



# On the relation between onset of bubble nucleation and gas supersaturation concentration



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## ABSTRACT

The time taken for gas bubbles to start forming on an electrode operating in a stagnant aqueous solution is driven by the dissolved gas mass-transfer near the electrode. This is the result of two processes that compete with one another. One adds dissolved gas molecules from the chemical reactions at the electrode surface and the other diffuses these molecules towards the bulk. Using this mechanism, a model is proposed that can predict the dissolved gas supersaturation concentration up to the onset of bubble nucleation at the electrodes (heterogeneous nucleation). Experimental measurement of the bubble onset nucleation time is incorporated within this model to calculate the critical supersaturation concentration for dissolved hydrogen and oxygen gas. The results show a strong link between the applied current density and the supersaturation concentration at the electrode surface. A relation was obtained that predict the onset of bubble nucleation showing an excellent agreement with the measurement.

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## 1. Introduction

During electrochemical reaction processes such as electrolysis of water, electrons flow from the anode to the cathode where they are consumed by hydrogen ions to form hydrogen gas. The dissolved gas builds up until a critical supersaturation concentration is reached at the electrode surface which marks the onset of bubble nucleation and undergoes a phase change [1,2]. To balance the electrical charge, hydroxide ions move through the electrolyte solution to the anode, where they give away electrons. Recent work has aimed at preventing or controlling gas bubble generation. For example, in electro-osmotic pumps, the flow rate is restricted due to the formation of bubbles at the membrane [3]. In electrophoretic deposition the bubbles generated at the electrodes may yield damaged and poor quality coatings [4]. One approach at controlling gas generation has been performing the electrochemical process under modulated electric fields such as pulsed direct current and alternating current [5–7]. A better understanding of the relation between the dissolved gas supersaturation concentration and the bubble nucleation time at the electrode surface during the electrochemical reaction could be used to suppress or eliminate the gas generation.

The dissolved gas concentration is governed by the rate at which the electroactive species are brought to the electrode surface, by the process of desorption from the liquid phase to the gaseous phase and by the diffusion of the dissolved gas towards the bulk [8–10]. At a gas-evolving electrode the gas concentration is dependent on the mass transfer due to single-phase free convection from the density gradients and also it is dependent on the two-phase free convection induced by rising bubbles [11,12]. Many studies have considered the different mechanisms that affect the mass transfer at gas-evolving electrodes and the efficiency when bubbles adhere to the electrode surfaces [13–16]. Present studies model the bubble production using empirical correlations with current density [17,18] without solving for the concentration distribution. These models implicitly assume that the nucleation and growth of bubbles is very fast. Other models assume that the bubbles nucleation and growth is governed by a linear rate law which depends on the change of the dissolved gas supersaturation concentration [19,1].

During electrolysis, the mass transfer of the electroactive species (radicals) is controlled by their migration, diffusion and convection and it can be modeled by the Nernst-Planck equation [20] [9,10,21]. These radicals convert to dissolved gas by losing or gaining electrons at the electrodes. At the short initial stage of the bubble nucleation in a stagnant electrolyte (the focus of the present work), the single-phase free convection mass-transfer can be neglected, and the dissolved gas concentration at the electrode is governed by the diffusion equation (Fick's second law) [22,20]. This simplification required a convectionless liquid. The dissolved

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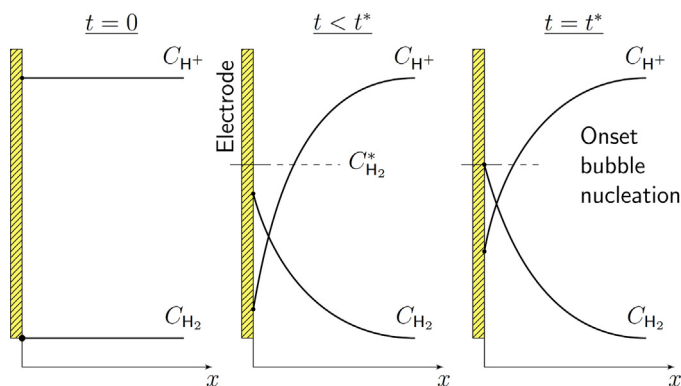


Fig. 1. Graphical illustration of  $C_{H^+}$  and  $C_{H_2}$  mass transfer near the electrode.

gas concentration increases with time up to the critical supersaturation concentration when the onset of bubble nucleation occurs. Since the bubbles do not nucleate infinitely fast, some time elapses until the appearance of the gas phase [23]. This differs substantially from what happens in continuous electrolysis where nucleation time is very small or possibly inexistent. While bubble production and growth has received much attention, there is a lack of information on the prediction of onset of bubble formation. Only the work by Dinkelacker [24] reported the bubble formation time as a function of current density. The present work relates the onset gas formation time with the critical supersaturation concentration near the electrode in a stagnant electrolyte. A supersaturation model is proposed that uses Fick's law and results from experimental measurements of the bubble formation time.

## 2. Theoretical model

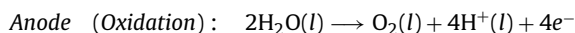
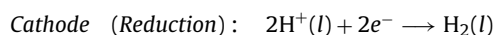
### 2.1. Chemistry of water electrolysis

The present study models the increase in the dissolved gas concentration  $C_i$ , of species  $i$  from basic principles to solve for the critical supersaturation concentration  $C_i^*$ . The number of dissolved gas moles generated at the electrode,  $n$ , is related to the current drawn by Faraday's law,

$$n = \frac{It}{zF} \quad (1)$$

where  $I$  is the constant current drawn by the electrolyte,  $z$  is the valency number of ions of the substance (electrons transferred per ion), and  $F$  is the Faraday's constant.

In our experiments we have chosen to work with simple, low ionic concentration aqueous buffers and inert platinum electrodes so that the electrodes half-reactions (acid) is,



The dissolved  $H_2$  and  $O_2$  gas, formed at the electrodes, build up until it reaches the critical supersaturation  $C_{H_2}^*$  and  $C_{O_2}^*$  respectively. Beyond this threshold and in the presence of a nucleation site, crack or cavity in the electrode surface, bubbles are initiated [25].

### 2.2. Concentration gradient of dissolved gas

The dissolved gas generated at the electrodes diffuses away towards the bulk. This produces a higher concentration near the electrode than at the bulk solution resulting in a concentration

gradient as shown in Fig. 1. The temporal evolution of the dissolved gas concentration can be written in terms of Fick's second law as,

$$\frac{\partial C_i(x, t)}{\partial t} = D_i \frac{\partial^2 C_i(x, t)}{\partial x^2}, \quad (2)$$

where  $D_i$  is the diffusion coefficient of species  $i$  in the working electrolyte. At the electrode boundary, the dissolved gas flux,  $J_i(x, t)$ , is proportional to the concentration gradient

$$J_i(x, t) = -D_i \frac{\partial C_i(x, t)}{\partial x}. \quad (3)$$

The analytical solution to Eq. 2 provides the evolution of the concentration,  $C_i(x, t)$  sketched in Fig. 1 but it can not predict the onset of bubble nucleation  $t^*$ . The goal is then to combine the solution to Eq. 2 with experimental measurements of the bubble formation time  $t^*$  to calculate  $C_i^*$ . To solve Eq. 2, the boundary and initial conditions are needed. We can assume that, before the electric field is applied, the species concentration,  $C_i$ , is equal to the bulk saturation concentration of the dissolved gas,  $C_i^\infty$ . Considering that the electrolysis cell is large compared to the diffusion thickness, the concentration far from the electrode reaches the bulk concentration,  $C_i^\infty$ . This can be written as,

$$C_i(x, 0) = C_i^\infty$$

$$\lim_{x \rightarrow \infty} C_i(x, t) = C_i^\infty. \quad (4)$$

When a constant current,  $I$ , is applied across the electrolysis cell, the resultant flux across the electrode surface,  $J_s$ , is constant and given by

$$-J_s = -J_i(0, t) = \frac{I}{zFA} = D_i \left( \frac{\partial C_i(x, t)}{\partial x} \right)_{x=0}$$

We can now solve Eq. 2 to obtain the concentrations of oxidized and reduced species at the electrode (Sand [22] and Karaoglanoff [26]) giving

$$C_i(x, t) = C_i^\infty + \frac{J_s}{D_i} \left\{ 2 \left( \frac{D_i t}{\pi} \right)^{1/2} \exp\left(-\frac{x^2}{4D_i t}\right) - x \operatorname{erfc}\left(\frac{x}{2(D_i t)^{1/2}}\right) \right\} \quad (5)$$

This equation can be written in terms of the non-dimensional parameter  $\eta$  as

$$C_i(x, t) = C_i^\infty + \frac{J_s x}{D_i} \left\{ \frac{1}{\sqrt{\pi \eta}} \exp(-\eta^2) - \operatorname{erfc}(\eta) \right\} \quad (6)$$

where  $x$  is nondimensionalized by a diffusion thickness  $\delta$ , with a general scaling of  $\delta \sim \sqrt{Dt}$ , so that  $\eta = x/\sqrt{4Dt}$ . Further details about the choice of  $\delta$  will be given next. We assume that before the onset of bubble formation, this diffusion equation (Eq. 6) dominates the mass transfer. Once bubbles are formed, other mass transfer mechanisms such as single-phase and two-phase convection and gas adsorption can dominate. These have been widely considered in the study of the gas-evolving electrodes [8–12,27,28], but will not be considered here since our analysis of the problem stops at the onset. This diffusion equation is plotted in Fig. 2, showing how the concentration of the dissolved gas,  $C_i(x, t)$ , varies as we move away from the electrode as well its variation at the electrode  $C_i(0, t)$ . As time increases, the concentration at the electrode surface increases and also the the boundary layer thickness from the surface where the dissolved gas concentration  $C_{H_2}$  is larger than the bulk concentration. This region of influence corresponds to a diffuse layer thickness  $\delta$  which can be shown to scale as  $\sim \sqrt{D_i t}$ .

The results in Fig. 2, show that the concentration of dissolved gas at the electrode increases with time. In such an environment rich in excess dissolved gas molecules, the conditions are being set for bubble nucleation. The process is not well understood with the traditional view being that the onset of nucleation is the result of

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