View Article Online / Journal Homepage / Table of Contents for this issue

Published on 04 October 2010. Downloaded by Universitat Politècnica de València on 29/10/2014 11:18:14.

Electrochemical absorption and oxidation of hydrogen on palladium alloys with platinum, gold and rhodium

Mariusz Łukaszewski, Katarzyna Hubkowska and Andrzej Czerwiński*

Received 12th May 2010, Accepted 4th August 2010
DOI: 10.1039/c0cp00542h

Thin layers of Pd and its alloys with Pt, Au and Rh were prepared by electrodeposition on a Au substrate. Hydrogen electrosorption by the obtained electrodes was studied in 0.5 M H_2SO_4 solution using cyclic voltammetry and chronoamperometry. The influence of the alloying process on selected thermodynamic (the amount of absorbed hydrogen, the stability of the β-phase, the extent of the absorption/desorption hysteresis) and kinetic aspects (the rate of hydrogen absorption and absorbed hydrogen oxidation) of hydrogen absorption and desorption was examined. It was found that the addition of the non-absorbing elements to Pd results in faster kinetics of the hydrogen electrosorption process and a smaller absorption/desorption hysteresis.

1. Introduction

Interest in metal–hydrogen systems has been growing continuously during recent years. Hydrogen is regarded as a fuel of the future; however, its storage remains a problem.[1,2] Metal hydrides seem to be the most promising for that purpose. Hydrogen-absorbing materials are also employed in electrochemical power sources, *e.g.* in rechargeable nickel-hydride batteries (Ni–MH)[3] or supercapacitors,[4] and in other branches of science and technology, *e.g.* as hydrogenation catalysts, membranes for hydrogen purification and isotope separation, neutron moderators and sources of highly pure hydrogen. Thus, studies of their chemical and electrochemical properties are important not only from a fundamental but also a practical point of view.

It has been known for almost 150 years that many transition metals can react with hydrogen forming non-stoichiometric hydrides, in which hydrogen occupies interstitial voids in the metal crystal lattice.[5] Under normal conditions these compounds are solid substances characterized by a series of metallic properties such as good electrical and thermal conductivity, opacity and metallic sheen, although they also exhibit hardness and brittleness. In most metal–hydrogen systems one can distinguish various phases, stable within a given range of hydrogen pressures and temperatures. The highest hydrogen solubility is observed for metals absorbing it exothermically, *i.e.* elements in Groups 3, 4 and 5 of the periodic table (*e.g.* Zr, Ti, V, lanthanides and actinides) and Pd.

Since 1866, when Graham published his pioneering report on hydrogen dissolved in Pd and Pd–Ag alloys,[5] the properties of the Pd–H system have been widely investigated. Although high atomic mass and high cost are the main reasons for the limited practical application of the Pd–H system, it can be treated as a model system for other hydrogen-absorbing materials and a knowledge of its electrochemical behavior allows us to better understand the processes occurring on electrodes of this type.

Pd easily absorbs large amounts of hydrogen both from the gas phase and electrochemically,[5–7] forming a non-stoichiometric compound, PdH_x. Hydrogen absorbed by Pd can exist in two phases: the hydrogen-poor α-phase (*i.e.* a solid solution of hydrogen in Pd) and the hydrogen-rich β-phase (*i.e.* a non-stoichiometric Pd hydride).[5,8–11] The ability of Pd to absorb hydrogen starts at a thickness of 3 atomic layers.[12] Under normal conditions, when Pd is in equilibrium with gaseous hydrogen, the H/Pd ratio is 0.69.[8] A similar value (0.73) is obtained at room temperature for a Pd electrode polarized at a potential slightly higher than the hydrogen evolution potential.[13] As demonstrated by structural data by Sakamoto *et al.*,[10,11] two phases of absorbed hydrogen can also exist in Pd-rich alloys with elements which do not absorb hydrogen under normal conditions, *e.g.* Pt, Au, or Rh. Experiments by Skorodumov *et al.*[14] established the picture of the phase transition process, according to which during the coexistence of both phases of absorbed hydrogen there is a movement of a sharp α–β phase boundary inside the metal, leading to a discontinuous hydrogen concentration gradient.

Electrochemical hydrogen insertion into metals and alloys has been commonly applied since the work by Graham. Pd is especially attractive and convenient for electrochemical experiments due to the fact that hydrogen absorption can be realized at room temperature without corrosion of the electrode material.[3] However, one of the important problems in electrochemical studies on hydrogen absorption processes in Pd electrodes made of wires or foils is the generation of absorption/desorption currents which are a few orders of magnitude higher than those originating from surface processes. This problem has been eliminated by Czerwiński[13,15–21] by the use of a thin (of the order of microns) metal layer deposited on a hydrogen-neutral matrix, *e.g.* Au or carbon. These electrodes are called 'limited volume electrodes' (LVEs). Such an approach allows for the limitation and control of the amount of absorbed hydrogen. Using this kind of electrode it is possible to distinguish between various forms of electrosorbed hydrogen as well as simultaneously study hydrogen absorption and surface processes. Thus, Pd-LVEs create new possibilities for electrochemical studies of hydrogen-absorbing materials. The methodology elaborated for fundamental studies on hydrogen electrosorption by Pd can be utilized

---

Warsaw University, Department of Chemistry, Pasteura 1, 02-093 Warsaw, Poland. E-mail: aczerw@chem.uw.edu.pl; Fax: +48-22-8225996; Tel: +48-22-8220211

Published on 04 October 2010. Downloaded by Universitat Politècnica de València on 29/10/2014 11:18:14.

for applied research, as was demonstrated in the examination of commercial AB_5 type alloys for hydride batteries.[22,23]

Czerwiński's idea has been adopted by other research groups[12,24–28] and the application of a thin metal layer in electrochemical experiments on hydrogen absorption by Pd has led to some interesting observations that could not have been made when bulk electrodes were used for that purpose (see ref. 12, 13, 15–21, 24–28).

In this paper we present our results of investigations on selected aspects of hydrogen electrosorption by thin layers of Pd and its alloys with Pt, Au and Rh, prepared by electrodeposition on a Au substrate. We demonstrate the influence of the alloying process on various absorption/desorption characteristics, such as the amount of absorbed hydrogen, the stability of the β-phase, the absorption/desorption hysteresis, and the rate of oxidation of absorbed hydrogen. We confirm our earlier suggestions that the rate of the $\alpha \rightarrow \beta$ phase transition is the decisive factor affecting the kinetics of hydrogen absorption by and desorption from thin Pd-based electrodes.

2. Experimental

All the experiments were performed at room temperature (25 °C) in 0.5 M H_2SO_4 solutions prepared from analytical grade reagents and triply distilled water additionally purified in a Millipore system. The solutions were deoxygenated with an argon stream for 20 min; during the experiments the argon stream was directed above the solution level in order to avoid contact with air. A platinum gauze and $Hg|Hg_2SO_4|0.5$ M H_2SO_4 were used as the auxiliary and reference electrodes, respectively. All the potentials in the text and in the figures are referred to the reversible hydrogen electrode (RHE) in the working solution.

Thin films of Pd and its alloys (limited volume electrodes, LVEs) were deposited potentiostatically on a gold wire (0.5 mm diameter) from an aqueous bath containing a respective mixture of $PdCl_2$ in HCl and H_2PtCl_6, $HAuCl_4$ or $RhCl_3$. The details of deposition conditions and deposit characterization are given in our recent papers.[29–31] All alloy compositions given in this work are bulk compositions expressed in atomic percentages, determined using atomic absorption spectroscopy (AAS) or energy dispersive analysis of X-rays (EDAX).

At the beginning of the hydrogen absorption experiments each 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 insertion/removal. Hydrogen absorption was performed at a constant potential for a period sufficient to ensure full hydrogen saturation, determined by chronoamperometry.

3. Results and discussion

Fig. 1 shows anodic voltammetric scans recorded after hydrogen electrosorption at −0.05 V by Pd and its alloys with Pt, Au

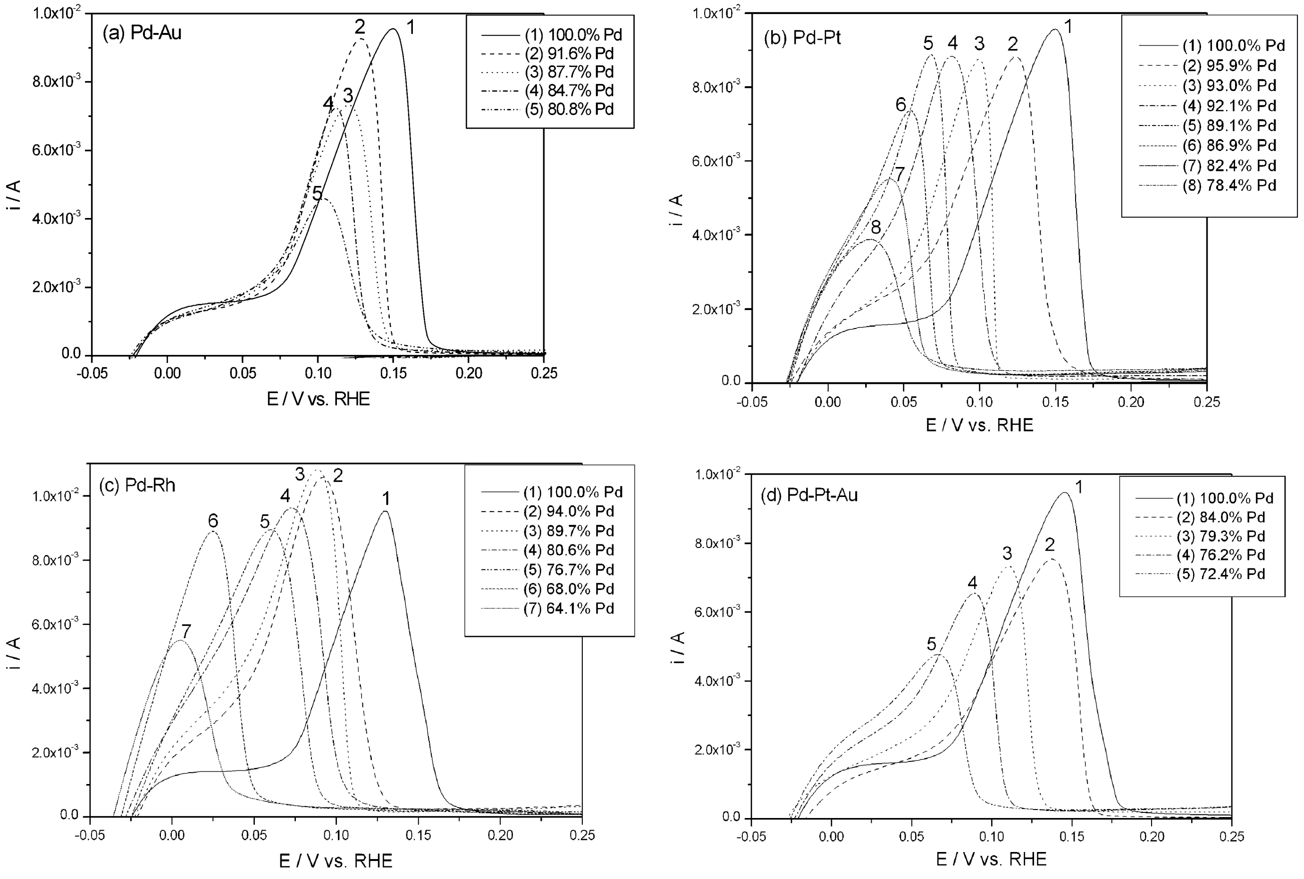

Fig. 1 Anodic voltammetric scans (0.01 V s^{-1}) recorded in 0.5 M H_2SO_4 after hydrogen electrosorption at −0.05 V by Pd and its alloys with Pt, Au and Rh. Electrode thickness in the range: 0.5–0.8 μm for Pd–Rh, 0.9–1.1 μm for Pd–Au, 0.7–0.9 μm for Pd–Pt, and 0.9–1.5 μm for Pd–Pt–Au.

View Article Online

Published on 04 October 2010. Downloaded by Universitat Politècnica de València on 29/10/2014 11:18:14.

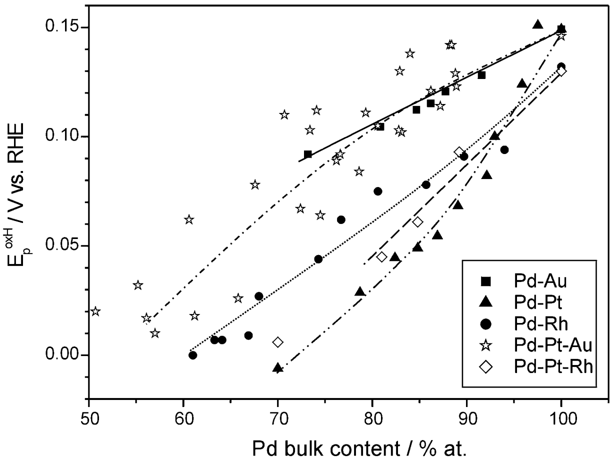

Fig. 2 The influence of alloy bulk composition on the potential of the absorbed hydrogen oxidation peak (0.01 V s^{-1}) after electrosorption at −0.05 V in 0.5 M H_2SO_4. Electrode thickness in the range: 0.5–0.8 μm for Pd–Rh and Pd–Pt–Rh, 0.9–1.1 μm for Pd–Au, 0.7–0.9 μm for Pd–Pt, and 0.9–1.5 μm for Pd–Pt–Au.

and Rh of various bulk compositions. It should be noted that the changes in electrode constitution result in the changes in the height, shape and position of absorbed hydrogen oxidation peaks. In particular, the potential of the hydrogen oxidation peaks is different for different types of alloys but with increasing amount of the alloying metal it is always shifted negatively with respect to the position of the same signal for pure Pd. The dependence of the potential of the absorbed hydrogen oxidation peak on the bulk composition of various alloys is shown in Fig. 2. An approximately linear decrease in the peak potential with decreasing Pd bulk content is observed. This fact indicates that on the alloys absorbed hydrogen can be oxidized more easily than on pure Pd. Moreover, the overall shape of the hydrogen oxidation peak is also changed in the case of the alloys compared to Pd. As seen in Fig. 1, for Pd the hydrogen oxidation peak is preceded by a region of a current plateau (around 0–0.05 V), while for most of the alloys this region is much less pronounced and both the ascending part of the peak and the peak itself are placed at potentials lower than for Pd.

Fig. 3 shows plots of the amount of electrosorbed hydrogen (expressed as the hydrogen-to-metal atomic ratio, H/M) as a function of electrode potential, obtained from chronoamperometric absorption/desorption experiments. Three characteristic potential regions can be distinguished, namely corresponding to hydrogen adsorption and absorption in the α-phase, the α→β phase transition, and hydrogen absorption in the β-phase (together with a small contribution from hydrogen adsorption).

An important feature of the data presented in Fig. 3 is the different position of the phase transition region on the potential scale. In the case of Pd–Au and Pd–Pt–Au alloys with high Au/Pt ratios (Fig. 3a) the α→β phase transition is shifted to higher potentials, while in the case of Pd–Pt, Pd–Rh, Pd–Pt–Rh and Pd–Pt–Au alloys with lower Au/Pt ratios (Fig. 3b) it is shifted to lower potentials compared with pure Pd. These tendencies for Pd binary alloys with Pt, Au and Rh are shown in Fig. 4a. Fig. 4b demonstrates that the trends observed for binary systems are also present in the case of a ternary Pd–Pt–Au system. For a series of Pd–Pt–Au alloys of comparable Pd bulk content the potential of the phase transition decreases with increasing relative bulk contribution of Pt. It can also be seen that the potential of the reverse β→α phase transition depends on alloy bulk composition, although with a different slope. As we proposed in our earlier communication,[32] the dependence of the potential of the α→β phase transition on Pd bulk content can be utilized for *in situ* determination of the bulk composition of Pd-rich alloys.

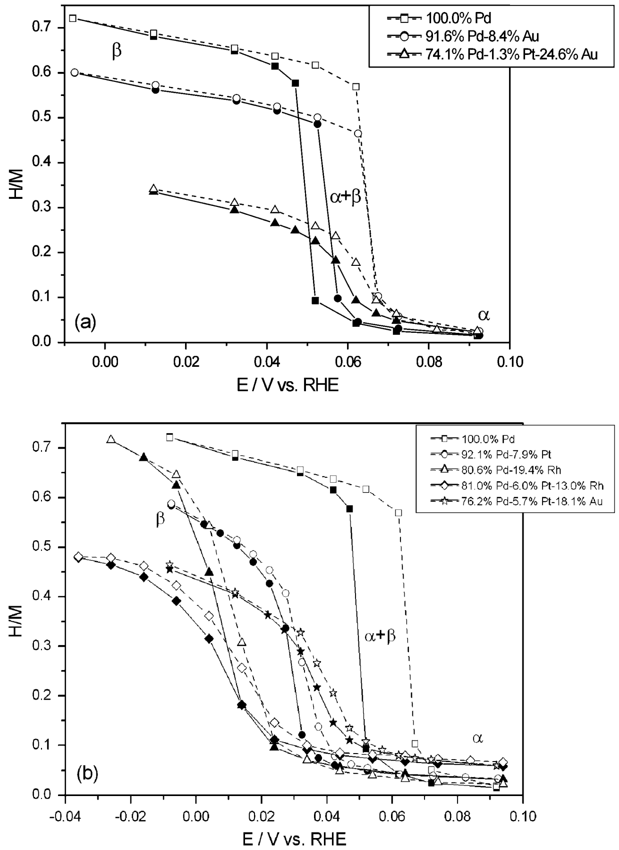

Fig. 3 The amount of electrosorbed hydrogen (expressed as the hydrogen-to-metal atomic ratio, H/M) *versus* the electrode potential for Pd and its alloys in 0.5 M H_2SO_4: (a) Pd–Au and Pd–Pt–Au, (b) Pd–Pt, Pd–Rh, Pd–Pt–Rh and Pd–Pt–Au. Solid symbols/solid lines: absorption course, open symbols/dashed lines: desorption course.

According to the literature, the changes in the position of the phase transition region can be explained mainly by the geometric effect connected with changes in the crystal lattice due to alloy formation.[10,11,33,34] Pd alloying with Au leads to an increase in the volume of the unit cell, while alloying with Rh causes an opposite effect. In the former case the additional work needed for the crystal lattice expansion during the α→β phase transition is smaller than in the latter case,[34] which results in different trends in the changes in the position of the phase transition region with alloy bulk composition. However, despite the unit cell expansion upon Pd alloying with Pt, the Pd–Pt system behaves similarly to the contracted Pd–Rh system. This effect is probably due to an alteration of the electronic[34,35] or elastic properties,[36,37] which are more important factors here than the geometric effect alone.

Published on 04 October 2010. Downloaded by Universitat Politècnica de València on 29/10/2014 11:18:14.

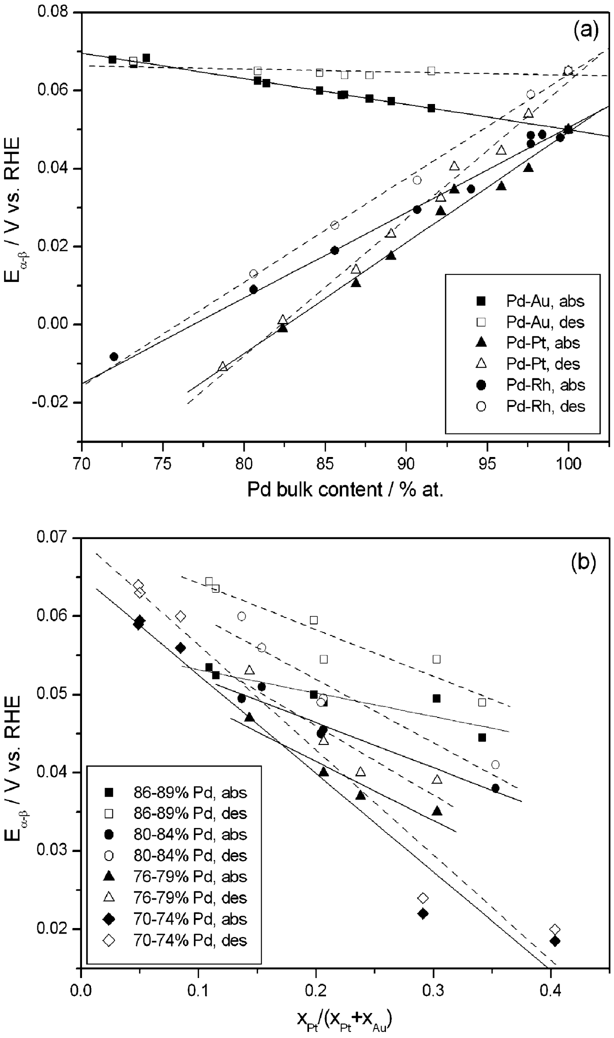

Fig. 4 The influence of the alloy bulk composition on the potentials of the α → β (absorption, solid symbols/solid lines) and β → α (desorption, open symbols/dashed lines) phase transitions in 0.5 M H_2SO_4: (a) Pd binary alloys with Pt, Au and Rh, (b) Pd–Pt–Au ternary alloys.

Since for the electrochemical absorption the potential (above the hydrogen evolution potential) corresponds to the equilibrium hydrogen pressure in gas-phase experiments,[38,39] the potential of the α → β phase transition can be converted into the Gibbs free energy of the hydride formation[3,5] and its position on the potential scale can serve as a measure of the thermodynamic stability of the β-phase. Therefore, on the basis of Fig. 3 and 4 it can be concluded that the β-phase generated electrochemically in Pd–Au and Au-rich Pd–Pt–Au alloys is more stable than in pure Pd, while for the other systems it is less stable. However, Fig. 1 and 2 clearly demonstrate that the tendency towards the easier oxidation of absorbed hydrogen is observed for all the above alloys, regardless of the changes in the thermodynamic stability of the β-phase. Thus, it indicates that the effect illustrated in Fig. 1 is a true kinetic effect. Another effect of the alloying process on the hydrogen electrosorption properties concerns the influence of the alloy bulk composition on the maximum absorption capacity. These trends for various alloys are shown in Fig. 5.

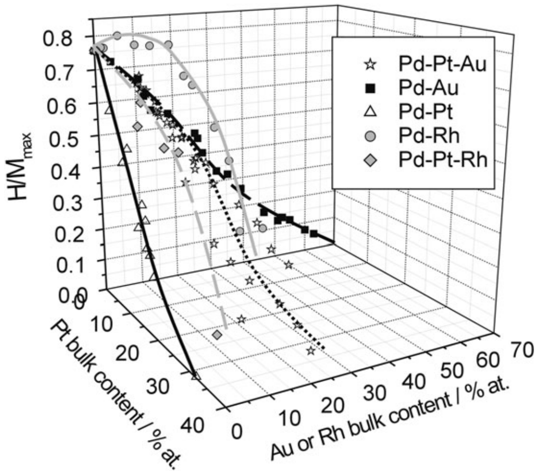

Fig. 5 The influence of the alloy bulk composition on the maximum amount of electrosorbed hydrogen in Pd and its alloys: Pd–Au,[40] Pd–Pt,[41] Pd–Pt–Au,[42] Pd–Pt–Rh,[43] and Pd–Rh.[44]

The systems investigated can be divided into two groups. For Pd–Au,[40] Pd–Pt,[41] Pd–Pt–Au[42] and Pd–Pt–Rh[43] alloys the maximum hydrogen solubility is always lower than in Pd and decreases with the increase in the bulk concentration of non-absorbing components. On the other hand, for Pd–Rh alloys[44] containing up to 20% Rh the amount of absorbed hydrogen is greater than in Pd. The changes in the maximum hydrogen absorption capacities are explained by the electronic effect, *i.e.* the alteration of the number of vacancies in the Pd d-band after the addition of the alloying element, or are related to changes in crystal lattice geometry and elastic properties.[10,11,33–37] In the context of the data presented in Fig. 5 it should be stressed that faster kinetics of hydrogen oxidation, illustrated in Fig. 1 and 2, cannot be ascribed simply to the decrease in the amount of hydrogen absorbed by the alloy, since the same effect is also observed for Pd-rich Pd–Rh alloys despite the increase in their hydrogen absorption capacities.[44]

The next feature of the plots presented in Fig. 3 is a difference between the potentials of the α → β and β → α phase transitions, similar to the hysteresis between the hydrogen plateau pressure in the absorption and desorption courses observed in gas-phase measurements.[5,45–49] The effect of hysteresis is important from a practical point of view in the context of energy storage as one of the factors determining energy loss in a charging/discharging cycle of hydride batteries[3] or supercapacitors.[4] The beneficial effect of the alloying metal on the hysteresis is observed for all the alloys studied (Fig. 6). In the case of the alloys sufficiently low in Pd the hysteresis disappears, *i.e.* the potential of the α → β phase transition becomes identical to the potential of the β → α phase transition. This is in line with the fact that after the addition of a certain limiting amount of the alloying metal the pure β-phase can no longer be formed[10,11] and the alloy absorbs hydrogen in a single α-phase, and therefore no phase transition occurs.

From an analysis of the changes in the course of chronoamperometric curves with the potential applied during hydrogen absorption/desorption it was found[43,44] that the process dependent on potential, rather than diffusion alone, controls the

This journal is © the Owner Societies 2010

Published on 04 October 2010. Downloaded by Universitat Politècnica de València on 29/10/2014 11:18:14.

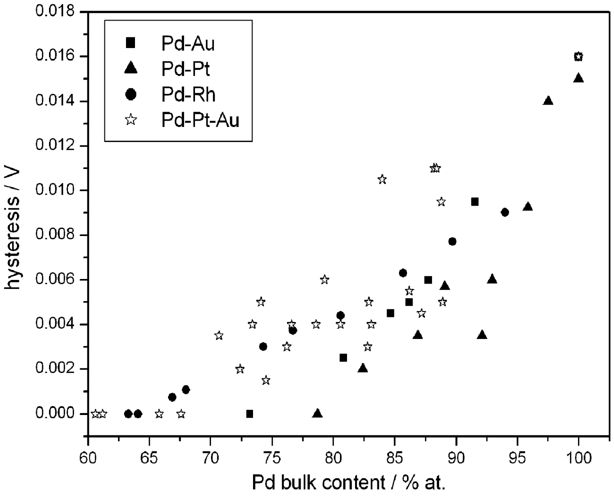

Fig. 6 The influence of the alloy bulk composition on the absorption/desorption hysteresis in 0.5 M H_2SO_4 for Pd alloys with Pt, Au and Rh.

overall rate of hydrogen absorption by and desorption from thin Pd-rich electrodes. As we proposed in earlier papers[43,44] at potentials where the α- and β-phases coexist, the processes of α→β and β→α phase transitions are probably the slowest steps of hydrogen absorption by and desorption from thin Pd-based layers. The slow rates of the phase transitions were manifested by the existence of sharp maxima on the potential dependence of hydrogen absorption and desorption time, placed at potential values where both phases coexist, *i.e.* in the hysteresis region (see ref. 43 and 44 for details).

Fig. 7 shows the relationship between the maximum absorption or desorption time, determined in chronoamperometric experiments, and the Pd bulk content in the alloys. It should be noted that these times for the alloys are generally lower than the values for pure Pd and decrease with decreasing Pd bulk content. This is in line with the easier oxidation of absorbed hydrogen on the alloys shown in Fig. 1. This behavior suggests that this effect may result from the accelerated phase transition in the alloys compared to Pd. Further arguments for this conclusion come from a comparison of the potentials of the absorbed hydrogen oxidation peak and the maximum desorption time for alloys of different compositions and different hysteresis effect. A careful analysis of Fig. 6 and 7 reveals that alloys exhibiting smaller hysteresis are also characterized by lower potentials of the absorbed hydrogen oxidation peak and shorter maximum absorption/desorption times. Thus, hydrogen removal is facilitated by a decreasing hysteresis effect. The lowest potentials of the absorbed hydrogen oxidation peak and lowest absorption/desorption times are observed for samples for which the hysteresis disappears and a single phase of absorbed hydrogen is present in the system.

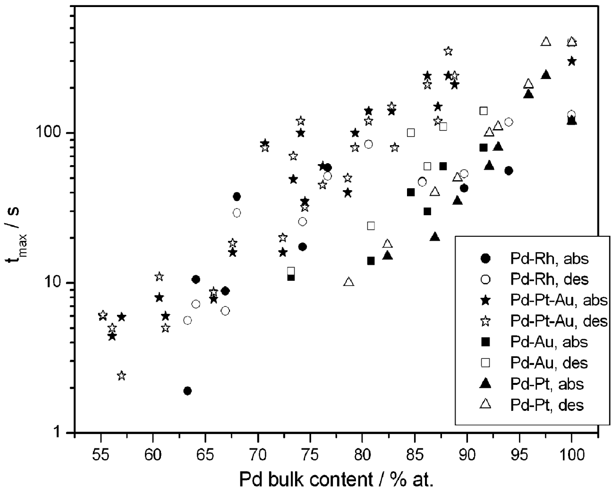

Fig. 7 The influence of the alloy bulk composition on the maximum absorption (solid symbols) and desorption (open symbols) time in chronoamperometric experiments in 0.5 M H_2SO_4 for Pd alloys with Pt, Au and Rh.

The influence of the rate of the α→β phase transition on the measured hydrogen absorption/desorption current was demonstrated by Zhang *et al.*[50] by theoretical modelling of CV curves for a thin Pd electrode. The characteristic shape of the hydrogen signals and a significant separation between cathodic and anodic peaks was explained assuming the α→β phase transition as the slowest step in the overall electrosorption process in thin Pd layers. According to this model, the changes observed in the slope of CV curves in the potential region before the main hydrogen oxidation peak (see Fig. 1) with an increasing amount of alloying metal may be ascribed to a faster phase transition in the alloys compared to pure Pd. This result together with the decrease in absorption/desorption hysteresis seems to be promising for a possible application of Pd-based systems in supercapacitors.[4,51]

It should be stressed here that the effect of improved kinetics of hydrogen electrosorption in the alloys in comparison with pure Pd cannot result simply from changes in the rate of hydrogen diffusion. According to the literature data,[52–56] the hydrogen diffusion coefficient in Pd-rich alloys with other noble metals is not higher than in Pd and decreases with decreasing Pd bulk content, regardless of the trends in the changes in the crystal lattice dimensions caused by the alloying process. This fact suggests that diffusion itself is not a decisive factor determining the rate of the oxidation of hydrogen absorbed by thin Pd-based films. More detailed studies on hydrogen diffusion in Pd alloys under electrochemical conditions are in progress in our laboratory.

4. Conclusions

Selected thermodynamic and kinetic aspects of hydrogen electrosorption by Pd and its alloys with Pt, Au and Rh were studied in acidic solution with the use of thin electrodes prepared by electrochemical deposition. It was found that the slow process of the α→β phase transition rather than surface kinetics or bulk diffusion controls the rate of hydrogen absorption by and desorption from thin Pd-based electrodes. The addition of other noble metals to Pd accelerates the phase transition, which is mirrored in a lower potential of absorbed hydrogen oxidation and shorter hydrogen absorption and desorption times. The trend of the changes in the stability of the β-phase depends on the particular alloying metal; however,

Published on 04 October 2010. Downloaded by Universitat Politècnica de València on 29/10/2014 11:18:14.

in all cases the absorption/desorption hysteresis becomes smaller compared to pure Pd.

Acknowledgements

This work was financially supported by the Department of Chemistry, Warsaw University.

References

1 G. W. Crabtree, M. S. Dresselhaus and M. V. Buchanan, *Phys. Today*, 2004, **57**, 39.
2 L. Schlapbach and A. Züttel, *Nature*, 2001, **414**, 353.
3 J. Kleperis, G. Wójcik, A. Czerwiński, J. Skowroński, M. Kopczyk and M. Bełtowska-Brzezińska, *J. Solid State Electrochem.*, 2001, **5**, 229.
4 M. Łukaszewski, A. Żurowski and A. Czerwiński, *J. Power Sources*, 2008, **185**, 1598.
5 F. A. Lewis, *The Palladium/Hydrogen System*, Academic Press, New York, 1967.
6 G. Jerkiewicz, *Prog. Surf. Sci.*, 1998, **57**, 137.
7 G. Jerkiewicz and A. Zolfaghari, *J. Electrochem. Soc.*, 1996, **143**, 1240.
8 R. Woods, in *Electroanalytical Chemistry*, ed. A. J. Bard, Marcel Dekker, New York, 1976, vol. 9, pp. 2–162.
9 T. B. Flanagan and Y. Sakamoto, *Plat. Met. Rev.*, 1993, **37**, 26.
10 Y. Sakamoto, K. Baba and T. B. Flanagan, *Z. Phys. Chem. N. F.*, 1988, **158**, 223.
11 Y. Sakamoto, K. Yuwasa and K. Hirayama, *J. Less Common Met.*, 1982, **88**, 115.
12 M. Baldauf and D. M. Kolb, *Electrochim. Acta*, 1993, **38**, 2145.
13 A. Czerwiński, R. Marassi and S. Zamponi, *J. Electroanal. Chem.*, 1991, **316**, 211.
14 B. G. Skorodumov, V. N. Serebryakov, V. G. Ulanov, E. V. Zhukovska and O. A. Zhukovsky, *Int. J. Hydrogen Energy*, 1996, **21**, 961.
15 M. Grdeń, J. Kotowski and A. Czerwiński, *J. Solid State Electrochem.*, 1999, **3**, 348.
16 M. Grdeń, J. Kotowski and A. Czerwiński, *J. Solid State Electrochem.*, 2000, **4**, 273.
17 A. Czerwiński, S. Zamponi and R. Marassi, *J. Electroanal. Chem.*, 1991, **304**, 233.
18 A. Czerwiński, I. Kiersztyn, M. Grdeń and J. Czapla, *J. Electroanal. Chem.*, 1999, **471**, 190.
19 A. Czerwiński, I. Kiersztyn and M. Grdeń, *J. Electroanal. Chem.*, 2000, **492**, 128.
20 A. Czerwiński, I. Kiersztyn and M. Grdeń, *J. Solid State Electrochem.*, 2003, **7**, 321.
21 M. Łukaszewski, M. Grdeń and A. Czerwiński, *J. Phys. Chem. Solids*, 2004, **65**, 5.
22 P. Piela, Z. Rogulski, M. Krebs, E. Pytlik, M. Schmalz, J. Dłubak, M. Karwowska, A. Gumkowska and A. Czerwiński, *J. Electrochem. Soc.*, 2010, **157**, A254.
23 Z. Rogulski, J. Dłubak, M. Karwowska, M. Krebs, E. Pytlik, M. Schmalz, A. Gumkowska and A. Czerwiński, *J. Power Sources*, 2010, **195**, 7517.
24 H. Duncan and A. Lasia, *Electrochim. Acta*, 2007, **52**, 6195.
25 M. H. Martin and A. Lasia, *Electrochim. Acta*, 2009, **54**, 5292.
26 A. Lasia, *J. Electroanal. Chem.*, 2006, **593**, 159.
27 C. Gabrielli, P. P. Grand, A. Lasia and H. Perrot, *J. Electrochem. Soc.*, 2004, **151**, A1925.
28 P. N. Bartlett and J. Marwan, *Phys. Chem. Chem. Phys.*, 2004, **6**, 2895.
29 M. Łukaszewski, T. Kędra and A. Czerwiński, *J. Electroanal. Chem.*, 2010, **638**, 123.
30 M. Łukaszewski and A. Czerwiński, *Thin Solid Films*, 2010, **518**, 3680.
31 M. Łukaszewski, K. Klimek and A. Czerwiński, *J. Electroanal. Chem.*, 2009, **637**, 13.
32 M. Łukaszewski, A. Żurowski, M. Grdeń and A. Czerwiński, *Electrochem. Commun.*, 2007, **9**, 671.
33 Y. Sakamoto, F. L. Chen, M. Ura and T. B. Flanagan, *Ber. Bunsenges. Phys. Chem.*, 1995, **99**, 807.
34 E. Wicke and K. Frölich, *Z. Phys. Chem. N. F.*, 1989, **163**, 35.
35 I. Moysan, V. Paul-Boncour, S. Thiébaut, E. Sciora, J. M. Fournier, R. Cortes, S. Bourgeois and A. Percheron-Guégan, *J. Alloys Compd.*, 2001, **332**, 14.
36 S. Thiébaut, A. Bigot, J. C. Achard, B. Limacher, D. Leroy and A. Percheron-Guégan, *J. Alloys Compd.*, 1995, **231**, 440.
37 J. D. Clewley, J. F. Lynch and T. B. Flanagan, *J. Chem. Soc., Faraday Trans. 1*, 1977, **73**, 494.
38 T. B. Flanagan and F. Lewis, *Trans. Faraday Soc.*, 1959, **55**, 1409.
39 T. B. Flanagan, *J. Phys. Chem.*, 1961, **65**, 280.
40 M. Łukaszewski, K. Kuśmierczyk, J. Kotowski, H. Siwek and A. Czerwiński, *J. Solid State Electrochem.*, 2003, **7**, 69.
41 M. Grdeń, A. Piaścik, Z. Koczorowski and A. Czerwiński, *J. Electroanal. Chem.*, 2002, **532**, 35.
42 M. Łukaszewski, T. Kędra and A. Czerwiński, *Electrochim. Acta*, 2010, **55**, 1150.
43 M. Łukaszewski, M. Grdeń and A. Czerwiński, *J. Electroanal. Chem.*, 2004, **573**, 87.
44 A. Żurowski, M. Łukaszewski and A. Czerwiński, *Electrochim. Acta*, 2006, **51**, 3112.
45 F. A. Lewis, *Plat. Met. Rev.*, 1960, **4**, 132.
46 D. Wang, T. B. Flanagan and T. Kuji, *Phys. Chem. Chem. Phys.*, 2002, **4**, 4244.
47 T. B. Flanagan, C.-N. Park and W. A. Oates, *Prog. Solid State Chem.*, 1995, **23**, 291.
48 R. Balasubramaniam, *J. Alloys Compd.*, 1997, **253–254**, 203.
49 T. B. Flanagan and J. D. Clewley, *J. Less Common Met.*, 1982, **83**, 127.
50 W.-S. Zhang, X.-W. Zhang and X.-G. Zhao, *J. Electroanal. Chem.*, 1998, **458**, 107.
51 A. Czerwiński, M. Łukaszewski and A. Żurowski, Patent P-375062.
52 A. Maestas and T. B. Flanagan, *J. Phys. Chem.*, 1973, **77**, 850.
53 H. Barlag, L. Opara and H. Züchner, *J. Alloys Compd.*, 2002, **330–332**, 434.
54 L. Opara, B. Klein and H. Züchner, *J. Alloys Compd.*, 1997, **253**, 378.
55 D. Artman and T. B. Flanagan, *J. Phys. Chem.*, 1973, **77**, 2804.
56 Y. Sakamoto, S. Hirata and H. Nishikawa, *J. Less Common Met.*, 1982, **88**, 387.

This journal is © the Owner Societies 2010