

Reactor analysis of series and parallel electrochemical reactions during galvanostatic operation

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The purpose of this paper is to address the problem of galvanostatic operation of irreversible electrochemical series and parallel reactions. The application of a constant current is known to be the preferred mode of industrial, electrochemical reactor operation. However, variations in product yields and current efficiencies are not easily predicted for this operational mode, except for simple limiting situations. By numerical solution of the governing first-order differential equations for batch and plug flow reactions, product yields have been predicted as a function of reactant conversion for a wide range of kinetic parameters. The effect of mass transport limitations and solvent decomposition is an integral feature of the analysis.

The performance characteristics obtained give a general description of the behaviour of most series and parallel electrochemical reactions. The possibility of a kinetic analysis of these electrochemical reactions from experimental yield data has been broadly demonstrated using published experimental data.

Nomenclature

C_{AO}	initial concentration of species A (mol m ⁻³)	k_{FH}	of step <i>i</i> (m s ⁻¹) electrochemical rate constant for the solvent decomposition reaction (m s ⁻¹)
C_j	bulk concentration of species <i>j</i> (mol m ⁻³)	k_{Lj}	mass transfer coefficient for species <i>j</i> (m s ⁻¹)
C_{js}	surface concentration of species <i>j</i> (mol m ⁻³)	n_i	number of electrons in step <i>i</i>
E	electrode potential (V)	t	reaction time or residence time (s)
F	Faraday number (C mol ⁻¹)	T	dimensionless time
i_H	partial current density for solvent decomposition (A m ⁻²)	X_A	fractional conversion
i_i	partial current density of step <i>i</i> (A m ⁻²)	α_i	constant describing potential dependency of reverse reaction rate constant (V ⁻¹)
i_T	total current density (A m ⁻²)	β_i	constant describing potential dependency of forward reaction rate constant (V ⁻¹)
k_{fi}	forward electrochemical rate constant of step <i>i</i> (m s ⁻¹)	β_H	constant describing potential dependency of the solvent decomposition reaction (V ⁻¹)
k_{bi}	backward electrochemical rate constant	σ	electrode area per unit volume (m ⁻¹)

1. Introduction

Electrochemical reductions and oxidations often proceed via complex reaction sequences involving electrocatalytic reaction, homogeneous electron transfer and chemical reaction. A variety of

important chemicals are produced by this means, especially in inorganic synthesis. However, only relatively few electro-organic reactions have achieved commercial development [1], but with the recent interest in this area several candidate syntheses are emerging [2].

Two important categories of reaction which frequently appear in electro-organic synthesis, are multiple competing reactions [3] and consecutive reactions [4]. Recent reported studies of such reactions are the electrochemical preparation of 3-bromothiophen [5], the electrochemical reduction of benzene [6], the synthesis of 2,5-dimethoxyphenyl acetate in a thin film contactor cell [7] and the electrochemical reduction of oxalic acid to glyoxylic acid [8].

Fleischmann *et al.* [7] analysed experimental data from the synthesis of 2,5-dimethoxyphenyl acetate in a two-phase batch reactor, giving intermediate product yield versus conversion curves for both potentiostatic operation and galvanostatic operation. However, three major assumptions inhibit the general use of the approach; that is, the assumption that the Tafel slopes for both electrochemical steps are equal, that mass transport resistance effects are absent and that solvent decomposition does not occur. The second of these assumptions was also made by Sakellaropoulos [3, 4] in his plug flow reactor models, which were additionally restricted to potentiostatic operation. The inclusion of mass transport resistance at the electrode surface has recently been incorporated in batch and plug flow reactor models of series and parallel electrochemical reactions [9], which again was restricted to potentiostatic operation. Galvanostatic operation of these reaction types has recently been described for restricted kinetic conditions, i.e. equal Tafel slopes [10, 11].

The purpose of this work is to investigate the general performance of series and parallel electrochemical reactions in batch and plug flow reactors during galvanostatic (constant current) operation. This method of current supply is known to be the preferred mode of industrial operation of electrochemical reactors because of its lower cost and ease of control. It is also frequently used for laboratory electrosyntheses. However, unlike potentiostatic operation where control of electrode potential and kinetics is inherent, galvanostatic operation gives rise to variations of electrode potential with time. This inevitably changes the magnitude of the electrochemical kinetic 'constants' and thus product yields may well be quite different to those experienced during potentiostatic operation. The effects of

variation in the parameters of the Tafel equations of the reactions are considered. Mass transport resistance close to the electrode surface is included and so is the influence of simultaneous solvent decomposition. Brief consideration is given to the effect of reversibility in the electrochemical kinetics.

2. Theoretical reactor analysis

The mathematical description of batch and plug flow electrochemical reactors during galvanostatic operation is developed below. Reactor operation will concentrate on only one region of electrode activity, and reactions at the secondary electrode are assumed to not adversely affect performance. For plug flow reactors it is assumed that variations in current density over the reactor due to concentration changes etc. are negligible.

The other main assumptions in the analysis are as follows (others will be noted where applicable).

- (i) Steady state, isothermal conditions apply.
- (ii) Constant volume conditions prevail.
- (iii) Ideal flow characteristics, either plug flow or well mixed are assumed.
- (iv) Mass transport is described through the use of a mass transfer coefficient k_{Li} for each species i in the following equation

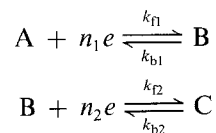
$$\frac{i_i}{nF} = k_{Li}(C_i - C_{is}) \quad (1)$$

where i_i is the partial current density and C_i and C_{is} are bulk and surface concentrations of species i .

- (v) Migration effects are negligible.
- (vi) Reactions are first order and Butler-Volmer kinetics apply.

2.1. Series reactions

The usual three component series reaction scheme considered is



The reaction rates for both steps following [9] are

$$i_1 = n_1 F(k_{f1} C_{AS} - k_{b1} C_{BS}) \quad (2)$$

$$i_2 = n_2 F(k_{f2} C_{BS} - k_{b2} C_{CS}) \quad (3)$$

where the rate constants are defined as

$$k_{f1} = k_1 \exp(\beta_1 E) \quad (4)$$

$$k_{b1} = k_1 \exp(-\alpha_1 E) \quad (5)$$

for the first reaction step and similarly for the second reaction step. E is the electrode potential with respect to any convenient reference electrode and k_1 is a constant independent of potential, though the value will depend on the reference electrode system chosen.

In this work it is convenient for the purpose of numerical solution to choose the reference potential to be such that the electrode potential at the beginning of the electrolysis is $1/\beta$, i.e. $\beta_1 E_{\text{initial}} = 1$. This convention is adopted to allow the changes in potential to be followed during the course of the reaction. At any time we have

$$\frac{E}{E_{\text{initial}}} = \ln\left(\frac{k_{f1}}{k_1}\right) = 1 + \ln\left[\frac{k_{f1}}{(k_{f1})_0}\right] \quad (6)$$

where $(k_{f1})_0$ is the initial value of k_{f1} .

As a consequence, the values k_1 and k_2 have some potential dependence in that, if the reaction were to be carried out at a different initial potential, then $(k_{f1})_0$ and $(k_{f2})_0$ would have changed. If the Tafel parameters of the two reactions are different this would mean that the ratio k_2/k_1 for a given electrochemical reaction would be dependent on the starting potential and, hence, different performance characteristics would be expected if the reaction were operated at a different current density.

By combining Equations 2 and 3 with mass transport expressions similar to Equation 1 to eliminate surface concentrations, reaction rates for both steps following [9] are

$$\frac{i_1}{n_1 F} = a_1 C_A + a_2 C_B + a_3 C_C \quad (7)$$

$$\frac{i_2}{n_2 F} = b_1 C_A + b_2 C_B + b_3 C_C \quad (8)$$

where

$$a_1 = \frac{y''}{y' y'' - \left(\frac{k_{b1}}{k_{f1} k_{LB}^2}\right)}$$

$$a_2 = \frac{\frac{k_{b1}}{k_{f1}} \left(\frac{1}{k_{LB}} - y''\right)}{y' y'' - \left(\frac{k_{b1}}{k_{f1} k_{LB}^2}\right)}$$

$$a_3 = - \frac{k_{b1} k_{b2}}{k_{f1} k_{f2} \left[y' y'' k_{LB} - \left(\frac{k_{b1}}{k_{f1} k_{LB}}\right) \right]}$$

$$b_1 = \frac{a_1}{k_{LB} y''}$$

$$b_2 = \frac{1}{y''} \left(\frac{a_2}{k_{LB}} + 1 \right)$$

$$b_3 = \frac{a_3}{k_{LB} y''} - \frac{k_{b2}}{y'' k_{f1}}$$

with

$$y' = \frac{1}{k_{f1}} + \frac{1}{k_{LA}} + \frac{k_{b1}}{k_{f1} k_{LB}}$$

$$y'' = \frac{1}{k_{f2}} + \frac{1}{k_{LB}} + \frac{k_{b2}}{k_{LC} k_{f2}}$$

For electrolysis in a batch reactor or plug flow reactor of electrode area per unit volume, σ , the reactor design equations are

$$\frac{dC_A}{dt} = -\sigma \frac{i_1}{n_1 F} \quad (9)$$

$$\frac{dC_B}{dt} = \sigma \left(\frac{i_1}{n_1 F} - \frac{i_2}{n_2 F} \right) \quad (10)$$

Here, t represents either the batch reaction time or plug flow reactor residence time.

The final equation of the analysis is that of constant total current density, i_T , given by

$$i_T = i_1 + i_2 \quad (11)$$

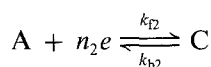
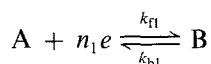
Equation 11 essentially controls the variation of electrode potential during electrolysis.

These equations are solved using a procedure illustrated in the accompanying block diagram for the case of a series reaction with no decomposition of the solvent. Analytical solutions can be obtained under certain simplified conditions of no mass transport resistance and equal Tafel slopes [7], but in general the requirement that potential (and hence k_{f1} and k_{f2}) is governed by Equation 11 precludes analytical solution. Instead, Runge-Kutta numerical integration is

used, with each step followed by an iterative procedure to recalculate k_{f1} and k_{f2} . The analytical expressions are used to check the accuracy of the numerical solution under the limiting conditions.

2.2. Parallel reactions

The concurrent reaction of species A forming two products B and C by electron transfer is considered.



The reaction rates for the two steps are given by equations similar to Equations 2 and 3.

For irreversible electron transfers, the reaction current densities following [9] become

$$\frac{i_1}{n_1 F} = \frac{C_A}{\frac{1}{k_{LA}} + \frac{1}{k_{f1}} + \frac{k_{f2}}{k_{f1} k_{LA}}} \quad (12)$$

and

$$\frac{i_2}{n_2 F} = \frac{C_A}{\frac{1}{k_{LA}} + \frac{1}{k_{f2}} + \frac{k_{f1}}{k_{f2} k_{LA}}} \quad (13)$$

The reactor design equations for this reaction sequence are

$$-\frac{dC_A}{dt} = \sigma \left(\frac{i_1}{n_1 F} + \frac{i_2}{n_2 F} \right) \quad (14)$$

$$\frac{dC_B}{dt} = \sigma \frac{i_1}{n_1 F} \quad (15)$$

For galvanostatic operation the condition of total current density, Equation 11, applies.

Generally, the solution of the reactor design equations is achieved numerically as described in Section 2.1.

2.3. Extension to accommodate solvent decomposition

A situation which occurs frequently in electrochemical reaction systems is decomposition of the solvent. This simultaneous reaction, which often results in the generation of a gaseous

product (e.g. H_2), invariably causes a negligible change in the reactant (solvent) concentration and hence the reaction can be considered to be of zero order. To accommodate this reaction in the present analysis the total current density is written as

$$i_T = i_H - i_1 + i_2 \quad (16)$$

where i_H is the current density for solvent decomposition and is given by a Tafel equation of the form

$$i_H = n_H F k_H \exp(\beta_H E) \quad (17)$$

For convenience, this reaction current density will often be referred to as that for the hydrogen evolution reaction.

3. Results and discussion

It is well known that single Tafel reactions in batch or plug flow reactors exhibit a linear decrease in reactant concentration with time (or residence time) during galvanostatic operation. With reactions giving two or more products, the behaviour is more complicated as to satisfy the constant current criterion, electrode potential is free to vary. This variation is dictated by the kinetic parameters for all reactions involved.

The inevitable variation of electrode potential during galvanostatic operation causes the values of the electrochemical rate 'constants' to change continually and, in most instances, their respective ratios also vary. Because of this, the variation of product distribution for multiple reaction systems is expected to be quite different to that for the equivalent conditions of potentiostatic operation. During potentiostatic operation the values of the electrochemical rate constants are, in fact, maintained constant. The respective ratios of the rate constants are governed by the electrode potential of operation and, hence, so is the product distribution. The magnitude of any solvent decomposition is also fixed by the value of electrode potential.

3.1. Series electrochemical reactions

In the series reaction sequence, the product of interest will be the intermediate B. The predicted behaviour will, therefore, concentrate on the

yield of B (C_B/C_{AO}), expressed as a function of reactant conversion X_A ($= 1 - C_A/C_{AO}$). From an overall material balance,

$$C_{AO} = C_A + C_B + C_C \quad (18)$$

information, such as current efficiency, the concentration of by-product C and concentration time characteristics, can be readily determined. The latter can be obtained from the expression

$$2X_A - \frac{C_B}{C_{AO}} = \frac{(i_T - i_H)\sigma t}{C_{AO}nF} \quad (19)$$

obtained from Equations 9, 10 and 16, when $n_1 = n_2$. Considering first the situation when the series reaction takes place in a potential range outside the region of solvent decomposition and without mass transport limitation, Fig. 1 shows a set of yield versus conversion curves for a series of ratios of Tafel slopes β_2/β_1 from 3 to 0.333 ($n_1 = n_2$). The main parameter in these charts is the ratio of initial rate constants k_2/k_1 (The ratio of initial rate constants $(k_{r2})_0/(k_{r1})_0$ is written now as k_2/k_1). As might be expected the yield of B goes through a maximum under all conditions, this maximum being greater the smaller the ratio of k_2/k_1 .

In Fig. 1, two types of behaviour are evident as the ratio β_2/β_1 , decreases.

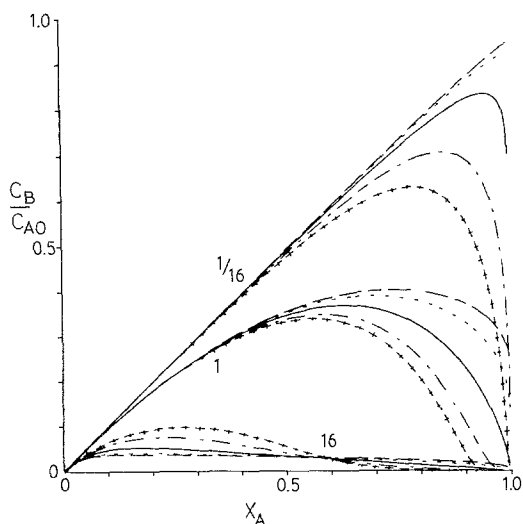


Fig. 1. Intermediate product yield versus conversion for series Tafel reactions showing the effect of the ratio of Tafel slopes β_2/β_1 and rate constants k_2/k_1 . Values of k_2/k_1 are shown on curves. Values of β_2/β_1 : $\frac{1}{3}$ (---); $\frac{1}{2}$ (···); 1 (—); 2 (- - - -); 3 (+ + +).

(i) For values of $k_2/k_1 \leq 1$, the maximum yield of B increases and occurs at higher conversions. At very low ratios of β_2/β_1 of 0.33 and $k_2/k_1 = 1/16$, the maximum yield of B is in excess of 0.9 and occurs at almost complete conversion of A. The behaviour is almost that of a single Tafel reaction, because the low value of β_2/β_1 causes the actual ratio of rate constants k_{r2}/k_{r1} to decrease to values less than the initial ratio k_2/k_1 as the potential increases to maintain constant current operation.

(ii) For values of $k_2/k_1 > 1$, yields are generally low, with maximum values decreasing with an increase in k_2/k_1 and occurring at lower conversions. At low values of β_2/β_1 , yields of B may vary very little over a large range of conversions.

The characteristic behaviour described above can be readily interpreted from the variation of electrode potential during operation. This variation of electrode potential is shown in Fig. 2 for a wide range of rate parameters. In the case of values of the initial ratio $k_2/k_1 > 1$, the potential must rise continuously during the course of the reaction to maintain constant current as the reactants are depleted. Hence when $\beta_2/\beta_1 < 1$, the value of k_{r2} increases less rapidly than k_{r1} , leading to the decrease in k_{r2}/k_{r1} and the greater yield of B.

When $k_2/k_1 > 1$, it is found that there is a fall in electrode potential over the early stages. This can be understood by considering times just after the electrolysis has started. The conversion of A is δX_A and all the reacted A has formed B. If $C_{BO} = 0$ then the concentration of B now present is $C_{AO}\delta X_A$ and the total current is

$$\begin{aligned} i_T &= n_1 F k_{r1} C_{AO} (1 - \delta X_A) + n_2 F k_{r2} C_{AO} \delta X_A \\ &= F C_{AO} (n_1 k_{r1} + (n_2 k_{r2} - n_1 k_{r1} \delta X_A)) \quad (20) \end{aligned}$$

If $n_2 k_{r2} > n_1 k_{r1}$, then if the rate constants k_{r1} and k_{r2} have their initial values, i_T is greater than its original value. To counteract this, and maintain galvanostatic conditions, the potential must initially fall. As the total amount of electroactive species falls with the production of C, this decrease in potential is eventually reversed.

The fall in potential as the intermediate concentration increases towards its peak value causes the behaviour with different Tafel slopes to be reversed compared to the case when $k_2/k_1 \leq 1$.

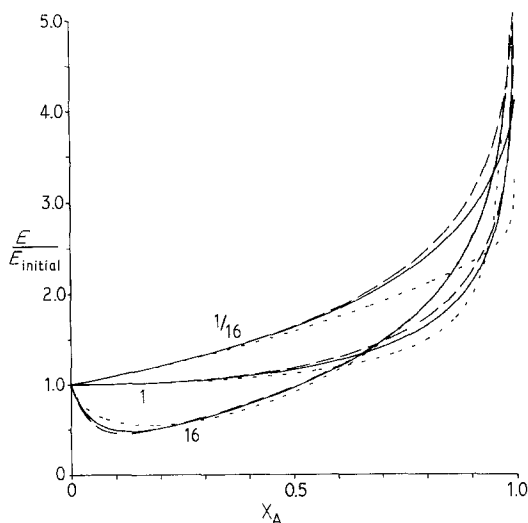


Fig. 2. Variation of electrode potential with conversion in the course of series Tafel reactions showing the effect of the ratio of Tafel slopes β_2/β_1 and rate constants k_2/k_1 . Potentials are measured relative to the reference system described following Equation 5. Values of k_2/k_1 are shown on the figure. Values of β_2/β_1 : $\frac{2}{3}$ (---); 1 (—); 2 (···).

Thus, when $\beta_2/\beta_1 < 1$, k_{r2} falls less rapidly than k_{r1} , increasing k_{r2}/k_{r1} and decreasing the yield of B.

The two main assumptions applied in obtaining the characteristics in Fig. 1 (i.e., no mass transport limitations and no solvent decomposition) will now in turn be lifted. Both factors will be more significant at high conversions.

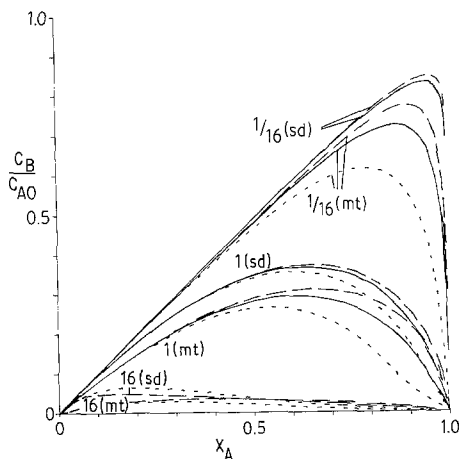


Fig. 3. The effect of mass transport and solvent decomposition on the yield-conversion curves for series Tafel reactions. Values of k_2/k_1 are shown on the figure. In addition, for curves marked mt, $k_L/k_{f10} = 5$ and for those marked sd, $k_H/k_1 = 1.0$ and $\beta_H/\beta_1 = 1.0$. Values of β_2/β_1 : $\frac{2}{3}$ (---); 1 (—); 2 (···).

3.1.1. The effect of mass transport. Fig. 3 shows the typical effect of varying degrees of mass transport on yield conversion behaviour. It is assumed that the mass transfer coefficients for species A and B are approximately equal. Two parameters feature in Fig. 3: the ratio k_2/k_1 and the ratio β_2/β_1 , with the effect of the latter on yield being highlighted.

The main effect of a decrease in mass transport rate is to reduce the yields obtained under similar conditions, due to intermediate B being more susceptible to further reduction. When $k_2/k_1 > 1$, the maximum value of B occurs at higher conversions as mass transport rate decreases and vice versa for $k_2/k_1 \leq 1$. The poorer yields experienced with low mass transport rates make current efficiencies low.

With low rates of mass transport and at high conversions, limiting currents for the reactions are approached. Hence, at some point, the condition of constant total current cannot be satisfied. In the performance characteristics this appears as a cut off in yield. In practice, however, the reaction will proceed, as the current balance will be maintained by the onset of solvent decomposition. This is considered in Section 3.1.2.

3.1.2. The influence of solvent decomposition. The influence of solvent decomposition (now referred to as hydrogen evolution) on the yield of B is also presented in Fig. 3. Four parameters feature, the ratio of rate parameters; k_2/k_1 , β_2/β_1 , k_H/k_1 and β_H/β_1 . With equal Tafel slopes for all reactions, yield-conversion characteristics are independent of the magnitude of the hydrogen evolution reaction because the ratio of rate constants k_{r2}/k_{r1} is unaffected by changes of electrode potential. When $\beta_2 < \beta_1$, increasing k_H decreases the yield of B because hydrogen evolution tends to hold down the electrode potential rise, reducing the relative increase in k_{r1} with respect to k_{r2} . When $\beta_2 > \beta_1$, increasing k_H increases the yield of B. The general effect of increasing hydrogen evolution is to reduce the variations in yields obtained with reactions of different Tafel slope ratios. This effect is more pronounced when $\beta_H > 2\beta_1$.

Although there are detectable differences in yield at varying amounts of hydrogen evolution,

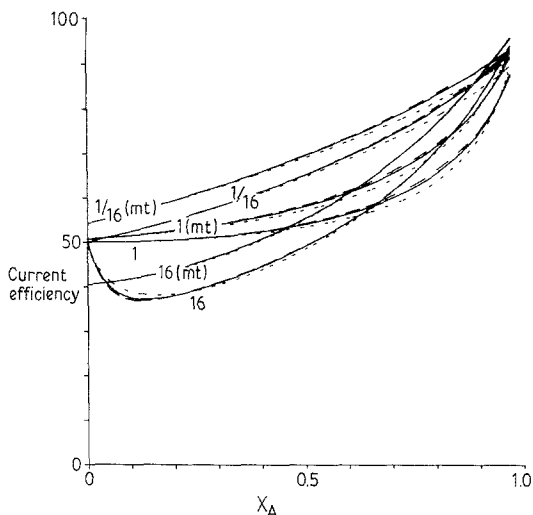


Fig. 4. The variation of hydrogen current efficiency for a series reaction accompanied by solvent decomposition: $k_H/k_1 = 1.0$, $\beta_H/\beta_1 = 1.0$, values of k_2/k_1 are shown on the figure. In addition, for curves marked mt, $k_L/k_{f10} = 5$.

the major effects of this reaction are with regard to the concentration–time characteristics (discussed later) and the current efficiency of the hydrogen evolution reaction (Fig. 4).

From Fig. 4 it can be seen that hydrogen current efficiency increases as the ratio k_2/k_1 decreases and as both the value of k_H and conversion increases. As might be expected, hydrogen current efficiency rises rapidly when high conversions are approached.

The effect of Tafel slope ratios is also seen to have some influence on hydrogen current efficiency. When $k_2/k_1 = 1$ and $1/16$, higher hydrogen current efficiencies are obtained with smaller β_2/β_1 , owing to k_{pH} increasing faster relative to k_{p1} and k_{p2} . With $k_2/k_1 = 16$, lower hydrogen current efficiencies tend to result, with smaller β_2/β_1 values. An interesting feature in this system is the minimum in hydrogen current efficiency experienced at intermediate conversions when $k_2/k_1 = 16$. This low hydrogen current efficiency corresponds to the region of maximum yield of B. This behaviour produces a maximum in overall current efficiency for the reaction of A to B when $k_2/k_1 > 1$.

When the Tafel slope of the hydrogen evolution reaction is greater than that of the first reaction step, hydrogen current efficiency is greater than that when $\beta_H = \beta_1$, for $k_2/k_1 < 1.0$.

When $k_2/k_1 > 1.0$ hydrogen current efficiency is lower than that for equal Tafel slopes ($\beta_H = \beta_1$).

3.1.3. The effect of solvent decomposition and mass transport. In most practical cases both mass transfer and solvent decomposition influence the course of the reaction, but their combined effects interact to make characterization of the behaviour with alteration of Tafel slopes or initial rate constant ratios difficult. Included in Fig. 4 are examples of the combined effects of variation in mass transfer coefficients and the ratios of rate constants of the two reactions of interest and that for solvent decomposition on the current efficiency for hydrogen evolution. It should be mentioned that the effect of mass transport resistance is to increase the rate of solvent decomposition and hence decrease the rate of the reactions involving the species of interest.

3.1.4. Concentration time characteristics. A typical set of yield versus time curves (using a dimensionless variable, $T = (i_T \sigma t)/(nFC_{A0})$ for the condition of equal Tafel slopes of both steps (i.e. β_2/β_1) are given in Fig. 5. The effect of mass transport and solvent decomposition has been ignored. Published experimental data for the anodic trifluoro-acetoxylation of chlorobenzene are included in Fig. 5 [12]. Here chlorobenzene

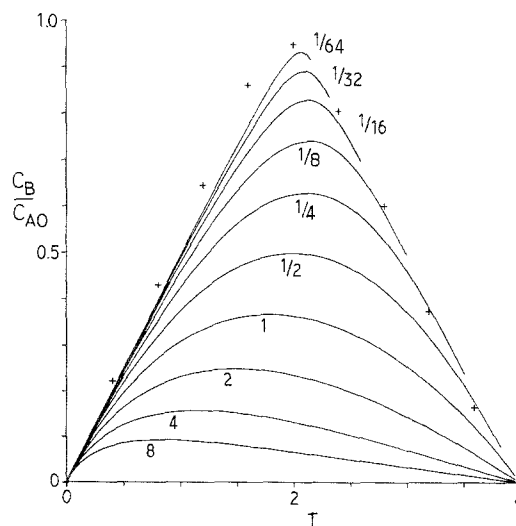


Fig. 5. Variation of yield with dimensionless time for a series reaction with equal Tafel slopes. Values of k_2/k_1 shown on figure. +, Experimental data for the anodic trifluoro-acetoxylation of chlorobenzene [12].

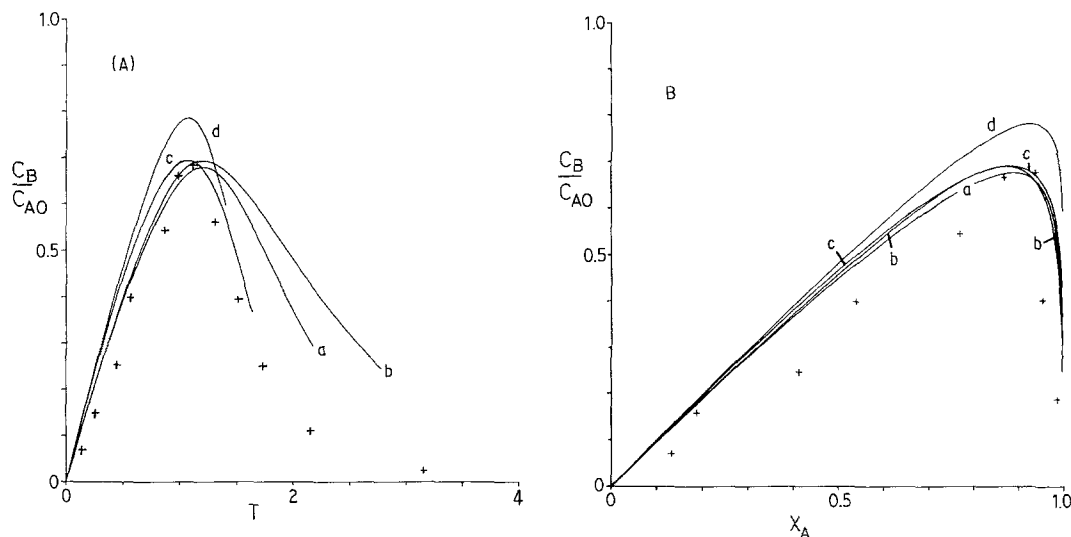


Fig. 6. Variation of product yield for a series reaction influenced both by mass transport and solvent decomposition. (A) Yield versus time; (B) yield versus conversion. (a) $k_2/k_1 = 0.17$; $\beta_2/\beta_1 = 0.5$; $k_L/(k_{f1})_0 = 5.0$; $k_H/k_1 = 0.05$; $\beta_H/\beta_1 = 0.5$. (b) $k_2/k_1 = 0.09$; $\beta_2/\beta_1 = 0.5$; $k_L/(k_{f1})_0 = 2.5$; $k_H/k_1 = 0.05$; $\beta_H/\beta_1 = 0.5$. (c) $k_2/k_1 = 0.17$; $\beta_2 = \beta_1$. (d) $k_2/k_1 = 0.09$; $\beta_2 = \beta_1$. +, Experimental data for the synthesis of 2,5-dimethoxyphenylacetate [7].

undergoes the series reaction to mono-trifluoroacetate and then di-trifluoroacetate (this species will produce tris-trifluoro-acetates on further oxidation). In this system, solvent decomposition only occurs at potentials 500 mV more positive than for the organic reactions and hence can be ignored. The behaviour of this oxidation appears to fit approximately into this category of series reaction with a ratio of $k_2/k_1 = 0.015$. This ratio is consistent with experimental polarization curves [12].

As mentioned previously, one of the main influences of solvent decomposition on series reactions is with regard to the yield versus time characteristics. Fig. 6a shows two yield versus time curves under conditions of solvent decomposition and also mass transport limitations. Also shown is the equivalent data for the condition $\beta_2 = \beta_1$ with solvent decomposition and no mass transport limitations. This clearly shows that the major effect of solvent decomposition is a tailing in the yield-time curve. The equivalent yield conversion curves for this system are shown in Fig. 6b. Little difference in the behaviour for the three conditions can be seen. Hence, accurate mass transport characterization, coupled with a knowledge of solvent decomposition kinetics, is a pre-requisite of experimental data analysis or product yield specification.

Even then inherent errors in experimental procedures may tend to obscure differences in kinetics. Hence, the yield versus time curves are likely to prove a necessary feature.

Experimental data for the synthesis of 2,5-dimethoxyphenylacetate from 1,4-dimethoxybenzene [7] are also shown in Fig. 6. A general fit of these data to predicted behaviour is exhibited, especially with regard to the tailing in the yield curve. However, it is not possible to improve the correlation of the data through manipulation of electrode kinetics, mass transport, etc. The difference between experimental data and predicted behaviour seems to lie in an imbalance of reactant and products reported in the organic phase. This first appears at low conversions where, regardless of the conditions of operation, yield should approximately equal the consumption of reactant. One explanation of the apparent unaccounted loss of product is the low solubility of the product in the aqueous phase to its saturation level.

3.1.5. Reduction of benzene. The electrochemical reduction of benzene using a dispersion of hydrocarbon and aqueous quaternary ammonium hydroxide has been investigated by Coleman and Wagenknecht [6]. Benzene reduction proceeds by a two electron transfer to 1,4-cyclo-

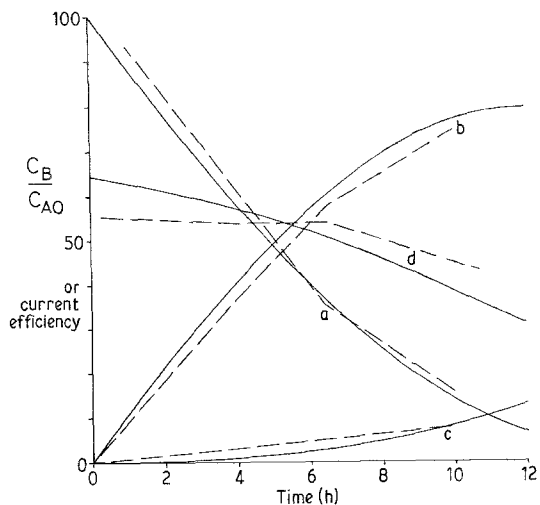
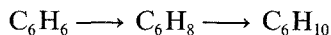


Fig. 7. Variation of yield and total current efficiency with time for a series reaction using the following kinetic parameters: $k_2/k_1 = 0.08$; $\beta_2 = \beta_1$; $k_H/k_1 = 1.1$; $\beta_H/\beta_1 = 0.5$. (a) Benzene; (b) 1,4-cyclohexadiene; (c) cyclohexene; (d) total current efficiency. Model predictions (—); experimental data [6] (---).

hexadiene, followed by a further two-electron transfer to cyclohexene:



This series reaction occurs simultaneously with the hydrogen reduction reaction. Typical published experimental batch reaction data [6] obtained at 60°C and 500 A m^{-2} is presented in Fig. 7 in the form of product distributions and the total current efficiency. Using the previously described reaction model the reaction behaviour is well represented by the following kinetic parameters (Fig. 7): $k_2/k_1 = 0.08$; $\beta_2 = \beta_1$; $k_H/k_1 = 1.1$; $\beta_H/\beta_1 = 0.5$.

The ratio k_H/k_1 relating to the hydrogen reduction reaction was obtained from the initial reported current efficiency. In the absence of polarization characteristics, the assumption of equal Tafel slopes for the two series reaction steps seemed to be reasonable. However, an improved fit to the experimental data can be achieved by adjusting the ratio of Tafel slopes.

3.1.6. Reversible electrochemical reactions. At low electrode potentials, electrochemical reactions exhibit reversible characteristics, the kinetics of which can frequently be expressed by the Butler–Volmer equation. The magnitude of the

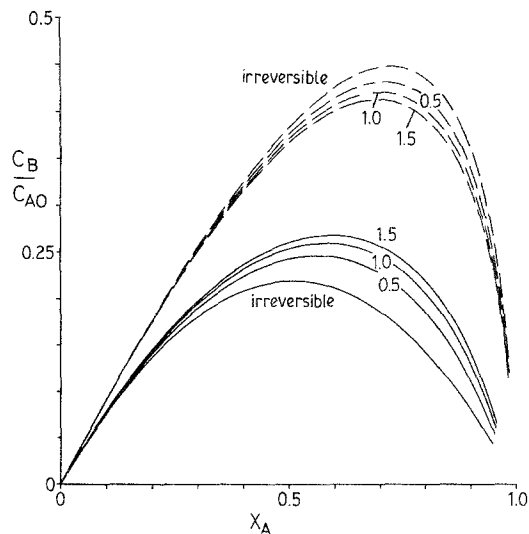


Fig. 8. Yield versus conversion curves for series reaction obeying a symmetric Butler–Volmer rate law. $\beta_1 = \alpha_1 = \beta_2 = \alpha_2$. Values of $(k_{b1})_0/(k_{r1})_0$ shown on figure. Values of k_2/k_1 : 2.0 (—); 0.5 (---).

reverse reaction in series reactions is likely to influence product yield and current efficiency as well as the overall rate of reaction. With potentiostatic operation series electrochemical reactions will exhibit characteristics akin to their chemical counterparts, i.e. equilibrium concentrations will be achieved. However, with galvanostatic operation the application of a constant current density will force the series reactions to completion, as conversion increases due to an ever increasing rise in electrode potential.

Typical yield versus conversion characteristics for a reversible series reaction following a symmetric Butler–Volmer rate law with equal Tafel slopes (i.e. $\beta_1 = \alpha_1 = \beta_2 = \alpha_2$) are given in Fig. 8. Two values of the initial ratio of the forward rate constants k_{r2}/k_{r1} are used, namely 2.0 and 0.5.

The effect of solvent decomposition and mass transport is not considered. When $k_{r2}/k_{r1} > 1$ the effect of an increasing degree of reversibility ((k_{b10}/k_{r10}) increasing) improves intermediate yields, i.e. low potential favours selectivity and current efficiency. Thus the performance of irreversible series reactions (which tend to exhibit relatively low intermediate yields) can be improved by operating at low potentials. When $k_{r2}/k_{r1} < 1$ the effect of increasing reversibility is to the detriment of product yield. High electrode

potentials are therefore imperative for good reactor performance.

3.2. Parallel electrochemical reactions

Consider the irreversible parallel reactions of A to produce components B and C unaffected by solvent decomposition or mass transport. Point selectivity of this parallel reaction is given by the ratio of the two reaction current densities, i_1/i_2 (assuming equal numbers of electrons transferred in each step), which is also equal to the ratio k_{f1}/k_{f2} . With potentiostatic operation this is fixed by the electrode potential. With galvanostatic operation, where potential varies, point selectivity varies uniquely with conversion depending on reaction kinetics. This variation will control overall selectivity, product yields and current efficiencies.

Product yields for the parallel reaction scheme are presented in Fig. 9 as a function of fractional conversion for a range of ratios of Tafel slopes, β_2/β_1 , and rate parameters, k_2/k_1 . When $\beta_2 = \beta_1$, product yield varies linearly with conversion [10]. With $\beta_2/\beta_1 > 1$, curvature in the product yield behaviour reflects the increase in electrode potential which increases the ratio k_{f2}/k_{f1} . More component C and less component B is formed at the same k_2/k_1 ratio as the ratio of Tafel slopes

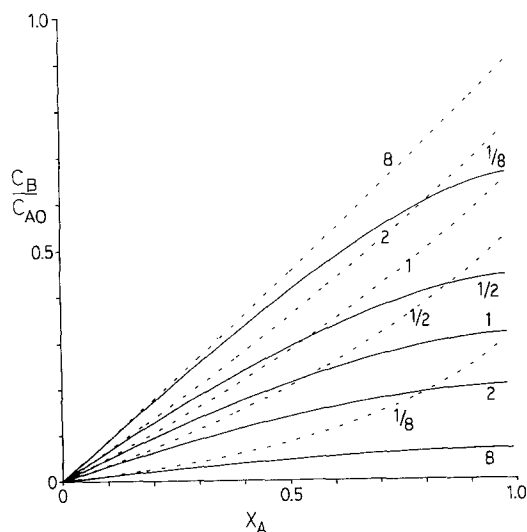


Fig. 9. Product yields versus conversion for parallel Tafel reactions. The effect of the ratio of Tafel slopes β_2/β_1 and rate constants k_2/k_1 . Values of k_2/k_1 shown on figure; $\beta_2/\beta_1 = 3.0$. C_C/C_{A0} , yield of C (---); C_B/C_{A0} , yield of B (—).

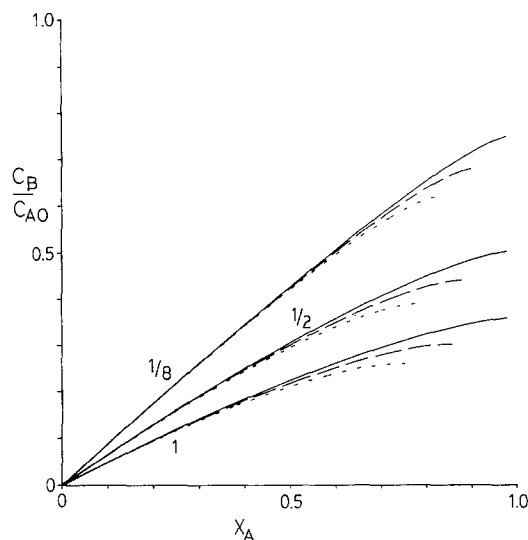


Fig. 10. The effect of mass transport on the yield of B for parallel Tafel reactions as a function of fractional conversion. Values of k_2/k_1 shown on figure; $\beta_2/\beta_1 = 2$. $K_L = \infty$ (—); $k_L/(k_{f1})_0 = 10$ (---); $k_L/(k_{f1})_0 = 5$ (···).

β_2/β_1 increases. At high values of k_2/k_1 , the effect is small as this ratio already tends to dictate product distribution.

However, at low values of k_2/k_1 (e.g. 1/8) product yields at complete conversion are almost equal when $\beta_2/\beta_1 = 3.0$. Even with a low Tafel slope ratio of 1.5, the ratio of product yields at complete conversion is approximately 3.7 (cf. 8 when $\beta_2 = \beta_1$). Overall, it is seen that the ratio of Tafel slopes in competing electrochemical reactions has considerable influence on reactor operation and product distribution.

3.2.1. The effect of mass transport. The influence of mass transport on product yield for the parallel reaction scheme can be seen in Fig. 10. The yield B is plotted as a function of conversion for different levels of mass transport expressed as the ratio k_L/k_{f10} . When $\beta_2/\beta_1 = 2$, the yield of B is seen to decrease with decreasing rate of mass transport. The reverse is true when $\beta_2/\beta_1 = 1.0$, with a slight increase of B at high conversions. As with the equivalent situation in the series reactions there comes a point at which practical operation (at or near limiting current) cannot be maintained without the onset of solvent decomposition. This will now be considered.

3.2.2. Onset of solvent decomposition. The effect of solvent decomposition on operation will be

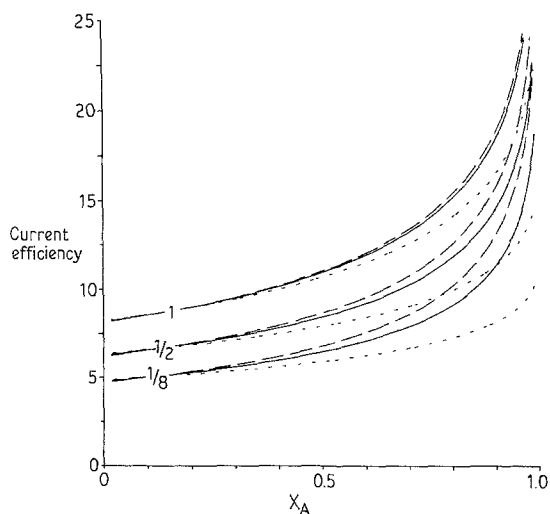


Fig. 11. Variation of hydrogen current efficiency as a function of conversion for a parallel reaction accompanied by solvent decomposition. Values of k_2/k_1 shown on figure; $k_H/k_1 = 0.1$, $\beta_H/\beta_1 = 1.0$. Values of β_2/β_1 : $\frac{2}{3}$ (---); 1.0 (—); 2.0 (···).

confined to the variation of the current efficiency of that reaction (hydrogen evolution) with conversion. Typical current efficiency curves are presented in Fig. 11 for a wide range of kinetic parameters of the parallel reactions. Hydrogen current efficiency, as expected, increases with conversion. It is also higher the smaller the difference between k_1 and k_2 , and when the ratio of Tafel slopes is such that this difference decreases during the course of the reaction (i.e. $\beta_2 > \beta_1$ when $k_2/k_1 < 1$ or $\beta_2 < \beta_1$ when $k_2/k_1 > 1$) this further increases the current efficiency for hydrogen evolution.

The effect of both a larger Tafel slope for hydrogen evolution and of the ratio k_H/k_1 is also, as expected, to increase the hydrogen current efficiency.

4. Conclusions

The present work has described the general behaviour of series and parallel electrochemical Tafel type reactions operating galvanostatically in plug flow or batch reactors. Variations in kinetic parameters, such as Tafel slopes, have been shown to have a significant effect on product yield and current efficiency. The initial

electrode potential and its subsequent variation with time can drastically affect product distribution.

For electrochemical reactors with known mass transport characteristics the behaviour of series reactions can be deduced from polarization characteristics. Where such characteristics are obscured by solvent decomposition or otherwise, an analysis of yield versus conversion and time data can provide the necessary kinetic information to provide subsequent predictions of behaviour. For parallel reactions this is a necessary requirement of any analysis.

It has also been shown that the performance of series and parallel reactions during galvanostatic operation differs markedly from that during potentiostatic operation, not least in the behaviour for reversible reactions where, for galvanostatic operation, the attainment of equilibrium concentrations is not possible. The major application of the work lies in the prediction of the performance of electrochemical processes during industrial operation.

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References

- [1] D. Pletcher, 'Industrial Electrochemistry', Chapman and Hall, London (1982).
- [2] N. L. Weinberg (ed.), 'Technique of Electro-organic Synthesis', Vol. 5, Part III, John Wiley and Sons, New York (1982).
- [3] G. P. Sakellariopoulos and G. A. Francis, *J. Electrochem. Soc.* **126** (1979) 1928.
- [4] G. P. Sakellariopoulos, *AIChE J.* **25** (1979) 781.
- [5] D. Pletcher and M. Razaq, *J. Appl. Electrochem.* **10** (1980) 575.
- [6] J. P. Coleman and J. H. Wagenknecht, *J. Electrochem. Soc.* **128**, (1981) 322.
- [7] M. Fleishmann, C. L. K. Tennakoon, P. Gough, J. H. Stevens and S. R. Korn, *J. Appl. Electrochem.* **13** (1983) 603.
- [8] F. Goodridge, R. E. Plimley, K. Lister and K. Scott, *ibid.* **10** (1980) 55.
- [9] K. Scott, *Electrochim. Acta* **30** (1985) 235.
- [10] *Idem*, *J. Appl. Electrochem.* **15** (1985) 837.
- [11] *Idem*, *ibid.* **15** (1985) 859.
- [12] G. Bockmair, H. P. Fritz and H. Gebauer, *Electrochim. Acta* **23** (1978) 21.