JOURNAL OF APPLIED ELECTROCHEMISTRY 21 (1991) 781–784

Effect of silicate on the membrane-type chlor-alkali cell

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Received 13 September 1990; revised 12 January 1991

The effect of silicate in the electrolyte solution in a chlor-alkali cell on a fluorocarbon ionomer, Nafion® 901, was studied. Calcium silicate precipitated and damaged the membrane during electrolysis when the anolyte and/or the catholyte was contaminated with Ca^{2+} and Mg^{2+}. The service lifetime of the membrane was thus shortened greatly.

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1. Introduction

Membrane cell technology in the chlor-alkali industry has been recognized as an energy saving means for producing high quality caustic with minimum labour costs. However, the membrane cell requires extra pure brine and water as the feeds to the anode and cathode compartments, respectively, otherwise the membranes are seriously affected by impurities in the electrolytic solutions. The effect of the hardness ions in the brine, especially Ca^{2+}, has been investigated extensively [1–5]. These cations penetrate the membrane, precipitate as hydroxide, and the polymer structure of the membrane is destroyed. It is said that the hardness in the feed brine must be kept as low as 20 p.p.b. Other impurities such as mercury have also been studied. The effect of mercury was investigated when the Japanese chlor-alkali industry converted amalgam cell rooms to membrane cells because the brine treatment yard and the flowsheet for the amalgam cell plant were utilized with minimum modification. This problem has been solved by use of ion-exchange resin columns [6].

Another concern is the effect of anions other than Cl^-, such as Br^-, I^-, and SO_4^{2-}, commonly existing in crude salt. The Du Pont research group has pointed out the damage to membranes caused by silicate [3, 7]. The purpose of this work is to investigate the effect of silicate in both the anolyte and the catholyte on the high performance membrane Nafion® 901.

2. Experimental details

Tests were performed in the manner previously reported [8, 9], that is, electrolysis was conducted at a current density of $50\,A\,dm^{-2}$, and the *iR* drop through the membrane was recorded until the membrane was damaged by impurities in the electrolyte.

The voltage drop through the membrane is relatively small and almost unchanged for many hours when the pure brine is electrolysed. On the other hand, the voltage drop increases gradually with time, and finally rises steeply when the brine is contaminated. Therefore, the two branches of the *iR* drop against time curve are extrapolated, and the time to convergence is defined as the time-to-degradation (TTD). The caustic current efficiency decreases when the membrane is damaged by the brine impurities. Since these phenomena depend on the membrane and the operating conditions, it is desirable to measure both the voltage drop and the current efficiency. However, the membrane *iR* drop was mainly measured to obtain the TTD for simplicity [9]. These experiments were repeated three to five times to obtain reproducible results.

The anolyte and the catholyte were 5 M NaCl and 4 M NaOH, respectively, and these solutions were circulated between the respective compartment and the reservoir at a flow rate of $0.8\,dm^3\,day^{-1}$. Alkaline sodium silicate (Na_2SiO_3) solution was added to the anolyte or the catholyte. The anolyte pH was adjusted by adding HCl solution.

The membranes were inspected after electrolysis by X-ray diffraction analysis (XDA), scanning electron microscopy (SEM), and electron probe microanalysis (EPMA) to investigate the silica deposits.

3. Results and discussion

Figure 1 shows the TTD as a function of the SiO_2 concentration in the electrolyte. The anolyte contained Ca^{2+} of $30\,mg\,dm^{-3}$ in concentration in all cases. With the anolyte free of silica, the TTD of the membranes affected by Ca^{2+} was about 300 h, and agreed with previously reported values [8]. The TTD was greatly reduced by addition of small amounts of silicate (open points) up to some $1\,mg\,dm^{-3}$ as SiO_2, but was almost unchanged thereafter. Above $2\,mg\,dm^{-3}$ SiO_2 or $\sim 0.03\,mM$, silica has no effect on the TTD, even though the Ca^{2+} is at $30\,mg\,dm^{-3}$ ($\sim 0.75\,mM$). It is hard to see any reasonable stoichiometry for the interaction. Perhaps the calcium silicate crystals are "seeding" the precipitation of the calcium hydroxide [10]. It is interesting that the TTD against silica con-

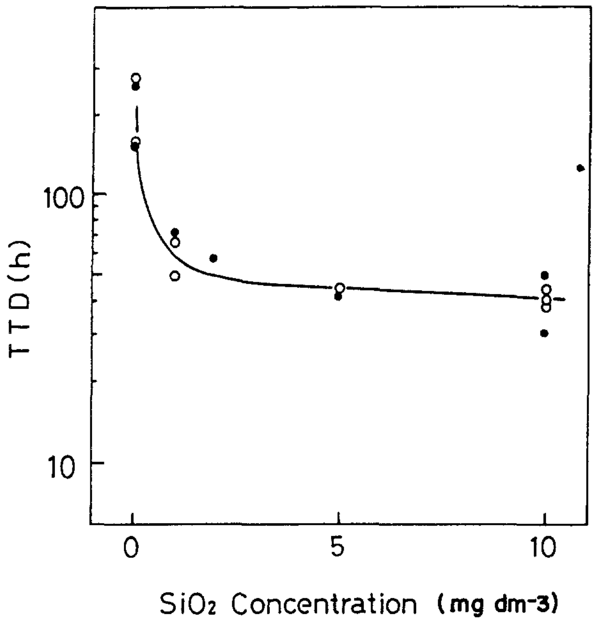

Fig. 1. Time-to-degradation as a function of the SiO_2 content in the electrolytic solution. (○) Anolyte = 5 M NaCl + 0.03 g dm^{-3} Ca^{2+}. (●) Catholyte = 4 M NaOH.

centration curve obained with the catholyte contaminated with silicate (closed points) was almost the same as with the contaminated anolyte. This is attributed to the same mechanism of degradation in both cases.

Figure 2 shows some examples of the SEM photographs of the cross-section of a degraded membrane. In Fig. 2a, heavy deposits can be seen close to the anode side. The deposit consists of Ca_2SiO_4 H_2O, with a small amount of $Ca(OH)_2$ according to the results of XDA and EPMA. In Fig. 2b, the anolyte contained Ca^{2+} but was free of SiO_3^{2-} whereas the catholyte was contaminated with SiO_3^{2-}. The heavy deposit at the anode side was mainly $Ca(OH)_2$. It is evident that silicate in the catholyte (also in the anolyte) is not destructive to the membrane if the electrolyte solution, either the anolyte or the catholyte, is free of Ca^{2+} (Fig. 2c). The experimental conditions of Fig. 2d are the same as those for Fig. 2b except that the anolyte contained both Ca^{2+} and Mg^{2+}. With the XDA and the EPMA results, the deposit in the sulphonate polymer layer of the anode side consisted of $Ca(OH)_2$ with some calcium silicate while the SEM photograph (d) was dissimilar to (b). Fig. 2c and d, no magnesium compound was found in the deposit.

The X-ray diffraction patterns of the anode side and the cathode side of a degraded membrane is shown in Fig. 3. The cathode side pattern of a virgin specimen is also illustrated as reference. The cathode side pattern is almost the same as that of a virgin membrane. On the other hand, sharp diffractions corresponding to Ca_2SiO_4 H_2O and $Ca(OH)_2$, (Labels 1 and 2 respectively), were obtained on the anode side. It is clear that the deposit on the anode side consists of a mixture of these compounds. The results for a degraded membrane examined in the anolyte contaminated with Ca^{2+} and SiO_3^{2-} were almost the same as those for Fig. 3.

In parallel with this experiment, a degraded specimen of Nafion® 901 after the life test was examined by XRD. The specimen was electrolysed at 50 A dm^{-2} at ~ 50° C for 965 h. The anolyte was 5 M NaCl containing 30 mg dm^{-3} Ca^{2+} and 10 mg dm^{-3} SiO_2, and the catholyte was 4 M NaOH free of impurity. The X-ray diffraction pattern of the cathode side was similar to that for the anode side, and showed peaks for $Ca(OH)_2$, Ca_2SiO_4 H_2O, and $Na_8Ca_3Si_5O_{17}$.

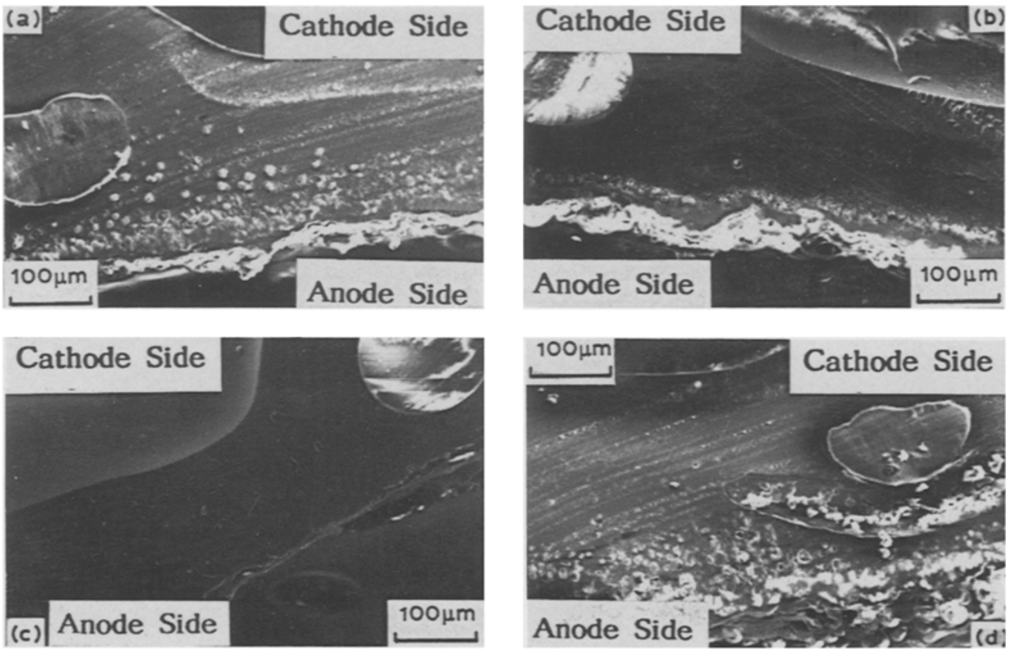

Fig. 2. SEM photographs of degraded specimen. Concentrations (mg dm^{-3}): (a) anolyte: Ca^{2+} (0.03), catholyte: SiO_2 (none present) (b) anolyte: Ca^{2+} (0.03), catholyte: SiO_2 (0.01), (c) anolyte: Mg^{2+} (0.1), catholyte: SiO_2 (0.1), and (d) anolyte: Ca^{2+} (0.03), Mg^{2+} (0.005), catholyte: SiO_2 (0.01).

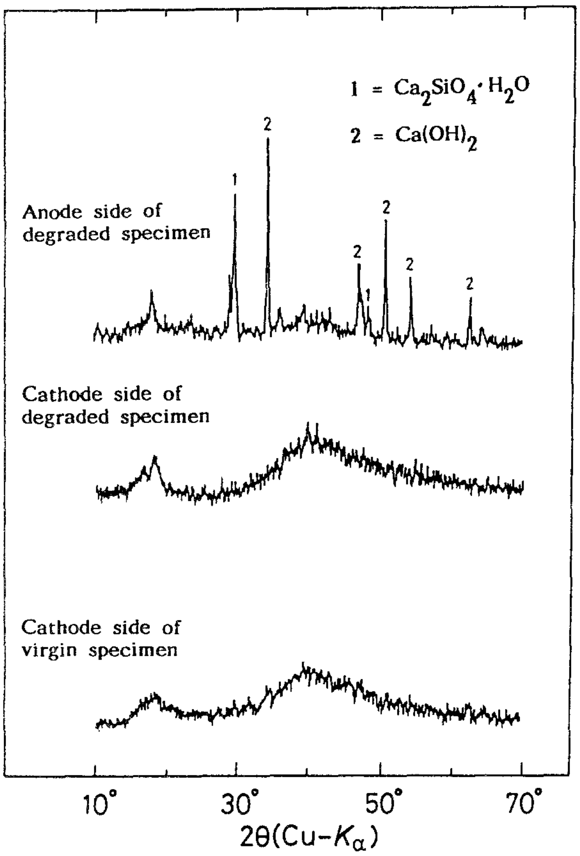

Fig. 3. X-ray diffraction chart of the cross-section of a degraded specimen and the cathode side of a virgin specimen. Anolyte impurity = 30 mg dm^{-3} Ca^{2+}. Catholyte impurity = 2 mg dm^{-3} SiO_2.

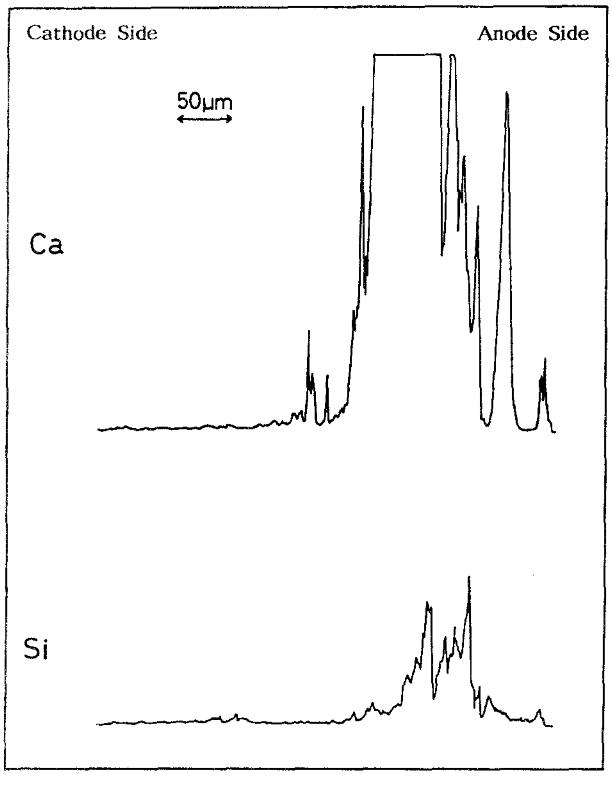

Fig. 4. EPMA results of the cross-section of a degraded specimen. Anolyte impurities = 30 mg dm^{-3} Ca^{2+} + 10 mg dm^{-3} SiO_2.

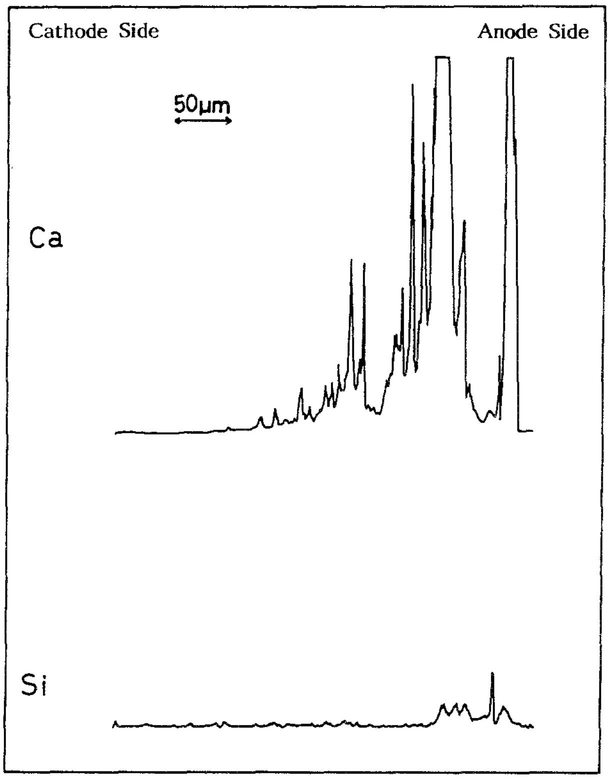

Fig. 5. EPMA results of the cross-section of a degraded specimen. Anolyte impurity = 30 mg dm^{-3} Ca^{2+}. Catholyte impurity = 10 mg dm^{-3} SiO_2.

Figures 4 and 5 are the EPMA results of the cross-section of degraded membranes. The anolyte contained both Ca^{2+} and SiO_3^{2-} and the catholyte was pure caustic solution in the case of Fig. 4. On the other hand, the anolyte contained Ca^{2+} but the catholyte was contaminated with silicate in another case (Fig. 5). It is obvious that the impurities (Ca and Si) accumulate on the anode side in both cases while the peak heights differ.

Bissot reports the formation of a complex calcium silicate, $Na_2Ca_2Si_2O_7 \cdot H_2O$, when the concentration ratio of NaOH to Na_2SiO_3 is relatively small: 35/1 at 90° C, whereas a mixture of $Ca(OH)_2$ and silicate is obtained at relatively large ratios of $NaOH/SiO_2$ [3]. Silicate ions may permeate through the membrane with water transport from the anode side to the cathode side. On the other hand, silicate ions in the catholyte migrate to the anode side during electrolysis. Although it is difficult to know the NaOH concentration in the membrane, Ogata et al. estimate the OH^- concentration distribution in the membrane [8]. Assuming that the solution pH adjacent to the membrane surface on the anode side is 10–12, the $NaOH/SiO_2$ ratio is of the order of 10^{-1} to 10^2. Therefore, it is possible to form either the complex silicate or $Ca(OH)_2$, or a mixture, but no formation of SiO_2 deposit in the membrane is assured. A significant difference between our results and Du Pont's report is the location of the deposit. We obtained a heavy deposit composed of Ca_2SiO_4 H_2O and $Ca(OH)_2$ on the anode side whereas the Du Pont group reported the formation of calcium silicate on the cathode side

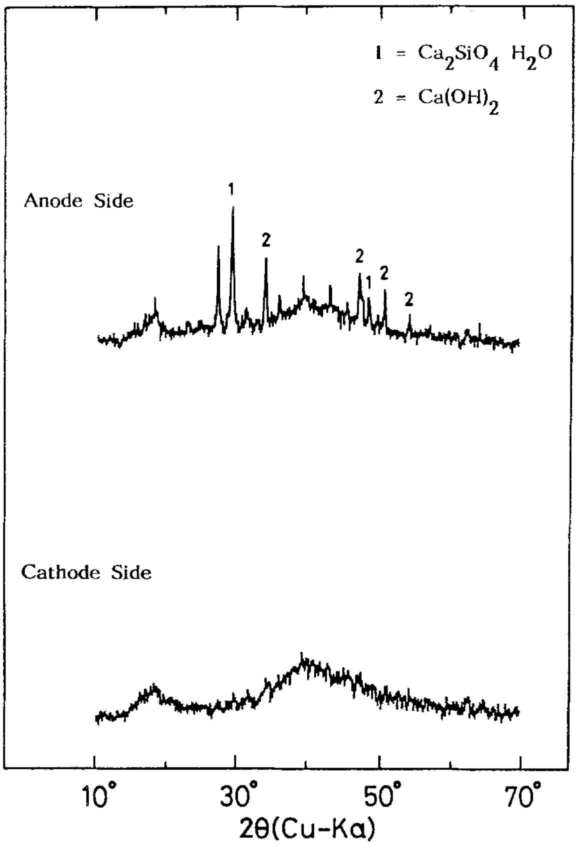

Fig. 6. X-ray diffraction chart of the cross-section of a degraded specimen. Anolyte impurities = 30 mg dm^{-3} Ca^{2+} + 5 mg dm^{-3} SiO_2. Catholyte impurity = 10 mg dm^{-3} SiO_2.

instead of the anode side [7]. Although the discrepancy has not been fully clarified, Keating has suggested the possible reasons [10]. Our work was conducted with 4 M NaOH (~ 15%). Nafion® 901 has its best anion rejection at + 30% NaOH. At 15% NaOH, more hydroxide ion and presumably silicate can pass through the membrane. This may account for the precipitation of the calcium close to the anode side, and would explain the difference between Bissot's report and ours. Another factor may be the higher concentration of calcium used in these experiments, which would cause the precipitate to form sooner or closer to the anode side.

Electrolysis was contained for many hours even after the membrane was damaged by Ca in the anolyte and silica in the catholyte. Figure 6 is the XDA chart of the membrane after the life test. It is clear that the peaks with respect to both Ca_2SiO_4 H_2O and $Ca(OH)_2$ appear on the anode side. The EPMA chart also showed small Si peaks on the cathode side.

Therefore, we consider that Ca^{2+} in the anolyte migrates into the membrane, and precipitates as $Ca(OH)_2$ since the OH^- concentration in the membrane is sufficiently high. Silicate ions also enter the membrane with water transport when silicate exists in the anolyte, and they precipitate together as calcium silicate.

A major portion of the Ca^{2+} entering the membrane is deposited near the anode side, and only a small amount of Ca^{2+} reaches the cathode side when the membrane is relatively new. Silicate ions in the catholyte may pass through the membrane and are attacked by Ca^{2+} and/or calcium hydroxide near the anode surface.

These precipitates grow in size and destroy the polymer structure, resulting in the stimulation of transport of chemical species through the voids and/or defects formed in the membrane. Calcium silicate can deposit on the anode side when the Ca^{2+} concentration increases.

Nafion® 901 was unaffected by silicate when the calcium content in the anolyte was less than 0.1 mg dm^{-3}. No precipitate was deposited in the membrane even if the silicate concentration was high under such conditions. It is therefore concluded that the presence of both Ca^{2+} and SiO_3^{2-} in the anolyte is harmful to the ion-exchange membrane at silicate concentrations as low as 2 mg dm^{-3} as SiO_2. The effect of silicate existing in the catholyte was also detrimental if the anolyte contains Ca^{2+}. Silicate ion migrates through the membrane, combines with Ca^{2+} come from the anode side, and deposits as calcium silicate.

The mass transfer of chemical species through the membrane becomes large when the membrane is damaged by precipitates. Calcium ion pass through the membrane from the anode side to the cathode side, meet with silicate, and the formation of unwanted calcium silicate occurs over the whole membrane.

Acknowledgement

The authors wish to express thanks to Dr James T. Keating at the Experimental Station of the E. I. du Pont de Nemours & Company, Wilmington, DE, for useful discussions. The Nafion® membrane was supplied by Du Pont Japan Limited. A part of this work was supported by the Japan Soda Industry Association.

References

[1] C. J. Molnar and N. N. Dorio, Abstract No. 442, Electrochemical Society meeting, Atlanta, GA (October 1977).
[2] T. C. Bissot, Abstract No. 417, Electrochemical Society meeting, Toronto, Canada (May 1985).
[3] T. C. Bissot, Abstract No. 439, Electrochemical Society meeting, Boston, MA (May 1986).
[4] K. Yamaguchi, T. Ichisaka and I. Kumagai, paper presented at the Chlorine Institute's Plant Operations Seminar, Tampa, FL (February 1986).
[5] K. Sato, M. Nakao and T. Ishii, Abstract No. 438, Electrochemical Society meeting, Boston, MA (May 1986).
[6] K. Yamaguchi, Dr. Eng. Thesis, Nagoya Institute of Technology, Nagoya (1990) p. 116.
[7] D. L. Peet, paper presented at the Chlorine Institute's Plant Operations Seminar, New Orleans, LA (1988).
[8] Y. Ogata, T. Kojima, S. Uchiyama, M. Yasuda and F. Hine, *J. Electrochem. Soc.* **136** (1989) 91.
[9] Y. Ogata, S. Uchiyama, M. Hayashi, M. Yasuda and F. Hine, *J. Appl. Electrochem.* **20** (1990) 1093.
[10] J. T. Keating, private communication.