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*Effect of operational parameters on gas evolution in electrolyte bulk: possibilities for lowering interelectrode resistance**

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Two facts form the basis of the present investigation. Firstly: generally, only a fraction of the total quantity of dissolved gas generated at a gas-evolving electrode is evolved in gaseous form directly at the electrode. Secondly: commonly, only a fraction of the complementary amount of dissolved gas reaching the bulk of electrolyte is evolved in the interelectrode gap. This paper analyses the conditions in which a major portion of the total amount of dissolved gas generated at the electrode remains in dissolved form when being withdrawn from the interelectrode gap. Increasing this amount results in lowering the effective resistivity of the gas–electrolyte dispersion.

Nomenclature

$A_{\rm B}$	gas–electrolyte interfacial area in bulk ($\rm m^2$)
c	gas concentration in electrolyte bulk ($\rm mol\ m^{-3}$)
d	mean diameter of gas bubbles in bulk (m)
$f_{\rm G}$	gas evolution efficiency at electrode (–)
F	Faraday constant, $F = 96\,487\ \rm A\ s\ mol^{-1}$
H	length of interelectrode gap in flow direction (m)
I	current of generation of dissolved gas (A)
j	current density ($\rm A\ m^{-2}$)
k	liquid mass transfer coefficient ($\rm m\ s^{-1}$)
K_1	dimensionless parameter, Equation 5
K_2	dimensionless parameter, Equation 6
K_3	dimensionless parameter, Equation 7
n	charge number of the electrode reaction (–)
$N_{\rm E}^{\square}$	flux to the bulk of liquid ($\rm mol\ s^{-1}$)
$N_{\rm F}^{\square}$	flux of gas evolved in bulk ($\rm mol\ s^{-1}$)
$N_{\rm G}^{\square}$	flux of gas evolved at the electrode ($\rm mol\ s^{-1}$)
$N_{\rm O}^{\square}$	flux of dissolved gas removed from the interelectrode gap ($\rm mol\ s^{-1}$)
p	pressure ($\rm kg\ m^{-1}\ s^{-2}$)
R	gas constant, $R = 8.314\ \rm kg\ m^2\ s^{-2}\ mol^{-1}\ K^{-1}$
T	temperature (K)
v_0	electrolyte velocity at cell entrance ($\rm m\ s^{-1}$)
$\dot{V}_{\rm L}$	volumetric flow rate of electrolyte ($\rm m^3\ s^{-1}$)
W	width of flow channel (m)
x	coordinate in flow direction (m)
Y	electrode-membrane clearance (m)
ν	stoichiometric number (–)
ϕ	volumetric gas fraction (–)

Subscripts

H	exit cell
o	entrance cell
s	saturation

1. Introduction

The problem to be treated here may be elucidated by a survey of recent findings. Commonly, the rate of gas evolution at an electrode is simply linked to the current density of the particular reaction. However, a direct quantitative link according to Faraday's law involves an inadmissible simplification. In fact, there are several additional parameters which affect the rate of gas evolution

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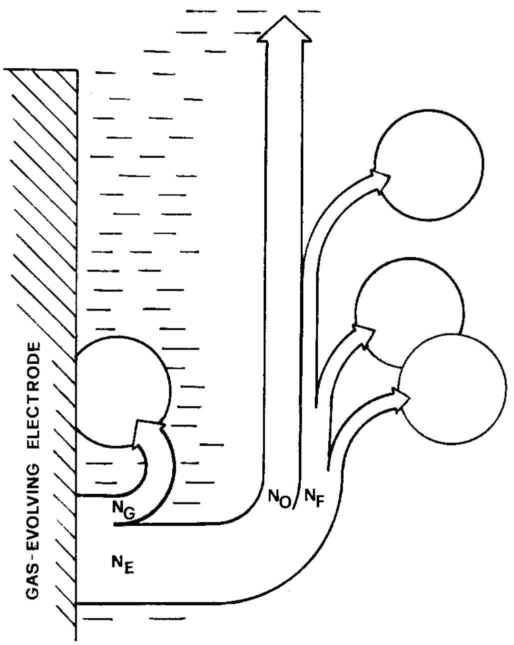

Fig. 1. Flow of dissolved gas to adhering bubble, N_G, and to freely moving bubble, N_F, with phase transformation. Flow of dissolved gas, N_O, out of the interelectrode gap.

in electrochemical reactors. (The term 'gas evolution' as used here and in previous papers by the authors is restricted to the physical process of phase transformation of dissolved substance from the liquid to the gaseous phase [1]. The meaning of the term is explicitly restricted to make a distinction from the process of the electrochemical and chemical formation of a substance to be subsequently transformed to the gaseous phase, since this latter process, although in the literature often termed gas evolution, is not characteristic of the gas phase. In this respect an electrode never generates 'gas'.) As shown, [2, 3] gas evolution at electrodes is also governed by the material and state of the electrode and by the properties and flow condition of the electrolyte. Not only in the range of very low values of current density but in the total industrial range of nucleate gas evolution, the rate of gas evolution at electrodes is significantly lower than that to be expected from calculations of the current density on the basis of Faraday's law. Uncoupling the gas evolution rate from the current density became necessary since it was evident that a substantial proportion of the dissolved gas is transported from the electrode to the bulk and does not therefore contribute to gas evolution at the electrode (Fig. 1).

In addition to the conditions directly at the electrode, represented particularly by the electrode–electrolyte interfacial concentration of electrolyte and the concentration governing bubble growth, and to obtain a closer insight into gas evolution in the interelectrode gap as a whole, we must consider the bulk of the electrolyte. Since some gas is transported from the electrode in dissolved form the bulk concentration increases and builds up a supersaturation (except where electrolyte enters the cell heavily undersaturated with gas). Bulk supersaturation is unstable since the freely moving bubbles continue to grow in the bulk owing to desorption of dissolved gas. Strictly speaking, this type of gas formation in the bulk is always incomplete since it requires a concentration difference between the bulk and the bubble–electrolyte interface, and it also takes time. The bulk of electrolyte will therefore always be supersaturated to a certain extent when leaving the cell. This finding has been confirmed by recent analysis [4] and raises an interesting engineering problem.

The question is: under what conditions is a substantial proportion of the total quantity of dissolved gas formed at the electrode not evolved in the interelectrode gap either at the electrode or in bulk, but remains in dissolved form when it is carried off from the cell? Ohmic resistance due to gas bubbles contained in the interelectrode gap is diminished the larger the amount of dissolved gas that remains untransformed to the gaseous stage inside the cell. The amount of substance maintained in dissolved form when withdrawn from the cell acts favourably on the terminal voltage. It is the object of the present analysis to investigate the conditions of removal of the dissolved gas, assess the effect of the decisive operational parameters and provide the answer to this question for industrially operated electrochemical reactors.

2. Discussion of relevant parameters

The relevant operational parameters which allow a quantiative treatment of the problem can be found from the consideration of a cell as shown

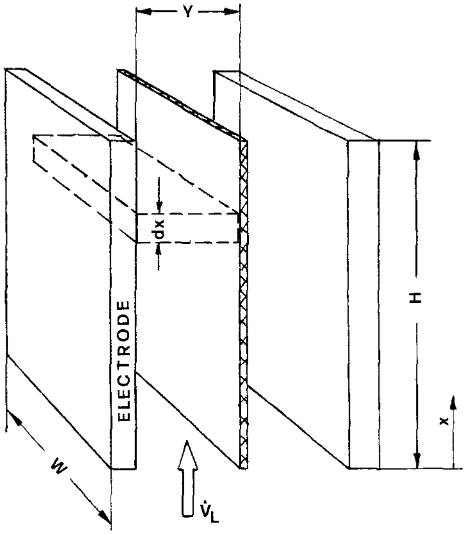

Fig. 2. Geometry of cell with gas-evolving electrode(s) and upward electrolyte flow.

in Fig. 2. The interelectrode gap is formed of a planar, non-perforated electrode and a parallel membrane. Electrolyte flows through the gap and carries off gas bubbles together with dissolved gas. Such systems are usual in industrial electrochemical reactors and represent a more problematic condition than perforated electrodes where gas release is usually facilitated.

A system similar to that shown in Fig. 2 was studied on the basis of a model used to obtain an answer to the question as to whether the bulk is in fact supersaturated and if so to what extent [4]. The amount of substance (e.g. hydrogen) transported in dissolved form from the electrode is given in Equation 1. This tacitly assumes tht the current density of the hydrogen-generating reaction is unity and that no hydrogen is lost through diffusion in or reaction with the electrode material, and that the total amount of substance generated enters the electrolyte in dissolved form.

$$\mathrm{d}N_E^{\square} = (1 - f_G)\frac{jW\mathrm{d}x}{(n/\nu)F} \tag{1}$$

The amount desorbed from the bulk inside the interelectrode gap is given by

$$\mathrm{d}N_F^{\square} = k\,\mathrm{d}A_B(c - c_s) \tag{2}$$

and the amount carried off from the gap in dissolved form (Fig. 1) by

$$\mathrm{d}N_O^{\square} = \dot{V}_L\mathrm{d}c \tag{3}$$

A balance of these amounts, together with some assumptions discussed in detail in reference 4 and not repeated here, yields an expression

$$\frac{1}{K_1} = 1 + \frac{3}{K_2}\left\{1 - 2\left[1 - \frac{\ln(1 + K_3)}{K_3}\right] \times \left[\frac{1}{K_3} - c_s\frac{c_0/c_s - 1}{c_H - c_0}\right]\right\} \tag{4}$$

The dimensionless groups denote

$$K_1 = \frac{(n/\nu)F(c_H - c_0)v_0}{j(1 - f_G)}\frac{Y}{H} \tag{5}$$

$$K_2 = \frac{v_0 d}{kH} \tag{6}$$

$$K_3 = \frac{RT}{p}\frac{j}{(n/\nu)Fv_0}\frac{H}{Y}\left[1 - K_1(1 - f_G)\right] \tag{7}$$

where the liquid velocity at the entrance of the interelectrode gap, $x = 0$, is

$$v_0 = \frac{\dot{V}_L}{WY} \tag{8}$$

The gas evolution efficiency f_G in Equation 1 represents the flux of dissolved gas evolved in the form of bubbles adhering to the electrode, divided by the flux of dissolved gas formed at the electrode [2],

$$f_G = \frac{\mathrm{d}N_G^{\square}}{[jW/(n/\nu)F]\,\mathrm{d}x} \tag{9}$$

By definition, the total flux $N_E^{\square}$ of dissolved gas transported from the electrode to the bulk is divided into a part $N_F^{\square}$ evolved in bulk within the interelectrode gap and a part $N_O^{\square}$ carried off in dissolved form out of the cell (Fig. 1).

$$N_E^{\square} = N_F^{\square} + N_O^{\square} \tag{10}$$

For the present purpose, it is useful to define a flux ratio representing the fraction which is carried off from the interelectrode space without being evolved as gas:

$$\frac{N_O^{\square}}{N_E^{\square}} = \frac{\int_{c_0}^{c_H}\dot{V}_L\mathrm{d}c}{\int_0^H(1 - f_G)\frac{jW}{(n/\nu)F}\mathrm{d}x} \tag{11}$$

This ratio Equation 11 represents the fraction of dissolved gas in bulk which is not transformed to the gaseous phase in the interelectrode gap.

Any increase in this ratio diminishes the rate of gas evolution within the cell and has a favourable effect on the ohmic interelectrode resistance.

Assuming, for simplicity's sake, a linear increase of the bulk concentration from the entrance to the exit side of the cell,

$$\mathrm{d}c = (c_\mathrm{H} - c_0)\mathrm{d}x/H \tag{12}$$

and further assuming constant current density ($\mathrm{d}j/\mathrm{d}x = 0$) and constant gas evolution efficiency ($\mathrm{d}f_\mathrm{G}/\mathrm{d}x = 0$), we obtain after integration of Equation 11

$$\frac{N_\mathrm{O}^\square}{N_\mathrm{E}^\square} = \frac{\dot{V}_\mathrm{L}(c_\mathrm{H} - c_0)}{I(1 - f_\mathrm{G})/[(n/\nu)F]} = \frac{(n/\nu)F(c_\mathrm{H} - c_0)v_0}{j(1 - f_\mathrm{G})} \times \frac{Y}{H} \tag{13}$$

Comparison of Equation 13 with 5 shows that the ratio coincides with the parameter K_1 obtained earlier.

$$\frac{N_\mathrm{O}^\square}{N_\mathrm{E}^\square} = K_1 \tag{14}$$

Thus, Equation 5 is the required expression which contains all parameters relevant to the present problem. K_1 is determined by the system of Equations 4, 6 and 7 shown in Fig. 3 for the special case $c_0/c_\mathrm{s} = 1$, i.e. for an electrolyte saturated with dissolved gas at the entrance to the interelectrode gap. To linearize the lines a logarithmic scale was chosen for the ordinate for the value $K_1/(1 - K_1) = N_\mathrm{O}^\square/N_\mathrm{F}^\square$.

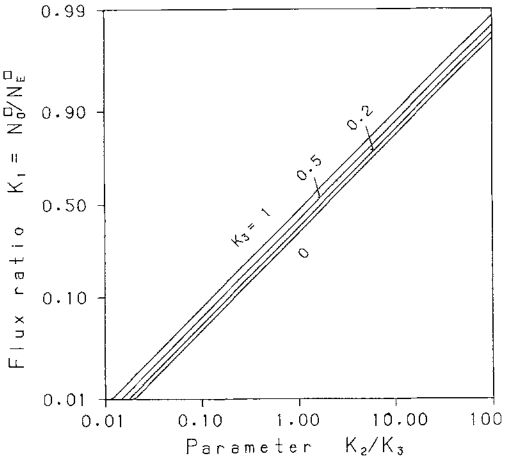

Fig. 3. The fraction K_1 of dissolved gas in bulk remaining in dissolved form at electrolyte outlet relative to parameter K_2/K_3 at various values of parameter K_3. Data from Equation 4 for saturated electrolyte at entrance, $c_0 = c_\mathrm{S}$.

A value $K_1 = 0$ would mean that no gas is carried off from the cell in dissolved form. The electrolyte at the outlet is saturated (or undersaturated). On the other hand, $K_1 = 1$ represents the case of zero desorption in bulk. The total amount of dissolved gas transferred from the electrode to the bulk is transformed into the gaseous phase before it leaves the cell. Both these extreme cases are unrealistic, i.e.:

$$0 < K_1 < 1 \tag{15}$$

3. The velocity–pressure–current system

Series extension of the logarithm in Equation 4 for the special case of $c_0 = c_\mathrm{s}$ results in

$$\frac{1}{K_1} = 1 + 6\frac{K_3}{K_2}\sum_{m=3}^{\infty}\frac{(-K_3)^{m-3}}{m} = 1 + 2\frac{K_3}{K_2} \times (1 - \tfrac{3}{4}K_3 + \tfrac{3}{5}K_3^2 - \ldots) \tag{16}$$

where $K_3 \leqslant 1$. As shown earlier [4], the parameter K_3 is the ratio of the flow rates of gas at the cell exit and of electrolyte (assuming zero slip between the two fluid phases).

$$K_3 = \frac{\dot{V}_\mathrm{G,H}}{\dot{V}_\mathrm{L}} \tag{17}$$

Since in commercial cells the gas fraction at the electrolyte outlet is maintained at low values for the sake of low interelectrode resistance, the parameter K_3 is generally much smaller than unity and the effect of the quantities in brackets in Equation 16 is small. It will be seen from Equation 16 that in this case the flux ratio K_1 is mainly controlled by the dimensionless ratio

$$\frac{K_2}{K_3} = \frac{v_0^2 p}{j}\,\frac{(n/\nu)FYd}{RTH^2k}\,\frac{1}{1 - K_1(1 - f_\mathrm{G})} \tag{18}$$

This means that for any given cell geometry, temperature and type of evolved gas, the fraction K_1 of dissolved gas in the bulk which remains in dissolved form until the electrolyte leaves the cell is predominantly governed by the dimensional group $(v_0^2 p/j)$.

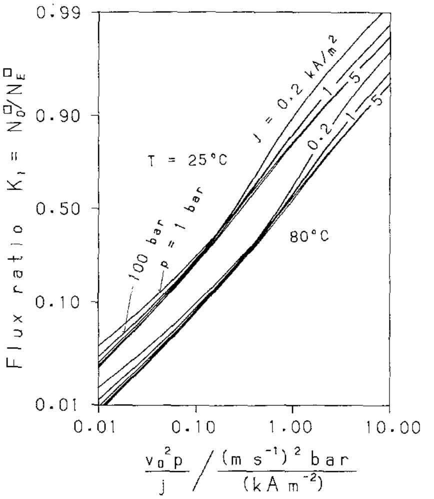

Fig. 4. The flux ratio K_1 relative to the relevant dimensional group $v_0^2 p/j$. Hydrogen evolution at 25 and 80° C, pressure $p = 1$ and 100 bar, current density $j = 200$, 1000, and 5000 A m^{-2}, saturated electrolyte at entrance.

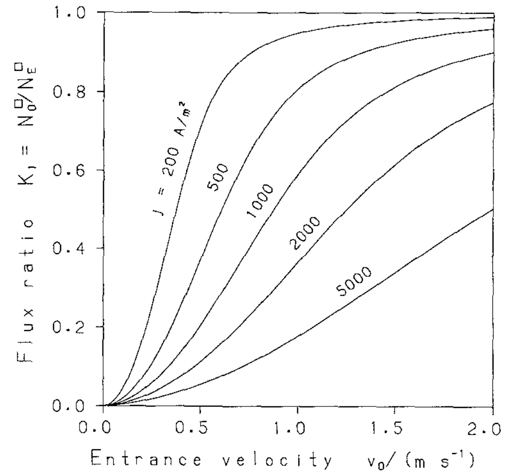

Fig. 5. Effect of entrance velocity v_0 of electrolyte and current density j on the flux ratio K_1. Hydrogen evolution at $p = 1$ bar and $T = 80°$ C, saturated electrolyte at entrance.

In order to test this finding and to obtain realistic values on the basis of a cell geometry representative of commercial electrochemical reactors, we consider the cell geometry of Fig. 2 with a total length $H = 1000$ mm and an electrode–membrane clearance of $Y = 3$ mm. The electrolyte is considered to be an aqueous solution of 25% KOH. Data for the mass transfer coefficient k were calculated from reference [5]; the mean bubble diameter was assumed to be $d = 50\ \mu m$, a reasonable value [6, 7]. Results obtained from Equations 4 and 16 when these values are inserted into Equation 18 are shown in Fig. 4, confirming that K_1 is enhanced approximately equally by the electrolyte pressure, the square of the electrolyte velocity and the reciprocal value of the current density. A separate and more thorough analysis of the effect of the most important parameters on the flux ratio K_1 should prove extremely interesting for industrial operational conditions.

4. Effect of electrolyte velocity

Values of K_1 obtained from Equation 4 when the above geometrical data and the mass transfer coefficient are inserted in Equations 6 and 7 are shown in Fig. 5 for hydrogen evolution and in Fig. 6 for oxygen.

At low electrolyte velocity the fraction of substance not desorbed inside the cell is small but increases substantially as the velocity is increased. In industrial hypochlorite cells and in low-rate chlorate cells with current densities of $j = 1500$ A m^{-2} and an electrolyte velocity of $v_0 = 1$ m s^{-1} [8, 9] about 50% of the dissolved hydrogen entering the bulk of electrolyte remains in dissolved form inside the gap. Taking into consideration that only about 30% of the

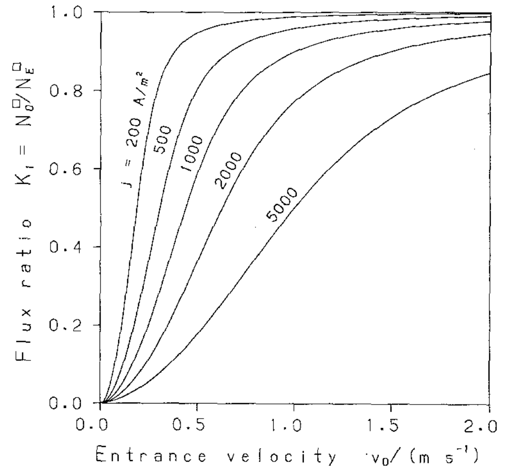

Fig. 6. Effect of entrance velocity v_0 of electrolyte and current density j on the flux ratio K_1. Oxygen evolution at $p = 1$ bar and $T = 80°$ C, saturated electrolyte at entrance.

total hydrogen formed is evolved as bubbles directly at the electrode at such current densities [2, 3], it will be seen that under these conditions only two-thirds of the total amount of hydrogen appears in the form of (adhering and freely moving) bubbles in the gap. It is only this proportion which yields the notorious 'bubble effect'. High electrolyte velocity turns out to be beneficial not only in that it causes gas bubbles to be removed quickly from the interelectrode gap, thus decreasing the mass transfer area in desorption, but also in that it reduces the time available for bubble growth.

In Equation 5, H/v_0 is a fictitious residence time for the electrolyte in the interelectrode gap. Shortening the cell length H in the flow direction is therefore equally effective whenever a further increase of flow velocity is not feasible, e.g. for commercial reasons.

5. Effect of current density

Current density is a complex variable since it acts both on the volume rate of gas evolved, hence on the liquid–gas interfacial mass transfer area, and on the residence time of electrolyte in the cell.

Parameter K_1 is affected by the current density through K_3 where it appears directly, and indirectly in the concentration difference $(c_H - c_0)$. As seen from Figs. 5 and 6, increasing the current density decreases the parameter K_1. Obviously, the effect on the interfacial area predominates. The overall effect is more pronounced with lower values of the entrance velocity v_0.

6. Effect of temperature

The effect of temperature on the parameter K_1 is not discussed fully since a choice of the operational temperature is usually limited by factors such as the conductivity of electrolyte, reaction conditions and the corrosion resistance of the material. However, it is important to obtain an idea of the effect of temperature in reaching conclusions from laboratory results obtained at considerably higher temperatures.

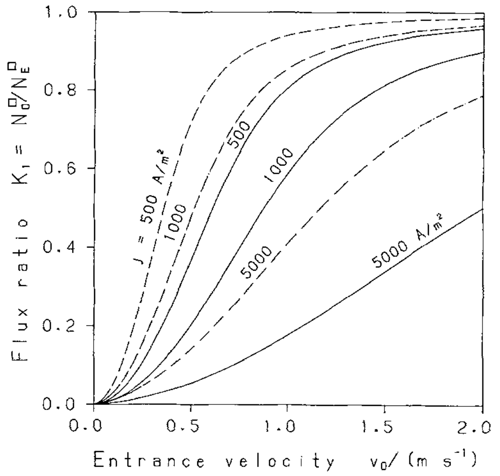

Fig. 7. Effect of temperature on the flux ratio K_1. Hydrogen evolution at $p = 1$ bar, $T = 25°$ C (broken line), $T = 80°$ C (full line) and various current densities j. Saturated electrolyte at entrance.

Temperature acts directly on K_3 and indirectly on K_2 through the mass transfer coefficient. Increasing temperature thus increases K_3 and reduces K_2, and both of these decrease K_1. Hydrogen data for 25° C are compared in Fig. 7 with data for 80° C taken from Fig. 5, under otherwise identical conditions.

It will be seen that a lower temperature increases the proportion of hydrogen withdrawn from the interelectrode gap in dissolved form.

7. Effect of pressure

It has been known for a long time that the terminal voltage of gas-evolving cells is reduced as the pressure of electrolyte is increased. The effect was formerly attributed to increased depolarization of the electrode process owing to the greater solubility of gases in the electrolyte adjacent to the electrode [10, 11]. At the same time, the direct effect of pressure on the gas volume has also been pointed out [12]. The effect of increased system pressure has since been shown conclusively to be caused solely by compression of the volume of gas bubbles. Increased pressure reduces the volume fraction of gas in the gas–electrolyte dispersion and acts favourably on the effective ohmic resistance of the dispersion in the bulk and near the electrode. Though widely accepted and doubtless correct this interpretation is incomplete, as may be shown on the basis of Equation 7.

Since the parameter K_3 represents the ratio of the flow rates of gas at the cell exit and of the

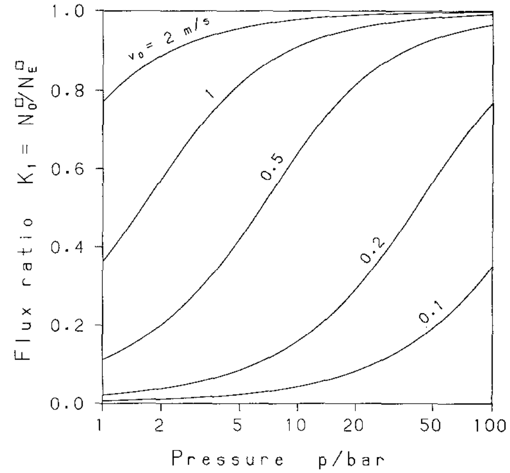

Fig. 8. Effect of pressure on the flux ratio K_1. Hydrogen evolution at $T = 80°$ C, $j = 2000$ A m^{-2}, and various entrance velocities v_0. Saturated electrolyte at entrance.

electrolyte, it expresses the volumetric gas fraction $\phi = \phi_H$ at $x = H$,

$$K_3 = \frac{\dot{V}_{G,H}}{\dot{V}_L} = \left(\frac{1}{\phi_H} - 1\right)^{-1} \qquad (17a)$$

and is thus a means for estimating the mean proportion of gas and the ohmic resistivity of the dispersion between the electrodes, e.g. from Bruggeman's or Maxwell's equation [7]. From Equations 7 and 4 it will be seen that neither K_3 nor ϕ_H are linear functional relationships of pressure (for all values $f_G < 1$). It is not only the compressed bubble volume which contributes to lowered resistivity but also the smaller bubble surface area which impedes bubble growth in the bulk of the electrolyte.

Again based on usual operational data of commercial electrochemical reactors, values of K_1 are shown in Fig. 8. It will be seen that the greater pressure used in certain water electrolyser systems considerably increases the proportion of dissolved gas not desorbed inside the cell. With the cell geometry under consideration and the electrolyte leaving the gap at a pressure of 20 bar, a current density of 2000 A m^{-2} and electrolyte velocity greater than 0.5 m s^{-1} more than 80% of the total amount of hydrogen reaching the bulk of the electrolyte remains dissolved. Due to the uncertainty in determining the mass transfer coefficients in Equation 6 and certain inevitable inaccuracies of the model [4], the numerical results given should not be regarded as 100% reliable before confirmation by experiment is available. However, they claim to give at least a qualitatively representative picture of the true conditions in electrochemical reactors.

8. Conclusions

The view that all or practically all the gas generated in dissolved form evolves to the gaseous phase within the interelectrode gap under normal industrial operational conditions is erroneous.

The proportion of dissolved gas carried off with the electrolyte from the cell increases with;

increasing flow velocity of the electrolyte,
decreasing current density,
decreasing temperature,
increasing pressure.

This fact should not be overlooked in the design of cells and in determining optimum operational conditions, for it is the amount of dissolved gas in the bulk which at a given current density contributes to lowering of the ohmic resistance of the gas–electrolyte dispersion.

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