

High Acid Retention Properties of Composite Membranes prepared from Anion Exchange Membranes and Poly(pyrrole)

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Composite membranes prepared from conventional anion exchange membranes and poly(pyrrole) show high current efficiency in the electro-dialytic concentration of hydrochloric acid solution.

The relatively high permeability of common anion exchange membranes to HCl limits their efficiency for the electro-dialytic concentration of dilute HCl solutions. In order to solve this problem, several improved anion exchange membranes have been reported: having a high crosslinked layer of epoxide compounds and amines,¹ made of a porous membrane and styrene-divinylbenzene type copolymer,² having imidazole groups as anion exchange groups,³ having thin anionic charged layers,⁴ made of a polymer having weakly basic anion exchange groups and of which T_g is below 70 °C,⁵ and with anion exchange groups which have hydrophobic groups such as octyl and dodecyl groups.⁶ However, high acid concentrations cannot be obtained by electro-dialytic concentration because blocking of the acid leakage is not enough in these membranes.⁷

Conducting polymers such as poly(aniline), poly(pyrrole), poly(thiophene) and other related polymers have been widely studied as functional materials.⁸⁻¹² Recently, conducting polymers have been evaluated from the viewpoint of not only electron conductivity, but also as materials to prepare separation membranes.¹³⁻¹⁶ Pyrrole especially is easy to polymerize by chemical oxidation and provides poly(pyrrole) with very tight and rigid properties. It was reported that pyrrole is readily absorbed in the anion exchange membranes by immersing the membranes into an aqueous pyrrole solution and readily polymerized on the membrane surfaces by immersing the membranes in an aqueous ferric chloride solution.¹⁷ It is expected that acid permeation through the anion exchange membrane decreases by formation of poly(pyrrole) layers on the membrane surfaces. In this work, improvement of the current efficiency of electro-dialytic concentration of hydrochloric acid solution is reported by forming poly(pyrrole) layers on conventional anion exchange membranes [by the composite membrane of the anion exchange membranes and poly(pyrrole)].

Anion exchange membranes used were Neosepta AM-1 (electric resistance: 1.7 Ω cm²; ion exchange capacity: 1.96 mequiv. per g dry membrane; water content: 0.25; strongly basic) and Neosepta AM-2 (electric resistance: 2.3 Ω cm²; ion exchange capacity: 1.84 mequiv. per g dry membrane; water content: 0.24; strongly basic) which are made by Tokuyama Soda Co., Ltd. Both membranes are reinforced by PVC fabric. Thickness of the membranes was 0.13 mm. Pyrrole was used as a monomer to prepare the composite membrane with the anion exchange membranes. After the membrane had been equilibrated with an aqueous 0.500 mol dm⁻³ pyrrole solution (for 97 h), the membrane was immersed in an 0.370 mol dm⁻³ ferric chloride solution for 22 h. Poly(pyrrole) was found only on surfaces of the anion exchange membrane as layers because pyrrole absorbed homogeneously in the membrane was excluded and polymerized on the membrane surfaces (pH of the ferric chloride solution is *ca.* 1). After polymerization, the excess poly(pyrrole) on the membrane surfaces was removed, the diffusion coefficient of hydrochloric acid through the membrane was measured by using a two compartment cell (effective membrane area: 4.0 × 5.0 cm) with stirring at 1500 ± 100 revolutions per min (rpm) at 25.0 °C for 2 h. The concentrated compartment was filled

with 6.0 mol dm⁻³ hydrochloric acid solution and the dilute compartment with pure water. Diffusion coefficient of hydrochloric acid was determined by analysing the amount of acid in the water that had diffused. The composite membranes prepared under the similar conditions were used in electro-dialytic concentration of the dilute hydrochloric acid solution. Electro-dialysis was carried out in the presence of concentration gradient across the membrane at the current density of 10 mA cm⁻² at 25 °C for 90 min in order to evaluate properties of the membranes under severe conditions. A two compartment cell with silver-silver chloride electrodes was used (capacity of each compartment was 120 cm³; effective membrane area: 2.0 cm × 5.0 cm). The anode compartment was filled with 6.0 mol dm⁻³ hydrochloric acid solution and the cathode compartment with 0.5 mol dm⁻³ hydrochloric acid solution. Both compartments were stirred at 1500 ± 100 rpm during electro-dialysis. After electro-dialysis, current efficiency of the acid concentration was calculated from the change in the concentration of the catholyte. Electric resistance of the membrane was measured in a 0.5 mol dm⁻³ hydrochloric acid solution at 25.0 °C at 1000 Hz alternating current.

Table 1 shows the diffusion coefficients of hydrochloric acid through Neosepta AM-1 and AM-2 with and without poly(pyrrole) layers. The diffusion coefficient decreased remarkably with formation of poly(pyrrole). The last column of Table 1 shows the ratio of the diffusion coefficient of the composite membranes against corresponding anion exchange membranes. Decrease in the diffusion coefficient by forming poly(pyrrole) layers was remarkable in the case of Neosepta AM-2. Weight increases after polymerization of Neosepta AM-1 and AM-2 were 15.5 and 15.3%, respectively. Though there was no remarkable difference in mass increase, the crosslinkage of Neosepta AM-2 is higher than that of AM-1. Table 2 shows current efficiency in electro-dialytic concentration of hydrochloric acid solution. Negative current efficiency means that the amount of hydrochloric acid diffused through the anion exchange membrane by concentration gradient exceeded that transported by electric current. The current efficiency became positive with formation of the poly(pyrrole) layer on the anion exchange membrane. Poly(pyrrole) layers on the membrane surfaces were markedly effective at decreasing the diffusion coefficient of hydrochloric acid through the anion exchange membranes. Electric resistance of the composite membranes is also shown in Table 2. The change in

Table 1 Comparison of diffusion coefficient of hydrochloric acid between anion exchange membranes and composite membranes prepared from the membranes and poly(pyrrole)

Membranes	Diffusion coefficient/ cm ⁻² s ⁻¹	Ratio
Neosepta AM-1	1.72 × 10 ⁻⁶	1.0
Neosepta AM-1 with poly(pyrrole)	0.91 × 10 ⁻⁹	0.00053
Neosepta AM-2	1.10 × 10 ⁻⁶	1.0
Neosepta AM-2 with poly(pyrrole)	0.69 × 10 ⁻¹⁰	0.00006

Table 2 Current efficiency of hydrochloric acid in electrodialysis

Membranes	Poly(pyrrole)	Current efficiency (%)	Electric resistance/ Ω cm ²
Neosepta AM-1	No	-554	1.34
	Yes	48.1	2.03
Neosepta AM-2	No	-336	2.04
	Yes	57.7	2.10

electric resistance was minute despite the remarkable improvement in the current efficiency. It is thought that this is due to thinness of the poly(pyrrole) layers formed on the surfaces. Poly(pyrrole) is a weakly basic anion exchangeable polymer. Since the membranes were used in hydrochloric acid solution, all pyrrole units of the polymer ought to be protonated. Calculated ion exchange capacity of poly(pyrrole) is 9.76 mequiv. per g dry polymer. If the anion exchange membrane crosslinked with divinylbenzene had the same ion exchange capacity, the membrane would swell considerably. Though it is not clear whether or not all pyrrole units of poly(pyrrole) on the membrane surfaces dissociate, the poly(pyrrole) layers did not delaminate from the anion exchange membrane because of any difference in swelling degree between the anion exchange membrane and the layers. Poly(pyrrole) which is polymerized by chemical oxidation is an amorphous polymer. Though it is well known that poly(pyrrole) is a rigid and tight polymer, its power against the high swelling pressure is not clear. The reason why the current efficiency increased with formation of poly(pyrrole) layers on the membrane surfaces might be based on specific properties

of the polymer, *i.e.* electron conductivity, and rigidity of the polymer, for example.

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References

- 1 S. Nishihara and S. Koike, *Japan Tokkyo Koho* (examined application), JP 43-10,060.
- 2 T. Gunjima, T. Ichiki and Y. Sugaya, *Japan Kokai Tokkyo Koho*, JP 51-103,089, November 11, 1976.
- 3 T. Misumi and S. Tsushima, *Japan Tokkyo Koho*, JP 56-21,052.
- 4 T. Sata, R. Izuo and F. Kurokawa, *Japan Tokkyo Koho*, JP 54-10,938.
- 5 T. Asawa and T. Gunjima, *Japan Kokai Tokkyo Koho*, JP 52-52,189, April 26, 1977.
- 6 T. Sata, Y. Kagiya, F. Kurokawa and K. Takata, *Japan Tokkyo Koho*, JP 61-18,930; JP 1-19,923.
- 7 M. Boudet-Dumy, A. Lindheimer and C. Gavach, *J. Membrane Sci.*, 1991, **57**, 57.
- 8 A. F. Diaz, K. K. Kanazawa and G. P. Gardini, *J. Chem. Soc., Chem. Commun.*, 1979, 653; K. K. Kanazawa, A. F. Diaz, R. H. Geiss, W. D. Gill, J. F. Kwak, J. A. Logan, J. F. Rabolt and G. B. Street, *J. Chem. Soc., Chem. Commun.*, 1979, 854.
- 9 P. Pratesi, *Gazz Chim. Ital.*, 1937, **67**, 188.
- 10 K. C. Khulbe and M. S. Mann, *J. Polymer Sci., Polym. Chem. Ed.*, 1982, **20**, 1089.
- 11 C. K. Baker, Y. Qui and J. R. Reynolds, *J. Phys. Chem.*, 1991, **95**, 4446.
- 12 L. H. Shi, F. Garnier and J. Roncali, *Macromolecules*, 1992, **25**, 6425.
- 13 T. Sata, H. Iwamoto and S. Ogura, *Japan Kokai Tokkyo Koho*, JP 63-270,505, November, 8, 1988.
- 14 T. Sata, *Japan Kokai Tokkyo Koho* JP 4-222,623, August 12, 1992.
- 15 P. Burgmayer and R. W. Murray, *J. Phys. Chem.*, 1984, **88**, 2515.
- 16 D. L. Feldheim and C. M. Elliot, *J. Membrane Sci.*, 1992, **70**, 9.
- 17 T. Sata and K. Saeki, *J. Chem. Soc., Chem. Commun.*, 1989, 230.