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ARTICLE TYPE

Preparation and properties of composite separator with asymmetric structure for alkaline batteries

Wei Xiao*, Lina Zhao, Yaqun Gong, Hong Wang, Jianguo Liu and Chuanwei Yan

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A novel asymmetric separator with high electrolyte wettability and chemical stability was developed for alkaline batteries. This separator was fabricated from an electrolyte-absorbing layer (cellulose nonwoven, CN) and an alkali-resistant layer (PVdF-ZrO₂ matrix), which were integrated together by point-bonded method using polyvinyl alcohol fibers as binder. The characteristic properties of the composite separator have been studied by structural characterization, contact angle testing, weight and dimensional stabilities, electrolyte-absorbing rate, and electrochemical behavior. Results showed that the composite separator had uniform surface morphology and highly gradient three-dimensional porous structure, which led to low electrolyte contact angle of 35° and area electrical resistance of 0.08Ω·cm². Moreover, it showed low weight reduction rate of 7.5% and area shrinkage rate of 2.0% in 40 wt% KOH solution at 333 K for 120 h. Due to the electrolyte-philic macroporous layer, the composite separator exhibited high electrolyte-absorbing rate, which was higher than 55 mm for 5 min. These characteristics endowed the composite separator with excellent electrochemical performances, including short activation time and long dry/wet storage life. It is demonstrated that the composite separator exhibits as a good candidate for alkaline batteries, especially for self-activated zinc-silver oxide battery.

Introduction

Alkaline battery systems have been under-represented in current scientific literatures, but their market potential is high which can supply energy to a wide range of devices from small portable music players to substantial power tools and electric vehicles.¹ Different from other alkaline batteries, zinc-silver oxide system already has a well-documented history of safe and reliable service for a broad variety of applications. Many power system designers still employ zinc-silver oxide to fulfill many critical applications where low weight and/or volume and high specific energy are required.²⁻⁴

In the elementary construction, a battery comprises two plates (anode and cathode), a separator and an electrolyte. Separators play a key role in all batteries. The requirements for separators differ between the various battery technologies. But in every case, some basic requirements must be fulfilled such as the followings: (1) preventing the internal short circuit between the positive and negative electrodes; (2) retaining high electrolyte absorbing property; (3) taking less occupancy and (4) having the durability that prevents shrinkage and degradation in battery environment.⁵ In zinc-silver oxide batteries any one of monovalent and divalent silver oxides has a strong oxidizing power and tends to be dissolved partly in the form of colloidal silver ions, resulting in the separator to be deteriorated accompanying precipitation and penetration of metallic silver even when used in multiple layers.⁶ Moreover, the electrolyte

absorbing performance of the separator is much more important than other properties for zinc-silver oxide reserve batteries, which is related to the activation rate and has been and continue to be the focus of concerted efforts in many battery groups, both in industry and academia.⁴

As the commonly used main separator in zinc-silver oxide batteries, cellulose semi-permeable separator can prevent migrating silver ions from reaching the anode by reducing them to insoluble silver metal. But at the same time the separator will be oxidized and destroyed, making it less effective for long-life batteries.⁷ So the life of zinc-silver oxide battery is very limited, even with the best separators in multiple layers. In addition, the electrolyte absorbing and retaining properties of cellulose separator are relatively poor, which result in much longer activation time for self-activated zinc-silver oxide batteries. On the contrary, some fiber-structured separators exhibit better electrolyte absorbing and retaining properties. However, they can hardly provide sufficient protection from interplate short circuit of the battery for several hours due to low alkali resistance and relatively large pore size of the separators.⁵ The separator has been the major obstacle for producing high quality zinc-silver oxide batteries with cycle life, calendar life and performances comparable to other alkaline batteries.⁶

In order to improve the comprehensive properties of separators used in zinc-silver oxide battery, a variety of other separators have been proposed and developed to replace or complement the cellulose separator, such as polyvinyl alcohol (PVA) films,⁸ polyethylene films,^{9, 10} microporous polypropylene separators,¹¹

inorganic separators and composite separators.¹²⁻¹⁵ Adamson et al prepared a composite separator which comprised a polymer, a ZrO_2 powder, and a conductivity enhancer. This separator showed excellent alkali resistance.¹² Maurya et al investigated the thermal and chemical stability of a pore-filled PE separator under alkaline environment. Results showed the triethylamine-filled PE composite separator exhibited a higher oxidative stability.¹³ Recently, Wang et al fabricated a high performance alkaline battery with PVA-polyacrylic acid copolymer separator. This composite membrane not only was an effective separator but also served as a means of electrolyte storage, ensuring the flexibility of the battery.¹⁴ However, it is difficult to satisfy simultaneously both of the aforementioned requests of high physicochemical stabilities and excellent electrolyte absorbing/retaining properties, which are key parameters for activation rate and discharge time for self-activated alkaline batteries.

Inspired by the above discussions, a new composite separator with asymmetric structure was designed to satisfy the requirements of self-activated zinc-silver oxide battery. Different from the conventional separators, this composite separator is fabricated by combining a macroporous layer and a microporous layer, which can provide excellent electrolyte wettability and high physicochemical stabilities to the separator, respectively. Thus, a fine balance between the above conflicting requirements can be maintained.

Experimental

Preparation of the microporous layer

A coating solution was prepared by mixing ZrO_2 particles (average particle size 40 nm, HiCharm, Ltd., China) and PVdF polymer (Solef 21216, Belgium) in acetone, wherein the ZrO_2 : PVdF composition ratio was fixed at 80/20 (wt %/wt %). To obtain a homogeneous suspension, intensive ultrasonic treatment was employed to disperse the inorganic particles uniformly. Then dip-coating method was used to coat the PVdF- ZrO_2 suspension on PVA nonwoven (thickness = 20 μm , Wanbang special material Co., Ltd, China), followed by room temperature drying for 4 h and vacuum drying at 333 K for 2 h. Fig. 1 shows the schematic depiction of the preparation process. After that, the microporous layer was immersed in 15wt % KOH solution (ethanol/water = 50 wt %/50 wt %) at 323 K for 3 h. Finally, the alkali-treated microporous layer with the colour changing from white to brown was washed with deionized water repeatedly, and then it was dried at 373 K for 8 h.

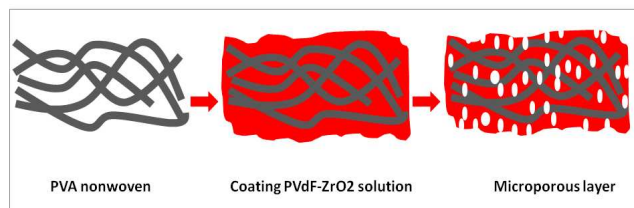


Fig. 1 Schematic illustrating the preparation process of the microporous layer

Fabrication of the composite separator

In this novel separator, the properties of electrolyte-absorbing and alkali resistance were provided by the macroporous layer

(cellulose nonwoven) and the microporous layer (PVdF- ZrO_2 mixed matrix membrane), respectively. An artful method to combine the two layers without affecting their functions was designed. PVA fibers (HWS-9, Hope Way Chemical Co., Ltd, China) with fineness of 1.0 dtex (15 μm in diameter) and length of 3 mm as binder were dispersed in deionized water (5wt %) at 353K for 0.5 h. Then the fiber-shaped binders were coated on one side of the cellulose nonwoven (conventional paper-based separator, Nippon Paper Papyrus Co., Ltd, Japan) followed by overlapping the microporous layer on the nonwoven. Finally, the overlaid layers were pressed with rollers of a drier at 393 K and a composite separator with asymmetric structure was obtained. A scheme for the combining process was shown in Fig. 2.

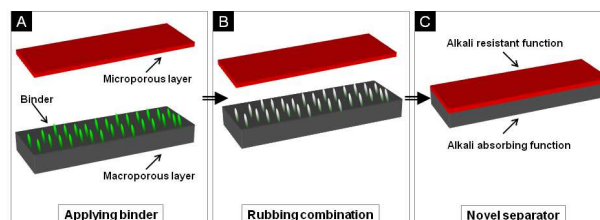


Fig. 2 Schematic illustrating the combination process of the separator

Characterization of the composite separator

Morphologies of the functional layers and the separator were examined using field emission scanning electron-microscopy (FE-SEM, S-4300, Hitachi). The weight reduction rate and area shrinkage rate were evaluated according to the reference.¹¹ The areas of the previous sample and immersed sample in 40wt % KOH aqueous solution were marked as A1 and A2, respectively. The area shrinkage rate was calculated by the formula of $(A1 - A2)/A1 \times 100$. When the areas were replaced by weight of the previous sample and dried sample (immersed in 40wt % KOH electrolyte), the weight reduction rate can be obtained by the above formula. The electrolyte impregnate ratio of the separator was tested,¹⁶ where samples (50 mm×50 mm) were immersed in 40% KOH aqueous solution (298 K) for 4 h. After draining for 30 s spontaneously, the samples were weighed. The weight of the solution retained in the sample was divided by the weight of the sample before immersing to determine a quantity of the absorbed solution. To measure the liquid aspiration samples (a height of 150 mm and a Width of 25 mm) were immersed in 40% KOH aqueous solution (298 K), and the time that the solution required to reach each height was determined. The adhesion strength between microporous layer and macroporous layer was tested at room temperature with a universal testing machine (Zwick Z100). Finally, the composite separator, conventional nonwoven separator and cellulose semi-permeable separator were assembled in flat type zinc-silver oxide batteries to evaluate their electrochemical properties.

Results and discussion

Fig. 3 shows the schematic illustrations of the separators with different structures. Different from the paper-based separator and semi-permeable separator (Fig. 3 A, B), the novel separator in present study exhibits asymmetric cross-section structure as shown in Fig. 3 (C), which is formed from a microporous layer and a macroporous layer. The microporous layer is composed of

PVdF polymer and ZrO_2 fillers which can improve the separator resistance to attack by the alkaline electrolyte and by the active materials in electrodes. Moreover, the tunable microstructure was beneficial for the prevention of colloidal silver migration and dendrites formation, resulting in prolonging the lifetime of zinc-silver oxide battery. Cellulose nonwoven as an electrolyte absorbing layer can improve the wettability of the separator with its better affinity to the alkaline electrolyte, resulting in shortening the activation time of self-activated zinc-silver oxide battery. In addition, instead of the commonly used binders in liquid form, the above two functional layers were integrated by partly dissolved PVA fibers. The two layers were bonded together at the contact points only by this fiber-shaped binder and the structures and properties of them can be reserved.

Hence, it is reasonably speculated that for the present composite separator, after being filled with alkaline electrolyte, the microporous layer is more effective in improving battery lifetime and the macroporous layer is more effective in facilitating electrolyte absorption in comparison with conventional separators.

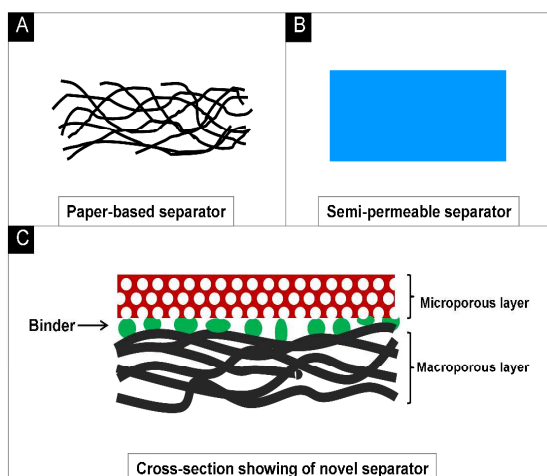


Fig. 3 Schematic illustrations of the separators with different structures

Morphological characteristics of the microporous layer, macroporous layer and the composite separator were shown in Fig. 4. It is obvious that the PVdF- ZrO_2 microporous layer has smooth and uniform surface morphology as well as a large number of nano-sized pores (Fig. 4 A). The ZrO_2 nano-particles adhered by PVdF are closely packed, which allows for the evolution of highly-percolated interstitial voids including gaps between the inorganic particles and pores from the phase inversion of PVdF during the evaporation of the solvent. The cellulose nonwoven exhibits rough surface and excessively large-sized pores which are arbitrarily distributed between the thick fibers as shown in Fig. 4 (B). After integration of the two layers with PVA-based binder, upper surface of the composite separator shows almost the same surface morphology as that of the microporous layer, indicating that the structure of the PVdF- ZrO_2 layer was not damaged during the integration process (Fig. 4 C). And the average pore diameter of the composite separator was about 240 nm.

The composite separator was further characterized by observing the cross-sectional morphology. Fig. 4 (D) confirms that consistent with the schematic structure as shown in Fig. 3 (C),

the composite separator has asymmetric structure as marked with red lines. The PVdF- ZrO_2 layer and the cellulose nonwoven layer are tightly packed together without obvious interlayer formed by partly dissolved PVA fibers. The adhesion strength between the two layers was about 13.5 MPa, which is larger enough to endow the composite separator with much more outstanding performances compared with the conventional separators.⁴

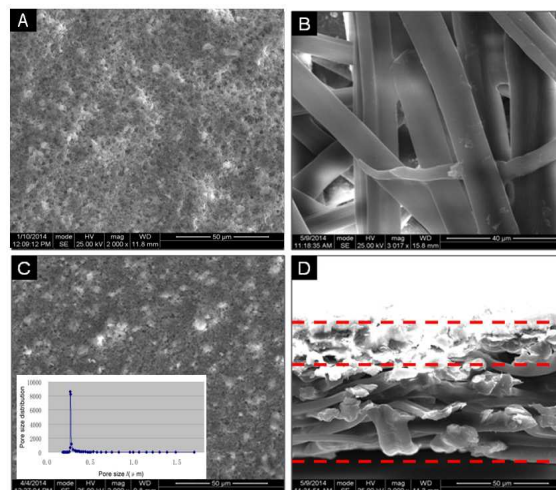


Fig. 4 SEM images of the microporous layer (A), macroporous layer (B), composite separator (C, upper surface; D, cross-section). The pore size distribution of the separator is inserted

The electrolyte wettability of the composite separator was compared with that of the untreated microporous layer by simultaneously dropping a drop of electrolyte onto the surface of each separator and observing the spread of the electrolyte as well as measuring the contact angle. As shown in Fig. 5, it is obvious that the electrolyte remains as a bead on the untreated microporous layer with contact angle of 90°, showing intensive hydrophobicity and great transporting resistance for alkaline electrolyte through the layer as well as long activation time for self-activated batteries.

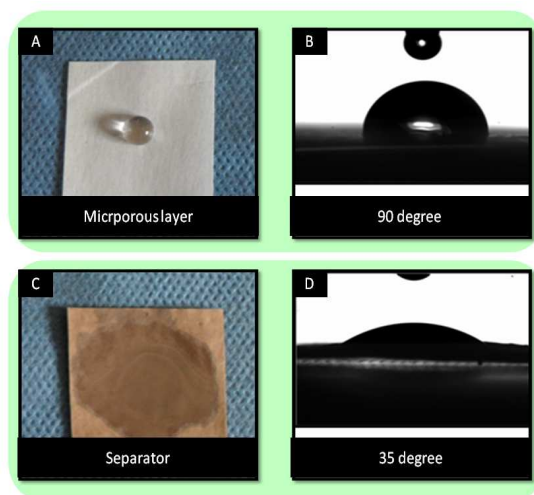


Fig. 5 Electrolyte wettability of the untreated microporous layer and the composite separator

However, after alkaline treatment and integration of the two

functional layers, the composite separator is quickly wetted with the alkaline electrolyte. The contact angle of the composite separator is only about 35° much lower than that of the untreated microporous layer. In addition, this separator affords large electrolyte uptake of 400%. It means that alkaline treatment is an effective method to enhance the affinity between the composite separator and the electrolyte by improved hydrophilicity and more amorphous structure of the polymer.¹⁷ So for this novel composite separator fast and uniform wetting of the alkaline electrolyte over the entire separator can be realized. Table 1 lists some basic properties of different separators.

Table 1. Properties of different separators

Samples	Characteristics	Thickness / (μm)	Average pore size (μm)	Electrical resistance / (Ω·cm ²)	Electrolyte uptake (%)	Electrolyte absorbing rate (s)
Microporous layer	Microporous	25	0.25	0.05	310	---
Macroporous layer	Fiber-structured	75	>20	0.02	450	60
Composite separator	Asymmetric Porous	95	0.24	0.08	400	60
[11]	Semi-permeable	40	---	0.106	240	---
[13]	Fiber-structured	131	>5	---	490	112

The separator used in alkaline batteries should lay flat and not bow or skew when it is laid out and soaked with electrolyte. So it is required to have good mechanical and chemical stabilities in the presence of strong alkaline electrolytes, such as high dimensional stability and low deterioration rate.

The alkali resistance of the microporous layer, macroporous layer and the composite separator were compared by measuring the weight reduction rate and area shrinkage rate, where they were immersed in 40wt % KOH solution at 333K for 6h. Fig. 6 shows that the weight reduction rate and area shrinkage rate of the macroporous layer are up to 4.5% and 10% respectively due to its loose fabric structure, which are much higher than those of the microporous layer. The microporous layer composed of PVdF polymer and nano-sized ZrO₂ fillers presents higher chemical and mechanical stabilities in strong alkaline electrolyte with both of weight reduction rate and area shrinkage rate lower than 1%. So the composite separator exhibits compromised weight reduction rate of 2% and area shrinkage rate of 1.8%, which are about four times lower than that of most semi-permeable separators used in alkaline batteries.¹⁸⁻¹⁹

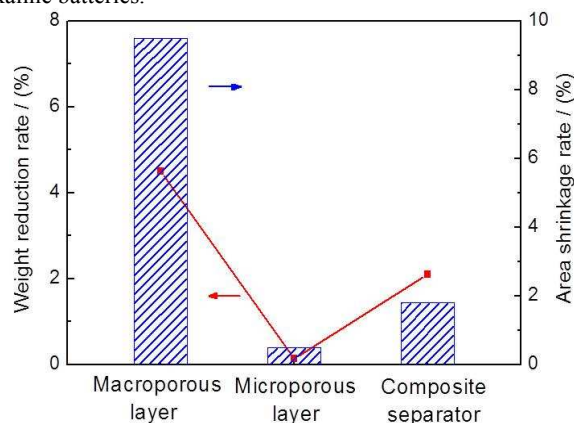


Fig. 6 Alkali resistance of different layers in 40wt % KOH solution at 333K for 6h

Fig. 7 demonstrates the alkali resistance of the composite separator in electrolyte as a function of immersion time at 333K. Consistent with the above discussion, the composite separator is difficult to be alkali deformed over a long time, which presents strong stabilities in alkaline electrolyte. Even for 120 h, the weight and area reserve percents are still as high as 92.5% and 97% confirming the superior chemical and mechanical stabilities of the novel separator, as compared to other separators with weight and area changes over 15%.¹⁶ This preferable alkali resistance provides high performance to the battery, such as preventing internal short circuit of the alkaline batteries.²⁰

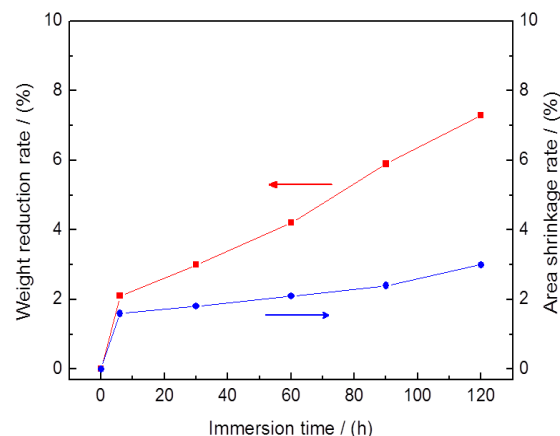


Fig. 7 Alkali resistance of the composite separator as a function of immersion time in 40wt% KOH solution at 333K

In addition to the mechanical and chemical stabilities, the electrolyte absorbing rate of the separator is another key property for self-activated batteries, which can affect the activation time of these batteries. This composite separator was examined by evaluating the electrolyte immersion-height as shown in Fig. 8.

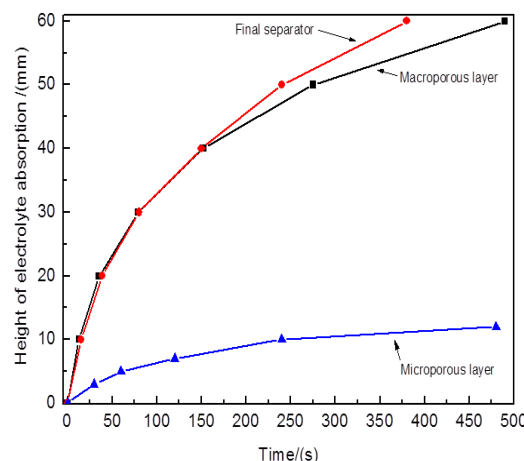


Fig. 8 Electrolyte-absorbing rate in 40wt% KOH solution at 298K

It can be seen that the composite separator presents similar electrolyte absorbing rate to that of the macroporous layer, which indicates that the combination process did not destroy the structures and properties of cellulose nonwoven. In other words, the partly dissolved PVA fibers as binder only adhere the two

functional layers without penetrating into their pores. Moreover, after three minutes the composite separator shows higher electrolyte absorbing rate due to the facile capillary intrusion of the electrolyte into the pores of the asymmetric separator. After five minutes, the electrolyte absorbing height of the composite separator is over 55 mm higher than those of the microporous layer (10 mm) and the macroporous layer (50 mm) as well as most of the conventional separators.⁴ This improvement in electrolyte absorbing rate of the present separator is attributed to its relatively electrolyte-philic constituents and the highly gradient porous structure, which may facilitate capillary intrusion of the electrolyte into the separator.²¹

Based on the above investigations, zinc-silver oxide batteries with different separators were assembled to determine the electrochemical properties of the composite separator as the procedures of the reference¹⁷ and the configuration of the battery is shown in Fig. 9.

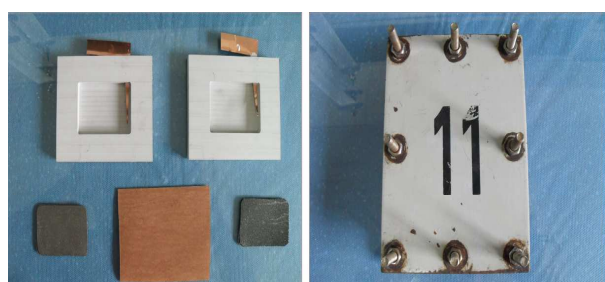


Fig. 9 Configuration of the test zinc-silver oxide battery

Open circuit voltage (OCV) drop can reflect the self-discharge behavior of batteries and predict the risk of internal short circuit in a certain extent. In this study, the OCV test began at the stage of 100% state of charge and stopped when the OCV value was lower than 1.0V. Fig. 10 shows that there are remarkable differences in OCV profiles between the batteries assembled from the composite separator, cellulose nonwoven (commercial paper-based separator) and cellulose acetate membrane (commercial semi-permeable separator). The OCV value of the battery with cellulose nonwoven marginally declines with storage time prolonging at initial phase and then drops rapidly. After 1.5 h storage time, the OCV value drops to 1.0 V due to its high self-discharge rate which can be explained by the poor structures of this type separator (Fig. 4 B). It indicates that the commonly used fiber-structured separators cannot afford the requirement of zinc-silver oxide reserve batteries with sufficient discharge time.

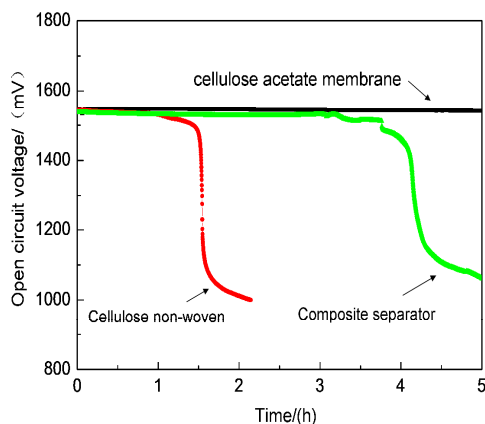


Fig. 10 OCV profiles of zinc-silver oxide batteries assembled from different separators

The battery assembled from the composite separator presents more than 4 h storage life, which is two times longer than that of the battery with nonwoven separator. This can be attributed to the limitation of colloidal silver ion transportation by the microporous layer and the excellent chemical stabilities of the composite separator. Due to the semi-permeable feature of cellulose acetate membrane, the battery assembled from which shows almost no change in OCV value during the test period. However, this type separator is only suitable for rechargeable zinc-silver oxide battery and is incompetent for self-activated zinc-silver oxide batteries because of its low electrolyte absorbing rate and poor electrolyte wettability.⁵

To further investigate the above differences in OCV profiles, the separators assembled in the tested batteries were characterized by SEM and EDX measurements as shown in Fig. 11. It is observed that there are no obvious changes in morphologies of these separators before and after the OCV test. However, the EDX results (Fig. 11 D) indicate that after OCV test the Ag content on the surface (facing the cathode) of each separator is different. The Ag atomic percent on upper surface of the composite separator is only about 0.06% due to the oxidation resistance of the PVdF-ZrO₂ layer, which is about four times lower than that presents on semi-permeable separator. Though the chemical stability of cellulose nonwoven is relatively high, the large pores cannot prevent the migration of colloidal silver ion from cathode to anode and its poor structure may also cause internal short circuit of the battery with single layer separator. All these would lead to intensive self-discharge, resulting in short storage life for zinc-silver oxide battery.

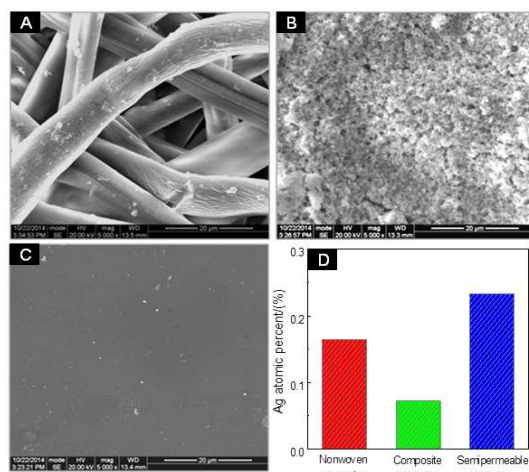


Fig. 11 SEM and EDX images of three types of separators after OCV test

This OCV behavior further confirms the present composite separator with asymmetric structure exhibits higher chemical resistance to the corrosive zinc-silver oxide battery environment compared with other separators.

To evaluate the effects of structural differences of these separators on the discharge performance of zinc-silver oxide batteries, the test batteries were assembled from the same cathode, anode and electrolyte except for the separators. The discharge test

was carried out at 0.25 C-rate at room temperature. Fig. 12 shows the comparison results of the primary zinc-silver oxide batteries with three types of separators, such as the cellulose nonwoven, cellulose acetate membrane and the composite separator. It is obvious that the battery with cellulose nonwoven shows discharge capacity of 3.5 mAh about 30% lower than those of the batteries with composite separator and semi-permeable separator. As discussed in Fig. 11, during the discharge process the poor structures of cellulose nonwoven may lead to intensive self-discharge, resulting in low discharge capacity.²² Though the pore size of the composite separator is larger than that of the semi-permeable separator, for this type battery the function provided by the microporous layer is quite enough to maintain the normal discharge process, presenting almost the same discharge capacity as that of the cellulose acetate membrane.

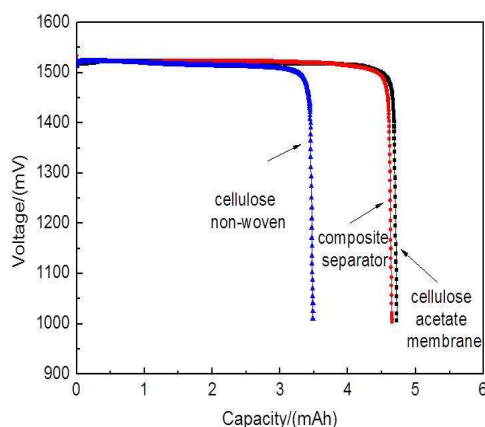


Fig. 12 Discharge performance of zinc-silver oxide batteries assembled from different separators

Conclusions

This study reports on the preparation of composite separator for primary zinc-silver oxide battery. The composite separator comprises an alkali resistance layer with PVdF/ZrO₂-based microporous structure and a macroporous layer with nonwoven structure, which are integrated together by a point-bonded method. The microporous layer provides the composite separator superior alkali resistance, oxidation resistance and high mechanical stability compared with the conventional separators. It shows very low weight reduction rate and area shrinkage rate of 7.5% and 3% respectively after immersion in 40wt% KOH aqueous solution at 333 K for 120 h. The macroporous layer trapping more electrolytes ensures the composite separator low electrical resistance and excellent wettability with electrolyte-adsorbing height higher than 55 mm for 5 min. The discharge capacity test further confirms the battery assembled from the composite separator exhibits preferable comprehensive performance compared with other separators for primary zinc-silver oxide battery. Combining the features of good electrolyte wettability and high stabilities, the composite separator is expected to be attractive for alkaline battery systems. Of course, further systematical evaluations of the composite separator are needed in order to optimize its performances.

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- Laboratory for Corrosion and Protection, Institute of Metal Research, Chinese Academy of Sciences, China.
Tel.: +86 24 2399 8320; fax: +86 24 2388 0201.
E-mail: wxiao@imr.ac.cn
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