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SHORT COMMUNICATION

Bubble effects on ion exchange membranes — an electrochemical study

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Nomenclature

C'_e, C''_e, C'_m, C''_m	supersaturation of dissolved gas
D, D_b	diameter of bubble
I, I_f	current
I(mean)	the mean current
I(max)	the current that passes when no bubbles are present, i.e., the current at the point of nucleation
S	area
S(mean)	the area of the membrane not obscured by bubbles
S(max)	90 mm^2 (the chosen membrane area)
Greek characters	
σ_{s-l}	surface tension at the solid liquid interface
ρ_L, ρ_G	density of liquid and gas, respectively

1. Introduction

Bubble attachment on ion exchange membranes during electrolysis in chlor–alkali cells is of great concern because it has a marked influence on the cell voltage. Du Pont and the Asahi Glass Corporation have developed new membranes, Nafion 961 and Flemion 775, respectively. By introducing inorganic compounds onto the membrane surface they have been made hydrophilic to such a degree that the bubble effect can be ignored even when the cathode and the anode touch the membrane during electrolysis. Thus, such an advanced membrane gap cell (MGC) has been developed that the membrane can be prevented from shrinkage and vibration, and the cell voltage is reduced. Although gas evolution on electrodes has been widely studied (e.g. [1–5]), little information exists on the bubble effect on ion exchange membranes. Bergner [6] has proposed a simple method to ascertain whether there is serious bubble accumulation on a membrane surface during electrolysis, or whether the membrane is suitable for MGC technology, according to whether the cell voltage decreases continuously as the distance between the membrane and the cathode is decreased to zero. Here, a new method to investigate the bubble effect on membranes during electrolysis is reported which uses conventional electrochemical linear sweep voltametry (LSV) and a four electrode system.

2. Theory

Consider the relationship among the bubbles occupying an area of membrane, the free membrane area and the membrane resistance. The bubble effect should be measurable in a U–I experiment. Unfortunately the marked overlap of bubbles during most electrode processes makes the experiment difficult, but in the case of a single bubble on a membrane surface, information should be accesible. According to nucleation theory [7], the nucleation rate of bubbles at the electrode is determined by C'_e, the supersaturation of dissolved gas at the interface between electrode and the liquid. By analogy we can say that the nucleation rate at the membrane is governed by C'_m. The bubble growth rate is however determined by C''_e and C''_m at the electrode and membrane respectively, where the supersaturation is that of the dissolved gas at the bubble/liquid interface of a bubble with radius R. It is obvious that the nucleation and growth of bubbles on an electrode is different from that on a membrane because of the different dissolved gas concentration profiles in the two situations. From Fig. 1, it can be seen that, $C'_e > C''_e$, and $C'_m < C''_m$. Thus on a membrane, the nucleation of bubbles is more difficult but their growth is easier than on an electrode.

On a liquid/solid interface, the more hydrophobic the solid, the greater the surface tension, σ_{s-l}, and the larger the bubbles grow before detachment. Janssen [8] reported bubble diameters as large as 2.4 mm on a PTEE coated nickel electrode, 48 times larger than on a metal or graphite electrode ($d = 50\,\mu$m) [9]. This phenomenon also favours the formation of large bubbles on the surface of perfluorocarbon ion exchange membranes. It is possible to observe the influence on

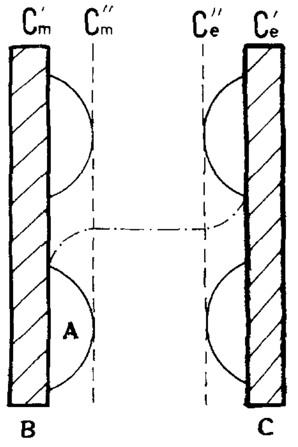

Fig. 1. Dissolved gas concentration profile between membrane and electrode: (–·–·–) gas concentration profile, (– – – –) bubble layer limit, A. bubble, B. membrane, C. electrode.

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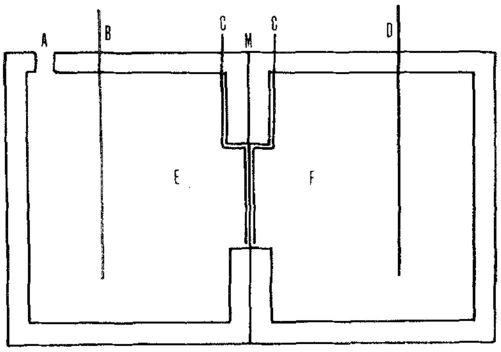

Fig. 2. Cell configuration: A. to vacuum pump, B. Ru–Ti net, C. Pt wire, D. stainless steel net, E. anode compartment, F. cathode compartment, M. membrane.

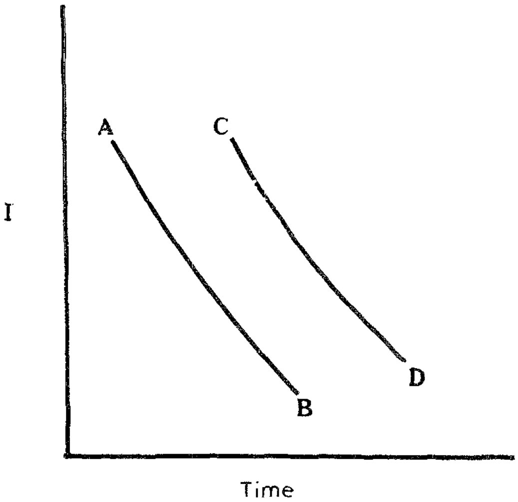

Fig. 3. Bubble effect on the I–t curve (schematic): A, C, nucleation of bubble, A–B, C–D, bubble growth, membrane area decrease, I, decrease, B, D, detachment of bubble.

the U–I curve of the formation of a single bubble if an appropriate membrane area and suitable experimental conditions are chosen, e.g. sweep rate.

3. Experimental details

A small model cell was made, with a cathode of stainless steel net and an anode of Ru–Ti net (Fig. 2). The two reference electrodes were platinum wires. Nafion 901 and Flemion 775 were obtained from Du Pont and Asahi Glass Corporation, respectively. The potentiostat was an EG&G Parc M273. An IBM computer was used to control the potentiostat and for the data acquisition. The cathode solution was NaOH (G.R., doubly distilled water) and the anode solution was saturated NaCl (315 g dm^{-3}, pH 2–3, Ca^{2+}, Mg^{2+} content below 50 p.p.b.). During the experiment, the anode compartment was connected to a vacuum pump to give a 5–20 mm water gauge negative pressure, which both ensured that the membrane remained in position and was the key to isolate the hydrogen bubble effect from the interference of chlorine bubbles. If the negative pressure of the anode compartment were not used, each undulation of the U–I curve would contain deviations reflecting chlorine bubble interference. In addition, the greater solubility of chlorine and the greater hydrophilicity of the sulphonated surface of the membrane facing the anode minimize the chlorine bubble effect.

4. Discussion

4.1. *Explanation of the measuring curve*

In the system of double reference electrodes shown in Fig. 2

$$U = U_{\mathrm{RNaCl}} - U_{\mathrm{RNaOH}} = IR_s + IR_m + U_0 \qquad (1)$$

Here U does not include the decomposition voltage and overvoltage. R_m is the membrane resistance including the resistance caused by bubble formation on the membrane, R_s is the solution resistance and U_0 is given by

$$U_0 = (U_{\mathrm{RNaCl}} - U_{\mathrm{RNaOH}})_{I=0} \qquad (2)$$

U_0 was determined by measuring the potential difference between the two reference electrodes at zero current ($I = 0$). In this system U_0 is approximately 0.5 V, hence the sweep starts at this voltage. Since $R_m \geqslant R_s$, it follows that

$$\Delta U = \Delta(U_{\mathrm{RNaCl}} - U_{\mathrm{RNaOH}}) = \Delta IR_m \qquad (3)$$

In LSV experiments it is customary to record the current as a function of potential, which is equivalent to recording current against time. Equation 3 shows that as U changes linearly with time, the current measured also changes linearly. But when bubbles form, R_m is no longer constant because the membrane area occupied by bubbles changes as they form, grow and detach. Under these conditions the U–I curve is not a straight line, but shows undulations reflecting the bubble influence. From the schematic Fig. 3, the bubble process is seen to affect the I–t (and hence I–U) curve.

In Fig. 4, Nafion 901, the range of undulations on the U–I curve is large, indicating that hydrogen bubbles grow to a large size on the hydrophobic surface of the perfluorocarboxylic layer, and some bubble coalescence takes place. In the case of Flemion 775, which has a modified porous hydrophilic layer on the fluorocarboxylic surface, the range of these is smaller (Fig. 5). The difference in the range of undulation gives the criterion for differentiating the two kinds of membrane and provides a simple, fast method to identify whether the test membrane is suitable for MGC electrolysis. It also indicates that on the modified surface of a MGC membrane, bubbles leave readily before they become large.

From LSV, it is also possible to obtain information of the bubble process at various current densities. In Fig. 4, there is a peak in the U–I curve. According to [10–12], this phenomenon may be accounted for by the formation of a gas film when the gas flux has reached a sufficiently high value. This indicates that when Nafion 901 is used for MGC technology, it may cause a marked bubble effect and lead to a high cell voltage. In the present experiment, the peak can only be observed when Nafion 901 is used in 30% NaOH.

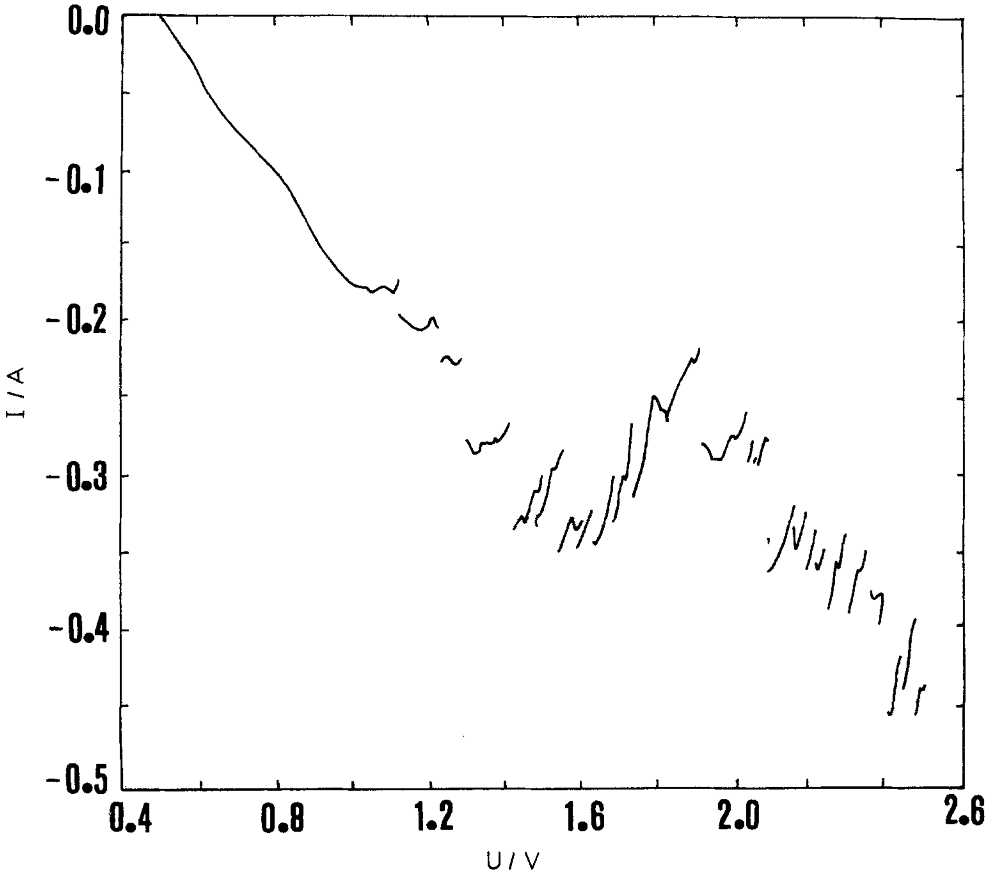

Fig. 4. *U–I* curve for Nafion 901(MGC), 30% NaOH(wt. %), sweep rate: 100 mV s^{-1}, 70°C.

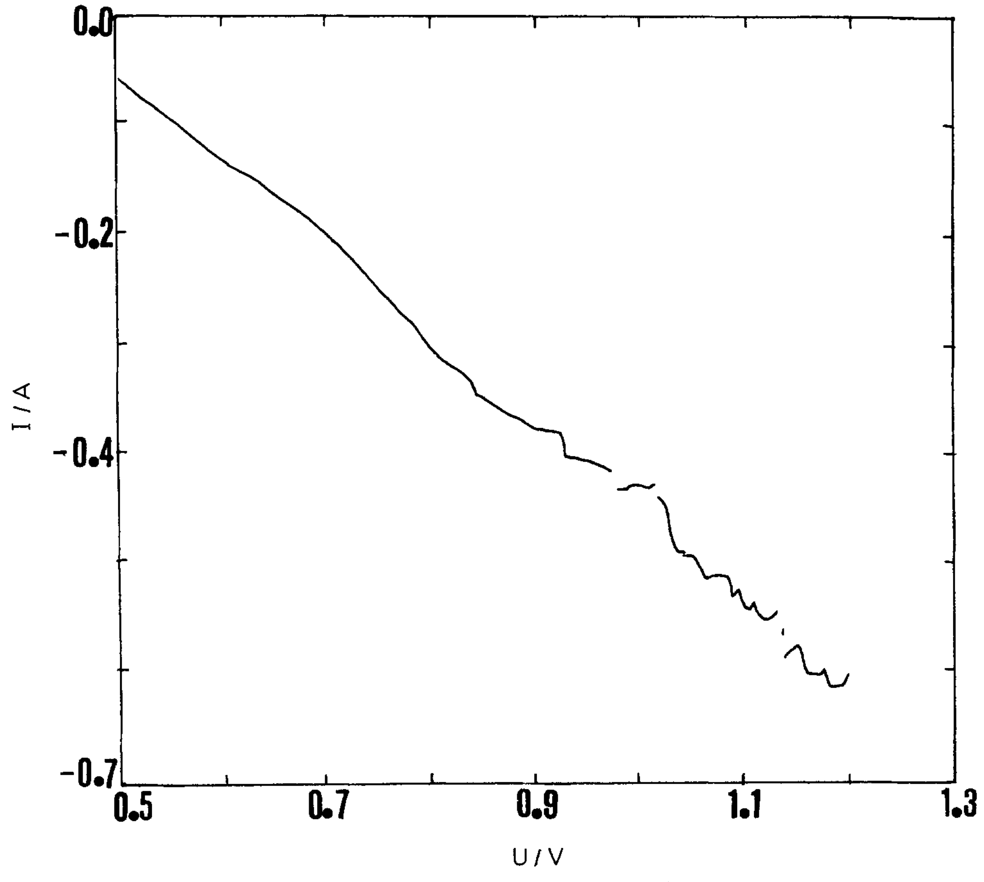

Fig. 5. *U–I* curve for Flemion 775(MGC), 30% NaOH(wt. %), sweep rate: 100 mV s^{-1}, 70°C.

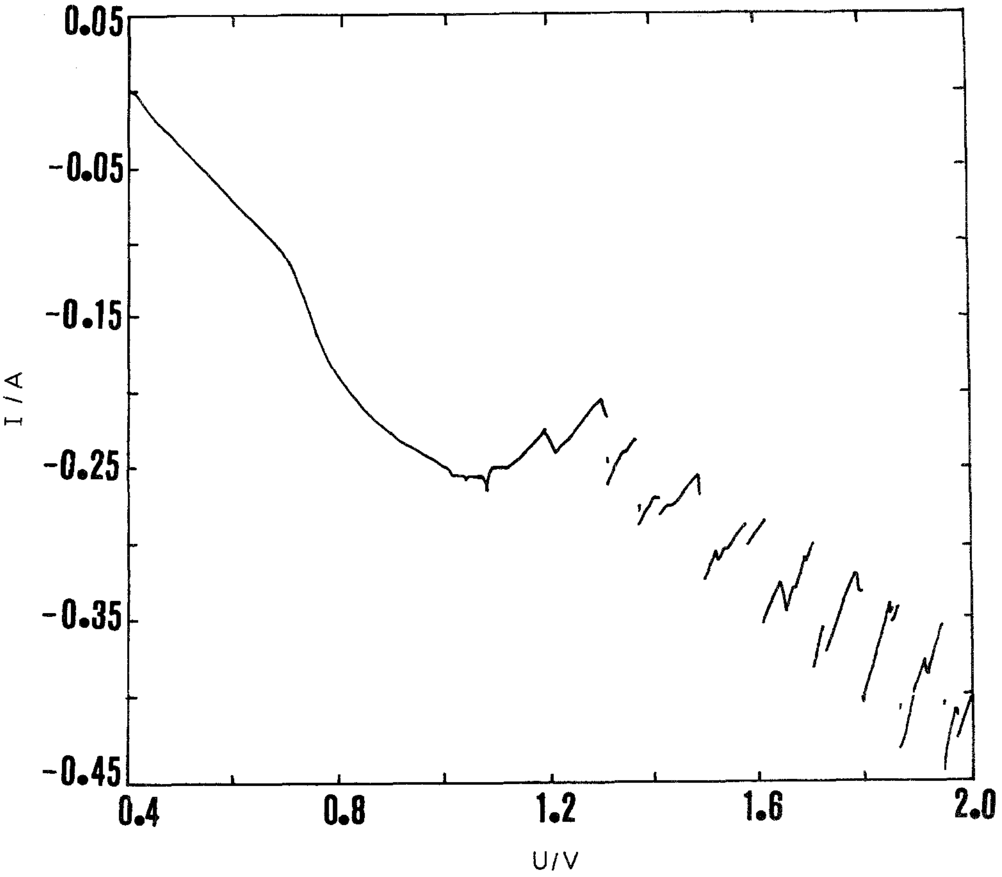

Fig. 6. U–I curve for Nafion 901 (2 mm gap between membrane and cathode), 30% NaOH(wt. %), sweep rate: 100 mV s^{-1}, 70°C.

This is consistent with the fact that the bubble effect is far more serious in concentrated NaOH solution.

In a membrane modification process, a key aim is to introduce a suitable quantity of inorganic modifying compound. If this is insufficient, the bubble effect remains large; however, if it is too great, the membrane resistance is increased. Both effects lead to an increase in cell voltage. It is difficult for other techniques to discriminate between the above cases, and hence the cause of cell voltage increase, but this method can do so. In the former situation, the U–I curve carries greater undulations; whereas in the latter, the whole U–I curve moves upward (I decreases). Hence, this technique is useful in membrane modification processes.

4.2. *Estimating the hydrogen bubble diameters*

If it is assumed that a bubble no longer occupies the membrane surface area when it leaves then according to [13]

$$R \propto 1/S \qquad (4)$$

In a certain range of U

$$\frac{I(\text{mean})}{I(\text{max})} = \frac{S(\text{mean})}{S(\text{max})} \qquad (5)$$

when $(U_{\text{RNaCl}} - U_{\text{RNaOH}})$ = a constant. It can be concluded that

$$D_b = 1.07\sqrt{I(\text{max})/I(\text{mean})} \qquad (6)$$

The formation of a bubble not only increases R_m but also changes the current distribution in its vicinity. Sides [13] presented an analytical solution and used I_f against distance data, where I_f represents the current density far from the bubble. Thus, Equation 6 should be corrected by a factor of $1/(1 + 0.3)$ calculated from [13] and becomes

$$D_b = 0.82\sqrt{I(\text{max})/I(\text{mean})} \qquad (7)$$

Since the diameter of a bubble depends on the current density, D_b has an average value. D_b as calculated from Equation 7 has the same order of magnitude as that in [8]. Tables 1 and 2 give values of D_b under various conditions. D_b decreases as the concen-

Table 1. Bubble diameter on Flemion 775(MGC)

Concentration of NaOH (wt %)	10%	20%	30%
$\bar{D}_b$/cm	0.22	0.16	0.15

Table 2. Bubble diameter on Nafion 901(MGC)

Concentration of NaOH (wt %)	10%	20%	30%
$\bar{D}_b$/cm	0.30	0.26	0.25

tration of NaOH increases. According to [14]

$$D_b \propto 1/[g(\rho_L - \rho_G)] \qquad (8)$$

When the concentration of NaOH increases ρ_L increases, so that there is a consequent decrease in D_b.

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