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SHORT COMMUNICATION

A population balance approach to the study of bubble behaviour at gas-evolving electrodes

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Nomenclature

d	volume average bubble diameter at break-off (m)
D	molecular diffusivity of dissolved gas ($\mathrm{m^2\,s^{-1}}$)
$f(x)\,\mathrm{d}x$	fraction of bubbles attached to the electrode in the size range x to $x + \mathrm{d}x$
F	Faraday's constant ($\mathrm{A\,s\,mol^{-1}}$)
$g(x)\,\mathrm{d}x$	fraction of bubbles leaving electrode in the size range x to $x + \mathrm{d}x$
$h(x)\,\mathrm{d}x$	fraction of bubbles nucleating on electrode in the size range x to $x + \mathrm{d}x$
i	current density at electrode surface ($\mathrm{A\,m^{-2}}$)
n	positive digit
N	number of bubbles on electrode surface per unit area ($\mathrm{m^{-2}}$)
P	pressure of the gas (atm)
q	rate of nucleation of bubbles per unit area ($\mathrm{m^{-2}\,s^{-1}}$)
r	radius of a single bubble after a time t (m)
R	gas constant ($\mathrm{atm\,m^3\,mol^{-1}}$)
t	age of the bubble after nucleating (s)
T	temperature of the fluid in the cell (K)
$u(x)$	growth rate of a bubble of size x ($\mathrm{m\,s^{-1}}$)
V	volume of gas evolved per unit area per unit time ($\mathrm{m\,s^{-1}}$)
x	diameter of a bubble (m)
β	parameter in Scriven's model

1. Introduction

A knowledge of the factors affecting the nucleation, growth, detachment and coalescence of electrogenerated bubbles is of importance in the design and performance of many industrial cells. Recent developments in this field are reviewed by Vogt [1] and it is clear that there are many analogies between gas-evolving electrodes and other particulate processes. Since population balance models have been found to be a useful way of analysing such diverse multiparticle systems as crystallization, comminution and solvent extraction [2], the aim of this paper is to explore the application of these concepts to electrolytic bubbles.

2. Population balance

The population balance is based on an equation for the continuity of particle numbers in a dispersed phase and is developed from the general conservation equation:

$$\text{accumulation} = \text{input} - \text{output} + \text{net generation} \quad (1)$$

This is applied to particles in a macroscopic system having a specific set of properties, e.g. size, shape or chemical composition [2, 3]. For gas-evolving electrodes this equation could be applied over the full range of behaviour from nucleation on the electrode to the bursting of bubbles at the electrolyte surface with the atmosphere. To illustrate the principles involved a simpler sub-system is chosen, the extent of which is limited to bubbles adhering to an electrode. It will be assumed that the current density is sufficiently low so that coalescence on the surface is negligible (coalescence can be accounted for [3, 4], but it complicates the mathematical development quite considerably). Although local variations occur, it will be assumed that the system is sufficiently large that, from a macroscopic point of view, the process is at steady state and the accumulation term in Equation 1 is zero.

The bubble property to be investigated is its diameter, x. Although bubbles attached to the surface are not fully spherical, this deviation will be neglected for the purposes of the study. To express Equation 1 mathematically it is also necessary to define three density functions, namely:

$h(x)\,\mathrm{d}x$ = fraction of bubbles nucleating on the electrode in the size range x to $x + \mathrm{d}x$,

$f(x)\,\mathrm{d}x$ = fraction of bubbles attached to the electrode in the size range x to $x + \mathrm{d}x$,

$g(x)\,\mathrm{d}x$ = fraction of bubbles leaving the electrode in the size range x to $x + \mathrm{d}x$.

Equation 1 thus becomes [2, 3, 5]:

$$0 = qh(x) - qg(x) - \mathrm{d}[Nu(x)f(x)]/\mathrm{d}x \quad (2)$$

where N = total number of bubbles on the electrode per unit area ($\mathrm{m^{-2}}$); q = number of bubbles nucleating per unit area per unit time ($\mathrm{m^{-2}\,s^{-1}}$); $u(x)$ = growth rate of a bubble of size x ($\mathrm{m\,s^{-1}}$).

There are a number of ways of approaching the solution of Equation 2 depending on the information available and the properties of the system that are of interest. One is the method of moments, which reduces Equation 2 to a relationship between certain average values. This is accomplished by multiplying Equation 2

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by x^n and integrating over the range of x, i.e.

$$\int_0^\infty x^n g(x)\,\mathrm{d}x = \int_0^\infty x^n h(x)\,\mathrm{d}x + \frac{nN}{q}\int_0^\infty x^{n-1}u(x)f(x)\,\mathrm{d}x \qquad (3)$$

At this stage it is necessary to postulate a functional form for $u(x)$. The growth of single bubbles at microelectrodes has been extensively studied and in a recent paper by Brandon and Kelsall [6] various regimes are identified. From this it would seem appropriate to use Scriven's model [7] for diffusion controlled spherical growth provided moderate current densities are used (i.e. $< 500\,\mathrm{A\,m^{-2}}$) [8]. The radius of a bubble r at time t after it enters this growth regime is given by:

$$r = 2\beta(Dt)^{1/2} \qquad (4)$$

where D is the molecular diffusivity of the dissolved gas and β a coefficient which is dependent on the degree of supersaturation of the gas in the surrounding solution [8, 9]. From this the growth rate can be determined as follows:

$$u(x) = \mathrm{d}x/\mathrm{d}t = 2\,\mathrm{d}r/\mathrm{d}t = 8\beta^2 D x^{-1} \qquad (5)$$

Substitution of Equation 5 in Equation 3 yields:

$$\int_0^\infty x^n g(x)\,\mathrm{d}x = \int_0^\infty x^n h(x)\,\mathrm{d}x + \frac{8\beta^2 DnN}{q}\int_0^\infty x^{n-2}f(x)\,\mathrm{d}x \qquad (6)$$

The average size of a bubble leaving the surface is usually much larger than the average size at nucleation. Thus for $n \geqslant 1$, the first term on the right hand side of Equation 6 makes a negligible contribution to the bubble departure properties, i.e.

$$\int_0^\infty x^n g(x)\,\mathrm{d}x \approx \frac{8\beta^2 DnN}{q}\int_0^\infty x^{n-2}f(x)\,\mathrm{d}x \qquad (7)$$

Equation 7 relates the moments of the size distribution of departing bubbles to lower order moments of the distribution attached to the electrode.

3. Experimental details

As it is not the objective of this paper to present an extensive set of experimental results, the techniques used will only be described very briefly. Further details are given by Hofman [10].

The cell was constructed of perspex with one side wall consisting of a vertical copper plate which acted as cathode. On the opposite wall a narrow strip of lead was embedded in a perspex sheet to form essentially a line anode. This enabled photographs to be taken of the cathode surface from the anode side without interference from the anode reaction. A small flow of electrolyte also helped to keep stray bubbles from moving into the section being photographed. The temperature of the electrolyte was 25° C. Smoothing sections were provided at the flow entrance and exit of the cell to minimize turbulence. A plan view of the cell is shown diagrammatically in Fig. 1.

Photographs of the bubbles on and near the cathode were taken with still and cine cameras. The microscope arrangement for the still camera had a very shallow depth of field which was focused on bubbles attached to the electrode. On the other hand the cine camera could differentiate between stationary and moving bubbles and was used to obtain an estimate of the size distribution of detached bubbles. The developed photographs were placed on a plotter which was fitted with a digitizing sight and the positions of the edges of the bubbles were recorded and stored in a computer file. The computer was programmed to sort the bubbles into size ranges and to determine the distributions $f(x)$ and $g(x)$ and the parameter N. Further details are given by Hofman [10].

4. Results and discussion

A typical set of results for hydrogen evolution from a 0.1 M sulphuric acid solution is shown in Fig. 2. The average velocity of the electrolyte was $0.1\,\mathrm{m\,s^{-1}}$. The current density at the position of observation was $33\,\mathrm{A\,m^{-2}}$ which was computed using an equation

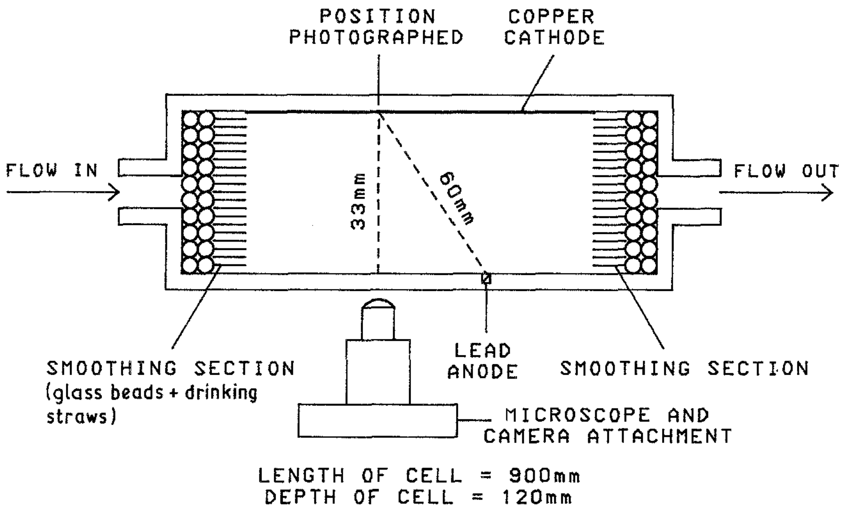

Fig. 1. Plan view of cell.

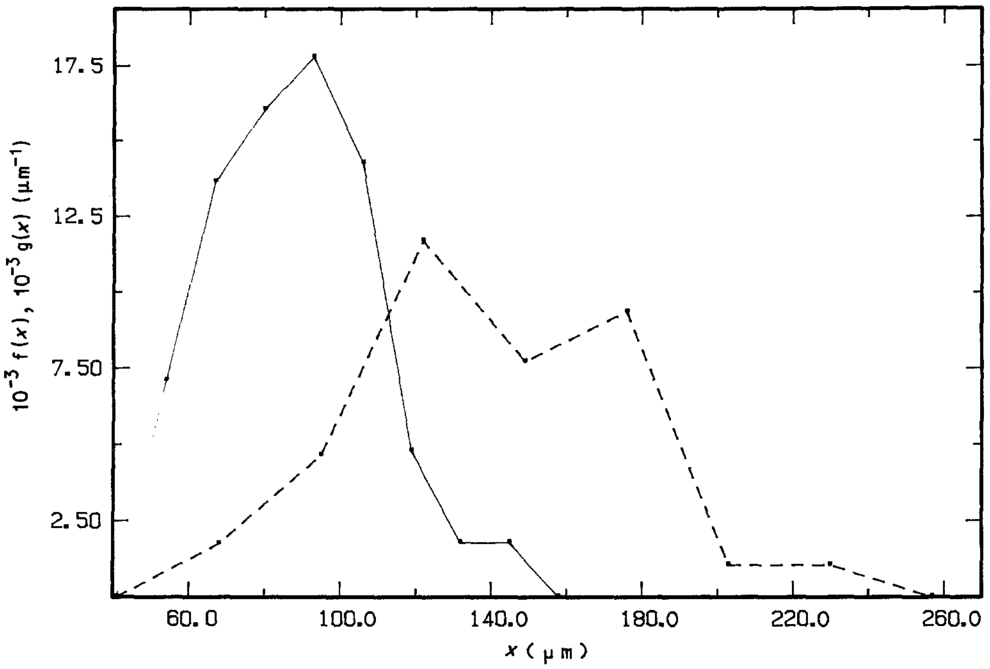

Fig. 2. Bubble size distributions: $f(x)$ (——), on the electrode; $g(x)$ (- - -), detached from electrode.

given by Kasper [11] for the cell geometry used. Although Kasper's model does not include the presence of bubbles it should give a reasonable estimate under the low current density conditions used.

From Fig. 2 it is clear that a significant fraction of bubbles that have left the electrode are larger than the largest size detected on the cathode. Visual observation through the microscope indicates that the detached bubbles photographed to produce $g(x)$ originate close to, or slightly upstream of, the point where they are nucleated. As the current density is lower in the upstream region where the bubbles are, if anything, smaller then it must be concluded that further growth occurs after detachment. This confirms the findings of Krause and Vogt [12] that the bulk electrolyte is supersaturated with hydrogen and that bubbles will continue to grow after they leave the electrode even in the absence of coalescence. It is therefore not advisable to insert the experimental values of $g(x)$ from Fig. 2 into Equation 7. However, there are a number of interesting results that can be derived from $f(x)$.

In Fig. 2 it appears that no bubble could be detected on the electrode below 40 μm. This is almost certainly due to the limitation of the photographic equipment used. It is fortunate, however, that the analytical technique used (i.e. the method of moments) is not very sensitive to the early part of the curve for $n \geqslant 1$.

According to Vogt [13], the fractional current efficiency for hydrogen evolution on an electrode is approximately 0.3 at the current density used in the present work. If V is the volume of gas evolved per unit area per unit time, then by Faraday's law (assuming hydrogen behaves as an ideal gas under the conditions in the cell):

$$V = \frac{0.3iRT}{2FP}\,(\mathrm{m\,s^{-1}}) \tag{8}$$

where i is the total current density, T and P the temperature and pressure of the gas and R and F the gas and Faraday's constants, respectively. V can also be determined from Equation 7, i.e.

$$\begin{aligned} V &= (q\pi/6)\int_0^\infty x^3 g(x)\,\mathrm{d}x \\ &= 4\pi\beta^2 DN\int_0^\infty x f(x)\,\mathrm{d}x \end{aligned} \tag{9}$$

From the data in Fig. 2 the above integral can be evaluated numerically:

$$\int_0^\infty x f(x)\,\mathrm{d}x = 8.8 \times 10^{-5}\,\mathrm{m}$$

and N is estimated from the still photograph as $9 \times 10^6\,\mathrm{m}^{-2}$. The value of $D = 6.9 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$ is taken as that for hydrogen in water at 25° C using the data of Davidson and Cullen [14]. P is assumed to be atmospheric pressure which is approximately 0.82 atm in Johannesburg. Equating Equations 8 and 9 gives a calculated value of $\beta = 0.15$. This is within the range reported by Glas and Westwater [9] for hydrogen generation at microelectrodes.

Another important parameter associated with gas-evolving electrodes is the bubble break-off diameter as it affects, among other things, the mass transfer coefficient at the electrode [15]. Several types of average break-off diameters could be determined, e.g. number average and volume average. The latter would appear to be more appropriate for mass transfer studies [16] and can be defined as

$$d = \frac{\int_0^\infty x^4 g(x)\,\mathrm{d}x}{\int_0^\infty x^3 g(x)\,\mathrm{d}x} \tag{10}$$

Inserting Equation 7

$$d = \frac{4\int_0^\infty x^2 f(x)\,\mathrm{d}x}{3\int_0^\infty x f(x)\,\mathrm{d}x} \tag{11}$$

These integrals can be evaluated numerically from Fig. 2 to give $d = 1.24 \times 10^{-4}$ m. This is in fair agreement with the data of Brandon and Kelsall [6] for a pH in the neighbourhood of unity.

5. Conclusions

Population balance modelling provides a useful analytical method of describing the size distributions of electrogenerated bubbles. It provides a link between processes which are occurring locally at the microscopic level to the overall effect these have on a macroscopic system. Two examples are presented in this paper to illustrate this link. A bubble growth rate model is examined by determining its characteristic parameter β from bubble size distribution data. It is interesting to note that β is related to the number average size of bubbles on the surface according to Equation 9. In the other example, the volume average break-off diameter is related to the ratio of the second to the first moment of $f(x)$ as described by Equation 11.

If the technique is to be extended to higher current densities where coalescence is likely to occur both on the electrode and in the bulk of the electrolyte, bubble volume rather than diameter should preferably be chosen as the characteristic property. The advantages can be clearly seen in the study of an analogous process involving liquid drop coalescence [2, 4].

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