



Short communication

Spin effects in oxygen electrocatalysis: A discussion

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ABSTRACT

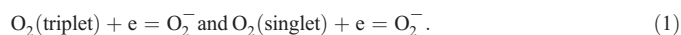
The reduction of molecular oxygen in triplet and singlet spin states at metal electrodes is analyzed in the framework of quantum mechanical theory of charge transfer. Both outer- and inner-sphere mechanism is considered. Singlet oxygen is argued to be considerably more active in electron transfer processes. It is demonstrated that spin polarization may play a catalytic role, parallel with the effect of overlap of reactant orbitals with the d-band of a metal electrode. Our model is based on two main assumptions: (i) some metal surfaces favor the existence of singlet molecular oxygen in adsorbed state; and (ii) short-living singlet O₂ molecules may appear as intermediates at some reduction steps. These two reasons are expected to increase the local concentration of active singlet molecular oxygen in reaction layer.

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The ground state of molecular oxygen is known to be triplet ($^3\Sigma_g^-$), where two unpaired electrons occupy antibonding – molecular orbitals forming a paramagnetic molecule [1,2]. At the same time in its lowest excited state (singlet, $^1\Delta_g$) a diamagnetic O₂ molecule appears as well. A singlet oxygen molecule is chemically more active and plays a very important role in a variety of biochemical processes (see reviews [2,3]); for example, an O₂ molecule becomes singlet being bound to the heme center of hemoglobin. Singlet molecular oxygen can be produced by photoexcitation of a suitable dye, which subsequently transfers its energy to a triplet oxygen and converts it into a singlet. The latter is not only more reactive because its energy is higher, but also because it removes spin conservation difficulties in certain reactions. In addition, singlet oxygen is expected to appear at metal surfaces. Experimental data by means of the UPS, ELS, LEED and work function measurements on the adsorption of molecular oxygen at Cu(100) and Cu(110) surface [4] were interpreted in terms of a chemisorbed singlet. The same conclusion was made in the work [5], where oxygen adsorption was studied at polycrystalline Ag and Cu surfaces (in the presence of adsorbed chlorine atoms) using X-ray and UV photoelectron spectroscopy. Some additional evidence can be also gained from periodical Density Functional Theory (DFT) calculations [6–8]. It has been predicted that a diamagnetic O₂ molecule (nearly neutral) exists in a stable adsorbed state on the Pt(111) surface (fcc hollow position); a difference in the adsorption energies between this surface place and the most preferable bridge position (for the triplet molecule) is small and amounts to 0.12 eV [6]. The authors of Ref. [7] have argued about the formation of a singlet O₂ molecule at Ag(100)

surface at short metal–O atom distances. In work [8] a diamagnetic state has been found for molecular oxygen strongly adsorbed at Ru(0001) surface.

Nowadays the oxygen reduction belongs to one of the most important and challenging research fields in electrocatalysis science, first of all because of its role in fuel cells [9]. In this communication an attempt is made to attract attention to some effect of spin nature which might play a role in this complicated multi-step electrode process. Let us consider the first electron transfer step for molecular oxygen in two different spin states:



This simple electron transfer is usually the first and rate-determining step in alkaline solutions (see e.g. Ref. [10]). On many substrates it seems to take place in an outer-sphere or near outer-sphere mode [11]. For the sake of simplicity, we consider first the normal outer-sphere mechanism. For further analysis it is convenient to write the rate constant (k) in terms of the Marcus theory:

$$k = \nu_{\text{eff}} \gamma \exp(-\sigma) \exp\left(-(\lambda - F\eta)^2 / 4\lambda k_B T\right), \quad (2)$$

where λ is the solvent reorganization energy; η is the overpotential with respect to the equilibrium potential; ν_{eff} is effective frequency factor; γ and $\exp(-\sigma)$ are additional pre-exponential factor which will be discussed below.

A value of -0.33 V was found experimentally for the standard electrode potential of the process $\text{O}_2 + e = \text{O}_2^-$ [12] for the triplet on the

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SHE scale. On the other hand, the energy of the molecular oxygen $^1\Delta_g$ state is 0.98 eV higher than the $^3\Sigma_g^-$ ground state [1]. The E_0 value for singlet oxygen can be readily estimated as $0.98 - 0.33 = 0.65$ V (see Table 1). The striking difference between the two E_0 values can be discussed in terms of the energy of Coulomb repulsion of electrons on the reactant orbital (U); this parameter plays an important role when constructing reaction free energy surfaces on the basis of the Newns–Anderson Hamiltonian [13]. In the case of the triplet oxygen an electron is transferred from a metal electrode to a half-occupied antibonding π -orbital ($U > 0$), while at the reduction of singlet oxygen an electron is transferred to an empty molecular orbital ($U = 0$). Therefore, the reduction of singlet molecular oxygen starts at significantly more positive electrode potentials. Assuming comparable work terms for the both oxygen forms (which is reasonable for the outer-sphere mechanism) a higher reactivity of singlet O_2 molecules becomes evident.

So, in the outer sphere mode there is a potential range of about 1 V in which the reactive singlet can be reduced to the superoxide ion, and the triplet state cannot. In aqueous solutions the lifetime of the singlet is short, of the order of pico- to at most a few milliseconds, which makes it difficult, though not impossible, to study electron transfer to a singlet oxygen in the outer sphere mode. In some organic solvents the lifetime of singlet oxygen is of the order of several ms, long enough for its detection. As shown in Ref. [14] singlet oxygen can be produced by a strong electric field in the gas phase, and can subsequently react in a suitable solvent. Obviously, the standard electrode potentials would be different in a non-aqueous solvent, but the difference between the potentials for the two oxygen species should remain the same.

However, the situation in the inner sphere mode is quite different. As a triplet oxygen molecule approaches a metal electrode surface, the Coulomb repulsion U decreases, because it is shielded by the s - and p -electrons of the metal. This entails a spin depolarization, the extent of which depends on the metal. Thus, on Cu(100) and Cu(110) the adsorbed state molecular oxygen is singlet [4,5], on Ag(100) [7] and Pt(111) [6] there can be two adsorbed states: a singlet and a paramagnetic state with a spin polarization of about 1, the latter on Pt(111) being slightly more favorable energetically (by about 0.12 eV).

There is no evidence for a stable, adsorbed, fully charged superoxide ion O_2^- ; earlier suggestion for its existence on Pt(111) proved to be unfounded. Sizable negative excess charges are known for the adsorption of halides on mercury, but even in this case, the magnitude of the electroreduction valence is notably less than one. Reaction (1) usually proceeds with a transfer coefficient of about 1/2, and the reaction order with respect to oxygen is unity. This is in line with the near outer-sphere mechanism, which we recently theoretically predicted on Au(100) electrode. In this case the reaction takes place close to the metal surface, but neither the reactant nor the product is chemisorbed [11]. We have suggested that the produced O_2^- ion reacts rapidly, which explains why reaction (1) is rate determining.

Thus the electron transfer happens in the region close to the metal surface, where the spin polarization decreases. It is worthwhile to study the two limiting cases of a triplet and singlet oxygen and compare some of their reactivity properties. The energy of reorganization should be nearly the same for both states. The tunneling factor $\exp(-\sigma)$ in Eq. (2) results from the fact that the equilibrium O–O distance differs for the reduced (f) and oxidized (i) states, and the vibration frequencies fall in quantum region, $\hbar\omega_{i(f)} \gg k_B T$. Assuming the linear response theory the parameter σ can be calculated as follows [13]:

$$\sigma = \frac{m(r_f - r_i)^2}{\hbar} \frac{\omega_i \omega_f}{(\omega_i + \omega_f)}, \quad (3)$$

where $r_{i(f)}$ are the O–O bond length in oxidized and reduced states and m is the effective oscillator mass.

For the reduced oxygen form (O_2^-) the ground state is $^2\Pi_g$, where $r_f = 1.348$ Å and $\omega_f = 1108$ cm^{-1} [15,16]. As can be seen from Table 1,

Table 1

Standard electrode potential E_0 , pre-exponential factor γ , bond length, vibration frequency (ω_i), tunneling factor $\exp(-\sigma)$ calculated for a molecular oxygen in two different spin states.

Spin state	$E_0(\text{SHE}), \text{V}$	γ	$r_{\text{O-O}}, \text{Å}$ [1]	ω_i, cm^{-1} [1]	$\exp(-\sigma)$
Triplet	−0.33 [11]	2/3	1.208	1580	0.23
Singlet	+0.65	1	1.2155	1509	0.27

the tunneling factor for the singlet oxygen is only 15% higher as compared with that for the triplet form. These simple estimations were made for gas phase. In a strongly adsorbed state the O–O bond length and vibration frequency of singlet oxygen can differ from those for gas phase; for example, $r_i = 1.39$ Å; $\omega_i = 826$ cm^{-1} (Pt) [6] and $r_i = 1.42$ Å; $\omega_i = 750$ cm^{-1} (Ru) [8]. However the qualitative conclusion is expected to remain the same.

In general, an additional pre-exponential factor (γ) should be addressed in Eq. (2) as well, when considering reaction (1). The physical meaning of this factor is the probability of the event that a transferred electron can occupy the acceptor π -orbital of molecular oxygen in accordance with the Pauli principle. The probability that the transferred electron has a certain spin projection is 1/2. For a singlet O_2 molecule it can occupy an empty acceptor orbital with probability 1. In turn, there are three different states for a triplet oxygen molecule: $\alpha(1)\alpha(2)$ ($M_s = 1$), $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$ ($M_s = 0$) and $\beta(1)\beta(2)$ ($M_s = -1$), where α and β are spin functions and M_s notes projections of the total spin (1). As only two states can be occupied by an electron taken from an electrode, the corresponding probability is, therefore, $1/2 * 2/3 = 1/3$. As the same situation takes place for the opposite spin projection, the resulting probability is $1/3 + 1/3 = 2/3$ (see Table 1).

The results compiled in Table 1 clearly demonstrate that singlet molecular oxygen is considerably more active in electroreduction as compared with its usual triplet form. For adiabatic electron transfer reactions the orbital overlap effect can noticeably smooth and reduce the activation barrier [13]. This effect is practically the same for both the singlet and triplet forms, because of the identical final electronic state, O_2^- .

On some electrode surfaces reaction (1) may proceed according to an inner-sphere mechanism with bond breaking:

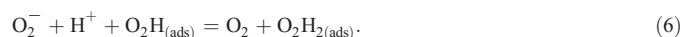


A simple analysis can be done in terms of Savéant's theory [17]. Then the activation barrier (ΔE_a) at zero electrode overvoltage can be recast in the form:

$$\Delta E_a = \frac{(\lambda + D + W_f - W_i)^2}{4(\lambda + D)}, \quad (5)$$

where D is the dissociation energy of O_2 molecule in gas phase; W_i the adsorption energy of O_2 molecule; W_f is the adsorption energies of O atom and O^- anion.

It is evident that the singlet spin state facilitates the O–O bond breaking and, therefore, decreases the intra-molecular contribution to the activation barrier (Eq. (5)). Catalytically active molecular oxygen in singlet state may also arise in further steps of the oxygen reduction. As an example, we consider the following reaction as a possible second step:



Since this is a reaction between two radicals, one of the products (O_2) can be both in triplet and singlet state. At the absence of an external

magnetic field the probability of formation of a singlet O_2 nearly amounts to 1/4. If the magnetic field can be neglected no longer, we have to consider time dependent probabilities to find O_2 in a certain spin state [18]. We have estimated additionally the free energy of process (6); Au(111) and Au(100) were considered as model electrode surfaces. It can be seen from Table 2 that reaction (6) is feasible for the both spin states of molecular oxygen, as well as for the both faces of gold electrode.

We also have to analyze the expression for the free energy (ΔG) of reaction (6) in more detail:

$$\Delta G = \Delta G_0 + 2.3 k_B T \text{pH} + k_B T \ln \frac{\theta_{H_2O_2}}{\theta_{HO_2}} + k_B T \ln \frac{[O_2]}{[O_2^-]}, \quad (7)$$

where θ notes the surface coverage; $[O_2]$ and $[O_2^-]$ are the equilibrium concentrations of molecular oxygen and O_2^- ion.

It is evident that step (6) becomes energetically more favorable at lower pH. More interesting, however, is the effect of the last term. Because the concentration of the singlet species is lower than the triplet molecules (under similar conditions), ΔG becomes more negative. Being significantly less stable than the triplet species, due to the spin conservation law singlet O_2 molecules may exist nevertheless as intermediate in some time scale (comparable with the elementary act time). Thus, singlet O_2 molecules generating by reaction (6) can participate in the electroreduction processes and facilitate the first electron transfer step.

Thus, spin polarization may play a catalytic role, parallel with the effect of overlap of reactant orbitals with the d-band of a metal electrode [9,13]. In conclusion, another theoretical attempt to investigate possible spin effects in the elementary act of electron transfer should be mentioned [20]. The authors [21] performed mixed quantum-classical molecular dynamics simulations to investigate the sticking of singlet O_2 molecules from a beam on Al(111) surface; it would be worthwhile to extend a similar approach to electrochemical interfaces. Most of computational efforts are focused to design new materials which are catalytically active in oxygen reduction (see, for example, Ref. [22]). We believe that it is tempting to predict “spin-catalysts” (metal surfaces, modified electrodes, nanoparticles etc.) which stabilize a singlet molecular oxygen, as well as to set up experiments for testing such catalysts. This will offer new horizons in electrocatalysis. A challenging problem is the influence of a substrate magnetic field on the spin states of adsorbed O_2 molecules. It is well-known that paramagnetic species are attracted by an external magnetic field (B_0), while diamagnetic molecules having a negative susceptibility are repelled. A magnetic field can, therefore, affect the diffusion transport of triplet and singlet molecular oxygen, although one needs rather high B_0 values to observe this effect. At the same time even a slight magnetic field can control directly the elementary act of electrocatalysis steps. As already was mentioned above, the probability of the formation of intermediate singlet O_2 molecules depends on the B_0 magnitude and oscillates as a function of time [18,23]. This problem deserves more detailed theoretical and experimental studies. Another interesting and important example of spin polarization effects in electrochemistry was investigated both theoretically and experimentally in work [25]. The authors of this article have analyzed for the first time the problem of ortho- and para-H conversion at electrochemical hydrogen evolution. Finally, we mention very briefly possible experiments which could be set up, in order to study the spin effects in electrocatalysis we discussed. If one wants to study singlet

oxygen electroreduction in aqueous solutions, the electrolyte pH has to be chosen in such a way that the reaction $O_2 + e^- \rightarrow O_2^-$ is still the dominant mechanism (a pH near 9 should be optimal). We can then expect to see a peak in the CV near 0.65 V, provided the current is sufficiently high. The strategy for such an experiment may follow the elegant work he strategy for such an experiment may follow the elegant work [12]. Measurements using in situ Electron Paramagnetic Resonance (EPR) technique may be also of worth, because the EPR signal intensity should depend on a ratio between paramagnetic and diamagnetic reactants and intermediates.

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Appendix A

The DFT calculations were performed by means of Gaussian 09 program suit [24]. A basis set of DZ quality was employed to describe the valence electrons of the Au atoms, while the effect of inner electrons was addressed by the Effective Core Potential developed by Hay and Wadt (LanL2). The standard basis set 6–31 g(d, p) was used for the electrons of O and H atoms. The Au(111) and Au(100) electrode surfaces were described using two-layer clusters ($Au_{15}(10 + 5)$ and $Au_{14}(8 + 6)$, respectively, see Fig. 1A). The hybrid exchange–correlation functional with vdW corrections [24] was used to model the adsorption of a hydrogen peroxide molecule; the adsorption of a HO_2 radical was investigated with the help of the hybrid B3PW91 functional. The open shell systems were treated in terms of the unrestricted formalism. The geometry of the adsorbates was optimized without symmetry restrictions. Some results of the calculations are shown in Fig. 1A and Table 1A. Since the adsorption energies depend in general on the cluster size, we performed additional test calculations (see the footnote to Table 1A). The ΔE_{ads} values for a H_2O_2 molecule are practically not sensitive to the cluster size, while for a neutral radical O_2H this effect is significantly stronger. The O_2H adsorption energy was found to have a non-monotonous character and the ΔE_{ads} value obtained for the smallest cluster Au_{14} is close to that calculated for a larger Au_{47} cluster. The cluster size effect does not change, therefore, our qualitative conclusion on the feasibility of reaction (6) on the Au(111) and Au(100) surfaces. Some pertinent thermodynamical estimates used in the article are collected in Table 2A as well.

Table 1A

Adsorption energy of the O_2H_2 and O_2H molecules on the Au(111) and Au(100) surface (ΔE_{ads} , eV) and the nearest Au–O distance (\AA , in parentheses) obtained on the basis of cluster DFT calculations.

adsorbed molecules	Au(111) ^a	Au(100) ^{a,b}
O_2H_2	–0.22 (3.014)	–0.37 (2.689)
O_2H	–0.303 (2.256)	–0.88 (2.206)

^a The ΔE_{ads} values calculated for a O_2H_2 molecule using Au clusters of different size: $Au_{22}(14 + 8)$, –0.24 eV; $Au_{24}(12 + 12)$, –0.3 eV; $Au_{35}(12 + 12 + 12)$, –0.35 eV.

^b The ΔE_{ads} values calculated for a O_2H radical using Au clusters of different size: $Au_{24}(12 + 12)$, –0.14 eV; $Au_{36}(12 + 12 + 12)$, –0.43 eV; $Au_{47}(16 + 15 + 16)$, –0.65 eV.

Table 2A

Standard Gibbs energy (ΔG_0) calculated for several reactions proceeding in the aqueous solution bulk (see Refs. [1,12,19]).

Reaction	ΔG_0 , eV
$O_2^- = O_2 + e$	–0.33 (0.65) ^a
$O_2H + e = O_2H^-$	–0.76
$O_2H^- + H^+ = O_2H_2$	–0.67
$O_2^- + O_2H + H^+ = O_2 + O_2H_2$	–1.76 (–0.78)

^a Data for singlet molecular oxygen are given in parentheses.

Table 2

Free energy (eV) of process (6) obtained by using standard electrode potentials (Refs. [1,12,19]) and the results of model Density Functional Theory calculations^a (see Appendix A for details).

Au(111)	Au(100)
–1.68 (–0.67)	–1.25 (–0.27)

^a Data for singlet molecular oxygen are given in parentheses.

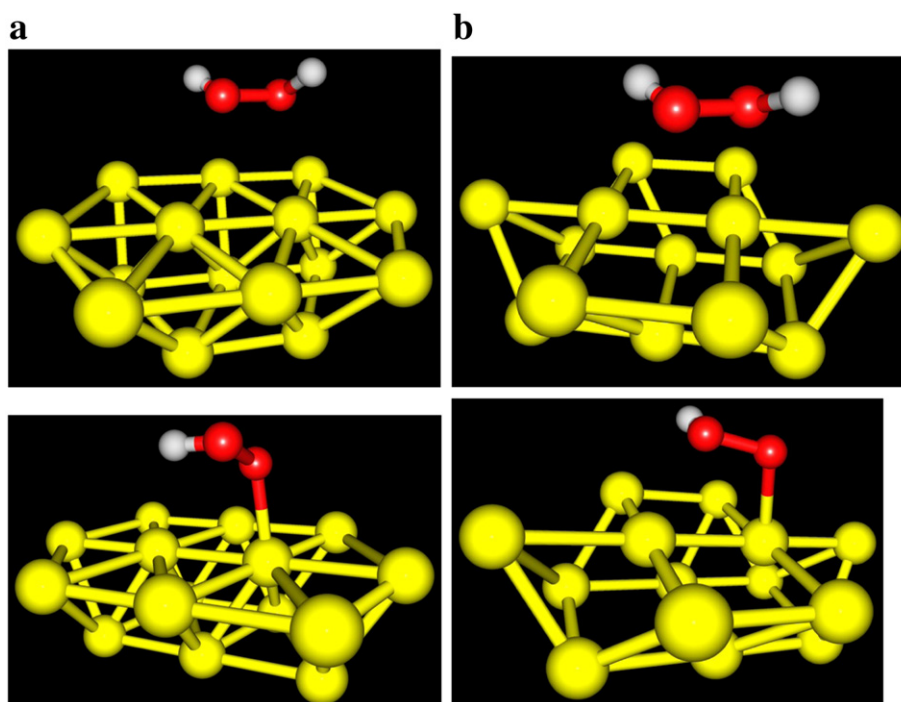


Fig. 1A. Optimized geometry of H_2O_2 (upper) and HO_2 (lower) molecules adsorbed on the Au(111) (a) and Au(100) (b) surface obtained on the basis of the cluster DFT calculations.

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