Polish J. Chem., **78**, 1121–1133 (2004)

Electrosorption of Carbon Dioxide on Rh Binary Alloys with Pt and Pd*

by H. Siwek[1,2], M. Łukaszewski[1] and A. Czerwiński[1,2]**

[1] *Warsaw University, Department of Chemistry, Pasteura 1, 02-093 Warsaw, Poland*
[2] *Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warsaw, Poland*

(Received March 8th, 2004; revised manuscript April 6th, 2004)

Pt-Rh and Pd-Rh alloys were prepared by electrochemical codeposition. Surface compositions of the alloys were determined from the potential of surface oxides reduction peak. Carbon dioxide was electrosorbed at constant potential in the range where underpotentially deposited hydrogen exists on the electrode surface. The presence of adsorbed CO_2 causes remarkable diminution of hydrogen adsorption signals on the voltammograms recorded after CO_2 adsorption for both Pt-Rh and Pd-Rh alloys. In the case of hydrogen-absorbing Pd-Rh electrodes adsorbed CO_2 does not influence significantly hydrogen insertion into the alloy bulk. Oxidative removal of CO_2 adsorbed on Pt-Rh and Pd-Rh results in a characteristic voltammetric peak, whose potential and shape depend on alloy surface composition. Eps (electron per site) values calculated for the oxidation of CO_2 adsorbed at a fixed potential (0.015 V) and alloy surface composition, being higher for alloys containing more Rh, with a maximum for pure Rh. It suggests that the structure and composition of CO_2 adsorption product vary with electrode surface properties and experimental conditions.

Key words: binary noble metal alloys, carbon dioxide electrosorption, cyclic voltammetry

The main part of electrochemical studies on noble metals and their alloys have concerned their electrocatalytic properties. Among the reactions investigated there have been the processes of electrosorption of hydrogen and oxygen, as well as small carbon-containing molecules, including carbon dioxide. The last subject is strictly linked to the constant search for new electrode materials for methanol fuel cells, in which CO_2 is one of the fuel oxidation products.

Platinum group metals are known to electrochemically adsorb hydrogen at potentials positive to the reversible hydrogen potential, *i.e.* underpotential deposition of hydrogen occurs on these materials [1–6]. Pd can additionally absorb hydrogen while for Pt and Rh bulk hydrogen dissolution is negligible [7]. Binary alloys formed by Pt, Rh and Pd possess various properties towards hydrogen adsorption and absorption, depending on their surface and bulk compositions [1,3,7–13]. All the elements also differ between each other in their electrochemical behavior at sufficiently high poten-

---

[*] Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday
[**] Corresponding author. Tel: +48-22-8220211; Fax: +48-22-8225996. E-mail: aczerw@chem.uw.edu.pl

tials where oxidation processes take place, involving the formation of surface oxides (oxygen adsorption) and the electrochemical dissolution of the electrode material [1,3,14–18]. Surface oxides generation and reduction on Rh electrode occurs at potentials markedly lower than on Pd and particularly Pt [1,3,14,16,17], while Pt is much more resistive to electrochemical dissolution than Pd and Rh [1,18]. Under cyclic voltammetric conditions the process of surface oxides reduction gives a well-defined peak whose potential is characteristic for a particular noble metal and varies linearly with surface composition in the case of a homogeneous binary noble metal alloy [1,3,18–23]. The latter fact allows for *in situ* determination of surface composition of such alloy electrodes as Pt-Rh, Pd-Pt, Pd-Rh and Pd-Au.

The process of electrosorption of carbon dioxide on platinum group metals has been a subject of numerous investigations [*e.g.* 24–57] carried out electrochemically as well as using electrochemistry combined with an additional technique such as IR spectroscopy, mass spectrometry, radiochemistry and gas chromatography. It has been established that in acidic solutions Pt and Rh can adsorb CO_2 at potentials from the hydrogen adsorption region, in a relatively slow reaction of CO_2 molecules with atoms of underpotentially deposited hydrogen (UPD H). Electrosorption of CO_2 is electrochemically irreversible; the potential of the adsorbate oxidative removal is much higher than the adsorption potential. It was proved in radiometric experiments that the adsorbate did not exchange with CO_2 molecules from the bulk of the solution [32], which indicates the chemical irreversibility of the reaction between CO_2 and adsorbed hydrogen. CO_2 adsorption on Rh is much slower than on Pt and results in a lower surface coverage with the adsorbate [35]. Due to a narrower hydrogen region [1,3,4] and stronger anion adsorption [58] the potentials of CO_2 adsorption on Rh in sulfuric acid solution are shifted into negative direction with respect to Pt [35,52,54].

In contrast to Pt and Rh, Pd electrode in acidic solutions is totally inert in CO_2 electrosorption reaction at potentials positive to the reversible hydrogen potential [40,59], despite the existence of UPD H on its surface [2]. CO_2 is adsorbed on Pd only at potentials considerably lower than the reversible hydrogen potential [60].

There have been many reports and discussions on the nature of the product of CO_2 electrosorption (denoted in the literature as adsorbed CO_2, "reduced CO_2" or "CO_2") on polycrystalline Pt and Rh electrodes in acidic solutions [see *e.g.* 24,27–33,36–38,40,41,43–45,47–50,52,53,56,57,61]. Although there is a general agreement on the presence of linearly and bridge bonded CO species on Pt surface after CO_2 electrosorption [27–29,36,38,48,50–53,56,57], other adsorbates have also been postulated in the literature, namely COH [28,38,40,45], HCO [43] and COOH species [24,28,30–33,41,47,50]. In particular, the results of combined electrochemical and radiochemical experiments suggest a dominant contribution of COOH radicals in the CO_2 adsorption products on Pt electrode [30–33]. It was also postulated that CO_2 molecules only block hydrogen atoms, becoming blocked itself by water molecules and anions [26,44,46,51]. In the case of Rh electrode the product of CO_2 adsorption is regarded as generally more reduced than on Pt [34,35,37,52,54,61]. It indicates the existence of a mixture of a CO-type adsorbate with a reduced form of adsorbed CO [52,54] or such species as CH_2 [34], CH, COH or even C radicals [35,61]. The process of CO_2 electrosorption on Pt and Rh depends on various factors, namely: potential and time of adsorption [28–35,38–40,45,46,50–55], electrode surface morphology [41,51,55], method of electrode pretreatment [51,55] and solution composition [39,46,51,53,54].

The process of CO_2 electrosorption on noble metal alloy electrodes has not been studied as extensively as on pure metals. The results of experiments performed on smooth Pt-Rh alloys [62] showed that in general the surface coverage, structure and composition of the adsorption product are dependent on the alloy surface composition. It was found that the product of CO_2 adsorption on Pt-Rh alloys containing several percent of Rh is more homogeneous than in the case of smooth Pt or Rh. However, these studies were restricted only to Pt-rich alloys and a more thorough examination is needed for that system in the aspect of CO_2 adsorption.

Recently, CO_2 electrosorption on Pd-Pt alloys has been studied [8]. It has been demonstrated that Pt and Pd retain their individual properties towards CO_2 despite forming a homogeneous alloy. These results suggest that CO_2 can be adsorbed only on Pt surface sites, which means that UPD hydrogen adsorbed on Pd atoms in the alloy is still inactive in the reaction with CO_2 molecules. On the other hand, only hydrogen generated on Pd surface atoms is the precursor state for hydrogen absorption in the alloy, the process occurring unaffected by the presence of adsorbed CO_2 on Pt sites. These findings have been confirmed for the Pt-Pd-Rh system [63].

In this paper we present the results of cyclic voltammetric studies on electrosorption of carbon dioxide on Pt-Rh and Pd-Rh binary alloy electrodeposits of rough surfaces. We show the data for a wide range of alloy surface compositions, including Rh-rich electrodes. We demonstrate the influence of the presence of adsorbed CO_2 on the processes of hydrogen adsorption and absorption. We also describe some general electrochemical properties of Pt-Rh and Pd-Rh alloys under conditions of cyclic voltammetry.

EXPERIMENTAL

Pt-Rh and Pd-Rh alloys were prepared by potentiostatic deposition on gold wires (99.9%, 0.5 mm diameter) from baths containing $RhCl_3$ and HCl with H_2PtCl_6 or $PdCl_2$, respectively. The thickness of the deposited alloy layers was of the order of microns (0.3–0.8 μm). The roughness factor of the deposits, as estimated from adsorbed hydrogen oxidation [1,62] and surface oxides reduction charge measurements [1,16,17], was *ca.* 50–200. Surface compositions were determined using the literature method [1,3,21,22] based on a linear dependence of the potential of surface oxides reduction peak on the surface content of an alloy component. Various surface compositions were obtained utilizing different dissolution rates of the metals during the procedure of potential cycling through the oxygen region. Selective removal of alloy components during potential cycling allowed for in situ preparation of alloy electrodes possessing various electrosorption properties towards hydrogen and CO_2. Such electrochemical treatment produced Pt-Rh and Pd-Rh alloys enriched with Pt and Pd, respectively, in both cases at the expense of Rh, which is much less resistive to oxidation under the conditions applied [1,3,18,21]. Prolonged potential cycling enabled us to obtain Pd-Rh electrodes constituting of two separate surface phases, *i.e.* superficially heterogeneous Pd-Rh alloys. All experiments were performed at room temperature in 0.5 M H_2SO_4 solution deoxygenated using an Ar stream. A three electrode cell was used with $Hg|Hg_2SO_4|0.5$ M H_2SO_4 as the reference electrode and a Pt gauze as the auxiliary electrode. All potentials are recalculated with respect to the SHE. All alloys compositions given in this work are expressed in atomic percentages.

In CO_2 adsorption experiments the solution was saturated with 99.9% purity gas at a potential from the hydrogen region (0.015 V). After completing the adsorption, which took 45 min, CO_2 was always removed from the solution with Ar and a voltammogram was recorded at a scan rate 0.05 V s^{-1}.

The purity of the system was checked using Pt electrode. The fact that no additional currents were recorded after electrode polarization at potential in the double layer charging region indicated that both solutions and CO_2 gas supply were free from impurities like CO or "organics".

RESULTS AND DISCUSSION

General voltammetric behavior of Pt-Rh and Pd-Rh alloys. Figs. 1a and 1b present cyclic voltammograms recorded in the full hydrogen-oxygen potential range for Pt-Rh and Pd-Rh alloys, respectively. The CV curves are similar to those reported previously in the literature [1,3,21,22,64]. One can distinguish hydrogen adsorption (1) and desorption (2) signals (the hydrogen region), then a potential range free from faradaic processes (the double layer region – 3), followed by surface oxides generation (4) and oxides reduction (5) currents (the oxygen region).

The hydrogen region on CV curves of Pt-Rh alloys (Fig. 1a) is narrower for higher Rh content and it is getting wider when the increasing surface contribution of Pt makes alloy surface properties closer to Pt. In the case of Pt-rich electrodes split hydrogen signals resemble two peaks attributed to strongly and weakly adsorbed hydrogen, typical of pure polycrystalline Pt [1–4]. On the other hand, Pd-Rh alloys can absorb hydrogen [3,11,65], which is mirrored by the presence of additional current signals (Fig. 1b) due to electrochemical hydrogen insertion (1′) and removal (2′).

In the oxygen region one should note various potentials of the onset of the processes of surface oxidation (oxygen adsorption) and surface oxides reduction (oxygen desorption). For the Pt-Rh system surface oxidation starts at potentials intermediate between those for pure Rh and Pt. The enrichment of the alloy surface with Pt results in the onset of surface oxides generation markedly shifted to higher potentials. Interestingly, in the case of Rh-rich Pd-Rh alloys the process of surface oxides formation happened to begin at a potential as low as for pure Rh. As it can be seen in Fig. 1a, a single peak of surface oxides reduction (5) was observed for all Pt-Rh electrodes independently of surface composition indicating phase homogeneity of the alloy surface [1]. According to the method of surface composition analysis of homogeneous binary noble metal alloys [1,3,18–23], the potential of the oxygen desorption peak (5) is a linear function of the surface composition. Since the surface oxides on Rh are reduced at much lower potentials than on Pt, a lower peak potential indicates a higher Rh content on the alloy surface. In contrast, the Pd-Rh system is not homogeneous over the whole potential range [3,65]. The occurrence of a miscibility gap is probably the reason for an asymmetric, wide signal of surface oxides reduction observed on CV curves for some Pd-Rh electrodes (see dotted line in Fig. 1b).

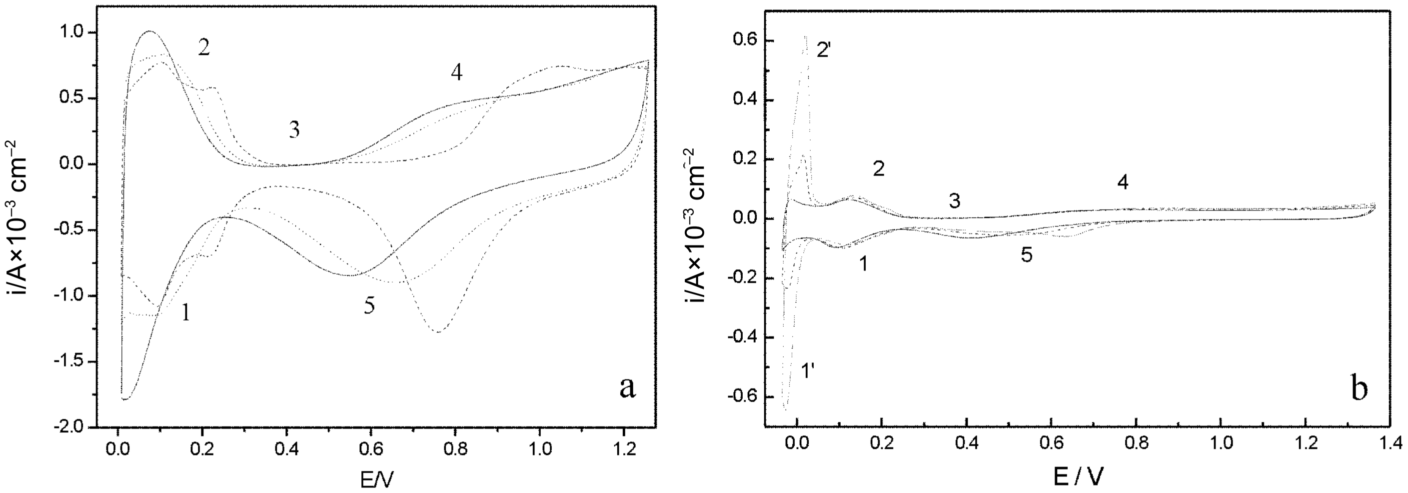

Figure 1. Cyclic voltammograms recorded in the full hydrogen-oxygen potential range, scan rate 0.05 V s^{-1}. The surface compositions are calculated from the potential of surface oxides reduction peak (signal 5). **a**) Pt-Rh alloys: — 62% Rh on the surface, ··· 32% Rh on the surface, --- 3% Rh. **b**) Pd-Rh alloys: — 86% Rh on the surface, --- 62% Rh on the surface, ··· superficially heterogeneous alloy with phases containing *ca*. 61% Rh and 23% Rh.

Long potential cycling of Pd-Rh alloys resulted in the electrode surface becoming heterogeneous, reflected by the splitting of the surface oxides reduction peak into two signals [1]. Such surface modifications were not observed in the case of Pt-Rh alloys subjected to the same procedure. The presence of two rather poorly separated surface oxides reduction peaks causes certain problems with reliable accurate determination of surface composition of a superficially heterogeneous Pd-Rh electrode. However, when Rh content is high, this signal appears as a symmetric peak, whose potential can be easily defined (solid line in Fig. 1b).

Carbon dioxide electrosorption. It has been found that carbon dioxide can be adsorbed on the surface of Pt-Rh and Pd-Rh alloys in the range of potentials, where underpotential deposition of hydrogen takes place. In the case of the Pt-Rh system both elements are active in CO_2 adsorption and the reaction proceeds for the full composition spectrum, although the potential range of UPD H, *i.e.* the range accessible for CO_2 adsorption, is narrower for higher Rh surface concentration. On the other hand, in the case of the Pd-Rh system the decrease in Rh content on the surface markedly weakens the alloy affinity to CO_2, since hydrogen adsorbed on Pd atoms does not take part in the reaction with CO_2 molecules [8,40,59,63]. For Pd-rich Pd-Rh alloys, containing less than *ca.* 20% Rh on the surface, the amount of adsorbed CO_2 was negligible.

Figs. 2a–2d present voltammograms recorded after CO_2 adsorption (solid line) together with blank curves (dotted line) recorded in the absence of adsorbed CO_2, for Pt-Rh alloys with various surface compositions. Figs. 3a–4e show the results of the same kind of experiment performed on Pd-Rh alloys. CO_2 electrosorption was performed for 45 min at 0.015 V, *i.e.* a potential low enough to obtain high surface coverage with adsorbed hydrogen [1,3,4], but higher than the potential of the hydrogen evolution reaction. The main features of the voltammograms recorded in the presence of the product of CO_2 adsorption are: (i) a decrease in hydrogen oxidation currents reflecting blocking hydrogen adsorption reaction on surface sites occupied by adsorbed CO_2 and (ii) a peak of the adsorbate oxidation, placed at potentials in the double layer or at the beginning of the oxygen region.

The influence of the presence of adsorbed CO_2 on hydrogen signals is different for both alloys. In the case of Pt-Rh alloys, on which hydrogen can be adsorbed but not absorbed in the bulk, all the oxidation currents in the whole hydrogen region are markedly diminished when adsorbed CO_2 is present on the surface. On the other hand, in the case of hydrogen-absorbing Pd-Rh alloys, the influence of adsorbed CO_2 on hydrogen signals is varied, depending on the origin of a particular peak. The peak at higher potentials originating from oxidation of adsorbed hydrogen again is significantly decreased, while the peak placed at lower potentials, attributed mainly to oxidation of absorbed hydrogen, is less affected by adsorbed CO_2. The lowering of the latter signal probably results from the fact that certain amount of adsorbed hydrogen is also oxidized in this potential range, although major part of the charge originates from oxidation of absorbed hydrogen. The little influence of the presence of ad-

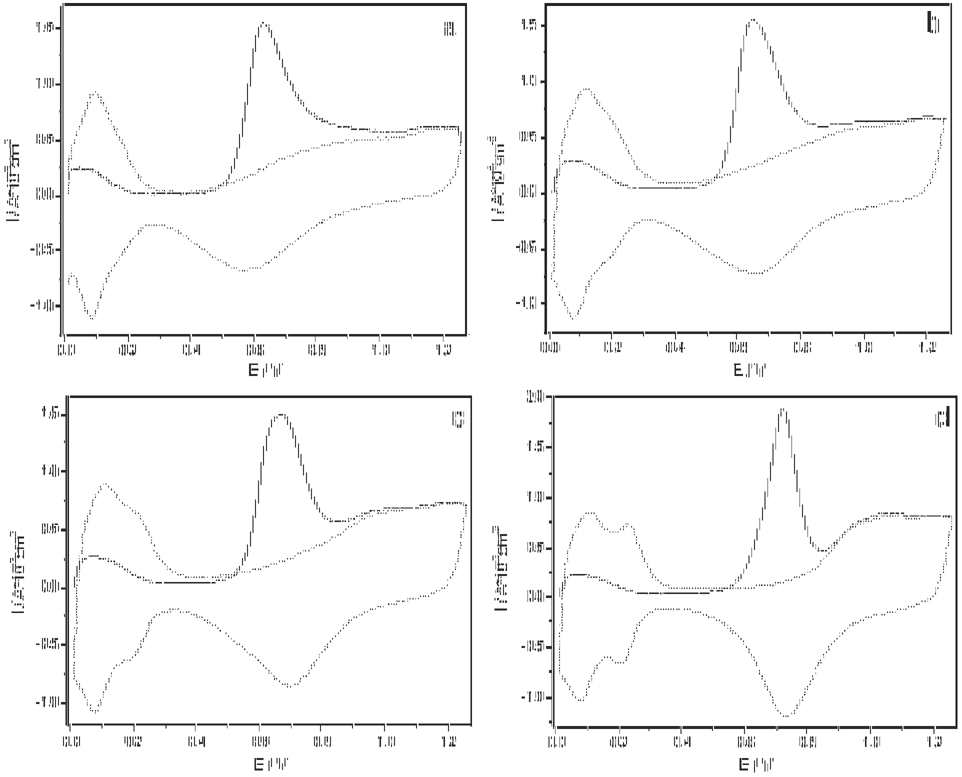

Figure 2. Cyclic voltammograms for Pt-Rh alloys after CO_2 adsorption for 45 min at 0.015 V: — 1st anodic scan, ··· next cycle; scan rate 0.05 V s^{-1}. Alloy surface composition: **a**) 62% Rh; **b**) 22% Rh; **c**) 32% Rh; **d**) 10% Rh.

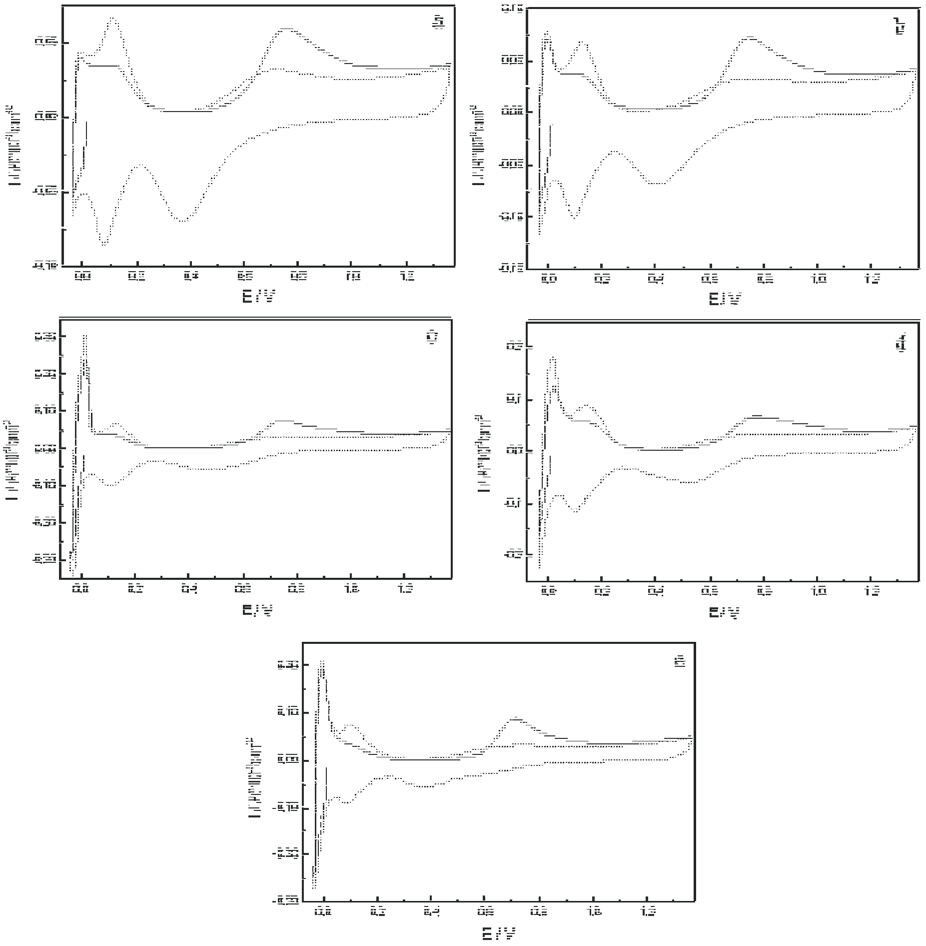

Figure 3. Cyclic voltammograms for Pd-Rh alloys after CO_2 adsorption for 45 min at 0.015 V: — 1st anodic scan, ··· next cycle; scan rate 0.05 V s^{-1}. Alloy surface composition: **a**) 97% Rh; **b**) 87% Rh; **c**) 71% Rh; **d**) 53% Rh; **e**) superficially heterogeneous alloy with phases containing *ca.* 96% Rh and 22% Rh.

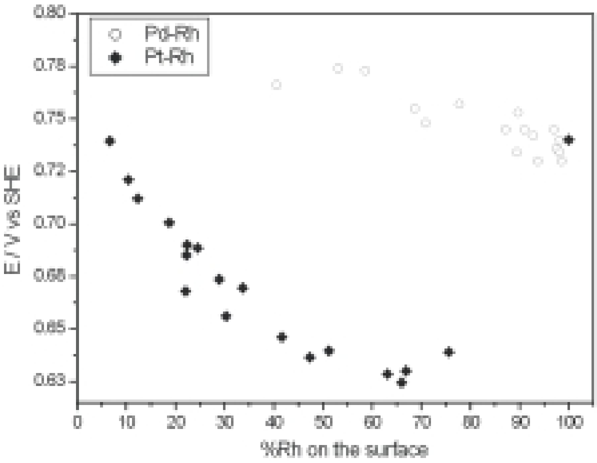

Figure 4. The influence of Rh surface concentration on the potential of the peak of adsorbed CO_2 oxidation (E) on Pt-Rh and Pd-Rh alloys. CO_2 adsorption potential 0.015 V, time 45 min, scan rate during adsorbate oxidation 0.05 V s^{-1}.

sorbed CO_2 on the bulk processes of hydrogen absorption/desorption has been demonstrated in recent reports [8,63].

The general shape and potential of the peak of adsorbed CO_2 oxidation are different for Pt-Rh and Pd-Rh alloys and for a given system change with surface composition. For the Pt-Rh system the increase in Rh surface content up to *ca.* 65% causes a negative shift of the oxidation signal of adsorbed CO_2 (Fig. 4). At this alloy composition the potential of adsorbed CO_2 oxidation peak reaches minimum values, and a further increase in Rh concentration shifts the position of that signal into higher potentials. It means that on Pt-Rh alloys containing *ca.* 65% Rh on the surface the oxidation of adsorbed CO_2 proceeds much easier than on pure Pt and Rh. Possibly for higher Rh surface concentration an additional product of CO_2 adsorption is formed, which is removed with a greater difficulty, *i.e.* at more positive potentials.

The comparison of CV curves recorded in the presence of adsorbed CO_2 (solid line in Figs. 2 and 3) with those for clean alloy surfaces (dotted line) shows that there are some differences in the mechanism of the adsorbate oxidation depending on the kind of alloy and its surface composition. When Rh content on the surface of a Pt-Rh electrode is high, the onset of adsorbed CO_2 oxidation overlaps with the beginning part of the oxygen region (see Fig. 2a), indicating on OH radicals (formed in the initial stage of the process of surface oxidation) as the main oxidant species. On the contrary, in the case of Pt-rich Pt-Rh electrodes CO_2 oxidation starts in the double layer region (Fig. 2d), which suggests that adsorbed water molecules participate in the process of adsorbed CO_2 oxidation. The position of CO_2 oxidation peak on Pt-Rh alloys with a dominant amount of a particular component is similar to its position observed for pure metals under similar experimental conditions [35,41,47,52,61]. One should also note that for alloys with high Rh surface content this signal is rather broad, in contrast to a sharp and narrow peak observed on Pt-rich electrodes. For Pd-Rh alloys the flat and broad peak of oxidation of adsorbed CO_2 is always placed at a potential higher than that corresponding to the onset of surface oxidation (see Figs. 3a–3e) and its descending part extends far into the oxygen region. The potential of the peak of oxidation of adsorbed CO_2 on superficially homogeneous Pd-Rh alloys also increases with the decrease in Rh surface content (Fig. 4). Interestingly, for Pd-Rh electrodes of heterogeneous surfaces (obtained after long potential cycling from an initially homogeneous Pd-Rh electrode) this peak potential was slightly lower than for the homogeneous ones (compare Fig. 3e with Figs. 3a–3d). However, it was very difficult to correlate the peak position with alloy surface composition, since due to splitting of surface oxide reduction peak into two wide and poorly defined signals it was possible to make only a rough estimation of the composition of particular surface phases.

In the case of Pt-Rh alloys of Rh surface content higher than *ca.* 80% the surface composition was very unstable, as could be concluded from changes in surface oxide reduction peak observed during CO_2 adsorption experiments. It might mirror the modifications of surface composition resulting from the interactions of Pt and Rh atoms with CO_2 molecules, which lead to the surface enrichment in one of alloy components. However, further investigations are needed to explain the nature of this phenomenon.

From the voltammetric signals it is possible to derive some quantitative data concerning the nature of the product of CO_2 adsorption. The ratio of the "CO_2" oxidation charge ($Q^{ox}_{CO_2}$) to the difference between the charges of hydrogen oxidation in the absence and presence of "CO_2" (ΔQ_H) can be treated as 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:

$$\text{eps} = Q^{ox}_{CO_2}/\Delta Q_H \tag{1}$$

If we assume that CO_2 adsorption does not influence the amount of absorbed hydrogen, *i.e.* all changes in hydrogen oxidation currents should be the result of reaction between CO_2 and adsorbed hydrogen, such a calculation also gives eps for CO_2 adsorption on Pd-Rh alloys. However, in the case of Pd-Rh alloys of Rh surface concentration lower than *ca.* 40% a reliable calculation of eps was impossible due to small amounts of adsorbed CO_2 resulting in a poorly defined oxidation signal.

Fig. 5 presents eps values plotted against Rh surface concentration for both Pt-Rh and Pd-Rh homogeneous alloys of stable and well defined surface compositions. In general the values are not integers indicating a mixed nature of the adsorbate, composed from at least of two kinds of species of different eps. In the case of eps values between 1 and 2 the products of CO_2 adsorption can be linearly (eps = 2) and bridge bonded (eps = 1) CO molecules in various relative amounts. When eps is higher than 2, additional products might be proposed, such as multi-bonded C–H or C–OH species, suggested earlier for Rh electrodes [34,35]. Recently, it has been confirmed spectro-

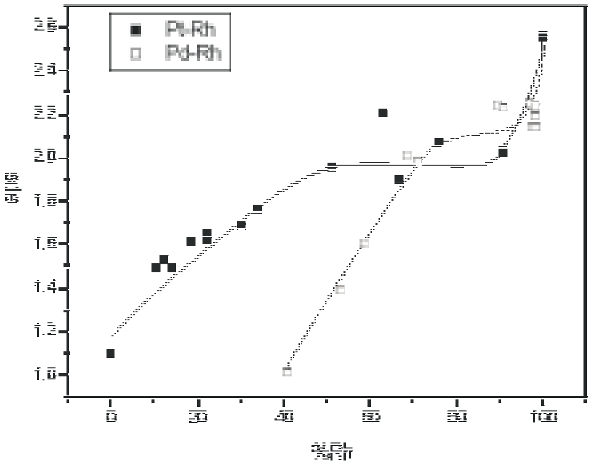

Figure 5. The influence of Rh surface concentration on the eps (electron per site) values calculated for CO_2 adsorption on Pt-Rh and Pd-Rh alloys. CO_2 adsorption potential 0.015 V, time 45 min, scan rate during adsorbate oxidation 0.05 V s^{-1}.

scopically that on Rh electrodes some additional CO_2 adsorption products exist which are more reduced than adsorbed CO [54].

We have found that the eps values (calculated for the same adsorption potential) are higher in experiments performed on alloys containing more Rh on the surface than for those conducted on alloys with lower Rh content (see Fig. 5). Although on the basis of the eps values obtained from electrochemical experiments we cannot determine definitely the structure and composition of adsorbed CO_2, we can state that the alloy surface composition affects the nature of the adsorbate. Interestingly, for a fixed Rh content, eps calculated for Pd-Rh alloys are lower than those for Pt-Rh alloys. This quantitative difference might reflect a qualitatively different nature of the adsorbate present on each alloy. Such behavior is possible due to the fact, that in the Pt-Rh system both components can adsorb CO_2, while in the Pd-Rh system only one component does, *i.e.* Rh. However, the changes in eps values for Pd-Rh alloys with Pd content suggest that despite the inertness of Pd atoms in CO_2 adsorption reaction their presence on the electrode surface affects the behavior of CO_2 molecules towards Rh atoms in Pd-Rh alloys.

It is noteworthy that for both alloys with the increase of the Rh content on the surface the eps values approach those obtained for pure Rh. It probably mirrors the fact, that the electrode surface of Rh-rich Pt-Rh and Pd-Rh alloys possesses adsorption properties similar to Rh. On the other hand, the behavior of the product of CO_2 adsorption on Pt-rich Pt-Rh alloys is similar to that observed for Pt, in respect of eps values close to unity and the adsorbate oxidation proceeding in the double layer region. The substantial differences in the processes of CO_2 electrosorption on Pt and Rh electrodes were proved earlier using radiochemical methods [35].

CONCLUSIONS

1. Carbon dioxide can be adsorbed on Pt-Rh and Pd-Rh alloys in a reaction of CO_2 molecules with underpotentially deposited hydrogen. In the case of the Pt-Rh system CO_2 adsorption occurs for the whole composition range. In the case of the Pd-Rh system the decrease in Rh surface content markedly weakens alloy ability to adsorb CO_2.
2. The presence of adsorbed CO_2 causes diminution of currents originating from hydrogen adsorption on both Pt-Rh and Pd-Rh alloys, but it has much less influence on signals connected with hydrogen absorption.
3. Under fixed experimental conditions (adsorption time, potential and scan rate) the shape and potential of oxidation peak of adsorbed CO_2 depend on the alloy surface composition. In the case of Pt-rich Pt-Rh alloys this signal is placed in the double layer region, while for Rh-rich Pt-Rh alloys and Pd-Rh alloys it is placed at the beginning of the oxygen region. It suggests some differences in the mechanism of the adsorbate oxidation depending on the kind of alloy and its surface composition. In the case of Pt-Rh alloys containing *ca.* 65% Rh on the surface the oxidation of adsorbed CO_2 occurs at potentials markedly lower than on pure Pt and Rh.
4. The number of electrons required for the oxidation of adsorbed CO_2 from one surface site (eps) calculated for given adsorption conditions increases with the increase in Rh content on the alloy surface. It means that the structure of the adsorbate is altered with alloy composition.

Acknowledgments

This work was financially supported by Department of Chemistry of Warsaw University and Industrial Chemistry Research Institute.

REFERENCES

1. Woods R., in: Electroanalytical Chemistry (Bard A.J., Ed.), Marcel Dekker, NY 1976, vol. 9, pp. 2–162.
2. Jerkiewicz G., *Prog. Surf. Sci.,* **57**, 137 (1998).
3. Rand D.A.J and Woods R., *J. Electroanal. Chem*., **36**, 57 (1972).
4. Woods R., *J. Electroanal. Chem*., **49**, 217 (1974).
5. Chevillot J-P., Farcy J., Hinnen Ch. and Rousseau A., *J. Electroanal. Chem*., **64**, 39 (1975).
6. Zolfaghari A., Villiard F., Chayer M. and Jerkiewicz G., *J. Alloy Compd.*, **253–254**, 481 (1997).
7. Lewis F.A., The Palladium-Hydrogen System, Academic Press, London-NY (1967).
8. Grdeń M., Paruszewska A. and Czerwiński A., *J. Electroanal. Chem*., **502**, 91 (2001).
9. Grdeń M., Piaścik A., Koczorowski Z. and Czerwiński A., *J. Electroanal. Chem.*, **532**, 35 (2002).
10. Maeland A. and Flanagan T.B., *J. Phys. Chem*., **68**, 1419 (1964).
11. Baranowski B., Majchrzak S. and Flanagan T.B., *J. Phys. Chem*., **77**, 35 (1973).
12. Lewis F.A., *Plat. Met. Rev*., **5**, 21 (1961).
13. Flanagan T.B. and Sakamoto Y., *Plat. Met. Rev*., **37**, 26 (1993).
14. Conway B.E., *Prog. Surf. Sci.*, **49**, 331 (1995).
15. Jerkiewicz G., in: Interfacial Electrochemistry (Wieckowski A., Ed.), Marcel Dekker, NY 1999, pp. 559–576.
16. Biegler T., Rand D.A.J. and Woods R., *J. Electroanal. Chem*., **29**, 269 (1971).
17. Rand D.A.J. and Woods R., *J. Electroanal. Chem*., **31**, 29 (1971).

18. Rand D.A.J. and Woods R., *J. Electroanal. Chem.*, **35**, 209 (1972).
19. Capon A. and Parsons R., *J. Electroanal. Chem.*, **65**, 285 (1975).
20. Kadirgan F., Beden B., Leger J-M. and Lamy C., *J. Electroanal. Chem.*, **125**, 89 (1981).
21. Baker B.G., Rand D.A J. and Woods R., *J. Electroanal. Chem.*, **97**, 189 (1979).
22. Aston M.K., Rand D.A.J. and Woods R., *J. Electroanal. Chem.*, **163**, 199 (1984).
23. Dalbay N. and Kadirgan F., *Electrochim. Acta*, **36**, 353 (1991).
24. Giner J., *Electrochim. Acta*, **8**, 857 (1963).
25. Giner J., *Electrochim. Acta*, **9**, 63 (1964).
26. Piersma B.J., Warner T.B. and Schuldiner S., *J. Electrochem. Soc.*, **113**, 841 (1966).
27. Breiter M.W., *Electrochim. Acta*, **12**, 1213 (1967).
28. Brummer S.B. and Cahill K., *J. Electroanal. Chem.*, **21**, 463 (1969).
29. Urbach H.B., Adams L.G. and Smith R.E., *J. Electrochem. Soc.*, **121**, 233 (1974).
30. Sobkowski J. and Czerwiński A., *J. Electroanal. Chem.*, **55**, 391 (1974).
31. Czerwiński A., Sobkowski J. and Więckowski A., *Int. J. Appl. Radiat. Is.*, **25**, 295 (1974).
32. Czerwiński A. and Sobkowski J., *J. Electroanal. Chem.*, **59**, 41 (1975).
33. Sobkowski J. and Czerwiński A., *J. Electroanal. Chem.*, **65**, 327 (1975).
34. Zakharian A.V., Osetrova N.V. and Vasiliev Yu.B., *Electrokhimiya*, **12**, 1854 (1976).
35. Sobkowski J., Więckowski A., Zelenay P. and Czerwiński A., *J. Electroanal. Chem.*, **100**, 781 (1979).
36. Beden B., Bewick A., Razaq M. and Weber J., *J. Electroanal. Chem.*, **139**, 203 (1982).
37. Vasiliev Yu.B., Andreev V.N., Osetrova N.V. and Yastrebova T.N., *Electrokhimiya*, **19**, 414 (1983).
38. Baruzzi A.M., Leiva E.P.M. and Giordano M.C., *J. Electroanal. Chem.*, **158**, 103 (1983).
39. Baruzzi A.M., Leiva E.P.M. and Giordano M.C., *J. Electroanal. Chem.*, **189**, 257 (1985).
40. Vassiliev Yu.B., Bagotzky V.S., Osetrova N.V. and Mikhailova A.A., *J. Electroanal. Chem.*, **189**, 311 (1985).
41. Sobkowski J. and Czerwiński A., *J. Phys. Chem.*, **89**, 365 (1985).
42. Czerwiński A., Sobkowski J. and Marassi R., *Anal. Lett.*, **18 (A14)**, 1717 (1985).
43. Willsau J. and Heitbaum J., *Electrochim. Acta*, **31**, 943 (1986).
44. Marcos M.L., Vara J.M., González-Velasco J. and Arvía A.J., *J. Electroanal. Chem.*, **224**, 189 (1987).
45. Kazarinov V.E., Andreev V.N. and Shlepakov A.V., *Electrochim. Acta*, **34**, 905 (1989).
46. Marcos M.L., González-Velasco J., Vara J M., Giordano M.C. and Arvía A.J., *J. Electroanal. Chem.*, **287**, 99 (1990).
47. Czerwiński A., *Polish J. Chem.*, **64**, 719 (1990).
48. Huang H., Fierro C., Scherson D. and Yeager E.B., *Langmuir*, **7**, 1154 (1991).
49. Westerhoff B. and Holze R., *Ber. Bunsen. Phys. Chem.*, **97**, 418 (1993).
50. Maier C.U., Bandi A.and Specht M., *J. Electrochem. Soc.*, **141 (1)**, L4 (1994).
51. Arévalo M.C., Gomis-Bas C., Hahn F., Beden B., Arévalo A. and Arvia A.J., *Electrochim. Acta*, **39**, 793 (1994).
52. Marcos M.L., González-Velasco J., Bolzán A.E. and Arvia A.J., *J. Electroanal. Chem.*, **395**, 91 (1995).
53. Marcos M.L., González-Velasco J., Hahn F., Beden B., Lamy C. and Arvia A.J., *J. Electroanal. Chem.*, **436**, 161 (1997).
54. Arévalo M.C., Gomis-Bas C. and Hahn F., *Electrochim. Acta*, **44**, 1369 (1998).
55. Mendez E., Martins M.E. and Zinola C.F., *J. Electroanal. Chem.*, **477**, 41 (1999).
56. Brisard G.M., Camargo A.P.M., Nart F.C. and Iwasita T., *Electrochem. Commun.*, **3**, 603 (2001).
57. Papageorgopoulos D.C. and de Bruijn F.A., *J. Electrochem. Soc.*, **149 (2)**, A140 (2002).
58. Zelenay P., Horanyi G., Rhee C. K. and Wieckowski A., *J. Electroanal. Chem.*, **300**, 499 (1991).
59. Czerwiński A., *J. Electroanal. Chem.*, **379**, 487 (1994).
60. Hoshi N., Noma M., Suzuki T. and Hori Y., *J. Electroanal. Chem.*, **421**, 15 (1997).
61. Czerwiński A., *Wiad. Chem.*, **42**, 437 (1988) (in Polish).
62. Czerwiński A. and Sobkowski J., *Anal. Lett.*, **17 (A19)**, 2175 (1984).
63. Łukaszewski M., Grdeń M. and Czerwiński A., *J. Phys. Chem. Solids*, **65**, 523 (2004).
64. Czerwiński A., Marassi R. and Sobkowski J., *Annali di Chimica*, **74**, 681 (1984).
65. Noh H., Clewley J.D., Flanagan T.B. and Craft A.P., *J. Alloy Compd.*, **240**, 235 (1996).