

Electrosorption of carbon dioxide on platinum group metals and alloys—a review

M. Łukaszewski · H. Siwek · A. Czerwiński

Received: 15 April 2008 / Accepted: 15 June 2008 / Published online: 12 July 2008
© Springer-Verlag 2008

Abstract The review summarizes the studies on the phenomenon of carbon dioxide electrosorption on platinum group metals and alloys. This subject is strictly linked to the research in the field of electrocatalysis and fuel cells. The work aims to present current knowledge on the processes of CO₂ electrosorption and the adsorbate oxidation on Pt, Rh, and their alloys as well as on the influence of various factors on the electrochemical behavior of reduced CO₂ on these materials. The experimental methods commonly applied in these investigations are characterized from the point of view of their ability to determine the nature of the adsorbate. The problem of similarities and differences between reduced CO₂ and adsorbed CO is also discussed.

Keywords Platinum group metals and alloys · Carbon dioxide electrosorption · Electrocatalysis · Fuel cells

Introduction

The continuous progress in the studies on fuel cells has resulted in a rapid increase in the number of papers devoted to the behavior of small-molecule organic compounds towards solid electrodes. The electrode reactions of methanol, ethanol,

formic acid, and carbon oxides on platinum group metals have been intensively investigated.

The process of organic fuel electrooxidation in a fuel cell typically consists of several steps, usually involving adsorbed CO as an intermediate and CO₂ as a final product [1]. The former species acts as strong surface poison inhibiting electrocatalytic processes on the anode and causing a decrease in cell efficiency. Although CO₂ itself is regarded as inert towards metallic electrodes, it can undergo further reactions with adsorbed hydrogen leading to adsorbed products, including CO, which also block active surface sites. Therefore, there is a constant search for such electrode materials, on which the carbonaceous species would not be adsorbed or their removal would be facilitated. It has been established [1–5] that the use of Pt alloys with such metals as Ru, Os, Ir, Re, Sn, Mo, and W leads to the improvement in the work of methanol fuel cells. Moreover, the investigations on electrode reactions of carbon oxides are also important in the context of the performance of hydrogen fuel cells, where in H₂ gas CO and CO₂ can be present as impurities [3, 6–10]. The effect of deterioration of cell voltage–current characteristic in the presence of carbon oxides is illustrated in Fig. 1 [3]. Furthermore, CO₂ is a substrate for reductive formation of many simple organic compounds of great practical significance [11–14]. Thus, the examination of the electrode reactions with the participation of CO₂ is an important part of applied electrochemistry. Simultaneously, fundamental studies are performed for better understanding the processes occurring in those systems leading to the extension of our knowledge on electrocatalysis and electrochemical properties of solid materials. In this context, CO₂ can be considered as a model for the examination of electrosorption of simple organic molecules.

M. Łukaszewski · A. Czerwiński (✉)
Department of Chemistry, Warsaw University,
Pasteura 1,
02-093 Warsaw, Poland
e-mail: aczerw@chem.uw.edu.pl

H. Siwek · A. Czerwiński
Industrial Chemistry Research Institute,
Rydygiera 8,
01-793 Warsaw, Poland

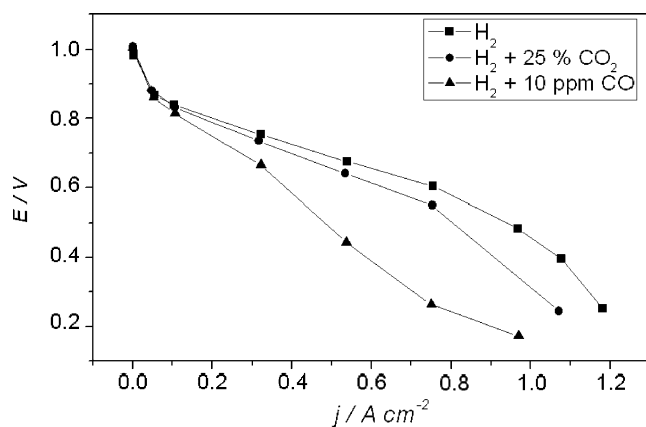
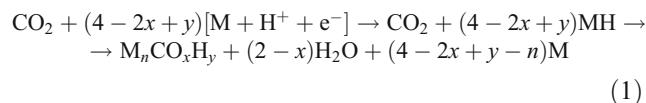


Fig. 1 Influence of the presence of CO₂ and CO in H₂ gas on the performance of the proton exchange membrane fuel cell with a Pt anode [3]

In Refs. [12–14], CO₂ reduction mainly on non-noble metals was discussed with respect to electrode material and process conditions. This paper focuses on CO₂ electroreduction occurring on platinum group metals and their alloys. The work aims to summarize current knowledge on the processes of CO₂ electroreduction and the adsorbate oxidation on Pt, Rh, and their alloys as well as on the influence of various factors on the electrochemical behavior of reduced CO₂ on these materials. The experimental methods commonly applied in these investigations are characterized from the point of view of their ability to determine the nature of the adsorbate. The problem of similarities and differences between reduced CO₂ and adsorbed CO is also discussed.

General characteristic of CO₂ electroreduction on platinum group metals in acidic solutions

CO₂ electroreduction on Pt was discovered by Giner in 1963 [15]. In 1976, Zakharian et al. [16] reported on a similar phenomenon on Rh. Further studies have confirmed that, in acidic solutions (e.g., H₂SO₄ and HClO₄) at potentials positive to the hydrogen reversible potential, CO₂ can be reduced on Pt, Rh, and their alloys in a reaction with underpotentially deposited hydrogen (UPD H), according to a general scheme:



where M stands for metal surface atoms, while M_nCO_xH_y represents the adsorption product of CO₂ reduction. Thus, hydrogen adsorption is a first and requisite step for CO₂ reduction to occur [15–45]. The product of the reaction between CO₂ molecules and hydrogen atoms (usually denoted as reduced CO₂ or r-CO₂) becomes adsorbed.

During CO₂ electroreduction in UPD H region, all products are bonded to the electrode surface [27, 34, 40, 42, 43, 46], i.e., no soluble species like CO, formaldehyde, or formic acid are observed [31]; however, when potential is shifted towards values of hydrogen evolution region, soluble products might also be formed such as HCOOH, CH₃OH, H₂CO, and CH₄ [47]. The adsorbed products cannot be further reduced nor desorbed even at more cathodic potentials [27, 40, 48]. These species are not removed from the surface either by bubbling with an inert gas or by washing procedure [27, 49]. The process of CO₂ electroreduction is electrochemically irreversible and the potential required for the adsorbate oxidative removal is significantly higher than the adsorption potential (see Fig. 2). Moreover, it was proved in radiometric experiments [49] that the adsorbate does not exchange with CO₂ molecules from the bulk of the solution, which indicates also the chemical irreversibility of the reaction between CO₂ and adsorbed hydrogen.

In contrast to Pt and Rh, other platinum group metals such as Pd, Ru, Os, and Ir do not adsorb CO₂ at potentials positive to the hydrogen reversible potential despite the existence of UPD H on these materials [16, 27, 42, 48, 50–52]; some interactions of CO₂ with adsorbed hydrogen were observed only on Ir (110) [53]. The lack of reaction between CO₂ and UPD H on Pd is particularly interesting, since this metal does not only adsorb but also absorbs large amounts of hydrogen. In fact, in the presence of UPD H, surface concentration of r-CO₂ on Pd is at least 50 times lower than on Pt [52]. No soluble species are generated during CO₂ interaction with Pd electrode in the UPD H potential region, either [27]. In acidic solutions, CO₂ is adsorbed on Pd only at potentials negative of the reversible hydrogen potential [50]. However, it is not clear whether this is a result of reduction of CO₂ by adsorbed hydrogen or hydronium ions.

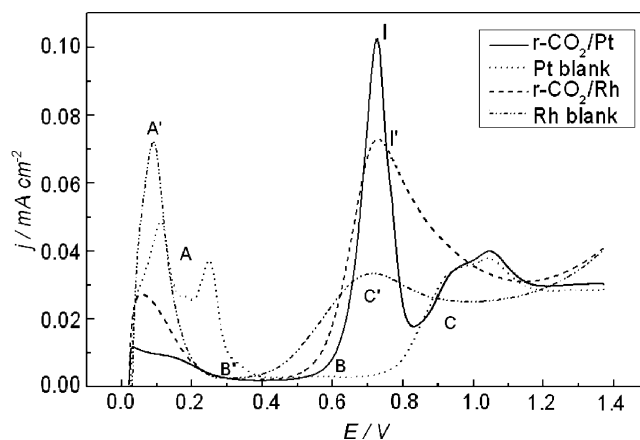


Fig. 2 Cyclic voltammograms recorded after CO₂ electroreduction at 0.02 V on Pt and Rh together with blank curves; scan rate 0.05 V s⁻¹, 0.5 M H₂SO₄. A, A'—adsorbed hydrogen oxidation region; B, B'—double layer region; C, C'—surface oxidation region; I, I'—r-CO₂ oxidation peak. Potential scale vs. SHE

In the literature, there were various attempts to explain why CO₂ is not adsorbed on Pd. In that context, it should be stressed that electronic work function for Pd is intermediate between the values for Pt and Rh, therefore one could expect Pd activity in CO₂ reduction similarly to its activity in hydrogenation reactions [22, 54]. According to Vassiliev et al. [16, 27, 44, 48], CO₂ must be first physisorbed on bare metal being activated before the reaction with hydrogen. Thus, the character of the interaction of CO₂ with the metal is essential. The reason of Pd inertness in CO₂ adsorption would be different bond energy of physisorbed CO₂ molecule with Pd surface in comparison with Pt and Rh. However, the significance of physisorption of CO₂ in its electroadsorption was questioned by Sobkowski et al. [28]. In fact, it should be noted that on Pt CO₂ adsorption still occurs even when major part of the electrode surface is covered with adsorbed hydrogen, i.e., when accessibility of a bare metal is small. Moreover, this phenomenon can play only a minor role when much stronger adsorption interactions take place. Another explanation of such unexpected behavior of Pd towards CO₂, as proposed by Grdeń et al. [55], might be the equilibrium between adsorbed and absorbed hydrogen. The consumption of adsorbed hydrogen in its reaction with CO₂ should force also desorption of absorbed hydrogen, which is energetically unfavorable. This proposal, however, does not explain the absence of r-CO₂ on metals not absorbing hydrogen, i.e., Ir, Ru, and Os. Therefore, the properties of hydrogen–metal bond itself can be suggested as a main reason of weak CO₂ adsorption on those materials [55]. Czerwiński [22] also pointed out the possibility of changes in metal surface properties due to adsorption of water and anions from the solution. Nevertheless, despite various proposals, there is still no generally accepted explanation of the fact that CO₂ electroadsorption on platinum group metals in the presence of UPD H is limited only to Pt and Rh.

Surface coverage with r-CO₂

The potential at which CO₂ electroadsorption starts is determined by the onset of hydrogen adsorption, which in acidic solutions is ca. 0.35–0.40 V vs. SHE for Pt (region A in Fig. 2) and ca. 0–0.25 V for Rh (region A'). The surface concentration of r-CO₂ on Pt initially increases with the potential decrease until it reaches a constant value below ca. 0.20 V [6, 22–24, 27, 37, 38, 49, 56–58] (Fig. 3). At potentials around the hydrogen reversible potential, a small decrease in surface coverage was reported [29]. The electrode coverage with the adsorbate obeys Temkin isotherm [27, 36, 59–61].

On the other hand, for Rh, the surface concentration of the adsorbate increases steadily with decreasing potential in

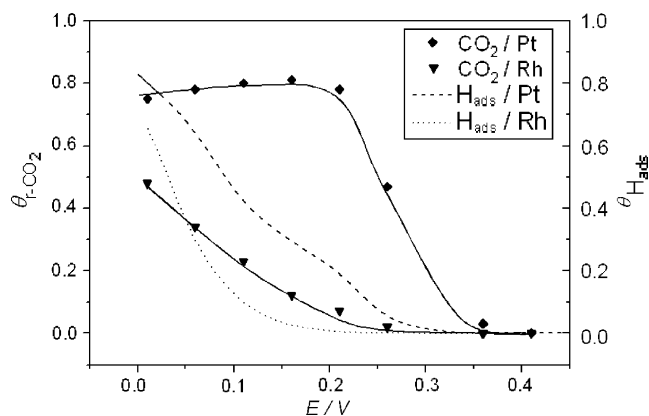


Fig. 3 Surface coverage with r-CO₂ and adsorbed hydrogen vs. adsorption potential for Pt and Rh in 0.5 M H₂SO₄. Potential scale vs. SHE

UPD H region [16, 27, 29], albeit some authors [28, 62] report that at ca. 0 V a plateau is attained. In general, the potential region of CO₂ electroadsorption on Rh is shifted negatively in comparison with Pt [16, 27–29, 56]. According to Marcos et al. [29], lower potential value related to maximum surface coverage with r-CO₂ on Rh with respect to Pt correlates with stronger adsorption of anions on the former metal. Martins [56] attributed this effect to different values of the potential of zero charge for both metals. Typical dependence of surface coverage with r-CO₂ and UPD H for Pt and Rh electrodes is shown in Fig. 3 [63].

The values of surface coverage with r-CO₂ were obtained mainly by electrochemical (e.g., from charging curves of voltammetry) or radiochemical methods. At room temperature, the maximum coverage between 0.70 and 0.80 [7, 16, 22, 27, 31, 36, 37, 44, 59, 64–67] is generally accepted for Pt electrode despite both higher (0.95 [68]) and lower values (0.45 [6], 0.52 [69]) sporadically found in the literature, while for Rh it does not exceed 0.60 [16, 22, 28, 65, 67]; the value as high as 0.82 reported in [62] does not seem realistic. For single crystal electrodes surface coverage with r-CO₂ depends on plane orientation [18, 33, 39, 53]. The fact that for every system this value is much lower than unity was explained by repulsive interactions between adsorbate molecules [36] or by steric effects [64]. Surface coverage with r-CO₂, in particular for Rh, is also affected by temperature [7, 16, 24, 27, 57, 66]; an increase with temperature is observed.

Kinetics of CO₂ electroadsorption

The kinetics of CO₂ adsorption on Pt has been studied by electrochemical techniques since the early works by Giner [70], Piersma et al. [71], and Brummer and Cahill [37]. Their data, together with later results of radiochemical

experiments performed by Urbach et al. [36] and Sobkowski and Czerwiński [24, 72], suggest strong dependence of adsorption rate with electrode potential. However, according to Vassiliev et al. [27], the rate of CO₂ adsorption is not directly affected by electrode potential but by hydrogen surface coverage, which is connected both with potential and pH. Various aspects of the kinetics of CO₂ electro-sorption on Pt were further examined by Marcos et al. [73], Kazarinov et al. [69], Martins [56], Smolinka et al. [6], Hoshi et al. [18, 20, 21], and Rodes et al. [19], while for Rh such studies were carried out by Zakharian et al. [16], Sobkowski et al. [28], and Hoshi et al. [53].

Surface concentration of r-CO₂ increases with time until a saturation coverage is reached [6, 19, 24, 53, 56, 71, 73]. Maximum reaction rate on Pt is in the range of 0.10–0.20 V [24, 37, 53] while on Rh it peaks around 0.05–0 V [28, 53]. Time needed for obtaining a steady-state surface coverage with r-CO₂ on Pt is shorter in comparison with Rh, which indicates higher electro-sorption rate in the former case [27, 56]. It was established that, on Pt electrode at potential range 0–0.15 V [22, 24] and on Rh [22, 28], the process of CO₂ electro-sorption followed second-order kinetics with respect to adsorbed hydrogen, while on Pt at potentials higher than 0.15–0.20 V first-order kinetics was observed [22, 24]. The order of the reaction with respect to CO₂ in solution is equal to 1 [22, 24, 37, 72]. The rate-determining step is the interaction between CO₂ molecule and atoms of adsorbed hydrogen [24, 27, 28, 37, 44], although for Pt there were suggestions that this is true only for the reaction of CO₂ with weakly adsorbed hydrogen, while its reaction with strongly adsorbed hydrogen under certain conditions might be controlled by mass transport [73]. Activation energy of the adsorption process depends mainly on the bond energy of adsorbed hydrogen with electrode surface and surface coverage with r-CO₂ [27, 44, 57]. Other factors influencing the kinetics of CO₂ electro-sorption are temperature [15, 16, 24, 27, 72], solution composition [20, 21, 72, 73], and pH [27, 29, 37, 44, 74] as well as plane orientation for single crystal electrodes [18–21, 44, 50, 53, 75, 76]. For instance, in the case of Pt in 0.5 M H₂SO₄ [53] and Pt [18] and Rh [53] in 0.1 M HClO₄, the rate of CO₂ reduction increases in the order: (111)<(100)<(110), while for Rh in 0.5 M H₂SO₄ [53]: (111)<(110)<(100).

During CO₂ reduction on Pt at potentials above 0.15 V a small cathodic charge (55 μC cm⁻² at 0.20 V) was detected [19, 22, 24], while at lower potentials no charge transfer was observed [15, 22, 24, 36, 38]. The flow of negative current is a result of the shift of equilibrium between adsorbed hydrogen and hydrogen ions from solution towards the adsorbed species [24, 38]. This is probably caused by the fact that in the presence of r-CO₂ surface centers normally not active in hydrogen adsorption process in that potential range become activated [24, 38]. Another

reason can be diffusion of r-CO₂ from the sites previously occupied by adsorbed hydrogen consumed in the reaction with CO₂ [21]; on liberated surface centers regeneration of adsorbed hydrogen takes place, whose further reaction with new CO₂ molecules is possible [19, 38]. Therefore, even at potentials corresponding to low initial electrode coverage with hydrogen, final surface coverage with r-CO₂ is relatively high, e.g., for 35% of a monolayer of adsorbed hydrogen surface concentration of r-CO₂ is still close to its maximum value, i.e. 70% [22–24, 28, 38]. During CO₂ electro-sorption on Rh electrode, the charge involved in the process did not exceed a few μC cm⁻² [28]. In fact, however, on the basis of Eq. (1), one can predict additional charge transfer due to hydrogen re-adsorption if free surface sites appear after CO₂ electro-sorption, i.e., when $4-2x+y-n>0$.

The nature of r-CO₂ and methods used for its examination

The nature of the product of CO₂ electro-sorption on polycrystalline Pt and Rh electrodes in acidic solutions has been widely discussed in the literature. This problem has been studied by the electrochemical methods (mainly cyclic voltammetry, chronoamperometry, and chronopotentiometry) as well as using electrochemistry combined with an additional technique such as IR spectroscopy [6, 17, 19, 29, 30, 33–35, 68, 75–78], mass spectrometry [6, 56, 47, 79], radiochemistry [22–24, 26–28, 36, 49, 69, 72], gas chromatography [80], and electrochemical quartz crystal microbalance [63, 67, 81, 82]. In Table 1, various adsorbates proposed in the literature for r-CO₂ together with techniques used for the adsorbate identification are summarized.

The authors generally agree on the presence of single-coordinated (linearly bonded) and multi-coordinated (bridge and triply bonded) CO species (Fig. 4 [83]) on Pt surface after CO₂ electro-sorption in the UPD H region [6, 15, 17, 19–21, 29–35, 37–39, 41, 47, 56, 66, 68, 70, 74–78, 80, 84–86]. However, some other adsorbates were also suggested like COH [27, 37, 42–44, 48, 69, 77, 85, 87], C(OH)₂ [36], CHO [79, 88, 89], and COOH [15, 22–24, 26, 32, 37, 49, 56, 64, 70, 72, 88, 90, 91] radicals, although these species have not been confirmed by most of spectroscopic data [6, 17, 19, 30, 33, 34, 68, 75, 76, 78]. It was also postulated that CO₂ molecules only block hydrogen atoms, becoming blocked itself by water molecules and anions [71]. The latter view, however, was questioned by the results of comparative experiments in H₂O and D₂O [72]. Another proposal for r-CO₂ was a clathrate-type structure denoted as Pt(H,CO₂,H₂O) [35, 59, 60, 73, 89, 92]. Traces of hydrocarbons were also taken into account [93].

Table 1 Different adsorption products of CO₂ electro sorption on Pt and Rh postulated in the literature

Adsorption product	Electrosorption scheme	Electrode	Experimental technique ^a
CO	CO ₂ + 2M + 2H ⁺ + 2e ⁻ → M _n CO + H ₂ O + (2 - n)M ^b	Pt, Rh	SNIFTIRS [34, 35, 62, 77], SPAIRS [34, 35, 62], FTIRRAS [17, 19, 33, 68, 75, 76, 78], DEMS [6, 47], SEIRAS [6], EMIRS [30], GC [80]
COOH	CO ₂ + M + H ⁺ + e ⁻ → MCOOH	Pt	R [22, 23, 49], SNIFTIRS [77]
CHO	CO ₂ + 3M + 3H ⁺ + 3e ⁻ → MCHO + H ₂ O + 2M	Pt	DEMS [79] ^c
COH	CO ₂ + 3M + 3H ⁺ + 3e ⁻ → M ₃ COH + H ₂ O	Pt, Rh	SNIFTIRS [77], DEMS [56], R [27, 28, 69]
C(OH) ₂	CO ₂ + 2M + 2H ⁺ + 2e ⁻ → M ₂ C(OH) ₂	Pt	R [36]
CH ₂	CO ₂ + 6M + 6H ⁺ + 6e ⁻ → M ₂ CH ₂ + 2H ₂ O + 4M	Rh	
CH	CO ₂ + 5M + 5H ⁺ + 5e ⁻ → M ₃ CH + 2H ₂ O + 2M	Rh	R [28]
C	CO ₂ + 4M + 4H ⁺ + 4e ⁻ → M ₄ C + 2H ₂ O	Rh	R [28]
H,CO ₂ ,H ₂ O	CO ₂ + H ₂ O + M + H ⁺ + e ⁻ → M(H, CO ₂ , H ₂ O)	Pt	SNIFTIRS [35], SPAIRS [35]

^a Besides electrochemistry; *R* radiochemistry, *GC* gas chromatography, *SPAIRS* single potential alteration infrared reflectance spectroscopy, *SNIFTIRS* subtractively normalized interfacial Fourier transform infrared reflectance spectroscopy, *FTIRRAS* Fourier transform infrared reflection absorption spectroscopy, *SEIRAS* surface enhanced infrared absorption spectroscopy, *EMIRS* electrochemically modulated infrared spectroscopy, *DEMS* differential electrochemical mass spectrometry

^b *n*=1 for linearly, 2 for bridge, and 3 for triply bonded CO

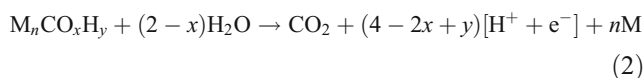
^c Coupled with isotope labeling

In the case of Rh electrode, the product of CO₂ electro sorption is regarded as generally more reduced than on Pt [22, 27, 28, 56]. A mixture of a CO-type adsorbate [29, 62] is proposed with an addition of species denoted as a reduced form of adsorbed CO [29, 62] or such species as COH [28, 56], CH₂ [22], CH [28], or even C radicals [28]. According to Sobkowski et al. [28], further reduction of CO₂ on Rh in comparison with Pt is caused by lower hydrogen–metal bond energy in the former case. Martins [56] attributed this behavior to different mechanisms during

the initial step of CO₂ electro sorption, involving a formation of a complex of CO₂ with H adatoms and water molecules at the interface in the case of Pt, in contrast to dissociative CO₂ adsorption in the case of Rh.

The fact that CO₂ adsorption product on Pt and Rh is not homogeneous is accepted by most of the authors. Indeed, taking into account the complexity of the electro sorption process, one simple product is unlikely [65, 94].

In general, from the electrochemistry alone it is not possible to unequivocally determine the structure of r-CO₂. However, one can obtain some information on the nature of the adsorbate on the basis of the analysis of the eps (electron per site) value, i.e., a number of electrons taking part in the process of the adsorbate oxidation from one surface site. Since the general scheme of r-CO₂ oxidation can be written as follows:



eps is defined as:

$$eps = (4 - 2x + y)/n \tag{3}$$

The value of eps can be calculated as the ratio of reduced CO₂ oxidation charge ($Q_{r-CO_2}^{ox}$) to the difference between the charges of adsorbed hydrogen oxidation in the absence and presence of reduced CO₂ ($\Delta Q_{H_{ads}}^{ox}$) [28, 55, 60, 66, 68, 88]:

$$eps = \frac{Q_{r-CO_2}^{ox}}{\Delta Q_{H_{ads}}^{ox}} \tag{4}$$

The method of eps calculation was discussed by Tokarz et al. [94], who modified this equation by taking into

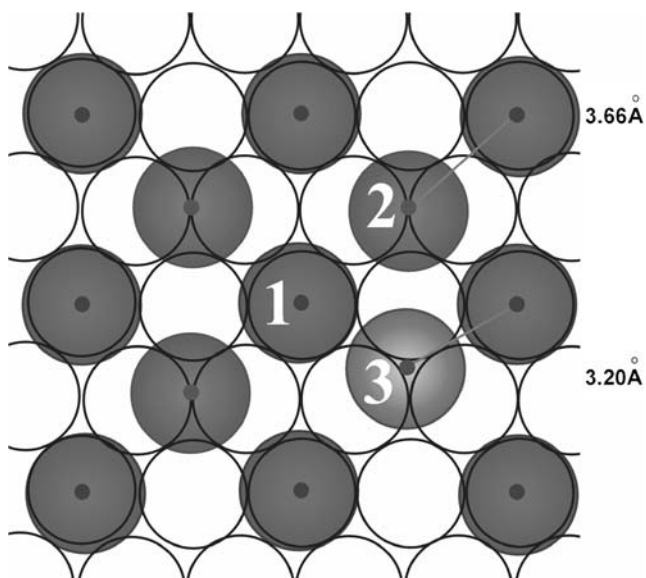


Fig. 4 Forms of CO adsorbate on Pt (111): 1—linearly boded CO, 2—bridge bonded CO, 3—triply bonded CO [83]

account a fractional surface coverage with adsorbed hydrogen ($\theta_{\text{H}_{\text{ads}}}$):

$$\text{eps} = \frac{Q_{\text{r-CO}_2}^{\text{ox}} \cdot \theta_{\text{H}_{\text{ads}}}}{\Delta Q_{\text{H}_{\text{ads}}}^{\text{ox}}} \quad (5)$$

Some other quantities related to eps also appeared in the literature, namely the inverse of eps [80], the ratio of reduced CO₂ oxidation charge to surface oxide reduction charge [89] or the number of metal atoms from which one r-CO₂ molecule displaces hydrogen [69].

Another parameter used for the characterization of the adsorbate is epm (electron per molecule), i.e., a number of electrons necessary for oxidation of one molecule of r-CO₂. This value cannot be determined in pure electrochemical experiment and other methods such as radiochemistry, gas chromatography, and mass spectrometry must be simultaneously applied. If the surface concentration of adsorbed species per area unit (Γ) is known, epm value can be calculated as [23]:

$$\text{epm} = \frac{Q_{\text{r-CO}_2}^{\text{ox}} \cdot N_{\text{A}}}{\Gamma \cdot S \cdot F} \quad (6)$$

where S is the real area of the electrode, N_{A} —Avogadro number and F —Faraday constant.

Figure 5 shows the epm–eps characteristic predicted for various structures of r-CO₂ together with respective values obtained experimentally [6, 16, 23, 24, 27, 28, 31, 37, 43, 45, 49, 56, 60, 66, 68, 69, 79, 80, 85, 88, 89, 94]. It is visible that for Pt the literature eps values are in the range 1–1.6, while for Rh a larger scatter of data is observed (1.3–3.5). On the other hand, the reported epm values differ significantly for both Pt (1–3.4) and Rh (3–5.7). The data

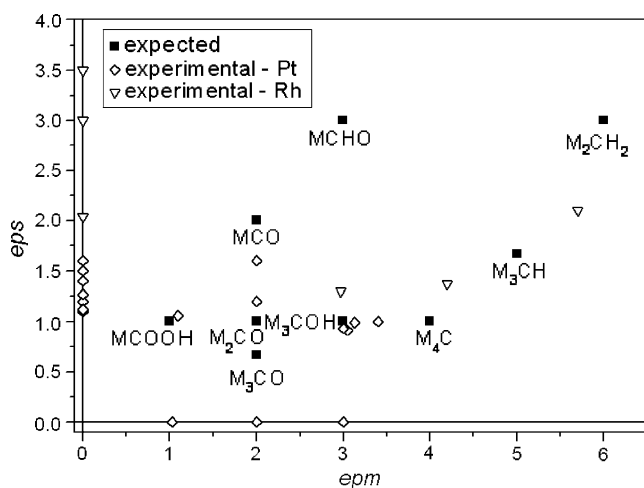


Fig. 5 Theoretical epm and eps values predicted for various structures of r-CO₂ together with experimental data obtained for Pt and Rh. Points on zero lines show data for which only one parameter was reported

for Pt and Rh might be interpreted assuming that the adsorbate generated on Rh is more reduced than on Pt, i.e., more electrons are exchanged per site or per molecule during the oxidation of r-CO₂ on Rh in comparison with Pt. Thus, different conclusions on the nature of r-CO₂ have been drawn by various authors. However, the possibility cannot be excluded that the discrepancy between eps or epm values originates from different contributions from anion re-adsorption to overall charge of the adsorbate oxidation [95–97], which is larger for higher coverages with the adsorbate and depends on the kind of metal. Moreover, the experiments with CO₂ reduction were performed in various electrolytes both containing specifically adsorbing species, like sulfates and those not exhibiting specific adsorption such as perchlorates. This can explain the fact that the comparison of the values reported for various metals and various electrolytes leads to significant disagreement. Nevertheless, since in a given electrolyte the surface coverage with r-CO₂ on Rh is always lower than on Pt, the higher eps and epm values for Rh cannot be totally ascribed to the above effects and therefore should at least partially result from differences in the adsorbate structure [67].

Each of the aforementioned methods has both its strong points and limitations, but they provide more complete information than the electrochemistry alone. The main advantage of radiochemical method is the possibility of determination of absolute surface concentration of the adsorbate and direct examination of the kinetics of CO₂ electrosorption and the adsorbate oxidation [23, 24, 26–28, 36, 49, 69, 72]. However, since all possible adsorbates discussed in the literature contain one carbon atom from the original CO₂, the method based on the carbon atom labeling is not selective with respect to the molecular structure of the species. The detection of hydrogen in the adsorbed species requires using tritium-labeled water and non-labeled CO₂ [98]. Other drawbacks of the radiochemical technique are: its limitation to electrodes of relatively large real surface area, since the number of impulses must be high enough, and the fact that the signal measured is an averaged value over the whole surface. On the other hand, gas chromatography [80] and mass spectrometry [6, 56, 79] allow for detection of soluble or volatile CO₂ reduction intermediates as well as monitoring the amount of CO₂ produced during the adsorbate oxidation rather than the species bonded to the electrode. More structural information about the adsorbate can be obtained when mass spectrometry is coupled with isotope labeling [79].

For the studies on CO₂ electrosorption, mainly on Pt electrodes, IR spectroscopy techniques have often been applied [6, 17, 19, 26, 30, 33–35, 62, 68, 75–78]. This group of methods is generally regarded as a powerful tool for in situ determination of the exact molecular structure of

the adsorbate and its evolution with potential changes. However, besides its unique features, they have several important limitations that should be stressed: first, the absolute value of the surface concentration of the adsorbate cannot be obtained; second, on the basis of IR spectra, only some chemical bonds can be identified and certain possible products of CO₂ reduction might not be detected (e.g., Beden et al. [30] failed to observe CO₂ electroadsorption on Pt at 0.25 V, which was in contradiction with most other results); third, due to very thin layer of the electrolyte used, the conditions of CO₂ reduction are markedly different than in other types of experiments. Willsau and Heitbaum [79] suggested that the process of photon absorption itself can lead to changes in the adsorbate structure. Martins [56] noted that in IR experiments the detection of thermodynamically stable products is favored, whereas e.g., differential electrochemical mass spectrometry (DEMS) analysis detects the first product, i.e., the one formed under kinetic control.

Another method that could seem promising for the studies on CO₂ electroadsorption is the electrochemical quartz crystal microbalance (EQCM), which has already been widely used as an in situ technique for the investigation of various electrode processes. Its high sensitivity to mass changes allows for monitoring even submonolayer phenomena connected with adsorption, deposition, and dissolution [99–104]. From a correlation between resonator frequency change (Δf) and charge consumed (Q), it is possible to obtain a parameter called “apparent molar mass” of species involved in the electrode process, according to the equation:

$$M/z = -(\Delta f \cdot C \cdot F)/Q \quad (7)$$

where C is calibration constant of the quartz crystal resonator, F is Faraday constant, and z is number of electrons exchanged. Unfortunately, because more than one species can participate in the charge transfer reaction and some other species can additionally be adsorbed/desorbed without charge transfer, the apparent molar mass is a resultant quantity of all those reactions. Moreover, apart from mass changes, there are other factors influencing the frequency of the quartz crystal resonator operating in liquid [99–104]. As a result, the analysis of the EQCM signal is difficult and can often lead to ambiguous conclusions. Recently [63, 67], an attempt has been made to predict the EQCM response during adsorption and oxidation of the adsorbate for various possible structures of r-CO₂. It was demonstrated that since the mass contribution to the measured frequency change is a resultant effect of various processes, including r-CO₂ adsorption/desorption, surface oxide formation, anion and water adsorption/desorption, and metal dissolution, the EQCM is not very specific about

the nature of the adsorbate. Due to not very great differences between apparent molar mass values predicted for various adsorbate structures, the exact composition of CO₂ reduction products cannot be unequivocally determined on the basis on the EQCM experiment. Nevertheless, the EQCM can be used as a valuable auxiliary method for comparative studies [63, 67, 81, 82].

Other promising techniques that might allow deeper insight into the problem of the nature of r-CO₂ are NMR and SFG, both already successfully applied to examine CO adsorption [105–110].

Factors influencing the properties of r-CO₂

The properties of r-CO₂ depend on such factors as: adsorption potential [6, 28, 37, 49, 65, 69, 78] adsorption time [6, 32, 56, 69], surface coverage with the adsorbate [37, 69], temperature [7, 27, 32], electrode surface morphology [29, 35, 49, 64] and method of electrode pretreatment [111], solution pH [27], and composition [34, 59, 62] as well as plane orientation for single crystal electrodes [19, 33, 75, 76]. The results of the experiments performed on noble metal alloys [55, 63, 65, 67, 81, 94, 112–120] have shown that in general the electrochemical characteristic of CO₂ adsorption product depends on the alloy surface composition.

The observed changes in eps and epm values with adsorption potential indicate the influence of that parameter on the structure of r-CO₂ [27, 28, 49, 65]. This is especially pronounced for Rh, where around 0 V some additional species more reduced than CO were detected [28, 29], confirmed by spectroscopic data [62]. For adsorption potentials below 0 V on Pt electrode an additional product ascribed to HCOOH was observed [25]. Some authors [29, 34, 35, 59, 60, 89, 111] suggest that the electrochemical properties of the adsorbate on Pt depend on whether it is a product of CO₂ interactions with strongly (s) or weakly (w) adsorbed hydrogen. According to Arévalo et al. [35], these reactions lead to ensembles denoted as Pt_s(H, CO₂, H₂O) and Pt_w(H, CO₂, H₂O), respectively; the former species can additionally undergo interconversion to yet another product, Pt_s(H, CO, OH, H₂O), which is, however, electrochemically undistinguishable.

According to Maier et al. [32] and Martins [56], the relative contributions from various forms of r-CO₂ on Pt depend on adsorption time and temperature: short periods (several minutes) and higher temperatures (70 °C) favor the formation of COOH, while for longer times and at lower temperatures (20 °C) CO species are dominant products. After prolonged polarization (several hours), HCOOH as an additional product was found [32]. Smolinka et al. [6] stated that electrode surface saturation with multi-coordinated CO

species requires shorter period than with single-coordinated CO species.

Sobkowski and Czerwiński [64] observed some influence of electrode roughness on the properties of r-CO₂ on Pt, which was explained by changes in energetic heterogeneity of the surface [22]. Mendez et al. [111] examined the influence of electrode morphology and pretreatment on the electrochemical properties of r-CO₂ on Pt and found that application of a appropriate potential cycling routine can lead to strengthening in the metal–adsorbate bond. Marcos et al. [29, 34, 59, 60, 73, 89] and Baruzzi et al. [61] studied CO₂ electrosorption and electrooxidation on Pt electrodes in different electrolytes, while Arévalo et al. [62] investigated the role of adsorbed anions on the r-CO₂ formation and electrooxidation on Rh. It was demonstrated that the anion effect on Rh was more remarkable than on Pt and a negative shift of the onset potential of CO₂ electrosorption and a positive shift of r-CO₂ oxidation potential was observed with the increase in adsorption strength of anions present in the electrolyte.

The characteristic of CO₂ electrosorption presented in the above sections concerns acidic solutions. Under these conditions, CO₂ gas is dissolved in a molecular form (CO₃²⁻ or HCO₃⁻ anions have extremely low concentrations [121]). In general, with the increase in pH in the range 0.4–6.0, surface coverage of Pt with r-CO₂ weakly decreases, but at pH>6 it rapidly drops [27, 42–44]. In neutral and basic solutions, CO₂ is converted into carbonates. These anions mainly undergo specific adsorption with a partial charge transfer, but without significant reduction [27, 122]. During strong cathodic polarization of Pt in KHCO₃ solution saturated with CO₂ at temperature around 273 K, small amounts of soluble species such as HCCOH, CO, CH₄, and H₂C₂O₆ were detected [123–125]. On Pd electrode in neutral and basic solutions at potentials below 0.05 V vs. RHE CO₂ (HCO₃⁻), reduction to HCOO⁻ [124, 126–129] and CO [17, 124, 127–129] was observed.

Is r-CO₂ identical with adsorbed CO?

In the literature, there is still a controversy about whether the adsorption products of CO₂ reduction on Pt, Rh, and their alloys are identical with the products of a direct CO adsorption. This question with respect to Pt electrode was raised first by Piersma et al. [71], who claimed that they are different. On the other hand, Breiter [80, 84] concluded that both adsorbates are the same. Also, Beden et al. [30] suggested that in both cases the adsorbed species are only CO radicals, although differently bonded to the surface: direct CO adsorption gives almost exclusively linearly bonded CO, while r-CO₂ consists of a significant amount

of more highly coordinated CO. Smolinka et al. [6] attributed the differences in CO adlayers formed by CO₂ reduction and CO adsorption to a different distribution of CO species on the surface rather than to the presence of other adsorbed species.

However, other authors believe that r-CO₂ cannot be totally identified with adsorbed CO alone. According to Brummer and Cahill [87], the interactions between adsorbed hydrogen and CO are repulsive at all potentials, which is not the case for r-CO₂. Westerhoff and Holze [130] found that CO₂ reduction on Pt resulted in the adsorbate with a vibrational behavior different from that of adsorbed CO. According to Kamath and Lal [88], Willsau and Heitbaum [79], Vassiliev et al. [27], Kazarinov et al. [69] as well as Papageorgopoulos and de Bruijn [66], r-CO₂ is more similar to the products of methanol, formaldehyde and formic acid adsorption than adsorbed CO. The last authors from a comparison of CV curves of r-CO₂ and adsorbed CO oxidation of the same coverage concluded that, due to differences in peak shape and potential as well as eps values, different adsorbate structures are expected in each case [66]. Also, Sobkowski and Czerwiński et al. [22, 64, 131–133] stated on the basis of analysis of surface coverage, eps, and epm values that the properties of r-CO₂ and adsorbed CO on Pt and Rh electrodes are not the same. In particular, the influence of electrode roughness on eps was different for CO₂ and CO [64]. Moreover, it was demonstrated [131] that charging curves recorded after CO₂ reduction and CO adsorption coincide only partially, confirming that the adsorbates are not totally identical. The differences in the rate of r-CO₂ and adsorbed CO oxidation were observed by Stonehart [134]. The existence of additional species more reduced than CO among the products of CO₂ reduction on Rh electrode was reported by Marcos et al. [29] and confirmed spectroscopically by Arévalo et al. [62]. Different adsorption characteristic of r-CO₂ in comparison with CO adsorbed on Rh was also observed by Martins [56]. Recent comparative studies [63, 67, 81] on CO₂ reduction and CO adsorption on various platinum metals and alloys performed by the electrochemical quartz crystal microbalance revealed deviations from proportionality between apparent molar mass and surface coverage with r-CO₂ and adsorbed CO indicating different nature of these adsorbates. Also, the influence of alloy composition on the adsorbate oxidation potential and eps was different for each carbon oxide [63, 65, 94, 119, 120].

Moreover, there are more general differences between electrosorption of both carbon oxides. In contrast to CO₂ reduction, the presence of adsorbed hydrogen is not necessary for CO adsorption, which can also take place in the double layer potential region, i.e., when the electrode is

free from adsorbed hydrogen or surface oxide [131]. Furthermore, CO adsorption occurs on all platinum group metals, including Pd [52, 135–138]. The influence of r-CO₂ and adsorbed CO on the processes of hydrogen electro-sorption in Pd-based electrodes is also different (see section below): in the former case, only hydrogen adsorption (but not absorption) is partially blocked [55, 67, 81, 82, 113–118], while in the latter case both hydrogen adsorption and absorption are strongly inhibited [52, 135–138]. It should be added that in an experiment when CO adsorption is performed on Pt previously covered with r-CO₂, the latter adsorbate is displaced by the former one [130]. Thus, r-CO₂ is probably less strongly bound in comparison with adsorbed CO. Moreover, since surface coverage with adsorbed CO is markedly higher than for r-CO₂ [22, 28, 131, 135], it was suggested [69, 113] that CO can be adsorbed on the surface sites that are not accessible for r-CO₂. Taguchi et al. [68] pointed at the differences in the initial stages of the electro-sorption process of both carbon oxides. Adsorbing CO₂ structure is more bulky than CO and therefore its adsorption is probably inhibited on some surface sites like defects or holes, while CO can adsorb with low steric hindrance up to full coverage.

All the above facts indicate that even if single- and multi-coordinated CO species are major products of both CO₂ reduction and CO adsorption, in each case there are various relative amounts of these forms and they are accompanied by different minor products.

The influence of r-CO₂ on hydrogen electro-sorption on platinum group metals and alloys

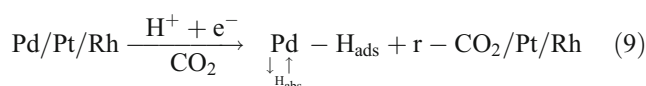
In the presence of r-CO₂, hydrogen adsorption in UPD H region is partially suppressed, i.e., hydrogen can be adsorbed only on the part of electrode surface not covered with r-CO₂. It is mirrored in the course of CV curves by lowering of hydrogen adsorption and desorption currents (see region A/A' in Fig. 2). This fact is utilized for the determination of surface coverage with the adsorbate calculated from the ratio of the difference between the charges of adsorbed hydrogen oxidation in the absence and presence of r-CO₂ ($\Delta Q_{H_{ads}}^{ox}$) to adsorbed hydrogen oxidation charge in the absence of reduced CO₂ ($Q_{H_{ads}}^{ox}$) [7, 27, 28, 65, 68, 94, 139]:

$$\theta = \frac{\Delta Q_{H_{ads}}^{ox}}{Q_{H_{ads}}^{ox}} \quad (8)$$

The presence of r-CO₂ modifies also the energy of hydrogen desorption, which drops as the coverage with the adsorbate rises [40]. With the decrease in electrode

potential the interactions between r-CO₂ and adsorbed hydrogen change from attractive into repulsive [87]. In the presence of r-CO₂ on Pt weakly and strongly adsorbed hydrogen become poorly distinguishable [59].

Although CO₂ cannot be reduced on pure Pd in the UPD H region, its adsorption is possible on Pd alloys with Pt and Rh [55, 63, 67, 81, 82, 113–118]. This behavior can be explained assuming that different adsorption properties of these metals towards CO₂ are retained in the alloy, i.e., CO₂ is adsorbed only on Pt and Rh surface atoms, but not on Pd atoms. Hydrogen bonded to Pd atoms does not participate in CO₂ reduction reaction, therefore its insertion into and removal from the alloy bulk can proceed despite the presence of r-CO₂ on neighboring Pt and Rh atoms, according to the scheme [55, 67]:



Since in a CO₂ reduction experiment performed on Pd alloys with Pt or Rh it is possible to block selectively hydrogen bonded to Pt and Rh surface atoms, without any significant effect on hydrogen bonded to Pd atoms, various current signals on CV curve are affected in a different way by the presence of the adsorbate. Thus, r-CO₂ can be applied as a diagnostic tool for the examination of the nature of complex hydrogen signals observed in cyclic voltammetric experiments for multi-component Pd alloys. As demonstrated by Łukaszewski et al. [115–117], CO₂ electro-sorption experiment performed on Pd–Pt–Rh electrodes allowed to distinguish between signals originating mainly from hydrogen absorption and those having significant contribution from hydrogen adsorption.

Marcos et al. [29] studied the influence of r-CO₂ on the hydrogen evolution reaction (HER) on Pt and Rh electrodes in 0.5 M H₂SO₄. In the presence of CO₂ in the solution, they observed an increase in the cathodic overvoltage for the HER. However, while on Pt the Tafel slope for the HER in the low current density range was –0.03 V/decade irrespective of the presence of CO₂ in the solution, on Rh the value increased from –0.03 V/decade for CO₂-free solution to –0.12 V/decade for CO₂-containing solution. The behavior observed for Rh suggests a change in the rate-determining step in the HER pathway, from a Tafel mechanism (i.e., H-atom recombination reaction) into a Volmer mechanism (i.e., electron transfer step).

Oxidation of r-CO₂

r-CO₂ is oxidized to CO₂ in a chemically and electrochemically irreversible process, which follows first-order kinetics

with respect to surface concentration of the adsorbate [26, 49]. The course of r-CO₂ oxidation depends on oxidation potential [49, 72], electrode surface state [18, 19, 75, 76, 89, 111], adsorption potential and time [6, 7, 29, 32, 59, 60, 62, 85, 89], surface coverage with r-CO₂ [69], temperature [7, 15, 32, 59, 72, 84], and solution composition [34, 59–62, 72, 73, 89] but is independent of the presence or absence of gaseous CO₂ in solution [27, 55, 63].

In cyclic voltammetric experiments, this process gives a characteristic peak placed at potential considerably higher than adsorption potential (signal *I/I'* in Fig. 2). On Pt and its alloys, the adsorbate oxidation starts in the double layer potential region (B in Fig. 2), while on Rh-based electrodes the oxidation peak coincides with the beginning part of surface oxidation currents (C'). In general, oxidation of r-CO₂ on Rh takes place over a potential range larger than on Pt [29] (see also Fig. 2). The position of the peak due to r-CO₂ oxidation on Pt electrode shifts negatively with the increase in temperature [7, 15, 32, 59]. This signal was found to be essentially composed of at least two overlapping signals [29, 34, 35, 59, 61, 69, 85, 89, 111]. Kazarinov et al. [69] ascribed this behavior to the presence of two forms characterized by similar chemical composition (COH) but different bonding energy. Martins [56], by deconvolution of r-CO₂ oxidation peak on Pt, found three adsorption products present, namely linearly and bridge bonded CO and COOH. Marcos et al. [29] related the presence of two closely located current peaks for r-CO₂ oxidation on Rh to tightly and weakly bound adsorbates. The result of CO₂ interactions with different forms of adsorbed hydrogen has also been taken into account [34, 35, 59, 60, 89, 111].

Moreover, the influence of scan rate on the multiplicity of r-CO₂ oxidation peak was observed [26, 35, 59–61, 85]. This behavior was explained by an interconversion of r-CO₂ during its potentiodynamic oxidation [59, 60, 85] or by different oxidation mechanisms [22, 26]. According to the first proposal, two chemically similar but energetically non-equivalent products of CO₂ electrosorption can transform in each other and at low scan rates only the less stable species can be detected, while at higher scan rates the exchange reaction is not fast enough and both forms can be oxidized. The rate of the interconversion between various r-CO₂ adsorbates depends also on solution composition, decreasing in the order: HClO₄>H₂SO₄>H₃PO₄ [59].

As far as the oxidation mechanism is concerned, it should be noted that r-CO₂ can be oxidized by adsorbed water or by adsorbed OH/O species formed during initial stages of surface oxide formation. The latter mechanism dominates for Rh [28, 56] and Rh alloys (Pd–Rh, Rh-rich Pt–Rh) [63, 67, 81, 113, 114], while for Pt-based electrodes

r-CO₂ is mainly oxidized by water [22, 26], although the participation of OH radical was also suggested [56, 61, 85]. According to Czerwiński [26], slow polarization additionally favors water as the oxidant species, while during fast potential changes a part of the adsorbate is oxidized also by OH or O species. These mechanisms were confirmed by the observation of large isotopic effects when the oxidation of r-CO₂ was performed in D₂O [72]. The rate-determining step of r-CO₂ oxidation is surface reaction between the oxidant and the adsorbate [26, 28, 61, 72, 85].

A different picture of r-CO₂ oxidation was presented by Marcos et al. [59, 70, 73] who claimed that at high coverage the electrooxidation proceeds initially as a first-order process involving decomposition of a clathrate-type structure of r-CO₂ and producing free surface sites. On these liberated centers, the reaction subsequently proceeds through second-order process, dependent on the anions and involving the adsorbate oxidation by adsorbed OH produced by decomposition of water.

It should be stressed that when comparing the activity of metals for CO₂ reduction and the adsorbate oxidation one needs to take into account different adsorption properties (adsorption energy) not only for CO₂, but also for hydrogen or oxygen (hydroxyl) and anions. The latter factor is discussed below. A detailed information on the processes of hydrogen electrosorption on noble metals as well as on metal oxidation itself can be found in the literature [140–144].

The influence of anions on electrochemical behavior of r-CO₂

The experiments on CO₂ reduction have been performed in various electrolytes, both containing specifically adsorbing anions (e.g., HSO₄[−] or SO₄^{2−}) and those not exhibiting specific adsorption (ClO₄[−]). The kind of anions and their adsorption strength have been found to affect the process of CO₂ reduction and the adsorbate oxidation.

Rodes et al. [19] and Hoshi et al. [20], from the comparison of data for H₂SO₄ and HClO₄, concluded that CO₂ reduction on Pt(110) is faster in the absence of adsorbed anions. The differences between these electrolytes were more significant above the potential where sulfate species start being adsorbed. The effect of the nature of the base electrolyte on CO₂ reduction was also reported for Pt(100) [76] as well as Rh(110), Rh(100), and Rh(poly) [53, 62], i.e., weaker adsorption of anions facilitated CO₂ reduction. It was explained by a competitive adsorption equilibrium between anions and hydrogen involved in the reaction with CO₂. On the other hand, for Pt(111) and Rh(111), low activity of CO₂ reduction was observed [75] in

both electrolytes indicating that in that case an intrinsic property of this specific plane orientation plays a more important role than the adsorption of anions. Marcos et al. [29] stated that since the onset of sulfate anion adsorption on Rh is shifted negatively in comparison with Pt, lower potential is required for maximum saturation of Rh surface with r-CO₂.

Due to the fact that CO₂ reduction is electrochemically irreversible, the adsorbate removal is shifted into higher potentials with respect to the adsorption potential. It means that at potentials from the double layer region the process of anion adsorption, if occurs, takes place in the presence of r-CO₂ on the surface, i.e., under conditions markedly different from those on a clean electrode. The studies performed with the use of the EQCM method [63, 67, 81, 82] have shown that in the anodic voltammetric scan taken after CO₂ reduction the resonator frequency decrease (corresponding to a resultant mass gain) is much slower than on the electrode free from r-CO₂. It was suggested that reduced CO₂ hinders adsorption of anions not only on the part of surface occupied by r-CO₂ but also on sites not covered by the adsorbate, causing the effective mass interacting with the electrode to be smaller than on an adsorbate-free surface. Anions can again be fully adsorbed only at potentials where the oxidation of r-CO₂ commences. A model for the EQCM data interpretation has been proposed taking into account the re-adsorption of anions during r-CO₂ removal [63, 67].

Marcos et al. [34, 59, 60, 73, 89] studied the kinetics and mechanism of electrooxidation of r-CO₂ on Pt in different acid media (H₂SO₄, HClO₄, and H₃PO₄). The influence of electrolyte composition on r-CO₂ oxidation peak potential, width, and multiplicity was found, with the lowest onset and smallest potential window of r-CO₂ removal observed for HClO₄ solution and the splitting of r-CO₂ oxidation peak enhanced in going from HClO₄ to H₂SO₄ to H₃PO₄. From subtle differences in wavenumber of IR absorption band ascribed to linearly bonded CO in various acids, the authors [34] concluded on the anion effect on the adsorbate properties and structure. The influence of anions on r-CO₂ electrooxidation was attributed mainly to interactions among anions and adsorbate complexes [34, 59] or through their impact on adsorbed OH species formation from adsorbed water [60, 61].

As found by Arévalo et al. [62] in the process of r-CO₂ electrooxidation on Rh, the anion effect is seen by a shift of the adsorbate oxidation potential towards more positive values as the anion strength increases. This behavior was interpreted both as the anion effect on the adsorbate structure or as a competitive reaction between the anions and OH_{ads}.

CO₂ reduction and the adsorbate oxidation on platinum metal alloys

With respect to CO₂ reduction, the investigated platinum metal alloys can be divided into two groups: (1) systems whose both components are active in CO₂ reduction, i.e., Pt–Rh [63, 65, 94, 112, 114, 119, 120] and (2) mixtures of elements active and inert in CO₂ reduction, i.e., Pt–Ru [3, 7–10, 66], Pd–Pt [55, 63, 67, 81, 117, 118], Pd–Rh [63, 67, 81, 113, 114, 117, 118], and Pd–Pt–Rh [63, 67, 115, 116].

As discussed above, Pd in the alloy remains inert to CO₂ reduction in the UPD H region. However, the alloy formation of Pd with Pt or Rh as well as Pt alloying with Rh alters the adsorbate properties, which is mirrored in the changes in surface coverage, eps, and oxidation potential.

On Pt–Rh [63, 65] and Pd–Pt–Rh alloys [67], surface coverage is intermediate with respect to the values on pure metals, while on Pd–Pt [55, 63, 67] and Pd–Rh alloys [63, 67] it is lower than on Pt and Rh (Fig. 6 [63, 65, 67]). Eps values for Pt–Rh and Pd–Rh alloys have been observed to increase with Rh surface content, while on Pd–Pt alloys they were similar to those for pure Pt. These findings have been summarized and discussed in detail in a recent report [63].

Although the potentials of r-CO₂ oxidation peak on pure Pt and Rh are similar (Fig. 2), when Pt is alloyed with Rh, a synergistic effect in the adsorbate oxidation is observed, i.e., r-CO₂ is removed from the Pt–Rh alloy at potentials lower than on pure metals (Fig. 7). The decrease in oxidation potential depends on alloy composition and adsorption potential. For electrodes containing ca. 60–65% Rh on the surface and adsorption potential slightly above 0 V, a negative shift of oxidation potential by 110 mV was reported

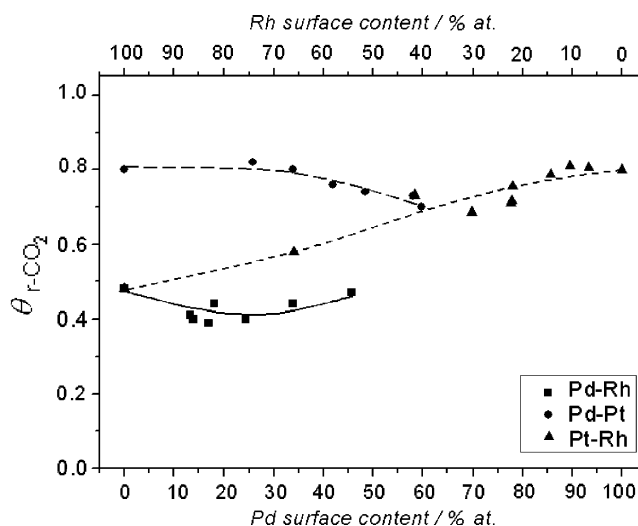


Fig. 6 Maximum surface coverage with r-CO₂ in 0.5 M H₂SO₄ vs. alloy surface composition [63]

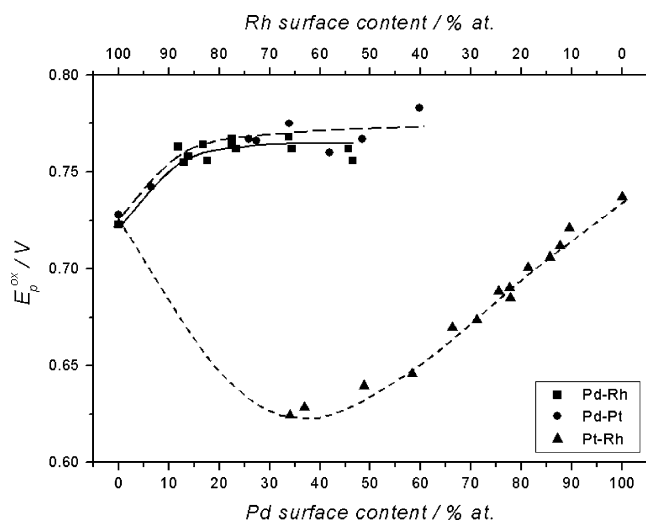


Fig. 7 Peak potential of r-CO₂ oxidation vs. surface composition of noble metal alloys; 0.05 V s⁻¹, 0.5 M H₂SO₄. Potential scale vs. SHE [63]

by Siwek et al. [63, 65, 94, 114, 119, 120]. On the other hand, even a small addition of Pd to Pt or Rh weakens the alloy activity in the oxidation of reduced CO₂ shifting its oxidation potential by ca. 50 mV into positive direction [63, 67, 118]. The possible reasons for such behavior were discussed by Łukaszewski and Czerwiński [67]. Probably alloy surface properties are here the most important factor affecting both the structure of the adsorbate and the mechanism of its oxidation. Pt–Ru electrodes have also been found to be more tolerant towards CO₂ than pure Pt, with the oxidation of r-CO₂ shifted into lower potentials [3, 7, 8, 67].

Concluding remarks

On the basis of numerous investigations on CO₂ electro-sorption on platinum group metals, the following facts have been established:

1. CO₂ electro-sorption occurs only provided that adsorbed hydrogen exists on electrode surface; however, this is a necessary but not a sufficient condition;
2. CO₂ electro-sorption at potentials positive to the reversible hydrogen potential is observed only for Pt, Rh, and their alloys but not for pure Pd, Ir, Ru, and Os;
3. The product of CO₂ electro-sorption on Pt is probably a mixture of mainly linearly, bridge and triply bonded CO species with additional minor products (COOH, COH, and CHO);
4. On Rh electrode, the product of CO₂ electro-sorption is more reduced than on Pt;
5. The process of CO₂ electro-sorption depends on such factors as: electrode material, potential and time of

adsorption, electrode surface morphology, method of electrode pretreatment, solution pH, and composition as well as plane orientation for single crystal electrodes;

6. CO₂ electro-sorption is irreversible;
7. The product of CO₂ electro-sorption cannot be totally identified with the product of a direct CO adsorption.

However, it is symptomatic that despite more than 40 years of intensive studies on that subject some important questions regarding the exact nature of r-CO₂ and mechanisms of its formation and oxidation are still open. In particular, a rather large scatter of eps and epm values obtained by various researchers is evident. Moreover, the inertness of Pd, Ir, Ru, and Os towards CO₂ still waits for explanation. Although a wide spectrum of methods applied in these investigations has provided complementary information, the conclusions are sometimes divergent. The differences between various authors can be ascribed to the following reasons:

1. The experimental conditions (adsorption potential and time, solution composition, electrode roughness and morphology, method of electrode preparation, and pretreatment) varied significantly, e.g., electrode roughness factor ranged from 1 (in the case of IR spectroscopy measurements) up to 800 (in the case of radiochemical experiments);
2. The reproducibility of the surface state of polycrystalline solid electrodes is worse than in the case of single crystals and we cannot directly transfer the findings on electrocatalytic behavior of single crystals to polycrystalline electrodes;
3. Due to its complexity, the gas–metal–solution system is more difficult to define than gas–metal system;
4. Each experimental method has its limitations, therefore some information can always be missed when the investigators rely on one technique only;
5. Different techniques used for the adsorbate identification might favor the detection of certain structures being not sensitive to others.

It seems that future investigations on CO₂ reduction should be performed in two ways. First, by coupling different techniques that provide information on the molecular level; second, by employing well-defined surfaces, e.g., well-ordered overlayers on single crystal electrodes, which could offer unique opportunities to modify the electronic properties of the upper layer by interaction with the substrate.

The study on CO₂ electrochemical behavior is of special interest because, similarly to adsorbed CO, reduced CO₂ might also be found among the intermediates in the anodic oxidation of simple organic molecules as well as the precursors in CO₂ electroreduction. Since the knowledge

on the electrode reactions of CO₂ on platinum group metals is important in the context of better understanding the processes occurring in electrocatalysis, in particular in fuel cells, the continuation of the studies on CO₂ electrosorption is of great significance from both fundamental and practical point of view.

Acknowledgements The research was financed within a framework of 6FP HydroNanoPol project and a SPB HydroNanoPol project financially supported by the Ministry of Science and Higher Education (MNiSW).

References

- Hogarth MP, Ralph TR (2002) *Plat Metab Rev* 46:146
- Petrij OA (2008) *J Solid State Electrochem* 12:609 doi:10.1007/s10008-007-0500-4
- Hogarth MP, Ralph TR (2002) *Plat Metab Rev* 46:117
- Leger J-M (2005) *Electrochim Acta* 50:3123 doi:10.1016/j.electacta.2004.11.063
- Liu H, Song C, Zhang L, Zhang J, Wang H, Wilkinson DP (2006) *J Power Sources* 155:95
- Smolinka T, Heinen M, Chen YX, Jusys Z, Lehnert W, Behm RJ (2005) *Electrochim Acta* 50:5189 doi:10.1016/j.electacta.2005.02.082
- de Bruijn FA, Papageorgopoulos DC, Sitters EF, Janssen GJM (2002) *J Power Sources* 110:117 doi:10.1016/S0378-7753(02)00227-6
- Tingelöf T, Hedström L, Holmström N, Alufors P, Lindbergh G (2008) *Int J Hydrogen Energy* 33:2064 doi:10.1016/j.ijhydene.2008.02.002
- Halseid R, Tunold R (2006) *J Electrochem Soc* 153:A2319 doi:10.1149/1.2360764
- Gu T, Lee W-K, van Zee JW, Murthy M (2004) *J Electrochem Soc* 151:A2100 doi:10.1149/1.1811080
- Sullivan BP (1989) *Plat Metab Rev* 33:2
- Jitaru M (2007) *J Univ Chem Tech Metab* 42:333
- Chaplin RPS, Wragg AA (2003) *J Appl Electrochem* 33:1107 doi:10.1023/B:JACH.0000004018.57792.b8
- Jitaru M, Lowy DA, Toma M, Toma BC, Oniciu L (1997) *J Appl Electrochem* 27:875 doi:10.1023/A:1018441316386
- Giner J (1963) *Electrochim Acta* 8:857 doi:10.1016/0013-4686(63)80054-7
- Zakharian AV, Osetrova NV, Vassiliev YB (1976) *Elektrokhimiya* 12:1854
- Taguchi S, Aramata A, Enyo M (1994) *J Electroanal Chem* 372:161 doi:10.1016/0022-0728(93)03287-Y
- Hoshi N, Hori Y (2000) *Electrochim Acta* 45:4263 doi:10.1016/S0013-4686(00)00559-4
- Rodes A, Pastor E, Iwasita T (1994) *J Electroanal Chem* 369:183 doi:10.1016/0022-0728(94)87097-7
- Hoshi N, Suzuki T, Hori Y (1996) *J Electroanal Chem* 416:61 doi:10.1016/S0022-0728(96)04726-2
- Hoshi N, Suzuki T, Hori Y (1996) *Electrochim Acta* 41:1647 doi:10.1016/0013-4686(95)00418-1
- Czerwiński A (1989) Habilitation thesis. Warsaw University
- Czerwiński A, Sobkowski J, Więckowski A (1974) *Int J Appl Radiat Isot* 25:295 doi:10.1016/0020-708X(74)90038-6
- Sobkowski J, Czerwiński A (1974) *J Electroanal Chem* 55:391 doi:10.1016/S0022-0728(74)80433-X
- Czerwiński A, Sobkowski J, Marassi R (1985) *Anal Lett* 18:1717
- Czerwiński A (1990) *Pol J Chem* 64:719
- Vassiliev YB, Bagotzky VS, Osetrova NV, Mikhailova AA (1985) *J Electroanal Chem* 189:311 doi:10.1016/0368-1874(85)80075-7
- Sobkowski J, Więckowski A, Zelenay P, Czerwiński A (1979) 100:781
- Marcos ML, González-Velasco J, Bolzán AE, Arvía AJ (1995) *J Electroanal Chem* 395:91 doi:10.1016/0022-0728(95)04098-9
- Beden B, Bewick A, Razaq M, Weber J (1982) *J Electroanal Chem* 139:203 doi:10.1016/0022-0728(82)85116-4
- Johnson PR, Kuhn AT (1965) *J Electrochem Soc* 112:599 doi:10.1149/1.2423615
- Maier CU, Bandi A, Specht M (1994) *J Electrochem Soc* 141:L4 doi:10.1149/1.2054719
- Nikolic BZ, Huang H, Gervasio D, Lin A, Fierro C, Adzic RR et al (1990) *J Electroanal Chem* 295:415 doi:10.1016/0022-0728(90)85033-2
- Marcos ML, González-Velasco J, Hahn F, Beden B, Lamy C, Arvía AJ (1997) *J Electroanal Chem* 436:161 doi:10.1016/S0022-0728(97)00342-2
- Arévalo MC, Gomis-Bas C, Hahn F, Beden B, Arévalo A, Arvía AJ (1994) *Electrochim Acta* 39:793 doi:10.1016/0013-4686(93)E0023-F
- Urbach HB, Adams LG, Smith RE (1974) *J Electrochem Soc* 121:233 doi:10.1149/1.2401787
- Brummer SB, Cahill K (1969) *J Electroanal Chem* 21:463 doi:10.1016/S0022-0728(69)80324-4
- Hoshi N, Mizumura T, Hori Y (1995) *Electrochim Acta* 40:883 doi:10.1016/0013-4686(94)00333-V
- Taguchi S, Aramata A (1994) *Electrochim Acta* 39:2533 doi:10.1016/0013-4686(94)00233-9
- Podlovchenko BI, Stenin VF, Yekibaeva AA (1968) *Elektrokhimiya* 4:1004
- Nanbu N, Kitamura F, Ohsaka T, Tokuda K (2000) *J Electroanal Chem* 485:128 doi:10.1016/S0022-0728(00)00104-2
- Mikhailova AA, Osetrova NV, Vassiliev YB (1985) *Elektrokhimiya* 21:1051
- Andreev VN, Vassiliev YB, Osetrova NV, Yastrebova TN (1983) *Elektrokhimiya* 19:381
- Osetrova NV, Vassiliev YB, Bagotzky VS (1977) *Elektrokhimiya* 13:512
- Kazarinov VE, Andreev VN, Tysiatschnaya GJ (1977) *Elektrokhimiya* 13:927
- Osetrova NV, Vassiliev YB, Bagotzky VS, Sadkova RG, Tscherechev AF, Hruszcz AP (1984) *Elektrokhimiya* 20:286
- Brisard GM, Camargo APM, Nart FC, Iwasita T (2001) *Electrochem Commun* 3:603 doi:10.1016/S1388-2481(01)00223-5
- Vassiliev YB, Andreev VN, Osetrova NV, Yastrebova TN (1983) *Elektrokhimiya* 19:414
- Czerwiński A, Sobkowski J (1975) *J Electroanal Chem* 59:41 doi:10.1016/S0022-0728(75)80044-1
- Hoshi N, Noma M, Suzuki T, Hori Y (1997) *J Electroanal Chem* 421:15 doi:10.1016/S0022-0728(96)01023-6
- Czerwiński A (1987) *Anal Lett* 20:503
- Czerwiński A (1994) *J Electroanal Chem* 379:487 doi:10.1016/0022-0728(94)87173-6
- Hoshi N, Ito H, Suzuki T, Hori Y (1995) *J Electroanal Chem* 395:309 doi:10.1016/0022-0728(95)04267-R
- Reshetnikov SM, Sokolska AM (1965) *Z F Ch* 39:1356
- Grdeń M, Paruszevska A, Czerwiński A (2001) *J Electroanal Chem* 502:91 doi:10.1016/S0022-0728(01)00351-5
- Martins ME (2005) *J Argent Chem Soc* 93:143
- Zakharian AV, Osetrova NV, Vassiliev YB (1977) *Elektrokhimiya* 13:1011
- Sidheswaran P (1973) *Electrochim Acta* 18:125 doi:10.1016/0013-4686(73)87022-7

59. Marcos ML, González-Velasco J, Vara JM, Giordano MC, Arvia AJ (1990) *J Electroanal Chem* 287:99 doi:10.1016/0022-0728(90)87162-D
60. Marcos ML, González-Velasco J, Vara JM, Giordano MC, Arvia AJ (1989) *J Electroanal Chem* 270:205 doi:10.1016/0022-0728(89)85037-5
61. Baruzzi AM, Leiva EPM, Giordano MC (1985) *J Electroanal Chem* 189:257 doi:10.1016/0368-1874(85)80072-1
62. Arévalo MC, Gomis-Bas C, Hahn F (1998) *Electrochim Acta* 44:1369 doi:10.1016/S0013-4686(98)00259-X
63. Siwek H, Łukaszewski M, Czerwiński A (2008) *Phys Chem Chem Phys* 10:3752 doi:10.1039/b718286b
64. Sobkowski J, Czerwiński A (1985) *J Phys Chem* 89:365 doi:10.1021/j100248a037
65. Siwek H, Tokarz W, Piela P, Czerwiński A (2008) *J Power Sources* 181:24 doi:10.1016/j.jpowsour.2007.11.033
66. Papageorgopoulos DC, de Bruijn FA (2002) *J Electrochem Soc* 149:A140 doi:10.1149/1.1430413
67. Łukaszewski M, Czerwiński A (2007) *J Electroanal Chem* 606:117 doi:10.1016/j.jelechem.2007.06.002
68. Taguchi S, Ohmori T, Aramata A, Enyo M (1994) *J Electroanal Chem* 369:199 doi:10.1016/0022-0728(94)87099-3
69. Kazarinov VE, Andreev VN, Shlepakov AV (1989) *Electrochim Acta* 34:905 doi:10.1016/0013-4686(89)80015-5
70. Giner J (1964) *Electrochim Acta* 9:63 doi:10.1016/0013-4686(64)80006-2
71. Piersma BJ, Warner TB, Schuldiner S (1966) *J Electrochem Soc* 113:841 doi:10.1149/1.2424132
72. Sobkowski J, Czerwiński A (1975) *J Electroanal Chem* 65:327 doi:10.1016/S0022-0728(75)80076-3
73. Marcos ML, González-Velasco J, Vara JM, Giordano MC, Arvia AJ (1990) *J Electroanal Chem* 281:257 doi:10.1016/0022-0728(90)87044-K
74. Hoshi N, Kawatani S, Kudo M, Hori Y (1999) *J Electroanal Chem* 467:67 doi:10.1016/S0022-0728(98)00476-8
75. Rodes A, Pastor E, Iwasita T (1994) *J Electroanal Chem* 373:167 doi:10.1016/0022-0728(94)03306-4
76. Rodes A, Pastor E, Iwasita T (1994) *J Electroanal Chem* 377:215 doi:10.1016/0022-0728(94)03424-9
77. Iwasita T, Nart FC, Lopez B, Vielstich W (1992) *Electrochim Acta* 37:2361 doi:10.1016/0013-4686(92)85133-6
78. Huang H, Fierro C, Scherson D, Yeager EB (1991) *Langmuir* 7:1154 doi:10.1021/la00054a022
79. Willsau J, Heitbaum J (1986) *Electrochim Acta* 31:943 doi:10.1016/0013-4686(86)80008-1
80. Breiter MW (1967) *Electrochim Acta* 12:1213 doi:10.1016/0013-4686(67)80036-7
81. Łukaszewski M, Czerwiński A (2006) *Electrochim Acta* 51:4728 doi:10.1016/j.electacta.2006.01.013
82. Łukaszewski M, Czerwiński A (2007) *Przem Chem* 86:846
83. Somorjai GA (1994) *Introduction to surface chemistry and catalysis*. Wiley, New York
84. Breiter MW (1968) *J Electroanal Chem* 19:131 doi:10.1016/S0022-0728(68)80196-2
85. Baruzzi AM, Leiva EPM, Giordano MC (1983) *J Electroanal Chem* 158:103
86. Chiu HC, Tseung ACC (1999) *Electrochem Solid-State Lett* 2:540 doi:10.1149/1.1390896
87. Brummer SB, Cahill K (1968) *Discuss Faraday Soc* 49:67 doi:10.1039/d9684500067
88. Kamath VN, Lal H (1968) *J Electroanal Chem* 19:137 doi:10.1016/S0022-0728(68)80197-4
89. Marcos ML, Vara JM, González-Velasco J, Arvia AJ (1987) *J Electroanal Chem* 224:189 doi:10.1016/0022-0728(87)85091-X
90. Czerwiński A, Marassi R, Sobkowski J (1984) *Ann Chim* 74:681
91. Vielstich W, Vogel V (1964) *Z Electrochem* 68:688
92. Arévalo MC, Gomis-Bas C, Pastor E, González S, Arvia AJ (1992) *Electrochim Acta* 37:1083 doi:10.1016/0013-4686(92)85226-B
93. Brummer SB, Turner MJ (1967) *J Phys Chem* 71:3902 doi:10.1021/j100871a026
94. Tokarz W, Siwek H, Piela P, Czerwiński A (2007) *Electrochim Acta* 52:5565 doi:10.1016/j.electacta.2006.12.016
95. Weaver M, Chang SC, Leung L-WH, Jiang X, Rubel M, Szklarczyk M et al (1992) *J Electroanal Chem* 327:247 doi:10.1016/0022-0728(92)80151-S
96. Orts JM, Fernández A, Feliu JM, Aldaz A, Clavilier J (1992) *J Electroanal Chem* 327:261 doi:10.1016/0022-0728(92)80152-T
97. Clavilier J, Albalat R, Gomez R, Orts JM, Feliu JM, Aldaz A (1992) *J Electroanal Chem* 330:489 doi:10.1016/0022-0728(92)80326-Y
98. Wieckowski A (1975) *J Electrochem Soc* 122:252 doi:10.1149/1.2134189
99. Tsionsky V, Daikhin L, Urbakh M, Gileadi E (2004) In: Bard AJ, Rubinstein I (eds) *Electroanalytical chemistry. A series of advances*, vol. 22. Marcel Dekker, New York, pp 2–99
100. Hepel M (1999) In: Wieckowski A (ed) *Interfacial electrochemistry*. Marcel Dekker, New York, pp 599–630
101. Buttry DA, Ward MD (1992) *Chem Rev* 92:1355 doi:10.1021/cr00014a006
102. Buttry DA (1991) In: Bard AJ (ed) *Electroanalytical chemistry. A series of advances*, vol. 17. Marcel Dekker, New York, pp 1–85
103. Schumacher R (1990) *Angew Chem Int Ed Engl* 29:329 doi:10.1002/anie.199003293
104. Deakin MR, Buttry DA (1989) *Anal Chem* 61:1147A doi:10.1021/ac00195a001
105. Lu GQ, Lagutchev A, Dlott DD, Wieckowski A (2005) *Surf Sci* 585:3 doi:10.1016/j.susc.2005.02.041
106. Lagutchev A, Lu GQ, Takeshita T, Dlott DD, Wieckowski A (2006) *J Chem Phys* 125:154705 doi:10.1063/1.2359446
107. Babu PK, Tong YY, Kim HS, Wieckowski A (2002) *J Electroanal Chem* 524–525:157 doi:10.1016/S0022-0728(02)00674-5
108. Vuissoz P-A, Ansermet J-P, Wieckowski A (1998) *Electrochim Acta* 44:1397 doi:10.1016/S0013-4686(98)00262-X
109. Babu PK, Kim HS, Oldfield E, Wieckowski A (2003) *J Phys Chem B* 107:7595 doi:10.1021/jp022679u
110. Tong YY, Rice C, Godbout N, Wieckowski A, Oldfield E (1999) *J Am Chem Soc* 121:2996–3003 doi:10.1021/ja9830492
111. Mendez E, Martins ME, Zinola CF (1999) *J Electroanal Chem* 477:41 doi:10.1016/S0022-0728(99)00387-3
112. Czerwiński A, Sobkowski J (1984) *Anal Lett* 17:2175
113. Łukaszewski M, Czerwiński A (2007) *J Solid State Electrochem* 11:339 doi:10.1007/s10008-006-0142-y
114. Siwek H, Łukaszewski M, Czerwiński A (2004) *Pol J Chem* 78:1121
115. Łukaszewski M, Grdeń M, Czerwiński A (2004) *Electrochim Acta* 49:3161 doi:10.1016/j.electacta.2004.02.029
116. Łukaszewski M, Grdeń M, Czerwiński A (2004) *J Phys Chem Solids* 65:523 doi:10.1016/j.jpcs.2003.09.023
117. Czerwiński A, Łukaszewski M, Grdeń M, Siwek H (2004) *Przem Chem* 83:508
118. Łukaszewski M, Czerwiński A (2007) *Przem Chem* 86:1231
119. Siwek H, Tokarz W, Kotowski J, Piela P, Czerwiński A (2005) *Przem Chem* 84:853
120. Siwek H, Piela P, Czerwiński A (2006) *Przem Chem* 85:1216
121. Iwasita T, Rodes A, Pastor E (1995) *J Electroanal Chem* 383:181–189 doi:10.1016/0022-0728(94)03708-B
122. Podlovchenko BI, Stenin VF, Yekibaeva AA (1968) *Elektrokimiya* 4:1374
123. Azuma M, Hashimoto K, Hiramoto M, Watanabe M, Sakata T (1989) *J Electroanal Chem* 260:441 doi:10.1016/0022-0728(89)87158-X
124. Hori Y, Wakebe H, Tsukamoto T, Koga O (1994) *Electrochim Acta* 39:1833 doi:10.1016/0013-4686(94)85172-7

125. Azuma M, Hashimoto K, Watanabe M, Sakata T (1990) *J Electroanal Chem* 294:299 doi:10.1016/0022-0728(90)87154-C
126. Podlovchenko BI, Kolyadko EA, Lu S (1994) 373:185
127. Yoshitake H, Kikkawa T, Ota K (1995) *J Electroanal Chem* 390:91 doi:10.1016/0022-0728(95)03948-G
128. Bandi A, Schwarz J, Maier CU (1993) *J Electrochem Soc* 140:1006 doi:10.1149/1.2056188
129. Hara K, Tsuneto A, Kudo A, Sakata T (1997) *J Electroanal Chem (Kyoto)* 434:239
130. Westerhoff B, Holze R (1993) *Ber Bunsenges Phys Chem* 97:418
131. Czerwiński A, Sobkowski J (1978) *J Electroanal Chem* 91:47 doi:10.1016/S0022-0728(78)80247-2
132. Czerwiński A, Sobkowski J, Kaczmarek A, Nowakowska M (1985) *Anal Lett* 18:1465
133. Czerwiński A (1988) *J Electroanal Chem* 252:189 doi:10.1016/0022-0728(88)85081-2
134. Stonehart P (1973) *Electrochim Acta* 18:63 doi:10.1016/0013-4686(73)87012-4
135. Czerwiński A, Zamponi S, Marassi R (1991) *J Electroanal Chem* 304:233 doi:10.1016/0022-0728(91)85505-J
136. Czerwiński A, Maruszczak G, Żelazowska M (1993) *Pol J Chem* 67:2037
137. Maruszczak G, Czerwiński A (1995) *Anal Lett* 28:2547
138. Breiter MW (1984) *J Electroanal Chem* 180:25 doi:10.1016/0368-1874(84)83566-2
139. Huang M, Faguy PW (1996) *J Electroanal Chem* 406:219 doi:10.1016/0022-0728(96)04560-3
140. Woods R (1976) Chemisorption at electrodes. In: Bard AJ (ed) *Electroanalytical chemistry*, vol. 9. Marcel Dekker, New York, pp 2–162
141. Jerkiewicz G (1998) *Prog Surf Sci* 57:137 doi:10.1016/S0079-6816(98)00015-X
142. Jerkiewicz G (1999) Surface oxidation of noble metal electrodes. In: Wieckowski A (ed) *Interfacial electrochemistry*. Marcel Dekker, New York, pp 559–576
143. Conway BE (1995) *Prog Surf Sci* 49:331 doi:10.1016/0079-6816(95)00040-6
144. Burke LD (1980) Oxide growth and oxygen evolution on noble metals. In: Trasatti S (ed) *Electrodes of conductive metallic oxides*. Elsevier, New York, pp 141–181