JOURNAL OF APPLIED ELECTROCHEMISTRY 11 (1981) 691–695

On the relative Coulombic effectiveness and profitability of electrolysis via intermittent current

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Received 29 December 1980

The current and energy utilization of intermittent current electrolysis is analysed, and feasibility regions in terms of product costs and profitability are discussed using the deposition of copper as an illustrative example.

Nomenclature

A	electrode area
b	geometric aspect ratio, W/L
c_0	bulk electrolyte concentration
C_E	Unit price or electricity, including generation of intermittent potential-drop train (MU J^{-1})
C_p	unit price of electrolysis product (MU kg^{-1})
D	electrolyte diffusivity
E	relative Coulombic effectiveness
F	Faraday's constant
h	chart recording heights (Fig. 1)
I	current
I_m	maximum allowable current in d.c. electrolysis
k	mass transfer coefficient
L	length of straight section in current response (Fig. 1)
MU	arbitrary monetary unit
m_e	electrochemical coefficient of product (kg C^{-1})
n	number of electrons involved in cathode reaction
N	number of cycles in intermittent potential train
P	unit profit (MU kg^{-1})
r	chart recording height ratio, or corresponding current ratio $h_1/h_2 = I_1/I_2$
S_I	root mean square of deviations about the fitted curve
t	time
V_c	magnitude of intermittent potential drop (V)
V_m	maximum allowable potential drop in d.c. electrolysis (V)
W	length of trapezoidal portion in response (c) (Fig. 1)
X	potential drop ratio V_c/V_m
Y	ratio of unit profits
Z_i	functions defined in Equation 9b (Z_1) and Equation 10b (Z_2)
γ	lumped parameter (Equation 4)
θ	chart response angle
τ	half-period of intermittent potential-drop train

1. Introduction

In some recent investigations of electrolysis via intermittent current (ICE) the analysis of current flow relative to d.c. current flow has received a good deal of attention, e.g., [1, 2]. Specifically, it was shown that under mass-transport control, any non-d.c. electrolysis (DCE) would have a maximum rate below that of d.c. electrolysis. Apart from this important finding, a number of questions arise with respect to the overall effectiveness of ICE, especially in the domain of mixed charge-transfer/mass-transfer control and simultaneous electrode reactions.

The purpose of this paper is to analyse the Coulombic effectiveness of ICE relative to DCE, on the basis of *experimental* current response to a finite-width, constant-potential pulse train of arbitrary frequency and pulse amplitude. Moreover, the profitability of ICE in terms of electricity and product costs is examined, and feasibility regions for ICE-oriented electrolytic processes are discussed.

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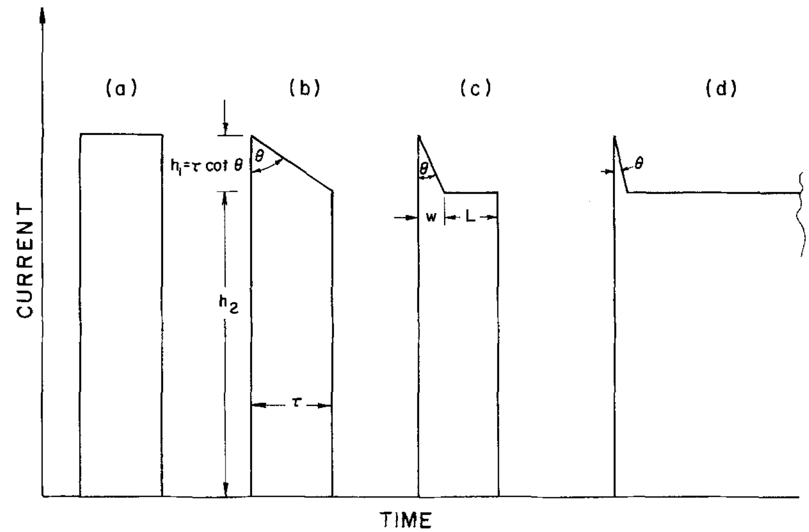

Fig. 1. Current responses to a rectified, finite-width, potential-drop train in steady state (only single cycles are shown). (a) Low voltage/high frequency; (b) high frequency; (c) low frequency; (d) d.c.

2. Results and discussion

Fig. 1 depicts typical current responses to a finite pulse width, constant-potential train imposed on two electrodes in an electrolytic cell. Responses (a) and (b) may be called type 1; response (c), type 2. The treatment of response (a) is trivial and will not be separately considered here. Response (d) is a general form of long-duration d.c. response where θ may reach 90° under certain conditions [degeneration to response (a)]. At low frequencies, the current response may be computed over a short time period from the outset of electrolysis by using the theoretical relationships

$$I = nFAc_0k_1 - \frac{2nFAc_0k_1^2}{(\pi D)^{1/2}}\, t^{1/2} \qquad (1)$$

in the case of kinetic control [3], and

$$I = \frac{nFAD^{1/2}c_0}{\pi^{1/2}} \frac{1}{t^{1/2}} \qquad (2)$$

in the case of diffusion control [4, 5]. Equation 2 does not include current flow due to hydronium-ion discharge at the cathode. At higher frequencies, theoretical analysis becomes rather cumbersome in as much as the input voltage train has to be represented by an appropriate Fourier expansion carrying an infinite series. The above equations can be applied, therefore, to response (c) in Fig. 1, as seen shortly below.

The relative Coulombic effectiveness E may be defined as the amount of electricity passed through the cell per cycle divided by the theoretical amount of electricity which would be passed, under steady-state conditions, during the same cycle period in d.c. electrolysis. One could also consider a number of cycles as basis.

2.1. *Type 1 response*

On the basis of the active half-cycle,

$$E_1 = \frac{h_1\tau/2 + h_2\tau}{(h_1 + h_2)\tau} = \frac{1 + r/2}{1 + r}. \qquad (3)$$

If N is the number of cycles considered in the wave train, then over a total time of $2N\tau$,

$$E_{1,N} = \frac{N(h_1\tau/2 + h_2\tau)}{2N\tau(h_1 + h_2)} = \frac{1}{2}E_1. \qquad (4)$$

The relative effectiveness is independent of θ and τ, and it depends only on the h_1/h_2 ratio (note that this ratio may be interpreted in terms of chart recording height as well as current flow).

2.2. *Type 2 response*

On the basis of the active half-cycle,

$$E_2 = \frac{h_1W/2 + h_2(W + L)}{(h_1 + h_2)(W + L)}$$

$$= \frac{\tan\theta + \frac{1}{2} r \tan\theta + L/h_1}{\tan\theta + r\tan\theta + (1/h_1 + 1/h_2) L}. \qquad (5)$$

Upon further algebraic manipulation, the much simpler expression

$$E_2 = \frac{1+\gamma r}{1+r}, \quad \gamma \equiv \frac{b}{2(1+b)}, \quad b = W/L \qquad (6)$$

is obtained, where b is the geometric aspect ratio of a type 2 response. The following limiting cases are of interest:

(a) $L \to 0$. Here $b \to \infty$, hence $\gamma \to \frac{1}{2}$ and $E_2 \to E_1$; a type 1 response is regained.

(b) $L \to \infty$. Here b and $\gamma \to 0$ and $E_2 \to 1/(1+r)$. This is the case of d.c. electrolysis [response (d) in Fig. 1]; the larger the value of θ the closer E_2 approximates to unity ($E_2 = 1$ when $\theta = \pi/2$). As expected, the relative Coulombic effectiveness is independent of θ in the limiting cases.

The effect of the aspect ratio on the variation of E with the ratio r is shown in Fig. 2. The relative effectiveness remains essentially unity up to $r \sim 0.01$, regardless of the numerical value of γ; however, as r increases E_2 will vary appreciably with γ.

If N cycles are taken as basis, a result similar to Equation 4 is obtained:

$$E_{2,N} = \frac{1}{2} E_2. \qquad (7)$$

3. Analysis of profitability for electrolysis with intermittent current

In a first approximation, relative profitability can be defined as the ratio of the difference between value of material produced and the cost of electricity expended in intermittent electrolysis, to the same difference in d.c. electrolysis during a reference time period. For a type 1 response,

$$Y_1 \equiv \frac{P_1}{P_2} = \frac{(\frac{1}{2} I_1 \tau + I_2 \tau)(C_p m_e - C_E V_c)}{2 I_m \tau (C_p m_e - C_E V_m)} \qquad (8)$$

or, by rearrangement,

$$Y_1 = \frac{1-(C_E V_m / C_p m_e) X}{1 - C_E V_m / C_p m_e} Z_1(X)$$

$$X \equiv \frac{V_c}{V_m} \qquad (9a)$$

where

$$Z_1(X) \equiv \frac{I_2}{2 I_m}\left(1 + \frac{r}{2}\right). \qquad (9b)$$

In the instance of a type 2 response, a similar derivation leads to the result

$$Y_2 = \frac{1-(C_E V_m / C_p m_e) X}{1 - C_E V_m / C_p m_e} Z_2(X) \qquad (10a)$$

$$Z_2(X) \equiv \frac{I_2}{2 I_m}(1 + \gamma r). \qquad (10b)$$

The $Z(X)$ functions have only positive values and

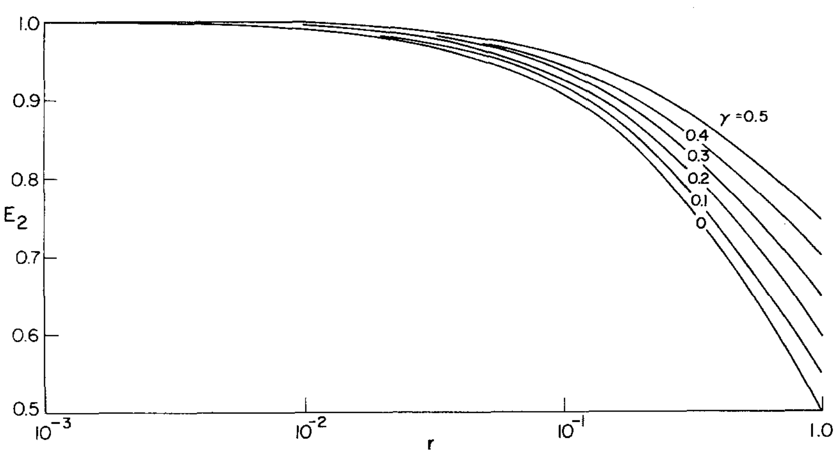

Fig. 2. The variation of relative Coulombic effectiveness with geometric parameters of the experimental current response of type 2.

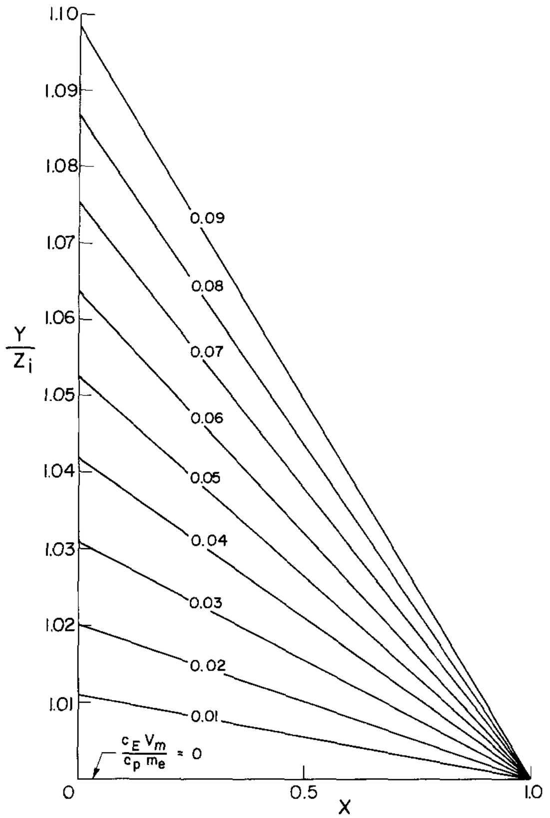

Fig. 3. Estimation chart for relative profitability of intermittent current electrolysis.

depend on the potential drop ratio. As shown in Fig. 3, the higher the electricity cost/product value ratio, the higher the numerical value of the relative profitability function, at a fixed potential-drop ratio, so long as $V_c < V_m$. If however, the electrode product is rather expensive and the unit cost of electricity is relatively low, the relative profitability will always equal the numerical value of $Z_i(X)$, $i = 1, 2$, regardless of the V_c/V_m ratio, and, depending on the cost factors and operation parameters, Y may be smaller or larger than unity.

4. An experimental example: electrolysis of copper

Fig. 4 illustrates the current response in an experimental cell [6] to a potential pulse of 2 V amplitude and 3 mHz frequency, obtained from a recorder chart (chart speed: 10 s cm^{-1}). The analysis of the initial current response indicates that both Equations 1 and 2 can be fitted to the experimental current–time variation with comparable statistical accuracy:

$$I = 320.176 - 7.2027\, t^{1/2} \qquad S_I = 5.96\,\text{mA}$$

$$I = 299.65 + 13.3757 \frac{1}{t^{1/2}} \qquad S_I = 5.08\,\text{mA}$$

over the first six seconds of response (t in seconds; I in milliamps). The ohmic contribution to the current, given the specific cell geometry and using an estimate [7] of the H^+-transference number, $t_{H^+} = 0.658$, is computed to be 248 mA, which is reasonably close to the second intercept. It appears that at the experimental pulse amplitude and frequency, the initial response is determined by a combined control of electrode kinetics and ionic diffusion; using the estimate [7] $D \cong 5.7 \times 10^{-6}\,\text{cm}^2\,\text{s}^{-1}$ for the electrolyte diffusivity, the apparent kinetic rate constant is calculated to be $k = 8.64 \times 10^{-4}\,\text{cm s}^{-1}$. Moreover, since the response is type 2 [response (c) in Fig. 1], the following numerical parameter values are calculated: $h_1 = I_1 = 34.43$ mA; $h_2 = I_2 = 282.47$ mA;

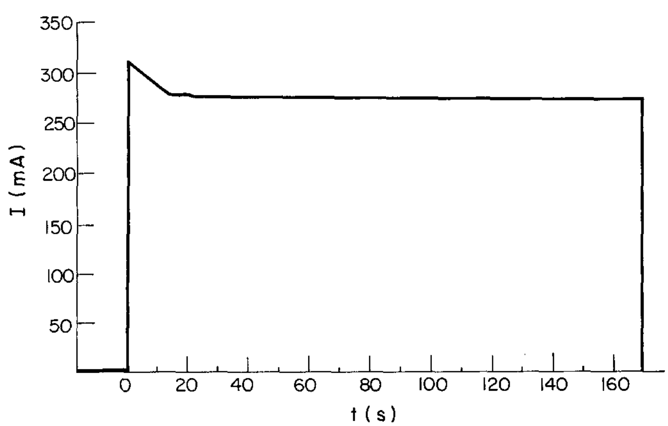

Fig. 4. A typical experimental current response to a rectified, finite-width, potential-drop train (single cycle). Electrolyte: 0.526 mol dm^{-3} $CuSO_4$ and 1.140 mol dm^{-3} H_2SO_4. Electrode area: 3.65 cm^2; electrode separation: 5.8 cm; pulse amplitude: 2 V; pulse frequency: 3 mHz.

$W = 13$ s; $L = 158$ s; $b = 0.0823$; $\gamma = 0.038$; $r = 0.1219$ and $E = 0.895$ (see also Fig. 2) Using $C_p = 270$ ¢ kg^{-1}; $C_E = 0.25$ ¢ J^{-1} [8, 9], and since $V_c = 2$; $V_m = 1.45$ [6]; $m_e = 0.3293$ kg C^{-1} and $I_m = 182$ mA [6], the numerical values $X = 1.38$, $Z_2 = 0.78$ and $Y_2 = 0.778$ can be computed.

While in this particular instance the numerical value of Y is below unity, in the case of noble metals one might typically have $V_c = 3$, $I_1 \cong 0.05$, $I_2 \cong 0.4$ and C_p may have the value of several thousands. Then $Z_i \cong Y_i$ and Y_i would vary from about 1.25 upwards. Thus intermittent current electrolysis may be more profitable than d.c. electrolysis under carefully chosen conditions, producing high-quality cathode deposits, specific electrochemical reaction products etc. at costs comparable to those associated with conventional d.c. electrolytic techniques.

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