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, \( i_T \), or for gas in bubbles, \( i_b \), and the effect of solution-flow velocity, \( v_{s.o} \), and temperature, \( T \), on the detached bubbles parameters, viz average Sauter bubble radius, \( R_{sdav} \), average bubble radius, \( R_{dav} \), average of the square of the bubble radii, \( (R^2)_{dav} \), average of the third power of the bubble radii, \( (R^3)_{dav} \), detached bubble frequency, \( \omega \), and efficiency of gas bubble evolution, \( \eta_b \), 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:

(a) The average Sauter bubble radius is proportional to \( i_T^{1/2} \) and decreases linearly with increasing \( v_{s.o} \) at constant \( i_b \). The constant \( n_b \) depends on the temperature, the nature of the gas evolved, the electrode material and the electrolyte and is independent of \( v_{s.o} \). Similar correlations were obtained for \( R_{dav} \), \( (R^2)_{dav} \) and \( (R^3)_{dav} \).

(b) The frequency of detached bubbles is proportional to \( i_T^{1/2} \) and increases linearly with increasing \( v_{s.o} \) at constant \( i_b \). The constant \( n_\omega \) depends on the temperature, the nature of the gas evolved, the electrode material and the electrolyte and is independent of \( v_{s.o} \).

(c) The efficiency of gas bubble evolution \( \eta_b \) increases with increasing \( i_b \) and approaches a limiting value.

NOMENCLATURE

\( A_{dav} \) average cross-section of detached bubbles
\( A_{dav} = \sum_{i=1}^{n} \pi R_{d,i}^2/n \) (m²)

\( d_b \) bubble population density (m⁻²)
\( F \) Faraday constant = 96487 C mol⁻¹

\( i \) electric current density (kA m⁻²)
\( i_T \) electric current density used for total gas evolution (kA m⁻²)
\( i_b \) electric current density used for gas in bubbles (kA m⁻²)

\( i_e \) electric current density for total gas evolution (kA m⁻²)
\( l \) electric current (kA)
\( n \) number of electrons involved in the electrode reaction to form one molecule of a species

\( n_b \) number of bubbles on a part of a moving film

\( n_f \) number of detached bubble on a part of a moving film

\( R_a \) radius of attached bubbles (m)
\( R_{d,i} \) radius of detached bubble (m)

\( R_{dav} \) average radius of detached bubbles,
\( R_{sdav} \) average Sauter bubble radius,
\( R_{dav} = \sum_{i=1}^{n} R_{d,i}/n \) (m)

\( (R^2)_{av} \) average of the square of the bubble radii,
\( (R^3)_{av} = \sum_{i=1}^{n} R_{i}^3/n \) (m³)

\( (R^2)_{dav} \) average of the third power of the bubble radii,
\( (R^3)_{dav} = \sum_{i=1}^{n} R_{d,i}^3/n \) (m³)

\( \omega \) detached bubble frequency
\( \omega = \sum_{i=1}^{n} \omega_i/n \)

\( \eta_b \) efficiency of gas bubble evolution
\( \eta_b = \sum_{i=1}^{n} \omega_i/n \)

\( v_{s.o} \) solution-flow velocity (m s⁻¹)

\( v_{p,b} \) theoretical production rate of gas bubbles when all the gas is evolved as bubbles,
\( v_{p,b} = i_b V_M \) (m s⁻¹)

\( v_{p,0} \) solution-flow velocity (m s⁻¹)

\( V_{dav} \) average volume of departed bubbles
\( V_{dav} = \sum_{i=1}^{n} \frac{4}{3} \pi R_{d,i}^3/n \) (m³)

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

\( V_g \) volume of gas (m³)

\( V(g + H_2O) \) volume of gas plus water vapor (m³)

\( p(H_2O) \) sum of the partial pressures of gas and water vapor (kPa)

\( p(g + H_2O) \) partial water vapor pressure (kPa)

\( \rho_{H_2O} \) density of water (g cm⁻³)

\( \rho_{gas} \) density of the gas (g cm⁻³)

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\[ \eta_b \text{ efficiency of gas bubble evolution,} \]
\[ \eta_s = \frac{v_{gs}}{v_{gs}} \]
\[ \delta \text{ thickness of Nernst diffusion layer (m)} \]

**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.

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, $i$, 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:

$$V_g = \frac{V(g + H_2O) - p(H_2O)}{p(g + H_2O)}$$

where $V_g$ is the volume of the gas (m$^3$), $V(g + H_2O)$ is the volume of gas plus water vapor (m$^3$), $p(g + H_2O)$ is the sum of the partial pressures of gas $g$ and water vapor where $p(g + H_2O)$ is supposed to be 101 kPa and $p(H_2O)$ is 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:

$$R_{d,av} = \frac{\sum n R_{d,i}}{n} \quad \text{and} \quad (R_s^2)_{av} = \frac{\sum n R_s^2}{n}$$

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

Effect of current density. Figure 2 shows the average Sauter radius of detached bubbles, $R_{s,av}$, 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$^{-1}$.](image-url)
From Fig. 2 it follows that the log $R_{sdav}$ 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, $R_{sdav}$, 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, $\omega$, as a function of current density, $i_b$, on double logarithmic scale are linear too. These linear relations can be expressed by:

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

and

$$\omega = a_5 i_b^{n_5}.$$  

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

The detached bubble frequency, $\omega$, that is the number of detached bubbles from the electrode per second and per m$^2$ 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, $R_{sdav}$, 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 $R_{sdav}$ for the three gases decreases linearly with increasing $v_{s,0}$ at 298 and 353 K.

In Fig. 5 the detached bubble frequency $\omega$ 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, $R_{sdav}$, for the three gases is shown as a function of the reciprocal temperature. The dependence of $R_{sdav}$ on the reciprocal temperature can be represented by:

$$R_{sdav} = a_6 \times 10^{n_6/T}.$$  

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 shown 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.
Efficiency of bubble evolution

The efficiency of bubble evolution is defined by:

\[ \eta_b = \frac{v_{g,b}}{v_{g,0}} \]

where \( v_{g,0} = (i_r T/nF 298)V_M \) (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 kPa = \( 24.5 \times 10^{-3} \) m\(^3\) mol\(^{-1}\), \( i_r \) = 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 \( \text{Cl}_2 \), \( \text{H}_2 \) or \( \text{O}_2 \) 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 \( i_r \). Hydrogen evolution has the highest \( \eta_b \) 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, \( i_r \), 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 \( \log i_r \) in the \( i_r \) range from 0.02 to 5 kA m\(^{-2}\). These linear relations are
expressed by:

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

The parameters $a_7$ and $m_7$ 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 $m_7$ 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 chlorine as a function of temperature for three different electrode materials, Pt, RuO$_2$/Pt, Pt and Co$_3$O$_4$ electrodes. The curves show that RuO$_2$/Pt electrode has the highest efficiency of gas bubble evolution.
evolution and Co$_2$O$_4$ electrode the lowest. The $n_b$ 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 filled just above the top of the working electrode, the number of which did not change, i.e., 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, i.e., coalescence of hydrogen bubbles in alkaline solution and of chlorine bubbles in acidic chloride solution occurs only to a limited extent.

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

where $\gamma$ = constant angle between bubble and wall in degrees, $\sigma$ = surface tension, $\rho_1$ = liquid density, $\rho_2$ = gas/vapour density and $g$ = gravitational acceleration. This equation is valid for a bubble with freely

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

<table>
<thead>
<tr>
<th>Gas</th>
<th>$T$ (K)</th>
<th>$v_{s0}$ (m s$^{-1}$)</th>
<th>Electrode material</th>
<th>Electrolyte</th>
<th>$a_7$</th>
<th>$n_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$_2$</td>
<td>298</td>
<td>0.05</td>
<td>RuO$_2$/Pt</td>
<td>4 M NaCl + 0.1 M HCl</td>
<td>0.5</td>
<td>0.39</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>353</td>
<td>0.05</td>
<td>RuO$_2$/Pt</td>
<td>4 M NaCl + 0.1 M HCl</td>
<td>0.4</td>
<td>0.39</td>
</tr>
<tr>
<td>H$_2$</td>
<td>353</td>
<td>0.05</td>
<td>Ni</td>
<td>6.8 M NaOH</td>
<td>2.0</td>
<td>0.39</td>
</tr>
<tr>
<td>H$_2$</td>
<td>298</td>
<td>0.12</td>
<td>Ni</td>
<td>1 M KOH</td>
<td>1.1</td>
<td>0.39</td>
</tr>
<tr>
<td>O$_2$</td>
<td>298</td>
<td>0.12</td>
<td>Ni</td>
<td>1 M KOH</td>
<td>0.6</td>
<td>0.39</td>
</tr>
</tbody>
</table>

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 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\(^{-1}\).

Fig. 13. Efficiency of gas bubble evolution as a function of temperature for chlorine-evolving electrode of RuO\(_2\)/Pt, Pt and Co, 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 m s\(^{-1}\).

Moving foot and a contact angle limited to 30\(^\circ\)[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

\[ R_d = c \sqrt[3]{\rho \frac{\sigma}{g (\rho_1 - \rho_2)}} \]

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

\[ V_{d,\text{max}} = 4\sigma \pi /\rho g \]

where \( r \) = cavity-mouth radius, \( \sigma \) = surface tension, \( \rho \) = 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 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 multibubble 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, \( v_{gb} \). Table 4 gives the results at \( v_{gb} = 0.126 \times 10^{-4} \) and 1.264 \( \times 10^{-4} \) m 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 \( v_{gb} = 0.12 \) 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 \( R_{d,\text{av}} \) 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 RuO$_2$/Pt electrode in 4 M NaCl + 0.1 M HCl at two volumetric rates of bubble evolution, viz $v_{b,0} = 0.126 \times 10^{-4}$ and $1.26 \times 10^{-4}$ m$^{-1}$ s$^{-1}$ and at $T = 298$ K and $v_{b,0} = 0.12$ m$^{-1}$ s$^{-1}$.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$v_{b,0} \times 10^4$ m$^{-1}$ s$^{-1}$</th>
<th>$i_b$ (kA m$^{-2}$)</th>
<th>$R_{bav}$ (m)</th>
<th>$(R_{bav}^2$ (m$^4$)</th>
<th>$R_{oav}$ (m)</th>
<th>$\sigma$ (m$^{-2}$ s$^{-1}$)</th>
<th>$\eta_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>0.126</td>
<td>1.26</td>
<td>0.126</td>
<td>1.26</td>
<td>0.126</td>
<td>1.26</td>
<td></td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.2</td>
<td>2.0</td>
<td>0.2</td>
<td>2.0</td>
<td>0.2</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>1.0</td>
<td>5.0</td>
<td>1.0</td>
<td>5.0</td>
<td>1.0</td>
<td>5.0</td>
<td></td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Gas</th>
<th>Diffusion coefficient m$^2$ s$^{-1}$</th>
<th>Saturation concentration mol m$^{-3}$</th>
<th>$i_b$ kA m$^{-2}$</th>
<th>$\eta_b$</th>
<th>$s_b$</th>
<th>$u_b$ (mm$^{-3}$)$t_b$</th>
<th>$R_d$ (mm)$R_o$</th>
<th>$2n_dR_o$ (mm$^{-1}$)$t_b$</th>
<th>$\delta$ (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>$3.0 \times 10^{-9}$</td>
<td>0.52</td>
<td>1.8</td>
<td>0.56</td>
<td>0.40</td>
<td>1500</td>
<td>8</td>
<td>76</td>
<td>$2 \times 10^{-5}$</td>
</tr>
<tr>
<td>O$_2$</td>
<td>$1.59 \times 10^{-9}$</td>
<td>0.89</td>
<td>4.7</td>
<td>0.43</td>
<td>0.40</td>
<td>250</td>
<td>17</td>
<td>27</td>
<td>$1 \times 10^{-5}$</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>$1.22 \times 10^{-9}$</td>
<td>22</td>
<td>3.6</td>
<td>0.28</td>
<td>0.80</td>
<td>19</td>
<td>110</td>
<td>13</td>
<td>$2 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

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 $i_b = 2$ kA m$^{-2}$, $T = 298$ K and $v_{b,0} = 0.12$ 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 $i_b^n$, where the exponent $n_b$ 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, $\eta_b$, 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, $2\pi R_o$. 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, $0.44R_o$ and $0.95R_o$ from the contact point where $R_o$ is the radius of the attached bubble. 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 $\eta_b$, 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, $\eta_b$, decreases in sequence of hydrogen, oxygen and chlorine. Since the dependence of $\eta_b$ on the current density $i$ is slight in evolution.

This rate corresponds to $i_2 = 1.8, 4.7$ and $3.6$ kA m$^{-2}$ for, respectively, hydrogen, oxygen and chlorine 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, $R_b$ 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, $\delta$, 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 $\eta_b$ 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 $\eta_b$ for the hydrogen- and 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 $s_b$, $R_b$ and $2\pi d_b R_b$ 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 $\eta_b$. 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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