A single-equation experimental model of electrode polarization

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A numerical method, based on the principle of modified asymptote superposition, is described which can represent electrode polarization data by a single equation.

Nomenclature

a, b, c	empirical constants
d	parameter in Equation 3
D'	transpose of parameter vector D
I	electric current flow between electrodes
q	modifying parameter
V	voltage drop between anode and cathode

1. Introduction

The variation of the current flow between an anode and a cathode in an electrochemical cell with the magnitude of the imposed electric field (or with one of the electrode potentials) is determined by more than one physical phenomenon. In consequence, even in the simplest case of a single-ion electrode reaction, individual sections of the I–V curve are interpreted in terms of the non-Faradaic and residual currents, a charge transport-controlled portion and a mass transport-controlled portion, within appropriate potential regions where one of the physical phenomena, represented by appropriate mathematical relationships, is predominant. In transition intervals between regions of predominance no single theoretical relationship applies. Yet, for the purpose of process design, analysis, simulation and optimization, a single-equation model would have obvious advantages, especially for pocket- and desk-size computing devices. The purpose of this paper is to present a fast and efficient method of constructing such a model from experimental polarization data. The method is one specific application of the recently developed [1, 2] technique of modified asymptote superposition (MAS). This technique is particularly well suited, although by no means confined, to instances where conventional deterministic model construction is cumbersome and computation is time-consuming.

2. Theory

The MAS technique is introduced by a relatively simple case where, in a certain range of the independent variable vector X, a physical system is governed by mutually independent phenomena $Y_A = f_A(X)$ and $Y_B = f_B(X)$. Then, the *asymptotic* system behaviour can be described as

$$y = y_1 = \max [f_A(X); f_B(X)] \qquad (1a)$$

or

$$y = y_2 = \min [f_A(X); f_B(X)]. \qquad (1b)$$

Real system behaviour, of course, falls between Y_A and Y_B, except in a certain subset of X where asymptotic behaviour is closely approached. Assume for the sake of argument, that

$$f_A(X) = a + bX \qquad (2a)$$

$$f_B(X) = c \qquad (2b)$$

where X is a single independent variable. Then, as shown in Fig. 1, f_A and f_B represent the two asymptotes, but not any transition between them. The transition range may be represented (among other, but less convenient choices) by exponential functions of the type $1/(1 + \epsilon^z)$ and $1/(1 + \epsilon^{-z})$. Thus, the single equation

$$y = \frac{a + bX}{1 + \epsilon^{d(X-X_0)}} + \frac{c}{1 + \epsilon^{-d(X-X_0)}} \qquad (3)$$
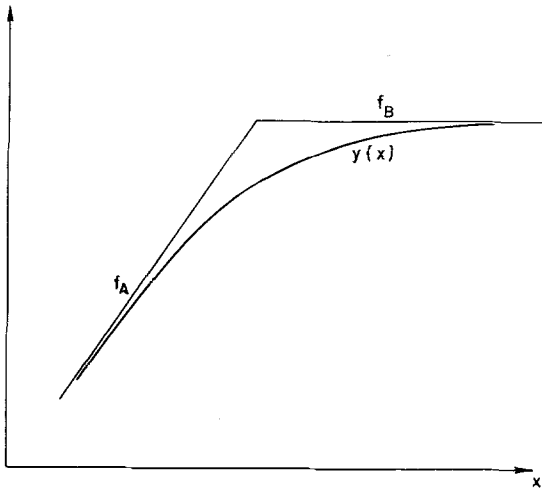
Fig. 1. Illustration of the asymptote superposition principle in the case of two distinct linear phenomena.

where X_0 is the appropriately chosen transition point, describes the *entire* behaviour within the range of interest of the independent variable. Not only is an exponential function representative of many physical (especially first-order) processes, but it also has a useful linear property for small deviations from X_0:

$$\frac{1}{1 + \epsilon^{\pm z}} \rightarrow \frac{1}{2} \mp \frac{z}{4} \qquad \text{for small } z. \quad (4)$$

This linear approximation ensures at least 0.001 accuracy for $|z| < 0.3$. The generalized form of Equation 3 may be written immediately as

$$y = \frac{f_A(X)}{1 + \epsilon^{D'(X - X_0)}} + \frac{f_B(X)}{1 + \epsilon^{-D'(X - X_0)}} \quad (5)$$

The 'sharpness' of transition depends on the numerical value of the D vector elements (or of the scalar d); for small values the predicted value of y at $X = X_0$ is the arithmetic average of the individual contributions. This property does not correspond to all known cases of physical superposition; in fact, if both independent phenomena are similar in magnitude about X_0, their intersection may result either in a dampening or in an augmenting effect on each other and the actual value of y may be appreciably different from the averaged values. In order to include this class, a modified form of asymptote superposition has to be used. Equations 1a and 1b are replaced by

$$y = Y_1 = \text{modified max } [f_A(X); f_B(X)] \quad (6a)$$

$$y = Y_2 = \text{modified min } [f_A(X); f_B(X)] \quad (6b)$$

and Equation 5 is modified to

$$y = \frac{f_A(X)}{1 + \epsilon^{D'(X - X_0) + q}} + \frac{f_B(X)}{1 + \epsilon^{-D'(X - X_0) + q}} \quad (7)$$

using the scalar-valued parameter q as modifier. The approach can be extended to more than two asymptotes without any conceptual difficulty and, indeed, electrode polarization corresponds to a three-asymptote case. Some of the important corollaries of the MAS principle are described in the following.

Let $z \equiv D'(X - X_0)$ and let X be in a close neighbourhood of the transition point X_0. Since within this neighbourhood f_A and f_B are nearly (but not truly) equal, one may write that $f_A \cong f_B = Y_A$ and Equation 7 may be written as

$$R_z \equiv \frac{y}{Y_A} \cong \frac{1}{1 + \epsilon^{z + q}} + \frac{1}{1 + \epsilon^{-z + q}} . \quad (8)$$

R_z is the fractional value of the actual system behaviour with respect to asymptotic behaviour at the transition point; if there were no deviation, R_z would be unity. Then, a deviation parameter $\alpha \equiv |R - 1|$ may be defined and Equation 8 rearranged to the form

$$\cosh(z) = \frac{1}{\alpha} \sinh |q| - \cosh |q| \quad (9)$$

regardless of the sign of q. One can plot a family of z versus $|q|$ curves with parameter α, as shown in Fig. 2. As z approaches zero, $|q| \rightarrow 2\alpha$ and the variation of z with $|q|$ becomes very steep; on the other hand, when $|q|$ becomes large, $\cosh(z)$ approaches the function $(\alpha^{-1} - 1)e^{|q|/2}$. Most importantly, the region of sharp variation is $|z| \leq 3$ and this fact will be important in establishing the single-equation polarization model. Finally, at $X = X_0$, $f_A = f_B$ and Equation 8 reduces to the simple relationship

$$R_0 = 2/(1 + \epsilon^q). \quad (10$$

3. A single-equation polarization model via the MAS principle

As shown in Fig. 3, where specific polarization data obtained in a previous study [1] have been plotted, the experimental I–V relationship may be approximated by three linear asymptotes in the
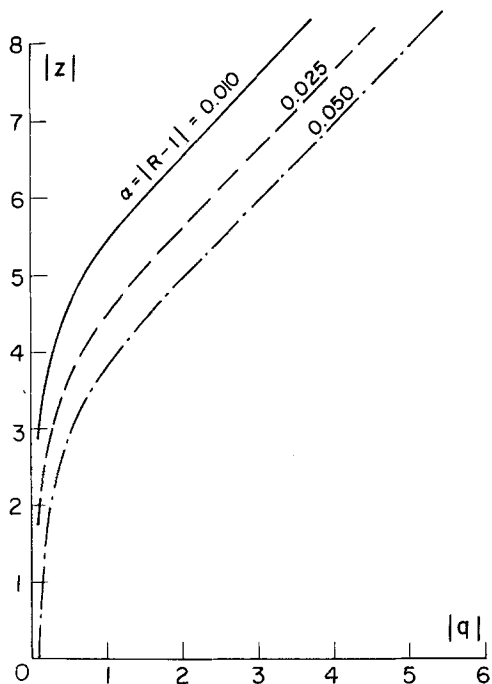
Fig. 2. The variation of $|z|$ with $|q|$ at selected values of α (Equation 9).

Fig. 3. Comparison of experimental polarization data with model prediction (Equation A4).

case of a single-ion cathode reaction followed by hydrogen generation:

$$I = a_1(V - b_1) \qquad I < I_{\mathrm{L}}$$

$$I = c \qquad\qquad I = I_{\mathrm{L}} \qquad (11)$$

$$I = a_2(V - b_2) \qquad I > I_{\mathrm{L}}.$$

Comparison with experimental data defines a lower deviation range (V_1, W_2) and an upper deviation range (V_2, W_2) at a predetermined error condition. The asymptote interception points are $V_1^* = b_1 + c/a_1$ and $V_2^* = b_2 + c/a_2$; the corresponding *experimental* current values are I_1^* and I_2^*. Let $R_1 = I_1^*/c$ and $R_2 = I_2^*/c$. Then, from Equation 10, $q_1 = \ln[(2 - R_1)/R_1]$ and $q_2 = \ln[(2 - R_2)/R_2]$. The next step is to establish the $(X - X_0)$ neighbourhood:

$$(X - X_0)_1 = \max \ [W_1 - V_1^*; V_1^* - V_1] \qquad (12a)$$

$$(X - X_0)_2 = \max \ [W_2 - V_2^*; V_2^* - V_2]. \qquad (12b)$$

Then,

$$z_1 = (X - X_0)_1 d_1 + q_1 \qquad (13a)$$

$$z_2 = (X - X_0)_2 d_2 + q_2. \qquad (13b)$$
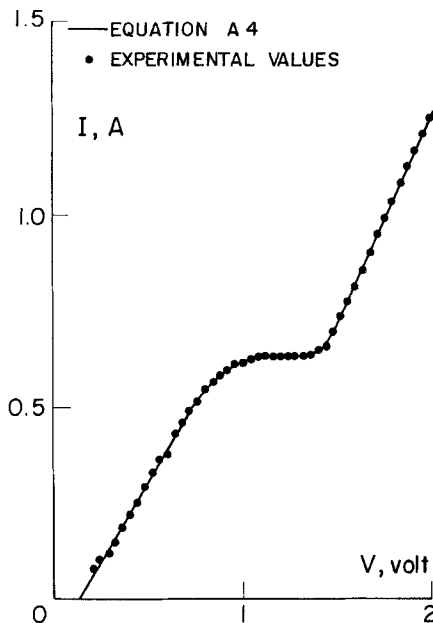
From Fig. 2, $|z| \leqslant 3$, hence one can obtain the

lowest and the highest possible values of d_1 and d_2:

$$(d_1)_{\min} = -\frac{3 + q_1}{(X - X_0)_1} \qquad (d_1)_{\max} = \frac{3 - q_1}{(X - X_0)_1} \qquad (14a)$$

$$(d_2)_{\min} = -\frac{3 + q_2}{(X - X_0)_2} \qquad (d_2)_{\max} = \frac{3 - q_2}{(X - X_0)_2}. \qquad (14b)$$

Rounding these values up to the *nearest integer* for the sake of convenience, their absolute values N_1 and N_2 are taken and the single-equation model may be written as

$$I = \frac{a_1(V - b_1)}{1 + e^{N_1(V - V_1^*) + q_1}}$$

$$+ \frac{c}{1 + e^{-N_1(V - V_1^*) + q_1} + e^{N_2(V - V_2^*) + q_2}} \qquad (15)$$

$$+ \frac{a_2(V - b_2)}{1 + e^{-N_2(V - V_2^*) + q_2}}.$$

Fig. 3 clearly indicates that the model can fit experimental data in the *entire* polarization range at high accuracy if the above steps are executed carefully. Details of the numerical illustration are described in the Appendix. It follows directly from the above that the method of modified

asymptotic superposition is appreciably faster and requires a good deal less computational effort than using conventional orthogonal polynomials when system behaviour is determined by competing and locally predominant phenomena. Polarization is a particularly good illustration of this statement, manifest by Equation 15 (and Equation A4 in the specific example quoted in the Appendix) which can readily be programmed into small computing devices. However, the usefulness of this approach is by no means confined to this instance and numerous applications in various areas of science and engineering can be envisaged.

Acknowledgement

Appendix. Numerical illustration

The first two columns in Table 1 contain experimentally observed current versus cell voltage drop data pertaining to an electrolytic cell [2] in which a $0.54 \, mol \, dm^{-3} \, CuSO_4 + 0.98 \, mol \, dm^{-3} \, H_2SO_4$ solution was electrolysed at $24° \, C$ between two cylindrical copper electrodes of $12.5 \, cm^2$ area each, placed vertically 1.5 cm apart. The graphically constructed asymptotes are as follows:

$$I = 0.813 \, (V - 0.1244) \qquad I < I_L \qquad (A1)$$

$$I = 0.632 \qquad I = I_L \qquad (A2)$$

$$I = 1.071 \, (V - 0.8347) \qquad I > I_L. \qquad (A3)$$

The experimental points are joined with a smooth curve (Fig. 3); one finds that $V_1^* = 0.1244 + 0.632/0.813 = 0.9108$ and $V_2^* = 0.8347 + 0.632/1.071 = 1.4248$. Hence, from the smooth curve, $I_1^* = 0.59$ and $I_2^* = 0.65$; hence $R_1 = 0.59/0.632 = 0.933$ and $R_2 = 0.65/0.632 = 1.0285$. Using Equation 10, $q_1 = \ln [(2 - 0.933)/0.933] = 0.134$ and $q_2 = \ln [(2 - 1.0285)/1.0285] = -0.057$ are computed. Comparing Equations A1–A3 with the experimental data, major deviations between asymptotes and experimental points appear in the $V_1 = 0.76$, $W_1 = 1.08$ and $V_2 = 1.36$, $W_2 = 1.48 \, V$ range. Hence, $(X - X_0)_1 = \max (1.08 - 0.9018; 0.9018 - 0.76) = 0.1782$ and $(X - X_0)_2 = \max (1.48 - 1.4248; 1.4248 - 1.36) = 0.0648$.

Table 1. Comparison of experimental and model-computed current flow in the experimental cell

Potential drop between electrodes (V)	Current (A)	
	Experimental	Computed by Equation A4
0.20	0.078	0.061
0.24	0.098	0.094
0.28	0.120	0.127
0.32	0.147	0.159
0.40	0.220	0.224
0.44	0.251	0.257
0.48	0.290	0.289
0.52	0.327	0.321
0.56	0.363	0.354
0.60	0.376	0.387
0.64	0.429	0.420
0.68	0.459	0.452
0.72	0.490	0.485
0.76	0.516	0.515
0.80	0.541	0.542
0.84	0.561	0.565
0.88	0.580	0.581
0.92	0.596	0.596
0.96	0.610	0.612
1.00	0.616	0.623
1.04	0.624	0.623
1.08	0.629	0.631
1.12	0.632	0.632
1.16	0.632	0.632
1.20	0.632	0.632
1.24	0.633	0.632
1.28	0.633	0.632
1.32	0.633	0.632
1.36	0.637	0.632
1.40	0.643	0.638
1.44	0.655	0.658
1.48	0.696	0.692
1.52	0.735	0.734
1.56	0.776	0.777
1.60	0.816	0.820
1.64	0.857	0.862
1.68	0.900	0.905
1.72	0.943	0.948
1.76	0.988	0.991
1.80	1.033	1.034
1.84	1.080	1.077
1.88	1.122	1.120
1.92	1.165	1.162
1.96	1.208	1.205
2.00	1.249	1.248

Then, using Equations 13 and $z = \pm 3$, $-17.586 < d_1 < 16.083$ and $-45.416 < d_2 < 47.175$. Since the numerical accuracy of the exponential terms is only mildly affected by doing so, the convenient

round numbers $|d_1| = 20$ and $|d_2| = 50$ are chosen. The single-equation model can now be written as

$$I = \frac{0.813(V - 0.1244)}{1 + \epsilon^{20(V-0.9018)+0.134}}$$

$$+ \frac{0.632}{1 + \epsilon^{-20(V-0.9018)+0.134} + \epsilon^{50(V-1.4248)-0.057}}$$

$$+ \frac{1.071(V - 0.8347)}{1 + \epsilon^{-50(V-1.4248)-0.057}} . \tag{A4}$$

Comparison of the variation of current with voltage drop predicted by Equation A4 in Table 1 with the experimental results indicates very close agreement.

References

[1]   M. S. Quraishi, PhD Thesis, University of Waterloo (1978).

[2]   M. S. Quraishi and T. Z. Fahidy, *Electrochim. Acta* **25** (1980) 591.