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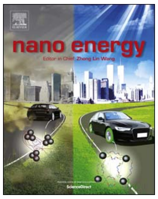

A scenario for oxygen reduction in alkaline media

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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 he 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.

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 [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

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et al. [7]. Finally, experimental and practical aspects of catalyst design for oxygen reduction, mainly in 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:

1. Results of DFT calculations for adsorbates must be taken into account. This rules out steps like $O_2 \rightarrow O_2(\mathrm{ads})$ on gold, because oxygen does not adsorb on this metal.
2. 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].
3. Species with low concentrations are not likely to meet and react.
4. 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]:

$$O_2 + e^- \rightarrow O_2^- \tag{1}$$

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:

$$2O_2^- + H_2O \rightleftharpoons HO_2^- + O_2 + OH^- \tag{2}$$

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:

$$O_2^- + H_2O + e^- \rightleftharpoons HO_2^- + OH^- \tag{3}$$

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:

$$O_2^- + H_2O \rightleftharpoons HO_2(\mathrm{ad}) + OH^- \tag{4}$$

$$HO_2(\mathrm{ads}) + e^- \rightleftharpoons HO_2^- \tag{5}$$

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:

$$HO_2^- + H_2O \rightleftharpoons 2OH(\mathrm{ad}) + OH^- \tag{6}$$

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

$$HO_2^- + H_2O + e^- \rightleftharpoons 2OH^- + OH(\mathrm{ad}) \tag{7}$$

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:

$$HO_2^- + H_2O + 2e^- \rightleftharpoons 3OH^- \tag{8}$$

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:

$$O_2 + e^- \rightarrow O_2^- \tag{9}$$

$$O_2^- + H_2O + e^- \rightleftharpoons HO_2^- + OH^- \tag{10}$$

$$HO_2^- + H_2O \rightleftharpoons 2OH(\mathrm{ad}) + OH^- \tag{11}$$

$$OH_{\mathrm{ad}} \rightarrow OH_{\mathrm{ad}}^- \tag{12}$$

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. Also, silver is known to be a good oxidation catalyst in uhv [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