Potential program invariant representation of voltammetric measurement results of reversible redox couples

Tamás Pajkossy

KFKI Atomic Energy Research Institute, H-1525 Budapest 114, POB 49, Hungary

Abstract

The use of a transformation is proposed by which the results of voltammetric measurements based on diffusion of reversible redox couples to an electrode of any geometry can be presented in the form of a standardized function T. To characterize the time dependence of the diffusion we define the function $G(s)$ by writing the Cottrell response of the species i in the form $\bar{I}_{i,\text{Cottrell}}(s) = \pm K_i c_i^* G(s)/s$ where K_i is a constant, c_i^* the bulk concentration of the diffusing species, s the Laplace variable; then we show that: (a) any voltammetric curve ($\bar{I}(s)$) measured in the same system can be transformed to potential program invariant form by computing the function $T = L^{-1}\{\bar{I}(s)/G(s)\}$; (b) the diffusional admittance of the same system is expressed by $Y(s) = G(s)\,\mathrm{d}T/\mathrm{d}E$; (c) one can perform the transformation yielding the potential program invariant form by passing the $I(t)$ function through a numeric filter having $1/G(s)$ transfer characteristics.

Keywords: Diffusion-controlled electrode process; Voltammetric measurements; Potential program invariant representation; Numerical transformation

1. Introduction

Diffusion-controlled electrode reactions are fairly frequent in electrode kinetics and a number of electroanalytical techniques employ these. The measured voltammetric results [1] tend to be presented in various ways: usually current I is plotted as function of time t, or electrode potential E. The $I(t)$ function, however, strongly depends on the shape of the $E(t)$ potential program function; thus the results measured with different $E(t)$ functions are not directly comparable with each other. Generally speaking, the measured response is characteristic not only of the measured system, but is also affected by the measurement conditions. Whenever possible, one should separate the effects due to the instrumental conditions from the measurement results, and the final results should contain parameters of the measured system only. In the context of voltammetry, in certain cases this can be achieved by transforming the measured $I(t)$ curve to a form which is

independent of the $E(t)$ potential program function, i.e. to a potential program invariant form, or, as in the case of small potential excursions from a steady value, to a perturbation-invariant form. For example, impedance is a perturbation-invariant function because the measured impedance does not 'remember' the actual perturbation function. Another example might be the semi-integration of the voltammetric results of reversible redox couples: the semi-integral of the current is independent of the potential sweep parameters.

The present communication is a synthesis of the statements of two previous papers. First, about a decade ago, Oldham [1] showed that under pure diffusion control the $I(t)^* g(t)$ convolution (where the $g(t)$ convolution function is characteristic of the electrode geometry) is a linear function of the surface concentrations of the (reversible) redox couple, and as such is a potential program invariant function. In the other publication [2], I dealt with various voltammetric (mostly polarographic) methods employing semi-infinite planar diffusion and showed how to transform their result into a form (being the Warburg coefficient of the redox couple) which depends only on solution parameters and does not depend on the instrumental conditions of the actual measurement.

Here I assume electrodes of any geometry at which

---

[1] The term voltammetry here is used to represent any type of electrochemical measurement in which the relations of current, electrode potential and time are investigated, e.g. cyclic voltammetry, chronocoulometry, chronopotentiometry, etc.

Table 1
Cottrell responses and transformations yielding potential program invariant forms for simple diffusion geometries: f_g, a factor of geometry [4]; $f_h = 0.620\nu^{-1/6}\Omega^{1/2}$, a hydrodynamical factor, where ν stands for kinematic viscosity and Ω is the angular frequncy of the rotating disk electrode (see Chapter 8.3.2 of Ref. [5])

Geometry of diffusion	Condition	Cottrell response, $\bar{I}(s)$	K_i	$G(s)$	$\exp(nF(E_0 - E_{1/2})/RT)$	$T(t)$
Semi-infinite (planar electrode)		$nFAc_i^* \sqrt{D_i}$	$nFA\sqrt{D_i}$	$\sqrt{s}$	$\sqrt{D_R/D_O}$	$\frac{1}{\sqrt{\pi}} \int_{-\infty}^{t} \frac{I(\tau)\,d\tau}{\sqrt{t-\tau}}$
Spherical (spherical electrode, radius r_0)	$t \gg r_0^2/D_i$	$nF(A/r_0)c_i^* D_i/s$	$nF(A/r_0)D_i$	1	D_R/D_O	$I(t)$
Convective diffusion (rotating disk electrode)	$t \gg D_i/\delta_0^2$	$nF(Af_h)c_i^* D_i^{2/3}/s$	$nF(Af_h)D_i^{2/3}$	1	$(D_R/D_O)^{2/3}$	$I(t)$
Bounded (thin layer cell, spacing l_0)	$t \gg D_i/l_0^2$	$\dfrac{nF(A/l_0)c_i^* D_i}{s + 2D_i/l_0^2}$	$nF(2Al_0)$	s	1	$\int_{-\infty}^{t} I(\tau)\,d\tau$
Fractal (fractal dimension of the electrode D_f)		$nF(Af_g)c_i^* D_i^{\alpha}s^{\alpha-1}$	$nF(Af_g)D_i^{\alpha}$	s^{α}	$(D_R/D_O)^{\alpha}$	$\frac{1}{\Gamma(\alpha)} \int_{-\infty}^{t} \frac{I(\tau)\,d\tau}{(t-\tau)^{1-\alpha}}$

charge transfer of pure diffusion control proceeds, and disregard all complications due to slow charge transfer reaction, *IR* drop, and double layer charging. In this way I show how the results of voltammetric measurement results are to be transformed to get the potential program invariant form, and show the connection between the potential program invariant form and the diffusional impedance. In the last part, the possibilities of the numerical transformation yielding the perturbation-invariant forms are outlined, and a demonstration experiment together with a numerical transformation are presented.

2. Potential program invariant forms and transformations

Keeping in mind that the case of pure diffusion control will be considered, let us start from the equation expressing that the surface concentrations and fluxes of the *i*th species are in linear connection with each other in the Laplace plane (throughout this paper the Laplace variable is denoted by *s*). This equation was first derived for the case of diffusion geometries with one spatial coordinate only, see Ref. [3]; a more general derivation is presented in Appendix A.

$$\bar{c}_i^* - \bar{c}_i^s = \bar{I}_i f_i(s) \tag{1}$$

where c_i^s, c_i^*, and I_i are respectively the surface and bulk concentrations, and the current carried by the *i*th species; the overlines here and hereafter indicate that these quantities are Laplace transformed ones. For the sake of later convenience, let us introduce the function $G_i(s)$ and the constant K_i through the equation

$$f_i(s) = \pm \frac{1}{K_i G_i(s)} \tag{2}$$

where all the constant terms of $1/f_i(s)$ are factored out to yield the positive K_i, and thus the sign is positive and negative for anodic and cathodic currents respectively. (The splitting of $1/f_i(s)$ to a constant and to an *s*-dependent term is not unique in certain cases; I shall return to this point in Section 3). Let us rewrite Eq. (1) to the form

$$\bar{c}_i^* - \bar{c}_i^s = \frac{\pm \bar{I}_i}{K_i G_i(s)} \tag{3}$$

Probably the simplest method of calculating (or measuring) K_i and $G_i(s)$ is to assume (or cause by employing a suitable potential jump) a step function of surface concentration $c^s(t)$, and then calculate (or measure) the $I(t)$, current–time, relationship (the Cottrell current) in the cell of a particular geometry. By taking it into account that the Laplace transform of a unit step function is $1/s$, it directly follows from Eq. (3) that

$$\bar{I}_{i,\text{Cottrell}} = \pm K_i c_i^* G(s)/s \tag{4}$$

The K_i and $G_i(s)$ expressions, along with the Cottrell responses for certain simple geometries, are listed in Table 1. In what follows, without restricting generality, we assume that there is one redox couple in the solution only; that is, *i* stands for O or R (oxidized and reduced species respectively). [2] Note that K_i and $G_i(s)$ are characteristics of the *i*th species; to obtain a simple formalism, we shall regard the $G_i(s)$ functions of the oxidized and reduced forms of the couple to be identical. (This is exactly true for the simple cases, e.g. in the case of semi-infinite planar diffusion, see Table 1; or can be regarded to be a reason-

---

[2] With the assumption of more than one redox pair, one gets equations containing sums of admittances and currents; however, these equations are otherwise of the same structure as those derived here.

able approximation for the complex cases, see Section 3.)
Thus, here we introduce the function

$$G(s) \equiv G_O(s) \approx G_R(s) \tag{5}$$

which is either independent of the diffusion coefficients or contains some combination of those. As the species cannot accumulate at the interface, the absolute values of the diffusional fluxes of the members of the redox couple are equal, and only one redox couple is present (see footnote 2) therefore index i of current I_i is omitted hereafter.

The $G(s)$ function is of central importance in characterizing voltammetry of reversible redox couples. First we show how to transform the $I(t)$ curves of voltammetric experiments carried out in a large potential range $(E - E_{1/2} \gg RT/F)$ of reversible redox couples into a potential program invariant form, and then calculate the diffusional (Warburg) admittance of the same system. During the latter calculation, small potential perturbation $(\delta E \ll RT/F)$ is used. I shall refer to these two regimes as large signal and small signal responses respectively.

2.1. Large signal response

The surface concentrations c_O^s and c_R^s can be calculated by using Eq. (3), i.e. this equation is to be applied to these two species. In the case of a reversible redox couple the ratio of the surface concentrations c_O^s and c_R^s is determined by the Nernst equation:

$$E = E_0 + \frac{RT}{nF} \ln\left(\frac{c_O^s}{c_R^s}\right) \tag{6}$$

where E_0 is the formal potential of the redox couple. By introducing the K constants defined by Eq. (3), the following form of this equation will also be used:

$$E = E_{1/2} + \frac{RT}{nF} \ln\left(\frac{K_O c_O^s}{K_R c_R^s}\right) \tag{7}$$

where $E_{1/2}$, the half-wave potential, is defined as

$$E_{1/2} = E_0 + \frac{RT}{nF} \ln\left(\frac{K_R}{K_O}\right) \tag{8}$$

c_O^s and c_R^s can be calculated by performing the inverse Laplace transform (L^{-1}) of the right-hand side of Eq. (3) then substituting the result into Eq. (6):

$$E = E_0 + \frac{RT}{nF} \ln\left\{\frac{c_O^* + L^{-1}[\bar{I}/(G(s)K_O)]}{c_R^* - L^{-1}[\bar{I}/(G(s)K_R)]}\right\} \tag{9}$$

Let us define the function T as

$$T = L^{-1}(\bar{I}/G(s)) \tag{10}$$

and define the constants $T_c = -K_O c_O^*$ and $T_a = K_R c_R^*$ (these are the cathodic and anodic limiting transformed currents respectively). By substitution we obtain an equation which has the same form as the well-known polarographic wave:

$$E = E_{1/2} + \frac{RT}{nF} \ln\left(\frac{T - T_c}{T_a - T}\right) \tag{11}$$

By expressing T we get the following equation:

$$T = \frac{T_a + T_c}{2} + \frac{T_a - T_c}{2} \tanh\left[\frac{nF}{2RT}(E - E_{1/2})\right] \tag{12}$$

It is useful also to give the function dT/dE:

$$\frac{dT}{dE} = \frac{nF}{4RT} \frac{T_a - T_c}{\cosh^2\left[\frac{nF}{2RT}(E - E_{1/2})\right]} \tag{13}$$

T and dT/dE are potential program invariant functions: the one and same $T(E)$ function is obtained if any voltammogram of a reversible redox couple is transformed by the appropriate transformation function.

2.2. Small signal response

Let us start from Eq. (6): in other words, by stating that the ratio of c_O^s and c_R^s is determined by the Nernst equation; however, the $\delta E(t)$ potential perturbation also causes the surface concentration terms to have a perturbation term:

$$E + \delta E(t)$$
$$= E_0 + \frac{RT}{nF} \ln\left(\frac{c_{O,a}^s + \delta c_O^s(t)}{c_{R,a}^s + \delta c_R^s(t)}\right)$$
$$= E_0 + \frac{RT}{nF} \ln\left(\frac{c_{O,a}^s}{c_{R,a}^s}\right) + \frac{RT}{nF} \ln\left(\frac{1 + \delta c_O^s(t)/c_{O,a}^s}{1 + \delta c_R^s(t)/c_{R,a}^p}\right) \tag{14}$$

Here, the subscript a refers to the fact that those concentrations are averaged over the period of perturbation. Let us separate the d.c. and perturbation terms; let us expand the latter into a series and drop all but the linear terms:

$$\delta E(t) = \frac{RT}{nF} \ln\left(\frac{1 + \delta c_O^s(t)/c_{O,a}^s}{1 + \delta c_R^s(t)/c_{R,a}^p}\right)$$
$$\approx \frac{RT}{nF}\left(\frac{\delta c_O^s(t)}{c_{O,a}^s} - \frac{\delta c_R^s(t)}{c_{R,a}^s}\right) \tag{15}$$

The Laplace transform for both sides of Eq. (15) yields

$$\overline{\delta E} = \frac{RT}{nF}\left(\frac{\overline{\delta c_O^s}}{c_{O,a}^s} - \frac{\overline{\delta c_R^s}}{c_{R,a}^s}\right) \tag{16}$$

The connection between perturbations of surface concentration and current can be calculated on the basis of Eq. (3):

$$\overline{\delta c_i^s} = \mp \overline{\delta I}/(G(s)K_i) \tag{17}$$

Let us combine Eqs. (16) and (17), keeping in mind the sign convention adopted:

$$\overline{\delta E} = \frac{RT}{nF} \frac{\overline{\delta I}}{G(s)}\left(\frac{1}{K_O c_{O,a}^s} + \frac{1}{K_R c_{R,a}^s}\right) \tag{18}$$

The admittance $Y(s)$ is of the following form:

$$Y(s) \equiv \frac{\bar{\delta I}}{\bar{\delta E}}$$

$$= \frac{nF}{RT} G(s) \left(\frac{1}{K_O c_{O,a}^s} + \frac{1}{K_R c_{R,a}^s} \right)^{-1} \tag{19}$$

Note that the surface concentrations are the steady state concentrations. They can be calculated by performing the inverse Laplace transform of Eq. (3) yielding

$$c_{O,a}^s = c_O^s(t) = c_O^* - L^{-1}[\bar{I}/(G(s)K_O)] \tag{20}$$

and

$$c_{R,a}^s = c_R^s(t) = c_R^* + L^{-1}[\bar{I}/(G(s)K_R)] \tag{21}$$

Multiplying Eqs. (20) and (21) by K_O and K_R respectively, then adding the two equations together, we find that

$$K_O c_{O,a}^s + K_R c_{R,a}^s = K_O c_O^* + K_R c_R^* \tag{22}$$

Taking into account the Nernst equation (Eq. (6)) as well we can express $c_{O,a}^s$ and $c_{R,a}^s$, and then by substituting these surface concentrations into Eq. (19) we obtain

$$Y(s) \equiv \frac{\bar{\delta I}}{\bar{\delta E}}$$

$$= \frac{nF}{RT} G(s) \left\{ \frac{K_O c_O^* + K_R c_R^*}{4\cosh^2\left[\dfrac{nF}{2RT}(E - E_{1/2})\right]} \right\} \tag{23}$$

or in another form:

$$\frac{Y(s)}{G(s)} = \frac{nF}{4RT} \frac{T_a - T_c}{\cosh^2\left[\dfrac{nF}{2RT}(E - E_{1/2})\right]} \tag{24}$$

The right-hand side of Eqs. (13) and (24) are of the same form: the dT/dE function is equal to the coefficient of the admittance, irrespective of the actual form of $G(s)$. The large signal and the small signal response functions are not independent of each other: they are connected to each other through differentiation. In other words, by changing from s to the usual $i\omega$ frequency variable of Y, the equation

$$\frac{Y(i\omega)}{G(i\omega)} = \frac{\partial T}{\partial E} \tag{25}$$

is valid for any diffusion geometry.

3. Discussion

(1) The fact that in the case of semi-infinite diffusion geometry, semi-integration yields a program potential independent form of the voltammetric results of reversible couples has been known since the early 1970s [6,7]; the

connection between the semi-integrated current and the Warburg coefficient for semi-infinite diffusion was demonstrated in Ref. [2]. The present paper gives a generalization of the former two ideas. However, if we consider other impedances which are relevant in electrochemistry, then the connection between the potential function invariant transformed current and the diffusional impedance is not surprising. Consider the following two cases:

(a) Whenever the current immediately follows, the potential changes (e.g. in the case of ideal, slow charge transfer), the current itself is a program potential invariant form, i.e. $T = I$; its derivative with respect to electrode potential is the reciprocal of the local differential resistance R. In other words, $dT/dE = Y_R$.

(b) If the interface is capacitive, the current depends, however, on the integral of the current; the charge Q does not depend on the potential program, i.e. $T = Q$. The dQ/dE derivative is the differential capacitance C; thus $dT/dE = C = Y_C/(i\omega)$.

In both cases Eq. (25) is obeyed; the connection of diffusional impedance and the transformed current fit into the same scheme.

(2) The use of potential perturbation invariant forms has the advantage of the easy IR_u drop correction (here R_u stands for the uncompensated solution resistance). Instead of plotting T vs. E, one should plot T vs. $E - IR_u$. (This statement is a triviality for polarization curves (when $T = I$); for convolution voltammetry this statement was first made in Ref. [6].)

(3) The splitting of $1/f(s)$ to a constant K_i and an s-dependent $G(s)$ function (see Eq. (2)) is unique in the simplest cases only. In Table 1 we summarize the 'textbook-cases' with simple functional forms of $\bar{I}(s)$ (these equations can be found in electrochemical textbooks, e.g. in Ref. [5], or can easily be derived). In these cases, by factoring out all constant terms, we obtain $G(s)$ as some power of s. Note that T depends on diffusion geometry: for example, the limits $(= K_i c_i^*)$, the half-wave potential, and the dimension of the T function are all different for planar and for ultramicroelectrodes. Therefore, one cannot compare directly the numerical values of the 'planar T' and the 'spherical T' functions, although their functional form is the same, cf. Eqs. (11)–(13).

The splitting of $1/f(s)$ is not unique when more complex cases of diffusion are considered (for analytical solutions, see e.g. Ref. [1]). This is the case, for example, with the full equation describing diffusion to a spherical electrode. The Cottrell response is given as

$$\bar{I} = nFAr_0 c_i^* \left(\frac{1}{\sqrt{s\tau_i}} + \frac{1}{s\tau_i} \right) \text{ with } \tau_i = \frac{r_0^2}{D_i} \tag{26}$$

thus

$$K_i G(s) = nFAr_0 \left(\sqrt{\frac{s}{\tau_i}} + \frac{1}{\tau_i} \right) \tag{27}$$

The constants can be factored out in one of two ways, yielding either

$$K_i = nFA\sqrt{D_i}; \quad G(s) = \sqrt{s} + \frac{1}{\sqrt{\tau_i}} \tag{28}$$

or

$$K_i = nF\frac{A}{r_0}D_i; \quad G(s) = 1 + \sqrt{s\tau_i} \tag{29}$$

Either can be used; however, the transforms based on Eqs. (28) and (29) yield the 'planar T' and the 'spherical T' functions respectively.

(4) The question arises how to perform numerically the transformations on actual data sets. In the simple cases listed in Table 1, the $G(s)$ function is independent of D_i, thus the same transform is to be applied in the numerator and the denominator of Eq. (9). The transformations are simple and can be carried out by using the equations in the rightmost column of Table 1. In the more complex cases the $G(s)$ functions are D_i-dependent (see Eq. (28) or Eq. (29)). This difficulty, however, can be overcome by applying the approximation of Eq. (5), i.e. instead of the $G_i(s)$ functions of the individual ions, we use some average $G(s)$.

Unfortunately, the transformation to be carried out in the time domain is far from being trivial. Algorithms can be based on the convolution integral discussed in Ref. [1]; however, this method requires a well defined, simple electrode geometry. Another disadvantage of this calculation method is that the computational time is proportional to N^2, where N is the number of data points. We suggest the use of numerical filters by which much faster calculations can be carried out (the computational time is proportional to $N \ln(N)$).

To obtain T we have to pass the digitized $I(t)$ signal through a numerical 'filter' which has a transfer function of $1/G(s)$. Such a numerical filter can be designed in two different ways.

The first is a widely accepted procedure for processing periodic data. Whenever the $I(t)$ function is, or can be regarded as, periodic, e.g. if it is the current response of a full cycle of some potential program, then a procedure based on the Fourier transform can be applied as follows:

• the $I(t)$ function is transformed to an $\tilde{I}(\omega)$ spectrum by Fourier transform;
• the $\tilde{I}(\omega)$ spectrum is then multiplied by $1/G(\omega)$;
• finally, the $\tilde{I}(\omega)/G(\omega)$ spectrum is inverse Fourier-transformed.

This procedure can, to some extent, also be used for filtering non-periodic data sets with various numerical approximations, e.g. 'windowing'.

The second procedure employs recursive numeric filters, an archetype of which is the following. Assume that an 'input' data set consists of data X_i; the numeric filter

produces 'output' data Y_i; the connection between them is defined by

$$Y_i = w_1 X_i + w_2 Y_{i-1} \tag{30}$$

where w_1 and w_2 are weighting factors. One can show that this recursive algorithm works as an amplifying (or attenuating) low-pass filter. We can construct arrays of such recursive filters with certain distributions of amplification factors and time constants; with suitably chosen parameters the overall transfer function may approximate the $1/G(s)$ characteristics to a reasonable extent. As to two examples, one can refer to papers showing that semi-integration [8] and Riemann–Liouville transform of order q [4] can be carried out in this way.

Calculation of the amplification factors and time constants of such a numeric filter array, in the general case, is not a simple task; this will be discussed in a separate paper. However, in certain cases, there exists an approximate solution of this problem: by slight modifications of the FRLT algorithm of Ref. [8] one can get filter transfer functions which fairly well approximate the $1/G(s)$ function. For example, this is the case when a small microdisk electrode of diameter in the order of magnitude of 10 to 100 μm is considered. In the usual time frame of the electrochemical experiments such electrodes show a transition between planar and spherical diffusion, that is $G(s) \propto s^{1/2}$ and $G(s) = $ constant at high and low s values respectively (cf. the first and second rows of Table 1). Accordingly, a numerical filter yielding the 'planar T' therefore has the characteristics of $1/G(s) \propto s^{-1/2}$ and $1/G(s) = $ constant in these s ranges.

Such characteristics can be obtained by slight modification of the semi-integration algorithm of Ref. [8]: the infinite distribution of the time constants of the numeric
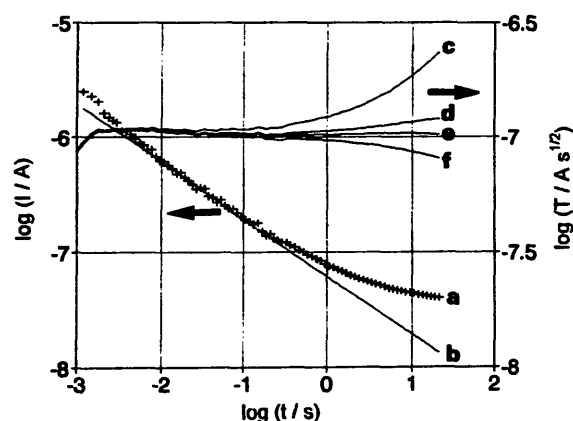

Fig. 1. Points **a**: Cottrell current transient on a platinum microdisk electrode of 100 μm diameter; solution 1 M Na_2SO_4 solution containing 5 mM $K_4Fe(CN)_6$; potential jump at $t = 0$ from -0.150 V to $+0.450$ V (vs. SCE). Line **b**: a line of slope $-1/2$ corresponding to ideal planar diffusion controlled current decay. Line **c**: the semi-integrated transient. Lines **d** to **f**: transformed transients, $\tau_{max} = 30$, 15, and 8 respectively. Either from the intercept of line **b** or from the average value of the points of line **e**, D_R was found to be 8×10^{-6} cm^2 s^{-1}.

filters is changed to a semi-infinite distribution, i.e. the maximum time constant of the filters is set to some $\tau = \tau_{max}$ value (rather than to $\tau_{max} \rightarrow +\infty$). In this case, as is illustrated below on an actual example, $1/G(s \ll 1/\tau_{max}) =$ constant and $1/G(s \gg 1/\tau_{max}) \propto s^{-1/2}$.

To achieve this goal, two modifications are made to the FRLT algorithm (see appendix of Ref. [8]):

line 2:

$t_0 = \tau_{max}$

where τ_{max} is some value close to the characteristic time separating the planar and spherical diffusion regimes. The exact value is determined by a trial-and-error procedure, as is shown later;

lines 4 and 13:

$i = 0,\ c_1 c_2$ rather than $i = 0,\ 2\ c_1 c_2$

To demonstrate the use of such a transformation, the following experiments and calculations were carried out.

First, a Cottrell current transient was measured on a platinum microdisk electrode of 100 μm diameter (Fig. 1, points a). Line b denotes a line of slope $-1/2$, i.e. this would be the decay curve if the diffusion were purely planar.

The 'ordinary' semi-integration (i.e. the application of parallel filters of time constants from $\tau \rightarrow -\infty$ to $\tau \rightarrow +\infty$) transforms the $I(t)$ curve to line c; lowering the upper limit of the time constant τ_{max} yields curves d to f. At one particular τ_{max} value the transformed function practically does not depend on the time: this is the transformation having the characteristics of $1/G(s)$, by the use of which we can obtain the potential program invariant functions.

Second, cyclic voltammograms (CVs) of a reversible redox system were measured on the same electrode. The CV curves of the first cycle are seen for three different scan rates. Note the different shape of the voltammograms: at 200 mV s^{-1} scan rate the curve looks like a CV charac-
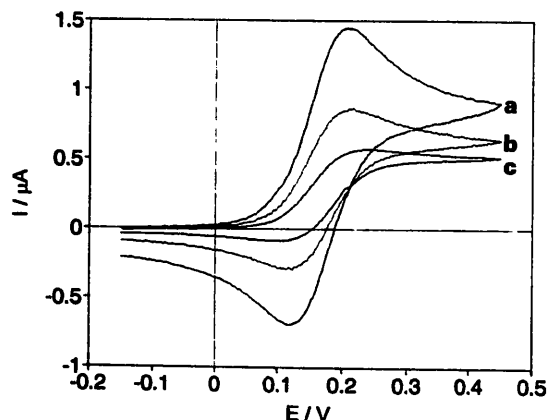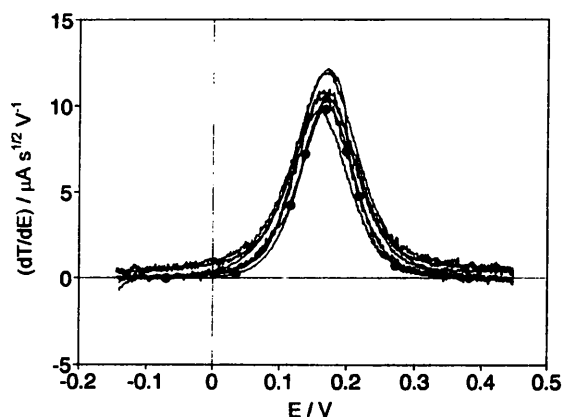

Fig. 3. The dT/dE curves calculated for the voltammograms of Fig. 2. The line marked with dots is the theoretical curve corresponding to Eq. (13), using $D_R = 8 \times 10^{-6}$ cm^2 s^{-1}, see the caption of Fig. 1.

teristic of planar diffusion, whereas at 10 mV s^{-1} scan rate the curve is 'polarographic wave'-like due to the pronounced spherical character of the diffusion.

Third, the transformed functions have been calculated by using the transformation algorithm developed above. These, calculated for the three CVs of Fig. 2, are plotted in Fig. 3. For comparison, based on Eq. (13), the theoretical dT/dE curve is also plotted. The curves coincide reasonably well, justifying the approximations used in the above way of carrying out the numerical transformation.

4. Summary

We have considered a purely diffusion-controlled electrode process; to characterize the time dependence of the diffusion we define the function $G(s)$ by writing the Cottrell response of species i in the form $\bar{I}_{i,\text{Cottrell}}(s) = \pm K_i c_i^* G(s)/s$. We have shown that:

1. any voltammetric curve $(\bar{I}(s))$ measured in the same system can be transformed to a potential program invariant form by computing the function $T = L^{-1}\bar{I}(s)/G(s)$ (see Eq. (12));
2. the diffusional admittance of the same system is expressed as $Y(s) = G(s)dT/dE$ (see Eq. (24));
3. the half-wave potential is related to the geometry of the diffusion through K_R/K_O (see Eq. (8));
4. one can perform the transformation yielding potential program invariant form by passing the digitized $I(t)$ function through a numeric filter having $1/G(s)$ transfer characteristics.

Acknowledgements

Fig. 2. CVs on the platinum microdisk. Solution 1 M Na$_2$SO$_4$ solution containing 50 mM K$_4$Fe(CN)$_6$. Scan rates: 200 mV s^{-1}, 50 mV s^{-1}, and 10 mV s^{-1} for curves a, b, and c respectively.

von Humboldt Foundation whose research fellowship made possible his stay in Ulm.

Appendix A

Consider a cell with a working electrode of arbitrary geometry and a solution containing a redox couple which is initially homogeneous, i.e. at point $r(x,y,z)$ the concentration $c(r,t \leq 0) = c_i^*$. In the $t > 0$ time range, a charge transfer reaction proceeds at the electrode surface the rate of which is sufficiently fast to be completely diffusion controlled. Then the surface concentrations of the oxidized and reduced species (in general the species i) are determined by the Nernst equation, and the diffusion of these species in the solution is described by Fick's second law:

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial r^2} \tag{A1}$$

One of the boundary conditions of this equation is $c(r_e,t) = c^s(t)$ where r_e denotes a point on the electrode surface; the other boundary condition depends on the actual geometry of the diffusion; it is not important to be specified here. The current density j_i at point r_e is expressed as

$$j_i(r_e) = -nFD_i \nabla c_i(r_e) \tag{A2}$$

The current is calculated by integrating $j(r_e)$ over the electrode surface A:

$$I_i = \int_A j_i(r_e) \, dA = -nFD_i \int_A \nabla c_i(r_e) \, dA \tag{A3}$$

With these assumptions we can calculate the final form of the $I_i(c_i^s)$ relation. First let us change to the Laplace plane; then perform a coordinate transform by introducing the following dimensionless quantities:

$$\xi = r\sqrt{s/D_i} \tag{A4}$$

$$\overline{\gamma}_i = \frac{\overline{c}_i(\xi) - \overline{c}_i^*}{\overline{c}_i^s - \overline{c}_i^*} \tag{A5}$$

Owing to the transform to dimensionless quantities, Eq. (A1) changes to

$$\overline{\gamma}_i = \frac{\partial^2 \overline{\gamma}_i}{\partial \xi^2} \tag{A6}$$

Since the concentration has been normalized, the $\gamma_i(s)$ function has spatial dependence only: it does not depend on the bulk and surface concentrations. Eq. (A2) and Eq. (A3) are changed to the following forms:

$$\overline{J}_i(r_e) = -nFD_i\left(\overline{c}_i^s - \overline{c}_i^*\right)\nabla\overline{\gamma}(r_e) \tag{A7}$$

$$\overline{I}_i = -nFD_i\left(\overline{c}_i^s - \overline{c}_i^*\right)\int_A \nabla\overline{\gamma}(r_e) \, dA \tag{A8}$$

Hence $\gamma_i(s)$ does not depend on the concentrations, the integral depends on s only; we can rearrange and simplify the latter equation to the form

$$\overline{c}_i^* - \overline{c}_i^s = \overline{I}_i\left(nFD_i\int_A \nabla\overline{\gamma}(r_e) \, dA\right)^{-1} = \overline{I}_i f_i(s) \tag{A9}$$

Note that while eq. (2a) of Ref. [3] refers to diffusion geometries of one spatial coordinate only, Eq. (A9) applies to any geometry.

References

[1] K.B. Oldham, Anal. Chem., 58 (1986) 2296.
[2] T. Pajkossy, J. Electroanal. Chem., 364 (1994) 229.
[3] H.E. Keller and W.H. Reinmuth, Anal. Chem., 44 (1972) 434.
[4] T. Pajkossy and L. Nyikos, Electrochim. Acta, 34 (1989) 181.
[5] A.J. Bard and L.R. Faulkner, Electrochemical Methods, Wiley, New York, 1980.
[6] J.C. Imbeaux and J.M. Savéant, J. Electroanal. Chem., 44 (1973) 169.
[7] K.B. Oldham, Anal. Chem., 44 (1972) 196.
[8] T. Pajkossy and L. Nyikos, J. Electroanal. Chem., 179 (1984) 65.