

Why is Gold such a Good Catalyst for Oxygen Reduction in Alkaline Media?*

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Fuel-cell technology faces a major problem: oxygen reduction is slow and requires a sizable overpotential, which reduces the efficiency of energy conversion. This is particularly true of the most common type of low-temperature cell, the PEM (proton exchange membrane) cell, which is designed for applications in automobiles and portable devices. The PEM works only in acid solutions, where platinum is still the best catalyst, and therefore there is presently an intensive search for better and cheaper oxygen catalysts in this medium. This experimental activity has been paralleled by much theoretical work into the reaction mechanism and the electronic properties of catalysts, but all have been restricted to acid media.^[1]

The first fuel cell that was ever put to practical use was the alkaline fuel cell operated by NASA. The reaction of oxygen is faster in alkaline solutions, and comparatively cheap materials, such as gold, silver, and a number of oxides, are better than platinum. What is missing for alkaline cells is a good, OH-conducting membrane, which would play the same role that PEMs play in acid cells. There are several very promising approaches to the design of such membranes, and they may soon be commercially available.^[2] In any case, there are good reasons to investigate oxygen reduction in alkaline media theoretically.

On most electrode materials the first electron transfer to the oxygen molecule determines the overall rate. In strongly alkaline media, this step is:



At low pH, the O_2^- ion can be protonated: $\text{HO}_2 \leftrightarrow \text{O}_2^- + \text{H}^+$, and the first step is a combined electron and proton transfer, to which we shall return below.

Sometimes, reaction (1) is written as two steps, with an adsorbed $\text{O}_2(\text{ad})$ as an intermediate state (see for example Ref. [3]). In any case, in strongly alkaline media this reaction does not depend on pH, and this has been verified experimentally.^[4,5] The lifetime of O_2^- is sufficiently long to appear in the reverse sweep of cyclic voltamograms if the electrode surface is passivated by a film.^[7] In contrast, in acid solutions the superoxide ion disproportionates rapidly.

It has also been suggested (see for example Ref. [8]) that in alkaline media the first electron transfer takes place by an outer sphere mechanism, where both reactants and products are close to the electrode but still solvated. The rates of outer sphere reactions, which take place at a distance of several Ångströms from the electrode, are independent of the electrode material,^[9,10] and such a mechanism would explain why in alkaline solutions the rates of oxygen reduction are similar on a fair number of electrodes such as silver, gold, and various oxides. On the other hand, on several metals, and in particular on gold, the reaction depends on the surface plane, and it is faster on Au(100) than on the other principle planes,^[6] and this is difficult to reconcile with an outer sphere mechanism.

Before investigating the kinetics, the thermodynamics should be mentioned briefly. At pH 14, the standard equilibrium potential for oxygen reduction is 0.401 V vs. SHE, and that of the O_2/O_2^- couple in the outer sphere mode lies at about -0.3 V;^[11] there is some uncertainty about the exact value. At a first glance, this difference of 0.7 V does not look promising. However, the value for the latter couple is for a 1 M solution of O_2^- . We know that the next reaction step is fast, so that the concentration of O_2^- has to be very much lower. For a concentration of 10^{-6} M the difference is only 0.34 V, and an outer sphere mechanism, setting in with an overpotential of this order of magnitude, seems feasible if the energy of activation is not too high. So at least this mechanism cannot be ruled out on the basis of thermodynamic arguments. These ideas are also supported by the experiments of Yang and McCreery.^[12] On a passivated carbon electrode, these authors observed the O_2/O_2^- reaction in an outer sphere mode. When the electrode surface was cleaned, the peak for the oxidation of the superoxide ion disappeared and the reduction of oxygen was shifted to higher potentials by several hundred millivolts.

To clarify the mechanism, we have investigated the electron transfer to the oxygen molecule by our own theory. We briefly summarize the main ideas; further details are given in the Supporting Information and the cited literature. The

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initial state is a weakly solvated molecule, and the final state is a strongly solvated ion. According to the Marcus^[13] and Hush^[14] theories, electron transfer requires a fluctuation of the solvent, which lowers the LUMO of the molecule to the Fermi level of the metal, where it accepts an electron, and the solvent configuration adapts itself further to the charge on the ion. The electronic energies of the molecule and of the ion can be obtained from density functional theory (DFT), but the solvent fluctuations and the resulting charge transfer cannot. We have therefore developed a theory^[15] containing ideas from Marcus–Hush and from Anderson–Newns theory.^[16,17] In essence, it extends electron-transfer theory to the case of arbitrarily strong coupling between the reactant and the electrode, and allows an explicit treatment of the interaction between the electronic bands of the metal and the valence orbitals of the reactant. We combine the DFT results with our theory to calculate Gibbs free-energy surfaces for the reaction.

As our model electrode we chose Au(100), which is one of the best catalysts in alkaline solutions.^[8] We first calculated the energy of the O₂ molecule in the vacuum as a function of the distance from the surface, optimizing the orientation and position parallel to the surface at each point. In accord with other researchers (see for example Ref. [18]), we found that the molecule interacts weakly with gold, with a binding energy of about −7 meV, which does not even show up in the corresponding graph (see Figure 1, which shows the behavior in the region relevant to electron transfer). As the molecule approaches the surface, its energy rises; at the same time spin polarization decreases slowly from the value of two, which it takes in the isolated molecule (Figure 1, top). We also investigated the breaking of the oxygen bond trying various pathways. The lowest activation energy we found was about 2.2 eV, and was obtained with fixed positions of the gold

surface. Obviously, bond breaking cannot be the first reaction step on Au(100).

DFT has well-known problems with the oxygen molecule. Also, performing DFT calculations with ions is not standard and requires several corrections. Therefore, it is difficult to obtain the absolute values for the electronic energies of the molecule and the ions. Fortunately, we only need the relative variations of both energies with distance; the absolute difference can then be obtained by adjusting the difference at large distances to the experimental value for the electron affinity of the molecule (−0.44 eV). Details are given in the Supporting Information.

The other quantities that we need are the energies of solvation of the ion and of the solvent reorganization. The energy of hydration of O₂[−] is 3.9 eV;^[11] according to the Marcus theory, the energy λ of reorganization is about half the solvation energy. The resulting value of 1.85 eV is close to the average value which Hartnig and Koper^[19] obtained from molecular dynamics for this redox couple, and is larger than the value estimated by Ignaczak et al.^[20] Thus the relevant properties of the solvent are known, and we can calculate the Gibbs free-energy surface of the reaction, which we shall plot as a function of the distance from the surface and of the solvent coordinate q . The latter is familiar from Marcus–Hush theory, where it is the only reaction coordinate. It indicates the configuration of the solvent, which during the reaction changes from that appropriate to the molecule to that corresponding to the ion, the activated complex being somewhere in between. We have normalized this coordinate in such a way that $q = 0$ corresponds to the solvent configuration in equilibrium with the molecule and $q = 1$ to the configuration corresponding to the ion. As explained in the Supporting Information, the solvation energy decreases as the particle approaches the surface, since its solvation sheaths breaks up.

Figure 2 shows the Gibbs free-energy surfaces calculated from our theory. The left panel shows the surface for the case, where the outer sphere pathway would be in equilibrium. At large distances there are two minima, one centered at $q = 0$, which corresponds to the oxygen molecule, and another one at $q = 1$ for the ion, and both have the same energy. The green dotted arrow between these minima indicates the outer sphere pathway. According to Marcus theory the corresponding energy of activation should be $\lambda/4 = 0.486$ eV; the small but noticeable interaction with the gold surface reduces it to 0.4 eV. However, the favorable reaction path is clearly not outer sphere, but towards the deep minimum for the ion that appears at short distances and $q = 1$, and has an activation energy of about 0.33 eV. Since the reaction occurs from a comparatively large distance, the difference in the energies of activation between the two paths is not large, and there is little difference in the rates for the direct pathway from the initial position of the molecule to the ion at the surface, or the indirect path starting with the outer sphere step and subsequent movement towards the surface.

The right panel of Figure 2 shows the situation when the outer-sphere step is endergonic by 0.3 eV, that is, when the electrode potential is 300 mV above the equilibrium potential for the outer sphere step. In view of the thermodynamic

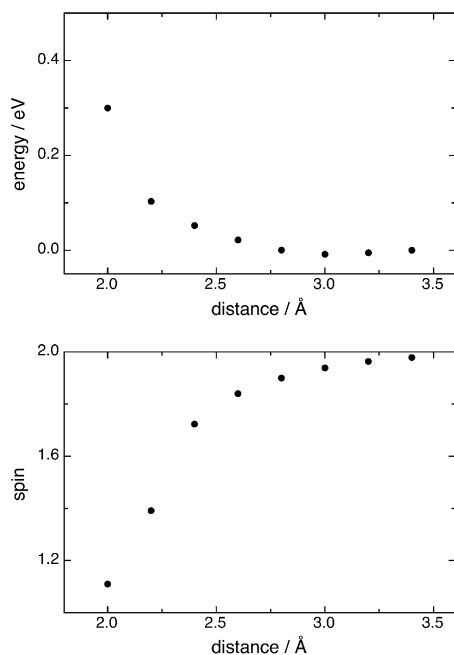


Figure 1. Energy (top) and spin polarization (bottom) of an oxygen molecule as a function of the separation from a Au(100) surface.

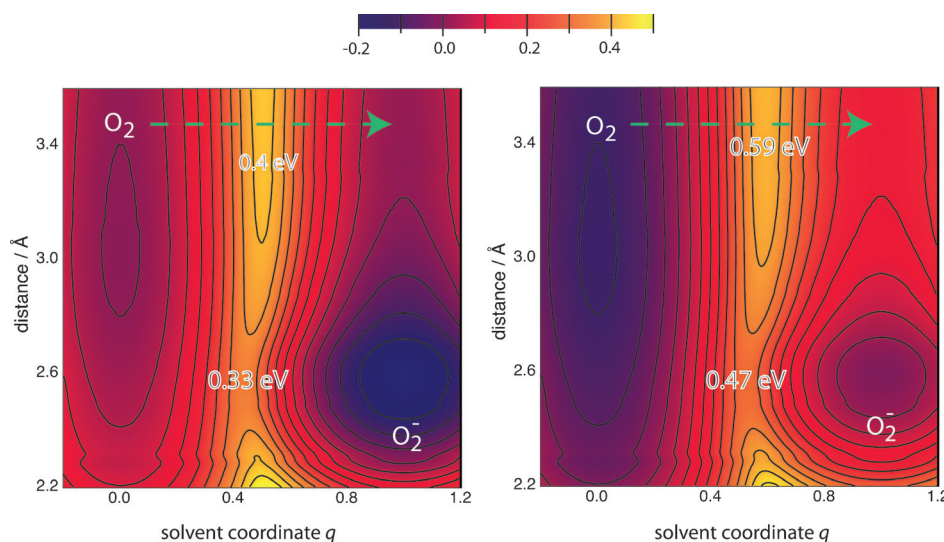


Figure 2. Gibbs free-energy surfaces for the reaction $\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^-$. Left: surface under equilibrium conditions for the outer sphere reaction; right: when the outer-sphere reaction is endergonic by 300 mV. The green dotted arrows indicate the outer sphere pathway.

considerations above, this would correspond to an overpotential for oxygen reduction (the total reaction) of a few hundred millivolts. Now the difference in the energies of activation for the two routes is somewhat larger, and the direct pathway, with an activation energy of about 0.47 eV, is clearly favored, a consequence of the fact that the outer-sphere step is uphill. From the change in the activation energy with potential we obtain a transfer coefficient of $\alpha = 0.46$, which compares well with the experimental value of about 0.5 observed on most materials. It is interesting to note that Marcus theory gives an activation energy of 0.65 eV for the outer sphere step, which is appreciably larger than predicted by our theory.

Because of the uncertainty in the energy of reorganization, which is based on a rough estimate, the absolute values of the calculated energies of activation are not very accurate. However, the order of magnitude should be correct, and, more importantly, the differences between the respective pathway. Therefore we conclude that the transfer of the first electron does not occur by an outer sphere mechanism, but by a direct transfer with the final state close to the electrode surface. However, the differences in the activation energies between the two pathways are small.

Our calculations have been performed for a bare gold surface. In the potential range where oxygen reduction takes place, metal electrodes are often partially covered by a layer of adsorbed OH, which may weaken the interaction between oxygen molecule and the electrode surface. In this case, we expect the outer-sphere path to dominate, which according to our calculations should be only a little slower than the direct path. On Au(100) the coverage with adsorbed OH is low in the region where oxygen reduction sets in,^[21] and this is one of the reasons that make it a good catalyst.

Au(100) is an excellent catalyst even though its interaction with the oxygen molecule is weak. All those effects that control catalysis in acid media, such as the position of the d band, long-range electronic interactions, or adsorption ener-

gies of intermediates, seem to play no role. So what makes a good catalyst for oxygen reduction in alkaline media? According to our model it is the rate of the reactions after the transfer of the first electron. The concentration of the superoxide ion must be very small to shift the O_2/O_2^- equilibrium potential closer to the equilibrium potential for the entire oxygen reduction reaction. These follow-up reactions will also determine if the reaction proceeds by the four-electron path leading to OH^- , or if it stops at peroxide. Prieto et al.^[21] have suggested that Au(100) is a particularly good catalyst because its surface is positively charged at small overpotentials

for oxygen reduction, so that negatively charged intermediates such as O_2^- are attracted to the electrode, where they react rapidly. However, a proper theoretical elucidation of the subsequent pathways is still missing, but this is not the subject here.

If Au(100) is such a good catalyst for oxygen reduction in alkaline solutions, the question arises as to why is it so bad in acid media. In these media, the first and rate-determining step is usually stated as:



This reaction has a standard equilibrium potential of -0.046 V at pH 0.^[11] As discussed before, fast subsequent reactions can lower the concentration of the product by a few hundred mV. In any case, the equilibrium potential for this reaction at pH 0 is about 0.5 V less favorable than that for reaction (1) at pH 14. As neither oxygen nor hydrogen adsorb chemically on gold, reaction (2) must take place in a near outer-sphere mode just like reaction (1). Indeed, DFT calculations performed by us clearly show that the formation of the product HO_2 takes place before its subsequent adsorption.

These theoretical arguments are in line with a recent experimental investigation by Ohta et al.^[22] of oxygen reduction on gold in acid media by surface-enhanced IR spectroscopy. These authors observed IR spectra of adsorbed HO_2 and O_2 . The band for the oxygen molecule is very close to the frequency of the free O_2 ; as the authors point out, this indicates that it is weakly adsorbed, without electron transfer, which is compatible with our DFT results.

These arguments in favor of alkaline media are based on thermodynamics, which could in principle be overcome by kinetics. However, the simple electron transfer in alkaline media is fast, with an activation energy of 0.33 eV at equilibrium, so that the unfavorable thermodynamics for acid media cannot possibly be overcome by faster kinetics.

In contrast, on transition metals such as Pt, the oxygen molecule is chemisorbed, with adsorption energies of the order of -0.6 eV (see for example Ref. [23]). This shifts the equilibrium potential for reaction (2) to correspondingly more positive values, and the overpotential for oxygen reduction is substantially reduced. Of course, the thermodynamics for reaction (2) have been investigated in several works (see Ref. [24] and references therein).

In conclusion, we have investigated the first and rate-determining electron transfer step for oxygen reduction on Au(100) in alkaline media. Even though this surface is an excellent catalyst, its electronic interaction with oxygen is weak, and d band effects, which dominate catalysis in acid media, play no role. The favored pathway leads directly to an adsorbed superoxide ion, but the activation energy for the outer sphere path, via a solvated ion, is not much higher. On a good catalyst, the subsequent reactions of the superoxide ion must be fast, keeping its concentration low. We suggest that this mechanism operates on a large variety of good catalysts, which exhibit similar reaction rates for oxygen reduction.

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