Heat-resistant poly (arylene ether nitriles) separator for high-safety lithium batteries via dual-functional modification

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Abstract. Herein, we report a dual-modified organic-inorganic separator as an alternative to polyolefin commercial separator for lithium metal batteries. This composite separator exhibits high thermal stability properties due to the use of an engineering plastic matrix of poly (arylene ether nitriles) (PEN). The dual hydrophilic modification strategy also allows the separator to have a high ionic conductivity and a low interfacial impedance. With this new separator, lithium-metal batteries have high charge/discharge capacity and high-rate performance. Moreover, Li/Li symmetric cells display long-term stability and phenomenon of suppressing the lithium dendrite in lithium-metal batteries.

1. Introduction

The energy problem is one of the biggest challenges facing the current social development[1]. With the increasing consumption of traditional fossil energy reserves and the increasingly prominent ecological environment damage caused by the large-scale use, the development and use of new energy gradually replace fossil energy has become a trend in the world. Lithium batteries have broad application prospects in various electronic devices and new energy vehicles for the advantages of long cycle life, high energy efficiency, and high capacity[2]. As one of the vital components of lithium batteries, the functions of separator include providing ion transport channels and storing liquid electrolytes[3]. Although the separator does not directly participate in the electrochemical reaction, it has a significant impact on the safety and performance of the battery. The currently used separators are mainly polyolefin-based microporous membranes[4]. However, they lack polar functional groups in the molecular chain, and have strong hydrophobic properties, resulting in poor affinity with the electrolyte, which affects the performance of the battery.

Modification through the matrix material of the separator is one of the best ways to solve the above problems[5-6]. Poly (arylene ether nitriles) is a special engineering plastic with aromatic rings containing cyano group and ether bond structure, which not only has high heat resistance, but also can be dissolved in common organic solvents at room temperature that laid a theoretical foundation for processing process[7]. Furthermore, the pore size and surface chemical structure of the separator are beneficial to the selectivity of ions, thereby improving the lithium-ion transmission efficiency and the performance of lithium batteries, so the interface between the separator and the electrolyte cannot be ignored.
In this work, PEN/TA-SiO₂/TA-PEI organic-inorganic composite separators were prepared by an internal-external double modification method. TA-SiO₂ was used as an inorganic filler to improve the heat resistance and insulation properties of PEN. Subsequently, tannic acid (TA) and polyethyleneimine (PEI) were self-assembled through layer by layer on the porous membrane to obtain a composite separator with surface chemical activity. The composite separator has high mechanical properties and electrolyte affinity, thereby improving the electrochemical performance of the separators.

2. Experimental section

2.1. Preparation of TA-SiO₂ nanoparticle
To form TA-SiO₂, 0.1g tannic acid powders were dissolved in 50 ml of tris-HCl buffer solution (PH=8.5), 1g SiO₂ nanoparticles (diameter size:50-100 nm) was then added to above solution to stirring for 24 h at room temperature. After TA-SiO₂ were washed by water and ethanol, they were dried at 80 ℃ for 12 h.

2.2. Preparation of PEN/TA-SiO₂/TA-PEI separator
To form porous PEN/TA-SiO₂/TA-PEI separator, the typical non-solvent induced phase separation and layer-by-layer self-assembly were used in this work. Briefly, 0.05g TA-SiO₂ nanoparticles, 0.05g LiCl, and 0.5g PEN were dissolved in 5 ml DMF to form a homogeneous solution, followed the solution was casted in a clean and flat glass plate. Then this glass plate was immersed in deionized water for 5 h to obtain porous PEN/SiO₂ separator. Furthermore, the PEN/SiO₂ separator was immersed into a tris-HCl buffer solution (PH=8.5) of TA (1.0 mg mL⁻¹) for 30 min, then subsequently immersed into PEI aqueous solution (1.0 mg mL⁻¹) for 20 min to obtain the PEN/TA-SiO₂/TA-PEI separator. The separators were dried at 60 ℃ for 12 h before using. When the amount of TA-SiO₂ in the composite is 3%, 5%, 10%, and 15%, the samples were named as 3%, 5%, 10% (PEN/TA-SiO₂), and 15%.

2.3. Characteristic
Thermogravimetric (TGA) was measured in a N₂ atmosphere form 40 ℃ to 800 ℃ on a Q-50 (TA instruments). The morphology was carried out on a scanning electron microscope (JEOL, JSM25900LV). The tensile strength and Young’s modules were obtained from a SANS CMT6104 series electromechanical universal testing machine. The porosity, electrolyte uptake, dimensional stability, ionic conductivity, and interfacial resistance of all the separators was obtained through previous literature[7]. Battey performance (rate or cyclability capability and cycle stability) of the LiFePO₄/separator/Li (LFP/separator/Li) and Li/separator/Li was carried out on battery testing system (Neware). The battery assemblies were carried out in an argon-filled glovebox.

3. Result and discussion
As demonstrated in Figure 1, to form porous PEN/TA-SiO₂/TA-PEI separator, firstly, the porous PEN/TA-SiO₂ membranes were obtained via a typical non-solvent induced phase separation, followed TA and PEI solution were used to coat on the surface of porous PEN/TA-SiO₂ to form functional coating on the PEN/TA-SiO₂/TA-PEI through layer-by-layer assembly. The TA-SiO₂ nanoparticle might tend to be distributed on the surface of the PEN/TA-SiO₂ separator due to the effect of the PEI species. The crosslinking structure between TA and PEI could strengthen the porous PEN/TA-SiO₂ membranes. Meanwhile, the TA-PEI structure on the surface of the separator could enhance the electrolyte wettability and uptake for the abundant active groups from TA-PEI.
The cross-section and surface morphologies of P-TS-E separator was shown in Figure 2a and b, respectively. As can be seen, abundant pores were found in the PEN/TA-SiO$_2$/TA-PEI separators, these pores were composed of micron pores (size: 10-20 µm) and nanopores (size: 100 nm-900 nm). Furthermore, plentiful porous structure and TA-SiO$_2$ particles was instituted on the surface of the P-TS-E. The highly porous P-TS-E separators might benefit to the enhanced ionic conductivity.

The thermal stability of separator is crucial for safety of the lithium-ion battery. Firstly, the TA coating amount on the surface of the SiO$_2$ was investigate by TGA, the result was shown in Figure 2c, a weight loss of 2.5% was found after TA coated on the SiO$_2$, it signified the TA coating amount of TA-SiO$_2$ was about 2.5%, and the TA-SiO$_2$ particles were successfully obtained. Figure 2d revealed the TGA curves of PP, PEN, PEN/TA-SiO$_2$, and P-TS-separators, the PEN, PEN/TA-SiO$_2$, and P-TS-E separators was superior than PP separator as a result of intrinsic thermal stability of the PEN polymer. Moreover, the dimensional thermos-stability of separators were evaluated through the images before and after treatment at 160 °C for 1h (Figure 2d inset), it can be seen that the PP separator exhibited an obvious dimensional shrinkage, whereas the PEN, PEN/TA-SiO$_2$, and P-TS-E separators displayed insignificant dimensional shrinkage, which implied the high-safety of separator using in the lithium ions battery.

The mechanical properties of these separators were shown in Figure 3a and b. The tensile strength of PEN and 10% separators were 7.8 MPa and 8.2 MPa, respectively. It indicated that the incorporation of TA-SiO$_2$ nanoparticles slightly enhance the mechanical properties. The P-TS-E separator exhibited a tensile strength and Young’s Modulus of 9 MPa and 180 MPa, respectively. This result might mainly be due to the crosslinking and hydrogen bonding sites of TA-PEI on the surface of the separators.

The porosity and Electrolyte uptake of various separators were shown in Figure 3c and d. As depicted, the PP separator showed a low porosity of 39% and electrolyte uptake of 180% result from its inconsecutive pores and inactive surface chemistry. Pure PEN membranes exhibited higher porosity and electrolyte uptake because of polar groups on the surface of PEN membranes. When TA-SiO$_2$ particles are introduced into PEN matrix, the porosity of the separator further increases. As the proportion of TA-SiO$_2$ particles increases, porosity and electrolyte uptake of separators increase to a certain extent, but when the addition amount is 15%, the electrolyte absorption rate had not changed. Meanwhile, after the PEN/TA-SiO$_2$ separator was treated with TA and PEI, the porosity of the separator decreased, but the electrolyte absorption rate increased, implying that the active chemical groups of the TA-PEI structure are conducive to absorbing electrolyte and increasing electrolyte infiltration, which contributes to the improvement of the electrochemical performance of the separators.
Figure 2. The cross section (a) and surface (b) SEM image of P-TS-E; TG curve (c) of PEN, PP, PEN/TA-SiO$_2$, P-TS-E separator (inset: dimensional stability of PP, PEN, PEN/TA-SiO$_2$, and P-TS-E); TGA curves (d) of SiO$_2$ and TA-SiO$_2$.

Figure 3. The tensile strength (a) and Young’s modulus (b) of PEN, 10%, and P-TS-E separators; Porosity (c) and Electrolyte uptake (d) of various separators.

The electrochemical properties of the separators were shown in Figure 4. The ionic conductivities of the PEN, PEN/TA-SiO$_2$, P-ST-E, and PP separators were 0.48, 0.78, 1.23, and 0.39 mS/cm. The P-TS-E separator exhibited the highest ionic conductivity due to its abundant pore size, electrolyte uptake, and active chemical surface. The interfacial impedance test structure of the separator was shown in Figure 4b. The interfacial impedance of the P-ST-E separator is about 180 Ω, which is much smaller.
than that of the PP and PEN separators. The smaller interfacial impedance is beneficial to the fast ion transfer between the electrode and the separator, thereby improving battery performance.

Figure 4. The ionic conductivity (a) and interfacial resistance (b) of PP, PEN, PEN/TA-SiO₂, and P-TS-E separators.

The battery performance was summarized in Figure 5. Figure 5a showed the long cycling of LFP/PP/Li and LFP/P-TS-E/Li batteries. As the number of cycles increases, the discharge capacity of the LFP/P-TS-E/Li battery was always higher than that of LFP/PP/Li. After 100 cycles, the discharge capacity of LFP/P-TS-E/Li was 146 mAh/g, while the discharge of LFP/PP/Li battery decayed from 139 mAh/g to 125 mAh/g. Furthermore, the rate cycling performances of LFP/PP/Li and LFP/P-TS-E/Li batteries were investigated to compare the performance of the batteries under high-rate charge-discharge conditions. The results were shown in Figure 5b. The discharge capacity of LFP/P-TS-E/Li battery is always higher than that of LFP/PP/Li battery under the various current density. Furthermore, in order to explore the inhibitory effect of the separator on Li dendrites, Li-Li symmetric cells were used to study the effect of separator, and the results were shown in Figure 5c and d. Li/P-TS-E/Li cells were very stable during the entire cycle number, thus P-TS-E can be safely used in lithium-metal batteries. The abundant amino, hydroxyl and nitrogen species on the surface of the P-TS-E separator are beneficial to regulate the distribution of lithium ions concentration and the deposition and stripping of lithium, thereby suppressing the lithium dendrite phenomenon in lithium batteries.

Figure 5. The long-time cyclability (a) and rate capability (b) of LFP/PP/Li and LFP/P-ST-E/Li coin-cells; Voltage profiles (c,d) of Li/PP/Li and Li/P-ST-E/Li symmetric cells at 1 mA cm⁻².
4. Conclusion

In this work, organic-inorganic separator modified by bi-hydrophilic method as an alternative to polyolefin commercial separator for lithium metal batteries. PEN/TA-SiO$_2$/TA-PEI separator showed more advantages than commercial separator. The engineering plastic matrix PEN give the material ultra-high thermal stability properties. The use of internal inorganic nano-SiO$_2$ and the layer-by-layer self-assembly of external TA-PEI layers give the separator perfect electrochemical properties. The abundant polar groups regulate the uniform distribution of lithium ions on the electrode surface, thus suppressing the lithium dendritic in lithium metal cells.

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