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Wet-laid Nonwoven Preparation a Separator for MH-Ni Battery

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Wet-laid nonwoven preparation method is simple and flexible in choosing raw materials and excellent uniformity. The separator for MH-Ni battery was preparation by wet-laid nonwoven with ES (PP/PE biocomponent) fibers and PPTA (poly- p- phenylene terephthamide) fibrillated fiber. The formation index of two kinds of separator manufactured by dry-laid method respectively is 161.5 and 83.3, but that made of wet laid can get 65.4.It is indicated that the wet-laid method could improve the formation of the separator. The results showed that the PPTA fibrillated fiber can decrease the pore size and reinforce the separator. Especially after hot pressing, the separator can be good tensile strength and small pore size in the meantime. The basic performances were: maximum pore size 36.1μm, average pore size 10.8μm, air permeability 353mm/s, tensile strength 2.85KN/m.

Keywords: MH-Ni; Battery separator paper; ES fiber； PPTA fibrillated fiber; Wet-laid nonwoven

1. INTRODUCTION

Nickel-metal hydride (Ni-MH) secondary battery comprises a positive electrode containing metal nickel hydroxide a negative electrode utilizes hydrogen-absorbing alloys. This battery has a long cycle life, high specific energy, high power density, tolerance for overcharge, fast charging and discharging, and many other outstanding characteristics. According to the analysis of Europe union, among all kinds of different fuels or the use of different energy of a car, hybrid electric vehicle has the highest fuel total efficiency (WTW). The personage inside course of study is generally believed that at present MH-Ni battery is a hybrid car is most realistic choice. It is a popular believe among insider that MH-Ni battery is the most realistic choice for hybrid electric vehicle at present. MH-Ni battery still has a huge market before lithium battery solve its safety problem.

The separator is another important part in the battery except electrode and electrolyte, permeable to ionic flow but preventing electric contact of the electrodes, so as to prevent the internal short circuit of the battery. They should be very good electronic insulators and have the capability of conducting ions by intrinsic ionic conductor or by soaking electrolyte, to realize the loop current of the battery [1, 2].

MH-Ni secondary battery separator was first obtained by nylon (polyamide) fiber [3-5], such as the US patents: USpat5935884, USpat5202178, USpat5089360, USpat4127703, USpat4699858 etc. Nylon fiber structure contains amide group, which can form hydrogen bonding with water easily, so nylon fiber separator has a good hydrophilia, and alkali absorbing amount is large, but it can easy degradation in the cyclic process, bad chemical stability, and also has self-discharge phenomenon, that seriously reduced the service life of the battery [2]. Later, vinylon fiber and polyolefin fiber come to use. Vinylon fiber structure contains hydroxide radical, has the good hydrophilicity, the separator paper has good absorbing property, and has a good alkali resistance performance, but its oxidation resistance is poorer, this reduces its service life.

In recent years, preferred material for MH-Ni secondary battery separator is polyolefin fiber or composite fiber[6-9]（such as ES fiber）which is reported in US patents: USpat5824430, USpat2010/0151325 A1, USpat6723467, USpat5645956, USpat5318866, USpat55591539. These patents are somewhat similar: they use ES fiber as the main raw material. Because ES fiber membrane has better alkali resistance, oxidation resistance, electrochemical performance is more stable compared with nylon and vinylon separator. Though it has shortage in hydrophilic performance but through the surface hydrophilic treatment, we can aggrandize its hydrophilic performance. Generally, hydrophilic treatment has the following several ways [10-15]: plasma discharge treatment; ultraviolet radiation grafting acrylic acid and its derivatives monomer; fluorinated or sulfonated processing etc. The basic principle is put hydrophilic groups on fiber surface through the free radical reaction. After the choose of some certain raw materials, the producers will then choose different separator production process, from the perspective of large, first is nonwoven preparation process, though some produces choose dry-laid process, most producers use wet-laid process nonwoven fabric preparation [16, 17].

ES fiber in the market has a “sheath-core” cross-section [18]. Because of the different melting point of the two components, the skin-layer melt while the core-layer does not melt when it is in a certain heating temperature, Such as sheath-core PP/PE composite fiber, cortex PE melting point is at 132.8～135℃, core layer PP is at 165℃. In order to enhance the absorbing and retention property, permeability and control the pore size the microfiber technology is applied. For example JP2005-183161A, use PFI mill to control the diameter of the 15μm fiber under 1μm, the retention property is increased. JP2005-228544A, use double disc grinding decreased the diameter of Twaron PPTA fiber from dozens of micrometer to 0.9 micrometer.

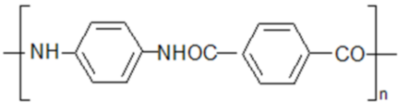


Figure 1. Aramid fiber structure diagram

PPTA-pulp[20] is one of the derivant of PPTA fiber(Kevlar) which is widely used as fillers and reinforcements, the diameter of the PPTA-pulp can reach nanoscale(100～500nm), so that we can use it to control the pore size, and it has a unique surface structure which can greatly enhance the grabbing force of the mixture.

This paper ES fiber was use as the main raw material. And PPTA fibrillated fiber was as reinforced fiber and to control the pore size at the same time. A method of making separator base material for MH-Ni battery with Wet-laid preparation was studied in this paper.

2. EXPERIMENTAL

2.1 Experimental material

(1)ES fiber 0.85dtex/f,6mm, Japan.

(2)PPTA fiber Kevlar29, standard 12μm×6mm, DuPont.

(3)Dispersing agent PEO(polyoxyethylene) molecular weight: 5million，Guangzhou.

(4)Antifoaming agents (Organic silicon class), surface tension: 22.35mN/m, Erosion point 39℃,Guangzhou.

(5)SDBS(sodium dodecyl benzene sulfonate) chemically pure，Guangzhou.

(6)Concentrated sulfuric acid, chemically pure，density: 98%，Guangzhou.

2.2 PPTA fibrillated pulp preparation

15 grams of the PPTA chopped fibers were immersed 80% to 85% concentrated sulfuric acid. The preprocessing time was about 8 minutes, then distilled water was used to wash these fibers. The pretreated fiber was refined with PFI disc refiner of 10% pulp consistency. The disc gap was 2.5mm. The revolution was 20000. [19-22]. The morphology of PPTA pulp were shown in Fig.2 and Fig. 3.

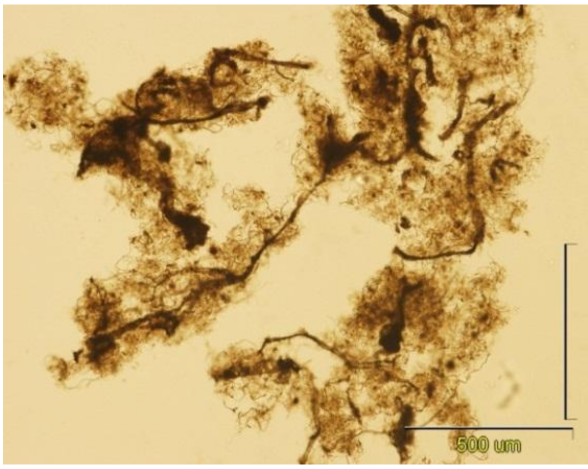


Figure 2. PPTA-pulp micro-photograph (100x)

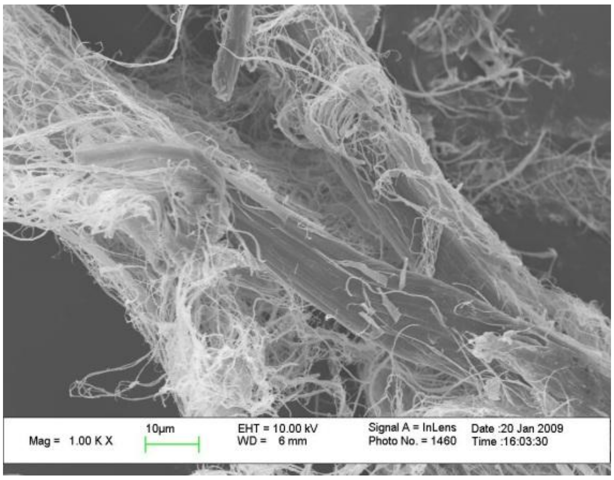


Figure 3. PPTA-pulp SEM micrograph (1.00kx)

2.3 Separator preparation

ES fiber was soaked in a solution of 60～65℃ SDBS for one hour to remove additives on the surface of fibers. Then the fibers were washed with distilled water, and then placed in a vacuum oven of 50~60℃ for drying[9]. Then the fibers were mixed with fibrillated PPTA pulp. The mixed pulp was dispersed with fruit juice machine for 5min. Then the mixed fiber was defibering with the standard slurry fluffer at 5000 rpm. Added PEO dispersant 0.5%～1% (weight based) to the mixed fiber. Laboratory handsheets (40 g/m^2) were prepared on a sheet former (TAPPI method T205 sp-02). The handsheets were dried on the plate dryer at temperature of 125℃～145℃. The hot pressing process with temperature 130℃～140℃ was used to reinforce strength and decrease thickness. The process of wet-laid method was shown in Fig. 4.

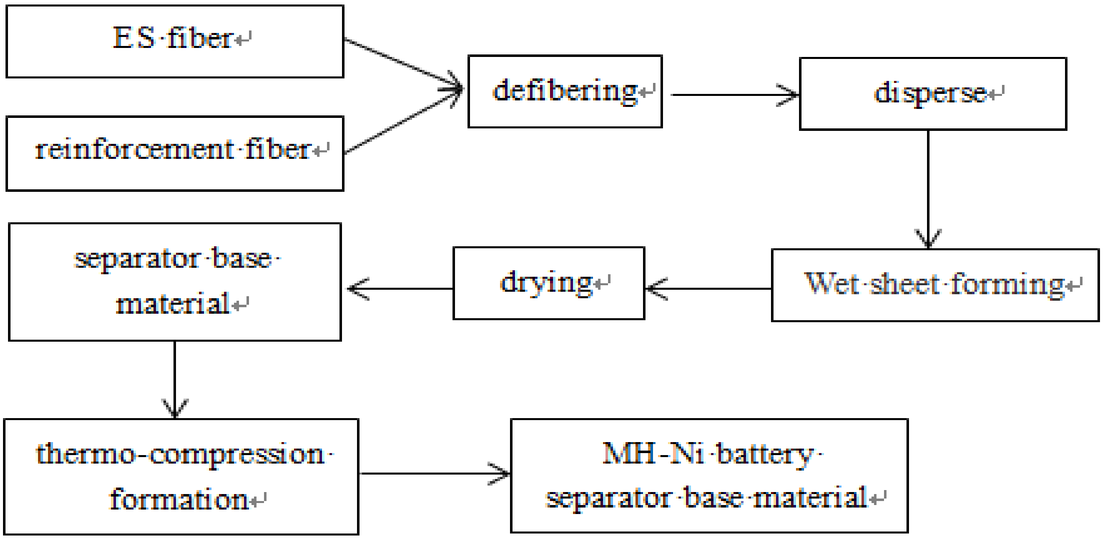


Figure 4. Technological process of separator preparation

2.4 Properties test

2.4.1 Basis weight and thickness

According to the GB451-79 standard，basis weight was tested by balance with sensitive quality: 0.1mg, thickness was tested by electric thickness tester form The Yangtze river papermaking equipment co. LTD.

2.4.2 Mean pore size and maximum pore size

Use Porous Materials, Inc.(PMI) of Capillary Flow Porometer to test.

2.4.3 Air permeability

Air permeability was tested by the computer type gas permeability tester：type:YG461E，Ningbo textile instrument factory.

2.4.4 Tensile strength and breaking elongation

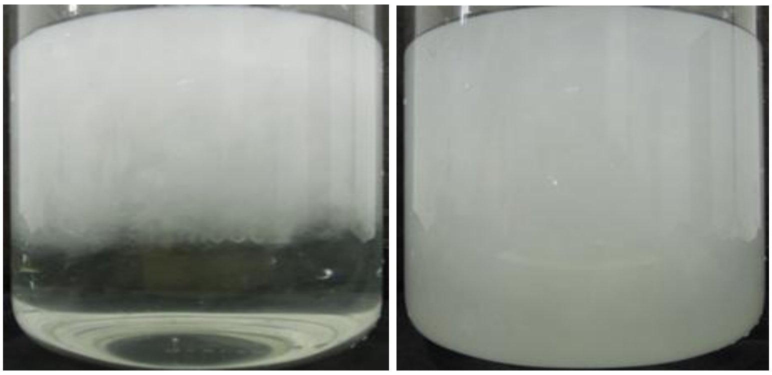
According to the GB453-89standard，tensile strength and breaking elongation was tested by LW Tensile strength tester.

3. RESULTS AND DISCUSSION

3.1 Fiber dispersion

ES fiber is organic synthetic fiber, which surface does not contain hydrophilic group. ES fiber is easier to flocculate when dispersed in water due to its strong hydrophobic nature, which causes bad paper evenness, poor interweaving and low strength. In order to use wet-laid papermaking process to produce separator with evenness, good quality and uniform performance, the fiber must be evenly dispersed in the water. After much trial and error we found that the fiber can be easily dispersed when add 0.1 %(percentage in bone dry pulp) high performance PEO (polyoxyethylene) as dispersant. Results were shown in Fig. 5. This result was in agreement with that in literature [23]. According to literatures[24,25] the mechanism of dispersion is: (1) Fiber flocculated together due to fiber interaction contact, and transmits acting force through contact point, makes the fibers emerge partial bending, these flexuous fibers forms continuous web or numerous flocculated group. (2) PEO is long chain high polymer, when added to the pulp system can increase the tensile viscosity of the fiber suspension, changed the rheological behavior of the fiber suspension, increased the fiber suspension property, so that the fiber have enough time to loose, weaken the mechanical force that holds fiber network together. And thereby reduced the flocculation, improved the forming.

ES fiber is synthetic fiber, with the transfer of fiber, it is easily to take air bubble into the water, Therefore, we need to add defoaming agent to remove bubbles, and then improve the fiber dispersion extent[26-28], after trying, organic silicone oil antifoaming agent is applicable to eliminate this kind of bubble, the dosage is 0.1% (percentage in bone dry pulp) or so.



(A) blank test (B) with dispersant and defoaming agent

Figure 5. The contrast of the fiber dispersion before and after adding additives (let stand for one minute after fiber relief)

ES fiber was easy to float due to the smaller density than water. A lot of bubbles would be born in the process of defibering. The bubbles attached to the fibers making the fiber easier to flocculate and float. From Figure 6 (A), without dispersing agents and antifoaming agents when dispersed the fiber, kept still for one minute after dispersing, and then the fiber floated and flocculated together in groups gradually. As shown in Figure 6 (B), when added 0.1% (oven dry pulp, pulp concentration 1%) PEO dispersant to the pulp and 0.1% (oven dry pulp) defoaming agent before dispersing, the fibers could be evenly dispersed. Kept still the suspension liquid of the fiber for one minute or longer (more than 5 minutes), the flocculation phenomenon were not going to happen.

3.2 Effects of PPTA-pulp dosage on formation

There were no hydrophilic groups in ES fiber structure. So the force of the wet sheet manufactured by PP/PE composite was weak. In order to improve the wet sheet strength, PPTA-pulp was added as reinforcement fiber [7, 29, 30]. The evaluation of the wet sheet strength was represented by paper injection. The results were shown in Table1. The wet sheet strength increased gradually with the increasing dosage of PPTA-pulp. When the dosage of PPTA-pulp is 7% of the total mass, the wet sheet strength is better than before, the web sticking phenomenon will not happen, we can tear off the sheet from the web easily.

Table 1. Effects of PPTA-pulp dosage on wet sheet strength

PPTA-pulp dosage	3%	5%	7%	9%
Paper injection(yes or not)	Y	N	N	N
wet sheet strength	bad（hard to tear off）	ordinary（can tear off）	good（easy to tear of f）	good（easy to tear off）

These results suggest that the best suitable dosage of PPTA-pulp is 7%. These results are similar with effects of PPTA-pulp dosage on structure and property of nylon material [31], a small amount of PPTA-pulp (< 5%) made a great influence on the tensile strength and elongation at break of the nylon material.

3.3 The best drying conditions

ES fiber is sheath-core PP/PE composite fiber, cortex PE melting point is at 132.8～135℃, core layer PP is at 165℃. In order to find the best drying temperature, the effects of temperature on the separator properties were studied with PPTA-pulp dosage of 7%.

The sheet was dried by flat hot-press machine which is different from the reported hot-air drying oven [32]. When the temperature was set at 125 ℃, the sheet surface was rough and has a hair slip phenomenon, and the strength was bad evidently. When the temperature was set at 145℃, the sheet shrinks clearly.

Table 2. Effects of different drying and temperature on the performance of the separator

Properties	130℃	135℃	140℃
Basic weight（g/m^2）	60	60	60
Thickness（mm）	346	341	340
Maximum pore size(μm)	42	42	41
Mean pore size(μm)	16	18	18
Air permeability(mm/s)	615	536	393
Tensile strength(KN/m)	2.64	2.54	2.18
Elongation (%)	10.4	10.2	8.3

The basic performance of the separator dried and solidified at the other temperature is showed in Table2. As the temperature increased, the thickness and maximum pore size of the separator did not change on the whole, the mean pore size somewhat increases, air permeability decreased dramatically. Tensile strength and elongation decreased as the temperature increased. Tensile strength and elongation reduced slowly from 130℃ to 135℃ and speeded up from 135℃ to 140℃. (Table 2). From Figure 6, it was indicated that the cortex of ES fiber has melted moderately. The contact points of ES fibers and ES fiber with PPTA-pulp formed effective spot gluing. The high temperature(⩾145℃) film phenomenon did not happen. These can explain why the tensile strength increased and the porosity was not decreased so much at the same time. Comprehensively, the separator base material can obtain the outstanding performance when set drying temperature at 135 ℃. This result is a little different from reported dry-laid ES nonwoven fabric with the best drying temperature at 140 ℃ [32]. The distinction could be caused by the difference of drying method.

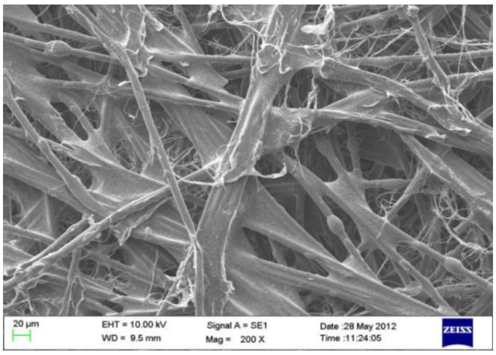


Figure 6. SEM picture(200x) of the separator (PPTA-pulp 7%) drying at 135℃

3.4 Separator property testing

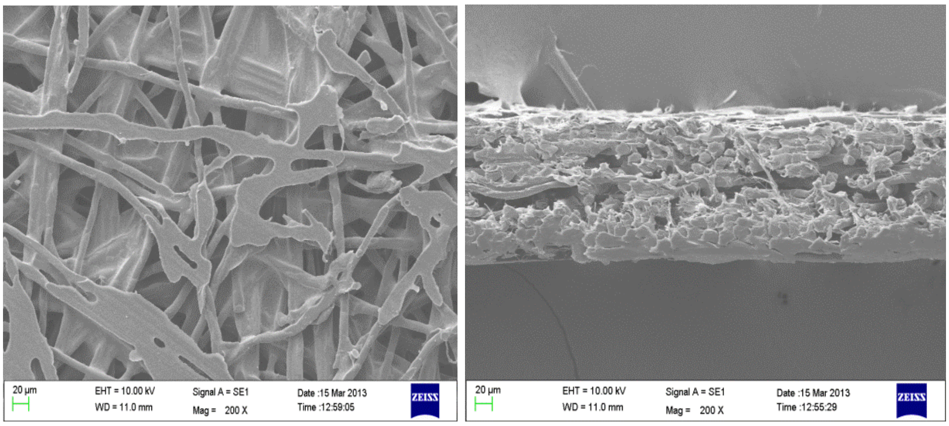
The effects of the PPTA-pulp dosage on the separator properties were shown in Table 3.

Table 3. Effects of dosage of PPTA-pulp on separator properties

Properties	3%	5%	7%	9%
Basic weight（g/m^2）	60	60	60	60
Thickness（mm）	294	315	340	327
Maximum pore size (μm)	48	42	41	45
Mean pore size (μm)	23	20	18	20
Air permeability (mm/s)	661	623	615	453
Tensile strength (KN/m)	2.19	2.23	2.31	2.69
Elongation	10.5	8.9	8.3	8.9

From Table 3, it indicated that as the PPTA-pulp dosage increased, the thickness was slightly different, but the impact was not big, air permeability decreased gradually and being faster from 7% to 9%. The maximum pore size and the mean pore size both presented the trends of first reduced and then increased, in addition there was a minimum value at the dosage of 7%. Tensile strength was increasing gradually, it was slowly from 3% to 5% and speeded up significantly from 5% to 7%. Elongation has a maximum value at the dosage of 3%, other conditions decreased a little bit, but has little changes between each other. In conclusion, we can obtain the separator basis material with excellent properties when the PPTA-pulp dosage is 7 %(Table 3). The usage of PPTA-pulp was a big difference from reported unmixed ES fiber sheet (1.2D/1.5D) [32].

3.5 Properties comparison



A(surface200x) B(section200x)

Figure 7. SEM picture of the separator (PPTA-pulp 7%) after hot pressing at 135℃

Figure 7 and Table 4 indicated that after hot pressing progress, the thickness was becoming thinner and the corresponding compactness increased. Due to the increased compactness the pore size and porosity reduced homologously. Hot pressing progress made more fibers on the surface melted and then the fibers formed a web as a whole.

Table 4. The comparison of basic properties between the wet-laid separator and dry-laid separator

Properties	Sample A	Sample B	Wet-laid separator
Basic weight （g/m^2）	58	55	60
Thickness（mm）	179	191	155
Maximum pore size (μm)	56.2	49.8	36.1
Mean pore size (μm)	20.3	23.3	10.8
Air permeability (mm/s)	396	423	353
Tensile strength (KN/m)	2.04	2.13	2.85

And the tensile strength was higher than before. According to Table 3 and Table 4, after hot pressing, we can found that the thickness was decreased by 54.3% and the tightness was increased in the meantime, the maximum pore size was decreased by 12.2%, meanwhile the mean pore size was decreased by 40.0%, the air permeability was decreased by 42.6%, the tensile strength was decreased by 23.4%.

The comparison between the wet-laid separator and the dry-laid separator is exhibited in Table4.

The wet-laid separator has a distinct advantage in strength index such as tensile strength than reported dry-laid separator [32]. The air permeability of the wet-laid separator was a little small, but still in the ideal within limits. The maximum pore size and the mean pore size are much smaller than domestic separator (sample A and B). Overall, the separator base material by wet-laid was better than those of dry-laid method.

4. CONCLUSIONS

Wet-laid nonwoven preparation method was successfully used to prepare separator base material for MH-Ni battery. The separator showed better evenness than dry-laid process. In order to enhance physical property and to control the pore size of the nonwoven separators, combining ES bicopoment fiber and PPTA fibrillated fiber were applied. The PPTA pulp can control the pore size and increase the physical properties. The separator with 7% of PPTA-pulp after hot pressing at the temperature 135℃ showed small average pore size about 10.8μm and large tensile strength about 2.85 KN/m. Compared with the samples by dry-laid nonwoven, the separator by wet-laid has a distinct advantage in mechanical strength such as tensile strength.

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