

## THE ELECTROCHEMICAL REDUCTION OF OXYGEN ON ELECTRODEPOSITED PALLADIUM CATALYST

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Oxygen reduction reaction was studied experimentally on palladium catalyst electrodeposited at glassy carbon in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution using the rotating disc electrode (RDE) method. Besides, *ab initio* quantum-chemical calculations have been carried out for the electronic structures of molecular clusters and adsorption complexes to model adsorption of molecular oxygen on palladium catalyst. It was shown that the value of adsorption energy of hydrogen peroxide influences the mechanism of oxygen reduction: at lower adsorption energies oxygen is reduced by the two-electron mechanism, which is followed by desorption of the peroxide molecule formed. At higher adsorption energies the reduction of oxygen occurs via the four-electron mechanism up to water formation. An explanation was proposed that the catalytic reaction of oxygen reduction proceeds on average via a 3.9-electron mechanism, which is verified experimentally by the rotating disc electrode method.

The problem of searching available catalysts for the oxygen electrode of fuel cells and metal-air batteries is one of the key issues in autonomous power systems developing. At present, platinum is known to be mainly used as a catalyst in the reaction of oxygen reduction. Besides their obvious scarcity and high cost, this material is easily poisoned by different impurities which make of power source term of life much shorter. Palladium may be a favored choice due to the almost similar catalytic properties with platinum where the mechanistic pathway of oxygen reduction is the same [1, 2]. Nevertheless, palladium has a lower price.

The aim of this paper is theoretical interpretation of experimental findings on oxygen reduction on palladium catalyst on the basis of quantum-chemical calculations. Quantum-chemical modelling of oxygen reduction on the Pd enables not only theoretical foundation for detailed mechanism of oxygen reduction, but also for increasing the efficiency of current-generating process.

## Research methodology

Oxygen reduction was studied in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution using the rotating disc electrode (RDE) method. Electrolyte were saturated with pure O<sub>2</sub> or deaerated with Ar gas. The silver/silver chloride reference electrode connected to the cell through a Luggin capillary was employed as a reference electrode. All potentials reported in this work are referred to the normal hydrogen electrode (NHE). A glassy carbon cell served as a counter electrode. The electrochemical investigations were done with VMP-3 potentiostat/galvanostat from Princeton Applied Research (UK). EM-04 rotator with speed control unit was used for the RDE experiments. All experiments were carried out at room temperature. The electrodeposition of palladium was carried out in deaerated 0.1 M H<sub>2</sub>SO<sub>4</sub> solution containing 0.1 mM PdCl<sub>2</sub>. Disk glassy carbon electrode was kept at 0.8 V during 5 minutes. During the deposition the electrode continuously rotated at 1000 rpm for faster mass transfer. After deposition the electrode was rinsed with water and transferred to another cell containing 0.1 M H<sub>2</sub>SO<sub>4</sub>. Electrode was kept at 0.1 V for 10 minutes in order to make full chloride desorption. Prior to the oxygen reduction studies the electrodes were electrochemically pretreated in Ar-saturated 0.1 M H<sub>2</sub>SO<sub>4</sub> by scanning the potential between 0.1 and 1.4 V. After this pretreatment the electrode was transferred into an oxygen-saturated electrolyte. The RDE measurements were carried out by scanning the potential between 1.0 and 0.1V at 20 mV/s with different electrode rotation rates.

*Ab initio* quantum-chemical calculations have been carried out for the electronic structures of molecular clusters and adsorption complexes to model physical and chemical adsorption of molecular oxygen on the surface of palladium catalyst. The quantum-chemical calculations were done using the Hartree-Fock-Roothan self-consistent field MO LCAO formalism in the 3–21 basis set of Gaussian functions.

## Results and Discussion

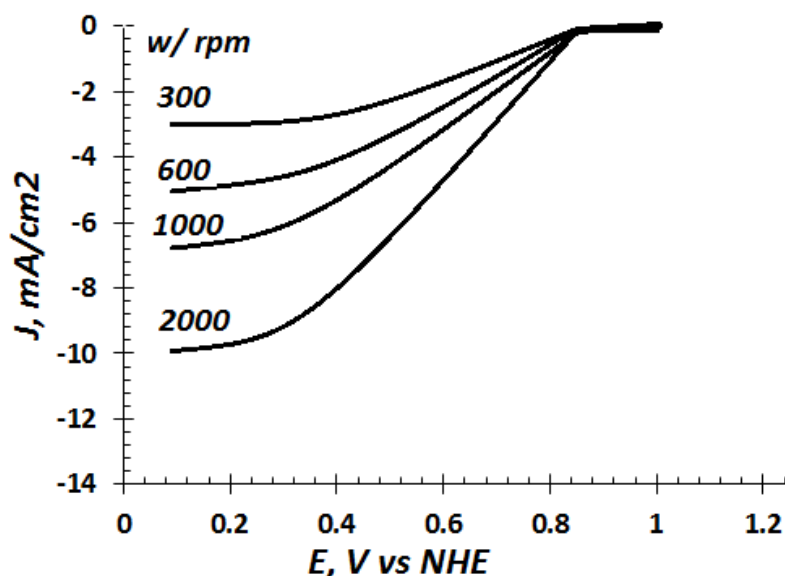
The electroreduction of oxygen on Pd electrodeposited on glass carbon electrodes was studied in oxygen saturated 0.1 M H<sub>2</sub>SO<sub>4</sub> using the RDE method. A polarisation curves of electrodeposited Pd is shown in Fig. 1.

The RDE data were analysed using the Koutecky—Levich equation:

$$\frac{1}{i} = \frac{1}{i_k} + \left( \frac{1}{0.620nFAD^{2/3}\nu^{-1/6}C} \right) \omega^{-1/2}$$

where  $i$  is the measured current density,  $j_k$  is kinetic current densities,  $n$  is the number of electrons transferred per oxygen molecule,  $F$  is the

Faraday constant (96,500 C/mol),  $w$  is the electrode rotation rate,  $C$  is the concentration of oxygen in the bulk ( $1.2 \cdot 10^{-6}$  mol/cc),  $D$  is the diffusion coefficient of oxygen ( $1.9 \cdot 10^{-5}$  cm<sup>2</sup>/s),  $\nu$  is the kinematic viscosity of the solution (0.01 cm<sup>2</sup>/s) and  $A$  is the electrode surface. According to the Koutecky—Levich equation the number of electrons transferred per O<sub>2</sub> molecule was calculated. The value of  $n$  was close to 3.9. This indicates that some amount of H<sub>2</sub>O<sub>2</sub> is produced in such conditions.



**Figure 1.** RDE voltammetry curves for oxygen reduction in oxygen saturated 0.1 M H<sub>2</sub>SO<sub>4</sub> on Pd deposited catalyst on glassy carbon electrode at various electrode rotation rates. Voltammetry scan rate is 20 mV/cm<sup>2</sup>

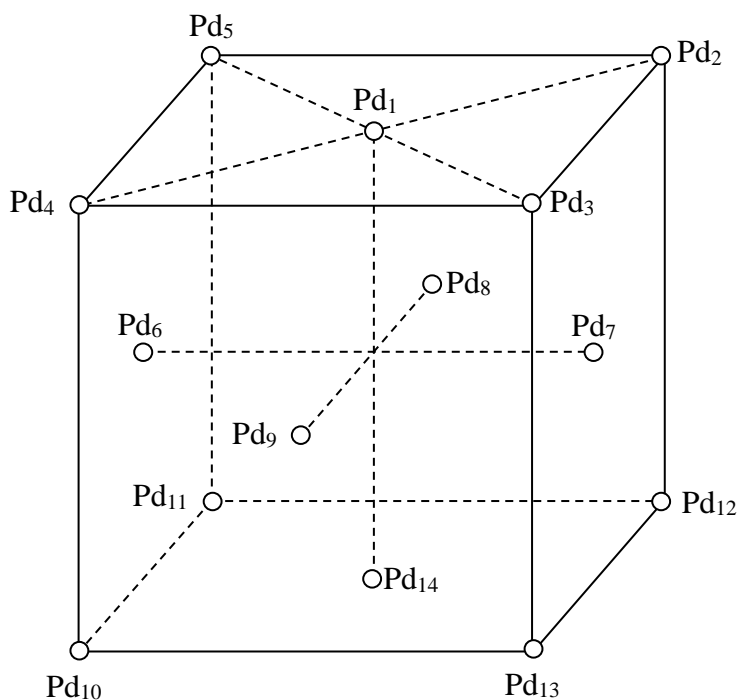
The  $n$  value smaller than 4 may be attributed to partial two-electron reduction of oxygen on glassy carbon. Also, this effect may be caused by decreased activity of hydrogen peroxide reduction on Pd in sulphuric acid solution.

The further theoretical interpretation of experimental findings on oxygen reduction on palladium catalyst carried out on the basis of quantum-chemical calculations.

Quantum-chemical calculations of electronic structures of the corresponding molecular clusters and Pd<sub>14</sub> AC adsorption complexes: Pd<sub>14</sub>-O<sub>2</sub>, Pd<sub>14</sub>-O<sub>2</sub>H, Pd<sub>14</sub>-H<sub>2</sub>O<sub>2</sub>, Pd<sub>14</sub>-H<sub>2</sub>O<sub>2</sub>H of two-centre bridge adsorption of molecular oxygen were carried out using the Hartree-Fock-Roothan self-consistent field MO LCAO formalism in the 3-21G basis set of Gaussian functions by the program [3]. The Pd<sub>1</sub>, Pd<sub>2</sub>, Pd<sub>3</sub>, Pd<sub>4</sub>, Pd<sub>5</sub> cations from (001) area were chosen as adsorption centers (Z<sub>i</sub>) (Fig. 2).

The accuracy of optimization of geometrical parameters was determined by a maximum value of 10<sup>-5</sup> Hartree/Bohr of energy

derivative with respect to Cartesian coordinates, whereas the energy was calculated with an accuracy of  $10^{-5}$  atomic units of energy.



**Figure 2.** A simplified model of the Pd<sub>14</sub> molecular cluster

The adsorption bond energy ( $\Delta E_{adb}$ ) was calculated as a difference between the total energy of adsorption complex ( $E_{ac}$ ) and the sum of the cluster energy ( $E_{cl}$ ) and adsorbate energy ( $E_{ad}$ ):

$$\Delta E_{adb} = E_{ac} - (E_{cl} + E_{ad}).$$

The transition metal atoms on the surface can have both donor and acceptor properties. The oxygen ions on the surface of oxides can also donate electron density. In the process of adsorption through the donor-acceptor mechanism, the adsorbed molecules enter the first coordination sphere of the adsorption centre, which causes an increase in coordination number. The increase in the coordination number of adsorption centre can lead to deformation of its coordination sphere and shift of atoms. The catalytic oxygen reduction on the surface of Pd catalysts proceeds through three stages: oxygen chemisorptions (Table 1.), hydrogen peroxide formation and water formation (Tables 2 and 3). Thus, the hydrogen peroxide molecule may be form on the surface of catalyst as a result of step-by-step addition of 2 protons and 2 electrons to the chemisorbed oxygen molecule.

In appropriate adsorption complexes  $O_2$  and  $H_2O_2$  adsorbates receive excessive negative electrical charges by partial replacement of the electron density from adsorbate to the surface (Table 1.).

**Table 1.** Charges on the atoms of Pd<sub>14</sub> clusters and their adsorption complexes

Atoms	Pd <sub>14</sub>	Pd <sub>14</sub> -O <sub>2</sub>	Pd <sub>14</sub> -O <sub>2</sub> H <sup>-</sup>	Pd <sub>14</sub> -H <sub>2</sub> O <sub>2</sub>	Pd <sub>14</sub> -H <sub>2</sub> O <sub>2</sub> H <sup>-</sup>
Pd <sub>1</sub>	-0.229	-0.130	+0.830	-1.102	-0.419
Pd <sub>2</sub>	+0.171	-0.165	-0.328	-0.029	-0.088
Pd <sub>3</sub>	+0.171	+0.170	-0.116	+0.004	-0.197
Pd <sub>4</sub>	+0.171	+0.356	+0.196	+0.374	-0.105
Pd <sub>5</sub>	+0.171	+0.221	-0.086	+0.118	+0.276
Pd <sub>14</sub>	+0.171	+0.118	+0.261	+0.184	+0.045
O <sub>15</sub>	-	-0.241	-0.339	-0.218	-0.569
O <sub>16</sub>	-	-0.257	-0.305	-0.238	-0.461
Δ(O <sub>2</sub> )	-	-0.498	-0.644	-0.556	-1.030

**Table 2.** The lengths of internuclear bonds R(A-B), Å and their corresponding bond orders p(A-B) in the clusters: Pd<sub>14</sub>-O<sub>2</sub>, Pd<sub>14</sub>-O<sub>2</sub>H<sup>-</sup>, Pd<sub>14</sub>-H<sub>2</sub>O<sub>2</sub>, Pd<sub>14</sub>-H<sub>2</sub>O<sub>2</sub>H<sup>-</sup>

The cluster Pd <sub>14</sub> -O <sub>2</sub>					
Bonds	R(A-B)	p(A-B)	Bonds	R(A-B)	p(A-B)
O <sub>15</sub> -O <sub>16</sub>	1.408	1.060	Pd <sub>3</sub> -O <sub>16</sub>	1.966	0.749
Pd <sub>1</sub> -O <sub>15</sub>	1.947	1.096	Pd <sub>2</sub> -O <sub>16</sub>	2.863	0.256
Pd <sub>3</sub> -O <sub>15</sub>	2.763	0.186	-	-	-
The cluster Pd <sub>14</sub> -O <sub>2</sub> H <sup>-</sup>					
Bonds	R(A-B)	p(A-B)	Bonds	R(A-B)	p(A-B)
O <sub>15</sub> -O <sub>16</sub>	1.506	0.883	Pd <sub>3</sub> -O <sub>16</sub>	2.650	0.443
Pd <sub>1</sub> -O <sub>15</sub>	2.037	0.800	Pd <sub>2</sub> -O <sub>16</sub>	2.677	0.329
Pd <sub>3</sub> -O <sub>15</sub>	3.076	0.144	Pd <sub>10</sub> -O <sub>15</sub>	4.602	0.095
The cluster Pd <sub>14</sub> -H <sub>2</sub> O <sub>2</sub>					
Bonds	R(A-B)	p(A-B)	Bonds	R(A-B)	p(A-B)
O <sub>15</sub> -O <sub>16</sub>	1.477	0.930	Pd <sub>3</sub> -O <sub>16</sub>	2.752	0.317
Pd <sub>1</sub> -O <sub>15</sub>	3.064	0.387	Pd <sub>5</sub> -H <sub>18</sub>	2.204	0.147
Pd <sub>2</sub> -O <sub>15</sub>	3.653	0.100	Pd <sub>2</sub> -O <sub>16</sub>	2.752	0.210
The cluster Pd <sub>14</sub> -H <sub>2</sub> O <sub>2</sub> H <sup>-</sup>					
Bonds	R(A-B)	p(A-B)	Bonds	R(A-B)	p(A-B)
O <sub>15</sub> -O <sub>16</sub>	2.700	-	O <sub>15</sub> -H <sub>17</sub>	1.762	0.060
Pd <sub>2</sub> -O <sub>15</sub>	2.751	0.110	O <sub>16</sub> -H <sub>17</sub>	0.961	0.787
Pd <sub>3</sub> -O <sub>16</sub>	2.754	0.301	O <sub>16</sub> -H <sub>19</sub>	0.941	0.906

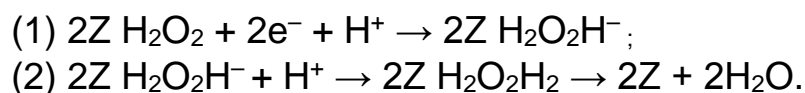
**Table 3.** Calculated adsorption bond energies in the following clusters: Pd<sub>14</sub>-O<sub>2</sub>, Pd<sub>14</sub>-O<sub>2</sub>H<sup>-</sup>, Pd<sub>14</sub>-H<sub>2</sub>O<sub>2</sub>, Pd<sub>14</sub>-H<sub>2</sub>O<sub>2</sub>H<sup>-</sup>

Adsorbate	O <sub>2</sub>	O <sub>2</sub> H <sup>-</sup>	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub> H <sup>-</sup>
ΔE <sub>adb</sub> , kJ/mole	-314.00	-417.44	-102.65	-501.15

Thus, in the adsorption complexes, due to interaction between the O<sub>2</sub>, O<sub>2</sub>H<sup>-</sup>, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>H<sup>-</sup>, 2H<sub>2</sub>O adsorbates and the cluster, the effective charges on the atoms and internuclear distances change, and redistribution of electron density occurs between the bonds and force centers (Tables 1, 2). A free oxygen molecule is a biradical, where two electrons with parallel spins occupy two antibonding degenerate highest occupied molecular orbitals (HOMO). The ground state of a free oxygen molecule is triplet. In the adsorbed oxygen molecule the degeneration is cancelled out under the influence of an electric field generated by the Pd cations. From the two half-filled HOMOs there are formed two frontier MOs of different energy: one lowest unoccupied (LUMO) and one HOMO, which is occupied by two electrons with paired spins. Owing to chemisorption the oxygen molecule takes a singlet state.

According to Table 2 in the Pd-O<sub>2</sub> adsorption complex the multi-coordination bond is formed between the unoccupied atomic orbital d<sub>x<sup>2</sup>-y<sup>2</sup></sub>-AO of the metal and the orbital of unshared pair of the adsorbed oxygen. In forming the σ-bond, the electron density shifts from the AO of adsorbed oxygen to the unoccupied d<sub>x<sup>2</sup>-y<sup>2</sup></sub>-AO of the metal. The occupied d<sub>xy</sub>-AO of the metal and the two-centre 2π\*-MO of adsorbed oxygen overlap forming a common 3-centre π-MO of the complex. The d-electron density, shifted from the surface as a result of reverse dative dπ-2pπ\* interaction, partially distributes in the unoccupied anti-bonding 2pπ-MO\* of the adsorbed oxygen molecule. The increase in electron population in the 2pπ-MO\* of the adsorbed oxygen molecule causes its transition to excited reactive state.

Depending on the value of energy of the adsorption bond between the cluster and hydrogen peroxide, ΔE<sub>adb</sub>, there are two possible ways for the reaction to continue: at lower ΔE<sub>adb</sub> values the peroxide molecule desorbs, and oxygen reduction proceeds via the two-electron mechanism to make peroxide; at higher ΔE<sub>adb</sub> values oxygen reduction proceeds via the 4-electron mechanism by the following reactions:



The higher the energy of bonding between the hydrogen peroxide and catalyst, the more likely the reactions are to occur in this way.

The second stage of the reaction is characterized by increased energy absorption (Table 3) resulting from the inclusion of two electrons to the adsorption complex. In formed H<sub>2</sub>O<sub>2</sub> molecule by the reaction 2ZO<sub>2</sub>H<sup>-</sup> + H<sup>+</sup> → 2ZH<sub>2</sub>O<sub>2</sub> under the influence of the electric field of the

addition proton the redistribution of electron density takes place. Thus intramolecular bond O<sub>15</sub>-O<sub>16</sub> becomes stabilized and the relationship between formed H<sub>2</sub>O<sub>2</sub> molecule and the cluster destabilizes greatly (Tables 2, 3).

### **Conclusions**

The electroreduction of oxygen on electrodeposited palladium on glassy carbon electrodes has been studied in acid solutions. Stable adsorption complexes of oxygen atoms and its compounds can form on the surface of palladium. In these complexes redistribution of electron density between the force centers and deformation of the catalyst surface occurs under the influence of adsorbates. Activation of the chemisorbed oxygen molecule is mainly due to a shift of electron density from the catalyst surface to the oxygen molecule. The adsorption energy of hydrogen peroxide influences the mechanism of oxygen reduction: at lower values of this energy oxygen is reduced via the 2-electron mechanism, which is followed by desorption of the newly formed molecule. At higher values oxygen reduction occurs via the 4-electron mechanism to form water. Thus, on average it may correspond to an effective value of  $n \sim 3.9$  on the surface of electrodeposited palladium on glassy carbon electrodes.

### **Acknowledgement**

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### **References**

- [1] M. Shao. Palladium-based electrocatalysts for hydrogen oxidation and oxygen reduction reactions/ M. Shao., E. Antolini// Journal of Power Sources., V.196. P2433, 2011.
- [2] L.M. Vracar. Palladium electrode in oxygen-saturated aqueous-solutions - reduction of oxygen in the activation-controlled region/ L.M. Vracar, D.B. Sepa, A. Damjanovic// Journal of the Electrochemical Society., V.133, P.1835, 1986.
- [3] <http://clssic.chem.msu.su./gran/gamess/index.html>