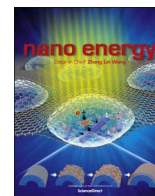




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A scenario for oxygen reduction in alkaline media



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ABSTRACT

We investigate oxygen reduction in alkaline solution with the focus on gold and silver electrodes. On the basis of theoretical considerations we propose a detailed mechanism, which we support by explicit calculations. In accordance with previous suggestions we conclude that the first step is an outer-sphere electron transfer to the oxygen molecule. The breaking of the oxygen-oxygen bond involves adsorption of OH on the electrode surface. This is much stronger on Au(100) than on Au(111), which explains why the former is a better catalyst.

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1. Introduction

When NASA looked for a reliable source of electricity for the Apollo mission and later for the space shuttle, they chose alkaline fuel cells. At that time, they were the best type of fuel cell available: robust, efficient – and expensive, but cost was not an issue for NASA. However, with the advent of the PEM (poly-electrolyte membrane) attention shifted to acid cells, and they have been the focus of research and development for the last decades.

The main problem of fuel cells is the sluggish reduction of oxygen; this reaction is faster in alkaline than in acid solutions, and it does not require expensive transition metals as catalysts. This advantage is offset by the fact that hydrogen oxidation is generally slower; however, recently electrodes modified by Ni(OH)₂ have proved to be almost as active in alkaline solutions as platinum in acid ones, so this may no longer be an obstacle to the development of efficient alkaline cells [1].

Following the trend in fuel cell development, theoretical investigations of oxygen reduction have focused almost entirely on acid solutions. But there is also a practical reason why alkaline solutions have been neglected: Nowadays theoretical studies are mostly based on DFT (density functional theory), and this has

great problems in treating ions and charge transfer. In acid solutions one can devise a reaction path, in which each step consists of a combined electron and proton transfer [2]. Thus the thermodynamics – though not the kinetics – of each step can be calculated by standard DFT. This option does not exist in alkaline solutions, which makes a treatment by pure DFT difficult.

Our group has developed its own theoretical method to study electrochemical charge transfer, which combines DFT with a theory of electrocatalysis and older theories of electron transfer. Recently, we have started to apply our theory to oxygen reduction in alkaline media with the focus on gold and silver [3,4]. In this paper we present a likely reaction path, which we support by explicit calculations. The reaction scheme is not new, but the theoretical support is original. Some of the calculations that we present have not yet been published; we shall give the results, but refer the technical details to future publications. So this article is a mixture of a review and a preview, and is meant to stimulate discussions and further investigations.

Before presenting our work we would like to place it into the context of other articles published in this issue. Rossmeisl et al. [5] also consider oxygen reduction, but in acid media, where every step can formally be written as a combined proton and electron transfer. As we shall see, the adsorption of intermediate plays a much larger role in acid than in alkali media; therefore in the latter there is no problem with scaling relations. Zeng and Greeley

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[6] also consider oxygen reduction in acid solutions, and investigate intermediate species on platinum by DFT, in particular the concomitant XPS spectra. They discuss the role of adsorbed OH, which we also treat below, but on different metals and in alkaline media. An extensive overview over interfacial effects in electrocatalysis has been presented by Herranz et al. [7]. Finally, experimental and practical aspects of catalyst design for oxygen reduction, mainly in acid solutions, are treated in the articles by Stamenkovic et al. [8] and by Strasser and Kühl [9].

2. The reaction scheme

A multitude of reaction schemes have been proposed for oxygen reduction; almost any scheme compatible with basic chemical laws – such as mass conservation and the absence of transmutation of elements – has been suggested at one time. In setting up a scheme for alkaline solutions, the following points must be considered:

- Results of DFT calculations for adsorbates must be taken into account. This rules out steps like $O_2 \rightarrow O_2(\text{ads})$ on gold, because oxygen does not adsorb on this metal.
- It is very rare that small adsorbates carry a sizable charge, O_2 on Ag being an exception. There is no known case in which a small adsorbate can exist both in a charged and in a neutral state. Note that earlier reports that O_2 adsorbed on platinum carries a negative charge have later been disproved [10].
- Species with low concentrations are not likely to meet and react.
- In each step not more than one electron can be transferred.

These points rule out quite a few mechanisms that have been proposed over the last decades.

Most researchers agree that in alkaline media usually the first electron transfer step according to [11,12]:



determines the overall rate. Often this reaction is written in terms of an adsorbed reactant and product, but this violates our rules. Since this reaction occurs roughly with the same rate on several electrode materials, it has been suggested that this step takes place in the outer sphere mode [13]. This view is compatible with thermodynamic considerations: In the outer sphere mode the standard equilibrium potential is about -0.3 V SHE, compared with a value of 0.4 V SHE for the overall reaction at pH 14. When this first step is slow and the subsequent steps are fast, the concentration of O_2^- is low, and for concentrations of the order of 10^{-6} – 10^{-7} M the overpotential is reduced to about 0.3 V, which is quite compatible with the onset potential observed on gold and silver [14–16]. The difference in reactivity between various metals would then not be caused by the first, but by the subsequent steps, which determine the concentration of O_2^- in front of the electrode. We shall return to this point below.

Several authors suggest:



as the second step. However, this step can only occur if the concentration of O_2^- is so high that two molecules can meet and react. As stated above, the concentration of this ion must be small on a good catalyst. Therefore we shall not investigate this step further. We prefer the alternative:



which at pH 14 has a very favorable standard potential at 0.2 V SHE [17], right in the voltage range where oxygen reduction takes

place on a good catalyst. Sometimes this is written as series of two steps:

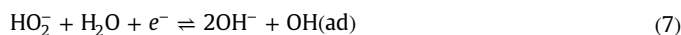


However, the standard equilibrium potential for the latter step lies at -0.744 V SHE [17] for the outer sphere mode, and adsorption of the reactant would make this even worse. Therefore, we propose that reaction (3) takes place in one step; since neither reactant nor product are adsorbed, this should occur in the outer sphere mode. This view is supported by theoretical calculations presented below.

In the literature, there are two suggestions for the fate of the HO_2^- ion:



which is a purely chemical step without electron transfer, and:



with subsequent electrochemical desorption of the adsorbed OH to OH^- . Both variants require empty sites on the electrode surface which can accept adsorbed OH. Reaction (7) and OH desorption can be combined to:



Since this does not involve an adsorbed species, its standard equilibrium potential is known: at pH 14 it lies at 0.867 V [17], and is therefore highly exothermic in the region of oxygen reduction. The simultaneous transfer of two electrons is, however, unlikely; we shall therefore disregard reaction (8).

This leaves us with reactions (6) and (7) as candidates for the step that breaks the oxygen-oxygen bond. We prefer step (6) for the following reason: The bond-breaking step must be highly sensitive to the surface structure. For example, on Au(100) the bond is broken, but on Au(111) not. The only place where the properties of the electrode enter is the adsorption of OH. In reaction (6) two OH are adsorbed, so this is more sensitive to the nature of the electrode. We also admit that this reaction, though difficult, is easier to treat theoretically than (7).

The final step is the desorption of OH. In summary, the reaction mechanism we consider is:



We shall now examine the individual steps in turn.

3. Step 1: $O_2 + e^- \rightarrow O_2^-$

We have considered this reaction on two different surfaces: on Au(100), where the oxygen molecule does not adsorb in the vacuum, and on Ag(100), where it adsorbs with an energy between -0.4 eV (our value and experiments) and -0.6 eV [18], in the adsorbed state it has a considerable negative charge of about -0.7 .

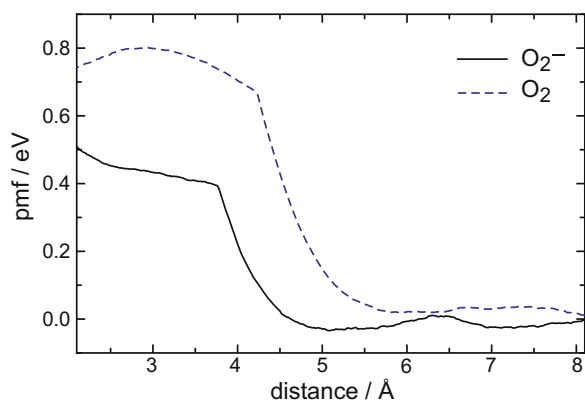


Fig. 1. Potentials of mean force for the approach of O_2^- and O_2 to the electrode surface. These curves are the same for Ag(100) and Au(100).

Also, silver is known to be a good oxidation catalyst in uvh [19], and is quite reactive to O_2 . Our intention was to study, if the different reactivity of these two surfaces entails a different electron transfer mechanism.

Besides the electronic interaction the reorganisation of the solvent plays a key role in electron transfer reaction. We have therefore studied the solvation energy of the molecule and the ion as a function of the distance from the electrode surface. Using classical molecular dynamics, we have calculated the potential of mean force (pmf) as these particles approach the surface – the pmf gives the change in the solvation energy as a function of the distance. The pmf of both the molecule and the anion increase towards the surface, as their hydration becomes weaker – see Fig. 1. 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 [17], the rise in energy towards the surface is moderate. In contrast, for the molecule the rise of the pmf is higher than the absolute value of the solvation energy in the bulk. We attribute this to an exclusion effect: Water likes to form a hydrogen bonded network on the surface, and expels the molecule, whose solvation shell is much weaker than that of the anion.

These pmfs determine two important quantities: the energy of reorganisation for electron transfer, and the work required to reach the reaction site – the so-called work terms in Marcus theory. The reorganisation energy refers to the interaction with the

slow part of the solvation energy, and is about half the absolute value of the solvation free energy [20].

Even without any further theoretical calculations it is obvious that on Au(100) neither the reactant nor the product can reach the electrode surface, so the reaction has to take place in the outer sphere mode. In contrast, on Ag(100) we may expect a competition between solvation, which tries to keep the reactant in the solution, and the electronic interactions, which attract the molecule. These expectations are borne out by the free energy surfaces which we calculated on the basis of our theory combined with DFT calculations. We usually plot these surfaces as a function of the distance of the reactant from the electrode surface, and of the solvent coordinate q . The latter is a concept derived from Marcus theory [21], and characterizes the state of the solvent. It takes on the value q , when the solvent would be in equilibrium with a reactant of charge $-q$ [20].

Fig. 2 shows these surfaces for the equilibrium electrode potential for the outer sphere mode. The surface for silver shows three minima. At $d=5$ Å and $q=0$ we see a minimum that corresponds to the uncharged O_2 molecule; towards the bulk of the solution this extends into a valley. We have chosen the reference energy 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 towards the bulk, but it does have a real shallow minimum which corresponds to the slight minimum in the pmf observed in Fig. 1. 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 theory [21] its activation energy should correspond to $\lambda/4$, where λ is the energy of reorganisation. As we have argued before [22,23], 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 in the bulk by about 0.5 eV (see Fig. 1). 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

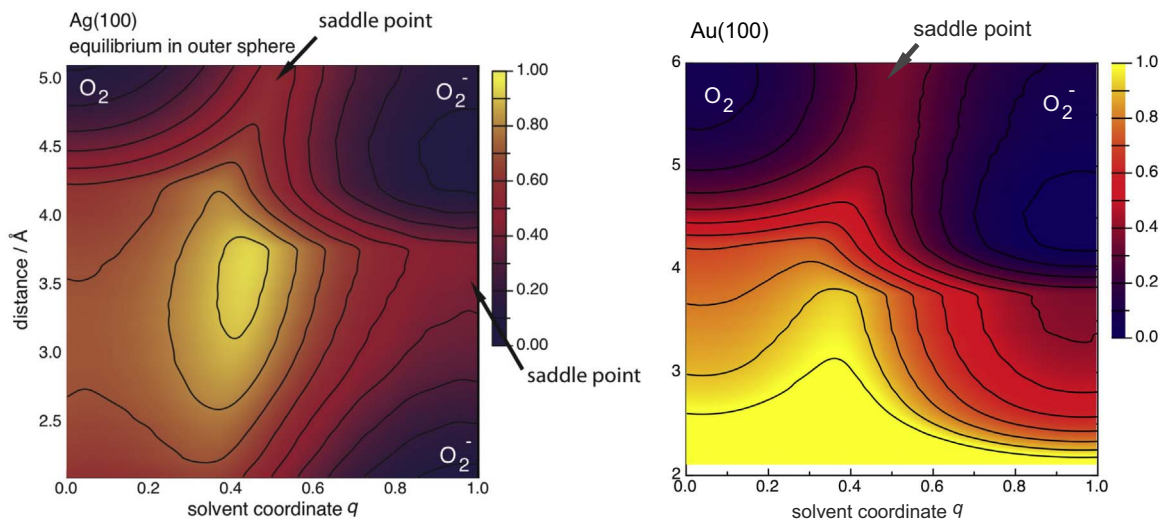


Fig. 2. Free energy surface for the reaction $\text{O}_2 + e^- \rightarrow \text{O}_2^-$ on Ag(100) and on Au(100). The electrode potential is for equilibrium in the outer sphere mode.

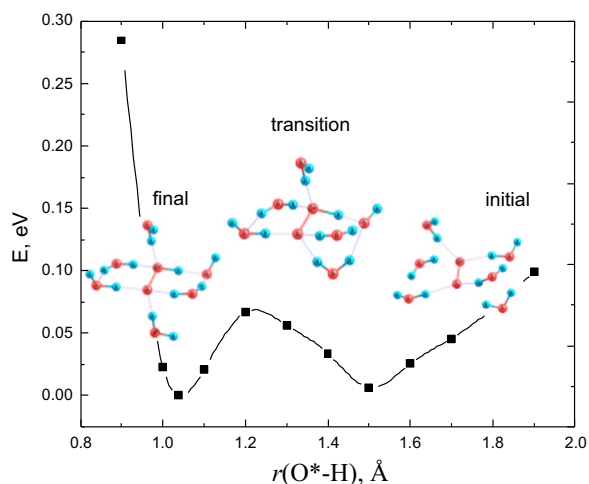


Fig. 3. Free energy curve for the reaction $\text{O}_2 + \text{H}_2\text{O} + e^- = \text{HO}_2 + \text{OH}^-$ calculated with 6 explicit water molecules; the barrier height is 0.06 eV.

point for the outer sphere step.

In contrast, on Au(100) there are only two minima, one for the molecule and one for the anion, and both are far from the electrode surface; they are separated by a barrier of 0.5 eV, which is the outer sphere value. In particular, there is no stable adsorbed state. So on this surface the reaction definitely takes place in the outer sphere mode. On Ag(100) the situation is somewhat more complicated, since we have three minima. Inspection of the free energy surface shows that the most favorable reaction path from O_2 to the adsorbed O_2^- is via an outer-sphere transfer to the O_2^- in the solution. The direct path is not favorable since the pmf for the O_2 rises steeply towards the surface (see Fig. 1). Thus, at the equilibrium potential two species of O_2^- coexist: one in the solution, the other adsorbed on the surface. On application of an overpotential the energy of the state in the solution is lowered, while the energy of the adsorbed state is largely unaffected. So on Ag(100) the reaction also takes place in the outer sphere mode, but there is an exchange with an adsorbed species.

4. Step 2: $\text{O}_2 + \text{H}_2\text{O} + e^- \rightleftharpoons \text{HO}_2 + \text{OH}^-$

After step 1 the O_2^- ion is in the outer sphere and surrounded by water, and the products of this reaction do not exist in an adsorbed form. We have therefore assumed that this reaction takes place in the outer sphere mode. Because of the charges on the reactants and products, DFT in the slab geometry is unsuitable.

Therefore we have investigated this reaction with the Gaussian suite of programs, which allows calculations with ions.

Solvation is important for electron transfer; we have therefore investigated this reaction with a variable number (1, 2, 4, and 6) of explicit water molecules; the rest of the solvation shell was treated by the polarizable continuum model (PCM). The electrode serves only as an electron donor, therefore it was not explicitly considered in the calculations.

The reaction can be considered as an H-atom transfer from the water molecule to the O_2^- with a simultaneous electron transfer to the OH radical. Therefore the distance between O_2^- and the nearest H-atom of water was taken as the reaction coordinate. When modeling the H-atom transfer in the $\text{O}_2(\text{H}_2\text{O})_n^{2-}$ form, the O^*-H distance was scanned, where O^* is an O-atom from the O_2 group; the other coordinates were allowed to relax. Thus the motion of the H-atom was treated as purely classical. As starting geometry we took the optimized initial cluster $\text{O}_2(\text{H}_2\text{O})_n^-$. The final state includes partially hydrated HO_2^- and OH^- ions coupled through H-bonds. This intermediate is assumed to dissociate with the formation of spatially separated $\text{HO}_2^-(\text{solv})$ and $\text{OH}^-(\text{solv})$.

The reaction barrier is low, but the results depended on the number of water molecules that were treated explicitly; generally, the larger this number, the lower the energy barrier. Full details will be reported elsewhere; here we show the free energy curve for equilibrium conditions calculated with 6 explicit water molecules – see Fig. 3. The barrier is very low, so that the reaction should proceed fast in both directions.

5. Step 3: $\text{HO}_2 + \text{H}_2\text{O} \rightleftharpoons 2\text{OH}_{ad} + \text{OH}^-$

This is the most difficult reaction to model: it involves the breaking of the oxygen-oxygen bond, a negative excess charge, and the simultaneous adsorption of two OH radicals, while one OH^- stays in the solution. Because of the negative excess charge we chose the Gaussian suite of programs for the calculations, and modeled the Au(100) surface by a gold cluster of 24 atoms (see Fig. 4). Since the cluster is finite, the surface sites are not all equivalent. Solvation was treated by the PCM model.

If we leave all of the atoms free to move they drift to the side of the cluster; this is unwanted since the center of the cluster is the best representation of the (100) surface. Therefore, in all calculations the OOH^- ion was kept at a bridge site with the O-O bond perpendicular to the metal surface. For the oxygen atom of the water molecule we tried several possible initial structures and so far a position at the neighboring bridge site gave the best results, i.e. the lowest energy – see Fig. 4. Note that in the initial structure one O-H bond in the H_2O molecule is stretched toward the OOH^- ion.

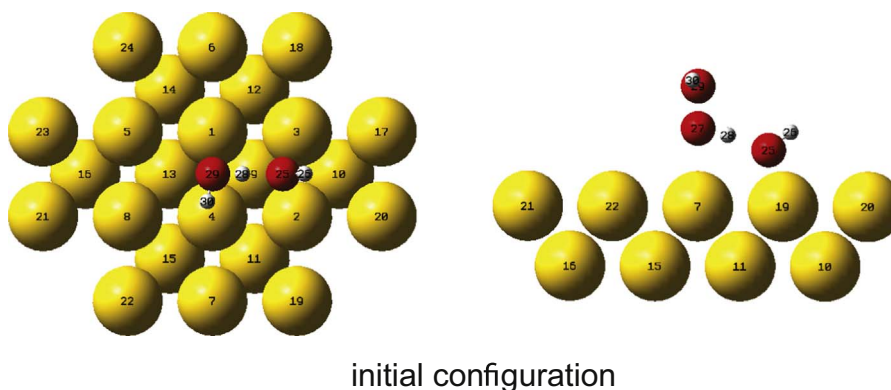


Fig. 4. Initial configuration for the reaction $\text{HO}_2 + \text{H}_2\text{O} = 2\text{OH}_{ad} + \text{OH}^-$.

As reaction coordinate we chose the distance between the two oxygen atoms in the HO_2^- anion. We first performed the calculations without the gold surface. In this case the reaction is endothermic with $\Delta H \approx 2.4$ eV and $\Delta G \approx 2.1$ eV; this is in reasonable agreement with an estimate of $\Delta H \approx 2.2$ eV obtained from tables [17]. Obviously, the spontaneous breaking of the O–O bond in solution will not occur. In contrast, on the Au(100) surface the reaction is exothermic by about 0.3 eV, and the barrier is 0.68 eV (see Fig. 5). The configurations at the top of the barrier and at the final state are shown in Fig. 6. Note that the calculations correctly result in two adsorbed OH radicals and an OH^- ion in solution. The energies contain the purely electronic energies resulting from DFT and the solvation energies, which have the nature of a free energy.

Because of the simplicity of the model system and the approximations involved these calculations are not quantitative. However, they clearly demonstrate that the breaking of O–O bond, which determines if the overall reactions involves four or only two electrons, requires a strong adsorption of OH on the electrode surface. We believe that this is the key to understanding the role of the catalysts, in particular to understanding the different behaviour of Au(100) and Au(111), to which we shall turn in the next section. Also, the value for the activation energy which we obtained, while by no means exact, indicates that the bond breaking reaction should occur with rate of a reasonable order of magnitude on Au(100). We note that this reaction is purely chemical, and hence does not depend on the electrode potential.

6. Step 4: $\text{OH}_{\text{ad}} + e^- \rightleftharpoons \text{OH}^-$

Both experiment [24] and theory [25] indicate that this

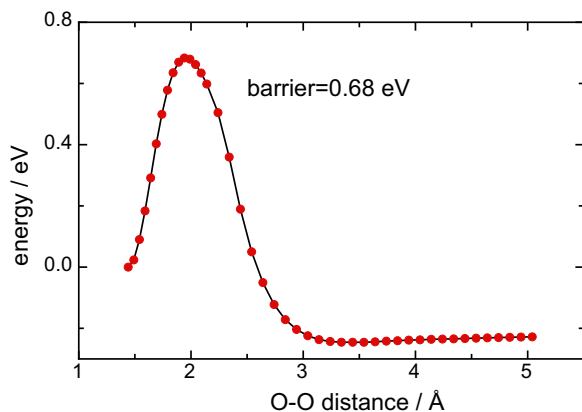


Fig. 5. Energy curve for the bond breaking step on a Au(100) surface.

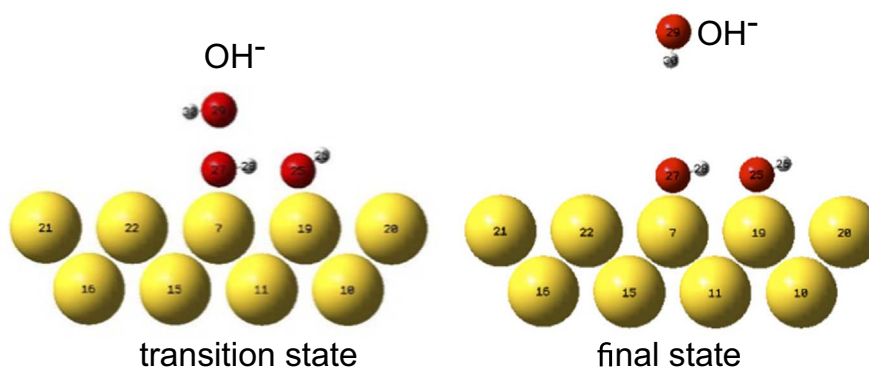


Fig. 6. Configurations at the transition state and at the final state.

reaction is fast. Therefore, and in view of the results of the previous section, we focus on the energy of adsorption of OH. Specifically, we want to compare Au(100) and Au(111); on the former surface, oxygen reduction proceeds all the way to OH^- , on the latter it stops after the transfer of two electrons. In the context of our proposed mechanism this means, that step 3 does not take place.

We have therefore calculated the adsorption energy of OH on both surfaces for various coverages; the results are shown in Fig. 7. The energies depend on the coverage, but adsorption on Au(100) is more favorable than on Au(111) by between 0.2–0.4 eV. Calculating adsorption energies of OH from aqueous solutions is somewhat problematic, since the adsorbate can form hydrogen bonds with the adjacent layer of water. Therefore we have performed additional calculation for adsorption in the presence of a layer of water, and have included van der Waals corrections, but adsorption on Au(100) remained more favorable by about the same amount.

OH adsorption on gold has been investigated by a fair number of researchers, principally on Au(111) [26–28], and most obtained a slightly higher, near -1.8 eV, value than we did. This difference can be traced to a different choice of pseudopotentials. However, the important point is that those researchers who investigated both surfaces also obtained a difference of about 0.4 eV at low coverages, with Au(100) being the more favorable surface [29,30]. Therefore, step 3 is by about 0.4–0.8 eV more favorable on Au(100) than on Au(111), which may explain while it takes place only on Au(100) and not on Au(111). Experimentally it is well established that OH adsorption is stronger on Au(100) than on Au(111) [24,31], although the cyclic voltammograms obtained in various groups differ in details. The adsorption of OH on Au(111) has been studied quantitatively by Chen and Lipkowski [32]; Fig. 3 of their work clearly shows that the coverage is low in the region

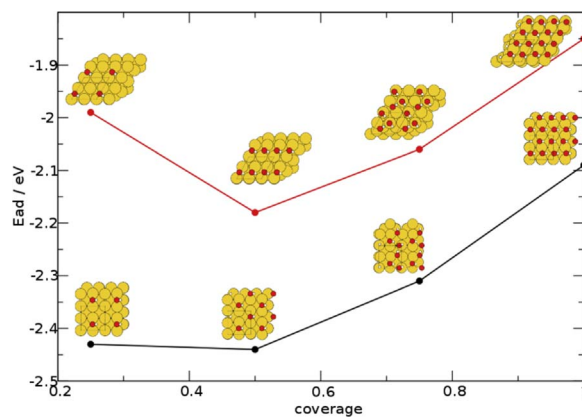


Fig. 7. Energy of adsorption of OH from the vacuum for Au(100) and Au(111) for various coverages.

relevant for oxygen reduction. Unfortunately, a similar quantitative study for Au(100) is missing, so we have to rely on the evidence from cyclic voltammograms.

As we have discussed in the introduction, the alternative to step 3 is the reaction (7), which involves the adsorption of one OH. Therefore this reaction is also more favorable on Au(100) than on Au(111), but the difference is smaller. So our analysis suggests that the step in which the oxygen-oxygen bond is broken involves OH adsorption. The same conclusion has been reached by Strbac and Adzic [33] in an early paper on the basis of extensive experimental investigations with vicinal surfaces. However, the mechanism suggested by these authors is quite different from ours.

7. Discussion and conclusions

As we stated in the introduction, the various steps in our mechanism have been proposed by other authors before; the new feature in this article are the theoretical investigations which support our scheme. Due to the different complexity of the steps, not all calculations have the same accuracy; in particular the bond breaking step is difficult to model, but we expect it to be qualitatively correct, and the energies should have the right order of magnitude.

One of our conclusions is that the breaking of the oxygen-oxygen bond requires a fairly strong adsorption of OH. In this way we explained the difference between Au(100), where the reaction involves four electrons, and Au(111), where it stops after two electrons. On the other hand the adsorption of OH must not be so strong that all of the surface is covered. However, the cyclic voltammograms of gold [24,31] and silver [14] surfaces indicate, that the coverage with OH is only partial in the region where oxygen reduction takes place. This is in agreement with our calculation, which show that adsorption becomes less favorable for higher coverages (see Fig. 7). In this context it is helpful, that the bond-breaking reaction does not depend on the electrode potential, while OH adsorption from the solution does.

It is sometimes assumed that the bond breaking occurs directly on the electrode surface: $O_2(\text{ads}) \rightarrow 2O(\text{ads})$. However, the activation energy for the breaking of this bond is 2.11 eV on Au(111) and 0.93 eV on Ag(111) [26] and thus prohibitively high.

Our calculations have been aimed at Au and Ag electrodes; nevertheless, we would like to add a word about Pt(111). Although it is difficult to compare the rates measured by different groups, there are experiments that seem to indicate that oxygen reduction in alkaline media is somewhat faster on Pt(111) than on Ag(100) or Au(100) (see e.g. [34]). The adsorption energy of O_2 on Pt(111) is about -0.7 eV [35]. The pmf for O_2 to arrive at the surface of Pt(111) can be expected to be roughly the same as on Ag(111), so that, judging from Fig. 1, the adsorption energy would offset the pmf, and the molecule could adsorb on the surface. This would open a direct path for the adsorption: $O_2 \rightarrow O_2(\text{ads})$, which does not exist on Ag(100) or Au(100), and a concomitant path $O_2(\text{ads}) + e^- \rightarrow O_2^-$, which could possibly be more favorable than the outer sphere mode. Whether this is a more favorable path than those on Au(100) and Ag(100), remains to be seen, but this difference should be kept in mind. The dissociation energy for O_2 on Pt(111) is about 0.6 – 0.8 eV [26,36] – the almost vanishing value in the much cited paper [2] is in error. This is higher than the activation energy for the outer sphere mode; in addition, this energy cannot be reduced by the application of an overpotential; this makes the simple dissociative path $O_2(\text{ads}) \rightarrow 2O(\text{ads})$ unfavorable both in alkaline and in acid solutions.

Whether alkaline fuel cells using silver or gold electrodes will ever be a commercial success remains to be seen. A recent study of porous silver electrodes by Kucernak et al. [37] gives reason for optimism, since the performance of the fuel cell was not limited by

the Ag catalyst but by mass transport. At the moment, doped carbon materials are much discussed as a comparatively cheap alternative – for a recent review see [38]. The mechanism of oxygen reduction on these materials is poorly understood, but experimental results obtained so far look promising.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen.2016.06.001>.

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