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Original Scientific Paper

The Electrode Kinetics of the Deposition and Dissolution of Me/Me²⁺ Electrodes

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It is shown that Vetter's equation for two successive transfer reactions applied to the elucidation of the electrode kinetics of the deposition and dissolution of Me/Me²⁺ electrodes yields a new interpretation of the intersections of Tafel lines for large anodic and large cathodic overvoltages with log *i* coordinates (*i*₀⁰, *i*_r⁰).

Vetter's equation, when applied to the kinetics of Me/Me²⁺ electrodes gives an explanation for the occurrence of two slopes in the anodic region, 2RT/3F and 2RT/F, and of the same slope for large anodic and large cathodic overvoltages, 2RT/F, for Fe/Fe²⁺ electrode in Ac⁻ and NO₃⁻ solution, and for the Cu/Cu²⁺ electrode in SO₄²⁻ solution, as well as for changes of *i*⁰ with *a*_{Cu²⁺} for the Cu/Cu²⁺ electrode.

Further application of this approach to electrochemical kinetics of Me/Me²⁺ electrodes is suggested.

INTRODUCTION

The overall electrochemical reaction



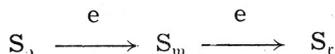
may be considered as composed of several separate successive steps (transfer reactions, surface diffusion). The rate of the overall reaction depends on the kinetic parameters of each of these reactions.

Very often it is possible to assume that in the series of consecutive reactions, such as those which can take place in metal deposition and dissolution there is only one rate determining step¹⁻⁵ (r. d. s.).

The overall electrochemical reaction involving 2 electrons



where S_r is the reduced form, S_o the oxidized form of substance S_i, and S_{in} the intermediate form in oxidised state, may be represented by two consecutive transfer steps



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Here we are interested in those cases where similar values of free energies of activation have to be considered for two successive transfer steps, for a given experimental condition.

In cases where similar values of free energy of activation are found for two or more steps one can expect that change of r.d.s. could occur with variation of experimental conditions⁶⁻⁸ (change of activation energy with potential).

Mattsson and Bockris⁹ proposed two different mono-electron transfer steps for the $\text{Cu}^{2+} + 2e \rightleftharpoons \text{Cu}$ overall electrode reaction with the intermediate form $S_m = \text{Cu}^+$. The calculated potential energy diagram for Cu^{2+} ion deposition^{6,7} via the redox step involving Cu^+ shows that, at overpotentials greater than 0.1 V, the free energy of the activated states of the transfer steps are similar. For the redox step Cu^{2+} the free energy of the activated state is about 15 Kcal mole⁻¹ and that for the transfer reaction $\text{Cu}^+ + e_M \rightarrow (\text{Cu}_{\text{adion}} + e_M)$ about 12 Kcal mole⁻¹ referred to the free energy of the initial state. Uncertainties in the free energy values calculated for a given model and reaction path is about ± 3 Kcal mole⁻¹.

Kabanov, Burstein, and Frumkin¹⁰, and Bockris, Drazic, and Despic¹¹ proposed two different mono-electron transfer steps for the $\text{Fe}^{2+} + 2e \rightleftharpoons \text{Fe}$ overall electrode reaction with the intermediate form $S_m = \text{FeOH}$.

In both cases the mechanism of the electrolytic deposition and dissolution of iron and copper was studied, for experimental conditions considered, using equation (1)

$$i = i^0 \left[\exp \left(\frac{\alpha z F}{RT} \eta \right) - \exp \left(- \frac{(1 - \alpha) z F}{RT} \eta \right) \right] \quad (1)$$

In these cases the function $\eta = f(i)$ is determined by i^0 and α , $\eta = f(i, i^0, \alpha)$.

Some experimental results, achieved in the study of the electrode kinetics of the deposition and dissolution of Fe and Cu, indicate that under certain experimental conditions it would be necessary to take into consideration the velocities of both the transfer reactions. It seems, that in some regions of experimental conditions, one can speak of two hindered transfer reactions, and of a change of r.d.s. brought about by changing the range of overpotentials.

In the case where it is necessary to consider the velocities of both the transfer reactions and have one equation for a wide range of overvoltages, which involves the change of r.d.s. and a region of two hindered transfer reactions, η is determined by the exchange current of both transfer reactions, i_o^0 and i_r^0 and by two transfer coefficients, α_o and α_r ,

$$\eta = F(i, i_o^0, i_r^0, \alpha_o, \alpha_r).$$

In this paper we intend to point out and to explain some of the experimental results using the general $\eta - F$ equation.

GENERAL CASE

For the overall electrochemical reaction



in the case of two successive transfer reactions





where S_r is the reduced form, S_o the oxidised form of substance S_j , and S_{in} the intermediate form in the oxidised state, i_r^0 the exchange current for the reaction (3), and i_o^0 the exchange current for the reaction (4), function $i = \varphi(\eta)$ is given by Vetter's^{12,13} equations (5a, b)

$$i = 2i_r^0 \exp\left(\frac{\alpha_r F}{RT} \eta\right) \frac{1 - \exp\left(-\frac{2F}{RT} \eta\right)}{1 + \frac{i_r^0}{i_o^0} \exp\left(-\frac{1 + \alpha_o - \alpha_r}{RT} F \eta\right)} \quad (5a)$$

$$i = -2i_o^0 \exp\left(-\frac{1 - \alpha_o}{RT} F \eta\right) \frac{1 - \exp\left(\frac{2F}{RT} \eta\right)}{1 + \frac{i_o^0}{i_r^0} \exp\left(\frac{1 + \alpha_o - \alpha_r}{RT} F \eta\right)} \quad (5b)$$

When $i_r^0 \gg i_o^0$, it is seen from equations (5a, b) that the velocity of metal dissolution for large anodic overvoltages is determined by the difference of kinetic parameters of reaction (3) — (reaction (3) r.d.s.) $i = f(i_r^0, \alpha_r, \eta)$ for small anodic overvoltages, when $i_r^0 \gg i_o^0$ is determined by kinetic parameters of reaction (4) — (reaction (4) r.d.s.), $i = f'(i_o^0, \alpha_o, \eta)$.

For the general cases, when $i_r^0/i_o^0 = 10$ and for $\alpha_r = \alpha_o = 0.5$ a function $i = \psi(\eta)$ calculated by equation (5a, b) is represented in Fig. 1. Fig. 1 represents one of the criteria for two successive hindered transfer reactions:

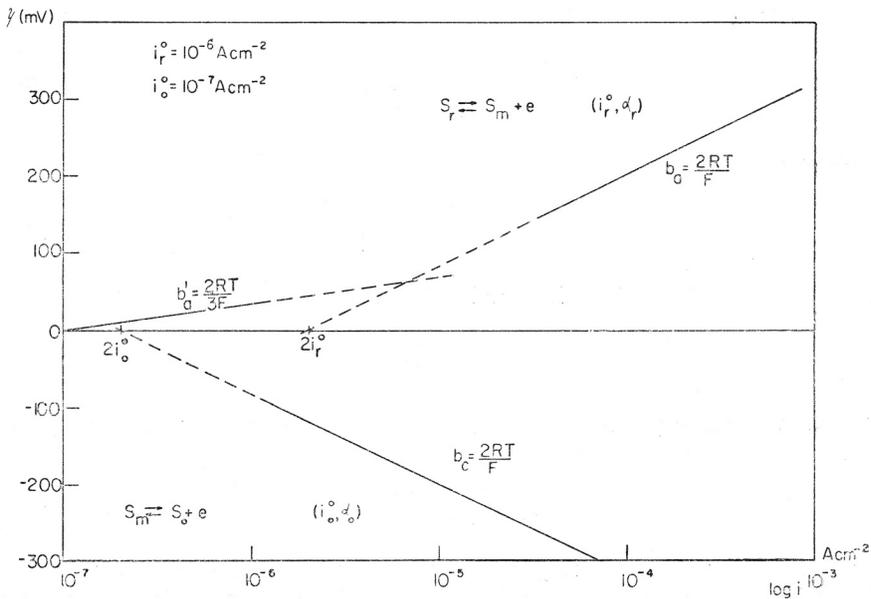


Fig. 1. Overpotential as a function of log current density for Eq. (5a, b).

Fe/Fe²⁺ ELECTRODE

For Ac⁻ and NO₃⁻ solutions (examined in a wider range of overpotentials, ± 200 mV) Bockris, Drazic and Despic¹¹ found that anodic Tafel slopes have two values, $2 RT/3F$ in the lower current densities ranges, and $2 RT/F$ in the higher ranges.

These results are in good agreement with equation (5a, b). When $i_r^0/i_0^0 = 10$ change of slope occurs from values of $\eta \gg RT/F 2.303 \log i_r^0/i_0^0$, i.e. for $i_r^0/i_0^0 = 10$ for $\eta \gg 59.2$ mV. The larger i_r^0/i_0^0 , the larger η of change of slope.

In the region of change of slopes (region of intersection of lines with two different slopes), velocity of metal dissolution is determined by both sets of kinetic parameters (reaction 3 and 4).

Existence of two values for anodic Tafel slopes when $i_r^0 \gg i_0^0$, besides the existence of two values of exchange currents, is just a criterion for two successive hindered transfer reactions.

Two slopes in the anodic region for dissolution of Fe, under some experimental conditions, were observed by Hurlen.¹⁴

Cu/Cu²⁺ ELECTRODE

In this case we would like to discuss only the change of exchange current with activity of Cu²⁺ ions, using experimental results available to this date.

Using equation (1) and assuming reaction $\text{Cu}^{2+} + e \rightarrow \text{Cu}^+$ as r.d.s., Mattsson and Bockris⁹ calculated: $\frac{\partial \log i^0}{\partial \ln a_{\text{Cu}^{2+}}} = 0.75$ for $\alpha = 0.5$, as a theoretical value,

and as an experimental value, 0.6. Bockris and Enyo¹⁵ found experimentally that $\frac{\partial \log i^0}{\partial \log a_{\text{Cu}^{2+}}} = 0.5$. They explained this result by pointing out that, at higher concentrations of Cu²⁺, the rate of reaction $\text{Cu}^+ + e \rightarrow \text{Cu}$ becomes increasingly important to the overall reaction rate, which is controlled by $\text{Cu}^{2+} + e \rightarrow \text{Cu}^+$ almost completely at lower concentrations.

The experimental value 0.5 (0.6) found by Bockris and Enyo can be considered as the mean value for $\frac{\partial \ln i_0^0}{\partial \ln a_{\text{Me}^{2+}}}$ and $\frac{\partial \ln i_r^0}{\partial \ln a_{\text{Me}^{2+}}}$ calculated by us, eq. (9) and (11).

In preliminary measurements, examining Tafel slopes in a wider range, up to +150 mV, in SO₄²⁻ solution, (Mattsson and Bockris⁹ and Bockris and Enyo¹⁵ up to +100 mV, Hurlen¹⁶ up to +30 mV, Turner and Johnson¹⁷ up to +50 mV) we have found¹⁸ two values for anodic Tafel slopes: $2 RT/3 F$ in the lower current densities ranges, and $2 RT/F$ in the higher ranges.

From these examples, it is seen that for some experimental conditions, equation (5a, b) is applicable to the electrode Cu/Cu²⁺.

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IZVOD

Kinetika elektrodnih procesa rastvaranja i deponovanja kod Me/Me²⁺ elektroda

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Pokazano je da Vetter-ova jednačina za višestepene elektrodne reakcije primenjena za objašnjenje kinetike elektrodnih procesa rastvaranja i deponovanja kod Me/Me²⁺ elektroda daje novi smisao preseka Tafel-ovih pravih za velike anodne i katodne nadnapone sa log i koordinatom (i_0^0 , i_1^0).

Vetter-ova jednačina primenjena na kinetiku Me/Me²⁺ elektroda daje objašnjenje za dva koeficijenta pravca Tafel-ove prave u anodnoj oblasti, $2RT/3F$ i $2RT/F$, i za isti koeficijent pravca za veliki anodni i katodni nadnapon, $2RT/F$, za Fe/Fe²⁺ elektrodu u Ac⁻ i NO₃⁻ rastvoru, i za Cu/Cu²⁺ elektrodu u SO₄²⁻ rastvoru, kao i promenu i^0 sa $a_{Cu^{2+}}$ za Cu/Cu²⁺.

Predlaže se dalja primena ovog metoda tretiranja elektrohemijske kinetike Me/Me²⁺ elektroda.

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