Flow-through and flow-by porous electrodes of nickel foam
Part III: theoretical electrode potential distribution in the flow-by configuration

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This paper deals with the theoretical potential distribution within a flow-by parallelepipedic porous electrode operating in limiting current conditions in a two-compartment electrolytic cell. The model takes into account the influence of the counter-electrode polarization and of the separator ohmic resistance. The results show that the design of the porous electrode requires the knowledge of the solution potential distribution within the whole cell volume.

Nomenclature

- $a_s$: specific surface area per unit volume of electrode
- $C_0$: entrance concentration ($y = 0$)
- $C_s$: exit concentration ($y = Y_0$)
- $E$: electrode potential ($= \phi_M - \phi_S$)
- $E_0$: equilibrium electrode potential
- $F$: Faraday number
- $i$: current density
- $j$: mean mass transfer coefficient
- $K$: parameter
- $L$: porous electrode thickness
- $n$: number of terms in Fourier series
- $P$: specific productivity
- $Q_v$: volumetric flow-rate
- $u$: mean flow velocity based on empty channel
- $V$: constant potential
- $V_e$: electrode volume
- $x$: thickness variable
- $X$: conversion
- $y$: length variable
- $y_0$: porous electrode length
- $z$: number of electrons in the electrochemical reaction

Greek symbols

- $\alpha$: parameter $[= zFk_d \alpha_c C_0 / y_c]$
- $\beta$: parameter $[= k_d \alpha / a]$
- $\gamma$: ionic electrolyte conductivity in pores
- $\phi_S$: solution potential
- $\phi_M$: matrix potential ($\phi_M = \text{constant}$)
- $\lambda$: parameter $[= \lambda + K]$
- $\eta$: overpotential

Suffices

- a: anodic
- c: cathodic
- eq: equilibrium
- s: separator
- S: solution

1. Introduction

The flow-by configuration of porous electrodes is known to be more adapted to industrial applications than the flow-through configuration [1, 2]. Indeed the former allows large residence times, high conversions per pass, and uniform potential distributions if the electrodes are sufficiently long in the electrolyte flow direction and thin in the current flow direction. In previous studies [3–5] a few aspects of the application of nickel foams as materials for flow-by porous electrodes were considered. These studies were completed by a study of the electrode potential distribution in conditions of limiting current, i.e. of maximum productivity.

The first deductions of theoretical potential distributions in highly conductive flow-by porous electrodes operating in the diffusional regime were due to Alkire and Ng for a cylindrical geometry [2] and to Tentorio and Casolo-Ginelli for a parallelepipedic geometry [6]. By assuming that only the current density vector normal to the electrolyte flow has to be taken into account, they obtained simple analytical expressions giving the local electrode potential. The maximum potential drop is localized at the electrode entrance and it is considered as a design criterion, a
Conclusion which was confirmed by other approaches [7] and which led Kreysa [8] to propose an electrode of variable thickness.

In order to improve the design of flow-by porous electrodes, the 2-dimensional electrode potential distribution was investigated by two groups [9, 10] at almost the same time. The analytical expressions obtained are complex and it seems that a one-dimensional approach similar to that of Tentorio [6] could be sufficient for the design of long thin electrodes [9] and/or for small conversions per pass [11]. These analyses suppose that the separator plane (x = L) is at a constant solution potential, $\bar{\phi}_s$, a situation which neglects the ohmic drop of the interelectrode space but also admits the equipotentiality of the counter-electrode. This anode equipotentiality may be obtained with anodic gas evolution and/or when the anode penetration by the current lines is very small (highly concentrated anolyte, very rapid anodic reaction, porous electrode of large specific surface area). It seems that only Fedkiw [9] examined, in a simple manner, the influence of the ohmic resistance of the interelectrode space on the potential distribution within porous electrodes.

2. Theoretical analysis for the diffusional regime

Let us consider the case of a cell containing two flow-through porous electrodes separated as shown in Fig. 1 (the presence of a separator is at least a hydrodynamical necessity in order to guarantee the percolation of each porous electrode by a given electrolyte flow). The problem is to investigate the potential distribution within the cathode working in limiting diffusion conditions. The porous electrode matrix is assumed to be equipotential (metal potential $\phi_M$ = constant).

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2.1. Potential distribution in the cell

The solution potential, $\phi_s$, in a porous electrode follows from the differential charge balance [6, 9, 10, 15]:

$$V^2 \phi_s = - \frac{\alpha_e}{\gamma} i_R$$  \hspace{1cm} (1)

where $\alpha_e$ is the specific electrode surface area (per unit volume of electrode), $i_R$ the local reaction current density and $\gamma$ the apparent electrolyte conductivity in the pores of the electrode matrix. For a diffusion controlled simple cathodic reaction with $z$ electrons, $i_R$ is related to the mean mass transfer coefficient, $\bar{k}_d$, (assuming that the local mass transfer coefficient does not depend on the position and is equal to the mean value $\bar{k}_d$), as:

$$i_R = - zF\bar{k}_d \bar{C}$$  \hspace{1cm} (2)

where $\bar{C}$ represents the local concentration of the reacting ions. If plug flow can be assumed in the porous electrode (no axial dispersion), the concentration only varies in the $y$ direction of the electrolyte flow. That is:

$$C(y) = C_0 \exp \left(- \frac{\bar{k}_d a_y}{\bar{u}} \right)$$  \hspace{1cm} (3)

where $C_0$ is the value of $C$ at the electrode entrance ($y = 0$) and $\bar{u}$ is the mean electrolyte flow velocity based on the empty cross-sectional area. Thus, the Poisson Equation 1, giving the cathodic solution potential, $\phi_{sc}$, follows from (2) and (3):

$$V^2 \phi_{sc} = \frac{zF\bar{k}_d a_y C_0}{\gamma} \exp \left(- \bar{k}_d a_y / \bar{u} \right)$$  \hspace{1cm} (4a)

In parallelepipedic flow-by porous electrodes, $\phi_{sc}$ may vary with two coordinates $x$ and $y$ (2-dimensional problem) and solution of the following differential