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Electrospun lignin/polyacrylonitrile nonwoven composite separator with high porosity and thermal stability for lithium-ion battery

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In this work, the lignin/polyacrylonitrile composite fiber-based nonwoven membranes (L-PANs) were prepared by ectrospinning with dispersing different amount of lignin in the polyacrylonitrile (PAN) solutions. The porosity of the L-PANs could reach 74%, which was significantly higher than that of the commercialized PP separator (42%). After exposure at 150°C for 15 min, the L-PANs showed no apparent dimensional change and no wrinkle, however, the commercialized PP separator shrank by 32%. At the same time, Li/LiFePO$_4$ battery using L-PANs as separator delivered superior the discharge C-rate capability and cycling performance compared to those using the commercialized PP separator at room temperature. More specifically, the discharge capacity of the cell containing L-PAN (3:7 by weight) could retain 148.9 mAh g^{-1} after 50 cycles at 0.2 C and the discharge capacity retention was 95%.

1 Introduction

Lithium-ion batteries with high energy density, wide operational voltage range, low self-discharge rate and long cycle life have been considered as one of the most promising power source for portable electronic devices, power tools such as cell phones, laptops, digital cameras, and electric vehicles in the future.[1-4]

As an indispensable part of lithium-ion batteries, separators play a key role in influencing on the performance of lithium-ion batteries. Their main function is to provide a physical barrier between the positive and negative electrodes to prevent electrical short circuits and simultaneously maintain liquid electrolyte between both electrodes.[5, 6] Separator materials must meet certain performance requirements for instance good mechanical, high wettability, low shrinkage and good chemical stability to make the battery safety and have high performance. Generally, polyolefin micro-porous membranes have been the major separators in current commercialized lithium-ion batteries due to their good mechanical and chemical stability.[7] However, there are many disadvantages in polyolefin membranes such as poor thermal stability, insufficient electrolyte wettability and low porosity of about 40%,[8] especially, low melting point of this type of separator can easily result in the shrink of separator and then internal short-circuiting of the electrodes, which limits the safety and stability of Li-ion batteries.[9, 10]

In order to address these issues and increase the thermal stability, electrolyte wettability and porosity of the separator, many researchers applied different materials and used novel methods to prepare the membranes for Li-ion batteries separators. Various approaches including phase inversion,[11] solution casting,[12] surface modification,[13] electrospinning[14] have been proposed for the preparation of polymer membrane. In comparison to other technologies, electrospinning can produce non-woven membranes including high porosity (60-90%),[15] which can increase electrolyte uptake, making them excellent candidates for Li-ion batteries separators. polymers can be used as a skeleton for separators due to their good performance for fiber-forming during electrospinning process, the frequently-used polymers used for investigating and developing separators include poly(ethylene oxide) (PEO), poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC), poly(vinylidene fluoride) (PVDF), etc..[16] Among various polymers, PAN is the most studied material for nanofiber separators due to its excellent flame resistance, processability, resistance to oxidative degradation and electrochemical stability. Most importantly, the oxidative stabilization of PAN is always very high even at high temperature.[17] Therefore, PAN is the most commonly used host polymer, which constituted a strong skeleton to work as a separator,[18] as a consequence, the safety and stability of batteries improved. Moreover, the electrolyte wettability and porosity of the separator can be further improved by introducing other polymers. Biocompatible and renewable natural macromolecule materials are highly motivated as suitable polymer.

Lignin, as the second most abundant component in nature, is separated from wood or to be as a co-product of the papermaking industry. Lignin with outstanding properties such as biodegradability and biocompatibility, low cost and environmental benignancy has considered to be used in various fields such as water purification[19], molecular sieving[20] and osmosis[21]. The most significant contribution to the sustainable development of lignin is

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that it provides the stable and sustainable source of organic substances, resulting in its very broad application prospects.[22, 23]

In this study, the lignin/polyacrylonitrile composite fiber-based nonwoven membranes (L-PANs) with different amount of lignin (lignin/PAN = 0:10, 1:9, 3:7, 5:5 by weight, respectively) were prepared by electrospinning method, which lignin was added to PAN to improve the porosity and wettability of the membranes. The physical properties and the electrochemical performance of the L-PANs were tested. Results showed that the L-PANs obviously improved the properties containing porosity, wettability, thermal stability and the electrochemical performance when compared to the commercialized PP separator. The high porosity and good electrolyte affinity of the L-PANs may further improve the electrochemical performance of Li-ion batteries, such as ionic conductivity, C-rate performance and cycling performance.

Experimental

Materials

Polyacrylonitrile (PAN, Mw = 150,000, Aldrich Co.) and lignin (Mw=10,000, Aldrich Co.) were vacuum dried at 60°C for 6 h before use. N,N-dimethylformamide (DMF, Sigma-Aldrich) was used solvent for electrospinning. The commercialized PP separator (Celgard 2400), provided by Celgard Company, was regarded as the separator of Li-ion batteries for comparison. The electrolyte was 1 M lithium hexafluorophosphate (LiPF$_6$) in ethylene carbonate and dimethyl carbonate (EC + DMC, 1:1 by volume). The EC and DMC solvent (battery grade, extra dry < 20 ppm of water) were purchased from Tianjin Jinniu power sources material Co. Ltd. (China) and used as received without further purification. All the other reactants were of analytical purity and used as received.

Separator Preparation

The lignin/polyacrylonitrile composite fiber-based nonwoven membranes (L-PANs) were fabricated by electrospinning method at room temperature. The PAN at a concentration of 12 wt% was prepared by adding PAN (1.44 g) into DMF (10.56 g) at 60°C to form a homogeneous polymer solution. Lignin/PAN solutions were prepared by dispersing different amount of lignin (0 g, 0.16 g, 0.62 g, and 1.44 g) into each PAN-DMF aqueous mixture under continuous mechanical stirring, the weight ratios of lignin/PAN were 0:10, 1:9, 3:7 and 5:5 (w/w), respectively.

The prepared solution was put into 10 ml syringes with metal needles. The needle-to-collector distance was 19 cm with two high voltages of +19kV and -4.00 kV applied to them, respectively. The collector drum rotation speed was 120 rpm and the solution feeding rate used was 2 ml/h, then the lignin/PAN membranes were dried under vacuum at 60°C for 12 h. After that, the lignin/PAN membranes were hot pressed with pressure and temperature setting to 16 MPa and 100°C, respectively. A commercialized PP separator (Celgard 2400) was chosen for comparison.

Structure Characterization

The morphology of the L-PANs and PAN membrane was observed by a field-emitting scanning electron microscope (SEM) (Hitachi S-4800, Japan).

The porosity of the membranes was measured by using n-butanol uptake tests. The porosity was calculated using the following equation:

$$\text{Porosity } (\%) = \frac{w_w - w_d}{\rho_b V}$$

where w_w and w_d are the weight of wet and dry membranes, respectively, ρ_b is the density of n-butanol, and V is the geometric volume of the membranes.

Performance Evaluation

The dimensional stability of the membranes was determined by thermal shrinkage tests at 150°C for 15 min.

Liquid electrolyte uptake was measured by soaking weighted the electrospun membranes and the commercialized PP separator in the liquid electrolyte of 1 M LiPF$_6$ in EC + DMC (1:1 in volume) for 2 h until an equilibrium at room temperature. The excess electrolyte solution on the membrane surface was removed with wipes. The electrolyte uptake (EU) was calculated by the equation:

$$\text{EU } (\%) = \frac{w_1 - w_0}{w_0} \times 100$$

where w_0 and w_1 are the weight of the dry and wet membranes, respectively.

The wettability of the separators was evaluated by contact angle measurements. The electrolyte (1 M LiPF$_6$/EC+DMC (1/1, v/v)) contact angle measurement was obtained using a commercialized drop shape analysis system (DSA100). Three parallel measurement were carried out for either separator under the same conditions.

The ionic conductivity of the liquid electrolyte-soaked membranes was measured by AC-impedance spectroscopy using stainless-steel (SS) cells with an electrochemical instrument (PGSTAT 128N, Metrohm). The frequency varied from 0.1 Hz to 1 MHz with AC amplitude of 5 mV at 20°C.

The ionic conductivity was calculated by:

$$\sigma = \frac{d}{R_b \times S}$$

where d is the membrane thickness, S is the contact area between membrane and steel electrodes, the bulk resistance (R_b) is obtained at the high frequency intercept of AC impedance intercept on the real axis.

The electrochemical stability of the liquid electrolyte-soaked membranes was determined by linear sweep voltammetry (CHI604D, China) using a stainless steel working electrode and a lithium metal as the counter electrode at the scanning rate of 5 mV s^{-1} at room temperature.

The charge-discharge performance of Li/LiFePO$_4$ cells containing liquid electrolyte-soaked membranes was evaluated using CR2430-type coin cells. The LiFePO$_4$ cathode was prepared by mixing LiFePO$_4$ power(80 wt%), carbon black conductor (10 wt%)

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and PVDF (10 wt%) in NMP and pasted on an aluminum current collector of 25 μm, and then dried in a vacuum oven at 120°C for 12 h. Battery testing system (Land, China) was used to measure the cycling performance with a potential window of 2.0-4.2 V at a current density of 0.2 C. The C-rate performance was also tested varying from 0.2 to 8 C.

Results and discussion

Morphologies

Fig. 1 showed the SEM images of the L-PANs and PAN membrane. With the increasing content of lignin in the membranes, the fiber diameter in average increased, ranging from 200 nm to 1000 nm. The diameter increase indicated that composition and viscosity of the solution had an effect on the fiber size. It was seen that all of the L-PANs and PAN membrane had a three dimensional network structure, which provided the membranes with good mechanical strength and high porosity.[24]
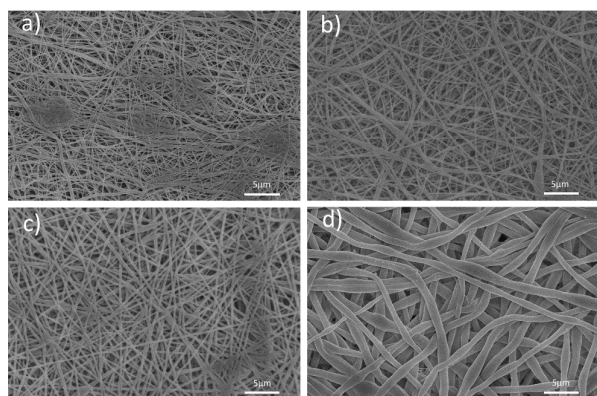
Fig. 1. SEM of membranes with different lignin/PAN weight ratio.a)PAN b)1:9 c) 3:7 d) 5:5

Porosity

Porosity is one of the important parameter for battery separator. Higher porosity leads to higher electrolyte uptake and increases the contact area between the liquid and the polymer, which is beneficial for the electrolyte retaining in the polymer membrane. Table 1 listed the porosities of the L-PANs, PAN membrane and the commercialized PP separator. It was found that the porosity of the electrospun membranes increased from 21% to 74% as the lignin/PAN weight ratio increased from 0:10 to 5:5. In particular, when the weight ratios of lignin/PAN were 3:7 and 5:5, the porosity of the L-PANs were higher than that of the commercialized PP separator (42%). This may be attributed to the fibrous morphology, the fiber diameter became larger with the increasing content of lignin, because larger fiber diameters lead to higher porosity.[8, 26]

Table 1 Membrane properties of a commercialized PP separator, PAN separator and L-PANs as a function of lignin content.

Property	PP	PAN	10 wt% Lignin/PAN	30 wt% Lignin/PAN	50 wt% Lignin/PAN
Porosity (%)	42	21	24	66	74
The contact angle	66.8 °	52.3 °	41.9 °	40.1 °	31.6 °
The ionic conductivity (S cm^{-1})	1.09× 10^{-5}	6.88 × 10^{-4}	9.94× 10^{-4}	1.24× 10^{-3}	7.75 × 10^{-4}

Thermal dimensional stability

A separator with good thermal dimensional stability might improve safety factor and have an active effect on the performance of battery, which can prevent the electrode from contacting the other at high temperature.[27, 28] Fig. 2 compared the morphology changes of the PAN membrane, the L-PANs (1:9, 3:7, 5:5 by weight) and the bcommercialized PP separator before and after thermal exposure at 150°C for 15 min. It can be seen the L-PANs showed no apparent dimensional change and no wrinkle, exhibiting superior thermal and dimensional stability. However, the commercialized PP separator could not maintain the original shape and shrank by 32%. The excellent thermal dimensional stability of the L-PANs could effectively prevent internal short-circuiting of the battery to improve battery safety performance at high temperature.[29]

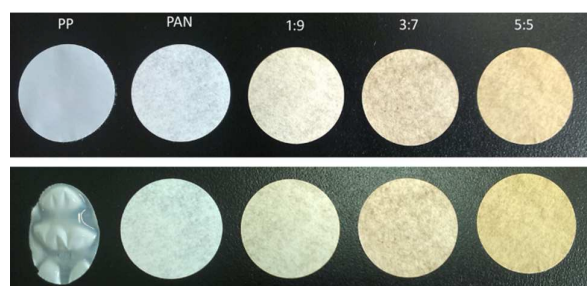Fig. 2 Photographs of the separators before and after thermal exposure at 150°C for 15 min.

Wettability

The separator with good wettability can retain the electrolyte effectively and increase the speed of absorbing electrolyte. To study the wettability of the separators, the contact angle measurement was performed, as shown in Table 1 and Fig. 3. It was clearly observed that the contact angles of the commercialized PP separator, the PAN membrane and the L-PANs (1:9, 3:7, 5:5 by weight) were 66.8 ± 1.6 °, 52.3 ± 1.5 °, 41.9 ± 1.2 °, 40.1 ± 1.1 °, 31.6 ± 1.4 °, respectively. It was clear that the L-PANs possessed better wettability comparing with the commercialized PP separator, which could be ascribed to high porosity, membranes morphology and good affinity to the electrolyte.

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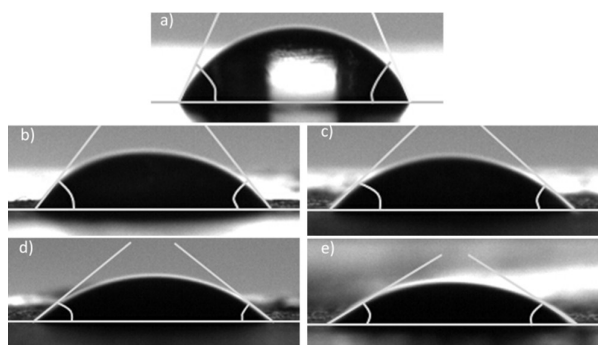
Fig. 3. Digital pictures of the contact angles of different separators. (liquid electrolyte: 1 M LiPF$_6$ in EC/DMC)a commercialized PP separator b) PAN c) 1:9 d) 3:7 e) 5:5

Electrolyte uptake and ionic conductivity

Fig. 4 showed the comparison of the electrolyte uptake process at room temperature. It can be seen from Fig. 3 the electrolyte uptake process of the L-PANs was fast and almost stabilized within 10 min. In contrast, the commercialized PP separator exhibited a low electrolyte uptake and the speed was slow. The maximum uptakes were 368%, 414%, 530%, 790% and 47% for the PAN membrane, the L-PANs (1:9, 3:7, 5:5 by weight) and the commercialized PP separator, respectively. The improvement in electrolyte uptake of the L-PANs should be caused mainly by the increased porosity, fully interconnected pore structure and good affinity to the electrolyte.[25] The low electrolyte uptake of the commercialized PP separator was attributed to the relatively low porosity and hydrophobic property. For lithium-ion batteries, high electrolyte uptake of separators accelerates the battery assembly process and achieves a low resistance.[27]

Table 1 showed the ionic conductivities of the PAN membrane, the L-PANs (1:9, 3:7, 5:5 by weight) and the commercialized PP separator at 20°C. It can be seen that the maximum ionic conductivity of the L-PAN (3:7 by weight) was 1.24×10^{-3} S cm^{-1}, however, the ionic conductivity of the commercialized PP separator was only 1.09×10^{-5} S cm^{-1}. The ionic conductivities of the L-PANs were significantly higher than that of the commercialized PP separator, this behavior ascribed to the high electrolyte uptake and optimal pore size of the electrospun membranes, which were favor of the easy migration of ion.[25]
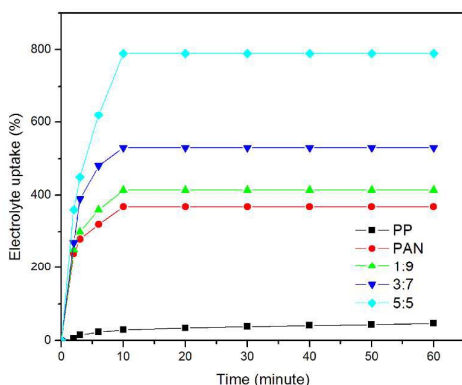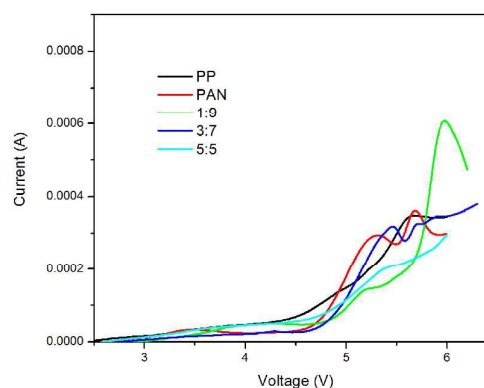

Fig. 4 Electrolyte uptake (%) of a commercialized PP separator and L-PAN membranes with different lignin/PAN weight ratio.

Electrochemical oxidation limit

The electrochemical stability window of the electrolyte is a key parameter to evaluate the battery performance. When observed the continuous rapid increase of current indicates the electrolyte starts to decompose.[30, 31] The electrochemical oxidation limit of liquid electrolyte-soaked membranes was evaluated by linear sweep voltammetry measurements (Fig. 5). It can be observed that all of the L-PANs exhibited an anodic stability greater than 4.5 V versus Li/Li$^+$, which were higher than that of the commercialized PP separator. It was indicated the L-PANs with a stability window up to 4.5 V were sufficient for the practical application in lithium ion battery with certain cathodes, for example, LiFePO$_4$ and S-based composites.[32] On the one hand, the high anodic stability could be ascribed the excellent affinity of the membranes to the electrolyte which can partially swell the fibers. On the other hand, the strong interaction of by nitrile (-CN) group of the PAN increased the electrochemical stability.[17, 18]

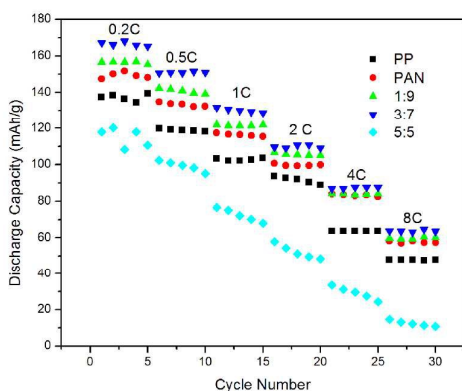Fig. 5 Electrochemcial stability windows of a commercialized PP separator and L-PAN membranes with different lignin/PAN weight ratio at the scanning rate of 5 mV s^{-1}.

C-rate performance

Fig. 6 showed the C-rate performance of Li/LiFePO$_4$ cells with the PAN membrane, the L-PANs (1:9, 3:7, 5:5 by weight) and the commercialized PP separator. The discharge capacity of the battery using the commercialized PP separator was around 137.5 mAh g^{-1} at 0.2 C and decreased to 48 mAh g^{-1} at 8 C, which exhibited a relatively low discharge capacity and the discharge capacity decreased quickly. Among the L-PANs, the cell with the L-PAN (3:7 by weight) had the best C-rate performance. For the cell with the L-PAN (3:7 by weight), the capacities were 167.1, 150.6, 131.8, 109.5, 86.9 and 63.8 mAh g^{-1} at the current densities of 0.2 C, 0.5 C, 1 C, 2 C, 4 C, and 8 C, respectively. The cell containing the L-PAN (3:7 by weight) exhibited less capacity fading when the current density increased. These results suggested that the higher wettability,

1 porosity and electrolyte uptake were beneficial for migration of the
2 lithium ion between the electrode and electrolyte interface, which
3 leaded to the better C-rate performance of the battery. At the same
4 time, it was clearly observed that discharge capacity of the cell with
5 the L-PAN (5:5 by weight) was relatively low and the capacities
6 decreased sharply, this might because system was unstable, too
7 much lignin could not react sufficiently with PAN so that some of
8 the lignin dissolved in the electrolyte salt, which had a negative
9 influence on battery performance.

10

11 Fig. 6 C-rate performance of Li/LiFePO₄ cells containing a commercialized PP
12 separator and L-PAN membranes with different lignin/PAN weight ratio.

13 **Cycling performance**

14 The cycling performance of L-PANs was investigated by using coin-
15 type Li/LiFePO₄ cells. Fig. 7(a) presented the initial charge-discharge
16 curves of the Li/LiFePO₄ cells at 0.2 C at room temperature. The
17 discharge capacity were 139.2, 152.6, 154.6, 156.9, 112.7 mAh g
18 for the cells containing the commercialized PP separator, PAN
19 membrane and L-PANs (1:9, 3:7, 5:5 by weight), respectively. It
20 could be seen that the cell using L-PAN (3:7 by weight) had the
21 highest discharge capacity (156.9 mAh g^{-1}).

22 To further investigate electrochemical stability of the L-PANs,
23 the cycling performance of the cells between 2.0-4.2 V at 0.2 C was
24 shown in Fig. 7(b). At the 50 th cycle, the discharge capacity of the
25 cell containing the L-PAN (3:7 by weight) was 148.9 mAh g^{-1}, which
26 was higher than that of other cells. After the 50 cycles, the
27 discharge capacity retentions were found to be 93.1%, 93.3%,
28 93.5% and 95% for the commercialized PP separator, PAN
29 membrane and L-PANs (1:9, 3:7 by weight), respectively. However,
30 the cell containing the L-PAN (5:5 by weight) still remained unstable
31 cycle. The better cycling performance of the L-PANs (1:9, 3:7 by
32 weight) was attributed to the increases of electrolyte uptake and
33 conductivity of lithium ions, which provided easier path for ions
34 transport and better electrolyte retention.[33] During the cell cycle
35 process, the capacity attenuation was due to active material
36 dissolution, electrolyte decomposition and the formation of
37 resistive layers on electrodes, leading to polarization between
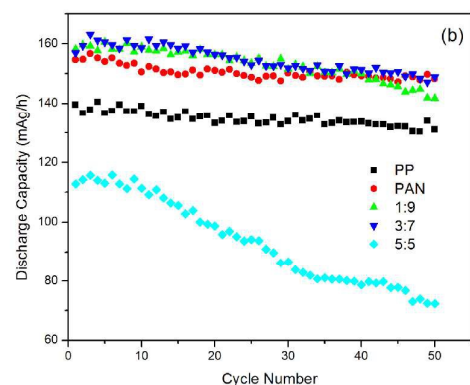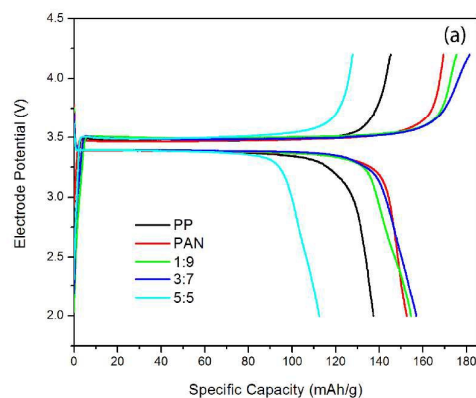38 electrolyte-electrode interface.[9, 34, 35]

Fig. 7 The initial charge-discharge curves (a) and cycling performance (b) of
Li/LiFePO₄ cells containing a commercialized PP separator and L-PAN
membranes with different lignin/PAN weight ratio at 0.2 C.

Conclusions

Lignin/polyacrylonitrile composite fiber-based nonwoven
membranes (L-PANs) were successfully prepared via electrospinning
method, followed by hot pressing with pressure and temperature
setting to 16 MPa and 100°C, respectively. The porosity of the L-
PANs could reach 74%, which was higher than that of the
commercialized PP separator (42%). After exposure at 150°C for 15
min, the L-PANs showed no apparent dimensional change and no
wrinkle. The cells using the L-PANs were evaluated for C-rate
performance and cycling performance. The results suggested that
the discharge capacity of the cell containing the L-PAN (3:7 by
weight) could retain 148.9 mAh g^{-1} after 50 cycles at 0.2 C and the
discharge capacity retention was 95%. The L-PANs could be suitable
for use as separator for lithium-ion batteries due to its low cost and
simple preparation process.

Acknowledgements

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