Preparation and Characteristics of Lithium Battery Separator Based on Cellulose Modification by Water-Soluble Polyimide Impregnated

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Abstract. In order to improve the comprehensive performance of lithium battery separator, cellulose based on lithium battery separator (mCNS) was prepared by cellulose/nylon 6 with ionic liquid [Emim]Ac as solvent and enhanced with polyimide (PI) as the impregnated solution. The properties of modified separator were investigated. As could be discovered from the experimental results that the addition of PI endowed the separators with more uniform and dense micro-pores, and the ions can pass through better, which was conducive to improving the electrical conductivity of the separator. Remarkable tensile strength (69 MPa) and elongation at break (35.3%) can be obtained at PI concentration of 40%. Meanwhile, the electrolyte absorption and retention rate reached 238.7% and 69.4%. The value of maximum thermo-shrinkage stress was 1.38 N and the thermo-shrinkage rate could reach 1.5%, which guaranteed the thermal stability of the battery. The electrochemical voltage was attained to 4.7 V and the ionic conductivity was improved to $0.61 \times 10^{-3}$ S cm$^{-1}$. The mCNS separator preparation process was simple and the performance was excellent, which provides a novel idea for the green development of lithium battery separator.

1. Introduction
With the energy massive consumption and environmental increasing pollution, the development and utilization of new energy and new materials has become a major problem of the whole society. Lithium ion batteries have their own advantages, which make it an ideal energy source in the 21st century. As a key component of lithium batteries, the separator affects the service life and safety performance of batteries. Most lithium battery membranes materials are polyolefin, however, there are problems such as low porosity, poor thermal shrinkage performance and easy leakage of electrolyte [1].

Cellulose is considered as an excellent membrane ideal material for separators of lithium battery, its strong intermolecular and intramolecular hydrogen bonding forces make it difficult to dissolve, which limits the application of cellulose [2]. Ionic liquid is a new type of “green” solvent, which has high stability and good solubility to cellulose. Nylon 6 has excellent chemical stability, mechanical properties, and is easy to be processed, which attracts many researchers to study its modification.

PI have the rigid rod-like structure, which makes it has excellent mechanical properties, dielectric properties, thermal stability and good toughness [3]. Based on these features, PI has been rapidly developed and widely used in the modification and preparation of separator, which is expected to satisfy the requirements of lithium battery separator. In this study, the advantages of PI were fully utilized to
improve cellulose membrane, and were incorporated in fabricating high-performance lithium battery separator.

Our research group has determined the optimal ratio of cellulose/nylon 6 lithium battery separator in previous studies [4]. On this base, a separator (mCNS) was put forward via the impregnated modification by PI of cellulose/nylon 6 (CNS). Corresponding tests and characterization were implemented to explore the influence of different PI concentration in the impregnated liquid on the comprehensive performance of the membrane. The best modification preparation conditions were obtained in the last.

2. Experimental

2.1. Materials

Hardwood pulp (with \( \alpha \)-cellulose content of approximately 90\%) was supplied by Shandong Sun Paper Industry Joint Stock Co., Ltd. Nylon 6 (density: 1.13 g/cm\(^3\)) was purchased from Dongguan huangjiang shengbang plastic material business department. Polyimide (YH-1066) was manufactured by Shanghai yehe industry and trade Co., Ltd. Polyvinylpyrrolidone (PVP K30, Mw~\(5.0 \times 10^4\) g\(\cdot\)mol\(^{-1}\)) was analytical grade and provided by Shanghai shanpu chemical Co., Ltd. Ionic liquid [Emim]Ac (1-ethyl-3-methylimidazole-3-ium, acetate, Mw~170.21 g\(\cdot\)mol\(^{-1}\)) was purchased from Shanghai chengjie chemical Co., Ltd.

2.2. Separators preparation

The fabrication of the modified separator was elaborated as follows. Cellulose/nylon6 separator was prepared before the modified separator was obtained. Firstly, the cellulose and nylon 6 were of desiccation in a drying oven at a certain temperature (70°C–80°C) for at least 8h for reserve use. Secondly, a definite magnitude of ionic liquid was put into a three-necked flask and heated in an oil bath pan to dissolve. Then nylon 6 was added into it at a certain temperature (180°C) for at least 2h. Thirdly, cellulose and PVP K30 were placed to the casting membrane solution and stirred for another 1h, when the temperature of the mixed solution dropped to 100°C. Then the mixture was scraped on the glass plate. The separator of cellulose/nylon 6 was prepared by the method of L-S phase inversion. Subsequently, the separator was immersed in tap water for 20h to make the solvent fully extracted, and the separator of CNS was obtained.

A series of PI concentrations (10%, 20%, 30%, 40% and 50%) were got intense agitation at 25°C for 1h. Subsequently, the CNS was immersed into the PI solution for 24h to make the separator to assimilate adequate quantity of PI. Then the separators were rinsed repeatedly with deionized water, and then dried for later use.

2.3. Analytical methods

Mechanical properties which included the tensile strength and breaking elongation of separator were conducted with electronic tensile testing machine (XLW, Labthink, China). The sample of the separator presoaked in liquid electrolyte for 2h. Five times were repeated to obtain the average value. The electrolyte absorption and retention rate of the separator were measured as previously described [5]. The contact angle was tested by a contact angle measuring instrument (SDC-100, Dongguan shengding precision instrument Co., Ltd) at room temperature.

The thermo-shrinkage was tested by a thermal shrinkage tester (FST-02, Labthink, China) at the temperature of 200°C. Thermogravimetric analysis (TGA) was implemented by adopting a thermogravimetric analyzer (STA2500, NETZSCH, Germany). Nitrogen adsorption isotherms were carried out to obtain isotherm and the pore structure of the separator sample with the porosity analyzer (NOVA, Quantachrome Instruments, American).

The electrochemical stability window and the electrochemical impedance spectroscopy were measured by the electrochemical workstation (CHI760E, Shanghai chenhua instrument co., Ltd) to investigate the electrochemical stability performance of the separator and the ionic conductivity of the separator. The test methods were carried as previously described [5].
3. Results and discussion

3.1. Morphology

Figure 1. SEM surface morphologies of CNS (a) and mCNS (b) (PI=40%); cross-section morphologies of CNS (c) and mCNS (d).

Figure 1 exhibited the SEM surface and cross-sectional morphologies of CNS and mCNS, and significant differences were observed. Compared with the CNS separator surface (a), the mCNS separator (b) demonstrated smoother and evenly distributed micro-pores on the surface, while the existence of the micro-pores was able to contribute to the effective absorption of the electrolyte solution. The SEM cross-sectional morphologies indicated that the mCNS separator cross-sectional (d) was a sponge-like structure with more and larger pores and exhibited greater smoothness than the CNS separator cross-sectional (c), which manifested that the structure of separators was extremely changed with the addition of PI. Therefore, it was concluded that the micro-pores structure of mCNS separators were easier to form ion channels [6], which were very important for ion transport of the lithium battery separators.

3.2. The electrolyte retention and absorption rate

Table 1. Effect of PI concentration on performance of the separators.

| PI concentration (%) | Absorption rate (%) | Retention rate (%) |
|----------------------|---------------------|-------------------|
| 0                    | 210.0               | 60.3              |
| 10                   | 225.6               | 63.8              |
| 20                   | 236.1               | 68.2              |
| 30                   | 240.4               | 70.9              |
| 40                   | 238.7               | 69.4              |
| 50                   | 230.9               | 67.8              |

Table 1 reported the electrolyte retention and absorption rate of the membrane with a series of PI concentration. It could be discovered that when the concentration of PI was 40%, the electrolyte absorption and retention rate reached the maximum value, which was 238.7% and 69.4% respectively. These data conformed the demands of lithium battery for a safety separator. The reasons could be ascribed as the PI macromolecular chain in the micro-pores of the separator increases the affinity of the membrane to the electrolyte, making the electrolyte easier to move in the micro-porous structure of the separator. As the PI concentration increased continue, a PI cladding was generated outside the separator. The electrolyte must pass through the PI cladding before entering the micro-pores, and the mechanical strength between the PI molecular chains had a certain hinder on it, thus reduced the electrolyte retention and absorption rate of the membrane. The addition of PI was made the micro-pore structure of the separator more compact and uniform, which has been reflected in the SEM images in 3.1. To a certain extent, these was beneficial to the transport of lithium ions and improved the charging and discharging performance of the separator.

3.3. Mechanical properties

The mechanical performances of separators were influenced by the PI concentration as shown in Figure 2. With the increased of the PI concentration, both the tensile strength and breaking elongation of mCNS separators exhibit a trend of first increasing and then decreasing. When the concentration of PI was 40%,
the tensile strength came up to the maximum value, which was 69MPa, at the same time, the elongation was 35.3%. Compared with the CNS separators, it was improved by 22.8% and 47.1%, respectively. The reason was depicted as follows, when the concentration of PI was less than 40%, the smaller viscosity of the impregnation solutions makes it easy to penetrate into the three-dimensional network of the separator. The conjugation effect was produced because the aromatic heterocycle structures in PI, coupled with the hydrogen bonding in nylon 6 and cellulose molecules, made the mCNS own strong bonding force. A certain number of ether bonds in PI main chain enable the molecular chain has certain flexibility through rotation, so the elongation was improved. When the concentration of PI increased continually, the viscosity of the impregnation solution increased. Therefore, it was difficult for PI to penetrate into the separator, resulted in the decreased of mechanical properties of the separators.

3.4. N2-adsorption experimental analysis
N2-adsorption tendency of CNS membrane and mCNS membrane were manifested following the date in Figure 3. As can be seen, the adsorption amount was very small in the low-pressure area (0~0.1) which was the adsorption produced, when the interaction between the adsorbent material and the adsorbed gas was very weak. The relative pressure range of 0.5~0.8 reflected the adsorption capacity of CNS separator was larger than the mCNS separator, made clear that the aperture of separator was smaller. As the relative pressure increasing, the adsorption competence of the separator also augmented, which showed multi-molecular layer adsorption and no monolayer saturation adsorption.

3.5. Thermal analysis
The thermo-shrinkage rate and stress could reflect the heat endurance of the separators. According to the change tendency of the separators at the temperature of 200°C in Figure 4 and the data in Table 2, it obtained that the maximum value of thermo-shrinkage stress of CNS membrane reached to 2.28N and the thermo-shrinkage rate was 3.1% at the same time, nevertheless the mCNS (PI= 40%) was decreased to 1.38N and 1.5% respectively. In contrast with the CNS separators, it decreased by 39.5% and 51.6%, respectively. When the concentration of PI increased, the maximum thermo-shrinkage stress and thermo-shrinkage rate began to increase, but they were still lower than the CNS separators. This result could be ascribed to the imine ring on PI main chain, which had an excellent interface performance when it was combined with cellulose/nylon6 and increased the bond energy between molecular. In addition, the existence of N-containing five-membered heterocyclic rings structure and the intermolecular conjugation effect of PI molecules improved the thermal stability of impregnated separator. It indicated that the heat endurance of the separators has been promoted after PI modification, which was more conductive to guarantee the safety of lithium battery during the process of use.

Table 2. Effect of PI concentration on the thermal shrinkage performance of separators.

| PI concentration (%) | Maximum thermo-shrinkage stress (N) | Thermo-shrinkage rate (%) |
|----------------------|-------------------------------------|---------------------------|
|                      |                                     |                           |

Figure 2. Effect of PI concentration on tensile strength and breaking elongation of the separators.

Figure 3. N2-adsorption isotherm of CNS separator and mCNS (PI=40%) separator.
Figure 4. Effect of PI concentration on the thermo-shrinkage stress of the separators.

Figure 5. TG curves of CNS separator (a) and mCNS (PI=40%) separator (b).

Thermogravimetric analysis presents the thermal degradation process. The TG curves were observed for the CNS and mCNS separators from Figure 5. The initial slight weight loss of curves A and B was due to the evaporation of the remained water in the separators. From curve (a) we could discovered that the first weightlessness period of CNS separators started at around 240°C, and the weight-loss of 55% due to the cellulose pyrolysis. The second stage of weightlessness initiated at approximately 320°C on account of thermal decomposition of nylon materials. However, as shown in curve (b), the weightlessness period of mCNS separators was the range of 310°C~455°C, and the weight-loss rate was about 75%. Compared with CNS separators, the initial degradation temperature of mCNS separators increased by about 70°C. This may be due to the increase of the binding strength between cellulose and nylon6 after PI entered the membrane structure. Through charge transfer, mixed layer stacking and other complexation, a force different from van der Waals force was formed in PI molecules or between molecules, which changed the decomposition process of the membrane and improved the heat endurance of the mCNS membrane [7].

3.6. Contact angle measuring
As shown in Figure 6, increasing the PI concentration minished the contact angle of the separators, indicating that the hydrophilicity of separators was boosted. At the same time, the contact angle of separators decreased to 22.258° when PI concentration was 40%. It could be seen that the liquid retention and uptake performance of the separators were enhanced, thus improved the delivery competence of the membrane to lithium ions in the electrolyte [6]. This result was consistent with the relevant results in 3.2.
Figure 6. Contact angles of CNS separator (a) and mCNS (PI=40%) separator (b).

3.7. Electrochemical analysis

Figure 7. Linear sweep voltammograms curves of the CNS and mCNS (PI=40%) separator.

Figure 8. Ac impedance curves of the CNS separator and mCNS (PI=40%) separator.

Table 3. Calculation results of ionic conductivity of separator.

| Separator sample | Thickness (cm) | Effective area (cm²) | Resistance (Ω) | Ionic conductivity (S·cm⁻¹) |
|------------------|----------------|----------------------|----------------|-----------------------------|
| CNS              | 3.50×10⁻⁵      | π×1²                 | 2.57           | 0.43×10⁻³                   |
| mCNS             | 3.50×10⁻⁵      | π×1²                 | 1.82           | 0.61×10⁻³                   |

The linear sweep voltammograms curves of the cellulose based membrane and the PI modified membrane was shown in Figure 7. The separator was in a steady state within a certain scanning voltage (3.0V~4.0V). When the voltage reached 4.2V, the steady state of the CNS separator began to be break, while the mCNS separator was basically stable and has small current value before 4.7 V. Compared with the CNS separator, the electrochemical stability was improved, this might be interpreted that the addition of PI delays the decomposition of the separator. The ac impedance spectrum of the separator was generated by EIS. It was obtained in Figure 8 that the ac impedance curves of the CNS and mCNS membrane were approximately straight line in the high frequency region, and the body resistance of the CNS membrane was lower than that of the mCNS separator. The calculated results of the ionic conductivity of the separator were shown in Table 3. It was demonstrated that the ionic conductivity of the mCNS separator reached to 0.61×10⁻³ S/cm, which was about 42% higher than that of the CNS separator.

It could be attributed that the absorption rate and porosity of the mCNS separator was increased, and the micro-pore structure of the separator was improved which leads to the stronger absorption and storage capacity of the separator to the electrolyte [6], thus improving the separator stability in the electrolyte. It could form more lithium ion migration channels. PI chain containing larger polar group was another important reason, and there was larger interaction force with the electrolyte. It was conducive to infiltration of the electrolyte to separator, thus the ionic conductivity was improved.
4. Conclusion
The lithium battery separator with excellent properties was prepared from PI impregnated modification cellulose membrane in this study. There was evidence that the separator performed best overall at a PI concentration of 40%. The involvement of PI boosted the ultimate tensile strength, water affinity, distribution of surface aperture, heat endurance and the electrochemical performance of the separator. SEM consequences exhibited that the number and distribution of micro-pores of the surface and cross-section of mCNS separators were compact and ideal than CNS, which made it easier to form ion channels. Meanwhile, TG curves appeared that the heat endurance of separator was enhanced after modification. According to N2-adsorption experiments, the absorbability of mCNS separator was smaller than CNS which manifested that the aperture diameter of mCNS separator was minished. The contact angle testing demonstrated that the water affinity of mCNS separators was aggrandized. Furthermore, the electrochemical stability of the modified separators was boosted and the ionic conductivity of the separators was advanced similarly, in which the charging and discharging performance of the separator was improved. It was noteworthy that these features made it possible to use it in the lithium battery. This new technology for preparing separator from PI impregnated modification cellulose membrane provides a new way to solve the limitations of lithium battery applications.

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