrease of the separator porosity. However, it is worth noting that changes of the separators' uptake of liquid electrolyte are smaller, relative to previous reports⁸, due to the thin hybrid layer.

The stability of liquid electrolyte was evaluated by determining the retention ratio of liquid electrolyte in the separators after being kept in sample bags for 6 h. The retention ratio represents the percentage of the separators' uptake of liquid electrolyte after separators being stored for 6 h and the initial saturated separators' uptake. Changes of the retention ratio with *COI* are shown in Fig. S3. It could be observed that the retention ratio increases obviously when *COI* is elevated, the retention ratio of the unmodified PP separator is only 51%, while the retention ratio reaches 82% when the *COI* is 16.2%, which means the stability of the liquid electrolyte entrapped in the separators is enhanced. The leakage of electrolyte solution mainly depends on the affinity of the electrolyte solvent with the separator matrix³³. As discussed above, the interactions of the liquid electrolyte with the PP separator are increased by the introduction of the hybrid layer which effectively prevents the loss of the liquid electrolyte. Since the retention behavior of the liquid electrolyte would largely influence the cycle life and safety of the batteries³⁴, the improved retention stability is of great significance for high performance of lithium ion batteries.

The ambient ionic conductivity of the separator-liquid electrolyte systems was determined and shown in Fig. 9. The ionic conductivities show a trend of increase at first and then decrease, which is similar with our previous work³⁵. The reason is deemed as the combination of liquid electrolyte uptake by the separators and pore structures. As is well known, the ionic conductivity relies on the amount and the mobility of lithium ions³⁶. In the case of low

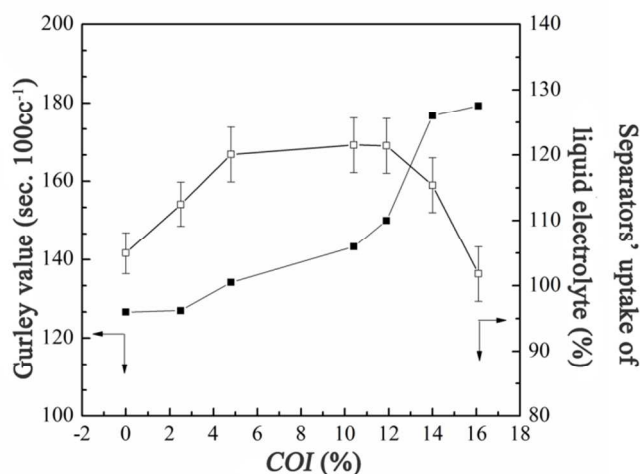


Fig. 8. The separators' uptake of liquid electrolyte and Gurley value of the separators with different *COI*.

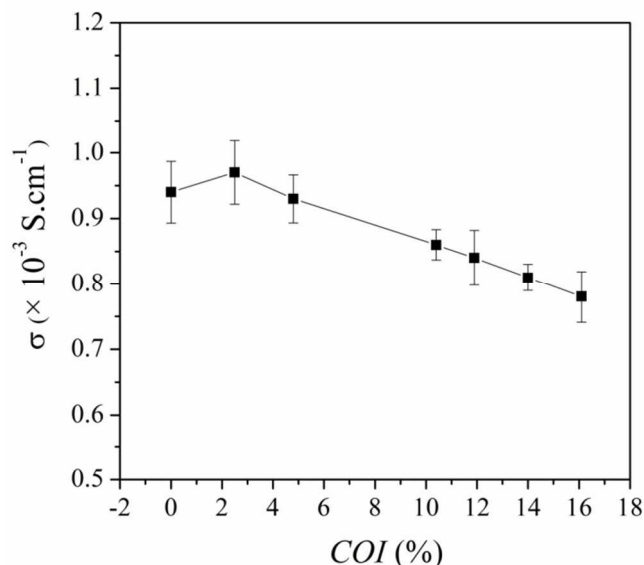


Fig. 9. The ionic conductivity of separator-liquid electrolyte systems.

COI, the uptake is dominant, and the increased uptake yields higher lithium ion content. So the ionic conductivity is elevated. The highest ionic conductivity reaches $0.97 \times 10^{-3} \text{ S cm}^{-1}$, while the ionic conductivity of the unmodified PP separator-liquid electrolyte system is $0.93 \times 10^{-3} \text{ S cm}^{-1}$. For higher *COI*, the pore structures become a dominant factor. Due to the pores being slightly blocked, the mobility of lithium ions is hindered, resulting in lower ionic conductivities.

The compatibility between electrodes and separators was evaluated by the interfacial resistance. The interfacial resistance is presented by the semicircle in Nyquist plot³⁷. Fig. 10 shows the Nyquist plots of the assembled cells with different separators. Compared to the cells containing PP separator and PP-PDA, the cell using hybrid layer coated PP (*COI*: 2.5%) possesses lower interfacial resistance, suggesting better affinity between hybrid layer coated PP and electrodes. That is due to the more intimate contact of hybrid layer coated PP after being soaked with liquid electrolyte, which is expected to a more facile ion transport through the interface of the electrode and the separator³⁸.

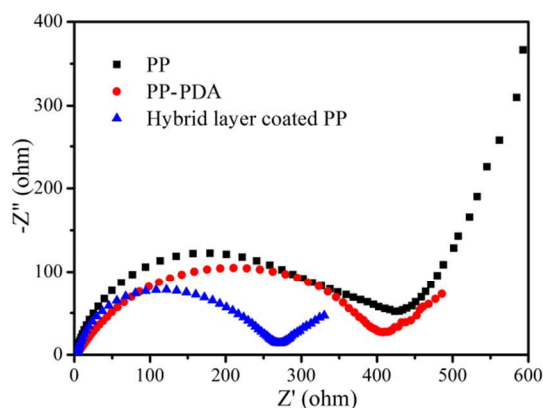


Fig. 10. Nyquist plots of Li/PP-liquid electrolyte/Li (Square), Li/PP-PDA-liquid electrolyte/Li (Circle) and Li/Hybrid layer coated PP (*COI*: 2.5%) -liquid electrolyte/Li (Triangle)

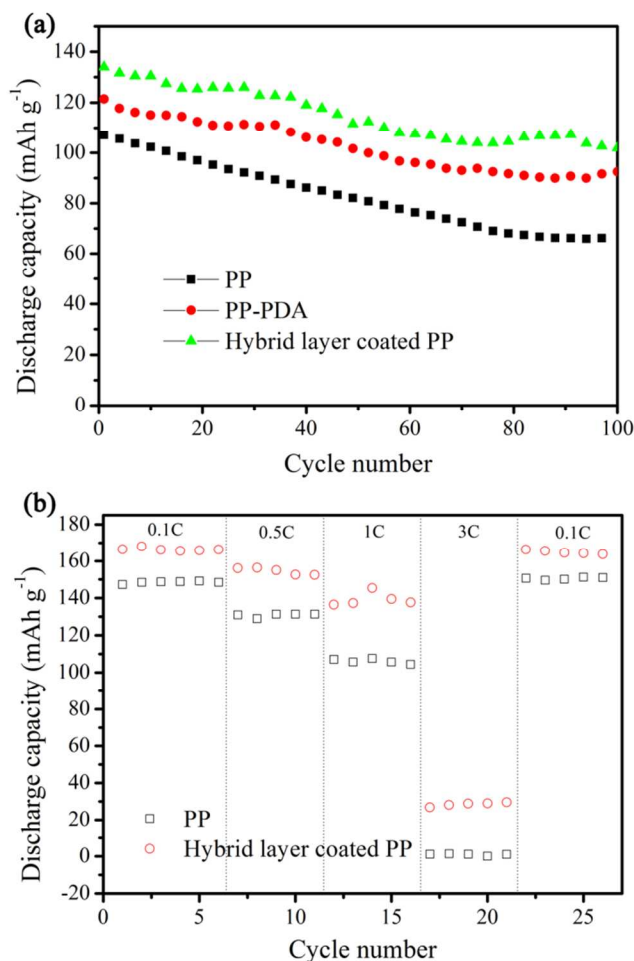


Fig. 11. (a) Change of the discharge capacities of coin cells containing unmodified PP separator and hybrid layer coated PP (*COI* 2.5%) during 100 cycles (1 C/1 C), (b) Comparison of discharge C-rate capability between different separators.

The effects of coating layers on the cycle performances of cells with different separators were also deeply studied. Here we choose unmodified PP separator, PP-PDA and hybrid layer coated PP (*COI*:2.5%) with the highest ionic conductivity for the following research. Fig.11a shows the charge-discharge capacities of $\text{LiFePO}_4/\text{PP}$ -liquid-electrolyte/lithium, $\text{LiFePO}_4/\text{PP-PDA}$ -liquid electrolyte/lithium, and $\text{LiFePO}_4/\text{hybrid layer coated PP}$ -liquid electrolyte/lithium at a rate of 1.0 C. The discharge capacities of all cells with PP, PP-PDA and hybrid layer coated PP decrease with increasing cycle number, which is attributed to the formation of the inert solid electrolyte interface (SEI) film in the interfacial layer between the separator and the electrodes, and thus the sequent consumption of the lithium ion in the electrolyte¹⁹. Especially when lithium metal was used as anode, the continuously generation of lithium dendrites would cause the too thick SEI layer which depressed ion diffusion and exhausted the electrolyte¹⁸, yielding decay of the cell capacity. Besides, self-discharge also may cause the loss of capacity³⁹, which depends on factors such as cathodes and cell preparation, nature and purity of electrolyte, temperature and so on. The discharge capacity retention of the cell containing hybrid layer coated PP (i.e., 76.3%) is much better than that of the cell using unmodified PP separator (i.e., 61.9%) after 100 cycles. The reason might be the uncovered pore structures on the separator and the strong affinity for liquid electrolyte. The former facilitates the lithium ion transportation across the separator-electrodes interface, and the latter prevents the electrolyte from leaking out of the separator during cycling^{40, 41}. Fig. 11b compares the discharge capacities of the cells employing unmodified PP separator and hybrid layer coated PP (*COI*: 2.5%) under various charge/discharge conditions. The discharge capacities of the cells decrease with the increase of charge/discharge rate. However, the cell with hybrid layer coated PP (*COI*: 2.5%) shows the higher capacity. It is attributed to the favourable ion transport between the electrodes and the separator in the cell, because of the firm adhesion of the separator to the electrodes after soaking in the electrolyte solution⁸. Moreover, the improved ionic conductivity of the hybrid layer coated PP bring to lower polarization at electrolyte-electrode interface at high rate, yielding better cycle performance^{38, 40, 42}.

Conclusions

We successfully developed a kind of composite separators by introducing a thin inorganic-organic hybrid coating layer onto a PP separator. Bioinspired PDA was incorporated and acted as an intermediate layer to connecting the hybrid layer onto the separator. The as-prepared composite separator kept its mechanical strength because of the mild modification method and the environmentally friendly reagents used in this method. The incorporation of the heat-resistant hybrid layers enabled the composite separators to show obvious reduction in the thermal shrinkage, as compared to the unmodified PP separator. The efficiently improved affinity of the modified separators with liquid electrolyte enhanced the stability of liquid electrolyte entrapped in the separators. Cells containing the hybrid layer coated PP (*COI*: 2.5%) showed better cycle performances, especially the reduced interfacial resistance. Considering the strong adhesion ability of PDA onto almost all types of surface, the surface modification strategy could be applied to nearly all kinds of membranes, especially separators, or even the new developed poly(ethylene terephthalate) (PET) and polyacrylonitrile (PAN) nonwoven separators.

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