Enhancement of Thermal Stability and Cycling Performance of Lithium-Ion Battery at High Temperature by Nano-ppy/OMMT-Coated Separator

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Abstract
Nanopolypyrrole/organic montmorillonite- (nano-ppy/OMMT-) coated separator is prepared by coating nano-ppy/OMMT on the surface of polyethylene (PE). Nano-ppy/OMMT-coated separator with three-dimensional and multilayered network structure is beneficial to absorb more organic electrolyte, enhancing the ionic conductivity (reach 4.31 mS cm⁻¹). Meanwhile, the composite separator exhibits excellent thermal stability and mechanical properties. The strong covalent bonds (Si-F) are formed by the nucleophilic substitution reaction between F⁻ from the thermal decomposition and hydrolysis of LiPF₆ and the covalent bonds (Si-O) of nano-ppy/OMMT. The Si-F can effectively prevent the formation of HF, POF₃, and LiF, resulting in the inhibition of the disproportionation of Mn³⁺ in LiNi₁/₃Co₁/₃Mn₁/₃O₂ material as well as reducing the internal resistance of the cell. Therefore, the nano-ppy/OMMT-coated separator exhibits outstanding capacity retention and cycling performance at 80°C.

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Nanopolypyrrole/organic montmorillonite-(nano-ppy/OMMT-)coated separator is prepared by coating nano-ppy/OMMT on the surface of polyethylene (PE). Nano-ppy/OMMT-coated separator with three-dimensional and multilayered network structure is beneficial to absorb more organic electrolyte, enhancing the ionic conductivity (reach 4.31 mS/cm). Meanwhile, the composite separator exhibits excellent thermal stability and mechanical properties. The strong covalent bonds (Si-F) are formed by the nucleophilic substitution reaction between F\(^{-}\) from the thermal decomposition and hydrolysis of LiPF\(_6\) and the covalent bonds (Si-O) of nano-ppy/OMMT. The Si-F can effectively prevent the formation of HF, POF\(_3\), and LiF, resulting in the inhibition of the disproportionation of Mn\(^{3+}\) in LiNi\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) material as well as reducing the internal resistance of the cell. Therefore, the nano-ppy/OMMT-coated separator exhibits outstanding capacity retention and cycling performance at 80°C.

1. Introduction

With the extensive application of lithium-ion battery (LIB) to electric vehicles and energy storage, the security of LIB at high temperature should be given more attention. It is worthy to note that the separator plays an essential part in permitting the transportation of Li-ion and preventing the contact of the electrodes in the LIB [1]. PE with excellent mechanical properties and electrochemical stability at room temperature is widely applied in the realm of LIB. However, the hydrophilic group of PE would lead to poor compatibility between PE and organic solution, thus increasing the internal resistance of the cell [1, 2]. A high thermal shrinkage of PE separator is usually found at high temperature, causing internal short circuit of the cell [3, 4]. LiPF\(_6\) is a common organic electrolyte. LiF, HF, and POF\(_3\) from the thermal decomposition and hydrolysis of LiPF\(_6\) at high temperature may be formed on the surface of the electrodes [5]. As insulating materials, LiF and POF\(_3\) may hinder the charge transfer reaction [6, 7]; HF can corrode the transition metals of cathode material [5, 8]. Hence, the electrochemical property and stability of LIB at high temperature depend on the thermal stability of organic electrolyte and separator. To handle these problems, inorganic materials, such as TiO\(_2\), Al\(_2\)O\(_3\), and SiO\(_2\), are coated on the surface of separator [9–12]. Although inorganic coatings can effectively improve the mechanical property and thermal stability of separators, inorganic particles would increase the interface resistance of the cell during the charge and discharge process. To ensure the safety of LIB and achieve its excellent performance at high temperature, it is essential to select proper inorganic coatings to enhance the thermal, mechanical, and electrochemical performances of the separator.

Compared with the conventional coated inorganic material, nano-organic montmorillonite (OMMT) layered silicates have a greater promising future for their functional advantages and structure [13–15]. OMMT, with the advantages of high specific surface area (~31.82 m\(^2\)/g), high aspect ratio large (~1000), high cation-exchange capacity (CEC~80 mequiv./100 g), length scale (clay channel width < 25 × 10\(^{-10}\) m), and appropriate interlayer charge (~0.55), is considered to be suitable for inorganic coating. The structure
of montmorillonite (MMT) consists of two fused silica tetrahedral sheets that sandwich an edge-shared octahedral sheet of either Al₂O₃ or Mg, Ca²⁺ and Na⁺ existing in the interlayer can be replaced by alkylammonium ions in the cation-exchange reaction to form the hydrophilic-layered and organophilic silicate. Alkylammonium ions in the interlayer can produce a nanopolymer-MMT, which increases the solubility of lithium salts and improves the mechanical properties of separators, because of its high dielectric property and huge interfacial area [16–18]. OMMT coated with high specific surface area can improve the absorbing ability of organic electrolyte, therefore enhancing the ion conductive ability of electrolyte membrane [17]. When polymer is mixed with MMT, the polymer chain can enter the layer of MMT, decreasing the pore diameter of the polymer electrolyte membranes [19]. OMMT can also react with impurities of the electrolyte, inhibiting the negative reaction between the impurities and Li-ion and then enhancing the stability of the interface between electrolyte and electrode [20–22]. High cation exchanges of OMMT regarded as Lewis acid centers can compete with lithium-ion to form complexes with the polymer. This would enhance conducting pathways for lithium-ion [23]. Therefore, OMMT, favorable inorganic coating for the separator, can improve the thermal stability and electrochemical performance of the cell.

In this study, under the interaction with FeCl₃ as the oxidant and Sodium p-toluenesulfonate (TSANa) as the swelling agents, pyrrole (py) was polymerized between molecular layers of MMT. Nano-ppy/OMMT was added to the poly(vinylidene fluoride) (PVDF) and N-methyl pyrrolidone (NMP) with different ratios. Then the mixed solution was coated onto the surface of PE separator. This method was used in the preparation of nano-ppy/OMMT-coated separator. The microstructure and the electrochemical performance of nano-ppy/OMMT-coated separator were explored and discussed in detail. The electrochemical performance of the cell assembled with nano-ppy/OMMT-coated separator and LiPF₆ was evaluated at high temperature. Then the contents of LiF, HF, and POF₂ in the cell after 100 cycles at 0.5 C and 80 °C were explored and studied, compared with those of the cell assembled with PE separator under the same conditions.

2. Experimental

2.1. Modified Principle and Preparation of Nano-ppy/OMMT. The OMMT was prepared by the cation-exchange reaction between Al³⁺ in the MMT and the Octadecyl Dimethyl Ammonium Chloride (ODAC) as organic intercalation agent. When the grain diameter of OMMT became smaller and its layer spacing was expanded, py enters the molecular layers of OMMT more easily. During the reaction with TSANa as the swelling agents and FeCl₃ as the oxidant, py was polymerized between molecular layers to expand layer spacing of OMMT. This method was applied to preparing nano-ppy/OMMT [24].

The nano-ppy/OMMT was prepared by mixing the MMT (AR, Aladdin) and ODAC (AR, Tianjin Guangfu) in deionized water and stirring at 60 °C for 12 h until the homogenous solution was obtained. The weight ratio between ODAC and MMT was 1:5. TSANa (AR, Tianjin Guangfu) and py (AR, Beijing J&K) were dissolved in the mixture solution and vigorously stirred at room temperature for 1 h (TSANa and py in the ratio of 1:8 by mass). 30 mL 1 mol/L FeCl₃ was added to the mixture solution with the dropping funnel and then stirred at the room temperature for 6 h. py was polymerized in situ under the action of TSANa and FeCl₃. At last, the resulting solution was washed, separated by centrifugal, and then putted into the high vacuum drying oven for 10 h at 80 °C.

2.2. The Preparation of Nano-ppy/OMMT-Coated Separator. The PVDF (Aladdin Chemistry Co., Ltd.) and NMP (AR, Tianjin Guangfu) (1:8 by mass) were mixed and stirred vigorously for 3 h until PVDF fully dispersed in NMP. And then nano-ppy/OMMT was added to the mixture solution (its mass ratio with PVDF is 0.04:1, 0.06:1, and 0.08:1) and stirred for 10 h until the homogenous solution was formed. The mixed solution was coated onto both sides of the PE separator (10 μm thick, WuHan XuHua) and dried in a vacuum oven at 50°C for 6 h. The nano-ppy/OMMT-coated separator was prepared in the way shown in Figure 1 [25,26].

2.3. Electrode Preparation and Cell Assembly. The positive electrode was prepared by mixing LiNi₀.₅Co₀.₅Mn₀.₅O₂ as active material powder, acetylene black, and PVDF binder (in the mass ratio of 8:1:1) in NMP solvent, which was stirred for 10 h until the viscous slurry was formed. The viscous slurry was coated on the aluminum foil (current collector) and dried at 100°C in the vacuum oven for 10 h. The liquid electrolyte consisted of 1 M LiPF₆ in diethyl carbonate (DEC)/ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (1:1:1 in mass, battery grade, Kejing. Co., Ltd.). The lithium metal served as the negative electrode (battery grade, Kejing. Co., Ltd.). A cell was assembled by sandwiching a nano-ppy/OMMT-coated separator between LiNi₀.₅Co₀.₅Mn₀.₅O₂, positive electrode, and the lithium metal, negative electrode. LiPF₆ liquid electrolyte was injected into the cell and pressed by the hydraulic press at the pressure of 10 MPa. All cells were implemented in a dry argon atmosphere glove box [27].

2.4. Characterization. The interlayer spacing and crystallization of both MMT and nano-ppy/OMMT were studied by X-ray diffraction (XRD), an automatic Japanese D/MAX-2500 powder diffract meter with monochromatic Cu Kα radiation; voltage pressure and current of 30 kV and 30 mA, respectively, scanning range of 1° ≤ 2θ ≤ 15°, and scanning speed of 3°/min; the incident X-ray wave length was 0.154 nm. The interlayer spacing was calculated by the following Bragg equation:

$$d = \frac{\lambda}{2 \sin \theta}$$

where $d$ is the layer spacing; $\theta$ is the incident angle; $\lambda$ is the wavelength of incident X-ray.
Transmission electron microscope (TEM, JEM-2100F) was adopted to study the surface morphology of MMT and OMMT. Scanning electron microscopy (SEM, NanoSEM 430) was adopted to study the cross-sectional structure of PE separator and nano-ppy/OMMT-coated separator. Nano-ppy/OMMT-coated separator and PE separator were measured after soaking the separators in LiPF$_6$ liquid electrolyte. The capacity of liquid electrolyte uptake was calculated with the following equation:

$$\varphi = \frac{w_1 - w_0}{w_0} \times 100\%$$

where $w_0$ is the weight of dry separator and $w_1$ is the weight of liquid electrolyte after removing excess electrolyte on the surface.

The tensile properties of nano-ppy/OMMT-coated separator and PE separator were evaluated by Universal Material Testing Machine (WDW5000) with a beam rate value of 10 mm/min and a load cell capacity of 5000 N. Thermogravimetric analysis (TGA, STA409EP, NETZSCH) was applied to investigate the thermal characteristics of nano-ppy/OMMT-coated separator and PE separator from 25°C to 600°C at a heating rate of 10°C/min under N$_2$ atmosphere. Impedance spectroscopy was used to test ionic conductivity of nano-ppy/OMMT-coated separator and PE separator with two stainless steel blocking electrodes in the frequency range from 0.01 Hz to $10^5$ Hz with the amplitude of 5 mV for an open circuit potential (CHI660E). The following equation was used to calculate ionic conductivity ($\sigma$):

$$\sigma = \frac{d}{R_b \times A},$$

where $R_b$ is the bulk resistance, $d$ is the film thickness, and $A$ is the surface area of electrode.

Charge/discharge performances and cycling behavior of cells assembled with nano-ppy/OMMT-coated separator and PE separator were tested by battery testing equipment CT2001A with the testing voltage between 2.7 V and 4.2 V at 0.5 C and 80°C. X-ray photo electron spectroscopy (XPS, PHI-5700, ESCA System) with an Al Kα X-ray source at 45° take-off angle was used to analyze the surface characteristic of the electrode after 100 cycles at 0.5 C and 80°C; residual electrolyte on the electrode was washed several times with anhydrous dimethyl carbonate in vacuum drying overnight at room temperature.

3. Results and Discussion

The XRD patterns of MMT and nano-ppy/OMMT are shown in Figure 2. The characteristic peak’s center is at $2\theta = 6.18^\circ$, corresponding to an interlayer spacing of 1.42 nm for the (0 0 1) plane of MMT. The cation-exchange reaction occurs between the ODAC and MMT. The long alkyl chain of ODAC can increase the interlayer spacing of MMT so that py can enter the layers of MMT easily. In the reaction with TSANa and FeCl$_3$, py is polymerized between molecular layers. The characteristic peak is shifted to $2\theta = 2.68^\circ$, corresponding to the interlayer spacing of 3.61 nm for nano-ppy/OMMT. Meanwhile, the diffraction peak becomes much smoother, meaning that the nano-ppy/OMMT is in amorphous state, which makes it much easier to enhance the ionic conductivity of polymer electrolytes [28, 29].

Figures 3(a) and 3(b) show the surface morphology of MMT and nano-ppy/OMMT by TEM. MMT is gathered into massive texture. The lamellar structure of nano-ppy/OMMT can be clearly seen, which would provide the basis for
the construction of three-dimensional and multilayered network structure of the composite separators. Figures 3(c)–3(f) exhibit the cross-sectional structure of PE separator and nano-ppy/OMMT-coated separator by SEM. Figure 3(c) shows that the polymer chain of PE is relatively dense so that it is not conducive to absorb organic electrolyte. Nano-ppy/OMMT is coated on the surface of PE separator (see Figure 3(d)), displaying the three-dimensional and multilayered network structure (see Figures 3(e) and 3(f)). Nano-ppy/OMMT-coated separator with high specific surface area and high aspect ratio can promote the separator to absorb more organic electrolyte. This would be beneficial for the migration of Li\(^+\) and the increase of the ionic conductivity.

Thermal stability is an important property for separator in Li-ion cell. PE separators are prepared by biaxial stretching so that they cannot maintain their dimensional stability at high temperatures (the melting temperature of PE is about 135\(^\circ\)C). The dimension of PE separator exposed to high temperatures will be changed, leading to the electric short circuit between electrodes. Therefore, it is essential to maintain the dimension of separators at high temperature. The thermal stabilities of nano-ppy/OMMT-coated separator and PE separator are, respectively, measured and evaluated after the exposure at 80\(^\circ\)C for 5 h, and the results are shown in Figure 4(a). There is no significant variation in dimension of nano-ppy/OMMT-coated separator. However, an evident thermal shrinkage (8\%) of PE separator is shown under the same condition. This can be explained by the fact that thermal shrinkage of the PE separator at 80\(^\circ\)C is prevented by nano-ppy/OMMT coated onto surface of PE separator.

The thermal stabilities of both PE separator (1.131 mg) and nano-ppy/OMMT-coated (5.640 mg) separator were assessed through thermogravimetric analysis at temperatures between 25\(^\circ\)C and 600\(^\circ\)C in N\(_2\) atmosphere. Figure 4(b) shows that PE has two weight loss processes. The first weight loss process (at about 233\(^\circ\)C) is due to the evaporation of vinylene carbonate. The second one (degrading process) is related to the evaporation of sulfolane (especially at 316\(^\circ\)C) [30]. However, the onset decomposition temperature of nano-ppy/OMMT-coated separator is much higher than that of PE separator. This might be related to several reasons. Firstly, the restricted chain motion in the nano-ppy/OMMT-coated separator requires higher thermal energy to initiate chain scission. Secondly, the exfoliated and well-dispersed nano-ppy/OMMT serves as an insulating surface and impedes the out-diffusion of decomposed products, which may slow down the weight loss of decomposed materials and the degradation of the underlying materials. At 255\(^\circ\)C (the start decomposition temperature of ppy is about 255\(^\circ\)C), the amount of nano-ppy/OMMT-coated separator reduces by 6\% and PE separator loses by 86\%, indicating that the decomposition temperature of the composite separator could be improved by coating the nano-ppy/OMMT. However, when the temperature is above 255\(^\circ\)C, ppy decomposes into gas, destroying the insulating surface and promoting the volatilization of PE. Thus, the weight loss of nano-ppy/OMMT-coated separator takes place rapidly at 255–410\(^\circ\)C. These results indicate that the nano-ppy/OMMT-coated separator could be available in Li-ion cell at temperatures below 80\(^\circ\)C [28, 30].

Figure 5 shows that, under the test condition, the elastic modulus and the yield stress of PE separator are both small, and its elongation at break is high. Nano-ppy/OMMT adheres to the surface and enters the internal structure of PE separator, combining the surface and structure of nano-ppy/OMMT-coated separator tightly. Molecular forces between the polymer chain of PE and inorganic molecules retard the movement and bend of the polymer chain under the action load, which results in the fracture of nano-ppy/OMMT-coated separator at the vicinity of yield point. In this way, both the elastic modulus and tensile strength of nano-ppy/OMMT-coated separator have been improved. The tensile strength of nano-ppy/OMMT-coated separator (3.39 MPa) is higher than that of PE separator (1.24 MPa). The tensile strength is calculated through the values of maximum load and displacement [31, 32]. The outstanding tensile property of nano-ppy/OMMT-coated composite separator is essential for the mechanical stability of batteries.

Table 1 lists the electrolyte uptake with different mass ratios of nano-ppy/OMMT-coated separators and PE separator immersed into the organic electrolyte in 24 h. The electrolyte uptake of PE separator is 146% without nano-ppy/OMMT-coating. The highest electrolyte uptake reaches 349% when the content of nano-ppy/OMMT is added up to 6\%, which is over twice higher than that of PE separator. The reason is that the hydrophobic group of PE makes PE separator have poor wettability in organic solution. However, nano-ppy/OMMT-coated separator with three-dimensional and multilayered network structure (see Figure 3(d)) and high specific surface area can absorb more liquid electrolyte and enhance the ion conductivity of LIB. In contrast, the electrolyte uptake of 8\% nano-ppy/OMMT-coated is lower than that of 6\% nano-ppy/OMMT-coated. The excess nano-ppy/OMMT makes the structure of nano-ppy/OMMT-coated separator tighter. So the 8\% nano-ppy/OMMT-coated separator absorbs less liquid electrolyte.

The ionic conductivity of separator with electrolyte is obtained by AC impedance spectroscopy. Figure 6(a) shows
Figure 3: (a) MMT. (b) Nano-ppy/OMMT. (c) The cross-sectional structure of PE separator. (d) The cross-sectional structure of nano-ppy/OMMT-coated separator. (e) The cross-sectional structure of PE in the nano-ppy/OMMT-coated separator. (f) The cross-sectional structure of nano-ppy/OMMT in the nano-ppy/OMMT-coated separator.

Figure 4: (a) Photographs of PE separator and nano-ppy/OMMT-coated separator. (b) TG curves of PE separator and nano-ppy/OMMT-coated separator.
that the ion conductivity of the bulk resistance can be calculated from the intercepts in the high-frequency range of the curves. As is shown in Figure 6(b), the ionic conductivity of PE separator (1.95 mS \cdot cm^{-1}) is lower than that of nano-ppy/OMMT-coated separators. The three-dimensional and multilayered network structure of nano-ppy/OMMT-coated separator can improve the electrolyte uptake, lower ionic coupling, and promote the formation of Li-ion conducting pathways on the surface and internal structure of nano-ppy/OMMT-coated separator [23, 31]. The ionic conductivities of 4%, 6%, and 8% nano-ppy/OMMT-coated separators are calculated to be 2.51 mS \cdot cm^{-1}, 4.31 mS \cdot cm^{-1}, and 2.36 mS \cdot cm^{-1} at room temperature. The ionic conductivity of 8% nano-ppy/OMMT-coating is lower than that of 6% nano-ppy/OMMT-coating. The excess nano-ppy/OMMT may adhere to Li-ion tightly, retarding the mobility of Li-ion and thereby increasing the bulk resistance of 8% nano-ppy/OMMT-coating [28].

The charge/discharge performances of the cell assembled with nano-ppy/OMMT-coated separator (6% nano-ppy/OMMT) and the cell assembled with PE separator are evaluated. The preconditioning cycles of cells are running in the voltage range of 2.7 and 4.2 V at 0.1 C. After ten cycles at room temperature, the charge/discharge performances of cells are evaluated at 0.5 C and 80°C. Figure 7(a) shows the cycling performance curves of the cells after 100 cycles. The first discharge capacity and coulombic efficiency of the cell assembled with nano-ppy/OMMT-coated separator are, respectively, 125.9 mAh/g and 99.6%, based on the active LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 material in the positive electrode. The first discharge capacity and coulombic efficiency of the cell assembled with PE separator are 123.7 mAh/g and 99.4%, respectively. After 100 cycles, discharge capacity of the cell assembled with nano-ppy/OMMT-coated separator slightly decreases to 99.12 mAh/g, close to 80% of the first discharge capacity. In contrast, the discharge capacity of the cell assembled with PE separator sharply decreases to 74.1 mAh/g, losing over 40% of the first discharge capacity. The coulombic efficiency of both cells is above 95%. Thus, the charge/discharge performances of the cells depend on the separator types. Nano-ppy/OMMT coated onto the surface of the PE separator is beneficial to prevent the loss of the discharge capacity at high temperature. Nano-ppy/OMMT-coated separator plays an important role in the charge/discharge performance of Li-ion cell.

Electrochemical impedance spectroscopy (EIS) is used to record different interfacial resistance of the cells assembled with PE separator and nano-ppy/OMMT-coated separator after 100th cycle at 0.5 C and 80°C. In Figure 7(b), two overlapping semicircles are exhibited in the spectra. One semicircle at high frequency range represents the formation of the solid-state interface resistance on the surface of electrode (R_{sei}). And the other one within the middle to the low frequency range corresponds to the charge-transfer resistance (R_{ct}). The high-frequency intercept on the real axis is defined as the electrolyte resistance. The internal resistance of the cell assembled with PE separator is higher than that of the cell assembled with nano-ppy/OMMT at 80°C in Figure 7(b). That can be explained by the loss of LiPF_6 in negative reactions between the positive electrode and organic electrolyte at high temperature [24, 33]. It is well known that HF is generated by thermal decomposition and hydrolysis of LiPF_6 by trace moisture in the electrolyte solution in (4) [5, 8]. Mn^{2+} and Mn^{4+} are generated by disproportionation of Mn^{3+} in LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 materials with the HF derived from LiPF_6. The passive film with Mn^{2+} and Mn^{4+} is formed on the surface of negative electrode material by (5). The result leads to the increase of the internal resistance and the decrease of discharge capacity at 80°C, as Hunter and Inoue reported [34, 35].

\[
\text{LiPF}_6 + H_2O \rightarrow \text{POF}_3 + 2HF + \text{LiF} \quad (4)
\]

\[
2\text{Mn}^{3+} + \text{HF} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+} \quad (5)
\]
In order to explore the effect of nano-ppy/OMMT, we examined the different contents of HF in LiPF$_6$ and in LiPF$_6$ with nano-ppy/OMMT, which were stored at 80°C for 72 h by an acid-base titration method [36]. The contents of HF in the electrolytes are analyzed and their results are shown in Table 2. The results in Table 2 show that the HF content of LiPF$_6$ is 227 ppm. And the HF content of LiPF$_6$ with nano-ppy/OMMT is 121 ppm. These results suggest that the nucleophilic substitution reaction between covalent bonds (Si-O) of nano-ppy/OMMT and HF derived from LiPF$_6$ can move and bend [37, 38]. The chemical bonds (Si-O) of ppy/OMMT can serve as HF scavengers to remove HF by the nucleophilic substitution reaction and to inhibit the dissolution of Mn$^{3+}$ from the active LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ materials at 80°C. This is essential to reduce the thickness of the passive film on the electrode surface and to increase the ionic conductivity during the charge and discharge process. As a result, nano-ppy/OMMT-coated separator exhibits good thermal stability and can improve discharge capacity of LIB.

POF$_3$ and LiF are insulating material on the electrode surface, which may hamper the charge transfer between the electrolyte and the electrode, increasing the charge-transfer resistance. To get the different contents of POF$_3$ and LiF in the negative electrodes of cells assembled with nano-ppy/OMMT-coated separator and PE separator, the surfaces of the negative electrodes are analyzed by XPS after 100 cycles at 80°C (see Figures 7(c)–7(f)). In the F 1s XPS spectra (see Figures 7(c) and 7(e)), the intensity of the relative peak, corresponding to LiF (685.1 eV) in the cell assembled with nano-ppy/OMMT-coated separator and PE separator, the surfaces of the negative electrodes are analyzed by XPS after 100 cycles at 80°C (see Figures 7(c)–7(f)). In the F 1s XPS spectra (see Figures 7(c) and 7(e)), the intensity of the relative peak, corresponding to LiF (685.1 eV) in the cell assembled with nano-ppy/OMMT-coated separator, is lower than that of the cell assembled with PE separator [39]. At the same time, the content of LiPO$_6$ of the negative electrodes of cell assembled with nano-ppy/OMMT-coated separator is higher than that of the negative electrodes of cell assembled with PE separator. So, nano-ppy/OMMT is effective to suppress LiPF$_6$ decomposition and reduce the contents of POF$_3$ and LiF in the negative electrodes, which can reduce the internal resistance of Li-ion battery at high temperature.

4. Conclusions

Nano-ppy/OMMT is prepared and then coated on the surface of PE separator, which is used to prepare nano-ppy/OMMT-coated separator. Nano-ppy/OMMT-coated separator with three-dimensional and multilayered network structure, high specific surface area, high aspect ratio, and good adsorption capacity can improve the absorbent ability of organic electrolyte and be beneficial for the migration of Li$^+$. Nano-ppy/OMMT-coated separator has excellent mechanical property (3.39 MPa) and ionic conductivity (4.31 mS·cm$^{-1}$). Nano-ppy/OMMT-coated separator can enhance thermal stability by retaining stable dimensions so that the composite separator can prevent the electric short circuit between electrodes. Since strong covalent bonds (Si-F) are formed in nucleophilic substitution reaction between F$^-$ (from the thermal decomposition of LiPF$_6$) and covalent bonds (Si-O) of nano-ppy/OMMT, nano-ppy/OMMT-coated separator can inhibit the disproportionation of Mn$^{3+}$ in LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$.

Table 2: HF contents in the electrolyte after storage at 80°C for 72 h.

<table>
<thead>
<tr>
<th>HF content (ppm)</th>
<th>LiPF$_6$</th>
<th>LiPF$_6$ with 6% with nano-ppy/OMMT</th>
</tr>
</thead>
<tbody>
<tr>
<td>227</td>
<td></td>
<td>121</td>
</tr>
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Figure 6: Relation between conductivity, impedance, and matrix: (a) relation between nano-ppy/OMMT matrix and impedance; (b) relation between nano-ppy/OMMT matrix and conductivity.
Figure 7: (a) Charge/discharge curves of cells assembled with PE separator and nano-ppy/OMMT-coated separator after 100 cycles at 80°C. (b) EIS of cells assembled with PE separator and nano-ppy/OMMT-coated separator after 100 cycles at 80°C. (c) F 1s XPS spectra and (d) P 2p XPS spectra of negative electrodes of cells assembled with PE separator. (e) F 1s XPS spectra and (f) P 2p XPS spectra of negative electrodes of cells assembled with nano-ppy/OMMT-coated separator.
materials and decrease the internal resistance of cell at high temperature. Nano-ppy/OMMT-coated separator is applied to the cell composed of LiPF$_6$ organic electrolyte and LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ positive electrode. The cell shows outstanding capacity retention and cycling performance at 0.5 C and 80°C. In conclusion, nano-ppy/OMMT-coated separator can serve as the applicable composite separator for lithium-ion battery at high temperature.

**Competing Interests**

The authors declare that they have no competing interests related to this study. They declare that they do not have any commercial or associative interest that represents a conflict of interests in connection with the work submitted.

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