Electrochimica Acta 56 (2011) 2344–2350

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Influence of temperature on hydrogen electrosorption into palladium-noble metal alloys. Part 2—Palladium–platinum alloys

K. Hubkowska, M. Łukaszewski, A. Czerwiński*,[1]

Warsaw University, Department of Chemistry, Pasteura 1, 02-093 Warsaw, Poland

ARTICLE INFO

Article history:
Received 24 August 2010
Received in revised form 8 November 2010
Accepted 9 November 2010
Available online 18 November 2010

Key words:
Pd–Pt alloys
Hydrogen absorption
Temperature
Phase transition
Hysteresis

ABSTRACT

Hydrogen electrosorption into Pd-rich (>75 at.% Pd in the bulk) Pd–Pt alloys obtained by electrodeposition was studied in acidic solutions (0.5 M H_2SO_4) using cyclic voltammetry and chronoamperometry. The influence of temperature (in the range between 283 and 328 K) on the amount of absorbed hydrogen, the potential of the α–β phase transition, the extent of absorption–desorption hysteresis and the potential of absorbed hydrogen oxidation was examined. It has been found that for the temperature range studied the potentials of the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ phase transitions are shifted negatively with both increasing temperature and decreasing Pd content in the alloy bulk. Thermodynamic parameters (Gibbs free energy, enthalpy and entropy) of the β-phase formation and decomposition were determined. With decreasing Pd bulk content the process of the β-phase formation becomes less exothermic and the thermodynamic stability of the β-phase decreases. The maximum hydrogen absorption capacity of Pd–Pt alloys decreases with increasing temperature and decreasing Pd bulk content. The potential of absorbed hydrogen oxidation is shifted negatively with increasing temperature and decreasing Pd bulk content.

1. Introduction

Palladium and platinum form a face centered cubic solid solutions, whose lattice parameter slightly increases with increasing Pt content with positive deviations from Vegard's law [1]. There is controversy in the literature whether there is a miscibility gap in the phase diagram of the Pd–Pt system [2,3]. However, according to most reports in the case of Pd-rich alloys homogeneous samples can be obtained by such methods as volume melting [1,4] or electrodeposition [5,6].

Hydrogen electrosorption into Pd–Pt alloys prepared by electrodeposition has been studied by Grdeń et al. [5] within the composition range between 70% and 100% Pd in the bulk. Żółtowski and Makowska [7] as well as Vigier et al. [8] studied hydrogen electrosorption in a Pd–Pt alloy containing 81% Pd in the bulk. However, these experiments were restricted to one temperature, i.e. 298 K. Noh et al. [9], Clewley et al. [10] and Yasumatsu et al. [11] carried out experiments on hydrogen absorption from the gas phase with Pd-rich Pd–Pt alloys in a wider temperature range. Maeland and Flanagan [12] and Carson et al. [13] reported on hydrogen absorption in Pd–Pt alloys from aqueous solutions saturated with gaseous hydrogen at temperatures between 273 and 333 K. Moysan et al. [1] and Thiébaut et al. [4] studied gaseous deuterium absorption in Pd–Pt alloys.

According to these studies Pd-rich Pd–Pt alloys can absorb hydrogen either from the gas phase or electrochemically, similarly to pure Pd. For sufficiently high bulk Pd content the β-phase of absorbed hydrogen can be formed, while the alloys with less Pd bulk content absorb hydrogen only in the single α-phase. The ability to absorb hydrogen decreases monotonically with increasing Pt bulk content and at room temperature it ceases when concentration of Pt in the alloy bulk reaches ca. 20–30 at.% [5,12,13]. Despite the crystal lattice expansion after Pd alloying with Pt the α–β phase transition in Pd–Pt alloys occurs at higher hydrogen pressure or lower electrode potential, as compared to pure Pd [1,4,5,9,11–13]. This unusual behavior is explained by a decrease in compressibility due to Pt addition [9] or by the effect of large broadening of the valence band upon alloying [1], which seems to play here a more important role than the geometric factor alone.

Recently, we have reported on the influence of temperature on hydrogen electrosorption in Pd–Au alloys [14]. In this paper we demonstrate the effect of temperature on the amount of absorbed hydrogen, the potential of the α–β phase transition, the extent of absorption–desorption hysteresis and the potential of absorbed hydrogen oxidation for Pd-rich Pd–Pt alloys prepared as thin electrodeposits (limited volume electrodes [15]). We have determined thermodynamic parameters of the β-phase formation and decomposition in the Pd–Pt system under electrochemical conditions.

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* Corresponding author. Tel.: +48 22 8220211; fax: +48 22 8225996.
E-mail address: aczerw@chem.uw.edu.pl (A. Czerwiński).

[1] ISE member.

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doi:10.1016/j.electacta.2010.11.026

2. Experimental

All experiments were performed in 0.5 M H_2SO_4 solutions at temperature of 283, 298, 313 and 328 K, controlled by a thermostat (Lauda RE 306, Germany). The solutions were prepared from analytical grade reagents (POCh, Poland) and triply distilled water, additionally purified in a Millipore system. The electrolyte was deoxygenated with an argon (99.999%, PRAXAIR) stream for 20 min; during the experiments the argon stream was directed above the solution level in order to avoid contact with air. All electrochemical experiments were performed with the use of a CH Instrument potentiostat, model 700C. A $Hg|Hg_2SO_4|0.5\ M\ H_2SO_4$ was used as the reference electrode. A Pt gauze was used as the auxiliary electrode. All potentials are recalculated with respect to the reversible hydrogen electrode (RHE) in the working solution. At 298 K in 0.5 H_2SO_4 the potential of $Hg|Hg_2SO_4|0.5\ M\ H_2SO_4$ was 0.665 V versus standard hydrogen electrode (SHE), and under the same conditions the potential of RHE was −0.028 V versus SHE.

The working electrode was a gold wire (99.99%, 0.5 mm diameter, supplied by Polish Mint) covered with a thin alloy layer electrodeposited at a constant potential from a bath containing 0.106 M $PdCl_2$ + 0.047 M H_2PtCl_6 + 0.96 M HCl. Various alloy compositions were obtained by changing deposition potential in the range of 0.25–0.50 V vs SHE (with higher deposition potential the obtained alloys were enriched with Pd). The alloy thickness was ca. $0.8 \pm 0.1\ \mu m$. At the end of the experiments the electrodes were dissolved in aqua regia and the amounts of Pd and Pt in the alloys were analyzed by atomic absorption spectroscopy. According to these results, the current efficiency of the deposition of Pd–Pt alloys was in the range 70–78%. All alloy compositions given in the text and figures are bulk compositions expressed in atomic percentages.

Hydrogen absorption was performed at a constant potential for a period sufficient to ensure full hydrogen saturation, determined by chronoamperometry. The amount of absorbed hydrogen was calculated from hydrogen sorption and oxidation charges obtained by the integration of chronoamperometric (CA) or cyclic voltammetric (CV) curves recorded during hydrogen absorption or desorption. The procedures of electrode saturation with hydrogen and the calculations of the amount of absorbed hydrogen were identical to those described earlier [14,16,17].

3. Results and discussion

Fig. 1 shows a comparison of CV curves recorded in the hydrogen electrosorption region for pure Pd and a Pd–Pt alloy (93.0% Pd in the bulk) during the first hydrogen absorption/desorption cycle performed on a fresh sample and for the same electrode after ca. 40 absorption/desorption runs in the potential range between −0.10 and 0.50 V at 298 K. In the case of Pd electrode there is a marked difference in the course of the voltammetric signals for the fresh and hydrogen-treated sample. For the fresh Pd deposit the cathodic signal due to hydrogen absorption (below 0 V) is poorly developed and the anodic peak due to hydrogen oxidative desorption (around 0.45 V) is broad and flat, while after repeated hydrogen absorption/desorption procedure a pair of well-defined peaks is observed and the potential difference between anodic and cathodic signals becomes smaller. On the other hand, for the Pd–Pt alloy both hydrogen peaks are already observed for the fresh sample and further hydrogen treatment leads to relatively small changes in the shape and position of these signals.

Fig. 1 indicates that hydrogen insertion into freshly deposited Pd occurs at a significantly negative overvoltage, while its removal requires the application of a markedly higher potential than in the case of a hydrogen-treated sample. A similar effect was also observed for Pd-rich Pd–Au [14] and Pd–Pt–Au [18] alloys and could be attributed to slower kinetics of hydrogen electrosorption in a freshly deposited electrode due to additional work necessary to expand the crystal lattice during the initial hydrogen ingress. The effect of hydrogen treatment on the rate of the electrosorption process was explained by Millet et al. [19] as a result of a successive creation of defects in the crystal lattice which could facilitate further transport of hydrogen in the metal. On the contrary, in the case of Pd–Pt alloys hydrogen electrosorption in a fresh electrode is not inhibited as compared to the aged sample. This behavior is in line with the observation made earlier for Pd–Pt–Au alloys [18], where with the increase in the content of alloying metals the difference between CV curves for fresh and aged Pd–Pt–Au deposits became smaller and for alloys with a moderate Pd content (below 70%) practically no retardation of hydrogen electrosorption in fresh samples was observed, particularly when the Pt/Au atomic ratio was high. The positive influence of Pt addition on the kinetics of hydrogen electrosorption probably results from much smaller absorption/desorption hysteresis (see text below). The fact that Pt alloying has a greater effect that the same amount of Au may be ascribed to an additional surface effect, i.e. by the acceleration of the adsorption step in the overall process of hydrogen electrosorption due to high Pt activity in the process of hydrogen adsorption (in contrast to Au) [20].

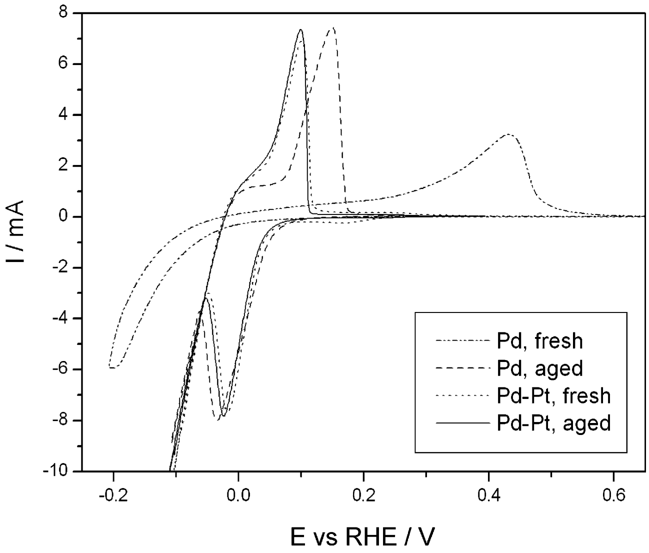

Fig. 1. The comparison of cyclic voltammograms recorded for a freshly deposited Pd–Pt alloy (93.0% Pd in the bulk) and after hydrogen treatment (ca. 40 runs of a repetitive hydrogen absorption/desorption between −0.10 and 0.50 V). Temperature 298 K, scan rate in cyclic voltammetry 0.01 V s^{-1}.

In order to minimize the effects of the further electrode ageing during the repetitive hydrogen insertion/removal in the experiment proper, at the beginning of the measurements each freshly deposited electrode was subjected at 298 K to a series of chronoamperometric and voltammetric runs between −0.10 and 0.50 V until a steady state voltammogram was obtained. All the results presented below concern Pd or Pd–Pt alloys after this procedure.

Fig. 2 shows cyclic voltammograms recorded in the potential range of hydrogen electrosorption at various temperatures for Pd and Pd–Pt alloys. It can be seen that with the increase in temperature the anodic peak due to oxidation of absorbed hydrogen becomes sharper and is shifted into lower potentials, while the temperature effect on hydrogen absorption (cathodic) current is much smaller and no distinct tendency in the peak potential changes can be observed. As a result of these trends the separation between hydrogen anodic and cathodic currents decreases with temperature, which indicates a lower degree of the electrochemical irreversibility of hydrogen absorption/desorption process at