

Preparation of Bipolar Membranes. II

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ABSTRACT: The bipolar multilayer membrane was prepared by a new technique. The interfacial layer and cation layer were formed by only one step. The anion and cation layers were made from the same material from which chloromethylated polysulfone was used as a basic material. The bipolar membranes were composed of a solvent-resistant anion layer with crosslinking matrix by the reaction of chloromethylated polysulfone in DMF with diamine; an ultrathin interfacial layer from chloromethylated polysulfone solution in DMF, containing cation-exchange resin and both quaternary and nonquaternary amine groups; and a cation layer from chloromethylated polysulfone dispersing cation resin powder. The prepared bipolar membrane exhibits a lower voltage drop over 100 mA/cm² and stable performances at a long-term operation. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1733–1738, 2001

Key words: bipolar membrane; polysulfone; electro dialysis; ion-exchange layers

INTRODUCTION

Bipolar membranes can be widely used for the production of acids and bases from the corresponding salt solution by electro dialytic water dissociation. The key element of the electro dialytic water dissociation system is the bipolar membrane. According to the principle of water dissociation with bipolar membranes, the structure of a bipolar membrane can be divided into three parts: a cation-exchange layer, an anion-exchange layer, and the interface between the two ion-exchange layers. Bipolar membranes, which may be commercially used in the production of acids and bases, should exhibit good mechanical strength, ability to operate at high current density, high permselectivity, low potential drop, and stable properties, to provide a long, useful life under operating conditions. These performances

depend critically on the chemical structure of the anion and cation layers and the degree of intimate contact between the two ion-exchange layers.

To realize the chemical structure and special physical structure of the bipolar membranes a lot of polymeric materials have been used for the preparation of bipolar membranes by a suitable procedure, in which the casting method is one of the most important and attractive methods and is the main method used for a few currently commercial bipolar membranes.^{1–7}

Bauer et al.³ prepared the bipolar membrane with good chemical stability in strong acids and bases, low electrical resistance at high current density, and a high water dissociation rate. The alkaline-resistant anion-exchange layers were prepared from a solution of chloromethylated polysulfone, by adding the mono-quaternary salt of 4,4'-diazabicyclo-[2.2.2]-octane (DABCO). The crosslinking density was adjusted by the ratio of DABCO to the chloromethylated polysulfone. This layer was then spray-coated with dilute solutions of poly(-4-vinylpyridine) and polyacrylic

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acid. After evaporation of the solvent cation-exchange layer from sulfonated polyetheretherketone was cast on top of the previously formed structure. The cation layer was crosslinked by transforming the sulfonic acid into the sulfochloride during the membrane formation process to avoid excessive swelling. The thickness of the intermediate layer was only several nanometers.¹⁻³

Naganuma et al.⁵ made the heat- and acid-resistant bipolar membranes from the quaternary ammonium salt-containing styrene-vinylbenzene copolymer anion layer and copolymer cation layer of $\text{CF}_2=\text{CF}_2$ and $\text{CF}_2=\text{CF}_2\text{OCF}_2=\text{CFOCF}_2=\text{CF}(\text{CF}_3)\text{O}(\text{CF}_2)_2\text{SO}_3\text{Na}$. The intermediate layer included a few different types, such as alkali earth metal, alkali-metal, H, polyelectrolyte ion exchanger, inorganic ion exchanger, and so forth.^{4,5}

The bipolar membranes invented by Chlanda et al.^{6,7} 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. The cation layer of the bipolar membrane was made from sulfonated polystyrene. The interfacial layer comprised ion-exchange resin dispersed in a polymer matrix having ionic groups of charge opposite to the charge of the ion-exchange resin. The inclusion of quaternary and nonquaternary amines in conjunction with the cation-resin-particle matrix in the interfacial region is critical to the production of low potential drop bipolar membranes.

However, until now the current method for making bipolar membranes comprised the three steps. The interfacial layer was formed by a separate step, and the anion and cation layers were made from different materials. Therefore, it is often very complicated to generate a very thin intermediate layer between the cation- and anion-selective sheet. Moreover, it is disadvantageous to keep the stable performances of bipolar membranes over a long-term period because the expansion coefficients of anion and cation materials are different and the adhesive strength between the anion and cation layers is not tight.

In this study we simplified the method for preparing the bipolar membranes to avoid the above-mentioned problems, which cast the bipolar membrane by only two steps, and the anion and cation layers are made of the same materials. Chloromethylated polysulfone was used as a basic mate-

rial for the anion, interfacial, and cation layers.⁸⁻¹² First, 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 and/or *N,N,N',N'*-tetramethyl-1,6-hexanediamine.¹⁰ Then chloromethylated polysulfone solution in *N,N*-dimethylformamide, containing the dispersed cation-exchange resin, was coated on the previously formed anion membrane. During this period the interfacial layer and cation layer formed simultaneously. The performances of the bipolar membrane were then investigated.

EXPERIMENTAL

Preparation of Anion-Exchange Layers^{9,10,12}

The solution of chloromethylated polysulfone (chloromethylated polysulfone was synthesized as previously described⁸; chloromethyl content, 2.4 meq/g) in *N,N*-dimethylformamide (DMF) was mixed with diamine, *N,N*-dimethyl-1,3-propanediamine, and/or *N,N,N',N'*-tetramethyl-1,6-hexanediamine. After mixing, the solution was poured on a glass plate and spread, with a blade, to a thickness of 100–200 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 to 20 min. Then solvent-resistant anion-exchange membrane with crosslinking matrix was obtained.

Preparation of Bilayer Bipolar Membranes by Two Steps¹¹ (Method I)

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

Preparation of Multilayer Bipolar Membranes by Traditional Three Steps¹¹ (Method II)

The anion-exchange membrane made earlier 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. The mem-

Table I Comparison of Multilayer Bipolar Membranes by New Technique to Bilayer Bipolar Membranes

Type of Bipolar Membrane (Method)	Membrane Thickness (mm)	Electrical Resistance (Ω)	Electrical Conductivity ($\Omega^{-1} \text{ m}^{-1}$)	Membrane Swelling (%)
Multilayer(III)	0.015	17.5	0.109	22
Bilayer(I)	0.011	21.3	0.066	19

brane was placed back in the oven for a period then removed.

New Method for Preparing Bipolar Membranes by Two Steps (Method III)

The anion-exchange membrane made earlier without cooling was removed and coated with chloromethylated polysulfone solution in *N,N*-dimethylformamide, dispersing the cation-exchange resin with high ion-exchange content of 4.5 meq/g instead of sulfonated polysulfone solution in DMF. The thickness of this layer was over 50 μm . The membrane was placed back in the oven for 8 to 20 min, then removed. During this period the interfacial and cation layers formed simultaneously.

Compared with the previously formed anion membrane the extra diamines were left in the anion layer to obtain an interfacial region with a crosslinking structure and to enhance the adhesive strength between the anion and cation layers by reacting between extra diamines with chloromethylated polysulfone as a basic material in the cation layer.

Properties of Bipolar Membranes

The measurement methods and experimental applications for membrane thickness, membrane conductivity, membrane electrical resistance, membrane swelling, and the voltage drop-current density curves were the same as previously reported.^{10,11}

RESULTS AND DISCUSSION

Comparison of Multilayer Bipolar Membranes by New Technique to Bilayer Bipolar Membranes

The bipolar membrane with interfacial region was produced by two steps as follows: 16.8 g of a 12% solution of chloromethylated polysulfone in

N,N-dimethylformamide was mixed with 2 ml *N,N,N',N'*-tetramethyl-1,6-hexanediamine. After mixing, the solution was poured on a glass plate and cast with a blade set at about 200 μm . The cast solution was allowed to stand at room temperature for several minutes, during which time a gel formed. The plate and gel were placed in a forced draft oven at 125°C for 8 to 20 min, removed, and coated without cooling, with a portion of a mixture formed by mixing 16.8 g of the above chloromethylated polysulfone solution dispersing 0.2 g cation-exchange resin, using a blade set to 200 μm . The membrane was placed back in the oven for 8 to 15 min then removed. After cooling, the plate was placed in NaCl solution and after several minutes the membrane was pulled free of the plate. The membrane performances are listed in Table I and Figure 1, and compared with performances of the bilayer bipolar membranes prepared by two steps.¹¹

Although the multilayer bipolar membrane made by the new technique and the bilayer bipolar membrane were prepared by the two-step casting method, the results are completely different. The electrical resistance of the multilayer

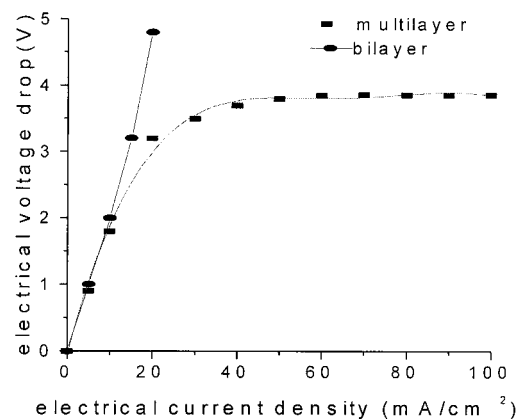


Figure 1 Voltage drop-current density curve of the multilayer bipolar membrane.

Table II Effect of Weak Basic Groups on Bipolar Membranes

Type of Bipolar Membrane (Method)	Weak Basic Group	Membrane Thickness (mm)	Electrical Resistance (Ω)	Electrical Conductivity ($\Omega^{-1} \text{ m}^{-1}$)	Membrane Swelling (%)
Multilayer(III)	Yes	0.015	11.6	0.165	23
Multilayer(III)	No	0.015	17.5	0.109	22
Bilayer(I)	No	0.011	21.3	0.066	19

bipolar membrane is lower than that of the bilayer bipolar membrane. The bilayer bipolar membrane showed a potential drop of approximately 5 V, even at a lower current density of 20 mA/cm² and the voltage drop–current density curve is linear. The bipolar multilayer membrane made by the new technique exhibits a potential drop of approximately 3.0 V at 20 mA/cm² and can be operated at current densities up to 100 mA/cm² without the voltage drop exceeding 3.7 V, demonstrating that the bipolar multilayer membrane has an obvious intermediate layer. The ionic groups in the intermediate layer catalytically dissociated water into proton and hydroxyl ion.

Effect of Weakly Basic Groups in the Anion and Interfacial Layers on Bipolar Membranes

The bipolar membrane was prepared by using a 2.23 g mixture of 3 mol of *N,N*-dimethyl-1,3-propanediamine and 1 mol of *N,N,N',N'*-tetramethyl-1,6-hexanediamine, instead of *N,N,N',N'*-tetramethyl-1,6-hexanediamine by the casting procedure as described earlier. *N,N*-dimethyl-1,3-propanediamine can react with chloromethyl into nonquaternary amine so that the intermediate layer can comprise both quaternary and nonquaternary amine groups. The results are shown in Table II and Figure 2.

The weakly basic groups act to catalyze the dissociation of water into H⁺ and OH⁻. The combination of strongly basic (quaternary amine) groups and weakly basic (nonquaternary amine) groups yields a membrane with significantly lower potential drops at the current density of 100 mA/cm², compared with the bipolar membrane without weakly basic groups.

In addition to quaternary and nonquaternary amine groups in the polymer matrix of the interface region, the composition of the matrix also influences the potential drop.⁷ Because the basic material both for the cation and anion layers is chloromethylated polysulfone, the extra diamine

in the anion layer will react with chloromethylated polysulfone in the cation layer after the chloromethylated polysulfone solution in *N,N*-dimethylformamide disperses the cation-exchange resin with high ion-exchange content of 4.5 meq/g cast on the top of the anion layer. Thus the interfacial layer of the bipolar membrane made by the new method should be obvious and ultrathin. The interfacial layer not only contains quaternary and nonquaternary amine groups, which catalyze the dissociation of water into H⁺ and OH⁻, but also forms the matrix that chemically crosslinks the anion layer and the cation layer. The ultrathin, crosslinking matrix maintains intimate contact between the anion and cation layers; and, at the same time, the degree of contact is controlled, such that the layers do not interpenetrate each other to a degree that would result in a high-resistance layer between the cation and anion permselective portions of the membrane. Such a matrix would make the bipolar membrane useful over a long-term period.

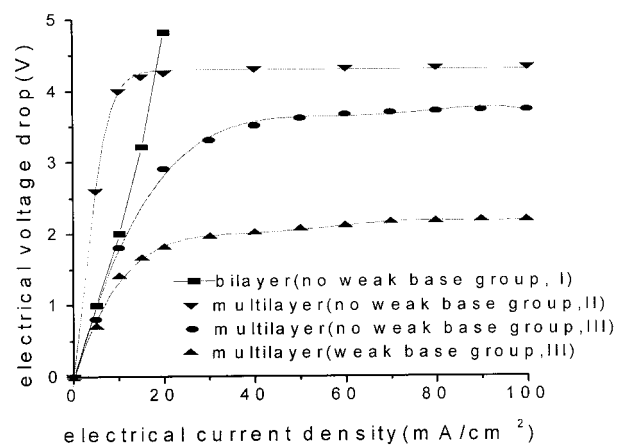


Figure 2 Voltage drop–current density curve of the multilayer bipolar membrane containing weak base groups.

Table III Effect of the Size of Cation Exchange Resin Particulates on Bipolar Membranes (Method III)

Particulate Size (mm)	Membrane Thickness (mm)	Electrical Resistance (Ω)	Electrical Conductivity ($\Omega^{-1} \text{ m}^{-1}$)	Membrane Swelling (%)
0.02	0.015	11.6	0.165	23
0.04	0.015	11.8	0.162	24
0.06	0.016	18.1	0.113	26

Effect of the Size of Cation-Exchange Resin Particulates on Bipolar Membranes

The performances of bipolar membranes prepared by different sizes of cation resin particles in the solution are shown in Table III and Figure 3.

The size of resin particulate did not exert a significant influence on the electrical resistance of bipolar membranes but had an obvious effect on the potential drop–current density relationship of the bipolar membrane. The electrical resistance of the membrane was mainly relative to the ion capacity of the membrane. Therefore the same amount of resin powder in the membrane did not bring about an obvious change on the electrical resistance, in spite of the different sizes of the resin particulates. However, in addition to the ion-exchange capacity in the anion, interfacial, and cation layers, the potential drop–current density relationship of the bipolar membrane was closely related to the membrane structure. The small particle size aids in the production of an interface layer, having a generally homogeneous dispersion of resin in the matrix and cation layer.

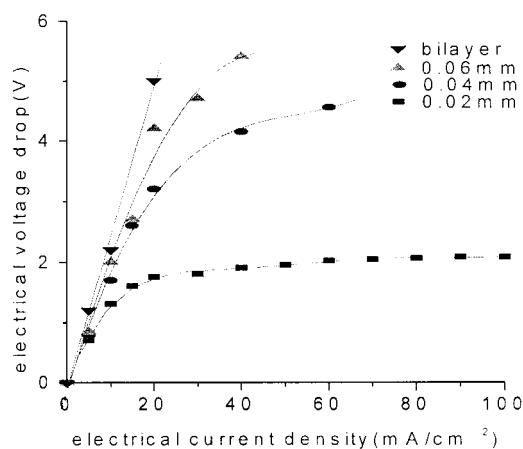


Figure 3 Voltage drop–current density curve of multilayer bipolar membranes containing different sizes of resin particulates.

The small particle size also yields a highly efficient water-splitting region in the interfacial layer. We hope to report on these data and analysis in future publications.

CONCLUSIONS

1. The multilayer bipolar membrane was prepared by a new technique. The interfacial layer and cation layers were formed simultaneously by only one step, which simplified the method for preparing the bipolar membrane compared to the previous casting method.
2. The bipolar membranes were composed of a solvent-resistant anion-exchange layer, an interfacial layer, and a cation layer. The anion-exchange membrane exhibited solvent resistance and contained the crosslinking matrix, which was prepared by the reaction of chloromethylated polysulfone in *N,N*-dimethylformamide with *N,N*-dimethyl-1,3-propanediamine and/or *N,N,N',N'*-tetramethyl-1,6-hexanediamine. The cation layer was made from chloromethylated polysulfone solution in DMF dispersing the cation-exchange resin. The interfacial layer was formed by the reaction of the extra diamine in the anion layer with the chloromethylated polysulfone in the cation layer, which yielded the crosslinking matrix containing quaternary and nonquaternary amine groups and dispersing cation-exchange resin.
3. Because the anion and cation layers were made from the same material and were characterized by intimate contact with the crosslinking matrix, the bipolar membrane exhibited stable performance even at a long-term operation.
4. The ultrathin interfacial layer, containing

sufficient quaternary, nonquaternary amine groups, and cation resin particles, yielded a low-resistance, highly efficient water-splitting region.

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REFERENCES

1. Bauer, B. Ger. Pat. 4026154, 1992.
2. Strathmann, H.; Rapp, H. J.; Bauer, B.; Bell, C. M. *Desalination* 1993, 90, 303.
3. Bauer, B.; Gerner, F. J.; Strathmann, H. *Desalination* 1988, 68, 279.
4. Umemura, K.; Naganuma, T.; Myake, H. Jpn. Kokai Tokyo Koho 06179757, 1994.
5. Naganuma, T.; Umemura, K.; Myake, H. Jpn. Kokai Tokyo Koho 06298964, 1994.
6. Chlanda, F. P.; Lee, L. T. C.; Liu, K. J. U.S. Pat. 4,116,889, 1978.
7. Chlanda, F. P.; Lan, M. J. U.S. Pat. 4,766,161, 1988.
8. Hao, J. H.; Wang, W.; Yang, P.; Zhao, Q. *Desalination* 1991, 83, 361.
9. Hao, J. H.; Chen, C. X.; Li, L.; Yu, L. X.; Jiang, W. J. Chin. Pat. Appl. 99125066.4, 1999.
10. Hao, J. H.; Chen, C. X.; Li, L.; Yu, L. X.; Jiang, W. J. *Desalination* 2000, 129, 15.
11. Hao, J. H.; Chen, C. X.; Li, L.; Yu, L. X.; Jiang, W. J. *J Appl Polym Sci* 2001, 80, 1658.
12. Hao, J. H. Ph.D. Thesis, Tsinghua University, 1997.