

Conversion Expressions for Electrochemical Reactors which Operate under Mass Transport Controlled Reaction Conditions, Part I: Batch Reactor, PFR and CSTR*

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Electrochemical reactors have become an established unit process for synthesis of materials and pollution control applications. Such reactors are often operated under mass transport controlled reaction conditions in order to maximise their productivity in which flow conditions in the reactor play a dominant role. We have developed a series of graphical plots that allow reactor performance to be quantified in terms of the reactant conversion for the cases of the idealised batch reactor and flow-through reactors in the single pass mode. Such plots avoid the need to integrate the material balance equations and provide useful working curves for those involved in the selection and design of electrochemical reactors, both in the laboratory and in industry.

SUMMARY OF EDUCATIONAL ASPECTS OF THE PAPER

1. This paper describes a new training tool in electrochemical engineering and the performance of electrochemical reactors.
2. The new approach is useful to the following courses: electrochemical engineering courses on electrochemical technology, reactor design and mass transfer, particularly in the areas of environmental treatment and clean synthesis.
3. The level of students involved in the use of the material has ranged from first and second year undergraduate chemistry and chemical engineering students through to Masters and Doctoral graduate programmes. The material has been given to a number of short courses in universities, industry and conferences in the subject areas of environmental treatment and clean processing.
4. What aspects of the contribution are new? Many students find it difficult to appreciate the fundamental principles of electrochemical reactor design and performance via traditional numerical calculations associated with the reactor design equations. Graphical presentation of conversion data, in the form of working curves, provides an immediate and attractive teaching aid that can be used as a live display on a PC

- microcomputer. Students can introduce data from laboratory experiments (or from industrial pilot plants) into a spreadsheet to compare their results with theoretical predictions of maximum reactor performance.
5. The material has been presented to many undergraduate, postgraduate and short courses in electrochemical technology. Feedback has been positive and students have appreciated the simple, graphical approach that avoids tedious calculations of maximum conversion in electrochemical reactors operating under complete mass transport controlled conditions.
6. Comments on the benefits for engineering education: these have included the ease of calculations on a simple, low-cost PC microcomputer running a short, QBASIC programme and the attraction of superimposing student results on a theoretical family of working curves. The generation of a family of conversion curves allows students to appreciate the envelope of possible reactor performance (and leads naturally to a discussion of modified reactor geometry and costs).

INTRODUCTION

ELECTROCHEMICAL ENGINEERING is a multi-disciplinary subject that concerns the design, characterisation and operation of electrochemical

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reactors and processes [1]. Electrochemical reactors are used for a wide range of applications, ranging from analytical determinations up to full-scale synthesis and environmental treatment [2]. Both in the laboratory and in industry, the electrochemical reactor is a key component of an electrochemical process and special attention must be taken in its design to achieve a high conversion rate of reactant to product as well as a high current efficiency for the desired reaction. In view of the diverse applications of electrochemistry, a wide range of different electrochemical reactor designs is possible, ranging from traditional plate-in-tank configurations up to more sophisticated designs using, for example, modern filter-press cells [3], porous three-dimensional [4], or rotating [5] electrodes. Extended reviews of electrochemical reactors are available in the literature [6, 7] and many text books on electrochemical engineering have recently appeared [6–12] demonstrating the continuous development of the subject, particularly in the areas of electrosynthesis [10–14] and environmental treatment [15–17].

Figure 1 shows an example of a filter-press type of electrochemical reactor [3], which consists of plate electrodes separated by insulating gaskets or spacers. The electrolyte to be treated is pumped between the electrodes where turbulence promoters or three-dimensional electrodes may be used to improve rates of mass transport of reactant to, and products from, the electrode surface. Amongst the important variables in the operation of a electrochemical reactor (flow rate, electrical connection, etc.), the electrode potential is a key parameter, since reactant conversion, selectivity and current efficiency depend directly of this parameter [1–2].

The material in this paper has been used in a number of courses, including: (i) an electrochemical engineering module to final year BSc Chemical Technology undergraduates at the

University of Strathclyde, (ii) an industrial chemistry module to final year BSc Applied Chemistry undergraduates at the University of Portsmouth, and (iii) various workshops at international symposia and short courses on electrochemical engineering. Students who have benefited from the material have ranged from chemical, materials, and mechanical engineers through to chemists and materials scientists. The teaching of conversion data in electrochemical reactors has proved to be important in early stages of PhD training for postgraduates pursuing research on the characterisation of electrochemical reactors. The material can be themed to suit the background and perspectives of the student. For example, environmental science and engineering students can consider the removal of toxic metal ion reactants, while chemical synthesis students find it more useful to work with the production of, for example, a pharmaceutical product from an organic precursor. Parts of the material have been presented in traditional lecture form (particularly to chemical engineering students). It is more common, however, to illustrate the conversion expressions by showing slides and videos of large-scale electrochemical reactors in industrial environments [1, 2] and to use workshop sessions to provide student confidence in the application of the conversion expressions to a particular industrial problem.

If the current through an electrode is recorded as a function of electrode potential (with respect to a reference electrode), current vs. electrode potential curves such as those presented in Fig. 2 can be achieved. In the general case, three zones can be observed [2, 12]. The first zone is characterised because the use of a larger overpotential leads to an increase in the current; this region is known as the charge transfer controlled zone because the rate of the process depends on the rate of electron

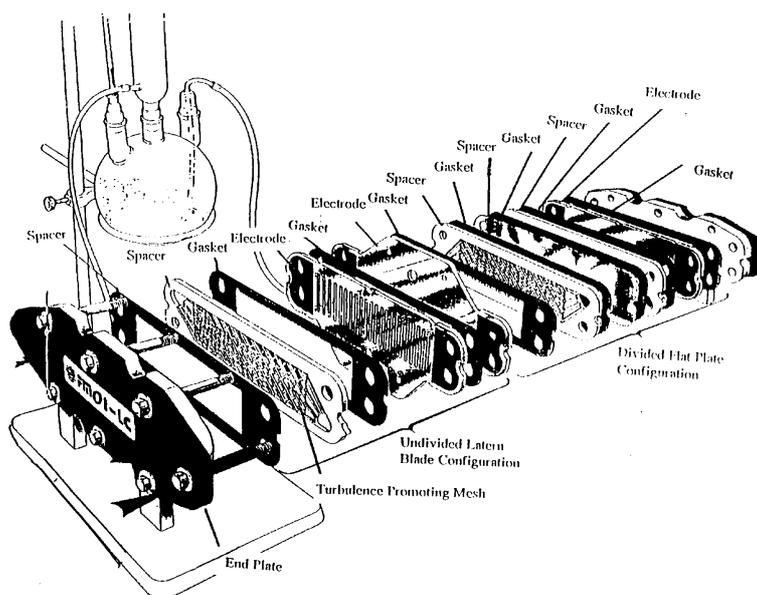


Fig. 1. An electrochemical filter-press reactor showing divided and undivided arrangements.

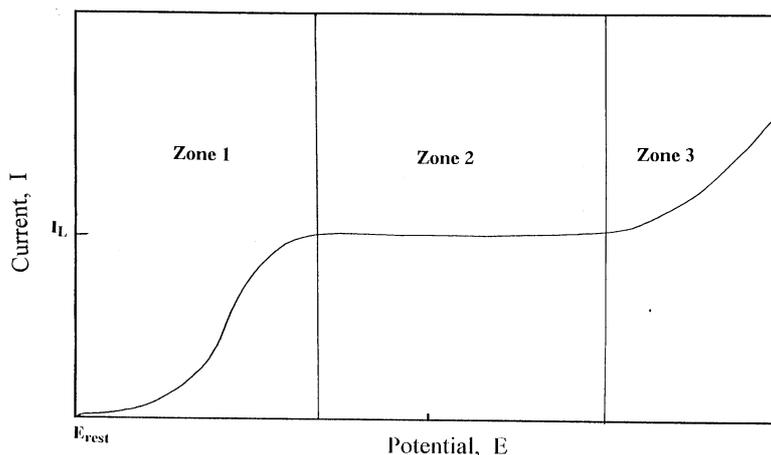


Fig. 2. A typical current versus overpotential curve for the single electrode process $O + ze^- \rightarrow R$, showing three zones of reaction rate control. Zone I: charge transfer control; Zone II: mass transport control; Zone III: a secondary reaction.

transfer. This zone extends until the overpotential is so large that the reaction rate over the electrodes is very rapid and is only dependent on the rate at which the reactant reaches the electrode, this being known as the mass transport controlled region. If the overpotential (η) is very high, an increase in the current is observed due to electrolysis of the supporting electrolyte. Three contributions to the mass transport are normally found due to diffusion, convection, and migration. Diffusion is the movement of species due to a concentration gradient in the solution and convection is the movement of species due to mechanical forces. Natural convection results if the forces are caused by localised temperature fluctuations and changes of density, whereas forced convection ensues if the solution is moved by external forces, such as electrolyte pumping or electrode movement.

In the case of migration, the movement of electrical charges is due to a potential gradient and this phenomenon is responsible for the passage of ionic current through the electrolyte. In many cases forced convection is the predominant factor due to the need to achieve high production rates, especially when treating dilute reactants. In practice, it is common to use a large concentration of a conductive background electrolyte and apply forced convection agitation; the conditions are then referred to as 'forced-convection'.

Electrochemical reactions are heterogeneous redox processes that occur via the transfer of charge across the interface between an electrode and an electrolyte [12]. A large range of important electrochemical reactions and industrial applications arises in chemical synthesis, pollution control, energy storage and monitoring of pollutants [1, 2, 12–17].

THEORY

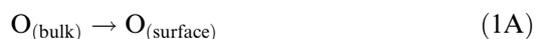
Many electrochemical reactors operate under limiting current conditions when the overall rate

of reaction is restricted by the rate of convective-diffusion of species towards the electrode surface. This mode of operation is found when the overpotential at the electrode is high and the rate of the process then depends on the rate of which the reactant reaches the electrode. The interconversion of an oxidised (O) and reduced (R) species of a redox couple O/R:



can be considered. The cathodic reaction may be considered to take place via a three-step mechanism [2, 12, 18]:

Mass transport of reactant towards the electrode:



Electron (or charge) transfer at the surface:



Mass transport of product away



For the case of the electrochemical reaction (1), in which the overpotential is sufficiently high, the rate of reaction becomes dependent only on the rate at which the reactant is supplied to the electrode. The limiting current conditions have then been achieved. In this case the process becomes completely mass transport controlled, i.e., reaction (1A) becomes the rate controlling step, and the production rate becomes highly dependent of the fluid flow conditions in the reactor [12].

Two types of ideal fluid flow through a reactor are commonly considered, namely, plug flow and perfect mixing. In the first case, it is assumed that the fluid flow is continuous through the reactor with no mixing of the electrolyte in the direction of the flow between inlet and outlet. The reactant and product concentrations are both functions of the distance but they are independent of time. As a result, the residence time must be equal for all species in the reactor. A

reactor with such properties is called a plug flow (or piston flow) reactor (PFR). Many practical reactors approximate well to PFR behaviour, including designs based on parallel plate and three-dimensional electrode cells [1–4, 9].

The most common example of a perfectly mixed reactor is the simple batch reactor in which the reactant is continuously stirred throughout a batch time during which reaction occurs. During the batch processing time the concentration of reactants and products will progressively change. At any instant, however, the electrolyte composition is uniform throughout the reactor. The batch reactor is widely used due to its simplicity and versatility. Batch reactors are used for small-scale operations where they are more economic than continuous reactors. They are also used as analytical devices, as rates of reaction can be followed as a function of electrolyte composition [2].

A perfectly stirred tank with a continuous flow through the reactor is called a continuously stirred tank reactor (CSTR). In this case, the concentration of reactants and products are uniform throughout the reactor. The reactant concentration within the reactor is equal to the outlet concentration, $c(\text{OUT})$, and is independent of time. A rotating cylinder electrode in turbulent flow can approximate well this model [5], as can a plate-in-tank design with provision for electrolyte agitation [11].

Figure 3 shows a sketch of three types of ideal reactor. It is very common to use the batch recirculation mode of operation, where a PFR or

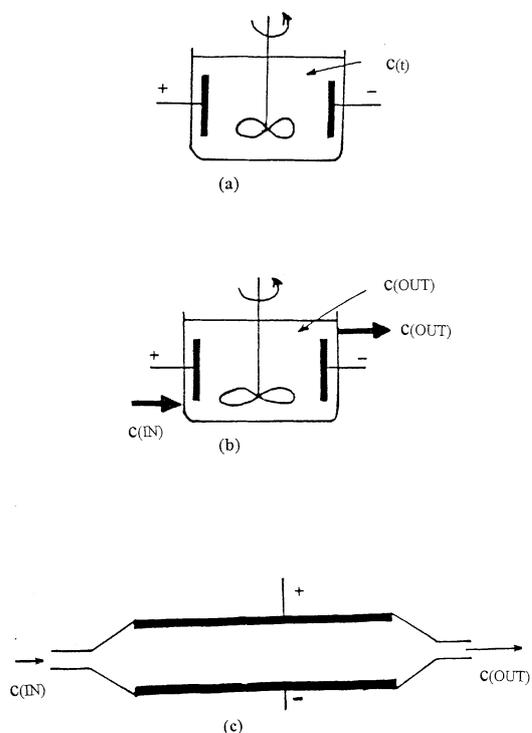


Fig. 3. Ideal types of chemical reactors: (a) Simple batch reactor; (b) Continuous stirred tank reactor; (c) Plug flow reactor.

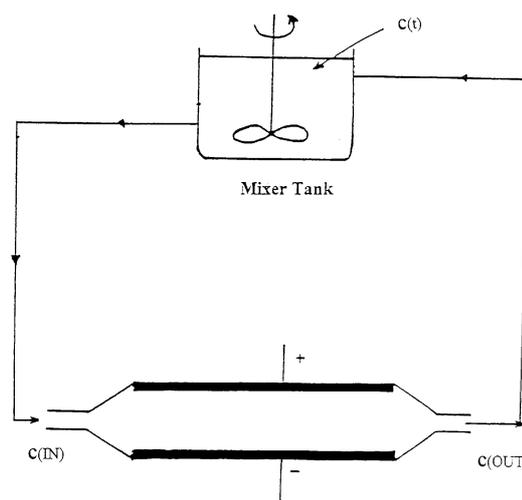


Fig. 4. Reactors in cascade and with recycle: (a) Cascade operation; (b) Reactor with recycle loop.

a CSTR can be connected in a loop containing a mixer tank (Fig. 4). The mixer tank provides the possibility of adjusting the volume of the system, aids reactant additions, process monitoring, product extraction and heat removal. On the other hand, it is common in industry to find cascade operation. In this case, several reactors are connected in hydraulic series to achieve a greater overall conversion. It is also common to use a reactor with recycle, in this case for a given reactor, it is possible to achieve a larger conversion using an appropriate recycle rate (Fig. 5). In all cases, it is important to consider figures of merit in order to rationalise the performance of a given reactor under similar operational conditions [12, 19, 20].

Here, we will consider batch reactors, PFRs and

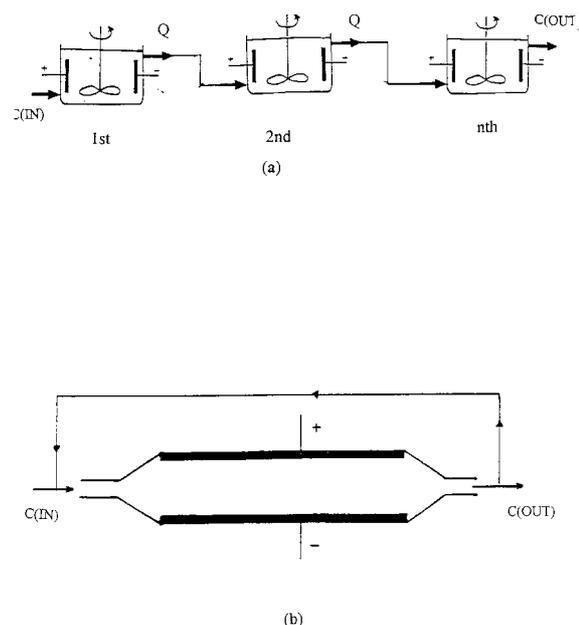


Fig. 5. Definition sketch for an electrochemical reactor in batch recirculation mode.

CSTRs under complete mass transport control of the reaction conditions; batch recycle and reactors with recycle will be considered in a second paper. Here, theoretical equations for the reactor design are provided and several figures are presented to enable reactor performance to be described in terms of conversion and as a function of the mass transport coefficient, k_m .

In reactor analysis, a material balance (per unit of time) is set up, in order to determine the reactor design equations. The material balance is based in the principle of the conservation of matter and in the case of the component O in reaction (1) can be written as:

$$\begin{aligned} \text{Rate of mass input} &= \text{Rate of mass output} \\ &+ \text{Rate of loss} \\ &= \text{Rate of accumulation} \quad (2) \end{aligned}$$

For the case of a batch reactor, there are no input or outputs and the expression simplifies to:

$$\begin{aligned} \text{Rate of accumulation of O} \\ &= -\text{Rate of disappearance of O} \quad (3) \end{aligned}$$

For the case of PFR and CSTR, there is no accumulation of materials and we can write for component O:

$$\begin{aligned} \text{Rate of mass input} - \text{Rate of mass output} \\ &= \text{Rate of mass disappearance} \quad (4) \end{aligned}$$

In an electrochemical reaction the rate of mass disappearance of O (i.e., $d[\text{O}]/dt$) is given by the expression:

$$I/zF = -d[\text{O}]/dt \quad (5)$$

where I is the cell current, z is the number of electrons involved in the electrode reaction and F is the Faraday constant. The quantity I/zF is the rate of material flow and has units of mol s^{-1} .

Here, the reaction is considered to take place under mass transport control and the value of I is the limiting current, I_L , is given by [16]:

$$I_L = zFk_m A c_B \quad (6)$$

where k_m is the mass transport coefficient (a type of heterogeneous rate constant), A is the electrode area and c_B is the concentration of the electroactive species in the bulk electrolyte.

It is useful to express reactor performance in terms of the fractional reactant conversion, X_A . In the case of a constant volume system, this may be defined as [20]:

$$X_A = \frac{c_{A0} - c_A}{c_{A0}} = \frac{[\text{O}]_0 - [\text{O}]_t}{[\text{O}]_0} = \frac{c_{(0)} - c_{(t)}}{c_{(0)}} \quad (7)$$

where c_{A0} is the initial concentration of reactant ($= [\text{O}]_0 = c_{(0)}$) and $c_A (= [\text{O}]_t = c_{(t)})$ is the final value. Design equations which express the fractional conversion under mass transport controlled reaction conditions have been derived [2, 7, 9, 12] and are summarised in Table 1 for the case of batch, PFR and CSTR reactors. The equations in this table indicate that the reactor performance, in terms of conversion, depends strongly upon the product of the mass transport coefficient and the electrode area, $k_m A$. In some cases, such as reactors using three-dimensional electrodes, it is difficult to separate the individual contributions of k_m and A . The value of k_m depends upon reactor geometry, the type of flow (laminar or turbulent) and volumetric flow rate. It is very important to calculate the value of the product $k_m A$ since this is the factor which determines the overall reactor performance under mass transport controlled reaction conditions. Several routes to the determination of empirical $k_m A$ values can be found in the literature and these are based on the determination of limiting current from steady-state current vs. electrode potential curves, from conversion vs. time data or from a mass transport correlation [9, 12, 21].

COMPUTER SIMULATIONS

We have used computer simulation to produce graphical displays showing reactor performance, in terms of reactant conversion, for reactions under mass transport control, with $k_m A$ as a parameter. Spreadsheet calculations and the resultant graphical plots have been performed using Microsoft EXCEL version 4.0, running on a 486 PC (or more recently a Pentium PC) microcomputer.

The expressions in Table 1 have been used to calculate a large number of points, followed by interpolation of a line through the data points. Normal plots have been obtained using up to 60 points per each line. It is important to realise that this procedure has been possible since the mass

Table 1. Summary of design equations for batch reactor, plug flow reactor and continuously stirred tank reactor in the single pass mode [2, 7, 12, 21]

Reactor type	Design equation	x	Equation number
Batch	$c_{(t)} = c_{(0)} \exp(-x)$	$k_m A t / V_R$	(8)
Batch	$\ln [c_{(t)} / c_{(0)}] = -x$	$k_m A t / V_R$	(9)
Batch	$X_A = 1 - \exp(-x)$	$k_m A t / V_R$	(10)
PFR	$c_{(x)} / c_{(IN)} = \exp(-x l)$	$k_m A' / Q$	(11)
PFR	$X_A = 1 - \exp(-x)$	$k_m A t / V_R$	(12)
CSTR	$X_A = 1 - 1 / (1 + x)$	$k_m A t / V_R$	(13)

balance leads to an expression that can be treated analytically. Numerical methods are then available to integrate the differential equations [7, 8]. A simple and short Microsoft QBASIC program has been developed (see the Appendix) to numerically integrate the relevant differential equations in the present case. The program uses a modified Euler method, this method being sufficiently accurate if a small step size is used [24].

The simple batch reactor

The reactant conversion expressions for a batch reactor, summarised in Table 1, were used to calculate values of normalised concentration ($X_A = c(t)/c(0)$) and conversion as a function of time. Figure 6 shows the normalised concentration decay for a batch system for several values of $k_m A/V$ (product of mass transport coefficient and area divided by reactor volume) versus time, t . An exponential decay is observed which becomes faster at higher values of $k_m A/V$. If the logarithm of the normalised concentration decay is plotted against time, then straight lines are observed of slope equal to the factor $k_m A/V$ (Fig. 7). This fact can be used to calculate a $k_m A$ value by recording the reactant concentration versus time behaviour.

It is interesting to consider the value of the fractional conversion. Figure 8 shows the fractional conversion versus time for a batch system. Calculation of the time required to reach a particular conversion is a major objective in the design of any batch reactor. This can be achieved via Fig. 6; by reading in the $k_m A/V$ value of the reactor in question, the reactant conversion can be found.

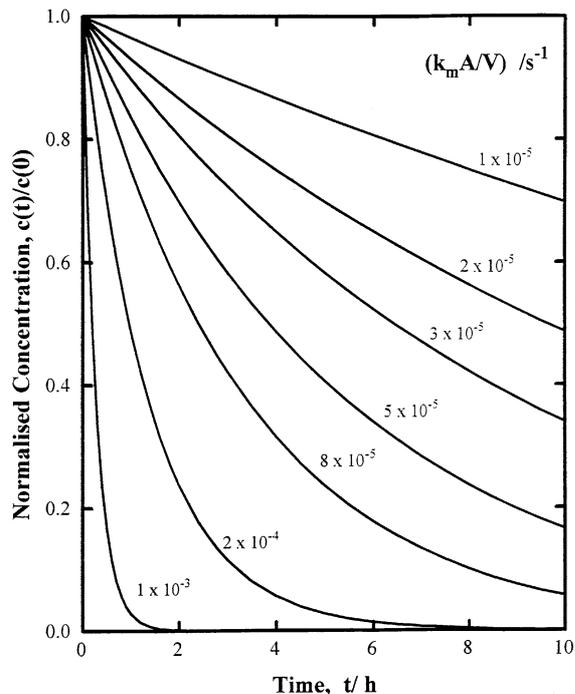


Fig. 6. Normalised reactant concentration versus time for a batch reactor.

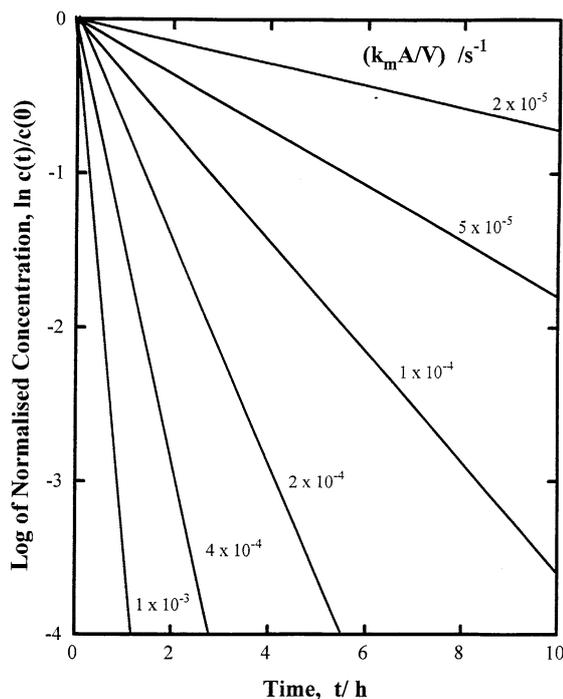


Fig. 7. Logarithm of normalised concentration versus time for a batch reactor.

So far, it has been assumed that all the cell current is used to drive the desired reaction. In practice, secondary reactions are common and the current efficiency, ϕ , is defined as the fraction of electrical charge used for the desired reaction (the 'charge yield'). Figure 9 shows current efficiency versus time and it is seen that the current efficiency falls with time (due to the decline in the reactant level) and it is a function of initial reactant

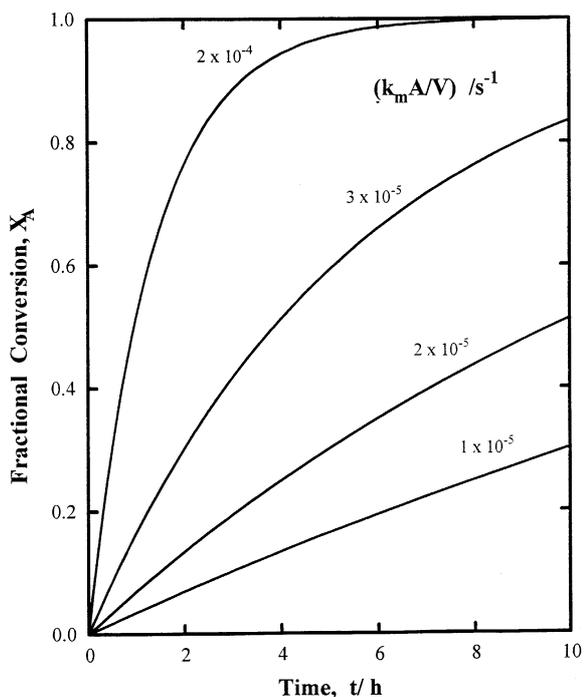


Fig. 8. Fractional conversion versus time for a batch reactor.

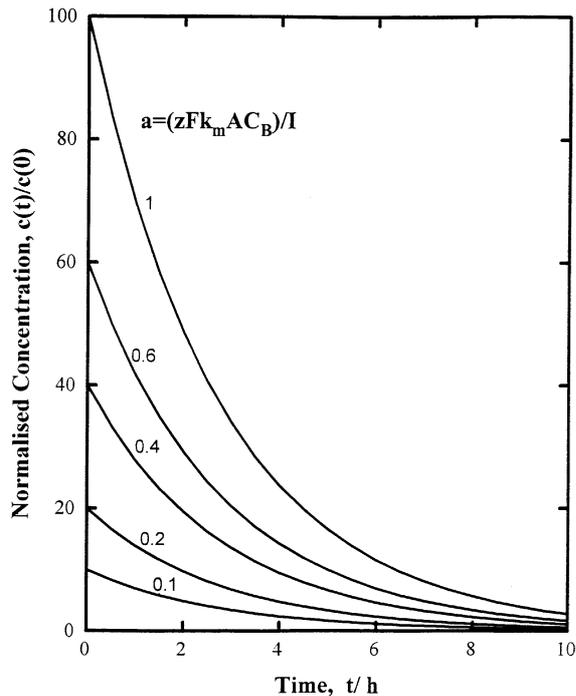


Fig. 9. Current efficiency as a function of time for a batch reactor showing the importance of the parameter $a = zFk_m A C_B / I$.

concentration. As can be seen in Figs 6–9, the batch reactor is a time-dependent system, where the reactant concentration continuously changes over the batch electrolysis time.

The continuous flow reactor (PFR and CSTR)

The plug flow reactor (PFR) assumes no mixing along the direction of electrolyte flow. Therefore, the reactant concentration will be a function of the distance, l , into the reactor from the inlet end. A mass balance for reactant loss, due to progress of the electrode reaction, leads to the equation:

$$\frac{dc(l)}{dl} = -\frac{k_m A'}{Q} c(l) \quad (14)$$

where $c(l)$ is the reactant concentration at a distance l into the reactor. Analytical solution leads to equation (10) which was used to calculate points $c(l)/c_{(IN)}$ versus l , but equation (14) can also be solved using a numerical method (as shown in the Appendix). Excellent agreement was obtained between the values obtained from these two methods. Figure 10 shows the concentration decay as a function of distance into the PFR. For given mass transport conditions, conversion is a function of the residence time (Fig. 11); obviously conversion increases for a larger residence time. For the case of the CSTR, the reactant concentration within the reactor is equal to that at the outlet and is a function of the residence time, as shown by equation (13) and Fig. 12.

It is interesting to compare a PFR and a CSTR which have the same values of mass transport coefficient and electrode area which operate

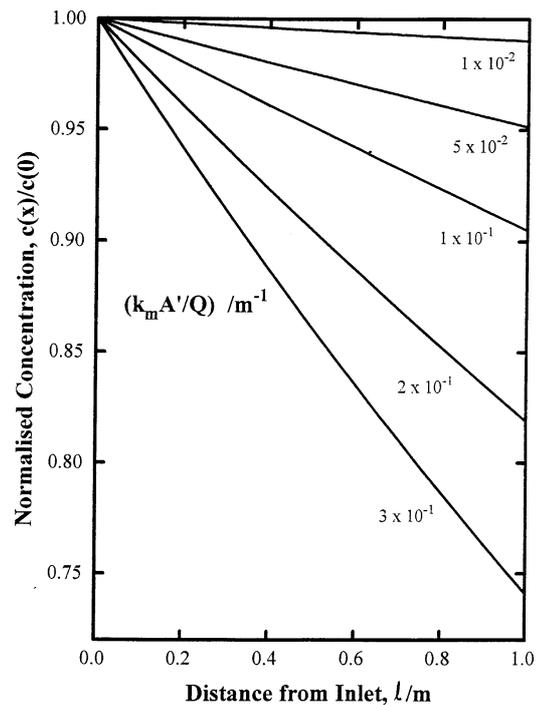


Fig. 10. Normalised concentration as a function of axial position along a plug flow reactor measured from the inlet end of the PFR.

under similar process conditions. Figure 13 compares the fractional conversion achieved for both reactors as a function of the performance parameter $k_m A/V$. To explain this behaviour we must consider the definitions given above. In the case of the CSTR, the reactant concentration within the reactor is the same as that at the

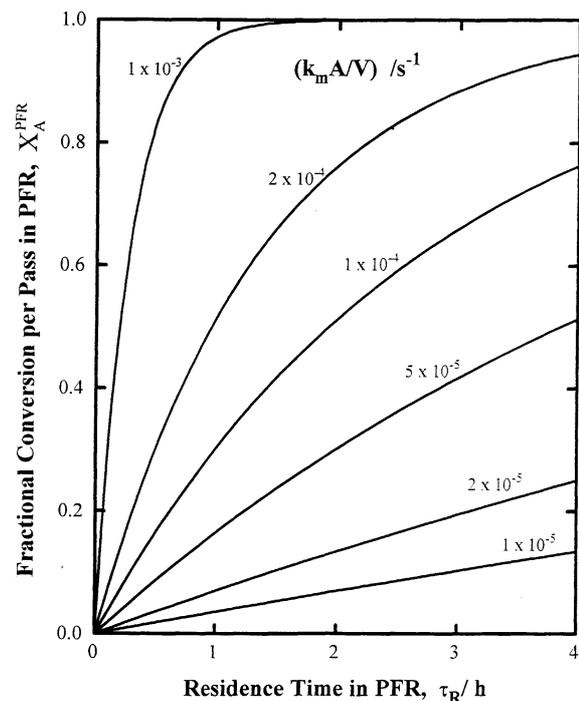


Fig. 11. Conversion achieved for a PFR as a function of residence time.

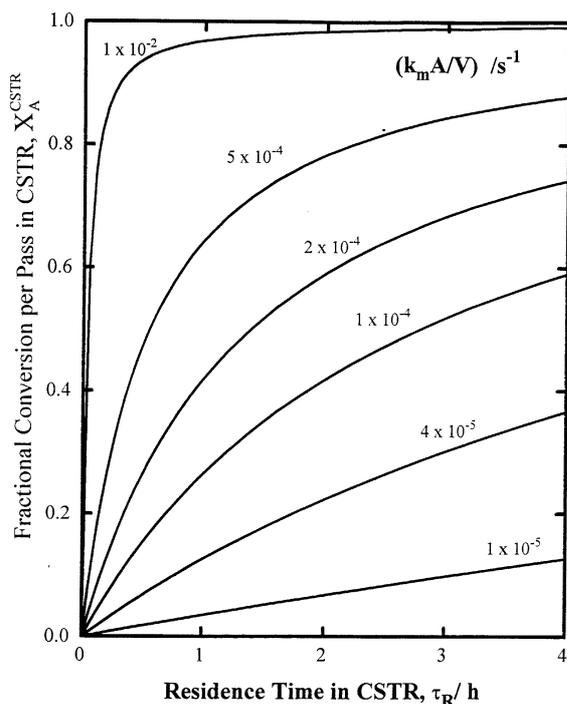


Fig. 12. Conversion achieved for a CSTR as a function of residence time.

outlet. Under mass transport controlled conditions, the reaction rate is proportional to the bulk reactant concentration via equation (6) and the reaction rate will be lower for a given value of $k_m A$ in a CSTR. The opposite case is achieved for the PFR where there is no mixing in the direction of flow and the reactant concentration remains as high as possible.

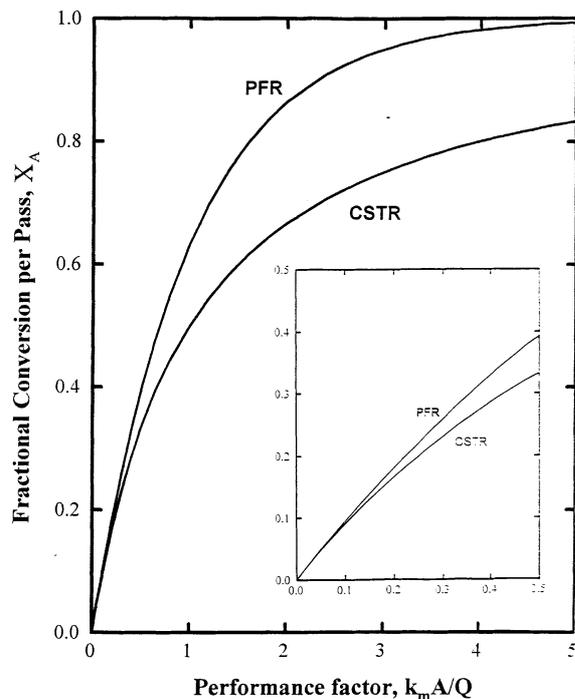


Fig. 13. Comparison between the conversion achieved for a PFR and a CSTR in the single pass mode.

It is important to consider the limit when PFR and CSTR models lead to the same conversion, i.e., the situation when both models have the same physical meaning. In the expressions shown in Table 1, a dimensionless factor, 'x', is repeated through batch, PFR and CSTR models. This factor is equal to $k_m A t / V_R$ for a batch reactor or $k_m A / Q$ for a continuous flow reactor. Reactant conversion depends strongly upon these factors. This factor also facilitates a comparison between models. Batch, PFR and CSTR will lead to the same conversion value for the values of x (defined in Table 1) in the following equation:

$$\exp(-x) \approx \frac{1}{1+x} \quad (15)$$

In other words, the approximation becomes an equality in the limit $x = 0$. For values around $x = 0$, a comparison between both sides of equation (1) can be made by expansion of $\exp(-x)$ and $1/(1+x)$ about the point $x = 0$, as a Maclaurin expansion, leading to:

$$\exp(-x) \approx 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \dots \quad (16)$$

$$\frac{1}{1+x} \approx 1 - x + \frac{x^2}{2} - \frac{x^3}{6} + \dots \quad (17)$$

Each side of equation (17) leads to the same series for very small values of x . Therefore, for small values of x , batch, PFR and CSTR models will predict the same conversion. It is important to realise that this analysis has been developed about the point $x = 0$. A general analysis, using a Taylor expansion for the general point $x = a$, will not lead to the same solution. For values of x appreciably greater than zero, equality (15) does not apply and the CSTR and PFR design equations will lead to the prediction of different conversion values, for given values of $k_m A$ and V . The errors involved in adopting simple batch models, rather than more sophisticated batch recycle ones, are considered elsewhere [2, 12, 21].

DISCUSSION

The hydrodynamic behaviour inside an electrochemical reactor and the averaged value of mass transport coefficient play a major role in determining the maximum reaction rate when electrochemical reactors are operated under mass transport conditions. The importance of maintaining high values of the product $k_m A$ (in order to achieve high reactor performance) has been highlighted through figures of merit [25] where it can be seen that this product is an extremely important factor. The time-dependence of conversion for the batch reactor (Figs 6–8) as well as the current efficiency are shown in Fig. 9. For the case of a PFR, Fig. 10 shows the position dependence of reactant concentration while Fig. 11 indicates the

conversion achieved for different $k_m A$ values. Figure 13 compares conversions achieved for a PFR and CSTR under identical flow rate, mass transport coefficient and electrode area conditions. It is found that a higher conversion is achieved in a PFR due to the flow characteristics of the reactor.

The idealised electrolyte flow and mass transport controlled reaction conditions considered in this paper are not encountered in laboratory and industrial practice. For example a common practice in organic and inorganic chemistry is to mix two reactants in a stirred beaker; a certain time is allowed to pass and finally the products are collected. This situation clearly corresponds to a fixed volume batch reactor. Practical examples of the PFR can be found in a HPLC column for analytical purposes or in flow injection analysis. Figures 6–13 allow the determination of fractional conversion of reactant for different flow situations. In all cases, it is considered that mass transport is the prevailing type of rate control. Some limitations of this approach must be taken into account. Firstly, this paper has considered only reactant depletion due to a single electrode reaction under complete mass transport control. In electrochemical reactors it is common to have a wide current vs. potential region under charge transfer or mixed (charge transfer and mass transfer) control, where the reaction rate is determined by

both charge transfer and mass transport rates. Adsorption phenomena at the electrode starting of the active electrode result in non-ideal behaviour and are considered elsewhere, as is the case of mixed control of the reaction rate [22, 23]. The use of a reservoir or multiple reactors in series hydraulic flow, as devices to increase the overall fractional conversion, will be treated in a second paper.

SUMMARY

We have provided a series of working curves to allow the calculation of reactant conversion in an electrochemical reactor supporting a reaction under complete mass transport control. This method is quick, simple and enables the conversion to be estimated for a wide range of hydrodynamic conditions and mass transport coefficient values. The graphical method is elegant and avoids the need for repetitive design calculations.

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APPENDIX

A material mass balance for each of the reactors considered leads to a differential equation that can be analytically integrated, leading to the solutions shown in Table 1. The resultant expression has been used to perform spreadsheet calculations and the results have been plotted graphically to produce working curves describing the reactor performance. Alternatively, the differential equations may be numerically integrated to directly obtain data points. Numerical integration is normally used when analytical solution is very difficult (or even impossible) for complex systems. Here, it is considered only as an example of an alternative method to obtain the data necessary to plot the Figures. The algorithm used is a modification of the Euler rule and the derivative is given in line 15 of the programme. The routine starts with the condition $x = x_0$ and runs until $x = x_n$ with a step h , all parameters being defined in line 30. The algorithm provides a sufficiently accurate calculation if a small step size is selected. More sophisticated methods such as the Runge-Kutta technique [24] are available but for the cases treated in this paper the following approach is sufficient and attractive in its simplicity. For a differential equation such as:

$$\frac{dy}{dx} = f(x, y) \quad (18)$$

Knowledge of an initial condition, say $x = x_0$ and $y = y_0$, enables a numerical solution of equation (18) to be obtained for a small step size, h , by projecting a tangent line at (x_0, y_0) to $(x_0 + h)$. In this case, the value of y_1 will be:

$$y_1 = y_0 + h \left(\frac{dy}{dx} \right)_{x=x_0} \quad (19)$$

or:

$$y_1 = y_0 + f(x_0, y_0) * h \quad (20)$$

The following expression may be used to calculate y_2 :

$$y_2 = y_1 + f(x_0 + h, y_1) * h \quad (21)$$

This method corresponds to a 'rectangle rule' which is commonly known as the Euler rule. An improvement in the technique is possible if the tangent is projected from a middle point between the initial conditions and the point y_1 . In this case, y_1 is given by the expression:

$$y_1 = y_0 + f(x_0 + h/2, y_{1/2}) * h \quad (22)$$

WHERE $(x_0 + h/2)$ is known and $y_{1/2}$ can be calculated via:

$$y_{1/2} = y_0 + f(x_0, y_0) * h \quad (23)$$

The programme below uses this improved method known as the 'middle point' rule:

```

1 REM numerical integration of differential equation
4 REM by using the midpoint-integration rule)
5 REM Trinidad P, Walsh F, Gilroy D
6 REM the function is defined in 15,  $x_0$ ,  $y_0$  is the initial condition
7 REM  $x_n$  is the final point, and  $h$  is the size of the interval.
15 DEF fnf(x, c) = -0.2 * c
20 READ  $x_0$ ,  $c$ ,  $x_n$ ,  $h$ 
30 DATA 0, 1, 10, 0.05
40 PRINT 'x', 'c'
50 PRINT
60 PRINT  $x_0$ ,  $c$ 
70 FOR  $x = x_0$  TO  $x_n - h$  STEP  $h$ 
80 LET  $d_1 = \text{fnf}(x, c)$ 
90 LET  $d_2 = \text{fnf}(x + h/2, c + d_1 * h/2)$ 
100 LET  $c = c + d_2 * h$ 
110 PRINT  $x + h$ ,  $c$ 
120 NEXT  $x$ 

```

NOMENCLATURE

A	Effective electrode area	m^2
A'	Electrode area per length of reactor	m
c_B	Bulk concentration of reactant	mol m^{-3}

$c_{(IN)}$	Reactant concentration at the reactor inlet	mol m^{-3}
$c_{(OUT)}$	Reactant concentration at the reactor outlet	mol m^{-3}
$c_{(0)}$	Initial concentration of reactant	mol m^{-3}
$c_{(t)}$	Reactant concentration at time t	mol m^{-3}
$c_{(l)}$	Concentration of reactant at position l into the reactor	mol m^{-3}
F	Faraday constant	$96,485 \text{ C mol}^{-1}$
I	Current	A
I_L	Limiting current (due to convective-diffusion)	A
l	Distance into the reactor from the inlet end	m
k_m	Mass transport coefficient	m s^{-1}
N	Number of identical reactors in a cascade arrangement	
Q	Volumetric flow rate of electrolyte	$\text{m}^3 \text{ s}^{-1}$
R	Recirculation rate of electrolyte	
t	Time	s
V_R	Volume of electrolyte within the reactor	m^3
X_A	Fractional conversion of reactant	
z	Number of electrons involved in the electrode reaction	
ϕ	Cumulative current efficiency	
τ_T	Mean residence time in the tank	s
τ_R	Mean residence time in the reactor	s

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