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The incremental ohmic resistance caused by bubbles adhering to an electrode

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Improved equations for the estimation of the increment of ohmic resistance due to gas adhering to the electrode surface are developed and compared with an earlier equation from the literature.

1. Introduction

Gas bubbles adhering to gas-evolving electrodes may substantially contribute to the interelectrode resistance. The phenomenon is vividly termed 'bubble curtain'. By shielding a portion of the electrode surface the true current density on the remaining surface is increased. Furthermore, the cross-sectional area of the (bubble-free) electrolyte is decreased raising the ohmic resistance. This behaviour is particularly undesirable owing to the fact that, in the usual range of current densities employed in industrial reactors, the gas fraction inside the 'bubble curtain' is far higher than the average taken over the entire interelectrode space. Models have been suggested which attempt to evaluate this effect when estimating interelectrode ohmic resistance [1, 2].

As pointed out by Sides and Tobias [3] the effect of the bubble layer differs from that of bubbles dispersed in the bulk electrolyte because the environment of a bubble adhering to the surface is asymmetric. These authors conducted a mathematical analysis of spherical bubbles contacting the electrode surface, and by considering the bubbles to be arranged regularly in a single surface layer they obtain the following expression.

$$\Delta R = \frac{z_B}{A}\pi R_M^2 A_0 \frac{2R_M}{\kappa_L A} \qquad (1)$$

where ΔR must be added to the ohmic interelectrode resistance calculated in the absence of gas. z_B denotes the number of bubbles simultaneously adhering to an electrode surface A, R_M the mean radius of adhering bubbles, κ_L the conductivity of the (bubble-free) electrolyte, A_0 is a dimensionless constant of value 0.9015.

A further resistance, not accounted for in Equation 1, is occasioned by the pinching of the field in the neighbourhood of bubbles sited close to one another. Introducing a pinching factor, $K_p \geqslant 1$, and a fractional electrode coverage

$$\theta_s = \frac{z_B}{A}\pi R_M^2 \qquad (2)$$

defined as the fraction of the electrode area shadowed by the adhering bubbles in orthogonal projection [4], Equation 1 may be written

$$\frac{\Delta R \kappa_L A}{2R_M} = 0.9015\theta_s K_p. \qquad (3)$$

The pinching effect was estimated by Sides and Tobias [3] to be $K_p = 2$–3 for a close-packed array of bubbles on the surface, i.e. for $\theta_s = \pi/4 = 0.785$ (cubic array) or $\theta_s = \pi/(12)^{1/2} = 0.907$ (hexagonal array).

It is the object of the present communication to show that ΔR, the increment in ohmic resistance, may be satisfactorily estimated by using the more conventional approach of assigning an effective conductivity, κ_b, to the layer comprising the bubble curtain,

$$\Delta R = \frac{b}{A\kappa_L}\left(\frac{\kappa_L}{\kappa_b} - 1\right), \qquad (4)$$

where b is the thickness of a layer adjacent to the electrode with increased resistivity. Assuming

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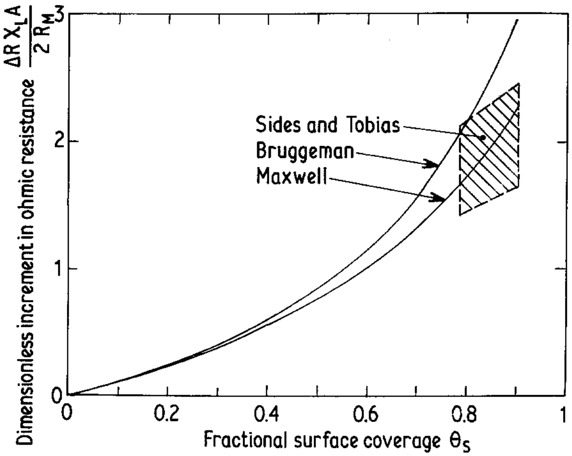

Fig. 1. Dimensionless increment in ohmic resistance incurred by a single-bubble layer adjacent to an electrode versus fractional surface coverage. Comparison of the method developed by Sides and Tobias, Equation 3, with the conventional method based on Bruggeman, Equation 8, and Maxwell, Equation 9, respectively.

spherical bubbles the layer will have a thickness of two bubble radii, $b = 2R_M$.

By departing from Sides and Tobias [3], it becomes possible to develop alternative expressions to Equation 3 by using effective conductivities tentatively calculated from equations for infinitely extended electrolytes containing bubbles in a uniform distribution. Equations of this nature are due to Bruggeman [5],

$$\frac{\kappa}{\kappa_L} = (1-\phi)^{1.5} \tag{5}$$

and Maxwell [6]

$$\frac{\kappa}{\kappa_L} = \left(1 + 1.5\frac{\phi}{1-\phi}\right)^{-1} \tag{6}$$

where ϕ is the volume fraction of gas. For a single-bubble layer (with a thickness of two bubble radii) one obtained from Equation 2

$$\phi = \frac{z_B}{A 2R_M}\frac{4}{3}\pi R_M^3 = \frac{2}{3}\theta_s. \tag{7}$$

The increment in ohmic resistance ΔR incurred by the bubble layer will, therefore, be given by

$$\frac{\Delta R \kappa_L A}{2R_M} = (1-\tfrac{2}{3}\theta_s)^{-1.5} - 1 \tag{8}$$

and

$$\frac{\Delta R \kappa_L A}{2R_M} = \left(\frac{1}{\theta_s} - \frac{2}{3}\right)^{-1}, \tag{9}$$

respectively. Note that these equations are free of a pinching factor, the value of which is most uncertain. Values of θ_s are known from various experiments and were tentatively collated for an extended range of current density [7].

In Fig. 1, Equations 8 and 9 are compared with Equation 3. It is seen that the agreement is satisfactory and therefore that the detailed analysis of Sides and Tobias, as far as it refers to the increment of resistance, has little, if any, advantage over the more conventional approach, the use of which simplifies matters by obviating the need for a pinching factor. It is therefore concluded that the conventional approach is quite serviceable until significantly more accurate methods are made available.

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