
THE APPLICATION OF THE RELAXATION METHOD TO THE STUDY OF Fe^{3+} , Fe^{2+} , $\text{H}_2\text{SO}_4/\text{Pt}$ ELECTRODE SYSTEM

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The paper presents the application of the relaxation theory of electrode reaction in a diffusional system. The theoretical equations derived are tested by the experimental results of a simple charge transfer reaction $\text{Fe}^{3+} + e = \text{Fe}^{2+}$ on Pt electrode in 1M- H_2SO_4 .

So far the relaxation theory of electrode process¹ has been applied successfully to electrode reactions in nondiffusional systems, e.g. metallic electrodes immersed in pure molten chlorides^{2,3}. Theoretical equations were also derived for the study of simple charge transfer electrode process⁴, electrode process coupled with chemical reactions⁵ and hydrogen evolution⁶. It has been assumed in all these derivations that the overall electrode process is not controlled by any diffusional transport. Although this may be certainly true in pure molten salts or totally irreversible electrode processes, reversible electrode reactions will be influenced by the diffusional transport.

In order to apply the relaxation method to such diffusional systems a new theory of relaxation method in diffusional systems is derived and applied to a simple charge transfer reaction. In contrary, however, to all classical electroanalytical methods^{7,8} in which the electrode response is measured simultaneously during its various type of polarization, in our relaxation method the studied electrode response is measured after the perturbation period. As shown theoretically⁹ the shape of the perturbing impulse is not important, but the current impulse has definitely an advantage over potential impulse.

Our relaxation method bears some analogy to the classical coulometric method derived by Delahay¹⁰ and Reinmuth¹¹, used recently for the investigations of fast redox systems by Vielstich et al.¹². However our galvanostatic perturbation is of longer duration and high voltage does not appear across the cell in the perturbation period. Also the theory of the overpotential decay is different.

THEORETICAL

Let us regard an electrode process which is a simple charge transfer electrode reaction in a diffusional system:



The oxidized O and reduced form R are at fairly high concentrations in a supporting electrolyte. In a perturbation period a galvanostatic current impulse I_p is imposed for a time t_p in such a way, that the perturbing charge $Q_p = I_p t_p$ is high enough to rise the equilibrium potential of the studied electrode to approximately 15 mV above its equilibrium value:

$$\Delta\eta_0 = E_p - E_{eq}. \quad (1)$$

Here $\Delta\eta_0$ is the overpotential of the studied electrode at the end of the perturbation impulse. The perturbation is followed by a free return back to equilibrium, which is traced by the recording of overpotential decay.

To derive an equation for the overpotential decay let us represent such an electrode process by an equivalent circuit presented in Fig. 1.

At the end of the perturbing period, which is the beginning of the registration of the overpotential decay ($t = 0$), the charged double layer capacitance (C_{dl}) starts to discharge through the charge transfer resistance (R_{ct}) and the diffusional impedance (Z_d).

Here:

$$R_{ct} = RT/nFAj_0, \quad (2)$$

$$Z_d = (RT/n^2F^2A) \sum_i (C_i \sqrt{D_i})^{-1}, \quad (3)$$

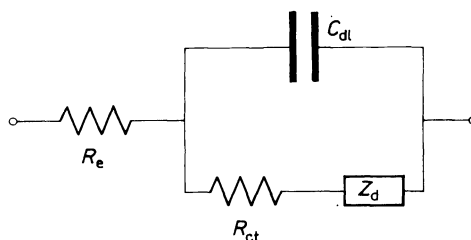
where j_0 is exchange current density, A electrode area, D_i diffusion coefficient of the ionic species i , c_i concentration of the ionic species i , R , T , n , F have their usual meaning.

In a Laplace domain the closed loop equation in Fig. 1 is:

$$\frac{\Delta\eta_0}{s} = \bar{I}(s) \left(R_{ct} + \frac{1}{sC_{dl}} + \frac{Z_d}{\sqrt{s}} \right), \quad (4)$$

FIG. 1

Equivalent circuit of an electrode process in a diffusional system. R_e electrolyte resistance, C_{dl} double layer capacitance, Z_d diffusional impedance. R_{ct} charge transfer resistance



where $\bar{I}(s)$ is the Laplace transform of the current within the loop during the relaxation of the circuit:

$$\bar{I}(s) = \frac{\Delta\eta_0}{s} \left[\left(R_{ct} + \frac{1}{sC_{dl}} + \frac{Z_d}{\sqrt{s}} \right) \right]^{-1}. \quad (5)$$

The Laplace transform of the overpotential is:

$$\Delta\eta(s) = \bar{I}(s) (R_{ct} + Z_d/\sqrt{s}) \quad (6)$$

which after small rearrangement gives:

$$\Delta\eta(s) = \Delta\eta_0 \frac{1}{(\sqrt{s+a})(\sqrt{s+b})} + \Delta\eta_0 \frac{Z_d}{R_{ct}} \frac{1}{s(\sqrt{s+a})(\sqrt{s+b})}, \quad (7)$$

where:

$$a = 2/(Z_d C_{dl}), \quad (8)$$

$$b = Z_d/(2R_{ct}). \quad (9)$$

It is seen that the desired kinetic parameter (R_{ct}) is contained in the constant b given by Eq. (9).

Taking the reverse transformation one obtains the time dependence of the measured overpotential:

$$\Delta\eta(t) = A \exp(a^2 t) \operatorname{erfc}(a\sqrt{t}) + B \exp(b^2 t) \operatorname{erfc}(b\sqrt{t}), \quad (10)$$

where A , B are constants. For a reversible or quasi-reversible electrode process, at high concentration of the depolarizer, the typical values of a and b are:

$$a = \frac{2}{Z_d C_{dl}} \sim \frac{2}{1 \cdot 10^{-5}} = 2 \cdot 10^5 \text{ s}^{-1/2},$$

$$b = \frac{Z_d}{2R_{ct}} \sim \frac{1}{2 \cdot 1} = 0.5 \text{ s}^{-1/2}.$$

It is thus seen that in a fairly long time range: $t \sim 0.01$ to 1 s, the first part of Eq. (10) vanishes to zero and the overpotential decay may be described by the second term of Eq. (10):

$$\Delta\eta(t) = B \exp(b^2 t) \operatorname{erfc}(b\sqrt{t}). \quad (11)$$

The constant b may be thus obtained from a single decay by a computer fit.

EXPERIMENTAL

Materials. Fe₂(SO₄)₃ (Analar, Riedel de Haen AG) has been used without further purification. FeSO₄·6 H₂O (Analar, POCH) has been crystallized from aqueous sulfuric acid solution in the presence of iron and dried in a desiccator over P₂O₅.

Apparatus and procedure. The relaxation decay curves in the studied system were obtained in a three electrode glass cell presented in Fig. 2.

All three electrodes were made of Pt sheets with the area of the indicator electrode being $A_{\text{geom}} = 0.27 \text{ cm}^2$ in good agreement with the chronopotentiometric value $A_{\text{chron}} = 0.30 \text{ cm}^2$. The latter quantity has been used for the calculation of the diffusional impedance. The temperature of the measuring cell was kept constant to 0.1°C. The solution was kept under nitrogen atmosphere.

The galvanostatic perturbing current impulse between indicator and auxiliary electrodes was supplied by a chronopotentiometer CHP-4C and the free decay of the resulting overpotential was recorded in a storage oscilloscope (Tektronix 434). The decay curve was then photographed by an Exacta VX 1000 camera.

RESULTS AND DISCUSSION

Typical decay of the anodically perturbed indicator electrode is presented in Fig. 3. A computer fit of the experimental decay curve $\Delta\eta = f(t)$ according to Eq. (11) is presented in Table I.

It is seen in Table I that the fit is indeed very good. The perturbation time was 1 s and the galvanostatic current intensity in the range 0.5 to 0.8 mA. It has been found

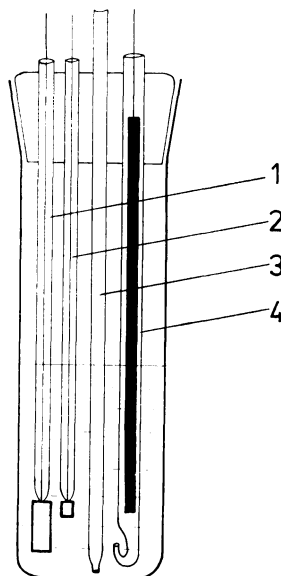


FIG. 2

The measuring glass vessel. 1 Pt reference electrode, 2 Pt indicator electrode, 3 graphite auxiliary electrode, 4 nitrogen inlet

experimentally that for the decay curves for which B of Eq. (11) was around 10 mV, the best fit was obtained.

TABLE I

Electrode reaction $\text{Fe}^{3+} + e = \text{Fe}^{2+}$, $[\text{H}_2\text{SO}_4] = 1 \text{ mol l}^{-1}$, $[\text{Fe}^{3+}] = [\text{Fe}^{2+}] = 1 \text{ mol l}^{-1}$, $A = 0.30 \text{ cm}^2$, $T = 358 \text{ K}$, $B = 9.183 \text{ mV}$, $b = 3.635 \text{ s}^{-1/2}$

t_i s	$\Delta\eta_{i,\text{exp}}$ mV	$\Delta\eta_{i,\text{calc}}$ mV	Difference mV
0.00833	6.73	6.54	0.19
0.0116	6.09	6.20	-0.11
0.0200	5.56	5.58	-0.02
0.0300	5.06	5.09	-0.03
0.0416	4.51	4.68	-0.17
0.0800	3.83	3.85	-0.02
0.135	3.29	3.22	0.07
0.203	2.79	2.76	0.03
0.281	2.43	2.42	0.01
0.376	2.16	2.14	0.02
0.470	1.99	1.95	0.04
0.566	1.83	1.79	0.04
0.666	1.68	1.66	0.02
0.760	1.53	1.56	-0.03
0.853	1.43	1.48	-0.05

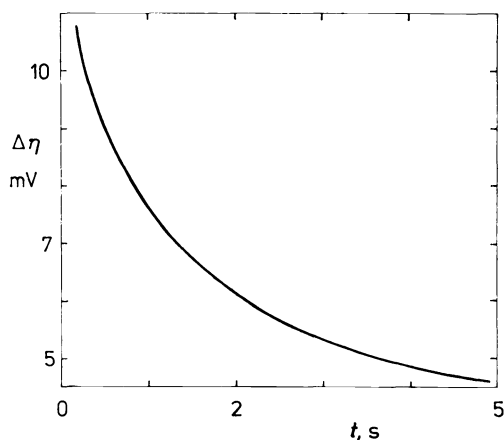


FIG. 3
The decay of the overpotential of the anodically polarized 1M-Fe^{3+} , 1M-Fe^{2+} , $1\text{M-H}_2\text{SO}_4/\text{Pt}$ electrode

Both cathodic and anodic perturbation pulses were employed although the results with anodic polarization in the perturbing period were more reproducible. It is possible that during cathodic perturbation some hydrogen might have been evolved at the Pt electrode.

Average values of b together with diffusional impedance and standard rate constants at several temperatures for 1M solutions of both Fe³⁺ and Fe²⁺ in 1M-H₂SO₄ are presented in Table II.

The diffusion coefficients of Fe³⁺ and Fe²⁺ ions in this solutions at several temperatures were measured chronopotentiometrically in a separate work¹³. The diffusional impedance Z_d has been calculated according to the Eq. (3) and the standard rate constant k^0 by the equation:

$$k^0 = 2bRT/F^2AcZ_d. \quad (12)$$

The activation energy at the equilibrium potential has been calculated according to an Arrhenius type equation^{7,14}:

$$U^* = -R \left[\frac{\partial \ln k^0}{\partial 1/T} \right]_p. \quad (13)$$

The temperature dependence of the standard rate constant obtained by the least squares method is: $k^0 = 1.845 \exp(-1551/T)$, ($r^2 = 0.994$), giving the activation energy: $U^* = 12.9$ kJ/mol.

This electrode process has been studied by many authors using different methods; the kinetic parameters are given by Tamamushi¹⁴ in an IUPAC publication. As given there, the standard rate constant of this electrode process^{15,16} ranges from

TABLE II

Kinetic parameters of the electrode reaction $\text{Fe}^{3+} + e = \text{Fe}^{2+}$ at Pt in 1M-H₂SO₄ for $[\text{Fe}^{3+}] = [\text{Fe}^{2+}] = 1 \text{ mol l}^{-1}$

T K	b $\text{s}^{-1/2}$	Z_d $\Omega \text{ s}^{-1/2}$	$k^0 \cdot 10^2$ cm s^{-1}
297	3.010	0.4780	1.00
318	3.050	0.4025	1.43
328	3.086	0.3742	1.61
337	3.125	0.3521	1.78
348	3.510	0.3285	2.21
358	3.601	0.3099	2.43

$1.5 \cdot 10^{-3}$ cm/s to $3.3 \cdot 10^{-2}$ cm/s. Although the literature data refer to the same sulfuric acid concentration (1 mol l^{-1}) the concentrations of the depolarizer ions in all papers are approximately 100 times lower than those in the present paper. This is because all nonrelaxational methods require for the measurements a low depolarizer concentration in a concentrated solution of the supporting electrolyte.

The relaxation method developed for the diffusional systems in this paper may be used for any solution, although for more concentrated solutions the reproducibility of the results is better.

It is seen from the comparison of the kinetic data of the studied electrode process with the literature data that the agreement is fairly good and the relaxation method may be recommended for the determination of kinetic parameters of fast electrode processes. It is especially useful in the case of the study of important technological electrochemical processes (e.g. electrorefining of metals, etc.) where concentrated solutions are frequently used.

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