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The Quantities Affecting the Bubble Coverage of Gas-Evolving Electrodes

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ABSTRACT

The fractional bubble coverage is the leading quantity required for information on the actual current density of gas-evolving electrodes at a given nominal current density I/A. As confirmed by experiments, the bubble coverage increases with increasing current density, provided the values are sufficiently small. At large values of the bubble coverage, both variables develop in opposite directions: The nominal current density decreases as the bubble coverage increases. However, the current density is not the single quantity acting on the bubble coverage. Additionally numerous other quantities impact. They are traced up and their interferences are discussed. Particularly their impact on the interrelation of bubble coverage and current density is studied. The outcome is significant particularly for understanding real processes occurring at elevate electrode potentials likewise in laboratory and in industrial electrochemical reactors.

1. Introduction

At gas-evolving electrodes, the fraction of the electrode area blanketed by adhering gas bubbles is inactive in the electrochemical reaction. Thus the nominal current density on its own, although commonly used in laboratory and industry, does not provide information on the actual current density representative of the processes at gas-evolving electrodes.

Therefore, dealing with gas-evolving electrodes necessitates taking account of a quantity inexistent at gas-free electrodes, i.e. the fraction of the electrode surface blanketed by adhering gas bubbles growing up until they reach a size sufficient to detach. This fraction Θ is termed fractional bubble coverage or simply bubble coverage. The value depends on the rate of gas evolution as can easily be reasoned. Replacing the rate with the nominal current density I/A gives a correlation to estimate Θ [1].

$$\frac{I/A}{I_{su}/A} = 3.08\,\Theta^{1.5}(1-\Theta)^{0.5} \tag{1}$$

where I_{su} denotes a maximum current. Eq. (1) takes into account that the bubble coverage at low values increases continuously with the current, but the current decreases at large values of the bubble coverage. This performance is reasonable. At $\Theta \to 1$, a gas layer isolates the electrode and the current breaks down.

It is an open question whether the bubble coverage is solely dependent on the current or further quantities interfere. Answering this question is the object of the present paper.

2. The fractional bubble coverage

Gas bubbles growing in contact with electrodes exert multiple impacts on the electrochemical process which they are the mediate product of. Bubbles within a layer adhering to the electrode block a fraction of the cross-sectional area available for current transport. The actual current density is larger than the nominal one. Therefore, the energy demand of the cell is affected. The overpotential of the electrode owing to both reactant and product increases as well as the ohmic interelectrode potential drop. A further relevant impact is that on mass transfer of reagent to and of dissolved product from the electrode. Since mass transfer is restricted to the active part of the electrode area, the mass transfer coefficient is lowered. On the other hand, bubbles growing at and detaching from the electrode induce microconvection in the boundary layer intensifying mass transfer. Moreover, the bubble coverage controls the area of the gas-liquid interface of adhering bubbles and affects the rate of dissolved product contributing to bubble growth, whereas the residual amount of product is transferred to the liquid bulk. All these processes are the more effective the larger the number and the size of bubbles. Therefore, the bubble coverage does not only serve to estimate the actual current density but exerts an important influence on the operation of gas-evolving electrodes.

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List of Symbols

A	electrode surface area [m^2]
c_e	concentration of dissolved product at electrode [mol m^{-3}]
c_s	saturation concentration of product [mol m^{-3}]
c	concentration of product in the environment of adhering bubbles [mol m^{-3}]
D_B	diffusion coefficient of product [$m^2\,s^{-1}$]
f_G	gas evolution efficiency [−]
F	Faraday constant, $F = 96485\,A\,s\,mol^{-1}$
Fo	Fourier number, Eq. (3)
I	current [A]
I_{su}	summit current [A]
Ja	Jakob number, Eq. (**11**)
k_B	mass transfer coefficient [$m\,s^{-1}$]
nr	number of adhering bubbles
p	pressure [$kg\,m^{-1}\,s^{-2}$]
p_s	vapour pressure of solvent [$kg\,m^{-1}\,s^{-2}$]
r	radial coordinate [m]
R	bubble radius [m]
R_m	universal gas constant, $R_m = 8.314\,kg\,m^2\,s^{-2}\,mol^{-1}\,K^{-1}$
R_r	bubble radius at $t = t_r$ [m]
$R_{I=0}$	bubble radius at zero current [m]
t	time [s]
t_r	residence time [s]
T	temperature [K]
V_r	bubble volume at $t = t_r$ [m^3]
$\dot{V}_G$	volume flow rate of gas [$m^3\,s^{-1}$]
Θ	fractional bubble coverage of the electrode surface [−]
ν_e/ν_B	ratio of the stoichiometric numbers of electrons and product B
Φ_B	current efficiency

The outstanding relevance of the bubble coverage gave rise to carry out experimental investigations confirming that the bubble coverage Θ distinctly depends on the nominal current density I/A [2–4]. Numerous attempts were made to present correlating functions [5–10]. Owing to experimental difficulties, all these relationships are restricted to a limited range of the current density. The semi-empirical Eq. (1) is based on experimental data and attempts an extension to the total range of the bubble coverage.

3. Quantities acting on he bubble coverage

The bubble coverage was defined by Ibl [11] as the fraction of electrode area in contact with adhering bubbles. This definition is satisfactory for non-wetting liquids but insufficient for aqueous electrolyte solutions that are mostly wetting. In this case the contact angles of bubbles are small, and the contact area is smaller than the inactive area. However, the current density below adhering bubbles is very small [12–14] and small enough to consider the area below bubbles inactive with sufficient accuracy allowing for the definition of the bubble coverage as the fraction of the total electrode surface area shadowed by orthogonal projection of the contour of adhering bubbles to the electrode in local and temporal average.

This definition allows for a fundamental mathematical formulation of the fractional bubble coverage Θ.

$$\Theta = \frac{n_r}{A}\int_0^{t_r}\int_0^{R(t)} 2\pi\, r\, dr\frac{dt}{t_r} \tag{2}$$

where n_r/A denotes the number of bubbles simultaneously adhering to the electrode area, and R denotes the radius of the circular area shadowed by a single bubble. The bubble radius varies during growth of the adhering bubbles. It is known from numerous experimental investigations that, except for a very short initial period, the bubble radius increases with the root of time. That can be expressed by the non-dimensional Fourier number

$$\mathrm{Fo} := \frac{D_B t}{R^2} \tag{3}$$

remaining essentially constant during bubble growth. Integration of Eq. (2) yields

$$\Theta = \frac{\pi}{2} {R_r}^2 \frac{n_r}{A} \tag{4}$$

On the other hand, the volume flux $\dot{V}_G$ of evolved gas on the total electrode area A can be described by the mean volume V_r of departing bubbles, the mean residence time t_r of bubbles at the electrode and the number of bubbles simultaneously present at the electrode.

$$\frac{\dot{V}_G}{A} = \frac{n_r V_r}{A\, t_r} \tag{5}$$

Combining Eqs. (4) and (5) gives

$$\Theta = \frac{\pi {R_r}^2}{2\, V_r} t_r \frac{\dot{V}_G}{A} \tag{6}$$

It is seen that the bubble coverage is controlled by the specific rate $\dot{V}_G/A$ of gas evolved at the electrode, by the residence time t_r of bubbles growing in contact with the electrode, by the radius R_r of the circular area shielding the electrode area immediately prior to the departure of the bubble, and by the volume V_r of the departing bubble. $0.5\,\pi\,{R_r}^2$ is the mean area shadowed by one bubble during the residence time. The gas flux density $\dot{V}_G/A$ transferred into adhering bubbles is

$$\frac{\dot{V}_G}{A} = f_G\, \Phi_B \frac{I/A}{(\nu_e/\nu_B)} \frac{R_m\, T}{F p - p_s} \tag{7}$$

where the gas evolution efficiency f_G denotes the fraction of the total product forming gas bubbles at the electrode, $p - p_s$ denotes the partial pressure of the product in the gaseous phase. Inserting Eq. (7) into (6) delivers comprehensive information of all quantities acting on the bubble coverage.

$$\Theta = \frac{\pi {R_r}^3}{2\, V_r} R_r \frac{t_r}{{R_r}^2} f_G\, \Phi_B \frac{I/A}{(\nu_e/\nu_B)} \frac{R_m\, T}{F p - p_s} \tag{8}$$

It is seen that Θ depends on much more quantities than taken into account by Eq. (1) that turns out to be a strongly simplified attempt. Eq. (8) is written in a form to exhibit a shape factor ${R_r}^3/V_r$, the radius R_r of the departing bubble, and a growth parameter ${R_r}^2/t_r$. It is instructive to study the behaviour of all relevant quantities in Eq. (8).

4. Bubble break-off radius R_r

The bubble break-off radius R_r in Eq. (8) is controlled by the balance of interfacial tensions and particularly by the solid-liquid interfacial tension depending on the electrode potential. Therefore,