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Hydrogen evolution reaction on a smooth iron electrode in alkaline solution at different temperatures

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The hydrogen evolution reaction (HER) has been studied on a rotating polycrystalline smooth iron disc electrode in the temperature range $20 \leqslant T/°C \leqslant 60$ in 2 M NaOH. It has been demonstrated that only for $|\eta| \geqslant 0.1$ V can the polarisation curve be considered as that corresponding to the HER, due to the corrosion process that takes place at low overpotentials. The experimental results were adequately correlated by the Volmer–Heyrovsky–Tafel mechanism with a Langmuirian adsorption, considering $\alpha_V \neq \alpha_H$. On this basis, two sets of kinetic parameters were found for each of the three elementary steps and the corresponding apparent activation energies were also evaluated. These results allowed the calculation of the experimental kinetic parameters, Tafel slope and extrapolated exchange current density, for all the temperatures studied.

Introduction

The HER on iron in alkaline solutions has been scarcely studied.[1–6] These works, except for two,[2,4] correspond to studies of permeation through iron membranes, based on the cell of Devanathan–Stachurski.[7] The thickness of the membranes used was $127 \leqslant d/\mu m \leqslant 770$ and an inverse dependence between the permeation flow and the thickness of the membrane was found.[3]

The most recent works[5,6] analyse the enhancement of inhibition of the HER by the adsorption of ions SH^- and AsO_2^-. A rigorous description of the reaction kinetics on the basis of the Volmer–Heyrovsky–Tafel mechanism was carried out, considering also the processes of absorption of hydrogen and adsorption of anions (inhibitors). The results obtained for the HER on pure iron showed two distinguishing aspects: the existence of a point of inflexion in the dependence of the logarithm of the current density (j) on overpotential (η),[5,6] and the dependence of the surface coverage (θ) on η that could be described by the Langmuirian adsorption model in spite of the large variation in θ values.

The present work deals with the evaluation of the elementary kinetic parameters of the Volmer–Heyrovsky–Tafel mechanism and their dependences on temperature for the hydrogen evolution reaction on a smooth polycrystalline iron electrode in the range $20 \leqslant T/°C \leqslant 60$.

Experimental

Experiments were carried out in a three-compartment, three-electrode cell. The working electrode was a rotating disc of Fe ARMCO 99.99%, 11 mm diameter and 3 mm thickness embedded into a Tacussel exchangeable electrode holder with an exposed surface of 0.26 cm^2 (5.8 mm diameter). This electrode was rotated at 4000 rpm by a rotating disc system (Tacussel EDI 10K). The electrolytic solution was 2 M NaOH, prepared with triply distilled water and purified by pre-electrolysis. The purity was verified through the independence of the current on the rotation rate at $\eta = -0.4$ V. The reference electrode was the reversible hydrogen electrode in the same solution (RHE), which allows direct reading of the overpotential, after the corresponding correction for the ohmic drop. The counterelectrode was a large area, platinised platinum wire located in an external separate compartment. Runs were carried out in a saturated solution by continuous bubbling of purified hydrogen and the selected temperature was controlled ($T \pm 0.1$ °C) by a thermostat Lauda R400.

(a) Electrochemical measurements

The experimental measurements were carried out using a potentiostat–galvanostat (Radiometer PGP201) and the VoltaMaster application software. Current–potential dependences were obtained by applying stationary voltammetry. This consisted of a potential scan, started at $\eta = -0.65$ V towards the anodic direction, with potential steps of 0.025 V with 240 s waiting time. Before each run, the working electrode was polished by the usual metallographic techniques using alumina powder up to 0.5 μm. Then, it was immersed in the electrolyte solution at -0.65 V and this potential was held for 15 min before the stationary voltammetry program was started. The experiment was continued until the current changed sign. Thus, it was possible to determine the corrosion potential for each temperature; this was always cathodic with respect to the RHE.

Results

The experimental current–potential dependences show at all temperatures that the inversion in the sign of the current is verified at a cathodic potential with respect to the reference hydrogen electrode in the same solution (Fig. 1). It can be inferred that at low overpotentials, corrosion of the Fe electrode occurs.[8,9] Therefore, for the correct analysis of the experimental current–potential dependence, the overpotential region where the experimental current density corresponds solely to that of the HER must be established ($j_{HER} = j_{exp}$). Fig. 2 illustrates qualitatively the different contributions to the experimental polarisation curve near the corrosion potential. They are the anodic current due to iron oxidation and the cathodic current corresponding to the HER. The corrosion

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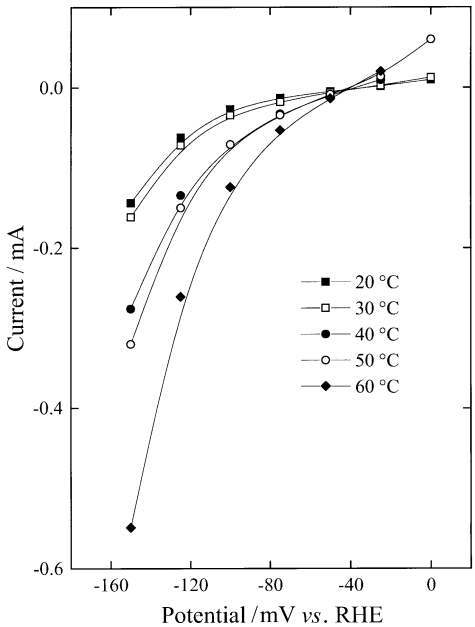

Fig. 1 Experimental current–potential dependence near the current sign inversion for the polarisation of Fe in 2 M NaOH at different temperatures.

potential can be evaluated from the experimental data shown in Fig. 1 and the corresponding corrosion current density by application of the Stern–Geary–Mansfeld method.[10] The results are summarised in Table 1. From these values and using the cathodic contribution to the Stern–Geary–Mansfeld equation, the corresponding values of j_{HER} were estimated near the corrosion potential. It can be concluded from these results that for $|E - E_{corr}| > 0.1$ V, the contribution of the corrosion process to the experimental current can be ignored. Therefore, the correct overpotential range for the determination of the kinetic parameters of the HER was $|\eta| \geqslant 0.1$ V.

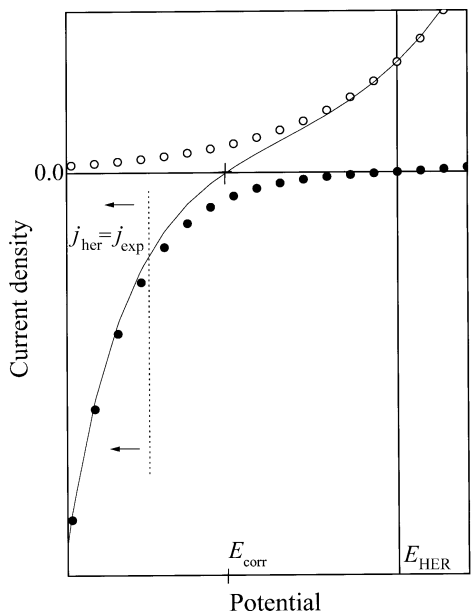

Fig. 2 Deconvolution of the experimental current–potential dependence near equilibrium for Fe in NaOH 2 M. (——) Experimental curve; (●) HER; (○) oxidation current.

Table 1 Values of the corrosion potential and current density on Fe in 2 M NaOH at different temperatures

T/°C	$-E_{corr}$/mV	j_{corr}/μA cm^{-2}
20	31.7	10.8
30	33.0	16.2
40	38.3	45.0
50	39.7	48.0
60	40.8	85.2

The experimental dependences log j *vs.* η of a smooth iron electrode in 2 M NaOH solution at 20, 30, 40, 50 and 60 °C and for $|\eta| \geqslant 0.1$ V are illustrated in Fig. 3 (symbols). It can be observed that in all cases the dependence exhibits an inflexion before it reaches the Tafelian region at high overpotentials. This behaviour is similar to that found previously for nickel in the same electrolyte solution.[11] The Volmer–Heyrovsky–Tafel kinetic mechanism is usually considered valid for the hydrogen evolution reaction. Due to the existence of the inflexion point, the stationary experimental dependence log j *vs.* η must be correlated by the simultaneous occurrence of the three steps. Volmer–Heyrovsky or Volmer–Tafel routes are not applicable to this case. The reaction steps in alkaline solutions can be written as:

$$H_2O + e^- \rightarrow H_{(ad)} + OH^- \text{ (Volmer)} \quad (1a)$$

$$H_2O + e^- + H_{(ad)} \rightarrow H_2 + OH^- \text{ (Heyrovsky)} \quad (1b)$$

$$H_{(ad)} + H_{(ad)} \rightarrow H_2 \text{ (Tafel)} \quad (1c)$$

Moreover, it is known that the adsorbed hydrogen can be embodied into the metal[1,3,5,6] as:

$$H_{(ad)} \rightarrow H_{(ab)} \quad (2)$$

It should be valid to consider that the permeation flow of hydrogen from the surface to the bulk of the electrode is zero at the end of the waiting time, when the current is read. This is because the electrode is rather thick (3 mm) and there is no anodic process on the opposite side of the electrode to promote diffusion. Therefore, the experimental results can be analysed considering the Volmer–Heyrovsky–Tafel mechanism in steady state and reaction (2) can be ignored. Consequently, the surface concentration $\theta(\eta)$ can be determined by the reaction steps (1a–c). In other words, it is considered that at the moment the current is read at each potential value, the

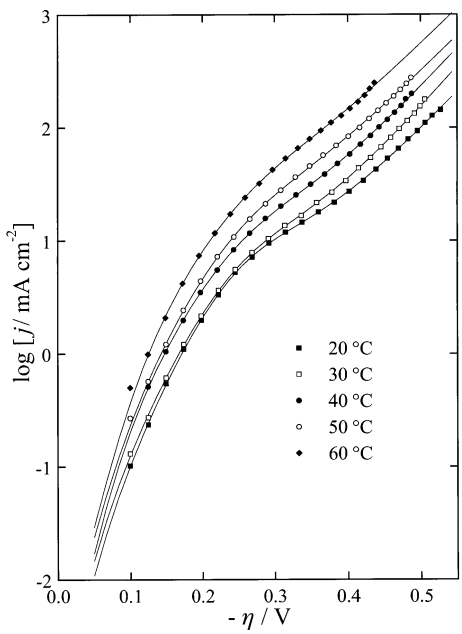

Fig. 3 Experimental dependence of the logarithm of the current density on overpotential for the HER on Fe in 2 M NaOH at different temperatures. Continuous lines correspond to simulation.

absorbed hydrogen is at equilibrium with the adsorbed hydrogen.

In this context, the experimental results were correlated at first through the Volmer–Heyrovsky–Tafel mechanism, being the behaviour of the reaction intermediate described by the Frumkin adsorption model with the symmetry factors $\alpha_V = \alpha_H$, using a generalisation of the equations derived previously.[12] Under these conditions, a reasonable fit of the experimental dependence was not achieved, even with the interaction parameter equal to zero (Langmuirian behaviour). Then, the Langmuir adsorption model was used, but considering $\alpha_V \neq \alpha_H$, attaining in this case an excellent fitting of the experimental data. The corresponding expressions of the current density and the surface coverage as a function of overpotential used for the correlation were:[13]

$$j(\eta) = \frac{F \exp(\alpha_V f\eta)}{(1-\theta^e)} \left\{ v_V^e \exp(-f\eta) - v_H^e \exp[(\alpha_H - \alpha_V) f\eta] - \left[[v_V^e \exp(-f\eta) - v_H^e \exp[(\alpha_H - \alpha_V) f\eta] + \frac{(1-\theta^e)}{\theta^e} \{v_V^e - v_H^e \exp[-(1-\alpha_H+\alpha_V) f\eta]\} \right] \theta(\eta) \right\} \quad (3)$$

$$a\theta^2 + b\theta + c = 0 \quad (4)$$

$$a = \frac{2v_V^e(1-2\theta^e)}{\theta^{e2}(1-\theta^e)^2} \quad (4a)$$

$$b = \frac{4v_T^e}{(1-\theta^e)^2} + \exp(\alpha_V f\eta) \times \left[\frac{v_V^e \exp(-f\eta) + v_H^e \exp[(\alpha_H - \alpha_V) f\eta]}{(1-\theta^e)} + \frac{v_V^e + v_H^e \exp[-(1-\alpha_H+\alpha_V) f\eta]}{\theta^e} \right] \quad (4b)$$

$$c = -\frac{2v_T^e}{(1-\theta^e)^2} - \exp(\alpha_V f\eta) \times \left[\frac{v_V^e \exp(-f\eta) + v_H^e \exp[(\alpha_H - \alpha_V) f\eta]}{(1-\theta^e)} \right] \quad (4c)$$

where $f = F/RT$; v_i^e is the equilibrium reaction rate of the step i ($i = {}_{V,H,T}$); α_i is the symmetry factor of i ($i = {}_{V,H}$) and θ^e is the surface coverage at equilibrium.

A non-linear least-squares fitting was applied to correlate the experimental results through eqn. (3) and (4a–c). This was done for $\eta \geqslant 0.1$ V, in order to avoid distortions in the dependence $j(\eta)$ due to the corrosion process. In these conditions, the kinetic parameters of the elementary steps (θ^e, α_V, α_H, v_V^e, v_H^e, v_T^e) were obtained. The regression generates two sets of kinetic parameter,[13] which are given in Table 2. It should be noticed that in spite of carrying out independent fitting for each temperature, the values of α_V and α_H were quite similar, which should indicate that they are independent of temperature and that the consideration about the difference in the α_i values is valid.

Discussion

The experimental determination of the current–potential dependence on a rotating disc electrode was used to evaluate the kinetic parameters of the hydrogen evolution reaction on iron. Special attention was paid to obtaining the correct polarisation curve and therefore the corrosion effect at low overpotentials was taken into account.

For the correct analysis of the dependences log j *vs.* η, it is convenient to evaluate also the variation of the surface coverage θ on η. It can be derived from data in Table 2 that two such relationships can be obtained, from Set I (θ_I) and Set II [$\theta_{II} = (1 - \theta_I)$], respectively. As the results obtained for each temperature are quite similar, Fig. 4 shows only the response at $T = 40$ °C. It can be observed that for Set I, θ_I varies from

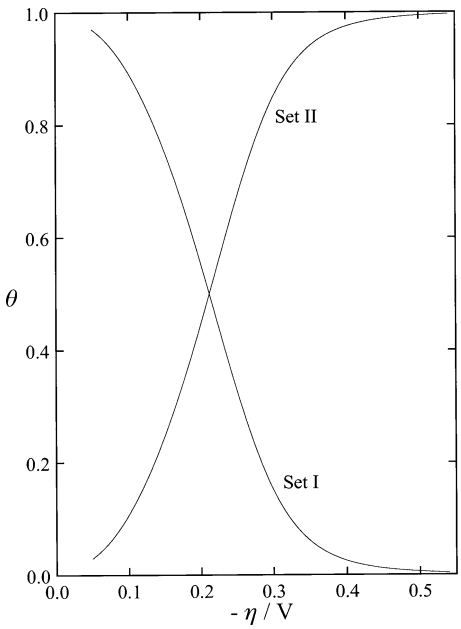

Fig. 4 Dependence of the surface coverage on overpotential for the HER on Fe in 2 M NaOH at 40 °C.

Table 2 Values of the elementary kinetic parameters obtained from simulation of the experimental results for Fe in 2 M NaOH at different temperatures

T/°C	Set	v_V^e/mol cm^{-2} s^{-1}	v_H^e/mol cm^{-2} s^{-1}	v_T^e/mol cm^{-2} s^{-1}	θ^e	α_V	α_H
20	I	5.878×10^{-10}	7.237×10^{-8}	1.895×10^{-9}	0.993 78	0.563 21	0.210 14
	II	7.237×10^{-8}	5.878×10^{-10}	1.895×10^{-9}	0.006 22	0.210 14	0.563 21
30	I	1.506×10^{-9}	9.544×10^{-8}	3.281×10^{-9}	0.991 56	0.563 51	0.211 60
	II	9.544×10^{-8}	1.506×10^{-9}	3.281×10^{-9}	0.008 44	0.211 60	0.563 51
40	I	2.123×10^{-9}	3.065×10^{-7}	2.260×10^{-9}	0.994 51	0.568 77	0.273 22
	II	3.065×10^{-7}	2.123×10^{-9}	2.260×10^{-9}	0.005 49	0.273 22	0.568 77
50	I	6.150×10^{-9}	2.828×10^{-7}	3.215×10^{-9}	0.993 82	0.576 98	0.194 61
	II	2.828×10^{-7}	6.150×10^{-9}	3.215×10^{-9}	0.006 18	0.194 61	0.576 98
60	I	7.214×10^{-9}	9.204×10^{-7}	2.897×10^{-9}	0.995 88	0.577 46	0.279 29
	II	9.204×10^{-7}	7.214×10^{-9}	2.897×10^{-9}	0.004 12	0.279 29	0.577 46

$\theta_I^e \cong 1$ to the limiting value $\theta_I^* \cong 0$ at $|\eta| \geqslant 0.40$ V. Conversely, for the case of Set II, θ_{II} varies from $\theta_{II}^e \cong 0$ to the limiting value $\theta_{II}^* \cong 1$ at $|\eta| \geqslant 0.40$ V. This behaviour was obtained for all temperatures studied.

The analysis of the dependences log j *vs.* η indicates the existence of a Tafelian domain at high overpotentials, where the surface coverage becomes independent of potential. Under these conditions, the terms in eqn. (4a–c) that do not depend on η can be neglected and thus a linear expression of $\theta(\eta)$ is obtained. Substituting it in eqn. (3), the following useful expression is obtained at $\eta \rightarrow -\infty$ (in this case $|\eta| \geqslant 0.40$ V). If Set I is considered, it is verified that $\alpha_{VI} > \alpha_{HI}$:

$$j(\eta) = \frac{2v_{VI}^e F}{(1-\theta_I^e)} \exp[-(1-\alpha_{VI})f\eta]; \quad \theta_I(\eta) = \theta_I^* = 0 \qquad (5)$$

Eqn. (5) can be rewritten in terms of the experimental kinetic parameters as:

$$j(\eta) = j_h^{ext} \exp[-\eta/b_h] \qquad (6)$$

where j_h^{ext} is the current density at $\eta = 0$ extrapolated from the high overpotential region, and b_h is the Tafel slope. They are defined as follows:

$$j_h^{ext} = \frac{2v_{VI}^e F}{(1-\theta_I^e)}, \quad b_h = 2.3026/(1-\alpha_{VI})f \qquad (7)$$

For Set II, it is necessarily verified that $\alpha_{VII} < \alpha_{HII}$ and the corresponding expression of $j(\eta)$ is:[13]

$$j(\eta) = \frac{2v_{HII} F}{\theta_{II}^e} \exp[-(1-\alpha_{HII})f\eta];$$

$$\theta_{II}(\eta) = [1-\theta_I^*] = \theta_{II}^* = 1 \qquad (8)$$

where j_h^{ext} and b_h are given by:

$$j_h^{ext} = \frac{2v_{HII}^e F}{\theta_{II}^e}, \quad b_h = 2.3026/(1-\alpha_{HII})f \qquad (9)$$

It should be noticed that both experimental kinetic parameters j_h^{ext} and the corresponding Tafel slope b_h are unique, independent of the set of elementary kinetic parameters from which they can be calculated, due to the relationships between both sets of kinetic parameters.[13] The experimental parameters were evaluated from data tabulated in Table 2 and are shown in Table 3.

The question about which of the two Sets (I or II) actually represents the behaviour of the hydrogen evolution reaction on iron is an open subject. Published results related to the dependence of the permeation rate on potential should be in favour of an increasing dependence of the surface coverage on overpotential (Set II).[5,6] Nevertheless, studies of the role of absorbed hydrogen on the corrosion of iron would indicate the inverse behaviour (Set I).[14] Moreover, it should be possible that the hydrogen involved as the intermediate in HER could be different from that involved in the absorption process. All these aspects should be the subjects of further studies.

Finally, the evaluation of the apparent activation energy of the elementary reaction steps was carried out, which is defined as:

$$\left.\frac{\partial \ln v_i^e}{\partial(1/T)}\right] = -\frac{E_{ai}^{app}}{R} \qquad (10)$$

Fig. 5 shows the linear dependences of ln v_i^e ($i = {}_{V,H,T}$) on the inverse of temperature for one of the sets of elementary kinetic parameters. The corresponding E_{ai}^{app} were calculated and the resulting values are illustrated in Table 4 for both sets of kinetic parameters. It can be noticed that Set II can be obtained from Set I by permutation of the Volmer and Heyrovsky parameters whilst holding the same value for the Tafel parameter, as has been demonstrated elsewhere.[13] It should be noticed that the apparent activation energies of the Volmer and Heyrovsky steps are quite similar, whilst that corresponding to the Tafel step is markedly lower. Although these kinds of data cannot be found in the literature, an estimation of an apparent activation energy, but in acidic solution, was made starting from experimental data obtained by Bockris *et al.*[1] on Fe, taking into account that the dependence of θ^e on temperature can be considered negligible. Extrapolating the Tafelian regions to the respective equilibrium potentials (calculated at each temperature), the corresponding values of ln j_h^{ext} were obtained, from which a value $E_a^{app} = 22.06$ kcal mol^{-1} was found. Taking into account that eqn. (7) and (9) are applicable in these conditions, it can be concluded that the value obtained corresponds to the Volmer or the Heyrovsky step.

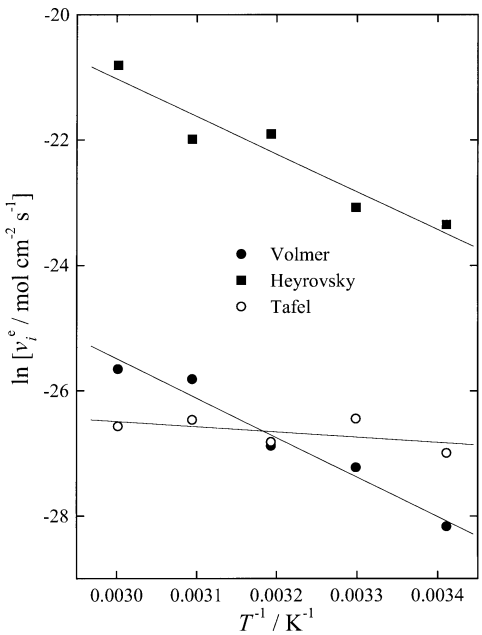

Fig. 5 Dependence of ln v_i^e on the inverse of temperature for the Volmer, Heyrovsky and Tafel steps.

Table 3 Values of the experimental kinetic parameters for Fe in 2 M NaOH at different temperatures

T/°C	j_h^{ext}/mA cm^{-2}	b_h/mV dec^{-1}
20	0.009 12	133.2
30	0.0172	137.8
40	0.0373	144.1
50	0.0960	151.6
60	0.1689	156.4

Table 4 Values of the apparent activation energy for the elementary kinetic steps

	E_a^{app}/kcal mol^{-1}	
Step	Set I	Set II
Volmer	24.494	23.814
Heyrovsky	23.814	24.494
Tafel	4.450	4.450

Furthermore, the value of the apparent activation energy calculated from the data of Bockris *et al.*[1] is surprisingly similar to those evaluated in the present work for the Volmer (24.5 kcal mol^{-1}) and Heyrovsky (23.8 kcal mol^{-1}) steps.

Acknowledgements

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