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Electrochemical reduction of oxygen on thin-film Pt electrodes in 0.1 M KOH

K. Tammeveski,[1] T. Tenno,[1] J. Claret[2] and C. Ferrater[3]

[1]Institute of Physical Chemistry, University of Tartu, Jakobi 2, EE 2400 Tartu, Estonia
[2]Department of Physical Chemistry, University of Barcelona, Av. Diagonal 647, E-08028 Barcelona, Catalonia, Spain
[3]Department of Applied Physics and Electronics, University of Barcelona, Av. Diagonal 647, E-08028 Barcelona, Catalonia, Spain

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Abstract—The electroreduction of oxygen has been studied on thin-film platinum using the rotating disk electrode technique. The kinetic parameters of oxygen reduction were determined for Pt films over the range of thickness from 1 to 50 nm. The kinetics of oxygen reduction were found to be slightly influenced by the platinum film thickness. Copyright © 1996 Elsevier Science Ltd

Key words: Oxygen reduction, thin-film Pt, morphology, electrocatalysis, kinetic parameters.

INTRODUCTION

Highly dispersed platinum on carbon supports has been widely used in various electrochemical systems, particularly in oxygen electrocatalysis [1]. The two aspects in supported Pt electrocatalysis that have deserved special attention in numerous investigations are particle size effect and metal-support interaction [2]. The particle size effect is closely connected with the structure sensitivity of oxygen reduction on platinum. The experimental results of O_2-reduction on Pt single crystal planes in acid media show a relatively small structure sensitivity [3, 4]; sometimes the structure effect was absent [5, 6]. Zinola *et al.* investigated the process of oxygen reduction in alkaline solution using Pt electrodes of preferred orientation. The amount of H_2O_2 produced was found to be dependent on the preferentially oriented Pt surface [7].

The application of thin metal films on carbon supports makes it possible to study the oxygen reduction kinetics in controlled diffusion conditions and enables us to carry out the structural characterization of Pt deposits more precisely. Poirier and Stoner found that the oxygen reduction activity on thin film Pt depends on the grain size, specific surface area and lattice parameter [8]. The experimental data in 1 M H_2SO_4 show that the specific activity of O_2-reduction decreases with the increasing grain size. The activity decrease is not in agreement with the previous observations in oxygen electrocatalysis on highly dispersed platinum [2, 9] and indicates that the examination of thin-film Pt catalysts can give novel insights into platinum electrocatalysis.

The majority of research in oxygen electrocatalysis on supported Pt electrodes has focused on the study of oxygen reduction in acid media. This is due to the fact that acid electrolytes are mainly used in fuel cell systems. Platinum is also the material of choice for technical application in alkaline fuel cells because of its high electrocatalytic activity and chemical stability. It is relevant to note that the oxygen reduction overpotential is lower in alkaline than in acid solutions [10]. Therefore, it is of particular interest to investigate the reduction of oxygen on finely divided platinum in alkaline media.

Our preliminary results revealed that the electrocatalytic activity of 50 nm-thick Pt film towards O_2 reduction was not much different from that of bulk Pt [11]. The objective of the present work is to study the kinetics of oxygen reduction on thin platinum films down to 1 nm in alkaline electrolyte.

EXPERIMENTAL

The glassy carbon (GC) electrodes SU-2000 were cut from rods (0.4 cm diam.) and embedded into a teflon holder. The exposed surface of the GC disk was polished to a mirror finish with alumina followed by ultrasonication in bidistilled water. Thin platinum films, 1–50 nm thick, were formed by electron beam evaporation onto glassy carbon substrate at 2×10^{-6} torr. The evaporation was made from a graphite crucible. The rate of evaporation was 0.8 Å sec^{-1}.

The GC substrate and quartz crystal oscillator were positioned at a distance of 20 cm from the evaporation source.

Electrochemical measurements were performed with an EG&G Princeton Applied Research M263 potentiostat by employing the rotating disk electrode technique (*rde*) and cyclic voltammetry (CV). The rotation rate was varied from 360 to 4600 r.p.m. by using a Tacussel CTV101T speed controller. Experiments were conducted in a three-electrode electrochemical cell. A Pt-wire was used as a counter electrode. Potentials are given *vs* the Hg/HgO, OH-reference electrode in alkaline solution and with respect to *sce* in acid media. For comparative purposes a bulk Pt disk and a Pt-bead electrode were used. The solutions used were 0.1 M KOH and 0.5 M H_2SO_4. The solutions were prepared from KOH pellets (p.a., Merck), sulfuric acid (Suprapur, Merck) and Milli Q water. Ar and O_2 were from SEO, quality N50 (99.999%). All experiments were conducted at room temperature (23 ± 1°C).

The morphology of Pt films was examined by transmission electron microscopy (TEM). The TEM images and selected area diffraction patterns were obtained with a Philips CM 30 microscope. Nominal resolution of the microscope was 1.4 Å. A conventional Au grid of 3 mm diam. was covered by a thin layer of formvar followed by coating with a very thin carbon film. After Pt evaporation the specimen was used to obtain the TEM micrographs.

X-ray photoelectron spectroscopy (XPS) was used to obtain the binding energy values for Pt 4*f* electrons of thin Pt film. XPS measurements were performed with a Perkin Elmer PHI-5500 apparatus.

RESULTS AND DISCUSSION

Transmission electron microscopy is a useful tool to study the surface morphology of thin metal films. However, it is unsuitable for the direct examination of conventional electrodes. In this work a very thin specimen was used for analysis. The TEM images for various Pt films are shown in Fig. 1. The film formation occurs in the island growth mode. Initial nuclei are formed *via* the processes of condensation and surface diffusion of Pt atoms reached the substrate surface. The Pt deposits of smaller thickness than 2 nm are formed by separated islands of nearly rounded shape, varying in diameter. The following stage of development consists in the islands growth and their merging (see Fig. 1(b)). For 10 nm-thick Pt films three-dimensional growth is evident. More particles satisfy Bragg conditions and black spots appear on the micrograph. For the film thickness of 20 nm small voids can be seen between Pt grains, whereas for 50 nm-thick film the substrate surface is covered by a continuous metal layer. The GC substrate has not been used in the morphological characterization of Pt films. Therefore, some differences from the above-given micrographs would

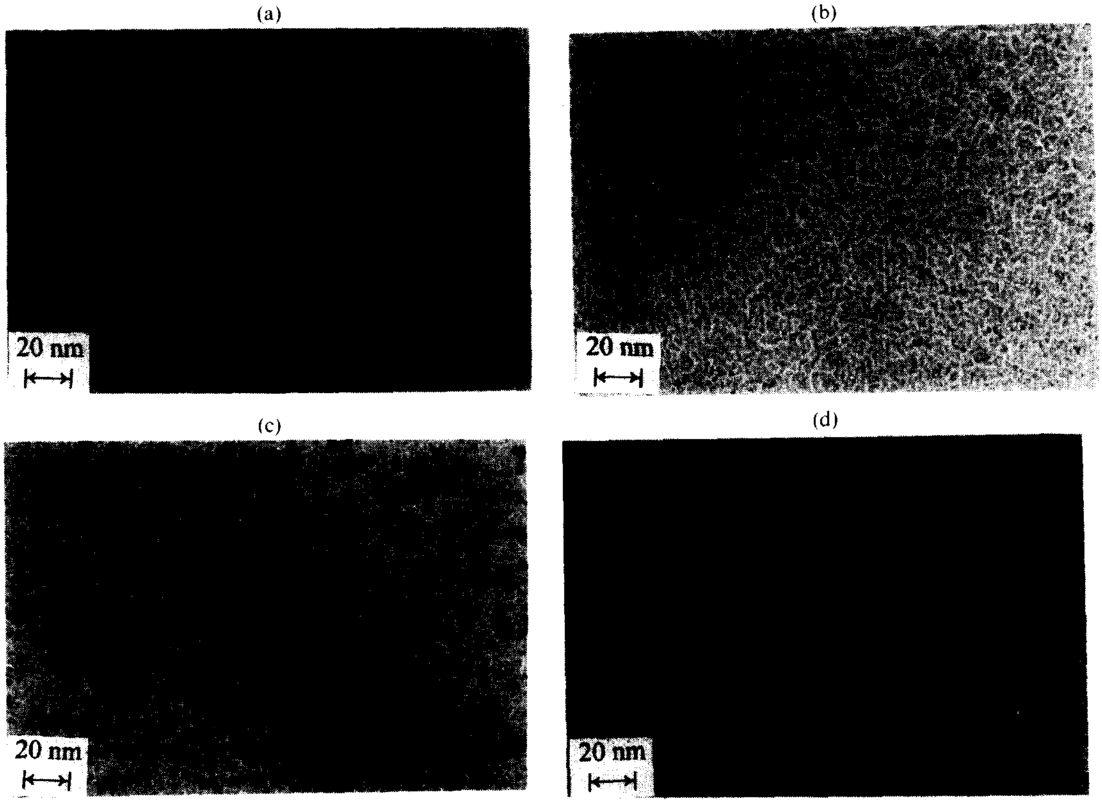

Fig. 1. TEM micrographs of thin Pt films: (a) 2 nm Pt; (b) 5 nm Pt; (c) 10 nm Pt and (d) 20 nm Pt.

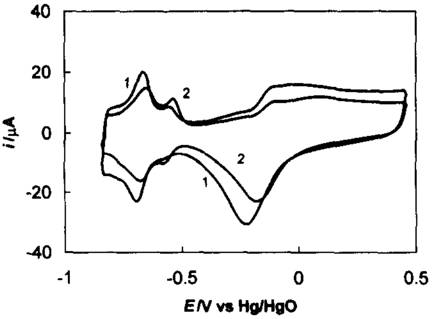

Fig. 2. Cyclic voltammograms for 5 nm thick Pt film (1) and Pt-bead (2) in Ar-saturated 0.1 M KOH at the sweep rate of 100 mV sec^{-1}.

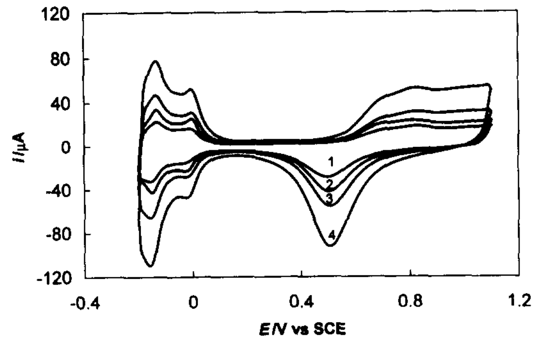

Fig. 3. Cyclic voltammograms for thin film Pt electrodes in Ar-saturated 0.5 M H_2SO_4: (1) 5 nm Pt; (2) 10 nm Pt; (3) 20 nm Pt and (4) 50 nm Pt. Sweep rate 100 mV sec^{-1}.

be expected for the GC surface, presumably not too large. Selected area diffraction patterns typical of polycrystalline platinum were obtained for all studied films. The diffraction line broadening was evident for thinner Pt films.

Cyclic voltammetry was used for the characterization of surface state and the determination of the real surface area of thin platinum films. Even for the thinnest Pt-film used (1 nm) two voltammetric peaks in the hydrogen adsorption region in both 0.1 M KOH and 0.5 M H_2SO_4 solutions were observed. Although the shape of cyclic voltammograms of thin film Pt on GC is similar to that for a polycrystalline platinum electrode, however, some finer differences on voltammograms were also evident. The platinum oxide reduction peak for thin Pt films (up to 5 nm thick) is shifted to more negative potentials as compared to that for the Pt-bead electrode (see Fig. 2). This is attributed to the differences in the oxidation state of the thin-film Pt electrodes. The dependence of the Pt oxide reduction peak potential on Pt loading was also observed by Peuckert *et al.* [12]. The ratio of a strongly adsorbed hydrogen peak to a weakly bound one is higher for the Pt-bead electrode in both electrolytes. This can be caused by the differences in structure, but also by a reduced contamination of the Pt-bead surface that was annealed before the measurements. For the measurement of the true surface area the sulfuric acid solution was preferred because in that case a better correction for the double layer charging is achieved (see Fig. 3). The amount of charge calculated from the area under hydrogen desorption peaks provides a basis for the determination of the true surface area of Pt electrodes. The roughness factor *fr* was determined by assuming that a monolayer hydrogen coverage is equivalent to 210 $\mu C\ cm^{-2}$.

The oxygen reduction data were collected by *rde* in O_2-saturated 0.1 M KOH. The potential profile used was the same for all thin-film Pt electrodes in order to assure a reproducible surface state. Before recording i,E-curves the electrode was held at the potentials of the second anodic oxidation peak (at 0.2 V for 1 min). Figure 4 presents the *rde* data for oxygen reduction on 2 nm thick Pt film. Standard voltammograms for O_2 reduction on platinum were obtained for all studied electrodes. For the reverse sweep the limiting currents were the same as those for the cathodic sweep, but higher currents were observed in the ascending (descending) region of the curve indicating that the reduced Pt surface is more active towards O_2-reduction. A small decay of current was observed at potentials prior to the hydrogen evolution reaction. The current decrease was observed at smaller Pt-film thicknesses and at higher rotation rates. Evidently, the number of surface sites that are needed for O_2 molecules to undergo reduction is decreasing due to hydrogen electrosorption. The diffusion limiting currents obey the Levich equation with the exception of 1 nm-thick Pt film, where i_d values were 5% lower than predicted. Whether this is due to the formation of hydrogen peroxide on the carbon surface not covered by Pt particles needs further investigated by using the *rrde* technique.

To analyse the kinetics of oxygen reduction reaction mass-transfer corrected Tafel plots were constructed. Two regions with different slopes are seen in Fig. 5 for thin Pt films and bulk Pt. At low current densities Tafel plots are linear with the slope ranging from −54 to −64 mV dec^{-1} for the studied electrodes. There is a clear tendency for the slope to

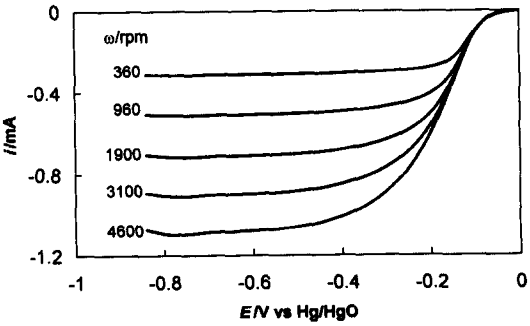

Fig. 4. Voltammetry curves for oxygen reduction on 2 nm thick Pt-film in O_2-saturated 0.1 M KOH. Sweep rate 10 mV sec^{-1}.

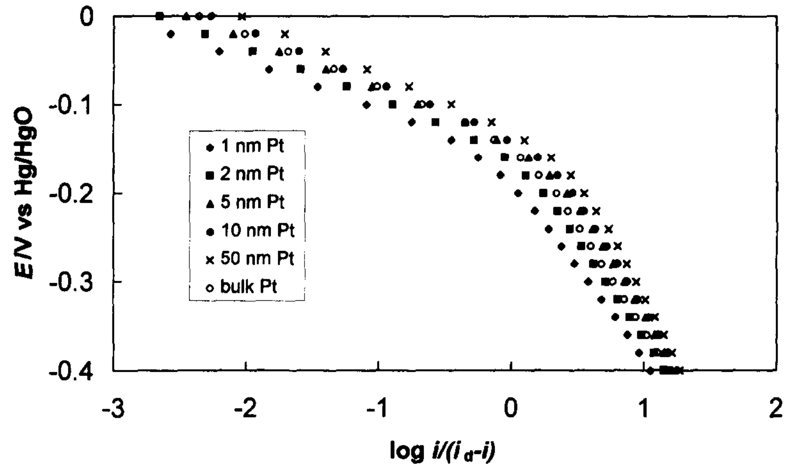

Fig. 5. Mass-transfer corrected Tafel plots for oxygen reduction on thin Pt films and bulk Pt in 0.1 M KOH.

increase with increasing film thickness. The Tafel slope close to $-60\,\mathrm{mV\ dec^{-1}}$ is typical of oxygen reduction on platinum electrodes at low overpotentials and is observed when there is a high coverage of platinum surface by oxygen-containing species [13]. At high current densities the slope value slightly changes with potential. In the potential range from -0.3 to -0.4 V the Tafel slope varied from -205 to $-290\,\mathrm{mV\ dec^{-1}}$, showing a larger degree of scatter. The slope values are considerably higher than those expected for the reaction mechanism involving the first electron transfer as the rate determining step. It has been proposed that the high slope can be caused by the slow O_2 adsorption step becoming rate-determining at higher overpotentials [14] or by the blocking of electrode surface with reaction intermediates (*eg* H_2O_2) [7]. The half-wave potential of oxygen reduction depends on the Pt film thickness. It should be noted that the $E_{1/2}$ values increase with increase in the true surface area of Pt film.

The exchange current densities (i_0) for oxygen reduction were obtained by the extrapolation of E *vs* log $i/(i_d - i)$ plots at the low current density region, to the reversible potential of the O_2/OH-couple in 0.1 M KOH (+0.305 V *vs* Hg/HgO), according to the equation:

$$\eta = \frac{2.3RT}{\delta F}\lg\frac{i_0}{i_d} - \left(\frac{2.3RT}{\delta F}\right)\lg\left(\frac{i}{i_d - i}\right). \qquad (1)$$

The i_0 values calculated per true surface area varied less than an order of magnitude for all studied electrodes. The i_0 values determined for the high current density region are not shown here because the data from the low overpotential region represent the main interest. The series of Tafel lines on the graph at low overpotentials follows the same order as that of the roughness factors for the corresponding electrodes. The Tafel line for bulk Pt lies between those for 5 and 10 nm-thick Pt film. The kinetic parameters of oxygen reduction on Pt films of various thickness are listed in Table 1.

A specific activity—SA (in μA/true surface area) and mass activity—MA (in A per gram of Pt) were calculated from the mass-transfer corrected currents of oxygen reduction at the potential of -0.02 V *vs*

Table 1.
Kinetic parameters for oxygen reduction on thin Pt film and bulk Pt in 0.1 M KOH. Region 1, low current densities; region 2, high current densities; $\omega = 1900$ rpm

Electrode	Tafel slope* Region 1 (mV dec^{-1})	Tafel slope Region 2 (mV dec^{-1})	$i_0 \times 10^{10}$** Region 1 (A cm^{-2})	$E_{1/2}$ *vs* Hg/HgO (mV)	i_k at -0.02 V** *vs* Hg/HgO (μA cm^{-2})
1 nm Pt	−54	−205 ± 13	0.6 ± 0.2	−192 ± 3	22 ± 4
2 nm Pt	−56	−224 ± 18	1.3 ± 0.5	−165 ± 3	31 ± 3
5 nm Pt	−57	−260 ± 12	2.2 ± 0.4	−151 ± 2	43 ± 5
10 nm Pt	−59	−257 ± 15	2.8 ± 0.3	−142 ± 2	40 ± 4
20 nm Pt	−61	−278 ± 23	3.4 ± 0.7	−137 ± 2	42 ± 6
50 nm Pt	−64	−283 ± 17	4.3 ± 0.3	−132 ± 2	39 ± 3
Bulk Pt	−59	−236 ± 12	2.5 ± 0.6	−154 ± 2	37 ± 4

*Entire column ± 2 mV dec^{-1}.
**Per true surface area.

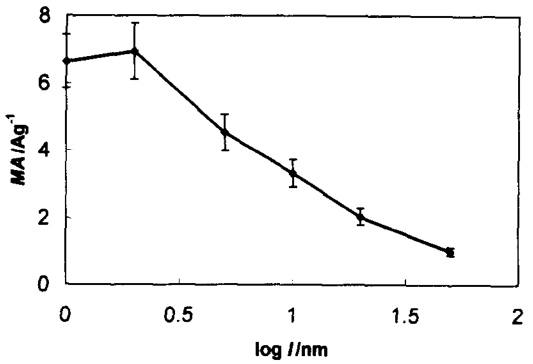

Fig. 6. Mass-activity of O_2-reduction as a function of Pt-film thickness.

Hg/HgO. The SA is nearly constant for the thin-film Pt electrodes more than 5 nm thick. It corresponds to 3.5 nm in grain size. This is in agreement with a large number of data obtained for oxygen reduction at highly dispersed platinum, showing a constant SA at grain sizes >4 nm [12]. Of course, differences in experimental techniques should be noted. Figure 6 shows a MA plot for oxygen reduction on thin Pt films. MA reaches its maximum at around 2 nm-thick Pt film with an average particle diameter of 3 nm. The earlier study of oxygen reduction on carbon-supported platinum in 8.5 M KOH revealed a similar dependence of electrocatalytic activity on Pt-grain size [15]. It is hardly possible to perform the further reduction of particle size in a reproducible manner. However, it would be of practical interest to know what is the electrocatalytic activity of Pt films thinner than 1 nm.

The XPS data indicate that the binding energy of Pt 4*f* level electrons depends on the Pt film thickness. Both the Pt $4f_{7/2}$ and Pt $4f_{5/2}$ peaks for 50 nm-thick Pt film were very close to those of bulk Pt, whereas for 1 and 2 nm-thick films a shift of spectra towards higher values of *ca.* 1 eV was observed. This observation is in agreement with the expectancy that the metal-support effect should be essential only for very thin films. It is not proven yet that the change in electrocatalytic activity is caused by a shift in binding energy, however, some correlation is evident. Recently, Antonucci *et al.* found that XPS spectra of highly dispersed Pt are affected by the presence and character of surface functional groups of the carbon support [16]. Thus, other factors besides the film thickness should be also taken into account.

CONCLUSIONS

Two Tafel regions were observed for both thin-film Pt and bulk Pt electrodes, with similar slope values. Therefore, no essential change in mechanism was considered for oxygen reduction on Pt films down to 1 nm thick. The slight effect of the Pt-film thickness on kinetic parameters was observed which is due to different adsorption properties of thin film and to the possible support effect.

On the basis of the results obtained it can be concluded that platinum being in the form of small particles retains its electrocatalytic activity towards oxygen reduction in 0.1 M KOH.

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