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Potentiodynamic Investigation of Oxygen Reduction Reaction on Polycrystalline Platinum Surface in Acidic Solutions: the Effect of the Polarization Rate on the Kinetic Parameters

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The time of exposure of potentiodynamically polarized platinum electrode to the potentials of oxide formation was considered quantitatively as a factor of kinetics of oxygen reduction reaction (ORR) in acidic, $HClO_4$ and H_2SO_4 solution. In general, the enhancement of catalytic activity towards ORR was measured upon increasing sweep rate. The results were discussed in terms of the amount of oxide formed on platinum surface, which decreased upon increasing sweep rate. The scope of view was confirmed that the Tafel slope for ORR on oxide-free Pt amounts to 120 mV dec^{-1}, while various values between 120 and 60 mV dec^{-1}, reported often in the literature, are governed by the site blocking/surface reorganization processes.

Keywords: ORR, Tafel slope, time effects, oxide formation, hydroxyl adsorption, place exchange

1. INTRODUCTION

Electrocatalytic processes commonly refer to such electrode processes where the charge-transfer depends on the nature of electrode material [1,2]. The term *electrocatalyst* denotes a substance able to increase the rate of a electrochemical reaction without modifying the overall standard Gibbs energy change, which upon entering catalytic cycle returns to its initial state [4]. As emphasized by Markovic and Ross [3], virtually every electrochemical reaction involving either breakage or formation of chemical bond is electrocatalytic in nature. This definition holds equally for simple reactions, such as hydrogen evolution/oxidation (HER/HOR), complex ones, such as oxygen reduction reaction (ORR), or bimolecular ones, such as CO oxidation (COOR). All these reactions are commonly investigated on platinum electrode surfaces, either single-crystalline or polycrystalline (Pt-poly) ones [3].

The studies of ORR, COOR and oxidation of low-molecular alcohols on Pt electrodes revealed the importance of the understanding of the role of species typically called "OH_{ads}" which are usually considered to be formed at potentials higher than ~700 mV *vs*. reversible hydrogen electrode (RHE) [5]. The initial stages of Pt surface oxidation were studied extensively from 1970's resulting in numerous scientific papers. For extensive discussion of these results up to mid 1990s the reader is referred to the work of Conway [5]. It is an actual experience that Pt oxidation is partly irreversible, as commonly observed by both cyclic voltammetry (CV) and chronoamperometric transients of oxide growth/reduction [5, 6]. In spite of the large number of studies published, the nature of so-called OH_{ads} species as well as the understanding of the Pt oxidation process remained somewhat controversial. Historically, work of Conway's groups established the viewpoint according to which hydroxyl/oxide formation is taking place in the "standard" oxide formation region, between 0.8 and 1.4 V *vs*. RHE, with a monolayer coverage (1 OH_{ads} per surface Pt atom) at about 1.1 V *vs*. RHE [5, 7]. Oxide formation was considered to be a stepwise process occurring through the formation of OH_{ads} by water discharge and subsequent oxidation to form O_{ads}. In addition, surface processes involving place-exchange were considered to take place simultaneously to the oxidation process, starting at a relatively low OH_{ads} coverage (θ > 5 %) [5, 8-10]. Other views have appeared too, considering that oxide without formation of OH_{ads} intermediate [11-13], but, again, above 700 mV vs. RHE. Other arguments came from the researcher working on COOR and low-molecular alcohols oxidation. Namely, in COOR experiments OH_{ads} was considered to react with CO_{ads} in a chemical Langmuir-Hinshelwood reaction [3, 14, 15]. The onset potential for COOR was found to be much lower than the "standard" onset potential for surface oxidation (150 mV vs. RHE for carbon-supported Pt [16]), leading to a conclusion that certain amount of OH_{ads} must be present at such low potentials where, in general, only H adsorption/desorption was considered to take place.

The role of OH_{ads} in ORR was a subject of a number of thorough studies [17-25]. Systematic studies of Markovic and Nørskov groups [17-20], combining electrochemical and ultra-high vacuum (UHV) techniques with theoretical density functional theory calculations, unveiled that OH adsorbed on Pt-based electrocatalysts surfaces acts as a spectator specie, while the metal – OH bond strength ($E_{M\text{–}OH}$) can be used as a catalytic descriptor. On the other hand, some evidences were provided that OH adsorption produced electronic effects, unwanted of a spectator only [21]. The work of Zhang et al. [22] related to a supported monolayer electrocatalysts, offered an another explanation of high electrocatalytic activity of Pt surfaces, invoking OH – OH repulsive force to be of a great importance. Extensive work of Gottesfeld [23] offers another important view. The author argued that a correct prediction of ORR activity (at a fixed potential) must account for both site availability and intrinsic catalytic activity, the former one being determined by standard potential of surface oxidation ($E^{o}_{\text{surface redox couple}}$), while the latter one being determined by ORR activation energy on clean surface (ΔH^{*}_{act}). Finally, Gottesfeld proposed that the quantity defined by $1/(1+Z)\exp(-\Delta H^{*}_{act}/RT)$ should be used for prediction of electrocatalytic activity at a specified potential E, where Z stands for $\exp(F(E - E^{o}_{\text{surface redox couple}})/RT)$. The work of Gottesfeld proposed intrinsic ORR Tafel slope to be 120 mV dec^{-1}, while the lower slope (60 mV) should be attributed to the action of $1/(1+Z)$ term, i.e. to the induced coverage changes in the kinetically controlled ORR region. This viewpoint was also supported by the work of Adzic's group [24]. The work of Arenz and Markovic [25], trying to reconcile different results of RDE (rotating disk electrode) and PEMFC (polymer electrolyte membrane fuel cell) studies, offered another viewpoint, claiming that intrinsic ORR Tafel slope on Pt should amounts to 60 mV dec^{-1}, while the higher values should be attributed to an artifact related to the problems of accurate kinetic analysis in the region of mixed kinetic-diffusion control, as well as to an inappropriately compensated electrolyte resistance. The later authors proposed guidelines for determining the activity of cathode catalysts *via* RDE measurements, and provided benchmark activities for ORR on Pt(111), Pt(100), Pt(110) and Pt-poly. As stated by Arenz and Markovic, well-established benchmark activities are necessary in order to have reliable comparison of activities of new electrocatalysts developed in different research groups [25]. Proposed guidelines for the measurement of ORR activity are closely connected to the problem of proper comparison of the results of different authors.

Typical ORR activity measurement *via* RDE is done in potentiodynamic regime, while background and ORR currents are recorded at the same potential sweep rate to enable correct subtraction of capacitive currents. Usually, when searching through the ORR literature, one finds that these experiments are done at 10, 20 or 50 mV s^{-1}, in the potential window between hydrogen evolution and extensive surface oxidation, i.e. from ~0.05 to 1 – 1.2 V *vs*. RHE.

In the current literature the consensus exists that oxide formation attenuates ORR on Pt surface. However, in the Gottesfeld's study [23], one simple question with no simple answer was raised: what is the nature of Pt surface in the region where initial stages of oxide formation take place (and ORR terminates)? A reasonable answer assumes that the time effects during surface oxidation process should play a role, causing that the kinetic and the thermodynamic parameters of surface oxidation may not be considered separately, what in turn should hold also to ORR. We emphasize this point in view of the fact that all the parameters mentioned thus far in the literature as predictors for ORR activity were essentially thermodynamic ones. First indications of the time effects were provided by Gasteiger et al. [26] and by Adzic's group [27]. The latter authors used RDE chronoamperometry and RDE voltammetry to demonstrate time and potential sweep effects on ORR voltammograms. Although clearly evidenced, such effects have not been discussed in many details.

In this contribution we demonstrated that time effects of oxide formation on Pt-poly in potentiodynamic experiments manifest themselves in ORR kinetics. Polycrystalline platinum (Pt-poly) was chosen for consideration in order to i) obey the nature of carbon-supported Pt nanoelectrocatalysts, and ii) to avoid complications connected to the catalyst loading and interparticle spacing characteristic of carbon-supported electrocatalyst [28]. In addition, Pt-poly electrodes with rather large real surfaces were prepared in order to diminish the effects of possible contamination of the electrode, as suggested by Gasteiger et al. [26]. The obtained results provided a basis for the discussion of different viewpoints on the application of Tafel slope as a diagnostic parameter of the mechanism of ORR. Throughout this text we rely to the picture of Pt oxidation process set by Conway and co-workers between 1970s and 1990s.

2. EXPERIMENTAL

The Pt-poly disk electrodes were prepared by potentiodynamic cycling of Pt disk electrode in 1.8 mM H_2PtCl_4 solution. Usually, 25 cycles with the sweep rate of 50 mV s^{-1} were performed. After platinization, electrodes were washed in deionized water stream and transferred into the cell filled by the de-aerated electrolyte solution (0.1M $HClO_4$ or 0.05 M H_2SO_4) and cycled between -0.25 and 1.15 V *vs*. SCE at 200 mV s^{-1} until stable cyclic voltammogram was obtained. After this surface stabilization, electrolytic solution was replaced by a fresh one. Blank cyclic voltammograms were recorded in N_2–purged 0.1M $HClO_4$ or 0.05 M H_2SO_4 with sweep rates from 200 to 10 mV s^{-1}, while ORR experiments were undertaken in the same solutions saturated with high purity O_2 with sweep rates amounting to 10, 20 and 50 mV s^{-1} and at electrode rotation rate of 600 rpm. In order to confirm that changes of recorded ORR currents under different sweep rates are not due to the changes of the electrode active surface in ORR operating conditions nor contamination, ORR currents have been recorded in the following cycle: 50 mV $s^{-1} \rightarrow$ 20 mV $s^{-1} \rightarrow$ 10 mV $s^{-1} \rightarrow$ 20 mV $s^{-1} \rightarrow$ 50 mV $s^{-1} \rightarrow$ 20 mV $s^{-1} \rightarrow$ 10 mV s^{-1} and their reproducibility was verified. Unless specially noted, presented ORR currents are recorded by sweeping potential in positive direction, starting from oxide-free surface towards oxide-covered surface.

All experiments were carried out at room temperature in a glass three-electrode electrochemical cell with Pt foil and double junction saturated calomel electrode (SCE) as counter and reference electrode, respectively. The instrument used was Gamry PCI4/750 potentiostat/galvanostat equipped with Pine rotator.

3. RESULTS AND DISCUSSION

3.1. Blank cyclic voltammograms of Pt-poly in acidic solutions and time effects during oxide formation in potentiodynamic regime

Blank cyclic voltammograms of Pt-poly in a given electrolyte actually represent adsorption isotherms, revealing different potential-dependent adsorption processes taking place on the electrode surface. Comparison of cyclic voltammograms recorded in $HClO_4$ and H_2SO_4 (Fig. 1) reveals, so far well established, differences regarding oxide formation and the effects of strongly adsorbing bisulfate ions. Oxide formation, evidenced on the CV curve as a deviation from extrapolated double layer region, in 0.05 mol dm^{-3} H_2SO_4 solution is shifted for ~100 mV due to anion adsorption, in comparison to 0.1 mol dm^{-3} $HClO_4$ (Fig. 1). Interesting behavior is observed if one takes a look on the corresponding differential coefficients of electrochemical adsorption isotherm, defined as $I(E)/v$ (v is the sweep rate, dE/dt) [5], as a function of applied potential, or integrated charge curves:

$$Q = \int_{E_1}^{E_2} \frac{I}{v} dE \qquad (1)$$

obtained with different sweep rates. Alternatively, apparent surface coverage θ can be evaluated using Eq. 1 and calculating Q/Q_H, where Q_H is total charge associated with hydrogen adsorption/desorption (Fig. 2).

As can be seen, upon progressive reduction of the sweep rate, more OH/O species are allowed to gather on the surface in the course of anodic scan. Such behavior can be understood quite well on the basis of a large body of experiments related to oxide formation on Pt surface, performed in the second half of 20th century [5].

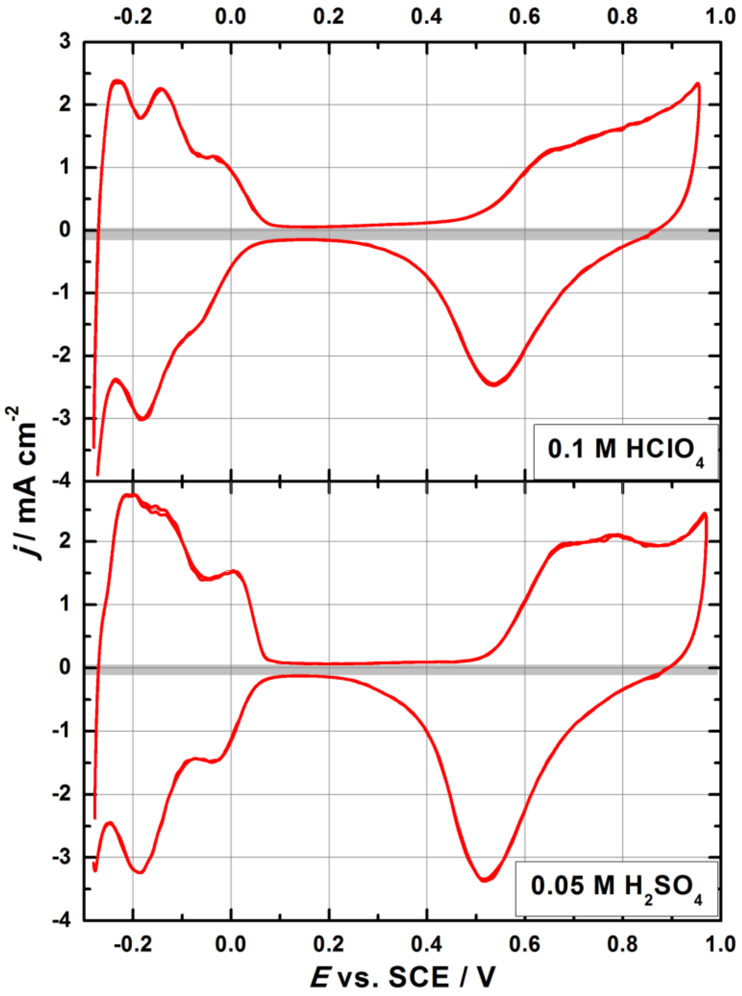

Figure 1. Blank cyclic voltammograms of Pt-poly electrodes recorded in N_2-purged 0.1 mol dm^{-3} $HClO_4$ (top) and 0.05 mol dm^{-3} H_2SO_4 (bottom); sweep rate 100 mV s^{-1}. Thickness of double-layer region is designated by gray shading.

The formation of surface oxide species on Pt is inevitably followed by a certain degree of irreversibility in CV experiments. The explanation of such behavior was sought in (slow) post-electrochemical process following fast initial formation of adsorbed OH, allowing deposition of much more OH/O species at a given potential than expected from a (reversible) 2D processes described by either Frumkin ($g \neq 0$) or Langmuir ($g = 0$) isotherm:

$$\frac{\theta}{1-\theta} = K_c \exp\left[\frac{F \cdot E}{R \cdot T} - g \cdot \theta\right] \tag{2}$$

Post-electrochemical process which was identified as being responsible for such behavior is place-exchange between initially adsorbed OH species and Pt atoms in the surface. As overviewed by Conway [5] place-exchange process starts to take place already at low coverage of approx. 5 – 15%. Place-exchange process has one interesting consequence: irreversibility of oxide formation on Pt is more pronounced with slower sweep rates in CV experiments as more time is left to surface oxide phase for place-exchange, as observed by Everett [9] some 50 years ago. Previously reported work on Pt-poly oxidation agrees that limiting amount of oxide formed on Pt-poly, after the appropriate correction for real surface area change, amounts to 880 μC cm^{-2} [5,29], corresponding to two equivalent Pt-O layers, or $Q/Q_H \approx 4$.

Different behavior of Pt-poly in $HClO_4$ and H_2SO_4 can be ascribed to difference in anion adsorption, where bisulfate ions are strongly bounded to the surface. In the absence of strongly adsorbed bisulfate ions (i.e. in $HClO_4$ solution) surface oxidation process commences at ~0.4 V *vs*. SCE (~0.7 V vs. RHE). The change of the sweep rate does not affect the onset potential of oxidation and the effect of sweep rate remains to be only the variation in the amount of oxide formed at a given potential, which can be ascribed to the place-exchange between the Pt atoms and the electroformed OH/O surface species. In contrast to an $HClO_4$ solution, strongly adsorbed bisulfate ions depress the surface oxidation process while lower amount of oxide is formed at the same potential when compared to Pt-poly in $HClO_4$ solution. Providing, by lower sweep rate, to the electrode to spend more time within an unchanged potential window, the onset potential for surface oxidation is being shifted to lower potentials, enabling more oxide to be formed.

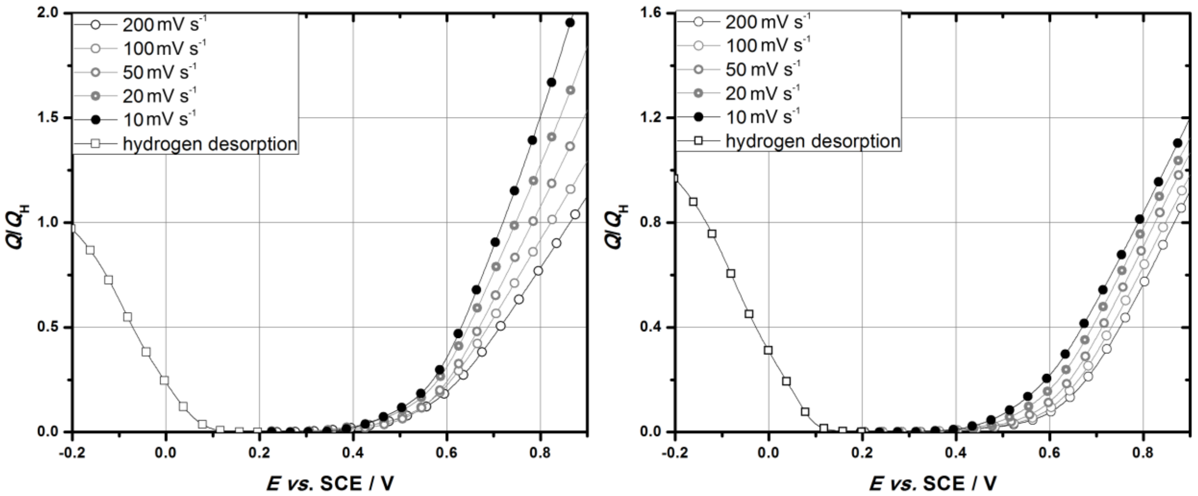

Figure 2. Total apparent surface coverage θ of Pt-poly electrode evaluated as Q/Q_H from the region of hydrogen desorption to extensive Pt oxide formation in 0.1 mol dm^{-3} $HClO_4$ (left) and 0.05 mol dm^{-3} H_2SO_4 (right). Different sweep rates are designated in the figure.

This can be explained again by time effects. In the presence of strongly adsorbing bisulfate ions, if more time is provided, the initial stages of oxide formation may be followed by desorption of bisulfate ions, and therefore, by place exchange process, higher amounts of oxide may be deposited on the electrode surface at the same potential, according to the equations:

$$(Pt_xA^-) + H_2O \rightarrow (x-1)Pt + PtOH + A^- + e \qquad (3a)$$

$$(x - 1)[Pt + H_2O \rightarrow PtOH + H^+ + e] \qquad (3b)$$

where A^- stands for strongly adsorbing bisulfate ion and x for the number of Pt sites occupied by the anion [30]. Nevertheless, a possibility that certain amount of bisulfate ions inserts within the oxide layer even at low sweep rates cannot be disregarded.

The kinetic effects of oxide formation demonstrated here must be accounted for in any discussion of Pt surface activity towards ORR. Namely, it is obvious that under potentiodynamic conditions one can, to a certain degree, control the state of surface oxide phase and stimulate both place exchange and ion adsorption/desorption processes, simply by tuning potential sweep rate. These effects arise within the timeframes in which ORR activity is evaluated using RDE technique coupled with cyclic voltammetry. This observation is supported by recent finding of Björling and Feliu [31] who quantified place-exchange process on Pt(111) in H_2SO_4 solution. The authors derived characteristic time constants which describe defect formation and place-exchange process on Pt(111) in potential-step experiments being of the order of 10^0 - 10^1 s, which matches the time frames in which Pt-poly spends under oxidation conditions during cyclic voltammetry experiment for ORR activity assessment (Section 3.2). In addition, it was assumed that the presence of various types of defects on Pt surfaces supports the formation of hydroxyl [31], which might indicate that this characteristic time constants might be even lower on a Pt-poly and supported Pt electrocatalysts than on a Pt(111) surface. Although the time effects we evidenced appear to be a quite undesired complication, it nevertheless could be used as a basis for discussion of different viewpoints about the ORR mechanisms on Pt surfaces [20,23-25], as will be done in the next sections.

3.2. ORR RDE currents on Pt-poly recorded in potentiodynamic regime

The differences are observable in the starting regions of ORR RDE currents recorded at different sweep rates in both 0.1 mol dm^{-3} $HClO_4$ (Fig. 3, left) and 0.05 mol dm^{-3} H_2SO_4 (Fig. 4, left). These differences in ORR currents should be discussed in conjunction with both the corresponding mass-corrected Tafel plots (Figs. 3 and 4, right) and the previously discussed oxidation state of Pt-poly surface in corresponding solutions (Section 3.1, Fig. 2).

First of all, in 0.1 mol dm^{-3} $HClO_4$ solution, the region of diffusion control becomes shorter when the sweep rate decreases. This can be correlated to an increasing amount of surface oxide evidenced in the integrated blank cyclic voltammograms (Fig. 2, left). The corresponding mass-corrected Tafel plots display sensitivity toward the sweep rate. In all three observed cases, double slope Tafel plots are evidenced, somewhat variable in values.

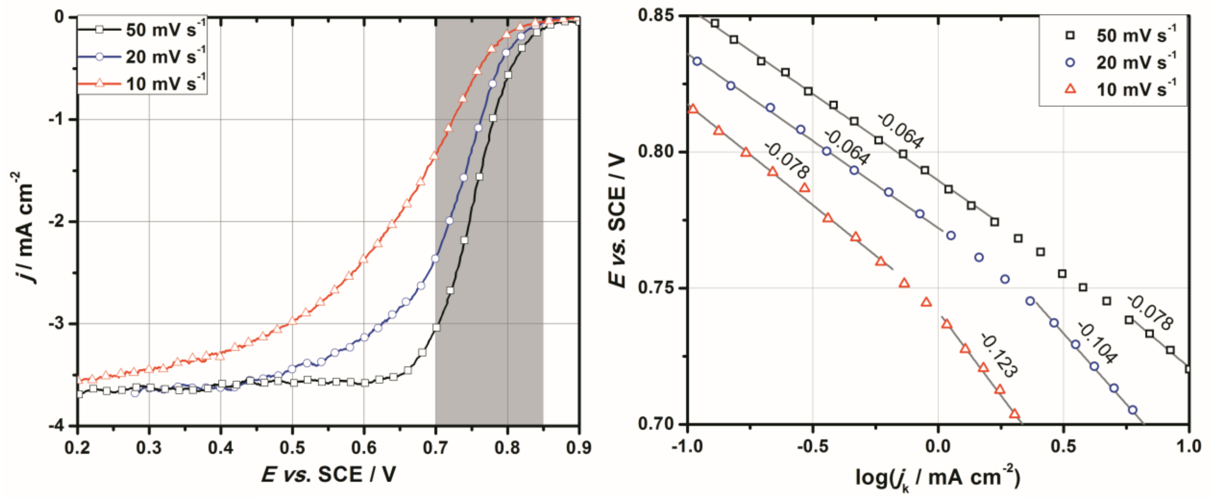

Figure 3. Background-corrected ORR-RDE currents recorded at Pt-poly in 0.1 mol dm^{-3} $HClO_4$ at different sweep rates (rotation rate 600 rpm) (left) with designated potential window where Tafel analysis is performed and corresponding mass-corrected Tafel plots (right).

For the scan rate 50 mV s^{-1}, the Tafel slope changes from -0.064 V to -0.078 V, in low- and high –current regions, respectively. These values do not differ much from the one reported by Markovic et al. [32], amounting to -0.076 V dec^{-1} for Pt(111) surface in 0.1 mol dm^{-3} $HClO_4$ solution in the region of kinetic control ($j_k > 0.2$ mA cm^{-2}), at a scan rate of 50 mV s^{-1}.

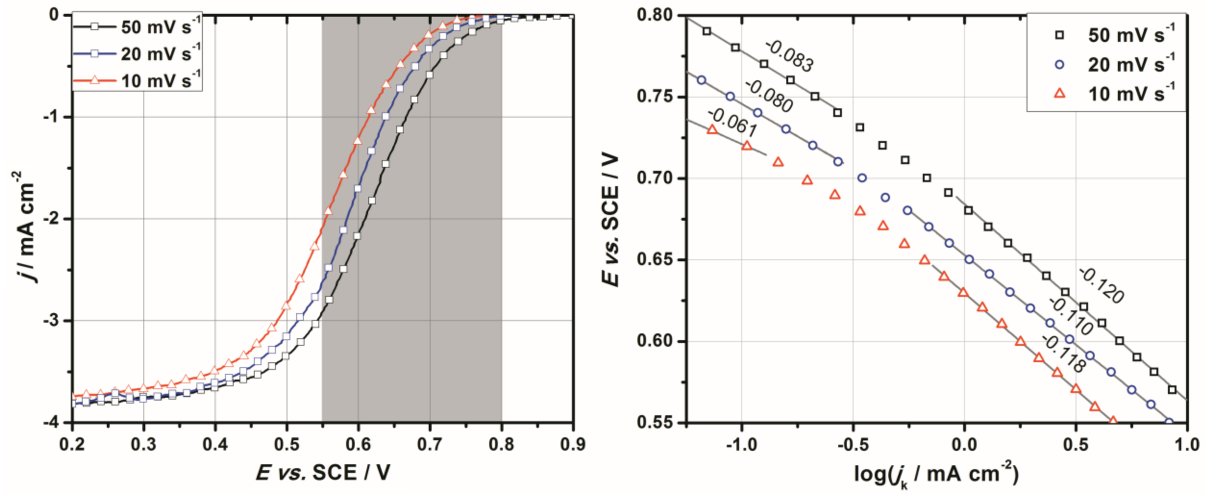

Figure 4. Background-corrected ORR-RDE currents recorded at Pt-poly in 0.05 mol dm^{-3} H_2SO_4 at different sweep rates (rotation rate 600 rpm) (left) with designated potential window where Tafel analysis is performed and corresponding mass-corrected Tafel plots (right).

Upon decreasing the sweep rate, Tafel slopes decreased too, amounting to -0.078 and -0.123 V dec^{-1}, when recorded at the sweep rate of 10 mV s^{-1} (Fig. 3). This may be correlated to the changes of the state of the surface (Section 3.1). Namely, when potential is swept at a rate 10 mV s^{-1}, in the potential region of both pure kinetic and mixed kinetic-diffusion control of ORR, electrode surface is not clean but significantly altered by place exchange processes, consisting of Pt-O layer with a fraction of reversibly adsorbed OH on top of it. These results agree perfectly with the ones of Wang et al. [27], where similar effects were evidenced in both potentiostatic and potentiodynamic conditions. A brief analysis shows that the observed decay of hronoamperometric currents recorded in the region of mixed kinetics of ORR [27] roughly follows a logarithmic law, which can be attributed to a surface oxide growth on Pt [5]. In addition, the effects of sweep rate on the kinetic parameters of ORR on Pt-based catalysts were recognized by Gasteiger et al. [26], and attributed to a hysteresis in the adsorption of oxygen containing species on Pt. Slow oxide formation was considered by Jarvi et al. [33] to be responsible for significant initial time decay of activity of cathode catalysts in PEMFCs at 0.9 V.

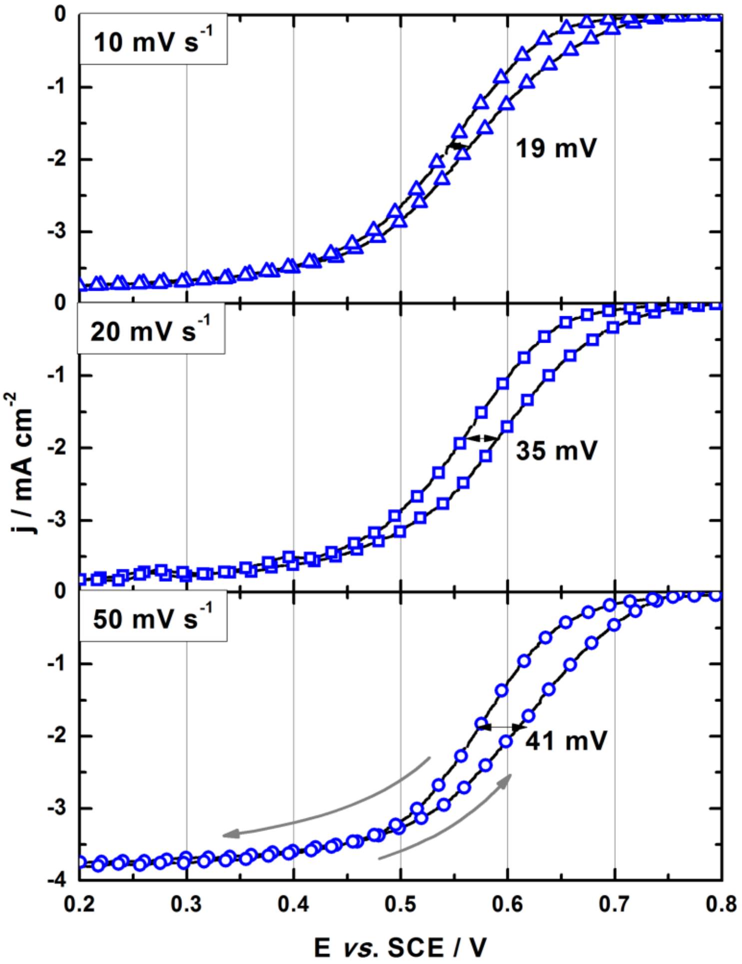

Figure 5. Background-corrected ORR-RDE currents recorded at Pt-poly in 0.05 mol dm^{-3} H_2SO_4 at different sweep rates (rotation rate 600 rpm) where both positive and negative going sweeps are indicated.

The here provided results support in a quantitative manner the statement that intrinsic Tafel slope for ORR on clean Pt is -0.120 V dec^{-1}, while deviations from this value should be ascribed to the potential-dependent changes of the number of available reactive surface sites, as indicated in earlier studies [23,24].

Yet again, behavior of Pt-poly in 0.05 mol dm^{-3} H_2SO_4 in ORR condition is very different from the case when ORR is investigated in 0.1 mol dm^{-3} $HClO_4$ (Fig. 4, left). Here we found that Tafel slope in high current density region varies between -0.110 and -0.120 V dec^{-1}, while in low current density region it increases from -0.083 V dec^{-1} to -0.061 V dec^{-1} when decreasing sweep rate from 50 to 10 mV s^{-1} (Fig. 4, right). When high sweep rate is applied Tafel slope changes from -0.120 V dec^{-1} to -0.083 V dec^{-1}. According to literature reports ORR Tafel slope in H_2SO_4 does not deviate from its intrinsic value (-0.120 V dec^{-1}). Such behavior of Pt electrode was ascribed to adsorption of bisulfate which saturates at a low potential, resulting in both site-blocking and electronic effects which remain nearly constant over the region of mixed control, holding Tafel slope close to -0.120 V dec^{-1} [27]. Nevertheless, if enough time is provided during potential sweep, strongly adsorbed bisulfate ions can be replaced by OH_{ads} followed by place exchange process as discussed earlier (Section 3.1), allowing ORR to take place at oxide-modified surface which, at least partially, resembles the one formed in the electrolytic solution free of strongly adsorbing ions. This can explain change of Tafel slope from -0.061 to -0.118 V dec^{-1} obtained with the sweep rate 10 mV s^{-1}, which should be expected in the absence of strongly adsorbing bisulfate ions.

The presented results indicate that under potentiodynamic conditions commonly used for evaluation of ORR activity of Pt–based electrocatalysts, surface of the catalyst cannot be considered as a static Pt surface covered to a certain extent with O_{ads} and OH_{ads}. On the other hand, provided results might account for wide range of values of Tafel slopes found experimentally. As demonstrated, kinetics of Pt surface oxidation process is extremely sensitive on the actual conditions during potentiodynamic experiment which in turn can favor certain surface processes such as place-exchange and ion adsorption/desorption. This can further result in the values of Tafel slope anywhere between -60 and -120 mV dec^{-1}, practically independently on the nature of electrolytic solution. Hence, if one uses a Tafel slope as a diagnostic parameter extreme caution must be taken if comparing different Pt-based surfaces in order to have similar oxidation conditions of different surfaces. In addition, we expect that surface oxidation process must be extremely sensitive on the size and shape of nanoparticle, and that the same potentiodynamic conditions can result in very different state of various electrocatalysts' surfaces during OH/O deposition.

When estimating ORR activity, usually positive going sweep is analyzed as, in this case, activity is not affected by oxide layer which is slowly removed when potential is decreasing. However, analyzing both positive and negative going sweep it can be observed that curves do not match and certain hysteresis is present (Fig. 5). This is commonly ascribed to slow removal of surface oxide which hinders ORR during negative going sweep.

As a measure of ORR activity different quantities are provided, such as half-wave potential ($E_{1/2}$) or mass-transfer corrected kinetic current at specified potential (usually at $E > E_{1/2}$) which can be normalized with respect to electrochemical active surface area or mass of Pt catalyst on the electrode [25]. However, these quantities are also dependent on the sweep rate (Table 1).

Table 1. Half-wave potential ($E_{1/2}$), hysteresis width and kinetic current for ORR measured in 0.1 M $HClO_4$ and 0.05 M H_2SO_4 at different sweep rates and unique rotation rate of 600 rpm. All potentials are referred to SCE.

Sweep rate, mV s^{-1}	0.1 M $HClO_4$			
	$E_{1/2}$ (+)* / mV	$E_{1/2}$ (-)* / mV	Hysteresis width** / mV	j_k (725 mV) / mA cm$^{-2}_{geo}$
10	613	546	67	-0.407
20	678	562	116	-0.647
50	722	591	131	-1.517
	0.05 M H_2SO_4			
	$E_{1/2}$ (+)* / mV	$E_{1/2}$ (-)* / mV	Hysteresis width** / mV	j_k (650 mV) / mA cm$^{-2}_{geo}$
10	563	544	19	-0.630
20	591	556	35	-1.080
50	614	573	41	-1.644

* + and – denote positive and negative going sweep, respectively
** measured as a difference of $E_{1/2}$ (+) and $E_{1/2}$ (-)

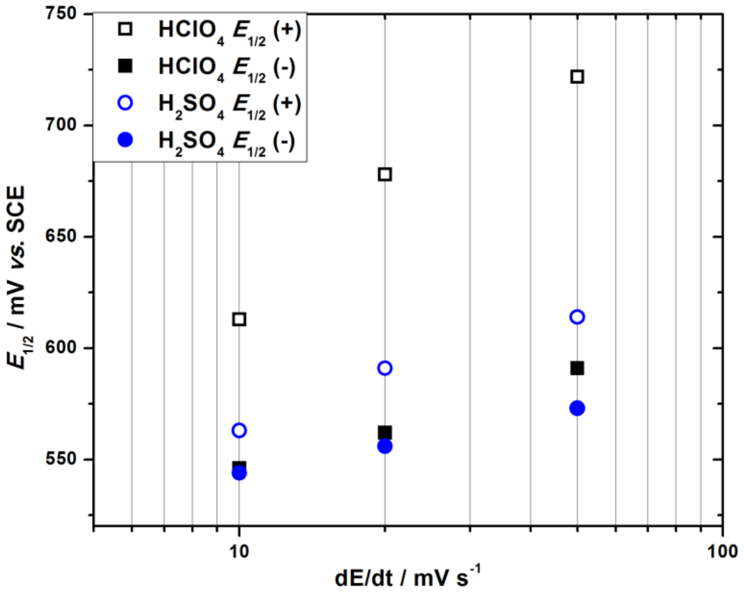

Figure 6. Dependence of the half-wave potential ($E_{1/2}$) for ORR on Pt-poly electrode on the potential sweep rate (d*E*/d*t*, *v*) in potentiodynamic experiment.

If observed differences are to be related to OH deposition/oxide growth one should expect that measured quantities should depend on the potential sweep rate in a similar manner as oxide growth. As potentiostatic experiments demonstrated logarithmic law for oxide growth on Pt [5] it is quite logical to expect that $E_{1/2}$ should be proportional to the logarithm of potential sweep rate. Indeed, such behavior is observed (Fig. 6).

It should be noted that, as defined, hysteresis width for ORR is highly dependent on the vertex anodic potential and its detail analysis might reveal important peculiarities of oxide growth on Pt and Pt-based surfaces which closely relate to ORR activity of these surfaces.

3.3. Practical vs. theoretical aspects

Practical aspects of provided results are quite clear: the same Pt catalyst will display different ORR activities if evaluated under different potentiodynamic conditions using RDE technique. Inspection of ORR currents presented in Figs. 3 and 4 points that differences in ORR activities (j_k, Table 1) could reach a factor of 2-3 or even more. Gasteiger et al. [26] reported both specific and mass activities of a series of various carbon-supported Pt catalysts obtained at 20 and 5 mV s^{-1} in 0.1 M $HClO_4$ at 60 °C, and the activities measured at 20 mV s^{-1} are typically higher than the corresponding activities at 5 mV s^{-1}. The same authors reported the activities of smooth Pt-poly disks (roughness factor lesser than 1.2) and the specific activities estimated from CV measurements at 20 mV s^{-1} are approximately twice the ones estimated from the experiments performed at 5 mV s^{-1}. Furthermore, benchmark ORR activities provided by Arenz and Markovic [25] were evaluated from potentiodynamic ORR curves recorded at 50 mV s^{-1} on single Pt(hkl) electrodes (h, k, l = 0, 1), which, according to here presented results, gives high ORR activity for particular electrocatalyst. This issue might be resolved if one more guideline is added to the list provided by Arenz and Markovic [25] with two possible options arising here. The first one is that ORR activity evaluation using RDE technique is always performed using the same potential sweep rate. In this sense differences in electrocatalytic activity can arise due to different thermodynamics of OH/O deposition but also the kinetics regarding surface restructuring processes. Another possibility, which is more complicated, but possibly more accurate, is to set potentiodynamic conditions during ORR measurements in such a way that the surfaces of studied electrocatalysts are in the same conditions, i.e. the same amount of oxide is formed on the surface. In this way intrinsic activities of different catalyst could be compared.

As explained by Gotesfeld [23], ORR rate expression, considering site blocking effect invoked by oxygen-species adsorption, is assumed to be:

$$j_{ORR} = j_0 \cdot (1-\theta) \cdot \exp\left\{-\frac{E-E^0}{b_{\mathrm{int}}}\right\} \tag{4}$$

where θ is the coverage by chemisorbed oxygen at potential E, and b_{int} is the intrinsic value of the ORR Tafel slope that would be measured at a Pt metal surface free of any blocking surface species. This intrinsic value of Tafel slope is taken to be 120 mV dec^{-1}, as mentioned earlier, while in this picture Tafel slope is determined by:

$$\frac{d(\log j_{ORR})}{d(E^0-E)} = \frac{1}{b_{\mathrm{int}}} + \frac{1}{1-\theta}\frac{d\theta}{dE} \tag{5}$$

The deviation of Tafel slope from its intrinsic value of 120 mV dec^{-1} is explained by the second term on the right-hand side of Eq. 5, resulting in apparent Tafel slope values below 120 mV dec^{-1}. This picture was supported by the work of Uribe et al. [34] who demonstrated the change of ORR Tafel slope from 120 mV dec^{-1} at clean Pt surface to its apparent value of 60 mV dec^{-1} at oxygen covered surface. The rate expressions similar to Eqs. (4) and (5) were also used to reconcile different values of ORR reaction order with respect to O_2 reported in the literature [23]. Uribe et al. [34] equalized the number of electrons passed through surface/electrolyte interface to the number of OH_{ads} at Pt surface sites, deriving surface coverage from voltammetric experiments to saturate at $\theta = 1$. However, saturation of surface coverage by adsorbed species at $\theta = 1$ is not plausible in the case of Pt-poly. Jerkiewicz et al. [13] combined cyclic-voltammetry, *in situ* electrochemical quartz crystal nanobalance and *ex situ* Auger electron spectroscopy measurements to show that charge associated with Pt-poly oxidation (in H_2SO_4) increases almost linearly, starting from surface oxidation onset potential (~ 0.85 V *vs*. RHE) to ~370 μC cm^{-2} at 1.40 V *vs*. RHE (recorded at 50 mV s^{-1}). These values correspond well to the ones in Fig. 2 (right). In addition, surface oxidation was found to proceed by a progressive coordination of O-containing species to the Pt substrate [13], while place-exchange process was proposed to take place at potentials above 1.15 V *vs*. RHE (i.e. ~0.85 V *vs*. SCE). In this sense, the actual state of the polycrystalline surface in the potentiodynamic experiment cannot be fully assessed, and the actual meaning of the second term at the right-hand side of Eq. (5) is somewhat indistinct, mostly due to the uncertain meaning/value of θ. Having in mind the potentiostatic experiments presented by Adzic's group [27] regarding chronoamperometric ORR transients, the evidences provided by Gasteiger et al. [26], the paper by Mentus et al. [35] considering the Pd/TiO_2 composite, and the results presented here, it appears that only true constant in Eq. (5) is b_{int}, while both left-hand side and the second term on the right-hand side of Eq. (5) should be considered rather as a function of time. ORR rate expression for stationary conditions can be colloquially rewritten as:

$$\frac{d(\log j_{ORR})}{d(E^0 - E)}(t) = \frac{1}{b_{\mathrm{int}}} + \frac{1}{1-\theta}\frac{d\theta}{dE}\cdot F(t) \tag{6}$$

in order to account for unavoidable time effects being present. The actual form of $F(t)$ depends on the state of the surface, presence of strongly adsorbing ions, as well as on the conditions to which electrode surface was subjected during potentiodynamic experiment. A question arises whether there is a proper basis to use ORR Tafel slope as diagnostic parameter regarding the actual ORR mechanism on a "restless" surface such as Pt-poly. At this point, it appears to be more sustainable that the measured values of Tafel slope reflect the state of the surface and its time- and potential- dependent rate of change, rather than the mechanism of ORR taking place at the same surface.

4. CONCLUSIONS

The effects of sweep rate on the kinetic parameters of ORR on Pt-poly electrode surfaces were considered quantitatively for the first time by means of RDE voltammetry in both 0.1 M $HClO_4$ and

0.05 M H_2SO_4 solutions. Following the qualitative literature indication, these effects were in this study correlated quantitatively to both the surface oxide formation and the adsorption of supporting electrolyte anions. By changing the sweep rate, the electrocatalytic performance of the same Pt-poly electrode toward ORR was altered. It appears that the time scales of surface reorganization processes match the ones of the potentiodynamic experiment in which ORR activity is evaluated, having huge effect on the results of the particular measurement. As worth mentioning, higher sweep rate provided an improved apparent ORR activity: the rate of ORR measured at 50 mV s^{-1}, can be two to three times higher than the one measured at 10 mV s^{-1}. The implication of these results can be divided in two groups. From the practical point of view, there is a necessity to add some more guidelines for ORR performance assessment of PEMFC catalysts: the rate of ORR on Pt surface should be estimated either by using the same sweep rate (which can be arbitrary selected), or by setting the unique initial state of the surface in all cases intended to be compared. From the theoretical point of view, in an estimation of kinetic parameters of ORR, if guided at different sweep rates, the experimenter must account with the differences in the state of the catalyst surface, which is both potential- and time-dependent. In this way, the Tafel slope of ORR on the clean Pt electrode surface can be considered to be intrinsically 120 mV (corresponding to oxide-free Pt state observable the region of mixed kinetic control of ORR) while the values between 120 and 60 mV, may be found in the region of kinetic control of ORR, as the results of the time dependent site blocking/surface reorganization processes, the most appropriately described by the work of Uribe et al. [34] and elaborated by Gotesfeld [23]. This study demonstrated that the measured values of the Tafel slope reflect the state of Pt surface and its dynamics rather than the mechanism of ORR on the observed surface.

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