B. Electrochem 4(5) May 1988, pp 475-479



# MODELLING AND SIMULATION OF ELECTROCHEMICAL PROCESSES

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[Received: 1987 July; Accepted: 1988 March]

Conventional reaction engineering technique may be applied to electrolytic process with emphasis on residence time distribution (RTD) method.

**Key words: Modelling and simulation, residence time distribution model, reactor model**

## INTRODUCTION

Mathematical modelling and simulation is a recognised technique in many process design, evaluation and control. The extent to which modelling is used varies throughout the process industries. Electrolytic reactors are in no way more difficult to model than the conventional chemical reactors. The main problem in the application of reaction engineering technique to electrochemical processes is that the kinetic data are in the form of polarization curves; reaction mechanism involves intermediates and current distribution may be nonuniform.

An attempt is made as to how conventional reaction engineering technique may be applied to an electrolytic process with emphasis on residence time distribution (RTD) method [1].

### Residence Time Distribution (RTD) function

The structure of the mathematical model for any process (either chemical or electrochemical) involving fluid flow is affected by the flow pattern prevailing in the system and is reflected in the RTD of fluid elements in their passage. The system may be an electrochemical flow cell. This distribution obeys statistical laws and can be ascertained from the form of a test signal passing through the system. A test signal may be simulated by injecting an amount of a tracer into the feed stream as a step input or as an impulse or a sine wave.

With a tracer injected instantaneously, its concentration is observed at the outlet of the system for series of interval, and these data are plotted to give a C - diagram. This is the RTD based on an impulse stimulus and can be defined as

$$C = \int_0^\infty t\, E(t)\, dt \qquad \ldots(1)$$

The RTD function E(t) gives the fraction of the tracer in exit stream of the reactor that has spent a time less than t within the reactor.

The average residence time $\tau$ is given by

$$\tau = \frac{\int_0^\infty t\, E(t)\, dt}{\int_0^\infty E(t)\, dt} \simeq \frac{\Sigma tC}{\Sigma C} \qquad \ldots(2)$$

The residence time distribution function may be written as

$$E(t) = \frac{C(t)}{t\, C_o} = \frac{C}{\Sigma\, C \Delta t} \qquad (3)$$

Where $\Delta t$ is the sampling interval. Once average residence time is known, the C - diagram may be described by an equation of the form

$$C = \frac{C(t)}{C_o} = t\, E(t) \qquad \ldots(4)$$

where $C_o$ is the initial concentration at the inlet of the system.

The spread or variance of a given variable about its means in the case of sample from a continuous distribution for a definite number of equidistance points, (equal sampling intervals) is given by

$$s_t^2 = \frac{\Sigma x^2_i\, f(x_i)}{\Sigma\, f(x_i)} - \frac{\Sigma\, x_i f(x_i)}{\Sigma\, f\,(x_i)} \qquad \ldots(5)$$

For variance in time units ( $S_t^2$)

$$\Sigma\, f\,(x_i) = \Sigma\, C_i$$

$$\Sigma\, x_i\, f\,(x_i) = \Sigma\, t_i\, C_i$$

$$\Sigma\, x_i^2\, f\,(x_i) = \Sigma\, t_i^2\, C_i$$

$$s_t^2 = \frac{\Sigma\, t_i^2\, C_i}{\Sigma\, C_i} - \left[\frac{\Sigma\, t_i\, C_i}{\Sigma\, C_i}\right]^2 \qquad \ldots(6)$$

The function E(t) gives the fraction of material in the reactor exit stream which has spent a time between t and t + dt within the reactor, multiplying by it by the concentration of material, $C_A$ that has been in the fluid element of the age t + dt gives the average concentration $C_A$ of the material leaving the reactor

$$C_A = \int_0^\infty C_A\, E(t)\, dt \qquad \ldots(7)$$

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The determination of residence times for fluid element from the above equation is based on the concept of statistical moments and probability density function. The zeroth moment of a probability density function is unity. The first moment is the expectation or mean value of the ensemble which gives a measure of location of the centre of the distribution. The second moment is variance which gives a measure of the spread of the distribution. The third moment is a measure of the symmetry or skewness of the distribution with respect to mean. The fourth moment characterises the sharpness of the peak about the mode. Theoretically, the moments are calculated in the range of zero to infinity. For a continuous distribution they have the form:

$$M_o = \int_0^\infty E(t)\,dt$$

$$M_1 = \frac{\int_0^\infty t\,E(t)\,dt}{\int_0^\infty E(t)\,dt}$$

$$M_m = \frac{\int_0^\infty t^m E(t)}{\int_0^\infty E(t)\,dt} \qquad \text{....(8)}$$

Since experimental distribution curves are step . wise approximated, it is assumed that the resultant distribution is discrete, and the expressions for the respective moments are as follows:

$$M_o = \sum_{i=1}^{n} C_i \Delta t$$

$$M_1 = \frac{\sum_{i=1}^{n} C_i t}{\sum_{i=1}^{n}}$$

$$M_m = \frac{\sum_{i=1}^{n} C_i\, t_i^m}{\sum_{i=1}^{n} C_i} \qquad \text{.. (9)}$$

If the experimental C - diagram nas an extended tail, Eq. (9) lacks in accuracy. A more accurate method for estimation of distribution parameter is given below. It is based on the use of average ordinates of the C - diagram with the limit of integration specified in advance. The procedure is as follows:

1. The moment for the experimental C - curve are found by the trapezoidal rule.

Then for the zeroth moment

$$M_0^E = \int_0^a C\,dt \simeq \sum_{i=1}^{n} C_{av,i}\,\Delta t$$

where $C_{av,i} = (C_{i+i} + C_i)/2$ is the average of the ordinate diagram in the interval 0 to a.

For any moment then

$$M_J^E = \frac{\int_0^a t^j\,C\,dt}{\int_0^a C\,dt} = \frac{\int_0^a \frac{C}{(j+1)}\,dt^{j+1}}{\int_0^a C\,dt}$$

$$= \frac{\sum_{i=1}^{n} \left(\frac{C_{av,i}}{j+1}\right) \Delta (t^{j+1})}{\sum_{i=1}^{n} C_{av,i}\,\Delta t}$$

$$= \frac{\sum_{i=1}^{n} \frac{C_{av,i}}{j+1} \left(t_{i+1}^{j+1} - t_i^{j+1}\right)}{\sum_{i=1}^{n} C_{av,i}\,(t_{i+1} - t_i)} \qquad \text{...(11)}$$

with the interval chosen to be $\Delta t < 0.02\,(t/\tau)$, the estimation of distribution parameters from, eq. (11) yields results practically the same as the exact expressions i.e. Eq. (8).

2. Moments are then found for models with the limit of integration from 0 to a and not from 0 to $\infty$, as is usually done, and a system of equations of the form:

$$M_1^E = M_1^M$$

$$M_2^E = M_2^M$$

$$M_j^E = M_j^M \qquad \text{... (12)}$$

$$M_n^E = M_m^M$$

is solved where the moment

$$M_j^M = \int_0^a t^j\,C\,dt \;/\; \int_0^a C\,dt \qquad \text{...(13)}$$

is found from a model.

The choice of the break point on the curve, t = a, depends on the conditions of measurement (th accuracy and sensitivity of elements) because the experimental curve is used to estimate the correctness of the model itself. The number of equations in the system equation (12) depends on the number of model parameters. For some models, such as cascade type or a tank with a stagnant zone, $M_j^M$ can be expressed analytically. In cases where this cannot be done because of complexity of analytical solution for equation of the model, $M_j^M$ should be found by directly integrating the model equations.

**Reaction environment and transfer function**

A knowledge of the reaction environment [2] in different electrolytic cells is important in the selection of the most appropriate cell

depending on the required contacting pattern and mode of operation to get high selectivity and useful current density. It is provided by RTD studies using tracer technique. The marker pulse technique is an analogue of the dye-injection technique of conventional chemical reaction engineering [3] with added advantage that the marker species may be generated at the electrode and therefore exactly experiences the same environment as the intermediate in the real reaction. This is not possible with dyes. For example, with well injection the momentum of the jet electrodes breaks through the sublayer so that the stream lines closest to the wall cannot be marked. The technique has been used successfully in parallel channel [4], battery model [5], packed bed [6], fluidized bed [7], trickle bed [8], disc stack cell [9], cell with differentially or co-rotating disc electrode [8,4] and cells consisting of fixing or moving coaxial cylinders. A pulse of current injects marker ions into the stream, and their direct arrival is detected by a pair of electrodes maintained at the potential of the limiting current; the current in the detector circuit is then a measure of distribution of marker concentration in time, which reflects residence time.

Delta function, step function or any wave form (like sine wave) can be used. When a tracer material is injected into the reactor under study as a pure sine wave at a particular frequency, the response is like a pure sine wave of the frequency and differs from the input stimulus only in magnitude and phase as dictated by the behaviour of the reactor. The resultant curve is called a frequency response. The frequency response is usually interpreted in the frequency rather than the time domain through the Laplace transform method. The ratio of the Laplace transform of an output time function to the Laplace transform of the respective input time function gives the transfer function of a system. From the transfer function developed for a wide range of frequencies, one can readily plot a frequency response diagram which can then be compared with that of the known frequency responses for standard reactor models. The transfer function of standard reactor models are summarized in Table I.

TABLE-I: Transfer function of standard idealized model

| Standard model | Transfer function |
|---|---|
| 1. Continuous stirred tank reactor (CSTR) | $\frac{1}{sT_1 + 1}$ |
| 2. Plug flow reactor (PFR) | $e^{-sTd}$ |
| 3. m equal-size CSTR in series | $\frac{1}{(sT_1 + 1)^n_m}$ |
| 4. m unequal-size CSTR in series | $\frac{1}{(sT_1 + 1)(sT_2 + 1) \ldots (sT_m + 1)}$ |
| 5. PFR and CSTR in series | $\frac{e^{-s_{Td}}}{(sT_1 + 1)}$ |

Remarks

$T_1 = \frac{V}{q}$, where V is the reactor volume, q is the fluid space velocity

$T_d = \frac{L}{U}$ where L is the length of reactor, U is the superficial velocity

$T_m = \frac{V_m}{q}$ and $s$ is the Laplace operator.

**Reaction model**

For developing a transfer function of a continuous stirred tank electrochemical reactor (CSTER), consider the reaction

$$A \xrightarrow{ne} B$$

Although the electrode reactions vary in their complexity, it can be represented by the diagram in Fig. 1, in which the reactant A is transported from the bulk electrolyte to the electrode surface where it undergoes reaction via a number of reactive intermediates to product B. Then, B is transported back to the bulk. Assuming that the reaction is of the "Tafel" type, the rate of reaction will be given by

$$-r_A = -\frac{1}{S}\frac{dN_A}{dt} = \frac{i_A}{nF} \qquad (14)$$

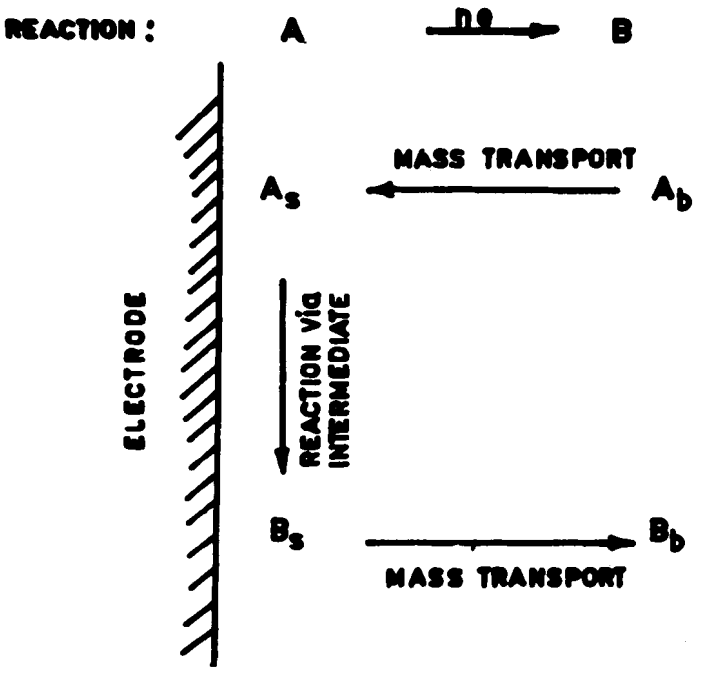


*Fig.1: Mass transfer and reaction at an electrode*

Further

$$\frac{i_A}{nF} = -k_h C_{A_s} e^{-bE} \quad \ldots(15)$$

$$\frac{i_A}{nF} = k_L (C_{Ab} - C_{AS}) \quad \ldots(16)$$

where $N_A$ is the number of moles of A transported to the electrode surface for reaction, t time, $i_A$ current density, S the electrode surface, $k_L$ the mass transfer coefficient, $k_h$ electrochemical rate constant, $C_A$ the concentration reactant A and b,s the subscript Elimination of $C_{As}$ from eqs. (15) and (16) leads to

$$\frac{i_A}{nF} = \frac{C_{Ab}}{\left(\frac{1}{k_L} + \frac{1}{k_h e^{-bE}}\right)} = kC_{Ab} \quad \ldots(17)$$

where

$$\frac{1}{k} = \frac{1}{k_L} + \frac{1}{k_h e^{-\beta E}}$$

and k is over all mass conversion constant.

For hydrogen evolution

$$i_H = 2Fk_H e^{-aE} \quad \ldots(18)$$

where $k_H$ and a are polarization constants for hydrogen evolution.

Then

$$i = i_A + i_H$$

$$= \frac{C_{Ab}}{\frac{1}{nFk_L} + \frac{1}{nFk_h e^{-\beta E}}} + 2Fk_H e^{-aE} \quad \ldots(19)$$

and the current efficiency, C, for the primary reaction will be

$$C = \frac{i_A}{i} \quad \ldots(20)$$

The current distribution is assumed to be uniform in the cell. The following procedure is used in the simulation.

(1) The cell operates at a fixed current and flow condition so that i and $k_L$ are known.

(2) Using eq.(19), E is found, which requires a numerical technique.

(3) The value for E obtained is then used in (17) to calculate $i_A$

(4) Knowing i and $i_A$, C is calculated

(5) Vary i and repeat the procedure 2 to 4

(6) Vary $k_L$ and repeat the procedure 2 to 5.The results are shown in Table II.

TABLE-II: Variation of current density and current efficiency on mass transfer coefficient

Reaction $A \xrightarrow{ne} B$, $\quad 2H^+ \xrightarrow{2e} H_2$

$2Fk = 10$, $2Fk_H = 0.1$, $1,a = 19V^{-1}$
$[A]_b = 1$ kmol/m$^3$

| i kA.m$^{-2}$ | Current efficiency (%) $k_L \times 10^{+3}$ cm.sec$^{-1}$ | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| 2.0 | 87 | 98 | 99 | 99 |
| 4.0 | 47 | 88 | 98 | 99 |
| 6.0 | 32 | 64 | 86 | 95 |
| 8.0 | 25 | 49 | 70 | 86 |
| 10.0 | 19 | 39 | 59 | 80 |

**Reactor model**

In case of CSTER, other quantities involved will be designated as follows: the volumetric flow rate or space velocity q; the reactor volume hold up V, the composition of A in the feed $C_i$, the composition of A in the exit stream as $C_o$ which is same as $C_A$ - the bulk concentration of A in reactor. Material balance gives:

$$q C_i - q C_o - k S C_o = V\frac{d C_o}{dt} \quad \ldots(21)$$

The Laplace transform of Eq. (21) gives:

$$q C_i(s) - q C_o(s) - k S C_o(s) = VsC_o$$

where s is the Laplace operator.

Dividing the output by the input, the resulting equation is

$$\frac{C_o(s)}{C_i(s)} = \frac{q/v}{(q/v) + k(s/v) + s} \quad \ldots(22)$$

on putting $V/q = T$, the space time and
$S/V = a$, the specific electrode area,

$$\frac{C_o(s)}{C_i(s)} = \frac{1}{sT + kaT + 1} \qquad \ldots(23)$$

The above expression describes changes in the state of the system with time, i.e. its transient response. Since $C_o/C_i$ measured under steady state condition under which s approaches zero, expression (23) may be reduced to the following form.

$$\frac{C_o(o)}{C_i(o)} = \frac{1}{kaT + 1} \qquad \ldots(24)$$

## CONCLUSION

From a comparison of Eq. (24) with transfer function of a CSTR (see Table I) it is readily seen that reactor model for an electrochemical reaction under steady state condition can be derived from transfer function by replacing s with k. This offers means of evaluating the kinetics of a process from its frequency response where there is steady state prevailing at the electrode surface, i.e. the rate of transport of reactant to the surface is equal to its rate of reaction.

The RTD model equations presented should provide a useful starting point for electrochemical reaction modelling which can be readily expanded and modified to incorporate more complex reaction schemes or more accurate reaction kinetics.

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