



Short communication

First insights of the electrocatalytical properties of stepped silver electrodes for the hydrogen evolution reaction

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ABSTRACT

The electrocatalytic properties of vicinal Ag(11n) surfaces for the hydrogen evolution reaction are investigated. An analysis of the reactivity as a function of the step density is performed. The rate constants for Volmer and Heyrovsky steps are evaluated from potentiostatic transients. A correlation between the anisotropy of hydrogen adsorption energy for different sites with the non-linear dependence on the step density is established.

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1. Introduction

The use of well-defined stepped surfaces has early been recognized as an experimental strategy to approach the behavior of nanoparticles [1], since sites at steps often seem to be much more active than those at terraces. Therefore, reactivity can be investigated as a function of density of defects by a systematic variation of the terrace width. The obtained trends can usually be interpreted as a combination of contributions from terraces and step sites.

The reactivity of stepped surfaces towards selected reactions of particular interest in electrocatalysis has been widely investigated. These studies included small organic molecules such as CO [2] and formic acid oxidation [3], NO and N₂O reduction [4,5], and ethanol oxidation [6], to mention some examples. In some cases, a linear relationship of the kinetic parameters with the density of steps is found [7]. Overviews of stepped metal surfaces and their stability and catalytic properties can be found in [8]. In a previous contribution [9], we have investigated the electronic properties for the series Ag(11n) surfaces by means of Density Functional Theory (DFT) and anisotropy maps of the resulting dipole moments have been calculated. The effect of steps and adsorbed hydrogen on the work function has been analyzed.

Experimentally, hydrogen adsorption on platinum stepped surfaces with different orientations of terraces and steps has been widely investigated [3,10,11]. Characteristic peaks can be identified in cyclic voltammograms, which were assigned to hydrogen adsorption and anion co-adsorption on different terrace and step sites. However, the kinetic parameters for the hydrogen evolution reaction (HER) on metallic electrodes of the Pt family are very difficult to obtain, since this reaction occurs too fast [12,13] and mass transport would interfere. In the case of slower processes, potentiostatic pulses appear as an attractive method to measure the kinetics, since current transients can be analyzed at short time without limitations of mass transport. Therefore, silver electrodes, where the HER is easily measurable, appear as an ideal system to investigate the effect of steps by this technique.

1.1. Experimental

Silver electrodes with vicinal surfaces of Ag(11n) orientations provided by Mateck have been employed. These surfaces have (100) terraces of different width and monoatomic (111) steps. We have investigated the Ag(115), Ag(119), and Ag(1 1 17) orientations, in comparison with the basal Ag(100) surface. The pre-treatment of the surface was previously described [13,14]. The measurements were carried out in 0.05 M H₂SO₄ at 25 °C using an Autolab model AUT 84233, controlled by NOVA 1.6 software.

The routine employed to obtain the kinetic parameters by means of potentiostatic transients is the same as that of a previous work [14]. First, the electrode is kept at a potential in the double layer

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region ($V_{\text{pl}})$ for 15 s, then the potential is changed to the region where the HER takes place (V_{trans}), and the current is recorded.

1.2. Computational details

DFT calculations based on plane waves were performed as implemented in DACAPO code. In a previous work, we have specified the details of these calculations [9]. Planar (100) and (111) surfaces have been described using (2×2) supercells with five metal layers. Vicinal Ag(11n) surfaces were modeled using unit cells with $m = (n + 1)/2$ silver atoms exposed to the surface, and two of them are located at the step. (1×1) and (2×1) supercells, containing 5 m metal layers, were used. All the adsorbate atoms and either the 2 or the 2 m topmost metal layers were allowed to relax in the case of planar or vicinal surfaces, respectively.

2. Results and discussion

We have demonstrated in a previous work [15] that hydrogen evolution reaction in silver surfaces occurs in two elementary steps:



We have also shown that the Tafel reaction ($\text{H}_{\text{ad}} + \text{H}_{\text{ad}} \rightarrow \text{H}_2$) is not a relevant process at high overpotentials. The characteristic shape for the experimental transients corresponds to a Volmer–Heyrovsky mechanism, Volmer being the rate-determining step. However, both reactions proceed with rate constants of the same order of magnitude. We note in passing that on silver hydrogen evolution is complicated by the simultaneous desorption of anions; in Ref. [15] we have shown how to eliminate this effect from the data.

Stepped surfaces are more active for the HER than the flat Ag(100), as can be observed from the current transients in Fig. 1a. The stationary currents observed at long times follow the order: Ag(115) > Ag(119) > Ag(117) > Ag(100). Using the procedure developed by Gerischer and Mehl [16] and our improvement to take into account the influence of anions [15], we have calculated the separate contributions of the Volmer and the Heyrovsky reactions. Briefly, the general expression for the current response when a potentiostatic pulse is applied is given by:

$$j(t) = nFk_V(\eta, C_{\text{H}^+})[1 - \theta_{\text{H}}(t) - \theta_{\text{A}}(t)] + nFk_{\text{H}}(\eta, C_{\text{H}^+})\theta_{\text{H}}(t).$$

The Volmer reaction with constant rate k_V (first term) is proportional to the density of vacant adsorption sites on the metal surface

$(1 - \theta_{\text{H}} - \theta_{\text{A}})$, while the Heyrovsky reaction with constant rate k_{H} (second term) is proportional to the hydrogen coverage θ_{H} . During the transient, anions that have been specifically adsorbed at the previous higher potential desorb and their coverage θ_{A} decreases to zero when the stationary state is reached. 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. We restrict ourselves to the Volmer – Heyrovsky steps for the HER, since on silver electrodes, as we have predicted from theoretical calculations [9] and it has been established from the experimental results [15,16], the Tafel reaction does not play any role at high overpotentials. Solving the corresponding differential equations assuming a Langmuir isotherm for the hydrogen adsorption, no contribution of the reverse reactions and disregarding mass transport at the time scale of our experiment, the current transients are fitted and the rate constants k_V and k_{H} are obtained. The use of Langmuir isotherm is justified because of the negligible interactions between adsorbed hydrogen, as we have confirmed by the DFT calculations.

An increase of the current with time has been obtained for all the surface orientations, indicating that Volmer reaction is the rate determining step and the electrochemical recombination (Heyrovsky reaction) the second step [15,16]. This result can be understood, because initially, only proton adsorption occurs, so that the coverage rises and electrochemical recombination sets in. As both reactions involve charge transfer, the current rises and becomes constant at long times. In contrast, chemical recombination does not involve charge transfer, so that the current would fall as the coverage rises. The stationary currents increase with the density of steps. Both reactions' constants (Volmer and Heyrovsky) also increase with the density of steps (see Fig. 1b). The simplest interpretation is that the reactions are faster on step sites than on terrace sites.

If we assume that on each type of site a reaction has a specific rate constant, a plot of the current versus the step density should result in a straight line. This is clearly not the case for the Ag(11n) surfaces. The decreasing slope with increasing step density indicates that either the step sites or the terrace sites become less active as the terraces get shorter.

A similarly complicated behavior has been observed before by Kajiwara et al. [12] who found that for stepped Pt surfaces, the value of the exchange current density j_0 for the HER/HOR increases linearly with the increase of the step atom density only from $n = \infty$ to $n = 9$. However, the values of j_0 for $(n - 1)(111)-(110)$, $n(100)-(111)$ and $n(100)-(110)$ series become constant on the surfaces with $n \leq 9$, whereas those of $n(111)-(100)$ series still increase linearly with the increase of L^{-1} .

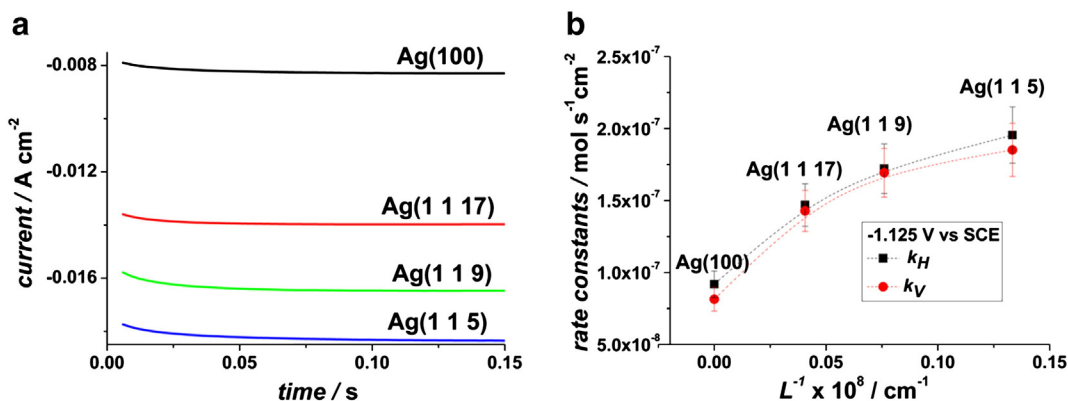


Fig. 1. (a) Potentiostatic transients for the HER on Ag(11n) electrodes at -1.125 V vs SCE. (b) Volmer and Heyrovsky rate constants as a function of the density of steps calculated by fitting the current transients shown on (a). (The density of steps was calculated from the mean distance between steps: $L_{11n} = \frac{a_{\perp}}{2} \sqrt{2 + n^2}$, where $a_{\perp} = 0.2889$ nm is the distance between densely packed atomic rows along [110] direction).

In order to understand the reasons for the non-linear behavior, we have investigated the interaction between hydrogen and the different possible adsorption sites on stepped surfaces. A quantitative evaluation requires first, the calculations of the activation barriers for both steps (Volmer and Heyrovsky) like the analysis we have previously performed with the low index single crystals of silver [17,18]; second, molecular dynamic simulations with these parameters must be carried out. In the present systems, this analysis is very complicated due to the variety of sites and the broken symmetry of stepped surfaces in comparison with the flat ones. We are optimizing this approach, but meanwhile we can make some estimation applying the Sabatier principle [19] and assuming that the adsorbed hydrogen is the intermediate resulting from the Volmer reaction as rate-determining step. Specifically, we have calculated by DFT the corresponding adsorption energies at various sites (bridge, hcp and fcc at the (111) steps, and hollow and bridge at the (100) terraces) using the expression:

$$\Delta E_{ads} = E_{surf+H} - E_{surf} - \frac{1}{2}E_{H_2}$$

where E_{surf+H} , E_{surf} and E_{H_2} are the energy of the H/surface system, the total energy of the surface, and of the hydrogen molecule, respectively. The highest activity for the adsorption is shown by the step sites, even though the central sites of the terraces also show appreciable minima for the adsorption energy. These results show a continuous energy gradient on the terraces directed from the upper to the bottom of the successive steps, even for surfaces with wide terraces like Ag(1 1 17). As an example, Fig. 2 shows the adsorption energy at the hollow sites of the terraces for the different stepped surfaces in comparison to the flat Ag(100). Similar tendencies have been found for the bridge sites perpendicular to the steps. The average energy difference between steps and terraces is not so large (about 0.1–0.2 eV). However, we have to keep in mind that according to the

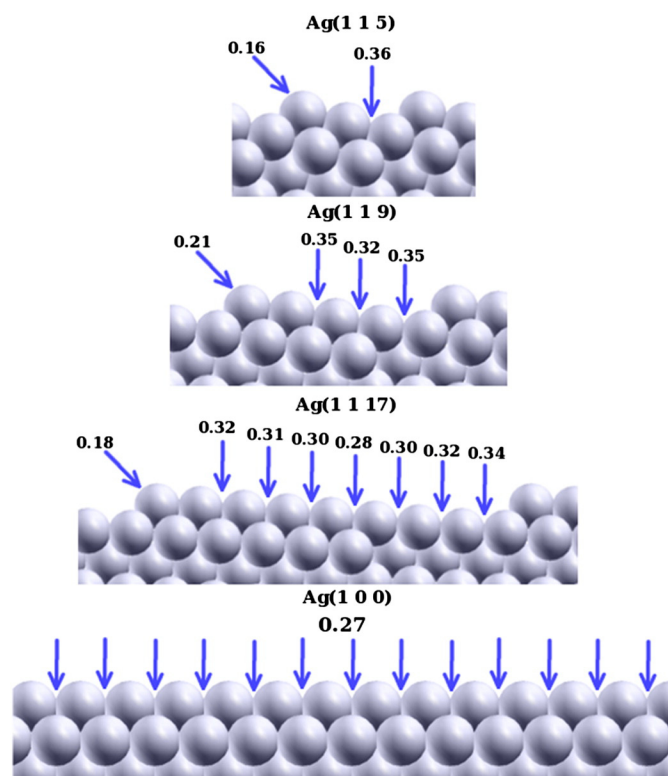


Fig. 2. Energetics for hydrogen adsorption on hollow sites of terraces and on bridge sites at steps of vicinal Ag(11n) surfaces. Adsorption energy at hollow sites of the flat Ag(100) surface is included for comparison. All the energy values are in eV.

Butler–Volmer law the energy of adsorption enters into the exponent for the rate constant.

At the upper part of steps, there are always two favorable sites with low coordination (bridge and hcp), with adsorption energies of about 0.16–0.18 eV independent of the width of the terrace. However, these values are somewhat higher than those at the corresponding sites of a flat (111) surface. The more coordinated fcc step–site at the bottom of steps shows higher values than the equivalent sites of a flat (111) surface, and only slightly lower than those of (100) terrace sites. On the terraces the adsorption energy at a given site depends both on the width of the terrace and on its position on the terrace, sites at the center being more favorable. The step–step interaction is evident from the break in the symmetry of the bridge sites of the terraces. The adsorption at bridge sites perpendicular to the steps is less favorable than at bridge sites parallel to the steps. The latter shows similar adsorption energies to the flat (100) surface and practically non-effect of the terrace length is observed, except at the sites closest to the step. This behavior could be due to the long-range order in the direction parallel to the step. On the contrary, the adsorption at hollow and bridge sites perpendicular to the steps is more affected by the length of the terraces, since the parallel steps break the two-dimensional symmetry of the surface. Clearly, as the terraces become shorter, adsorption on the terraces becomes less favorable. This complicated energetic picture explains the curvature observed in Fig. 1b, since less favorable adsorption energies result in lower rate constants according to the Sabatier principle.

3. Conclusions

We have shown that on stepped silver surfaces the rate of both the Volmer and the Heyrovsky reaction is faster on the steps than on the terraces. However, the rate constants of these reactions do not vary linearly with the step density. Our DFT calculations indicate that the adsorption energy at the step sites is independent of the terrace width, while the adsorption on the terrace sites depends both on the position along the terrace and the terrace length. Adsorption on shorter terraces is less favorable, and this qualitatively explains on the basis of Sabatier principle the non-linear dependence of the rate on the step density. The distribution of the adsorption energies on the surfaces is quite complicated. A quantitative analysis requires a detailed kinetic modeling for the barrier of both steps (Volmer and Heyrovsky), for which this work has laid the foundations.

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