Hydrogen Evolution on Single-Crystal Copper and Silver: A Theoretical Study

Elizabeth Santos,[a, b] Kay Pötting,[b] Angelica Lundin,[a] Paola Quaino,[a, c] and Wolfgang Schmickler*[a]

Dedicated to Prof. Dr. R. Jürgen Behm on the occasion of his 60th birthday

Hydrogen evolution on single-crystal copper and silver is investigated by a combination of density functional theory and a theory developed in our own group. At short times, the reaction rate is determined by the transfer of the first proton to the electrode surface. In accord with experiment, we find for both metals that this reaction proceeds faster on the (111) surfaces than on the (100) ones. The main cause is the lower, that is, more favourable, adsorption energy on the former surfaces. On both silver surfaces, the second step is electrochemical desorption. The same mechanism is likely to operate on copper.

1. Introduction

For a long time, it has been known that the rate of hydrogen evolution depends strongly on the electrode material. When clean, well-defined single-crystal electrodes became available in electrochemistry, an important question was whether the rate depends only on the nature of the electrode, or on the crystal face as well. Early experiments on silver[1,2] and copper[3] showed that in both cases the (111) surface was the better catalyst. This was not the case for gold,[4] but because the gold surfaces are known to be reconstructed in the potential region where hydrogen evolution takes place, it is not surprising that it behaves differently. The differences in the rate constants between various facets of Ag and Cu are not large, of the order of a factor of five; as yet, they are unexplained.

In a series of papers,[5,6] we have recently proposed a theory for electrocatalysis that combines elements of the Marcus[7] and Hush[8] theory, Anderson–Newns theory[9,10] and our previous work[11] with density functional theory (DFT). First applications to hydrogen evolution explained the dependence on the nature of the metal well[12,13,14] and gave a reasonable order of magnitude for the rate constants. More importantly, the catalytic activities of the metals could be explained in terms of the interaction of their d bands with the hydrogen 1s orbital as it passes the Fermi level. All our previous calculations have been performed for the densest crystal faces; for Ag and Cu this is the (111) face. Herein we test whether our theory can correctly reproduce the different catalytic activities of the (111) and (100) surfaces of these metals.

2. Free Energy of Proton Transfer

The first step in hydrogen evolution is always the transfer of a proton from solution according to Equation (1):

$$H^+ + e^- \rightarrow H_{ad} \tag{1}$$
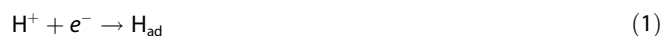
which is also known as the Volmer reaction. On copper and on silver electrodes, this is the step that determines the rate at short times, so we focus on this. Before considering the kinetics, we take a look at the thermodynamics, in particular the free energy of adsorption of the proton from solution. This is conveniently referred to the hydrogen scale, so that it gives the free energy required to adsorb a proton from the solution on the electrode when the latter is held at the equilibrium potential. Nørskov et al.[15] have compiled a list of adsorption energies for the fcc(111) surfaces of a number of metals using the following procedure: starting from a hydrogen molecule at a large distance from the surface, the energy of dissociation into two adsorbed hydrogen atoms is calculated. To obtain the corresponding free energy for this process, an amount of the order of 0.2 eV is added to correct for the entropy of hydrogen gas at ambient pressure and temperature. When the electrode is at the standard hydrogen potential, the protons in the solution, at a pH of 0, are in equilibrium with the gas. Hence this free energy equals the free energy for the adsorption of two protons. The free energies of adsorption given in the table have been calculated from the dissociation energy of the molecule and for a coverage of 1/4; because of the repulsion between adsorbed hydrogen atoms, the energies increase slightly with coverage.

In this way, we have calculated the free energies of adsorption on the four surfaces that we consider. For the technical

[a] Prof. Dr. E. Santos, Dr. A. Lundin, Dr. P. Quaino, Prof. Dr. W. Schmickler
Institute of Theoretical Chemistry, Ulm University
89069 Ulm (Germany)
Fax: (+49) 731 502 2819
E-mail: wolfgang.schmickler@uni-ulm.de

[b] Prof. Dr. E. Santos, K. Pötting
Faculdad de Matemática, Astronomìa y Fisica
IFFaMAF-CONICET
Universidad Nacional de Córdoba, Córdoba (Argentina)

[c] Dr. P. Quaino
PRELINE, Universidad Nacional de Literal
Santa Fe (Argentina)

details we refer to the appendix and to our previous work.[16,18] On the (111) surfaces, the fcc three-fold hollow site has the lowest adsorption energy, while on the (100) surfaces, it is the four-fold hollow site. Our results for the (111) surfaces are close to those of Nørskov et al.[15] On both metals, the energy of adsorption is higher—less favourable—on the (100) than on the (111) surface. At first glance, this is surprising, because the bond distances are shorter on the (100) surfaces, and the d band structure on the two surfaces is very similar (see Figure 1). However, the d bands lie well below the Fermi level,
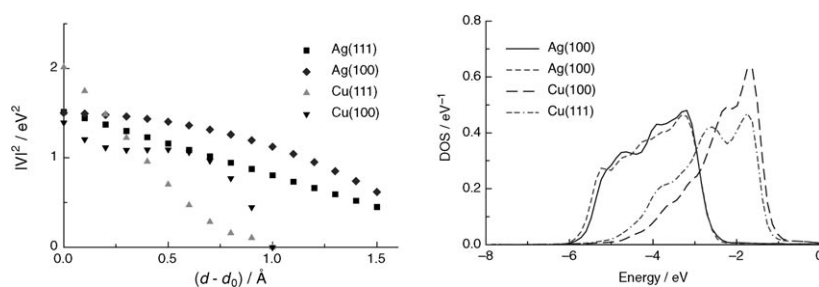

Figure 1. Left: Coupling constants of the metal surfaces under consideration with the 1s orbital of hydrogen as a function of the deviation from the equilibrium distance d_0. Right: Surface densities of states of the d bands. The Fermi level has been taken as the energy zero.

therefore they do not participate in the bonding. Though the interaction with the d band splits the hydrogen 1s orbital into a bonding and an anti-bonding part, both lie below the Fermi level. Therefore they are filled and do not contribute to the bonding. Thus, the adsorption is solely caused by the interaction with the sp band. In fact, because of Pauli repulsion, the interaction with the d band actually weakens the bond.[19] Therefore, the weaker adsorption on the (100) surfaces of Cu and Ag is probably caused by the greater Pauli repulsion of the d bands on the former surfaces, where the bond distance is shorter. For the case of copper, it had been shown previously that hydrogen adsorption is stronger on the (111) than on the (100) surface.[20] Hydrogen dissociation has been found to be about 0.1 eV more exothermic on the former surface, which is in line with our results. In passing we note that on platinum, adsorption is stronger on the (100) than on the (111) plane.[21] Since on platinum, the d band contributes to the bonding, Pauli repulsion plays a lesser role[22–25], and adsorption is favoured on the more open surface.

On all four surfaces the energy of adsorption is positive. Therefore, at zero overpotential proton adsorption is endergonic, and the adsorbed state is a short-lived intermediate. At sufficiently high overpotentials η, when $|e_0\eta| > \Delta G_{ad}$, it becomes exergonic, but even then the adsorbate will quickly react further to form hydrogen molecules.

3. Kinetics of Proton Transfer

As mentioned in the introduction, we have recently proposed a model for electrocatalytic reactions and applied it to the proton transfer from aqueous solutions to metal surfaces. The details of our method are given in ref. [18], but to make this

paper self-contained, we briefly outline the main ideas without going into mathematical details. The initial state in Equation (1) is a strongly solvated proton sitting in front of the electrode surface, the final state is an adsorbed non-solvated hydrogen atom. Thus, the reaction involves a reorganization of the solvent, in the spirit of the Marcus theory of electron transfer,[7] and the approach of the reactant to the surface. Therefore, we calculate free energy surfaces for the proton transfer as a function of the distance of reactant from the surface and of a generalized solvent coordinate q, which has the following meaning: a solvent configuration characterized by q would be in equilibrium with a reactant of charge $-qe_0$. In particular, in the initial state $q=1$, and in the final state $q=0$. As a basis, we first perform DFT calculations for a hydrogen atom at various distances d from the surface, which gives the energy for $q=0$. From the density of states of the hydrogen atom, we obtain the interaction constants with the d band of the metal as a function of the distance. The latter are needed to extend the results to solvent configurations with $q\neq0$, using our own theory.[16,18]

Electrocatalysis requires a metal d band which couples strongly with the valence orbital—in this case the hydrogen 1s orbital—of the reactant.[5,6] Both for copper and silver, the d band surface densities of states do not differ much for the two orientations (see Figure 1). In both metals, the d bands lie well below the Fermi level, indicating that they are likely to be mediocre catalysts. At short distances, the coupling constants to hydrogen are of the same order of magnitude for all four surfaces, but they fall off more rapidly on copper, which has the more compact d orbitals. Comparing the (111) and the (100) surfaces, we note that on the former the interaction falls off more rapidly, as the threefold hollow sites are shallower than the fourfold.

In order to calculate the free energy surfaces, we need to know the free energy of reorganization associated with the electron transfer. This is determined by the interaction of the proton with the solvent, and should be independent of the nature of the metal, because the interaction of copper and silver with water is weak. The appropriate value has been discussed extensively in our previous work.[12,18,26] Based on the solvation energy of the proton, we have estimated a value of the order of $\lambda=0.3$ eV. In ref. [18] we have performed calculations for several values of λ and also investigated a model in which λ decreases by a factor of two towards the metal surface for steric reasons, an effect which one of us had suggested before,[27] and which is supported by computer simulations.[28] As expected, we found that the order of the activity of the metals did not depend on the exact value of λ, and also was the same for a model with a spatially constant λ. However, the model with a varying λ gave surfaces which are more in line

with computer simulations.[28] Therefore, herein we give the results for an energy of reorganization which has a value of 0.3 eV for the proton in the initial state, and half that value at the adsorption site. For further details we refer to ref. [18] and we emphasize that the order of activity is the same for all the options we explored therein.

The resulting free energy surfaces for the adsorption of the proton (Volmer reaction) are shown in Figure 2. They have been calculated for the standard hydrogen potential. In all sur-
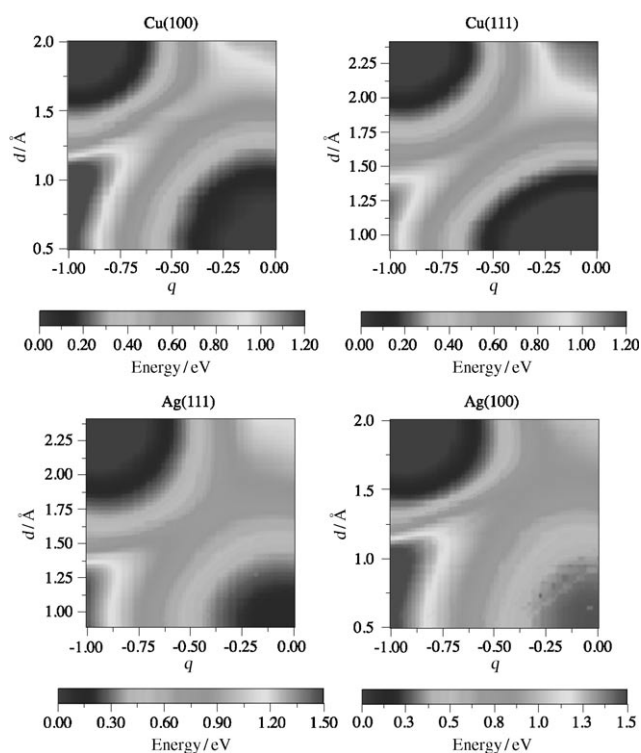
Figure 2. Free energy surfaces for hydrogen adsorption on single crystal surfaces of copper and silver.

faces, the minimum in the upper left corner, at $q = 1$, corresponds to the initial state, the solvated proton, and the minimum at the bottom right corner, at $q = 0$, to the final state, the adsorbed hydrogen atom. In all cases the final state has a higher free energy, which are the values given in Table 1. These two states are separated by an energy barrier; the energy of the saddle point gives the free energy of activation of the Volmer reaction, which is also given in the table. For

both metals, the energy of activation is higher for the surface with the higher free energy of adsorption, as may have been expected. Thus, in agreement with experimental data, we find higher activation energies, and hence lower rate constants, for the (100) than for the (111) surfaces.

Since the proton is a light particle, it can in principle tunnel through energy barriers. Since q is a collective solvent coordinate, tunnelling on the surfaces shown in Figure 2 could only occur along the distance coordinate d. Because of the shape of the free energy surfaces, there are no paths along which the proton could tunnel to achieve a transition rate greater than the classical rate. Therefore, tunnelling plays no role according to our model calculations. As we have discussed in a previous communication from our group,[29] this is in line with experimental data, which indicate that the isotope effect for hydrogen evolution is generally small.[30] According to a recent article, this could possibly be different on mercury.[31]

4. Chemical versus Electrochemical Recombination

The Volmer reaction is always the first step in hydrogen evolution. For the second step, there are two possibilities: chemical recombination, also known as Tafel reaction, according to Equation (2):

$$H + H \rightarrow H_2 \tag{2}$$

or electrochemical recombination (the Heyrowski reaction) according to Equation (3):

$$H + H^+ + e^- \rightarrow H_2 \tag{3}$$

The first reaction should be independent or weakly dependent on the electrode potential, while the rate constant k_H of the second one, just like the Volmer step [Eq. (1)], depends exponentially on the electrode potential given by Equation (4):

$$k_H \propto \exp - \frac{\propto e_0 \eta}{k_B T} \tag{4}$$

where η is the deviation of the electrode potential from the equilibrium potential. By convention, this is negative in the hydrogen evolution region. k_B is Boltzmann's constant, and α the transfer coefficient, typically of the order of 1/2.

The activation energy for the chemical reaction can be calculated by standard DFT. For copper, the activation energy for the reverse reaction, the dissociation, has been intensively investigated;[32] for Cu(111), the value is about 0.5 eV, for Cu(100) a little higher, 0.6 eV. Hydrogen dissociation is slightly exothermic on both surfaces, by about −0.1 eV for the (111) surface and slightly less for (100). Therefore the energies of activation should be slightly higher for the reverse reaction. Corrections for the free energy are difficult for the activation barrier, but should be minor. Thus, we would expect the free energy of activation for the chemical recombination not to be larger than that for proton adsorption. The frequency factor for surface re-

Table 1. Reaction free energy ΔG_{ad} and free energy of activation ΔG_{act} for the Volmer reaction on the hydrogen scale, and bond distances d_0. The latter are given with respect to the plane containing the centers of the top layer of atoms.

Metal	Ag(111)	Ag(100)	Cu(111)	Cu(100)
ΔG_{ad} [eV]	0.39	0.48	0.10	0.14
ΔG_{act} [eV]	0.71	0.81	0.71	0.79
Bond distance d_0 [Å]	0.9	0.5	0.9	0.5

actions is typically of the order of 10^{13} s^{-1}, while for proton adsorption it is at most of the order of 10^{11} s^{-1}. Therefore, at zero and small overpotentials, proton adsorption would be slower than chemical recombination, while at higher overpotentials the latter process would be slower.

Experimentally, in line with our results,[18] hydrogen evolution on copper is somewhat slow and therefore usually investigated at overpotentials $|\eta| > 0.3$ V. Older results on polycrystalline copper by Gerischer and Mehl[33] suggest an electrochemical recombination as the second step, which would be in line with our theoretical values. To the best of our knowledge, there are no experiments on single-crystal copper that have determined the mechanism, so these older results still require verification.

On single-crystal silver the situation is clearer. Experimental results from our group show that the current increases exponentially with the overpotential,[1] and on both surfaces current transients increase with time (see Figure 3). The latter fact
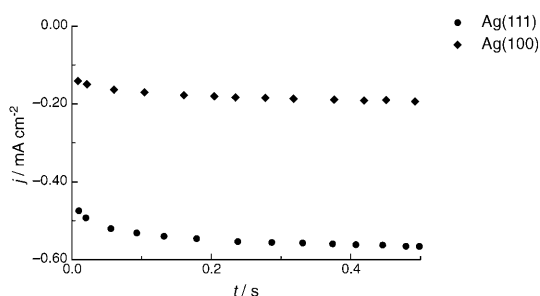

Figure 3. Current transients for hydrogen evolution on Ag(100) and Ag(111) for an overpotential of −0.65 V vs SHE in a solution of 0.1 M H$_2$SO$_4$.[34] By convention, currents and overpotential for hydrogen evolution are negative.

clearly indicates that the recombination occurs through the electrochemical reaction of Equation (3), the Heyrowski reaction. 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.[33] In contrast, chemical recombination does not involve charge transfer, so that the current would fall as the coverage rises.

According to DFT calculations, the energy of activation for the dissociation reaction on Ag(111) is about 1 eV;[35] this is in line with experimental results for D$_2$ dissociation, which indicate that the activation barrier is larger than 0.8 eV.[36] For Ag(100) we have also obtained an activation barrier of about 1 eV. These high values for he dissociation reaction explain why on both silver surfaces the second step is electrochemical desorption according to Equation (3).

5. Conclusions

Herein, we investigated hydrogen evolution on four single-crystal surfaces: Ag(111), Ag(100), Cu(111), and Ag(100) by a combination of DFT and a theory developed in our group. In accord with experimental data, we find that the first step, the

Volmer reaction, is faster on the (111) than on the (100) surfaces. The main cause is the higher, that is, more endergonic, adsorption energy on the more open surfaces. For silver, both theory and experiments suggest that the second step is the electrochemical desorption of the hydrogen atoms. On copper, the same mechanism is likely to operate, though we cannot rule out that low absolute values of the overpotential chemical recombination may occur. Thus, electrochemical desorption seems to be more prevalent than previously thought,[37,38] and there is a need for a theoretical description of this process. Corresponding work is in progress in our group.

Computational Methods

All calculations were performed using the DACAPO code.[39] This utilizes an iterative scheme to solve the Kohn–Sham equations of density functional theory self-consistently. A plane-wave basis set is used to expand the electronic wave functions, and the inner electrons were represented by ultrasoft pseudopotentials,[40] which allows the use of a low energy cut-off for the plane-wave basis set. An energy cut-off of 400 eV, dictated by the pseudopotential of each metal, was used in all calculations. The electron–electron exchange and correlation interactions are treated with the generalized gradient approximation (GGA) in the version of Perdew, Burke and Ernzerhof.[41] The Brillouin zone integration was performed using a 16×16×1 k-point Monkhorst–Pack grid[42] corresponding to the (1×1) surface unit cell. The surfaces were modelled by a (2×2) supercell with four metal layers and eight layers of vacuum. Dipole correction was used to avoid slab–slab interactions.[43] The first two layers were allowed to relax, while the bottom two layers were fixed at the calculated next neighbor distance. The optimized surfaces (pre-relaxed) in the absence of the hydrogen atom were used as input data to carry out the calculations to study the hydrogen desorption. For each system, we performed a series of calculations for a single hydrogen atom adsorbed on a hollow site, and varied its separation from the surface. The pre-relaxed surface was kept fixed while the H was allowed to relax in the xy-coordinates during these calculations. At each position we calculated the adsorption energy, and the DOS projected onto the 1 s orbital of hydrogen.

The adsorption energies for hydrogen have been calculated from the dissociation energies for the molecule; the difference between the two copper surfaces is 0.08 eV according to our calculations, and thus close to the uncertainty of DFT calculations. However, practically the same value has been obtained by another group.[20] In addition, it is the difference in adsorption energy for the same adsorbate on the same metal, only the structure of the surface is different. Therefore we believe that this difference is trustworthy.

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