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Preparation and performance of polypropylene separator modified by SiO_2/PVA layer for lithium batteries

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Abstract: An aqueous silica (SiO_2) dispersion was prepared by using silica as ceramic particles, polyvinyl alcohol (PVA) as a binder and deionized water as a dispersion medium. A SiO_2 ceramic layer was applied to the surface of the polypropylene (PP) separator by dip coating. The separators before and after modification were characterized by XRD, SEM, DTA, lyophilic performance test, contact angle test and heat resistance test. The separators were assembled into lithium-ion batteries for electrochemical performance test. The results show that after the successful introduction of SiO_2/PVA coating on the surface of PP separator, the lyophilic and heat resistance and electrochemical performance of PP separator have been improved significantly. The battery rate performance and cycle performance are significantly improved. Especially the capacity retention rate of the original separator was only 75.79% at 100 charge-discharge times, and that of the modified separator was as high as 87.18%.

Keywords: silicon dioxide; polypropylene separator; lithium ion battery; thermal resistance; electrochemical performance

1 Introduction

Lithium-ion batteries are widely used in the field of electronic equipment due to their high energy density and long cycle life (1,2). As a key component of lithium batteries, battery separators mainly serve to isolate positive and negative electrodes, retain electrolyte, and allow lithium ions to pass through (3,4). At present, commercial lithium battery separators are mainly polyolefin porous membranes such as polyethylene (PE) and polypropylene (PP) (5-9). Although these membranes have the advantages of chemical inert, easy processing and low cost, the low surface energy and hydrophobicity of polyolefin materials, as well as the stretching pore forming process, make this kind of membrane have poor heat resistance and poor wetting to electrolyte, which greatly affects the cycle and safety performance of the battery (10-12).

In order to solve the above problems, the simplest and most effective method is to introduce a ceramic layer on the surface of the membrane to prepare a ceramic composite separator. After the ceramic layer is applied to the surface of the polyolefin separator, the thermal stability of the composite separator is remarkably improved due to the excellent high temperature resistance of the ceramic particles. At the same time, since the surface of the ceramic particles contains a hydroxyl group, the wettability of the electrolyte to the separator can be remarkably improved. In addition, since the coating layer can additionally retain a part of the electrolyte, the liquid absorption of the composite separator is remarkably improved. Juang et al. used microwave method to deposit titanium dioxide on polymer film to prepare lithium ion battery composite film, which improved thermal and dimensional stability (13). Xu et al. prepared ultra-thin multifunctional films on polyethylene (PE) films by using polyacrylic acid (PAA) and zirconia (ZrO_2) through simple self-assembly process without destroying the special porous structure of the films (14). Compared with the original PE separator, the

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composite membrane has good electrolyte wettability and absorption, high ionic conductivity, which makes lithium ion batteries have excellent cycle performance. Shi et al. prepared a separator modified by nanometer ceramic powders for lithium-ion battery, which showed good high temperature stability, high absorption and wettability of electrolytes (15). Wang et al. applied the Al_2O_3/phenolphthalein polyetherketone (PEK-C) layer on the surface of the PP film to improve the thermal stability of the separator and the assembly safety performance of the battery, but did not significantly improve the hydrophilic performance of the membrane (16). A composite membrane as a separator for lithium-ion batteries was studied by Zhang et al. (17). The composite membrane is mainly composed of calcium carbonate powder and polymer binder. It has high porosity and good capillary properties, and has good wettability with liquid electrolyte. Among the above methods, composite coatings can improve the performance of separator to a certain extent, but the preparation process of composite coatings is complex and the cost is high. Polymer binders are the main binders used in some ceramic coatings. In order to dissolve these binders, a large number of organic solvents are used in ceramic dispersions. The use of organic solvents not only pollutes the environment and wastes energy, but also is harmful to human health.

Nano-silica (SiO_2) is one of the most widely used nano-materials, because SiO_2 not only has good heat resistance, lyophilicity and chemical inertness, it also has a higher dielectric ratio and lower dielectric loss than other inorganic fillers. Considering the liquid-philic and heat-resistant properties of the separator, in this work, SiO_2 is selected as inorganic ceramic filler. Polyvinyl alcohol (PVA) is a water-soluble polymer with excellent film-forming properties and strong adhesion. And SiO_2/PVA coating was introduced on the surface of PP separator with PVA as binder and deionized water as solvent. The heat resistances, hydrophilic and electrochemical properties of the composite separator were investigated.

2 Experimental

2.1 Preparation of modified separator

A suitable size PP (Celgard 2400) separator was completely immersed in absolute ethanol for about 20 min and dried at 60°C for use. 0.5 g of PVA (1788, 44.05 Mw, Aladdin) powders were added into 50 mL of deionized water, and continue stirring at 90°C until PVA was completely dissolved. 0.5 g of nano-SiO_2 (average particle 20 nm, Aladdin) powder was added in the PVA solution system. After stirring magnetically for 2 h, the PVA/nano-SiO_2 slurry dropped to room temperature. The coating slurry was prepared after standing for 3 h.

The suitable PP separator was cut off, and a suitable amount of coating solution was applied to the separator by dipping coating method. The modified coating separator was dried at room temperature until no obvious liquid existed. Then the coating film was dried in a vacuum oven at 60°C for 24 h.

2.2 Performance test

The native separator and modified separator were studied by XRD (D/max-2500ps, Regaku). Test conditions: room temperature, Ka diffraction of copper target, test voltage 40 Kv, current intensity 200 mA, scanning angle 5°-75°.

The PP separators before and after modification were characterized by scanning electron microscopy (Hitachi s4800). The surface of the sample was plated with gold before testing.

The electrolyte contact angle of separator is tested by drop shape analyzer (DSA 10-MK2, KRüss GmbH). The electrolyte was dripped directly on the surface of the film, and the contact angle was measured directly. All measurements were carried out at room temperature (25°C).

The electrolyte uptake of the separator was calculated by measuring the weight of separators before and after immersion into liquid electrolyte by Eq. 1:

$$\text{Electrolyte uptake} = \frac{W_t - W_o}{W_o} \times 100\% \qquad (1)$$

where W_0 is the mass of the original separator and W_t is the mass of the separator after the liquid electrolyte is completely absorbed (18).

The thermal shrinkage of the separators (2 cm × 2 cm) were calculated by measuring the size variation after being heat treated for 1 h at different temperatures (130-170°C), using Eq. 2:

$$\text{Thermal shrinkage} = \frac{S_o - S_t}{S_o} \times 100\% \qquad (2)$$

where S_o is the area of the original separator, and S_t is the area of the separator after being heat treated for 60 min (19).

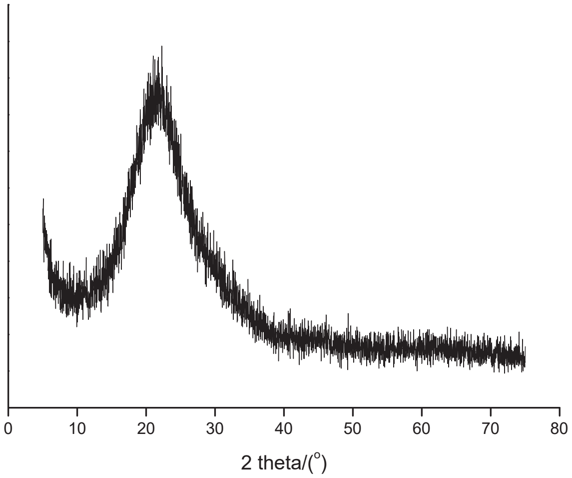

Figure 1: XRD spectrum of bare SiO_2.

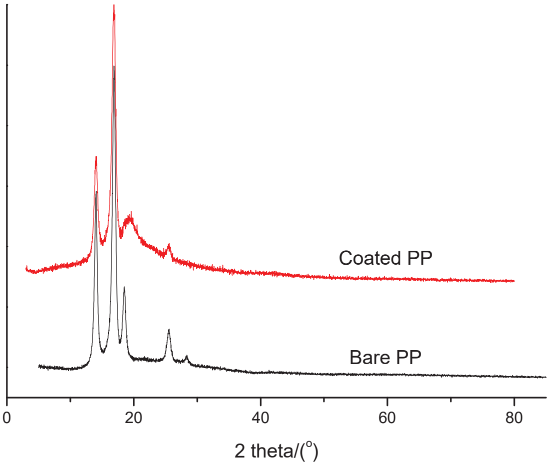

Figure 2: XRD spectrums of bare and coated PP separators.

The thermal stability of battery films were tested by thermal analyzer (Pyris Diamond TG/ DTA, Perkin-Elmer) at a temperature of 50-280°C and a heating rate of 10 K/min.

In order to study the effect of SiO_2/PVA coating on the performance of separator batteries, the rate performance and cycle performance of the original and composite separators were tested on a battery tester. The 2032 coin cell was assembled in a glove box with the separator. The cathode was prepared with a slurry composed of lithium iron phosphate ($LiFePO_4$), Super P and polyvinylidene fluoride (PVDF) [m(LiFePO4) : m(Super P) : m(PVDF) = 8:1:1], and lithium metal sheet was used as anode. LiPF6 was dissolved in a mixed solvent of EC, EMC and DMC with a ratio of 1:1:1 (w/w) to prepare liquid electrolyte with a concentration of 1 mol/L. Charging and discharging current densities used for rate performance testing are 0.2 C/0.2 C, 0.5 C/0.5 C, 1.0 C/1.0 C, 2.0 C/2.0 C, 3.0 C/3.0 C, 5.0 C/5.0 C, respectively. And the cycle performance of the battery was tested 100 times.

3 Results and discussion

3.1 X-ray diffraction analysis

The X-ray diffraction pattern of silica is showed in Figure 1. A broad diffraction peak can be seen indicating that SiO_2 is an amorphous structure. Figure 2 shows the XRD patterns of bare PP and coated PP separators. The diffraction peaks of coated PP separator appeared at 14.03°, 17.05°, and 18.55°, which are consistent with the PP characteristic peaks; meanwhile, a broad peak of silica appeared at 20-25°. It can be observed from Figure 2 that the composite film contains amorphous SiO_2 after the PP separator is modified by SiO_2/PVA coating, and the crystal form transformation of the silica is not caused during the coating process.

3.2 SEM analysis

The PP separators before and after modification were tested by scanning electron microscopy to analyze the surface appearance of the SiO_2/PVA coating layer. The surface image of bare PP separator without modification is shown in Figure 3. There are many fine and relatively regular voids in the PP film, which is due to the dry stretching method (20). Figures 4a-c show the surface images of the coated SiO_2 separator. A layer of nano-SiO_2 ceramic powder was firmly attached to the PP film, the distribution of nano-particles is more uniform, and there are voids between the particles. The existence of these voids will provide a channel for the passage of Li^+.

3.3 Determination of contact angle

The molecular state of the surface layer is different from that of its internal molecular state and the energy of the molecule in the surface layer is higher than that of its internal molecule. When the solid material contacts with the surface of the liquid material and the interface is formed, the adsorption phenomenon of reducing the surface energy will occur. As a result, the liquid material will spread out to reduce the surface energy, and the contact angle between the two phases is often very small. In practice, the contact angle is usually used to measure the hydrophilicity or hydrophobicity of the solid surface. Table 1 shows the contact angle formed by dropping

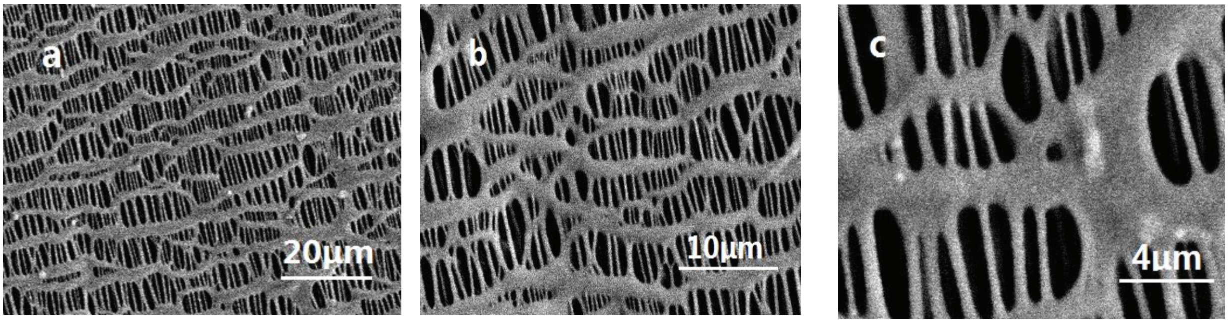

Figure 3: SEM images of bare PP surface.

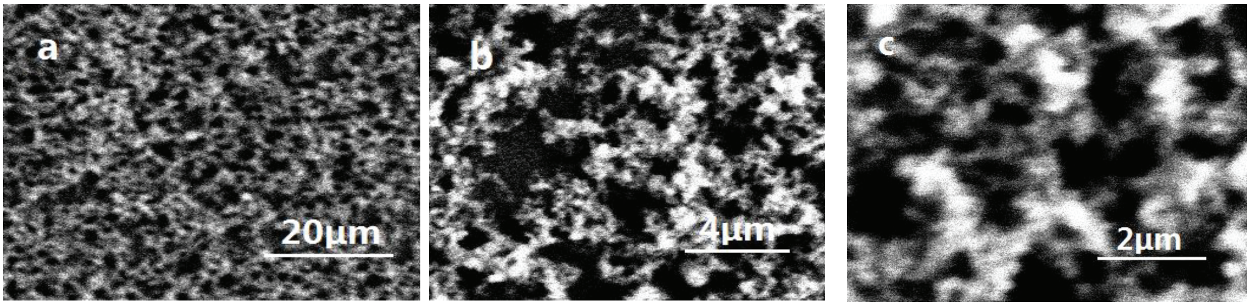

Figure 4: SEM images of PP separator surface after modification.

Table 1: Contact angle of bare and coated film.

Sample	Contact angle
Bare PP	117.5°
Coted PP	83.6°

electrolyte on the bare surface of PP film and coated PP composite film, respectively. All measurements were carried out at room temperature (25°C). The contact angle was measured at different points on the sample for several times to get the average value. The data in Table 1 show that the contact angle of PP separator decreased from 117.5° to 83.6° after coating, which indicated that the wettability of PP separator treated with SiO_2/PVA slurry was significantly improved compared with untreated one. The reason may be that there are abundant hydroxyl groups on the surface of SiO_2 ceramic nano-particles and a large number of hydrophilic hydroxyl groups on the molecular chain of PVA, which have good hydrophilic properties when they are fully mixed. When the composite slurry is coated on the PP film, the surface of the film is coated with a layer of "hydrophilic coating", which shows that the composite slurry has good hydrophilic properties. It is found that the compatibility of the electrolyte with the composite film has been greatly improved, which is of great significance to improve batteries' comprehensive performance.

3.4 Lyophilic properties of the separator

An important function of the separator is to provide lithium ion conducting channels after absorbing the electrolyte (21). Therefore, the separator should be rapidly wetted by the electrolyte and has a high volume of liquid absorption. The former can accelerate the assembly speed of lithium-ion batteries, while the latter can improve the ionic conductivity of the separator. The fluid uptake of the original and composite separator is shown in Figure 5. As can be seen from Figure 5, the liquid electrolyte absorptivity of the separator varied with the wetting time. Each group of data was averaged through three parallel tests.

The original PP separator needs about 250 s to reach saturated absorption. Compared with the original PP membrane, the introduction of the coating can significantly improve the wettability of the liquid electrolyte on the composite separator because of the large amount of hydroxyl groups on the surface of SiO_2. Therefore, the saturated absorption time of the composite separator is shortened (about 100 s). In addition, because the electrolyte can only be retained in the inner cavity of the original PP separator, the liquid absorption capacity of the original PP separator is only 91%. When the SiO_2/PVA slurry is introduced into the separator surface, the electrolyte can also be retained in the pores of the coating layer, so the

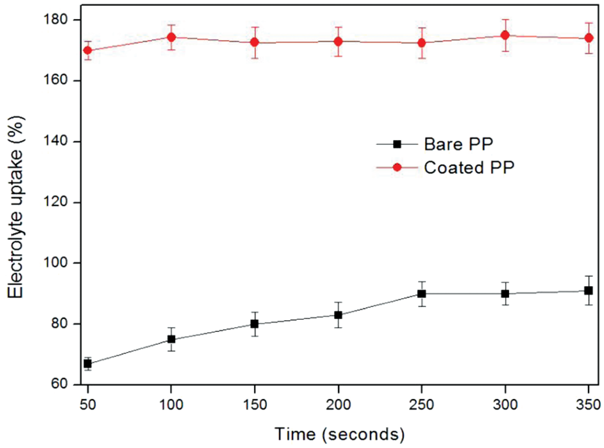

Figure 5: Effect of wetting time on electrolyte absorption by membrane.

liquid absorption capacity of the composite separator increases to 175%.

3.5 Thermal stability analysis

One of the functions of the polymer film is to separate the positive and negative poles of the battery and to prevent short circuit due to contact between the two poles (22). Therefore, for safety reasons, the separator needs to have excellent thermal stability. Figure 6 is a graph showing the thermal shrinkage of the separator as a function of temperature, and Figure 7 is the DTA curves of the separator. Each group of data was averaged through three parallel tests.

The thermal shrinkage of the bare PP film and the modified PP film increased with the increase of temperature, but the change of the thermal shrinkage of the original separator was greater than that of the modified separator. At the same temperature, the thermal shrinkage of the original separator was always greater than that of the modified separator. Especially at 170°C, the thermal shrinkage of the original separator was as high as 53%, while that of the modified separator was only 27%. The above results show that the heat resistance of the separator coated with SiO_2/PVA slurry is better than that of the untreated one. This is mainly because the coated ceramic particles and the adhesive PVA have excellent heat resistance, which can inhibit the deformation of the microporous film to some extent.

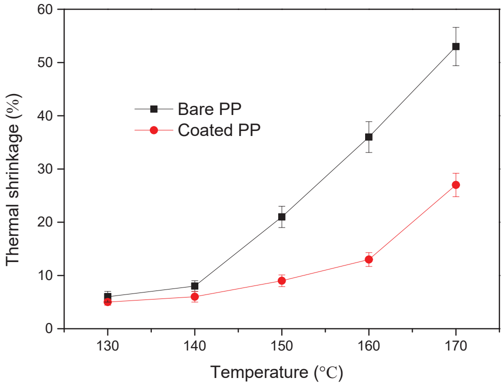

Figure 6: Comparison of thermal shrinkage of bare PP and coated PP separators as a function of temperature.

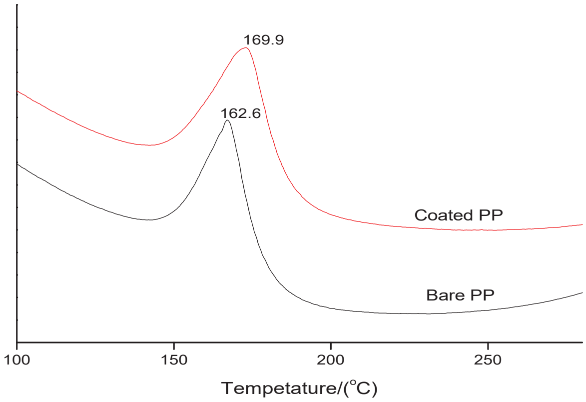

Figure 7: DTA curves of bare and coated PP separators.

From Figure 7, it can be seen that there is an endothermic peak near 162.6°C for PP separator, and the melting temperature of modified separator increases to 169.9°C, indicating that the thermal resistance of the separator can be improved by successfully coating SiO_2/PVA layer on the surface of the separator, which is consistent with the results of Figure 6.

3.6 Electrochemical performance

The cycle performance and rate performance of the battery are closely related to the ion transport capacity of the separator (23). For the modified separator, the diffusion path of lithium ions will increase with the increase of thickness, which may affect the ion transport and performance of batteries. Figure 8 shows the cycling performance of coin cell assembled with original film and modified film, respectively.

As shown in Figure 8a, the battery's discharge capacity gradually decreases with the increase in the number of cycles. This is because during the cycle performance test of the battery, some physical changes will inevitably occur inside the battery, which will lead to the increase of resistance and the decrease of discharge capacity of the battery. However, compared with the original separator, the modified one exhibits

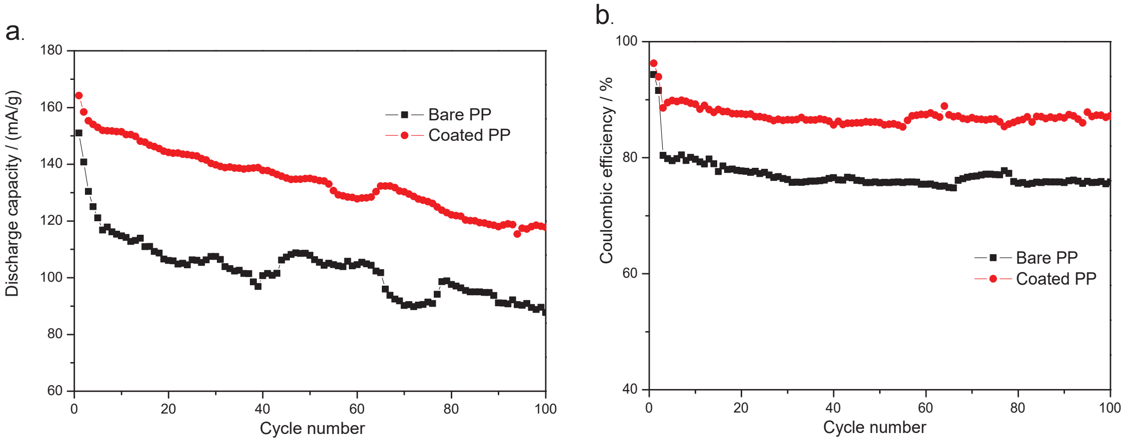

Figure 8: Cycling performance of cells using the bare PP and coated PP separators: (a) cycling capacity, (b) coulombic efficiency.

a greater discharge capacity and stronger capacity retention during the whole cycle. Especially the capacity retention rate of the original separator was only 75.79% at 100 charge-discharge times, and that of the modified separator was as high as 87.18%. In addition, as displayed in Figure 8b, the Coulombic efficiency exhibits a similar trend compared to the capacity shown in Figure 8a. The Coulombic efficiency for the case of the coated PP significantly exceeds that of the bare one. As seen, the Coulombic efficiency for the coated PP remains at about 90%; whereas the efficiency is less than 80% for the bare one. It is ascribed to the enhanced ion transfer through the modified diaphragm, which enables an improved environment for the reversible reactions at electrode during charge and discharge.

As shown in Figure 9, the discharge capacity of the battery gradually decreased with the increase of the charge/discharge current density, which was due to the decrease in the diffusion rate of lithium ions at high current density (24). Compared with the original separator, the discharge capacity of the modified separator is higher, and the higher the current density, the greater the difference between the discharge capacity of the bare PP film and that of the coated PP film. For example, the discharge capacity of the modified separator was about 158 mAh/g at 1.0 C/1.0 C charge and discharge and 91.9% at 0.2 C, while that of the original PP separator was about 119 mAh/g and 88.1% at 0.2 C. The composite separator had higher ionic conductivity and easier interfacial charge transfer, so it had higher discharge capacity at different rates. When the 0.2 C discharge test was re-performed after the high rate discharge, the discharge capacity of the battery basically returned to the initial value, indicating that the battery was not damaged after the high rate discharge test and could still be used.

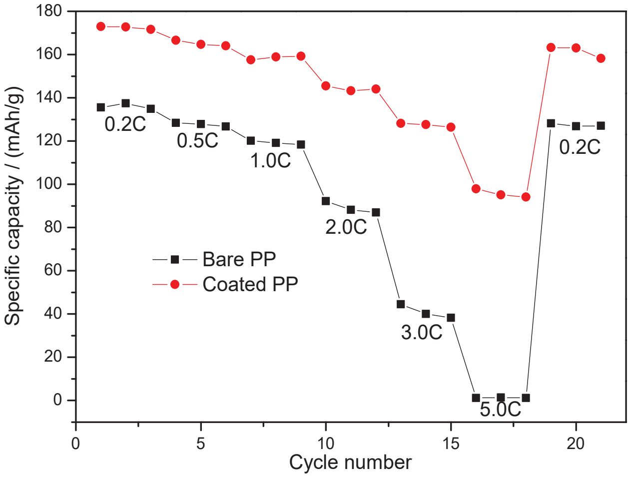

Figure 9: Variation of specific capacity of the cells using the bare PP and coated PP separators with C rate.

In summary, the cycling performance and rate performance of the battery assembled by modified separator have been improved, indicating that the coating has little effect on the diffusion of Li^+. The reasons are as follows:

(a) There are uneven gaps between the particles in the coating, which are beneficial to the intercalation and release of Li^+, and the capillary effect is also beneficial to the diffusion of Li^+;

(b) Modified separator has good wettability to electrolyte and higher liquid absorption rate, which increases the diffusion ability of Li^+ in battery.

The above results show that the wettability and liquid absorption of the separator to the electrolyte are improved by introducing SiO_2/PVA coating on the surface of PP separator, which makes the coated separator have better cycling performance and rate performance. And the performance of the battery has reached the level reported in the literature (15-17).

4 Conclusion

SiO_2/PVA slurry was prepared by using nano-SiO_2 ceramic powder as filler, PVA as binder and deionized water as solvent. The contact angle of electrolyte was reduced from 117.3° to 83.6° and the absorption rate was increased from 98% to 175% after the SiO_2/PVA coating was successfully introduced on the surface of traditional PP separator by dip coating. Shrinkage decreased from 53% to 27%. Compared with the original separator, the modified separator has higher discharge and stronger capacity retention capacity. Especially when the charge-discharge cycle is 100 times, the capacity retention rate of the original film is only 75.79%, while the capacity retention rate of the modified one is as high as 87.18%. The battery rate performance and cycle performance are significantly improved.

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