JOURNAL OF APPLIED ELECTROCHEMISTRY **19** (1989) 566–570

# Material properties of cation exchange membranes for chloralkali electrolysis, water electrolysis and fuel cells*

T. ASAWA

*Asahi Glass Co. Ltd, 2-1-2 Marunouchi, Chiyoda-ku, Tokyo 100, Japan*

Received 3 August 1988; revised 2 November 1988

Owing to the development of perfluorinated ion-exchange membranes, the application of the membranes in electrochemical cells has advanced greatly, especially in chloralkali electrolysis. Material properties of perfluorinated carboxylate membranes used for chloralkali electrolysis are described in relation to the conditions of their use. Some new membranes for water electrolysis and fuel cells are briefly described.

## 1. Introduction

The application of ion-exchange membranes in the field of chloralkali electrolysis originated with their use in fuel cells. Du Pont had developed a perfluorosulfonate membrane for fuel cells in spacecraft, and introduced it commercially in 1969, later calling it Nafion [1].

In the early 1970s, strong incentives for development of a new technology in the chloralkali industry came from the rapid rise in energy costs and environmental concern about mercury pollution, especially in Japan. Perfluorosulfonate membranes were tested in chloralkali cells, but the loss of current efficiency due to the back migration of hydroxyl ions was as high as 20–50%. Many attempts were made to reduce this back migration of hydroxyl ions.

In 1975, the development of a perfluorocarboxylate membrane created a breakthrough. The membrane achieved a current efficiency as high as 95%, producing a strong caustic solution. Next, an important improvement was made in the early 1980s for reduction of cell voltage. The surfaces of the membranes were modified to increase the hydrophilicity and prevent the adhesion of gas bubbles. Using the surface-modified membrane with a small gap between electrodes, a reduction of about 0.2 V in cell voltage was achieved.

Perfluorinated membranes played a big role in chloralkali electrolysis, but they are not so widely used in water electrolysis or fuel cells because of their high cost. Some new membranes, aimed at such uses, are under development in pursuit of low resistance and low cost.

## 2. Membranes for chloralkali electrolysis

The key to success in chloralkali electrolysis is a perfluorocarboxylate membrane. Asahi Glass synthesized a perfluorocarboxylate polymer as a pioneer. Based on this polymer, Asahi Glass has developed a membrane for the chloralkali process and named it Flemion. In the following, the material properties of the membrane are described in relation to the conditions of chloralkali electrolysis [2, 3].

### 2.1. *General features of the perfluorocarboxylate membrane*

As the membrane is made of a perfluorinated polymer, it is resistant against chlorine and strong caustic solution at high temperature, meeting a fundamental requirement for use in chloralkali electrolysis.

When the membrane is used in chloralkali electrolysis, it demonstrates a higher current efficiency than a perfluorosulfonate membrane, as shown in Fig. 1. This is due to the fact that the fixed anion concentration within the carboxylate membrane is higher than that in the sulfonate membrane, and hydroxyl ions in a catholyte are effectively excluded from the carboxylate membrane.

As shown in Fig. 2, the water content of the membrane decreases with increase in the concentration of the caustic solution in which the membrane is equilibriated. In other words, the fixed anion concentration within the membrane increases with the caustic concentration.

In Fig. 3, the results of brine electrolysis using two grades of carboxylate membrane are shown. Both of the membranes are homogeneous, single-layer carboxylate. The ion-exchange capacity of one membrane is higher than that of the other. The reason for the change in current efficiency with caustic concentration can be explained in relation to the previous figure. As the caustic concentration increases, the water content of the membrane decreases and back migration of hydroxyl ion is reduced. However, as the water content of the membrane becomes too low, ion

---

* Paper presented at the meeting on Materials Problems and Material Sciences in Electrochemical Engineering Practice organised by the Working Party on Electrochemical Engineering of the European Federation of Chemical Engineers held at Maastricht, The Netherlands, September 17th and 18th 1987.

0021-891X/89 $03.00 + .12

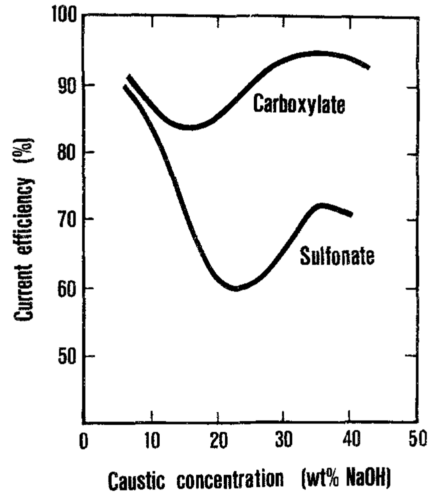


Fig. 1.

pairs are formed between carboxylate and sodium ion to some extent, and current efficiency is reduced.

For the membrane of higher ion-exchange capacity, the water content is higher than that for the other membrane at a given caustic concentration. As a result, optimum current efficiency, in other words, optimum water content for a high charged membrane, shifts to a higher caustic concentration.

### 2.2. *Design and performance of commercial membranes*

Taking into consideration the change in performance with ion-exchange capacity, an efficient membrane can be designed with a two-layered structure. On the cathode side is applied a thin perfluorocarboxylate membrane of an ion-exchange capacity most suitable for attaining the highest current efficiency with the required caustic concentration. The other thicker membrane facing the anode is made of a copolymer with a high ion-exchange capacity so as to attain a high conductivity. With this design, both a high current efficiency and a high conductivity can be realized.

Regarding reinforcement, it is essential that the amount of non-conductive reinforcing material be as little as possible. Woven cloth made of thin and strong PTFE fibres has been adopted. It is also advantageous to use sacrificial fibres, which dissolve during electrolysis, in combination with PTFE fibres.

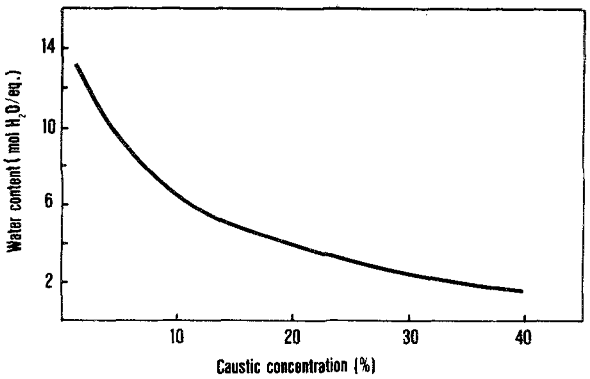


Fig. 2.

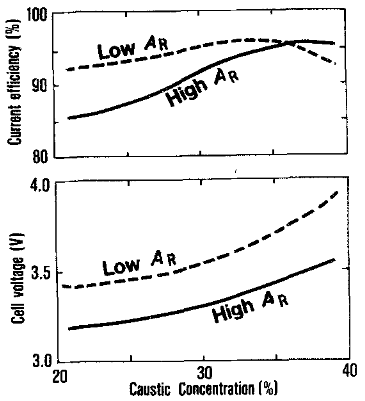


Fig. 3.

Asahi Glass's DX processing of membrane surfaces is an innovative technology for a reduction of cell voltage. In Fig. 4, the dependence of cell voltage upon electrode gap for a Flemion DX is shown in comparison with that for a Flemion 230, without DX. The cell voltage for Flemion DX is lower than that for Flemion 230, and decreases monotonously with decrease of the gap. This confirms the absence of gas bubble adhesion to the surface of Flemion DX, and indicates the feasibility of using the membrane with little gap between electrodes. By these means, cell voltage is reduced by nearly 0.2 V.

Summing up the above, the design elements of commercial membranes are shown in Table 1. The membrane is composed of two layers. Facing the cathode, a thin carboxylate layer of an optimum composition is selected. As for the thicker layer, a carboxylate polymer or a sulfonate polymer may be used as long as its electric resistance is low. The membrane is reinforced and surface treated.

Though membrane resistance and current efficiency is already close to the practical limit, we are still trying to improve the membrane, aiming at operation with a higher current density and adaptability to various user conditions.

We now have several commercial membranes widely used in our AZEC system, in other filter-press cells and also in retrofitting of diaphragm cells. Standard Flemion for use in any type of filter-press cells, producing 35% NaOH, is numbered as 865. In Fig. 5, the performance of Flemion 865 under normal operating conditions is shown. The low content of NaCl in

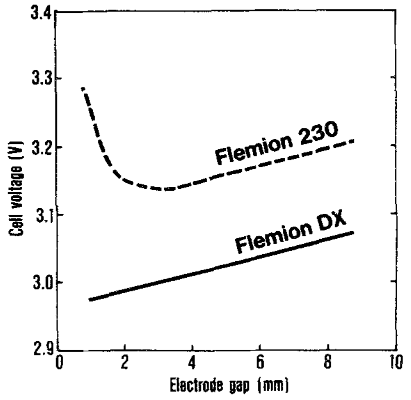


Fig. 4.

*Table 1.*

| | |
|---|---|
| Cathode side layer | Optimum ion-exchange capacity for:<br>(a) 20–25% NaOH<br>(b) 30–35% NaOH<br>(c) >45% NaOH<br>(d) 30–35% KOH |
| Anode side layer | High conductivity<br>carboxylic acid<br>(sulfonic acid) |
| Reinforcement | High strength and low resistance<br>thin and strong fibre<br>(sacrifice (soluble) fibre) |
| Abatement of gas blanketing | Improvement of hydrophilicity<br>porous inorganic layer |

*Table 2.*

| | |
|---|---|
| Mechanical damage (regarding cell strcture) | Abrasion with anode or cathode due to the membrane fluttering<br>Strong compression with anode and cathode<br>Misalignment of gasket<br>Chlorine gas stagnation |
| Undesirable operation (regarding operating conditions) | Brine impurities<br>Upset operation |

NaOH is the feature of the performance of the Flemion membrane. This is attributed to the high carboxylate concentration within the two layers of the carboxylate membranes.

### 2.3. *Proper usage of the membrane*

Fundamentally, perfluorocarboxylate polymer is chemically stable under normal electrolytic conditions [4]. Very slow relaxation of the polymer chain leads to a gradual decrease in current efficiency of less than 1% per year. However, in order to realize a full-life use of the membranes in a commercial cell, it is necessary to design and construct the cell to secure every membrane from damage, and to operate the cell under the recommended conditions for the best performance, avoiding upsets in operation [5].

In Table 2, detrimental factors to a membrane life are summarized. Mechanical damage of the membrane is caused by inadequate structure of a cell. In cell design, it is essential to prevent the stagnation of chlorine gas on the surface of a membrane. The chlorine gas diffuses into the membrane and reacts with caustic soda to form sodium chloride crystals within the membrane, resulting in blistering or delamination.

It is also important to avoid undesirable conditions in operation. Impurities in brine should be reduced to below allowable limits, and upsets in operation such as blockage of brine feed to anolyte or water feed to catholyte should be prevented [6].

For a membrane in an operating chloralkali cell, an assymetric profile of water content occurs across its thickness (Fig. 6). When electric current is passed, water is forced into the membrane by electro-osmosis, and the water content of most of the membrane approaches the equilibrium value with anolyte, while a small part on the cathode side resists swelling and maintains low water content, which is essential for rejection of hydroxyl ion.

Fluctuation in the caustic strength directly affects the water content on the cathode side and also current efficiency. The effect of the anolyte concentration is indicated in Fig. 7. As the anolyte concentration decreases, the water transfer coefficient, expressed as mole per Faraday, increases. This fact indicates that the water content of the bulk layer facing the anolyte increases with decrease in brine strength.

The effect of temperature should be considered in combination with caustic concentration (Fig. 8). Where cells must be operated under irregular conditions, it is essential to avoid a high temperature with weak caustic, which leads to membrane swelling, or a low temperature with strong caustic, which may cause dehydration resulting in ion pair formation.

The effect of impurities in brine on membrane performance can also be understood in relation to the

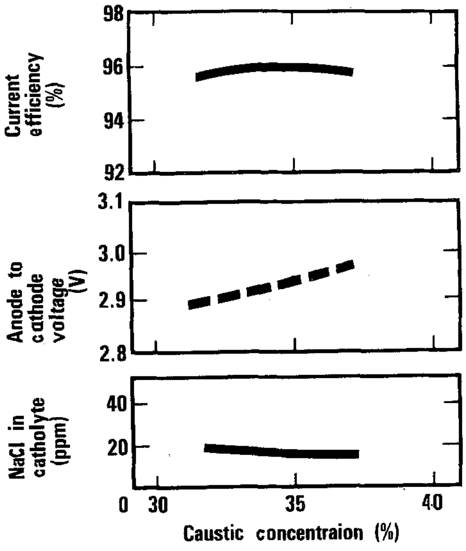


Fig. 5.

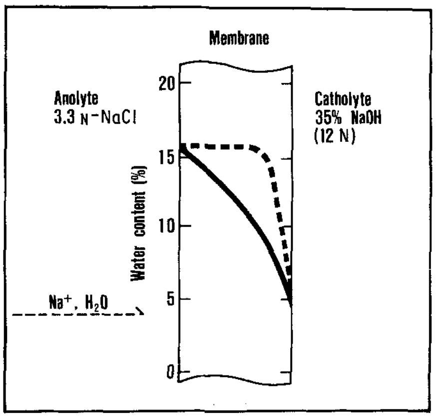


Fig. 6.

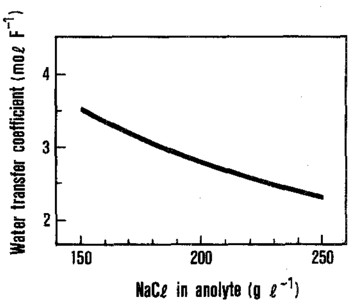


Fig. 7.

profile of water content within the membrane. The calcium ions travelling through the membrane from the anolyte may precipitate as $Ca(OH)_2$ in the cathode side layer of the membrane, where water content is at its lowest and caustic strength is at its highest. The precipitate breaks the structure of the hydroxyl-rejecting surface skin so that current efficiency drops. If the concentration of calcium in the anolyte is below a limiting value, calcium ions pass through the membrane without forming a precipitate. The limiting value for calcium in the anolyte rises with decrease in catholyte strength, in accord with the explained mechanism (Fig. 9).

### 2.4. *Progress of the membrane process [7]*

The membrane cell chloralkali process made a considerable advance during the first decade of commercialization. It can now be regarded that this energy-saving system is 'fully commercialized' [8].

In Japan, following government policy, the operation of the mercury cell process ended by August 1986, and the membrane cell process, including the rectrofitting of diaphragm cells, covers 80% of the total production capacity.

Now the membrane chloralkali process has a strong foothold to prosper throughout the world. The energy consumption for the membrane process is about 30% less than those for the mercury or diaphragm cell processes. The construction cost for membrane cell plant is also about 20% less than those for other plants. Worldwide, the capacity of membrane processes has reached 10% of the total capacity. It is expected that the membrane process will be predominant in the world chloralkali industry in the near future.

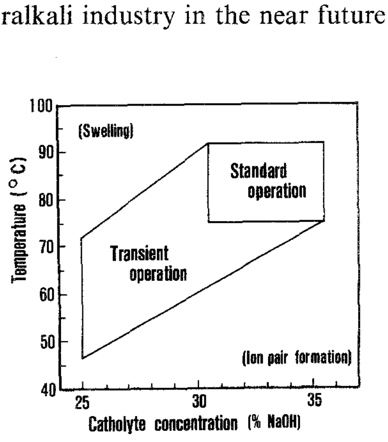


Fig. 8.

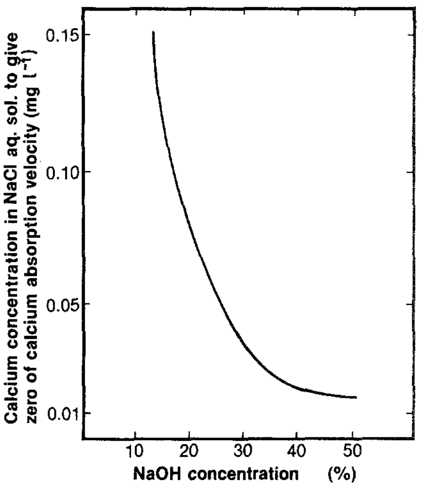


Fig. 9. The limiting value for calcium in anolyte NaCl solution.

## 3. Application of ion-exchange membranes for water electrolysis and fuel cells

### 3.1. *Perfluorinated membranes*

GE developed a novel use of membranes called the SPE cell [9]. In the SPE cell, catalytic materials are attached to both surfaces of the membrane so that the membrane plays a role as the sole electrolyte between the electrodes. Current collectors are pressed onto both surfaces of the membrane to provide electric current over the whole area. SPE systems have been applied in fuel cells and small-scale water electrolysis so far. For a large-scale water electrolysis system, the AZEC system, which had been developed originally for chloralkali electrolysis, seems to be a better candidate. In the Sunshine Project under MITI, Asahi Glass studied the performance of the AZEC cell in water electrolysis [10]. A perfluorocarboxylate membrane with a DX surface coating was used in alkaline electrolytes. With nearly zero gaps between electrodes and the membrane, a low voltage comparable to that for the SPE cell can be obtained (Fig. 10). With AZEC cells, contact of the membrane and an electrode is not required so that scale-up for a large-sized cell is easier than with an SPE cell.

### 3.2. *New membranes for water electrolysis and fuel cells*

In these applications, the membranes are exposed to

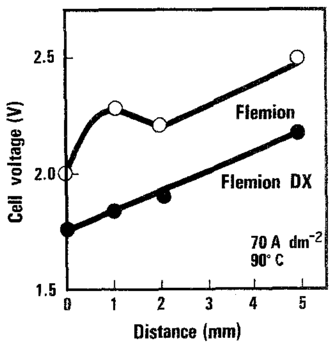
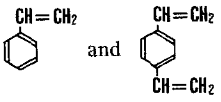
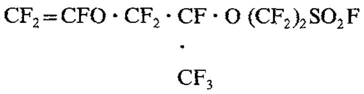
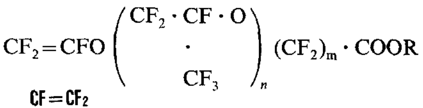
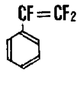
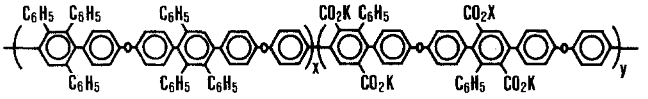


Fig. 10.

*Table 3.*

| | |
|---|---|
| (1)  | Copolymerization<br>Graft polymerization |
| (2)  $CF_2{=}CFO\cdot CF_2\cdot \underset{CF_3}{CF}\cdot O\,(CF_2)_2SO_2F$ | Copolymerization<br>with TFE |
| (3)  $CF_2{=}CFO\left(CF_2\cdot \underset{CF_3}{CF}\cdot O\right)_n(CF_2)_m\cdot COOR$ | Copolymerization<br>with TFE |
| (4)  | Graft polymerization |
| (5)  | |

less severe conditions than in chloralkali electrolysis where chlorine is evolved at the anode. In pursuit of a low electric resistance and a low cost, some new membranes have been developed and tested (Table 3).

The first of these is an aromatic carboxylate. The polymer was originally prepared for possible use as a windshield material on supersonic aircraft. It can be cast into tough, flexible films that display outstanding chemical and thermal stability. The feature of the membrane made from this polymer is a high conductivity. It is highly conductive even in strong caustic solutions, regardless of current density [11].

Another series of new membranes are those which are prepared by radiation grafting of functional monomers onto films. Grafting of styrene or acrylic acid on polyethylene was established earlier, but the resulting membranes were not resistant against oxidants. In recent studies, fluorine-containing monomers or fluorine-containing films are used in order to endow resistance against oxidation [12, 13].

All the above membranes are rather expensive. Mass production may lead to future cost reduction of the membranes.

## 4. Conclusion

Summing up, the application of ion-exchange membranes has resulted in an innovative process in chloralkali electrolysis, but in water electrolysis and fuel cells the situation is not yet so promising. However, further development in ion-exchange membranes aimed at applications in these fields, based on the advanced knowledge obtained through the past development of membranes from styrene-divinylbenzene types to perfluorinated types, is expected to contribute to solving problems related to future energy supply.

## References

[1] W. G. F. Grot, G. E. Munn and P. N. Walmsley, paper presented at the 141st ECS Meeting, Houston (1972).

[2] H. Ukihashi, T. Asawa and H. Miyake, 'Ion Exchange Membranes', Ellis Horwood, London (1983) pp. 165–177.

[3] H. Ukihashi, M. Yamabe and H. Miyake, *Prog. Polym. Sci.* **12** (1986) 229.

[4] D. Bergner, *Chem. Zeit.* **107** (1983) 281.

[5] K. Sato, M. Nakao, T. Ishii, Proc. Symp. Diaphragms Sep. Ion-Exch. Membr. (1986) pp. 28–41.

[6] T. C. Bissot, Proc. Symp. Diaphragms Sep. Ion-Exch. Membr. (1986) pp. 42–51.

[7] K. H. Simmrock, E. Griesenbeck, J. Jörissen and R. Rodermund, *Chem.-Ing.-Tech.* **53** (1981) 10.

[8] H. Ukihashi and K. Sato, 'Modern Chlor-Alkali Technology', Ellis Horwood, London (1986) Vol. 3, p. 196.

[9] J. F. McElroy, US DOE Rep. No. CONF-830974 (1983) pp. 127–130.

[10] T. Morimoto, M. Yoshitake, S. Morikawa and Y. Oda, *Int. J. Hydrogen Energy* **11** (1986) 503.

[11] A. Steck and H. L. Yeager, *Int. J. Hydrogen Energy* **11** (1986) 443.

[12] L. J. D'Agostino, V. Fried and R. Diebolde, Proc. Symp. Diaphragms Sep. Ion-Exch. Membr. (1986) pp. 102–119.

[13] USP 4, 605, 685 (1986) August 12.