

Cellulose/Polysulfonamide Composite Membrane as a High Performance Lithium-Ion Battery Separator

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ABSTRACT: Battery separators have drawn considerable attention due to their vital roles for the safety and electrochemical performance of lithium-ion batteries. In this paper, the cellulose/polysulfonamide composite membrane was successfully fabricated from a mixture of microfibrillar cellulose and polysulfonamide via a facile papermaking process. And its potential application was explored as a high performance lithium-ion battery separator by characterizing their electrolyte wettability, heat tolerance, and electrochemical properties. Lithium cobalt oxide/graphite cells using the separator displayed better capacity retention ratios of 85% after 100 cycles and superior rate capability compared with those of a commercial polypropylene separator. Furthermore, the lithium iron phosphate/lithium half cell using cellulose/polysulfonamide separator exhibited stable charge–discharge capability even at 120 °C. It was demonstrated that the composite separator possessed an enhanced thermal dimensional stability. This research provides a promising new strategy for large-scale fabrication of high performance lithium-ion battery membranes.

KEYWORDS: Cellulose, Polysulfonamide, Composite membrane, Papermaking process, Lithium-ion battery separator



INTRODUCTION

The market of lithium-ion batteries (LIBs), due to their high energy density, excellent cycle performance, and low self-discharge rate, has grown tremendously over the past decade to keep pace with consumer electronics.^{1–6} High-power density lithium-ion batteries are finding their application in the power tool market and stationary and transportation applications.^{1,4,7–12} These new markets have aroused new demands and challenges on separators for lithium-ion batteries. A separator plays two main roles during the application of cells: (1) preventing internal short circuiting between the cathode and anode to maintain the safety of batteries and (2) providing a path for ionic conduction in the liquid electrolyte throughout the interconnected porous structure.^{13,14} The polyolefin microporous separators have been widely used in LIBs due to their excellent properties such as electrochemical stability, mechanical strength, and thermal shutdown; however, their intrinsically hydrophobic character, low surface energies, and low porosity raises serious concerns, especially for high-power density.^{13,15–18} In order to tackle these problems, intensive efforts have been made to modify their surface including a polymer coating lyophilic layer, grafting process, and incorporating inorganic nanoparticles.^{19–24} Nevertheless, these strategies which could improve wettability and thermal stability are limited in practical applications due to high manufacturing cost and inherent low thermal dimensional stability of polyolefin based membranes.

In general, separator cost accounts for a fair portion of the total cost of LIBs which can exceed by about 20% due to the expensive raw materials and complicated fabrication technology.¹⁴ Therefore, it is urgent to explore cost-effective materials and facile large-scale fabrication to reduce cost. Natural cellulose, the most important skeletal component in plants, is an inexhaustible and renewable raw material with fascinating properties. Composed of repeated units of D-glucose, cellulose is a very promising material due to its hydrophilicity, renewability, environment friendly and thermal dimensional stability.^{25–28} Polysulfonamide (PSA) is a kind of high performance synthetic polymer known for excellent thermal, mechanical, dielectric properties, along with superior chemical resistance.^{29–32} In our previous reports, a PSA-based membrane has been successfully investigated as an LIB separator via an electrospinning process.^{32,36} The PSA-based separator presented excellent thermal dimensional stability, wide chemical window, high porosity, and uniform pore structure; however, the pristine material was expensive and, in addition, the electrospinning process made it difficult to produce separators on a large scale. It has been proven that the papermaking process could in large scale produce membranes with lower manufacturing cost.¹⁴ To the best of our knowledge,

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cellulose/PSA composite membranes have not yet been explored as high performance LIB separators by a facile paper-making method.

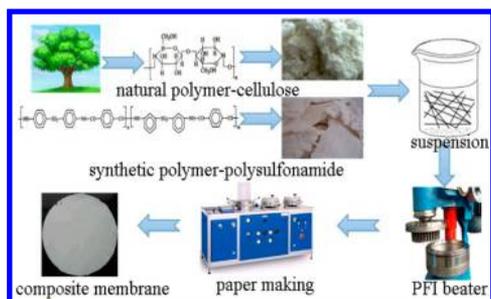
Herein, a facile papermaking process was applied to fabricate cellulose/PSA composite membrane for a cost-effective and high performance LIB separator. Cellulose was used as the original material which could greatly reduce the material cost of LIBs, and the papermaking process could alleviate the processing cost for a large scale application. PSA was used to enhance the mechanical property and thermal dimensional stability of composite membrane. It was demonstrated that the cellulose/PSA composite membrane possessed excellent thermal stability, low interfacial resistance, superior rate capability, and better cycle performance. These excellent properties and facile large-scale fabrication process could endow this cellulose/PSA composite membrane a very promising application as high-performance lithium-ion battery separator.

EXPERIMENTAL SECTION

Materials. Cotton cellulose pulp (DP 750–1000, Shandong Yinying Co., Ltd.), polysulfonamide pulp (DuPont Company), propylene carbonate (PC) (Capchem Technology Co., Ltd.), 1 M lithium hexafluorophosphate (LiPF₆) in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1/1, v/v) (Guotai-huarong New Chemical Materials Co., Ltd.), lithium bis(oxalato)borate (LiBOB) (Suzhou Fotai New Materials Co., Ltd.), and polypropylene (PP) separator (Celgard 2500) were received from their respectively indicated suppliers. Other chemical reagents were all purchased commercially and used without further purification.

Preparation of the Cellulose/PSA Composite Membrane. The schematic illustration for the cellulose/PSA composite membrane was shown in Scheme 1. A 12 wt % suspension of cellulose and PSA

Scheme 1. Schematic Illustration for the Preparation of Cellulose/Polysulfonamide Composite Membrane



pulps with the mass ratio of 3/1 (w/w) was stirred for 10 h. Then, the mixed pulp was beaten in a PFI beater (PL11-00, Xianyang Taisite) at 20 000 rpm to disperse fibers. The dispersed fibers were grinded into fibrillated fibers with ultrafine friction grinding machine (MKZA6-S, Masuko Sangyo Co., Ltd.). Finally, the obtained homogeneous slurry was added into a papermaking machine (Rapid Koethen BB) to fabricate a wet cellulose/PSA composite membrane. The wet composite membrane was subsequently dried in a hot-oven at 95 °C for 30 min and, then, calendered at 120 °C under 20 MPa. After that, the final cellulose/PSA composite nonwoven membrane was dried under vacuum at 120 °C for 12 h. The average thickness of the resultant membrane was $40 \pm 1 \mu\text{m}$.

Membrane Characteristics. The surface morphology of cellulose/PSA composite membrane was observed by a Hitachi S-4800 field emission scanning electron microscope (SEM). The air permeability of the membrane was examined with a Gurley densometer (4110N, Gurley) by measuring the time for air to pass through a determined volume (100 cm³). The porosity of the

membrane was measured using the method of *n*-butyl alcohol immersion by immersing in *n*-butanol 1 h, and then calculating the porosity using the equation: porosity = $(m_a/\rho_a)/(m_a/\rho_a + m_b/\rho_b) \times 100\%$, where m_a and m_b are the mass of *n*-butanol and the membrane and ρ_a and ρ_b are the density of *n*-butanol and the membrane, respectively. The electrolyte uptake was measured through the weight of membranes before and after liquid electrolyte (1 M LiPF₆ in EC/DMC (1/1, v/v)) soaking for 1 h and calculated using following equation: electrolyte uptake = $(W_c - W_d)/W_d \times 100\%$, where W_d and W_c are the weight of the membrane before and after soaking in the liquid electrolyte, respectively. Thermal stability of the membrane was tested by a differential scanning calorimeter (Diamond DSC, PerkinElmer) ranging from 50 to 300 °C at 10 °C min⁻¹ under N₂ atmosphere. The thermal shrinkage behavior of the membrane was determined by an oven test at 200 °C for 0.5 h. The stress–strain curves of the separators were tested using an Instron-3300 universal tensile tester (USA) at a speed of 10 mm min⁻¹ with the samples of 1 cm wide and 4 cm long.

Electrochemical Measurements. In order to measure electrochemical performance, two types of electrolyte (1 M LiPF₆ in EC/DMC (1/1, v/v) and 0.5 M lithium bis(oxalato)borate (LiBOB) in propylene carbonate (PC)) were prepared. The ionic conductivity of PP and cellulose/PSA composite separator between two stainless-steel plate electrodes were evaluated using the electrochemical impedance spectroscopy (EIS) measurement in combination with a Zahner Zennium Electrochemical Workstation by applying an AC voltage of 10 mV amplitude in the frequency range of 1–10⁶ Hz. The interfacial resistances between two lithium plates were also investigated by EIS measurement. The electrochemical stability window of the separators were measured by a linear sweep voltammograms (LSV) on a working electrode of stainless-steel and a counter electrode of lithium metal at the potential range between 2.5 and 6.0 V under the scan rate of 1.0 mV s⁻¹ at 20 °C.

LiCoO₂ cathode (LiCoO₂/carbon black/PVDF = 90/5/5, w/w/w), LiFePO₄ cathode (LiFePO₄/carbon black/PVDF = 80/10/10, w/w/w) and a natural graphite anode (natural graphite/carbon black/PVDF = 90/5/5, w/w/w) were prepared by a doctor-blading process and then dried under vacuum at 120 °C for 12 h. A half cell (2032-type coin) was assembled by sandwiching separator between a lithium metal foil and LiFePO₄ electrode and activated by filling it with the liquid electrolyte of 0.5 M LiBOB/PC. A unit cell (2032-type coin) was composed of a LiCoO₂ cathode, a natural graphite anode, separator, and 1 M LiPF₆/EC+DMC electrolyte. All assembly of cells were carried out in an argon-filled glovebox. The charge/discharge rate capability and cycle performance of cells were detected using a LAND battery test system at 20 and 120 °C. The discharge current densities were varied from 0.2 to 8.0 C under a voltage range between 2.75 and 4.2 V. The cells were cycled at a fixed charge/discharge current density of 0.5 C/0.5 C for cycle performance testing.

RESULTS AND DISCUSSION

Prior to exploring cellulose/PSA composite membrane as LIBs separator, membrane properties were characterized. Typical SEM images of PP separator and cellulose/PSA composite separator were shown in Figure 1. It was observed that the PP separator possessed elliptic pores which were formed via a uniaxially stretching technology.^{13,14} By comparison, the cellulose/PSA composite membrane without applying pressure possessed large-sized and irregular pores, which was not beneficial to improve the battery safety because of self-discharge and the formation of lithium dendrites.³¹ And the corresponding mechanical performance of this separator was poor. When the cellulose/PSA membrane was hot calendered under pressure of 20 MPa, the interwoven pores became smaller and generated tortuous nanosized pores between compact cellulose fibers. The nanosized pores played critical roles in preventing internal short circuits and avoiding self-discharge. In addition, the tortuous pores were advantageous to prevent the

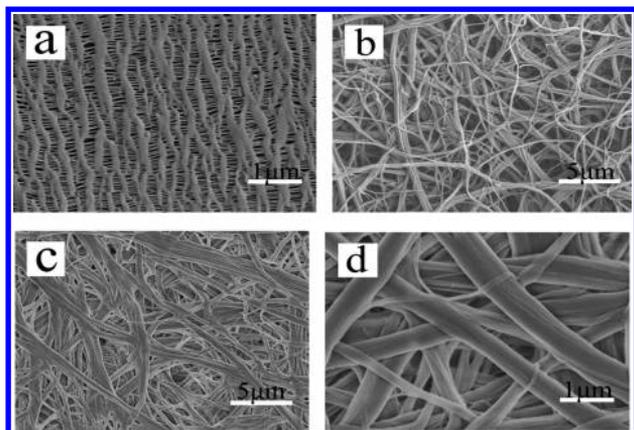


Figure 1. Typical SEM images of (a) commercial PP separator, (b) cellulose/PSA composite membrane without exercising pressure, (c and d) cellulose/PSA composite membrane with the pressure of 20 MPa.

growth of lithium dendrites and enhance the mechanical properties which were favorable to enhance the safety performance of battery.^{15,31}

The battery separator should be robust to withstand the high tension after casual collisions.^{15,25} With the change of mass ratio between cellulose and PSA, the mechanical strength of the composite membrane was varied. As shown in Figure 2, when

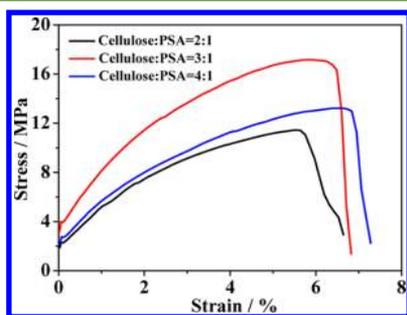


Figure 2. Stress–strain curves of cellulose/PSA composite separator with the different mass ratio.

the mass ratio was 3:1, the cellulose/PSA composite membrane exhibited the highest strength of 17 MPa. The cellulose provided a skeleton well bonded by PSA. The synergy between cellulose and PSA was beneficial to improve the mechanical performance.

The thickness, porosity, air permeability, and electrolyte uptake of the separators were summarized in Table 1. The porosity of cellulose/PSA (66%) was higher than that of PP separator (55%) indicating an enhanced permeability.³³ It was remarkable that the Gurley value of cellulose/PSA composite membrane (60 s) was much lower than that of PP separator (235 s). This result could be ascribed to the higher porosity and

Table 1. Physical Properties of PP Separator and Cellulose/PSA Composite Membrane

sample	thickness (μm)	Gurley value (s)	porosity (%)	electrolyte uptake (%)
PP separator	25	235	55	120
cellulose/PSA composite membrane	40	60	66	260

interwoven porous structure of cellulose/PSA membrane. As is well-known, high porosity can result in high electrolyte uptake which is beneficial to facilitate rapid ionic transportation.¹³ Due to the lyophilic group of cellulose and high porosity, the electrolyte uptake of cellulose/PSA composite membrane was up to 260% which was much higher than PP separator. These excellent properties were favorable to improve wettability and electrochemical performance of the lithium-ion battery.

It was obvious in Figure 3 that the wettability of PP separator with liquid electrolyte was poor because of its hydrophobic

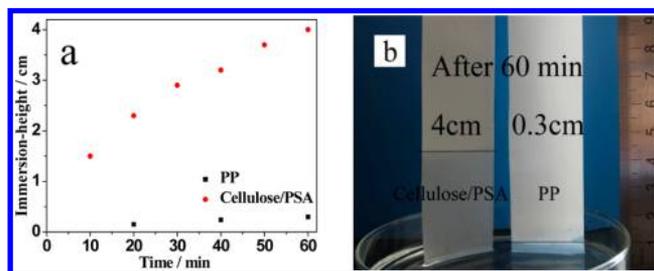


Figure 3. (a) Immersion-height evolution of liquid electrolyte (1 M LiPF₆ in EC/DMC (1/1, v/v)) in PP separator and cellulose/PSA composite membrane, (b) photograph showing liquid electrolyte immersion-height after 60 min.

surface and low surface energy,¹⁵ while the cellulose/PSA composite membrane exhibited better electrolyte immersion-height (4 cm) than PP separator (0.3 cm). The cellulose/PSA composite separator was easily accessible to liquid electrolyte which was closely related to the physical properties. The superior wettability facilitated facile of electrolyte filling in battery during the charge/discharge test.

Thermal stability of separators played an important role for the safety of lithium-ion batteries because they could prevent short-circuits by keeping anode and cathode apart. PP separator had better advantages at elevated temperature due to shutdown properties, however, the separator suffered from severe thermal shrinkage at higher temperature which could cause internal short-circuits; furthermore, it could lead to fire outbreak and even explosion. As shown in Figure 4, the cellulose/PSA

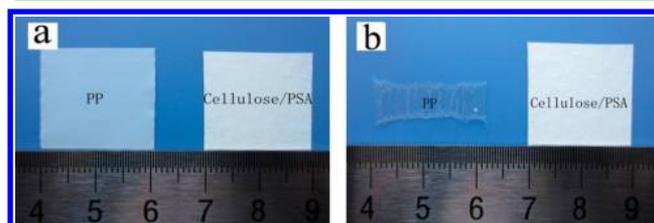


Figure 4. Photographs of PP separator and cellulose/PSA composite membrane (a) at 20 °C and (b) after exposure to 200 °C for 0.5 h.

composite membrane maintained original dimension after thermal treatment at 200 °C while the PP separator displayed severe thermal shrinkage (>50%). This superior thermal tolerance could effectively prevent internal short-circuit at evaluated temperature.

According to the DSC measurement in Figure 5, PP separator began to melt at 150 °C and had an endothermic peak at 165 °C; however, cellulose/PSA membrane did not show any obvious peak below 300 °C. This significantly suppressed thermal shrinkage of cellulose/PSA membrane was mainly attributed to the high thermal stability of PSA and close-

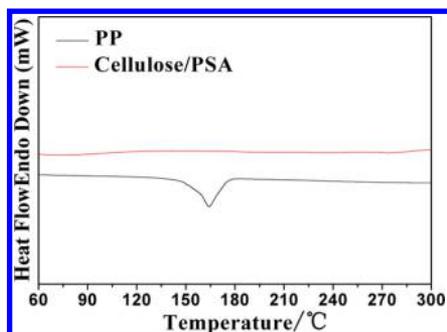


Figure 5. DSC curves of PP separator and cellulose/PSA composite membrane.

packed polysaccharide chains which were highly stabilized by hydrogen bonds;³⁵ meanwhile, a papermaking process also contributed to improve thermal stability. Thus, the thermal dimensional stability endowed the cellulose/PSA composite membrane a promising application as high performance lithium-ion battery separator.

The ionic conductivity and interfacial resistance played important roles in the performance of lithium-ion batteries. The porous structure and Gurley value were closely related to the ionic conductivity and useful parameters to predict the ionic conductivity.^{15,34} The ionic conductivity of electrolyte-soaked PP separator was calculated to be $0.68 \times 10^{-3} \text{ S cm}^{-1}$ according to the equation: $\sigma = L/RS$, where L is the thickness of the separator and S is the contact area between the separator and stainless steel blocking electrodes, while that of cellulose/PSA composite membrane was $1.2 \times 10^{-3} \text{ S cm}^{-1}$. The higher ionic conductivity was closely related to above-mentioned physical properties and underlines the successful evolution of highly interconnected nanoporous network channels in the cellulose/PSA composite membrane.²⁵ In addition, higher ionic conductivity was beneficial to ensure better rate capability of the battery. Figure 6 depicted the interfacial compatibility of

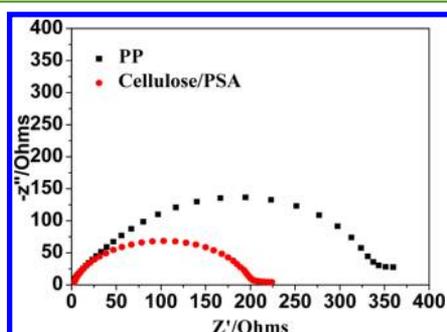


Figure 6. Nyquist plots of Li/electrolyte-soaked separator/Li cells at 20 °C.

separators between lithium plates. The interfacial resistance of cellulose/PSA composite membrane was 200 Ω while that of PP separator was 340 Ω . The lower interfacial resistance indicated that the cellulose/PSA separator possessed better interfacial compatibility with electrode materials.

The electrochemical stability window of separators were measured by linear sweep voltammograms (LSV). Figure 7 displayed the LSV curves of PP and cellulose/PSA separator using liquid electrolyte of EC/DMC. It was suggested that no significant decomposition of any components in the cell using cellulose/PSA separator took place below 4.9 V vs Li/Li⁺ while

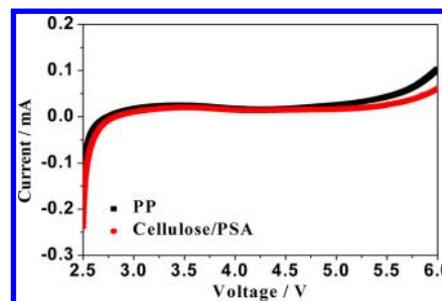


Figure 7. Linear sweep voltammograms of the PP separator and cellulose/PSA composite membrane at 1.0 mV s^{-1} from 2.5 to 6.0 V.

that of PP separator began to decompose at about 4.7 V. The cellulose/PSA composite separator could be chemically stable against the liquid electrolyte. This result indicated that cellulose/PSA separator had better interfacial compatibility with carbonate electrolyte and anodic stability.¹⁰

In order to evaluate the practical application properties of the cellulose/PSA composite membrane, cycling performance and rate capability tests were carried out. As shown in Figure 8, the

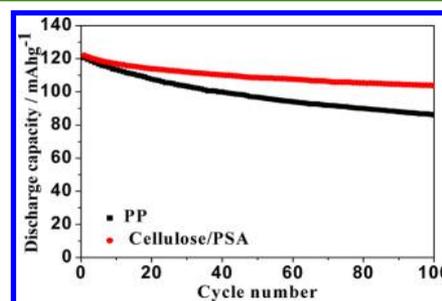


Figure 8. Cycle performance of the cells using PP separator and cellulose/PSA composite separator.

LiCoO₂/graphite cells using cellulose/PSA composite separator displayed stable cycling performance and higher capacity retention (85%) than that of PP separator (73%) after 100 cycles. The better capacity retention was ascribed to the excellent electrolyte uptake, higher ionic conductive, and lower interfacial resistance which could allow facile ionic transport and better electrolyte retention during charge–discharge test.^{12–15,25}

To investigate the enhanced cycle performance of cells using cellulose/PSA separator, AC impedance measurements were carried out after the first and 100th cycles. It is well-known that the semicircle at high frequency zone represents the charge-transfer resistance accompanied with migration of lithium ion.^{14,19} As shown in Figure 9a, the charge-transfer resistance of cell with cellulose/PSA separator was 18 Ω which was slightly lower than the cell with PP separator (20 Ω) after the first cycle. However, after 100 cycles, the remarkable differences were observed in Figure 9b. The charge-transfer resistance of cells using cellulose/PSA separator and PP separator increased by 11 Ω and 30 Ω , respectively. The lower charge-transfer resistance was related to the higher electrolyte uptake and better interface compatibility which were beneficial to improve cycle performance and rate capability.¹⁹

Figure 10 exhibited the discharging capacities of cells with PP separator and cellulose/PSA separator at different current densities ranging from 0.2 to 8 C. The discharge capacity using PP separator and cellulose/PSA composite separator dropped

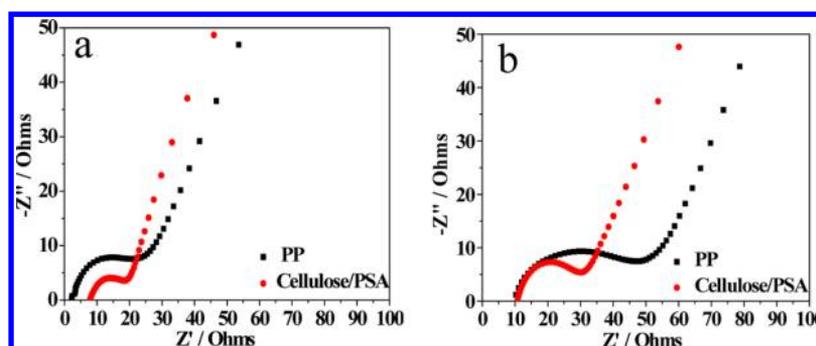


Figure 9. Nyquist plots for cells measured after the (a) first cycle and (b) 100th cycle.

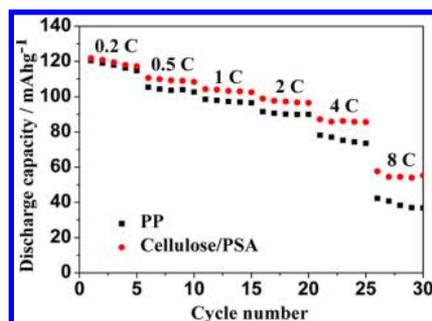


Figure 10. Rate capability of LiCoO₂/graphite cells using PP separator and cellulose/PSA composite separator.

following discharging current densities from 0.2 to 8 C; however, the discharging capacities of a cell with cellulose/PSA separator was higher than PP separator at various rates. The superior rate capability could be ascribed to higher ionic conductivity and better interfacial compatibility of electrolyte-soaked cellulose/PSA composite membrane. The excellent cycle performance and rate capability of lithium-ion battery using cellulose/PSA composite membrane were significant for commercial application as high performance lithium-ion battery separator.

To further illustrate the thermal dimensional stability of separator at high temperature, cycle performance of LiFePO₄/Li cells using PP separator and cellulose/PSA composite separator were evaluated under 0.5 C at 120 °C. As shown in Figure 11, the cell with cellulose/PSA separator displayed excellent and stable cycling performance while the cell using PP separator could not be charged and discharged stably. The thermal shrinkage of the PP separator caused internal short-circuits of the cell at 120 °C. The obtained discharge capacity of cell using cellulose/PSA separator after 20 cycles was 132.6

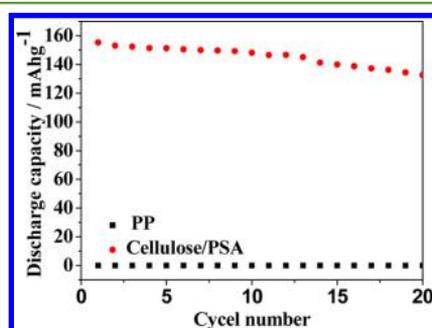


Figure 11. Cycle performance of LiFePO₄/Li cells using PP separator or cellulose/PSA composite separator at 120 °C.

mAh g⁻¹. From the foregoing experimental results, cellulose/PSA composite separator could maintain better performance at elevated temperature. This result demonstrated that the cellulose/PSA composite membrane possessed better thermal dimensional stability during cycling at evaluated temperature which would enhance safety characteristic of high performance lithium-ion battery.

CONCLUSION

In summary, we explored renewable, environment friendly, natural cellulose and synthetic PSA to fabricate cellulose/PSA composite membrane via a facile papermaking process as a lithium-ion battery separator, which could greatly reduce the cost of the separator in a large scale. The electrolyte-soaked cellulose/PSA composite membrane delivered superior ion conductivity ($1.2 \times 10^{-3} \text{ S cm}^{-1}$) owing to the synergetic effect between electrolyte and composite material. Furthermore, it was demonstrated that the cellulose/PSA composite membrane exhibited excellent thermal dimensional stability, which could significantly enhance the safety of lithium-ion batteries. The superior electrochemical performance contributed by cellulose/PSA composite membrane at 20 °C and even at an elevated temperature could endow it a very promising application as high-performance lithium-ion battery separator.

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Notes

The authors declare no competing financial interest.

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