Preparation of Bipolar Membranes (I)

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ABSTRACT: The bipolar membranes were prepared by charged material of polysulfone as a base. The bipolar membranes were composed of a solvent-resistant anion exchange layer with a crosslinking matrix prepared by the reaction of chloromethylated polysulfone in DMF with diamine, an interfacial layer made from chloromethylated polysulfone solution in DMF containing cation exchange resin and amine, and a cation exchange layer made from sulfonated polysulfone dispersing cation resin powder. The prepared bipolar membrane can exhibit lower voltage drop over 100 mA/cm^2. The critical requirement for producing bipolar membranes of low potential drop is the creation of a thin interfacial region with a low electrical resistance and a suitable chemical structure, which act to catalyze water splitting. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1658–1663, 2001

Key words: bipolar membrane; polysulfone; electrodialysis

INTRODUCTION

Interest in the use of electrodialytic water splitting employing bipolar membranes to produce acids and bases from salts has existed for a number of years. There could exist great potentialities in the recovery of resources, the control of pollutants, and the chemical processing because of the simple process, high efficiency, and low disposal of wastes.[1–3]

The most crucial of these is the bipolar membrane, so called because it is composed of two distinct parts, which are selective to ions of opposite charges. Under the influence of an applied direct current, such a sandwich membrane is capable of forcibly dissociating water to form equivalent amounts of hydrogen and hydroxyl ions.

Bipolar membrane can be made by many different methods.[4]

Bipolar membranes have been prepared by adhering together, with heat and pressure or with an adhesive paste, two membranes consisting of oppositely charged ion exchange resins in an inert matrix.[5] Anion and cation exchange membranes have also been fused together by means of heat and pressure to form bipolar membranes.[6] The application of an anionic polyelectrolyte paste to a cation membrane, which is then cured to yield a bipolar membrane, has been described. Further, bipolar membranes from a single sheet of polymeric material, which is selectively functionalized on one side to give cation selectivity and on the other side to give anion selectivity, have been prepared.[7]

But the most attractive method for preparing bipolar membrane is the casting method. The bipolar membrane with good mechanical strength, ability to operate at high current density, high permselectivity, low potential drop, and stable properties were prepared by this method, which

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made the bipolar membrane water-splitting technology commercialize.[8,9]

A critical factor in the production of bipolar membranes exhibiting low potential drop by the casting method is the degree of intimate contact between the anion and cation layers. The degree of contact must be controlled such that the layers do not interpenetrate each other to a degree, which would result in a high resistance layer between the cation and anion permselective portions of the membrane. To solve this problem, Bauer[10] first cast an interfacial layer of polyelectrolyte with ion exchange resin in a matrix polymer having ionic groups of charge opposite the charge of the ion exchange resin on the first ion exchange layer. The bipolar membrane invented by Chlanda, etc.,[9] were characterized by an anion permselective layer comprising a crosslinked reaction product of poly(styrene-vinylbenzyl halide) copolymer between vinylbenzyl halide and diamine, which limited the degree of interpenetration to the extent necessary to produce quality bipolar membranes.

In this article, bipolar membranes were prepared from polysulfone as a base material by the casting method. Compared to polystyrene, polysulfone is an excellent membrane material in terms of physical and chemical stability. It is easy that polysulfone was modified into charged material, such as sulphonated polysulfone,[11,12] quaternized polysulfone,[13] which have been widely used in the process of ultrafiltration, reverse osmosis, and electrodialysis. First, the cation and anion exchange membranes were prepared. The solvent-resistant anion exchange membranes were prepared by the reaction of chloromethylated polysulfone in N,N-dimethylformamide with diamine, such as N,N-dimethyl-1, 3-propanediamine, or N,N,N',N'-tetramethyl-1, 6-hexanediamine, etc. The cation exchange membrane with low resistance and high permselectivity were made from sulfonated polysulfone containing the dispersed cation exchange resin. Then the bipolar membranes were cast by the use of the solvent-resistant anion exchange membrane and sulfonated polysulfone containing the dispersed cation exchange resin above. The performances of the membrane were investigated.

METHODS AND EXPERIMENTS

Experimental

Preparation of the Anion Exchange Membranes[14]

The solution of chloromethylated polysulfone (chloromethylated polysulfone was synthesized in ref. 13. The chloromethyl content is 2.4 mEq/g. in N,N-dimethylformamide (DMF) was mixed with diamine, N,N-dimethyl-1, 3-propanediamine. After mixing, the solution was poured on a glass plate and spread, with a doctor blade, to a thickness of 200–400 μm. The cast solution was allowed to stand at room temperature for 5 min. Thereafter, the plate with the cast layer was placed in an oven at 125°C for 8–20 min. Then solvent-resistant anion exchange membrane with a crosslinking matrix was obtained.

Preparation of the Cation Exchange Membranes[15]

Sulfonated polysulfone with an ion exchange content of 0.69 mEq/g was dissolved in DMF at room temperature. After defoaming, the polymer solution was cast into a film on a flat glass plate with a blade. The casting solution and plate were placed in a oven at 125°C for 10 min. Because the ion exchange content of sulfonated polysulfone is not high enough to get the cation exchange membrane with low electric resistance, the cation exchange membranes were improved by dispersing the cation exchange resin with high ion exchange content of 4.5 mEq/g into the casting solution.

Preparation of the Bipolar Membranes by Two Steps

The anion exchange membrane made above without cooling was removed and coated with sulfonated polysulfone solution in DMF in which cation exchange resin was dispersed as shown above. The membrane was placed back in the oven for a period, then removed.

Preparation of the Bipolar Membranes by Traditional Three Steps

The anion exchange membrane made above without cooling was removed and coated with chloromethylated polysulfone solution in DMF in which cation exchange resin and amine were dispersed. The membrane was placed back in the oven for a period then removed and coated with a sulfonated polysulfone solution in DMF in which cation exchange resin was dispersed as shown above. The membrane was placed back in the oven for a period then removed.

Membrane Properties

The Anion and Cation Exchange Membranes

The measurement methods and experimental applications for membrane thickness, membrane
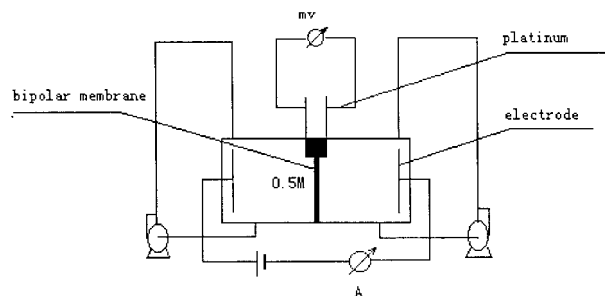
Figure 1 Voltage–current density curve measurement apparatus.

conductivities, membrane electrical resistance, membrane permselectivities to anion or cation (membrane permselectivity is equal to the ratio of actual membrane potential between the calomel electrodes to the theoretical membrane potential), and membrane swelling were same as reported earlier.[14]

The Voltage–Current Density Curve of the Bipolar Membranes

The voltage–current density curve measurement apparatus for bipolar membrane was shown in Figure 1. The exposed area of the bipolar membrane was 100 cm^2. Each compartment of the cell was filled with 0.5 *M* Na$_2$SO$_4$ aqueous solution by circulation at room temperature. The voltages between the electrodes at several current levels were recorded. The membrane was then removed, and the voltages across the solution in the combined compartment was measured at different current levels. The difference between the voltage across the calomel electrodes with the bipolar membrane and the voltage across the electrodes without the membrane is the potential drop of the membrane.

RESULTS AND DISCUSSIONS

Anion Exchange Membrane Performances[14]

A critical factor in the production of bipolar membranes exhibiting low potential drop is the degree of intimate contact between the anion and cation layers. The degree of contact must be controlled without interpenetration of each other. To meet this purpose, the solvent-resistant anion membranes were cast by the use of a polymer matrix containing crosslinked material. The anion exchange membranes with crosslinking matrix were prepared by the reaction of chloromethylated polysulfone in *N,N*-dimethylformamide with diamine, such as *N,N*-dimethyl-1,3-propanediamine, or *N,N,N',N'*-tetramethyl-1, 6-hexanediamine. Because the chloromethyl content on chloromethylated polysulfone is excessive to diamine in the casting solution, the crosslinking matrix degree of anion exchange membrane mainly depend on the quantity of diamine in the casting solution. In addition, the solvent-resistant anion exchange membranes with the good performances were obtained by a controlling reaction condition, such as the concentration of polymer solution, reaction temperature, and reaction time.
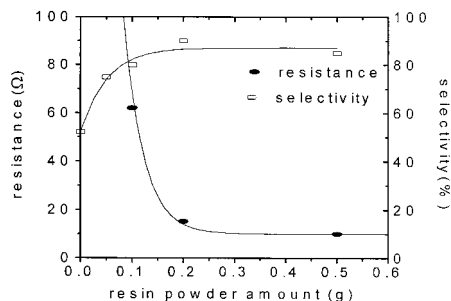
The prepared anion membrane exhibited the electrical resistance of 1.28–12.5 Ω and the permselectivities of 93.1–98.5%.[14]

Cation Exchange Membrane Performances

To increase the ion exchange content of sulfonated polysulfone, the cation exchange membrane with low electrical resistance, the cation exchange membranes were improved by adding the cation exchange resin of high ion exchange capacity into the casting solution. The dispersed cation resin membrane performances were rela-

Table I   The Effect of Resin Powder Content in Sulfonated Polysulfone Solution on Cation Exchange Membrane (Resin Powder Diameter 0.02 mm)

Resin Content (g)	Membrane Thickness (mm)	Electrical Resistance (Ω)	Permselectivity (%)	Membrane Swelling (%)
0	0.029	>1K	52	2
0.05	0.030	123	75	4
0.1	0.035	62	80	9
0.2	0.036	15	90	15
0.5	0.040	10	85	20

Figure 2   The effect of resin powder amount on cation membrane performances.

tive to the size of cation exchange resin particulate and its quantity in the membrane.

As shown in Table I and Figure 2, with an increase in the resin powder amount on the cation membrane, the ion-exchange capacity in the membrane increased. In general, increasing the ion exchange capacity leads to the decrease in resistance and the increase in selectivity. Therefore, the resistance of the cation exchange membrane decreased rapidly, but its selectivity increased at first, and then become more stable.

As shown in Table II, the size of resin particulate had not much more influence on the electric resistance of the cation exchange membrane. But increasing the size of resin particulate led to the decrease on the permselectivity. The electrical resistance of the cation membrane was mainly relative to the ion capacity of the membrane. Therefore, the same amount of resin powder in the membrane had not brought the obvious change on the electrical resistance. However, the membrane selectivity had a close relation to the membrane structure. With an increase to the size of resin particulate, the interspace between the resin particulates increased, which easily made the membrane uneven.

The cation exchange membranes of sulfonated polysulfone with low electrical resistance and

Table II   The Effect of the Size of Cation Exchange Resin Particulate on the Cation Exchange Membrane Performances

Resin Size (mm)	Membrane Thickness (mm)	Electrical Resistance (Ω)	Perm-selectivity (%)	Membrane Swelling (%)
0.02	0.030	12	90	14
0.04	0.035	14	80	13
0.06	0.040	18	40	13

Table III   The Effect of Resin Powder Content in Sulfonated Polysulfone Cation Exchange Layer on the Bipolar Membranes (Resin Powder Diameter 0.02 mm)

Resin Content (g)	Membrane Thickness (mm)	Electrical Resistance (Ω)	Electrical Conductivities ($\Omega^{-1}\,m^{-1}$)
0	0.115	>1K	0
0.05	0.110	260	0.005
0.1	0.109	98.5	0.014
0.2	0.110	21.4	0.065
0.5	0.118	20.2	0.074

high selectivity were prepared by dispersing the cation exchange resin with high ion capacity and particulate size.

Bipolar Membrane Performances Prepared by Two Steps

On the basis of the preparation of the anion exchange membrane containing a crosslinked matrix and cation exchange membrane dispersing cation resin powder, the bipolar membranes were prepared by casting the dispersed resin sulfonated polysulfone solution in DMF directly on the anion exchange layer.

As shown in Table III and Figure 3, with the increase of the cation resin powder amount, the electrical resistance of the bipolar membrane decreased rapidly, then become stable, which is similar to the cation exchange monolayer. The voltage–current density curve of bipolar membranes were shown in Figure 4. At the low electrical density the voltage drop of bipolar membranes was high. Although increasing the amount of the
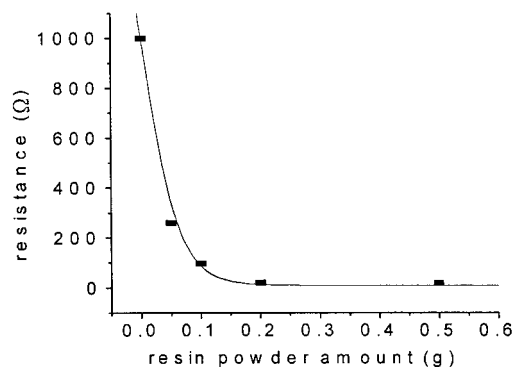
Figure 3   The effect of resin powder amount on bipolar membrane resistances.
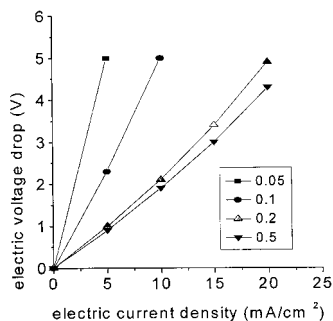
Figure 4 The effect of resin powder amount on bipolar membrane voltage-current density curves.

cation exchange resin in sulfonated polysulfone solution can improve the voltage drop of bipolar membranes, the bipolar membrane cannot be used at higher current density. Because the anion exchange layer and the cation exchange layer themselves exhibited good performances, the high potential drop at low current density was aroused from the interfacial region between the anion and cation portion of the membrane. It is shown that producing bipolar membranes of a low potential drop is not only relative to the creation of an interfacial region, which does not exhibit a high resistance layer, but also depends on the chemical structure of an interfacial region. There are two possibilities for the bipolar membrane prepared by two steps with a result in the high potential drop at low current density: (1) it has not an obvious interfacial region; (2) even if it has an interfacial region, its structure has not met the need of water-splitting capacity of bipolar membrane.

Bipolar Membrane Performances Prepared by Three Steps

To improve the structure of bipolar membrane and enhance the water-splitting capacity of the bipolar membrane we prepared the bipolar membrane with an interfacial layer of special chemical structures by three steps.

As shown in Table IV and Figure 5, although the electrical resistance of the bipolar membrane prepared by three steps is higher than that prepared by two steps, the bipolar membrane prepared by three steps can operate at higher current density over 100 mA/cm^2 and reach the constant. Instead, the potential drop of the bipolar membrane prepared by two steps reached 5 V only at a current density of 20 mA/cm^2. These results demonstrated that the chemical structure

Table IV   Comparison between Bilayer and Traditional Trilayer Bipolar Membranes

Interfacial Layer	Membrane Thickness (mm)	Electrical Resistance (Ω)
Yes	0.15	100
No	0.11	21

in the interfacial region was more critical to the production of bipolar membranes.

Compared to the bipolar membrane prepared by the two steps, the bipolar membrane prepared by the three steps can obtain the distinct interfacial layer by an additional step. The interfacial layer composed of cation exchange resin dispersed in a polymer matrix containing quaternary and nonquaternary amine groups. The chemical structure of the interfacial region included the cation group of SO$_3$Na, strong basic groups of the quaternary amine, and weakly basic groups of the nonquaternary amine. Sufficient anion exchange capacity of the interfacial region in conjunction with cation resin particles in the interface yield a low resistance, highly efficient water-splitting region. The weakly basic groups act to catalyze the dissociation of water into H$^+$ and OH$^-$. However, because the interfacial layer was thicker, and there existed possibly the mixing between the interfacial region and anion exchange layer or cation exchange layer, the electrical resistance of the bipolar membrane was still higher, which resulted in the rapid increase on potential drop at lower current density and still higher potential
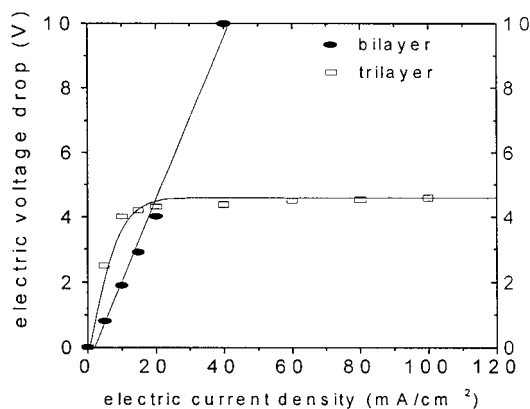
Figure 5 Comparison of the voltage–current density curve between bilayer and traditional trilayer bipolar membranes.

drop over 20 mA/cm^2. We hope to report on the new method for preparing bipolar membranes with a thin interfacial region to improve bipolar membrane performances on the low electrical resistance and low potential drop in future publications.

CONCLUSION

The bipolar membranes consisted of a solvent-resistant anion exchange layer with a crosslinking matrix prepared by the reaction of chloromethylated polysulfone in DMF with diamine, an interfacial layer made from chloromethylated polysulfone solution in DMF containing a cation exchange resin and amine, and a cation exchange layer made from sulfonated polysulfone dispersing a cation resin powder. The prepared bipolar membrane can exhibit a lower voltage drop over 100 mA/cm^2.

The anion exchange layer and the cation exchange layer themselves exhibited good performances. The critical requirement for producing bipolar membranes of a low potential drop is the creation of a thin interfacial region with a low electrical resistance and a suitable chemical structure that act to catalyze water splitting.

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