Hydrogen Fuel Cells

DOI: 10.1002/anie.200702338

Electrocatalysis of Hydrogen Oxidation—Theoretical Foundations**

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The oxidation of hydrogen is one of the fundamental reactions of electrochemistry. It is the anodic reaction of the most common type of fuel cell, which many expect to form the basis of a future hydrogen economy.[1] Because of its importance, it has been the subject of numerous investigations; indeed, it has been claimed that an overobsession with this reaction has delayed the development of electrochemistry by a decade.[2]

The rate of hydrogen oxidation at different metals varies over more than six orders of magnitude. On metals like mercury and lead it is extremely slow and not observable near thermodynamic equilibrium, while on platinum it proceeds so quickly that this system has been used to define the standard reference electrode. Thus, the behavior of this reaction is completely different from that of outer-sphere electron-transfer reactions, for which rate is practically independent of the nature of the metal[3,4] and which are well described by Marcus theory.[5]

In the past, there have been several attempts to relate the catalytic activity of metals for hydrogen oxidation to their physical or chemical properties. Thus, phenomenological correlations have been established, with limited success, between the reaction rate and the work function,[6] the strength of the metal–hydrogen bond,[7,8] and the presence of unfilled d orbitals.[9] Recently, concepts familiar from gas-phase catalysis have been invoked, in particular the position of the center of the d band.[10] As we demonstrate below, the principles governing gas-phase catalysis do influence electrochemical reactions as well, but because of the different course of electrochemical reactions, they act in a different manner.

The overall reaction is $H_2 \rightarrow 2H^+ + 2e^-$. The initial state is the stable molecule, and the final state consists of two protons stabilized by interaction with the solvent. For most metals, the first step results in a proton on the metal surface. This situation is not stable, and the proton desorbs into the solution. In the critical stage of this reaction, a thermal fluctuation raises the energy of the bonding orbital of the molecule to the Fermi level E_F of the metal, two electrons are transferred from the molecule to the metal, the molecular bond is broken, and the system relaxes into two solvated protons.[11] Thus, a good catalyst must lower the energy of the system as the bonding orbital passes E_F.

In contrast to gas-phase reactions, it is not possible to treat electrochemical hydrogen oxidation solely by ab initio methods for several reasons: 1) The interaction of the proton with water is very strong, so a realistic calculation would require a large number of water molecules. 2) There is no consistent way to introduce the electrode potential into such calculations. 3) It is not possible to represent the solvent fluctuations that raise the electronic level of the reactant past the Fermi level. Therefore, in previous studies[11–13] we developed a formalism for electrochemical bond-breaking reactions, which was based on a combination of tight-binding theory, the Anderson–Newns model,[14] and electrochemical electron-transfer theory.[15] Model calculations with idealized band shapes suggested a mechanism by which a d band centered near the Fermi level can lower the activation energy. However, the proof of any theory lies in its ability to explain experimental data. Herein, we apply our ideas to the hydrogen oxidation on a series of real metals. At this stage, our aim is not to calculate absolute values for the activation energy but to determine its variation with the nature of the metal.

The theoretical background has been given elsewhere,[11,12] so herein, we focus on the application of our theory to hydrogen oxidation. The most important quantities that characterize the metal–molecule interactions are the so-called chemisorption functions $\Delta(\varepsilon)$ and $\Lambda(\varepsilon)$, which depend on the electronic energy ε.[14,16] The former determines the width of the molecular density of states (DOS) and is defined in Equation (1), where $V_{a,k}$ is the coupling constant between a hydrogen atom and an electronic state k on the metal:

$$\Delta = \pi \sum_k |V_{a,k}|^2 \delta(\varepsilon - \varepsilon_k) \tag{1}$$

We are interested in the interaction with the d band; for this purpose, we can ignore the k dependence of the coupling constants and replace them by a single effective value $|V_{\text{eff}}|^2$. Lists of such effective coupling constants for hydrogen and various metals have been published by Hammer and Nørskov.[10,17] The sum over k then reduces to the surface density of states $\rho_d(\varepsilon)$ of the d band of the metal [Eq. (2)]:

$$\Delta(\varepsilon) = |V_{\text{eff}}|^2 \rho_d(\varepsilon) \tag{2}$$

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[**] We thank Cristian Sanchez (University of Cordoba, Argentina), Axel Groß, Kay Pötting, and Florian Wilhelm from the University of Ulm for supplying us with the metal densities of states. Financial support by the Deutsche Forschungsgemeinschaft (Schm 344/34-1, Sa 1770/1-1), by the European Union (NENA project), by COST D36, and by CONICET (Argentina) is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

The other chemisorption function $\Lambda(\varepsilon)$ gives the shift of the reactant level that arises from interaction with the metal. It can be obtained from $\Delta(\varepsilon)$ through a Hilbert transformation (see the Supporting Information). The densities of states of the common metals are available in the literature, or they can be calculated with standard DFT programs. Thus, we are able to calculate the chemisorption functions, and these quantities determine the variation of the rate of hydrogen oxidation with the nature of the metal.

The values of the other parameters are less critical, because they are the same for all metals and therefore do not affect the trend. Their choice is described in the Supporting Information. We note only that the reorganization energy for a proton is about $\lambda = 3$ eV and therefore has a large effect on the reaction.

The relative position of electronic energy levels in solution with respect to the Fermi level E_F depends on the electrode potential. At present it is not possible to establish an absolute scale of energies in our model, because important quantities, such as the energy of reorganization or the double-layer properties of the various metals, are not known with sufficient accuracy. However, we do not attempt to calculate absolute values for the energies of activation; our aim is to calculate relative values and to explain the great variation in catalytic activity. Therefore, we only have to choose the same, well-defined reference state for all metals. For this purpose we have chosen the electrode potential at which a hydrogen molecule in solution has an energy of -4λ, which roughly corresponds to the energy of the final state of this reaction (two protons on the electrode surface).

We have obtained the coupling constants $|V_{\mathrm{eff}}|^2$ and the electronic densities of states for (111) surfaces of the sd metals Cu, Ag, Au, and for several transition metals. Within this group, the coupling constants vary by about a factor of five (see the Supporting Information); they increase down the columns of the periodic table, because the valence orbitals become more extended and the overlap with hydrogen increases. Figure 1 shows the density of states of several metal surfaces; the two transition metals shown (Ni and Pt) have a high density of d-band states near the Fermi level E_F, while those of the sd metals lie much lower.

With these data we have calculated potential-energy surfaces as a function of the bond length r between the two hydrogen atoms and the generalized solvent coordinate q. The latter concept denotes the configuration of the solvent and is familiar from Marcus theory.[5] Briefly, a solvent coordinate q corresponds to a solvent configuration that would be in equilibrium with a particle of charge $-q$. Thus, the neutral molecule is in equilibrium with a solvent configuration $q = 0$, and two fully charged protons correspond to a solvent configuration of $q = -2$. Two examples of such potential-energy surfaces are shown in Figure 2. On these surfaces, the system initially consists of a molecule situated in the valley near $q = 0$, $r = r_0$, where r_0 is the equilibrium bond length. The

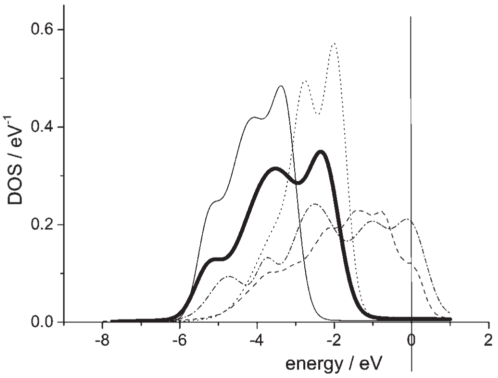

Figure 1. Surface densities of d-band states of some of the metals considered. The integral over the densities has been normalized to unity; the vertical line represents the Fermi level. Thin line: Ag(111); thick line: Au(111); dotted line: Cu(111); dashed-dotted line: Pt(111); dashed line: Ni(111).

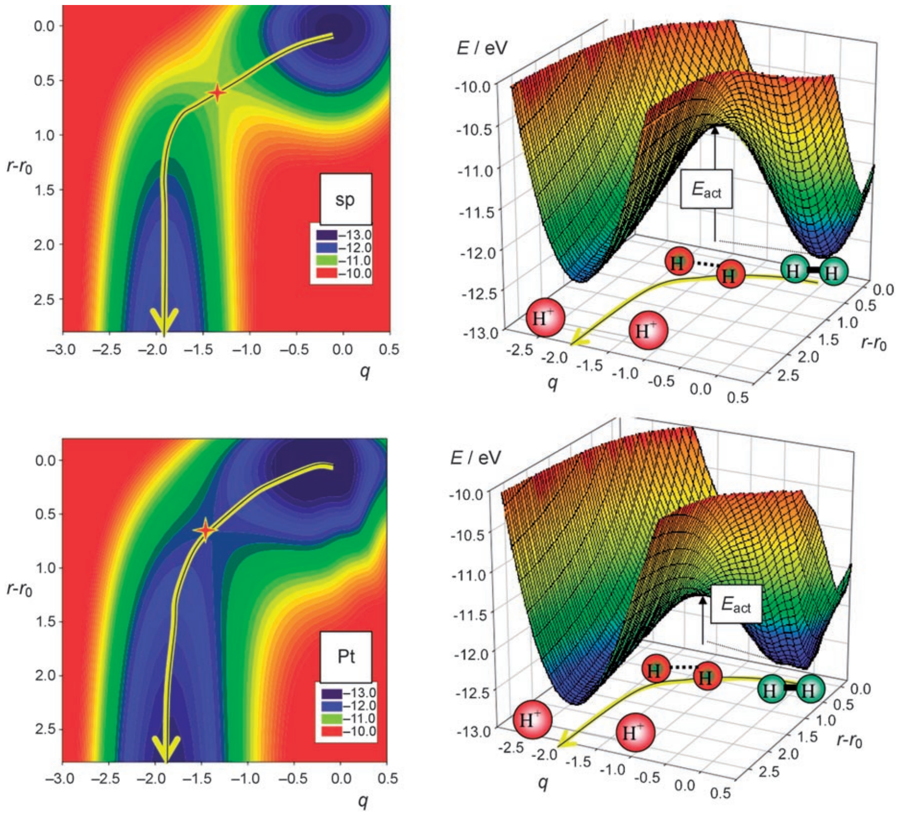

Figure 2. Potential-energy surfaces for the oxidation of H_2 as a function of the bond length r and the solvent coordinate q. The equilibrium bond length is denoted by r_0; r is given in atomic units (1 a.u. = 0.529 Å). Upper panels: sp metal, lower panels: platinum. The red crosses denote the saddle points.

final state, two protons, corresponds to the valley centered near $q=-2$. This valley becomes deeper for increasing r because of the Coulomb repulsion between the two protons. The initial and the final states are separated by a barrier whose saddle point determines the activation energy. As can be seen from Figure 2, the nature of the metal has a pronounced effect on the shape of the surfaces. In particular, owing to d-band catalysis, the barrier on platinum is very much lower than on sp metals.

From these surfaces we have calculated the activation energy for hydrogen oxidation and compared it to experimental values for the logarithm of the exchange current density; the results are shown in Figure 3. The activation energies are given with respect to the energy of the molecule in the bulk of the solution; they are not meant to be absolute values but to give the relative trend. In addition to the sd and transition metals listed, we have also performed calculations for a generic sp metal by setting the coupling constant $|V_{\text{eff}}|^2=0$, and we compared this result with experimental values for typical sp metals such as Cd and Pb, whose exchange current densities are of the order of 10^{-9} A cm^{-2}. Unfortunately, there is a large scattering of experimental data that cannot only be due to the fact that many of these values refer to polycrystalline electrodes. The scattering is mostly due to different methods of electrode preparation and to different measuring techniques. As a general rule, the higher rate constants are more likely to be correct, since the most common contaminations tend to inhibit the reaction, and the use of inadequate techniques (i.e. those that are too slow) generally results in values that are too low. However, there is a good correlation between the calculated activation energies and the experimental rates. In particular, our calculations explain very well the large difference in the catalytic activity of transition metals like Pt, Re, Ir on one hand and Ni and Co on the other hand. Even though all these metals have a high DOS near the Fermi level, Ni and Co are very much less active, because their coupling constants (2.82 eV^2 and 3.4 eV^2) are much smaller than those of the former group, which lie between 8 eV^2 and 14.6 eV^2. The behavior of the three sd metals can be seen to be more strongly influenced by their coupling constants, which increase from Cu to Au, than by their densities of states. The low rate of the sp-metals is, of course, due to the absence of d-band catalysis.

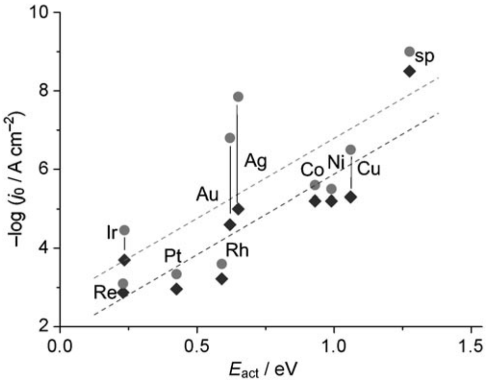

Figure 3. Experimental data for the exchange current density j_0 of the hydrogen oxidation versus our calculated values for the activation energy. The experimental data have been taken from the compilation of Nørskov et al.;[8] values for Ni and Cu have been taken from reference [9]. Where more than two experimental values existed, the extreme values have been taken to indicate the range. For the sp metals, we have taken the values for Cd and Pb. The lines are fits to the two sets of experimental data.

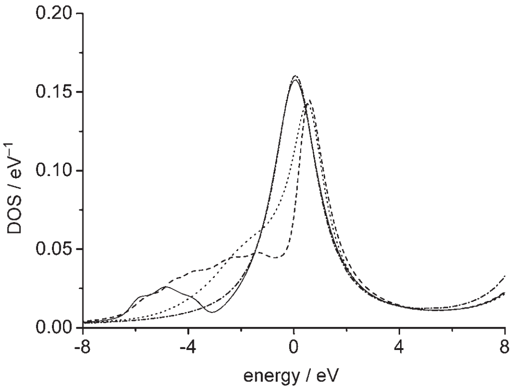

Figure 4. Density of states of the hydrogen molecule in the activated state; only the bonding orbital is shown. Solid line: Ag(111); dashed line: Pt(111); dotted line: Ni(111); dashed-dotted line: sp metal.

The activation energy is determined by the interaction of the bonding orbital of the hydrogen molecule with the d band as it passes the Fermi level E_F of the metal. At this critical stage, the occupation probability of the bonding orbital is about one, so that one electron has already been transferred to the metal. Figure 4 shows a few examples for the DOS of the H_2 molecule at this activated state. At Pt(111), the DOS of the bonding orbital is considerably broadened. There is a large peak, which has already passed the Fermi level and hence does not contribute to the energy of the molecule, and a part about 4-eV wide that lies below E_F. In contrast, Ni(111), in spite of its high density of d states near E_F, affects the molecule's DOS only weakly because of its low coupling constant. Ag(111), in spite of the low position of its d band, splits the bonding orbital into a large peak near E_F and a smaller peak that is roughly centered in the middle of the d band. In this case, the larger coupling constant of Ag(111) plays a greater role than the favorable position of the d band in Ni(111). In the absence of a d band, the bonding orbital is only broadened. An important contribution to the energy of the molecule is obtained by integrating the electronic energy over the occupied part of the DOS.[17] Therefore, a substantial broadening or splitting of the bonding orbital in the activated state will significantly lower the activation energy and thus catalyze the reaction.

Finally, there is a group of metals, such as Ta, Nb, and Ti, that we have not considered although they have a high density of states at the Fermi level. These metals are covered by oxide films in aqueous solutions and therefore are poor catalysts.

Our calculations are based on the assumption that the breaking of the bond results in two protons on the electrode surface. This assumption should be sound for the metals Cu, Ag, Au, Co, and Ni, which do not adsorb atomic hydrogen in the potential range of the oxidation. However, on Group 10 metals (e.g. Pt), hydrogen is known to adsorb at low overpotentials, and the desorption of hydrogen may be the rate-determining step. If this is the case, our calculation would explain why the breaking of the bond is faster than the desorption.

Obviously, our method of estimating rate constants is only approximate, even though it seems to be at least as accurate as the available experimental data. The accuracy of the calculations can be much improved by calculating the density of states of hydrogen on the metal surface as a function of its bond length using common quantum-chemical programs. This approach will give better estimates but will probably add little to our understanding.

Bond breaking with simultaneous electron transfer plays a major role in many important electrochemical reactions, such as the reduction of oxygen and of chlorine. The critical step occurs when the antibonding orbital passes the Fermi level of the metal and picks up electrons. Thus, these reactions can be described by the same theoretical framework. In particular, a good catalyst for these reactions should have a high density of d states near the Fermi level.

In summary, we have shown that the catalytic activity of metal electrodes for hydrogen oxidation can be understood in terms of two concepts: their d-band density of states and the strength of their interaction with the molecule. Hammer and Nørskov have shown that the same concepts can explain the dissociation of H_2 on metals in the vacuum.[17] There is, however, a decisive difference. In the electrochemical oxidation, the splitting of the bond involves the transfer of two electrons; therefore, the activated state occurs when the bonding orbital passes the Fermi level, and the DOS of the molecule at this state is crucial. Nevertheless, it is pleasing that the same principles, even if they act in a different way, can be used to explain this reaction both in a vacuum and in an electrochemical cell.

Received: May 29, 2007

Keywords: electron transfer · fuel cells · heterogeneous catalysis · hydrogen oxidation

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