Oxygen reduction on single crystal platinum electrodes in phosphoric acid solutions

A. TANAKA,1 R. ADŽIĆ2* and B. NIKOLIĆ3

1University of Sao Paulo, Caixa Postal 780-CEP 13560-970, Sao Carlos, Brasil,
2ICTM-Center for Electrochemistry and Center for Multidisciplinary Studies, University of Belgrade, Belgrade, Yugoslavia and 3Faculty of Technology and Metallurgy, University of Belgrade, P.O.Box 3503, YU-11120 Belgrade, Yugoslavia

(Received 18 June 1999)

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% H₃PO₄ 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.2–6 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 electro-reduction by Adžić10 addresses also some aspects of the reaction on single crystal surfaces.

Hanging meniscus rotating disc electrode technique introduced by Cahan and Villellas11 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 dislocation electrode with a platinum single crystal disk, which does not have some limitations of the hanging meniscus rotating disk electrode.

* Present address: Brookhaven National Laboratory, Upton NY 11973, USA
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, but also on high surface area and on supported platinum electrodes. Studies using rotating ring-disc method have shown that in 85% H$_3$PO$_4$ the parallel mechanism of O$_2$ reduction takes place, with the dominant four-electron reaction path.

The aim of this study is to gain the information on O$_2$ reduction on Pt low index single-crystal planes in both 85% and diluted H$_3$PO$_4$ solution. An attempt is also made to examine the structural dependence of O$_2$ reduction, as it already has been found in 0.1 M HClO$_4$, 0.05 M H$_2$SO$_4$, and 0.1 M KOH solution, which is at variance with the early results by Ross.

**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 pure water. The crystals were mounted in a Kel-F collet holder, designed to fit a Pine rotator (Pine Instrument Co.). H$_3$PO$_4$ 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 cm$^2$, 0.332 cm$^2$ and 0.327 cm$^2$, respectively.

**RESULTS AND DISCUSSION**

Figure 1 shows voltammetry curve of Pt (111) surface in 85% H$_3$PO$_4$. 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 H$_2$SO$_4$ solution, and it has been concluded that the peak in both cases is caused by anion adsorption and ordering of the adsorbed anions. Voltammetry curve for Pt (111) in diluted, 0.1 M H$_3$PO$_4$, 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 HClO$_4$ and different amount of H$_3$PO$_4$ (4.0 x 10$^{-6}$ M – 1.5 x 10$^{-5}$ M) the electrosorption valence of H$_2$PO$_4^-$, $\gamma_{H_2PO_4^-}$ = -1, has been obtained.

A particularly interesting appears the behavior of Pt (111) in 85% H$_3$PO$_4$ 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 H$_2$O in this solution limits the oxidation at very positive potentials in Fig. 1. This behavior has a consequence on the O$_2$ reduction, as will be discussed below.

Figure 2 gives current–potential curves (cathodic direction) for O$_2$ reduction on Pt (hkl) in 85% H$_3$PO$_4$ 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% H₃PO₄. Inset: Voltammetry curve of the same surface in 0.1 M H₃PO₄. 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 O₂ reduction current and that of H₂ 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% H₃PO₄ at 1600 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 H₃PO₄, 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 O₂ reduction on Pt (hkl) in 0.1 M H₃PO₄ (cathodic scan) at 1600 rpm. The diffusion limiting currents have different values (the same in 85% H₃PO₄ – Fig. 2) simply because of the different surface areas. The different behaviour of the Pt (hkl) faces in both 0.1 M and 85% H₃PO₄ 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 HClO₄ and H₂SO₄. Rotating ring – Pt (hkl) disc experiments in H₂SO₄ reported by Marković et al. showed that this decrease in the hydrogen adsorption region coincides with the appearance H₂O₂ 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. 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 H₃PO₄ 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

\[ \Gamma' = \Gamma_k^{-1} + B^{-1} \omega^{-1/2} \]  

(1)

where \( \Gamma_k \) denotes kinetic current, \( B \) is Levich constant and \( \omega \) is rotation speed in rpm. Levich constant is given by:

\[ B = 0.62 \left( \frac{2\pi}{60} \right)^{1/2} nFAcD^{2/3} \nu^{-1/6} \]  

(2)

in which \( n \) is the number of electrons exchanged per O₂ molecule, \( F \) – Faraday constant, \( A \) is electrode surface area, \( c \) is bulk concentration (solubility) and \( D \) diffusion coefficient of oxygen, while \( \nu \) is kinematic viscosity of the electrolyte.

---

**Fig. 4. \( \Gamma' - \omega^{-1/2} \) plots for oxygen reduction on Pt (hkl) planes in 85% H₃PO₄ at indicated potentials obtained from current – potential curves.**

Figure 4 and 5 give \( \Gamma' - \omega^{-1/2} \) dependence is obtained from polarization curves for oxygen reduction on Pt (hkl) surfaces in 85% and 0.1 M H₃PO₄ solutions, respectively. Fairly well parallel straight lines indicate first-order kinetics with respect to O₂ 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 O₂ reduction in 85% H₃PO₄ 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(001) planes in 0.1 M H$_3$PO$_4$ at indicated potentials obtained from current-potential curves. One could conclude that oxygen reduction in 85% H$_3$PO$_4$ proceeds dominantly via a four-electron pathway on all three Pt low-index faces. The same conclusion holds for 0.1 M H$_3$PO$_4$. The values of $B \cdot 10^2$, mA(rpm)$^{-1/2}$, calculated assuming that the solubility and viscosity data for 0.1 M HClO$_4$ are close to those for 0.1 M H$_3$PO$_4$ 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.

(a) 

(b)

Fig. 6. Potential dependence of the rate constants for oxygen reduction dependencies in 85% H$_3$PO$_4$, a), and 0.1 M H$_3$PO$_4$ b), calculated from kinetics currents obtained from $I^1 - \omega^{1/2}$ plots.
From the intercepts in Figs. 4 and 5 the first-order rate constant \( k = I_q/AtnFe \) 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 \( \text{H}_3\text{PO}_4 \) 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 \( \text{H}_3\text{PO}_4 \) adsorption does not prevent PtOH formation on these two surfaces, contrary to the Pt (111) surface. \( \text{H}_3\text{PO}_4 \) adsorption on Pt (111) is strong, stronger than adsorption of \( \text{H}_2\text{SO}_4 \) or \( \text{HClO}_4 \).\(^{19}\) The existence of oxygen containing species on Pt(hkl) in concentrated \( \text{H}_3\text{PO}_4 \) 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 Genushaw 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 \( \text{O}_2 \) adsorption and that the change of the coverage affects the adsorption of oxygen molecule on platinum.\(^{23,24}\) The same view was expressed by Adzic\(^{25}\) and Uribe et al.\(^{26}\) According to this opinion, PtOH formation is not due to the interaction of \( \text{O}_2 \) with Pt, but rather from the reaction of \( \text{H}_2\text{O} \) with Pt, which causes inhibition of \( \text{O}_2 \) reduction. In this situation it should be expected that there is no slope change on
Pt(111) surface when tetrahedral anions, such as sulfates\(^7\) 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 \(O_2\) 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 \(O_2\) 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 \(\text{H}_3\text{PO}_4\) 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 \textit{et al.} for \(O_2\) reduction on Pt\((hkl)\) in 0.1 M \(\text{HClO}_4\).\(^4\) They concluded that the activity for \(O_2\) 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 \(O_2\) electroreduction can make the conditions for \(O_2\) adsorption quite different in comparison with gas phase. Yeager and coworkers suggest dissociative adsorption of \(O_2\) as rate-determining step in \(O_2\) reduction.\(^27,28\) The high activity of Pt\((110)\) plane is due to the lower activation energy for dissociative \(O_2\) adsorption, which is connected with stronger interaction of \(O_2\) and the surface.

The order of activity in \(\text{H}_3\text{PO}_4\), both 8.5% and 0.1 M, Figs. 6–8, is \((110) > (100) > (111)\). This differs from the sequence found in the case of \(\text{HClO}_4\) solution,\(^4\) but is the same as that one found in \(\text{H}_2\text{SO}_4\) solution.\(^7\) The most active plane in all mentioned electrolytes is the \((110)\) plane while the lowest activity in \(\text{H}_2\text{SO}_4\)\(^7\) and \(\text{H}_3\text{PO}_4\) is found for the \((111)\) surface. The activity of Pt \((hkl)\) is higher in \(\text{HClO}_4\)\(^4\) than in \(\text{H}_2\text{SO}_4\)\(^7\) and \(\text{H}_3\text{PO}_4\). This implies that adsorption of acid anions, which
proceeds with different intensity,\textsuperscript{19,29} should be responsible for the activity of Pt \((hkl)\) for \(O_2\) reduction in those electrolytes.

The adsorption of \(\text{H}_3\text{PO}_4\) anion appears structure sensitive, which is probably similar to the structure sensitivity of the adsorption of \(\text{H}_2\text{SO}_4\) anion considering their common tetrahedral structure.\textsuperscript{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 \(O_2\) reduction. Adsorption of phosphoric acid anion probably inhibits oxygen reduction by blocking initial adsorption of \(O_2\) 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 \(\text{H}_3\text{PO}_4\) follows the first-order kinetics, which proceeds similar as found for polycrystalline platinum\textsuperscript{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 \(\text{H}_3\text{PO}_4\), 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 \(\text{H}_2\text{SO}_4\) on the basis of the results obtained with rotating ring-Pt(hkl) disc\textsuperscript{7} In the region of positive potentials, Tafel slopes for \(O_2\) reduction reaction on Pt (110) and (100) surfaces in 0.1 M \(\text{H}_3\text{PO}_4\) 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% \(\text{H}_3\text{PO}_4\).

*Acknowledgement.* A part of this work was performed during the summer of 1989 and spring of 1990 at Case Western Reserve University, Cleveland, Ohio, USA, financial support of CWRU is acknowledged.
ИЗВОД
РЕДУКЦИЈА КИСЕОНИКА НА МОНОКРИСТАЛНИМ ПЛАТИНСКИМ ЕЛЕКТРОДАМА У РАСТВОРIMA ФОСФОРНЕ КИСЕЛИНЕ

А. ТАНАКА, Р. АДШИЋ и Б. НИКОЛИЋ

1 University of Sao Paulo, Caixa Postal 780-CEP 13560-970, Sao Carlos, Brasil,
2 ИХТМ - Институт за химичарство и техника, Београд, Београд, Југославија
3 Технолошки институт у Београду, Београд, Југославија

Испитивана је реакција редукције кисеоника на индикаторским монокристалном платини у 85% и 0.1 М раствору H₃PO₄ техником ротирајућег мениска. Утврђено је да је у оба раствора реакција првог реда и да се одиграја 4-електронским путем у коме је првобројно електронска спора ступањ. Катодичка активност за редукцију кисеоника следи низ Pt(110) > Pt(100) > Pt(111). Структурна зависност активности доминантно је одређена структурно зависном адсорбцијом аниона фосфорне кисеолине на Pt(hkl) ривима.

(Примењено 18. јуна 1999)

REFERENCES
23. M. Tarasevich, Elektrokhimiya 9 (1973) 599

* Sadaštija adresa: Brookhaven National Laboratory, Upton NY 11973, USA