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Studies of the pH of the membrane surface in a laboratory chlor-alkali cell

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The pH on the surface of an ion-exchange membrane was measured with a microprobe in a laboratory scale chlor-alkali cell to study the leakage of OH^- through the membrane. The solution pH in the vicinity of the membrane facing the anode was found to be considerably higher than that in the bulk solution because of penetration and leakage of OH^-. The pH varied with the membrane type. This explains why the carboxylate membrane is not protonated and can be used as a separator in chlor-alkali cells.

1. Introduction

The anolyte of the membrane chlor-alkali cell is a concentrated NaCl solution saturated with dissolved chlorine at a pH of approximately 3. The catholyte is a NaOH solution of 30–40% by weight. The electrolytes are separated by a cationic membrane 0.1–0.2 mm thick. Although the membrane retards the passage of OH^-, a small amount of OH^- passes through the membrane to the anode compartment and causes current inefficiency. It is evident that the membrane is exposed to caustic solution and that a NaOH concentration gradient through the membrane is established. The gradient depends on factors such as the chemical composition of the polymer and the EW (equivalent weight) or the ion exchange capacity, as well as cell operating conditions, such as current density and solution composition. It is difficult to measure the OH^- concentration distribution in such a thin layer but a mathematical simulation is possible [1].

Another reason for studying the caustic gradient in the membrane is that the alkaline earth metal ions in the anolyte penetrate into the membrane and are precipitated as hydroxides, resulting in the almost irreversible degradation of the membrane [2].

Sulphonate membranes, such as Nafion 117, have high electrical conductivity but permit leakage of OH^- under the operating conditions of a chlor-alkali cell. On the other hand, carboxylate polymer membranes can retard OH^- effectively, but may be protonated and become non-conductive when exposed to acidic solution [3]. Bilayer membranes such as Nafion 901 are composed of a thick layer of sulphonate resin on the anode side and a thin layer of carboxylate resin on the cathode side to ensure both high current efficiency and low voltage drop through the membrane. In fact, Flemion, which consists entirely of a carboxylate polymer, can be utilized in industrial cells because the pH on the membrane facing the anode is sufficiently high due to leakage of OH^-.

This paper deals with solution pH measurement near the membrane. The current efficiency of a laboratory cell equipped with sulphonate, carboxylate, and bilayered membranes under various operating conditions is also discussed.

2. Experimental details

Three types of perfluorinated carbon ionomer membrane were employed: a sulphonate membrane 180 μm thick having 1100 EW (Nafion 117), a carboxylate membrane 270 μm thick having 700 EW (Flemion EX), and a bilayer membrane, Nafion 901. Nafion 901 is composed of a thick layer of sulphonate polymer with almost the same characteristics as Nafion 117 on the anode side and a thin layer of carboxylate polymer such as Flemion EX on the cathode side, and is also reinforced with Teflon fabric. These membranes were converted into the Na-form prior to experiment.

2.1. *pH measurements*

A plastic cell (Lucite resin) with three compartments was fabricated. The membrane to be tested was mounted between the cathode compartment and the centre compartment as shown in Fig. 1. The effective area of the membrane was 0.12 dm^2. The centre compartment was separated by Nafion 315 from the anode compartment to prevent any disturbance by dissolved chlorine on the pH measurement near the membrane being tested. A RuO_2–TiO_2 coated Ti anode and a Ni sheet cathode were positioned in the respective compartments. A pH microelectrode was located near the

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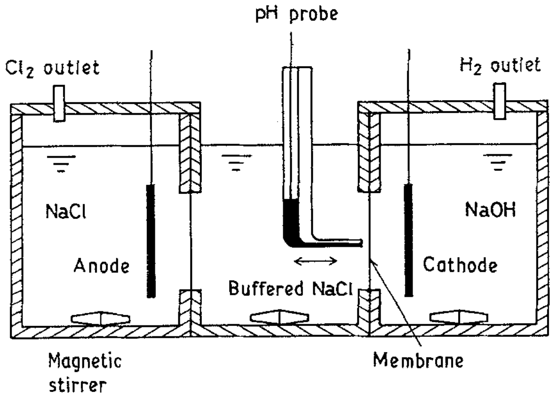

Fig. 1. Cell configuration for the pH measurement.

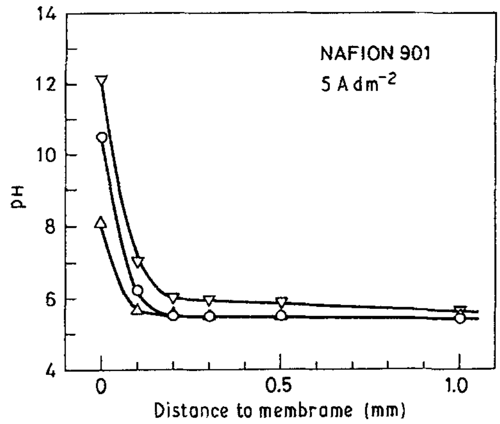

Fig. 2. Examples of the pH against distance curves. Concentration of NaOH: △ 0.1 M; ○ 4 M; ▽ 15 M.

membrane facing the centre compartment with a holder equipped with a vernier to move the microprobe perpendicularly to the membrane surface. However, it was difficult to make measurements at zero distance from the membrane (see Discussion section).

The anolyte was 5 M NaCl for all the experiments, but the NaOH concentration in the cathode compartment was varied in the range 0.1–1.5 M. A buffered solution of 5 M NaCl with M/15 KH_2PO_4 and M/15 Na_2HPO_4 was fed to the centre compartment at a rate of about 30 ml min^{-1} for 1 A dm^{-2} of current density from the level tank about 2 m above the cell, and the solution pH was kept constant at 5.5. The solution volume of these compartments was about 500 ml. Experiments were conducted at room temperature.

A pH microprobe was fabricated with a glass capillary of about 0.5 mm diameter containing a solid antimony electrode [4] in parallel with a Luggin tip of about 0.5 mm diameter connected with a Ag/AgCl reference electrode.

The microprobe was calibrated with standard pH solutions: the potential varied linearly with solution pH in the range 8–12 but deviated somewhat in acidic ($pH < 7$) and alkaline ($pH > 12$) solutions.

2.2. *Current efficiency*

The caustic current efficiency of a two compartment cell was obtained. The cell structure and the experimental procedure were similar to that in the previous paper [2]. However, the cathode compartment was made smaller (150 ml) to allow the cell to reach steady state more quickly after start-up.

Acidified 5 M NaCl was fed to the anode compartment at the rate of 3 l day^{-1}, and distilled water to the cathode compartment at 1.3 l day^{-1} by a metering pump. Electrolysis was conducted at a current density of 50 A dm^{-2} based on the membrane surface (0.10 dm^2) or at a total current of 5 A under room temperature conditions. The cell temperature rose to about 45–50° C due to resistance heating.

Chlorine was liberated at the oxide coated Ti anode, and hence the NaCl concentration decreased from 5 M to 3.8 M. Hydrogen and hydroxyl ion were generated at the Ni cathode and the catholyte concentration was about 2.8 M when the cell reached steady state. The catholyte effluent was collected every hour and titrated with a HCl standard solution to evaluate the caustic current efficiency. The anolyte concentration and the pH were also measured.

3. Results and discussion

The potential of the microprobe and the solution pH varied significantly in the vicinity of the membrane, but the potential no longer changed when it touched the surface, indicating zero distance.

The effect of the non-conductive glass tip of the microprobe on the current distribution near the membrane was investigated. The current distribution was unaffected even when the microprobe touched the surface since the ion exchange membranes had relatively large conductivities. Therefore, the suitability of the microprobe for pH measurement near the membrane was verified by these preliminary experiments.

Fig. 2 shows examples of the solution pH in the vicinity of the membrane on the anode side. Although the pH on the membrane was high, it dropped sharply with increasing distance, becoming 5.5 at 0.2 mm from the surface.

Table 1 summarises the experimental results obtained under various conditions of catholyte strength and current density. The solution pH in the bulk solution was kept constant at 5.5 in all cases. The current density was varied only in the range 0–10 A dm^{-2} since the potential of the pH microprobe fluctuated at current densities above 10 A dm^{-2}. With Nafion 117 the microprobe potential fluctuated and was unmeasurable even at 10 A dm^{-2}, probably due to an excessive leakage of OH^-. The pH near a carboxylate membrane (Flemion EX) was low compared to Nafion 117 and 901, reflecting the order of rejection of OH^- of these membranes [5]. The 'degraded' membrane in Table 1 was made by electrolysis with 5 M NaCl solution containing 0.1 g l^{-1} Ca^{2+} at 10 A dm^{-2} for 400 h in a separate cell prior to the pH measurement. Calcium ions penetrated and calcium hydroxide was deposited in the membrane, damaging the microstructure of the polymer. Hydroxyl

Table 1. pH on the membrane facing the anode

Membranes	*Catholyte concentration, (M)*	*Current density, (A dm^{-2})*				
		0	0.5	2	5	10
Nafion 117	0.1	7.1	6.9	8.4	10.3	–
	0.5	7.5	7.1	9.1	10.9	–
	4	12.1	11.9	12.5	–	–
	15	12.5	12.6	–	–	–
Nafion 901	0.1	6.1	6.0	6.9	8.1	10.4
	0.5	6.2	6.1	7.9	9.4	10.5
	4	9.9	9.3	9.8	10.5	11.5
	15	11.5	11.3	12.1	12.3	12.7
Nafion 901, degraded	4	11.6	12.4	–	–	–
Flemion EX	0.1	5.6	5.5	5.8	6.4	9.8
	0.5	6.1	6.1	6.8	8.0	9.9
	4	8.9	8.8	9.5	10.1	10.9
	15	8.8	8.4	9.1	9.9	9.9

rejection declined and the pH on the membrane at the anode side rose.

The higher the catholyte strength the higher was the pH on the anode side with the exception of Flemion EX, as shown in Table 1. In the case of Flemion EX, the pH increased with increasing the catholyte strength in the range 0.1–4 M, but then decreased in the concentration range 4–15 M, probably due to the distinctive characteristics of water uptake of these membranes [6–8]. The water content of Flemion EX is small, especially in concentrated NaOH solutions: 12% and 4% in 4 M and 13 M NaOH solution, respectively [8], compared to 18% and 10% in Nafion 901 in the same solutions [7]. The diffusion of OH^- is controlled not only by the OH^- concentration of catholyte but the water content in the polymer. In other words, the diffusion coefficient of OH^- decreases with the decrease of the water content.

The pH on the membrane surface was unchanged, or even decreased at low current densities, then increased at high current densities in most cases. The hydration of Na^+ in the membrane, the electrical conductivity, and the flow rate of water molecules are functions of current density since the microstructure of the polymer is related to the current density [9, 10]. Hydroxyl ion migration from the cathode side to the anode side is in opposition to water flow, but is stimulated by electrolysis at high current densities, resulting in a complicated variation of the pH. Once the membrane is damaged by impurities in the brine, the microstructure of the ionomer changes almost irreversibly, and a monotonic increase of pH with current density results from the undesirable leakage of OH^-.

The carboxylate polymer membrane is protonated and becomes non-conductive in acidified solution: at pH $\simeq$ 4 when pK_a = 1.9 (for example [3]). However, since the catholyte of the chlor-alkali cell is a concentrated NaOH solution, the membrane is saturated with caustic solution, and is not protonated even on the anode side. In fact, the solution pH on and near the membrane is high, as stated above.

Figure 3 shows the OH^- current efficiency of the cell equipped with a carboxylate membrane (Flemion EX) and the IR drop across the membrane as functions of the anolyte pH. Low current efficiency (approx. 91%) in this experiment is due to the difference in electrolyte conditions and current density from those in industrial cells. Both the current efficiency and the *IR* drop were almost unchanged in the pH range 1.5–5. The current efficiency decreased and the *IR* drop increased dramatically at pH less than 1.5 (open points). Of course, both the current efficiency and the *IR* drop recovered to the regular levels when the anolyte pH increased (filled points). From these results, it is clear that carboxylate membrane is alkaline and is not protonated at anolyte pH above 2.

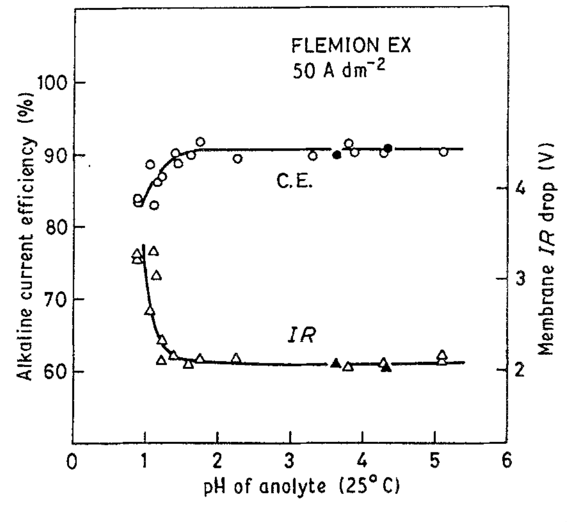

Fig. 3. Current efficiency and *IR* drop as functions of the anolyte pH at 50 A dm^{-2}. Membrane: Flemion EX.

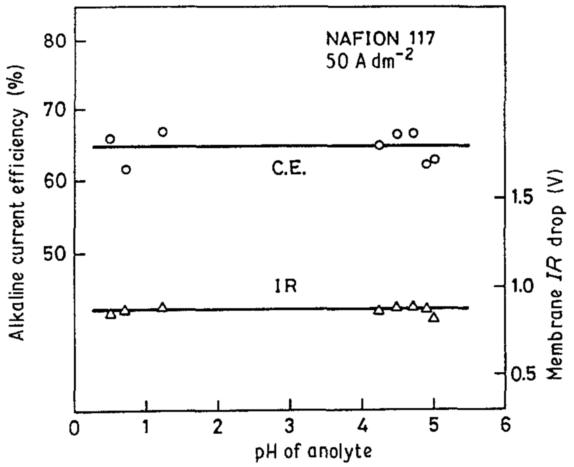

Fig. 4. Current efficiency and *IR* drop as functions of the anolyte pH at 50 A dm^{-2}. Membrane: Nafion 117.

On the other hand, the current efficiency of the membrane having the more acidic sulphonate group, Nafion 117, did not increase even with brine acidified as low as pH = 0.5, as shown in Fig. 4.

4. Conclusions

The pH adjacent to the anode side of perfluorinated cation exchange membranes during electrolysis of NaCl solution was measured with a microprobe consisting of an antimony electrode and a Ag/AgCl electrode.

The ohmic resistance of a carboxylate polymer membrane in a laboratory cell increased and the caustic efficiency decreased when the anolyte pH was lowered to 1.5. Therefore, the anolyte pH must be higher than 2 to avoid the protonation of the carboxylate resin facing the anode. In fact, in industrial cells Flemion membranes composed of carboxylate polymer work even when the anolyte pH is as low as 2–3 because the membrane is penetrated by caustic solution from the cathode compartment. On the other hand, a sulphonate polymer membrane such as Nafion 117 maintains high electrical conductivity even in acidified solution.

It is difficult to investigate the behaviour of membranes in operation, and only the *IR* drop through the membrane is instantaneously measureable. Since the measurement of the pH on the membrane surface provides valuable information, further improvement of the experimental technique is worthwhile.

Acknowledgements

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References

[1] C. W. Walton and R. E. White, paper presented at the Electrochemical Society meeting, Honolulu, HI, October 1987.

[2] Y. Ogata, T. Kojima, S. Uchiyama, M. Yasuda and F. Hine, *J. Electrochem. Soc.* **136** (1989) 91.

[3] Z. Twardowski, H. L. Yeager and B. O'Dell, *J. Electrochem. Soc.* **129** (1982) 328.

[4] D. J. G. Ives, 'Reference Electrodes', (edited by D. J. G. Ives and G. J. Janz), Academic Press, New York (1961) Chapter 7.

[5] R. S. Yeo and H. L. Yeager, 'Modern Aspects of Electrochemistry', Vol. 16, (edited by B. E. Conway, R. E. White and J. O'M. Bockris), Plenum Press, New York (1985) Chapter 6.

[6] W. G. F. Grot, G. E. Munn and P. N. Walmsley, paper presented at the Electrochemical Society Meeting, Houston, Texas, May 1972.

[7] R. R. Chandran, R. S. Yeo and D-T. Chin, *Electrochim. Acta* **30** (1985) 158.

[8] Information supplied by Asahi Glass Co.

[9] E. Heitz and G. Kreysa, 'Principles of Electrochemical Engineering', VCH, Weinheim (1986) p. 197.

[10] S. Rodinini and M. Fettari, 'Proceedings of the Symposium on Diaphragms, Separators, and Ion-Exchange Membranes', Electrochem. Soc., Pennington, NJ (1986) p. 120.