

## Electroreduction of oxygen on Nafion<sup>®</sup>-coated thin platinum films in acid media

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### Abstract

Electrocatalytic oxygen reduction reaction (ORR) kinetics on vacuum-evaporated thin platinum films in sulfuric acid solution is thoroughly investigated employing the rotating disc electrode (RDE) method. The nominal thickness of the Pt films is varied from 0.25 to 20 nm and the effect of applied Nafion<sup>®</sup> layer on the ORR activity in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution is evaluated. The electroactive surface area of Pt and the corresponding overall ORR activity decreases with the nominal film thickness. An increase in the hydrogen peroxide yield and a decrease of the ORR specific activity of Pt with decreasing the film thickness is also observed. The Nafion<sup>®</sup> coating slightly increases the hydrogen peroxide production, but does not affect the electrocatalytic activity of Pt. The results obtained with the model system employed herein are important for elucidating the influence of Nafion<sup>®</sup> layer on the ORR kinetics on Pt-based electrocatalysts.

**Keywords:** Oxygen reduction; Electrocatalysis; Pt film; Nafion; Kinetics.

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## 1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are considered to be highly promising energy conversion devices, thanks to their high efficiency and low environmental impact. At present, commercialization of the fuel cells is still hindered, as expensive Pt-based catalysts are required to overcome the sluggish oxygen reduction reaction (ORR) kinetics on the fuel cell cathode. In order to reduce the Pt loading, the utilization of Pt should be further improved and the composition of the cathode catalyst layer should be optimized. Nafion<sup>®</sup> ionomer is commonly added to carbon-supported Pt catalysts (Pt/C), in order to create a proton-conducting network for efficient Pt utilisation [1]. The ionomer content has a great effect on the ORR performance of the catalyst, as it provides an additional resistance to the mass transport of reactants and products [2-5]. Moreover, Nafion can also affect the kinetics of the ORR on Pt surface [6-12].

Nafion<sup>®</sup> consists of hydrophobic polytetrafluoroethylene backbone and side chains containing hydrophilic sulfonic acid groups [13, 14]. In the presence of water, the latter are clustered to form an interconnected proton-conducting network. The sulfonate groups adsorb rather strongly on Pt, as confirmed by in-situ spectroscopic methods [10, 15, 16] and by electrochemical CO displacement experiments [17]. Similarly to the adsorbed (bi)sulfate anions in sulfuric acid solution [18], the adsorbed sulfonate groups can block the active centers of Pt and thereby influence its electrocatalytic activity for ORR [6] and methanol electrooxidation [19]. Inhibition of the ORR on bulk Pt in the presence of Nafion<sup>®</sup> in HClO<sub>4</sub> solution that contained only weakly adsorbing anions has been noted in several studies [6-11]. The surface coverage and adsorption strength of the sulfonate strongly depends upon the

crystallographic orientation of Pt surface [6, 17, 20]. Thus, for Pt single crystal surfaces the largest decrease in the ORR activity due to the Nafion<sup>®</sup> layer has been noted on Pt(111) facet, which also shows the strongest adsorption of (bi)sulfate ions [6]. The inhibition of the ORR also depends upon the structure of the ionomer, as the adsorption of sulfonate moieties is facilitated for the ionomers with longer and more flexible side chains [10]. On the other hand, no effect of Nafion<sup>®</sup> on the ORR rate in HClO<sub>4</sub> solution was observed by Yano *et al.* [21]. In sulfuric acid solution, the adsorption of (bi)sulfate anions on Pt leads to a considerably lower ORR activity as compared to that in perchloric acid [22]. In 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, a slight enhancement of the ORR current by Nafion<sup>®</sup> at low overpotentials was observed, but the current decreased at higher overpotentials due to the mass transport limitations [2]. Improved kinetics of the ORR in 0.5 M H<sub>2</sub>SO<sub>4</sub> has been attributed to the higher O<sub>2</sub> solubility or a higher proton activity in the polymer film as compared to sulfuric acid solution [12]. However, comparable ORR rates on Nafion<sup>®</sup>-free and Nafion<sup>®</sup>-covered Pt electrodes in H<sub>2</sub>SO<sub>4</sub> solution have been observed on bulk polycrystalline Pt [4, 23] as well as on Pt(111) single crystal surface [6].●

In several works, the influence of Nafion<sup>®</sup> on the electrochemical oxygen reduction behavior of nanostructured Pt catalysts has been studied by RDE method. For example, Curnick *et al.* [24, 25] showed a facile method for the preparation of electrocatalysts from Nafion<sup>®</sup>-stabilized colloidal Pt nanoparticles (Nafion<sup>®</sup>-Pt/C), offering synthetically-directed formation of the Pt-ionomer interface and providing unprecedented control over the morphology of Pt particles on the carbon support. Their study revealed that Nafion<sup>®</sup>-Pt/C catalysts possessed similar specific activity and mass activity towards the ORR as commercial

Pt/C catalysts, whilst requiring lower overall ionomer loadings. For nanostructured thin Pt films, a 7–10% decrease of the ORR rate in the presence of Nafion<sup>®</sup> film was noted, which is comparable with that observed on Pt(110) and Pt(100) surfaces [6]. Antoine *et al.* have shown that the ORR mechanism on carbon-supported Pt nanoparticles inside Nafion<sup>®</sup> is similar to that on bulk Pt [26]. The kinetic current density depends on Nafion<sup>®</sup> content in the catalyst layer, being the highest at the ionomer fraction of 10-55 wt% [27]. The specific activity (SA) for O<sub>2</sub> reduction of Pt in ultrathin uniform Pt/C layers in 0.1 M HClO<sub>4</sub> decreased with increasing the ionomer/carbon ratio, which was attributed to the adsorption of sulfonate groups [7, 28]. The decrease of SA in the presence of Nafion<sup>®</sup> did not depend upon the Pt particle size [7]. However, in case of very low Nafion<sup>®</sup>/catalyst ratios (<0.04), it was shown that the effect of ionomer on the SA was negligible [29]. Ultra-microelectrode with cavity technique was used to show that in 1 M H<sub>2</sub>SO<sub>4</sub> solution, the ORR activity of Pt/C catalyst was enhanced by Nafion<sup>®</sup> at low current densities, presumably as a result of the higher acidity, but decreased at high current densities [30]. The studies of the ORR on Nafion<sup>®</sup>-containing Pt/C electrodes by channel flow double electrode method have demonstrated a decrease in the O<sub>2</sub> reduction activity and increase in H<sub>2</sub>O<sub>2</sub> yield with increasing SO<sub>4</sub><sup>2-</sup> concentration in HClO<sub>4</sub> solution, which was attributed to the strong specific adsorption of sulfate anions [31].

The effect of Pt particle size on the ORR electrocatalytic activity has been extensively studied [32]. For thin Pt films, the dependence of the ORR activity on the Pt film thickness and particle size was observed in HClO<sub>4</sub> solution, but not in H<sub>2</sub>SO<sub>4</sub> [33]. Although in some studies no particle size effect for small (<5 nm) Pt particles has been noted [34-36], a decrease in the specific activity with decreasing particle size and maximum mass activity (MA) at about 2-5

nm has often been observed [26, 29, 37-43]. This size effect has been attributed to the changes in the distribution of Pt surface facets and edge sites with particle size [29, 39, 40, 43, 44] or to stronger adsorption of oxygenated species on smaller particles due to the electronic effects [41, 42]. These experimental observations are also supported by theoretical calculations, where particles were modelled as truncated cubo-octahedra [45]. In contrast, Nesselberger *et al.* have found only small differences in SA for carbon-supported Pt catalyst with the particle size between 1-5 nm, but observed much higher SA for polycrystalline Pt and 30 nm unsupported Pt black particles [36]. They modelled the activities of Pt particles of different sizes based upon the distribution of surface planes and respective SA values. The results obtained were in contradiction with the measured activities, which showed that these simple models are not sufficient to describe the electrocatalytic ORR behavior of Pt nanoparticles.

There are also several reports discussing the dependence of the ORR activity on the Pt interparticle distance, as reviewed in Ref.[32]. In some works, a decrease of the ORR activity with decreasing the distance between Pt particles has been observed, which can be explained by the effect of O<sub>2</sub> diffusion and shielding of particles [46]. However, more recently an increase of the specific activity with a decrease in the interparticle distance was observed [47, 48], which was explained to be possibly due to the decrease in the potential drop within the electrochemical double layer [48].

Thus, despite of the extensive work on the effect of Pt particle size and the presence of Nafion<sup>®</sup> to ORR kinetics, some contradictions between the reports still exist, which can possibly be due to the complex O<sub>2</sub> mass-transport conditions in Pt/C catalyst layers. Our aim was to use planar electrodes as model systems, in order to elucidate the influence of Nafion<sup>®</sup>

layer to the ORR kinetics on Pt films of different morphology at controllable mass-transport conditions. The nanostructured thin Pt films were prepared by electron-beam evaporation and these consist of Pt nano-islands, the size of which increases with nominal film thickness.

## 2. Experimental

Glassy carbon (GC) disc electrodes with the geometric surface area of  $0.132 \text{ cm}^2$  were prepared by mounting the GC discs into Teflon holders and polished with 1.0 and  $0.3 \text{ }\mu\text{m}$  alumina slurries (Buehler). After polishing, the GC electrodes were cleaned in an ultrasonic bath Branson 1510E-MTH (42 kHz, 70 W) in Milli-Q (Millipore, Inc.) water for 5 min. Thin Pt films with the nominal thickness of 0.25–20 nm were prepared onto GC electrodes by electron-beam evaporation using Vacuum Service OY evaporation system at a base pressure of  $2 \times 10^{-6}$  Torr. The thin-film Pt electrodes were coated by a Nafion<sup>®</sup> layer by applying a droplet of 0.5% Nafion<sup>®</sup> solution in ethanol, which was prepared from 5 wt% Nafion<sup>®</sup> solution in lower alcohols (Aldrich). The solvent was allowed to evaporate yielding a  $0.5 \text{ }\mu\text{m}$  Nafion<sup>®</sup> layer, as calculated by assuming the density of  $2 \text{ g cm}^{-3}$  for dry Nafion<sup>®</sup> [49-51]. For transmission electron microscopy (TEM) studies, the Pt films were evaporated onto TEM grids (formvar/carbon-coated copper grids) and studied on a Tecnai 12 instrument at 120 kV accelerating voltage.

The electrochemical experiments were carried out in a glass cell in 0.5 M  $\text{H}_2\text{SO}_4$  solution at room temperature ( $23 \pm 2^\circ\text{C}$ ). The solution was prepared from 96%  $\text{H}_2\text{SO}_4$  (Suprapur, Merck) and deaerated with argon (Ar, 99.999%, AGA) or saturated with  $\text{O}_2$  (99.999%, AGA); the gas flow over the electrolyte solution was maintained during the experiments. A saturated

calomel electrode (SCE) was used as a reference, which was calibrated against the reversible hydrogen electrode (RHE) as follows:  $E_{\text{RHE}} = E_{\text{SCE}} + 0.270 \text{ V}$ . The calibration was performed in 0.5 M  $\text{H}_2\text{SO}_4$  solution saturated with  $\text{H}_2$  and using Pt wires as both working and counter electrodes. All potentials are quoted with respect to the RHE. A Pt wire was employed as the counter electrode and the counter electrode compartment was separated from the working electrode compartment by a glass frit. The potential was controlled with an Autolab potentiostat/galvanostat (PGSTAT30, Eco Chemie B.V., The Netherlands) using the General Purpose Electrochemical System (GPES) software. The electrodes were electrochemically pre-treated by scanning the potential between 0.02 and 1.47 V at  $100 \text{ mV s}^{-1}$  until reproducible cyclic voltammograms were obtained. The electroactive surface area (ESA) of Pt on the electrodes was determined by integrating the charge under the hydrogen desorption peaks, assuming a charge density of  $210 \text{ C cm}^{-2}$  for  $\text{H}_{\text{upd}}$  monolayer [52].

After potential cycling the electrodes were directly transferred into another cell containing  $\text{O}_2$ -saturated solution, in order to minimize the surface contamination in air. Electroreduction of  $\text{O}_2$  was studied by rotating disc electrode (RDE) measurements using an EDI101 rotator and a CTV101 speed control unit (Radiometer) at electrode rotation rates ( $\omega$ ) between 360 and 4600 rpm. The potential was scanned between 1.07 to 0.07 V vs. RHE at  $10 \text{ mV s}^{-1}$ . The anodic background-corrected scans are presented and analyzed.

### **3. Results and Discussion**

#### **3.1. TEM studies**

The TEM micrographs of vacuum-evaporated thin Pt films are presented in Figure 1. The

images clearly show that Pt is not growing epitaxially but is forming small nano-islands. This corresponds to the Volmer–Weber growth mode and was previously observed for vacuum-evaporated Pt and Pd films [53, 54]. The island diameter slightly increases with the nominal film thickness, from  $1.7\pm 0.2$  nm for 0.25 nm film to  $2.8\pm 0.4$  nm for 1 nm film and  $3.5\pm 0.5$  for 5 nm film. The number on islands per unit surface area rises and for the 5 nm film the particles are merged.

### 3.2. Cyclic voltammetry (CV)

Thin-film Pt electrodes were subjected to potential cycling in O<sub>2</sub>-free 0.5 M H<sub>2</sub>SO<sub>4</sub> solution in order to clean and characterize the Pt surface. Figure 2 shows stable cyclic voltammograms for Nafion<sup>®</sup>-coated and uncoated Pt films. The CV curves show the characteristic features of polycrystalline Pt. Two pairs of reversible peaks corresponding to the hydrogen adsorption/desorption (H<sub>upd</sub>) at about 0.13 and 0.26 V vs. RHE have been attributed to H<sub>upd</sub> on Pt(110) and Pt(100) step sites, respectively, but recently shown to be due to replacement of adsorbed hydrogen by adsorbed hydroxyl on those surface sites [55]. The third peak located at ca 0.21 V has been associated with oxidation of H<sub>upd</sub> on reconstructed two-dimensional (110)-(2×1) domains that appear on anodically oxidised polycrystalline Pt or Pt(110) surfaces [55, 56]. The broad peak of oxide formation starts at about 0.8 V vs. RHE and the oxide reduction peak shifts from 0.76 to 0.69 V vs. RHE as the film thickness decreases. This effect is experimentally well-established and has been attributed to stronger adsorption of oxygen-containing species on smaller Pt particles [42] or to decrease in the kinetics of the Pt/PtO couple with decreasing Pt particle size [57, 58]. The charges corresponding to the H<sub>upd</sub>

and oxide formation/reduction considerably increase with Pt film thickness. The CVs of uncoated and Nafion<sup>®</sup>-coated Pt films look rather similar, the  $H_{\text{upd}}$  peaks being only slightly less pronounced for the latter, similar to that observed on polycrystalline Pt [4, 5]. It has been suggested that the adsorption of sulfonate groups is suppressed by strongly adsorbing (bi)sulfate anions from the electrolyte solution [6, 17]. It has been proposed that for the sulfonate groups the metal-anion interactions are counter-balanced by the bonding of the anions to the polymer matrix and sulfonate-counter-cation interactions [17].

The *ESA* of Pt determined by integrating the charge of  $H_{\text{upd}}$  desorption peaks increased with increase in film thickness (Table 1). Although the 5 nm Pt film completely covers the GC substrate surface, the *ESA* value is still considerably higher for 20 nm film, indicating that the roughness of the Pt film increases with the film thickness. It is also noteworthy that the *ESA* values are up to 18% lower for Nafion<sup>®</sup>-coated electrodes. This is in accordance with the studies on bulk polycrystalline Pt, where about 15-20% decrease of the *ESA* is due to the blocking of surface-active sites by Nafion<sup>®</sup> has been observed [2, 4].

### **3.3. CO oxidation studies.**

CO stripping behavior on Pt films of various thicknesses, coated with Nafion were investigated as presented in Figure 3. CO stripping experiment was performed by electrochemical oxidation of the pre-adsorbed CO on the electrode surface in N<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. It can be seen in the inset of Figure 3 that the CO stripping peaks on 20 nm, 5 nm and 0.25 nm Pt films are located at 0.72, 0.77 and 0.86 V, respectively. The shift of the peak potential may be related to the distinct morphology of Pt films. Very similar results

have been obtained for Pt films with the nominal thickness of 0.2 to 2.5 nm on carbon and TiO<sub>2</sub> substrates and the peak shift has been attributed to more difficult oxidation of Pt surface sites of smaller Pt clusters [57, 58]. Maillard et al. also observed a positive peak shift for Pt particles smaller than 3.3 nm [59], therefore, the most positive peak potential of 0.25 nm film can be due to the small Pt island size. The particle size effects in CO monolayer oxidation were attributed to the particle size-dependent interaction between adsorbed CO and OH as well as to the size-dependent surface diffusion coefficient of adsorbed CO [60]. On the other hand, the appearance of a CO oxidation peak at more negative potentials than that of polycrystalline Pt has been attributed to the high defect density of nanograined structures or agglomerated Pt particles [59, 60]. This explains the negative peak shift for the 5 nm and 20 nm films that also appear to consist on agglomerates of Pt grains (Figure 1). For Nafion-covered 20 nm, 5 nm and 0.25 nm Pt films a small negative shift of the CO stripping peak to 0.71, 0.72 and 0.82 V, respectively, was observed. This is in contradiction with the results of IR reflectance absorption spectroscopy studies, which have shown that the CO oxidation proceeds at higher potentials on Pt nanoparticles [61] and Pt(111) [16] covered by Nafion.

### ***3.4. Oxygen reduction studies***

The electroreduction of oxygen on thin Pt films was studied in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution by the RDE method. The representative ORR polarization curves for Nafion<sup>®</sup>-coated and uncoated electrodes are presented in Figures 4 and 5. S-shape voltammograms were observed for all the electrodes studied and for the 1 nm and thicker Pt films, the reduction currents reached

plateau values. It is evident that the plateau current is considerably lower for Nafion<sup>®</sup>-coated electrodes, which is caused by the resistance of the Nafion<sup>®</sup> layer to the mass-transfer of oxygen. A small decrease of the current at negative potentials is due to the adsorbed hydrogen, which partly block the O<sub>2</sub> reduction centres [18].

For the Koutecky-Levich (K-L) analysis of the RDE polarization curves of Nafion<sup>®</sup>-coated electrodes, the diffusion of O<sub>2</sub> in the film should be taken into account according to the following equation [3, 4, 50, 51]:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_f} + \frac{1}{j_d} = \frac{1}{j_k} + \frac{1}{j_f} + \frac{1}{0.62nFD_{O_2}^{2/3}\nu^{-1/6}C_{O_2}^b\omega^{1/2}} \quad (1)$$

where  $j$  is the experimentally measured current density,  $j_k$  is the kinetic current density,  $j_f$  is the diffusion-limited current density controlled by the diffusion of O<sub>2</sub> in the Nafion<sup>®</sup> layer,  $j_d$  is the diffusion-limited current density determined by the mass-transport properties of the RDE in the boundary layer,  $n$  is the number of electrons transferred per O<sub>2</sub> molecule,  $F$  is the Faraday constant (96,485 C mol<sup>-1</sup>),  $\omega$  is the electrode rotation rate,  $C_{O_2}^b$  is the concentration of oxygen in the bulk solution (1.13×10<sup>-6</sup> mol cm<sup>-3</sup>) [2],  $D_{O_2}$  is the diffusion coefficient of oxygen in 0.5 M H<sub>2</sub>SO<sub>4</sub> (1.8×10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>) [2] and  $\nu$  is the kinematic viscosity of the electrolyte solution (0.01 cm<sup>2</sup> s<sup>-1</sup>) [62]. For Nafion<sup>®</sup>-coated electrodes, the limiting current density  $j_{lim}$  appears as a combination of  $j_d$  and  $j_f$  ( $1/j_{lim} = 1/j_d + 1/j_f$ ) and in case the value of  $n$  is independent of the potential, the kinetic current density can be calculated from the experimental values by the following equation:

$$j_k = \frac{j \times j_{lim}}{j_{lim} - j} \quad (2)$$

From the slopes of the K-L plots (inset to Figure 4), the values of  $n$  were calculated. The  $n$  values close to 4 were obtained for bare 1 nm and thicker Pt films (Table 1), indicating that

the product of O<sub>2</sub> reduction is water. At  $E > 0.2$  V vs. RHE the  $n$  value was independent of the potential for all electrodes, but at the most negative potentials the H<sub>2</sub>O<sub>2</sub> production sharply increased due to the blocking effect of adsorbed hydrogen. For the Nafion<sup>®</sup>-coated films, slightly lower  $n$  values were observed. Higher peroxide yield on Nafion<sup>®</sup>-coated Pt electrodes has been explained by blocking of some O<sub>2</sub> adsorption sites on Pt surface by fluorocarbon polymer network of Nafion<sup>®</sup> [8]. On the 0.25 nm Pt films, the  $n$  value was also lower, which can be attributed to the increased interparticle distance, which decreases the probability of H<sub>2</sub>O<sub>2</sub> re-adsorption and reduction on neighbouring Pt nano-islands.

It can be noted that the electrocatalytic activity of the Pt films increases with the film thickness (Figure 5) and the half-wave potential ( $E_{1/2}$ ) for O<sub>2</sub> reduction shifts to higher values (Table 1). This is an expected result, as the  $ESA$  of Pt also considerably increases for the thicker films. In order to evaluate the dependence of intrinsic electrocatalytic activity of Pt on the morphology of the films and on the presence of Nafion<sup>®</sup>, the specific activity (SA) of Pt was calculated at 0.9 V vs. RHE:

$$SA = \frac{I_k}{ESA} \quad (3)$$

where  $I_k$  is the kinetic current calculated from the K-L equation. Comparison of the  $ESA$  values presented in Table 1 shows that the Nafion<sup>®</sup> coating does not remarkably influence the ORR activity of Pt in H<sub>2</sub>SO<sub>4</sub> solution, except for the 20 nm film, which shows slightly increased SA when coated by Nafion<sup>®</sup>. This is in accordance with previous observations that the ORR kinetics on Nafion<sup>®</sup>-covered and bare Pt surface is similar in H<sub>2</sub>SO<sub>4</sub> solution, where the (bi)sulfate anions are present in a large excess and show stronger adsorption as compared to sulfonate groups [6, 21]. Thus, in H<sub>2</sub>SO<sub>4</sub> solutions the electrocatalytic activity of both bare

and Nafion<sup>®</sup>-coated Pt is mainly determined by the adsorption of the (bi)sulfate, whereas in HClO<sub>4</sub> solution, a significant decrease of ORR kinetic currents in the presence of Nafion<sup>®</sup> is observed due to the adsorption of sulfonate groups [6, 7]. This effect is most remarkable on Pt(111) that shows strongest adsorption of sulfonate, but can be observed also on Pt nanoparticles [6].

It is also evident that the SA values decrease with decreasing the Pt loading, both for Nafion<sup>®</sup>-coated and uncoated electrodes. This can be due to morphological differences of the Pt films, such as decreasing the size of Pt islands with Pt nominal thickness, as the dependence of the ORR specific activity on Pt particle size has been observed in many studies [32]. It is known that the ORR is a structure-sensitive reaction and strongly influenced by the adsorption of spectator species, such as (bi)sulfate anions that show the strongest adsorption on Pt(111) facet and consequently this Pt single crystal plane is the least active for ORR in H<sub>2</sub>SO<sub>4</sub> [18]. For cubo-octahedral particles, the proportion of Pt(111) surface facets increases with decreasing the Pt particle size, resulting in declined ORR activity [44]. Lower ORR activity of smaller Pt particles has also been attributed to higher prevalence of low-coordinated Pt sites, which show stronger adsorption of OH that inhibits the ORR rate [39, 41]. Another reason for lower activity of 0.25 nm Pt film might be higher interparticle distance, as Nesselberger *et al.* have demonstrated that the SA of Pt nanoclusters decreases significantly when the average edge-to-edge distance increases to 1-2 nm [48], as seen in Figure 1(a). In addition, part of the decreased SA observed for the thinnest Pt film is presumably due to the higher peroxide yield.

The mass-transfer corrected Tafel plots constructed from the RDE polarization data at

1900 rpm are presented in Figure 6. The slope of these plots gradually increases from -68...-106 mV dec<sup>-1</sup> at low current densities to -135...-203 mV dec<sup>-1</sup> at high current densities, the Tafel slope values are given in Table 1. For Pt catalysts, the slope values close to -60 and -120 mV dec<sup>-1</sup> at low and high current densities, respectively, have been obtained in many studies [18, 26, 27, 51, 63-65]. The transfer of the first electron to O<sub>2</sub> molecule has been suggested to be the rate-determining step (rds) in both potential regions and the slope change has been attributed to the change of the adsorption conditions of reaction intermediates, following Temkin or Langmuirian type adsorption [26, 27, 63]. The lower Tafel slope values have also been related to the site-blocking effect of chemisorbed oxygen at higher potentials [22, 66]. In this work, Tafel slope values are higher in both regions and are rather similar for Nafion<sup>®</sup>-coated and uncoated electrodes. It has been observed for Pt single crystal electrodes that the Tafel slope of ORR does not change when the electrode is coated with Nafion<sup>®</sup> [6]. It can be concluded that the ORR mechanism does not depend on the Pt loading or on the presence of Nafion<sup>®</sup> layer on the electrode surface.

#### **4. Conclusions**

The effect of Nafion<sup>®</sup> layer on the ORR activity of thin Pt films with the nominal thickness between 0.25-20 nm was studied in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. According to the TEM studies, the thinnest films (0.25 nm and 1 nm) consist of separate Pt nano-islands with the diameter of a few nanometers. The electrocatalytic ORR activity of the Pt films decreased with decreasing the nominal film thickness, as a result of decreasing the electroactive surface area of Pt. However, the specific activity of Pt was also lower for the thinnest film, which was attributed

to the effect of the decreasing particle size and/or increasing the inter-particle distance. The H<sub>2</sub>O<sub>2</sub> production also slightly increased for the thinnest Pt film. Applying a thin layer of Nafion<sup>®</sup> onto the Pt films resulted in a decrease in the diffusion-limited current density, but it did not affect the specific activity of Pt for O<sub>2</sub> reduction. H<sub>2</sub>O<sub>2</sub> yield was slightly higher for Nafion<sup>®</sup>-coated electrodes. The results show that the adsorption of sulfonate anions does not impact the ORR activity of nanostructured Pt films in sulfuric acid solutions.

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**Table 1.** Kinetic parameters for O<sub>2</sub> reduction on bare and Nafion<sup>®</sup>-coated thin-film Pt electrodes in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.

Nominal Pt film thickness	<i>ESA</i> (cm <sup>2</sup> )	<i>n</i> at 0.2 V vs. RHE	<i>E</i> <sub>1/2</sub> (V vs. RHE)	<i>SA</i> at 0.9 V vs. RHE (mA cm <sup>-2</sup> )	Tafel slope I* (mV dec <sup>-1</sup> )	Tafel slope II* (mV dec <sup>-1</sup> )
<b>bare Pt</b>						
0.25 nm	0.044 ± 0.015	3.53 ± 0.22	0.635 ± 0.002	0.079 ± 0.010	-91 ± 8	-135 ± 2
1 nm	0.156 ± 0.003	4.05 ± 0.07	0.732 ± 0.001	0.114 ± 0.003	-79 ± 3	-135 ± 3
5 nm	0.273 ± 0.029	3.73 ± 0.04	0.769 ± 0.008	0.126 ± 0.009	-87 ± 2	-139 ± 4
20 nm	0.458 ± 0.025	3.94 ± 0.19	0.792 ± 0.005	0.142 ± 0.005	-86 ± 1	-168 ± 8
<b>Nafion<sup>®</sup>-coated Pt</b>						
0.25 nm	0.038 ± 0.019	3.05 ± 0.07	0.533 ± 0.032	0.092 ± 0.025	-106 ± 1	-203 ± 28
1 nm	0.142 ± 0.005	3.75 ± 0.24	0.717 ± 0.007	0.114 ± 0.015	-68 ± 5	-152 ± 2
5 nm	0.224 ± 0.010	3.52 ± 0.08	0.751 ± 0.017	0.148 ± 0.038	-85 ± 1	-171 ± 3
20 nm	0.454 ± 0.044	3.83 ± 0.06	0.805 ± 0.013	0.199 ± 0.019	-81 ± 1	-197 ± 10

\*Region I corresponds to low current densities (0.9 V < *E* < 1 V; 0.85 V < *E* < 0.95 V for 0.25 nm film) and region II to high current densities (0.6 V < *E* < 0.8 V).

## Figure Captions

**Figure 1.** TEM images of thin Pt films with the nominal thickness of (a) 0.25 nm, (b) 1 nm and (c) 5 nm.

**Figure 2.** Cyclic voltammograms for (a) bare and (b) Nafion-coated thin Pt films in Ar-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.  $\nu = 100 \text{ mV s}^{-1}$ .

**Figure 3.** Cyclic voltammograms for oxidation of pre-adsorbed CO on Nafion-coated thin Pt films and bare Pt films (inset) in Ar-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.  $\nu = 20 \text{ mV s}^{-1}$ .

**Figure 4.** RDE voltammetry curves for O<sub>2</sub> reduction on bare and Nafion-coated 1 nm Pt film in O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at various electrode rotation rates (360, 610, 960, 1900, 3100 and 4600 rpm).  $\nu = 10 \text{ mV s}^{-1}$ . The inset displays the Koutecky-Levich plots of O<sub>2</sub> electroreduction at 0.2 V.

**Figure 5.** RDE voltammetry curves for O<sub>2</sub> reduction on (a) bare and (b) Nafion-coated thin Pt films in O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> at 1900 rpm.  $\nu = 10 \text{ mV s}^{-1}$ .

**Figure 6.** Mass-transfer corrected Tafel plots for O<sub>2</sub> reduction on (a) bare and (b) Nafion-coated thin Pt films in O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>.  $\omega = 1900 \text{ rpm}$ .