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Analysis of the performance of packed-bed electrochemical reactors

Y. VOLKMAN

Atomic Energy Commission, Nuclear Research Centre – Negev, POB 9007, Beer-Sheva 84190, Israel

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The performance of a packed-bed electrochemical reactor with a parasitic reaction is analysed. Current efficiency and energy consumption are calculated using a linear approximation to the polarization equation. The results are presented as a function of dimensionless variables, which are characteristic of electrode and process parameters. The adverse effects of the parasitic reaction are estimated and ways to avoid them are discussed.

Nomenclature

a	specific interfacial area of the electrode bed ($\text{cm}^{-2}\,\text{cm}^{-3}$)
c	concentration of reactants (g-mol cm^{-3})
F	Faraday constant ($96\,500\ \text{As g-mol}^{-1}$)
I	superficial current density in the solution (A cm^{-2})
I_d	superficial current density in the solution at the diaphragm (A cm^{-2})
I_R	superficial current density in the solution of the useful reaction (A cm^{-2})
j	interfacial current density within the electrode (A cm^{-2})
j_0	interfacial current density of the useful reaction within the electrode (A cm^{-2})
j_1	interfacial current density of the parasitic reaction within the electrode (A cm^{-2})
k_m	mass transfer coefficient (cm s^{-1})
L	thickness of electrode bed (cm)
L_1	Thickness of the 'single reaction zone' (Equation 6) (cm)
m	dimensionless variable (Equation 14)
n	number of electrons transferred in the electrochemical reaction
ΔW	excess specific power consumption (W/useful A)
w	dimensionless excess power consumption (Equation 21)
x	length variable (cm)
α	proportionality constant (Equation 2)
ϵ_I	current efficiency
η	electrode–electrolyte voltage difference (V)
η_1	'decomposition voltage' for the parasitic reaction (V)
ϕ	dimensionless voltage drop variable (Equation 14)
k	effective conductivity of the electrolyte ($\Omega^{-1}\,\text{cm}^{-1}$)

Subscripts

0	the useful reaction; values at $x = 0$.
1	the parasitic reaction; values at $x = L_1$.
L	values at $x = L$.

1. Introduction

Packed-bed or porous electrodes, offering a high specific surface area, have been suggested as suitable means for carrying out electrochemical reactions with low current densities [1–3], especially when the reaction rate is limited by mass-transfer.

The theory of such electrodes was reviewed by Newman and Tiedeman [3]. More technical and practical aspects were summarized by Kreysa and Heitz [4].

Armstrong [5] pointed out that the main drawback of porous electrodes is the excessive potential drop in the electrolyte. Assuming that voltage losses in the electrode matrix are negligible, the potential difference across the electrode–electrolyte interface increases as the potential of the solution decreases.

Such potential variations cause changes in overvoltage and may induce parasitic reactions, thus having an adverse effect on the performance of packed-bed electrochemical reactors. In several experimental works it was noted [6, 7] that when aqueous solutions are treated, water decomposition occurs within the porous electrode, along with the useful reaction. Recently, Alkire and Gould [8] analysed multiple reaction sequences in packed-bed electrodes, but the practical aspects of parasitic reactions were not studied.

In this work, a linear approximation to the electrochemical reaction rate equation is used to study the effects of a parasitic reaction on the current efficiency and energy consumption of packed-bed electrochemical cells. Conclusions are drawn, concerning the construction and operation of such electrolytic reactors.

2. The mathematical model

2.1. *Assumptions*

The mathematical model for evaluating the performance of a packed-bed electrode is based on the following assumptions.

(a) The electrode is a packed bed of interconnected electrically-conducting particles having an interfacial area a per unit volume. It has the form of a slab with thickness L. All gradients are unidirectional (the x-direction). A conducting backplate at $x = 0$ supplies the electrical current to the electrode. The other side (at $x = L$), is separated from the counterelectrode compartment by a porous non-conducting diaphragm (Fig. 1).

(b) The electrode is so operated that the useful reaction is mass-transfer controlled [9]. The voltage at the backplate is sufficient to assure interfacial limiting current density for the useful reaction.

Knowing the mass-transfer coefficient, k_m, this limiting interfacial current density, j_0 is given by

$$j_0 = Fnk_mc \tag{1}$$

where c is the bulk concentration of the reactant, F is the Faraday constant, and n is the number of electrons which are transferred in the reaction.

(c) The parasitic reaction is not limited by mass transport but by the rate of the electrochemical reaction which is assumed to follow a linear approximation of the polarization law:

$$j_1 = \alpha(\eta - \eta_1) \tag{2}$$

where j_1 is the current density of the parasitic reaction, η is the local electrode–electrolyte voltage difference, η_1 is a 'decomposition voltage', below which the rate of this reaction may be neglected, and α is a proportionality constant characteristic of the reaction. No other reactions, which affect current efficiency, take place.

(d) The voltage drop in the electrode matrix is insignificant. The electrolyte solution in the electrode has an effective conductivity, k, which depends on the supporting electrolyte and on the porosity of the electrode.

(e) The electrode is assumed to operate as a differential reactor at steady state. Therefore, the concentration gradients of the reactants of the useful reaction can be neglected. This implies that j_0 is almost constant within the electrode.

2.2. *Potential and current distribution*

Using the above assumptions, it is concluded that the electrode thickness can be divided into two zones: the 'single reaction zone', where $\eta < \eta_1$ and only the useful reaction is significant; and the 'parasitic reaction zone' where $\eta \geqslant \eta_1$, thus both the useful and the parasitic reactions have significant rates. The thickness at which $\eta = \eta_1$ is assigned by $x = L_1$ (Fig. 1).

Following Coeuret [10], the differential equation for the voltage difference distribution in the 'single reaction zone' is

$$\frac{d^2\eta}{dx^2} = \frac{a}{k}j_0 \quad (0 \leqslant x \leqslant L_1) \tag{3}$$

and the boundary conditions are

$$\begin{aligned} \frac{d\eta}{dx} &= 0 \text{ at } x = 0 \\ \eta &= \eta_0 \text{ at } x = 0. \end{aligned} \tag{4}$$

This equation is solved by direct integration assuming that j_0 is constant. The result is

$$\eta = \frac{aj_0}{2k}x^2 + \eta_0 \quad (0 \leqslant x < L_1). \tag{5}$$

L_1 can be calculated by setting $\eta = \eta_1$:

$$L_1 = \sqrt{\left[\frac{2k}{aj_0}(\eta_1 - \eta_0)\right]}. \tag{6}$$

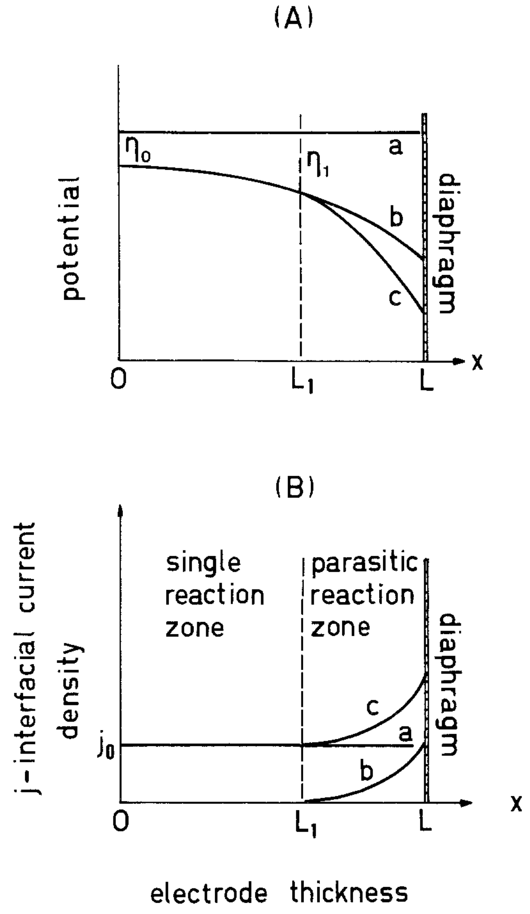

Fig. 1. Schematic description of the electrode.
A. Potential distribution in a packed-bed electrode.
(a) electrode matrix potential
(b) solution-phase potential without parasitic reaction
(c) solution-phase potential with parasitic reaction.
B. Interfacial current density distribution.
(a) useful reaction
(b) parasitic reaction
(c) total reaction.

The differential equation for the 'parasitic reaction zone' accounts for the presence of two reactions:

$$\frac{d^2\eta}{dx^2} = \frac{a}{k}(j_0 + j_1) = \frac{a}{k}[j_0 + \alpha(\eta - \eta_0)] \quad (L \geqslant x \geqslant L_1). \tag{7}$$

The boundary conditions require continuity of the voltage and its derivative at $x = L_1$. Thus, the voltage-difference distribution in the 'parasitic reaction zone' is given by the expression:

$$\eta = \frac{1}{\alpha}\left(j_0\left\{\cosh \sqrt{\left(\frac{\alpha a}{k}\right)}(x - L_1) + \sqrt{\left[\frac{2\alpha}{j_0}(\eta_1 - \eta_0)\right]} \sinh \sqrt{\left(\frac{\alpha k}{k}\right)}(x - L_1)\right\} - (j_0 - \alpha\eta_1)\right) \quad (L \geqslant x \geqslant L_1) \tag{8}$$

The superficial current density in the solution at a cross-section normal to the current flow as a function of x is calculated by Ohm's law:

$$I = k\frac{d\eta}{dx} = j_0 \sqrt{\left(\frac{ak}{\alpha}\right)} \times \left\{\sinh \sqrt{\left(\frac{\alpha a}{k}\right)}(x - L_1) + \sqrt{\left[\frac{2\alpha}{j_0}(\eta_1 - \eta_0)\right]} \times \cosh \sqrt{\left(\frac{\alpha a}{k}\right)}(x - L_1)\right\} \quad (L \geqslant x \geqslant L_1) \tag{9}$$

and

$$I = k\frac{d\eta}{dx} = aj_0x \quad (L_1 > x \geqslant 0). \tag{10}$$

3. Results

3.1. *Current efficiency*

The superficial current density at the diaphragm (I_d), is calculated by substituting $x = L$ in Equation 9.

The total useful current density at the diaphragm (I_R) is

$$I_R = aj_0L. \tag{11}$$

The current efficiency ϵ_I for the electrode is

$$\epsilon_I = \frac{I_R}{I_d}. \tag{12}$$

From Equations 9 and 11 one obtains

$$\epsilon_I = L\sqrt{\left(\frac{\alpha a}{k}\right)} \Big/ \left\{\sinh L\sqrt{\left(\frac{\alpha a}{k}\right)}\left(1 - \frac{L_1}{L}\right) + \sqrt{\left[\frac{2\alpha}{j_0}(\eta_1 - \eta_0)\right]} \cosh L\sqrt{\left(\frac{\alpha a}{k}\right)}\left(1 - \frac{L_1}{L}\right)\right\} \quad \text{for } (L > L_1). \tag{13}$$

Two dimensionless variables are now introduced:

$$m = L\sqrt{\left(\frac{\alpha a}{k}\right)}$$

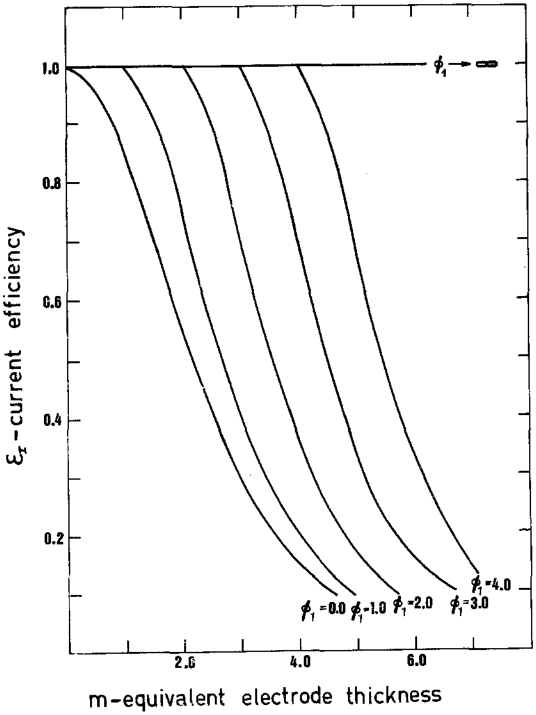

Fig. 2. Current efficiency of a packed-bed electrode with a parasitic reaction.

and

$$\phi = \sqrt{\left[\frac{2\alpha}{j_0}(\eta - \eta_0)\right]} \tag{14}$$

$$\text{especially: } \phi_1 = \sqrt{\left[\frac{2\alpha}{j_0}(\eta_1 - \eta_0)\right]}.$$

Equations 6 and 13 are re-written using these parameters:

$$\frac{L_1}{L} = \frac{\phi_1}{m} \tag{15}$$

$$\epsilon_I = \frac{m}{\sinh(m - \phi_1) + \phi_1 \cosh(m - \phi_1)} \tag{16}$$

The dependence of the current efficiency on m and ϕ_1 is shown in Fig. 2.

It should be remembered that $\epsilon_I = 1.0$ when $L < L_1$ (i.e., $m < \phi_1$).

3.2. *Potential losses*

The potential loss in the electrolyte phase along the packed-bed electrode is the difference $\eta_L - \eta_0$, where η_L is the voltage difference at $x = L$. It is calculated using Equation 8 or 5, according to the value of L.

Rearranging the terms in Equation 8 after substituting $x = L$ and the dimensionless parameters m and ϕ, yields, for the case $L \geqslant L_1$ $(m \geqslant \phi_1)$:

$$\tfrac{1}{2}(\phi_L^2 - \phi_1^2) = \cosh(m - \phi_1) + \phi_1 \sinh(m - \phi_1) - 1 \tag{17}$$

where

$$\phi_L^2 = \frac{2\alpha}{j_0}(\eta_L - \eta_0)$$

according to the definition of ϕ (Equation 14).

Therefore:

$$\phi_L^2 = 2[\cosh(m - \phi_1) + \phi_1 \sinh(m - \phi_1) - 1] + \phi_L^2. \tag{18}$$

This is the dimensionless form of the potential drop in the electrode, when $L \geqslant L_1$ $(m \geqslant \phi_1)$. When $m < \phi_1$ (i.e., there is no parasitic reaction), the voltage drop is given by a modified form of Equation 5:

$$\phi_L^2 = L^2\left(\frac{\alpha a}{k}\right) = m^2. \tag{19}$$

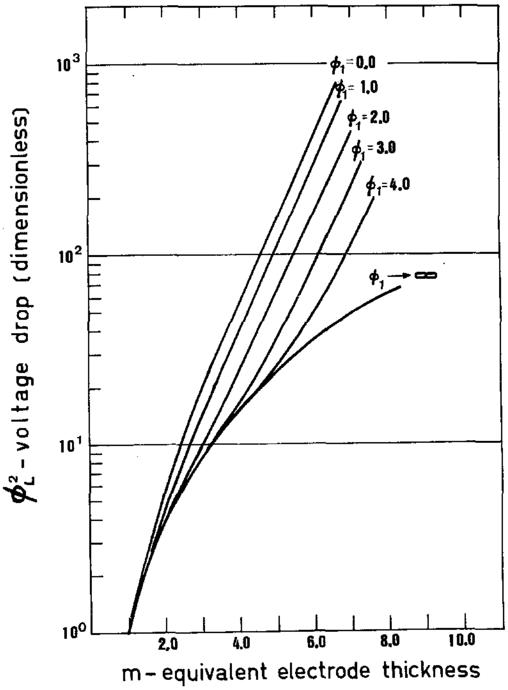

Fig. 3. Voltage drop in a packed-bed electrode with a parasitic reaction.

The dimensionless potential drop, ϕ_L^2, was calculated as a function of m and ϕ_1, using Equations 18 and 19. The results are shown in Fig. 3.

3.3. *Excess energy consumption*

The voltage drop in the electrolyte of a packed-bed electrode is higher than the voltage drop expected from a planar electrode cell. Usually, planar electrodes are kept close to the diaphragm, to minimize ohmic voltage losses.

Therefore, operating a packed-bed electrode cell results in excess energy consumption as compared to a planar electrode. Excessive consumption of energy results also from the parasitic reaction which lowers the current efficiency.

The excess energy consumption per unit of the useful reaction product is proportional to:

$$\Delta W = \frac{(\eta_L - \eta_0)I_d}{I_R} = \frac{\eta_L - \eta_0}{\epsilon_I}. \qquad (20)$$

(For simplicity, the useful reaction rate is expressed as the current that is required for the useful reaction).

Using the dimensionless variables, a dimensionless parameter w, which is related to ΔW, is defined by

$$w = \frac{\alpha}{j_0}\Delta W = \frac{\phi_L^2}{\epsilon_I}. \qquad (21)$$

The dependence of w on m and ϕ_1 is calculated from the values of ϕ_L^2 and ϵ_I, obtained with Equations 16, 18 and 19. The results are shown in Fig. 4.

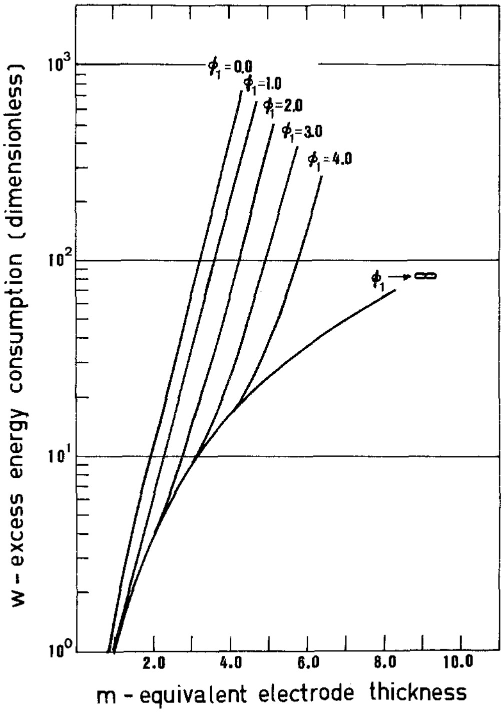

Fig. 4. Excess energy consumption (per product unit) of a packed-bed electrode with a parasitic reaction.

3.4. *Limiting cases*

The results of the above calculations can be bounded between two limiting cases.

(a) If $\eta_L < \eta_1$, then $\phi_1 \rightarrow \infty$. This means that there is no parasitic reaction within the electrode bed. In this case:

$$\epsilon_I = 1.0$$
$$\phi_I^2 = m^2 \qquad (22)$$
$$w = m^2.$$

(b) If $\eta_0 = \eta_1$ then $\phi_1 = 0$, and this means that the parasitic reaction starts at the backplate ($x = 0$). In this case the following results are obtained:

$$\epsilon_I = \frac{m}{\sinh m}$$
$$\phi_L^2 = 2(\cosh m - 1) \qquad (23)$$
$$w = \frac{2(\cosh m - 1)\sinh m}{m}.$$

(c) The case where $\eta_0 < \eta_1$ is insignificant, since in practice it is impossible to carry out the useful reaction when its overvoltage is higher than the overvoltage of the parasitic reaction.

These limiting cases are included in Figs. 2–4.

4. Discussion and conclusions

Using dimensionless variables, the combined effects of the technological parameters of the electrode (through m) and the parameters of the electrochemical reactions (through ϕ_1) can be studied.

The variable m, which is proportional to L, can be regarded as the dimensionless equivalent thickness of the electrode. Its definition (Equation 14) incorporates the effect of the specific surface area of the electrode and the effective conductivity of the electrolyte in the pores. De la Rue and Tobias [11] showed that k is a function of the specific conductivity of the electrolyte and the porosity of the packed bed.

The variable ϕ is a dimensionless form of voltage drop in the electrode, and its definition includes j_0 (the limiting current density of the useful reaction), η_0 (the electrode–electrolyte voltage difference required for achieving this limiting current density), and η (the local voltage differences). Especially, ϕ_1 is characteristic of η_1 (the 'decomposition voltage' of the parasitic reaction).

Both m and ϕ include α, the proportionality constant of the linearized rate equation (Equation 2).

Comparing the results for $\phi_1 \to \infty$ (no parasitic reaction) with those of the other cases, it is concluded that the performance of a packed-bed electrochemical reactor is very sensitive to the presence of a parasitic reaction. The adverse influence of the parasitic reaction becomes stronger with increased equivalent thickness of the electrode. Excess energy consumption is significant when a packed-bed electrode is used, even without parasitic reactions.

High values of ϕ_1 reduce energy consumption and increase current efficiency. This can be done by choosing an electrode material with high η_1, or by operating the cell at low current densities.

For practical uses, parasitic reactions should be avoided. According to the analysis in the preceding paragraphs, the equivalent thickness of the electrode should be small and limited to L_1 (in the dimensionless notation: $m \leqslant \phi_1$). Therefore, the electrode has to be thin, with a small specific surface area and with high porosity (for high solution conductivity).

Those conclusions contradict the main advantage of packed-bed electrodes; namely, high reaction rates due to high specific surface area. Thus, the expected gain in cell volume is offset by the excess energy consumption which is associated with the use of packed-bed electrodes. The selection of packed-bed electrodes for specific applications and their quantitative design must be based on the economical balance between the expected low investment and high operating costs.

Recently, two papers that treat similar problems of packed-bed electrolyses have been published [12, 13].

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