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STUDIES ON THE MECHANISM OF HYDROGEN ELECTRODE REACTION

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Rezumat

În acest articol se tratează câteva studii teoretice legate de mecanismul de descărcare a hidrogenului la catod, în procesul de electroliză a apei. S-a demonstrat că dependenţa densităţii de curent de suprapotenţial pentru reacţia de descărcare a hidrogenului, descrisă prin mecanismul Volmer – Heyrowsky – Tafel, poate fi corelată prin două seturi de parametri cinetici. Relaţiile care evidenţiază ambele grupuri de parametri au fost analizate atât pentru situaţia desfăşurării simultane a celor trei etape ale mecanismului, cât şi pentru căi cinetice diferite ale acestuia.

Résumé

Cet article présente quelques études théorétiques concertant le mécanisme de déchargement de l'hydrogène au cathode dans le processus de l'électrolyse de l'eau. On a demande que la dépendance de la densité du courrant de sur potentiel pour la réaction de déchargement de l'hydrogène, décrite par le mécanisme Volmer – Heyrowsky – Tafel, peut être corrélée par deux groupes de paramètres ont été analyse aussi pour la situation du développement simultané de ces trois étapes du mécanisme, que pour différentes voies cinétiques pour celui-ci.

Abriss

In diesem Werk würden einige theoretische Studien über dem Entlademechanismus des Wasserstoffes beim Kathode während der Wasserelektrolyse dargestellt. Es wurde demonstriert dass die Abhängigkeit der Stromdichte von Überpotential für den Entlademechanismus des Wasserstoffes, beschrieben durch den Volmer-Heyrowsky-Tafel Mechanismus, kann durch zwei Sätze kinetischen Parameter korreliert sein. Die Relationen die zwei Parametersätze beschreiben wurden für das gleichzeitige Aufrollen den drei Stufen sowie auch für unterschiedliche kinetischen Wege analysiert.

1. Introduction

The existence of two sets of kinetic parameters that produce the same dependence of the current density (j) on overpotential (η) for the Volmer – Heyrowsky route was found [La'90], studying the kinetics of the hydrogen evolution reaction on nickel electrodes. They have shown that, when the symmetry factor of the Volmer and Heyrowsky steps are equal ($\alpha_V = \alpha_H$), the simultaneous permutation of the kinetic constants $k_{+V} \rightleftarrows k_{+H}$ and $k_{-V} \longleftrightarrow k_{-H}$ does not alter the dependence $j(\eta)$, but transforms the dependence of the surface coverage on overpotential $\theta(\eta)$ into $[1 - \theta(\eta)]$. This statement was extended for different values of the symmetry factor [La'94]. Analyzing the application of the Volmer – Heyrowsky route to the oxidation of metals and considering both steps irreversible, also concluded that the permutations $k_{+V} \longleftrightarrow k_{+H}$ and $\alpha_V \longleftrightarrow \alpha_H$ do not alter the dependence $j(\eta)$.

The property pointed out by these reports is very important for its consequence on the correlation of experimental j vs. η needs a more detailed study. Therefore, the present work extends the analysis to the simultaneous occurrence of the three steps of the Volmer – Heyrowsky – Tafel mechanism, solved without kinetic approximations for the case of a Langmuir – type adsorption. The relations obtained are applied to the simulation of the dependence of the surface coverage on overpotential from one set of kinetic parameters. Furthermore, the conditions leading to a particular kinetic route are indicated.

2. Theoretical Analysis

The hydrogen electrode reaction in alkaline media ca be written as:

$$H_2O + 2e^- \rightleftarrows H_2 + 2OH^- \tag{1}$$

The corresponding elementary steps for the Volmer – Heyrowsky – Tafel mechanism are:

$H_2O + e^- \rightleftharpoons H_{(a)} + OH^-$ Volmer (2a)

$H_2O + e^- + H_{(a)} \rightleftharpoons H_2 + OH^-$ Heyrowsky (2b)

$H_{(a)} + H_{(a)} \rightleftharpoons H_2$ Tafel (2c)

The kinetics of the hydrogen electrode reaction for the simultaneous occurrence of the Volmer – Heyrowsky and the Volmer – Tafel routes in a steady state can be described on terms of the reaction rate of the elementary steps by the following equalities[Ch'96]:

$$2\nu = \nu_V + \nu_H = 2(\nu_H + \nu_T) = 2(\nu_V - \nu_T) \tag{3}$$

where ν is the overall reaction rate and ν_s is the reaction rate of the step s, being positive for the reduction process and negative for the oxidation one. The rate of the elementary steps, when a Langmuir – type adsorption is considered for the adsorbed hydrogen, in the absence of mass-transfer limitations, can be written as:

$$\nu_V = \nu_V^e \frac{(1-\theta)}{(1-\theta^e)} \exp[-(1-\alpha_V) f\eta] - \nu_V^e \frac{\theta}{\theta^e} \exp(\alpha_V f\eta) \tag{4}$$

$$\nu_H = \nu_H^e \frac{\theta}{\theta^e} \exp[-(1-\alpha_H) f\eta] - \nu_H^e \frac{(1-\theta)}{(1-\theta^e)} \exp(\alpha_H f\eta) \tag{5}$$

$$\nu_T = \nu_T^e \frac{\theta^2}{\theta^{e2}} - \nu_T^e \frac{(1-\theta)^2}{(1-\theta^e)^2} \tag{6}$$

where the superscript e indicates equilibrium, $f = F/RT$, and η is negative for reduction and positive for oxidation. The following implicit equation $f(\theta, \eta) = 0$ can be obtained from the second or third equality of equation 3.

$$a\theta^2 + b\theta + c = 0 \tag{7}$$

where

$$a = \frac{2\nu_T^e (1-2\theta^e)}{\theta^{e2}\ (1-\theta^e)^2} \tag{7a}$$

$$b = \frac{4\nu_T^e}{(1-\theta^e)^2} + \exp(\alpha_V f\eta) \left[\frac{\nu_V^e \exp(-f\eta) + \nu_H^e \exp[(\alpha_H - \alpha_V) f\eta]}{(1-\theta^e)} + \frac{\nu_V^e + \nu_H^e \exp[-(1-\alpha_H + \alpha_V) f\eta]}{\theta^e} \right] \tag{7b}$$

$$c = -\frac{2\nu_T^e}{(1-\theta^e)^2} - \exp(\alpha_V f\eta) \left[\frac{\nu_V^e \exp(-f\eta) + \nu_H^e \exp[(\alpha_H - \alpha_V) f\eta]}{(1-\theta^e)} \right] \tag{7c}$$

Starting from eq. 7 – 7c, it has been demonstrated that $\theta(\eta)$ reaches a limiting value (θ^*) for both anodic and cathodic potentials. The expressions of θ^*, according to the relative values of α_V and α_H, for $\eta >> 0$ (θ^*_a) are [Ch'00]

$$\theta^*_a = 1 \qquad (\alpha_V < \alpha_H) \tag{8a}$$

$$\theta^*_a = \frac{\theta^e \nu_H^e}{(1-\theta^e)\nu_V^e + \theta^e \nu_H^e} \qquad (\alpha_V = \alpha_H) \tag{8b}$$

$$\theta^*_a = 0 \qquad (\alpha_V > \alpha_H) \tag{8c}$$

The corresponding expressions for $\eta << 0$ (θ^*_c)

$$\theta^*_c = 0 \qquad (\alpha_V < \alpha_H) \tag{9a}$$

$$\theta^*_c = \frac{\theta^e \nu_V^e}{(1-\theta^e)\nu_H^e + \theta^e \nu_V^e} \qquad (\alpha_V = \alpha_H) \tag{9b}$$

$$\theta^*_c = 1 \qquad (\alpha_V > \alpha_H) \tag{9c}$$

Furthermore, the dependence $j(\eta)$ can be also obtained from eq. 3 taking account that $j = 2F\nu$

$$j(\eta) = \frac{2F\exp(\alpha_V f\eta)}{(1-\theta^e)}\{\nu_V^e \exp(-f\eta) - \nu_H^e \exp[(\alpha_H - \alpha_V)f\eta] - [\nu_V^e \exp(-f\eta) - \nu_H^e \exp[(\alpha_H - \alpha_V)f\eta] +$$

$$+ \frac{(1-\theta^e)}{\theta^e}\{\nu_V^e - \nu_H^e \exp[-(1-\alpha_H + \alpha_V)f\eta]\}]\theta(\eta)\} \tag{10}$$

Analysis of the dependence $\theta(\eta)$

For a given set of kinetic parameters θ^e, ν_V^e, ν_H^e and ν_T^e, a unique dependence $\theta(\eta)$ is obtained, corresponding to the following solution of eq. 7.

$$\theta(\eta) = \frac{-b+\sqrt{b^2-4ac}}{2a} \tag{11}$$

because the second analytic solution corresponding to the minus sign does not verify the condition $0 \le \theta(\eta) \le 1$. Under these conditions, the dependence of the surface coverage on overpotential is studied for the following two sets of parameters (S_j)

$$S_1(\theta_1^e,\ \nu_{V1}^e,\ \nu_{H1}^e, \nu_{T1}^e,\ \alpha_{V1},\ \alpha_{H1}) \tag{12a}$$

$$S_2(\theta_2^e, \nu_{V2}^e, \nu_{H2}^e, \nu_{T2}^e,\ \alpha_{V2},\ \alpha_{H2}) \tag{12b}$$

The corresponding expressions for a_j, b_j and c_j (j =1,2) can be obtained from eq. 7a-c. Then, considering the following relationships between the parameters of the two sets

$$\theta_2^e = (1\text{-}\theta_1^e) \tag{13a}$$

$$\nu_{V2}^e = \nu_{H1}^e \tag{13b}$$

$$\nu_{H2}^e = \nu_{V1}^e \tag{13c}$$

$$\nu_{T2}^e = \nu_{T1}^e \tag{13d}$$

$$\alpha_{V2} = \alpha_{H1} \tag{13e}$$

$$\alpha_{H2} = \alpha_{V1} \tag{13f}$$

The relationships between the constants are straightforwardly obtained

$$a_2 = -\ a_1 \tag{14a}$$

$$b_2 = b_1 + 2a_1 \tag{14b}$$

$$c_2 = -\ (c_1 + b_1 + a_1) \tag{14c}$$

Consequently, if θ_1 is the solution of the equation $a_1\theta_1^2 + b_1\theta_1 + c_1 = 0$, it can be verified from eq. 14a-c that

$$\theta_2(\eta) = 1 - \theta_1(\eta) \tag{15}$$

is the solution of the equation $a_1\theta_1^2 + b_1\theta_1 + c_1 = 0$. Therefore, the dependence $\theta(\eta)$ can be transformed into the dependence $[1 - \theta(\eta)]$ by replacing the kinetic parameters θ^e, ν_V^e, ν_H^e, ν_T^e, α_V and α_H according to eq. 13a-f. The first consequence of such replacement is related to the behavior of the steady-state pseudocapacitance, which is defined as

$$C = q\left|\frac{d\theta}{d\eta}\right| \tag{16}$$

Where q is the charge needed to complete one monolayer of adsorbed hydrogen. If $C_1(\eta)$ and $C_2(\eta)$ correspond to the set of kinetic parameters $S_1$and S_2, respectively, then

$$C_1(\eta) = C_2(\eta) \tag{17}$$

Analysis of the dependence $j(\eta)$

The expressions of the current density can be obtained by replacing the two sets of kinetic parameters given in eq. 12a and 12b, respectively in eq. 10.

$$j_1(\eta) = j(\eta, S_1) \tag{18a}$$

$$j_2(\eta) = j(\eta, S_2) \tag{18b}$$

Taking in account eq. 13a-f and that the dependence of the surface coverage on overpotential for the two sets of parameters verifies eq. 15, it can be demonstrated from eq. 18a-b that

$$j_1(\eta) = j_2(\eta) \tag{19}$$

Equation 19 indicates that there are two sets of kinetic parameters that can be reproduce a given dependence $j(\eta)$. It can also be demonstrated from eq. 19 that the polarization resistance (R_p) is invariant to the permutation of the two sets of the kinetic parameters. This fact can be verified taking into account that R_p for the hydrogen electrode reaction described by the Volmer-Heyrowsky-Tafel mechanism is given by [Ch'96]

$$R_p = \frac{RT}{4F^2}\left[\frac{4v_T^e + v_H^e + v_V^e}{v_H^e v_V^e + v_T^e v_V^e + v_H^e v_T^e}\right] \tag{20}$$

Considering the two sets of kinetic parameters as in the previous item and taking into account eq.13a-f, it can be verified that $R_{p1} = R_{p2}$, a result that derives directly from eq. 19. Furthermore, the exchange current density for the Volmer-Heyrowsky-Tafel mechanism is given by [Ch'96]

$$j^0 = 2F\frac{v_V^e v_H^e + v_V^e v_T^e + v_H^e v_T^e}{v_V^e + v_H^e + 2v_T^e} \tag{21}$$

and is also invariant to the permutation of the two sets of kinetic parameters.

4. Conclusions

The two sets of kinetic parameters that fit the same $j(\eta)$ dependence of the hydrogen electrode reaction through the Volmer –Heyrowsky-Tafel mechanism was established. In this context, there are two cases, which can be derived from eq. 13a-f.

1. The equilibrium reaction rate for the Tafel step equal to zero in S_1. Taking into account eq. 13d, it follows that in this case both sets of parameters characterize the reaction through the Volmer-Heyrowsky route.
2. The equilibrium reaction rates for the Heyrowsky step equal to zero in S_1. Taking into account eq. 13b, it follows that in this case set S_1 defines the route of Volmer-Tafel. The dependence $\theta_1(\eta)$ increases with the displacement of the overpotential toward negative values, as is well known. [Ba'93] When set S_2 is analyzed, the same dependence $j(\eta)$ is described by the less known Tafel-Heyrowsky route. [Ch'99] On the other hand, if the equilibrium reaction rate for the Volmer step is equal to zero in S_1, according to eq. 13c, S1 defines the Tafe-Heyrowsky route, and S_2 the Volmer-Tafel route, respectively.

An alternative that could give some evidence on the distinction between the two sets of kinetic parameters should be the study of the hydrogen evolution reaction on membrane electrodes, where the hydrogen absorption reaction takes place.

References

[Ba'93] Bai L., J. Elecroanal. Chem., 355, 37 1993

[Ch'96] Chialvo M.R.G., Chialvo A.C., J. Electroanal. Chem., 415, 97, 1996

[Ch'00] Chialvo M.R.G., Chialvo A.C., Journal of the Electrochemical Society, 147 (5), 1619 – 1622, 2000

[Ch'99] Chialvo M.R.G., Chialvo A.C., Electrochem. Commun., 1, 379, 1999

[La'90] Lasia A., Rami A., Electroanal. Chem., 294, 123, 1990

[La'94] Lasia A., Proceedings of the Symposium on Electrochemistry and Material Science of the Cathodic Hydrogen Absorption and Adsorption, PV 94/21, 261, The Electrochemical Society Proceedings Series, Pennington, 1994