On the Theory of Electrocatalysis

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Abstract A theory of electrocatalysis developed in our group is presented and related to other theories of electrochemical electron transfer. As an example, the theory is applied to the first step in oxygen reduction on silver in alkaline media. It is shown, that this step occurs in the outer sphere mode.

1 Introduction

In the first approximation, scientists can be grouped into two classes: specialists, who work in a small field that they analyze profoundly, and generalists, who cover a broad area, and are less concerned with small details. Prof. John O'M. Bockris was a generalist, and, what is more important, a generalist with a vision. The breadth of his work is exemplified by his large number of publications, and by his seminal books on *Surface Electrochemistry* [1] and *Quantum Electrochemistry* [2] (both with S. Khan), each encompassing between 500 and 100 pages. His textbook on Modern Electrochemistry [3] (with K.N. Reddy) educated generations of electrochemists, and contrasts in style and spirit with the equally influential *Electrochemical Methods* by Bard and Faulkner [4]. As early as 1976, he presented his vision of the hydrogen economy based on solar energy and electrochemical energy conversion, which he later published as a book [5]; he returned to this topic in several of his later books aimed at a general audience. When he presented his ideas, he was a lonely prophet, but now, about 50 years later, they belong to the mainstream.

The theory of electrocatalysis was among the many topics on which he worked. At that time, the theory of electrochemical reactions was limited to outer sphere electron transfer, and he pointed out correctly, that these could not be applied to catalytic reactions. Throughout his life he worked on various topics of electrocatalysis. Obviously this is not the place to review his work, but we would like to draw attention to one of his early works, together with Brian Conway, entitled: *Electrolytic hydrogen evolution kinetics and its relation to electronic and adsorptive properties of metals*

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[6],which discusses in an intelligent way the relation between the kinetics and the energy of adsorption of hydrogen, and related quantities. It precedes the works of Gerischer [7] and Parsons [8] on volcano plots by about a year, and the standard work by Trasatti [9] by 15 years. Nowadays, the most cited work on this topic seems to be the article by Nørskov et al. [10], who provided DFT data for this venerable topic. Conway and Bockris did not only discuss the Sabatier principle, but made the useful distinction between *sp* and *d* metals, and furthermore pointed out the importance of the filling of the *d* band, which at that time was called *d* character—all these topics were rediscovered at the beginning of this millennium. In addition, they discussed current-potential relationships in terms of potential energy curves for the transition of the proton. Unfortunately, the extensive work of Bockris and his school on electrocatalysis never resulted in a quantitative theory, because the computational tools were missing at that time, and even the experimental values were not very reliable.

In this chapter, we review our own theory of electrocatalysis, which, we are sure, John O'M. Bockris would have approved, because it is based on the type of molecular description which he favored during his lifetime.

2 Elements for a Theory of Electrocatalysis

Before presenting our own theory, we would like to discuss a few concepts pertinent to electrocatalysis. The first quantitative theory for electrochemical reactions was for outer sphere electron transfer. It came in two flavors: The work of Levich, Dogonadze, and their school [11, 12] was primarily based on perturbation theory and weak interactions. The theories of Marcus [13] and Hush [14], which preceded the Soviet works, concern the weakly adiabatic limit, in which the interaction between the reactant and the electrode is strong enough to make the reaction adiabatic, but so weak that it does not affect the reaction barrier. A characteristic feature of the latter class of reactions is that the rate does not depend on the electrode material [15, 16]. Neither version is applicable to electrocatalysis, where the interactions are strong, and where often the rate on various materials can vary over eight orders of magnitudes [1]. Already in 1986, I had proposed a version of electron transfer theory based on Green's functions [17], which could be applied to interactions of arbitrary strengths, but in absence of a way to calculate strong electronic interactions this did not result in a theory of electrocatalysis. Nowadays, with density functional theory we have the computational means to calculate such interactions. So one essential aspect of theories of electrocatalysis is, that they must be able to treat strong interactions, and this will usually imply that DFT plays an important role.

However, even though the classical electron transfer theories cannot be applied to electrocatalysis, we must not forget the most important lesson that they taught us, the role of solvent reorganization. By definition, all electrochemical reactions involve charge transfer, and thus at least one of the reactants changes its charge, and hence its solvation. The accompanying changes in solvation energy are usually of the order of a few electron volts; in the case of the discharge of the proton it reaches about 11.3 eV! The concomitant energy of solvent reorganization makes an important contribution to the activation energy—indeed, in outer sphere electron transfer it alone determines the barrier height—and fluctuations of the solvent trigger the reaction. Therefore theories of electrocatalysis must contain an explicit treatment of the solvent, which must include statistical fluctuations. A simple model of a water bilayer at zero temperature is not enough.

As a reacting ion moves toward an electrode surface, its energy of solvation changes. The magnitude of this effect depends on the ion under consideration; for small ions such as Ag^+ and Li^+, which fit well into the structure of water, it is quite small [18], while it can be appreciable for larger ions like I^- [19]. In any case, it is an effect which must be considered. If both the reactant and the product are solvated, we require the energy of solvation as a function of position for both of them.

Finally, a rather trivial point: electrochemical reactions are governed by the electrode potential, which determines the rate, the activation energy, and even the direction. Since so far there is no consistent way to include the electrode potential in DFT calculations, a treatment that is based on DFT alone lacks a fundamental aspect.

3 Our Model for Electrocatalytic Reactions

We have presented our theory for electrocatalytic reactions in various publications [20–22], where we also give the mathematical details. Here we want to demonstrate the various effects that enter, and present our model Hamiltonian step by step. In order to focus on the main points, we present the version where spin plays no role, such as in the Volmer reaction or in the deposition of monovalent ions like Ag^+. Thus we consider one orbital labeled a on the reactant, and a continuum of states k on the metal. Generally, the index k runs both over the *sp* band and the d band of the metal. Denoting electronic energies by ϵ, and the operator for the occupation number by n, the electronic terms without interactions are:

$$H_1 = \epsilon_a n_a + \sum_k \epsilon_k n_k \tag{1}$$

Electron exchange between reactant and electron is effected by a combination of annihilation c and creation operators c^* for the electronic states:

$$H_2 = \sum_k \left(V_k c_k^* c_a + V_k^* c_a^* c_k \right) \tag{2}$$

The first term transfers an electron from the reactant to the metal state k with an amplitude of V_k, the second term effects the reverse process. The sum $H_1 + H_2$ describes the spinless version of the Anderson–Newns theory [23, 24].

Next we introduce the coupling with the solvent. Electron transfer theory distinguishes between two kinds of modes: slow modes, which in the case of water correspond to the motion of the molecular dipole moment, and the fast modes, which correspond to the electronic polarizability of the molecule, and which follow any charge transfer almost instantaneously. Electron transfer is triggered by thermal fluctuations of the slow modes, which are described as a bath of harmonic oscillators—in fact, any other model based on a harmonic approximation gives identical results. There is an infinite number of such oscillator modes, but in the harmonic approximation the minima for the initial state, the activated state, and the final states lie on a straight line, and this can be used to define a single solvent coordinate q; details are given in Ref. [25]. It is convenient to normalize q in such a way that the minima occur at integral values. Specifically, we normalize q in such a way that a solvent configuration characterized by q would be in equilibrium with a charge number of $-q$ on the reactant. For simplicity, we assume that the initial state with $\langle n_a \rangle = 0$ carries unit positive charge, and the final state is an adsorbed neutral atom, whose energy of solvation we neglect. Then the corresponding terms in our Hamiltonian are:

$$H_{\text{sol}} = \lambda q^2 + 2(z - n_a)\lambda q \tag{3}$$

The first term describes the slow solvent modes when the charge on the reactant is zero; the second term is a linear coupling of these modes with the charge. λ is the energy of reorganization familiar from Marcus theory, and z is the charge number of the reactant when the orbital a is empty. We have left out the kinetic energy, since it plays no role in the determination of the saddle point. To be specific, we discuss the case where $z = 1$, so that the reaction is the transfer of one electron to a cation.

Since we neglect the solvation of the final state, the interaction with the fast solvent modes affects only the energies of the initial state i, which is the cation. We denote the corresponding solvation energy by G^i_{fast}, and it contributes a term:

$$H_{\text{fast}} = (1 - n_a)\Delta G^i_{\text{fast}} \tag{4}$$

As a reactant approaches the electrode, its solvation energy changes; this effect can be obtained by molecular dynamics simulations, and the corresponding change is called the *potential of mean force* (pmf). In terms of the notation of Marcus theory, the potentials of mean force correspond to work terms, so we denote them by w_i and w_f, and introduce a term $n_a w_f + (1 - n_a) w_i$. Since in the case considered here the final state is an adsorbed atom, $w_f = 0$; however, we shall first keep this term in order to show the correspondence with Marcus theory for the case of weak interactions.

Finally we include the electrode potential ϕ, which simply shifts the energy of the ion, and gives a term $(1 - n_a)e_0\phi$. Collecting the various terms gives:

$$\begin{aligned} H = {} & (\epsilon_a - e_0\phi - \Delta G^i_{\text{fast}} + w_f - w_i - 2\lambda q)n_a + \lambda q^2 + 2\lambda q \\ & + \Delta G^i_{\text{fast}} + w_i + \sum_k \epsilon_k n_k + \sum_k (V_k c^*_k c_a + V^*_k c^*_a c_k) \end{aligned} \tag{5}$$

In the limit of weak interactions, the coupling to the metal has no effect on the energy, and we should retrieve Marcus theory. In this case, the initial state with $\langle n_a \rangle = 0$ has its minimum at $q = -1$, with an energy:

$$G_i = w_i - \lambda + \Delta G^i_{\text{fast}} = \Delta G_{\text{sol}} + w_i \tag{6}$$

where we have used the fact that $-\lambda$ is the slow part of the total solvation energy ΔG_{sol}. The interpretation is obvious: the only energy is the solvation energy modified by the work term.

In the final state $\langle n_a \rangle = 1$, the minimum is at $q = 0$, with an energy:

$$G_f = \epsilon_a - e_0\phi + w_f \tag{7}$$

This is the electronic energy shifted by the electrode potential, plus the work term. This gives the following free energy difference for the electron transfer step:

$$\Delta G^{\text{el}} = \epsilon_a - e_0\phi + w_f - \Delta G^i_{\text{sol}} - w_i \tag{8}$$

The free energy difference for the overall reaction does not contain the work terms:

$$\Delta G = \epsilon_a - e_0\phi - \Delta G^i_{\text{sol}} \tag{9}$$

The energy of activation is easily obtained calculating the value of q where the energies for the two states are equal. This results in the Marcus expression [13] for the reaction rate, which we will discuss below when we relate our theory to other works.

3.1 Density of States

When the reactant is far from the electrode, its valence level is sharp and characterized solely by its energy ϵ_a. However, when it approaches the surface, it begins to interact with the electronic states of the metal, with which it can exchange electrons. Consequently the valence level is no longer sharp, but characterized by a *density of states* (DOS). In the simplest case, which we shall discuss below, this takes on the shape of a Lorentzian, and the DOS can be considered as a consequence of the lifetime broadening.

The mathematical analysis of our model in based on the consideration of the Green's function, which is defined as $G(z) = \frac{1}{z-H}$, where z is the energy variable and H the Hamiltonian of Eq. (5). The calculations are facilitated if we split the Hamiltonian in two parts: The non-interactive part H_0, which comprises all of the terms of Eq. (5) except the last sum, which in the interacting part denoted by V. The Green's function can then be obtained via the identity:

$$G(z) = G_0(z) + G(z)VG_0(z), \tag{10}$$

where $G_0(z)$ is the Green's function pertaining to the Hamiltonian H_0.

The density of states can be calculated exactly from the Green's function, and expressed in terms of the two so-called *chemisorption functions* which describe the interaction [26]:

$$\Delta(\epsilon) = \pi \sum_k |V_k|^2 \delta(\epsilon - \epsilon_k) \qquad \Lambda(\epsilon) = \frac{1}{\pi}\mathcal{P}\int \frac{\Delta(\epsilon')}{\epsilon - \epsilon'}\, d\epsilon', \tag{11}$$

where $\mathcal{P}$ denotes the principle part. The corresponding density of states of the reactant is:

$$\rho_a(\epsilon) = \frac{1}{\pi}\frac{\Delta}{\left[\epsilon - (\tilde{\epsilon}_a - \Lambda - 2\lambda q)\right]^2 + \Delta^2}, \tag{12}$$

where we have collected the terms that modify ϵ_a:

$$\tilde{\epsilon}_a = \epsilon_a - e_0\phi - \Delta G^i_{\text{fast}} + w_f - w_i \tag{13}$$

In the simplest case, which we shall discuss in more detail below, Δ and Λ are constant. In this case the density of states $\rho_a(\epsilon)$ takes the form of a Lorentzian of width Δ, whose center has been shifted by Λ. In addition, the center fluctuates with the solvent coordinate q. In the general case, Δ and Λ depend on the energy ϵ, and the form is more complicated.

The occupancy of the valence state a is obtained by integrating the DOS up to the Fermi level E_F:

$$\langle n_a \rangle = \int_{-\infty}^{E_F} \rho_a(\epsilon)\, d\epsilon \tag{14}$$

From now on, we shall set $E_F = 0$. The electronic part of the energy is obtained by multiplying the DOS with the energy ϵ and integrating again to the Fermi level:

$$E_{\text{el}} = \int_{-\infty}^{0} \epsilon\, \rho_a(\epsilon)\, d\epsilon \tag{15}$$

3.2 *Wide Band Approximation*

As already mentioned, in the simplest case Δ does not depend on the energy; in this case $\Lambda = 0$. This is known as the *wide band approximation*, because physically it corresponds to the interaction of the reactant with a wide, structureless band of the electrode. The integrals in Eqs. (14) and (15) can be performed explicitly. This gives for the occupancy:

$$\langle n \rangle = \frac{1}{\pi} \operatorname{arccot} \frac{\epsilon_a - 2\lambda q}{\Delta} \tag{16}$$

This simple approximation can be used to nicely explain a basic effect of catalysis due to the width Δ of the reactant's DOS. For this purpose, we ignore the fast solvation and the work terms for the moment—they become important for quantitative calculations on real systems—and focus on electron transfer and solvent reorganization. Then the energy can be written as a function of the solvent coordinate q:

$$E(q) = \lambda q^2 + 2\lambda q + (\epsilon_a - 2\lambda q)\langle n \rangle + \frac{\Delta}{2\pi} \ln \frac{\left[\epsilon_a - 2\lambda q\right]^2 + \Delta^2}{\epsilon_a^2 + \Delta^2} \tag{17}$$

It is easy to verify that equilibrium occurs for $\epsilon_a = -\lambda$, and this is the case we shall now consider. The corresponding free energy curve has been examined in detail in [17]. For not too strong interactions, for $\Delta < 2\lambda/\pi$, the curve has two minima corresponding to the initial and the final state, separated by a maximum at the transition state. The corresponding energy of activation is:

$$E_{\text{act}} = \lambda/4 + \frac{\Delta}{2\pi} \ln \frac{\Delta^2}{\lambda^2 + \Delta^2} \tag{18}$$

For $\Delta \to 0$, we recover the Marcus result of $\lambda/4$; for finite values of Δ, the argument of the logarithmic term is smaller than unity, and hence this terms decreases the energy of activation. The reason can be visualized in Fig. 1: According to Eq. 15, the electronic energy is obtained by integrating $\epsilon \rho_a(\epsilon)$ up to the Fermi level. At the activated state, the DOS is centered directly at the Fermi level, which is the energy at which the electron transfer takes place. For a sharp DOS, i.e., for $\Delta \approx 0$, the electronic energy at the saddle point would be equal to E_F, and hence equal zero with our

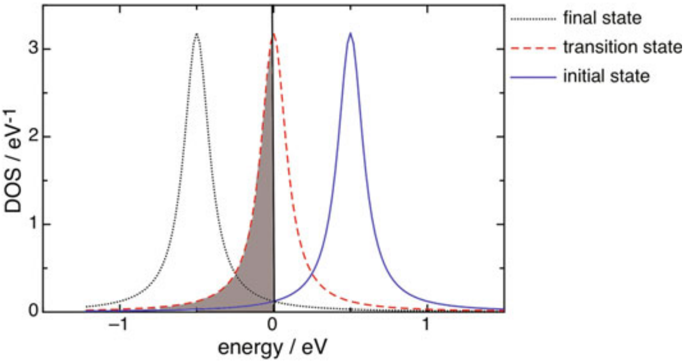


Fig. 1 DOS for the initial, the activated, and the final state for the case of equilibrium; parameter: $\lambda = 0.5$ eV. The shaded portion of the DOS for the transition state reduces the energy of activation. After [25]

choice of reference energy. For a finite width Δ, the shaded part which lies below the Fermi level contributes to the energy of the activated state. Obviously, it is smaller than zero, and the lower, the greater Δ. In this way, a strong interaction with the metal lowers the activation energy, and thus catalyzes the reaction. We shall meet the same effect when we discuss electrocatalysis in real system.

4 Relation to Other Theories

4.1 Marcus Theory

Marcus theory corresponds to the weakly adiabatic case: The interaction with the metal is strong enough, to make the electron transfer adiabatic, but too weak to have an effect on the activation energy. The latter is easily derived by calculating the intersection point between energy curves of the initial ($\langle n_a \rangle = 0$) and the final ($\langle n_a \rangle = 1$) states, both considered as a function of the solvent coordinate q. The result is:

$$E_{\mathrm{act}} = w_i + \frac{(\lambda + \Delta G + w_f - w_i)^2}{4\lambda} \tag{19}$$

which is familiar from Marcus theory. The properties of the metal and its interaction with the reactant do not enter; so there is no catalysis. Indeed, experimental results show that in this case the rate is independent of the nature of the metal [15, 16]. We shall not discuss the pre-exponential factor, which is usually obtained from Kramers theory [27].

4.2 Levich and Dogonadze Theory

The first quantum mechanical theory of electrochemical electron transfer was developed by the Soviet group led by Levich and Dogonadze [11]. In essence, it is based on a Hamiltonian like ours, but without the work terms. However, the interacting part V is considered as weak and treated by first-order perturbation theory. A systematic perturbation theory can be based on an iteration of Eq. (10), which results in a series in terms of V:

$$G(z) = G_0(z) + G_0(z)VG_0(z) + G_0VG_0(z)VG_0(z) + \cdots \tag{20}$$

In the first-order perturbation only the first two terms are retained. As a consequence, the width Δ and the shift Λ do not figure in the theory. The standard procedure is to perform a Fourier transform, from which Fermi's golden rule is obtained after some calculations. The final expression for the rate constant contains the same energy of activation as Marcus theory, though without the work terms. However, the pre-exponential factor contains the matrix element of V_{if} between the initial and final states, and is given by $|V_{if}|^2/h$. The element V_{if} has the meaning of an effective value of V_k.

In Marcus theory as well as in ours the reactant shares its electrons with the metal. In contrast, in perturbation theory electron transfer is a rare event, and the theory traces the transition of a single electron with a definite energy. Thus one obtains an *energy resolved rate* $W(\epsilon)$ for the transfer an electron of an energy ϵ, to the metal, and a corresponding expression for the reverse direction. Since electron transfer from the reactant can only occur to empty levels, the total rate k_{r} of reduction is obtained by multiplying with the probability of finding an empty level, and integrating over energy:

$$k_{\mathrm{a}} = \int [1 - f(\epsilon)] W_a(\epsilon, \eta)\, d\epsilon, \tag{21}$$

where we have expressed the fact that the rate depends on the overpotential η as well; $f(\epsilon)$ is the Fermi–Dirac distribution. The index 'a' indicates that this is the rate for the anodic reaction, which is the oxidation. The energy resolved rate takes the form:

$$W_a(\epsilon, \eta) \propto (4\pi\lambda kT)^{-1/2} \exp - \frac{(\lambda - \epsilon + e_0\eta)^2}{4\lambda kT} \tag{22}$$

The term $(-\epsilon + e_0\eta)$ is the free energy for the transfer of an electron of energy ϵ to the electrode. Thus, the energy of activation is given by the Marcus expression of Eq. (19), but without the work terms. The pre-exponential factor contains the perturbation $|V_{if}|^2$, and a factor which converts normal concentrations to surface concentrations [25].

For the cathodic reaction, the free energy of the reaction in the energy resolved rate takes the opposite sign:

$$W_c(\epsilon, \eta) \propto (4\pi\lambda kT)^{-1/2} \exp - \frac{(\lambda + \epsilon - e_0\eta)^2}{4\lambda kT} \tag{23}$$

and this has to be multiplied with the probability to find an occupied state on the metal from which the electron can be transferred:

$$k_{\mathrm{a}} = \int f(\epsilon) W_c(\epsilon, \eta)\, d\epsilon \tag{24}$$

4.3 Gerischer's Theory

Gerischer's theory [28] is essentially a re-interpretation of the theories of Marcus and of Levich and Dogonadze. Just like the latter, it considers electron exchange with specific energy levels ϵ. For the anodic direction, we introduce the electronic density of states $\rho_e(\epsilon)$ of the electrode; the product $\rho_e(\epsilon)[1 - f(\epsilon)]$ is then the probability of finding an empty state on the electrode. The term:

$$W_{\text{red}}(\epsilon, \eta) = (4\pi\lambda kT)^{-1/2} \exp - \frac{(\lambda - \epsilon + e_0\eta)^2}{4\lambda kT} \tag{25}$$

is then interpreted as the *density of reduced states* of the reactant. Apart from the pre-exponential factor, this is the same as the energy reduced rate of Eq. (22) given above. The total rate is then obtained by multiplying the density of empty states on the electrode with the density of reduced states of the reactant, and integrating over energy:

$$k_a = \int \rho_e(\epsilon)[1 - f(\epsilon)] W_{\text{red}}(\epsilon, \eta) d\epsilon \tag{26}$$

Since at room temperature the Fermi–Dirac distribution is almost a step function, in practice the integral is taken from the Fermi level to the top of the conduction band; the upper limit can be extended to infinity, since the integrand drops off rapidly for high energies.

Similarly, the density of oxidized states of the reactants is introduced as:

$$W_{\text{ox}}(\epsilon, \eta) = (4\pi\lambda kT)^{-1/2} \exp - \frac{(\lambda + \epsilon - e_0\eta)^2}{4\lambda kT} \tag{27}$$

and the cathodic rate is given by:

$$k_a = \int \rho_e(\epsilon) f(\epsilon) W_{\text{ox}}(\epsilon, \eta) d\epsilon \tag{28}$$

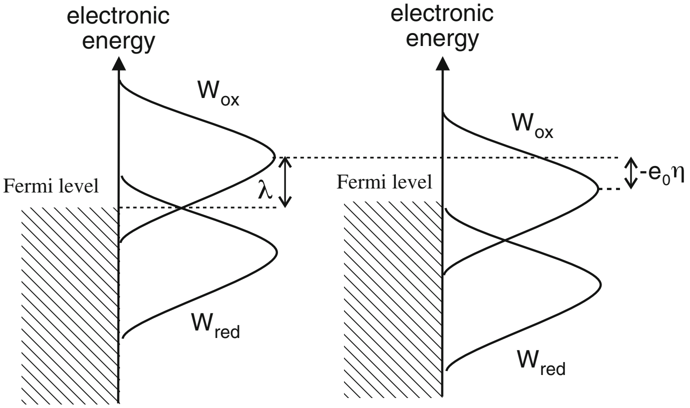


Fig. 2 Densities of reduced and oxidized states at equilibrium (*left*) and after the application of a cathodic overpotential (*right*). After [25]

In practice, the integral goes from minus infinity to the Fermi level. Gerischer's theory is for adiabatic transitions, since the perturbation $|V_{if}|$ does not enter into the rate equation. On the other hand, it uses the concept of electron exchange with specific energy levels of the metal. Equations (26) and (28) have a nice graphical representation shown in Fig. 2. In this picture, the application of an overpotential simply shifts the densities of states of the redox couple with respect to the Fermi level of the metal. This model has the further advantage that it can be readily applied to semiconductors. Equations (26) and (28) stay the same, but the electronic density of states $\rho_e(\epsilon)$ of the electrode now has a band gap.

5 Application to Real Systems: Oxygen Reduction in Alkaline Media

We now return to our theory of electrocatalysis as presented in Sect. 2, and show how it can be applied to real systems, where simple approximations like the wide band approximation do not hold. For this purpose, we need a number of quantities, which we obtain from DFT and from molecular dynamics. We start with the parameters that relate to the interaction of the reactant with the metal. As a concrete example, we chose the first step in oxygen reduction on Ag(100) in alkaline media [29], which occurs according to:

$$O_2 + e^- \rightarrow O_2^- \tag{29}$$

The reasons for choosing this particular reaction are the following: The rate of reaction (29) is very similar on a variety of electrode materials. It has therefore been suggested, that it occurs by an outer sphere mechanism, in which neither the reactant nor the product are adsorbed [30]. On the basis of our theory, we have recently shown that on Au(100) it indeed occurs in the outer sphere mode [31]. However, gold is special in that the oxygen molecule is not adsorbed on the surface. In contrast, silver is much more reactive to oxygen; in the vacuum the molecule adsorbs with an energy of about −0.4 eV [32]. We therefore want to investigate, if the reaction mechanism on Ag(100) is inner or outer sphere.

5.1 *Interaction with the Metal*

The parameters for the interaction with the metal can be determined by DFT. Calculations for a slab of metal performed with one of the common packages yield the electronic structure of the metal surface. For most metal of interest, this consists of a *sp*- and a *d* band. Usually, it is a good approximation to assume that the interaction of the reactant is constant for each band. Therefore we can write:

$$\Delta = \pi |V_{\rm sp}|^2 \rho_{\rm sp}(\epsilon) + \pi |V_{\rm d}|^2 \rho_{\rm d}(\epsilon), \tag{30}$$

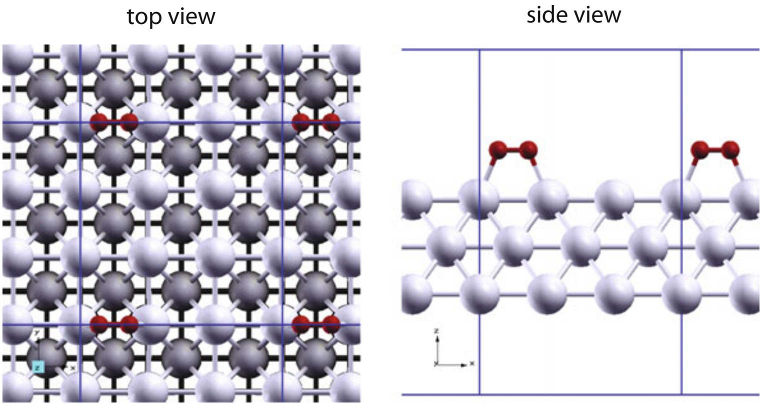


Fig. 3 Configuration of O_2 adsorbed on Ag(100). After [29]

where $\rho_{\mathrm{sp}}(\epsilon)$ and $\rho_{\mathrm{d}}(\epsilon)$ are the electronic densities of states of the metal *sp* and *d* bands. The function $\Lambda(\epsilon)$ is then obtained by integration according to Eq. (11). In addition, we need the energy ϵ_a of the reactant. In order to construct the free energy surface for the reaction, we require these three parameters as a function of the distance. For this purpose, we perform DFT calculations for the O_2 molecule in front of the Ag(100) surface at various distances. This gives us the energy as a function of the distance, and also the densities of states of the molecule. In order to obtain V_{sp}, V_{d} and ϵ_a for a given distance, we fit the theoretical density of states as given by Eq. (12), taken at $q = 0$, to the DOS obtained by DFT. The technical details are given in [29].

In our example, the approaching O_2 molecule has two empty antibonding spin orbitals; only the one which is directed perpendicularly to the metal surface interacts with the silver surface. As it approaches Ag(100), it becomes partially filled, and acquires a charge of about $-0.7\ e_0$ when it is adsorbed. The configuration of the adsorbed molecule is shown in Fig. 3. As an example of the fitting procedure, we show the DOS when the molecule is adsorbed, and the theoretical DOS according to Eq. (12) with the fitted values in Fig. 4. The fit is excellent, and this is true for larger separations as well. We must admit that the fitting procedure does not always work quite as well as in this example. In a few cases, for example, for the adsorption of OH on Pt(111), we have to introduce an energy dependence of the coupling constants [33].

5.2 *Solvent and Work Terms*

The energy of reorganization and the work terms are obtained from the energies of solvation of the reactant and the product. The bulk values of these energies are known

Fig. 4 DOS of the O_2 antibonding orbital that binds to the Ag(100) surface; the full curve has been obtained by DFT, the *dashed curve* by fitting. The fitted parameters are: $|V_{\mathrm{sp}}|^2 = 0.96$ eV^2, $|V_{\mathrm{d}}|^2 = 0.09$ eV^2, $\epsilon_a = -0.33$ eV. After [29]

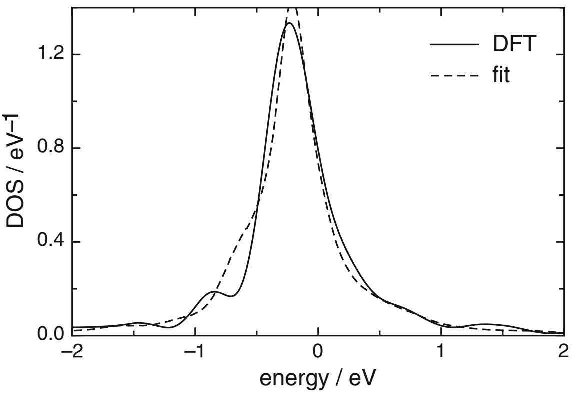
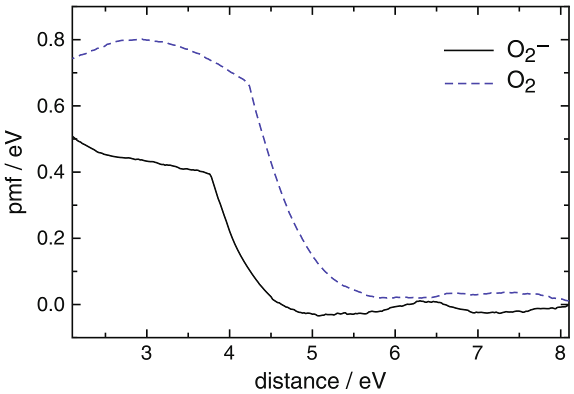


Fig. 5 Potentials of mean force for the approach of O_2^- and O_2 to the electrode surface. These curves are the same for Ag(100) and Au(100). After [29]



from experiment; as these particles approach the electrode surface they lose a part of their solvation sheets. The concomitant change in energy is known as the *potential of mean fore* (pmf), and can be obtained by molecular dynamics. For the details, we refer to the literature [29, 33].

We have calculated the pmf of both the molecule and the anion for the approach to the Ag(100). As expected, both increase toward the surface, as their hydration becomes weaker—see Fig. 5. This effect is stronger for the molecule, where the pmf begins to rise at about 6 Å, than for the anion, where it even has a slight minimum near 5 Å before it starts to rise. Considering that the hydration energy of the anion is about −3.9 eV, the rise in energy toward the surface is moderate.

The energy of solvation must be split into two parts: the slow part, which determines the energy of reorganization, and the fast part, which enters into the work terms. For this purpose, we note that the Marcus expression for the energy of reorganization is related to the energy of solvation, as given by Born's theory, by the relation:

$$\lambda = -\frac{1/\epsilon_\infty - 1/\epsilon_s}{1 - 1/\epsilon_s} \Delta G_{\mathrm{sol}}, \tag{31}$$

where ϵ_∞ is the optical dielectric constant of the solvent, and ϵ_s the static constant. For aqueous solutions, λ is about one half of the absolute value of the energy of solvation.

5.3 *The First Step in Oxygen Reduction on Ag(100)*

We now have the ingredients which we need to calculate the free energy surface for reaction (1). In Fig. 6 we present the surface for the potential, when the reaction is in equilibrium in the outer sphere. As usual, we have plotted the free energy as a function of the distance d of the reactant from the surface and of the solvent coordinate [25]. A quick reminder: The solvent coordinate characterizes the state of the solvent; it takes on the value q, when the solvent would be in equilibrium with a reactant of charge $-q$. At $d = 5$ Å and $q = 0$, we see a minimum that corresponds to the uncharged O_2 molecule; toward the bulk of the solution this extends into a valley. We have chosen the energy zero such that the energy is zero at this minimum. Likewise at large distances, but at $q = 1$, lies the minimum for the anion; again this extends into a valley toward the bulk, but it does have a real shallow minimum which corresponds to the slight minimum in the pmf observed in Fig. 5. These two minima are separated by a saddle point with an energy of 0.5 eV. A transition between these minima corresponds to an outer sphere electron transfer, so according to Marcus

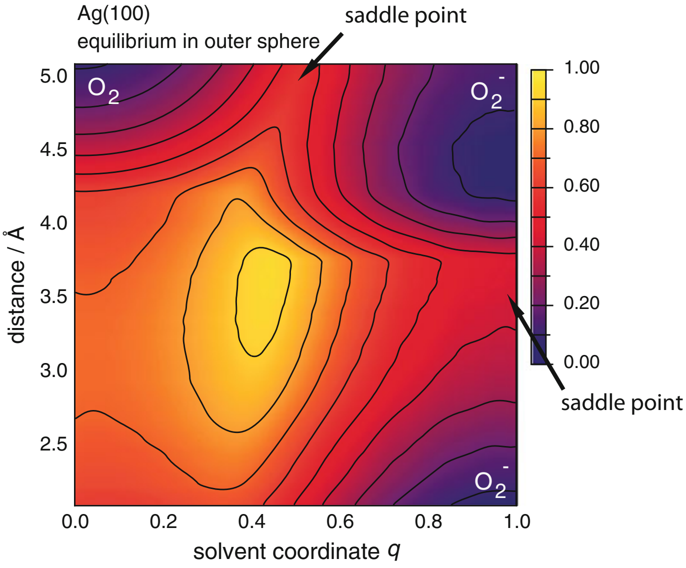


Fig. 6 Free energy surface for the reaction $O_2 + e^- \rightarrow O_2^-$ on Ag(100). The electrode potential is for equilibrium in the outer sphere mode. After [29]

theory [13], its activation energy should correspond to $\lambda/4$, where λ is the energy of reorganization. As we have argued above [20, 21], in aqueous solutions λ is half the absolute value of the energy of hydration (−3.9 eV in the bulk), so this activation energy agrees with Marcus theory. We note that close to the surface, λ decreases a little as the absolute value of energy of solvation becomes smaller in accord with the pmf for the anion.

Right on the electrode surface, at $q = 1$, there is a third minimum corresponding to the adsorbed state. Due to the effect of solvation, which favors charged particles, its charge is −1, somewhat lower than for the adsorbed state in the vacuum. Its energy is practically the same as that of the other two minima. This is the result of a compensation effect: The interaction with the metal lowers the energy by 0.4 eV, but the pmf is higher than that in the bulk by about 0.5 eV (see Fig. 5). A little bit of extra energy is gained by the change in the charge. The saddle point that separates the ionic state in the bulk from the one at the surface has an activation energy of about 0.4 eV. Within the accuracy of our calculations, this is of the same order of magnitude as the saddle point for the outer sphere step.

We have also performed calculations for a cathodic overpotential of $\eta = 0.2$ V making the reduction more favorable. The effect on the outer sphere pathway is straightforward: The energy of the ion is lowered by $-e_0\eta$, that of the molecule is unchanged, and the saddle point is lowered by the order of 0.1 V, giving a transfer coefficient of $\alpha \approx 0.5$. The effect on the rest of the surface requires a model for the variation of the potential near the surface. We have chosen a simple model in which the effect of the overpotential decays linearly between $d = 5.1$ Å, and the electrode surface, where its effect vanishes. However, the qualitative conclusions are independent of the details of this decay. The corresponding surface is shown in Fig. 7. Since the effect of the overpotential vanishes right on the surface, the energy of the adsorbed state is unchanged, and is now higher than that of the anion in the solution.

Blizanac et al. [34] have performed a thorough investigation of oxygen reduction on single crystal silver in alkaline solutions. They observed onset potentials of the order of 0.9 V RHE, which is compatible with an outer sphere mechanism. The onset potential should be close to the potential at which the outer sphere transfer is in equilibrium. From the temperature dependence of the currents, they determined the activation energies. For an electrode potential of 0.8 V RHE, which translates into an overpotential of about 0.1 V for the outer sphere reaction, they observed activation energies of the order of 0.3 eV, which are quite compatible with our theoretical values. The measured transfer coefficients are close to 0.5, in agreement with our results and typical for an outer sphere mechanism.

Thus our results suggest the following pathway: At equilibrium, the first step in oxygen reduction takes place in the outer sphere mode. The energy of the adsorbed species is about the same as that of the anion in solution, so the two species can interchange. The direct pathway from O_2 to the adsorbed anion is not favorable because of the strong rise of the pmf of the molecule near the surface (see Fig. 5). Application of a cathodic overpotential favors the anion in the solution, so that the adsorbed state becomes less favorable.

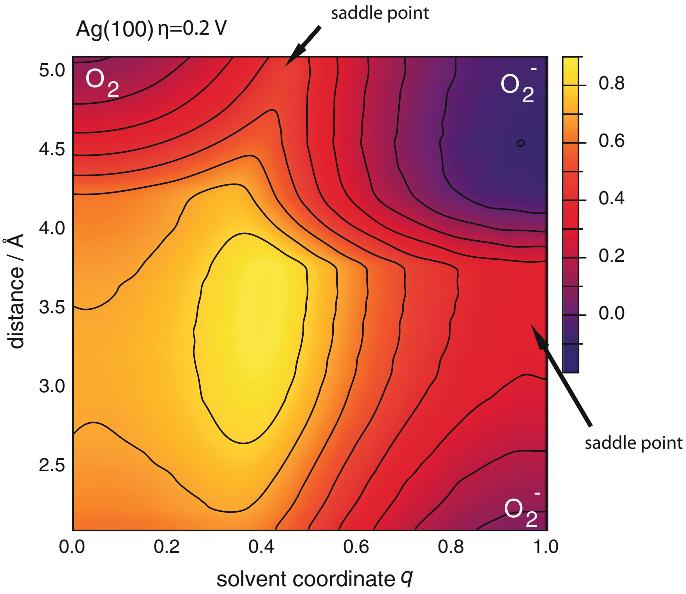


Fig. 7 Free energy surface for the reaction $O_2 + e^- \rightarrow O_2^-$ on Ag(100) for a cathodic overpotential of $\eta = 0.2$ V. After [29]

6 Conclusions

In this article, we have briefly reviewed the theory of electrocatalysis as developed in our group. It is related to older theories for outer sphere electron transfer. The new feature is that we have developed the theory so that it applicable to strong interactions between the electrode and the reactants, and are able to extract the system parameters from DFT calculations and molecular dynamics. As an example, we have presented recent results for oxygen reduction in alkaline media. For applications to other reactions, in particular to hydrogen evolution, we refer to our published works [20–22].

So far, we have mainly performed model calculations for the case where a single atom or molecule reacts. Obviously, the application of our method becomes more complicated when the number of reactants is larger. We have taken first step in this direction in our investigation of the Heyrovsky reaction on Ag(111) [35].

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