

# Hydrogen Evolution Reaction on Nanostructures Electrodes—a Scenario on Stepped Silver Surfaces

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**Abstract** We have investigated the scenario for the hydrogen evolution reaction at stepped silver surfaces in acid solutions at high overpotentials using a simple kinetic model. Two independent types of sites, at the steps and at the terraces, were considered. The rate constants for the Volmer and Heyrovsky reactions were estimated. Both reactions occur with rate constant about two orders of magnitude larger at step sites than at terrace sites. Calculations of the activation energy for these reactions using our theory of electrocatalysis give similar results.

**Keywords** Electrocatalysis · Stepped surfaces · Silver · Hydrogen evolution reaction · DFT · Kinetic · Monte Carlo

## Introduction

It is a challenge to describe the hydrogen reactions (evolution and oxidation) in an electrochemical environment [1]. The best catalysts are metallic electrodes of the Pt family. However, the kinetic parameters for the hydrogen evolution reaction (HER) on these electrode materials are very difficult

to obtain, since this reaction occurs too fast [2–9]. Another practical complication in the investigation of the HER is the mass transport. An appropriate method to investigate the kinetics of the HER is the application of potential pulses [10]. The analysis of the response at short times avoids complications produced by diffusion processes, and the kinetic processes can be investigated.

In this study, we chose silver because this material shows an intermediate reactivity and is therefore well suited to investigate in detail different effects. The use of well-defined stepped surfaces has early been recognized as an approach to understand the behaviour of nanoparticles. The rate of electrocatalytic reactions depends not only on the chemical nature, but also on the structure of the electrode surface, and in particular it is usually different on defects. Since vicinal surfaces [11] can be considered as monoatomic steps periodically spaced and separated by flat terraces of low-index surfaces, catalytic properties of defects can be systematically investigated varying the relative size of terraces and steps [2, 3, 12]. However, it is difficult to determine the contribution of steps and terraces in a continuous reaction like hydrogen or oxygen evolution, where the adsorption of a species is only an intermediate process. The current that is measured comes from all reaction sites, and there is no obvious way to separate it into different contributions. We believe that a combination of experiment and theory is the best approach to investigate such structural effects.

In previous works [13, 14], we have performed a detailed analysis of the electronics and energetics of vicinal Ag(11n) surfaces ( $n = 5, 9, 17$ ) using density functional theory (DFT). However, in an electrochemical environment, not only metal–hydrogen interactions play a role, but additional complications must be considered. To mention some concerns, electron transfer processes take place; the interaction with the solvent involves reorganization of the hydration shells; specifically

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adsorbed ions can interfere with the reaction. In order to better describe these processes, we have developed our own theory of electrocatalysis [15, 16]. We have applied this theory to the HER at silver electrodes [17, 18], and concluded that the reaction mechanism involves the Volmer and Heyrovsky reactions, with the first as rate determining step. These results are in agreement with older experimental works [19, 20], which we have been recently confirmed in systematic studies using flat and stepped silver electrodes [21–23].

Within this scenario, in the present contribution, we have focused on the hydrogen evolution reaction at vicinal Ag(11n) electrodes in acid solutions using different approaches. We combine experimental work with a theoretical analysis, which involves kinetic Monte Carlo simulations and our own electrocatalysis theory.

## Experimental and Calculation Details

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(1 1 5), Ag(1 1 9), and Ag(1 1 17) orientations. Figure 1 shows the geometrical structures of these surfaces and the corresponding unit cells for terrace (pink lines) and step sites (yellow lines).

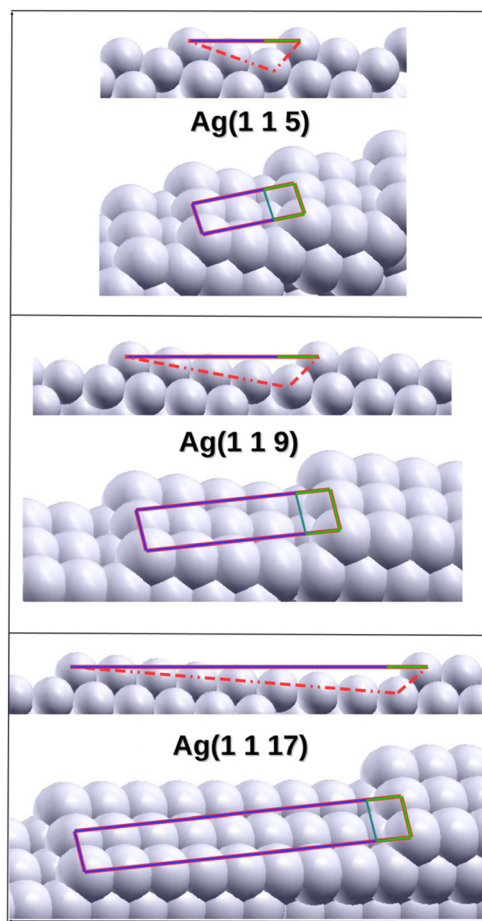
The pre-treatment of the surface and the routine employed to obtain the kinetic parameters by means of potentiostatic transients are the same as previously described [21, 22]. The measurements were carried out in 0.05 M H<sub>2</sub>SO<sub>4</sub> at 25 °C.

The theoretical methods used to investigate the hydrogen evolution reaction (HER) on the silver nanostructures included Density Functional Theory (DFT), Kinetic Monte Carlo (KMC) and molecular dynamics (MD) simulations, and our own electrocatalysis theory. The details of each method will be discussed separately.

## DFT Calculations

The adsorption energy of hydrogen and the corresponding projected density of states (PDOS) were calculated by periodic DFT calculations as implemented in the DACAPO [24] code. Ultrasoft pseudopotentials [25] have been used to describe the electron-ion interactions for all atomic species. The wave functions and charge densities were expanded by plane-wave basis sets with cut-offs of 350 and 600 eV, respectively. The Perdew, Burke, Ernzerhof (PBE) [26] formulation has been employed for the exchange and correlation functionals.

The vicinal Ag(1 1 17) surface was modelled using a unit cell with nine silver atoms exposed to the surface, 45 metal layers, and a 10 Å vacuum layer. Hydrogen atoms and the 18 topmost metal layers were allowed to relax. Brillouin-zone



**Fig. 1** Geometrical structures and unit cells for terrace and step sites of the Ag(11n) vicinal surfaces. The corresponding sizes are the following: (7.51 Å × 2.89 Å), (13.17 Å × 2.89 Å), and (24.67 Å × 2.89 Å) for the (1 1 5), (1 1 9) and (1 1 17) orientations, respectively

(BZ) integrations were performed with the  $8 \times 1 \times 1$  Monkhorst-Pack mesh [27].

According to the previous work [13], the most favourable sites are the hollow and the bridge positions for the adsorption on terraces and steps regions, respectively.

## KMC Simulations

Kinetic Monte Carlo simulations were performed in order to obtain the nanoscopic description of the reactions (Volmer and Heyrovsky elementary steps) on step and terrace sites. The kinetic parameters obtained by fitting the experimental current transients were used as input for these simulations. In order to reproduce the experimental transients, the simulations were run for about 15,000 steps. The unit cells are shown in Fig. 1. The surfaces were modelled using the following super-cells: (150.3 Å × 144.6 Å), (237.1 Å × 144.6 Å), and (246.7 Å × 144.6 Å) for the (1 1 5), (1 1 9), and (1 1 17) silver orientations, respectively.

## MD Simulations

The reorganization of the solvent when the proton approaches the (1 1 17) surface was obtained by steered-molecular dynamics [28] (SMD) using a canonical ensemble (constant NVT) as implemented in LAMMPS (large-scale atomic/molecular massively parallel simulator) code [29]. The SMD method employs a pulling force to produce conformational changes (or displacements) during a MD simulation [28]. This external force changes the free energy of the system in order to accelerate processes that will take longer to occur. The potential of mean force (PMF) along the assumed reaction coordinate [30] is calculated using the Jarzynski's equality [31].

All the simulations were performed using periodic boundary conditions with a simulation box containing a silver slab (size: 28.9 Å × 49.4 Å), an ensemble of 1671 water molecules, and a proton. The systems were equilibrated during 100 ps at 298 K. Afterwards, ten independent SMD simulations were performed during 900 ps (time step = 1.0 fs), and the results were averaged to obtain the corresponding PMF. The average temperature of 298 K was maintained by using a Nose-Hoover thermostat with a relaxation time of 0.1 ps.

The interactions between species were described using 12–6 Lennard–Jones pairwise potential. For water, we used the SPC/E (extended simple point charge) model, and the corresponding parameters for oxygen and hydrogen were taken from Yoshida et al. [32]. The Lennard–Jones parameters for silver were taken from Agrawal et al. [33] and those for the H<sup>+</sup> (as a zundel or hydronium ion) were taken from Ricci et al. [34]. The cross interactions were computed through the Lorentz–Berthelot mixing rules.

The solvent reorganization energy  $\lambda$  at different distances to the surface (coordinate  $z$ ) was calculated according to the eq. [35]:

$$\lambda(z) = \frac{|\Delta G_{\text{solv(bulk)}} - \text{PMF}(z)|}{2} \quad (1)$$

$\Delta G_{\text{solv(bulk)}}$  is the solvation energy of the proton in the bulk of the solution (water), and  $\text{PMF}(z)$  is the Potential of Mean Force of the proton approaching at a distance  $z$  to the adsorption site of the surface.

## Electrocatalysis Theory

Our theory of electrocatalysis is based on a model Hamiltonian, quantum statistics, DFT, and MD simulations. The formalism is the same as that presented previously [15, 16]. We summarize the most important aspects. Applying the adsorption model of Anderson–Newns [36, 37], and introducing the interaction with the solvent according to Marcus–Hush

[38, 39], the density of states corresponding to the orbital of the H-atom assumes the following form:

$$\rho_{\text{H}}(\varepsilon, q, z) = \frac{1}{\pi} \frac{\Delta(\varepsilon, z)}{[\varepsilon - (\varepsilon_{\text{H}}(z) + \Lambda(\varepsilon, z) - 2\lambda(z)q)]^2 + \Delta(\varepsilon, z)^2} \quad (2)$$

where  $\varepsilon$  is the electronic coordinate;  $z$  and  $q$  are the solvent coordinates according to Marcus–Hush [38, 39]. The latter is zero for the neutral hydrogen atom and  $-1$  for the proton.

The chemisorption functions  $\Delta(\varepsilon, z)$  and  $\Lambda(\varepsilon, z)$ , which are split into the interaction with the d and with the sp. bands, produce a broadening and a shift of the electronic states of the H-atom, respectively, and are given by

$$\begin{aligned} \Delta(\varepsilon, z) &= \sum_k |V|^2(z) \pi \delta(\varepsilon - \varepsilon_k) \approx |V|^2(z) \pi \rho_{\text{Met}}(\varepsilon) = \Delta_{\text{sp}}(\varepsilon, z) + \Delta_{\text{d}}(\varepsilon, z) \\ &= |V_{\text{sp}}|^2(z) \pi \rho_{\text{Met-sp}}(\varepsilon) + |V_{\text{d}}|^2(z) \pi \rho_{\text{Met-d}}(\varepsilon) \\ \Lambda(\varepsilon, z) &= \frac{1}{\pi} P \int \frac{\Delta(\varepsilon')}{\varepsilon - \varepsilon'} d\varepsilon' = \Lambda_{\text{sp}}(\varepsilon, z) + \Lambda_{\text{d}}(\varepsilon, z) \end{aligned} \quad (3)$$

where  $|V_{\text{sp}}|^2$  and  $|V_{\text{d}}|^2$  are the coupling constants of the H-atom with the sp. and d band, respectively, (overlap interaction integrals:  $\langle k|V|H \rangle$ ), and  $\varepsilon_{\text{H}}$  is the position of the energy level of the 1 s-orbital of the H-atom. These three parameters are calculated for each distance to the surface by fitting the PDOS obtained by DFT using Eq. (2) with  $q = 0$ .

Therefore, the total energy of the H-atom and the solvent is as follows:

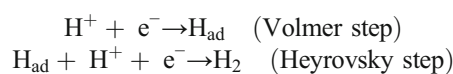
$$E(q, z) = \int_{-\infty}^{\varepsilon_{\text{F}}=0} \rho_{\text{H}}(\varepsilon, q, z) \cdot \varepsilon d\varepsilon + \lambda(z)q^2 + 2\lambda(z)q \quad (4)$$

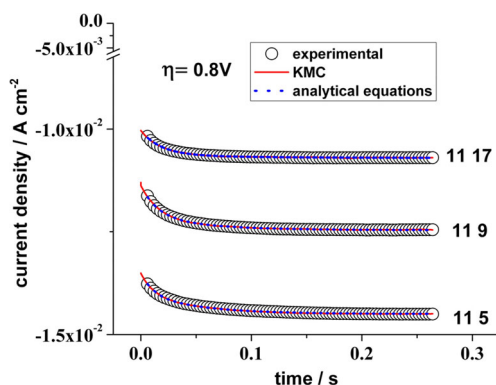
We have to introduce some corrections due to the electronic correlation and exchange, and add an entropic term [15].

Finally, we can obtain potential energy surfaces as a function of the distance to the electrode and the solvent coordinate using Eq. (4). Contours plots of this equation are very useful to analyse the course of the reaction, as the charge on the adsorbate and its solvation evolve. This will be discussed in detail below.

## Results and Discussion

The mechanism involved in the HER depends on the electrocatalyst. We have demonstrated in previous work [18, 21, 22] that this reaction at silver surfaces occurs in two elementary steps:





**Fig. 2** Potentiostatic transients for the HER on Ag(11n) electrodes obtained in 0.05 M H<sub>2</sub>SO<sub>4</sub> at  $\eta = 0.8$  V. The circles correspond to the experimental data, the red lines to curves obtained by kinetic Monte Carlo simulations, and the blue dotted lines to curves obtained by fitting the experimental data with Eq. (5)

The Volmer reaction seems to be the rate-determining step. We have also shown that the Tafel reaction ( $H_{ad} + H_{ad} \rightarrow H_2$ ) is not a relevant process at high overpotentials.

Figure 2 shows the current transients obtained at high overpotentials ( $\eta = 0.8$  V) for different stepped silver surfaces. The characteristic shape for the experimental transients corresponds to a Volmer–Heyrovsky mechanism, Volmer being the rate-determining step, as previously found.

According to our previous DFT calculations [13], the adsorption is more favourable at step sites than at terrace sites by about 0.2 eV. The lowest energy at the step corresponds to the bridge site, while at terraces it is the hollow site. However, for both terrace and step, there is a variety of different possible sites, and they show slight anisotropy in the hydrogen adsorption energy. The diffusion from terrace sites to step sites requires a barrier of at least 0.1 eV.

We shall consider a kinetic model involving only two distinct sites for the adsorption of hydrogen: at step and terrace

sites. In this first approach, the processes take place independently at these two regions. We neglect the diffusion of hydrogen between sites. Also, we shall not consider the effect of anions present during the reaction. Therefore, the total current is the addition of the currents due to the processes occurring at terrace ( $j_{terr}$ ) and step sites ( $j_{step}$ ):

$$j = j_{terr} + j_{step} = F \left\{ f_{terr} \left[ k_{terr}^V (1 - \theta_{terr}) + k_{terr}^H \theta_{terr} \right] + f_{step} \left[ k_{step}^V (1 - \theta_{step}) + k_{step}^H \theta_{step} \right] \right\} \quad (5)$$

Here  $k^V$  and  $k^H$  are the rate constants for Volmer and Heyrovsky reactions, respectively. The coverage at terrace and step sites is independently defined between 0 and 1 as the fraction of occupied sites ( $n^{occ}$ ) with respect to the total number of either, terrace and step sites ( $n^{tot}$ ),

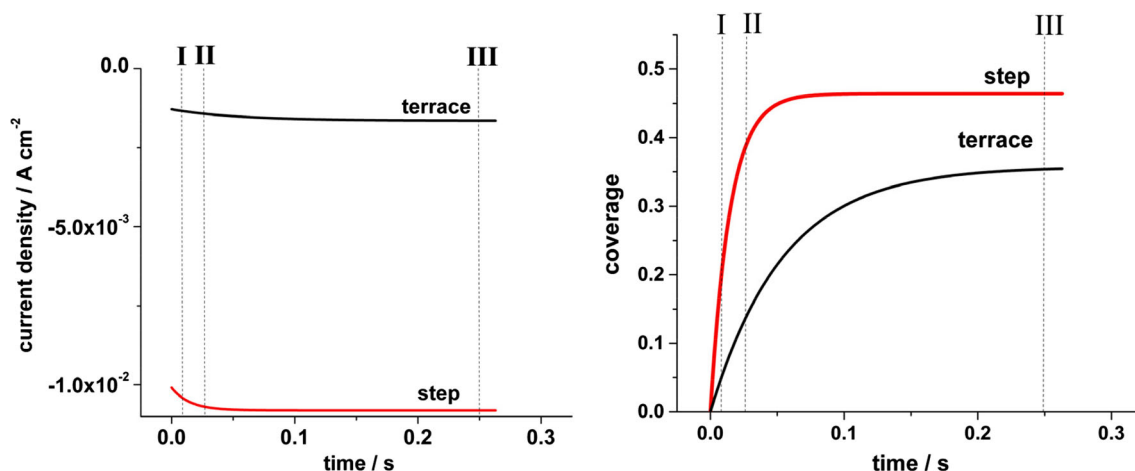
$$\theta_{terr} = \frac{n_{terr}^{occ}}{n_{terr}^{tot}}, \quad \theta_{step} = \frac{n_{step}^{occ}}{n_{step}^{tot}} \quad (6)$$

$f_{terr}$  and  $f_{step}$  are the fractions of geometrical area of the stepped surfaces corresponding to terrace and step sites, respectively. Since the experimental data were obtained at a high overpotential, the reverse reactions are not considered.

Both kinetic Monte Carlo simulations (KMC) and kinetic analysis using Eq. (5) can reproduce very well the experimental data.

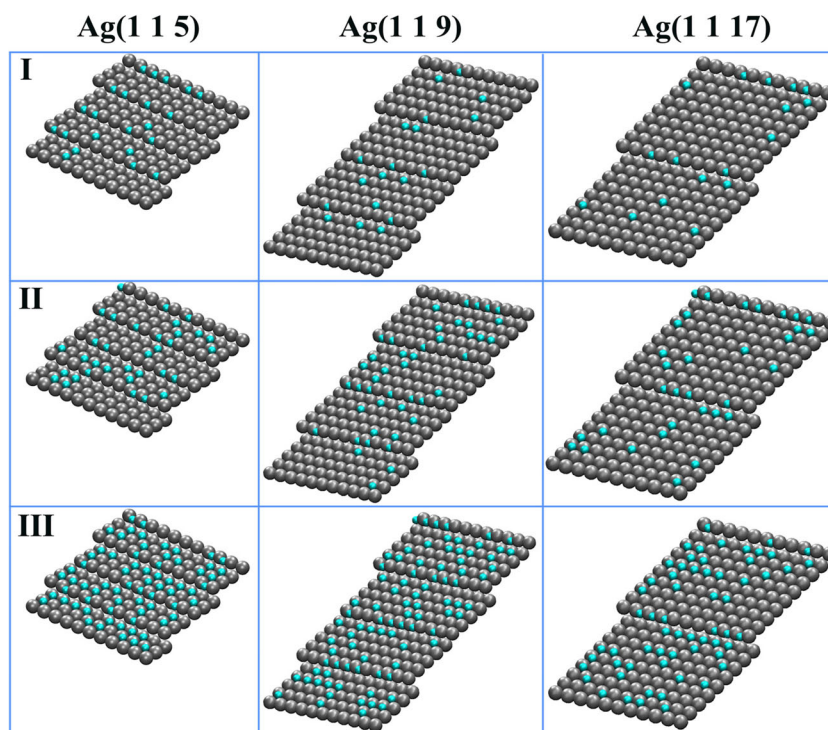
Figure 3 shows the contributions to the current of the processes occurring at terrace and step sites (at left), and the gradual occupation of the different sites (at right).

The absolute value of the current for the processes occurring at step sites is much larger than that corresponding to terrace sites, even when the surface fraction of step is smaller than that of the terrace ( $f_{step} < f_{terr}$ ). The occupation of step sites is faster than that of terrace sites. At the stationary states,



**Fig. 3** Separation of the processes occurring at terrace and step sites for the Ag(1 1 9) surface. Contribution of the current components (at left) and partial coverage of terrace and step sites (at right)

**Fig. 4** Snapshots showing the hydrogen coverage of the stepped silver surfaces at three different times during a current transient (labels I, II, and III of Fig. 3) obtained by KMC simulations



the step sites are almost half occupied, while only about a third of the terrace sites are covered by hydrogen. Similar results were obtained for the other surface orientations.

It is interesting to compare these results with the energetics obtained by DFT [13]. According to thermodynamics, it is more favourable to completely fill up the steps with hydrogen and subsequently the terrace sites. However, the present results reflect the kinetics of the processes, therefore, at the stationary state, the coverage is determined by the relative values of the rate constants.

Figure 4 shows nanoscopic images obtained by KMC simulations at three different times during the current transient for the three investigated surfaces (labelled in Fig. 3 as I, II, and III).

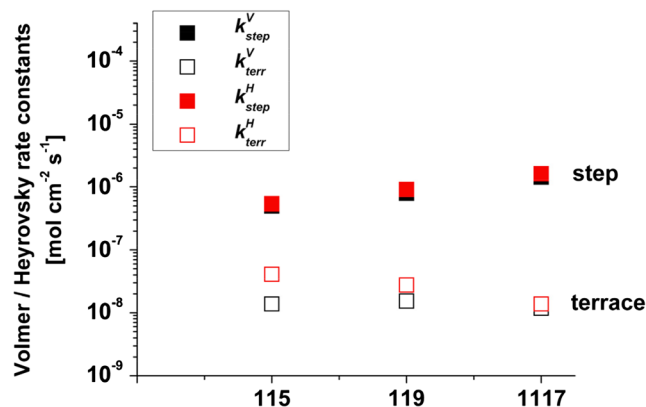
The rate constants for Volmer and Heyrovsky reactions are calculated by fitting the transients with Eq. (5), and used for the KMC simulations, are shown in Fig. 5.

Both Volmer and Heyrovsky reactions proceed with rate constants of the same order of magnitude, but the latter is always slightly faster. Therefore, the Volmer reaction is the rate-determining step. Both rate constants are about two orders of magnitude larger for step than for terrace sites and similar for all surface orientations.

We have also investigated the Volmer reaction at the bridge step site and at the hollow terrace site of the stepped Ag(1 1 17) surface applying our theory of electrocatalysis [15, 16], which combines electronic parameters calculated by DFT, the Marcus–Hush theory to treat the solvent, and the Anderson–Newns adsorption

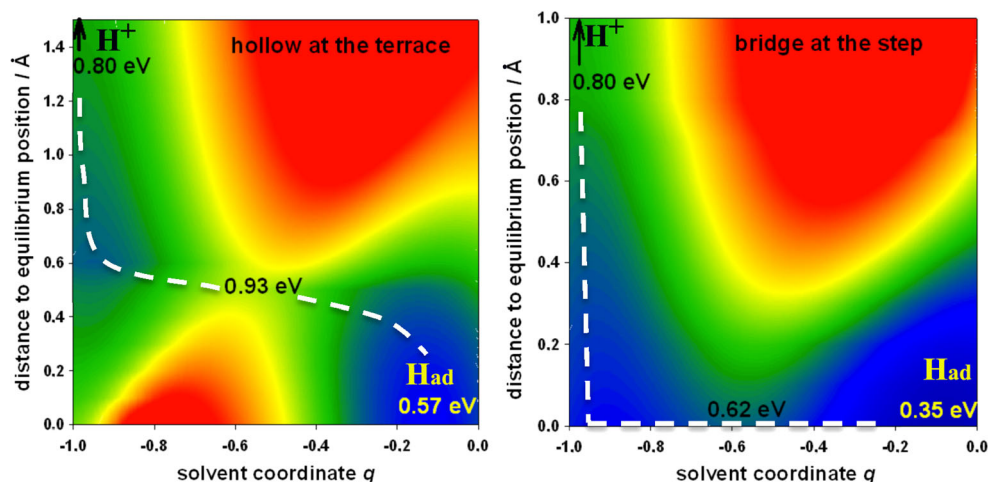
model. The solvent reorganization was modelled by molecular dynamics as described above.

Contour plots of the potential energy surfaces obtained by Eq. (4), and taking into account all interactions mentioned above are shown in Fig. 6. The valleys at short distances and near  $q = 0$  correspond to the adsorbed hydrogen. In this region, the energy is basically determined by the electronic interactions. The free energy of adsorption is about 0.2 eV larger for a hollow site placed on the terrace than for the bridge site at the step. At large distances and for a solvent coordinate of  $q = -1$ , the proton is solvated forming a Zundel ion with two water molecules, and the electronic interactions with the electrode do not play any role. When the proton approaches the surface, it gradually loses its solvation shell. In this region and for



**Fig. 5** Volmer and Heyrovsky rate constant obtained by fitting current transients for stepped Ag(11n) surfaces

**Fig. 6** Contour plots of the potential energy surfaces for the Volmer reaction at the bridge step site and at the hollow terrace site of the stepped Ag(1 1 1) surface. The calculations are for an overpotential of  $\eta = 0.8$  V.



values of  $q$  more negative than  $-0.4$  where the proton still retains a considerable amount of positive charge, the environment governs its solvation. When it is near the step, it can retain a larger amount of water around, since the steric hindrance is less (see Fig. 7). Contrary, when it approaches the flat terrace, it loses a larger number of water molecules from its solvation shell. Therefore, the increase in the energy due to the reorganization of the slow solvent modes is lower for the step than for the hollow site at the terrace. The interplay between all these factors, electronic interactions, solvent environment, and applied potential finally determines the reaction paths and the activation barriers.

At the overpotential of  $\eta = 0.8$  V, the Volmer reaction is exergonic on both sites of the step and of the terrace, resulting in a net gain of energy after the adsorption. However, at the bridge site of the step, it is downhill without activation barrier, while at the hollow site of the terrace it requires about 0.13 eV.

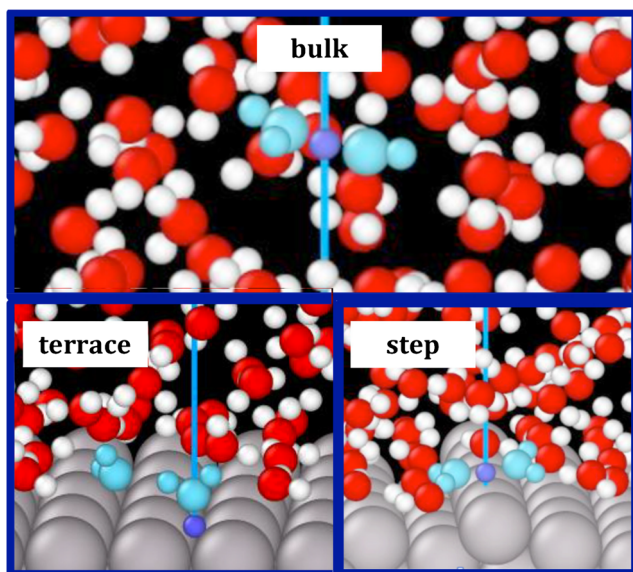
The reaction paths follow a completely different course. In the first case, the proton first approaches the step up to a very short distance of the equilibrium position for the adsorption, and then the electron transfer takes place; in the second case, the proton approaches the terrace up to about 0.5 Å of the equilibrium distance and starts to lose gradually its positive charge.

In order to compare these results with the rate constants obtained by fitting the experimental data, we have assumed that the pre-exponential factors are of the same order of magnitude, and we have estimated the relationship between the processes at both sites. The rate constant for the terrace site results about two orders of magnitude smaller than for the step site. This is in good agreement with the rate constants estimated from the experimental data.

## Conclusions

We have investigated a scenario for the hydrogen evolution reaction at the stepped silver surfaces in acid solutions at high overpotentials by a combination of experiment, ab initio theory, and computational tools such as DFT, KMC, and MD simulations. For the analysis, we used a relatively simple model in which only two types of sites, terrace and step, were considered. On this basis, we could experimentally determine the respective contributions of these sites to the Volmer and Heyrovsky reactions—the Tafel reaction plays no role. Both reactions are by about two orders of magnitude faster on steps than on terraces, and the Heyrovsky reaction is always somewhat faster than the other.

It is gratifying that these results agree quite well with estimates of the rate constants based on our theory of electrocatalysis, which is a totally different approach. An analysis of the current transients, in combination with KMC simulations, gave a nanoscopic view of the gradual occupation of reaction sites while the reaction proceeds.



**Fig. 7** snapshots from simulation applying molecular dynamics

Of course, our model is basic, and there are complications that we did not consider. Thus, a more realistic model should take into account the anisotropy in the energetics of adsorption sites and the co-adsorption of anions. However, the satisfactory agreement between our experiments and our theoretical treatment suggests that the model captured the essential aspects of hydrogen evolution on stepped silver surfaces.

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