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Approximate analytical design procedures for plug flow electrochemical reactors

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Approaches to the approximate design of plug flow electrochemical reactors are described. In one approach the local reactor voltage balance is combined with the associated material balance to give a single variable equation for the reactor residence time. Other approaches consider qualitatively situations when potentiostatic or galvanostatic conditions may be used as approximations to constant voltage operation.

Nomenclature

a	specific electrode area (m^{-1})
C_{AO}	initial concentration of a ($mol\,m^{-3}$)
C_j	concentration of species j ($mol\,m^{-3}$)
d	equivalent interelectrode spacing (m)
E_D	decomposition voltage (V)
E_{cell}	total cell voltage (V)
F	Faraday number
i_x	local current density ($A\,m^{-2}$)
i_T	total current density ($A\,m^{-2}$)
k	electrochemical rate constant ($m\,s^{-1}$)
$\bar{k}$	rate constant ratio $= k_2/k_1$
n	number of electrons
X_A	fractional conversion
β	$\alpha nF/RT$
κ	effective conductivity ($mho\,m^{-1}$)
η	overpotential (V)
τ	residence time (s)

Subscripts

a	anode
c	cathode

1. Introduction

The concept of plug flow, although idealized, is a convenient and often good representation of fluid mechanic behaviour in continuous electrochemical reactors based on parallel plate, annular and other electrode configurations. It is well known that such reactors operate with a fixed potential between the electrodes and that local current density and electrode potential are free to vary according to specific operating parameters used such as terminal voltage, flow rate, temperature, etc. In reactor design this condition constrains the approach in that, apart from the most simple of situations [1], there is no quick analytical procedure for predicting or assessing reactor performance. The general approach relies on the application of numerical procedures centred around the local voltage balance. Although this in principle does not present a real problem, the time involved can prove relatively expensive in manpower, where a quick, relatively accurate 'first order' design is all that is required. This paper describes methods which allow an analytical approach to the design of plug flow reactors or which, at least, considerably reduce the labour involved.

2. The plug flow reactor general design

A schematic model of the plug flow reactor (PFR) is shown in Fig. 1. With steady state operation and a fixed inlet concentration C_{AO} a mass balance for species A over an incremental length of the reactor can be written as

$$-\mathrm{d}C_A = \frac{ai_x}{nF}\,\mathrm{d}\tau \tag{1}$$

where τ is the residence time and a is the specific electrode area. The cell voltage in plug flow electrolytic reactors is spatially constant (assuming negligible electrode ohmic losses), with local current densities determined by the voltage balance and the current balance, if more than one electrode reaction occurs. The voltage balance for a PFR is written as

$$E_{cell} = E_D + \eta_a + |\eta_c| + i_x \sum \frac{d}{\kappa} \tag{2}$$

where η_a and η_c are the anodic and cathodic overpotentials, E_D is the decomposition potential and the last term is the sum of the ohmic voltage losses.

For high field Tafel-type kinetics the voltage balance [1] becomes (for single electrode reactions)

$$E_{cell} = E_D + \frac{1}{\beta_a}\ln\left(\frac{i_x}{n_a F k_a C_a}\right) + \frac{1}{\beta}\ln\left(\frac{i_x}{nFkC_A}\right) + i_x \sum \frac{d}{\kappa} \tag{3}$$

where $\beta = \alpha nF/RT$ and the subscript, a, refers to anodic terms assuming the main reaction to be cathodic.

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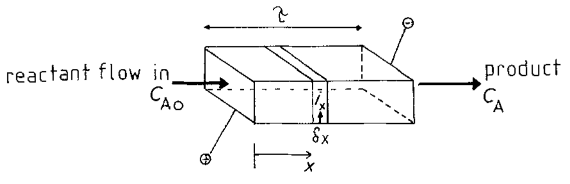

Fig. 1. Schematic view of the plug flow electrochemical reactor.

The PFR design is accomplished by subdividing the reactor into a small number of increments (see Fig. 1) in which a local current density, i_N, flows. In each increment the concentration of active species changes by an amount ΔC_N. By specifying suitably small changes in concentration we can determine local current density, i_N, from Equation 3 by iteration. This step requires prior knowledge of the variation of electrolyte conductivity with concentration. If gas evolving reactions occur, then the effect of gas bubbles on conductivity must also be incorporated [2]. Usually changes in concentrations of counter electrode reactants are considered negligible. For an overall specified change in reactant concentration we obtain a set of data of i_x as a function of C_A. This is then used to integrate Equation 1 and evaluate the residence time.

3. Approximate analytical procedure

The above design procedure is ideally suited to a computer solution, especially if multiple reactions occur and a number of iterative calculations are required. A considerable simplification to the design method is possible if ohmic voltage losses are relatively small in comparison to electrode potentials and if local current density variations are not large. In this case we assume that the ohmic voltage terms are constant and write Equation 3 as

$$E_{\text{cell}} - E_D - i_x \sum \frac{d}{\kappa} = E^*_{\text{cell}} = \frac{1}{\beta_a} \times \ln\left(\frac{i_x}{n_a F k_a C_a}\right) + \frac{1}{\beta_c} \ln\left(\frac{i_x}{nFKC_A}\right) \tag{4}$$

For a cathodic reaction and assuming C_a is constant this rearranges as

$$i_x^{(1/\beta_a + 1/\beta)} = \exp(E^*) C_A^{1/\beta} \tag{5}$$

where

$$E^*_{\text{cell}} + \frac{1}{\beta_a} \ln(n_a F k_a C_a) + \frac{1}{\beta} \ln(nFk) = E^*$$

Combining this with Equation 1 and integrating gives

$$C_A^{(-\beta/\beta_a)} - C_{AO}^{(-\beta/\beta_a)} = \beta a \tau \exp \frac{(\beta \beta_a E^*)}{(\beta_a + \beta)} \tag{6}$$

4. Example and extension of the approximate method

To illustrate the general treatment for multiple reactions consider a typical consecutive reaction sequence. The analysis ignores any side reactions other than those occurring at the counter electrode. These latter reactions are assumed to be concentration independent. Variations in electrolyte conductivity with position are, for simplicity, ignored.

The material balance equations for the following consecutive reaction

$$\mathrm{A} \xrightarrow{i_1} \mathrm{B} \xrightarrow{i_2} \mathrm{C}$$

are

$$\frac{dC_A}{d\tau} = -a \frac{i_1}{n_1 F} \tag{7}$$

$$\frac{dC_B}{d\tau} = a\left(\frac{i_1}{n_1 F} - \frac{i_2}{n_2 F}\right) \tag{8}$$

There is a twofold objective in this design: (i) to determine the required reactor size and associated current density distribution; (ii) to evaluate the product distribution, yield and current efficiency.

At this point two often quite reasonable assumptions are adopted to simplify the procedure and reduce the number of calculations. These are that mass transport is not rate limiting and that the coefficients β_1 and β_2 are equal [3]. With these assumptions the current density ratio $(i_1/i_2) = (n_1/n_2)(k_1/k_2) = 1/\bar{k}$ and the yield versus conversion (X_A) characteristics obtained from equations 10 and 11 are given by

$$\frac{C_B}{C_{AO}} = \frac{(1 - X_A) - (1 - X_A)^{\bar{k}}}{\bar{k} - 1} \tag{9}$$

A current balance can be written as

$$i_T = (n_1 F k_1 C_A + n_2 F k_2 C_B) \exp(\beta \eta) \tag{10}$$

Combining with Equation 9 gives

$$\frac{i_T \exp(-\beta\eta)}{n_1 F k_1 C_{AO}} = \frac{(1 - X_A)\left(\bar{k}\left(\frac{n_2}{n_1} + 1\right) - 1\right) - (1 - X_A)^{\bar{k}}}{\bar{k}} \tag{11}$$

A major aim in reactor design is to minimize energy consumption which is often achieved by minimizing cell internal resistance. Therefore the internal resistance is low compared to the electrode potentials, i.e. $E_{iR} \ll \eta_a + |\eta_c|$. If, in addition, the change in total current is not too great along the reactor then, as a first approximation, $i_T = i_{TO}$ and therefore the voltage balance [4] becomes

$$E^*_{\text{cell}} = \frac{1}{\beta_a} \ln\left(\frac{i_T}{n_a F k_a C_a}\right) + \frac{1}{\beta} \ln\left(\frac{i_T}{F(n_1 k_1 C_A + n_2 k_2 C_B)}\right) \tag{12}$$

Substituting in turn for electrode potential and total current in Equation 7 gives

$$\frac{-dC_A}{d\tau} = P_1 C_A (n_1 k_1 C_A + n_2 k_2 C_B)^{(-\beta/\beta_a/(1+\beta/\beta_a))} \tag{13}$$

where

$$P_1 = ak_1F^{(-\beta/\beta_a/(1+\beta/\beta_a))}$$

$$\times \{(n_aFk_aC_a)^{\beta/\beta_a} \exp(\beta^*E_{cell})\}^{(1/1+(\beta/\beta_a))}$$

Substituting Equation 9 in Equation 13 gives

$$\frac{dX_A}{d\tau} = P_2(1 - X_A)\left[(1 - X_A)\left(-\bar{k}\left(\frac{n_2}{n_1} + 1\right) + 1\right) + \frac{n_2}{n_1}\bar{k}(1 - X_A)^{\bar{k}}\right]^{(-\beta/\beta_a/1+(\beta/\beta_a))} \quad (14)$$

where

$$P_2 = P_1\left[\frac{n_1k_1C_{AO}}{(1-\bar{k})}\right]^{(-\beta/\beta_a/1+(\beta/\beta_a))}$$

For specified values of β/β_a, this on integration gives the fractional conversion as a function of residence time. Equations 9 and 10 enable the yield of B, total current and current efficiency to be determined.

4.1. *Numerical example*

Estimation of residence time and conversion under conditions of maximum yield of intermediate: the rates of reaction are given by the following expressions

$$i_1/2F = 3 \times 10^{-15} \exp(10E)C_A$$

$$i_2/2F = 1 \times 10^{-15} \exp(10E)C_B$$

The reactor has an interelectrode gap of 2.5 mm, a specific area of 8000 m^{-1} and operates at a voltage of 4 V and at a nominal current density of 2000 A m^{-2}. The anodic counter electrode reaction has the following kinetics

$$\frac{i_a}{F} = 10^{-9}\exp(10E)$$

The specific conductivity of the electrolyte is 40 mho m^{-1}. The initial concentration of A = 1000 mol m^{-3}.

4.2. *Solution*

The conversion at which the maximum yield on B is obtained from Equation 9 is given by

$$X_A = 1 - (\bar{k})^{(1/(1-\bar{k}))} = 1 - (\tfrac{1}{3})^{1/(1-1/3)} = 0.80755 \quad (15)$$

Combining Equations 9 and 15 gives the yield as

$$\left(\frac{C_B}{C_{AO}}\right)_{max} = \left(\frac{1}{\bar{k}}\right)^{(1/\bar{k}-1)}$$

Hence

$$\left(\frac{C_B}{C_{AO}}\right)_{max} = (\tfrac{1}{3})^{(1/(3-1))} = 0.5773$$

The voltage contribution from the cell internal resistance is

$$E_{IR} \simeq 2000\frac{2.5 \times 10^{-3}}{40}$$

$$\simeq 0.125\,V$$

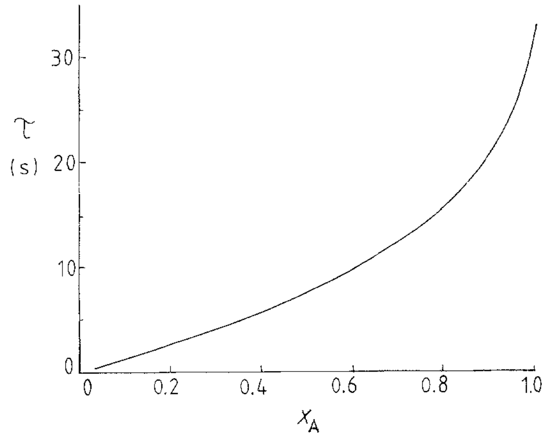

Fig. 2. Variation of residence time with conversion for the given numerical example.

Therefore

$$E^*_{cell} \simeq 4.0 - 0.125 = 3.875\,V.$$

The initial current density is estimated from

$$i^2_{To} = (F \times 10^{-9})F(2 \times 3 \times 10^{-15} \times 10^3) \times \exp(10 \times 3.875)$$

Hence $i_{To} = 2011.5\,A\,m^{-2}$.

In Equation 14 the parameter P_2 is

$$P_2 = 8000 \times 3 \times 10^{-14}F[10^{-8}\exp(10 \times 3.875)]^{1/2} \times F^{-1/2}\left[\frac{2 \times 3 \times 10^{-14} \times 1000}{(1 - 1/3)}\right]^{-1/2}$$

$$= 0.0657$$

The conversion residence time behaviour is therefore obtained from

$$\frac{dX_A}{d\tau} = 0.0657(1 - X_A)(1 - X_A) \times [(1 - \tfrac{1}{3}(1 + 1) + \tfrac{1}{3}(1 - X_A)^{1/3}]^{-1/2} \quad (17)$$

Letting $y = C_A/C_{AO} = 1 - X_A$ this equation can be written as

$$\tau = 8.79\int[y^{-1} + y^{-5/3}]^{1/2}\,dy \quad (18)$$

This integration is numerically straightforward and when performed shows the variation of conversion with residence time (Fig. 2).

Figure 2 shows that after a conversion of some 50% the required reactor residence time starts to rise rapidly due to the fact that greater amounts of current are used to convert B to C. The required residence time to achieve maximum yield conditions is 16.1 s.

In principle the reactor design continues by estimating the current density distribution from Equation 21 which also enables energy consumption to be obtained. At low conversions when $C_B \simeq C_{AO}X_A$ the total current density is given approximately by

$$i_T \propto \left(1 - \frac{2X_A}{3}\right)^{1/2} \quad (19)$$

Up to a conversion of some 50% the current density falls approximately by a factor of 0.81 and thus near galvanostatic conditions exist.

Compare the residence time obtained above to that required for galvanostatic operation by combining Equations 7 and 8 in the form

$$\tau = \frac{FC_{\mathrm{AO}}}{ai_{\mathrm{T}}}((n_1 + n_2)X_{\mathrm{A}} - n_2 C_{\mathrm{B}}/C_{\mathrm{AO}}) \quad (20)$$

Under maximum yield conditions

$$\tau = \frac{96500 \times 10^3(4 \times 0.80755 - 2 \times 0.5773)}{8000 i_{\mathrm{T}}} = \frac{2.50 \times 10^4}{i_{\mathrm{T}}}\,\mathrm{s}$$

Now the current density at the reactor exit under constant voltage operation is 1240.0 A m^{-2}. Taking a mean current density of 1620 A m^{-2} for galvanostatic operation gives a residence time $\tau = 15.55$ s which is in reasonable agreement to the 'exact' value of 16.1 s. The next section therefore, considers when this may be a useful approximation to the exact constant voltage operation.

5. Approximate operating condition for the PFR

The previous numerical example has indicated that, under appropriate conditions, the current supplied to the reactor may be approximated by a galvanostatic mode of operation. If this is the case, then design procedures can be greatly simplified in comparison to a 'constant voltage' mode and indeed more so if a potentiostatic approximation can be adopted. Firstly, however, the conditions at which either galvanostatic or potentiostatic operation is a reasonable approximation to actual operation must be decided upon, albeit from a qualitative view.

During a potentiostatic electrolysis, current generally falls with conversion. With a PFR, if effective electrolyte conductivity decreases with reactor length, then this will cause a decrease in current and go some way to meeting this requirement. Now the interconversion of reacting species and the use of supporting electrolytes means electrolyte conductivity remains almost constant. The generation of gases at either anode or cathode will decrease effective conductivity due to the bubble effect. Therefore, reactors in which the counter electrode reaction is a gas evolving reaction, itself quite a common situation, will tend to approach the requirement for approximate potentiostatic control.

Conversely to approach a galvanostatic condition, effective electrolyte conductivity should not decrease with conversion and, in principle, should increase, to offset the rise in electrode potential generally associated with galvanostatic operation. Thus reactors where gas evolution is small will tend to approximate this condition. The rise in electrolyte temperature with conversion, associated with most electrolytic reactors, which generally increases conductivity may be beneficial. Alternatively, reactors with diaphragms in which anolyte and catholyte flow counter-currently, or are in cross flow [5], may also approach galvanostatic conditions, especially if a gas evolution reaction is involved.

Overall the adoption and applicability of either of the above approximations should be checked with reference to a 'voltage balance' applied at the end conditions of the reactor. That is, the calculated voltage at the reactor inlet and exit should be in reasonable correspondence.

6. Conclusions

This paper shows that the design methods for plug flow electrochemical reactors can be greatly simplified by adopting approximations which correspond to a number of practical situations. Notably the desirable situation of a low internal ohmic voltage is one situation when the design can be accomplished using analytical equations.

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