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Short communication

Wet-laid non-woven fabric for separator of lithium-ion battery

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ABSTRACT

In this paper, a wet-laid non-woven material consisted of fibrillated fibers is presented, which is potential to be separator for lithium-ion battery. Average pore size of the separators calendered at different line pressures is 0.180 μm and 0.372 μm, respectively. The results show that the pore size of non-woven separator could be controlled efficiently by fibrillated fiber and pressure of calender which could help to reduce the internal short circuit. The permeability and the rate of absorption of non-woven separator are higher than those of the conventional polyolefin separator.

1. Introduction

Separator is a kind of porous materials placed between positive and negative electrodes. Its function is to keep the electrodes apart to prevent electrical short circuits and at the same time allow rapid transport of ion [1]. The property of separator is one of the main factors affecting the charge and discharge process and safety of lithium-ion batteries.

The microporous polyolefin membranes (PP, PE and laminates of PP and PE) are the most widely used Li-ion battery separators, which attributes to their thin thickness, small pore size (0.03–0.1 μm) and good electrochemical stability [2]. But the heat-resistant properties of polyolefin are not good enough which limits its use in power batteries because of safety problems.

In recent years, some kinds of novel non-woven materials have been developed for lithium-ion batteries [3–10]. Compared to the polyolefin membranes, non-woven materials have more choices in the compositions and structure so that the characteristics of separator can be designed to satisfy the needs.

The main reason that prevents non-woven separator for lithium-ion battery to commercialize in large scale is that it is very difficult to control the pore size, uniformity and the thickness. For lithium-ion batteries, separator must have minimal thickness usually in range of 15–40 μm as well as small pore dimension below 1 μm for preventing short circuits. The maximum pore dimension of non-woven separator with thickness below 40 μm is commonly several decade micron meters because the diameter of the fibers in non-woven is normally larger than 5 μm. Ordinary non-woven material cannot prevent short circuits sufficiently in lithium-ion batteries. Some research has been done to solve this problem.O Hennige et al. [4] have developed a kind of separator by coating ceramic particles having an average size of 0.5–7 um such as alumina, silica, or zirconia on the surface of PET non-woven. In another patent [5], they coated PE wax on the non-woven to form a shut down layer which melts at desired temperature to insure the safety.

In JP2004031084 [7], the separator for rechargeable lithium-ion batteries is characterized by containing a macromolecule resin enveloping layer in one side of the base material.

In JP2003123728 [8], the separator was prepared by wet paper making method. The diameter of the fibers, which composed the separator is between 1 μm and 10 μm. In JP2003129393 [9], a non-woven containing microfibers with diameter of 0.05–0.5 μm and super-thin fibers with diameter of 1–10 μm was manufactured by wet papermaking method. The microfibers were prepared by fibrillating the fiber, which had the sea island structure of polyvinyl alcohol and polyacrylonitrile. In JP2006019191 [10], separator consisted of heat-resistant aramid pulp was prepared by multilayer wet-laid formation.

Wet-laid non-woven separators show a high homogeneity. This means that dendrite growth can be avoided efficiently because of uniform current density in lithium-ion batteries using these separators.

In this work, a kind of separator consisted of fibrillated fibers was prepared by wet-laid process. Because the diameter of most

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fibrils is small, the pore size can be well controlled. The structure and performance of this material were investigated as follows.

2. Experimental

2.1. Materials

Para-phenylene terephthalamide (PPTA) fibers, 5–10 mm in length, were fibrillated by refiner until the pulp's Canadian Standard Freeness was about 150 ml. Polyethylene terephthalate (PET) fiber with diameter 3–4 μm was chosen as thermo bonding fiber. PPTA pulp and PET fiber were mixed in an aqueous suspension and randomly laid down on a screen belt. The wet-laid non-woven materials were calendered at 120 °C with different pressure for thermo bonding. Separator A was calendered with linear pressure of 200 kg cm^{-1}. Separator B was calendered with linear pressure of 20 kg cm^{-1}. Comparison samples were Clegard 2340, polyolefin separator produced by Celgard and Separion®, non-woven separator coated by ceramic particles produced by Degussa.

Half cells were made to compare the differences of impedance among separator A, separator B and polyolefin separator. Raw materials of half-cell in present paper included pure Li cathode, $LiCoO_2$ anode, and mixed solution of EC and MC electrolyte and monolayer separator.

2.2. Measurements

Pore dimensions were tested using a model CFP1100A Capillary Flow Porometer (CFP) manufactured by PMI. In a typical CFP experiment, separator is filled with Porewick® and subjected to gas pressure. The pressure on the separator is increased in controlled fashion while the flow rate of gas through the separator is simultaneously monitored. Pore size information can be obtained from these two values. The pore size was calculated based on Eq. (1):

$$D = \frac{4\gamma \operatorname{Cos}\theta}{p} \tag{1}$$

where D is the diameter; γ is the surface tension; θ is the contact angle; p is the pressure difference.

The pore size of microporous separator cannot be measured using CFP1100A because its pore size is less than 50 nm which is lower than 60 nm, the limit of measurement range. So the pore size of Celgard separator was measured by B.E.T method in ASAP 2010 porosimeter.

Permeability studies were also carried out using CFP. Gurley number can be obtained by monitoring the rate at which the gas escapes through the pores of the separator.

Porosity was determined by mathematical calculation by Eq. (2):

$$\text{Porosity}\,(\%) = \frac{1-(W/\rho)}{L1 \times L2 \times t} \times 100 \tag{2}$$

where W is the weight of specimen; ρ is the density of specimen; $L1$ is the length of specimen; $L2$ is the length of specimen; t is the thickness of specimen.

Separator samples were soaked into electrolyte for 6 h at ambient temperature. Electrolyte retention value (ERV) were calculated by Eq. (3):

$$\text{ERV}\,(\%) = \frac{\text{Wd} - \text{Wt}}{\text{Wt}} \times 100 \tag{3}$$

where Wt: weight of 4 mm × 4 mm separator sample; Wd: weight of 4 mm × 4 mm separator sample after filled with electrolyte.

Rate of absorption was used to determine the wettability of separator. Separators, cut into $W15 \times L200$ mm specimens, were hanged vertically and sucked into electrolyte for 30 min at ambient temperature. Finally the heights sucked by electrolyte were measured.

Surface morphology of separator was observed by the field emission scanning electron microscope (SEM) LEO1530VP from German. Its resolution is 1 nm.

AC impedance measurements were carried out at a frequency of 1 Hz using electrochemical workstation.

3. Results and discussion

3.1. Pore dimensions

The pore size must be smaller than the particle size of the electrode components, including the electrode active materials and the conducting additives. In practical cases, separators with submicron pore sizes have been proven to be adequate to prevent the internal short circuits since the tortuous structure of the pores assists in blocking the particles from reaching the opposite electrode [3].

Table 1 shows that the pore sizes of three kinds of non-woven separators are much larger than that of polyolefin separator. Average pore sizes of separators A and B are 180 nm and 372 nm, respectively, which are smaller than the pore size of Separion®. The results show the fibrillated fibers which have diameter in range of 10 nm–1 μm could control the pore size efficiently. It is also proved that the pressure of calendering affects the pore structure of non-woven dramatically. Micron-size pores still exist in the separators A and B, because the thermo bonding fibers' diameter is 3–4 μm and there are some PPTA fiber trunks with several microns diameter. Further study is needed to make sure that this non-woven separator can prevent short circuits in batteries sufficiently.

3.2. Porosity

An appropriate porosity is necessary to hold sufficient liquid electrolyte for the ionic conductivity between the electrodes which ensure small internal resistance of batteries [6]. Typically, the commercialized lithium-ion battery separators have a porosity of 40%.

Table 1 shows that the porosity of separator A is 36%, which is lower than those of the other three kinds of separators due to the high calender linear pressure. The small porosity will result in high separator resistance in battery.

3.3. Permeability

Air permeability is expressed by the Gurley number, which is defined as the time required for a specific amount of air to pass through a specific area of the separator under a specific pressure. The separator with uniform permeability is essential for the long

Table 1
Physical properties of separators.

	A	B	Separion®	Polyolefin membrane
Type	Non-woven	Non-woven	Non-woven	Membrane
Basis weigth/g m^2	30	30	30	20
Thickness/μm	30	40	40	40
Maximum pore diameter/μm	1.23	2.39	5.99	0.159
Average pore diameter/μm	0.180	0.372	0.430	0.0295
Porosity/%	36	46	40–55	40–45
Gurley number/s $(100\,cm^3)^{-1}$	150	10.0	0.483	420

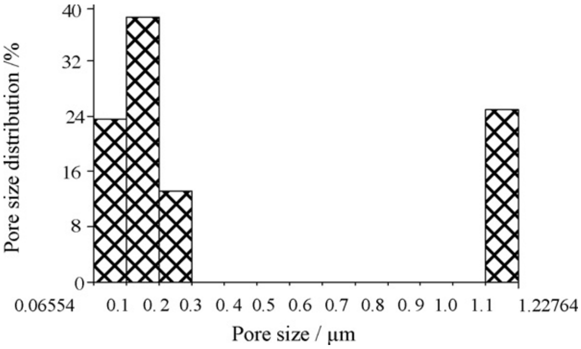

Fig. 1. Pore distribution of separator A.

cycle life of a battery. Variations in permeability will result in uneven current density distribution, which has been verified as the main reason for the formation of dendrite Li on the negative electrode [6]. Table 1 shows that the three kinds non-woven separators have much smaller Gurley number than that of polyolefin separator which could be good for batteries' charging and discharging properties.

3.4. Pore size distribution

Pore size distributions of three kinds of non-woven separators were shown in Figs. 1–3. From Fig. 1 it can be found that separator A's pore size distribution is discontinuous. Most of its pore dimensions are less than 300 nm, but about 30% of them are in the range of 1.2–1.3 μm. Most of separator B's pore dimensions are less than 1.4 μm, and about 6% of them are in the range of 2.0–2.4 μm. Fig. 3 shows that about 10% pores of Separion® have diameters higher than 4 μm.

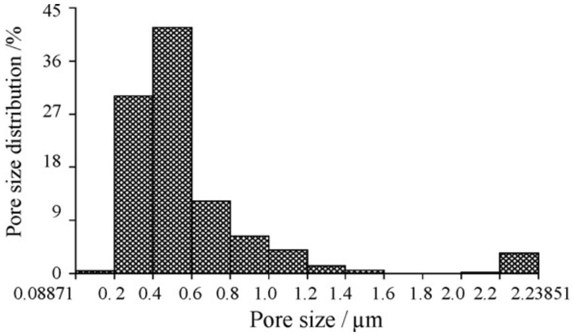

Fig. 2. Pore distribution of separator B.

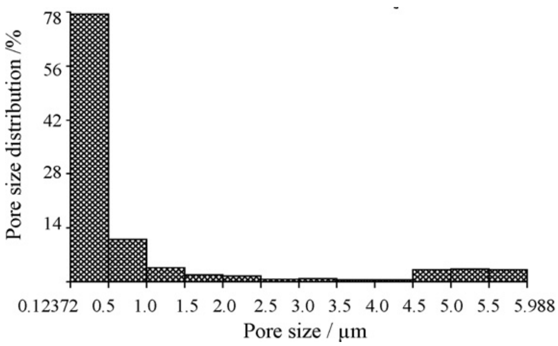

Fig. 3. Pore distribution of Separion®.

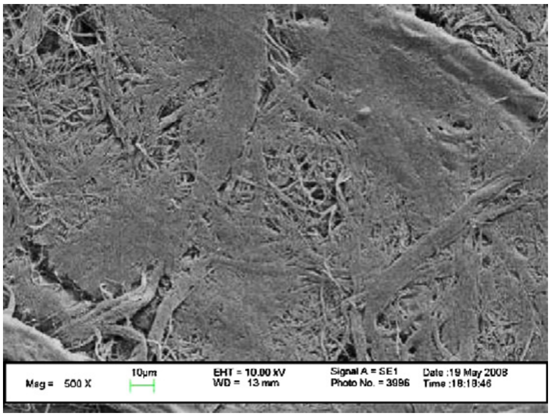

Fig. 4. SEM pictures of non-woven A (500×).

3.5. Morphology

Surface morphology of separators was observed by SEM. In Figs. 4–7 it can be found that the pores of PO separator are more uniform than those of non-woven separators. The pore structure of the separators are very different. The non-woven separators have labyrinth-like pore structure which seems to be more tortuous than that of polyolefin separator. The pore sizes are controlled by the fibrils in non-woven A and B and the pore size is controlled by the nanoparticles in Separion®. Decreasing the diameter of fibrils could improve the uniformity of non-woven separators, which helps to

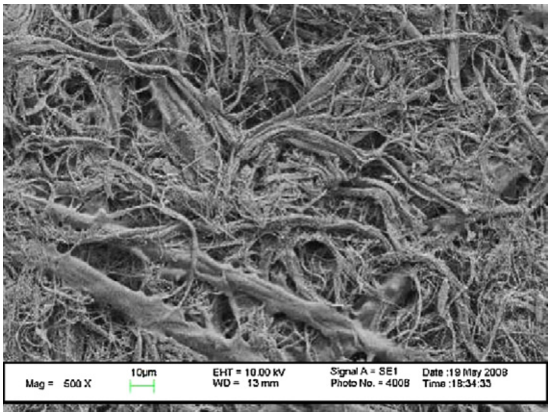

Fig. 5. SEM pictures of non-woven B (500×).

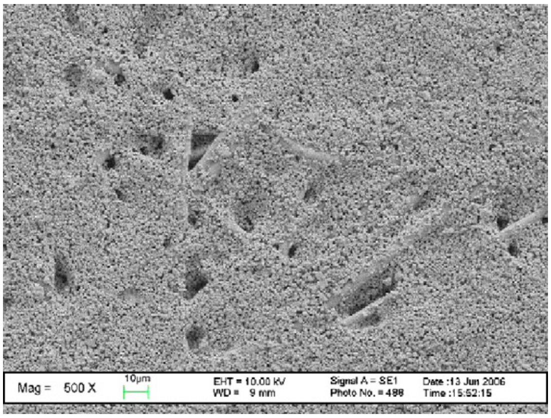

Fig. 6. The SEM picture of Degussa non-woven (500×).

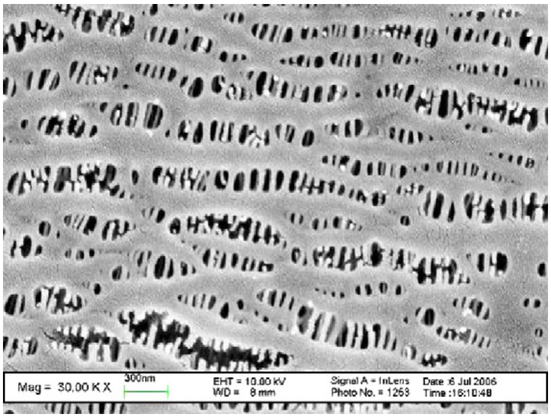

Fig. 7. The SEM picture of polyolefin film (30,000×).

Table 2
Electrolyte absorptivity and electrolyte retention property of separators.

	A	B	Separion®	Polyolefin membrane
Rate of absorption/mm (30 min)$^{-1}$	5	9	9	2
Electrolyte retention value/%	370	670	710	655

prevent the formation of dendrite Li. Further research in refining process is needed.

3.6. *Electrolyte absorptivity and electrolyte retention property*

As we know, separators should wet easily in the electrolyte and retain the electrolyte permanently which helps to fill electrolyte in battery assembly and increase cycle life of the battery [6]. Table 2 shows that separator A has the lowest rate of absorption and electrolyte retention value which attributes to its highest density and lowest porosity.

3.7. *Impedance*

The AC impedance spectroscopy of half-cells with different separators is shown in Figs. 7–9. From the impedance spectra, it can be found that semicircle's intercepts of non-woven separators A and B were 1600 Ω and 1800 Ω, respectively, which were larger than that of polyolefin separator 1200 Ω. The results indicated that the resistance of non-woven separator was larger than that of polyolefin separator (Fig. 10).

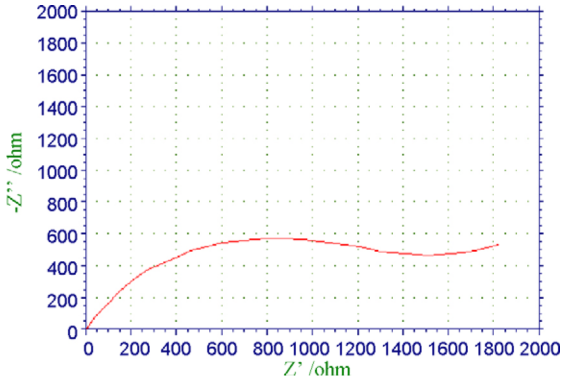

Fig. 8. AC impedance spectroscopy of non-woven separator A.

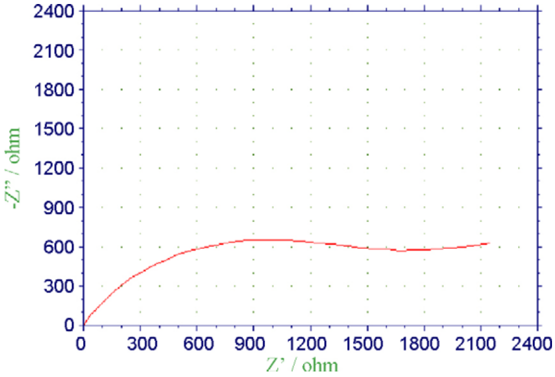

Fig. 9. AC impedance spectroscopy of non-woven.

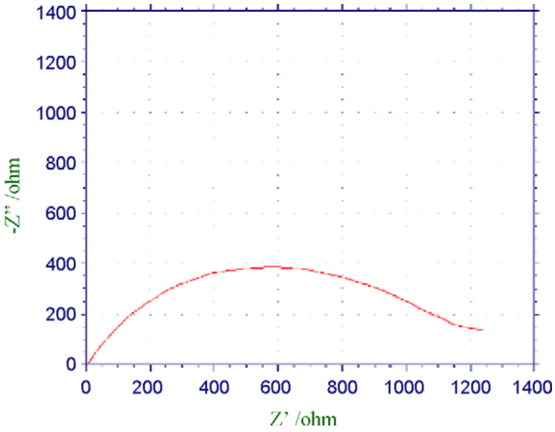

Fig. 10. AC impedance spectroscopy of polyolefin separator.

4. Conclusions

Non-woven consisted of fibrillated fibers which has average pore size below 1 μm could be used as separator for Li-ion battery. Pore size, porosity, permeability, rate of electrolyte absorption, electrolyte retention property and SEM of self-made wet-laid non-woven separators and two kinds of commercial separators were studied. Average pore sizes of separators A and B are 180 nm and 372 nm, respectively, which are larger than that of the polyolefin separator. It was proved that fibrillated fiber and pressure of calender could control the pore size efficiently. The porosity of non-woven A is 36%, which is the lower than those of the other three separators because of its high density. The Gurley numbers of non-woven separator A and separator B are 150 s/100 cm^3 and 10 s/100 cm^3, which are smaller than that of polyolefin separator 420 s/100 cm^3. From SEM observation, it can be found that non-woven separator has labyrinth-like pore structure.

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