



# Local microprocesses at gas-evolving electrodes and their influence on mass transfer



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## ARTICLE INFO

### Article history:

Received 14 October 2014

Received in revised form 1 January 2015

Accepted 2 January 2015

Available online 9 January 2015

### Keywords:

gas-evolving electrodes  
mass transfer  
microconvection  
convectionless diffusion

## ABSTRACT

Mass transfer controlled by gas evolution at electrodes has previously been widely studied. However, the resulting correlations deviate considerably from each other, mainly because they did not take into account the various interacting mechanisms. The present paper gives an overview of these models.

A model is then presented taking into account all the decisive mechanisms and their interactions. As a result, a new mass transfer correlation is derived suitable for industrial and basic applications.

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## 1. Introduction

Mass transfer at gas-evolving electrodes is of great importance to numerous electrochemical reactors. There, mass transfer of the reagent, say hydrogen ion, from the bulk to the electrode surface is different from mass transfer of the product, say dissolved hydrogen. The latter one splits into two paths. One of them, the transfer from the electrode to the liquid bulk, varies with the distance from the electrode [1]. The other one is the transfer of the dissolved product to the gas-liquid interface causing bubble growth. This mass transfer rate can be assessed [2]. The present study focuses on mass transfer from the bulk to the electrode.

Mass transfer at gas-evolving electrodes may be affected by a variety of mechanisms [3]. Single-phase free convection [4] and free convection of the gas-liquid dispersion [5–8] act on mass transfer. Furthermore, strong superimposed forced convection past the electrode surface can interact with other mass transfer mechanisms [9,10], mainly at small values of the current density [11]. All these phenomena are based on continuous macroconvective processes facilitating a theoretical approach.

However, operational conditions involving high values of current density are of major relevance. Here several consecutive and strongly different microprocesses induced by growing and detaching bubbles are active.

- Bubbles adhering to the electrode surface start growing from active nucleation sites and continue growing until break-off from the surface. Then a new bubble starts growing at the same site. During bubble growth in contact with the electrode, liquid is pushed off in the radial direction and with varying intensity past the surrounding area. This flow affects convective mass transfer.
- At break-off from the electrode, the volume previously occupied by the bubble is filled inducing additional convective mass transfer.
- This wake flow transports liquid to the electrode surface. Then the concentration boundary layer in a confined area around the nucleation site is strongly disturbed. Non-steady diffusion results acting on mass transfer irrespective of liquid flow.

These microprocesses influence the rate of mass transfer of reagents to the electrode and of products away from the electrode.

Attempts to describe these processes have been made in two different ways. Non-steady state diffusion following departure of bubbles from the electrode was assumed to be the only mass transfer mechanism. Ibl considered convectionless diffusion during the waiting time between departure and growth of the subsequent bubble [12] and succeeded in establishing a first mass transfer correlation for gas-evolving electrodes [13]. His model was later modified by Roušar and Cezner [14]. In another attempt, convective mass transfer induced by bubble growth was regarded as the controlling mechanism [15,16]. The influence of the wake flow on convective mass transfer was briefly discussed by Tomasoni [17]. All these previous studies have substantial

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## Nomenclature

### List of Symbols

$A$	electrode surface area [m <sup>2</sup> ]
$A_a$	active area [m <sup>2</sup> ]
$c$	concentration [mol m <sup>-3</sup> ]
$d$	equivalent bubble break-off diameter [m]
$D_B$	diffusion coefficient of dissolved product [m <sup>2</sup> s <sup>-1</sup> ]
$D_i$	diffusion coefficient of transferred species [m <sup>2</sup> s <sup>-1</sup> ]
$f_G$	gas-evolution efficiency [-]
$F$	Faraday constant, $F = 96485 \text{ A s mol}^{-1}$
$I$	current [A]
$I_{su}$	summit current [A]
$k$	mass transfer coefficient [m s <sup>-1</sup> ]
$k_d$	local mass transfer coefficient in pure diffusion [m s <sup>-1</sup> ]
$k_r$	local mass transfer coefficient in convection [m s <sup>-1</sup> ]
$L$	radius of the microarea, Eq.id=6#(1) [m]
$L_a$	outer radius of the active area [m]
$n_b$	number of bubbles in contact with electrode
$\dot{N}$	flux of substance [mol s <sup>-1</sup> ]
$p$	pressure [kg m <sup>-1</sup> s <sup>-2</sup> ]
$p_{H_2O}$	vapour pressure of solvent [kg m <sup>-1</sup> s <sup>-2</sup> ]
$r$	radial coordinate [m]
$r_0$	radial coordinate inside bubble, Fig.id=6#2 [m]
$R$	bubble radius [m]
$R_a$	inner radius of active area [m]
$R_m$	universal gas constant, $R_m = 8.314 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ K}^{-1}$
$R_r$	radius of departing bubble [m]
$t$	time [s]
$t_b$	bubble break-off time [s]
$t_c$	cycle time [s]
$t_r$	residence time [s]
$T$	temperature [K]
$v$	liquid flow velocity [m s <sup>-1</sup> ]
$v_0$	varying flow velocity within the boundary layer [m s <sup>-1</sup> ]
$v_b$	bubble break-off velocity [m s <sup>-1</sup> ]
$\dot{V}_G$	volume rate of evolved gas [m <sup>3</sup> s <sup>-1</sup> ]
$\dot{V}_L$	liquid flow rate [m <sup>3</sup> s <sup>-1</sup> ]
$V_r$	volume of departing bubble [m <sup>3</sup> ]
$z$	orthogonal coordinate [m]
$\infty$	liquid bulk
$\delta$	boundary layer thickness [m]
$\delta_N$	Nernst diffusion layer thickness [m]
$\eta$	dynamic viscosity of liquid [kg m <sup>-1</sup> s <sup>-2</sup> ]
$\Theta$	fractional bubble coverage of the electrode surface [-]
$\nu_e/\nu_b$	ratio of the stoichiometric numbers of electrons and product
$\nu_L$	kinematic viscosity of liquid [m <sup>2</sup> s <sup>-1</sup> ]
$\rho$	liquid density [kg m <sup>-3</sup> ]
$\tau$	shear stress [kg s <sup>-2</sup> m <sup>-1</sup> ]
$\varphi_B$	current efficiency
Fo	Fourier number, Eq.id=6#(2)
Re <sub>b</sub>	Reynolds number of wake flow, Eq.id=6#(37)
Re <sub>G</sub>	Reynolds number of gas evolution, Eq.id=6#(13)
Sc	Schmidt number, Eq.id=6#(12)
Sh	Sherwood number

limitations. They were confined to the action of a single micro-mechanism as made evident in a critical evaluation [18].

In the following analysis, the previous models of convectionless microdiffusion and of microconvection are again reconsidered and,

with the aid of our present knowledge of the microprocesses, a mass transfer correlation suitable for practical application will be derived.

## 2. Mass transfer induced by convectionless diffusion

In a first step, we study the mechanism of diffusion after bubble departure. Any convection is excluded. As the bubble breaks off from the electrode, the concentrations of reagent and product in the boundary layer are significantly disturbed. Immediately after break-off, liquid with approximately the bulk concentration reaches the area around the previous site of the bubble. A sufficiently large electrode potential effects a rapid drop of the interfacial concentration to almost zero. As long as the bubble does not break-off from the electrode surface, the Nernst diffusion layer thickness, initially being very small, increases and the mass transfer coefficient decreases. The process is analyzed on a small definite part of the electrode area, a microarea, the processes on which are considered as representative of the total electrode area.

### 2.1. Microarea and bubble growth

Each growing bubble adhering to the electrode occupies a certain microarea of the electrode. A number of  $n_b$  bubbles is simultaneously adhering to the electrode surface. The bubble population density is  $n_b/A$  and the related microarea assumed to be circular with a radius  $L$  is

$$\frac{A}{n_b} := \pi L^2 \quad (1)$$

In addition to physical properties, the growth velocity of the bubble radius, is controlled by supersaturation of dissolved product, e.g. H<sub>2</sub>, exerting its maximum effect immediately at the electrode surface [19]. The average value in the environment of the adhering bubble is controlling the bubble growth [20]. The velocity of bubble growth is described by the Fourier number

$$Fo := \frac{D_B t}{R^2} \quad (2)$$

depending on the concentration [21].  $D_B$  is the diffusion coefficient of the dissolved product and is not necessarily identical with the diffusion coefficient  $D_i$  of the species of interest. Shortly after the start of bubble growth, the Fourier number remains constant [10,22–25]. In this case we obtain

$$R \frac{dR}{dt} = \frac{1 D_B}{2 Fo} \quad (3)$$

The residence time  $t_r$  is the time between start of bubble growth and break-off from the electrode surface. When the Fourier number is almost constant, the bubble ratio is directly interrelated with time. From Eq. (2) there follows the important relationship

$$\frac{R}{R_r} = \sqrt{\frac{t}{t_r}}, \quad (4)$$

where  $R_r$  is the bubble radius at the time of break-off from the electrode. Particularly for the condition of bubble break-off with  $R = R_r$  at the end of the residence time  $t = t_r$ , Eq. (3) reduces to

$$R \frac{dR}{dt} = \frac{1 R_r^2}{2 t_r} \quad (5)$$

This term will be used below. The Fourier number turns out to be no longer of interest.

During the residence time, the bubble adhering to the electrode shields a certain part of the total microarea. The fraction of that

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