Technical Paper

Membrane Asymmetry and Effect of Colloidal Additive on Reverse Osmosis Properties of Cellulose Acetate Membrane

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The asymmetric properties of Batch-47 type reverse osmosis membrane seem to arise from the asymmetric two-layer structure of the membrane, similar to the case of Batch-18 type membrane. The feed solution containing colloidal additives at 10^{-4} ~ 10^{-3} *M* was circulated over the porous layer of the membrane under pressure. Dynamically formed membrane prepared in this way exhibited an increase of salt rejection and decrease of flow rate as compared with the case without additives. Additives which had a marked effect were the hydrous Zr and Th while those of minor effect were the hydrous Fe, Si, Al and Cu additives, Na-polyacrylate, polyethyleneimine and polyphosphoric acid.

1 Introduction

Various membranes have been tested for reverse osmosis performance, but the cellulose acetate membrane developed by Loeb and Sourirajan is still the promising one for desalination^{1),2)}. This membrane is prepared from one of two different type of casting solutions¹⁾. One type, Batch-18 type consists of a solution of cellulose acetate, acetone, water and Mg (ClO₄)₂. The other type consists of a solution of cellulose acetate, acetone, and formamide. This type membrane is called Batch-47. The asymmetry of Batch-18 type membrane in which the flow rate and salt rejection are dependent on the direction of flow through the membrane, was noted by Loeb and Sharples^{1),3)}. Desalination can be achieved only when the surface of the membrane, which had been in contact with air during the course of casting, is in contact with the feed solution. Koppers et al. found that the salt rejection property of cellophane substantially increased, though its permeation rate decreased by a pretreatment with a feed solution containing colloid⁴⁾. Shor et al. also found that with dynamically formed zirconium oxide membrane, which in a typical case initially rejected about 20% and finally over 90% of salt in the presence of 10^{-3} *M* colloidal zirconium oxide, the permeation rate usually decreased by a factor of 2~3⁵⁾.

The authors investigated the asymmetric reverse

osmosis properties of Batch-47 type membrane and studied a reverse osmosis performance on the porous structure layer (non-effective in desalination) of the membrane facing the feed solution containing colloidal additives.

2 Experimental

Membranes were prepared according to the procedure of Loeb previously described^{1),6)}. The casting solution was prepared by mixing cellulose diacetate (Wakō Pure Chem. Co. Ltd.), formamide and acetone in the proportion 25 : 30 : 45 by weight. The membranes were cast at room temperature on a glass plate with a casting knife for thin layer chromatography. After the solvent was allowed to evaporate for one minute, the membranes were immersed in ice cold water for two hours. They were then removed from the plate and dipped in a water bath 60~80°C for five minutes (annealing step).

Reverse osmosis performance test was carried out as shown in the flow diagram (Fig. 1)⁶⁾. The feed solution is injected into the desalination cell *C* by a pressure pump, through a surge tank *S* and filter *F*. Water permeated through the membrane is collected into the center of the cell through a spiral path. *P_r* is a pressure regulator, for which the necessary pressure is supplied from a nitrogen cylinder. The membrane was supported on a porous disk of stainless steel. Salt rejection, *R*, is calculated by

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Fig. 1 Diagram of equipment used for reverse osmosis performance

$$R(\%) = \frac{C_1 - C_2}{C_1} \times 100,$$

where C_1 and C_2 refer to the concentration of the feed and the permeated solution, respectively. The concentration of chloride ion was determined by titration with silver nitrate solution, using K_2CrO_4 solution as indicator. A dynamic membrane was formed on the porous structure layer of the membrane which was in contact with the glass plate during casting, by circulating a feed solution containing $10^{-4} \sim 10^{-5} M$ colloidal additive. The porous layer of the membrane is put toward the high pressure feed side of the cell. The progress of the dynamic membrane formation then can be followed by its salt rejection. Circulation of the feed was kept enough to eliminate concentration polarization (20 cm/sec).

The colloidal additives were prepared as follows:^{5),7),8)} Hydrous thorium and zirconium oxides; They were prepared by boiling 0.03 M salt ($ZrOCl_2$ or $ThCl_4$) solution for several hours, until the onset of visible turbidity. Hydrous ferric oxide; 30% $FeCl_3$ solution (5 ml) was added dropwise under agitation to 500 ml of boiling water, and brownish colloidal solution was immediately obtained. Hydrous aluminum oxide; The precipitate prepared from $AlCl_3$ and NH_3 solution was washed with water. 3 ml of acetic acid was added to it. It was then refluxed for 24 hours until the appearance of colloidal solution was observed. Cu; $CuCl_2 \cdot 2H_2O$ was dissolved in 500 ml water, and refluxed for 24 hours until the appearance of green turbid solution was observed. Si; This was prepared from aqueous Na_2SiO_3 solution (S.G. 1.15) and 6 M HCl solution. Polyethyleneimine, Na-polyacrylate, polyphosphoric acid; They were obtained commercially from Wako Pure Chemical Co. Ltd and were diluted with water in use.

Fig. 2 Asymmetry of flow rate and salt rejection
Feed: 3.5% NaCl solution, pH of feed:
6.2~6.5, Operating temp.: $24 \pm 1^\circ C$

3 Results and Discussion

The membrane has a thickness of 200μ and consists of a thin dense layer and a porous substructure. The existence of the two regions has been established by means of electron microscopy⁹⁾. The flow rate and salt rejection were determined as a function of pressure, which was applied alternately to the dense layer and to porous layer of the membrane facing the feed solution. The pressure was applied in succession without stopping the operation. Typical results for the membrane annealed at $80^\circ C$ are given in Fig. 2. Positive and negative pressures imply that the thin dense layer contacts with the feed solution under pressure, respectively. In the positive region, the flow rate is almost proportional to pressure and the salt rejection increased smoothly. However, in the negative region, once a critical pressure, represented by the point C had been passed, the flow rate increases rapidly with increasing pressure, and then becomes approximately linear with respect to pressure. The flow rates are symmetrical up to 30~40 atm, and are represented by the straight lines OC and OC'. Salt rejection in the negative region decreases rapidly at point C. This may be due to salt accumulation in the porous layer, or opening and widening of the smaller pores by applied pressure. The asymmetry of flow and salt rejection, as shown in Fig. 2, might arise from the asymmetric structure of the membrane described before. The behavior is similar to that reported earlier for Batch-18 type membrane by Banks et al.³⁾, being almost the same for other membranes annealed at different temperatures.

It was previously observed that salt rejection occurs

Table 1 Effect of colloidal additive on reverse osmosis properties of cellulose acetate membrane under 50 atm (operating temp. : 25°C)

Run	Feed (0.5 N)	Annealing temp (°C)	Additive	Salt rejection (%)		Additive rejection (%)	Flow rate (m ³ /cm ² ·hr)	
				no additive	additive		no additive	additive
1*	NaCl	80	Fe	5.1	18.5		1.89	0.57
2	NaCl	80	Si	5.2	18.9		2.09	0.58
3	NaCl	80	Al	5.9	20.5		2.07	0.42
4	NaCl	80	Cu	9.8	13.2		1.78	0.32
5	NaCl	80	PA·Na	4.7	22.4		1.94	0.62
6	NaCl	80	PEI	7.9	27.4		1.23	0.34
7	NaCl	80	TPA	9.2	13.5		1.64	0.46
8*	NaCl	80	Zr	3.8	32.2		0.78	0.40
9*	NaCl	80	Zr	2.3	32.8	99	0.46	0.32
10*	NaCl	—	Zr	12.8	29.8	94	0.53	0.48
11	NaCl	80	Zr	10.6	31.3	97	0.69	0.47
12*	NaCl	75	Zr	11.3	79.2	94	0.91	0.61
13*	NaCl	75	Zr	6.2	79.6	98	2.05	1.15
14	NaCl	70	Zr	8.4	18.3	98	1.57	0.59
15*	NaCl	70	Zr	9.0	20.8	98	0.98	0.46
16*	NaCl	80	Th	5.7	21.8		1.91	1.01
17*	NaCl	80	Th	6.2	33.0		2.02	1.10
18	NaCl	80	Th	6.3	38.5		1.90	0.92
19*	NaCl	80	Th	7.5	43.2		1.75	0.83
20*	NaCl	80	Th	10.0	40.7		1.57	0.79
21*	CaCl ₂	80	Th	15.2	78.8		1.35	0.68
22*	CaCl ₂	80	Th	14.8	70.5		1.65	0.70
23*	CaCl ₂	80	Th	14.4	72.2		0.91	0.50
24*	CaCl ₂	80	Zr	12.3	83.7	99	0.98	0.46
25	CaCl ₂	80	Al	8.5	33.4		1.83	0.86
26	CaCl ₂	80	Si	9.8	29.8		1.27	0.87
27*	CaCl ₂	80	Fe	10.1	26.3		1.09	0.76
28	CaCl ₂	80	Cu	9.7	17.6		1.36	0.89

* pH of feed : 2.7~3.5

PA·Na : Sodium polyacrylate, PEI : Polyethyleneimine, TPA : Tripolyphosphoric acid

when the feed solution containing an additive is forced through the membrane under pressure. Shor et al. presented the performance of a dynamically formed zirconium oxide membrane⁹. Sacks and Lonsdale found that a membrane formed by casting polyacrylic acid on the surface of a porous supporting membrane showed salt rejection considerably¹⁰. The authors investigated the effect of various colloidal additives on flow rate and salt rejection for the porous layer of the membrane facing the feed solution under 50 atm. The results are summarized in Table 1. A typical time dependency of salt rejection due to the presence of additive is given in Fig. 3. As shown in Fig. 3 and Table 1, the salt rejection increases as the flow rate falls, a higher flow rate thus being associated with lower salt rejection. It is apparent that in the case of unhydrous polyphosphoric acid, the plugging is caused by the addition and there may be little or no salt rejection. In the cases of hydrous zirconium and

Fig. 3 Effect of colloidal additive on reverse osmosis properties of cellulose acetate membrane under 50 atm (Salt rejection vs. time from the start of run)
Operating temp. : 24±1°C

thorium oxide additives, the results are not explicable clearly, but at least in line with the Donnan exclusion effect³⁾, viz, Ca^{++} ion being better rejected than Na^{+} ion. However, in such a case, the plugging effect as distinguished from ion exclusion effect might in part caused by the presence of an additive. The additive seems to have covered the surface or to have penetrated into the pores. This might depend on the porosity, pore size distribution and affinity of the supporting cellulose acetate membrane to an additive. Additives which had a marked effect were the Zr and Th additives.

<E 357> (Received Aug. 1, 1973)

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< 図 書 案 内 >

電 極 反 応 の 基 礎

玉虫伶太・伊豆津公佑・本多健一・藤嶋 昭・藤平正道・篠塚則子・長 哲郎著 共立出版株式会社
共立出版株式会社発行 A 5 判 218ページ 1,400円 共立化学ライブラリー 5

最近の電極反応の研究では、測定法や測定技術の新しい進歩、解析法の発展などによって電極反応の基礎的な問題の解明が試みられているが、非水溶媒の使用は電極反応の領域を大きく進展させることになった。従来の電解質溶液や電極反応の理論はほとんど水溶液を対象としたものであるが、非水溶液の場合は Debye-Hückel の強電解質理論もそのまま適合できないし、電極界面の電気二重層構造も異なり、電極反応の挙動は非常に異なる。したがって非水溶媒における電極反応の体系化は未だしの状態であるが、できるだけこの問題に取り組むことは現時点で大いに有意義なことと考えられる。

本書の執筆者はそれぞれ電極反応の研究において非水溶媒を念頭において研究をされたり、積極的に非水溶媒に取り組んでおられる方々である。

電気化学というと過去の遺物ととられやすいが、本書を読んでいただければ、電気化学の現象や理論の発展が、化学の分野のみならず科学全般に如何に寄与するか理解していただけるものと信じている。 (序文より)

〔内容〕 ☐電極反応とは ☐非水溶媒 ☐半導体電極および回転リング・ディスク ☐プロトン付加反応 ☐電極への吸着 ☐支電解質 (〒112 東京都文京区小日向 4-6-19 共立出版株式会社)

日本金属学会会報「金属電気化学とその応用」特集号

(社) 日本金属学会発行 B 5 判 154ページ 850円 (送料36円)

本書は、日本金属学会会報の10月号 (Vol. 12 No. 10) の「金属電気化学とその応用」をテーマにした特集号です。この問題はきわめて広範囲な領域にわたって編集されております。

〔内容〕 ☐腐食反応の電気化学 (佐藤教男) ☐防食法の電気化学 (加藤正義) ☐金属表面処理の電気化学 (永山政一) ☐金属の構造と電気化学 (大谷南海男) ☐スラグ・メタル反応における電気化学的解析 (萩野和巳・大谷正康) ☐溶融金属と溶融スラグ間の界面現象と界面電気現象 (萩野和巳・原 茂太) ☐溶融スラグの物性と構造 (杉之原幸夫・柳ヶ瀬勉) ☐水溶液の電気化学 (増子 昇) ☐溶融塩電気化学の応用 (緑川林造・石川達雄) ☐高温液体および固体酸化物電解質の化学 (後藤和弘) ☐その他

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