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Primary Potential and Current Distribution
Around a Bubble on an Electrode

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ABSTRACT

An analytical solution for the primary potential and current distribution around a spherical bubble in contact with a plane electrode is presented. Zero at the contact point, the current density reaches only one percent of its undisturbed value at thirty percent of the radius from that point and goes through a shallow maximum two radii away. The solution obtained for spherical bubbles is shown to apply for bubbles having contact angles smaller than 17.5° . The incremental resistance caused by dilute arrays of bubbles is evaluated.

* Electrochemical Society Active Member

Key words: potential field, current distribution, electrolytic
gas evolution

Introduction

The evaluation of effective thermal or electrical conductance of heterogenous systems from the conductivities of the individual phases is a commonly occurring problem in science and technology. For suspensions of gas bubbles generated by discharge processes at electrodes, the problem is tractable because the discontinuous phase consists of spherical, nonconducting particles. As early as 1892 Maxwell (1) presented an analytical solution for the effective conductivity of a dilute random, suspension of spherical particles. Rayleigh (2) developed an exact solution for a cubic array of spheres. Using an ingenious approximate treatment by Bruggeman (3), Tobias and co-workers (4,5) proposed useful approximations for treating concentrated, random suspensions of spheres and applied these results in the evaluation of the effect of gas bubbles on the resistance and current distribution in electrolytic gas generators (6). Hine and co-workers (7) differentiated between a relatively concentrated dispersion of gases near the electrodes and the more dilute suspension in the bulk electrolyte. These semi-empirical models, however, do not consider the effect of bubbles attached to the electrode surface. The effect of this layer of bubbles, present during electrolysis, differs from that of bubbles dispersed in the bulk electrolyte because the environment of a bubble sitting on the surface is asymmetric; the electrode, an equipotential surface, is in contact with a planar array of bubbles, while electrolyte extends to a large distance on the opposite side of this array.

In the following an analytical solution is presented which describes the potential field around a spherical bubble in point contact with a planar equipotential surface when the field far from the sphere is linear. The current distribution on the electrode plane and the incremental resistance caused by a dilute array of bubbles are also evaluated.

Theoretical

We use tangent sphere coordinates to solve Laplace's equation for the potential field and current distribution on the planar electrode around the insulating sphere. The coordinate planes are spheres tangent to a plane and toroids without center openings; they are related to Cartesian coordinates by

$$z = \frac{v}{v^2 + \mu^2}, \quad r = \frac{\mu}{\mu^2 + v^2}. \quad [1]$$

The coordinates and their relations to the geometry appear in Figure 1.

The variables, defined in dimensionless form, are as follows:

$$\begin{aligned} z^* &= z/2a \\ x^* &= x/2a \\ v^* &= 2av \\ \mu^* &= 2a\mu \\ \phi^* &= \phi/2a\phi_0 \\ i^* &= i/\kappa\phi_0. \end{aligned} \quad [2]$$

The distance variables are normalized to the bubble diameter; therefore, $x^* = 1$ defines a plane parallel to the $y^* z^*$ plane and located one bubble diameter from the axis passing through the center of the bubble and the contact point.

We write the potential as the sum of a disturbance and a linear term:

$$\phi^* = \phi_d^* + z^* \quad [3]$$

The second term already satisfies Laplace's equation and all boundary conditions except the one on the bubble surface; therefore,

$$\nabla^2 \phi_d^* = 0. \quad [4]$$

The disturbance must vanish both on the electrode and far away; the potential must be symmetric about an axis passing through the center of the bubble and the contact point; finally, no current passes through the bubble. In tangent sphere coordinates equation [4] and these boundary conditions are:

$$\frac{(\mu^{*2} + \nu^{*2})^3}{\mu^*} \left[\frac{\partial}{\partial \mu^*} \left(\frac{\mu^*}{\mu^{*2} + \nu^{*2}} \frac{\partial \phi_d^*}{\partial \mu^*} \right) + \mu^* \frac{\partial}{\partial \nu^*} \left(\frac{1}{\mu^{*2} + \nu^{*2}} \frac{\partial \phi_d^*}{\partial \nu^*} \right) \right] = 0 \quad [5]$$

$$\phi_d^* \Big|_{\nu^*=0} = 0 = \phi_d^* \Big|_{\substack{\nu^*=0 \\ \mu^*=0}} \quad [6]$$

$$\frac{\partial \phi_d^*}{\partial \mu^*} \Big|_{\mu^*=0} = 0 \quad [7]$$

$$\left. \frac{\partial \phi^*}{\partial v^*} \right|_{v^*=1} = 0 . \quad [8]$$

Moon and Spencer (8) give the separation criteria, the separated equations, and their general solutions. After applying conditions [6] and [7], we obtain

$$\phi_d^* = A \sinh(qv^*) J_0(q\mu^*) (\mu^{*2} + v^{*2})^{1/2} . \quad [9]$$

Because the domain is infinite, the solution must include all values of q ; therefore, [9] passes to an integral.

$$\phi_d^* = (\mu^{*2} + v^{*2})^{1/2} \int_0^\infty A \sinh(qv^*) J_0(q\mu^*) dq . \quad [10]$$

The insulation condition [8] determines A as a function of q . Upon differentiating the complete potential ϕ^* , evaluating this expression at $v^* = 1$, and equating it to zero, we obtain

$$\begin{aligned} 0 = & \frac{1}{(\mu^{*2} + 1)^{1/2}} \int_0^\infty A \sinh q J_0(q\mu^*) dq \\ & + (\mu^{*2} + 1)^{1/2} \int_0^\infty A q \cosh q J_0(q\mu^*) dq \\ & + \frac{(\mu^{*2} - 1)}{(\mu^{*2} + 1)^2} . \end{aligned} \quad [11]$$

Following Witze, Schrock, and Chambré (9), we use the differential equation satisfied by J_0 and integrate twice by parts to obtain

$$\frac{1 - \mu^{*2}}{(\mu^{*2} + 1)^{3/2}} = \int_0^{\infty} q H J_0(q\mu^*) dq \quad [12]$$

where

$$H(q) = \frac{1}{q} \left\{ -\frac{d}{dq} \left[q \frac{d}{dq} (A \cosh q) \right] + A(q \cosh q + \sinh q) \right\} . \quad [13]$$

After inverting the transform with the help of the Erdelyi Tables (10) and rearranging the equations, we obtain

$$\frac{dA}{dq} = \frac{1 - q + e^{-2q}}{2 \cosh^2 q} + \frac{C}{2q \cosh^2 q} . \quad [14]$$

C must be zero for the derivative to remain finite at $q = 0$.

$$A = \int_{\infty}^q \frac{1 - q + e^{-2q}}{2 \cosh^2 q} dq . \quad [15]$$

The potential is now given by

$$\phi^* = (\nu^{*2} + \mu^{*2})^{1/2} \int_0^{\infty} A J_0(q\mu^*) \sinh q (\nu^*) dq + \frac{\nu^*}{(\mu^{*2} + \nu^{*2})} \quad [16]$$

and the primary current distribution is

$$i^* = \mu^{*2} \left. \frac{\partial \phi^*}{\partial \nu^*} \right|_{\nu^*=0} = \mu^{*3} \int_0^{\infty} q A dq J_0(q\mu^*) dq + 1 . \quad [17]$$

Equations [16] and [17] were numerically evaluated by routines that calculated the Bessel functions and integrated their products with the hyperbolic functions over the appropriate domains.

DISCUSSION

The electric field appears in Figures 2(a) and (b). The potential is normalized so that equipotentials far from the bubble coincide with distance from the electrode (see [3]). As required by the insulation condition, [8], the equipotentials meet the bubble at right angles; they approach their undisturbed values far away. One can see from Figure 2(a) that the displacement of equipotentials caused by the insulating sphere becomes negligibly small beyond one and a half diameters from its contact point along the electrode and three diameters perpendicular to the electrode.

The current distribution as a function of dimensionless distance appears in Figures 3(a) and (b). The current density is normalized to be 1.0 at a great distance from the sphere; we call this the "undisturbed" value. The value .5 on the abscissa of Figure 3 marks the outermost circle on the electrode shadowed by the bubble; here, the current density is eighty percent of its undisturbed value. The current density farther from the bubble exceeds 1.0 because the upper half of the sphere deflects the flux and thereby creates a maximum current density two percent greater than the undisturbed value at one diameter from the contact point. We conclude that fields around spheres separated by more than three diameters affect each other negligibly.

A detail of the current distribution near the contact point appears in Figure 3(b). Zero at the axis, the current density reaches only one percent of its undisturbed value at thirty percent of the radius from the contact point; therefore, we can insulate the area inside this distance with a surface which coincides with a surface of flow. Thus the effect of a tangent insulating sphere on the current distribution approximates that of a bubble having a nearly spherical shape and a contact area less than $.09 \pi a^2$. Calculating the contact angle for this base area according to the geometry in Figure 4,

$$\theta = 90^\circ - \cos^{-1} (b/a) = 17.5^\circ, \quad [18]$$

we conclude that the effect of a sphere on a plane approximates that of a nearly spherical bubble having a contact angle less than 17.5° .

The bubble increases the resistance by deforming the otherwise straight lines of current. We evaluate the effect by integrating the potential disturbance over a plane far from the electrode and parallel to it.

$$\Delta\phi = 4a^2 \int_0^\infty 2\pi x^* \phi_d^* \Big|_{z^* \rightarrow \infty} dx^* = A_o \pi a^2 \quad [19]$$

where

$$\begin{aligned} A_o &= 8 \int_0^\infty q A d q \\ &= .9015 . \end{aligned} \quad [20]$$

$\Delta\phi$ does not depend on distance from the electrode; it is the net disturbance of potential integrated with area. "n" bubbles per unit area, distributed such that their contributions are independent, cause a net potential disturbance

$$\Delta\phi^* = nA_o \pi a^2 . \quad [21]$$

One cannot deduce a conductivity analogous to Maxwell's because the layer of bubbles is two-dimensional; the effect must be characterized as a polarization at the electrode surface. The increment of resistance caused by the bubbles on an electrode of area S is the net potential disturbance, [21], divided by the total current to the electrode, $\kappa\phi_o S$.

$$\Delta R = \frac{\Delta\phi^*}{\kappa S \phi_o} = \frac{2A_o n \pi a^3}{\kappa S} \quad [22]$$

ΔR is a resistance increment related only to the disturbance caused by the bubbles. Its sum with the cell's resistance in the absence of gas gives the net cell resistance.

Bubbles whose contact points are three diameters apart in a planar hexagonal array give a number density $.0321/a^2$. If the bubble diameter is a tenth of the interelectrode gap in a parallel plane cell geometry, [22] predicts a resistance increase of only 1 percent. This means that the resistance caused by a sparse collection of small bubbles is negligible. When closer than three diameters, the bubbles interact

significantly and thereby disturb the potential more than predicted by [22]; nevertheless, this equation establishes that when the diameters are a tenth of the interelectrode spacing, the minimum added resistance caused by a close-packed array of bubbles on a surface is at least eight percent of the cell resistance. In reality, because of the severe pinching of the field between bubbles, the effect must be substantially larger than this, perhaps by a factor of two to three. Experiments and additional theory are in progress which will determine the effect of dense single and multiple surface layers of bubbles on the resistance at electrodes.

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NOMENCLATURE

- a bubble radius, cm
- A_0 .9015, dimensionless
- A Fourier constant, dimensionless
- b radius of bubble base, cm
- C constant of integration
- i current density, Amp/cm²

n	number density of bubbles, cm^{-2}
q	separation parameter, dimensionless
ΔR	net resistance increase caused by the layer of bubbles, ohm
S	area of electrode, cm^2
x	distance parallel to electrode, cm
z	distance perpendicular to electrode, cm
ϕ	potential, volt
ϕ_0	slope of linear potential field far from the bubble, volt/cm
$\Delta\phi$	net potential disturbance far from the electrode integrated with area $\text{volt}\cdot\text{cm}^2$
ν	tangent sphere coordinate, cm^{-1}
μ	tangent sphere coordinate, cm^{-1}
κ	conductivity $(\text{ohm}\cdot\text{cm})^{-1}$
θ	contact angle, degrees

Subscripts and Superscripts

d	disturbance
*	dimensionless quantity

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FIGURE CAPTIONS

- Figure 1. Tangent sphere coordinates in two dimensions.
- Figure 2(a). Potential around an insulating sphere tangent to an electrode.
- Figure 2(b). Detail of potential close to sphere.
- Figure 3(a). Current distribution near a spherical insulator tangent to a surface.
- Figure 3(b). Detail of current distribution near the contact point.
- Figure 4. Geometry for calculation of contact angle θ .

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Figure 1. Tangent sphere coordinates in two dimensions.

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Figure 2(a). Potential around an insulating sphere tangent to an electrode.

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Figure 2(b). Detail of potential close to sphere.

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Figure 3(a). Current distribution near a spherical insulator tangent to a surface.

Figure 3(b). Detail of current distribution near the contact point.

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Figure 4. Geometry for calculation of contact angle θ .

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