

THE RATE OF GAS EVOLUTION AT ELECTRODES—I. AN ESTIMATE OF THE EFFICIENCY OF GAS EVOLUTION FROM THE SUPERSATURATION OF ELECTROLYTE ADJACENT TO A GAS-EVOLVING ELECTRODE

H. VOGT

Fachbereich Verfahrens- und Umwelttechnik, Technische Fachhochschule Berlin, D-1000 Berlin 65, Federal Republic of Germany

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Abstract—The rate of gas evolution immediately at the electrode has a great effect on heat and mass transfer (of any substance) at gas-evolving electrodes. The question of how much of the gas generated in dissolved form is transformed into the gaseous phase of bubbles adhering to the electrode is studied on the basis of calculations of mass transfer of dissolved gas. Contrary to the established view of the matter it is found that only a fraction of the dissolved gas is transformed into bubbles at the electrode. This fraction, expressed as the efficiency of gas evolution, increases as the current density increases but is far smaller than unity in usual industrial current density values and remains different from unity in the whole range of nucleate gas evolution.

NOMENCLATURE

A	electrode area (m^2)
A_w	wetted part of the electrode area (m^2)
Δc	concentration difference of dissolved gas, Equation (22) (mol m^{-3})
c_e, \bar{c}_e	concentration of dissolved gas at the electrode-electrolyte interface, local and mean value, respectively (mol m^{-3})
c_0	bulk concentration of dissolved gas (mol m^{-3})
d	bubble departure diameter (m)
d_h	hydraulic diameter (m)
D	diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
f_G	efficiency of gas evolution
F	Faraday constant, $F = 96487 \text{ As mol}^{-1}$
g	acceleration of gravity (m s^{-2})
j_{tot}	total current density (A m^{-2})
j	current density of formation of dissolved gas (A m^{-2})
k_E	mass transfer coefficient, Equation (5) (m s^{-1})
k_E'	mass transfer coefficient, Equation (4) (m s^{-1})
k_{Eh}	mass transfer coefficient due to microconvection (m s^{-1})
k_{Ec}, k_{Ec}'	mass transfer coefficients due to macroconvection (m s^{-1})
K_1	parameter, Equation (23) ($\text{m}^4 \text{s}^{-1} \text{mol}^{-1}$)
K_2	dimensionless parameter, Equation (26)
K_3	dimensionless parameter, Equation (27)
L	characteristic length (m)
M_G	molar mass of gas (kg mol^{-1})
n	charge number of the electrode reaction
N_D	flux density of formation of dissolved gas ($\text{mol m}^{-2} \text{s}^{-1}$)
N_E	flux density to the bulk of liquid ($\text{mol m}^{-2} \text{s}^{-1}$)
N_E^D	flux to the bulk of liquid (mol s^{-1})
N_G	flux density to bubbles adhering to the electrode ($\text{mol m}^{-2} \text{s}^{-1}$)
p	pressure ($\text{kg m}^{-1} \text{s}^{-2}$)
R_m	gas constant, $R_m = 8.314 \text{ kg m}^2 \text{s}^{-2} \text{mol}^{-1} \text{K}^{-1}$
T	temperature (K)
v_G^*	volumetric flux density of gas evolved at the electrode (m s^{-1})
v_L	flow velocity of electrolyte (m s^{-1})

Dimensionless groups

Ar	Archimedes number, Equation (13)
Re_G, Re_L	Reynolds numbers, Equations (17) and (10)
Sc	Schmidt number, Equation (11)
Sh_h, Sh_c	Sherwood numbers, Equations (16), (9) and (12)

Greek characters

ε	current efficiency of formation of dissolved gas
θ	fractional surface coverage
ν	kinematic viscosity of electrolyte ($\text{m}^2 \text{s}^{-1}$)
ν_D	stoichiometric number
ρ_G	density of gas (kg m^{-3})
φ	volumetric gas fraction

1. INTRODUCTION

How much gas is evolved *as such* at a gas-evolving electrode? The question may seem to be amazingly simple since it is understood that the amount of dissolved gas formed at the electrode due to Faraday's law coincides quantitatively with the amount transformed into the gaseous phase in form of bubbles adhering to the electrode. However, there is evidence that in reality this established view is far too inaccurate. A closer look at the transport mechanisms at gas-evolving electrodes may be applied to point out a problem that has not been given enough weight.

2. TWO COMPETING TRANSPORT MECHANISMS

A substance, as for example molecular hydrogen, formed at an electrode in the sequel of an electrochemical reaction, must be transported away from the electrode. As a prerequisite, a sufficiently large concentration gradient of dissolved hydrogen builds up. In steady-state operation, the interfacial electrolyte con-

centration is (far) larger than in liquid bulk. Hydrogen is transported to the bulk by molecular diffusion and superimposed convection. Under ordinary circumstances the interfacial concentration increases as the current density is raised, thus balancing the greater mass flux density. The concentration, however, does not grow infinitely.

If the interfacial concentration exceeds a certain value (depending on the properties of the electrolyte, the gas and the surface morphology of the electrode) nuclei at the electrode surface become active and hydrogen is transformed into the gaseous phase. The electrode starts working as a gas-evolving electrode. Gas bubbles grow and depart from the electrode when they have reached a sufficient size and thus provide a second transport mechanism. At the same nucleation site a new bubble forms [1, 2]. Hence, hydrogen is transported from the electrode *via* two competing mechanisms (Fig. 1):

- (i) convective mass transfer of dissolved substance from the electrode surface to the bulk of electrolyte and
- (ii) primary mass transfer of dissolved substance from the region near the electrode to the gas-liquid interface of growing bubbles adhering to the electrode, subsequent transformation into the gaseous phase and bubble departure from the electrode.

Dissolved substance is, at least partly, further transformed into the gaseous phase outside the electrode concentration boundary layer by means of desorption from a supersaturated bulk liquid. This fact, however, can be left out of consideration since this discussion is restricted explicitly to the transport mechanisms from the electrode. They are of particular importance as will be shown later.

It is an established view that soon after gas bubble formation has started the first transport mechanism becomes unimportant as compared with the second one. Transport of the substance in gaseous form from the electrode is believed to be predominant, whereas the transport of dissolved substance from the electrode to the bulk is considered negligible, except for a smaller range of current density situated immediately above

the current density characterizing the onset of gas bubble formation.

This view can be found in numerous papers dealing with mass transfer at gas-evolving electrodes, a process which is customarily understood as the transport of substances other than dissolved gases to or from the electrode. Apart from very rare exceptions [3] no distinction has been made so far between the rate of formation of dissolved gas—which is interconnected with the (partial) current density—and the rate of evolution of the same substance in gaseous form at the electrode. Attempts to estimate quantitatively the fraction of the total amount of dissolved gas which is not transformed into the gaseous phase at the electrode do not appear to have been published.

An investigation of the role of the two competing transport mechanisms as listed above is intended to have a double aim. Firstly, an improved insight into the complex microevents at gas-evolving electrodes is expected, mainly with respect to the supersaturations and their effect on nucleation and bubble population data. Secondly, and perhaps more important, is to make possible the prediction of the rate of gas evolution in form of bubbles adhering to the electrode. This quantity, being interconnected with the second of the mechanisms listed, is the controlling one (or, under extraordinary conditions, at least a most important one) in mass transfer at gas-evolving electrodes, but defies direct experimental assessment. The question whether the second mechanism is really the predominant one is, therefore, of fundamental importance for any comparison of experimental mass transfer data with results from equations based on theory.

To clarify the role of the two mechanisms by straight experiments would be virtually impossible or could only be done with extraordinary difficulties because bubbles do not cease growing after being detached from the electrode but continue to absorb gas from the supersaturated electrolyte when rising remote from the electrode. In stationary electrolytes operated under steady-state condition the total quantity of gas evolved (at electrode and other walls as well as in bulk) obeys exactly Faraday's law and conclusions on the mechanisms are completely impossible. It is the object of the present paper to present an analysis on the basis of mass transfer calculations under consideration of available experimental supersaturation data already published.

Hydrogen is referred to in this paper as an example for every dissolved gas formed electrochemically at a gas-evolving electrode. Apart from the numerical examples which explicitly refer to hydrogen, the treatment applies equally to oxygen, chlorine and other gases.

3. EFFICIENCY OF GAS EVOLUTION

Let us consider a reaction which yields a flux density N_D of a substance "D" (*eg* molecular hydrogen) at a current density

$$j = N_D(n/v_D)F. \quad (1)$$

In case of competing electrode reactions, j is the partial current density. In this case, the current efficiency ε

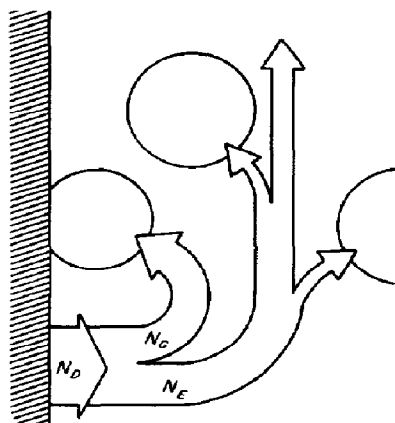


Fig. 1. Transport mechanisms of dissolved gas from the electrode.

$= j/j_{\text{tot}}$ can be calculated from a relationship derived earlier[4][†].

j and N_D will be defined as referred to the electrode area A with no regard to the fact that A may be partly blocked by adhering bubbles; j and N_D thus represent the nominal current density and the nominal flux density, respectively.

The electrode area A is sufficiently larger than given by the dimensions of departing bubbles, but, possibly smaller than the total geometric area of the electrode. This distinction is reasonable whenever the current density varies over the total electrode area, as commonly happens in gas-evolving electrochemical reactors.

As illustrated in Fig. 1, the total flux density N_D composes of a flux density N_E transported in dissolved form to the bulk and a flux density N_G transformed into the gaseous phase at the electrode[‡]

$$N_D = N_E + N_G \quad (2)$$

We define a fraction f_G which is evolved as gas in form of bubbles grown at the electrode surface,

$$f_G = \frac{N_G}{N_D} = 1 - \frac{N_E}{N_D} \quad (3)$$

This fraction f_G denotes the efficiency of gas evolution. Its quantitative evaluation will be the object of the following investigation. The generally established view of the role of the transport mechanisms would be represented by $f_G = 1$.

4. MASS TRANSFER OF DISSOLVED SUBSTANCE TO THE BULK

The flux N_E^D of a substance transported in dissolved form from the wetted part A_w of the electrode area to the bulk of electrolyte may be given by

$$N_E^D = k_E A_w (\bar{c}_e - c_0) \quad (4)$$

where k_E is a mean mass transfer coefficient and $(\bar{c}_e - c_0)$ is the concentration difference of dissolved substance at the electrode and in bulk. All these quantities demand some discussion.

It was pointed out earlier[5] that the concentration c_e of the electrolyte at zero distance from the electrode varies with the position on the electrode, particularly with the centre of the contact area of the adhering bubble. Strictly \bar{c}_e is, therefore, a mean value of c_e over the wetted part of the electrode area.

N_E^D/A_w is the effective flux density on the wetted area, ie the total electrode area minus the contact areas of all adhering bubbles. Therefore k_E is the effective mass transfer coefficient referred to the wetted area. It may, however, be useful to define an apparent mass transfer coefficient k_E referred to the total area A ,

including the non-wetted partial areas.

$$N_E = \frac{N_E^D}{A} = k_E (\bar{c}_e - c_0) \quad (5)$$

The interrelation between the two mass transfer coefficients is therefore,

$$k_E = k_E \frac{A_w}{A} = k_E (1 - \theta) \quad (6)$$

where θ is the fractional surface coverage, ie the fraction of the electrode area A covered by adhering bubbles.

There are again two mechanisms acting on mass transfer of dissolved substance to the bulk; k_E is affected by the (macro)convective mass transfer owing to electrolyte flow past the electrode and, whenever gas evolution proceeds, by superimposed microevents due to growing and detaching bubbles. Both mechanisms may separately be described by particular mass transfer coefficients k_{Ec} and k_{Eb} , respectively. The combined action of both mechanisms may be taken into account by[6]

$$k_E = (k_{Ec}^2 + k_{Eb}^2)^{0.5} \quad (7)$$

Equations for microconvective mass transfer depend on the particular flow conditions of the bubble-electrolyte dispersion (natural or forced flow). For forced convective mass transfer well-known relationships may be used, eg for laminar flow the extended Léveque equation[7]

$$Sh_c = 1.615 (Re_L Sc d_h / L)^{1/3} [1 + 0.1 (Re_L d_h / L)^{1/4}] \quad (8)$$

where d_h is the equivalent hydraulic diameter for non-circular ducts and L is the length of the interelectrode gap in flow direction. The dimensionless groups are

$$Sh_c = \frac{k_{Ec} d_h}{D} \quad (9)$$

$$Re_L = \frac{v_L d_h}{\nu} \quad (10)$$

$$Sc = \frac{\nu}{D} \quad (11)$$

Equation (8) is applicable to all Schmidt numbers Sc but restricted to $Re_L Sc d_h / L > 50$.

In the case of gas-sparged electrodes, ie electrodes exposed to a flow induced by gas inserted from outside the cell, mass transfer can be described quantitatively by the relationship of Ibl and coworkers[8, 9]

$$Sh_c = \frac{k_{Ec} L}{D} = 0.19 (Ar Sc)^{1/3} \quad (12)$$

where

$$Ar \equiv \frac{gL^3}{\nu^2} \frac{\varphi}{1 - \varphi} \quad (13)$$

and L is a characteristic (but in this case inconsequential) length, and φ is the volumetric gas fraction near the electrode.

Equations for microconvective mass transfer at gas-evolving electrodes were derived for, and are usually applied to, a species under limiting current density

[†] Strictly, j is the current density representative of the formation of the substance "D" as primarily dissolved in electrolyte. Thus, any possible reactions of the substance at or with the electrode or a diffusion through or an absorption by the electrode material are explicitly excluded.

[‡] Any homogeneous or heterogeneous chemical reactions of "D" in electrolyte will also be excluded.

conditions†. The application is, of course, not restricted to the condition of zero concentration at the electrode and the equations are equally useful for any other species in the transport from the bulk to the electrode or in reverse direction. Out of the available equations we base on [11]

$$Sh_b = 0.93 Re_G^{0.5} Sc^{0.487} \quad (14)$$

for a mean current density range ($100-10^4 \text{ A m}^{-2}$) or, preferably, to its more extended and more universal form [11]

$$Sh_b = 1.89 Re_G^{0.5} Sc^{0.487} [\theta^{0.5} (1 - \theta^{0.5})]^{0.5}. \quad (15)$$

The meaning of the dimensionless groups is

$$Sh_b \equiv \frac{k_{Eb} d}{D} \quad (16)$$

$$Re_G \equiv \frac{v_G^* d}{\nu} \quad (17)$$

where v_G^* denotes the volumetric flux density of gas evolved at the electrode.

$$v_G^* = N_G \frac{M_G}{\rho_G} \approx N_G \frac{R_m T}{p}. \quad (18)$$

The characteristic length d is the mean bubble departure diameter. For a Schmidt number of about $Sc = 300$, Equation (15) may be written in the simpler form

$$Sh_b = 1.75 (Re_G Sc)^{0.5} [\theta^{0.5} (1 - \theta^{0.5})]^{0.5}. \quad (19)$$

The derivation from (15) is moderate in other realistic Schmidt numbers of dissolved gases in liquids.

The combined mass transfer coefficient, Equation (7) follows from (6), (16) and (19).

$$k_E = \left[k_{Ec}^2 (1 - \theta)^2 + 1.75^2 \left(\frac{D}{d} \right) \theta^{0.5} (1 - \theta^{0.5}) v_G^* \right]^{0.5}. \quad (20)$$

From (5) follows the (nominal) flux density referred to the area A .

$$N_E = [k_{Ec}^2 (1 - \theta)^2 + K_1 N_G]^{0.5} \Delta c \quad (21)$$

with the abbreviations

$$\Delta c = (\bar{c}_e - c_0) \quad (22)$$

$$K_1 = 1.75^2 \frac{D}{d} \theta^{0.5} (1 - \theta^{0.5}) \frac{M_G}{\rho_G}. \quad (23)$$

It may be more convenient to replace the flux density of dissolved gas, N_G , for the flux density of the total amount of substance formed at the electrode, N_D , which is known from the current density j according to Equation (1):

$$N_E = \Delta c \{ [K_1 N_D + 0.25 K_2^2 \Delta c^2 + k_{Ec}^2 (1 - \theta)^2]^{0.5} - 0.5 K_1 \Delta c \}. \quad (24)$$

5. A RELATIONSHIP FOR THE EFFICIENCY OF GAS EVOLUTION

The efficiency of gas evolution, understood as the fraction of the total amount of substance formed which is transformed into the gaseous phase of bubbles adhering to the electrode and defined by Equation (3), results immediately from (24) as

$$f_G = 1 + K_2 - [K_2 (2 + K_2) + K_3^2]^{0.5} \quad (25)$$

where the following dimensionless parameters are used:

$$K_2 = 1.53 \frac{D}{d} \frac{R_m T}{p} \theta^{0.5} (1 - \theta^{0.5}) \Delta c^2 \frac{(n/v_D) F}{j} \quad (26)$$

$$K_3 = k_{Ec} (1 - \theta) \Delta c \frac{(n/v_D) F}{j}. \quad (27)$$

It is easily seen from Equation (27) that the parameter K_3 represents the fraction of the total amount of substance formed which is transported in dissolved form to the bulk through macroconvective mass transfer, hence $0 \leq K_3 \leq 1$. The parameter K_2 represents the effect of the flux density ($k_{Eb} \Delta c$) of substance transported in dissolved form to the bulk through microconvective mass transfer in the form

$$K_2 = \frac{(k_{Eb} \Delta c)^2}{2 N_D N_G} = \frac{K_1 \Delta c^2}{2 N_D}. \quad (26a)$$

Equation (25) is shown in Fig. 2.

The question under what condition gas is not evolved, $f_G = 0$, can be answered from (25). The condition is given for $K_3 = 1$ (and arbitrary values of K_2). As seen from (27) this is the case when, in absence of bubble growth, the whole amount of substance is transported to the bulk through macroconvective mass transfer, ie at current densities below the onset of nucleate gas evolution.

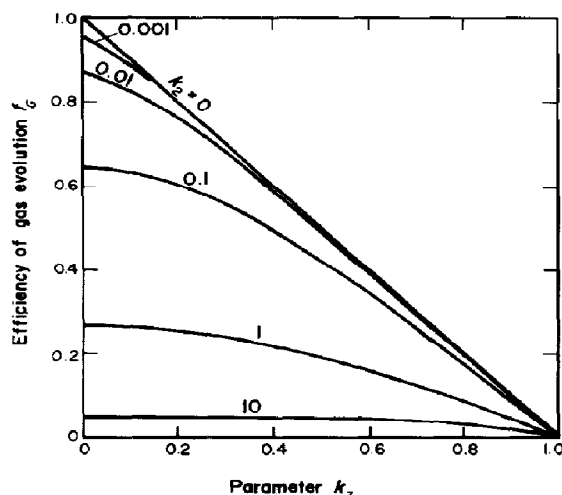


Fig. 2. Efficiency of gas evolution as a function of the parameters K_2 and K_3 .

† "Microconvection" does not explicitly refer to a special model for mass transfer at gas-evolving electrodes but takes up a term established in heat transfer [10].

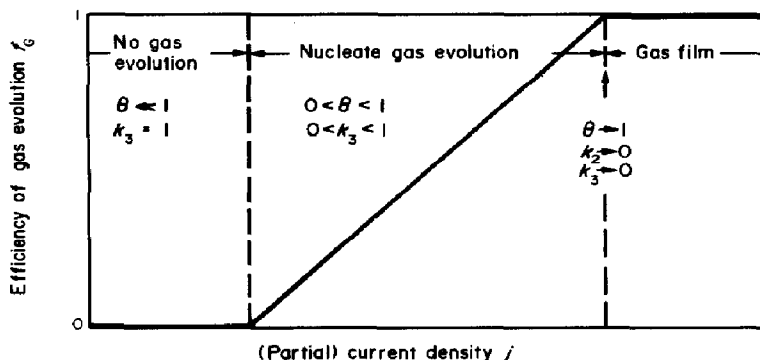


Fig. 3. The three stages of operation of gas-evolving electrodes in qualitative presentation.

It is informative to examine under what condition the efficiency of gas evolution, f_g , will equal unity. From Equation (25) follows the condition $K_2 = 0$ and $K_3 = 0$. Substance is not transported to the bulk, neither by macroconvective nor by microconvective mass transfer. It is seen from Equation (26) that $K_2 \rightarrow 0$ for $\theta \rightarrow 0$ as well as $\theta \rightarrow 1$; Equation (27) shows that $K_3 \rightarrow 0$ is attained in values of the fractional surface coverage $\theta \rightarrow 1$ only. Hence, the condition $f_g \rightarrow 1$ can only be verified for that current density which is linked with a complete blocking of the electrode surface due to adhering bubbles, i.e. for a current density which marks the upper bound of nucleate gas evolution. The condition thus provides the interesting answer that in the whole range of nucleate gas evolution, the efficiency of gas evolution is smaller than unity; only a fraction of the total amount of substance is evolved as gas at the electrode. The approach of f_g close to unity signalizes the formation of a gas film, i.e. the onset of what is called the anode effect in alumina electrolysis.

The trend of f_g is qualitatively illustrated in Fig. 3.

6. EXPERIMENTAL RESULTS

Reasonable values of the efficiency of gas evolution, f_g , can be obtained by inserting realistic concentration differences Δc into Equation (25). Values of Δc are available from various experimental investigations conducted by Shibata [12–14] who studied the concentration of hydrogen and oxygen immediately at the cathode and the anode respectively. Two different methods of investigation were used and gave excellent agreement [12]. The data cover a wide range of current density from 3 to 10^4 A m^{-2} . The electrolyte was sparged with hydrogen or oxygen introduced from outside, so that the bulk concentration c_0 was very near the saturation concentration. The concentration values c_e given are mean values over the wetted area, $c_e = \bar{c}_e$.

6.1. Hydrogen evolution

Shibata's experimental results [12, 13] were evaluated using a diffusion coefficient of hydrogen in 0.5 M H_2SO_4 and 25°C of value $D = 3.7 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. The bubble diameter used was $d = 50 \mu\text{m}$, assumed to be

independent of the current density. The departure diameter is a question not settled so far. The problem is discussed in detail in [1, 2]. The diameter used is, however, a reasonable value with satisfactory accuracy for this field of application and agrees with careful investigations of Janssen and Hoogland [15].

The fractional surface coverage θ was taken from [16] where experimental findings of various investigators are collated. These values depend, indeed, on the particular experimental conditions and need not necessarily coincide with the unknown coverage data in Shibata's runs. This uncertainty, however, does not involve serious problems for the following reasons. The term $[\theta^{0.5}(1-\theta^{0.5})]$ in Equation (26) exhibits small variations ($\pm 10\%$) in the coverage range of $0.08 < \theta < 0.5$, representative of a current density range of about $10\text{--}30,000 \text{ A m}^{-2}$. The parameter K_2 is, therefore, only slightly affected in the whole range of experimental investigation. It is further seen from (25) or Fig. 2 that the parameter K_3 has a strong effect on f_g for all small values of K_2 ($K_2 \rightarrow 0$) and for mean values of K_2 ($K_2 \approx 1$) together with large values of K_3 ($K_3 \rightarrow 1$). Inserting experimental data shows that the coincidence of mean values of K_2 with large values of K_3 is verified only in small values of the current density where $\theta \ll 1$ and thus $(1-\theta) \approx 1$. As the current density increases, values of K_2 increase until, at large values of the current density, they decrease to values $K_2 \rightarrow 0$. In this latter case, values of K_3 are very small, $K_3 \rightarrow 0$. Their effect on f_g becomes negligible. The precarious question of reliable fractional surface coverage data is thus meaningless in this context.

The unknown mass transfer coefficient k_{Ec} due to macroconvection required for the parameter K_3 can be obtained as follows. If it is correct that in low values of the current density the efficiency of gas evolution is $f_g = 0$, the parameter must be $K_3 = 1$, irrespective of the fact that the fractional surface coverage θ and the concentration difference Δc vary as the current density j varies. Inserting data for θ , Δc and j into

$$k_{Ec}(1-\theta)\frac{\Delta c}{j}\frac{n}{v_D}F = K_3 = 1 \quad (28)$$

permits the determination of reasonable values of k_{Ec} without knowledge of the experimental particularities. Unfortunately experimental assessment of the interfacial concentration c_e is necessarily the more inac-

curate the lower the current density. The procedure to find k_{Ec} can be facilitated and improved by plotting the experimental data in a log-log diagram as shown in Fig. 4. From Equation (28) it follows that the range of no gas evolution must be represented by a slope of unity. The derivation of the line from this slope marks the onset of nucleate gas evolution.

The values obtained were $k_{Ec} = 15 \times 10^{-6} \text{ m s}^{-1}$ and $k_{Ec} = 20 \times 10^{-6} \text{ m s}^{-1}$ for two different experimental set-ups ([12] and [13]) with unstirred electrolyte and $k_{Ec} = 220 \times 10^{-6} \text{ m s}^{-1}$ with vigorous stirring [13]. The latter value is in approx. agreement with the results from Equation (12).

The efficiency of gas evolution as obtained from Shibata's supersaturation data is shown in Fig. 5.

6.2. Oxygen evolution

The diffusion coefficient used in Equation (26) was $D = 2.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for oxygen in 1 M H_2SO_4 at

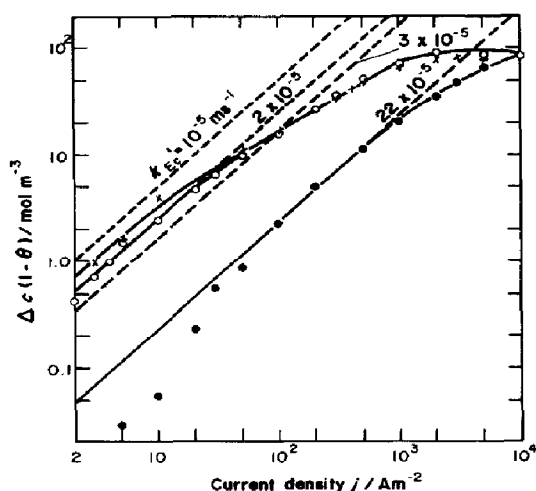


Fig. 4. Assessment of the macroconvective mass transfer coefficient k_{Ec} for various experiments of Shibata. Hydrogen evolution from 0.5 M H_2SO_4 , 25°C. No stirring: + [12], o [13]; vigorous stirring: • [13].

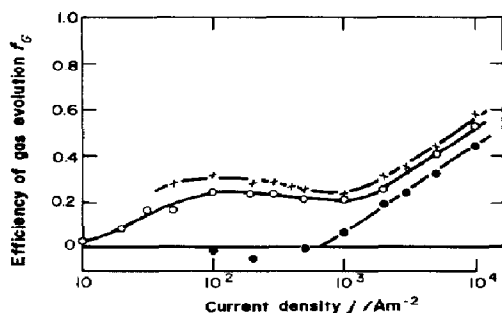


Fig. 5. Efficiency of hydrogen gas evolution vs current density, calculated from Equation (25) based on experimental supersaturation data of Shibata; smooth platinum electrodes. +, unstirred electrolyte [12]; o, unstirred [13]; •, stirred [13].

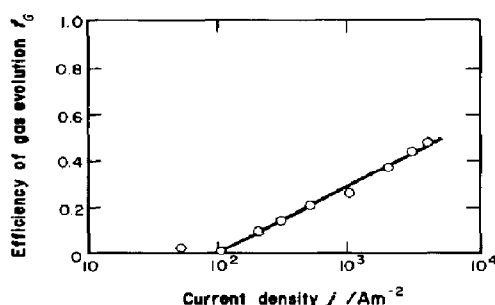


Fig. 6. Efficiency of oxygen gas evolution vs current density, calculated from Equation (25) based on experimental supersaturation data of Shibata [14]; smooth platinum electrode, unstirred electrolyte.

25°C [14]. The same constant bubble departure diameter was used as for hydrogen and the same surface coverage data due to lack of reliable data for anodes. The mass transfer coefficient k_{Ec} was estimated as outlined above, $k_{Ec} = 10 \times 10^{-6} \text{ m s}^{-1}$. Results are plotted in Fig. 6.

7. DISCUSSION

The diagrams show that the onset of nucleate gas evolution, *ie* the upper bound of the range of electrolysis without gas evolution at the electrode, depends strongly on whether the electrolyte is stirred or not (this is well-known from experience) and that the gas evolution does not start below $j = 10 \text{ A m}^{-2}$ under the conditions of experimentation. This, of course, does not exclude the possibility that a few single bubbles are formed at lower current densities since the supersaturation Δc measured by Shibata [12-14] and used in Equations (26) and (27) represents an average value over the wetted area. Local concentrations may notably exceed the average, thus permitting a nucleation site to become active. Presumably these are rare and exceptional events at the electrode below the current density representing the real onset of gas evolution.

It is arguable that the mass transfer equation (15) or its special forms (14) and (19) are not experimentally verified with a Reynolds number defined by Equation (17) together with (18). Indeed (15) is a fully theoretical equation based on the rate of gas evolved as bubbles growing at the electrode, but was verified [11] with a Reynolds number formed with a volumetric flux density of evolved gas being equal to the total quantity generated:

$$v_G^* = N_D \frac{M_G}{\rho_G} \quad (29)$$

A distinction between N_D and N_G , as proposed in the present paper, was not made. Since Equation (19) is one of the basic equations used in the present paper, one might be compelled to conclude that the outcome of this investigation may be strongly deficient. However, this suspicion is not confirmed by the following consideration.

One may suppose that the f_g values as obtained for unstirred electrolyte (Fig. 5) reflect the real conditions

of experiments used to test the mass transfer equation (15). Reynolds numbers formed with these f_G values will then represent the experimental values more realistically than the values used in the original paper [11]. A comparison of Equation (15) with the new (corrected) data points shows that (15) yields mass transfer coefficients which are, in fact, somewhat too small. In the range of usual industrial current density values, the deviation is about 30%. It might, therefore, be advisable to choose a larger numerical factor in Equation (19) and to repeat the procedure to obtain values of f_G . Since the value of a corrected numerical factor is doubtful, we refrain from carrying out the complete procedure and confine ourselves to the tendency to be expected; the parameter K_2 would be increased, whereas K_3 remains unchanged. As seen from Fig. 2, resulting values of f_G would be somewhat lower. Hence, using Equation (19) in a slightly modified form rather tends to lower the efficiency of gas evolution predicted but does not contribute to invalidate the discrepancy between N_D and N_G noted.

It must be pointed out that Figs 5 and 6 represent the particular conditions of Shibata's experiments. The numeric results of the efficiency of gas evolution depend in particular on the supersaturation data and cannot be generalized. Above all, the behaviour of the efficiency of gas evolution (owing to k_{ec}) in small values of the current density is somewhat doubtful. All results, however, suggest a striking conclusion; in the

whole range of industrial current density, the efficiency of gas evolution is far smaller than unity.

This result does not agree with the established view and it appears that a customary term as "current density of gas evolution" represents an erroneous view. Before conclusions will be drawn it would be useful to test the result by a second independent method. This will be done in a second part of this paper dealing with bubble growth data. Detailed conclusions will be given there.

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