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The polyvinyl alcohol/phosphomolybdic acid membrane for Zinc bromine redox flow battery

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ABSTRACT

A novel membrane of the flow zinc-bromine battery is designed and fabricated to improve the energy density of zinc-bromine flow battery. Polyvinyl alcohol/ phosphomolybdicacid (PVA/POM) membrane which is a kind of ordinary high water-content of non-ionic membrane is fabricated for zincbromine redox flow battery. Themicrostructure and properties of the membrane were characterized by water uptake test, swelling rate test, UV spectrum test, infrared spectroscopy test and thermal stability test. The electrochemical of the membrane was examined by electrochemical analyzer. Compared with the performance of the traditional zinc-bromine flow battery, the results show that PVA/POM acid membrane is a promising material for zinc-bromine redox flow battery.

KEYWORDS

Polyvinyl alcohol membrane;
Phosphomolybdic acid;
Zinc bromine battery;
Conductivity.

INTRODUCTION

The adoption of intermittent renewable energy sources, such as solar energy and wind power, more than 20% of total energy capacity will require electric-energy storage systems to be deployed[1]. The zinc-bromine redox flow battery, an electrochemical system which stores energy in the solution, was considered to be highly attractive for energy storage.

Since Thaller[2] proposed theredox flow batteries in the early 1970s, a number of redox flow battery systems including Fe/Cr, all-vanadium, Zn/Br2(ZBB) and polysulfide/Br2 have been successively proposed and developed[3-6]. The materialsof zinc-bromine redox flow battery could lower the cost of flow batteries, while increasing the energy density[7]. Zinc-bromine redox flow battery can charge quickly, and can be used thousands of times in deep discharge situation[8-10]. Zinc-bromineredox flow battery can be used in new energy vehicles, an emergency power supply and some other fields. Although, people have done a lot about the components of the battery at present[11-14], there are still some technical problems unresolved[15].

Nowadaysthere are two kinds of membranes in the battery. One is the ion exchange membrane which was used in the zinc bromide liquid flow battery, such as Nafion. Another is microporous membrane, such as Daramic[16]. In this article, we mainly studied the aqueous non-ionic non-porous membrane in the application of zinc bromide liquid flow battery,

opening up some new routes for the diversification of zinc bromide battery membrane.

Polyvinyl alcohol (PVA) membrane has strict linear structure, strong hydrogen bonding between molecules, chemical stability and sufficient thermal stability. However, because of the poor water resistance, high temperature resistance and creep of faults,the use of the PVA membraneis limited[17]. It is necessary to make chemical modification process for PVA membrane has water resistant, high temperature resistant. Compared with the PVA membrane, which is condensed by PVA solution, PVA/ POM membrane is better and can be used as new type materials of ion exchange membrane of zinc-bromine redox flow battery. Additionally, with the critical material phosphomolybdic acid(POM), which already has been prepared to be battery membrane, single cell and cell stack are assembled[18-20].

This paper mainly studied the physical-chemical properties and electrochemical properties of the PVA/POM membrane. The results show that PVA/ POM membrane is a promising material for zinc-bromine redox flow battery.

EXPERIMENTAL

Materials

Polyvinyl alcohol (PVA, alcoholization degree 97%-98%,average degree of polymerization of 2400-2500) was purchased from Tianjin Bo Di Chemicals Co. (Tianjin, China). phosphomolybdic acid (POM, average Mw=2257.6 g mol^{-1}) was from Tianjin chemical reagent factory (Tianjin, China). All commercial chemicals were used without additional purification. The water used was purified through a general pure water system.

Preparation of PVA/ POM membrane

The membrane synthesis route was based on the method reported in Ref.[21]. PVA (5 g) was dissolved in distilled water, then POM (2.5 g) was added with constant stirring at 80!until the homogeneous solution was obtained. The resulting solution was cast on a glass plate. when the solution completely solidify into a film at room temperature, dried it at 110! for 12 hours. Added ethyl silicate on the wet membrane and dried in a vacuum oven. In order to make the membrane thicker, repeated this step three times.

Water uptake and swelling rate

Water uptake and swelling rate of the membrane refer to the intrinsic water which is bound with active groups of the membrane, and it is represented as per gram of dry membrane mass in grams of the water.

Cut a piece of membrane to 5cm × 5cm, the membranewas immersed in an excess of deionized water (500 ml) at ambient temperature for two days. Their surface water was mopped with absorbent papers and the fully hydrated membranewas immediately weighed. Then the membrane was dried at 40! under vacuum until the quality of the membrane remain stable, weighed it. Water uptake(W1) was calculated using the following Eq. (1).

$$W_1 = \frac{M_{wet} - M_{dry}}{M_{dry}} \times 100\% \quad (1)$$

M_{wet} is wet weight of membrane;

M_{dry} is dry weight of membrane.

Swelling rate of the membrane(W2) is calculated as Eq. (2).

$$W_2 = \frac{S_{wet} - S_{dry}}{S_{dry}} \times 100\% \quad (2)$$

TABLE 1 : The water absorption

	Wet weight(g)	Dry weight(g)	Water absorption rate （%）
PVA Membrane	0.2159	0.1990	8.4925
PVA/ POM Membrane	0.5500	0.3600	52.7778

TABLE 2 : The swelling rate

	Wet area(cm^2)	Dry area(cm^2)	The Swelling Rate （%）
PVA Membrane	26.1121	24.9001	4.8674
PVA/ POM Membrane	36.0012	24.9995	44.0076

S_{wet} is the area of wet membrane;
S_{dry} is the area of dry membrane.

Conductivity measurement

The characteristics of the membrane was carried out with electrochemical impedance spectroscopy. Cut the membrane into a size of 1.5× 1.5cm square. The membrane was soaked into deionized water. The membrane was hold at the desirable temperature and humidity for 0.5h to ensure that a steady state is achieved. When the membrane swells, removes it and measures the thickness of membrane. Conductivity of computation formula is as following Eq. (3).

$$K = \frac{L}{R \times S} \quad (3)$$

K is the conductivity of the membrane;
L is the thickness of the membrane;
S is the area of the membrane;
Ris the resistor of the membrane.

RESULTS AND DISCUSSION

The research of physical-chemical properties of membrane

The water uptake of themembranes

The proton conductivity of proton exchange membrane is closely related with the moisture content of membrane. There are two reasons that the water content affects the proton conductivity of membrane. One is the water molecules of proton in the film-fixed under the influence of the interaction of the sulfonic acid root. Another is in different water content, the cluster of membrane structure changes. It is the advantage of the proton to transfer between clusters with high hydration degree, ion cluster size, the spacing of cluster size bigger[22].

Cut the prepared membrane into 5cm × 5cm square. According to the above methods, compared with the PVA membrane, we can find that the PVA/ POM membrane can hold more water than thePVA membrane, water absorption is relatively better and ion conduction is fairly easy.

The swelling rate of the membranes

We should make the membrane size change as small as possible in order to guarantee the stability of the battery performance of the membrane. We can see from TABLE 2, compared with the PVA/POM membrane, PVA membrane has better dimensional stability in the process of the water absorption of dry swelling, and consistent lateral length change. The PVA/POM membrane transverse length has a certain difference. This is due to the different membrane process, which makes its anisotropy.

UV spectra of the membranes

Ultraviolet spectrum was carried on the Shimadzu UV-2550. The characteristics of ultraviolet absorption spectrum can be used to qualitative analysis and simple analysis of the structure by using absorption peak. The same material under different condition has different wavelength of absor-

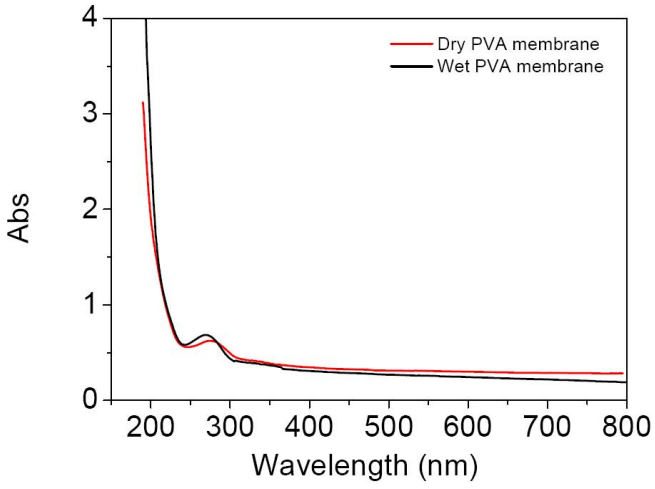

Figure 1 : UV-VIS spectra of dry and wet PVA membrane

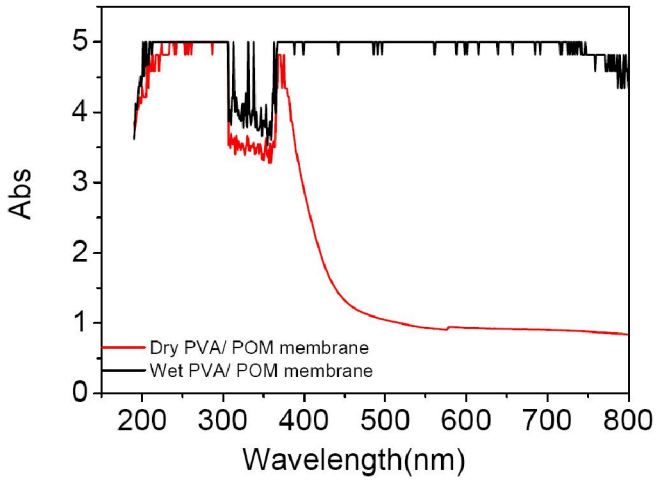

Figure 2 : UV-VIS spectra of dry and wet PVA/ POM membrane

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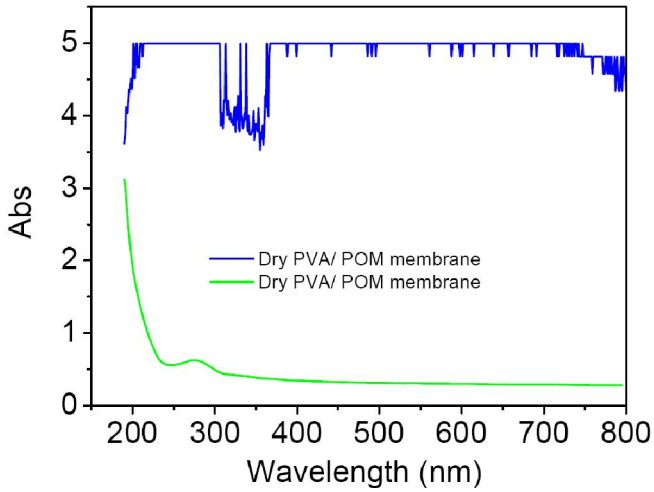

Figure 3 : UV-VIS spectra of dry PVA membrane and PVA/ POM membrane

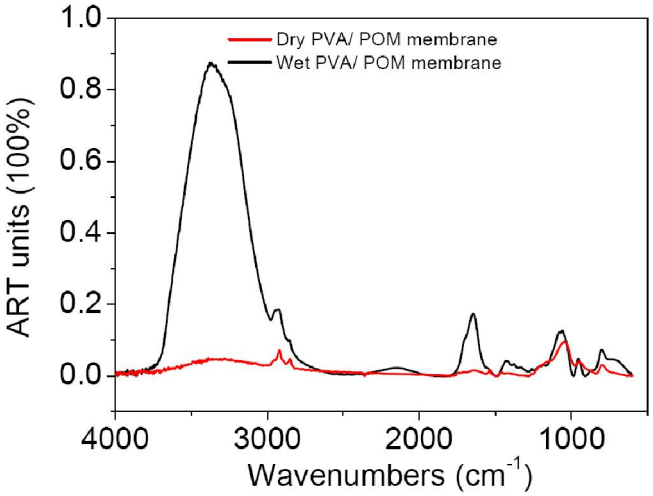

Figure 5 : FT-IR spectra of dry and wetPVA/ POM acidmembrane

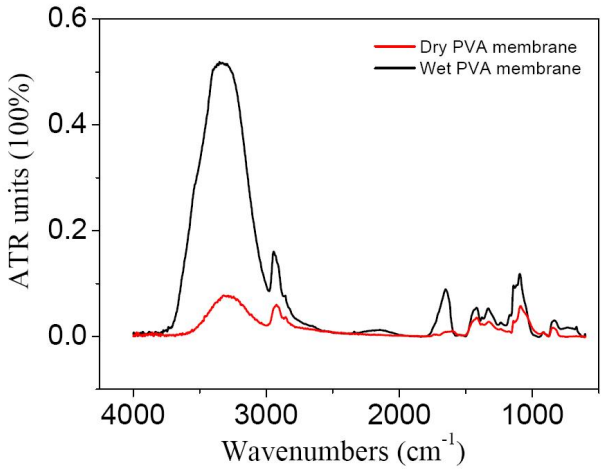

Figure 4 : FT-IR spectra of dry and wet PVA membrane

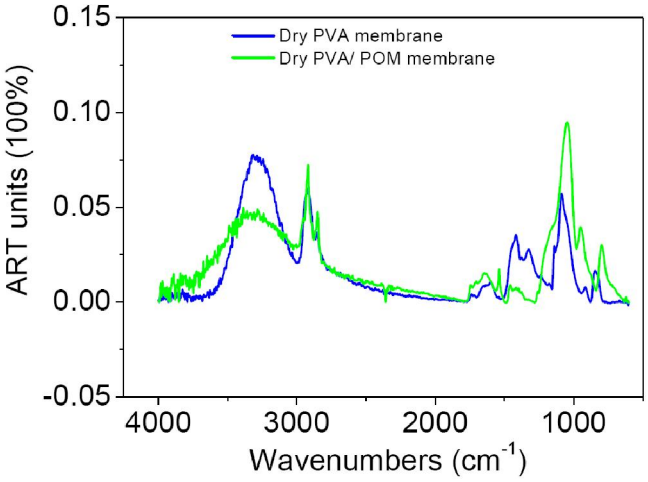

Figure 6 : FT-IR spectra of dry PVA membrane and PVA/ POMmembrane

bance. Figure 1 shows that the UV spectra of dry and wet PVA membrane. Figure 2 shows the PVA/ POM membrane. Ultraviolet spectrum has absorption band in the end. Because containing one or a few lone pair electrons, absorption band of saturated halogenated hydrocarbon, amine or impurity atom single compounds have resulted n-zeta * transition, its scope from the far end of the ultraviolet to the near ultraviolet area, near the 200-nm. Alcohol is of easy to form hydrogen bonds between molecules association, absorption wavelength and intensity will change with the degree of association.

Through the UV-visible spectra, it can be seen that dry and wet membrane both have characteristic peaks at 200-300nm, which is similar to 2,4-pentanediol[23]. Besides,since the head-tail structure of the five-carbon unit group is similar to 2, 4-pentanediol,it can be considered that PVA is the head-tail structure instead of the head-head structure. And the peak of wet film is higher than that of dry film, because hydroxyl groups of the wet film and water molecules form hydrogen bonds.

Infrared spectroscopy of the membranes

Infrared spectrum carried on the EQUINOX55. Figure 4 and Figure 5 show that the infrared spectrum of dry and wet of the PVA membrane and the PVA/ POM membrane. Through the infrared spectrum of the film, we can see that the dry membrane has a strong absorption peak at 3350.5cm^{-1}[24], and it is caused by the presence of hydroxyl groups of the film; wet membrane also has a strong absorption peak at 3350.5cm^{-1}. Since the hydroxyl groups of the wet film and water molecules form hydrogen

bonds, the absorption peak is much higher than the absorption peak of the dry membrane. Dry membrane and wet membrane both have an absorption peaks at 2943cm^{-1}, it is caused by the presence of methylene.

Figure 6 shows the absorption peak of dry PVA membrane and the PVA/POM membrane is almost similar, but the height of the peak is different. The dry PVA membrane has higher absorption peaks, it is related to the concentration of the absorption.

TGA of the membranes

The METTLER-TOLEDO is usedfor thermogravimetric analysis. Set the air flow at 100ml/min and rose the temperature at 40!/min. The samples of the membranewas placed in the thermal gravimetric analyzer. Heated the samples from 50! to 1000! and recorded the change of mass percentage of the samples, then the thermogravimetric curves of the samples was obtained. From the thermogravimetric curves of the samples, we can visually see the whole process of thermal decomposition of the samples, and thermal stability can be seen.

Figure 7 shoes that in the whole temperature range, membranes is totally weightless. PVA membraneis very stable from 0! to 250!. With the water loss in PVA membrane, a small amount mass of PVA membrane is lost. A sharp decline in the quality of PVA membrane occurs from 250!. More than 90 percent of the mass of the film is lost in the range of 250!~ 500!. It is mainly caused by the thermal decomposition of the PVA membrane. While the PVA/POM membraneremain stable when the temperature is below 200!. The quality of the membrane has a sharp decline at 200!. As described above, the thermal stability of PVA membrane is at 250! and PVA/POM membrane with the thermal stability temperature is at 200!. PVA membrane has a better thermal stability.

Conductivity measurement

CHI604D electrochemical analyzer is a type of internal contain fast digital signal generator, the high speed data acquisition system, general electrochemical measurement system, the IR drop compensation potential and the potentiostat. In the experiment, electrochemical impedance spectroscopy is used to test the characteristics of the prepared membrane. The polymer membranes were held at the desired temperature and humidity for 0.5 h, and measurements were taken at 1min intervals when the steady state was achieved.

Cut the membrane into a size of 1.5cm × 1.5cm square, then soaked the membrane into deionized water. When the membrane was swelling, removed it and measured the thickness of membrane. The result of which is 0.100cm. Adjust the radio frequency of the electrochemical analyzer, the low frequency and amplitude, and at ambient temperature, the membrane was measured by electrochemical analyzer for AC impedance analysis. Then we got the nyquist plot of the membrane (Figure 8). The nyquist plot shows that the resistance value of the measured PVAmembrane is 26Ω, and the PVA/POM membrane is 1.1Ω.

From the experiment system we can calculate the conductivity of PVA membrane is 0.171S/m, and the conductivity of PVA/POM membrane is 4.0404S/m. The conductivity of the PVA/POM membrane is relatively good.

Battery performance

The battery is made of membrane, carbon felt, bipolar plates, end plates and other materials[25]. Membrane is the key to the battery internal material. Performance of the membrane has a great influence on the performance of the battery, we use the PVA/POM membrane to assemble the battery.

Battery outer gap seal with glass glue to ensure that the battery liquid leakage was not occurred. After the battery assembly, we use the peristaltic pump to pump a lot of water into the battery inside in case of cleaning the inside of the battery. Continue pumping, deionized water will be from the battery drainage discharge mouth, so that impurities inside of the battery will be out. At the same time also can verify the battery without liquid leakage and blockage. Repeat the above operation several times, until the battery internal impurities completely ruled out, and then close the peristaltic pump, the battery internal deionized water completely ruled out clean.

We do some charge and discharge test to detect

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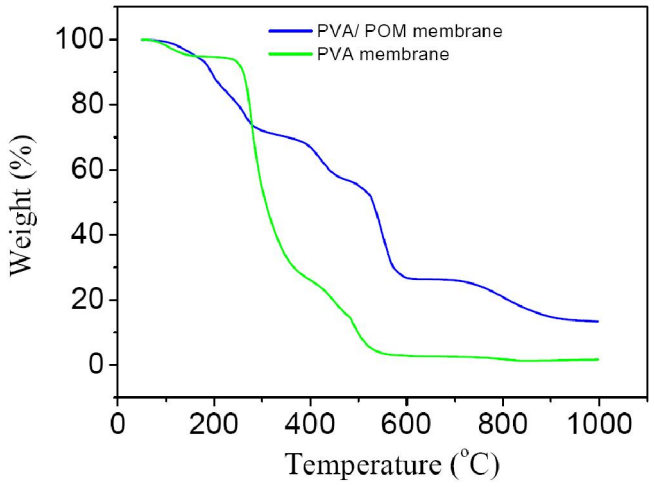

Figure 7 : Thermogravimetric analysis diagram of PVA membrane and PVA/ POMmembrane

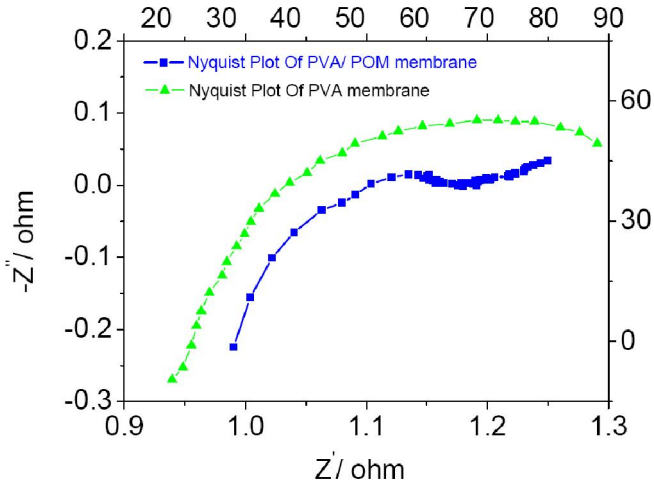

Figure 8 : Nyquist plot of PVA membrane and PVA/ POMmembrane

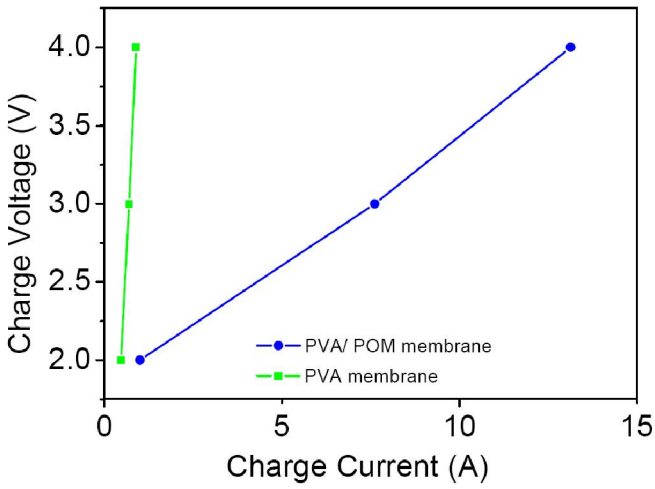

Figure 9 : Polarization curves of the battery at different charge voltage

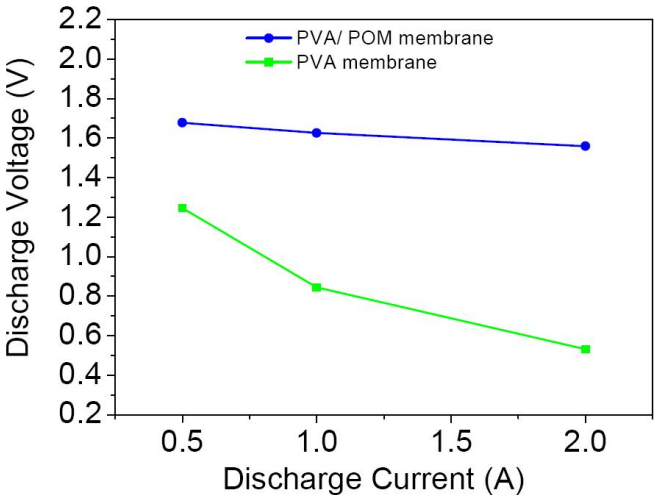

Figure 10 : Polarization curves of the battery at different discharge current

the performance of the PVA and the PVA/ POM membrane. The name of the instrument is CT-3002W-60V40A-N which is a new generation of battery testing system made from Shenzhen new will electronic co., LTD. The electrolyte is a solution of 2mol/L ZnBr2. We use 2V, 3V, 4V to constant voltage charging battery for at most ten minutes, and then respectively with 0.5 A, 1 A, 1.5 A current to constant discharge the battery. You can get Figure 9 and Figure 10 to show the charging and discharging process of polarization curves.

Through drawing, we can see that as the charge voltage increases, the charging current also increases. As the discharge current increases, the discharge voltage decreases. Compared to the PVA membrane, the PVA/POM membrane increased faster when charging and decreased slower when discharging. Its high performance of zinc bromide can be traced to the ion on the hydrogen bond. The establishment of the water channel is the main reason.

CONCLUSIONS

In this paper, we successfully synthesize the aqueous non-ionic non-porous membrane that called the PVA/POM membrane, and be used in the zinc bromide liquid flow battery. After a zinc bromine battery with this PVA/POM membrane is operated at different current when discharging to examine the performance of the membrane, it is found that in 0.5A current electricity, the maximum discharge voltage is 1.6778 V; in 1A current electricity, the maximum

discharge voltage is 1.6257 V. the new battery shows much lower weight andbetter charge-discharge performance than traditional membrane, as well as improved energy density. Therefore, the PVA/POM membrane is an attractive candidate material of membrane being worthy to make great efforts to investigate deeply further.

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