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# Thermodynamic aspects of hydrogen electrosorption into Pd–Rh alloys

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ABSTRACT

Pd–Rh alloys were electrodeposited potentiostatically from baths containing a mixture of aqueous solutions of $PdCl_2$, $RhCl_3$ and HCl in various proportions. The thickness of the deposited layers was ca. 1 μm. The processes of hydrogen electrosorption were studied in 0.5 M $H_2SO_4$ solution in the temperature range of 283–328 K, using chronoamperometry and cycling voltammetry. Thermodynamic parameters of hydride formation and decomposition (Gibbs energy — $\Delta G_{\alpha \to \beta}$, $\Delta G_{\beta \to \alpha}$, enthalpy — $\Delta H_{\alpha \to \beta}$, $\Delta H_{\beta \to \alpha}$ and entropy — $\Delta S_{\alpha \to \beta}$, $\Delta S_{\beta \to \alpha}$) were calculated from the potentials of the $\alpha \to \beta$ and $\beta \to \alpha$ phase transitions. The absolute values of Gibbs energy and enthalpy distinctly decrease with increasing bulk content of Rh, while the entropy values are only slightly affected by the alloy bulk composition. It means that with increasing bulk content of Rh the hydride phase formation in Pd–Rh alloys becomes less exothermic and the hydride itself becomes thermodynamically less stable. Absorbed hydrogen probably occupies both Pd and Rh neighboring interstices.

## 1. Introduction

The fact that palladium is able to absorb large amounts of hydrogen has been known since the nineteenth century, i.e., when Graham published his first report (1866) [1]. Since then an increasing number of studies have been performed on hydrogen sorption into Pd and its alloys, as well as in other metals [2,3]. Among all these systems Pd and Pd alloys are particularly important as model systems, which are helpful in understanding the complexity of processes of hydrogen absorption/desorption into/from metallic materials designed for hydrogen storage [4–6] and used in Ni–MH batteries [7,8] or other energy sources [9].

In most Pd-based systems the additive of a metal that does not absorb hydrogen in its pure state leads to a decrease in the maximum alloy absorption capacity [2,3,10–14]. This kind of a behavior is exhibited by such alloys as Pd–Ag, Pd–Au, Pd–Cu, Pd–Pt and Pd–Ni [2,3]. However, there are exceptions to this rule. Pd–Rh alloys containing more than 80 at.% of Pd in the bulk are able to absorb more hydrogen than pure Pd [2,3,9,15–30]. Recently, a similar situation has been observed for Pd–Ru alloys containing ca. 1% Ru in the bulk [31,32].

The Pd–Rh–H system was a subject of numerous studies [9,15–30, 33–38]. Hydrogen absorption was performed from the gas phase or from solutions saturated with gaseous hydrogen, as well as electrochemically. It was found [2,3,9,15–17,21–30] that for Pd–Rh alloys containing ca. 2–10% Rh in the bulk the maximum hydrogen-to-metal atomic ratio (H/M) exceeded 0.80 in comparison with the values of 0.69–0.75 for pure Pd [39–41]. Even for the alloys containing 20% Rh the amount of absorbed hydrogen can be as large as for Pd [27]. The values of H/M ratio reaching 1 were observed for Pd–Rh alloys containing up to 40% Rh, exposed to high hydrogen pressures [29].

For Pd-rich alloys two phases of absorbed hydrogen can exist, i.e., the α- and β-phases, while for lower Pd bulk contents the Pd–metal–H system is homogeneous [42,43]. With the increasing amount of Rh in the alloy bulk the α–β phase transition is shifted into higher gas pressure or lower electrode potential [2,3,10–12,15–24,28,30,37,38]. This behavior is typical of Pd alloys with metals of a smaller lattice parameter than those of pure Pd (contracted alloys) [2,3,10–12,42,43]. The extent of absorption/desorption hysteresis decreases with increasing Rh bulk content in Pd–Rh alloys [16,17,19,20,23,30].

Several research groups determined the thermodynamic parameters of hydrogen absorption in Pd–Rh alloys from the temperature dependence of the position of the phase transition region on the pressure/potential scale [19,20,22,30,37,38,44]. According to these results, hydrogen absorption in Pd–Rh alloys becomes less exothermic with increasing amounts of Rh in the alloy bulk. On the other hand, the changes in absorption entropy with alloy composition do not usually reveal a distinct tendency.

The present article deals with the results of electrochemical determination of thermodynamic parameters of hydrogen absorption in Pd–Rh alloys prepared in the form of limited volume electrodes (LVE), i.e., thin

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layers (ca. 1 μm) electrodeposited on a conducting substrate [45]. This is a continuation of our recent investigations on hydrogen electrosorption in Pd–Rh alloys [15–18] and thermodynamic characteristic of Pd–noble metal systems [46–48].

## 2. Experimental

All experiments were performed in acidic solutions (0.5 M $H_2SO_4$) at temperatures of 283, 298, 313, and 328 K which were controlled by a thermostat (Lauda RE 306, Germany). The solutions were prepared from analytical grade reagents and triply distilled water additionally purified in a Millipore system. The electrolyte was deoxygenated with an argon (99.999%) stream for ca. 20 min; during the experiments Ar was flowing above the solution level to prevent from the contact with air.

All experiments were performed in a three-electrode cell with a $Hg|Hg_2SO_4|0.5$ M $H_2SO_4$ as the reference electrode, a Pt gauze as the auxiliary electrode and a gold wire covered with a thin Pd–Rh alloy layer (limited volume electrode) as the working electrode. All potentials were recalculated with respect to the RHE according to a procedure described earlier [16,49]. The working electrodes were obtained by electrodeposition at a constant potential from a bath containing a mixture of aqueous solutions of $PdCl_2$, $RhCl_3$ and HCl. The thickness of the working electrode layer was ca. 1 μm. The bulk composition of the alloys was controlled by the application of a given value of deposition potential and/or by using a given composition of the deposition bath. Bath 1 contained 0.06 M $RhCl_3$, 0.10 M $PdCl_2$ and 0.89 M HCl, while bath 2 contained 0.10 M $RhCl_3$, 0.09 M $PdCl_2$ and 0.80 M HCl (see [15] for details). In order to eliminate a simultaneous hydrogen penetration into the alloy being formed, the deposition potential was always higher than the value required for hydrogen sorption, i.e., it ranged from 0.27 to 0.37 V vs. SHE.

Hydrogen electrosorption into Pd and Pd–Rh alloys was studied using cyclic voltammetry and chronoamperometry. Hydrogen was electrosorbed at a given potential for a period sufficient for full hydrogen saturation, determined for each potential in separate experiments, and then it was oxidized at constant potential or during a positive voltammetric scan with 0.01 V $s^{-1}$. This sequence was repeated for each temperature studied. The amount of absorbed hydrogen was calculated from hydrogen sorption and oxidation charges obtained by the integration of chronoamperometric or voltammetric curves [16]. After the electrochemical experiments the total amounts of Pd and Rh in the alloys were analyzed by atomic emission spectroscopy (Analytic Laboratory of Polish Mint). All alloy compositions given in the text and figures are bulk compositions expressed in atomic percentages.

In order to obtain reproducible results and to avoid the effects of alloy aging during further hydrogen insertion/removal, before hydrogen absorption experiments each electrode was subjected to a series of voltammetric and chronoamperometric scans/steps through the potential region of hydrogen adsorption and absorption until a steady-state voltammogram was obtained [16,46,47].

## 3. Results and discussion

Fig. 1 presents the influence of the electrode potential on the amount of electrosorbed hydrogen, expressed as the hydrogen-to-metal atomic ratio (H/M), in Pd and selected Pd–Rh alloys, at various temperatures. As reported earlier for other hydrogen-absorbing systems [15–18,31, 32,40,41,45–49], the course of the H/M vs. E dependence can be explained taking into account the presence of particular forms of electrosorbed hydrogen. Lower values of H/M ratio at higher potentials are related to the α-phase (i.e., a solid solution of hydrogen in metal) and adsorbed hydrogen, while higher H/M ratios at lower potentials correspond mainly to the β-phase (i.e., a non-stoichiometric hydride) with a small contribution from adsorbed hydrogen. Between these two regions a narrow region of a sharp increase in the H/M value is visible that is due to the α–β phase transition. Fig. 1 shows that in the α- and β-phase coexistence region the potential of the α → β transition is lower than the potential of the β → α transition, analogously to the experiments in the gas phase, where the equilibrium hydrogen pressure during absorption is higher than that during desorption. This is the well-known phenomenon of the absorption/desorption hysteresis, observed for many metal–gas systems and widely discussed in the literature [2,3,50–59].

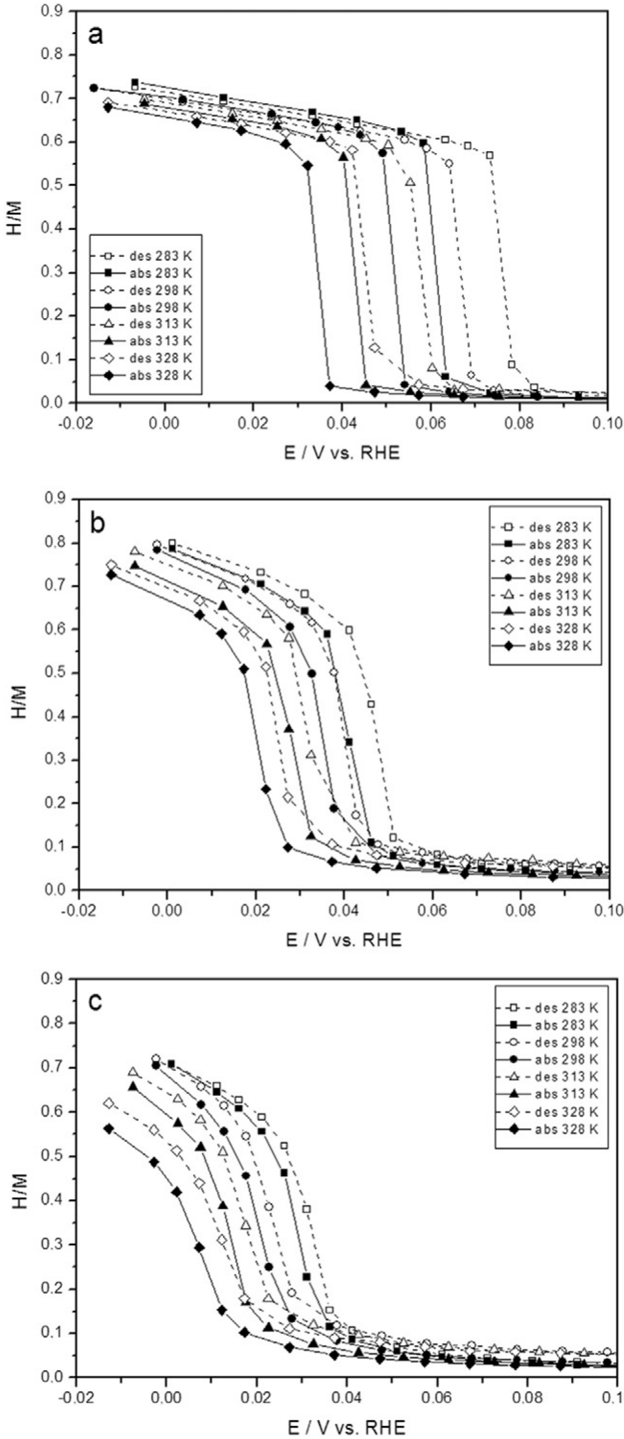

**Fig. 1.** Influence of electrode potential and temperature on the amount of hydrogen absorbed in (a) Pd and Pd–Rh alloys: (b) with 92.6% Pd in the bulk, and (c) with 88.0% Pd in the bulk. Full symbols, solid lines — absorption course, open symbols, dashed lines — desorption course.

The analysis of the curves presented in Fig. 1 for various samples and temperatures reveals the following facts:

1) For a given electrode composition, the H/M–E plots are shifted into lower potentials as the temperature increases. This behavior corresponds to the increase in the equilibrium hydrogen pressure with temperature in gas-phase experiments [2]. A similar tendency was also observed in our earlier experiments with other Pd alloys [46–48].
2) For a given electrode composition, the maximum amount of absorbed hydrogen in the β-phase decreases with increasing temperature. This tendency is a consequence of the fact that hydrogen absorption into Pd-rich alloys is an exothermic process and therefore the temperature increase shifts the reaction equilibrium towards desorption [2,19,20,22,30,37,38,44].
3) For a given temperature, the phase transition regions are shifted into lower potentials with increasing the bulk content of Rh in the alloys. Analogously, in gas-phase experiments the phase transition plateau is shifted into higher hydrogen pressures. This phenomenon is explained in the literature by the decrease in alloy lattice parameter (geometric effect) with increasing Rh bulk content [2,10–14,42,43].
4) For a given temperature, the maximum amount of absorbed hydrogen in Pd–Rh alloys containing small amounts of Rh is higher than in pure Pd. A similar behavior was earlier reported by many authors [2,3,9,15–17,21–30] and was attributed to the electronic effect originating from an increased number of free electron states below Pd Fermi level upon alloying with Rh [12].
5) The extent of absorption/desorption hysteresis decreases with increasing Rh bulk content for each temperature studied, as reported also by other researchers [19,20,23,30].
6) With increasing Rh bulk content the phase transition becomes less and less pronounced and finally disappears, which mirrors the fact that above a particular Rh substitution the β-phase is no longer formed [42,43].

The values of the potentials of the α → β and β → α phase transitions can be converted into Gibbs energy of the process of the β-phase formation and decomposition at a given temperature. From the temperature dependence of ΔG values one can determine other thermodynamic parameters of the β-phase formation and decomposition, i.e., enthalpy and entropy.

However, the existence of the hysteresis between absorption and desorption processes complicates the analysis of the thermodynamics of the Pd/alloy–H system. In general, two approaches can be found in the literature. One of them assumes that the thermodynamic functions can be calculated separately for absorption and desorption processes [19,20,30,37,38,44]. The other approach assumes that only one of the curves, i.e., the absorption or (usually) desorption curve represents the true equilibrium [60,61], or the true equilibrium is represented by pressures/potentials located between absorption and desorption curves in the hysteresis region [38,50,59,62–65].

Different values of thermodynamic functions for absorption and desorption are the result of the fact that in the hysteresis region Gibbs phase rule is not fulfilled [58]. We have discussed that point in our earlier papers [46,47]. Since most of the literature reports concerning the Pd–Rh system present separate values of thermodynamic functions for absorption and desorption processes [19,20,30,37,38,44], for the sake of comparison the same procedure has been applied in the present work.

According to Flanagan and Luo [20,66,67], the reaction occurring in the region of the phase transition is given by the equation (for the gas phase):

$$1/2\ H_2(g) + [1/(b-a)]\ MH_a \rightarrow [1/(b-a)]\ MH_b \tag{1}$$

where M is hydrogen-absorbing metal/homogeneous alloy, while a and b are the H/M ratios corresponding to the α- and β-phase boundaries, i.e., the maximum hydrogen concentration in the α-phase and the minimum hydrogen concentration in the β-phase. The relation between the equilibrium hydrogen pressure at the phase transition plateau ($p_{\alpha-\beta}$) and the changes in enthalpy and entropy during the phase transition are given by the equation:

$$1/2\ RT\ \ln\left(p_{\alpha-\beta}\right) = \Delta H_{\alpha-\beta} - T\Delta S_{\alpha-\beta}. \tag{2}$$

In the electrochemical experiment the potential of the phase transition expressed with respect to the RHE scale can be recalculated into Gibbs energy of the β-phase formation ($\Delta G_{\alpha\rightarrow\beta}$) or decomposition ($\Delta G_{\beta\rightarrow\alpha}$), according to the equations:

$$\Delta G_{\alpha\rightarrow\beta} = -2 \cdot F \cdot E_{\alpha\rightarrow\beta} \tag{3}$$

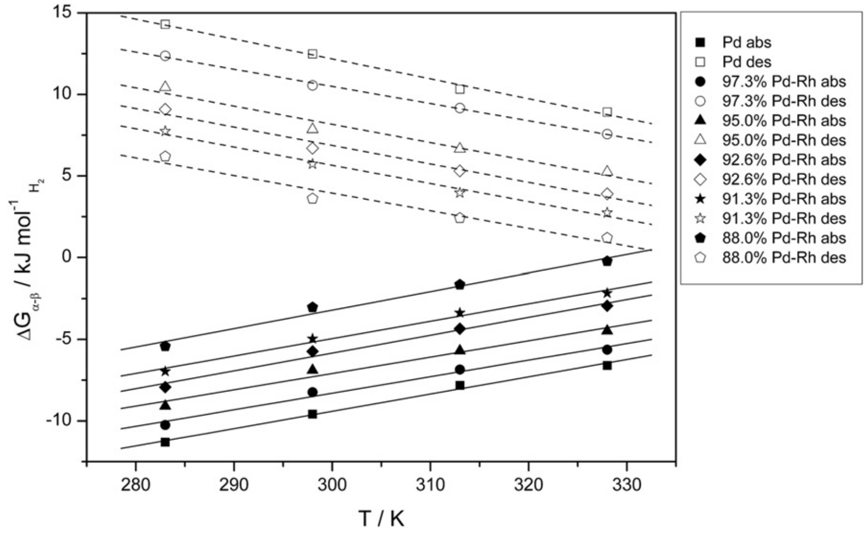

**Fig. 2.** Influence of temperature on the values of Gibbs energy of hydride formation (full symbols, solid lines) and decomposition (open symbols, dashed lines) into/from Pd and Pd–Rh alloys of different bulk compositions (indicated in the legend).

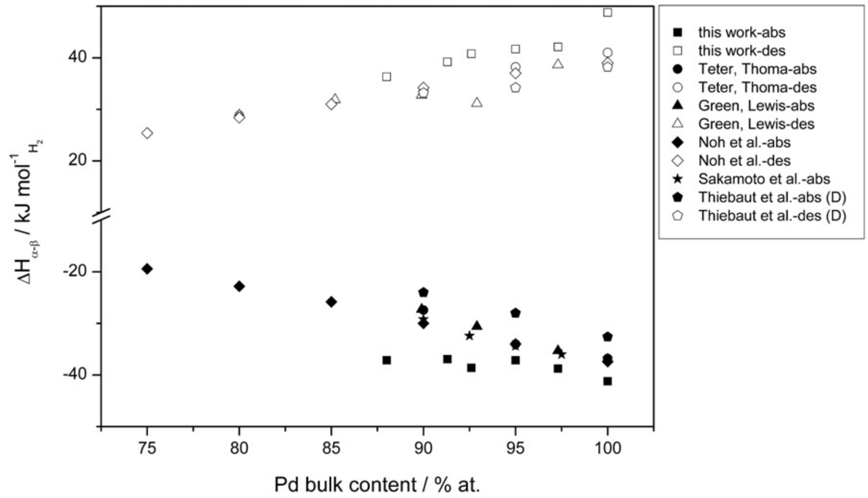

**Fig. 3.** Influence of alloy bulk composition on the values of enthalpy of hydride formation (full symbols) and decomposition (open symbols) into/from Pd and Pd–Rh alloys, obtained by various authors (this work, Thiebaut et al. [19], Sakamoto et al. [22], Noh et al. [30], Green and Lewis [37], Teter and Thoma [44]).

$$\Delta G_{\beta\to\alpha} = 2 \cdot F \cdot E_{\beta\to\alpha} \qquad (4)$$

where:

F Faraday's constant;
$E_{\alpha\to\beta}$ the potential of the α → β phase transition expressed with respect to the RHE;
$E_{\beta\to\alpha}$ the potential of the β → α phase transition expressed with respect to the RHE.

It should be noted that the values of Gibbs energy calculated using Eqs. (3) and (4) are related to 1 mol of molecular hydrogen and are twice greater than the values related to 1 mol of atomic hydrogen (Eq. (2)). This remark should be remembered when data from various literature sources are compared, as both ways of ΔG expression are practiced.

Fig. 2 shows the influence of temperature on the values of Gibbs energy of the β-phase formation and decomposition in Pd and Pd-rich Pd–Rh alloys, i.e., for the alloy composition range where two phases can exist in the Pd–Rh–H system (only for those compositions the determination of the phase transition thermodynamic functions makes a physical sense), calculated according to Eqs. (3) and (4). The phase transition potentials were determined at the midpoints of the respective plateau regions on H/M vs. E curves.

It can be seen that with increasing temperature the absolute values of Gibbs energy decrease, i.e., become less negative for hydride formation and less positive for hydride decomposition. A similar tendency is observed at each temperature with increasing Rh bulk content in the alloy. These results indicate that the β-phase becomes thermodynamically less stable as the temperature and Rh bulk concentration increase. This tendency is in line with the gas-phase data [19,20,22–24,28,30,37] and is coherent with our earlier studies on the temperature influence on hydrogen electrosorption in Pd–Rh alloys [15,16].

The dependence between temperature and Gibbs energy can be utilized to calculate enthalpy and entropy of the β-phase formation and decomposition. Assuming a linear function of the plot of ΔG vs. T, the values of ΔH and ΔS (averaged over the temperature range) can be obtained according to a basic thermodynamic equation:

$$\Delta G = \Delta H - T\Delta S \qquad (5)$$

Figs. 3 and 4 show the thermodynamic parameters of the β-phase formation and decomposition as a function of Pd–Rh alloy bulk composition. Our data are compared with the results taken from the literature [19,22,30,37,44]. Fig. 3 indicates that with decreasing Pd bulk content the values of enthalpy of the hydride formation (absorption) become less negative, while the values of enthalpy of the hydride decomposition

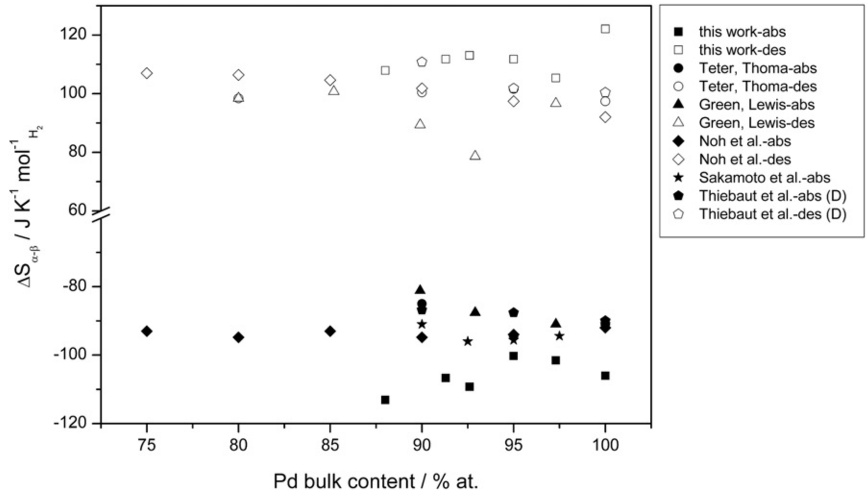

**Fig. 4.** Influence of alloy bulk composition on the values of entropy of hydride formation (full symbols) and decomposition (open symbols) into/from Pd and Pd–Rh alloys, obtained by various authors (this work, Thiebaut et al. [19], Sakamoto et al. [22], Noh et al. [30], Green and Lewis [37], Teter and Thoma [44]).

**Table. 1**
Conditions of hydrogen absorption in Pd–Rh alloys reported in the literature.

| Reference | Method of sample preparation and pretreatment | Sample form | Absorption conditions | Temperature range |
|---|---|---|---|---|
| This work | Electrochemical codeposition, several tens of absorption/desorption cycles | 1 μm thick layer on Au substrate | Electrochemical from 0.5 M $H_2SO_4$ aq. | 283, 298, 313, 328 K |
| Thiebaut et al. [19] | Annealing at 1000 °C under Ar for 24 h and quenched in water, activation by 5 absorption/desorption cycles | Bar-shaped, $\Phi = 1$ cm, $L = 10$ cm | Gas phase, deuterium absorption | 283–373 K |
| Sakamoto et al. [22] | Annealing at 1123 K for 2 h in vacuo and cooling to room temperature | 60–70 μm thick foil | Gas phase | 273–433 K |
| Noh et al. [30] | Arc melting under Ar, annealing at 1173 K in vacuum for 72 h and re-annealing for 72 h at 1173 K, slow quenching in air | 140 μm thick foil | Gas phase | 273, 303, 323 K |
| Green and Lewis [37] | Melting under Ar, anodization in 1 M HCl for 5 min at 2 mA or palladization | Wires of 0.0122 and 0.0274 cm diameter, 8–12 cm long | From hydrogen saturated 0.002 M HCl aq. | 273, 298, 323 K |
| Teter and Thoma [44] | Powder mixing and pressing, arc melting, homogenizing for 72 h at 1200 °C, annealing for 2 h at 900 °C, activation by several absorption/desorption cycles | 100 μm thick foil | Gas phase | 303–363 K |

(desorption) become less positive. It means that the process of hydride formation in Pd–Rh alloys is less exothermic than in pure Pd, and the greater the Rh bulk content is, the weaker the thermal effect of the hydride formation.

According to the literature [7], the heat of the hydride formation is an important parameter that characterizes an alloy for its possible applications as a hydrogen absorber. For instance, for the use of an alloy in hydride batteries the value of enthalpy of the hydride formation should be lower than ca. $-25 \div -15$ kJ mol$^{-1}$ and higher than $-50 \div -40$ kJ mol$^{-1}$of $H_2$ [7]. For high enthalpy values the hydride is not stable enough for charging, while for very low values it is too stable for discharging at room temperature. The fact that Rh additive makes the Pd–Rh alloy hydride less stable than Pd hydride means that the Pd–Rh–H system may be more suitable for practical applications, all the more that its hydrogen absorption capacity is greater than that of pure Pd.

The trends in the enthalpy changes with alloy bulk composition observed in our studies are qualitatively similar to other literature data [19,22,30,37,44]. However, the absolute values of enthalpy found in our studies are greater than those reported for other authors. The same situation took place for our results on thermodynamic parameters for hydrogen absorption/desorption into/from Pd alloys with Au, Pt and Ru. In earlier papers [46,47] we have discussed the possible reasons for these differences, i.e., various ways of sample preparation and pretreatment, sample structure and thickness, experimental conditions and temperature ranges used for thermodynamic calculations. Those remarks remain valid also for the case of the Pd–Rh system. Most literature data concern hydrogen absorption from the gas phase in bulk samples of a large volume, while in our studies hydrogen absorption in thin layers was studied under electrochemical conditions. These differences are listed in Table 1. There are several reports indicating that the size effects may affect the thermodynamic characteristic of the process of hydrogen absorption in Pd-based systems [68–71]. It was demonstrated that Pd hydride formation and decomposition in the case of nanosized Pd are characterized by different thermodynamic parameters as compared with bulk Pd hydrides [72–75]. Theoretical predictions also suggest that the smaller is the size of hydrogen-absorbing particles, the greater are the absolute values of enthalpy and entropy of the hydride formation/decomposition [73]. More detailed investigations on the effect of the form and properties of hydrogen-absorbing samples on the thermodynamics of hydrogen absorption are planned to be performed soon in our laboratory and will be reported separately.

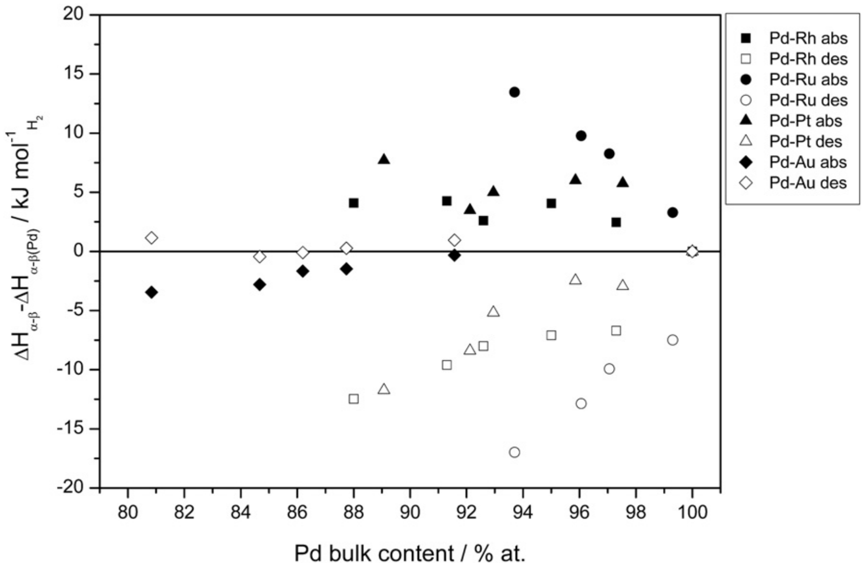

**Fig. 5.** Influence of alloy bulk composition on the values of enthalpy of hydride formation (full symbols) and decomposition (open symbols) into/from Pd alloys [46–48], expressed as the difference with respect to the value for pure Pd.

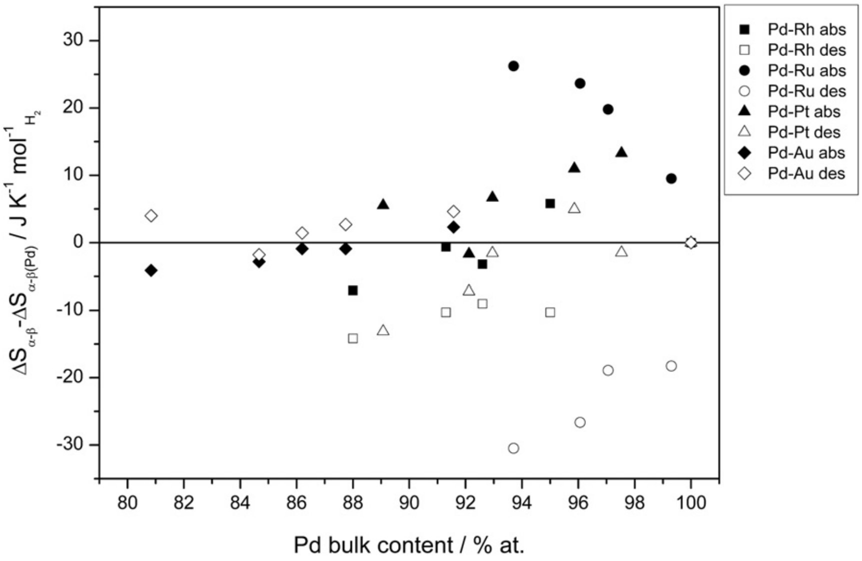

**Fig. 6.** Influence of alloy bulk composition on the values of entropy of hydride formation (full symbols, solid lines) and decomposition (open symbols, dashed lines) into/from Pd alloys [46–48], expressed as the difference with respect to the value for pure Pd.

Fig. 4 shows the changes in entropy of hydride formation/decomposition as a function of alloy bulk composition. As can be observed, the entropy values weakly depend on Pd content in the alloy. This behavior is in line with most of the literature data. Again, the absolute values of entropy changes are greater for our results than for the reports concerning hydrogen absorption from the gas phase in relatively thick samples.

Entropy changes accompanying hydrogen absorption in Pd–noble metal alloys can be considered as an indicator of the number of energetically different types of lattice interstices to be occupied by hydrogen atoms [20,38]. The almost constant values of $\Delta S_{\alpha\rightarrow\beta}$ with the increasing Rh content may suggest that hydrogen occupies both Pd and Rh neighboring interstices. This observation is coherent with the results of Flanagan and Luo [20], who stated that absorbed hydrogen can be located also near Rh atoms. Nevertheless, a slight increase in $|\Delta S_{\alpha\rightarrow\beta}|$ with the increasing Rh content may suggest that the latter ones may be preferred, as suggested by Lewis [14].

It may be interesting to compare our results for Pd–Rh alloys with the earlier data obtained in our laboratory for other Pd alloys prepared in the form of thin electrodeposits [46–48]. Figs. 5 and 6 present the values of enthalpy and entropy, expressed as their differences with respect to the values of pure Pd, for Pd–Rh, Pd–Ru, Pd–Pt and Pd–Au alloys. It can be seen that the direction of absorption enthalpy changes for Pd–Au alloys differ from those for other systems. In the case of Pd–Au alloys the process of hydrogen absorption becomes more exothermic with increasing amounts of the alloying metal, while for Pd–Pt, Pd–Rh and Pd–Ru alloys an opposite trend is observed. This difference is a result of a different influence of the additive element on the lattice constant of the Pd-based alloy [42,43]. Pd–Au alloys are expanded systems with the lattice constant higher than for pure Pd, while Pd–Ru and Pd–Rh alloys are contracted systems with the lattice constant smaller than pure Pd. However, the Pd–Pt system is an exception to the expanded/contracted classification of Pd alloys, since it behaves as a contacted system despite a small expansion of the lattice constant [2]. This unusual behavior was explained in terms of electronic effects [76] and factors connected with elastic properties [77]. It should also be noted that the highest slope of the changes in hydride formation/decomposition enthalpy with alloy bulk composition is observed for Pd–Ru alloys. Our earlier studies [31,32,48] have demonstrated that for that system the influence of the additive metal on hydrogen absorption behavior is particularly strong and its hydrogen absorption properties are very sensitive even to very small changes in Ru bulk content.

Fig. 6 indicates that the influence of alloy bulk composition of the entropy changes for Pd–Ru alloys is also much more significant than for other alloys. The addition of Ru to Pd results in a distinct increase/decrease in entropy values of hydride formation/decomposition suggesting that in those alloys hydrogen atoms occupy preferably Pd neighboring interstices, avoiding Rh atom neighborhood. Smaller differences between entropy changes for other systems suggest that although Pd neighboring interstices are still preferred, hydrogen may also occupy the interstices with neighboring additive metal atoms. This conclusion is partially consistent with the results of Mössbauer measurements [20], which show that absorbed hydrogen rather avoids interstices with Au and Pt as the nearest neighbors, but does not avoid interstices with Rh nearest neighbors. No such data on Pd–Ru alloys can be found in the literature.

## 4. Conclusions

Thin electrodeposited layers of Pd and Pd–Rh alloys were studied in the aspect of electrochemical absorption of hydrogen. The experiments carried out at various temperatures allowed us to calculate the thermodynamic parameters of hydride formation/decomposition. It was found that the thermodynamic stability of the hydride formed during hydrogen absorption in Pd–Rh alloys is lower as compared with that of the hydride formed in pure Pd and decreases with increasing Rh additive. The enthalpy of hydride formation becomes less negative with increasing Rh bulk content, which means that hydrogen absorption in Pd–Rh alloys becomes less exothermic with Rh additive. The addition of Rh to Pd has a very small effect on entropy values of hydride formation, suggesting that absorbed hydrogen atoms occupy both Pd and Rh neighboring interstices.

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