Bubble parameters and efficiency of gas bubble evolution for a chlorine-, a hydrogen- and an oxygen-evolving wire electrode

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BUBBLE PARAMETERS AND EFFICIENCY OF GAS BUBBLE EVOLUTION FOR A CHLORINE-, A HYDROGEN- AND AN OXYGEN-EVOLVING WIRE ELECTRODE

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Abstract—The effect of current density used for total gas evolution, i_g , or for gas in bubbles, i_b , and the effect of solution-flow velocity, $v_{s,0}$, and temperature, T , on the detached bubbles parameters, viz average Sauter bubble radius, $R_{s,d,av}$, average bubble radius, $R_{d,av}$, average of the square of the bubble radii, $(R_d^2)_{av}$, average of the third power of the bubble radii, $(R_d^3)_{av}$, detached bubble frequency, ω , and efficiency of gas bubble evolution, η_b , for a chlorine-, a hydrogen- and an oxygen-evolving electrode at forced convection have been determined experimentally. The electrodes consist of a thin wire electrode with a small height. It has been found that:

- The average Sauter bubble radius is proportional to $i_g^{n_4}$ and decreases linearly with increasing $v_{s,0}$ at constant i_g . The constant n_4 depends on the temperature, the nature of the gas evolved, the electrode material and the electrolyte and is independent of $v_{s,0}$. Similar correlations were obtained for $R_{d,av}$, $(R_d^2)_{av}$ and $(R_d^3)_{av}$.
- The frequency of detached bubbles is proportional to $i_g^{n_5}$ and increases linearly with increasing $v_{s,0}$ at constant i_g . The constant n_5 depends on the temperature, the nature of the gas evolved, the electrode material and the electrolyte and is independent of $v_{s,0}$.
- The efficiency of gas bubble evolution η_b increases with increasing i_g and approaches a limiting value.

NOMENCLATURE

$A_{d,av}$ average cross-section of detached bubbles

$$A_{d,av} = \sum_{i=1}^n \pi R_{d,i}^2 / n \text{ (m}^2\text{)}$$

d_b bubble population density (m⁻²)

F Faraday constant = 96487 C mol⁻¹

i electric current density (kA m⁻²)

i_b electric current density used for gas in bubbles (kA m⁻²)

i_g electric current density for total gas evolution (kA m⁻²)

I electric current (kA)

n number of electrons, involved in the electrode reaction to form one molecule of a species

n number of bubbles on a part of a moving film

R_a radius of attached bubbles (m)

$R_{d,i}$ radius of detached bubble i (m)

$R_{d,av}$ average radius of detached bubbles,

$$R_{d,av} = \sum_{i=1}^n R_{d,i} / n \text{ (m)}$$

$(R_d^2)_{av}$ average of the square of the bubble radii,

$$(R_d^2)_{av} = \sum_{i=1}^n R_{d,i}^2 / n \text{ (m}^2\text{)}$$

$(R_d^3)_{av}$ average of the third power of the bubble radii,

$$(R_d^3)_{av} = \sum_{i=1}^n R_{d,i}^3 / n \text{ (m}^3\text{)}$$

$R_{s,d,av}$ average Sauter bubble radius,

S_b

degree of screening of the electrode by attached bubbles

T

temperature (K)

$v_{g,b}$

gas bubble production rate (ms⁻¹)

$v_{g,0}$

theoretical production rate of gas bubbles when all the gas is evolved as bubbles,

$$v_{g,0} = \frac{i_g V_M}{nF} \times \frac{T}{298} \text{ (ms}^{-1}\text{)},$$

where $V_M = 24.510^{-3}$ m³ mol⁻¹ at 298 K and 101 kPa

$v_{s,0}$

solution-flow velocity (ms⁻¹)

$V_{d,av}$

average volume of departed bubbles

$$V_{d,av} = \sum_{i=1}^n \frac{4}{3} \pi R_{d,i}^3 / n \text{ (m}^3\text{)}$$

V_M

volume of 1 mol gas is 24.5 10⁻³ m³ at 298 K (m³ mol⁻¹)

V_g

volume of the gas (m³)

$V(g + H_2O)$

volume of gas plus water vapor (m³)

ω

detached bubble frequency is the number of detached bubbles from the electrode per second and per m² electrode surface (m⁻² s⁻¹)

$p(H_2O)$

partial water vapor pressure (kPa)

$p(g + H_2O)$

sum of the partial pressures of gas g and water vapor (= 101 kPa)

η_b efficiency of gas bubble evolution,

$$\eta_b = \frac{v_{g,b}}{v_{g,0}}$$

δ thickness of Nernst diffusion layer (m)

Subscripts

av	average
b	bubble
Cl	chlorine
d	detached
g	gas
H	hydrogen
O	oxygen
s	solution

INTRODUCTION

Electrogenerated bubbles at gas-evolving electrodes have received much attention, because of their industrial importance. All theoretical work performed in the past concerns the departing mechanism of a single growing bubble on a horizontal wall in convectionless solution. The detached bubble radius of a relatively large bubble can be calculated with the theoretical Fritz equation[1]. It is quite difficult to verify the calculated result experimentally, because the required contact angle of the bubble is usually unknown and hardly determinable. For practical purpose the multi-bubbles system is important. At present no theoretical treatment of the multi-bubbles system is available, only a few experimental results are known and at some points they appear to be poor and questionable[2]. Because of industrial importance it has been decided to determine the bubble behaviour in a more thorough and comprehensive manner. So far, little has been done on efficiency of gas bubble evolution at a gas-evolving electrode. Only some experimental results have been published about the bubble behaviour and the efficiency of gas bubble evolution[2-5]. Vogt[6] had reported some calculated results about the efficiency of gas bubble evolution. The main objective of this investigation is to determine experimentally the bubble parameters and the efficiency of gas bubble evolution under (semi-)industrial conditions.

EXPERIMENTAL

Determination of detached bubble parameters and efficiency of gas bubble evolution

The experimental set-up of the electrolytic cell, circuit and optical arrangements used to perform the bubble measurements is almost the same as described in[2, 7, 8]. A schematic diagram of the set-up is shown in Fig. 1. The working-electrode compartment and the two counter-electrode compartments were separated by a membrane (Nafion, type 117). The working-electrode compartment had an inner cross-section of 1.35 cm² and a length of about 10 cm, and a wire working electrode was placed vertically in the middle of the tube opposite both membranes. Two platinum plates of about 30 mm² each were used as counter electrodes.

Fig. 1. Electrolysis set up.

The current was adjusted galvanostatically. The volume of solution in the working-electrode compartment was about 2000 cm³. The volumetric flow-rate of the thermostated solution through the working-electrode compartment was measured with a calibrated flowmeter (F & P. Co. Precision Bore flowmeter, tube No. FP.-3/8-25-G-5/36, stainless steel or glass float). The detached chlorine, hydrogen and oxygen bubbles were filmed in a space from the top of the working electrode to 1.7 mm above the working electrode with a high-speed film camera of 3000 frames per second to obtain sharply pictured bubbles. The film pictures were analyzed and the efficiency of gas bubble evolution was calculated as described in[7, 8].

For the chlorine experiments a solution of 4 M NaCl plus 0.1 M HCl was used as anolyte. A 1 M KOH solution has been used as catholyte for the hydrogen evolution at 298 K and as anolyte for the oxygen evolution at 298 K, and for hydrogen evolution at 353 K a 6.8 M NaOH solution has been used as catholyte.

The solution-flow circuits containing the counter-electrode compartment were generally filled with 10 M NaOH. The choice of the electrolysis conditions is based on the industrial operation conditions of the chlor-alkali process. The working electrode consists of a nickel or platinum wire (diameter 0.5 mm) with or without a coating layer of RuO₂ or Co₃O₄. The length of the wire was varied between 2 and 4 mm.

Preparation of electrodes

Preparation of RuO₂-electrode[9]. The platinum-wire was placed for 10 min in concentrated caustic and after that in concentrated hydrochloric acid, both solutions at 353 K. The wire was coated by dipping it into a solution of 0.1 M RuCl₃ and 20% HCl. The wire was then dried at 353 K and heated for 10 min at 723 K. The procedures were repeated six times. Then the wire was heated for 1 h at 723 K.

Preparation of Co₃O₄-electrode[10]. The platinum-wire was etched for 10 min in concentrated hydrochloric acid at 353 K. The wire was dipped in a 0.5 M Co(NO₃)₂ solution; dried for about 1 min at 353 K, and heated for 3 to 5 min at 623 K. The procedure was repeated three times. The heating procedure was finished at 623 K for 1 h.

RESULTS

Characteristics of detached chlorine, hydrogen and oxygen bubbles

Only a part of the gas formed during electrolysis is evolved as bubbles and the rest of the gas dissolves in the solution. The rate of the gas bubble evolution corresponds to the current density, i_b , being a fraction of the current density, i_g , used for the total gas production. The bubble behaviour can be characterized by bubble parameters, such as bubble radius, bubble cross-section, bubble volume and bubble frequency. Assuming that the bubbles formed during the electrolysis are saturated with water vapor, the volume of the gas is calculated by:

$$V_g = V_{(g+H_2O)} \frac{[p(g+H_2O) - p(H_2O)]}{p(g+H_2O)},$$

where V_g = the volume of the gas (m^3), $V_{(g+H_2O)}$ = the volume of gas plus water vapor (m^3), $p(g+H_2O)$ = the sum of the partial pressures of gas g and water vapor where $p(g+H_2O)$ is supposed to be 101 kPa and $p(H_2O)$ = the partial water vapor pressure. The hydrostatic head was not taken into account in the gas volume calculation because its value was negligible. The $p(H_2O)$ of different kinds of solution are given as a function of temperature in the literature[11].

The characteristics of attached bubbles at the electrode surface fluctuate around a quasi-stationary state[7]. Due to changes in nucleation properties of the electrode surface, the extent of the fluctuation depends for instance on electrode orientation, nature of the gas evolved and electrolytic conditions. Similar phenomena are expected to happen with the detached bubbles. Moreover, the quasi-stationary state changes with increasing electrolysis time and finally it becomes practically constant.

The measured bubble parameters are averaged, because of their fluctuations. A common method for this purpose is as follows: the bubble behaviour on a small surface is filmed during a certain period of time.

To cover the bubble behaviour in different stages, an adequate number of frames of the film has to be used to obtain sufficiently accurate bubble parameters. Consequently, the bubble parameters are averaged in time.

It has been found that about 500 frames of the film are required to obtain reliable average values of the bubble parameters, at a film speed of 3000 frames per second. At the beginning of the filming the camera is not running steadily, it requires some time before it becomes stable, therefore the first thousand frames of the film are not measured. Additionally, for each set of electrolysis conditions a pre-electrolysis time of about 30 min is required to enable the electrolytic system to be stabilized. From the experimental bubble radii we calculated:

$$R_{d,av} = \sum_{i=1}^n \frac{R_{d,i}}{n} \quad R_{s,d,av} = \frac{\sum_{i=1}^n \frac{R_{d,i}^3}{n}}{\sum_{i=1}^n \frac{R_{d,i}^2}{n}},$$

$$(R_d^2)_{av} = \sum_{i=1}^n \frac{R_{d,i}^2}{n} \quad \text{and} \quad (R_d^3)_{av} = \sum_{i=1}^n \frac{R_{d,i}^3}{n}$$

where $R_{d,av}$ = the average radius of detached bubbles, $R_{d,i}$ = the radius of detached bubble i , n = the number of bubbles, $R_{s,d,av}$ = the average Sauter radius of detached bubbles, $(R_d^2)_{av}$ = the average of the square of the bubble radii, and $(R_d^3)_{av}$ = the average of the third power of the bubble radii.

In the formula of $R_{d,av}$ the contribution of the small bubbles dominates too much and the bigger bubbles are underestimated. Therefore it is preferable to use $R_{s,d,av}$.

Effect of current density. Figure 2 shows the average Sauter radius of detached bubbles, $R_{s,d,av}$, as a function of the current density i_b , on a double logarithmic scale for chlorine and hydrogen evolution at two temperatures and for oxygen evolution at only one temperature.

Fig. 2. Average Sauter bubble radius vs the current density i_b on double logarithmic scale for a hydrogen-evolving nickel electrode in 1 M KOH, at 298 K and a solution-flow velocity of 0.12 m s^{-1} and in 6.8 M NaOH, at 353 K and a solution-flow of 0.05 m s^{-1} and for an oxygen-evolving nickel electrode in 1 M KOH, at 298 K and a solution-flow velocity of 0.12 m s^{-1} and for a chlorine-evolving RuO_2/Pt electrode in 4 M NaCl + 0.1 M HCl, at 298 and 353 K and a solution-flow velocity of 0.05 m s^{-1} .

From Fig. 2 it follows that the log $R_{s,d,av}$ for all three gases increases linearly with increasing log i_b , for i_b from about 0.01–5 kA m⁻². The experimental results showed that the average radius, $R_{d,av}$, the average square of radius, $(R_d^2)_{av}$, the average third power of radius, $(R_d^3)_{av}$, and the frequency of detached bubbles, ω , as a function of current density, i_b , on double logarithmic scale are linear too. These linear relations can be expressed by:

$$R_{d,av} = a_1 i_b^{n_1}, \quad (R_d^2)_{av} = a_2 i_b^{n_2}, \\ (R_d^3)_{av} = a_3 i_b^{n_3}, \quad R_{s,d,av} = a_4 i_b^{n_4}$$

$$\text{and} \quad \omega = a_5 i_b^{n_5}.$$

The constants a_1 – a_5 and n_1 – n_5 are tabulated in Table 1.

The detached bubble frequency, ω , that is the number of detached bubbles from the electrode per second and per m² electrode surface, for chlorine, hydrogen and oxygen is plotted *vs* the current density, i_b , on a double logarithmic scale in Fig. 3. The parameters a_5 and n_5 are strongly dependent on the temperature.

Effect of solution-flow velocity. The average Sauter radius, $R_{s,d,av}$, for chlorine, hydrogen and oxygen bubbles is plotted as a function of solution-flow velocity, $v_{s,0}$, for a constant i_b in Fig. 4. From Fig. 4 it can be concluded that in the solution-flow velocity range from 0 to 0.2 m s⁻¹ the $R_{s,d,av}$ for the three gases decreases linearly with increasing $v_{s,0}$ at 298 and 353 K.

In Fig. 5 the detached bubble frequency ω *vs* $v_{s,0}$ at constant i_b is given for hydrogen, chlorine and oxygen. The results obtained show that in the solution-flow velocity range from 0 to 0.12 m s⁻¹ the detached bubble frequency for the three gases increases linearly with increasing solution-flow velocity, at 298 and 353 K.

Effect of temperature and electrode material. In Fig. 6 the logarithm of average Sauter radius, $R_{s,d,av}$, for the three gases is shown as a function of the reciprocal temperature. The dependence of $R_{s,d,av}$ on the reciprocal temperature and can be represented by:

$$R_{s,d,av} = a_6 \times 10^{n_6/T}.$$

The parameters a_6 and n_6 of the three gases are given in Table 2.

The constants a_6 and n_6 depend on the solution-flow velocity, the current density, the nature of the gas evolved, the electrode material and the electrolyte. The dependence of the detached bubble frequency on the temperature for chlorine, hydrogen and oxygen is showed in Fig. 7. The curves show that in the temperature range from 298 to 353 K at constant i_b the detached bubble frequency for the three gases increases linearly with increasing temperature.

For only the chlorine experiment the temperature was extended to 363 K. In the temperature range from 353 to 363 K the detached bubble frequency for chlorine increases rapidly with increasing temperature, probably due to water vapour formation.

Table 1. $R_{d,av}$, $(R_d^2)_{av}$, $R_{s,d,av}$ and ω as a function of current density, i_b , at different working conditions and i_b is given in kA m⁻²

Gas	T (K)	$v_{s,0}$ (m s ⁻¹)	Electrode material	Electrolyte	$a_1 \times 10^5$	n_1	$a_2 \times 10^9$	n_2	$a_3 \times 10^{13}$	n_3	$a_4 \times 10^5$	n_4	$a_5 \times 10^{-6}$	n_5
Cl ₂	298	0.05	RuO ₂ /Pt	4 M NaCl + 0.1 M HCl	7.2	0.17	6.0	0.46	5.3	0.60	9.4	0.19	57	0.3
Cl ₂	353	0.05	RuO ₂ /Pt	4 M NaCl + 0.1 M HCl	4.7	0.13	3.2	0.14	2.9	0.13	10.5	0.07	220	0.9
H ₂	298	0.12	Ni	1 M KOH	4.0	0.20	2.2	0.49	1.3	0.74	6.0	0.26	260	0.2
H ₂	353	0.05	Ni	6.8 M NaOH	4.6	0.22	2.5	0.43	1.6	0.55	6.6	0.15	330	0.4
O ₂	298	0.12	Ni	1 M KOH	4.8	0.24	2.7	0.50	1.5	0.63	5.7	0.21	180	0.4

Fig. 3. Detached bubble frequency vs the current density i_b on double logarithmic scale for a hydrogen-evolving nickel electrode in 1 M KOH, at 298 K and a solution-flow velocity of 0.12 m s^{-1} and in 6.8 M NaOH, at 353 K and a solution-flow velocity of 0.05 m s^{-1} and for an oxygen-evolving nickel electrode in 1 M KOH, at 298 K and a solution-flow velocity of 0.12 m s^{-1} and for a chlorine-evolving RuO_2/Pt electrode in 4 M NaCl + 0.1 M HCl, at 298 and 353 K and a solution-flow velocity of 0.05 m s^{-1} .

Fig. 4. Average Sauter radius of detached bubbles vs the solution-flow velocity for a hydrogen-evolving nickel electrode in 1 M KOH, at 298 K and 1 kA m^{-2} and in 6.8 M NaOH, at 353 K and 1 kA m^{-2} and for an oxygen-evolving nickel electrode in 1 M KOH, at 298 K and 1 kA m^{-2} and for a chlorine-evolving RuO_2/Pt electrode in 4 M NaCl + 0.1 M HCl, at 298 and 353 K and respectively, at 2 and 4 kA m^{-2} .

Efficiency of bubble evolution

The efficiency of bubble evolution is defined by:

$$\eta_b = \frac{v_{g,b}}{v_{g,0}}$$

where $v_{g,0} = (i_g T / nF 298) V_M$ (theoretical gas production rate, when the gas formed is completely taken up by bubbles), V_M = the volume of 1 mol gas at 298 K and a pressure of $101 \text{ kPa} = 24.5 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$, i_g = the current density used for the total gas production in kA m^{-2} , n = the number of electrons, involved in the reaction to form one molecule of Cl_2 , H_2 or O_2 and $v_{g,b}$ = the experimental bubble volume production rate corrected for the effect of vapour. The efficiency of

gas bubble evolution vs the current density for oxygen and hydrogen evolution is plotted in Fig. 8 and for chlorine in Fig. 9. The results obtained show that the efficiency of gas bubble evolution increases in decreasing rate with increasing current density i_g . Hydrogen evolution has the highest η_b and chlorine evolution the lowest.

Effect of current density. In Fig. 10, $\eta_b/(1 - \eta_b)$ is plotted as a function of the current density, i_b , on double logarithmic scale for chlorine and hydrogen evolution at 298 and 353 K and for oxygen evolution at 298 K. Figure 10 shows that $\log \eta_b/(1 - \eta_b)$ for all three gases increases linearly with increasing $\log i_b$ in the i_b range from 0.02 to 5 kA m^{-2} . These linear relations are

Fig. 5. Detached bubble frequency *vs* the solution-flow velocity of an oxygen-evolving nickel electrode in 1 M KOH, at 298 K and 1 kA m⁻² and for chlorine-evolving RuO₂/Pt electrode in 4 M NaCl + 0.1 M HCl, at 298 and 353 K and, respectively, at 2 kA m⁻² and 4 kA m⁻² and for a hydrogen-evolving nickel electrode in 1 M KOH, at 298 K and 1 kA m⁻² and in 6.8 M NaOH, at 353 K and 1 kA m⁻².

expressed by:

$$\frac{\eta_b}{1 - \eta_b} = a_7 i_b^{n_7}.$$

The parameters a_7 and n_7 of the three gases are given in Table 3 where i_b is given in kA m⁻².

The constant a_7 depends on the temperature, the solution-flow velocity and the nature of the gas evolved, the electrode material and the electrolyte. The constant n_7 is 0.39.

Effect of solution-flow velocity. Figure 11 shows $\eta_b/(1 - \eta_b)$ for the three gases *vs* the solution-flow velocity at constant i_b . From Fig. 11 it follows that $\eta_b/(1 - \eta_b)$ for chlorine, hydrogen and oxygen decreases slightly with increasing solution-flow velocity.

Effect of temperature and electrode material. In Fig. 12 the efficiency of gas bubble evolution for chlorine, hydrogen and oxygen is plotted as a function of temperature. The curves show that in the temperature range from 298 to 368 K the $\eta_{b,H}$ for hydrogen evolution on a nickel electrode in 1 M KOH solution at 1 kA m⁻² and $v_s = 0.12$ m s⁻¹ is independent of T , while $\eta_{b,H}$ for hydrogen evolution on a nickel electrode in 6.8 M NaOH solution at 0.5 kA m⁻² and $v_s = 0.05$ m s⁻¹ increases slightly with increasing temperature. $\eta_{b,O}$ for oxygen evolution on a nickel electrode in 1 M KOH solution at 1 kA m⁻² and $v_s = 0.12$ m s⁻¹ increases strongly with increasing temperature. Figure 13 shows the efficiency of gas bubble evolution for three different electrode materials, *viz* RuO₂/Pt, Pt and Co₃O₄ electrodes. The curves show that RuO₂/Pt electrode has the highest efficiency of gas bubble

Fig. 6. Average Sauter radius *vs* reciprocal temperature on single logarithmic scale for a hydrogen-evolving nickel electrode in 1 M KOH, at 1 kA m⁻² and a solution-flow velocity of 0.12 m s⁻¹ and in 6.8 M NaOH, at 0.5 kA m⁻² and a solution-flow velocity of 0.05 m s⁻¹ and for an oxygen-evolving nickel electrode in 1 M KOH, at 1 kA m⁻² and a solution-flow velocity of 0.12 m s⁻¹ and for chlorine-evolving electrode of RuO₂/Pt, Pt and Co₃O₄ in 4 M NaCl + 0.1 M HCl, at 2 kA m⁻² and a solution-flow velocity of 0.05 m s⁻¹.

Table 2. Average Sauter radius, $R_{s,d,av}$, in dependence of $1/T$ and T is given in K

Gas	i_a (kA m ⁻²)	$v_{s,0}$ (m s ⁻¹)	Electrode material	Electrolyte*	$a_6 \times 10^6$	n_6
Cl ₂	2	0.05	RuO ₂ /Pt	4 M NaCl + 0.1 M HCl	13.2	229
Cl ₂	2	0.05	Pt	4 M NaCl + 0.1 M HCl	13.2	229
Cl ₂	2	0.05	Co ₃ O ₄	4 M NaCl + 0.1 M HCl	9.8	295
H ₂	0.5	0.05	Ni	6.8 M NaOH	112	-200
H ₂	1	0.12	Ni	1 M KOH	34.7	40
O ₂	1	0.12	Ni	1 M KOH	15.9	-182

*Saturated with Cl₂, H₂ or O₂.

Fig. 7. Detached bubble frequency vs the temperature for a hydrogen-evolving nickel electrode in 1 M KOH, at 1 kA m^{-2} and a solution-flow velocity of 0.12 m s^{-1} and for an oxygen-evolving nickel electrode in 1 M KOH, at 1 kA m^{-2} and a solution-flow velocity of 0.12 m s^{-1} and for a chlorine-evolving RuO_2/Pt electrode in 4 M NaCl + 0.1 M HCl, at 2 kA m^{-2} and a solution-flow velocity of 0.05 m s^{-1} .

Fig. 8. Efficiency of gas bubble evolution as a function of current density for hydrogen evolution on a nickel electrode in 1 M KOH, at 298 K and a solution-flow velocity of 0.12 m s^{-1} and in 6.8 M NaOH, at 353 K and a solution-flow velocity of 0.05 m s^{-1} , and for oxygen evolution on a nickel electrode in 1 M KOH at 298 K and a solution-flow velocity of 0.12 m s^{-1} .

Fig. 9. Efficiency of gas bubble evolution as a function of current density for chlorine evolution on a RuO_2/Pt electrode in 4 M NaCl + 0.1 M HCl, at 298 and 353 K and a solution-flow velocity of 0.05 m s^{-1} .

evolution and Co_3O_4 electrode the lowest. The η_b of all three types electrodes increases with increasing temperature till it reaches a maximum at about 348 K and then decreases by increasing temperature.

DISCUSSION

Behaviour of detached bubbles and detached bubble frequency.

Bubbles rise in the space filmed just above the top of the working electrode, the number of which did not change, *ie* no coalescence occurred in the space just above the working electrode. Since the electrode is very short (about 3 mm), it can be assumed that during the period between the detachment of a bubble and the filming of this bubble, coalescence of detached rising bubbles is negligible. This agrees with other results, *ie* coalescence of hydrogen bubbles in alkaline solution and of chlorine bubbles in acidic chloride solution occurs only to a limited extent[4, 13]. Probably the growth of a bubble can be neglected after detachment until the moment of filming, since no bubble growth rate was detected in the observed space (picture height 1.70 mm). It can be concluded that pictured bubbles are almost the same size as bubbles departing from the electrode surface. Much attention has been paid to the radius of a bubble departing from the electrode. Two types of bubble-evolving electrodes can be distinguished, *viz* the single-bubble system (only one bubble is present on the electrode) and the multi-bubble system (many bubbles on the electrode). Up till now the theoretical relations for bubble departure radius concern only the departure mechanism of a single bubble growing on a horizontal wall in a convectionless liquid solution. Fritz[14] had derived an equation for the bubble departure radius, R_d , for slowly growing bubbles on a horizontal wall, in which the bubble-foot radius exceeds the cavity mouth radius. He obtained

$$R_d = 0.014 \gamma [\sigma / g(\rho_1 - \rho_2)]^{1/2},$$

where γ = constant angle between bubble and wall in degrees, σ = surface tension, ρ_1 = liquid density, ρ_2 = gas/vapour density and g = gravitational acceleration. This equation is valid for a bubble with freely

Fig. 10. $\eta_b/(1-\eta_b)$ is plotted vs the current density i_b on double logarithmic scale for a hydrogen-evolving nickel electrode in 1 M KOH, at 298 K and a solution-flow velocity of 0.12 m s^{-1} and in 6.8 M NaOH, at 353 K and a solution-flow of 0.05 s^{-1} and for an oxygen-evolving nickel electrode in 1 M KOH, at 298 K and a solution-flow velocity of 0.12 m s^{-1} and for a chlorine-evolving RuO_2/Pt electrode in 4 M NaCl + 0.1 M HCl, at 298 and 353 K and a solution-flow velocity of 0.05 m s^{-1} .

Table 3. $\eta_b/(1-\eta_b)$ in dependence of i_b

Gas	T (K)	$v_{s,0}$ (m s^{-1})	Electrode material	Electrolyte	a_7	n_7
Cl_2	298	0.05	RuO_2/Pt	4 M NaCl + 0.1 M HCl	0.5	0.39
Cl_2	353	0.05	RuO_2/Pt	4 M NaCl + 0.1 M HCl	0.4	0.39
H_2	353	0.05	Ni	6.8 M NaOH	2.0	0.39
H_2	298	0.12	Ni	1 M KOH	1.1	0.39
O_2	298	0.12	Ni	1 M KOH	0.6	0.39

Fig. 11. $\eta_b/(1-\eta_b)$ as a function of solution-flow velocity for a hydrogen-evolving nickel electrode in 1 M KOH, at 1 kA m^{-2} and 298 K and in 6.8 M NaOH, at 1 kA m^{-2} and 353 K and for an oxygen-evolving nickel electrode in 1 M KOH, at 1 kA m^{-2} and 298 K and for a chlorine-evolving RuO_2/Pt electrode in 4 M NaCl + 0.1 M HCl, at 2 and 4 kA m^{-2} and, respectively, at 298 and 353 K.

Fig. 12. Efficiency of gas bubble evolution as a function of temperature for a hydrogen-evolving nickel electrode in 1 M KOH, at 1 kA m^{-2} and a solution-flow velocity of 0.12 ms^{-1} and in 6.8 M NaOH, at 0.5 kA m^{-2} and a solution-flow velocity of 0.05 ms^{-1} and for an oxygen-evolving nickel electrode in 1 M KOH, at 1 kA m^{-2} and a solution-flow velocity of 0.12 ms^{-1} .

Fig. 13. Efficiency of gas bubble evolution as a function of temperature for chlorine-evolving electrode of RuO_2/Pt , Pt and Co_3O_4 in 4 M NaCl + 0.1 M HCl saturated with Cl_2 , at 2 kA m^{-2} and a solution-flow velocity of 0.05 ms^{-1} .

moving foot and a contact angle limited to 30° [15]. Various expressions were derived [16–18] for faster growing bubbles. The effect of subatmospheric pressure on the departure radius has been expressed by Cole and Shulman [19] as

$$R_d = c\gamma/p[\sigma/g(\rho_1 - \rho_2)]^{1/2},$$

where c = a pressure-dependent constant and p = subatmospheric pressure. Slooten [20] developed an equation for the maximal bubble departure volume, $V_{d,\max}$, for a bubble growing on a horizontal wall with its foot attached to the mouth of the cavity, a "cavity bubble". He found that

$$V_{d,\max} = 4r\sigma/\rho g,$$

where r = cavity-mouth radius, σ = surface tension, ρ = liquid density and g = gravitational acceleration. An extensive discussion about the size of departure bubbles is presented by Van Stralen [22]. Brandon and Kelsall [21] had given experimental bubble departure radii for a hydrogen-, oxygen- and chlorine-evolving micro electrode on which only one bubble was present. Their results cannot be explained by the present theoretical relations. They proposed that electrostatic

Fig. 14. Growth of a "cavity" bubble.

interaction between the bubble and electrode double layers controlled the bubble departure radius and that the two phases *viz* the gas and the solid phase, were separated by a thin liquid film of electrolyte. However, a direct contact between bubble and electrode surface is probable (cf. Fig. 14) [23, 25]. Bubbles are formed on cavities in the electrode surface. The question whether a cavity is active or nonactive, depends on its mouth radius and the supersaturation concentration of evolved gas at the electrode surface. Cavities with smaller mouth radius become active with increasing supersaturation concentration [24]. Probably both the contact area between the bubble and the electrode surface and the bubble departure radius are affected by the cavity size. At present a model which takes into account the electrostatic interaction and the cavity size, is not yet available even for a single-bubble system.

The radius of bubbles departing from the gas-evolving electrode used in this investigation (a multi-bubble system) varied widely due to fluctuations in the solution flow induced by departure, rise and coalescence of bubbles and to differences in cavity sizes.

To determine the effect of the nature of the gases on bubble departure radii, they should be compared at the same volumetric rate of bubble evolution, $v_{g,b}$. Table 4 gives the results at $v_{g,b} = 0.126 \times 10^{-4}$ and $1.264 \times 10^{-4} \text{ m}^3 \text{ s}^{-1}$, corresponding to $i_b = 0.1$ and 1.0 kA m^{-2} for hydrogen and chlorine, respectively, and to $i_b = 0.2$ and 2.0 kA m^{-2} for oxygen, and at 298 K and $v_{s,0} = 0.12 \text{ m s}^{-1}$. From Table 4 it follows that at the same rate of volumetric gas evolution, the hydrogen bubbles are the smallest and the chlorine bubbles the largest. The $R_{d,av}$ results obtained for hydrogen and oxygen show good agreement with the results of Janssen *et al.* [2]. Those reported by Bongenaar *et al.* [12] and Janssen *et al.* [8] are smaller; however, their experimental conditions differ totally from those used in the present experiment. It has been found that, in alkaline solution, hydrogen bubbles slip over the electrode surface more frequently than oxygen bubbles [8]. This means that the adhesion of hydrogen bubbles to the electrode surface is much weaker than that of oxygen bubbles. Further, it is known that hydrogen bubbles in alkaline solution do not coalesce as easily as oxygen bubbles do [13, 24]. Consequently, it is expected that small hydrogen and big oxygen bubbles will be formed. A theoretical description of the bubble departure radius will be very complex, due to a number of factors, such as that coalescence of bubbles results in large bubbles. However, the detachment of these large bubbles causes a strong flow of solution near the electrode surface which sweeps a lot of small bubbles from the electrode surface. Consequently, the average bubble departure radius for a multi-bubble system is determined in a complex way by many factors.

Table 4. The bubble parameter for hydrogen and oxygen evolution at a Ni electrode in 1 M KOH and for chlorine evolution at a RuO₂/Pt electrode in 4 M NaCl + 0.1 M HCl at two volumetric rates of bubble evolution, viz $v_{g,b} = 0.126 \times 10^{-4}$ and $1.26 \times 10^{-4} \text{ m s}^{-1}$ and at $T = 298 \text{ K}$ and $v_{s,0} = 0.12 \text{ m s}^{-1}$

Gas	H ₂		O ₂		Cl ₂	
$v_{g,b} \times 10^4 \text{ m s}^{-1}$	0.126	1.26	0.126	1.26	0.126	1.26
$i_b \text{ (kA m}^{-2}\text{)}$	0.1	1.0	0.2	2.0	0.1	1.0
$R_{d,av} \text{ (m)}$	25×10^{-6}	40×10^{-6}	31×10^{-6}	55×10^{-6}	36×10^{-6}	59×10^{-6}
$(R_d^2)_{av} \text{ (m}^2\text{)}$	7×10^{-10}	22×10^{-10}	12×10^{-10}	38×10^{-10}	14×10^{-10}	41×10^{-10}
$(R_d^3)_{av} \text{ (m}^3\text{)}$	2.3×10^{-14}	13×10^{-14}	4.7×10^{-14}	26×10^{-14}	7×10^{-14}	29×10^{-14}
$R_{s,d,av} \text{ (m)}$	32×10^{-6}	60×10^{-6}	40×10^{-6}	67×10^{-6}	51×10^{-6}	79×10^{-6}
$\omega \text{ (m}^{-2} \text{ s}^{-1}\text{)}$	120×10^6	260×10^6	74×10^6	180×10^6	36×10^6	84×10^6
η_b	0.30	0.56	0.22	0.43	0.13	0.28

Table 5. Parameters for hydrogen, oxygen and chlorine gas-evolving electrodes at a volumetric rate of bubble evolution of $1.26 \times 10^{-4} \text{ m s}^{-1}$, a solution-flow velocity of 0.12 m s^{-1} and at 298 K

Gas	H ₂	O ₂	Cl ₂
Diffusion coefficient $\text{m}^2 \text{ s}^{-1}$ [26, 28]	3.0×10^{-9}	1.59×10^{-9}	1.22×10^{-9}
Saturation concentration mol m^{-3} [26, 27, 28]	0.52	0.89	22
$i_g \text{ kA m}^{-2}$	1.8	4.7	3.6
η_b	0.56	0.43	0.28
s_b [8]	0.40	0.40	0.80
$d_b \text{ (mm}^{-2}\text{)} [8]$	1500	250	19
$R_a \text{ (}\mu\text{m)} [8]$	8	17	110
$2\pi d_b R_a \text{ (mm}^{-1}\text{)} [8]$	76	27	13
$\delta \text{ (m)} [25]$	2×10^{-5}	1×10^{-5}	2×10^{-5}

A comparison of bubble parameters under standard conditions of current density, solution-flow velocity and temperature is of interest for practical applications, *eg* separation of bubbles from a solution. It has been found that under the condition $i_g = 2 \text{ kA m}^{-2}$, $T = 298 \text{ K}$ and $v_{s,0} = 0.12 \text{ m s}^{-1}$, the average detached bubble radius for hydrogen and oxygen is practically the same and clearly smaller than for chlorine. It takes much longer to obtain a solution free from bubbles for hydrogen than for oxygen and chlorine bubbles. It is well known that, in alkaline solution, oxygen bubbles coalesce much more easily than hydrogen bubbles. It has been found that practically no coalescence of chlorine bubbles occurs [4]. Finally, it follows that the separation of bubbles and solution is determined not only by the detached bubble radius but also by the coalescence behaviour of bubbles.

The frequency of detached bubbles is proportional to $i_g^{n_s}$, where the exponent n_s depends strongly on both the nature of the gas evolved and the electrolytic conditions.

Efficiency of bubble evolution

Experimentally it was found that size of a detached bubble remains almost constant during its rise in the film region, so that it is reasonable to assume that the efficiency of bubble evolution determined from the pictures just above the top of the working electrode, equals that near the surface of the gas-evolving electrode. Figs 8 and 9 show that hydrogen has the highest efficiency of bubble evolution and chlorine the

lowest. Janssen *et al.* [2] had found a similar result. The theoretical results calculated by Vogt [6] are much lower. Consequently, a large part of the gas formed at the electrode surface is dissolved in the solution. Since the solution at the inlet of the cell is saturated, the solution becomes supersaturated by gas evolution. The supersaturation decreases with increasing distance from the gas-evolving electrode by absorption of dissolved gas by bubbles.

For a single-bubble electrode system Van Stralen *et al.* [30] and Brandon *et al.* [21] had found experimentally that the efficiency of bubble evolution, η_b , increases with increasing ratio of bubble to electrode radius, increasing degree of screening of the electrode, s_b , by the attached bubble or with increasing circumference of the cross-section of the attached bubble, $2\pi R_a$. The current distribution around a spherical bubble in contact with a plane electrode has been calculated by Sides and Tobias [31]. They had found that the current density is zero at the contact point and the current density reaches 10 and 80% of its undisturbed value at, respectively, $0.44 R_a$ and $0.95 R_a$ from the contact point where R_a is the radius of attached bubbles. From the results of Dukovic and Tobias [32] it follows that, for a multi-bubble system, the dissolved gas is formed mainly on the electrode surface which is not screened off by attached bubbles.

To elucidate the parameters determining η_b , some relevant parameters for hydrogen-, oxygen- and chlorine-evolving electrodes are given in Table 5. The solubility and diffusion coefficients for hydrogen and oxygen in 1 M KOH and chlorine in 4 M NaCl + 0.1 M

HCl are tabulated [27, 28, 29]. From Table 4 it follows that the efficiency of bubble evolution, η_b , decreases in sequence of hydrogen, oxygen and chlorine. Since the dependence of η_b on the current density i_g is slight in the high current density i_g range, the relation between η_b and parameters of attached bubbles is investigated at a high volumetric rate of bubble evolution, viz $v_{g,b} = 1.26 \times 10^{-4} \text{ m s}^{-1}$ at 298 K and $v_{s,0} = 0.12 \text{ m s}^{-1}$. This rate corresponds to $i_g = 1.8, 4.7$ and 3.6 kA m^{-2} for, respectively, hydrogen, oxygen and chlorine evolution.

Parameters describing the behaviour of bubbles present on transparent nickel electrodes in 1 M KOH are given for hydrogen and oxygen in [8]. From their results the degree of screening of the transparent electrode by attached bubbles, s_b , the bubble population density, d_b , the radius of attached bubbles, R_a and the total circumference of the cross-sections of bubbles attached to the electrode have been obtained. Bubble parameters for chlorine bubbles attached to a transparent platinum electrode have been taken from unpublished work of a number of authors. The thickness of the diffusion layer, δ , at a gas-evolving electrode for indicator ions is a measure for the rate of the solution-flow velocity near the electrode surface. For the oxygen, hydrogen and chlorine-evolving electrode, used in this investigation, the results are given in Table 5 [26].

For the chlorine-evolving electrode, the highest s_b and the lowest η_b have been found. Table 5 shows that the diffusion coefficient increases in sequence of chlorine, oxygen and hydrogen and the solubility for chlorine is much higher than those for hydrogen and oxygen. Apparently, both the diffusion coefficient and the solubility of the gas evolved are important factors determining the efficiency of gas bubble evolution. The great difference in η_b for the hydrogen- and the oxygen-evolving electrode cannot be explained by the relatively slight difference in solubilities and diffusion coefficients for hydrogen and oxygen. Table 5 shows a great difference in d_b , R_a and $2\pi d_b R_a$ between hydrogen and oxygen. In an analogous way to the transport of gas in a fuel-cell electrode, where the length of the three-phase boundary (electrode solution gas) mainly determines the transport of gas to the electrode, the total circumference of the cross-sections of bubbles attached to the electrode, is also an important factor determining η_b . This means that the ancillary electrode surface for a bubble attached to the electrode surface is a ring around the contact point of the bubble with the electrode. This ring has a surface area which is proportional to the radius of the bubble.

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REFERENCES

- W. Fritz, Berechnung des maximalen Volumes von Dampfblasen, *Phys. Zeitschrift* **11**, 379 (1935).
- L. J. J. Janssen and E. Barendrecht, *Electrochim. Acta* **30**, 683 (1985).
- N. Ibl, E. Adam, J. Venczel and E. Scholok, *Chem. Ing. Tech.* **43**, 202 (1971).
- L. J. J. Janssen, E. Barendrecht and S. J. D. van Stralen, 36th ISE-meeting, Salamanca, Spain, September 23–28, 4020–4022 (1985).
- S. Shibata, *Electrochim. Acta* **23**, 619 (1978).
- H. Vogt, Ext. Abstracts 34th ISE-meeting, Erlangen 413 (1983).
- C. W. M. P. Sillen, Thesis, Eindhoven University of Technology (1983).
- L. J. J. Janssen, C. W. M. P. Sillen, E. Barendrecht and S. J. D. van Stralen, *Electrochim. Acta* **29**, 633 (1984).
- S. Trasatti, *Electrodes of Conductive Metallic Oxides*, part A, Elsevier Publishing Company, Amsterdam, Oxford, New York, 315 (1980).
- V. V. Shalaginov, D. M. Shub, N. V. Kozlova and V. N. Lomova, Effect of conditions of preparation on anodic behaviour of $\text{Ti/Co}_3\text{O}_4$ electrodes in chlorine solution, *Elektrokhimiya* **19**, 537.
- C. J. West, *International Critical Tables* Vol. III, 370, McGraw-Hill, New York (1933).
- B. E. Bongenaar-Schlechter, L. J. M. Konings, C. J. Smeyers, J. H. G. Verbunt, E. Barendrecht, L. J. J. Janssen, W. M. Sluyter and S. J. D. van Stralen, *Hydrogen as an Energy Carrier*, Proc. 3rd Int. Seminar, Lyon 25–27, May 1983, 206. D. Reidel, Dordrecht (1983).
- L. J. J. Janssen, *Electrochim. Acta* **23**, 81 (1978).
- W. Fritz, *Phys. Zeitschrift* **11**, 379 (1935).
- A. K. Chesters, in *Boiling Phenomena*, (Edited by S. J. D. van Stralen and R. Cole) Chap. 26, Hemisphere, Washington (1979).
- J. S. Saini, C. P. Gupta and S. Lal, *Int. J. Heat Mass Transfer* **18**, 472 (1975).
- A. P. Hatton, D. D. James and T. L. Liew, Measurements of bubble characteristics for pool boiling from single, cylindrical cavities, 4th Int. Heat Transfer Conference 5, Paris-Versailles (1970).
- A. M. Kiper, *Int. J. Heat Mass Transfer* **14**, 931 (1971).
- R. Cole and H. L. Shulman, Bubble departure diameters at subatmospheric pressures, Chemical Engineering progress symposium series, *Heat transfer*, Los Angeles **62**, 6 (1966).
- W. Zijl, Thesis, Eindhoven University of Technology (1979).
- N. P. Brandon and G. H. Kelsall, *J. appl. Electrochem.* **5**, 475 (1984).
- S. J. D. van Stralen, in *Boiling Phenomena* (Edited by S. J. D. van Stralen and R. Cole), Hemisphere, Washington (1979).
- W. Zijl, in *Boiling Phenomena* (Edited by S. J. D. van Stralen and R. Cole), Hemisphere, Washington (1979).
- R. Cole in *Boiling Phenomena* (Edited by S. J. D. van Stralen and R. Cole), Hemisphere, Washington (1979).
- S. J. D. van Stralen and W. M. Sluyter, *J. appl. Electrochem.* **15**, 527 (1985).
- L. J. J. Janssen and J. G. Hoogland, *Electrochim. Acta* **15**, 1013 (1970).
- A. M. Yatkovski and N. A. Fedotov, *R. J. Phys. Chem.* **43**, 575 (1969).
- F. T. B. J. van den Brink, Thesis, Eindhoven University of Technology (1981).
- I. V. Kadija, *J. Electrochem. Soc.* **127**, 599 (1980).
- S. J. D. van Stralen, R. de Jonge and H. Verhaart, in *Boiling Phenomena* (Edited by S. J. D. van Stralen and R. Cole), Hemisphere, Washington (1979).
- P. J. Sides and C. W. Tobias, *J. electrochem. Soc.* **127**, 288 (1980).
- J. Dukovic and C. W. Tobias, *Proc. Electrochem. Soc.* (86–12) 122 (1986).