

Current transients for the hydrogen evolution reaction at high overpotentials on silver electrodes in acid solutions: Experiments and modelling



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ABSTRACT

The hydrogen evolution reaction has been investigated on Ag(1 0 0) by potentiostatic current transients at high overpotentials ($\eta > 0.7$ V) in acidic solutions. The reaction proceeds via the Volmer–Heyrovsky mechanism, simultaneously coupled with desorption of sulphate/disulphate anions. Volmer is the rate determined step, although the Heyrovsky reaction is only slightly faster. The kinetic parameters have been obtained under various conditions of pH and concentration of anions. A catalytic effect due to the presence of anions has been observed.

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1. Introduction

The hydrogen-evolution reaction (HER) is one of the best-investigated reactions in electrochemistry (for a noteworthy overview see [1]). There are two important motivations for its study. On one side, the practical interest in using hydrogen as a renewable fuel. On the other side, it is considered to be a classical prototype of an electrocatalytic process due to the apparent simplicity of its mechanism. For many decades, a considerable effort has been made to develop a theoretical framework that explains the experimental results. Also, much of surface science has focused on the metal–hydrogen interactions [2,3]. These interaction energies have been the basis of the popular ‘volcano plots’ which have been widely used as criteria for electrocatalytic activity. However, this oversimplified approach frequently does not take into account the differences in the mechanisms and the existence of various forms of adsorbed hydrogen [1] depending on the electrode material.

We can distinguish three groups of metals with different behaviours. (1) Metals like platinum, which show a high reactivity; the hydrogen molecule dissociates spontaneously, and the oxidation reaction occurs very fast. (2) Metals like mercury, which are practically inactive, and finally (3) the coinage metals (Au, Ag and Cu), which show an intermediate behaviour, and are therefore well suited to investigate in detail different effects [4–9]. Considerably attention has been paid to mechanistic aspects on platinum electrodes (see for example [10–15]). In the case of the less active electrodes, changes in the Tafel slopes are frequently observed. Several alternatives have been proposed, including the theory of barrierless discharge [16].

Although hydrogen is the simplest atom (single valence electron), the difficulties in the fundamental understanding of its reactivity have been recognized a long time ago (see for example the introductory remarks in [1,2]). When Gerischer and Mehl wrote their seminal paper in 1955 [8], they observed that many features of hydrogen evolution were not yet understood, even though fifty years had passed since the first thorough investigation of this reaction by Tafel [17]. Now, another fifty years later, after myriads of articles have been published on this subject, important issues still remain controversial.

In the case of an electrochemical environment, not only metal–hydrogen interactions play a role, but additional complications must be considered: In the reaction mechanism, electron

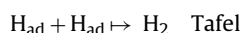
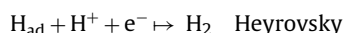
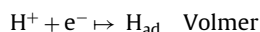
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transfer processes take place; the interaction with the solvent involves reorganization of the hydration shells; specifically adsorbed ions can interfere with the reaction. In our group, we have developed a theoretical approach for the investigation of electrochemical processes, which explicitly considers solvent interactions and electron transfer [18]. We have applied this theory to a large variety of metal surfaces; amongst others, we have explained why (1 1 1) surfaces of copper and silver are better catalysts for HER than (1 0 0) surfaces [19].

Another practical complication in the investigation of the HER is the mass transport. Frequently, cyclic voltammetry is used to characterize the electrocatalytic activity. Although this technique can give first qualitative insights, more precise measurements are necessary for a quantitative analysis. Thus, besides rotating disc electrodes under hydrodynamic control, electrochemical impedance spectroscopy and potential pulses are appropriate methods to investigate the kinetics of the HER. The analysis of the response at short times avoids complications produced by diffusion processes, and the kinetic processes can be investigated.

The mechanism involved in the HER depends on the electrocatalyst. There are three possible elementary reaction steps:



The rate of the Erdey-Gruz - Volmer reaction [20] reaction depends on the vacancies of the surface sites, while the rates of Heyrovsky [21] and Tafel [17] reactions depend on the hydrogen coverage. On silver electrodes, it is well known that the HER goes through a two-steps mechanism, involving Volmer and Heyrovsky as elementary steps [8,9]. We have also investigated with our own theory Volmer and Heyrovsky steps on Ag(1 1 1). According to our calculations, both reactions have similar rate constants, the Heyrovsky step being slightly faster [22].

In this contribution, we aim to improve the kinetic models for the HER to describe the behaviour of Ag(1 0 0) electrodes over the entire relevant potential region and under various operating conditions, and compare with theoretical calculations based on our own model of electrocatalysis. Basically, we have analyzed the effect of pH and the influence of adsorbing anions. We have used an approach that improves the formalism previously proposed by Gerischer and Mehl [8] and includes the simultaneously desorption of anions. We have separated the contributions of the two elementary steps, evaluated their rate constants, and compared their potential dependence with theoretical predictions. We have applied this approach to the HER on Ag(1 0 0), but an extension to other orientations is straightforward. We like to stress here, that the approach proposed by Gerischer and Mehl is valid only if the adsorbed intermediates formed electrochemically obey the Langmuir isotherm throughout the range of coverage studied, and the reverse reactions can be neglected [23]. These restrictions are fulfilled if the measurements are performed at high overpotentials and the adsorption energy of the intermediates does not depend on the coverage.

2. Experimental

The Ag(100) single crystal electrode with an exposed area of 0.1706 cm² has been provided by Mateck (orientation accuracy <1°). The silver electrode was pre-treated by a three-step procedure. First, by cyclic polarization in a solution containing 0.1 M CrO₃ [24], then by chemical polishing in a NaCN + H₂O₂ solution, and finally exposing the electrode to hydrogen-flame annealing

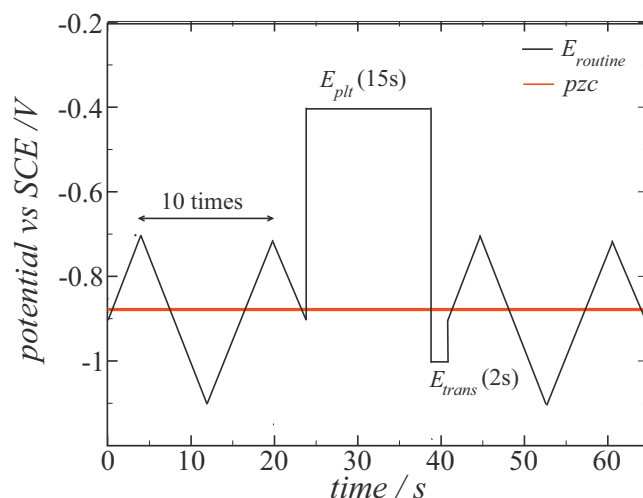


Fig. 1. Potential routine programme for measurements of transients to obtain kinetic parameters for the HER on Ag(100). $E_{\text{plt}} = -0.400$ V is the previous potential applied for stabilization, E_{trans} the potential where the transient was recorded, and $pzc = -0.865$ V is the potential of zero charge for the Ag(1 0 0) electrode [18] (red line).

[25]. The crystal was transferred with a drop of ultrapure water to the electrochemical cell and immersed into the electrolyte under potential control at a potential below the potential of zero charge ($pzc = -0.865$ V). In this way, contact of the crystal with air was kept to a minimum. Electrodes treated with this procedure yield nearly ideal voltammetric responses for the underpotential deposition of Pb monolayers according to the literature. Prior to each measurement the surface was stabilized performing several potential cycles in the potential range of -1.1 V to -0.7 V vs SCE at 100 mV/s.

The supporting electrolyte was prepared with H₂SO₄ and Na₂SO₄ suprapure products (Merck) and water from a Barnstead Nanopure TOC-UV Ultrapure Water System (18.2 MΩ, TOC < 5 ppb). The electrolyte was deaerated with N₂ before each measurement. Also, we have carried out some test experiments in hydrogen-saturated electrolytes. However, no appreciable changes in the transients have been observed, at least in the period of time necessary to record the transients.

Indeed, a simple estimate shows that at the high overpotentials which we applied the hydrogen oxydation is entirely negligible. Therefore, all the measurements for the HER presented here have been performed in the absence of hydrogen in the electrolyte.

The electrochemical measurements were carried out at $T = 298$ K in a conventional electrochemical cell. The counter electrode was a platinum sheet (1 cm²), and the reference electrode was a saturated calomel electrode (SCE) mounted inside a Luggin capillary.

All potentials in this study were referred to the SCE. In the case of the theoretical data calculated for different overpotentials, a comparative SCE-scale is included. The electrochemical measurements were carried out with an Autolab model AUT 84233, controlled by NOVA 1.6 software.

The chronoamperometric transients were obtained applying a systematic consecutive potential routine (see Fig. 1).

3. Kinetic modelling

3.1. Current response to potentiostatic pulses

The measured current density during a potential step for the HER considering the three possible steps mentioned in the introduction

(Volmer, Heyrovsky, Tafel), and neglecting double layer charging, transport contribution and the reverse reactions, is given by:

$$j(t) = nFk_V(\eta, C_{H^+})[1 - \theta_H(t)] + nFk_H(\eta, C_{H^+})\theta_H(t) \quad (1)$$

The only two steps that contribute to the electrochemical current are Volmer (first term) and Heyrovsky (second term), whose rate constants k_V and k_H depend on the overpotential η and the concentration of protons C_{H^+} ($k_V = k_V^0 C_{H^+} \exp(\alpha_V F \eta / RT)$, $k_H = k_H^0 C_{H^+} \exp(\alpha_H F \eta / RT)$). The Volmer reaction rate is proportional to the density of vacant adsorption sites on the metal surface ($1 - \theta_H$), while the Heyrovsky reaction rate is proportional to the hydrogen coverage θ_H . The Tafel reaction rate depends quadratically on the hydrogen coverage and its rate constant k_T is independent of the overpotential. This reaction does not contribute directly to the current, but indirectly through the change in the hydrogen coverage.

The general expression for the time dependence of current and hydrogen coverage is according to Gerischer and Mehl [8] (for simplicity, from now on, we shall omit the parenthesis (η, C_{H^+})):

$$j(t) = nFk_V + nF(k_H - k_V) \left[P \frac{e^{\lambda_G t} - S}{e^{\lambda_G t} + S} - R \right] \quad (2)$$

$$\theta_H = P \frac{1 - Se^{-\lambda_G t}}{1 + Se^{-\lambda_G t}} - R \quad (3)$$

where

$$P = \frac{\sqrt{(k_V + k_H)^2 + 4k_V k_T}}{2k_T} \quad (4)$$

$$R = \frac{k_V + k_H}{2k_T} \quad (5)$$

$$S = \frac{\sqrt{1+X} - 1}{\sqrt{1+X} + 1} \quad (6)$$

$$X = \frac{4k_V k_T}{(k_V + k_H)^2} \quad (7)$$

$$\lambda_G = 2nF \frac{k_T P}{Q_H^0} \quad (8)$$

Q_H^0 is the charge density corresponding to a monolayer (ML) of hydrogen and for the case of Ag(100) is $1.92 \times 10^{-4} \text{ C/cm}^2$, $n=1$ since for every of both steps (Heyrovsky and Volmer) only one electron is transferred.

According to (3) the hydrogen coverage monotonically increases with the time from zero reaching the stationary value of:

$$\theta_H^\infty = P - R \quad (9)$$

Therefore, the cathodic current decays if $k_V > k_H$ whereas it increases if $k_H > k_V$, independent of the value of k_T . Consequently, it is possible to infer only from the transient shape if Volmer or Heyrovsky is the rate-determining step. This is one of the advantage of using potentiostatic pulses. Fig. 2 shows some examples of transients for different conditions of the rate constants simulated using Eq. (2). Another interesting aspect of potentiostatic pulses is, that at the start of the transient the current is given by the Volmer process ($j_{t=0} = j_V = nFk_V$), while the stationary value is given by:

$$j_\infty = j_V \left[1 + \theta_H^\infty \left(\frac{j_H}{j_V} - 1 \right) \right] \quad (10)$$

where $j_H = nFk_H$. This equation allows a clear separation of both processes, which is more difficult to obtain with stationary techniques, since both processes are measured simultaneously. The relationship between initial and final currents (j_∞/j_V) varies between two and zero depending on the kinetic parameters.

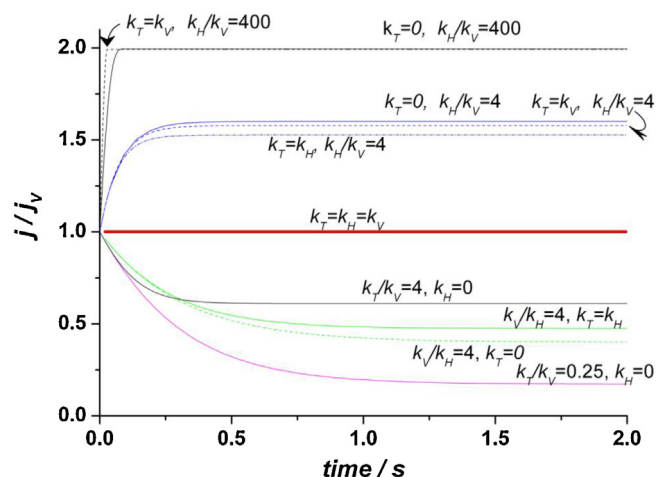


Fig. 2. Simulated current transients with Eq. (2) for different relationships between the kinetic parameters. The current has been normalized to the Volmer current j_V (Volmer rate constant $k_V = 5 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$). k_T : Tafel rate constant, k_H : Heyrovsky rate constant.

If the three rate constants have the same values ($k_V = k_H = k_T$), then $j_\infty/j_V = 1$ for the whole interval of time, and the maximum coverage of hydrogen is $\theta_H^\infty = 0.41$. However, if the electrochemical recombination is the only reaction that occurs in the second step ($k_V = k_H$; $k_T = 0$), this value increases to $\theta_H^\infty = 0.5$. As we shall see below, in our measurements (and also according to our theoretical predictions) we are close to this limit, with the Heyrovsky step being only slightly faster than the Volmer step.

If $k_H > k_V$, independent on the value of k_T , the relationship between initial and final currents is $1 < (j_\infty/j_V) < 2$, and the stationary hydrogen coverage cannot reach a value higher than $\theta_H^\infty = 0.5$. It is interesting to note here, that even when $k_T > k_H$, the current increases with time until the stationary value. However, we have to keep in mind, that while the Tafel reaction does not depend on the potential, for the Heyrovsky reaction the activation energy decreases with the potential. Therefore, it is expected that at higher overpotentials the second step happens predominantly through the electrochemical recombination.

Only if the second step, either Heyrovsky or Tafel, is the rate-determining step is $(j_\infty/j_V) < 1$, and the hydrogen coverage can reach values larger than $\theta_H^\infty > 0.5$.

There are other processes that can also affect the hydrogen reactions. Here, we analyze the effect on the transients, when a previously adsorbed species A desorbs simultaneously during the hydrogen evolution reaction, with the rate constant k_D . We shall see in the next sections that this is the case for silver electrodes, when anions are specifically adsorbed. Now, expression (1) becomes:

$$j(t) = nFk_V(\eta, C_{H^+})[1 - \theta_H(t) - \theta_A(t)] + nFk_H(\eta, C_{H^+})\theta_H(t) \quad (11)$$

where

$$\theta_A(t) = \theta_A^0 e^{-\lambda_A t} \quad (12)$$

$$\lambda_A = nF \frac{k_D}{Q_H^0} \quad (13)$$

We restrict ourselves to the Volmer–Heyrovsky steps for the HER, since on silver electrodes, as we have predicted from theoretical calculations [22], and we shall see later from the experimental results, the Tafel reaction does not play any role. Then, considering that the Tafel reaction is negligible, the differential equation to be solved with the boundary condition $\theta_H^0 = 0$ (at $t=0$) is:

$$Q_H^0 \frac{d\theta_H}{dt} = nFk_V[1 - \theta_H(t) - \theta_A(t)] - nFk_H\theta_H(t) \quad (14)$$

Replacing (12) in (14) the solution is trivial, and expression (3) becomes:

$$\theta_H(t) = \theta_H^\infty (1 - e^{-\lambda_{VH}t}) + \frac{\theta_A^0 k_V}{k_V + k_H + k_d} (e^{-\lambda_{VH}t} - e^{-\lambda_A t}) \quad (15)$$

where

$$\lambda_{VH} = nF \frac{(k_V + k_H)}{Q_H^0} \quad (16)$$

and

$$\theta_H^\infty = \frac{k_V}{k_V + k_H} \quad (17)$$

$$j_\infty = nF \frac{2k_V k_H}{k_V + k_H} \quad (18)$$

In both expressions above, the stationary hydrogen coverage (17) and stationary current (18) do not depend on the kinetic parameters for the desorption of anions. Note that the limits for hydrogen coverage for $t \rightarrow 0$, and $t \rightarrow \infty$ are the same as before ($\theta_H^0 = 0$ and (15) reduces to the expression (17), respectively).

However, the initial current depends on the initial surface concentration of the blocking species A:

$$j_0 = nF k_V (1 - \theta_A^0) \quad (19)$$

In all the cases described above, interactions between adsorbed species have been neglected. This should be a good approximation at low coverage, and only at high coverage some deviations, due to the repulsion between adsorbed neighbours, should be expected. As we have already mentioned, hydrogen adsorption on silver is weak. Density Functional Theory (DFT) calculations suggest that at 0 V NHE and pH 0 the adsorption of the hydrogen atom is endergonic by about 0.4 eV. This implies, that it should be exergonic for potentials more negative than -0.4 V, and thus over the whole potential range in which we have performed our experiments. For the Tafel reaction, our DFT calculations give a value of about 1.3 eV for the energy of activation, much higher than for the Volmer and the Heyrovsky steps. This is in line with our experimental results, which show no contribution of the Tafel reaction. In the rest of this work, we shall therefore focus on the Volmer–Heyrovsky mechanism. In another contribution [27], we have also studied the coverage dependence of the adsorption energy of hydrogen and simulated its effect on the transient. At coverages below 0.5 it is so small that it is completely negligible. A similar weak adsorbate interaction has been observed by Karlberg et al. for the adsorption of hydrogen on platinum [28]. Therefore, the interaction between adsorbed hydrogen can be considered weak for these conditions, and Langmuir isotherms are applicable.

4. Results and discussion

Fig. 3 shows voltammograms in acidic solutions for Ag(100) in the potential region where the HER takes place. Besides the high overpotential for the HER and the expected decrease of the current with pH, although this reaction occurs below the potential of zero charge ($pzc = -0.865$ V for Ag(100) [26]), a markedly catalytic effect of the anions is also observed. This effect appears for both pH values. For the highest concentration of anions and lowest pH, a shoulder at about -0.8 V is observed.

A similar behaviour has been observed by Schweizer and Kolb [29], and it was attributed to a catalytic effect in the hydrogen evolution, which is favoured by the adsorbed sulphate. Comparable effects were also reported for sulphate on Cu(111) surfaces [30–32].

These voltammograms give a first insight into the influence of anions on the HER at Ag(100). However, as mentioned in

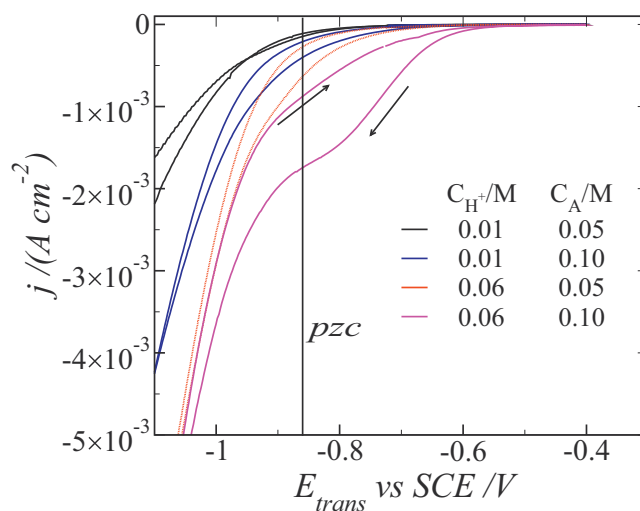


Fig. 3. Cyclic voltammograms for Ag(100) in the potential range where the HER takes place. The electrolyte was prepared by different combinations of H_2SO_4 and NaHSO_4 . $C_A/M = [\text{SO}_4^{2-}] + [\text{HSO}_4^-]$. Potential sweep: 50 mV/s.

the introduction, current transients obtained by potentiostatic pulses are more appropriate for a quantitative analysis than cyclic voltammetry.

Fig. 4a shows a typical experimental current transient obtained by applying a potential step in the region of the HER in

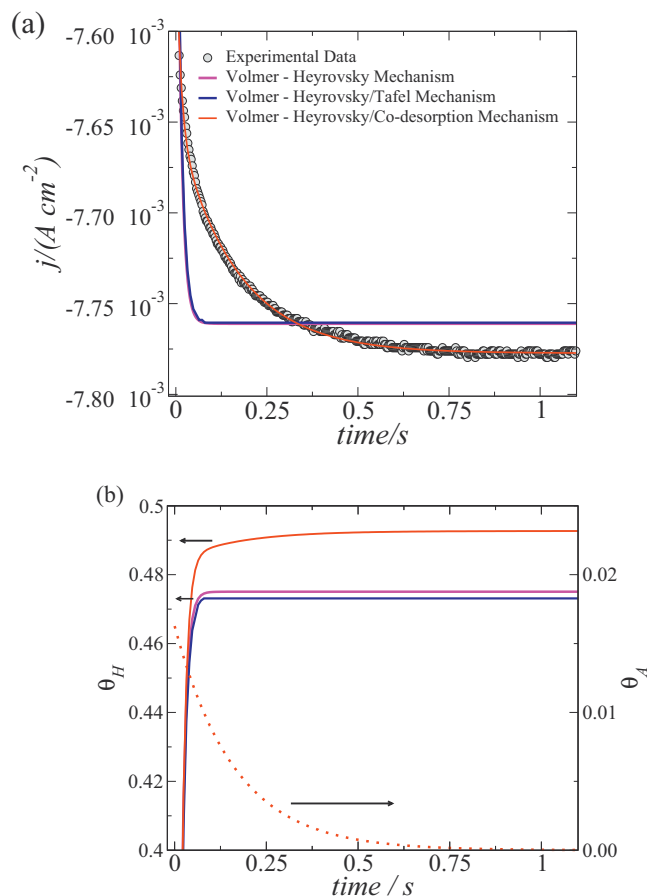


Fig. 4. (a) Typical potentiostatic current transient obtained for the HER at $E_{trans} = -1.2$ V, in $0.03 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ solution. The lines are the best fits performed with different kinetic models. (b) Evolution with time of the hydrogen and anions coverages obtained applying the different kinetic models to fit the experimental data (the colours correspond to those of (a)).

Table 1Kinetic parameters obtained from the fit of the experimental data shown in Fig. 4 with the different models. $V_{trans} = -1.2$ V, electrolyte: 0.03 mol/dm³ H₂SO₄.

| Kinetic model | k_V (mol cm ⁻² s ⁻¹) | k_H (mol cm ⁻² s ⁻¹) | k_T (mol cm ⁻² s ⁻¹) | k_D (mol cm ⁻² s ⁻¹) | λ_{VH}^{-1} (s) | λ_A^{-1} (s) |
|--------------------------------|---|---|---|---|-------------------------|----------------------|
| Volmer–Heyrovsky | 8.04×10^{-8} | 8.89×10^{-8} | – | – | 1.17×10^{-2} | – |
| Volmer–Heyrovsky/Tafel | 7.64×10^{-8} | 8.48×10^{-8} | 5.2×10^{-12} | – | 1.23×10^{-2} | – |
| Volmer–Heyrovsky/co-desorption | 7.94×10^{-8} | 8.18×10^{-8} | – | 1.22×10^{-8} | 1.23×10^{-2} | 0.163 |

comparison to different fits. Fig. 4b shows the corresponding time evolution of the adsorbed species. The increasing cathodic current indicates that Heyrovsky reaction plays an important role in the formation of H₂ during the second step of the HER, with the Volmer reaction as rate determining step ($k_H > k_V$). However, attempts to fit this curve considering the Volmer–Heyrovsky, or the more general mechanism considering both chemical and electrochemical recombination as further steps (Volmer–Heyrovsky/Tafel mechanism, Eq. (2)) failed (see pink and blue lines in Fig. 4a). The only way to obtain an almost good fit using Eq. (2), is considering a larger time constant λ_{VH}^{-1} containing an unrealistic value for Q_H^0 . It seems that the experimental current decays more slowly to the stationary value than the predictions by the two considered mechanisms. Successful results can be obtained if we consider desorption of foreign species to occur simultaneously with the hydrogen recombination (see Eq. (11), red lines in Fig. 4a and b). Table 1 shows the kinetic parameters obtained by fitting the experimental data of Fig. 4 with the different models. Although the Volmer step is rate determining, the Heyrovsky reaction has a rate constant of the same order of magnitude. Therefore, the terms proportional to the hydrogen coverage in Eq. (11) practically compensate each other, and the main contribution to the current comes from the term: $(j(t) \approx nFk_V[1 - \theta_A(t)])$. This explains the delay to achieve the stationary current, since the time constant corresponding to the anion desorption (λ_A^{-1}) determines the shape of the transient (see also the coverage decay of the desorbing species A in Fig. 4b).

A more detailed exploration of the transients shows interesting effects (Fig. 5). Here, the results obtained under different conditions of pH and concentrations of anions are shown, using normalized scales for both current and time. The current has been normalized by the experimental stationary value j_∞ , while the time constant λ_{VH}^{-1} given by Eq. (16) has been used for the normalization of the time scale. When the concentration of anions increases, a pronounced delay, up to 30 times the value of the time constant λ_{VH}^{-1} , can be

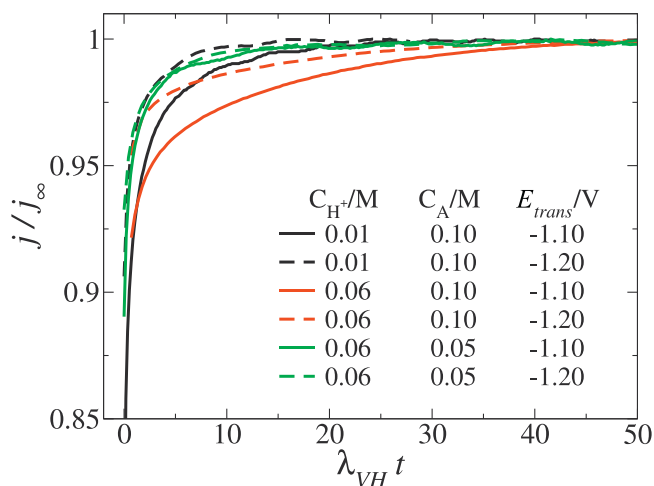


Fig. 5. Normalized current transients obtained at two different potentials E_{trans} , using electrolytes with two different pH and two different concentrations of anions (sulphate/bisulphate). The current was normalized with the stationary current j_∞ , while the time with the time constant of the Volmer–Heyrovsky mechanism λ_{VH}^{-1} (see Eq. (15)).

observed. This demonstrates the effect of the anions already mentioned above. At the beginning of each transient the surface is slightly blocked by anions, so that the initial current is less negative than that of a perfectly clean surface. The decay of the transient is affected by the anion coverage and the rate at which the anions desorb. Consequently, the equilibrium current is achieved only when the anion coverage is zero. This effect is weaker at higher overpotentials, since the anions coverage desorb faster.

Other interesting effects can be inferred from the analysis of transients such as those shown in Fig. 5. The rate of Volmer and Heyrovsky reactions increases with the proton concentration in the solution. However, instead of the expected reaction order of 1, we obtained values of about 0.5 for both steps in all the analyzed cases. Doubova and Trasatti [5] have also obtained a low order reaction of 0.8 varying the concentration of HClO₄ at constant ionic strength. We shall return to this point later.

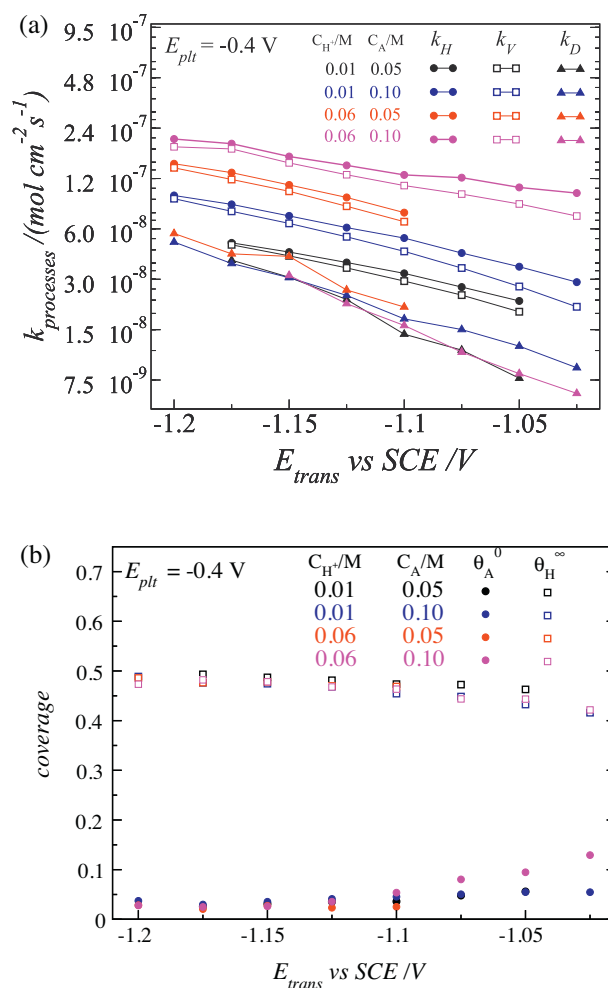


Fig. 6. Potential dependence of kinetic parameters for HER obtained by fitting current transients under different conditions of pH and anions concentration. (a) Rate constant for Volmer step k_V , Heyrovsky step k_H , and anions desorption k_D . (b) Surface coverage for hydrogen at the stationary state θ_H^0 , and initial coverage for anions (immediately after set the potential at E_{trans}).

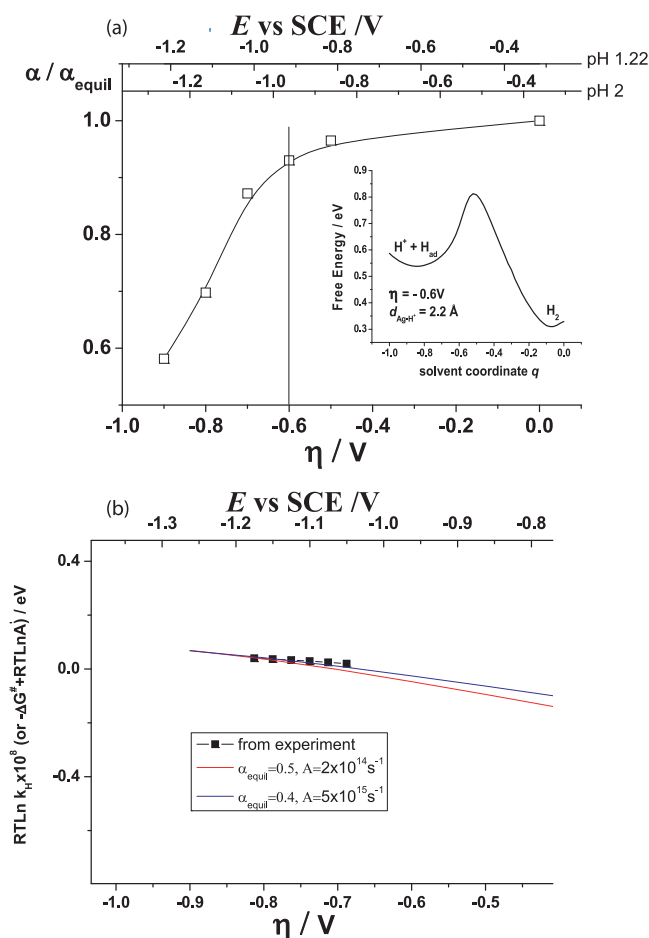


Fig. 7. (a) Predicted decrease of the charge transfer coefficient α with increasing negative overpotentials for the Heyrovsky step according to our electrocatalysis theory [15]. Inset: free energy curve for the Heyrovsky step at $\eta = -0.6$ V as a function of the solvent coordinate, and at a constant distance to the surface ($d = 2.2$ Å). The α values were calculated from the derivative of the free activation energy. (b) Comparison between experimental current – overpotential data (symbols) and theoretical predictions assuming different values of the equilibrium charge transfer coefficient and pre-exponential factor A . Experimental data correspond to the black filled circles of Fig. 6.

The rate constants, obtained by fitting the transients using Eq. (11), are shown in Fig. 6a as a function of the potential E_{trans} . According to these results, Volmer and Heyrovsky rate constants are of the same order of magnitude for all the systems analyzed, the Heyrovsky reaction always being slightly faster. Both rate constants are larger for higher concentration of anions. This effect appears at all pH investigated, and quantitatively confirmed the catalytic influence of the presence of anions on the HER, as already mentioned above from the qualitative analysis of the cyclic voltammograms (see Fig. 3). The charge transfer coefficient α for both steps, Volmer and Heyrovsky reactions, is always considerably lower than 0.5. Doubova and Trasatti [5] and our group in a previous work [9] have reported values near 0.5. However, the overpotentials investigated in the present contribution are considerably higher than those reported in the previous works. It is well known from theoretical approaches of Marcus [33] and Dogonadze et al. [34,35], that transfer coefficients different of 0.5 can be obtained depending if the elementary steps are endergonic or exergonic. In order to verify this effect, we have calculated the overpotential dependence of the charge transfer coefficient for the Heyrovsky step applying our previous theoretical approach [22]. We have obtained it from the derivative of the activation energy. Fig. 7a shows the relative decrease of α from the value at equilibrium to higher

overpotentials. In the same figure, the free energy as a function of the solvent coordinate for the reactions path at $\eta = -0.6$ V is included as an example. Effectively, at overpotentials far from equilibrium the reaction becomes exergonic. These results clearly show that a considerable effect on the transfer coefficient is expected at high overpotentials, as we have experimentally observed. Fig. 7b shows two estimated current–potential curve obtained by considering the overpotential dependence of α shown in Fig. 7a, assuming two different values of the equilibrium value of α and two estimated values of the pre-exponential coefficient A , in comparison with one of the set data of Fig. 6 [33]:

$$k_H = k_H^0 e^{-\left[\int_{\eta_{equil}}^{\eta} \alpha d\eta - \Delta G_{equil}^\# \right] / kt} \quad (20)$$

Although this is an approximation, since the theory yields relative values, the agreement is very good, and it demonstrates that the large Tafel slopes obtained experimentally have a physical basis.

Returning to Fig. 6a, the rate constants for the anions desorption process are considerable lower than the kinetic constants of the elementary steps corresponding to the HER. They are independent of the protons and anions concentrations in the solution but they increase with the overpotential. At potentials well below pzc , the negative charge on the surface is larger, increasing the repulsion between the surface and the anions. Therefore, the desorption rate increases as well.

Fig. 6b shows the potential dependence of the stationary hydrogen coverage θ_H^∞ , and the initial anion coverage θ_H^0 obtained by the fit. θ_H^∞ values are slightly potential dependent, and always lower than 0.5 ML. In view of the weak interaction between hydrogen and silver, these coverages may seem rather high. However, as mentioned above, the electrochemical potential is the driving force, and our values refer to a range of overpotentials in which hydrogen adsorption is exergonic. Also, our results are in line with the values reported by Gerischer and Mehl [8], who obtained values of 0.8 and 0.3 for polycrystalline copper and silver electrodes, respectively. Also the pseudocapacity curves shown by Doubova and Trasatti [5] suggest coverages in this range, if we analyze them in the framework of the well known kinetic models (for example, compare Fig. 2 in [5] with Fig. 2 in [13]).

θ_A^0 values are below 0.15 ML and slightly decrease at higher overpotentials. Pioneering works of Valette [26] and Vitanov and Popov [36], exclusively based on electrochemical measurements, have shown that perchlorate and also sulphate adsorb specifically on Ag(1 0 0) around the pzc . Valette [26] suggested, that in the case of weak ion-metal interactions, like those between sulphate or perchlorate and silver, the role of the ion–solvent interactions may determine the relative adsorbability. Therefore, it can overcome the specific co-adsorption of hydronium and sulphate.

More recently, it has been experimentally verified by several other methods, that sulphate/bisulphate adsorbs specifically on silver: Marinković et al. [37] by in situ FTIR spectroscopy, Smoliński et al. [38] by radiometric and electrochemical methods, Shingaya and Ito [39] by IRAS measurements, Schweizer and Kolb [29] by STM. Adsorption isotherms were calculated [38] and the maximal adsorption coverage was estimated to be around 0.15–0.20 ML, i.e. of the same order of magnitude as obtained by us.

Effectively, incommensurate (1.3×3) superstructure of sulphate or bisulphate similar to the structure of this anion on Au(1 0 0) found by Kleinert et al. [40], was molecularly resolved by in situ STM by Schweizer and Kolb [29] on Ag(1 0 0). They derive a sulphate coverage of 0.25 at -0.2 V vs SCE. More interesting, since measurements in neutral 0.1 M Na_2SO_4 solutions showed a disordered sulphate adlayer, it is evident that H_3O^+ hydrogen-bonded to sulphate is required to stabilize the sulphate structure, such as also suggested by Kleinert et al. [40] for gold. Bridging hydrogen

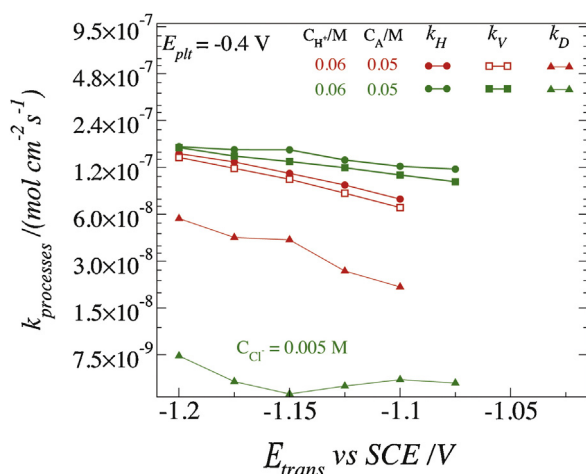


Fig. 8. Potential dependence of kinetic parameters for HER obtained with two solutions of the same pH and same concentration of sulphate, but at one of them an aliquot of chloride was added (green lines and symbols).

bonds would diminish the Coulomb repulsions between adjacent sulphate anions. They have attributed secondary spots observed in the STM images to the hydronium co-adsorption.

Although the HER occurs at potentials below the pzc , the presence of a certain amount of adsorbed sulphate is expected, since the interaction with hydronium ions stabilizes this adlayer. Therefore, the previously formed adlayer during the pre-treatment procedure performed at E_{plt} still survives for a while when the potential has been set at E_{trans} . Desorption of the anions occurs simultaneously with the HER (see the time-dependences of θ_A and θ_H in Fig. 4b). As demonstrated in Figs. 4 and 5, the presence of a small amount of adsorbed anions is enough to produce a marked delay in the establishment of the stationary current. The co-adsorption of hydronium can also explain the fractional order obtained at different pH. The distribution of these cations in the interface should be different than in the bulk of the electrolyte. Doubova and Trasatti [5] have also invoked this possible explanation.

Finally, in order to explore the role of anion adsorption further, we have added a small amount of chloride anion, which is known to adsorb strongly on Ag(1 0 0), also below the pzc [41,42]. Fig. 8 shows these results in comparison with those obtained in the presence of sulphate. The corresponding desorption rate constant of chloride is about one order of magnitude lower than that for desorption of sulphate at a concentration ten times lower. A catalytic effect on the HER is also observed, although it is not as strong as expected. This result indicates, that the catalytic effect is not directly related to the presence of any sort of anions, but to those who can be stabilized by hydronium. Probably, halides interactions with hydronium are weaker than those with oxanions, like sulphate or perchlorate, due to the absence of hydrogen bonds formation.

5. Conclusions

We have investigated the kinetics of HER on Ag(1 0 0), and found that within the entire range of overpotentials investigated, the reaction proceeds via the Volmer–Heyrovsky mechanism with a simultaneous slow desorption of anions specifically adsorbed during the pre-treatment at potentials in the double layer region. Probably, these anions are stabilized by the co-adsorption of hydronium. We have separated the contributions of the elementary steps and the corresponding rate constants have been obtained. The rate-determining step is the Volmer reaction, although the Heyrovsky step is only slightly faster. This fact is the reason why the anion effect is so strong. In Eq. (11) the terms depending on the

hydrogen coverage compensate each other, and the time constant of the anions desorption determines how fast the stationary state is achieved.

The small values of the anion desorption constant has an important consequence in the shape of the transients even if the anion coverage is not large. The rate constants for the anions desorption process are considerable lower than the kinetics of the HER. Therefore, the HER could reach quickly the stationary state if the anions were absent as is evident from the simulated curves in Fig. 4. However, since there are adsorption sites that must be released by the anions in order the HER takes place, about 95% of the transient is determined by the kinetics of the anions desorption process.

For most of the measurements in this work, the initial coverage of anions on Ag(1 0 0) is below 0.1 ML. Although this is a relatively small coverage with respect to final hydrogen coverage (between 0.4 and 0.5 ML), it was found that the influence of anion desorption drastically changes the shape of the transient.

The high values of hydrogen coverage (about 0.5) can be understood because of both rate constants, corresponding to Volmer and Heyrovsky steps are almost of the same order of magnitude. Furthermore, at the investigated overpotentials, both reactions are exergonic.

A catalytic effect by sulphate adsorption has been observed for the HER, as it is evident from the higher rate constants obtained for both processes (Volmer and Heyrovsky) in the presence of adsorbing anions. The proposed model for the evaluation of the rate constants is based on the sites inhibition by anions and cannot explain by itself an increase in the catalytic activity. A quantitative analysis of this effect requires a detailed theoretical modelling for the barrier of both steps.

A strong decrease of the transfer coefficient α at higher negative overpotentials has been observed in accordance with theoretical predictions [33–35].

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