Electrochimica Acta 113 (2013) 575–582

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

# Mass-transfer characterization in a parallel-plate electrochemical reactor with convergent flow

A.N. Colli, J.M. Bisang*

*Programa de Electroquímica Aplicada e Ingeniería Electroquímica (PRELINE), Facultad de Ingeniería Química, Universidad Nacional del Litoral, Santiago del Estero 2829, S3000AOM Santa Fe, Argentina*

ARTICLE INFO

*Article history:*
Received 12 June 2013
Received in revised form 4 October 2013
Accepted 7 October 2013
Available online 14 October 2013

*Keywords:*
Convergent flow
Current distribution
Mass-transfer coefficient
Parallel-plate electrodes

ABSTRACT

A continuous reduction in the cross-section area is analysed as a means of improving mass-transfer in a parallel-plate electrochemical reactor. Experimental local mass-transfer coefficients along the electrode length are reported for different values of the convergent ratio and Reynolds numbers, using the reduction of ferricyanide as a test reaction. The Reynolds numbers evaluated at the reactor inlet range from 85 to 4600 with interelectrode gaps of 2 and 4 mm. The convergent flow improves the mean mass-transfer coefficient by 10–60% and mass-transfer distribution under laminar flow conditions becomes more uniform. The experimental data under laminar flow conditions are compared with theoretical calculations obtained by a computational fluid dynamics software and also with an analytical simplified model. A suitable agreement is observed between both theoretical treatments and with the experimental results. The pressure drop across the reactor is reported and compared with theoretical predictions.



## 1. Introduction

Reactors with parallel-plate electrodes are frequently used in applied electrochemistry. In many cases the reaction of interest is under mass-transfer control and several strategies are proposed to improve the reactor performance. One alternative is to place obstacles in the interelectrode gap to disturb hydrodynamics [1,2]. These are called turbulence promoters and mass-transfer conditions are strongly dependent on their geometric patterns [3]. The use of turbulence promoters makes the current distribution more uniform [3], but they increase the pressure drop along the reactor length [4] and can reduce the overall electrode surface area in the points where they make contact with the electrode [5]. They can also alter the residence time distribution in the reactor [6] and, depending on the turbulence promoter type, can produce the channelling of the electrolyte [7]. Another option is the increase of the roughness of the electrode [8], which enlarges the specific surface area and the mass-transfer coefficient, though Sedahmed and Shemilt [9] reported an insignificant influence under laminar flow conditions. A third alternative is the sparging of gas in the interelectrode gap or its generation at the electrode surface. In this last case the mass-transfer coefficient is increased owing to the disruption of the mass-transfer boundary layer, called bubble-induced convection [10]. This procedure increases the ohmic drop in the interelectrode gap [11] and modifies the current distribution at the electrode surface [12,13]. Mass-transfer due to bubble-induced convection was enhanced by the use of a rough electrode. However, when a turbulence promoter was placed in the flow channel, the influence upon the two-phase inert-gas mass-transfer was negligible [14]. Finally, another strategy to increase the efficiency of the equipment is changing its geometry. Thus, a sudden change in the flow cross-sectional area, as it may occur at the entrance and exit of electrochemical flow cells, produces important variations in the local mass-transfer coefficient [15]. Likewise, the use of corrugated ducts [16,17] increases the mass-transfer characteristics in relation to a smooth circular pipe. However, its implementation is difficult in the case of parallel-plate electrochemical reactors. Convergent and divergent ducts of rectangular cross-section were proposed to enhance heat transfer in the gas flow [18,19]. This paper is focused on this last alternative. Thus, the reduction in the cross-section inside the reactor is analysed in order to increase the flow velocity along the equipment to enlarge the mass-transfer coefficient. The main advantages of the proposal are the ease of construction and the fact that the electrode surface area is not modified in comparison when turbulence promoters are used.

## 2. Mathematical model

The stationary concentration of minority species in an electrochemical reactor with parallel-plate electrodes in the presence

* Corresponding author. Tel.: +54 342 4571164; fax: +54 342 4571164.
*E-mail address:* jbisang@fiq.unl.edu.ar (J.M. Bisang).

0013-4686/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2013.10.005

of supporting electrolyte is given by the convective mass-transfer equation as

$$D\left(\frac{\partial^2 c}{\partial x^2}+\frac{\partial^2 c}{\partial y^2}+\frac{\partial^2 c}{\partial z^2}\right)=u_x\frac{\partial c}{\partial x}+u_y\frac{\partial c}{\partial y}+u_z\frac{\partial c}{\partial z} \quad (1)$$

here $x$, $y$ and $z$ are the axial coordinates, $c$ is the concentration of the reactant ion, $D$ is the diffusion coefficient of the reactant in the solution, $u_x$, $u_y$ and $u_z$ are the velocities of fluid along the axial coordinates.

The numerical solution of the Navier–Stokes equations together with the continuity equation shows that, as demonstrated later, $u_y$ for the present convergent reactor is negligible in comparison with the other components of the velocity vector. Then, assuming that

$$u_y = 0 \quad (2)$$

neglecting the change in concentration along the electrode width

$$\frac{\partial c}{\partial z}=0 \quad (3)$$

and

$$\frac{\partial^2 c}{\partial y^2}\gg\frac{\partial^2 c}{\partial x^2} \quad (4)$$

Eq. (1) is simplified to

$$D\frac{\partial^2 c}{\partial y^2}=u_x\frac{\partial c}{\partial x} \quad (5)$$

with the following boundary conditions [20]:

$$x=0,\quad c=c_{in}\quad \text{for}\quad 0<y<g \quad (6)$$

$$y=0,\quad c=c_s\quad \text{for}\quad x>0 \quad (7)$$

and a further condition is that the local concentration becomes uniform away from the vicinity of the electrode. Here $c_{in}$ is the concentration at the reactor inlet, $c_s$ at the electrode surface and $g$ the interelectrode gap.

For a parallel-plate reactor with infinitely wide electrodes and fully developed laminar flow the Lévêque equation is [20]

$$u_x=\frac{12u_{av}}{d_h}y \quad (8)$$

here $d_h$ is the hydraulic diameter and $u_{av}$ is the average fluid velocity. Eq. (8) is supposed to be valid for convergent flow and, due to the small value of the interelectrode gap, $d_h$ is not considered as a function of the position. Eq. (8) is a rough approximation, but it provides a very useful simplification for the modelling, which must be experimentally verified. Thus, the average fluid velocity in convergent flow is given by

$$u_{av}(x)=\frac{u_{av}(0)}{(1-\lambda x/L)} \quad (9)$$

where the convergence ratio, $\lambda$, is defined as

$$\lambda=1-\frac{W(L)}{W(0)} \quad (10)$$

here $W$ is the electrode width.

Introducing Eqs. (8) and (9) into Eq. (5) results in

$$\frac{\partial^2 c}{\partial y^2}=\frac{12u_{av}(0)}{Dd_h(1-\lambda x/L)}y\frac{\partial c}{\partial x} \quad (11)$$

Likewise, the local mass-transfer coefficient, $k_{m,x}$ is given by

$$k_{m,x}=\frac{D}{(c_{in}-c_s)}\left.\frac{\partial c}{\partial y}\right|_{y=0} \quad (12)$$

**Table 1**
Values of the incomplete Beta functions and Ψ as a function of λ.

| λ | $B_{\lambda/2}(2/3, 2/3)$ | $B_{\lambda/2}(5/3, 2/3)$ | Ψ |
|---|---|---|---|
| 0.25 | 0.3816 | 0.0193 | 1.5680 |
| 0.50 | 0.6175 | 0.0631 | 1.6507 |
| 0.75 | 0.8269 | 0.1283 | 1.7547 |

Solving Eq. (11) with the boundary conditions given by Eqs. (6) and (7) and introducing the result into Eq. (12) yields

$$Sh_x=1.232\left[Re(0)Sc\frac{d_h}{x}\frac{1}{1-(\lambda x/2/L)}\right]^{1/3} \quad (13)$$

where the local Sherwood number, $Sh_x$, the Reynolds number evaluated at the reactor inlet, Re(0), and the Schmidt number, Sc, are defined as

$$Sh_x=\frac{k_{m,x}d_h}{D} \quad (14)$$

$$Re(0)=\frac{u_{av}(0)d_h}{\nu} \quad (15)$$

and

$$Sc=\frac{\nu}{D} \quad (16)$$

The mean Sherwood number, Sh, is given by

$$Sh=\frac{1}{A}\int_0^A Sh_x\,dA \quad (17)$$

here $A$ is the active electrode surface area. Taking into account Eq. (10), Eq. (17) yields

$$Sh=\frac{1}{L(1-\lambda/2)}\int_0^L Sh_x(1-\lambda x/L)\,dx \quad (18)$$

Introducing Eq. (13) into Eq. (18) and solving results in

$$Sh=1.232\left[Re(0)Sc\frac{d_h}{L}\right]^{1/3}\Psi(\lambda) \quad (19)$$

being

$$\Psi(\lambda)=\frac{B_{\lambda/2}(2/3,2/3)-2B_{\lambda/2}(5/3,2/3)}{(1-\lambda/2)(\lambda/2)^{2/3}} \quad (20)$$

where $B_{\lambda/2}(2/3, 2/3)$ and $B_{\lambda/2}(5/3, 2/3)$ are the incomplete Beta function defined as

$$B_\omega(a,b)=\int_0^\omega t^{a-1}(1-t)^{b-1}\,dt \quad (21)$$

Table 1 reports $B_{\lambda/2}(2/3, 2/3)$, $B_{\lambda/2}(5/3, 2/3)$, and Ψ for different values of λ.

Likewise, for low values of λ Eq. (13) yields

$$\lim_{\lambda\to 0}Sh_x=1.232\left[Re(0)Sc\frac{d_h}{x}\right]^{1/3} \quad (22)$$

and from Eq. (19)

$$\lim_{\lambda\to 0}Sh=1.85\left[Re(0)Sc\frac{d_h}{L}\right]^{1/3} \quad (23)$$

Eqs. (22) and (23) were previously reported by Pickett [20] for a parallel-plate reactor with infinitely wide electrodes and developed laminar flow.

The OpenFOAM free software was also used to calculate the velocity and concentration fields. The velocity profiles inside the reactor were calculated, with the use of the simpleFoam routine, by solving numerically in laminar flow the Navier–Stokes equations