

Review

Electrochemical Methods of Real Surface Area Determination of Noble Metal Electrodes – an Overview

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The electrochemical methods of real surface area determination of noble metal electrodes and their alloys are summarized. These methods utilize hydrogen adsorption, surface oxide reduction, double layer capacitance, adsorbed carbon monoxide stripping and underpotential deposition of metals. The principles, advantages and limitations of the methods are discussed. The examples of their use are shown. The comparison between various methods is presented.

Keywords: Real surface area; Noble metals; Alloys; Electrodes; Adsorption

1. INTRODUCTION

Noble metals and their alloys have been intensively studied as electrode materials for electrocatalytic purposes [1-35]. They possess the ability to adsorb various species on their surfaces and to facilitate various reactions that are of great importance in the context of energy conversion, in particular, in fuel cells. For many years it has been known that platinum and its alloys are excellent catalysts for hydrogen oxidation/evolution reaction (HOR/HER) [1-4, 32] and oxygen reduction reaction (ORR) [5-7, 16, 18, 33] as well as for the oxidation of small-molecule alcohols, like methanol and ethanol [8-15, 17, 19, 23, 25, 26]. On these processes the work of low-temperature fuel cells (Direct Alcohol Fuel Cells, Proton Exchange Membrane Fuel Cells) is based. On the other hand, palladium exhibits good catalytic properties in the process of formic acid oxidation, which recently has often been regarded as an alternative fuel for methanol or ethanol [20, 27-31, 34, 35]. Pd and Pt are also components of the catalyst for automotive exhausts, especially for NO reduction [36]. Moreover,

palladium is an efficient hydrogen absorber [37] and is treated as a model system for other hydrogen-absorbing materials [38]. The examination of the behavior of the palladium-hydrogen systems allows us to understand better the processes occurring in other metal-hydrogen systems, which are utilized in many fields of science and technology, e.g. in Ni-MH cells [38] or as hydrogen storage materials [39].

One of the most important parameters characterizing the surface of solid electrodes is the real surface area (RSA) [40-42]. In contrast to liquid electrodes (i.e. mercury), the surface of a solid electrode is always not smooth and its real area exceeds the geometric one [40]. In the case of electrocatalytic materials the RSA may be even 1000 times greater than the geometric area [43] and differs for different electrodes. The ratio between the real and geometric area is called "roughness factor", R_F . Since the catalytic processes occur on surface active centers, all the extensive quantities obtained in an experiment, such as electric current, electrode reaction rates and other interfacial parameters have to be normalized with respect to the RSA. Therefore, the precise knowledge on the value of RSA is crucial for the comparison of the behavior and activity of various catalytic systems examined in various laboratories. The possibility of the RSA monitoring during the experiment is also important under conditions where the experiment itself may alter the electrode surface state [41]. By measuring the loss of the catalyst active area one can check the catalyst durability during its operation, e.g. in a fuel cell [44].

Numerous methods of the RSA determination for various materials have been summarized by Trasatti and Petrii [40]. In this review we limit to the in situ methods of the RSA determination of polycrystalline noble metal electrodes and their alloys in acidic environment. We purposely limit our discussion to polycrystalline materials due to their high practical importance in electrochemical power sources.

Under the term "RSA" we mean the true, electrochemically active surface area (ECSA). We characterize the main procedures based on such electrochemical phenomena as hydrogen adsorption, surface oxide reduction, double layer capacitance, adsorbed CO stripping and underpotential deposition of metals. The principles, advantages and limitations of these methods are discussed and the comparison between various methods is made. We believe that a careful systematisation in this field is required and hope that our paper may help other researchers in the choice of a proper method of the RSA determination for the materials studied.

All figures demonstrated in the following review show electrochemical behavior of polycrystalline Pt electrodes as an example of well-known, typical trends of volt-ampereometric responses presented by noble metals in various environments. The plots were prepared using data collected by authors and presented in the form, which, authors believe, is the most suitable for the illustrative purposes. They have not been published before.

2. HYDROGEN ADSORPTION

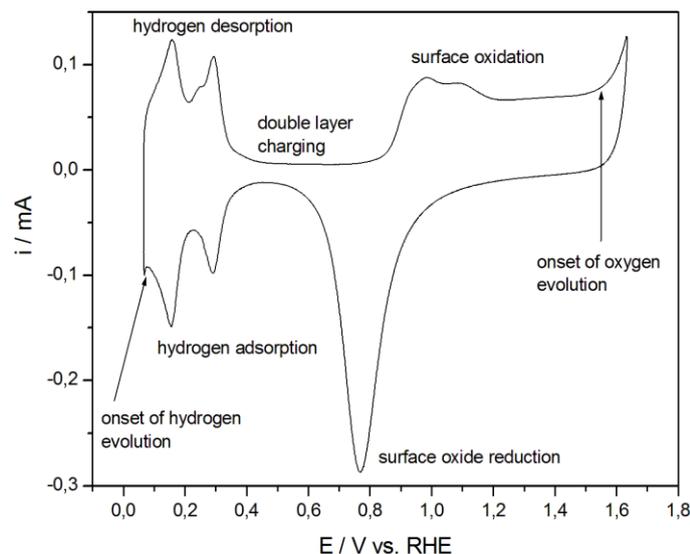


Figure 1. Cyclic voltammogram (scan rate 0.1 V s^{-1}) recorded for a polycrystalline Pt electrode in $0.5 \text{ M H}_2\text{SO}_4$ (temperature 298 K).

Fig. 1 presents a cyclic voltammetric curve for a polycrystalline Pt electrode in $0.5 \text{ M H}_2\text{SO}_4$. Its well-known course has been widely discussed in the literature [41]. Three potential ranges can be distinguished here, namely:

- a region of hydrogen adsorption/desorption (so-called “hydrogen region”)
- a region of surface oxide formation/reduction (so-called “oxygen” or “oxide region”)
- a region free from faradaic processes (so-called “double layer legion”)

The most important facts concerning the electrochemistry of a Pt electrode in the hydrogen region can be summarized as follows:

- 1) Hydrogen adsorption on Pt starts at potentials positive to the reversible potential of the H^+/H_2 redox couple, preceding the process of molecular hydrogen evolution, therefore it can be regarded as a particular case of underpotential deposition phenomenon (UPD);
- 2) The process is fast and electrochemically reversible, the equilibrium surface coverage depends on electrode potential;
- 3) Various forms of adsorbed hydrogen are observed, namely the strongly and weakly adsorbed H species.

Similarly to Pt, the phenomenon of hydrogen UPD is also observed for rhodium, palladium and iridium. However, in the case of palladium, hydrogen adsorption on the surface proceeds simultaneously with hydrogen absorption in the bulk [37, 41]. The separation between these two processes is not easy and requires special procedures [45, 46]. Therefore, it is not possible to extract hydrogen adsorption contribution in a single voltammetric experiment on a Pd electrode and to determine the RSA of a Pd electrode from hydrogen adsorption charge. A negligible hydrogen

adsorption on Au electrode (only 2-4% of a monolayer [41]) also excludes the applicability of this method of the RSA determination for that metal. Although ruthenium adsorbs hydrogen, in that case the hydrogen region is overlapped with the oxygen adsorption region [47-51], which prevents the possibility of utilizing both these processes for the RSA determination. Moreover, Green and Kucernak [52] showed that the total charge in the hydrogen region does not refer to the adsorption process only because ruthenium can absorb some amounts of hydrogen and store it in the subsurface layers.

For Pt, Rh and Ir the charge consumed in adsorbed hydrogen oxidation, measured by the integration of the voltammetric peaks in the hydrogen region or by chronopotentiometry, can be recalculated into the value of the RSA, according to the equation:

$$\text{RSA} = Q_{\text{ox}}^{\text{H}} / (\theta_{\text{H}} Q_{\text{ox,ML,S}}^{\text{H}}) \quad (1)$$

where Q_{ox}^{H} is the measured charge due to the oxidation of adsorbed hydrogen for a given cathodic vertex potential, θ_{H} is the surface coverage with adsorbed hydrogen at that potential and $Q_{\text{ox,ML,S}}^{\text{H}}$ is the charge due to oxidation of a monolayer of adsorbed hydrogen per unit area. Bett et al. [53] as well as Sobkowski and Umiński [54] have found from the charge needed for adsorbed hydrogen oxidation and BET measurements that for platinum black one hydrogen adsorption center (a platinum atom) adsorbs one hydrogen atom.

Usually, the charge due to the anodic process of hydrogen desorption is used instead of the cathodic adsorption charge. In an ideal case both these values should be the same, however, some differences of the order of ca. 10% are observed [48, 55-57]. The cathodic charge is more difficult to estimate due to overlapping with the onset of hydrogen evolution [55]. Sometimes, the average between adsorption and desorption charges was used for the RSA calculation [1].

This method assumes that one hydrogen atom can be adsorbed on a single Pt surface center and a total charge transfer occurs between the adsorbing hydrogen and the metal surface [40, 41, 58]. The value of $Q_{\text{ox,ML,S}}^{\text{H}}$ can be calculated on the basis of surface atom density of a given metal and for polycrystalline electrodes it is an averaged values for various crystal planes. Commonly, an equal distribution of the three low-index planes, i.e. (100), (111) and (110) is assumed. However, in real conditions, different polycrystalline samples may differ in respect of the distribution of the various planes on the surface. The accepted values of $Q_{\text{ox,ML,S}}^{\text{H}}$ for polycrystalline Pt, Rh and Ir are $210 \mu\text{C cm}^{-2}$, $221 \mu\text{C cm}^{-2}$ and $218 \mu\text{C cm}^{-2}$, respectively. In the case of Pt, this value corresponds to the surface atom density of $1.31 \cdot 10^{15} \text{ cm}^{-2}$ [40, 41].

According to Eqn. (1), the surface coverage with adsorbed hydrogen has to be known for the calculation of the RSA. In a typical experimental conditions it is not possible to attain a full monolayer of adsorbed hydrogen, since earlier hydrogen starts to evolve and the evolution charge dominates over the adsorption charge. It has been proposed that the electrode should be polarized up to a current minimum placed at the potential just before the onset of hydrogen evolution. This minimum is better defined on Pt and Rh than on Ir. The minimum position depends on the electrode surface roughness and temperature as well as the scan rate used in a cyclic voltammetric experiment. The identification of this end-potential for electrode polarization is easier at low temperature and using slower scan rate [58].

There were also attempts to separate hydrogen adsorption and evolution contributions by extrapolating the hydrogen charge to infinite scan rate [59, 60]. Using ac techniques it is possible to separate adsorption and evolution components by analyzing the frequency dependence [41].

For voltammetric polarization to the current minimum potential just before the onset of hydrogen evolution, the θ_H values given in the literature for Pt, Rh and Ir are 0.77, 0.59 and 0.65, respectively [41]. The fact of an incomplete surface coverage with adsorbed hydrogen should be emphasized. However, quite many authors [48, 52, 56, 61-71] do not take it into account and ascribe the measured hydrogen desorption charge to a full monolayer, using the conversion factor equal to $Q_{ox,ML,S}^H$ without the correction for the fractional θ_H value. Such a calculation leads to the underestimation of the RSA.

According to Jerkiewicz [72], the value of $Q_{ox,ML,S}^H$ cannot be treated as a firm constant for all types of Pt electrodes. Up to now the role of corner and edge atoms in hydrogen adsorption is not sufficiently understood. These factors are particularly important in the case of nanoparticles. Jerkiewicz concludes that it is still unclear whether the conversion factor of $Q_{ox,ML,S}^H$ for polycrystalline Pt can be used for the RSA determination of Pt nanoparticles [72]. The possibility of the underestimation of the RSA of small Pt nanoparticles when calculated from hydrogen adsorption charge was also raised by Maillard et al. [73].

Another important problem concerns the correction of the measured charge for the double layer charging contribution. Typically, the value of capacitive current flowing in the double layer region is subtracted from the total oxidation current measured in the hydrogen region [40, 41, 58, 67, 69, 71, 74, 75, 76]. This is an arbitrary procedure based on an assumption that double layer charging current is constant over the entire hydrogen region, i.e. the double layer capacity is not changed in the presence of adsorbed hydrogen and does not depend on surface coverage with hydrogen. It is also assumed that the current present in the double layer region has no faradaic contributions.

In principle, the capacitive current in potentiodynamic measurements may be eliminated by applying staircase voltammetry, where the current is probed at the end of the potential step [77, 78]. Under these conditions the double layer charging current is negligible and the measured current originates from faradaic processes only. However, this approach cannot be used for hydrogen adsorption measurements. Since hydrogen adsorption is very fast, it starts from the very beginning of the potential step and rapidly decays in time. Therefore, the current measured after some time delay is significantly underestimated [78].

In order to obtain reliable RSA measurements, the process of hydrogen adsorption cannot be disturbed by any other competitive adsorption processes. High purity of the electrode and solution is needed. Therefore, the electrolyte must be free from any surface poisons like halide ions, sulfur or traces of carbon oxides [79, 80]. The effect of the ion adsorption from supporting electrolyte also occurs but it is inevitable, thus H adsorption charge contains contribution from ion adsorption [48], which is different in different electrolytes. The solution has also to be deoxygenated to eliminate oxygen reduction reaction.

The method of RSA determination from hydrogen adsorption has been established as a standard for Pt and Rh electrodes, making possible the normalization of the experimental data for those metals. According to the literature [40], the accuracy of that method is within 10%. It is noteworthy

that hydrogen adsorbate can be completely removed from the surface and it usually does not alter the surface state of the electrode. However, in some cases the contact of electrode surface with hydrogen may lead to significant changes. In the literature one can find reports on the phenomenon of surface segregation of Pd-Ag alloys after hydrogen treatment, leading to alloy surface enrichment with Pd [81]. Also, for other Pd alloys hydrogen electroadsorption coupled with absorption may lead to the changes in the surface roughness and the stability of the surface oxides [82,83].

It should be noted that the number of surface centers determined from hydrogen adsorption measurement corresponds to the number of the centers able to bond hydrogen. Since hydrogen atom is the smallest adsorbate, the RSA determined from hydrogen adsorption is the maximum surface area accessible for adsorption [41, 44]. For larger molecules the accessible area will be smaller [62]. Moreover, it was suggested that the number of readily accessible surface sites for Pt is ca. 92% of a total number of sites [41].

In the case of the alloys between Pt and Rh the method of the RSA determination based on hydrogen adsorption can still be applied. The following equation has been proposed for the Pt-Rh system [84]:

$$\text{RSA} = Q_{\text{ox}}^{\text{H}} / [(x_{\text{Pt}} \cdot 210 + x_{\text{Rh}} \cdot 220) (x_{\text{Pt}} \cdot 0.77 + x_{\text{Rh}} \cdot 0.59)] \quad (2)$$

where x_{Pt} and x_{Rh} are atomic fractions of the metals on the alloy surface. Thus, it was assumed that alloy adsorption properties towards hydrogen are intermediate with respect to those of pure metals, being a linear function of the alloy surface composition. Therefore, for the RSA determination the surface composition of the Pt-Rh alloy should be known.

As in the case of Pd, the RSA of Pt and Rh alloys with Pd cannot be determined from hydrogen adsorption charge. Some attempts have been made to separate hydrogen adsorption and absorption currents for those Pd alloys, which contain low concentration of Pd and therefore absorb small amounts of hydrogen [85]. The multiple currents in the hydrogen region were deconvoluted in a computer program and the peaks placed at higher potentials were ascribed to adsorbed hydrogen while those at lower potentials were attributed to absorbed hydrogen. The results were used for the calculation of surface coverage with carbon oxides adsorption products [85]. However, the comparison with the results with other techniques of the RSA determination led to the conclusion that such a procedure can give only an estimation of the RSA and cannot be utilized for more accurate measurements.

Czerwiński [86, 87] observed that during a decrease in the RSA of a Pd electrode the charge under a smaller hydrogen peak, placed at higher potentials, alters proportionally to the change in the RSA and its change is approximately a half of the difference in the surface oxide reduction charge. Therefore, it was suggested that the smaller hydrogen oxidation peak can be related to the current necessary for the oxidation of adsorbed hydrogen. However, further analysis of the experimental data obtained for Pd and its alloys with other noble metals [88, 89] has led to the conclusion that none of the voltammetric signals can be unequivocally attributed to the oxidation of exclusively one form of electroadsorbed hydrogen.

Interesting results were obtained for a Pd-Si alloy containing 80% Pd in the bulk [90]. Due to the presence of Si, this alloy did not absorb large amounts of hydrogen and it was possible to distinguish H adsorption signals in the hydrogen region. Thus, the RSA of the Pd-Si electrode was

calculated assuming the charge for the oxidation of a hydrogen monolayer as $210 \mu\text{C cm}^{-2}$. The value of the RSA determined in this way was very close to that obtained from surface oxide reduction charge [90].

3. SURFACE OXIDE REDUCTION

The process of surface oxide formation (oxygen adsorption) on a Pt electrode and other noble metals occurs at potentials more negative than that of the onset of molecular oxygen evolution. In contrast to hydrogen adsorption, surface oxide formation is significantly slower and much more irreversible [41]. The surface coverage with adsorbed oxygen depends on the electrode potential and time. A detailed characteristic of this process on noble metal surfaces can be found in the literature [41, 91-107].

The initial stages of surface oxidation of platinum are usually described as Pt-OH formation, followed by conversion to PtO. The experiments carried out by Jerkiewicz et. al [104] with the use of the EQCM, however, led to the conclusion that PtO species are present on the surface already at the very beginning of the oxidation process. According to Biegler et al. [102] the limiting coverage with the surface oxide on Pt is reached at 2.2 V vs. RHE and corresponds to PtO₂ stoichiometry. At this potential surface oxide formation occurs simultaneously with molecular oxygen evolution. Before the onset of oxygen evolution a monolayer of PtO is reached (at. ca. 1.5 V vs. RHE). For rhodium the formation of RhOH, Rh(OH)₃ and RhO(OH) species was postulated by Jerkiewicz and Borodzinski [103], while elsewhere the layer of chemisorbed oxygen on Rh was treated as RhO [41]. The latter stoichiometry has been confirmed in EQCM experiments [108]. Similar findings on the MO-type oxide formation were reported for Pd [106] and Au [107] oxidation.

As in the case of the previous method of the RSA determination, the one based on oxygen adsorption relies on the surface oxide reduction (oxygen desorption) charge measurement ($Q_{\text{red}}^{\text{O}}$), which can be converted into the RSA by applying the equation:

$$\text{RSA} = Q_{\text{red}}^{\text{O}} / (\theta_{\text{O}} Q_{\text{red,ML,S}}^{\text{O}}) \quad (3)$$

where θ_{O} is the surface coverage with surface oxide (adsorbed oxygen) and $Q_{\text{red,ML,S}}^{\text{O}}$ is the charge due to the reduction of a monolayer of surface oxide per unit area. The values of $Q_{\text{red}}^{\text{O}}$ and θ_{O} depend on the potential of electrode polarization and time scale of the experiment, i.e. scan rate in voltammetric measurements. The exact potential of a monolayer formation is affected by scan rate, electrolyte composition and electrode surface roughness [62, 96].

Typically, the charge corresponding to the monolayer of surface oxide of 1:1 stoichiometry is utilized. The conditions of a monolayer formation can be determined by analyzing the dependence of $Q_{\text{red}}^{\text{O}}$ on electrode potential for other fixed parameters. The potential, at which a monolayer of adsorbed oxygen atoms is formed is indicated by a characteristic inflexion point on the $Q_{\text{red}}^{\text{O}}$ vs. E relationship, where the slope changes [90, 101, 109-111]. For metals that can adsorb hydrogen, the oxygen desorption charge may also be compared with the charge due to hydrogen monolayer desorption charge, assuming that a for a monolayer of surface oxide the ratio between these two values should 2:1 [112]. The electrode polarization into the oxygen evolution region should be avoided since multilayer oxide films of an undefined stoichiometry can be formed, which are difficult to reduce.

For the RSA determination the cathodic charge of the oxide reduction should be utilized rather than the anodic charge of the oxide formation. This is due to the fact that in the oxygen region two additional anodic processes occur, namely the electrochemical dissolution of the electrode material and molecular oxygen evolution, both contributing to the total measured oxidation charge [113]. Therefore, the anodic charge usually exceeds the cathodic charge [62, 113, 114], which could lead to the overestimation of the RSA. According to the results of the EQCM experiments, the amount of dissolved metals at potentials just before the onset of oxygen evolution corresponds to ca. 15% of a monolayer for Pd, 4% for Rh and 0.2% for Pt [115].

The method based on oxygen adsorption is generally regarded as less reliable than that based on hydrogen adsorption [40]. Again, the high purity of the studied system is needed [41]. Similarly to the first method, the second one also required the correction for double layer charging. The same assumptions are usually made [40, 41].

The method of RSA determination based on surface oxide reduction is used mainly for Pd and Au electrodes, for which the first method cannot be applied. Thus, for those metals it is the most applicable method, regarded as a standard one [41]. $Q_{\text{red, ML,S}}^{\text{O}}$ values for Pd and Au are $424 \mu\text{C cm}^{-2}$ and $390 \pm 10 \mu\text{C cm}^{-2}$, respectively [41]. The potentials of PdO and AuO monolayer formation are ca. 1.45 V and 1.70 V vs. RHE, respectively [41, 101, 116].

For Pt and Rh this method is rather rarely used, since it has no advantages over that based on hydrogen adsorption. In our earlier report [108] we have compared the data obtained for a Rh electrode with both methods and found a good agreement between them. The values of $Q_{\text{red, ML,S}}^{\text{O}}$ values were taken as twice higher than the respective $Q_{\text{ox, ML,S}}^{\text{H}}$ values, i.e. $442 \mu\text{C cm}^{-2}$ for Rh. Analogously, for Pt $Q_{\text{red, ML,S}}^{\text{O}}$ is equal to $420 \mu\text{C cm}^{-2}$.

The method of the RSA determination based on surface oxide reduction has been applied for Pd alloys with Pt, Rh and Au [117, 118]. Due to similar values of $Q_{\text{red, ML,S}}^{\text{O}}$ for Pt and Pd, Kadirgan et al. [117] used the conversion factor of $420 \mu\text{C cm}^{-2}$ for an oxide monolayer reduction (formed at ca. 1.5 V) on Pd-Pt alloys. However, in general, since alloy formation modifies the electrochemical properties of the components, such factors as $Q_{\text{red, ML,S}}^{\text{O}}$, θ_{O} and the potential of a monolayer formation may differ from the values for pure metals being the function of the alloy surface composition [111, 119].

Our recent studies [119] have revealed that the potential of a monolayer formation of surface oxide on homogeneous Pd-Au alloys or on the Pd-rich phase in heterogeneous Pd-Au alloys depends almost linearly on Pd surface content in that phase. Therefore, it can be expected that also $Q_{\text{red, ML,S}}^{\text{O}}$ and θ_{O} values are approximately a linear function of Pd surface content in the alloy phase. Thus, a following equation was postulated for the determination of the RSA of the Pd-Au alloy phase:

$$\text{RSA}^{\text{Pd-Au}} = Q_{\text{red}}^{\text{O}} / (\theta_{\text{PdO}} \cdot Q_{\text{red, ML,S}}^{\text{PdO}} \cdot X_{\text{Pd}} + \theta_{\text{AuO}} \cdot Q_{\text{red, ML,S}}^{\text{AuO}} \cdot X_{\text{Au}}) \quad (4)$$

On the other hand, in the case of the Au-rich phase in heterogeneous Pd-Au alloys it was demonstrated that its electrochemical properties resemble those of pure Au [41]. Thus, a simplified equation can be used for the RSA determination of that phase:

$$\text{RSA}^{\text{Au}} = Q_{\text{red}}^{\text{O}} / (\theta_{\text{AuO}} \cdot Q_{\text{red, ML,S}}^{\text{AuO}}) \quad (5)$$

The total surface area of heterogeneous Pd-Au alloys was obtained as a sum of the areas occupied by both surface phases [118, 120].

The above idea was extended to the RSA determination of Pd-Pt-Rh ternary alloys [118, 121]. The following equation was utilized:

$$\text{RSA} = Q^0 / \sum (Q_{\text{ML}, S}^0 \cdot x_M \cdot \theta_M^0) \quad (6)$$

where M denote the metallic alloy components.

An approach based on the coupling of the methods of the RSA determination based on hydrogen and oxygen adsorption was applied to Pt-Au alloys [122-126]. These alloys consist of two surface phases, which have electrochemical properties similar to pure metals [124]. Thus, the RSA of a Pt-Au electrode was calculated as a sum of the RSAs occupied by both phases, where the RSA of the Pt-rich phase was determined from hydrogen adsorption and the RSA of the Au-rich phase was determined from surface oxide reduction [122-126].

Prolonged electrode polarization to the oxygen region, causing surface oxide formation/reduction, metal electrodisolution/redeposition and oxygen evolution may alter the surface state of the material studied. In the literature there are numerous reports demonstrating that depending on the exact potential program applied, involving surface oxidation, the surface can significantly roughen or smooth during such an experiment [127, 128]. Additionally, in the case of the alloys the polarization to high potential inevitable for RSA determination can lead to the changes in the alloy surface composition due to a preferential dissolution of alloy components [41]. Surface segregation and phase separation of initially homogeneous alloys was observed in the case of Pd-Au, Pd-Pt-Au and Pd-Pt-Rh electrodes [41, 120, 129-131]. All these possibilities should be excluded when this method of the RSA determination is applied.

4. DOUBLE LAYER CAPACITANCE

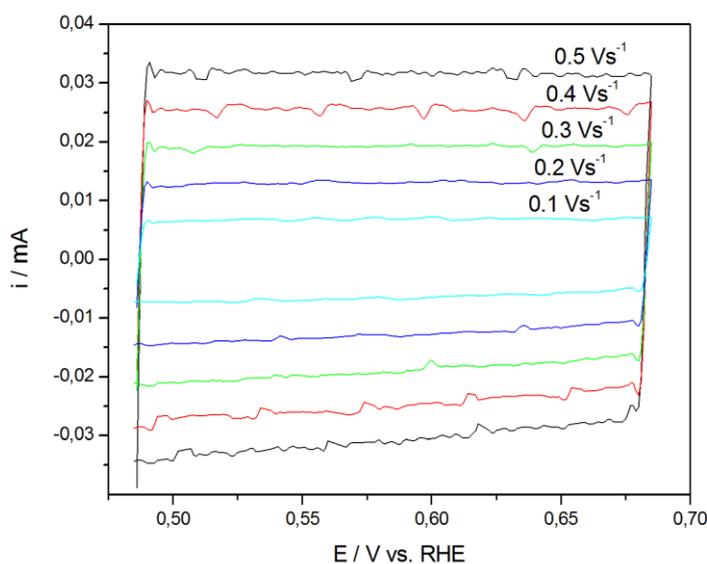


Figure 2. Double layer charging currents recorded with various scan rates for a polycrystalline Pt electrode in 0.5 M H₂SO₄ (temperature 298 K).

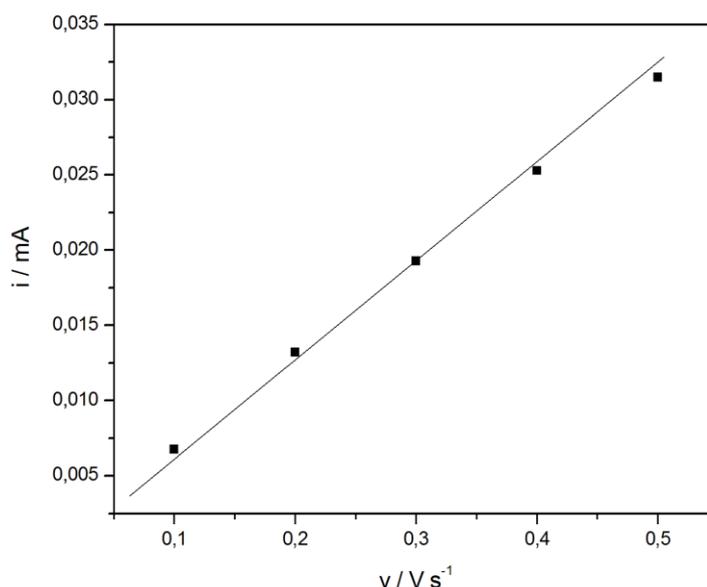


Figure 3. Dependence of double layer charging current at potential of 0.60 vs. RHE on scan rate for a polycrystalline Pt electrode in 0.5 M H_2SO_4 (temperature 298 K).

The potential region, where electrical double layer charging is the only electrochemical process, is called “double layer region” and for noble metal electrodes is placed between the hydrogen and oxygen regions. For Pt and Pd it corresponds to the potential range from ca. 0.40 V to 0.70 V vs. RHE, while for Au it is wider and is placed between 0 and ca. 1.35 V vs. RHE. In contrast, on Rh this region is very narrow [132] or even absent [133], while on Ru such a region cannot be distinguished at all due to a partial overlapping of hydrogen and oxygen regions [49, 50].

Usually, in the method of the RSA determination based on double layer capacity voltammetric curves are recorded in the mere double layer region at various scan rates (Fig. 2). Then, a plot of the current in the middle of the potential window vs. scan rate is constructed (Fig. 3). Under the condition, where the double layer charging is the only process occurring in that potential range, this plot is a straight line, whose slope gives the value of double layer differential capacity, according to the equation:

$$i = dQ/dt = (dQ/dE) \cdot (dE/dt) = C \cdot v \quad (7)$$

In fact, the capacity value obtained by the above procedure contains contributions both from double layer charging and pseudocapacity of the process of electrolyte ion adsorption [109]. There should be no faradaic contributions to the current flowing in the double layer region.

RSA can be calculated by referring the obtained capacity to the reference value of capacity per the unit area (C_{ref}):

$$\text{RSA} = C / C_{\text{ref}} \quad (8)$$

The greatest difficulty of that method and the main source of the error is the fact that the precise value of C_{ref} should be known, which is often not the case. In general, the values of capacity per the unit area reported in the literature range from several tens to even 60 or more $\mu\text{F cm}^{-2}$, being

typically between 20 and 40 $\mu\text{F cm}^{-2}$ [40, 77]. This discrepancy may lead to the 100% errors. Differential capacity of the double layer depends strongly on the electrode potential, surface structure, electrolyte composition and concentration, and is very sensitive to even small changes in experimental conditions. It means that C_{ref} has to be determined in an independent experiment, under given conditions, on the basis of other, well defined method of the RSA determination. For noble metals such a standard method can be that based on hydrogen adsorption (Pt, Rh, Ir) or oxygen adsorption (Pd, Au). Such a procedure was applied by Conway et al. [125] in the studies on Pt-Au alloys and by Łukaszewski and Czerwiński [118, 120] for Pd-Au alloys.

Using the above approach for Pd and Au electrodes in 1 M H_2SO_4 solution for potential of -0.09 V vs. RHE the value of 44.5 $\mu\text{F cm}^{-2}$ was obtained by Łukaszewski and Czerwiński [118, 120], while in 0.5 M H_2SO_4 solution this value for Pd and Pt was equal to 34 $\mu\text{F cm}^{-2}$ [118]. These values were then utilized for the RSA determination of Pd-Au and Pd-Pt-Rh alloys. A similar value (28 $\mu\text{F cm}^{-2}$) was used for the RSA measurements of Pt-Au alloys in the same electrolyte [122]. However, other research groups found different values of C_{ref} . Chen et al. [62] calculated the capacitance of ca. 53 $\mu\text{F cm}^{-2}$ for Pt electrode in 0.5 M H_2SO_4 , while Fang et al. [109] obtained the capacitance of 23 $\mu\text{F cm}^{-2}$ for Pd electrode in 0.5 M H_2SO_4 . Tremblay et al. [48] and Łosiewicz et al. [49] reported on the values of ca. 60 $\mu\text{F cm}^{-2}$ and 66 $\mu\text{F cm}^{-2}$ for Pt, and Ru, respectively (determined from impedance spectroscopy measurements). They estimated the relative error of this method of the RSA determination as 50%. For Rh, Łosiewicz et al. [132] found the value of ca. 25 $\mu\text{F cm}^{-2}$. All these results show that even for a given metal/alloy there is no general agreement on the value of the capacitance per unit area.

Although much less reliable than two previous methods and limited to the RSA estimation rather than its precise determination, the method based on the double layer capacity has some advantages. It enables the measurements of the RSA without the need of electrode polarization to the oxygen region, where the processes of oxide formation/reduction and metal dissolution/redeposition could lead to the changes in the surface state. It is not destructive and allows to measure the total surface area accessible to the electrolyte [48]. For the alloys it gives the value of the RSA corresponding to all alloy components [118, 120, 134]. However, in the case of metallic electrodes dispersed in a matrix this method gives the overall value of the whole area instead of the electrochemically active area of the metal [47].

5. CO ADSORPTION

Carbon monoxide is known as a strong surface poison of catalytic electrodes [135]. It has high affinity to many metals, including all platinum group metals. As one of the intermediates in the oxidation of various organic compounds it becomes adsorbed on the electrode surface and blocks the surface centers taking part in the electrochemical process, which leads to the deterioration of the catalyst activity. The electrode poisoning by CO adsorption products is responsible for a still unsatisfactory efficiency of methanol and ethanol fuel cells [136, 137].

However, the unfavorable phenomenon of CO adsorption can be utilized for the RSA determination of solid electrodes. CO strongly adsorbs on all noble metals and their alloys in the

potential range corresponding to the hydrogen and double layer regions [43, 84, 138-142]. It can be fully desorbed by its oxidation to CO₂ by applying sufficiently high potential to the electrode.

The RSA determination based on CO adsorption is a particular case of the use of adsorption of probe molecules from the solution [40]. The amount of the adsorbate is measured from the charge needed for its oxidation during anodic stripping and the RSA is calculated according to the equation:

$$\text{RSA} = Q_{\text{CO}} / (z F \Gamma_{\text{CO}}) \quad (9)$$

where Q_{CO} is the charge of the oxidation of CO adsorption product, z is the number of electrons exchanged in the oxidation, F is Faraday constant and Γ_{CO} is the saturation coverage with adsorbed CO in mol cm⁻².

Under the conditions of a cyclic voltammeteric experiments the charge due to adsorbed CO oxidations is equal to:

$$Q_{\text{CO}} = \text{eps} \cdot n \cdot F \cdot \theta_{\text{CO}} \quad (10)$$

where eps is the number of electrons required for the adsorbate oxidation from one surface site occupied by the adsorbate (electron per site), n is the total number of surface sites and θ_{CO} is the surface coverage with adsorbed CO. Since n/RSA is the surface atom density, the above equation can be converted into:

$$\text{RSA} = Q_{\text{CO}} / (\text{eps} \cdot Q_{\text{ox,ML,S}}^{\text{H}} \cdot \theta_{\text{CO}}) \quad (11)$$

which for a Pt electrode gives:

$$\text{RSA} = Q_{\text{CO}} / (\text{eps} \cdot 210 \cdot \theta_{\text{CO}}) \quad (12)$$

The conversion factor in the denominator of Eq. (11) can be calculated provided that eps and θ_{CO} are known. eps is a function of the structure of CO adsorption product. The exact structure of CO adsorbate depends on the kind of metal and, in the case of the alloys, on their surface composition. The main product of CO adsorption on Pt are linearly and two-fold bridge-bonded CO species [43, 56, 140-147], for which the eps values are equal to 2 and 1, respectively, together with multi-fold bridge-bonded CO [43]. According to many authors [44, 52, 68, 144, 148, 149] CO is adsorbed on Pt exclusively as 1:1, linearly bonded species. However, it may be to much simplification. In fact, other adsorbate structures were also postulated in the literature, such as COOH radicals ($\text{eps} = 1$) [140, 141, 150]. In the case of Rh the product of CO adsorption is more reduced than for Pt and probably contains a mixture of various forms of CO species [43, 146, 151-153] together with CHO or COH radicals ($\text{eps} = 3$) [138], or C intermediates [139]. For Pd, Ir and Ru a mixture of linearly and bridge-bonded CO is postulated [43, 83, 146, 154, 155]. However, there were suggestions, that under certain conditions the ratio of adsorbed CO species to surface Ru atoms may reach even 2:1 [156, 157].

CO stripping as a standalone method of real surface area determination has been used in studies of a number of bi- and trimetallic systems. Amongst them, one can mention such interfaces like binary Pt/Ru, Pt/Au, Pd/Pt, ternary Pt/Rh/Sn nanoparticles and core shell structures, unsupported or deposited on various carbon supports [158-166]. Many reports present calculations of the RSA which refers to the charge of CO desorption per unit area, $Q_{\text{ox,ML,S}}^{\text{CO}} = 420 \mu\text{C cm}^{-2}$.

The use of this parameter carries an assumption on the identity of CO_{ads} structure for all metallic surfaces. In theoretical situation, where a surface of an hypothetical electrode is fully covered with two-fold bridge bonded CO_{ads} the value of $Q_{\text{ox,ML,S}}^{\text{CO}}$ should be twice greater than the value of $Q_{\text{ox,ML,S}}^{\text{H}}$. This may be the case only for a Pt electrode under certain potential conditions [167]). For

other situations and other electrochemical systems a deviation from that value might be expected due to different structures of adsorbed CO. Thus, one should be aware of possible errors when comparing such determined RSA of various kinds of electroactive materials. Still, however, most of the authors do not consider this issue, leaving it without any discussion.

For single crystals, CO oxidation charge and surface coverage is different for different crystal planes [168, 169]. It is unknown how these values contribute to the value of the conversion factor for a given polycrystalline electrode. Only arbitrary assumptions can be made when calculating the value for the polycrystalline electrode [32].

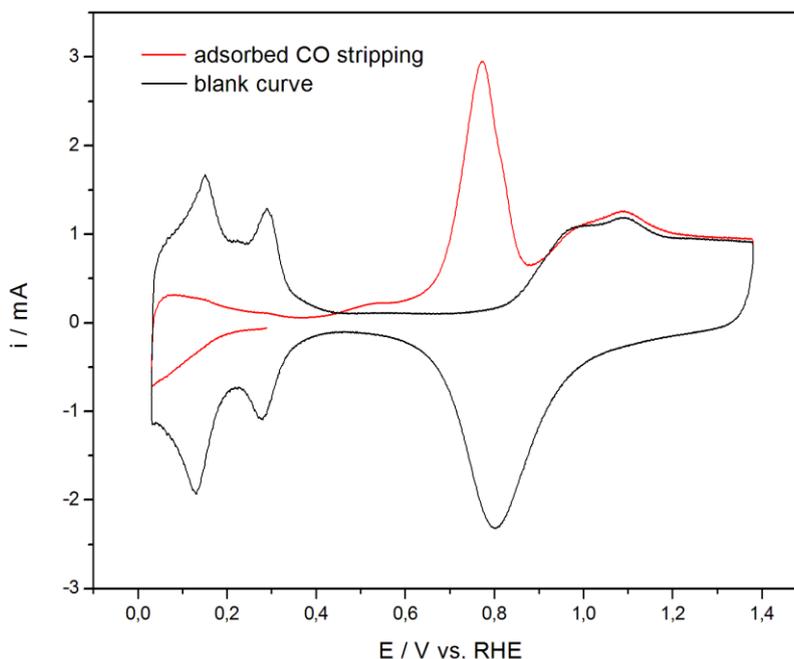


Figure 4. Adsorbed CO stripping current (red line) recorded for a polycrystalline Pt electrode in 0.5 M H_2SO_4 (temperature 298 K) together with a blank curve (black line). CO adsorption potential 0.29 V vs. RHE, adsorption time 20 min, scan rate 0.05 V s^{-1} .

For a given metal, the adsorbate structure and composition, its coverage and oxidation charge are affected also by the adsorption potential, adsorption time, temperature, electrode surface roughness and surface pretreatment as well as electrolyte composition and pH [43, 44, 138, 144, 147, 150, 170]. According to Vidaković et al. [44], a saturated monolayer of CO adsorbate on Pt electrode is formed after 15 min, while Sobkowski and Czerwiński reported on saturation adsorption time of 25-35 min. [150]. In the case of a Pt-Ru catalyst the CO saturated coverage was achieved in ca. 60-120 min. [44, 149] However, some authors used much shorter times of CO adsorption, e.g. 10 min or less [1, 52, 57, 66, 109, 171, 172]. The maximum value of θ_{CO} , although very high, may be not equal to unity [44, 84, 138, 140, 142, 144, 145, 149, 150, 173-177]. This fact has not always been taken into account [52, 67, 178].

In particular, for Pt and its alloys the nature of adsorbed CO depends on whether the adsorption was performed in the hydrogen or double layer region. In the former case two forms of the adsorbate are electrochemically distinguishable [81, 141, 142, 144, 147, 148, 150, 157, 172, 173, 178-182] (Fig. 4), characterized by different θ_{CO} values [85]. In the case of the alloys the adsorption parameters are

additionally a function of alloy surface composition [84, 85, 154, 181, 183, 184]. Thus, the values of θ_{CO} and ϵ_{ps} depend on the experimental conditions and no single, constant conversion factor can be applied to recalculate Q_{CO} into the RSA. One cannot simply transfer the findings for pure Pt to other metals and alloys, either. A weighted average between the values of the conversion factors corresponding to the electrooxidation charge of a monolayer of adsorbed CO on pure alloy components may be used [185].

To determine accurately the CO stripping charge one has to make correction for other background processes like double layer charging and metal oxide formation. It may be assumed that double layer charging and surface oxidation proceed in the same way in the presence and absence of adsorbed CO [55, 74]. Then, Q_{CO} is measured as the difference in the total anodic charge in the potential range of CO stripping and the charge passed in the same range in the absence of the adsorbate [1, 40, 75]. However, more complex procedures of the base line subtraction were also evaluated [44, 57, 66, 67, 149]. The possibility of accurate CO charge determination using differential electrochemical mass spectroscopy (DEMS) was demonstrated [148, 172-174, 176, 180, 181, 186]. Another method of the determination of the amount of adsorbed CO, which is independent of both faradaic and nonfaradaic background, relies on infrared spectroscopic technique [47].

It is important that during the anodic removal of adsorbed CO there should be no CO present in the solution, since in the presence of CO dissolved in the electrolyte a compressed monolayer is formed of a higher surface coverage [47, 187].

It should be remembered that adsorbed CO may cause changes in the electrode surface state leading to the changes in the RSA [62]. This is particularly important when using this method for the RSA determination of nanoparticles, when the possibility of particle agglomeration may occur. On the other hand, CO adsorption method of the RSA determination is claimed to be more appropriate for nanoparticles than that based on hydrogen adsorption [1, 73]. In the case of alloys the presence of adsorbed CO can also induce surface segregation and changes in the phase arrangement and surface composition [129]. These effects are usually irreversible. Thus, the RSA determination from CO adsorption can significantly modify the electrode surface and its catalytic properties [66, 67], which rather should be avoided. Moreover, adsorbed CO oxidation at high potentials can be accompanied by metal dissolution from the electrode surface, additionally leading to changes in the electrode surface state and, in the case of alloys, surface composition [188].

Another fact that should be taken into account are the steric effects connected with the size of CO adsorption products. The adsorbed species are larger than adsorbed hydrogen atoms and they may not have access to the whole exposed area of the electrode. Moreover, for various adsorption procedures this effect may be different, since different adsorbate structures are generated under various adsorption conditions [40].

When applied for the RSA determination of Pd and Pd alloys, CO adsorption has to be performed at potentials in the double layer region in order to avoid simultaneous hydrogen absorption in the electrode bulk. In the presence of adsorbed CO the removal of adsorbed hydrogen is strongly retarded and its oxidation signal is overlapped with that of CO stripping [86, 189-191].

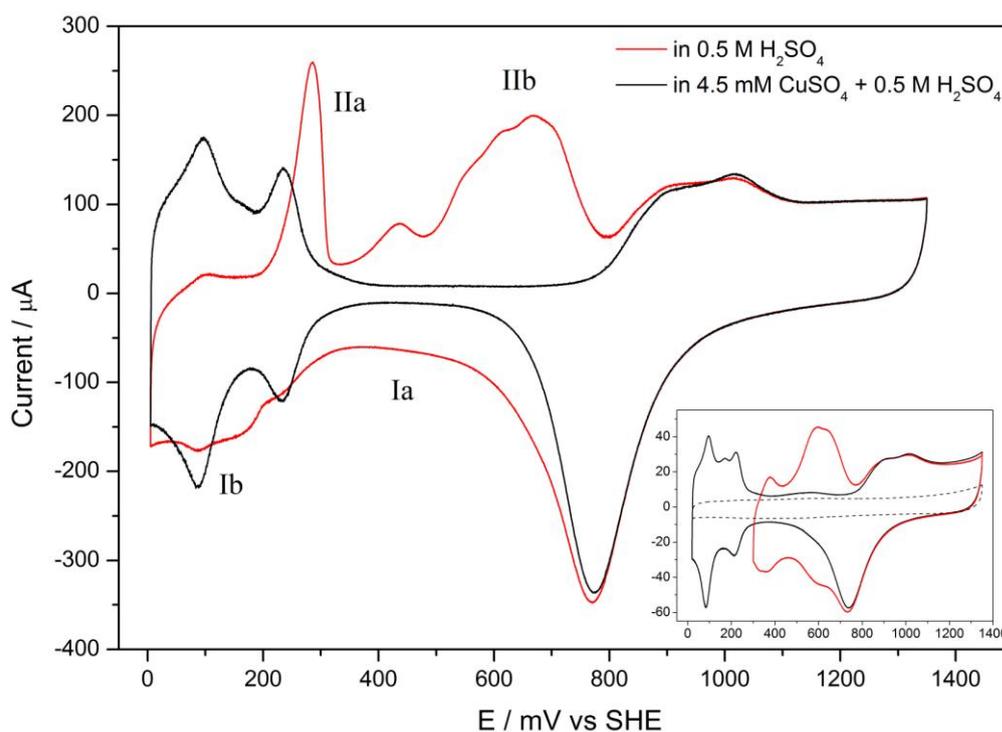
Since adsorbing CO displaces other previously adsorbed species, such as anions and hydrogen, it is possible to utilize this process for the RSA determination. According to the literature [192, 193],

the charge density for CO/H displacement on Pt(111) at 0.08 V is $152 \pm 5 \mu\text{C cm}^{-2}$. Chen et al. [62] pointed out that the advantages of this method are little effects from anion adsorption, hydrogen evolution and double layer charging. Using this method one has to pay attention to avoid the interference from the reduction of oxygen dissolved in the solution.

6. UNDERPOTENTIAL DEPOSITION OF METALS

Underpotential deposition (UPD) of metals occurs at potentials positive to the reversible potential of the M^+/M redox couple, below which a bulk deposition of the metal phase starts. From the thermodynamic point of view UPD takes place, when the affinity of the adsorbing metal to the substrate is greater than the affinity of the adsorbing metal to itself in its metallic phase [56, 79, 194-196].

In perfect conditions, where atomic diameters of the adsorbed (underpotentially deposited) metal and the substrate are of a similar value, the UPD deposit forms a monolayer which perfectly reproduces the morphology of the underlying substrate. The idea of implementing the underpotential deposition to measure the surface area of metals was proposed by Franklin et al., who studied the UPD of Pb on Ag catalysts [197]. Since then the underpotential deposition phenomenon has been widely studied and discussed in the literature. It has been shown that the coverage of the adatom layer is strongly dependent on deposition conditions, type of the deposited metal and substrate, and trace amounts of inorganic anions (in particular halides) or organic impurities [198].



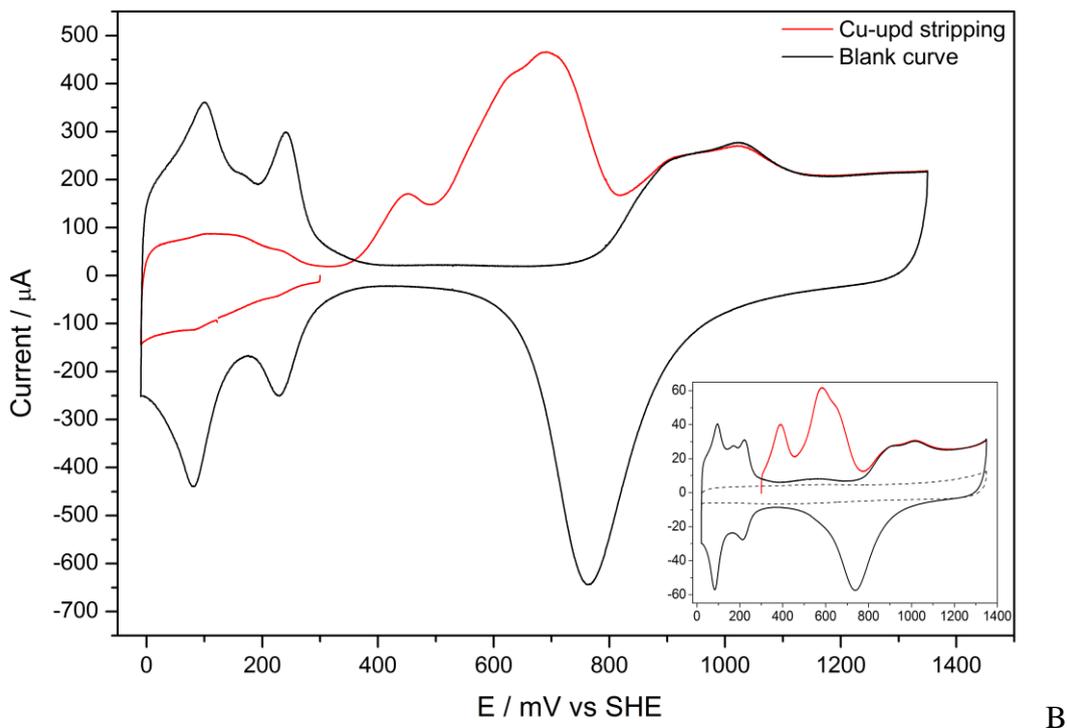


Figure 5. (a) Cyclic voltammograms (0.01 V s^{-1}) recorded for a polycrystalline Pt electrode in pure $0.5 \text{ M H}_2\text{SO}_4$ solution (black line) and solution containing 4.5 mM CuSO_4 in $0.5 \text{ M H}_2\text{SO}_4$ (red line). (b) Stripping current of Cu-UPD layer on Pt. Inner plots represent CV scans for 40 % wt Pt / C electrodes (dashed line shows the CV for pure carbon support). The Pt electrode was held in 4.5 mM CuSO_4 in $0.5 \text{ M H}_2\text{SO}_4$ solution at 0.33 V vs RHE for 15 min. After deposition the Cu containing solution was replaced with pure supporting electrolyte and cyclic voltammograms were performed with a scan rate 0.01 V s^{-1} (1st scan – red line, 2nd scan – black line). Temperature 298 K.

From a practical point of view, for a monolayer of a deposited metal, the charge consumed in that process (Q^M), usually measured during voltammetric stripping of the adatoms, can be converted into the RSA using the equation:

$$\text{RSA} = Q^M / Q^M_{\text{ML,S}} \quad (13)$$

where $Q^M_{\text{ML,S}}$ is the charge corresponding to a monolayer of deposited metal per unit area.

The underpotentially deposited metals most often used for the RSA determination are Cu, Ag and Pb. In those cases the values of $Q^M_{\text{ML,S}}$ are 420 , 210 and $300 \mu\text{C cm}^{-2}$ respectively [52, 199]. Figure 5a shows an example of a cyclic voltammogram recorded on a typical polycrystalline Pt electrode (inner figure contains CV for 40 % wt. Pt/C electrode) during continuous potential cycling in a solution containing 4.5 mM CuSO_4 and $0.5 \text{ M H}_2\text{SO}_4$ (solid line) as well as the background CV recorded in a pure supporting electrolyte ($0.5 \text{ M H}_2\text{SO}_4$, red line). No faradaic process is observed related to the deposition and oxidation of Cu above the potential of ca. 800 mV , where the formation of platinum surface oxides occurs - reduction of Cu ions to its metallic form is preceded by the oxide reduction reaction. The analysis of cathodic current density in the “Cu region” does not allow to distinguish between the underpotential and the bulk Cu crystal growth modes translating into broad,

irregular signal (Ia), partially overlapping the H-UPD related currents (Ib on Fig 5a). In the positive scan, two separated regions are attributed to the oxidation of bulk phase (IIa) and the Cu-UPD (IIb). The plot in Fig. 5b (solid line) shows a typical stripping signal of underpotentially deposited Cu on polycrystalline platinum (inner figure contains a stripping signal for 40 % wt. Pt/C) recorded in the absence of Cu ions in the supporting electrolyte. Cu-UPD desorption signal can be deconvoluted into several peaks due to different bonding strength of Cu at different Pt crystal planes.

The main problems with the calculation of the charge corresponding to the deposited metal are the proper correction for background processes (double layer charging, hydrogen or oxygen adsorption) [62, 109] and the proper identification of the potential, where the formation of a monolayer of metal adatoms is completed [52, 62, 109]. In some cases the exact achievement of a true monolayer is not possible [200], and a multilayer deposition can start before the full monolayer is formed [201-203]. In general, the arrangement of adatoms on the electrode surface may not correspond to 1:1 atomic ratio, i.e. the number of surface sites occupied by foreign atoms is not equal to 1 [204]. For instance, on Pt electrode this condition is fulfilled for Cu and Ag UPD, while for other depositing metals (e.g. Cd, Sn, Pb) the ratio is 1:2 or 1:3 [205]. Schumacher et al. [206] determined the surface coverage with Cu adatoms on Pt to be in the range between 0.44 (for pure H₂SO₄ supporting electrolyte) and 0.8 (for the supporting electrolyte with an addition of small amounts of Cl⁻ ions). Zhang et al. [207] found that for metallic Ru, Cu deposit reaches a coverage of a half of monolayer, while for electrochemically treated conductive-RuO_xH_y surface, the coverage plateau is obtained at ca. 0.9 ML.

Another unfavorable situation appears, when a partial charge transfer occurs during deposition [208-212], resulting in the undefined value of $Q_{ML,S}^M$. Deakin and Melroy [213] used quartz crystal microbalance in order to calculate electrodeposition valencies (γ) of underpotentially deposited Pb, Bi, Cu and Cd on polycrystalline gold. They found that in contrast to bulk deposition, the values of γ deviate for Bi and Cu adatoms from valencies of their ions during UPD. The Cu-UPD γ remained on the level of 1.4 suggesting a presence of partial charge on the Cu atoms. Similar effects regarding Cu UPD on polycrystalline Pt were found by Schumacher et al. [206]. The authors claim that the electrosorption valency of 1.2 ± 0.3 reflects a situation where a positive charge of +1 is localized per adsorbed Cu atom. On the other hand, Chierchie and Mayer [214] discovered that Cu UPD forms completely discharged, epitaxial layer on polycrystalline Pd.

One should also take into account the possibility of a retention of the deposited adatoms in the crystal lattice of the substrate, which leads to the alteration of the structure of the electrode surface [215, 216]. A surface alloy formation between the matrix and the deposited metal may occur [217-219]. If the traces of deposited adatoms are not removed during its stripping, their presence may further modify the catalytic activity of the electrode studied [79, 220-222].

The advantage of the method of the RSA determination based on UPD is its high reproducibility [40]. Generally, this method is regarded as a more sensitive than that based on double layer charging. This method can be applied for those systems where other methods cannot be used. Cu UPD is very suitable for the RSA determination of Ru electrode [40, 48, 49, 51, 52, 202], where hydrogen and oxygen region are overlapped and the charges due to hydrogen and oxygen adsorption cannot be separated. The similarity of atomic radii of Cu and Rh is here a favorable factor [51, 52].

7. COMPARISON BETWEEN VARIOUS METHODS OF RSA DETERMINATION.

In the literature there are reports where different methods of the RSA determinations were applied for the same electrode. Therefore, the comparison between various methods could be made. Below some examples of such studies are briefly reviewed.

Green and Kucernak [52, 154, 223] compared the methods of the RSA determination based on Cu UPD, hydrogen adsorption and CO adsorption for Pt, Ru, Pt-Ru powder black and mesoporous Pt-Ru electrocatalysts. In the case of pure Pt and Pt-Ru alloys they found a good agreement between the RSA values obtained by CO stripping, Cu UPD and H adsorption (for Pt). These results were consistent with BET measurements. On the other hand, the RSA of Ru electrode calculated from CO stripping was ca. twice as large as that determined by Cu UPD and BET methods. According to the authors, this discrepancy indicates other than 1:1 stoichiometry between CO and Ru surface sites. Due to the fact that Cu does not deposit on Ru oxide, it was possible to distinguish between bare, metallic Ru and oxidized Ru sites on the surface of a Pt-Ru catalyst. On the other hand, Gavrilov et al. [224] made a suggestion that the Cu-UPD technique applied with longer time procedures becomes sensitive to all forms of reversibly oxidized ruthenium. The authors postulate that the RSA determination should be performed under various Cu deposition times in order to avoid errors related with the selectivity of the process. The changes in the electrode RSA in the process of Ru dissolution could also be studied using Cu UPD [52].

Real surface area of platinum nanoparticles (ca. 20 % wt.) deposited on carbon (C) and tungsten carbides (WC) was determined from carbon monoxide and hydrogen desorption charges by Jeon et al [225]. The authors found that the RSA value calculated from hydrogen region was 2.5 times higher than from CO experiments for WC supported platinum, while the discrepancy between surface areas for Pt/C obtained from both methods were less than 10 %. The high excess of H-UPD atoms found on Pt/WC comparing to Pt/C was explained by a surface spill-over of H⁺ from Pt to tungsten carbid. According to the CV profiles presented in the article, the ratio between the values of hydrogen and oxide desorption charge was markedly different for both catalysts, suggesting that oxygen sorption process was probably not affected by the spill-over phenomenon. Thus, a consideration on the surface oxide desorption charge as a more reliable basis for the RSA estimation in this particular case would be very attractive. Unfortunately, the authors did not comment on this.

A similar approach was presented by Vangatesan et al., who calculated the RSA referred to mass of platinum for Pt nanoparticles deposited on mesoporous carbon support [226]. In addition to electrochemical measurements, the authors calculated an average Pt particle size and estimated specific surface area using TEM technique. In this case, however, the discrepancy between CO and the hydrogen derived RSA values increased with increasing platinum loading and for the highest, 80 % wt. Pt, the RSA_{CO} was twice as high as the RSA_{H^+} and almost five times lower than RSA_{TEM} . The authors discuss such high differences as a result of pore size decrease in the case of Pt nanoparticles with higher loading. Such phenomenon would indeed explain the underestimated value of the electrochemically determined RSA in comparison to that obtained by TEM. However the differences between CO and H-upd stripping results were not clarified.

Fang et al. [109] applied 4 methods to determine the RSA of Pd electrode, namely: double layer capacitance, surface oxide reduction, Cu UPD and CO stripping. The results obtained by the second and third methods were consistent with deviations below 5%. The other methods results agreed with the previous one on condition that double layer capacity per unit area was taken as $23 \mu\text{F cm}^{-2}$ and surface coverage with adsorbed CO was assumed 0.66. (for the conversion factor of $420 \mu\text{C cm}^{-2}$). For Cu UPD the conversion factor of $407 \mu\text{C cm}^{-2}$ was used.

Elliot et al. [61] characterized the surface of nanostructured Pt films deposited on microelectrodes by hydrogen adsorption and Cu UPD. In the latter case they used the conversion factor of $410 \mu\text{C cm}^{-2}$. A good agreement between both methods was found.

Kim et al. [227] compared various methods of the RSA determination of nanoporous Pt layer with small pore diamensions characterized by different values of roughness factor (from 25 to 450). The RSA values determined by Cu-UPD and CO stripping methods were smaller than that estimated by the H-UPD) method, and the discrepancy became greater as the roughness factor increased. The authors concluded that the accessible surface area of the pores inside the Pt layers for the adsorbates decreases in the order of $\text{H} > \text{CO} > \text{Cu}$. The size of adsorption species may explain their accessibility into the pores.

Fiçicioğlu and Kadirgan [110] examined the surface of electrodeposited Pd-Pt alloys with the use of oxygen adsorption and Cu UPD. The differences in the RSA values obtained by both methods were ca. 10%. The authors concluded that the estimation of the RSA of a Pd-Pt alloy based on Cu UPD is more appropriate, while oxygen adsorption method led to overestimation of the RSA.

Łukaszewski and Czerwiński [118] compared the values of the RSA of Pd-Au alloys determined by oxygen desorption and double layer capacitance. They studied both superficially homogeneous and heterogeneous electrodes. The difference in the results obtained by both methods was within 30%. They suggested that the latter method is suitable rather for the estimation of the RSA and gives only the value of the total electrode area, while the former one enables the calculation of the RSAs of particular surface phases. In the same laboratory an agreement within ca. 20% was found for the values of the RSA of Pt-Au alloys determined for hydrogen and oxygen adsorption, and double layer capacitance [122].

Bogolowski et al. [174] determined the RSA of Ru electrocatalyst by CO stripping and Cu UPD. They assumed the same packing density of adsorbed CO on Ru as on Pt and used the conversion factor of $280 \mu\text{C cm}^{-2}$, i.e. corresponding to CO surface coverage equal to 0.66. In order to obtain an agreement with the RSA values determined from Cu UPD, in the latter case the conversion factor of $520 \mu\text{C cm}^{-2}$ was used.

The above methods were used by Nagel et al. [176] for the determination of the RSA of polycrystalline and nanoparticle Pt and Ru electrodes. They found 20% agreement between both methods, provided that CO oxidation charge was detected by DEMS and assuming a maximum coverage with adsorbed CO of 0.70 both for Pt and Ru, and for polycrystalline electrodes and nanoparticles as well.

Chen et al. [62] exploited numerous electrochemical methods to evaluate the RSA of Pt foils, thin Pt deposits and carbon-supported Pt nanoparticles. They found that for relatively smooth Pt electrodes all methods gave similar results. However, with increasing roughness factor the values of

RSA decreased in the method order: H adsorption > Cu UPD > CO/H displacement. For rough Pt surfaces ca. 21% of the surface sites being accessible for H adsorption could not be occupied by Cu UPD. These differences were explained by different size of the adsorbates. The smallest hydrogen atoms can be adsorbed even in pores inside rough surfaces, which are inaccessible to the species with a larger molecule size. Thus, the RSA determined by Cu UPD corresponds to the number of surface sites accessible for most reactants. The authors also concluded that the method based on double layer capacitance measurement enables only a rough evaluation of the RSA. CO adsorption methods was regarded as inappropriate for RSA determination of rough surfaces due to a significant annealing effect induced by adsorbed CO. Such a phenomenon was not observed in the case of Cu deposition.

Different results were obtained by Shao et al. [66] and Rudi et al. [67], who studied several methods of RSA determination of Pt-Ni nanoparticles. The values of RSA decreased in the order: Cu UPD > CO adsorption > H adsorption. The influence of history of the applied potential cycling program on the RSA values was also observed [67].

Guterman et al. [228] evaluated the RSA of carbon supported Pt and Pt₃Ni catalysts in three ways: (1) from the charge consumed during the desorption of the hydrogen monolayer; (2) from the half-sum of the charge consumed by the hydrogen monolayer adsorption and desorption; and (3) from the charge consumed by the CO desorption. The three results for any one of the catalysts were practically identical.

Lindström et al. [55] compared the RSA of porous Pt electrodes, used in PEFCs, determined from hydrogen adsorption and CO oxidation. The changes of hydrogen charges with temperature and humidity were reported. The effect of temperature on CO charges was the smaller the higher the relative humidity was. Thus, the authors regarded the method based on CO adsorption as a more accurate for the RSA determination in fuel cells, while the method based on H adsorption is limited rather to room temperature.

Watt-Smith et al. [56] determined the RSA of Pt/C PEM fuel cell electrodes using different adsorbates, i.e. hydrogen, CO and Ag UPD. They found the variations between the results obtained by different methods to be ca. 100% for highly rough electrodes and ca. 30% for less rough electrodes. In the former case H adsorption seemed to be more accurate for the RSA determination, while in the latter case both these methods worked. The data from CO adsorption were much less reliable.

Binninger et al. [57] examined the RSA of Pt catalysts on carbon and metal-oxide supports using H adsorption and CO oxidation. They developed a more sophisticated procedure of the baseline correction for H desorption and CO oxidation signals. Using these modifications they were able to obtain reproducible and consistent values of the RSA. However, the method based on H adsorption was regarded as a more reliable than the other.

The Cu-UPD technique was used in the electrochemical quantification of the electro-active surface area of other noble metals and metallic nanoparticles. Aldana-Gonzales et al. [229] found that the RSA of AuNPs/ITO determined from voltammetric and chronoamperometric measurements performed in CuSO₄/H₂SO₄ solution were in a good agreement with geometric surface area quantified by AFM technique. Similar values of RSA were obtained using Cu-upd and H-UPD techniques in studies of carbon supported Pd and Pd-Fe catalysts performed by Neergat et al. [230]. Colmenares et al. compared H-UPD, preadsorbed CO monolayer oxidation, Cu-UPD stripping and RuO_x formation

methods in surface area determination of Se-modified RuNPs/C [231]. They showed that for both – high and low Se concentration on the Ru surface, the most reliable information about the RSA value was obtained from CO_{ad} stripping, while Cu-UPD method led to the overestimation of the active surface area because of the formation of CuSe_x compounds.

8. CONCLUSIONS

The value of the RSA of a given electrode varies with the method used for its determination and the experimental conditions. Each method of the RSA measurement is based on specific theory and assumptions. Thus, even for the same electrode various “surface areas” can be defined [232].

Undoubtedly, no universal method exists that could be used for the RSA determination of all noble metal electrodes. Even for pure Pt, which has been the most frequently studied metal, different authors propose slightly different procedures. For other metals, and in particular, for their alloys, the situation is more complex and in many cases there is no standard way of the RSA determination that would be generally accepted in the literature.

For a Pt electrode the most recommended method is that based on hydrogen adsorption. The second one is probably that of Cu UPD. The latter method is also applicable for other metals and alloys and seems to be the most versatile. The RSA determination from oxygen adsorption is the most suitable for Au, Pd and Pd-rich alloys. The method utilizing double layer capacitance appears to be quite universal but it is only destined to a rough estimation of the RSA. The narrow double layer potential window, possible contributions from faradaic processes and often unknown conversion factor between the measured capacity and RSA are here the main problems.

The method based on CO adsorption needs a special comment. Although commonly used and potentially applicable for all platinum group metals and alloys, it seems to be very problematic. It requires the knowledge on the adsorption parameters, such as the surface coverage with the adsorbate and its exact structure and composition. These factors are dependent on the adsorption conditions and the electrode state. It means that in each case for a reliable RSA determination of a given type of the electrode the detailed investigations on the nature of the CO adsorption product should be carried out for given experimental conditions, which is very inconvenient. No fixed, standardized procedure of CO adsorption has been established for the RSA determination of various noble metals and their alloys of different composition.

A lot of further research is needed in order to understand better the electrochemical reactions that are utilized for the RSA determination of solid electrodes. Since more and more complex systems are now investigated as electrocatalysts and electrode materials, such a knowledge is crucial for obtaining true and reliable data. Only on condition that the RSA of these systems is properly determined one can reproduce and compare the results originating from different laboratories, different time periods, obtained by different techniques and concerning different materials.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest

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