

Oxygen reduction on single crystal platinum electrodes in phosphoric acid solutions

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Oxygen reduction reaction has been studied on Pt low index planes in 0.1 M and 85% H₃PO₄ using hanging meniscus rotating disc electrode technique. The first-order kinetics of O₂ reduction reaction was found for all three surfaces in a four-electron process with the first electron transfer rate determining in both 0.1 M and 85% H₂PO₄ solutions. Catalytic activity for O₂ reduction follows the sequence Pt (110)>Pt (100)>Pt (111). Structural dependence is predominantly determined by the adsorption of phosphoric acid anions, which is strongly structure-dependent on Pt surfaces.

Key words: oxygen reduction, Pt low-index single crystal, H₃PO₄, hanging meniscus rotating disc electrode, current-potential curves, Tafel plots.

Oxygen reduction reaction is one of the most important electrocatalytic reactions. Different electrode materials and electrolyte have been tested from kinetic as well as thermodynamic point of view,¹ but only a few recent papers deal with a structural dependence of this reaction on platinum single crystal surfaces.²⁻⁸ This is partly caused by difficulties in preparing clean rotating Pt single crystal electrodes, necessary for a reliable study of oxygen reduction. Until recently, single crystal studies in electrochemical systems have been mostly focused on adsorption phenomena and reaction of organic molecules.⁹ A recent review of oxygen electroreduction by Adžić¹⁰ addresses also some aspects of the reaction on single crystal surfaces.

Hanging meniscus rotating disc electrode technique introduced by Cahan and Villullas¹¹ provides one way to study oxygen reduction on single crystal planes under mass transfer control similar to that with standard rotating disk electrode. Single crystal planes can be prepared by hydrogen flame annealing method, which provides clean and well-oriented surface.¹² Most recently Marković *et al.*^{7,8} reported a study involving rotating disk-ring electrode with a platinum single crystal disk, which does not have some limitations of the hanging meniscus rotating disk electrode.

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Phosphoric acid is one of the most suitable electrolytes for the fuel cell applications. Consequently, oxygen reduction in concentrated phosphoric acid has been often studied on polycrystalline smooth platinum,^{13,14} but also on high surface area^{15–17} and on supported platinum electrodes.¹⁸ Studies using rotating ring-disc method^{13,14} have shown that in 85% H₃PO₄ the parallel mechanism of O₂ reduction takes place, with the dominant four-electron reaction path.

The aim of this study is to gain the information on O₂ reduction on Pt low index single-crystal planes in both 85% and diluted H₃PO₄ solution. An attempt is also made to examine the structural dependence of O₂ reduction, as it already has been found in 0.1 M HClO₄,⁴ 0.05 M H₂SO₄⁷ and 0.1 M KOH⁸ solution, which is at variance with the early results by Ross.²

EXPERIMENTAL

Cylindrical Pt single crystals were obtained from Metal Crystals Ltd. (Cambridge, UK). Surface preparation involved polishing with diamond paste (the last polishing with a 1 μm grade) and annealing in hydrogen flame. After cooling in hydrogen gas, the electrode surface was protected with a drop of ultra pure water.¹² The crystals were mounted in a Kel-F collet holder, designed to fit a Pine rotator (Pine Instrument Co.). H₃PO₄ was from Baker Ultrex. Platinum wire served as the counter electrode and reversible hydrogen in the same solution served as the reference. Measurements were done at room temperature. Electrode surface area of Pt (111), Pt (100) and Pt (110) were 0.358 cm², 0.332 cm² and 0.327 cm², respectively.

RESULTS AND DISCUSSION

Figure 1 shows voltammetry curve of Pt (111) surface in 85% H₃PO₄. A pair of sharp peaks appears at the potential $\approx 0.3 V_{RHE}$, with practically no separation in anodic and cathodic sweep directions. Similar observation has been observed for the Pt (111) face in concentrated H₂SO₄ solution, and it has been concluded that the peak in both cases is caused by anion adsorption and ordering of the adsorbed anions.¹⁹ Voltammetry curve for Pt (111) in diluted, 0.1 M H₃PO₄, solutions (Fig. 1, inset) has a shape indicative of a well oriented Pt (111) surface. It should be mentioned that from voltammetry curves for Pt (111) in the electrolyte which contained 0.1 M HClO₄ and different amount of H₃PO₄ ($4.0 \times 10^{-6} M - 1.5 \times 10^{-3} M$) the electroadsorption valence of H₂PO₄⁻, $\gamma_{H_2PO_4^-} \approx -1$, has been obtained.¹⁹

A particularly interesting appears the behavior of Pt (111) in 85% H₃PO₄ in the potential region where in other electrolyte solutions a monolayer of Pt oxide is formed, *viz.* $0.8 - 1.2 V_{RHE}$. A negligible oxidation current is observed up to $1.2 V_{RHE}$ is not reported before. This is a consequence of a strong adsorption of anions which effectively blocks the Pt (111) surface, since both the anion and the surface have the same three-fold symmetry. In addition to anion adsorption, a low activity of H₂O in this solution limits the oxidation at very positive potentials in Fig. 1. This behavior has a consequence on the O₂ reduction, as will be discussed below.

Figure 2 gives current – potential curves (cathodic direction) for O₂ reduction on Pt (*hkl*) in 85% H₃PO₄ at the rotation rate of 1600 rpm. A complete set of data has been recorded in the rotation range from 125 – 1600 rpm. The curve for Pt (111)

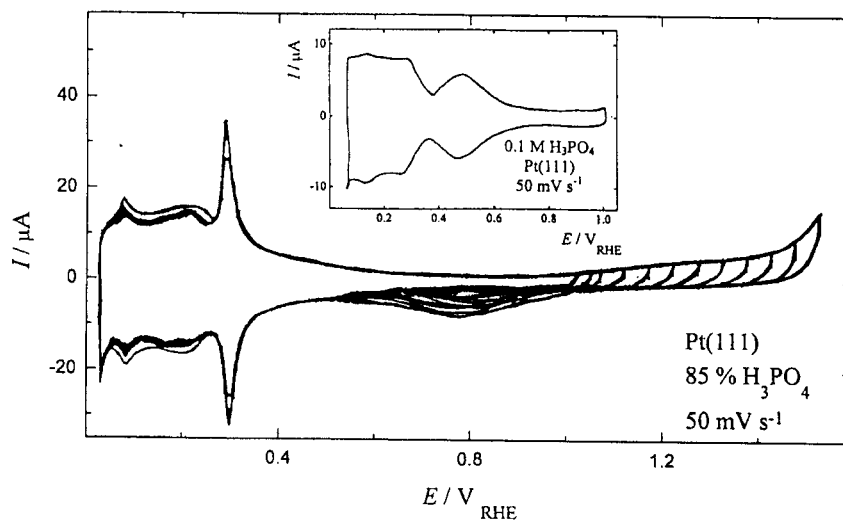


Fig. 1. Voltammetry curves of Pt(111) in 85% H_3PO_4 . Inset: Voltammetry curve of the same surface in 0.1 M H_3PO_4 . Sweep rate: 50 mV s^{-1} .

at potentials more negative than 0.4 V (beyond the limiting current of oxygen reduction) appears to be a sum of the O_2 reduction current and that of H_2 adsorption (*cf.* Fig. 1). It is also seen that the limiting current region is defined better for (110) and (100) faces, than for the (111) plane. This difference could be caused by the intensive oxygen transport through the thin film of electrolyte towards the edge of

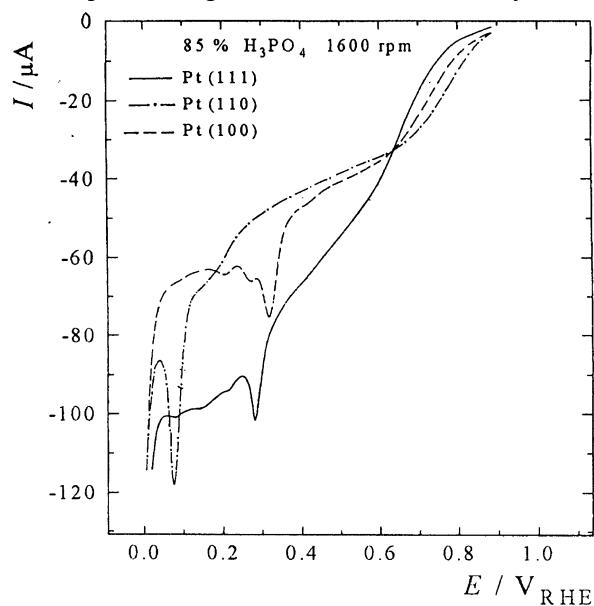


Fig. 2. Current – potential curves for oxygen reduction on low-index Pt planes in 85% H_3PO_4 at 1600 rpm. Sweep rate: 50 mV s^{-1} .

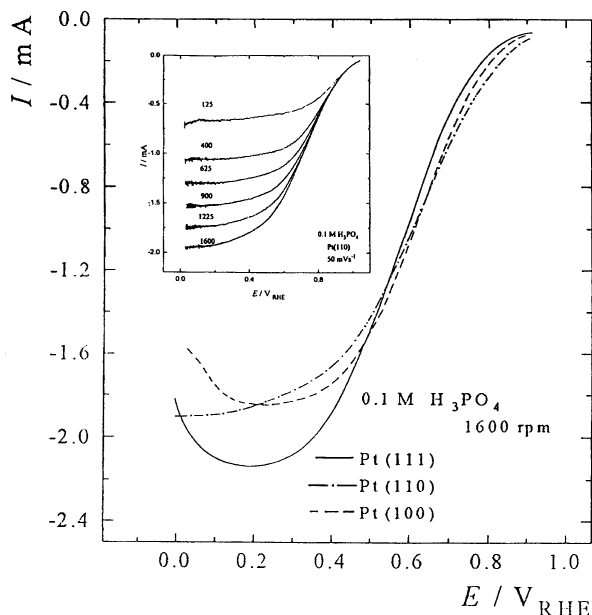


Fig. 3. Current – potential curves for oxygen reduction on low-index Pt planes in 0.1 M H_3PO_4 at 1600 rpm. Inset: Current – potential curves for oxygen reduction on Pt(110) plane at specified rotation rate (rpm). Sweep rate: 50 $mV s^{-1}$.

the electrode influenced by surface tension at three phase interface, which should be dependent on the Pt surface orientation. This effect is less pronounced in 0.1 M H_3PO_4 , as it is seen in Fig. 3 – inset, where current–potential curves of oxygen reduction on Pt (110) are given for different rotation rates. The well-defined diffusion limiting current plateau was registered in the whole range of rotation rates.

Figure 3 shows current – potential curves of O_2 reduction on Pt (hkl) in 0.1 M H_3PO_4 (cathodic scan) at 1600 rpm. The diffusion limiting currents have different values (the same in 85% H_3PO_4 – Fig. 2) simply because of the different surface areas. The different behaviour of the Pt (hkl) faces in both 0.1 M and 85% H_3PO_4 in the kinetic and mixed kinetic–diffusion control regions, implies a structural dependence of oxygen reduction reaction. In the potential region more negative than 0.1 V_{RHE} , there is a decrease of limiting diffusion currents for Pt(111) and Pt(100), while such a decrease is not seen for Pt(110). Similar observations were made for Pt (hkl) in $HClO_4$ ⁴ and H_2SO_4 .⁷ Rotating ring – Pt (hkl) disc experiments in H_2SO_4 reported by Marković *et al.*⁷ showed that this decrease in the hydrogen adsorption region coincides with the appearance H_2O_2 as a reduction product. This implies a change in the mechanism of oxygen reduction reaction from the direct four-electron to "parallel" or "peroxide" pathways. The state of underpotential deposited (adsorbed) hydrogen is different on different Pt planes.²⁰ Sites for hydrogen adsorption on Pt (110) plane are below the top rows of Pt atoms and main amount of adsorbed hydrogen is below the surface, while the surface of Pt (111) and (100) planes are

fully covered by hydrogen. The effect of adsorbed hydrogen on oxygen reduction is more pronounced on (111) and (100) faces than on Pt (110).

With the assumption that oxygen reduction is first-order reaction, the analysis of the data in mixed diffusion–kinetic control regions for the two H_3PO_4 solutions was carried out by using Levich-Koutecky equation, which has been already applied in the case of a hanging meniscus rotating disc electrode.⁴ According to this equation one has

$$I^{-1} = I_k^{-1} + B^{-1} \omega^{-1/2} \quad (1)$$

where I_k denotes kinetic current, B is Levich constant and ω is rotation speed in rpm. Levich constant is given by:

$$B = 0.621 \left(\frac{2\pi}{60} \right)^{1/2} nFAcD^{2/3} \nu^{-1/6} \quad (2)$$

in which n is the number of electrons exchanged per O_2 molecule, F – Farady constant, A is electrode surface area, c is bulk concentration (solubility) and D diffusion coefficient of oxygen, while ν is kinematic viscosity of the electrolyte.

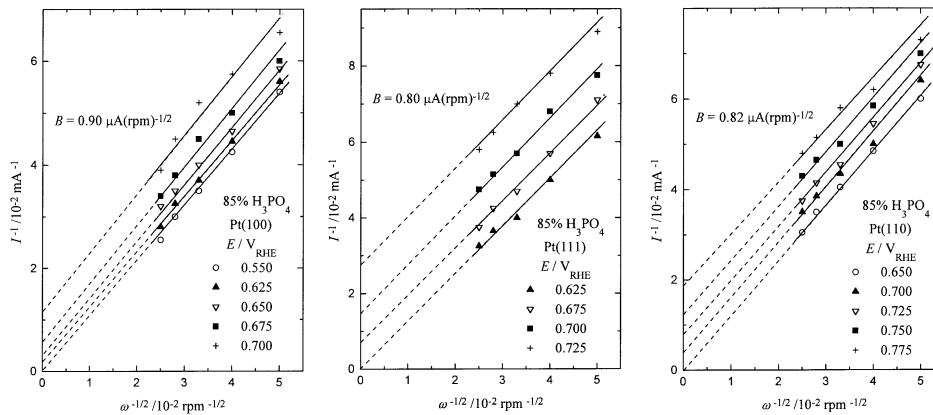


Fig. 4. $I^{-1} - \omega^{-1/2}$ plots for oxygen reduction on Pt (hkl) planes in 85% H_3PO_4 at indicated potentials obtained from current – potential curves.

Figure 4 and 5 give $I^{-1} - \omega^{-1/2}$ dependences obtained from polarization curves for oxygen reduction on Pt (hkl) surfaces in 85% and 0.1 M H_3PO_4 solutions, respectively. Fairly well parallel straight lines indicate first-order kinetics with respect to O_2 molecule. Taking the literature data for $c = 2.87 \times 10^{-7} \text{ mol cm}^{-3}$, $D = 7.61 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, $\nu = 0.23 \text{ cm}^2 \text{ s}^{-1}$ used by O'Grady *et al.*¹⁴ in the analysis of O_2 reduction in 85% H_3PO_4 , and assuming $n = 4$, the calculated values of B in $\mu\text{A}(\text{rpm})^{-1/2}$, are 0.87, 0.81 and 0.80, for the (111), (100) and (110) orientations, respectively. Experimental and calculated values are in fairly good agreement, so

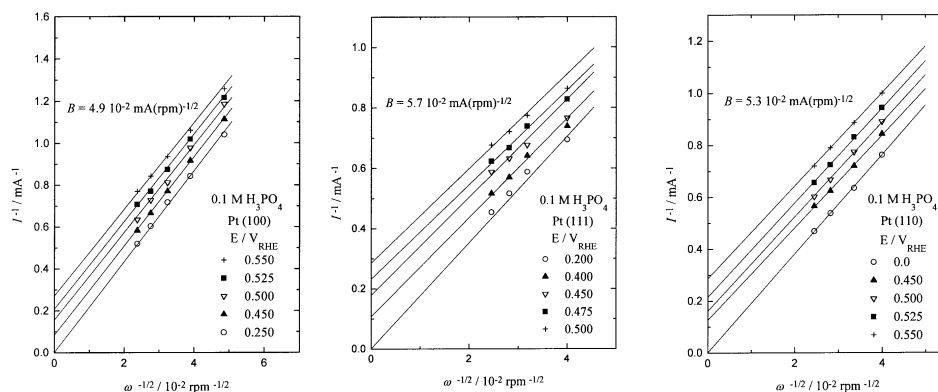


Fig. 5. $I^{-1} - \omega^{-1/2}$ plots for oxygen reduction on Pt(*hkl*) planes in 0.1 M H_3PO_4 at indicated potentials obtained from current – potential curves.

one could conclude that oxygen reduction in 85% H_3PO_4 proceeds dominantly *via* a four-electron pathway on all three Pt low - index faces. The same conclusion holds for 0.1 M H_3PO_4 . The values of $B \cdot 10^2$, $\text{mA}(\text{rpm})^{-1/2}$, calculated assuming that the solubility and viscosity data for 0.1 M HClO_4 are close to these for 0.1 M H_3PO_4 and $n = 4$, are 4.6, 4.2 and 4.3 for the (111), (110) and (100) faces, respectively. Experimentally obtained B values are larger than calculated (Eq. (2)). If n value is calculated from experimental B values (Eq. (2)), one obtains $n > 4$, which has no physical sense in oxygen reduction reaction.

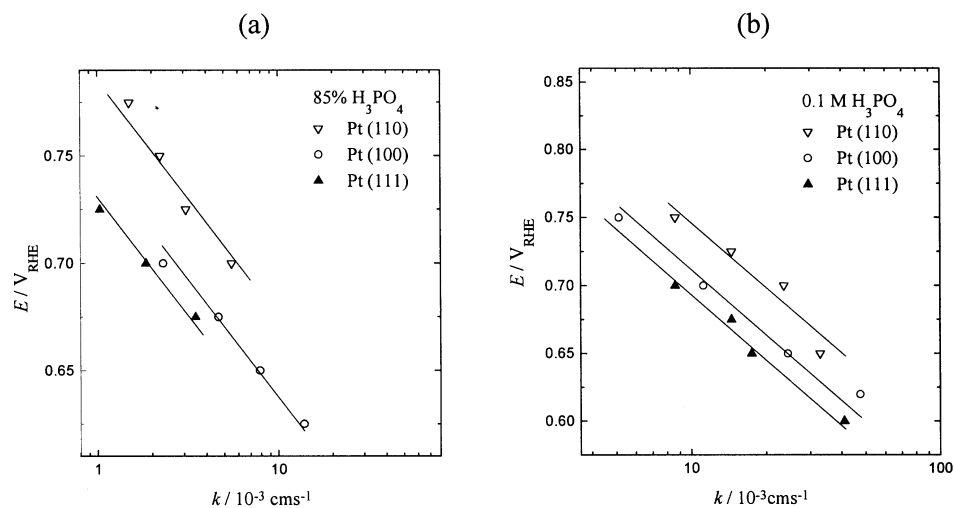


Fig. 6. Potential dependence of the rate constants for oxygen reduction dependencies in 85% H_3PO_4 , a), and 0.1 M H_3PO_4 b), calculated from kinetics currents obtained from $I^{-1} - \omega^{-1/2}$ plots.

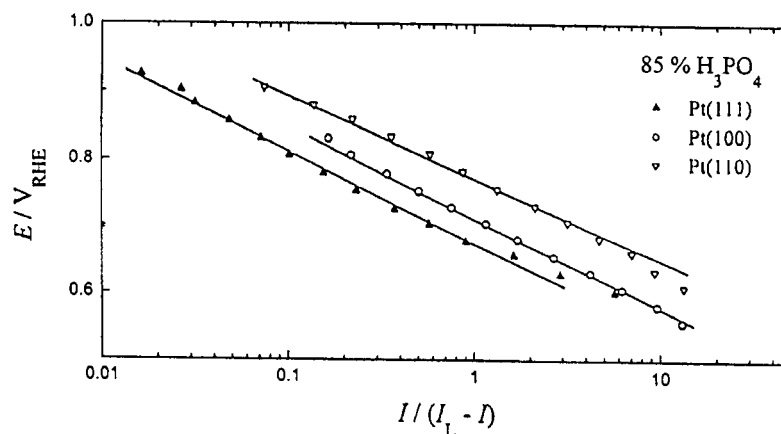


Fig. 7. Tafel plots for oxygen reduction on Pt(*hkl*) in 85% H₃PO₄ obtained from current–potential curves at 1600 rpm.

From the intercepts in Figs. 4 and 5 the first-order rate constant ($k = I_k/AnFc$) for oxygen reduction reaction are calculated and plotted in Fig. 6. The slopes of the plots for both solutions and all three faces are close to -120 mV. The same slope is seen for Tafel plots – Figs. 7 and 8, obtained from the data in Figs. 2 and 3. Structural dependence of the oxygen reduction rate is obvious. The most active plane is (110) and the smallest activity is seen for (111) plane. The slope of Tafel plots at more positive potential region for Pt (100) and Pt (110) in 0.1 M H₃PO₄ is close to -60 mV. This change of slope is certainly related to the existence of oxygen containing species, usually denoted as PtOH, in this potential range.²¹ The effect of PtOH on oxygen adsorption means that H₃PO₄ adsorption does not prevent PtOH formation on these two surfaces, contrary to the Pt (111) surface. H₃PO₄ adsorption on Pt (111) is strong, stronger than adsorption of H₂SO₄ or HClO₄.¹⁹ The existence of oxygen containing species on Pt(*hkl*) in concentrated H₃PO₄ is not easy to prove in the whole potential region of oxygen reduction, as can be seen for Pt (111) in Fig. 1.

The change of Tafel slope usually means the change in reaction mechanism, but for oxygen electroreduction it is known that first-electron transfer is rate-determining step in both low and high current density region.¹⁰ Damjanović and Genshaw ascribed the slope change to the change from Temkin conditions for reaction intermediates in the PtOH region (low current density region) to Langmuirian behaviour at less positive potentials, where the coverage of adsorbed oxygen species becomes negligible.²² A different explanation of the change of slope was offered by Tarasevich, who suggested that adsorbed oxygen species cause a decrease of O₂ adsorption and that the change of the coverage affects the adsorption of oxygen molecule on platinum.^{23,24} The same view was expressed by Adzic²⁵ and Uribe *et al.*²⁶ According to this opinion, PtOH formation is not due to the interaction of O₂ with Pt, but rather from the reaction of H₂O with Pt, which causes inhibition of O₂ reduction. In this situation it should be expected that there is no slope change on

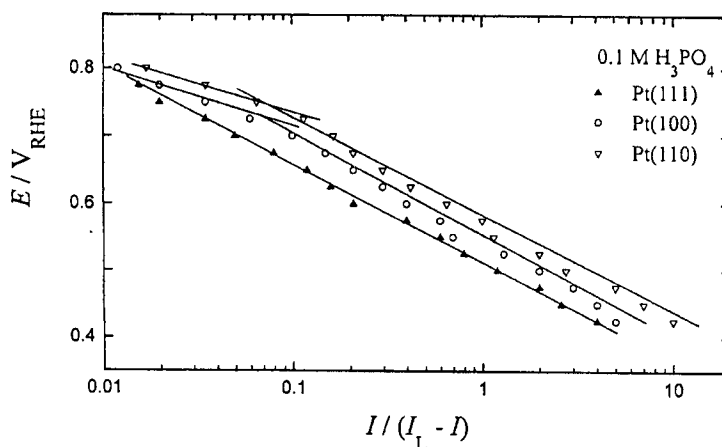


Fig. 8. Tafel plots for oxygen reduction on Pt(*hkl*) in 0.1 M H₃PO₄ obtained from current–potential curves at 1600 rpm.

Pt(111) surface when tetrahedral anions, such as sulfates⁷ or phosphates, are adsorbed. Other two low-index faces of Pt do not adsorb those anions and the formation of PtOH is not prevented at potentials 0.7–0.8 V_{RHE} so that O₂ reduction reaction is inhibited by them. The adsorption of PtOH follows the Temkin isotherm which causes such an effect on the reduction kinetics.

Considering kinetic and mixed kinetic – diffusion control region, it can be concluded that O₂ reduction reaction is first order with respect to dissolved oxygen, which proceeds dominantly in a four-electron reaction pathway with a first electron transfer as rate determining step. This is valid for all three planes in both concentrated and diluted H₃PO₄ solutions. The structural sensitivity of reaction does not affect these reaction parameters, except the half-wave potentials. This type of structural sensitivity could be considered similar to the one observed for the activity of Pt(*hkl*) for oxygen adsorption from the gas phase, as discussed by Marković *et al.* for O₂ reduction on Pt(*hkl*) in 0.1 M HClO₄.⁴ They concluded that the activity for O₂ reduction follows the order (110) > (111) > (100), which is also the order of activity for oxygen adsorption from gas phase, although the aqueous media in the case of O₂ electroreduction can make the conditions for O₂ adsorption quite different in comparison with gas phase. Yeager and coworkers suggest dissociative adsorption of O₂ as rate-determining step in O₂ reduction.^{27,28} The high activity of Pt(110) plane is due to the lower activation energy for dissociative O₂ adsorption, which is connected with stronger interaction of O₂ and the surface.

The order of activity in H₃PO₄, both 85% and 0.1 M, Figs. 6–8, is (110) > (100) > (111). This differs from the sequence found in the case of HClO₄ solution,⁴ but is the same as that one found in H₂SO₄ solution.⁷ The most active plane in all mentioned electrolytes is the (110) plane while the lowest activity in H₂SO₄⁷ and H₃PO₄ is found for the (111) surface. The activity of Pt (*hkl*) is higher in HClO₄⁴ than in H₂SO₄⁷ and H₃PO₄. This implies that adsorption of acid anions, which

proceeds with different intensity,^{19,29} should be responsible for the activity of Pt (*hkl*) for O₂ reduction in those electrolytes.

The adsorption of H₃PO₄ anion appears structure sensitive, which is probably similar to the structure sensitivity of the adsorption of H₂SO₄ anion considering their common tetrahedral structure.^{7,20} Adsorption of sulfuric or phosphoric acid anions on Pt (111) surface through three equivalent oxygen atoms is stronger than on other two low-index planes, where one or two oxygen atoms are involved in bonding to the surface. This difference in bonding (and coverage) leads to the corresponding variation in catalytic activity for O₂ reduction. Adsorption of phosphoric acid anion probably inhibits oxygen reduction by blocking initial adsorption of O₂ molecule, but does not affect the reaction pathway in the kinetic control region.

CONCLUSION

On the basis of the above results and data analysis one can conclude that the oxygen reduction on Pt(*hkl*) surfaces in 85% and 0.1 M H₃PO₄ follows the first-order kinetics, which proceeds similar as found for polycrystalline platinum^{13,14} *via* four-electron pathway with a first electron transfer as rate-determining step. The reaction exhibits a considerable structural sensitivity. The sequence in the activity is (110) > (100) > (111). This sensitivity is probably caused by structure sensitive phosphoric anion adsorption. In the region of hydrogen adsorption on (111) and (100) in 0.1 M H₃PO₄, oxygen reduction proceeds *via* two-electron pathway due to the effect of underpotential deposited hydrogen. Similar conclusions have been made for oxygen reduction in 0.05 M H₂SO₄ on the basis of the results obtained with rotating ring-Pt(*hkl*) disc.⁷ In the region of positive potentials, Tafel slopes for O₂ reduction reaction on Pt (110) and (100) surfaces in 0.1 M H₃PO₄ are close to -60 mV, which is caused by inhibitory effect of PtOH. In the more negative region slope for these two planes is close to -120 mV. This change of slope is not observed in the absence of PtOH formation, as observed with Pt(111) in both 0.1 M and 85% H₃PO₄.

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ИЗВОД

РЕДУКЦИЈА КИСЕОНИКА НА МОНОКРИСТАЛНИМ ПЛАТИНСКИМ ЕЛЕКТРОДАМА
У РАСТВОРИМА ФОСФОРНЕ КИСЕЛИНЕА. ТАНАКА,¹ Р. АЦИЋ^{2*} и Б. НИКОЛИЋ³¹ *University of Sao Paulo, Caixa Postal 780-CEP 13560-970, Sao Carlos, Brasil,*² *ИХТМ - Центар за електрохемију и Центар за мултидисциплинарне науке, Универзитет у Београду, Београд, Јужославија и*³ *Технолошко-металуришки факултет, Универзитет у Београду, б.бр. 3503, 1120 Београд, Јужославија*

Испитивана је реакција редукције кисеоника на нискоиндексним монокристалима платине у 85% и 0.1 М раствору H_3PO_4 техником ротирајућег мениска. Утврђено је да је у оба раствора реакција првог реда и да се одиграва 4-електронским путем у коме је пренос првог електрона спори ступањ. Каталитичка активност за редукцију кисеоника следи низ $Pt(110) > Pt(100) > Pt(111)$. Структурна зависност активности доминантно је одређена структурно зависном адсорпцијом анјона фосфорне киселине на $Pt(hkl)$ равнинама.

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