Electrochimica Acta 320 (2019) 134528

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

High thermal stability and low impedance polypropylene separator coated with aluminum phosphate

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ARTICLE INFO

Article history:
Received 25 April 2019
Received in revised form
1 July 2019
Accepted 9 July 2019
Available online 24 July 2019

Keywords:
Lithium ion batteries
$AlPO_4$
Polypropylene separator
Thermal stability

ABSTRACT

Separators with low ionic impedances and high thermal/electrochemical stability are desirable for high-performance Li-ion batteries. Herein, a composite layer consisting of $AlPO_4$, poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) and polymethyl methacrylate (PMMA) is coated on the polypropylene (PP) separator matrix. The coated PP exhibits an electrolyte uptake of 2.28%, leading to improved ionic conductivity and Li-ion diffusion coefficient. In addition, this separator has a wide electrochemical stability window, high peeling strength of 111.2 $N\ m^{-1}$ and superior thermal stability at 170 °C. By applying this coated separator in the cell with $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode, excellent cycling stability and rate performance can be also obtained. The improved electrochemical performances can be attributed to that $AlPO_4$ in the coating layer exhibits high electrolyte uptake and firmly combines with the PP matrix.

1. Introduction

Lithium-ion batteries are widely applied in portable electronics, electric vehicles and energy storage systems because of their high energy density, long cycle life and high operational voltage [1,2]. As one of main components of the battery, the separators play an important role on the electrochemical performance and safety during charge-discharge and stored processes [3]. The polyolefin (i.e., polyethylene (PE) or polypropylene (PP)) separators are widely used as the separator material for their advantages in the field of lithium-ion batteries, such as their good electrochemical stability, low cost and high thermal shutdown properties [4,5]. However, the polyolefin separators have still had many drawbacks [6–10] in a battery system. Especially, in a battery system, the layered $LiNi_xCo_yMn_zO_2$ is used as a cathode. While the battery is overheated, the polyolefin separators trend to shrink to result in short circuit and even explosion of the batteries [11,12]. To improve the thermal stability of the separators, what the many materials (i.e., polymer, SiO_2 [13], Al_2O_3 [14], TiO_2 [15], ZrO_2 [16], etc.) have been chosen to coat on the surface of the polyolefin. However, up till now, the as-prepared polyolefins still exhibit many disadvantages in the lithium ions battery for their high interfacial impedance and the tendency of peeling off the separator matrix to cause safe hidden-trouble. Considering that the melting point of $AlPO_4$ is as high as 1400 °C and the PO_4^{3-} exhibits high coordination ability, $AlPO_4$ might be an ideal coating material for polyolefins. Compared to the PE separators, the PP′ exhibit higher thermal shutdown temperature [4,5]. The PP separators coated with $AlPO_4$ may exhibit higher thermal stability and lower electrochemical impedance. In this study, a modified PP separator with micro-sphere and nanosized composite of polymer and aluminum phosphate was firstly prepared and the coating effects on the separator were further studied.

2. Experimental

2.1. Preparation of the coated PP separators

The coated PP separators were prepared by using below three steps: 1) To prepare a slurry by mixing 40 mL solvents with 0.5 g micro-sphere $AlPO_4$, 0.5 g PMMA (polymethyl methacrylate, Arkema Inc.) and 1.0 g PVDF-HFP (polyvinylidenefluoride-hexafluoropropylene, Arkema Inc.) under continuous stirring with a rate

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https://doi.org/10.1016/j.electacta.2019.07.039

of 1300 RPM for 12 h at 50 °C, in which the solvent is composed of acetone and dimethylformamide in the volume ratio of 2: 1; 2) To prepare the wet coated PP separators by coating the bare PP ones (Thickness: 20 μm, Xucheng Tech. Co., Ltd.) with the slurry; 3) To dry the wet coated PP separators for 12 h at 60 °C in a vacuum drying oven. The thickness of the as-prepared coated PP is 37 μm.

2.2. Physical characterization

Unless stated otherwise, the following measurements were performed at room temperature. A field emission scanning electron microscope (FESEM, TESCAN MIRA 3, Czech) was used to observe the morphology of the separators. A Thermo Nicolet Avatar 360 FTIR spectrometer was used to measure the Fourier transform infrared spectrometry (FTIR) by a pressing potassium bromide troche. Electrolyte uptake of the separator was measured using the following steps. The separator was soaked in the electrolyte for 2 h, and excess electrolytes were wiped off. The weights of the separator were measured before and after the soaking.

The shrinkages of the separator were measured based on the dimensional change ratio while the separators were heated under various temperature for 0.5 h, and were calculated from Eq. (1) [17,18]:

$$Shrinkage(\%) = (S_0 - S_T)/S_0 \times 100 \tag{1}$$

where S_O and S_T refer to separators area before and after heated, respectively.

Peeling strength of the coated PP separators was measured by using a Digital-Display dynamometer (DS2-50N, Japan).

2.3. Electrochemical performance

The ionic conductivities, diffusion coefficients of lithium ions, electrochemical stability of the separators were measured the electrochemical impedance spectroscopy (EIS) at 25 °C on an electrochemical work station CHI604E (Chenhua, Shanghai, China).

The ionic conductivities and diffusion coefficients of lithium ions were measured based on the EIS of cells in the frequency from 1.0×10^5 to 0.010 Hz. During the measurement of the ionic conductivities, the blocking-type cells ($S = 2.06\ cm^2$) were fabricated by sandwiching the separator between two stainless-steel electrodes.

To calculate the diffusion coefficients of lithium ions of the separator, a Li-symmetric cell was used to measure the EIS, in which the separator was sandwiched between two lithium metal electrodes. As a comparison, the diffusion coefficients of lithium ions of the $LiNi_{0.50}Co_{0.20}Mn_{0.30}O_2$ composite was calculated according to the EIS of the cell composed with lithium metal/separator/$LiNi_{0.50}Co_{0.20}Mn_{0.30}O_2$ composite, in which $LiNi_{0.50}Co_{0.20}Mn_{0.30}O_2$ composite is the mixture of $LiNi_{0.50}Co_{0.20}Mn_{0.30}O_2$/carbon (Super S)/PVDF in the weight ratio of 85: 10: 5. The electrolyte (No. 4477R) was purchased from China Guotai Huarong New Materials Ltd. of Chem. Ind..

The electrochemical stability of the separator was measured by using a linear sweep voltammetry on a cell, in which one separator was sandwiched between a lithium metal and a stainless-steel electrode. The measurement was done between 2 and 6 V (vs. Li^+/Li) at a scan rate of 1 mV s^{-1}.

The electrochemical performance of the separators was evaluated by using the CR2025 coin cells, which were assembled by sandwiching a separator between a $LiNi_{0.50}Co_{0.20}Mn_{0.30}O_2$ composite electrode ($LiNi_{0.50}Co_{0.20}Mn_{0.30}O_2$/carbon (Super S)/PVDF, 85/10/5 w/w/w) and a lithium metal. All cells were assembled in an argon-filled glove box with water and oxygen content lower than 0.1 ppm. The cycling performance of the cell was studied with a Neware Battery Tester (Neware BTS 7.6.0). The $LiNi_{0.50}Co_{0.20}Mn_{0.30}O_2$ bought from Energy Technology of Zhangzhou Wangbao Co. Ltd.

3. Results and discussion

SEM images and XRD patterns of the separators were shown in Fig. 1. It can be seen from Fig. 1a that the surface of the bare PP is relatively smooth, despite of its porous structure (with pore size between 0.1 and 0.4 μm). Fig. 1b show the SEM images of the coated PP after assembled in the battery. The surface of the coated PP is covered by the nanosized particles (Particle size: ~200 nm) and micro-sphere ones (Particle size: ~1 μm). XRD pattern confirmed that $AlPO_4$ exists in the coating layer. It can be conjectured that the PVDF-HFP can react with PMMA to form the polymer, then, the polymer and $AlPO_4$ form the composite after continuous stirring. The composite of $AlPO_4$ and polymer firstly forms the nanosized particles and then they further display larger analogous micro-sphere particles.

The coating layer may peel off from the PP matrix for its low surface energy and low polarity, leading to poor cycling and safety performance during long-term cycling. The stability of the coating layer is one of the key factors for the coated PP separators. It was determined by the thermal and electrochemical stability, and the peeling strength of the coated layer. The thermal stability of the coated PP determined by the shrinkage of the size during heating. Relationship between the shrinkage of the separator and heating temperature showed in Fig. 2a. It can be seen from Fig. 2a that the shrinkage of the coated PP is less than 50% after heated at 170 °C. However, the shrinkage of the bare PP is nearly 100% heated at the same condition. Therefore, the coating obviously improves the thermal stability of the PP separator.

In order to investigate the electrochemical stability window of the coated PP, the electrochemical system composed of lithium metal/separator/stainless-steel was scanned with the linear sweep voltammetry from 2 to 6 V (vs. Li^+/Li) at the scan rate of 1 mV s^{-1} on a electrochemical work station. The result shows that and the bare PP is stable in the voltage range between 2.0 and 4.97 V (vs. Li^+/Li), the coated PP is stable in the voltage range between 2.0 and 5.15 V (vs. Li^+/Li), indicating that the coating improves the antioxygenic property of PP separator (Fig. 2b). The reason is that the coating can avoid the PP matrix to contact with the electrolyte to improve its antioxidation in the high potential range.

The peeling strength of the coating layer indicates whether the coating layer firmly combine with the PP matrix. The experimental result shows that the peeling strength of the coated PP is 111.2 N m^{-1}. In comparison, the peeling strengths of P2 (PP coated Al_2O_3/PVDF-HFP/PMMA) and P3 (PP coated $AlPO_4$/PVDF/PMMA) are 93.6 N m^{-1} and 78.2 N m^{-1}, respectively. This result indicates that the coated layer of the coated PP firmly binded with the PP matrix.

To investigate the reason of coated layer firmly binded with the PP matrix, FTIR spectra of the coated PP with $P_{AlPO4/PVDF-HFP/PMMA}$ were measured. The FTIR spectra (Fig. 3) show that the peaks located at 700 cm^{-1} (stretching vibration of C–P) and 1110 cm^{-1} (characteristic absorption of PO_4^{3-}) confirm that the partial PO_4^{3-} may combine with the PP matrix to increase the combined force between the matrix and coating layer.

To investigate the cycling performance, the cells using various cathodes and separators were tested the charge-discharge performance at the rate of 1 C. Here, the separator prepared by coating PP with the mixture of $AlPO_4$, PVDF-HFP and PMMA ($P_{AlPO4/PVDF-HFP/PMMA}$) is abbreviated as P1. For comparison, the electrochemical performances of other three separator were also tested: P2, P3 and

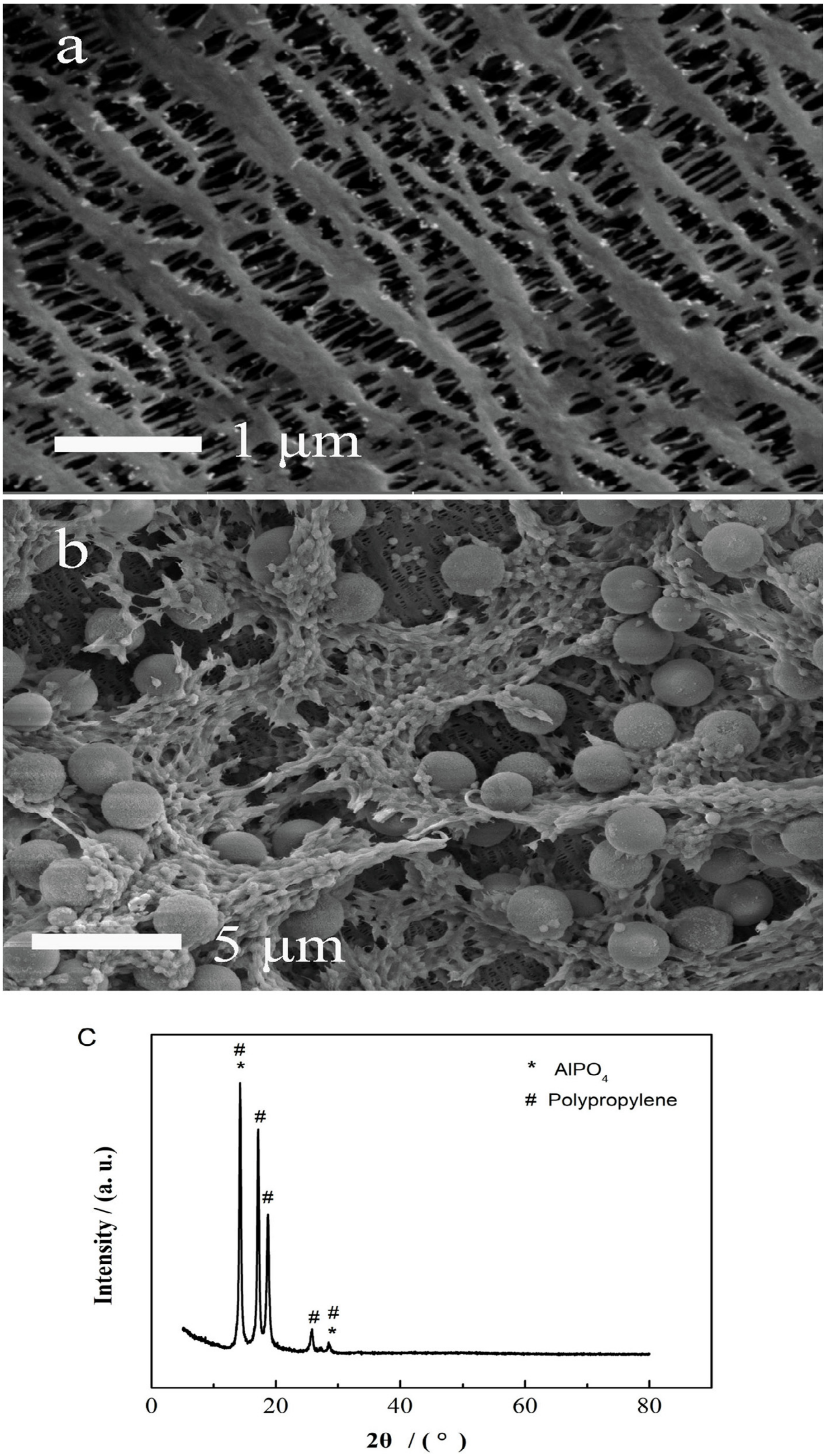

Fig. 1. SEM images and XRD patterns of the separators (Fig. 1a: Bare PP; 1b: Coated PP; 1C: XRD patterns of the Coated PP).

a bare PP. Fig. 4a shows that using $LiNi_{0.50}Co_{0.20}Mn_{0.30}O_2$ as cathode, P1, P2, P3 and bare PP exhibit 1st cycle capacities of 213, 202, 198 and 194 mAh g^{-1}, respectively. After 40 cycles, the capacities became 191, 178, 172 and 166 mAh g^{-1}, leading to capacity fading rates of 10.3%, 11.9%, 13.1% and 14.4%, respectively. The experimentl result further shows that using $LiNi_{0.50}Co_{0.20}Mn_{0.30}O_2$ as cathode,

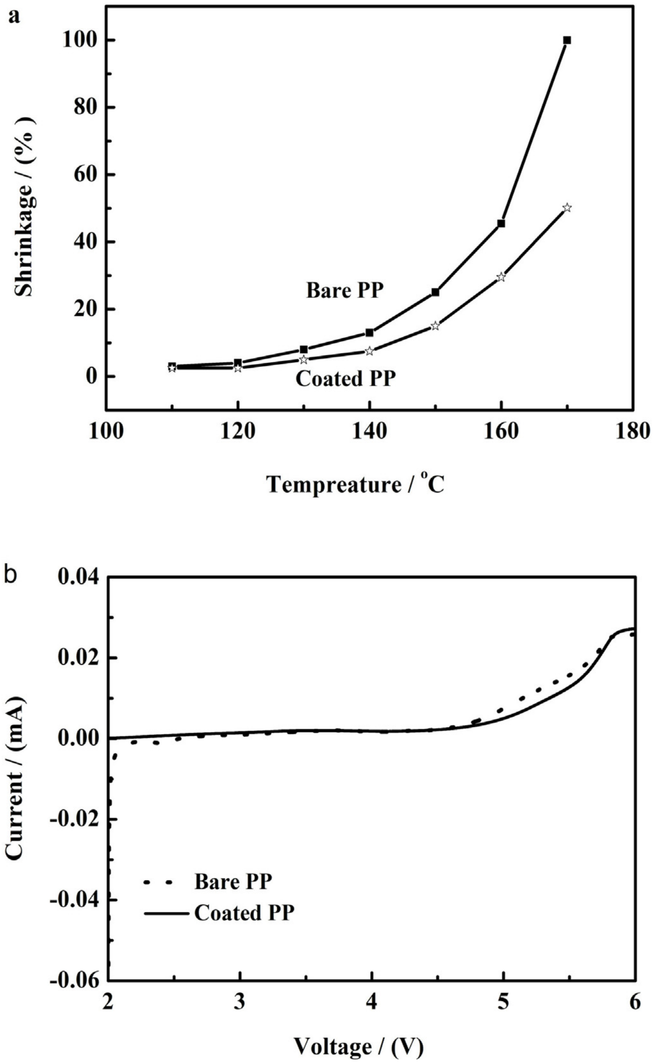

Fig. 2. (a) Shrinkage of the separators in the temperature range of 110–170 °C. (b) The linear scan voltammogram curves of the separators.

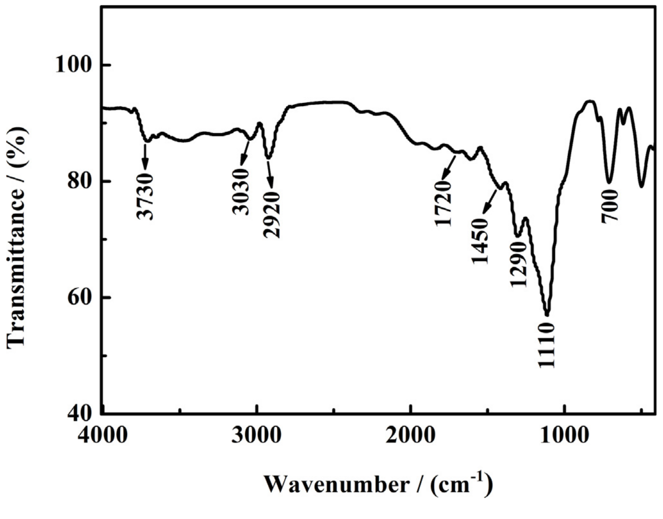

Fig. 3. FTIR spectra of the coated PP separator.

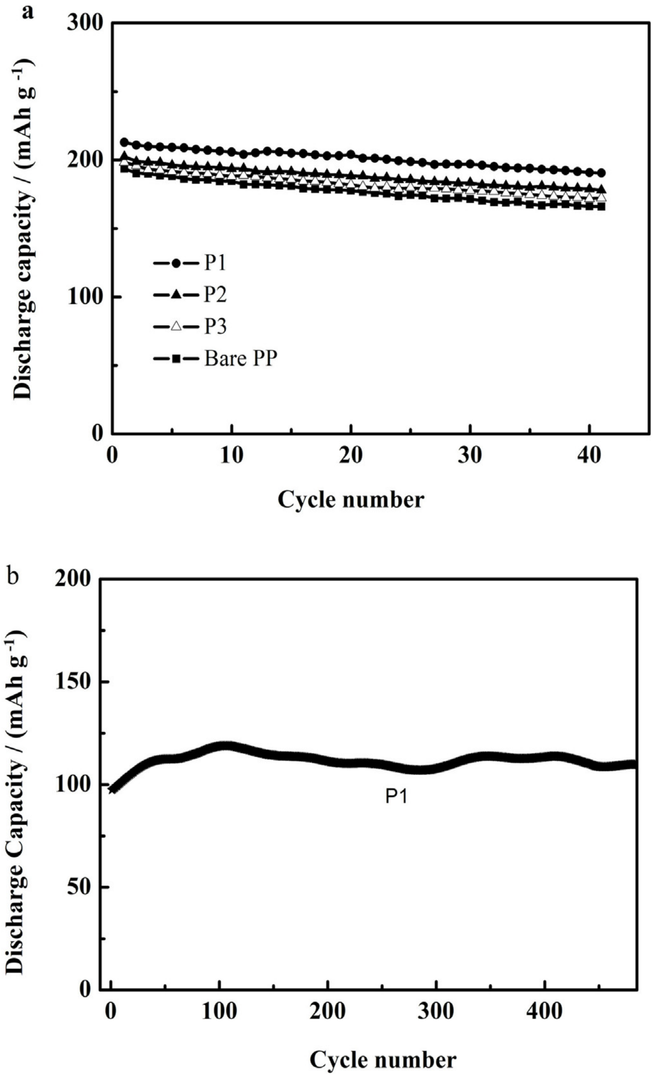

Fig. 4. Relationship curves between discharge capacity and cycle number (P1: $P_{AlPO4/PVDF\text{-}HFP/PMMA}$; P2: $P_{Al2O3/PVDF\text{-}HFP/PMMA}$; P3: $P_{AlPO4/PVDF/PMMA}$; a: $LiNi_{0.50}Co_{0.20}Mn_{0.30}O_2$ cathode discharge at the 1 C rate in the voltage range of 2.5–4.6 V; b: $LiFePO_4$ cathode discharge at the 2C rate in the voltage range of 2.5–3.9 V).

P1, P2, P3 and bare PP exhibit the 1st cycle coulombic efficiency (η) of 79.5%, 83.9%, 80.8% and 79.5%, respectively. After 40 cycles, the coulombic efficiency became 99.8%, 99.5%, 99.4% and 99.6%. Boriboon et al. [19] found that the cell using $LiNiMnCoO_2$ cathode and regenerated cellulose titania separator exhibit the capacity of 100 mAhg^{-1} which discharged at the 1C rate.

In order to further evaluate the electrochemicla performance of the coated PP avoiding the effect of $LiNi_{0.50}Co_{0.20}Mn_{0.30}O_2$ performance, the cells using $LiFePO_4$ cathode and coated PP with the mixture of $AlPO_4$, PVDF-HFP and PMMA was tested the long-term stability in the voltage range of 2.5–3.9 V. Fig. 4b shows that the cell exhibit the capacities of 93 mAh g^{-1} (1st cycle), 95 mAh g^{-1} (2nd cycle) and 110 mAh g^{-1} (485th cycle), and the 485 cycle' capacities is not fading while tested with the current as high as the rate of 5C (1C = 170 mA). The experimentl result further shows that the cell exhibit the coulombic efficiency (η) is 63% (1st cycle), 101.6% (2nd cycle), 99.6% (485th cycle), respectively. During the testing process, the capacities is firstly increasing to 120 mAh g^{-1} (101th cycle), then decreasing to 110 mAh g^{-1} (485th cycle). Compared to previous literature ($LiFePO_4$ cathode exhibits the discharge capacity

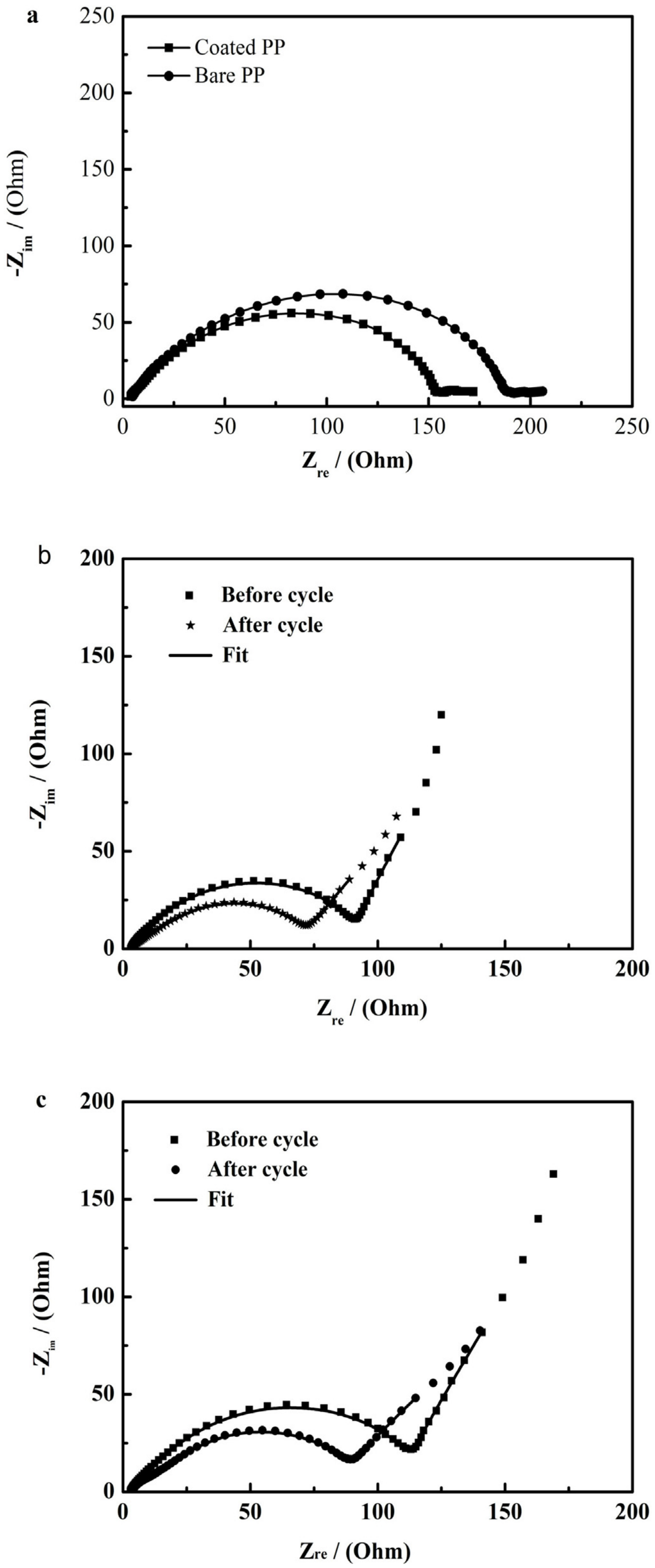

Fig. 5. EIS of the cells using various separators. (a: Li-symmetric cell; b: Half-cell with $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ composite and coated PP before cycle and after 40 cycles; c: Half-cell with $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ composite and bare PP before cycle and after 40 cycles).

of 120 mAh g^{-1} for the improved PE separator [20], 118 mAh g^{-1} for commercial Celgard 2400, and poly(vinylidene fluoride)/polyacrylonitrile blend separator (2C rate) [20]), the coated PP with the mixture of $AlPO_4$, PVDF-HFP and PMMA obviously improves the $LiFePO_4$ cathode discharged and cycling performance of the cell while the $LiNi_{0.50}Co_{0.20}Mn_{0.30}O_2$ cathode was used. Therefore, the cell using coated PP of $P_{AlPO4/PVDF-HFP/PMMA}$ exhibits the excellent cycling performance.

The electrolyte uptake, ionic conductivity, diffusion coefficients of Li ions and surface impedance of the separator were considered to be the important factors to result in the excellent charge-discharge performance of the cell. Electrolyte uptake of the separator was calculated from Eq. (2) [21].

$$\text{Uptake}(\%) = (W_1 - W_0)/W_0 \times 100 \tag{2}$$

where W_0 and W_1 are the weights of separator before and after the soaking, respectively.

Electrolyte uptakes for different separators are calculated to be 2.28% ($P_{AlPO4/PVDF-HFP/PMMA}$) and 1.51% (bare PP), indicating that the coating layer improves electrolyte uptake of the separator to

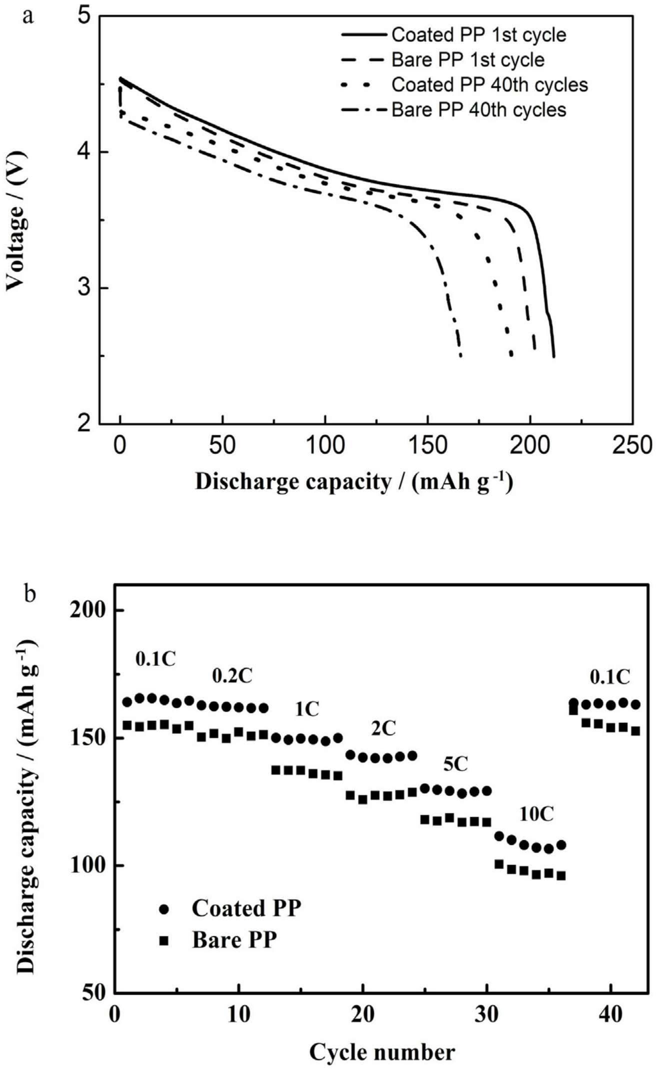

Fig. 6. (a) Discharge curves of the cells in the voltage range of 2.5–4.6V and (b) Rate performance of the cells in the voltage range of 2.5–4.3V while used $LiNi_{0.50}Co_{0.20}Mn_{0.30}O_2$ composite and coated PP or bare PP.

increases the ionic conductivities for the good compatibility between the PMMA in the coating layer and electrolyte.

In order to measure the diffusion coefficients of lithium ions, two kinds of the electrochemical systems were employed to measure the electrochemical impedance spectroscopy (EIS) of the samples. Li-symmetric cell is composed of Li metal/separator/Li metal, half cell with $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ composite is $LiNi_{0.50}Co_{0.20}Mn_{0.30}O_2$ composite/separator/Li metal. In the electrochemical system of Li metal/separator/Li metal, the EIS of the cells using various separators were shown in Fig. 5a. Fig. 5a shows that the charge transfer impedance of the coated PP is 154 Ω, and the bare PP is 188 Ω, indicating a reduced charge transfer impedance after coating.

In the electrochemical system of half-cell with $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ composite, the EIS of the half cell with $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ composite and coated PP before cycle and after 40 cycles were shown in Fig. 5b; the EIS of the half cell with $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ composite and bare PP before cycle and after 40 cycles were shown in Fig. 5c. The diffusion coefficients of lithium ions of the cells with the separators are estimated based on the following Eq. (4) [22,23]. according the data in Fig. 5b or 5c

$$D_{Li^+} = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2} \quad [4]$$

where R represents the gas constant ($8.314\,J\,K^{-1}\,mol^{-1}$), T is the

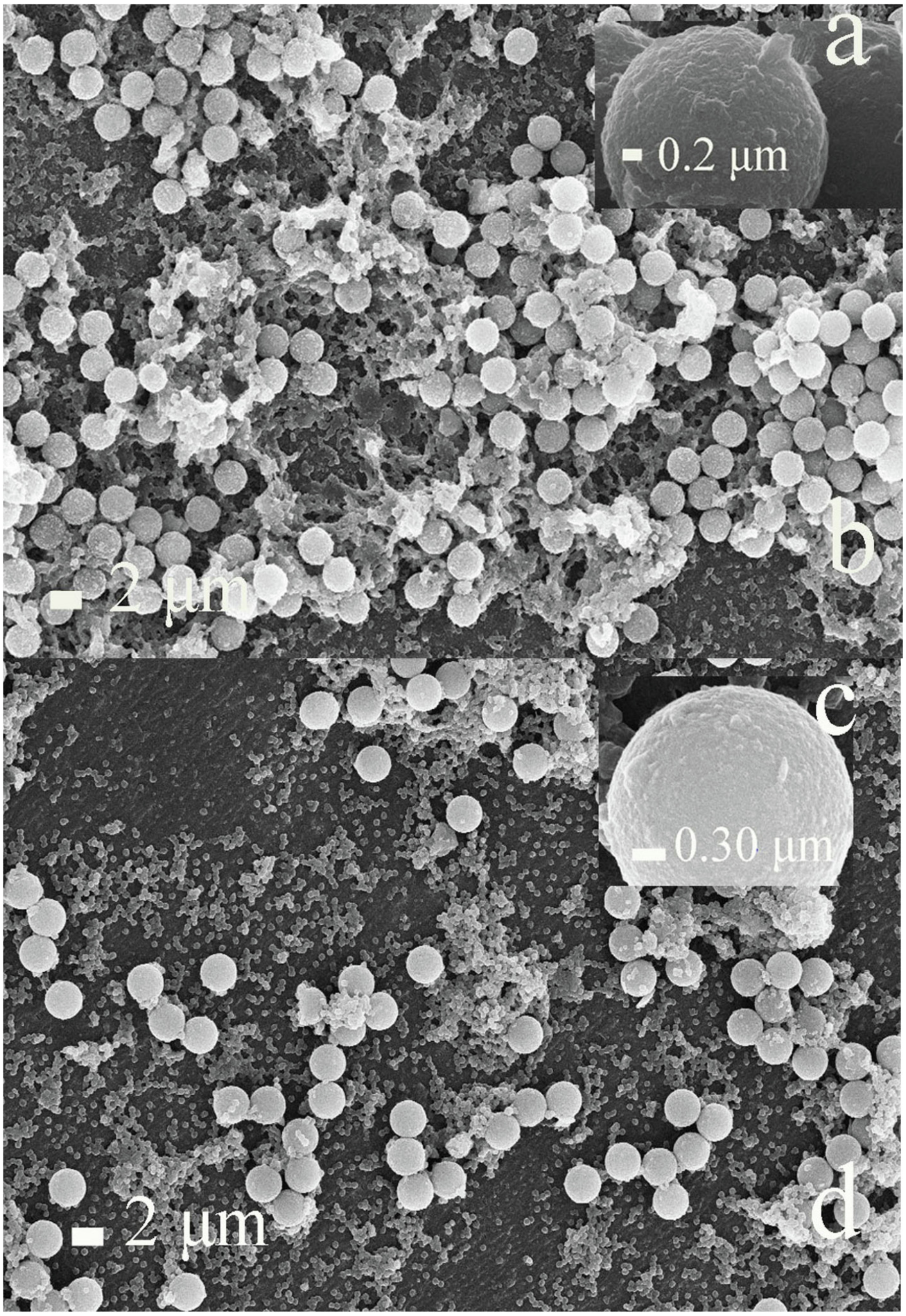

Fig. 7. SEM images of the coated PP separators after 40 cycles. (a and b: cycled in the voltage range of 2.5~4.6 V for 40 cycles; c and d: cycled at 55 °C in the voltage range of 2.5 ~ 4.3 V).

absolute temperature (298 K), A is the surface of the electrode (1.766 cm^2), n is the number of the electrons involved in the reaction (n = 1), F reflects the Faraday constant, C is the concentration of lithium ion (C is 4.90×10^{-2} mol cm^{-3} in this work), σ is the Warburg coefficient which can be calculated from relationship plot between Z_{re} and $\omega^{-1/2}$ (square root of the angular frequency) in the low-frequency region of the cells [24,25]. The diffusion coefficients of lithium ions of the cells with the coated PP ($D^{+}_{\mathrm{Li},\ \mathrm{coated\ PP}}$) are calculated to be $7.88 \times 10^{-13,}$ cm^2 s^{-1}. Compared to the coated PP, the D^{+}_{Li} of the cell with the bare PP ($D^{+}_{\mathrm{Li},\ \mathrm{PP}}$) is lower ($4.64 \times 10^{-13}$ cm^2 s^{-1}). Therefore, the coating can increase the diffusion coefficient of lithium ions in the separator, indicating that the mixture of $AlPO_4$, PVDF-HFP and PMMA increased the non-crystalline region of the separator to enhance the diffusion of lithium ions.

Fig. 5b shows that the impedance spectra of the cells using coated PP and $LiNi_{0.50}Co_{0.20}Mn_{0.30}O_2$ composite are 92 (before cycle) and 71.8 Ω (after 40 cycles), indicating that the impedance of the cells using coated PP and $LiNi_{0.50}Co_{0.20}Mn_{0.30}O_2$ composite decreased with cycling in 40 cycles. Here, the cell using coated PP and $LiNi_{0.50}Co_{0.20}Mn_{0.30}O_2$ composite prepared by charge-discharged the cell for 40 cycles at the 1 C rate. In comparison with coated PP, the impedance spectra of the cell using bare PP and $LiNi_{0.50}Co_{0.20}Mn_{0.30}O_2$ composite is 113.2 (before cycle) and 90 Ω (after 40 cycles) (Fig. 5c).

According to the Warburg coefficient (σ), which can be calculated from relationship plot between Z_{re} and $\omega^{-1/2}$, thus the diffusion coefficient of lithium ions for the coated PP is 3.28×10^{-16} cm^2 s^{-1} ($D^{+}_{\mathrm{Li},\ \mathrm{composite,\ coated\ PP}}$) and for the bare PP is 1.54×10^{-16} ($D^{+}_{\mathrm{Li},\ \mathrm{composite,\ PP}}$). $D^{+}_{\mathrm{Li},\ \mathrm{composite,\ coated\ PP}}$ is higher than $D^{+}_{\mathrm{Li},\ \mathrm{composite,\ PP}}$. Therefore, the coating with the mixture of $AlPO_4$, PVDF-HFP and PMMA increases the diffusion performance of lithium ions. Compared to the $D^{+}_{\mathrm{Li},\ \mathrm{composite,\ coated\ PP}}$, the $D^{+}_{\mathrm{Li},\ \mathrm{coated\ PP}}$ is larger. It can be conjectured that the coating cannot affect the diffusion of lithium ions for the good compatibility between the PMMA in the coating layer and electrolyte.

Fig. 6a shows that the cell using coated PP with $P_{\mathrm{AlPO4/PVDF\text{-}HFP/PMMA}}$ exhibits higher discharge voltage platform (~3.87V in the 1st cycle, ~3.77V in the 40th cycle) than those using bare PP (~3.80 V in the 1st cycle, ~3.70 V in the 40th cycle). Compared to bare PP, the coated PP with the mixture of $AlPO_4$, PVDF-HFP and PMMA obviously improves the discharged and cycling performance of the cell while the $LiNi_{0.50}Co_{0.20}Mn_{0.30}O_2$ cathode was used. Fig. 6b shows the rate performance of the cell with $P_{\mathrm{AlPO4/PVDF\text{-}HFP/PMMA}}$ separator in the voltage range of 2.5–4.3 V while continuously charge-discharged for 42 cycles at the current of 0.1 C, 0.2 C, 1 C, 2 C, 5 C, 10 C and 0.1 C rate. The cell using the coated PP with $P_{\mathrm{AlPO4/PVDF\text{-}HFP/PMMA}}$ exhibits a excellent high rate and cycling performance with discharge capacities of 166 mAh g^{-1} (0.1 C rate), 163 mAh g^{-1} (0.2 C rate), 150 mAh g^{-1} (1 C rate), 143 mAh g^{-1} (2 C rate), 130 mAh g^{-1} (5 C rate), 112 mAh g^{-1} (10 C rate) and 164 mAh g^{-1} (0.1 C rate), respectively. In comparison with coated PP, the cell with bare PP separator exhibits the discharge capacities of 155 mAh g^{-1} (0.1 C rate), 150 mAh g^{-1} (0.2 C rate), 137 mAh g^{-1} (1 C rate), 127 mAh g^{-1} (2 C rate), 118 mAh g^{-1} (5 C rate), 100 mAh g^{-1} (10 C rate) and 156 mAh g^{-1} (0.1 C rate), respectively. Therefore, the coating layer increases electrolyte uptake of the separator to improve the ionic conductivities and diffusion performqance of lithium ions, thus, the coated PP exhibits less electrochemical impedance. The cell using $LiNi_{0.50}Co_{0.20}Mn_{0.30}O_2$ cathode and coated PP with $P_{\mathrm{AlPO4/PVDF\text{-}HFP/PMMA}}$ exhibit higher discharge voltage platform and rate performance compared to the one using bare PP for the good compatibility between the PMMA in the coating layer and electrolyte.

Fig. 7 shows that the SEM images of the coated PP separators after charge-discharged for 40 cycles. Fig. 7a and b shows that the SEM images of the coated PP after 40 cycles in the voltage range of 2.5~4.6 V, and Fig. 7c and d shows that the SEM images of the coated PP charge-discharged for 40 cycles in the voltage range of 2.5~4.3 V and at 55 °C. Fig. 7 indicates that the coating layer composed of the nanosized and micro-sphere particles is stable duing cycling in the voltage range of 2.5~4.6 V and at 55 °C because the micrograph morphology of the coated PP is unchanged.

4. Conclusions

In this work, a composite coating layer consisting of $AlPO_4$, poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) and polymethyl methacrylate (PMMA) on a PP matrix is firstly prepared. The coated PP exhibits an electrolyte uptake of 2.28%, leading to improved ionic conductivity and Li-ion diffusion coefficient. In addition, this separator has a wide electrochemical stability window, high peeling strength of 111.2 N m^{-1}, ionic conductivity of 1.03×10^{-3} S cm^{-1}, the diffusion coefficient of lithium ions of 7.88×10^{-13} cm^2 s^1, and superior thermal stability at 170 °C. By applying this coated separator in the cell using $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ or $LIFePO_4$ cathode, excellent cycling stability and rate performance can be also obtained. The improved electrochemical performances can be attributed to that $AlPO_4$ in the coating layer exhibits high electrolyte uptake and firmly combines with the PP matrix.

Acknowledgements

This work was supported by the Fujian Provincial Science and Technology Department's University Industry Cooperation Project of China (grant numbers 2016H6006) and Fuzhou Science and Technology Bureau Project of China (grant numbers 2017-G-68).

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