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Comparison of the performance of flow-by three-dimensional cylindrical electrochemical reactors with inner or outer counter electrode under limiting current conditions

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ABSTRACT

The influence of the position of the counter electrode on the behaviour of a cylindrical electrochemical reactor with a three-dimensional electrode in flow-by configuration is analysed. Experimental results of the potential distribution are compared with theoretical predictions obtaining a close agreement between them. The best performance was observed for the arrangement with an outer counter electrode, where the largest bed thickness is obtained for a given potential difference in the three-dimensional structure; which, under limiting current conditions, tolerates a higher current increasing the conversion per pass. The reactor was also checked for the removal of copper from dilute solutions and the experimental results coincide with the theoretical predictions. The morphology of the electrodeposited copper is discussed as a function of the radial position inside the three-dimensional structure.

1. Introduction

Three-dimensional structures are required as electrodes to increase the space time yield of electrochemical reactors when the reactions take place at low current densities such as in the processing of contaminants from waste waters. These electrodes were recently reviewed [1] and a parallelepiped configuration is frequently preferred for the reactor. However, a cylindrical arrangement is necessary in some cases in the industrial practice. Thus, a pioneer cylindrical electrochemical reactor with a three-dimensional anode of lead pellets was used in the Nalco process for the production of lead alkyls [2]. Van der Heiden et al. [3,4] reported the removal of metals from dilute solutions by fluidised bed electrolysis using a cylindrical configuration with many anodic compartments made of a diaphragm with a central wire as anode, which are symmetrically placed in only one cathode. Around each diaphragm six bar-shaped contact feeders are installed to supply the fluidised bed with current. This type of cell construction presents a radial potential distribution around each anode. The Zadra-IMT process for the direct electrowinning of gold is based on a cylindrical three-dimensional cathode of steel wool [5].

The cylindrical configuration is also used in three-dimensional rotating electrodes. A rotating packed bed electrode [6] and a vertically moving particle bed electrode were proposed [7,8]. Reade et al. [9] studied the performance of a reticulated vitreous carbon rotating cylinder electrode, where an electrolyte jet impinged on the bottom central part of the electrode enhancing the mass-transfer coefficient. Likewise, the mass-transfer behaviour of rotating cylinder electrodes made of expanded metal sheets [10], woven wire meshes [11] and wedge wire screens [12] was also examined. Recently, a three-dimensional rotating electrode with a two phase flow induced by centrifugal force was studied for the production of alkaline peroxide by the electrochemical reduction of oxygen [13]. Alkire and Ng [14,15] proposed a mathematical model for cylindrical electrochemical reactors with a packed-bed of flow-by configuration.

In all these cases of cylindrical electrochemical reactors the outer or inner location of the counter electrode related to the three-dimensional structure is of crucial importance for the performance of the equipment [16], because in the cylindrical geometry, with current and electrolyte flow at a right angle, the cross-sectional area for the current flow in the solution phase depends on the radial position.

It is the purpose of the present contribution to analyse experimentally the potential distribution in a cylindrical geometry, either with outer or inner location of the counter electrode, in

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order to find the best arrangement for an electrochemical reactor with a three-dimensional working electrode and to assess the accuracy of the continuous model for these equipments.

2. Mathematical modelling

Fig. 1 shows schematically a cylindrical electrochemical reactor with a three-dimensional electrode. Part (a) corresponds to the configuration with outer counter electrode and Part (b) to the inner case. In the following theoretical analysis, based on the continuous model of three-dimensional electrodes, some usual simplifying assumptions are made: (i) the void fraction and the surface area per unit electrode volume are uniform and do not change with time, (ii) the effective resistivity of the metal phase is negligible in comparison to that of the solution phase, (iii) the electrolyte velocity is constant across the cross-section of the reactor, (iv) a single electrode reaction takes place under limiting current conditions, and (v) the reactor is isothermal and in steady state. Additionally, the change in concentration inside the three-dimensional electrode was considered negligible, which represents a rough approximation allowing a simplification in the modelling. The current balance in the solution phase yields

$$\frac{dI_s(r)}{dr} = j(r)A_s 2\pi r h \tag{1}$$

where I_s is the current in the solution phase at the radial position r, A_s is the surface area per unit electrode volume and h is the electrode length. Assuming all points under limiting current conditions, the total current drained by the electrode, I_L, can be obtained by integration of Eq. (1)

$$I_L = j_L A_S \pi h (r_e^2 - r_i^2) \tag{2}$$

where r_e and r_i are the external and internal radius of the three-dimensional electrode, respectively and the limiting current density, j_L, is given by

$$j_L = \nu_e F k_m c \tag{3}$$

here ν_e is the number of electrons interchanged, F is the Faraday constant, k_m is the global mass-transfer coefficient and c is the bulk concentration. Introducing Eq. (2) into Eq. (1) and integrating is

$$I_s(r) = I_L \frac{r^2 - r_{ref}^2}{r_e^2 - r_i^2} \tag{4}$$

being $r_{ref} = r_i$ for the outer counter electrode case and $r_{ref} = r_e$ when the counter electrode is internal.

The Ohm's law for the solution phase is

$$\frac{d\varphi_s(r)}{dr} = -\rho \frac{I_s(r)}{2\pi r h} \tag{5}$$

where φ_s is the potential in the solution phase and ρ is the effective electrolyte resistivity, evaluated by the Bruggeman equation

$$\rho = \rho^0 \varepsilon^{-3/2} \tag{6}$$

being ρ^0 the electrolyte resistivity and ε the void fraction of the three-dimensional structure. Defining the local electrode potential, E, against any reference electrode as

$$E(r) = \varphi_m - \varphi_s(r) \tag{7}$$

here φ_m is the potential in the metal phase, which is assumed isopotential. Thus, the mathematical model is valid for cylindrical electrochemical reactors with a three-dimensional electrode made of meshes, expanded metal sheets, felts, foams, clothes or packed beds of conductive particles. Combining Eqs. (4), (5), and (7) yields

$$E(r) = E(r_i) + \frac{\rho I_L}{2\pi h (r_e^2 - r_i^2)} \int_{r_i}^{r} \left(r - \frac{r_{ref}^2}{r}\right) dr \tag{8}$$

The potential distribution inside the three-dimensional electrode is obtained by integration of Eq. (8)

$$E(r) = E(r_i) + \frac{\rho I_L}{2V} \left(\frac{r^2 - r_i^2}{2} - r_{ref}^2 \ln \frac{r}{r_i} \right) \tag{9}$$

being V the volume of the three-dimensional structure and I_L is negative for a cathodic process and positive for an anodic one. Evaluating Eq. (9) at the external radius and rearranging yields

$$\frac{E(r_e) - E(r_i)}{\rho I_L} = \frac{1}{2V} \left(\frac{r_e^2 - r_i^2}{2} - r_{ref}^2 \ln \frac{r_e}{r_i} \right) \tag{10}$$

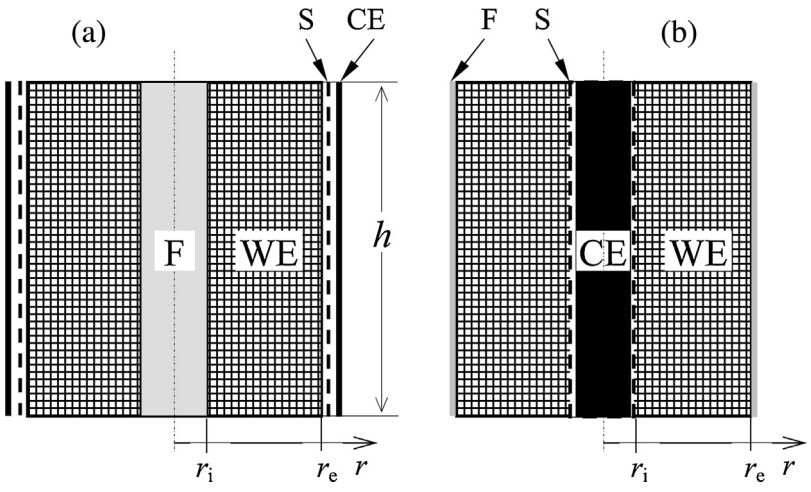

Fig. 1. Schematic view of the two arrangements of cylindrical electrochemical reactors with three-dimensional electrodes used in the mathematical model. (a) Outer counter electrode. (b) Inner counter electrode. CE: counter electrode, WE: three-dimensional electrode, F: current feeder, S: separator.