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Calculations on the effect of gas evolution on the current-overpotential relation and current distribution in electrolytic cells

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Gas evolution during electrode reactions has several effects on the electrode behaviour. One of these effects is the nonuniform increase of the resistivity of the electrolyte with the resultant increase of IR drop through the solution and the distortion of current distribution. Calculations of these effects are presented for an electrode built of vertical blades. This geometry has the peculiarity that it allows the inclusion of linear polarization and gas effects in the treatment, without the necessity to use numerical or approximate solutions of the differential equations. It is shown that the system parameters can be combined into a single dimensionless parameter to describe those aspects of the electrode behaviour which depend on the gas evolution. The parameters examined include the geometry of the electrode, the polarization resistance, gas bubble rise velocity, and solution resistivity. Expressions are given for optimization of the electrode geometry to achieve minimum overpotential.

Nomenclature

b	Polarization resistance ($\Omega\,\mathrm{cm}^2$)
C	Constant, $= RT(\delta + t)/\delta lPtFs$ ($\mathrm{A}^{-1}\mathrm{cm}$)
$E(x)$	Potential of the solution at point x (V)
f_{av}	Average volume fraction of gas (dimensionless)
$f(y)$	Volume fraction of gas at height y (dimensionless)
$f(Y)$	Volume fraction of gas at reduced height Y (dimensionless)
F	Faraday number (coulomb mol^{-1})
h	Height of the electrode (cm)
i	Nominal current density of the electrode $= I_{\mathrm{T}}/hw$ ($\mathrm{A\,cm}^{-2}$)
$i(y)$	Local electrode current density at height y ($\mathrm{A\,cm}^{-2}$)
$i(Y)$	Local electrode current density at reduced height Y ($\mathrm{A\,cm}^{-2}$)
$i_{\mathrm{f}}(x)$	Faradaic current density at point x ($\mathrm{A\,cm}^{-2}$)
$i_{\mathrm{f}}(X)$	Faradaic current density at reduced length X ($\mathrm{A\,cm}^{-2}$)
$i_{\mathrm{f,av}}$	Average faradaic current density in the slot $= I_{\mathrm{s}}/2hl$ ($\mathrm{A\,cm}^{-2}$)
I_{s}	Total current entering one slot (A)
I_{T}	Total current flowing to the electrode (A)
$I(x)$	Current flowing in the solution phase of one slot at point x (A)
k	Constant, $= (2\rho/b\delta)^{1/2}$ (cm^{-1})
K	Dimensionless parameter $= \eta hRT(2\delta/b\rho)^{1/2}/4\delta lPzFs$, or $= 1 - (1 - iCh)^{1/4}$
l	Horizontal length of the slot (cm)
n	Number of slots on the electrode (dimensionless)
P	Pressure of gas liberated on the electrode (assumed to be independent of height) (atm)
R	Universal gas constant ($\mathrm{cm}^3\,\mathrm{atm\,K}^{-1}\,\mathrm{mol}^{-1}$)
s	Bubble rise velocity ($\mathrm{cm\,s}^{-1}$)
t	Thickness of the blades (cm)
T	Temperature of the gas (K)
$dV(y)$	Volume of gas present in a volume element of the slot (cm^3)
w	Width of the electrode (cm)
x	Horizontal distance from the back plate (cm)
X	Reduced horizontal distance $= x/l$ (dimensionless)
y	Vertical distance from the bottom of the electrode (cm)

Y	Reduced vertical distance $= y/h$ (dimensionless)
z	Number of Faradays needed to produce one mole of gas (mol^{-1})
δ	Width of a slot (blade spacing) (cm)
η	Measured overpotential of the electrode $= \eta(l)$ (V)
$\eta(x)$	Overpotential at point x (V)
ρ	Resistivity of gas free electrolyte (Ω cm)
$\rho(y)$	Resistivity of gas filled electrolyte at height y (Ω cm).

1. Introduction

Electrochemical reactions involving the evolution of a gas have some special characteristics not shared by electrode reactions in general. During the course of the process, gas bubbles nucleate, grow in size, and rise in the solution. These phenomena introduce numerous effects which have to be taken into consideration when dealing with gas electrodes. One of these effects arises from the presence of bubbles in the electrolyte, the distribution of which will, in general, be nonuniform. This will cause a nonuniform resistance increase of the solution, resulting in an increase of the voltage drop and in a distortion of the current distribution.

In spite of the practical importance of this effect, it is only partially understood. A series of papers gave experimental information on the magnitude of the effects [1–6], and theoretical treatments were given by Tobias [7] for stagnant electrolyte, and by Funk, Thorpe, and Bong [8–9] for cells with forced circulation. The Tobias treatment resulted in a general, qualitative understanding of the effects, but analytical solutions were found only under restricted conditions. Some of the main restrictions were a simple geometry (parallel sheet electrodes), and the total neglect of polarization effects. Electrodes with much more complicated geometry are generally used in industrial practice, and the extension of the theoretical treatment to more complex shapes is desirable; at the same time, the removal of the restriction of constant polarization, if possible, would put the treatment on a more realistic basis. A large number of different electrode geometries are in use, or have been proposed, with the aim of decreasing the overpotential by an increase of active area, and with the aim of allowing easier gas removal from the interelectrode volume. However, the treatment of gas effects for these complex shapes is even more difficult than for the flat sheet electrode. The particular geometry considered in this work has the peculiarity that it allows the inclusion of a linear polarization relation in the calculations, without making it necessary to use a numerical or approximate solution. However, extension of the treatment outside the linear current density-overpotential range will require numerical solutions.

2. Calculations

2.1. *Model of the electrode*

The geometrical arrangement of the electrode configuration is shown in Fig. 1. The electrode consists of a number of parallel blades arranged vertically in the cell. The blades are supported by a back plate, which also serves as current conductor. The faradaic current is restricted to the sides of the blades and it is considered to be zero on the back plate (e.g., insulator layer on the back plate between the blades), but this restriction is removed at a later stage of the treatment. The blades are facing a diaphragm which separates the cell into two compartments and the phenomena occurring on the counter electrode are neglected.

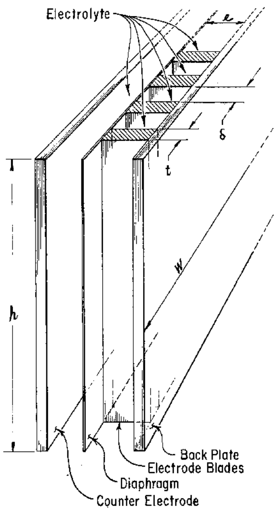

Fig. 1. Electrode geometry.

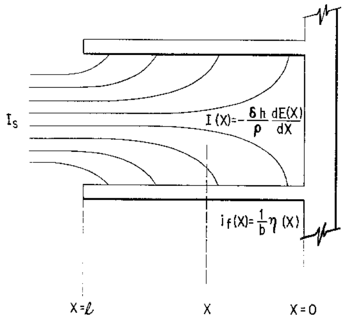

Fig. 2. Horizontal cross-section of one slot.

2.2. *Electrode reaction without gas evolution*

Before the effect of gas evolution can be considered, some relations will have to be determined for an electrode reaction involving no complications from gas bubbles. These are the current-potential relation of the electrode, and the current distribution in the slot. These relations will be needed as a starting point for the following calculations, and also as a comparison base to evaluate the change in the electrode characteristics caused by the gas evolution.

It is assumed that the overall cell arrangement is such that the vertical current distribution will be uniform, and only the horizontal current distribution needs to be determined. It is further assumed that the electrical resistance of the metallic phase is negligibly small compared to that of the solution; this assumption will be incorrect only if $t \ll \delta$, and, as will be shown later, this is not a favoured practice.

A horizontal cross section of a single slot is shown in Fig. 2. The total current entering the slot (I_s) is progressively transferred to the metallic phase by the faradaic reaction, which takes place on the surface of the blades at the distance-dependent rate of $i_f(x)$. Therefore, the current flowing in the solution phase, at point x, can be expressed as:

$$I(x) = I_s - 2h \int_x^l i_f(x)\mathrm{d}x = 2h \int_0^x i_f(x)\mathrm{d}x, \tag{1}$$

where $2h$ is the electrode area of the slot per unit length. Since the metal is considered an equipotential phase, the gradient of solution potential will be related to the gradient of overpotential as $\mathrm{d}E(x)/\mathrm{d}x = -\mathrm{d}\eta(x)/\mathrm{d}x$, and application of Ohm's law to the solution will give:

$$2h \int_0^x i_f(x)\mathrm{d}x = \frac{\delta h}{\rho}\frac{\mathrm{d}\eta(x)}{\mathrm{d}x}, \tag{2}$$

where δh is the cross-sectional area of the slot. If the relation between the faradaic current and the overpotential is now expressed by a linear approximation, $\eta(x) = bi_f(x)$, differentiation of Equation 2 will give the basic equation of the system:

$$\frac{\mathrm{d}^2\eta(x)}{\mathrm{d}x^2} = \frac{2\rho}{b\delta}\eta(x) = k^2\eta(x). \tag{3}$$

Solution of Equation 3, under the boundary conditions of:

$$\left[\frac{\mathrm{d}\eta(x)}{\mathrm{d}x}\right]_{x=0} = 0 \tag{4}$$

and

$$\left[\frac{\mathrm{d}\eta(x)}{\mathrm{d}x}\right]_{x=l} = \frac{I_s\rho}{\delta h}, \tag{5}$$

can be obtained as:

$$\eta(x) = \frac{I_s\rho}{\delta hk}\frac{\cosh(kx)}{\sinh(kl)}, \tag{6}$$

from which the horizontal current distribution in the slot follows*:

$$\frac{i_f(x)}{i_{f,\mathrm{av}}} = kl\frac{\cosh(kx)}{\sinh(kl)}. \tag{7}$$

Equation 6 can be rearranged in order to obtain the final current-overpotential relation in directly measurable quantities. The current will be expressed as the nominal current density of the electrode:

$$i = \frac{nI_s}{hw} = \frac{nI_s}{h[n(\delta + t)]}, \tag{8}$$

and the overpotential as $\eta(l)$, the value which one would experimentally measure. The final equation is:

$$\eta = i(\delta + t)\frac{\left(\frac{b\rho}{2\delta}\right)^{1/2}}{\tanh\left(\frac{2l^2\rho}{b\delta}\right)^{1/2}}. \tag{9}^*$$

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* Equations 7 and 9 have similar forms as some relations derived for porous electrodes (see e.g. Posey [10]), since the slot can, in effect, be compared to a one-dimensional pore.

2.3. *Optimization of electrode geometry*

Equation 9 can be used to optimize the electrode parameters to achieve the lowest overpotential at a given current density. The overpotential decreases with the increase of the horizontal length of the slot and approaches its lowest value asymptotically. Since the value of the tanh function approaches unity rather rapidly as its argument increases, an increase of l is not justified over

$$l = \left(\frac{8b\delta}{\rho}\right)^{1/2}. \tag{10}$$

At this length the lowest overpotential is reached within 0·1% (tanh 4 = 0·9993). Assuming that this value of l will be used, the current-overpotential relation can be simplified to:

$$\eta = i(\delta + t)\left(\frac{b\rho}{2\delta}\right)^{1/2}. \tag{11}$$

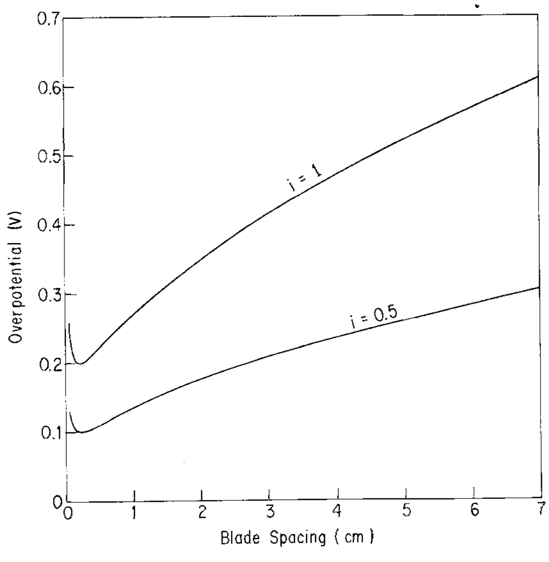

Fig. 3. Gas free overpotential (conditions: b = 0·1, ρ = 1, t = 0·2).

The effect of t and δ can be evaluated from Equation 11. No optimal value exists for t, which should be kept as small as practical. On the other hand, a minimum overpotential is found at $\delta = t$. (Fig. 3). These effects can be explained, considering the geometry of the system. Increase of the value of t decreases the surface area of the electrode available for faradaic reaction, per unit of norminal electrode area, and therefore causes an increase in overpotential. The minimum in the effect of δ is arising from the interplay of two effects: as its value decreases, the surface area of the electrode increases, decreasing the overpotential, but at the same time the electrolytic resistance of the slot increases, causing the opposite effect.

2.4. *Effect of gas evolution*

The derivation which follows is based on the same general assumptions as the treatment of Tobias for the simple sheet electrode [7]. The main assumption is that the gas bubbles can be characterized by a single, average rise velocity value, which is independent of height and current density; convection of the electrolyte (both natural and forced) is assumed to be negligible. It is also assumed that, at any given height, the bubbles are uniformly distributed in the horizontal cross-section of the electrolyte column, and only vertical distribution effects have to be considered.

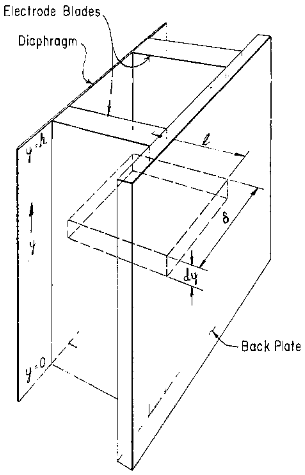

Fig. 4. Volume element in one slot.

The volume fraction of the gas in a given volume element of the electrolyte (Fig. 4) will be a function of height y (all the gas produced below the height y will have to pass through this volume element). The resulting nonuniform change of solution resistance will cause the local current density of the electrode to become a function of height. The volume of gas present in the volume element of $\delta l dy$ is related to the current density as:

$$dV(y) = \left[\frac{RT(\delta + t)}{PzF}\int_0^y i(y)\,dy\right]\frac{dy}{s}, \quad (12)$$

where $(\delta + t)\,i(y)$ is the current entering one slot at y per unit height, and the expression in the square brackets gives the volume of the gas produced in the slot per second between 0 and y. Since the gas bubbles rise with a uniform velocity of s cm s^{-1}, a dy/s fraction of the gas produced below point y will be present in the volume in question. From Equation 12, the volume fraction of the gas follows as:

$$f(y) = \frac{dV(y)}{\delta l\,dy} = C\int_0^y i(y)\,dy, \quad (13)$$

where all the constant terms are grouped in C. Differentiation gives:

$$df(y) = Ci(y)\,dy. \quad (14)$$

As in the gas-free treatment, the metal is considered an equipotential phase and only the current is a function of the position coordinates. The constant overpotential of the electrode (η) is related to the current through a relation similar to Equation 11, assuming that the condition given in Equation 10 is satisfied, but, in this case, the effect of gas bubbles on the resistivity of the electrolyte has to be taken into consideration. Using the Bruggeman [11] equation, which was shown to be applicable to electrolytic cells by De La Rue and Tobias [12]:

$$\rho(y) = \rho[1 - f(y)]^{-3/2}, \quad (15)$$

the current-overpotential relation at any height y will become:

$$i(y) = \frac{\eta}{(\delta + t)}\left(\frac{2\delta}{b\rho}\right)^{1/2}[1 - f(y)]^{3/4}. \quad (16)$$

Substituting Equation 16 into Equation 14 gives

$$\frac{\eta C}{(\delta + t)}\left(\frac{2\delta}{b\rho}\right)^{1/2} dy = [1 - f(y)]^{-3/4}\,df(y), \quad (17)$$

and integration between the respective limits of 0 to y, and 0 to $f(y)$, converting to reduced height ($Y = y/h$), and solving for $f(Y)$ results in:

$$f(Y) = 1 - (1 - KY)^4, \quad (18)$$

where K is a dimensionless constant including all parameters characterizing the electrode:

$$K = \eta\frac{hRT}{4\delta lPzFs}\left(\frac{2\delta}{\rho b}\right)^{1/2} = \eta\frac{hRT}{8\delta PzFsb}. \quad (19)$$

The volume fraction of gas, as a function of reduced height, is shown in Fig. 5 for several values of K.

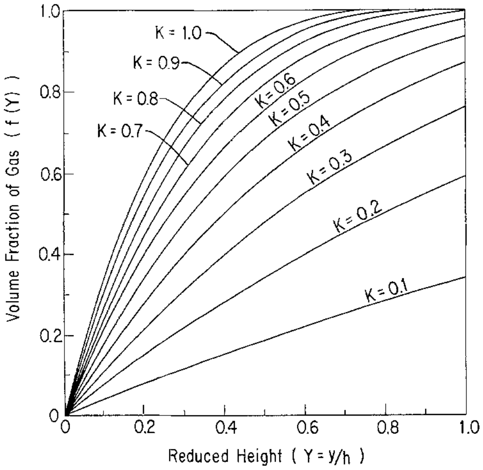

Fig. 5. Vertical gas distribution.

The current distribution can now be obtained from the combination of Equations 16, 18, and 19 as:

$$i(Y) = \frac{4K}{Ch}(1 - KY)^3. \quad (20)$$

The average, or nominal, current density of the electrode can be expressed with the help of Equations 13 and 18:

$$i = \int_0^l i(Y)\,dY = \frac{1}{Ch}[1 - (1 - K)^4], \quad (21)$$

from which another expression for K can be obtained:

$$K = 1 - (1 - iCh)^{1/4}. \quad (22)$$

Elimination of K between Equations 19 and 22 gives finally the basic current density-overpotential relation of the electrode:

$$\eta = \frac{4(\delta + t)}{Ch}\left(\frac{b\rho}{2\delta}\right)^{1/2}[1 - (1 - iCh)^{1/4}]. \quad (23)$$

Some further useful relations which can be derived are the relative current distribution:

$$\frac{i(Y)}{i} = \frac{4K(1 - KY)^3}{1 - (1 - K)^4}, \quad (24)$$

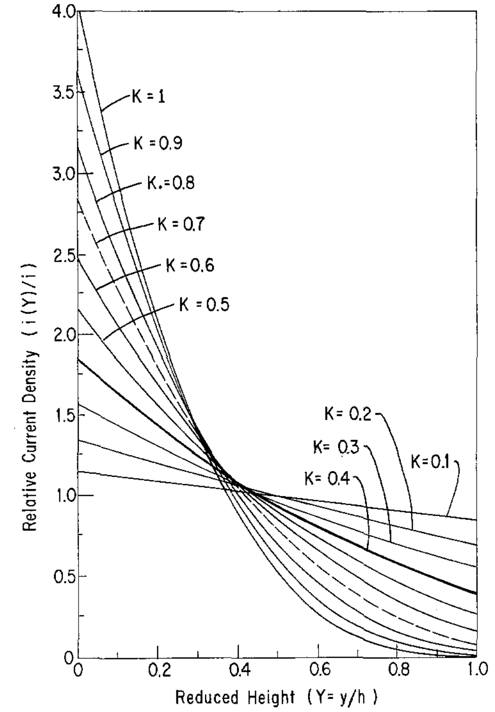

Fig. 6. Vertical current distribution.

shown in Fig. 6 for several values of K, and an expression for the average gas volume fraction, as a function of K:

$$f_{av} = \int_0^l f(Y)\,dY = 1 + \frac{(1-K)^5 - 1}{5K}. \quad (25)$$

3. Discussion

Relations derived in the previous sections can be used to examine the general effects of gas evolution, to optimize the parameters of electrode geometry, and to compare the behavior of this electrode with that of a simple flat sheet.

3.1. *Gas effects*

The effects caused by the presence of gas bubbles in the electrolyte can be described with the help of the dimensionless parameter K (Equations 19 and 22) which includes all system parameters: those describing the geometry of the electrode, and those characterizing the electrode reaction, the electrode surface, and the solution. The effects caused by the presence of the gas bubbles are all enhanced by an increase of K. The average volume fraction of gas (Equation 25), the nonuniformity of the gas distribution (Fig. 5), and the nonuniformity of the current distribution (Fig. 6) all increase with increasing K. The changes of system parameters which will cause an increase of K are those which either increase the volume of gas produced (increase of i, or T/Pz), decrease the volume (decrease of l, δ, per unit height or increase of t), decrease the rate of gas removal (decrease of s, or increase of h), or, indirectly, decrease l (decrease of b, or increase of ρ).

The effect of system parameters on the overpotential, on the other hand, is more complex (cf. Equation 23), and cannot be expressed with only the help of K. The reason for this is that a change in some of the parameters will not only cause a change in the gas effect, but also would change the overpotential of the electrode in the absence of the gas, and both of these effects show up in the final result. If one considers the relative overpotential change caused by the gas, by taking the ratio of Equations 23 and 11:

$$\frac{\eta\,(\text{with gas})}{\eta\,(\text{without gas})} = \frac{4K}{1-(K-1)^4}, \quad (26)$$

the effect can be expressed by K alone. It can be concluded that every effect caused by the presence of the gas can be described with the help of the dimensionless parameter K.

The behaviour of this electrode configuration with respect to the volume fraction of gas is generally the same as that described by Tobias [7] for the flat sheet electrode. The behaviour of the latter could also be completely described by a dimensionless parameter, similar to the present K. However, there are also some differences because of the different treatment of the polarization. The current is limited in each case by the model to $i = 1/Ch$; at this maximum current the volume fraction of the gas is unity at the top of the electrode, and any further increase would mean that the constant gas velocity assumed in the treatment is not sufficient to remove the gases produced. In the present model this also limits K to a maximum value of one, and the overpotential to a maximum value of four times that of the gas free value (Fig. 7). For the flat sheet electrode, because of the constant polarization assumption, K is not limited

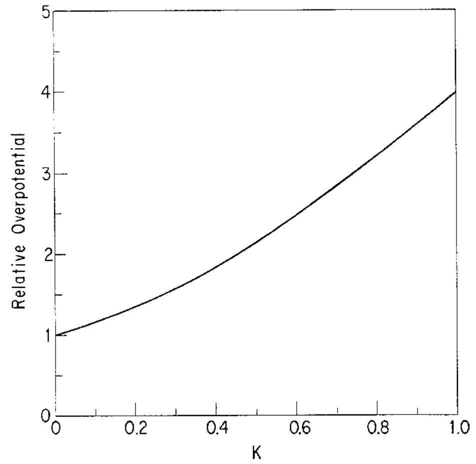

Fig. 7. Relative overpotential [η (with gas)/η (without gas)] as a function of K.

by the current and its value increases to infinity together with the value of the IR drop caused by the gas bubbles.

3.2. *Optimization of system parameters with respect to overpotential*

The basic current density-overpotential relation of the system is that of Equation 23, which takes into account the horizontal current distribution arising from the electrode geometry and the vertical current distribution caused by the gas evolution. It was necessary to assume a simple linear polarization equation for the faradaic current, rather than use the Tafel or the Butler–Volmer equations, in order to arrive at an analytical solution. While this is an approximation, it is a higher order one than the constant polarization assumption which was necessary in the case of the flat sheet electrode [7]. This equation can be used to optimize the system parameters to obtain the lowest possible overpotential at a given current density. A minimum in overpotential is found only with respect to blade spacing. The other variables affect the overpotential monotonously, but they also affect the position of the overpotential minimum with respect to δ. Both of these effects are demonstrated using η versus δ plots.

Some examples of the effect of blade spacing are shown in Fig. 8. The minimum is similar to that found for the flat sheet electrode [7] with respect to electrode spacing. It is the result of two opposing effects: the decrease of δ results in a higher volume fraction of gas and consequently a higher overpotential; on the other hand, a decrease of δ decreases the gas free overpotential of the electrode. At small blade spacing, the first effect predominates; at wide spacing, the second one. It is because of the interplay of these two effects that the minimum cannot be expressed as a function of K only. With the increase of K through the effects of any of the system parameters, the minimum is shifted toward higher η and δ values but the effect is also influenced by the gas-free overpotential behaviour of the electrode. In the case of the flat sheet electrodes, where the variables affected only the solution resistance and not the overpotential, the minimum was found to be at a constant average gas volume fraction of 0·36 (see Appendix). In the present case, the minimum is found near to this value (Table 1) but with a considerable spread ($\simeq \pm 0{\cdot}1$).

The other parameters will influence the position of this overpotential minimum either through only

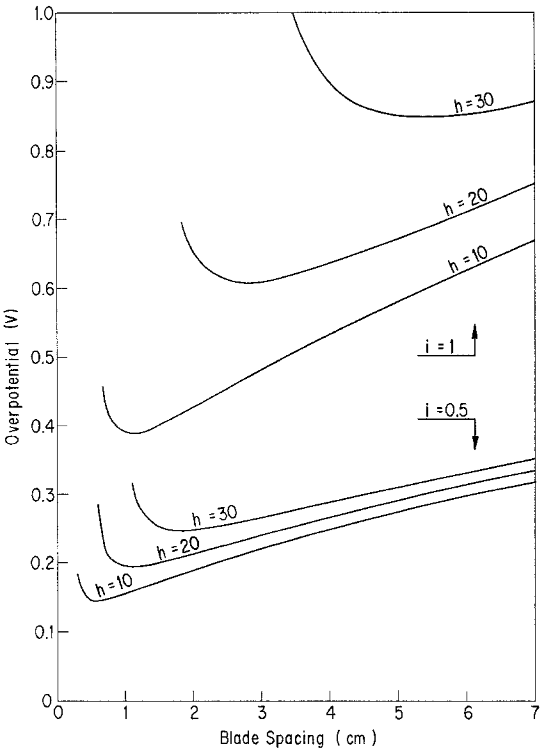

Fig. 8. Effect of current density and electrode height on overpotential (conditions: $b = 0{\cdot}1$, $s = 5$, $\rho = 1$, $t = 0{\cdot}2$, and $T/Pz = 298$).

Table 1. Variations of K and f_{av} at δ_{min}

i	h	t	b	ρ	δ_{min}	η_{min}	K (at δ_{min})	f_{av} (at δ_{min})
1	30	0·2	0·1	1	5·3	0·85	0·30	0·45
1	20	0·2	0·1	1	2·7	0·61	0·28	0·42
1	10	0·2	0·1	1	1·1	0·39	0·22	0·36
0·5	60	0·2	0·1	1	5·3	0·42	0·30	0·45
0·5	30	0·2	0·1	1	1·8	0·25	0·26	0·41
0·5	20	0·2	0·1	1	1·1	0·19	0·22	0·36
0·5	10	0·2	0·1	1	0·6	0·15	0·15	0·27
0·5	30	0·2	0·05	1	3·0	0·23	0·29	0·43
0·5	30	0·2	0·3	1	0·9	0·31	0·22	0·36
0·5	30	0·1	0·1	1	1·5	0·23	0·29	0·43
0·5	30	0·4	0·1	1	2·3	0·28	0·22	0·36
0·5	30	0·2	0·1	2	3·0	0·45	0·29	0·43
0·5	30	0·2	0·1	4	5·3	0·85	0·30	0·45

Constant parameters: $s = 5, l = (8b\delta/\rho)^{1/2}$, $T/Pz = 298$.

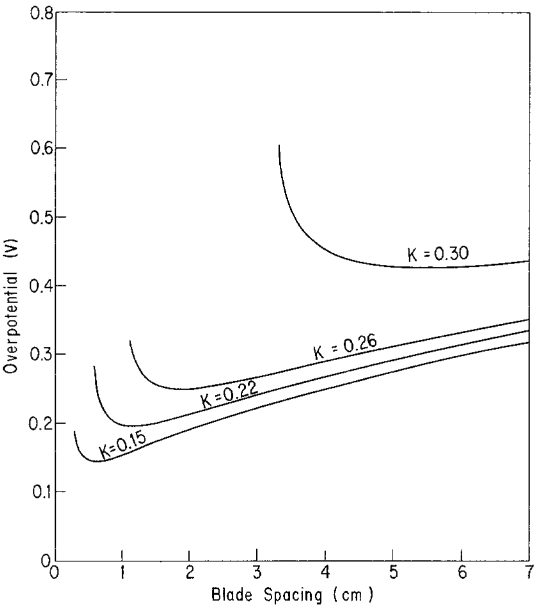

Fig. 9. Effect of electrode height, slot length, bubble rise velocity, and temperature-pressure on overpotential. Standard conditions: $i = 0{\cdot}5$, $b = 0{\cdot}1$, $s = 5$, $\rho = 1$, $t = 0{\cdot}2$, $h = 30$, $l = (8b\delta/\rho)^{1/2}$, $T/Pz = 298$. Varying one parameter, while keeping the others at standard values, will affect K as shown:

K	h	l	s	T/Pz
0·30	60	$1/2(8b\delta/\rho)^{1/2}$	2·5	594
0·26	30	$(8b\delta/\rho)^{1/2}$	5	298
0·23	20	$2(8b\delta/\rho)^{1/2}$	10	198
0·15	10	–	15	99

a gas effect (h, l, and s) in which case their effect can be described with the use of K, or through a combined gas and gas free overpotential effect (i, t, b, ρ, and T/Pz.).

The effect of electrode height is illustrated in Figs. 8 and 9. It is a straightforward gas effect since the gas-free overpotential is independent of h. The change of overpotential caused by a change in current density is also shown on Fig. 8. The direction of change agrees with that predicted from K, and the gas effect can be observed by comparing these curves with those of Fig. 3, where the gas-free overpotential is plotted. The high overpotential penalty to be paid for using a tall cell and/or high current density is clearly indicated by the graphs. Both of these variables should be kept at such a low value as practical based on economic considerations.

The change of plate thickness affects η only mildly (Fig. 10). Its value should be kept as small as practical. A condition of $t \ll \delta$ would invalidate the assumption of zero metal resistivity, but it will not occur at practical blade thicknesses.

The effect of horizontal length is already tacitly included in the effect of some of the other parameters, through Equation 10. Considerable deviations from the length required by Equation 10 will invalidate basic assumptions of the model. Decreasing the length will make Equation 11 a poor approximation, and increasing the length will

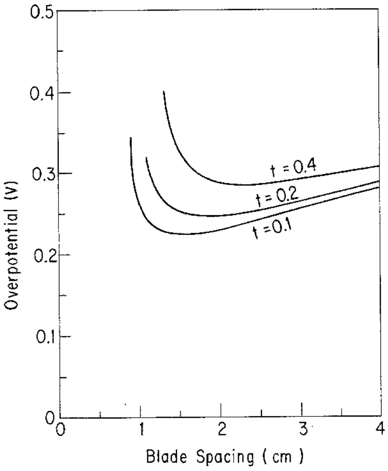

Fig. 10. Effect of blade thickness on overpotential (conditions as Fig. 9).

void the assumption of uniform horizontal gas distribution. The horizontal current distribution is strongly nonuniform (cf. Fig. 13) and the above assumption can be held valid only if $l \lesssim \delta$, which condition is satisfied by relying on Equation 10 (cf. Table 1). Deviations from the preferred value within narrow limits can be approximated as a straightforward gas effect (at these values the gas-free overpotential is hardly affected by a change in l), and are illustrated in Fig. 9.

The value of bubble rise velocity will be influenced by the bubble diameter, and, through this, by the surface characteristics of the electrode, and the surface tension and viscosity properties of the gas and the electrolyte. Values in the few cm/sec range have been reported [6]. This is strictly a gas effect, operating through the value of K (Fig. 9).

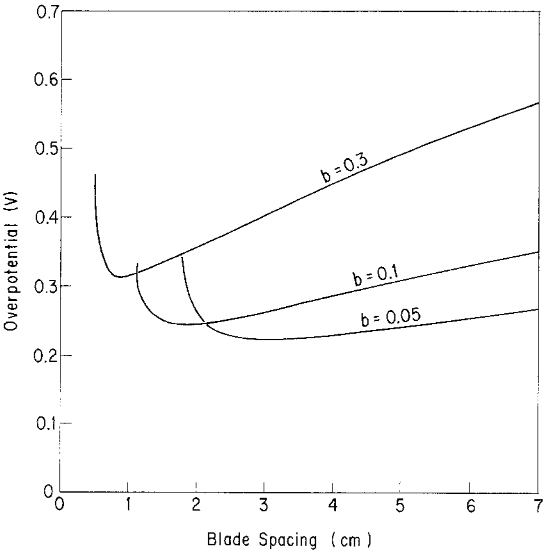

Fig. 11. Effect of polarization resistance on overpotential (conditions as Fig. 9).

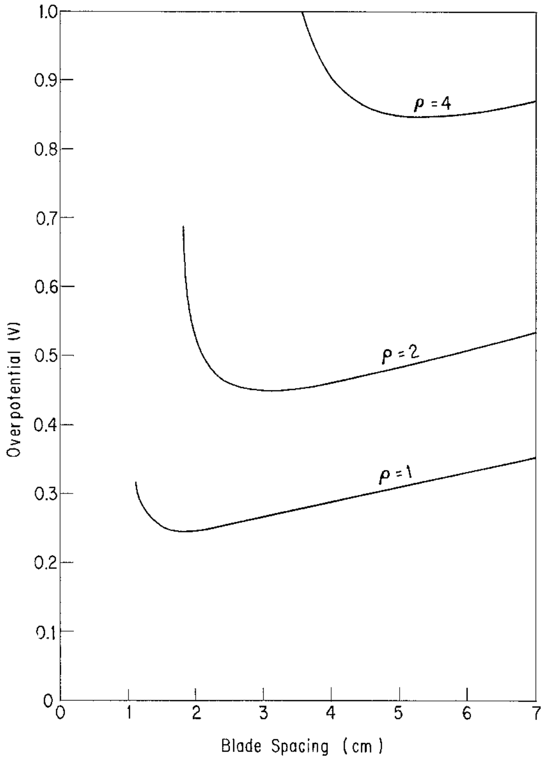

Fig. 12. Effect of the resistivity of the gas free solution on overpotential (conditions as Fig. 9).

The polarization resistance has a complex effect (Fig. 11). An increase of its value will decrease K because of its effect on l (Equation 10), and consequently the overpotential minimum will shift toward lower δ values, but, at the same time, the overpotential increases through the effect on the gas free value.

The solution resistance also has a complex effect (Fig. 12); it changes l through Equation 10, and also changes the gas free overpotential. The direct effect of T/Pz, acting through K, is shown in Fig. 9. However, this assumes that all other parameters are independent of T/Pz which is true only within a narrow range. In general, the values of b and s will depend on the temperature and pressure.

3.3. *Current distribution effects*

In this electrode geometry, the current distribution is a two-dimensional problem, varying both in the vertical and horizontal directions. The vertical current distribution is determined completely by the value of K, which in the range of variables considered is between 0·1 and 0·3 at the overpotential minimum (Table 1). The current distribution is relatively uniform at these K values (Fig. 6) ranging at most ±50% around the nominal. In the horizontal direction the current distribution is much more nonuniform as shown in Fig. 13; furthermore, the distribution is a function of height due to the varying resistance of the solution. This nonuniform current distribution allows the removal of an original restriction of the model, namely that the back plate should be isolated to avoid the occurrence of faradaic reaction on its surface. Since only a small fraction of the current reaches to the back of the electrode, the model is also a good approximation for an electrode where the back plate is not insulated.

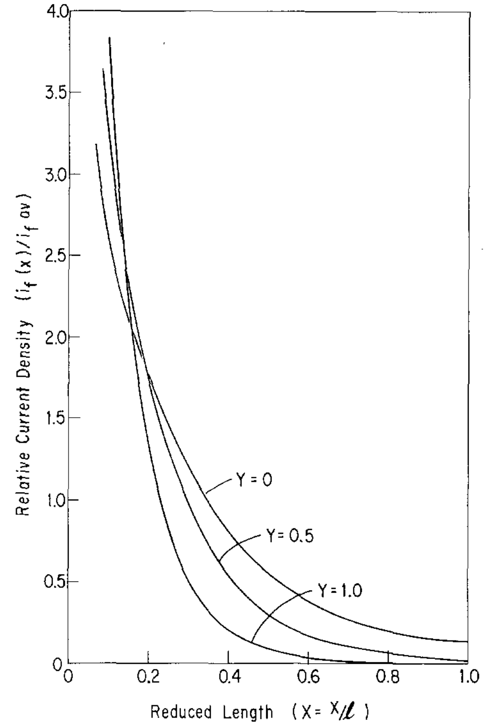

Fig. 13. Horizontal current distribution (conditions as Fig. 9).

Appendix

This opportunity is taken to include some discussion of the Tobias treatment [7] of the flat sheet electrode case. The relation predicting a minimum in the effective solution resistance at a fixed gas volume is one of the most practical results of the treatment. The equation given by Tobias seems to involve some unnecessary simplifications since the rigorous equations can be derived.

The effect of average gas volume fraction can be examined under two different conditions: keeping the current or the voltage constant while varying the interelectrode distance. Starting with Tobias' Equation 15 (the nomenclature of the original paper will be followed):

$$R_{\text{eff}} = \frac{\rho\delta}{hw}\frac{(K+2)^2}{K+4},$$

and using Equations 12 and 16 to express δ and K, respectively, one obtains:

$$R_{\text{eff}} = \frac{2RT\rho I_T}{hw^2PmFs}\frac{1}{f_{\text{av}}(1-f_{\text{av}})(2-f_{\text{av}})^2}.$$

Assuming that I_T is constant, differentiation yields minimum resistance at $f_{\text{av}} = 0{\cdot}36$. Proceeding again as above, but expressing δ from the definition of K gives:

$$R_{\text{eff}} = \left(\frac{2RT\rho E}{hw^2PmFs}\right)^{1/2}\frac{1}{f_{\text{av}}^{1/2}(1-f_{\text{av}})^{1/2}(2-f_{\text{av}})},$$

from which, assuming E = constant, the minimum resistance is again obtained at $f_{\text{av}} = 0{\cdot}36$. Neither of the above equations agrees with Tobias' Equation 17:

$$R_{\text{eff}} = \frac{A}{f_{\text{av}}(1-f_{\text{av}})^{3/2}}$$

which predicts a minimum at $f_{\text{av}} = 0{\cdot}40$.

Another useful expression, which can be obtained from the definition of K using the value corresponding to $f_{\text{av}} = 0{\cdot}36$, is the interelectrode spacing giving minimum resistance:

$$\delta_{\text{min}} = 1{\cdot}69\frac{RT}{PmF}\frac{i_{\text{av}}h}{s}.$$

The system parameter changes affecting δ_{min} correspond to those affecting the minimum overpotential of the electrode discussed in this paper, considering the gas effects only.

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