

Nickel–Metal Hydride Battery Separators Fabricated from Sulfonated Nonwovens

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ABSTRACT: In this study, we examined the sulfonation reaction of polyolefin nonwovens and their properties as battery separators. The occurrence of the sulfonation was confirmed by means of X-ray photoelectron spectroscopy, and the influences of the temperature and time of the sulfonation reaction on the properties of polyolefin nonwoven battery separators were studied. The results show that the process method for producing the separators of sulfonation was capable of realizing high water conservation properties and improving

the water absorption rate and K^+ exchange capacity while maintaining tensile strength. The nickel–metal hydride batteries with the sulfonated polyolefin as separators had a similar capacity but a lower internal impedance compared to batteries with H&V commercial separators. Furthermore, their properties were stable after 300 charge–discharge cycles. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 272–275, 2008

Key words: ESCA/XPS; graft copolymers; polyolefins

INTRODUCTION

Alkaline storage batteries have been used as power sources for portable information equipment and vehicles, such as cellular phones, notebook computers, and cars driven by electricity and hybrid energy.^{1–3} As a result, there has been an increasing demand for high-performance and, in particular, long-life alkaline storage batteries. To produce batteries with such desirable performances, it is important to ensure good liquid retention properties of the separator in the battery.

Polyolefin fibers have many advantages over other types of polymer fibers, including chemical and physical stability to alkaline electrolytes and excellent thermal resistance. On the other hand, nonwovens produced from polyolefin fibers have a three-dimensional network structure with a high porosity but small pore size. As a result, polyolefin nonwovens have been drawing attention as potential battery separators. However, most polyolefins are typically nonpolar and hydrophobic polymers, and therefore, their nonwovens have poor hydrophilicity and a low water absorption rate and liquid retaining ability. Consequently, they cannot be soaked enough in alkaline electrolyte, which limits the diffusion of electrolytes. To obtain Ni–MH batteries, nickel–metal

hydride batteries consist of a positive plate containing nickel hydroxide as its principal active material, a negative plate mainly composed of hydrogen absorbing alloys, a separator made of fine fibers, an alkaline electrolyte, a metal case and a sealing plate provided with a self-resealing safety vent. With desirable properties, polyolefin nonwovens should be modified to improve their wettability before they can be used as separators. Currently, there are generally two methods to improve the hydrophilicity of separators. One is surface treatment with wet chemicals, corona discharge, plasma,⁴ and so on, and another is the introduction of hydrophilic groups, such as carboxylic^{5,6} and sulfonic groups,^{7,8} onto the polymer through graft reactions. In this study, we improved the wettability of polyolefin nonwovens through sulfonation reactions and fabricated them into Ni–MH batteries as separators.

EXPERIMENTAL

Materials

Polyolefin [PE/PP sheath-core bicomponent fiber (ES) staple fiber] nonwovens were prepared by a calendar bonding process with a weight of 58 g/m². Sulfuric acid, hydrochloric acid, potassium hydroxide, and phenolphthalein reagent were purchased from Tianjin No. 3 Chemical Reagent Plant (Tianjin, China) and were used as received.

Preparation of the separators

Polyolefin nonwovens cut into 16 × 40 cm² pieces were immersed in fuming sulfuric acid for a desired

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period of time at a given temperature. During the sulfonation treatment, the nonwovens were slightly stretched to avoid shrinkage. The sulfonated nonwovens were then repeatedly washed with copious distilled water.

Preparation of the Ni-MH batteries

Each nickel-hydrogen storage battery was assembled with a separator, positive electrode, and negative electrode. Nickel hydroxide and a hydrogen-absorbing alloy (LaNi_5) served as the positive and negative electrode materials, respectively. Potassium hydroxide aqueous solution with a concentration of 30% was used as the electrolyte in the batteries.

Characterization

X-ray photoelectron spectroscopy (XPS) spectra were recorded with a PHI 5000C XPS spectrometer (PerkinElmer Instruments, Massachusetts, USA) with a monochromatic $\text{Al K}\alpha$ X-ray source at a 45° takeoff angle. The mechanical properties of the separators

were measured with tensile test machine (YG065, Laizhou Electron Instrument, Shan, Dong, China) at drawing speed of 200 mm/min. All measurements were performed five times for each sample to obtain an average. Air permeability was tested with a fabric densometer (YG461B, Ningbo, Textile Instrument, Zhe Jiang, China). The thickness of the separators was measured with a thickness test machine (YG141, Shuzhou Dalong Instrument, Jiang Su, China) under a pressure of $0.5 \pm 0.01\text{KPa}$. Liquid retaining ability, water absorption rate, and K^+ exchange capacity were measured with Japan VC58160 standards. Battery performance was detected by the International Electrotechnical Commission (IEC) 61951-2:2003 standard and carried out on Arbin electrochemical testing system (Texas, USA).

RESULTS AND DISCUSSION

XPS analysis of the polyolefin nonwovens

The XPS spectra of the blank and sulfonated polyolefin nonwovens samples are shown in Figure 1. As shown in Figure 1(a), there was a new peak with a

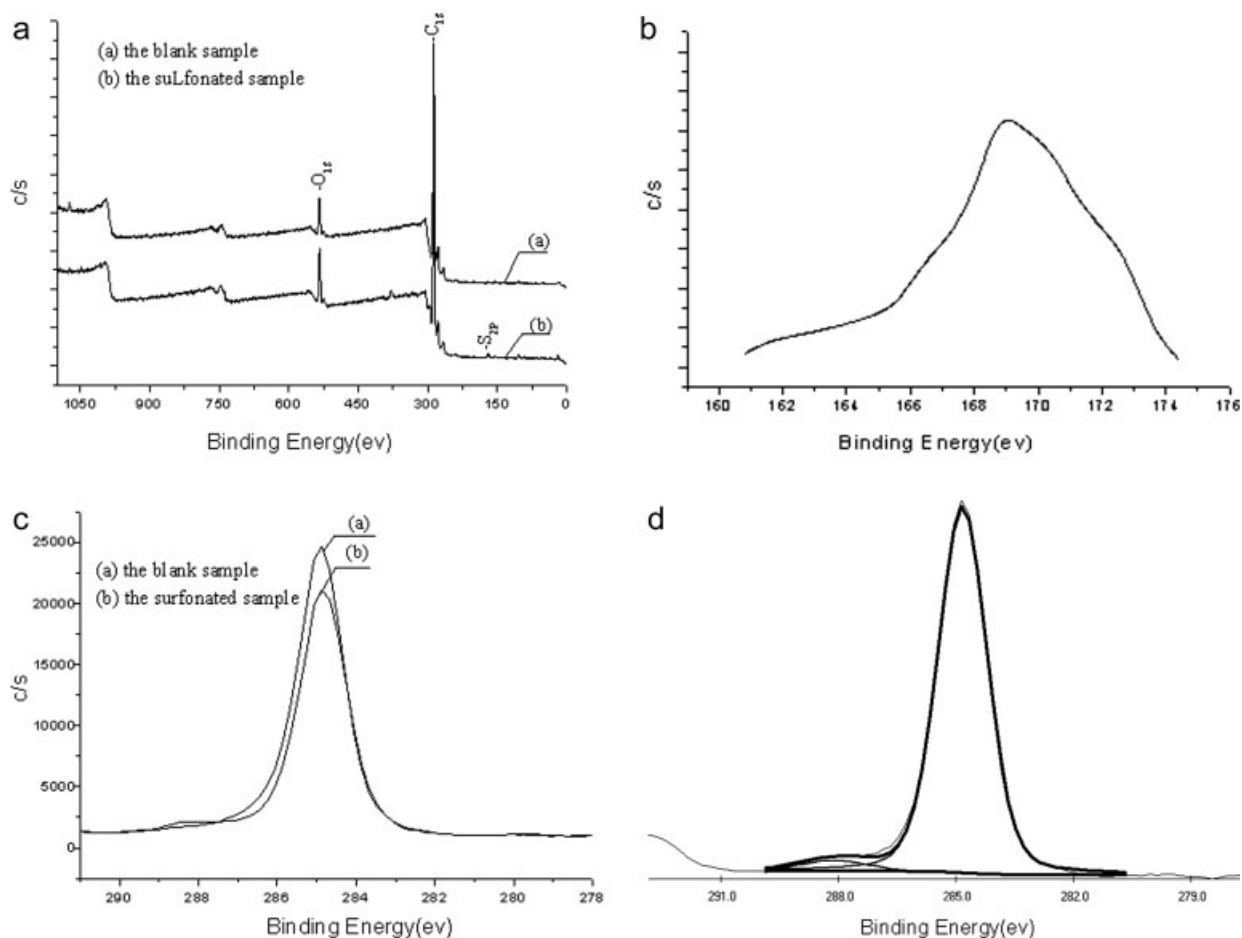


Figure 1 (a) XPS spectra of the blank and the sulfonated samples, (b) high-resolution XPS spectra of $\text{S } 2p$, (c) high-resolution spectra of $\text{C } 1s$, and (d) resolved spectra of $\text{C } 1s$ of the sulfonated sample.

TABLE I
Effect of the Reaction Temperature on the Water Adsorption Rate and K⁺ Exchange Capacity

Reaction temperature (°C)	120	125	130	135	140	143
Water adsorption rate (mm/30 min)	5.5	25.5	33.5	55.5	112	90
K ⁺ exchange capacity (mequiv/g)	0	0.011	0.032	0.049	0.155	0.115

Unit mass of the nonwovens = 58 g/m²; reaction time = 20 s.

TABLE II
Effect of the Reaction Time on the Water Adsorption Rate and K⁺ Exchange Capacity

Reaction time (s)	5	10	15	20	25	30
Water adsorption rate (mm/30 min)	28.0	78.3	90.4	125.5	116.5	110.2
K ⁺ exchange capacity (mequiv/g)	0	0.003	0.051	0.180	0.187	0.135

Unit mass of the nonwovens = 58 g/m²; reaction temperature = 140°C.

bonding energy of about 168.4 eV in the sulfonated sample, which was assigned to S_{2P} of —SO₃H. Figure 1(b) gives the high-resolution XPS spectra of S_{2P}. We can find that the oxygen amount in the two samples was different. The O_{1S} of the sulfonated sample increased to 10.7% from the initial 7.4% of the blank sample, which indicated that oxygen atoms were introduced into the polymer structure, which resulted from the sulfonation reaction. The O_{1S} peak in the blank sample was caused by exposure of the nonwovens to the atmosphere.

Figure 1(c) gives the high-resolution spectra of C_{1S}. The half-height width of the blank and sulfonated samples were 1.22 and 1.62 eV, respectively. The increasing half-height width indicated that the carbon atom in the sample had a chemical shift and might have existed in different states.

Figure 1(d) shows the resolved spectrum of carbon in the sulfonated sample, from which we can see that they were two types of carbon atoms whose bonding energies were 284.83 and 288.10 eV, respectively, corresponding to C—H or C—C and C—S, respectively. This indicated that C—S bonds originated in the ES macromolecule chains after sulfonation; in other words, —SO₃H groups formed during the sulfonation.

Effect of the reaction temperature on the water absorption rate and K⁺ exchange capacity

For high-performance batteries, it is necessary to enhance the degree of sulfonation because the impedance within the batteries will decrease with increasing liquid retaining properties, which depend on the increase of the hydrophilic properties of the separators.

The water adsorption rate and K⁺ exchange capacity reflected the degree of hydrophilicity of the sulfonated nonwovens to some extent. Table I shows the relationship of the sulfonation temperature with the water absorption rate and K⁺ exchange capacity. The water absorption rate and K⁺ exchange capacity

of the separators increased with reaction temperature ranging from 120 to 140°C because of the presence of —SO₃H groups but declined when the temperature was above 140°C. The possible reason was that the higher temperature accelerated the sulfonation, and more —SO₃H groups were grafted onto the samples; however, if the temperature was too high, for example, over 140°C, the nonwoven samples were partially carbonized in the presence of fuming sulfuric acid, and the —SO₃H groups could not be easily grafted. As shown in Table I, 140°C was the optimal reaction temperature.

Effect of the reaction time on the water absorption rate and K⁺ exchange capacity

Reaction time is another important parameter in sulfonation reactions. Table II shows the influence of reaction time on the water adsorption rate and K⁺ exchange capacity at 140°C. It was evident that a better separator was achieved when the reaction time was set to around 20 s. This was also caused by the potential carbonization occurring at higher temperatures or longer times.

TABLE III
Comparison of the Properties of the Blank Sample and the Sulfonated Separator

	Test item	
	Blank sample	Sulfonated separator
Unit mass (g/m ²)	58	63
Thickness (μm)	163	175 ± 25
Air permeability (L m ⁻² ·s ⁻¹)	548	Over 550
Tensile strength (N/50 mm)	187	Over 200
Water absorption rate (mm/30 min)	2	Over 80
Liquid retaining ability (%)	0	Over 250
K ⁺ exchange capacity (mequiv/g)	0	0.15–0.18

Sulfonation temperature = 140°C; sulfonation time = 20 s.

TABLE IV
Test Results of the Battery Properties

Sample	Weight of the anode (g)	Thickness of the anode (mm)	Thickness of the separator (mm)	Rolling pressure (atm)	Capability (mAh)	Internal impedance (mΩ)
1	8.69	0.74	0.20	3.0	1842	21.80
2	8.65	0.74	0.20	3.0	1825	21.30
3	8.64	0.745	0.17	3.0	1818	22.20
4	8.68	0.74	0.16	3.0	1830	24.50
5	8.63	0.74	0.16	2.5	1826	24.60
6	8.65	0.745	0.17	2.5	1806	23.21
7	8.66	0.74	0.15		1850	23.00
8	8.85	0.75	0.15		1812	26.84

The designed capability was 1800 mAh, the cathode plate was $120 \times 43.5 \times 0.3 \text{ mm}^3$, the weight of the battery was 9.7 g, and the amount of electrolyte was 2.50 g.

Properties of the separators

The properties of the separators after sulfonation compared to the blank sample are listed in Table III. The unit mass, thickness, mechanical properties, and air permeability of the separators were almost the same as those of the original nonwovens, whereas the water absorption rate, liquid retaining ability, and K^+ exchange capacity were remarkably improved, which could make them competent for Ni-MH battery separators, as shown in Table III.

Properties of the battery

We compared the properties of the batteries using our sulfonated nonwoven as separators (samples 1–6) and ones with H&V commercial separators (samples 7 and 8), and the results are listed in Table IV. All of the batteries made of our sulfonated separators achieved a capacity of 1800 mAh, which was close to that of the batteries with H&V separators, and their average value of internal impedance of about 22.71 mΩ were lower than that of batteries with H&V separators.

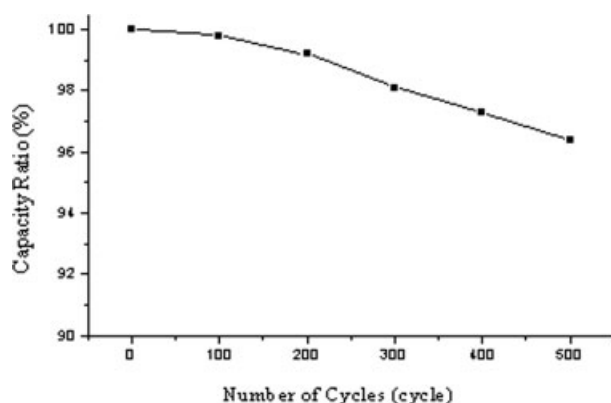


Figure 2 Dependence of the number of cycles on the capacity ratio.

Moreover, the test results of overcharging and cycle life found that the batteries with the sulfonated nonwovens as separators were just slightly hot without electrolyte leakage after high electric current charging, and the appearance and tensile strength of the separators remained stable. After 300 charge–discharge cycles, the capacity of the batteries did not decrease apparently, just about 4% after 500 cycles, as shown in Figure 2.

CONCLUSIONS

1. The method of sulfonation to improve polyolefin hydrophilicity was feasible, and the optimal sulfonation temperature and time of the process were about 140°C and 20 s, respectively.
2. Sulfonic acid groups, which increased the water conservation properties, water absorption rate, and K^+ exchange capacity of the separators, were confirmed by means of XPS to have been grafted onto the ES fibers.
3. The Ni/MH batteries with the sulfonated polyolefin separators had a capacity and internal impedance of about 1800 mAh and 22.71 mΩ, respectively, and were also stable after 300 charge–discharge cycles.

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