

A. Czerwiński · M. Grdeń · M. Łukaszewski

## Dual mechanism of hydrogen desorption from palladium alloys postulated on the basis of cyclic voltammetric studies

Received: 7 May 2003 / Accepted: 8 July 2003 / Published online: 19 December 2003  
© Springer-Verlag 2003

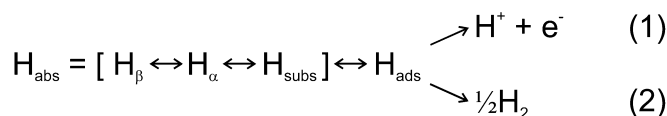
**Abstract** The process of hydrogen absorption/desorption in Pd-Pt and Pd-Pt-Rh alloys has been investigated using cyclic voltammetry. Hydrogen absorbed at constant potential was electrooxidized at various scan rates. The charge of hydrogen oxidation has been found to be dependent on the scan rate. The decrease in the oxidation charge observed for low scan rates indicates that, under these conditions, some amount of hydrogen may be removed via a non-electrochemical recombination reaction. The results suggest that the dual mechanism of hydrogen desorption, involving electrochemical oxidation and non-electrochemical recombination, confirmed for pure palladium, is valid also for palladium alloys.

**Keywords** Hydrogen absorption · Limited volume electrodes · Palladium alloys

### Introduction

In recent years, several reports have been presented on the results of cyclic voltammetric studies of the process of hydrogen absorption/desorption in/from palladium limited-volume electrodes [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. The investigations, including the influence on

hydrogen sorption of such factors as scan rate [4, 9, 10, 11, 14], thickness of the Pd layer [9, 10, 11, 14], temperature [14] and solution composition [14], have led to the conclusion that hydrogen absorption/desorption in/from the Pd electrode proceeds according to the following scheme [10, 11, 14]:



In the above,  $H_{\alpha}$  and  $H_{\beta}$  stand for the  $\alpha$ - and  $\beta$ -phases, respectively, i.e. two forms of hydrogen absorbed in the bulk of electrode, while  $H_{\text{subs}}$  denotes the subsurface hydrogen, i.e. a separate phase of hydrogen dissolved directly beneath the surface in a layer of the thickness not more than 20–50 nm [15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25]. An important stage of the hydrogen sorption process is that involving hydrogen adsorbed on the surface ( $H_{\text{ads}}$ ). When Pd is electrochemically saturated with hydrogen, hydrogen atoms are generated in the Volmer reaction. On the other hand, during hydrogen desorption both the Volmer (Eq. 1) and Tafel (Eq. 2) reactions can take place, which means that absorbed hydrogen is removed by an electrochemical surface process as well as a non-electrochemical one [4, 10, 11, 14].

A key argument for the validity of this mechanism was the characteristic dependence of the hydrogen oxidation charge on the scan rate in a cyclic voltammetric experiment. It has been found that the amount of hydrogen electrooxidized at the slowest scan rates is lower by 10–20% than the maximum amount measured at faster scan rates [10, 11, 14]. Since the rate of the electrooxidation reaction increases with potential and the rate of the recombination process depends on the surface coverage with hydrogen, which decreases with potential, the increase in electrode potential favors the

Contribution to the 3rd Baltic Conference on Electrochemistry, GDANSK-SOBIESZEWO, 23–26 APRIL 2003.

Dedicated to the memory of Harry B. Mark, Jr. (February 28, 1934–March 3rd, 2003)

A. Czerwiński (✉) · M. Grdeń · M. Łukaszewski  
Department of Chemistry,  
Warsaw University,  
Pasteura 1, 02-093 Warsaw,  
Poland

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

electrochemical process. When a very slow scan rate is applied, the electrode remains for a relatively long time in the potential region where the electrooxidation reaction is slow and the surface coverage with adsorbed hydrogen is high. Under these conditions, more hydrogen is removed via the recombination process, which decreases the amount of hydrogen desorbing via the charge transfer process. Thus, the total charge of hydrogen oxidation in the anodic scan is diminished [10, 11, 14].

The results reported for Pd-Au alloys [26] show that such behavior of absorbed hydrogen does not have to be exclusively the characteristic of pure Pd but may be a more general phenomenon typical of Pd-based absorbing systems.

In this paper we present the results of cyclic voltammetric studies on the hydrogen desorption process from Pd-Pt binary alloys and Pd-Pt-Rh ternary alloys, prepared as limited-volume electrodes. It seems that also for these systems it is possible to describe the process of hydrogen removal using the dual mechanism postulated earlier for Pd.

## Experimental

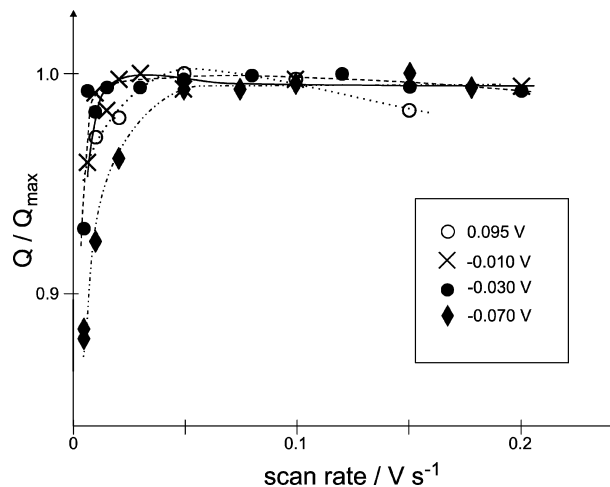
All experiments were performed at room temperature in 0.5 M  $\text{H}_2\text{SO}_4$  solutions previously deoxygenated using an argon stream. During the experiments an Ar atmosphere was maintained by gas passing above the solution level.  $\text{Hg}|\text{Hg}_2\text{SO}_4|0.5 \text{ M } \text{H}_2\text{SO}_4$  or  $\text{Ag}|\text{AgCl}$  was used as the reference electrode. A platinum gauze was used as the auxiliary electrode. All potentials are recalculated with respect to the SHE.

The working electrode was a gold wire (99.9%, 0.5 mm diameter) covered with a thin layer of alloy (limited-volume electrode). The alloys were prepared by electrodeposition at constant potential from a bath containing  $\text{PdCl}_2$ ,  $\text{H}_2\text{PtCl}_6$  and  $\text{HCl}$  (Pd-Pt) or  $\text{PdCl}_2$ ,  $\text{H}_2\text{PtCl}_6$ ,  $\text{RhCl}_3$  and  $\text{HCl}$  (Pd-Pt-Rh). The deposition potential was always higher than the value required for any hydrogen sorption in order to avoid hydrogen penetration into the alloy being formed. The thickness of the electrodes was between 0.20 and 0.60  $\mu\text{m}$ . The roughness factor, as estimated from double-layer capacity [27, 28] and surface oxide reduction charge measurements [29, 30, 31], was ca. 50–200. Bulk compositions of the alloys were analyzed using an EDAX analyzer (EDR-286) coupled with a LEO 435VP scanning electron microscope. All alloy compositions given in this work are bulk compositions expressed in atomic percentages.

At the beginning of the experiments, each alloy electrode was cycled continuously through the potential region of hydrogen adsorption and absorption until a steady-state voltammogram was obtained. This procedure was applied in order to avoid the effects of ageing during further hydrogen entering/removing in the experiment. Hydrogen absorption was performed at constant potential for a period sufficient to ensure full hydrogen saturation available under the given conditions. After completing the absorption, the voltammogram towards a potential of the double-layer region was recorded at a given scan rate. The oxidation charge was calculated from the integration of the anodic peak currents of the CV curve.

## Results and discussion

Figure 1 shows the influence of the scan rate on the charge due to the oxidation process of hydrogen previ-

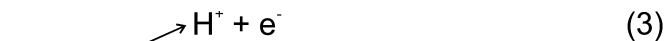


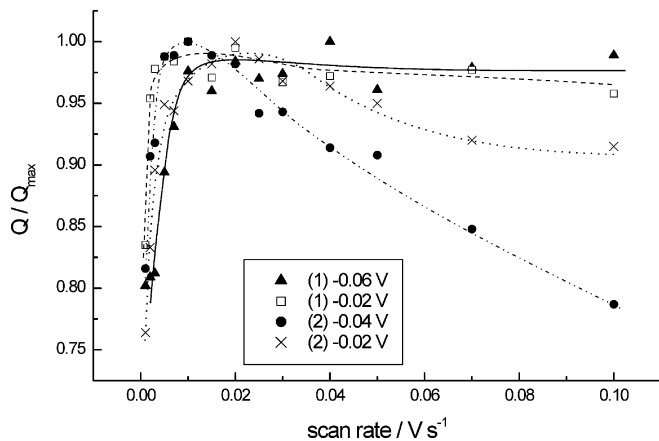
**Fig. 1** The influence of the scan rate on the oxidation charge of hydrogen absorbed in 86%Pd-14%Pt alloy (thickness 0.50  $\mu\text{m}$ ) at various potentials

ously absorbed in a Pd-Pt alloy containing 14% of Pt. The series of experimental data were taken for various potentials of hydrogen absorption; thus each series corresponds to the hydrogen removal from the electrode saturated with various amounts of hydrogen. For a better comparison of data, for each series the values of the oxidation charge were normalized by expressing them as a ratio of the charge measured at a given scan rate ( $Q$ ) to the maximum charge in that series ( $Q_{\text{max}}$ ). Similar plots are presented for two samples of Pd-Pt-Rh alloys, with various bulk compositions (Fig. 2), namely 81%Pd-6%Pt-13%Rh and 63%Pd-32%Pt-5%Rh.

The most important feature of these plots is the decrease in the oxidation charges occurring for slow scan rates, i.e. lower than 0.02  $\text{V s}^{-1}$  for the Pd-Pt alloy and 0.01  $\text{V s}^{-1}$  for the Pd-Pt-Rh alloys studied. With the increase in the scan rate the oxidation charges reach maximum values and then decrease again. The highest oxidation charge is obtained for scan rates from the range 0.025–0.1  $\text{V s}^{-1}$  in the case of the Pd-Pt system and 0.01–0.05  $\text{V s}^{-1}$  for Pd-Pt-Rh electrodes.

As has already been demonstrated for Pd [4, 9, 10, 13] and Pd-Au alloys [26], such a dependence of hydrogen oxidation charge on the scan rate can be explained on the basis of the assumption that electrochemical oxidation of hydrogen adsorbed on the surface is not the only way for removal of hydrogen dissolved in the bulk. The second reaction path, i.e. a non-electrochemical process of recombination of hydrogen atoms, should also be taken into account. Thus, the general scheme of hydrogen desorption from Pd alloys can be proposed as follows:





**Fig. 2** The influence of the scan rate on the oxidation charge of hydrogen absorbed in Pd-Pt-Rh alloys at various potentials: (1) 81%Pd-6%Pt-13%Rh, thickness 0.58  $\mu\text{m}$ ; (2) 63%Pd-32%Pt-5%Rh, thickness 0.26  $\mu\text{m}$

If both reactions 3 and 4 can proceed simultaneously, the amount of absorbed hydrogen measured electrochemically in an anodic CV scan (i.e. the amount of hydrogen leaving electrode in a charge transfer process) depends on the rates of the electrochemical and non-electrochemical surface processes, as well as on the rate of hydrogen diffusion from the bulk towards the electrode surface. The rate of electrooxidation of the adsorbed form of hydrogen depends on the electrode potential and increases with increasing potential. This means that under the conditions of a CV experiment, in which the electrode is polarized from the potential of hydrogen absorption in the positive direction, the sufficiently high potentials are reached faster and hydrogen is oxidized faster at high scan rates than at low scan rates. On the other hand, the rate of the recombination reaction depends on the surface coverage with hydrogen atoms, which decreases as the potential rises. Therefore the ratio of the rates of these two processes changes with the scan rate. The non-electrochemical hydrogen removal is expected to be important when the scan rate is low, owing to the fact that for quite a long time the electrode is in the potential region where the charge transfer process is slow, hydrogen concentration on the surface is high and relatively much time is allowed for the recombination process to occur. Thus, the lowering of the hydrogen oxidation charge, observed for slow polarization scans, is

evidence for the participation of the non-electrochemical reaction in the process of hydrogen desorption. When the scan rate increases, the ratio of the rate of electrooxidation to the rate of recombination rises, which is reflected in the increase in the hydrogen oxidation charge in a certain range of scan rates. Further decrease in hydrogen oxidation charge, observed for fast polarization, can be due to the diffusional limitations, i.e. not all hydrogen is transferred from the bulk to the surface during one fast anodic scan [4, 10, 11, 14].

The data obtained for Pd-Pt and Pd-Pt-Rh electrodes are summarized in Table 1. For each sample and a given absorption potential the maximum atomic ratio of hydrogen to metal,  $(\text{H}/\text{M})_{\text{max}}$ , and the difference between the extreme values of oxidation charge are presented.

It should be noted that the effect of the decrease in hydrogen oxidation charge is observed not only for high electrode saturation with hydrogen, i.e. when the  $\beta$ -phase exists, but also for lower amounts of absorbed hydrogen, corresponding to the existence of a mixture of  $\alpha$ - and  $\beta$ -phases or even to the pure  $\alpha$ -phase. A low amount of absorbed hydrogen and the lack of  $\beta$ -phase formation can be due to the absorption potential not being enough to generate a sufficiently high H/M ratio and/or because of a low Pd content in the bulk of alloy (see Table 1). Such behavior leads to the conclusion that the occurrence of the effect does not seem to be strictly connected with a particular phase of adsorbed hydrogen. Moreover, since the effect is still observed for potentials considerably higher than the reversible potential of the hydrogen evolution reaction,  $E_{\text{HER}}^{\text{r}}$  (see Fig. 1), the full surface coverage with adsorbed hydrogen is not a requisite condition for that phenomenon. It should be stressed that the form of adsorbed hydrogen participating in the hydrogen evolution reaction proceeding according to the Tafel mechanism (OPD H) is different from the form existing on the surface at potentials higher than  $E_{\text{HER}}^{\text{r}}$  (UPD H) [15, 18, 19]. Therefore it cannot be excluded that the exact mechanism of non-electrochemical hydrogen desorption also depends on whether the potential is higher or lower than  $E_{\text{HER}}^{\text{r}}$ . The kind of surface sites occupied by adsorbed hydrogen in a given potential range may play an even more important role in the process of hydrogen atoms recombination than a specific value of surface coverage with adsorbed hydrogen.

**Table 1** The values of the maximum amount of absorbed hydrogen measured electrochemically and the difference between the maximum and minimum hydrogen oxidation charges for Pd-Pt and Pd-Pt-Rh electrodes saturated with hydrogen at various potentials

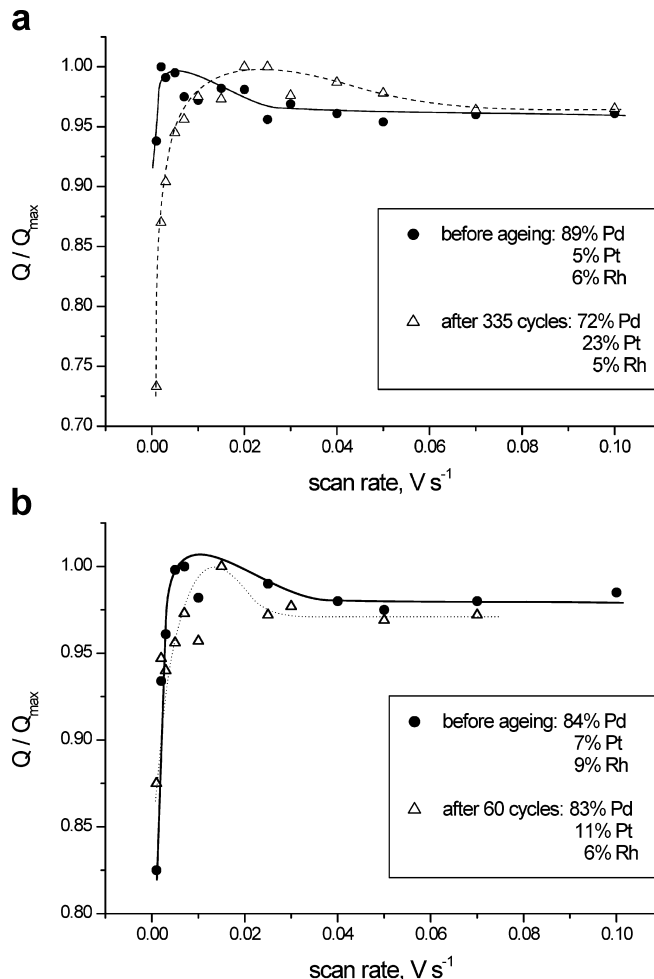
Bulk composition	Thickness ( $\mu\text{m}$ )	$E_{\text{abs}}$ (V)	$(\text{H}/\text{M})_{\text{max}}$	$(Q_{\text{max}} - Q_{\text{min}})/Q_{\text{max}}$
86%Pd-14%Pt	0.50	-0.07	0.25 ( $\alpha + \beta$ )	12%
		-0.03	0.17 ( $\alpha + \beta$ )	6%
		-0.01	0.09 ( $\alpha + \beta$ )	4%
		0.095	0.02 ( $\alpha$ )	3%
81%Pd-6%Pt-13%Rh	0.58	-0.06	0.48 ( $\beta$ )	20%
		-0.02	0.21 ( $\alpha + \beta$ )	17%
		-0.04	0.10 ( $\alpha + \beta$ )	21%
63%Pd-32%Pt-5%Rh	0.26	-0.02	0.07 ( $\alpha + \beta$ )	24%

It should be added that, according to earlier findings [10, 32], the presence of gaseous hydrogen generated during electrode polarization to the hydrogen evolution region does not influence oxidation charges recorded during an anodic CV scan. This could be interpreted as follows: first, the oxidation of gaseous hydrogen during an anodic CV scan is negligible; second, the presence or absence of gaseous hydrogen does not change any equilibrium processes involving hydrogen participation.

It is known that the surface of noble metal electrodes can be markedly altered by applying the procedure of continuous potential cycling in the oxygen region, as a result of the oxygen sorption/desorption processes accompanied by metal dissolution and subsequent recrystallization [29, 33, 34]. In the case of alloys, the changes are usually even more dramatic, since the surface composition is altered because of selective dissolution of less noble components [29, 30, 31, 35, 36]. For thin alloy electrodes the changes involve not only the surface but also some part of the bulk, i.e. layers close to the surface [36]. In this work the possibility of such alloy modifications has been utilized to examine whether they influence the unusual hydrogen oxidation charge/scan rate dependence. Figure 3a and Fig. 3b present  $Q/Q_{\max}$  vs.  $\nu$  plots obtained for Pd-Pt-Rh subjected to potential cycling in the oxygen region (0.36–1.36 V,  $0.1 \text{ V s}^{-1}$ ). Hydrogen absorption/desorption experiments were performed before and after the procedure of electrochemical ageing.

The comparison of the plots for fresh and aged electrodes shows that the effect of charge diminution for low scan rates can either increase (Fig. 3a) or decrease (Fig. 3b). However, now it is difficult to find a simple correlation between these changes and one of the various factors connected with the electrode state. Nevertheless, it is noteworthy that a significant increase of the effect was observed in the case of the alloy whose bulk composition was markedly affected by long potential cycling (see Fig. 3a). The alloy enrichment with Pt at the expense of Pd results in the diminution of the amount of absorbed hydrogen. Owing to a smaller bulk Pd content, the hydrogen/alloys system becomes less stable, which may facilitate hydrogen removal [37, 38, 39, 40].

If the dual mechanism of hydrogen desorption is applied to Pd alloys, a question arises whether the process of hydrogen atoms recombination proceeds exclusively on Pd surface atoms or whether hydrogen adsorbed on Pd atoms can recombine with hydrogen adsorbed on neighboring Pt or Rh atoms. The experiments with carbon dioxide adsorption on Pd-Pt [41] and Pd-Pt-Rh alloys [36] have shown that only Pd atoms are active in the electrochemical process of hydrogen desorption. If this remains true also for the recombination reaction, we may suppose that the contribution of the non-electrochemical desorption path in the process of hydrogen removal from a Pd alloy should be strictly connected with the surface composition and the distribution of atoms on the surface. In particular, it should depend on whether the Pd atoms are randomly located



**Fig. 3a, b** The influence of the scan rate on the oxidation charge of hydrogen absorbed in Pd-Pt-Rh alloys before and after potential cycling in the oxygen region (0.36–1.36 V,  $0.1 \text{ V s}^{-1}$ ). Absorption potential:  $-0.02 \text{ V}$ . (a) Initial composition: 89%Pd-5%Pt-6%Rh, thickness  $0.57 \mu\text{m}$ ; composition after 335 cycles: 72%Pd-23%Pt-5%Rh. (b) Initial composition 84%Pd-7%Pt-9%Rh, thickness  $0.48 \mu\text{m}$ ; composition after 60 cycles: 83%Pd-11%Pt-6%Rh

or form islands. The process of non-electrochemical hydrogen desorption would be effective only for the condition that there were sufficient neighboring Pd atoms on the electrode surface. Hydrogen adsorbed on isolated Pd sites, surrounded by Pt or Rh atoms, might not be removed via a recombination reaction.

It should be added that the possibility of the existence of subsurface hydrogen, proved for pure Pd [10, 11, 14], still waits for verification in the case of Pd alloys. It seems that such a phase might be present for alloys sufficiently rich in Pd and play an important role in the process of hydrogen removal.

## Conclusions

For both Pd-Pt and Pd-Pt-Rh electrodes the scan rate has an influence on the amount of absorbed hydrogen electrooxidized during a cyclic voltammetric experiment.

The decrease in hydrogen oxidation charge observed for low scan rates indicates the possibility of the existence of two paths of hydrogen desorption, i.e. an electrochemical oxidation step and a non-electrochemical recombination process.

The results show that the recombination reaction still takes place for a relatively low saturation of the electrode with hydrogen, i.e. when only the  $\alpha$ -phase is formed, as well as for relatively high potentials, i.e. when the surface coverage with hydrogen is far below unity. This means that the effect cannot be strictly linked either to a particular form of absorbed hydrogen or to a high surface concentration of adsorbed hydrogen.

The surface composition and atom arrangement might determine the rate of the recombination reaction on alloy electrodes. The potential cycling in the oxygen region altering the state of the alloy surface as well as modifying bulk compositions also influences the charge/scan rate dependence.

**Acknowledgements** This work was financially supported by the Polish State Committee for Scientific Research (KBN) Grant No. 3T09A 003 19.

## References

- Czerwiński A, Zamponi S, Marassi R (1991) *J Electroanal Chem* 304:233
- Czerwiński A, Marassi R, Zamponi S (1991) *J Electroanal Chem* 316:211
- Czerwiński A, Marassi R (1991) *J Electroanal Chem* 322:373
- Czerwiński A, Maruszczak G, Żelazowska M (1993) *Pol J Chem* 67:2037
- Czerwiński A (1994) *J Electroanal Chem* 379:487
- Czerwiński A (1994) *Electrochim Acta* 39:431
- Czerwiński A, Maruszczak G, Żelazowska M, Łańcucka M, Marassi R, Zamponi S (1995) *J Electroanal Chem* 386:207
- Czerwiński A (1995) *Pol J Chem* 69:699
- Czerwiński A, Grdeń M, Kiersztyn I, Kotowski J, Żelazowska-Zakrent M (1998) Extended abstracts, 49th annual ISE meeting, Kitakyushu, Japan, p 168
- Czerwiński A, Kiersztyn I, Grdeń M, Czapla J (1999) *J Electroanal Chem* 471:190
- Czerwiński A, Kiersztyn I, Grdeń M (2000) *J Electroanal Chem* 492:128
- Zhang WS, Zhang XW, Zhao XG (1998) *J Electroanal Chem* 458:107
- Zhang WS, Zhang XW, Li HQ (1999) *J Electroanal Chem* 474:123
- Czerwiński A, Kiersztyn I, Grdeń M (2003) *J Solid State Electrochem* 7:321
- Jerkiewicz G (1998) *Prog Surf Sci* 57:137
- Breiter MW (1979) *J Electroanal Chem* 109:253
- Bucur RV, Bota F (1982) *Electrochim Acta* 27:521
- Conway BE, Jerkiewicz G (1993) *J Electroanal Chem* 357:47
- Conway BE (1999) Electrochemical processes involving H adsorbed at metal electrode surfaces. In: Wieckowski A (ed) *Interfacial electrochemistry*. Dekker, New York, pp 131–150
- Bucur RV (1968) *Electrochim Acta* 31:385
- Szpak S, Mosier-Boss PA, Scharber SR, Smith JJ (1994) *J Electroanal Chem* 365:275
- Szpak S, Mosier-Boss PA, Scharber SR, Smith JJ (1992) *J Electroanal Chem* 337:147
- Bucur RV, Bota F (1984) *Electrochim Acta* 29:109
- Bucur RV, Bota F (1983) *Electrochim Acta* 28:1373
- Bucur RV, Bota F (1981) *Electrochim Acta* 26:1653
- Łukaszewski M, Kuśmierczyk K, Kotowski J, Siwek H, Czerwiński A (2003) *J Solid State Electrochem* 7:69
- Trasatti S, Petrii OA (1991) *Pure Appl Chem* 63:711
- Kuśmierczyk K, Łukaszewski M, Rogulski Z, Siwek H, Kotowski J, Czerwiński A (2002) *Pol J Chem* 76: 607
- Woods R (1976) Chemisorption at electrodes. In: Bard AJ (ed) *Electroanalytical chemistry*, vol 9. Dekker, New York, pp 2–162
- Capon A, Parsons R (1975) *J Electroanal Chem* 65:285
- Kadirgan F, Beden B, Leger JM, Lamy C (1981) *J Electroanal Chem* 125:89
- Grdeń M, Piaścik A, Koczorowski Z, Czerwiński A (2002) *J Electroanal Chem* 532:35
- Bolzan A, Martins ME, Arvia AJ (1986) *J Electroanal Chem* 207:279
- Perdriel CL, Custidiano E, Arvia AJ (1988) *J Electroanal Chem* 246:165
- Rand DAJ, Woods R (1972) *J Electroanal Chem* 36:57
- Łukaszewski M, Grdeń M, Czerwiński A (in preparation)
- Lewis FA (1967) *The palladium-hydrogen system*. Academic Press, New York
- Flanagan TB, Sakamoto Y (1993) *Platinum Met Rev* 37:26
- Sakamoto Y, Ohira K, Kokubu M, Flanagan TB (1997) *J Alloys Compd* 253:212
- Thiebaut S, Bigot A, Achard JC, Limacher B, Leroy D, Percheron-Guegan A (1995) *J Alloys Compd* 231:440
- Grdeń M, Paruszevska A, Czerwiński A (2001) *J Electroanal Chem* 502:91