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Growth and Decay of Activation Overpotential for Systems which Proceed by Two Different Successive Transfer Electrode Reactions

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Analysis of growth and decay of activation overpotential for systems involving two different successive hindered transfer reactions, for large values of η , has shown that there is a considerable difference between cathodic and anodic galvanostatic transients (for the same transfer coefficient) for such systems.

The ratio of rates of growth and decay of overpotentials for the cathodic and the anodic region, for the same transfer coefficients and the same overpotential as well as rise time and decay time is given by the ratio of exchange current densities, $i_r^0 : i_o^0$.

Occurrence of difference in galvanostatic transients for cathodic and anodic regions is suggested to be a new diagnostic criteria in studies of kinetics of electrode processes for occurrence of multi-electron transfer reactions.

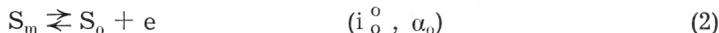
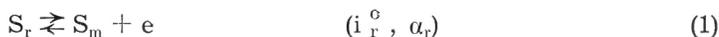
Growth and decay of activation overpotential have up to now been studied for one transfer reaction only, or for the case when it can be assumed that in the series of separate successive electrode reactions there is only one hindered transfer reaction.¹⁻³

It has been shown⁴⁻⁷ that in some cases the kinetics of electrode processes involving two different successive hindered transfer reactions in the series of separate successive electrode reactions must be treated. Here we propose to analyse the galvanostatic growth and decay of activation overpotentials in the case where it is necessary to consider the velocities of two transfer reactions.

The overall electrochemical reaction involving 2 electrons



where S_r is the reduced form, S_o the oxidized form of the substance S_j , and S_m the intermediate form in the oxidized state, may be represented by two consecutive transfer steps



where i_r^0 and α_r are the exchange current density and transfer coefficient for reaction (1) and i_o^0 and α_o the exchange current density and the transfer

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coefficient for reaction (2). In this case, the faradaic current i_F as a function of the activation overpotential η and the kinetic parameters of both transfer reactions is given by Vetter's equation,^{4,5}

$$i = 2 i_r^0 \exp\left(\frac{\alpha_r F}{RT} \eta\right) \frac{1 - \exp\left(-\frac{2F}{RT} \eta\right)}{1 + \frac{i_r^0}{i_o^0} \exp\left(-\frac{1 + \alpha_o - \alpha_r}{RT} F \eta\right)} \quad (3)$$

Vetter's equation refers to the steady state, *i.e.* it is a function $i = F(\eta)$. With this paper we want to extend present knowledge of electrode reactions which proceed by two different successive transfer electrode reactions by the study of a non-steady state, *i.e.* the study of $\eta = f(t)$ curves for galvanostatic conditions of charging of the electrode.

For $i_r^0 \neq i_o^0$, the first and general conclusion is that growth and decay curves, $\eta = f(t)$, are different for the cathodic and the anodic region. For a single transfer reactions, transients for the cathodic and the anodic region, are in general, the same, for the same transfer coefficients.¹⁻³

GROWTH OF ACTIVATION OVERPOTENTIAL

If a current of constant density (constant rate of supply of electrons) i is passed through an electrode, and if C is the double layer capacity, then the total current i , $i = i_C + i_F$, is given by:

$$i = C \frac{d\eta}{dt} + i_F \quad (4)$$

where η is the non-steady state overpotential.

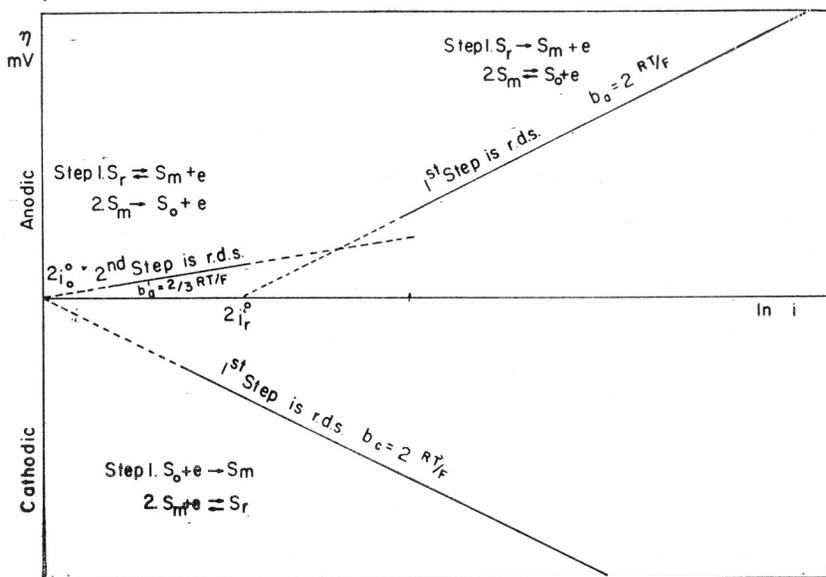


Fig. 1. Overpotential as a function of log current density for Eq. 3, for the case $i_r^0 \gg i_o^0$

In the case when $i_r^o \gg i_o^o$, there is a change of the reaction mechanism and of the Tafel slope, the slope of $\log i_r = f(\eta)$, in the anodic region, as seen in Fig. 1.

The equivalent circuit for the system studied is given⁸⁻¹⁰ in Fig. 2.

It appears from Fig. 1 and 2 that when $i_r^o \gg i_o^o$ for the cathodic region and for large anodic overvoltages $\left(b = 2 \frac{RT}{F}\right)$ the equivalent circuit is (a), and for small $\left(\frac{1}{2} \frac{RT}{F} \ll \eta \ll \frac{RT}{F} \ln \frac{i_r^o}{i_o^o}\right)$ anodic overvoltages $\left(b'_a = \frac{2}{3} \frac{RT}{F}\right)$ the equivalent circuit is (b).

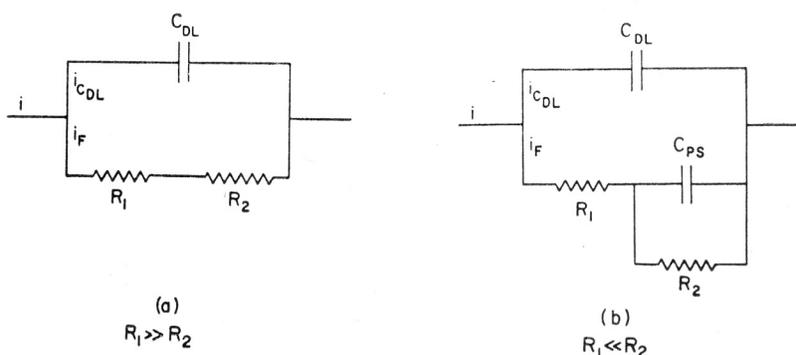


Fig. 2. Equivalent circuit for a system which proceeds by two different successive electrode transfer reactions.

(a) the first step is slow (r. d. s.), the second step is fast
 (b) the first step is fast, the second step is slow (r. d. s.)
 R_1 — transfer resistance of reaction 1; R_2 — transfer resistance of reaction 2; C_{DL} — capacity of double layer; C_{PS} — pseudocapacity; i — constant external current density; i_F — faradaic current

For the equivalent circuit in Fig. 2 (a), a galvanostatic transient can be represented as shown in Fig. 3(a). In the region where the first step is fast and the second step is the rate determining step (r.d.s.) the galvanostatic transient can be represented as in Fig. 3(b).

For sufficiently large values of η , in both cathodic and anodic regions, ($\Theta = \Theta_{max}$; where Θ , is the coverage by intermediate species) the system is represented by equivalent circuit Fig. 2(a).

Here we propose to analyse this region only, the region of large η

$$\eta \gg \frac{RT}{F} \ln \frac{i_r^o}{i_o^o} \text{ and the case when } i_r^o \gg i_o^o.$$

In order to compare the anodic and cathodic transients and rise times for the transients, in the anodic region as origin of time the time $t = 0$ is taken as indicated in Fig. 3. The inherent assumption that when a change of

mechanism occurs, the first part of a transient with the second step as r.d.s. does not influence (to an appreciable extent) the portion of the transient with the first step as r.s.d.,¹¹⁻¹² is sufficiently justified for large values of η and enables one to compare the cathodic and anodic transients for large values of η .

In the following text whenever an equation is given for the dependent variable for the anodic region a corresponding equation is valid for the cathodic region by taking i_o^o and α_o instead of i_r^o and α_r and changing sign.

According to Vetter, i_F for large anodic overpotentials, is given by:

$$i_F = 2 i_r^o \exp \left(\frac{\alpha_r F}{RT} \eta \right) \quad (5)$$

From equation (4) and (5) the rate of change of activation overpotential with time is given by:

$$(\partial\eta/\partial t)_{an} = 2i_r^o D(\eta) \quad (6)$$

where:

$$D(\eta) = \frac{1}{C} \left[\exp \left(\frac{\alpha_r F}{RT} \eta_\infty \right) - \exp \left(\frac{\alpha_r F}{RT} \eta \right) \right]$$

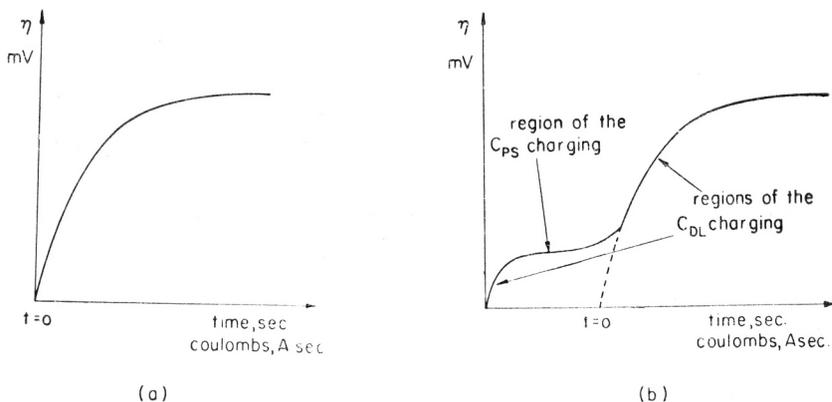


Fig. 3. Galvanostatic transients: (a) for equivalent circuit Fig. 2. (a); (b) for equivalent circuit Fig. 2 (b)

From equation (6) it can be seen that if the rate of growth of anodic and cathodic overpotentials are compared for the same transfer coefficients ($\alpha_r = \alpha_o$) and the same η_∞ and η , equation:

$$(\partial|\eta|/\partial t)_{an} = (\partial|\eta|/\partial t)_{cath} \frac{i_r^o}{i_o^o} \quad (7)$$

is obtained i.e. the ratio of the rates of growth of the activation overpotential is equal to the ratio of the exchange current densities.

Substituting i_F given by equation (5) into equation (4) and solving the resulting differential equation (assuming $C_{DL} = \text{const.}$), the following equation is obtained:

$$\eta = - \frac{RT}{\alpha_r F} \ln \left[\frac{i - 2i_r^o}{i} \exp \left(-i \frac{\alpha_r F}{RT} \frac{1}{C} t \right) + \frac{2i_r^o}{i} \right] \quad (8)$$

It appears from equations (6—8) that with different values of Tafel slopes (variations in Tafel slopes are small, a factor of 5 is high, in comparison with variations in exchange current densities^{6,7} i_r^o and i_o^o ; for the kinetics of deposition and dissolution of some metals this ratio is 10 : 1, for redox systems even 100 : 1 or 1000 : 1) the occurrence of two different successive transfer reactions gives rise to a considerable difference between the cathodic and the anodic growth curves. This difference is an additional diagnostic criterion for the occurrence of two different successive transfer reactions.

The rise time τ_{an} , defined as t for $\eta = a\eta_\infty$, where η_∞ is the steady state overpotential, is given by (neglecting i_r^o in the sum $i + i_r^o$):

$$\tau_{an} = \frac{1}{2i_r^o} A(\eta_\infty) \quad (9)$$

where

$$A(\eta_\infty) = - \frac{RT}{\alpha_r F} C \exp \left(- \frac{\alpha_r F}{RT} \eta_\infty \right) \ln \left[\exp \left(- \frac{\alpha_r F}{RT} a\eta_\infty \right) - \exp \left(- \frac{\alpha_r F}{RT} \eta_\infty \right) \right]$$

Comparing rise times for cathodic and anodic transients, for the same transfer coefficients and the same steady state overpotentials, one gets

$$\tau_{an} = \tau_{cath} \frac{i_r^o}{i_o^o} \quad (10)$$

i.e. the ratio of rise time values for cathodic and anodic transients is equal to the ratio of exchange current densities.

DECAY OF ACTIVATION OVERPOTENTIAL

For the decay curve $i = 0$ and therefore, according to equation (4)

$$\frac{d\eta}{dt} = - \frac{1}{C} i_F \quad (11)$$

Substituting corresponding values of i_F , rate of decay functions are obtained, i.e. $\eta = f(t)$ after integration.

The rate of decay of anodic overpotential is given by:

$$(\partial\eta/\partial t)_{an} = 2i_r^o B(\eta) \quad (12)$$

where:

$$B(\eta) = - \frac{1}{C} \exp \left(\frac{\alpha_r F}{RT} \eta \right)$$

and the decay time, defined as $\eta = b\eta_\infty$, is given by:

$$\tau_{an} = \frac{1}{2i_r^o} M(\eta_\infty) \quad (13)$$

where:

$$M(\eta_{\infty}) = C \frac{RT}{\alpha_r F} \left[\exp \left(- \frac{\alpha_r F}{RT} b \eta_{\infty} - \exp \left(- \frac{\alpha_r F}{RT} \eta_{\infty} \right) \right) \right]$$

Function $\eta = f(t)$ is given by the expression:

$$\eta = - \frac{RT}{\alpha_r F} \ln \left[- \frac{2i_r^{\circ}}{C} \frac{\alpha_r F}{RT} t + \exp \left(- \frac{\alpha_r F}{RT} \eta_{\infty} \right) \right] \quad (14)$$

for the anodic transients as well as, with known substitutions for the corresponding cathodic transients.

CONCLUSION

Analysis of growth and decay of activation overpotential for systems involving two different successive hindered transfer reactions has shown, that curves $\eta = f(t)$, galvanostatic transients, are different for the cathodic and the anodic region (for the same transfer coefficient). For a single transfer reaction the galvanostatic transients are, in general, the same for both regions.

Occurrence of a difference in galvanostatic transients for cathodic and anodic regions is characteristic for multitransfer reactions and can be used as a diagnostic criterion in studies of the kinetics of electrode processes. The difference between monotransfer transients and multitransfer transients stems from the fact that for multitransfer electrode reactions there is a set of different kinetic parameters corresponding to each transfer reaction.

The use of computer calculations and complete solutions of studied differential equations is desirable.

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IZVOD

Promena aktivacionog nadnapona sa vremenom za sisteme sa višestepenim elektrodnim reakcijama

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Analiza funkcija promene potencijala sa vremenom pod uslovima uključivanja i isključivanja konstantne struje za sisteme sa višestepenim elektrodnim reakcijama, za velike vrednosti nadnapona, pokazuje da postoji znatna razlika između katodnih i anodnih krivih kada se ove upoređuju za istu vrednost faktora simetrije i isti nadnapon.

Kod sistema sa jednoelektronskom elektrodnom reakcijom katodne i anodne funkcije, promene potencijala sa vremenom su iste (za istu vrednost koeficijenta simetrije).

Odnos vrednosti brzina promene potencijala sa vremenom u odgovarajućim tačkama katodne i anodne oblasti kao i vrednosti vremena postizanja jedne određene vrednosti nadnapona stoji u odnosu struja izmene, $i_r^0 : i_o^0$.

Analiza funkcija promene potencijala sa vremenom daje novi kriterijum za postojanje višestepenih elektrodnih reakcija.

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