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Perfluorosulphonic acid (Nafion) membrane as a separator for an advanced alkaline water electrolyser[*]

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Nafion membranes of two different equivalent weights (eq. wt) were evaluated as a separator in an alkaline electrolyser with nickel screen electrodes in both KOH and NaOH electrolytes over the concentration range of 10–30 wt % and at temperatures from 25 to 160° C. For the same current densities, the cell voltage with 30% KOH electrolytes was more than twice that with 30% NaOH. This result correlates with the water content of the membrane which is almost twice as high in NaOH electrolytes. Thinner membranes and membranes of lower equivalent weight give lower cell voltages. Materials and performance considerations indicate that a membrane of 1000 eq. wt is the optimum separator for an alkaline electrolyser. Indications are that LiOH may be an even better electrolyte than NaOH for use with Nafion membranes. Further improvements in performance can be expected by membrane pretreatment such as exposing the membrane to elevated temperature in water. Nafion membranes have excellent physical and mechanical properties in alkaline electrolyte and can be used at temperatures up to 250° C.

1. Introduction

For hydrogen production by water electrolysis to be competitive with conventional methods, it is vital to reduce the capital costs of the cells and approach 100% energy efficiency [1, 2]. Conventional water electrolysers operate at 80° C with chrysotile asbestos as the separator and 25–30% KOH as the electrolyte. The cell voltage is typically 2.0 V so that the energy efficiency is only 75%. It has been reported [3] that by raising the operating temperature to about 150° C, it should be possible to lower the cell voltage to about 1.6 V, which results in an energy efficiency of more than 90%. Appleby and Crepy [4] and Braun [5] have also shown that an increase of the operating temperature of advanced water electrolysers to temperatures in the range 120–150° C can improve the energy efficiency and lower hydrogen production costs.

One of the most serious problems in raising the operating temperature from 80° C to over 100° C is to find a substitute for chrysotile asbestos as the separator in water electrolysers. Alternate separator materials such as polyantimonic acid [6, 7] and potassium hexatitanate [8] have been investigated. These materials are stable at 150° C and have demonstrated satisfactory performance in alkaline water electrolysers. In a recent study [9], more than 50 separator materials, including organic and inorganic ion exchange membranes, porous membranes, woven materials, polypropylene felts, etc. have been evaluated in alkaline water electrolysers at temperatures ranging from 80° C to ~ 150° C. It was found that Nafion and Teflon-bond potassium hexatitanate paper are the most promising new materials. The results on Nafion, which are dependent on the electrolyte used, are presented and analysed in this paper.

A water electrolyser with Nafion as the electrolyte layer, namely the solid polymer electrolyte water electrolyser, is being developed at the General Electric Company [10]. Although pure water is the feed liquid in this electrolyser, the environment that the electrodes encounter is essentially highly acidic. This is because the electrodes are in contact with the sulphonic acid groups at the membrane surface [11, 12]. Owing

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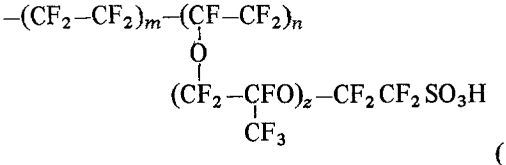
to the acidic environment, noble metals or their alloys are used as electrocatalysts for the hydrogen and oxygen evolution reactions [13].

On the other hand, Nafion finds promising application as a separator in chlor-alkali electrolysers [14]. Because of the hydroxyl ion rejection requirement for high current efficiency, the types of Nafion being considered are of low water content, such as Nafion-315, Nafion-amine [15] and Nafion carboxylate membranes [16].

In alkaline electrolyte, the sulphonic acid groups of the Nafion membrane are neutralized. Neutralization has a drastic effect on the physical properties of the membrane [17]. The glass transition temperature increases from 110° C to ~ 220° C. The thermal stability and tensile strength of the membrane increase markedly. As a result, the membrane will be suitable for use at temperatures up to 250° C. Of course, the maximum operating temperature will be limited by the instability of other cell components, such as cell frames and gaskets. Thus, it is of considerable interest to evaluate Nafion as a separator for alkaline water electrolysers, especially for high-temperature operations. Particular attention was paid in this study to the effect of the type of alkaline ions and alkali concentration on membrane swelling as well as on cell performance.

2. Experimental

The Nafion membranes were prepared by du Pont. The Nafions are co-polymers of tetrafluoroethylene and monomers such as perfluoro-3,6-dioxa-4-methyl-7-octene-sulphonic acid [18]



$$-(CF_2-CF_2)_m-(\underset{\substack{|\\O\\|\\(CF_2-\underset{\substack{|\\CF_3}}{C}FO)_z-CF_2CF_2SO_3H}}{C}F-CF_2)_n \qquad (1)$$

This polymer has exceptional thermal stability and oxidative and hydrolytic resistance. It is ideal for the use in water electrolysers.

Unless otherwise specified, all the measurements were made with Nafion-115, equivalent weight of 1100 and thickness of 0.12 mm. The membranes were evaluated as in their as-received condition. The equilibrium water content of the membrane was determined by a method previously described [19]. The cell performance was measured in a pressure vessel. The membrane was sandwiched between two Ni electrodes. The cell frame was constructed using either polypropylene or polysulphone depending on the operating temperature. The cell potential–current density measurements for water electrolysers were made in KOH and in NaOH as a function of concentration and operating temperature.

3. Results

Fig. 1 shows the water content of the membrane as a function of alkali concentration. The following empirical equation relating the water content of the membrane to the equivalent weight, salt

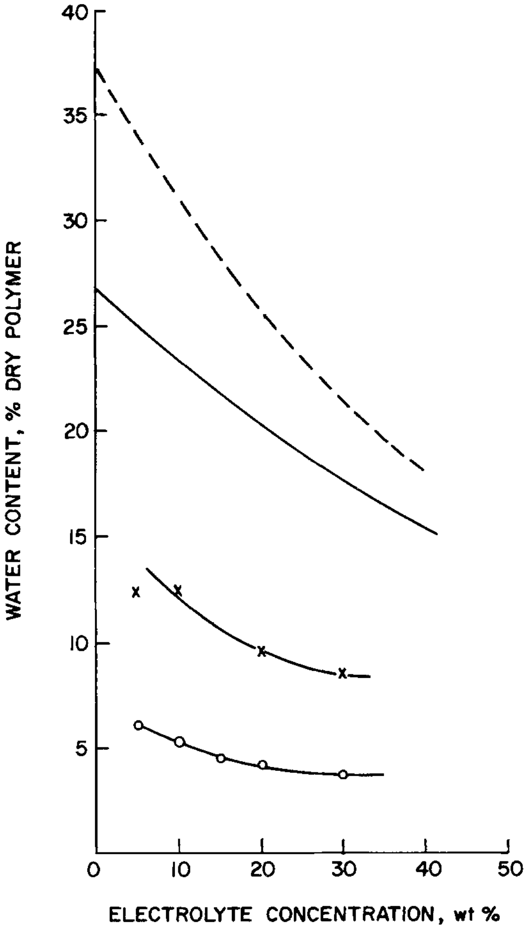


Fig. 1. Water content in Nafion membrane versus alkaline concentration. Experimental values, (o) KOH, (X) NaOH; calculated values from Equation 1, (——) KOH, (– – –) NaOH.

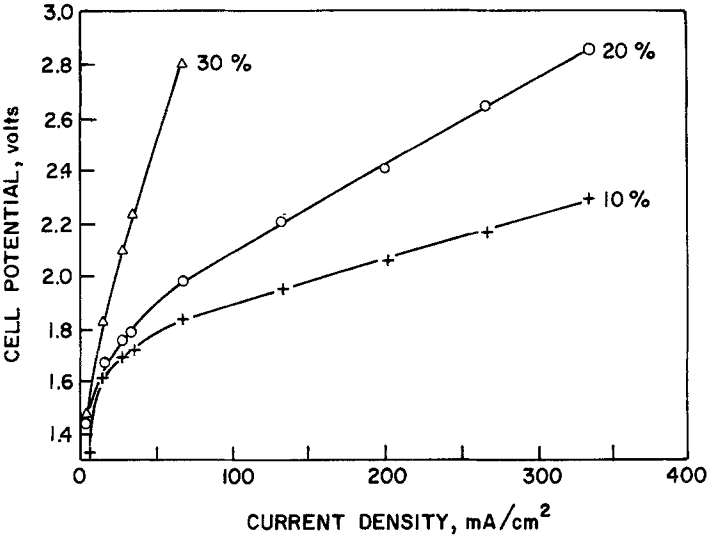


Fig. 2. Cell potential as a function of current density for water electrolysis at various KOH concentrations at 96° C.

form, and the prehistory of the membrane was reported previously [20, 21].

$$W = \frac{0.0126AB}{1 + 0.075M} \exp (3980/\text{eq. wt}) \qquad (2)$$

where W is the weight % water, based on the dry polymer weight, eq. wt the equivalent weight of the membrane, M the molarity of the electrolyte ($0 \leqslant M \leqslant 14$), A a constant ($H^+ = 1$; $Li^+ = 0.95$; $Na^+ = 0.79$; $K^+ = 0.57$) and B a constant, dependent on the history of pretreatment of the membrane.

The calculated values of W with $B = 1$ and eq. wt $= 1100$ are also shown in Fig. 1 for comparison. The water content decreases with increasing alkali concentration and is very low in KOH electrolyte. The prehistory of the membrane has a profound effect on the water content of the mem-

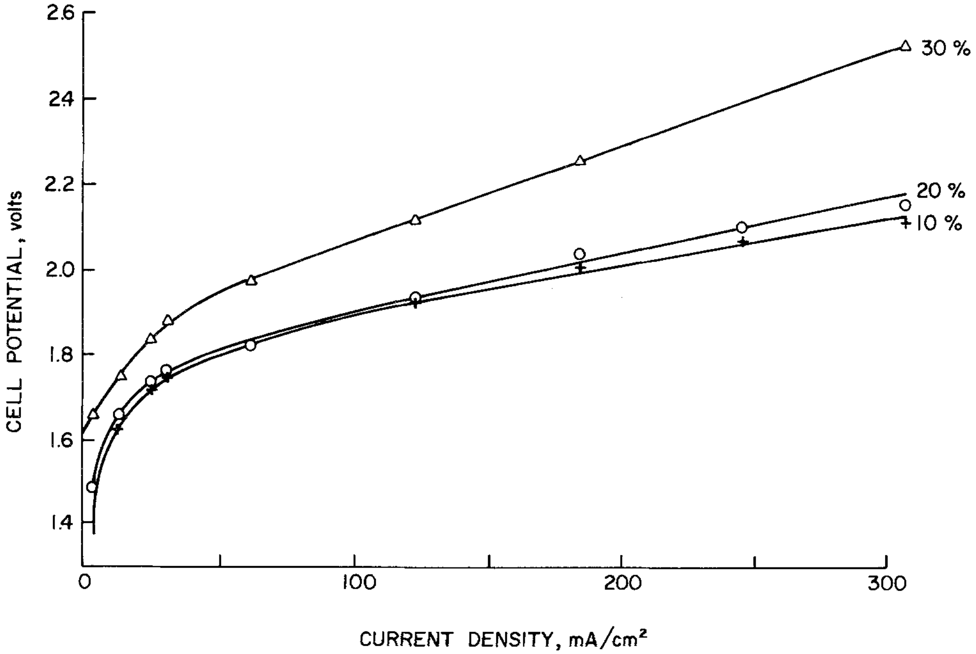


Fig. 3. Cell potential as a function of current density for water electrolysis at several NaOH concentrations at 95° C.

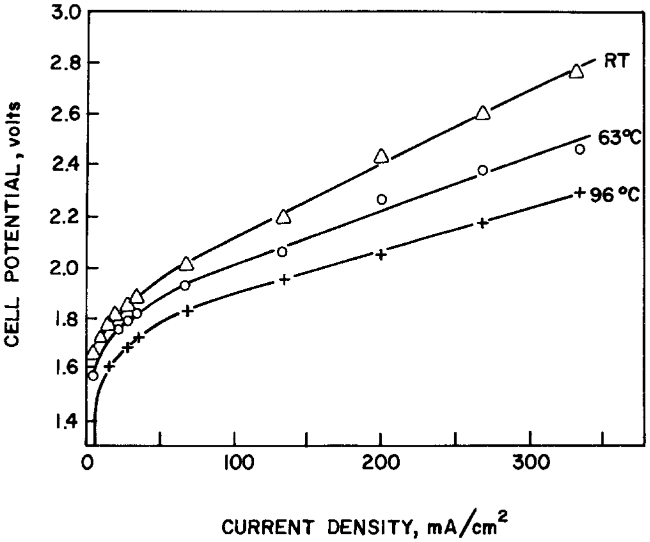


Fig. 4. Cell potential as a function of current density for water electrolysis in 10% KOH at various operating temperatures. Room temperature (RT) is 25° C.

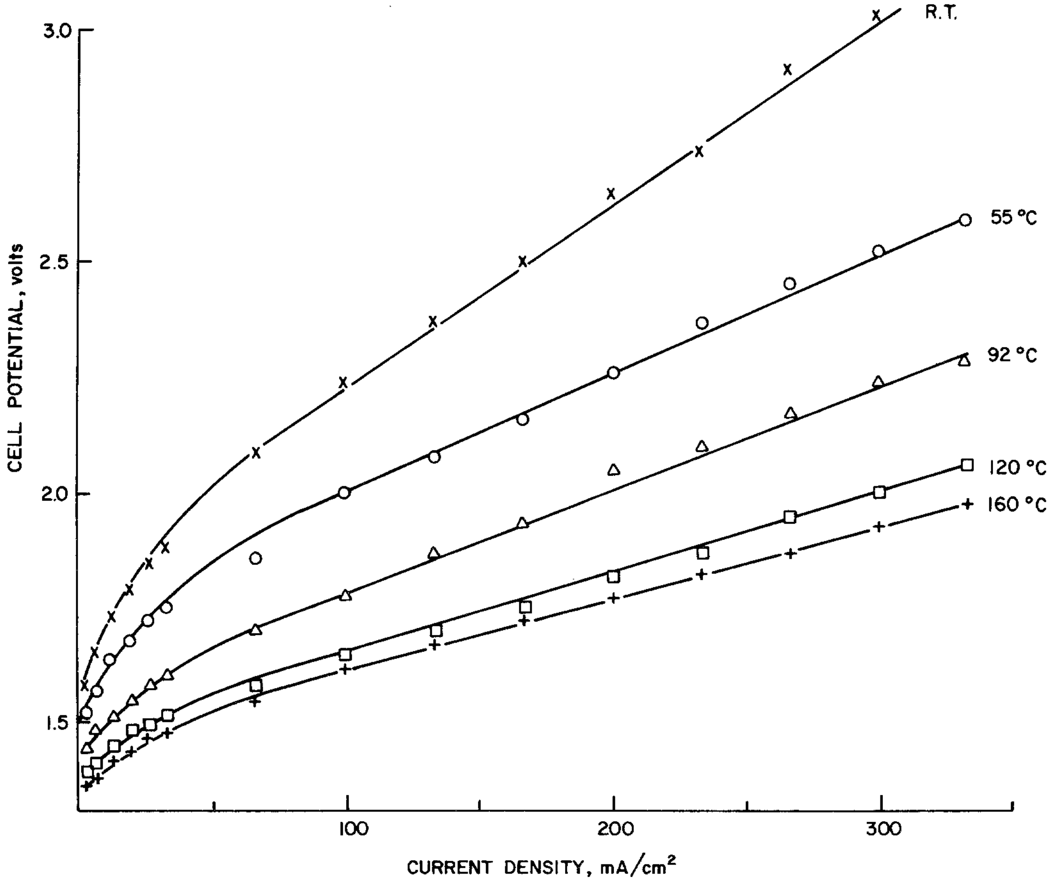


Fig. 5. Cell potential as a function of current density for water electrolysis in 20% NaOH at various operating temperatures.

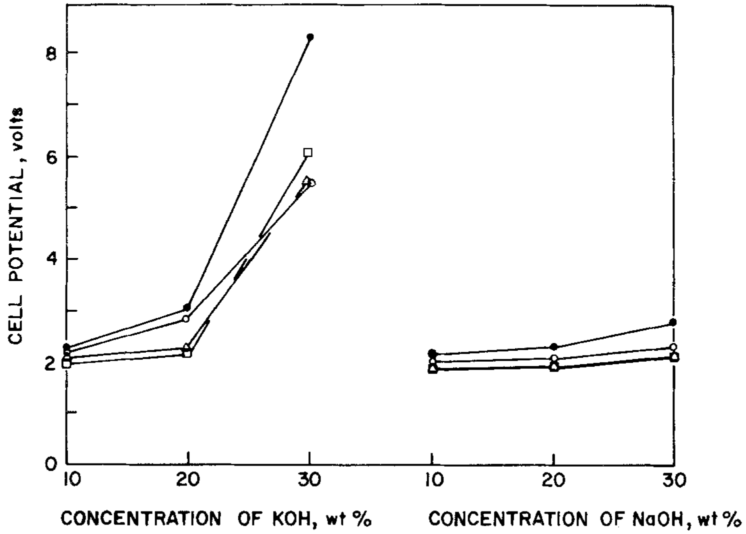


Fig. 6. Cell potential at a current density of 133 mA cm^{-2} for water electrolysis as a function of KOH and NaOH concentrations. (●) 25° C, (□) 54° C, (△) 63° C, (○) 95° C.

brane, and this probably explains the difference between the calculated and experimental results.

Fig. 2 presents the cell voltage as a function of current density for various KOH concentrations at 96° C. It is clear that the cell voltage increases markedly with increasing KOH concentration. Linear voltage–current relationships are observed in all cases at high current densities. Similar data are presented for NaOH electrolyte at 95° C in Fig. 3. The cell potentials are lower in NaOH than in KOH even for higher molar concentrations.

The temperature effect on cell performance in 10% KOH is shown in Fig. 4. The cell voltage decreases at elevated temperature. Again, a linear voltage–current relationship is observed at high current densities. The temperature effect on cell performance in 20% NaOH is shown in Fig. 5. Fig. 6 is a direct comparison of cell potentials in KOH and NaOH electrolytes at a current density of 133 mA cm^{-2}. The superior performance of NaOH electrolytes is quite evident.

Table 1. Cell resistance (Ω cm^2) for water electrolysis at various operating conditions when Nafion-115 is used as the separator

	Cell temperature (° C)			
Electrolyte	25	54	63	95
10% NaOH	2.2	1.5	–	1.0
20% NaOH	3.5	1.8	–	1.4
30% NaOH	9.4	4.7	–	2.2
10% KOH	3.1	–	2.1	1.7
20% KOH	6.5	–	4.2	3.6
30% KOH	44.0	–	24.0	17.0

The cell resistances at various operating conditions are summarized in Table 1. The cell resistances are lower in NaOH than in KOH. The cell resistances with Nafion of two different equivalent weights and thicknesses are presented in Table 2. The cell performance is superior at lower equivalent weight and with thinner membranes.

4. Discussion

In alkaline solution, the reaction at the cathode is:

$$2H_2O + 2e \rightarrow H_2 + 2OH^- \qquad (3)$$

and at the anode, it is:

$$2OH^- \rightarrow \tfrac{1}{2}O_2 + 2e + H_2O \qquad (4)$$

There are three possibilities for the charge-carrier transfer across the Nafion membrane, namely

*Table 2. Cell resistance for water electrolysis at 95° C when various Nafion membranes are used as the separators**

	Eq. wt	*Thickness* (mm)	*Cell resistance* (Ω cm^2)
Nafion-115	1100	0.12	17
Nafion-110	1100	0.25	22
Nafion-120	1200	0.25	46

* The electrolyte is 30% KOH.

Table 3. Nafion membrane and electrolyte conductivities at 25° C; eq. wt = 1100

Electrolyte	*Electrolyte conductivity* (Ω^{-1} cm^{-1})	*Membrane conductivity* (Ω^{-1} cm^{-1})
5% KOH	0.21	0.0017*
20% KOH	0.73	0.0021†
20% NaOH	0.33	0.0053†

* for eq. wt = 1200 (after [7]).

† Calculated by $\sigma = 1.4\sigma_{ex}(1-\theta)^{2.3}$ where σ and σ_{ex} are the membrane and free electrolyte conductivities, respectively, and θ is the volume fraction of the polymer (after [23]).

Table 4. Dependence of Nafion membrane conductivity on boiling in water at various temperatures and pressures, Nafion-125 [24]*

Temperature (° C)	*Pressure* (atm)	*Water content* (wt %)	*Conductivity* (Ω^{-1}cm^{-1} × 10^3)
100	1.0	28.2	0.115
150	4.9	38.8	11.0
150	35.2	86.4	46.0
175	35.2	116.2	71.0
200	703.0	370.0	200.0

* The electrolyte is 40% KOH.

OH^- ion transport from catholyte to anolyte, H^+ ion transport from anolyte to catholyte and alkali metal ion (such as Na^+) transport from anolyte to catholyte. Because of the negligible H^+ ion concentration in alkaline solution and the OH^- ion rejection behaviour of the cation-exchange membrane, the major charge carrier is the alkali metal ion. This is particularly true for high metal ion concentrations. The Donnan exclusion is increased by the lower water content of the membrane at high concentrations. However, in contrast to the case of a chloro-alkali cell, OH^- and H^+ transportation across the membrane does not affect the current efficiency of a water electrolyser.

The linear voltage–current relationship indicates that the cell overpotential is mainly due to ohmic losses. This is attributed to the membrane resistance, since it is two orders of magnitude higher than that of the free electrolyte, as shown in Table 3.

The membrane conductivity and cell performance are strongly related to the water content of the membrane [13, 22, 23]. The cell voltage decreases with decreasing alkaline concentration. Despite the fact that the conductivity of KOH is twice that of NaOH, the membrane conductivity is higher in NaOH than in KOH. This is primarily due to the extremely low water content when the membrane is in contact with KOH, as shown in Fig. 1. Since the conductivity of LiOH is about the same as that of NaOH, and the factor A in Equation 1 for Li^+ is larger than for Na^+, it is likely that LiOH will be an even better electrolyte for an alkaline ion-exchange membrane water electrolyser.

The cell performance improves with lower eq. wt Nafion, and with thinner membranes, again confirming that the membrane conductivity strongly determines the cell efficiency. Since the polymers with eq. wt below 1000 become too weak for use in the swollen form and may be soluble [24], the present choice of Nafion for an alkaline water electrolyser is one with an eq. wt of 1000. The decrease in cell voltage with increasing temperature is attributable to not only decreasing the membrane resistance, but also to increasing the kinetics of the electrode reactions, especially that of oxygen evolution.

It has been reported [24] that the membrane conductivity can be increased considerably by soaking the membrane in water at temperatures above 100° C and elevated pressure, as shown in Table 4. The membrane is fully swollen by such pretreatments. Even though the diffusion of hydrogen and oxygen through the membrane increases with increasing water content of the membrane, the resultant coulombic loss is insignificant in comparison with the gain in membrane conductivity [13, 22]. Furthermore, since hydroxyl ion exclusion is not a requirement in this application, the membranes could be tailored to have a high water content. It is very likely that, by optimizing the Nafion membrane characteristics, the cell voltage at 100° C for an alkaline water electrolyser with non-noble metal electrocatalysts could be reduced to less than 1.8 V at current density of 0.5 A cm^{-2}, i.e. approaching performance of characteristics solid polymer electrolyte water electrolysers, which use noble metal electrocatalysts.

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References

[1] S. Srinivasan and F. J. Salzano, *Int. J. Hydrogen Energy* **2** (1977) 53.

[2] P. W. T. Lu and S. Srinivasan, *J. Appl. Electrochem.* 9 (1979) 269.

[3] M. H. Miles, G. Kissel, P. W. T. Lu and S. Srinivasan, *J. Electrochem. Soc.* **123** (1976) 332.

[4] A. J. Appleby and G. Crepy, *Proceedings of the Symposium on Electrode Materials and Processes for Energy Conversion and Storage,* (edited by J. D. E. McIntyre, S. Srinivasan and F. G. Will) The Electrochemical Society, Princeton, New Jersey (1977) p. 382.

[5] M. J. Braun, *ibid,* p. 375.

[6] H. Vandenborre and R. Leysen, *Electrochim. Acta* **23** (1978) 803.

[7] H. Vandenborre and L. H. Baetsle, 'Development and Parametric Testing of Water Electrolysis Cells for Hydrogen Production Based on Inorganic-Membrane-Electrolyte Technology', Annual Report, Contract Number 342-77-9-EHB, December (1978).

[8] M. Klein, *Proceedings of IECEC,* San Diego, California, September (1972) p. 79 (Paper no. 729017).

[9] S. Srinivasan, P. W. T. Lu, G. Kissel, F. Kulesa and J. Orehotsky, DOE Chemical/Hydrogen Energy Systems Contractors Review, November (1978).

[10] J. H. Russell, *Proceedings of Symposium on Industrial Water Electrolysis,* (edited by S. Srinivasan, F. J. Slazano and A. Landgrebe) The Electrochemical Society, Princeton, New Jersey (1978) p. 77.

[11] S. Stucki and A. Menth, *ibid,* p. 180.

[12] R. S. Yeo, unpublished results.

[13] A. B. LaConti, A. R. Fragola and J. R. Boyack, *Proceedings of the Symposium on Electrode Materials and Processes for Energy Conversion and Storage,* (edited by J. D. E. McIntyre, S. Srinivasan and F. G. Will), The Electrochemical Society, Princeton, New Jersey (1977) p. 354.

[14] E. J. Peters, D. R. Pulver and E. H. Price, 'Extended Abstracts', Abstract no. 443, Vol. 77-2, The Electrochemical Society, Princeton, New Jersey (1977) p. 1149.

[15] C. J. Hora and D. E. Maloney, *ibid,* Abstract no. 441, p. 1145.

[16] H. Ukihashi, *Polymer Preprints* **20-1** (1979) 195.

[17] R. S. Yeo and A. Eisenberg, *J. Appl. Polym. Sci.* **21** (1977) 875.

[18] D. J. Vaughan, *du Pont Innovation* 4 (1973) 10.

[19] R. S. Yeo, Ph.D. Thesis, McGill University (1976).

[20] W. G. Grot, G. E. Munn and P. M. Walmsley, 'Extended Abstracts' Abstract no. 154, Vol. 72-1, The Electrochemical Society, Princeton, New Jersey (1972) p. 394.

[21] G. E. Munn, *ibid,* Abstract no. 436, Vol. 77-2, The Electrochemical Society, Princeton, New Jersey (1977) p. 1135.

[22] R. S. Yeo and J. McBreen, *J. Electrochem. Soc.* **126** (1979) 1682.

[23] R. S. Yeo and D-T. Chin, *ibid* **127** (1980) 549.

[24] R. L. Coalson and W. G. Grot, US Patent 3 684 747 (1972).