Influence on the electrolyte resistance of the contact angle of a bubble attached to a disk electrode

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ARTICLE INFO

ABSTRACT

In a previous work, the analysis of the electrolyte-resistance (ER) increment due to the presence of an insulating sphere above or in contact with a disk electrode, simulating a spherical particle, drop, or gas bubble close or attached to an electrode has been reported (Bouazaze et al., 2010) [17]. In the present work, the influence on the ER of the contact angle with the electrode surface, which plays for example a major role in the size of bubbles on gas-evolving electrodes, is quantitatively determined. The mathematical collocation method used in the previous work was improved to account for the change in geometry of the electrode-sphere system. The theoretical results show that the ER increment due to the presence of the sphere depends on its size, position, and contact angle. For a given size and position of spheres of aspect ratio less than 0.4, the ER increment due to the contact angle varies roughly between −45% and +35% of the increment due to a perfect sphere, depending on the interplay of the surface and volume competing effects influencing the ER. Despite their low values, the ER increments could be experimentally measured for spheres of different contact angle placed at the electrode centre, owing to a high-precision motorized translation stage and a specific low-noise ER measurement device. An excellent agreement was obtained between the theoretical and experimental results.

1. Introduction

Formation of electrolytic bubbles is encountered in many industrial electrochemical applications because gas molecules are often generated from electrochemical reactions. This phenomenon has important implications because a part of the active electrode surface is screened by the attached bubbles, which affects charge, mass, and heat transfers at the electrode/electrolyte interface. The screening effect of electrolytic bubbles and the influence of the contact angle of attached bubbles, defined as the angle between the liquid–gas interface and the electrode surface, have been studied in several papers. For example, the modification of the primary distribution of potential and current lines (ohmic effects) due to the presence of a single spherical bubble attached to an infinite plane electrode has been analytically derived by Sides and Tobias and the incremental electrical resistance was calculated for a sparse array of spherical bubbles [1]. The electrode current density, which is quite negligible on a small area around the contact point, was found to approximately apply for nearly spherical

bubbles having a contact angle lower than 17.5°. This analysis was later extended to bubbles making arbitrary contact angle with the electrode by Wilson and Hulme [2]. Dukovic and Tobias studied the effects of attached bubbles on the local distribution of current and on the potential drop at the electrode [3]. In addition to the increase in electrical resistance (ohmic effects), their model shows an increase in the surface overpotential due to the masked electrode area that increases the local current density, and a decrease in the concentration overpotential due to decreased local supersaturation near the bubbles. All these parameters have been shown to depend on the contact angle of the bubbles with the plane electrode.

The screening effect of attached electrolytic bubbles was also studied by Vogt et al. who introduced the bubble fractional coverage factor, defined as the area screened by the normal projection of the bubbles on the electrode surface. They showed this factor strongly depends on the electrolysis current density for both stagnant [4] and flowing [5,6] electrolytes. However, these authors neglected the influence of the contact angle when its value is lower than 90° (wetting electrolyte), considering that the actual current density on the shaded area below the attached bubbles is small.

Several authors have tried to take into account the influence of the contact angle on bubble growth rate, detachment diameter,

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and population density on the electrode, and to predict its dynamic variation at different stages of bubble evolution (nucleation, growth, and detachment). Trieu and Chandran studied hydrogen evolution formed by formaldehyde oxidation during electroless copper deposition on a vertical wall [7]. They theoretically showed the dependence of the side contact angle and bubble detachment radius and observed experimentally that the smaller the contact angle, the larger the evolving bubbles, which strongly affects the quality of the product plate.

Buehl and Westwater studied the effect of contact angle on the growth rate of bubbles in water supersaturated with carbon dioxide [8]. Their theoretical work and photographic observations of bubbles coming out from an artificial site drilled on a horizontal wall concluded that the effect of contact angle on bubble growth rates was small for contact angles between 0° and 90°, even if the contact angle changed during bubble growth. Baum et al. studied the influence of the attachment of hydrogen bubbles produced during the etching of Si (100) in aqueous KOH on the surface roughness of microstructures [9]. Indeed, these bubbles are one of the causes of the formation of pyramids on the Si surface. They showed that the decrease in contact angle of the attached bubbles due to alcohol or oxidizing agent addition improves the surface finish.

Gas evolution may also be studied using the electrochemical noise technique, which consists in measuring the potential or current or electrolyte resistance fluctuations generated by the growth and detachment of bubbles, in order to derive the size and departure rate of bubbles. Despite the ability of the technique to monitor gas evolution in real time, very few studies have been reported in the literature on this topic. Gabrielli et al. showed that the mean departure rate, the mean radius of detaching bubbles, and the gas evolution efficiency can be derived from the spectral analysis of the potential or current fluctuations [10]. Hodgson showed that the influence of various electrocatalysts on the departure rate of chlorine bubbles evolving on ruthenium–titanium oxide anodes could be monitored by current noise measurements [11]. Compared to the analysis of the potential or current fluctuations, which depend on several factors (ohmic, activation, concentration of dissolved gas) [3,12], the analysis of the fluctuations of the electrolyte resistance (ER) measured between the reference electrode and the working electrode is easier since only ohmic effects are concerned. Owing to the experimental set-up described in Ref. [13], Huet et al. simultaneously measured potential and ER fluctuations due to oxygen bubbles detaching from rough and porous horizontal Ni electrodes and showed that the size of detached bubbles depends on the electrode surface roughness [14]. Volanschi et al. studied the influence of various surfactants on the dynamic surface tension, which plays a significant role on the size and departure rate of evolving bubbles, from the simultaneous measurement of potential and ER on microcavity electrodes in aqueous solutions [15]. Benzaïd et al. also measured the ER fluctuations generated by hydrogen bubbles on cylindrical vertical carbon steel tensile specimens under cathodic polarisation [16]. However, their simplified model of the power spectral density of the ER fluctuations gave characteristic parameters of the gas evolution in only qualitative agreement with optical observations because of the complicated screening and dragging effects of rising bubbles for vertical electrodes.

In order to improve the theoretical models, it is necessary to quantify the effect of a bubble above or attached to a plane electrode of finite size on the ER. In a previous work, the ER increment due to the presence of an insulating sphere in contact with a disk electrode was calculated with the collocation mathematical method [17]. This configuration "single sphere – electrode" simulating a frozen bubble is the basic case in the study of gas evolution and can also find interest in other fields, such as when tracking the position of a moving spherical particle in a flow-channel [18]. However, only bubbles of contact angle equal to zero were concerned up to now. To extent the previous study, the influence of contact angle of an insulating sphere sitting at any position on a disk electrode is investigated in the present paper.

2. Theoretical treatment

The mathematical collocation method used to calculate the distribution of the potential ϕ in the electrolyte when an insulating sphere simulating a bubble with a zero contact angle lies on a disk electrode has been detailed in Refs. [17,19] and is summarized in Appendix A. This method applies as well when the contact angle θ of the bubble is different from 0. In that case, the bubble is simulated by a sphere cut off by a plane. Fig. 1 shows the notations used in this paper. The centre of the disk electrode of radius a_e is the origin O of the Cartesian coordinate system (x, y, z) and the centre O′ of the sphere of radius a_p corresponds to the point $(x_0, 0, z_0 = a_p \cos \theta)$, where θ is the contact angle of the truncated sphere, as defined in Fig. 1.

Once the coefficients A_{nm} and C_{nm} of the series expansion of the potential distribution in the electrolyte are determined (Appendix A), the ER can be calculated from the ratio of the potential ϕ_0 applied to the surface of the electrode and the current I flowing across the electrode, which is obtained by integrating the current density on the electrode $\kappa (\partial\phi/\partial z)|_{z=0}$, where κ is the electrolyte conductivity. The following expression of the ER is obtained for a sphere ($\theta = 0$) sitting on the electrode; it only depends on one coefficient (A_{00}) of the series expansion of the potential, which is a purely imaginary complex number (see Appendix D in Ref. [17]):

$$R_e = \frac{\phi_0}{I} = \frac{\phi_0}{2\pi \kappa a_e j A_{00}} \tag{1}$$

For a truncated sphere ($\theta \neq 0$), the derivation of the ER is more involved. Indeed, there is no analytical expression of the current I flowing across the electrode, in contrast with a perfect sphere, so that the current density must be numerically integrated on the electrode area not blocked by the sphere. When the truncated sphere is centred on the electrode axis, the expression of the ER depends on all coefficients A_{n0} of the potential series expansion but the numerical calculations are relatively simple. When the sphere is not centred, these calculations are much more complex and some convergence problems arise, especially when the sphere approaches the electrode edge. The convergence of the calculations was ensured for $x_0 < a_e - a_p \sin \theta$, that is, when the disk below the truncated sphere lies entirely on the electrode surface, at least for the largest spheres considered in this work ($a_p/a_e = 0.4$ or 0.5).

The ER change due to the presence of the sphere was compared to the value of the theoretical ER of the disk electrode in the absence of the sphere, which is given by Newman's formula when the counter electrode is at infinity [20]:
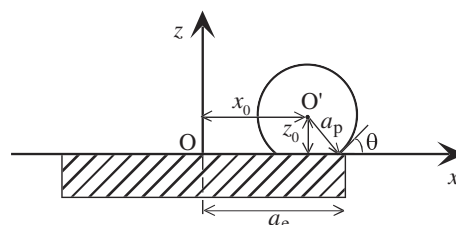
$$R_{e,N} = \frac{1}{4\kappa a_e} \tag{2}$$

Fig. 1. Schematic drawing of the truncated sphere in contact with the electrode.