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 N_2O 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 H_2SO_4 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$_{plt}$) 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:

$$H^+ + e^- \rightarrow H_{ad} \qquad \text{(Volmer)}$$

$$H_{ad} + H^+ + e^- \rightarrow H_2 \qquad \text{(Heyrovsky)}.$$

We have also shown that the Tafel reaction ($H_{ad} + H_{ad} \rightarrow H_2$) 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(11 17) > 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:

$$j(t) = nF k_V(\eta, C_{H^+})[1 - \theta_H(t) - \theta_A(t)] + nF k_H(\eta, C_{H^+})\theta_H(t).$$

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

($1 - \theta_H - \theta_A$), 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 = ∞ 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 ≤ 9, whereas those of n(111)–(100) series still increase linearly with the increase of L^{-1}.
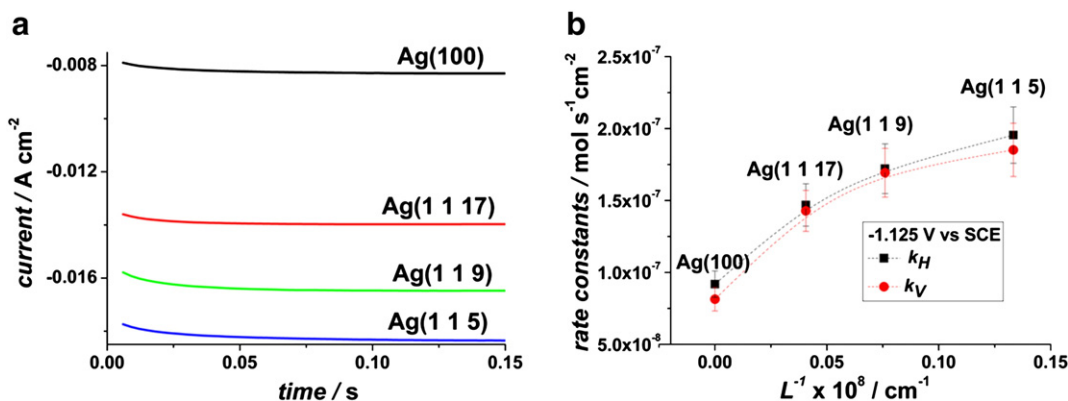

Fig. 1. (a) Potentiostatic transients for the HER on Ag(11n) electrodes at −1.125 V vs SCE. (b) Volmer and Heyrovsky rate constants as a function of the density of steps calculated by fitting the current transients shown on (a). (The density of steps was calculated from the mean distance between steps: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