Hydrogen electrosorption in palladium alloys

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Interest in metal–hydrogen systems has been growing continuously during recent years. Hydrogen is regarded as a fuel of the future. However, hydrogen storage still remains a problem. Metal hydrides seem to be the most promising for that purpose. Hydrogen-absorbing materials are also utilized in electro-chemical power sources, e.g. in rechargeable nickel-hydride batteries (Ni–MH) or supercapacitors. Since 1866, when Graham published his pioneering report [1] on hydrogen dissolved in Pd and Pd–Ag alloys 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.

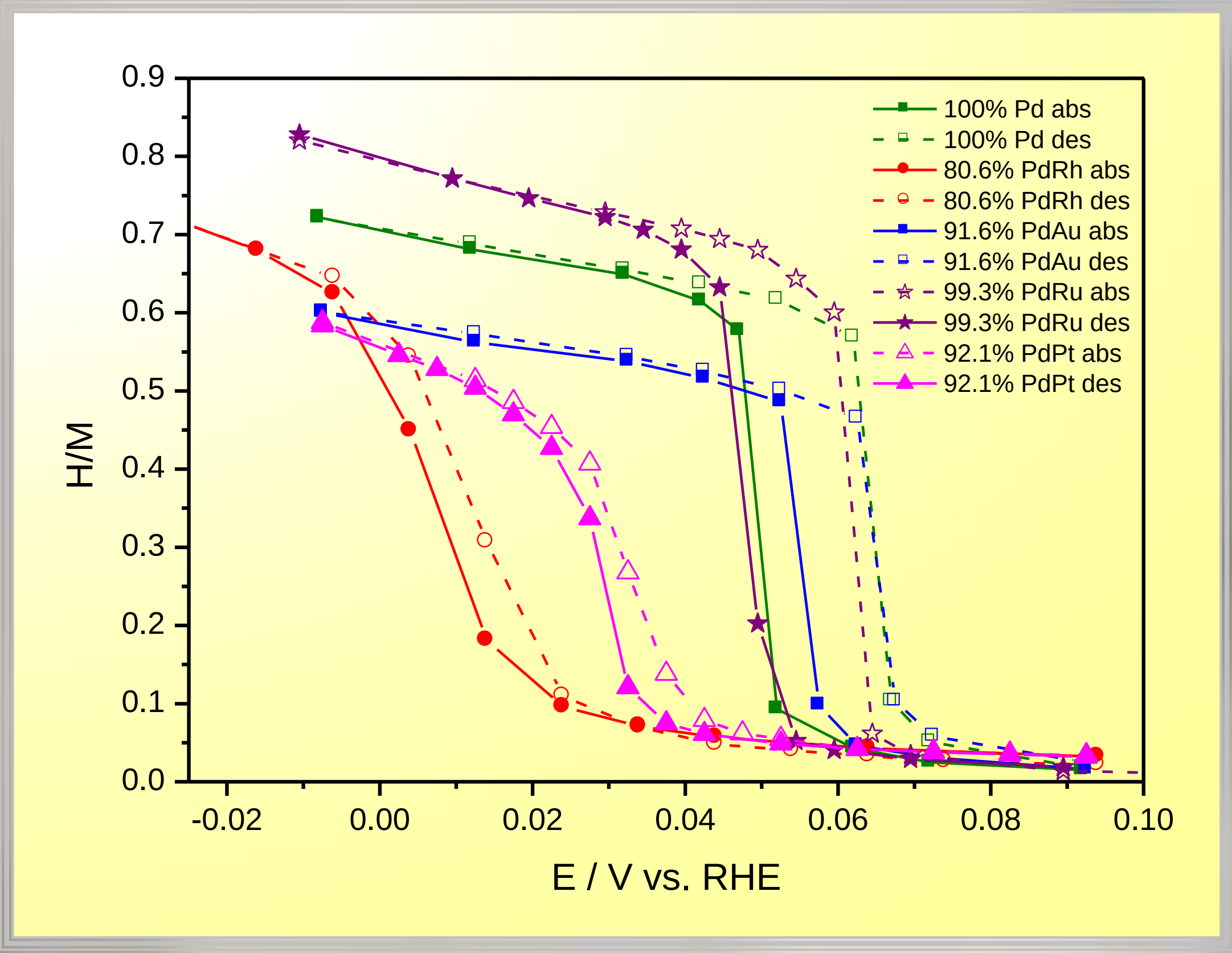

***Fig. 1.** Influence of electrode potential and alloy bulk composition on the amount of electrosorbed hydrogen (hydrogen-to-metal atomic ratio)*

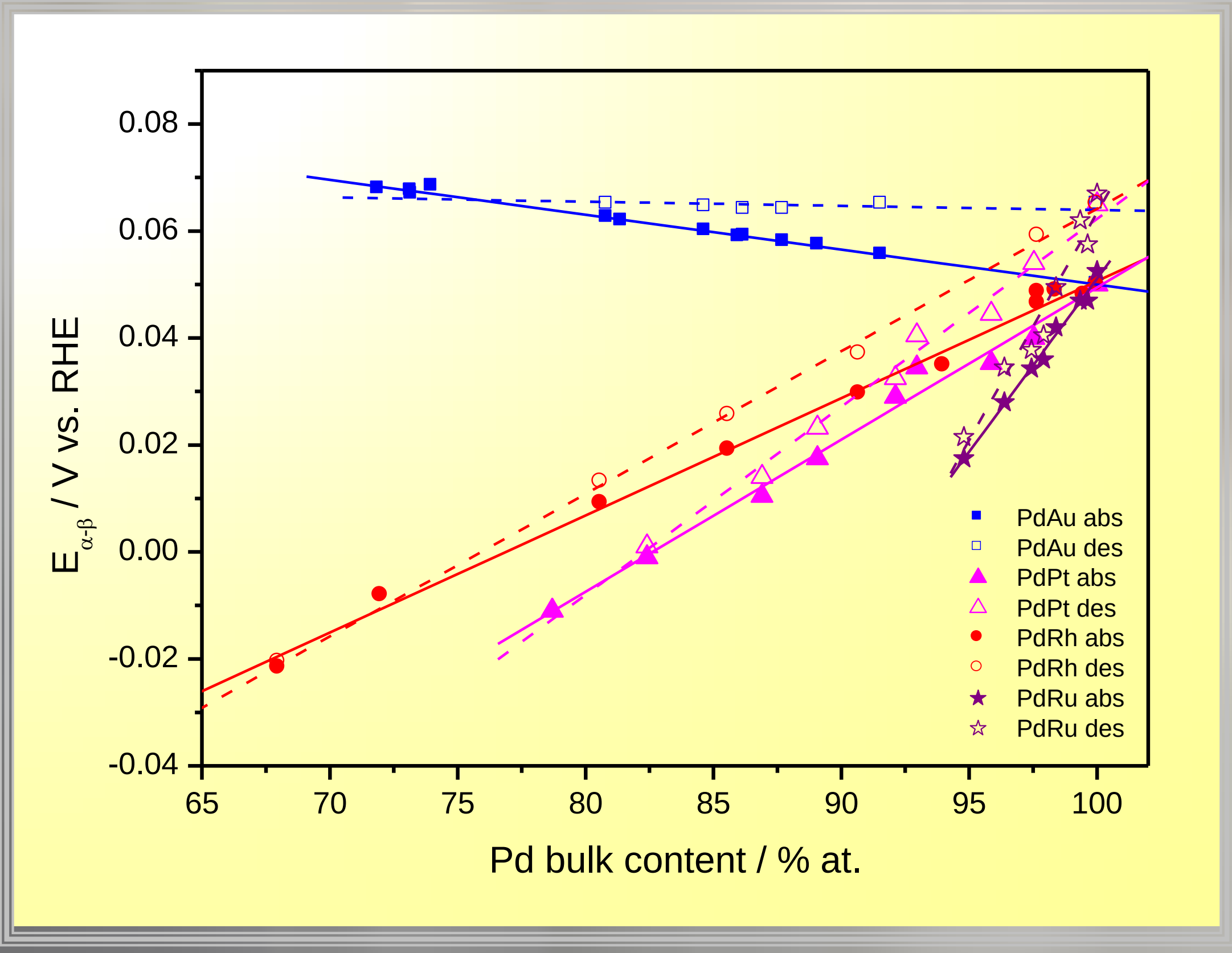

***Fig. 2.** The influence of the alloy bulk composition on the potential of α→β and β→α phase transition in Pd-noble metal alloys; E ± 2.5 mV*

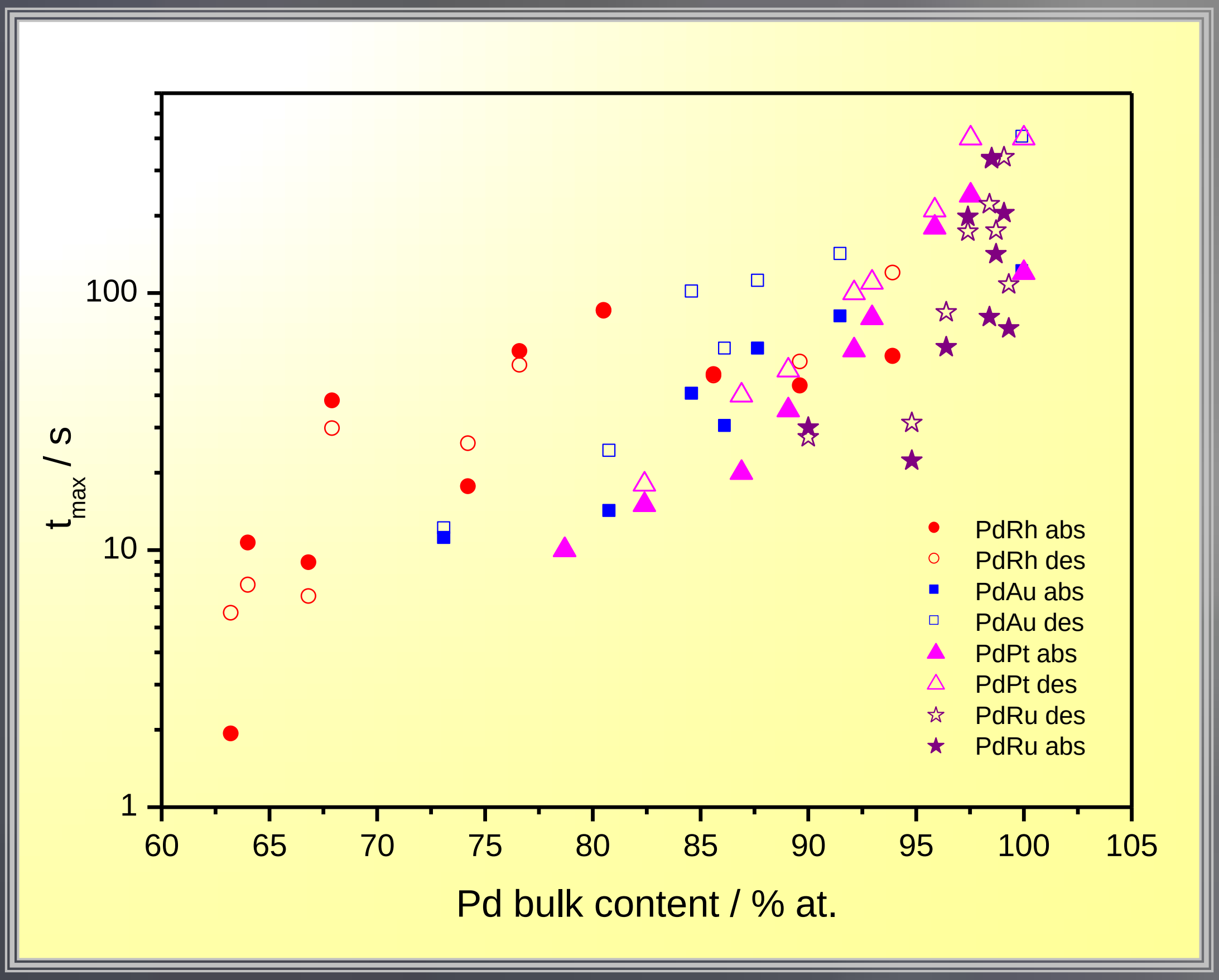

***Fig. 3**. The influence of alloy bulk composition on the maximum time needed for complete hydrogen saturation (solid symbols) and removal (open symbols) in chronoamperometric experoments.*

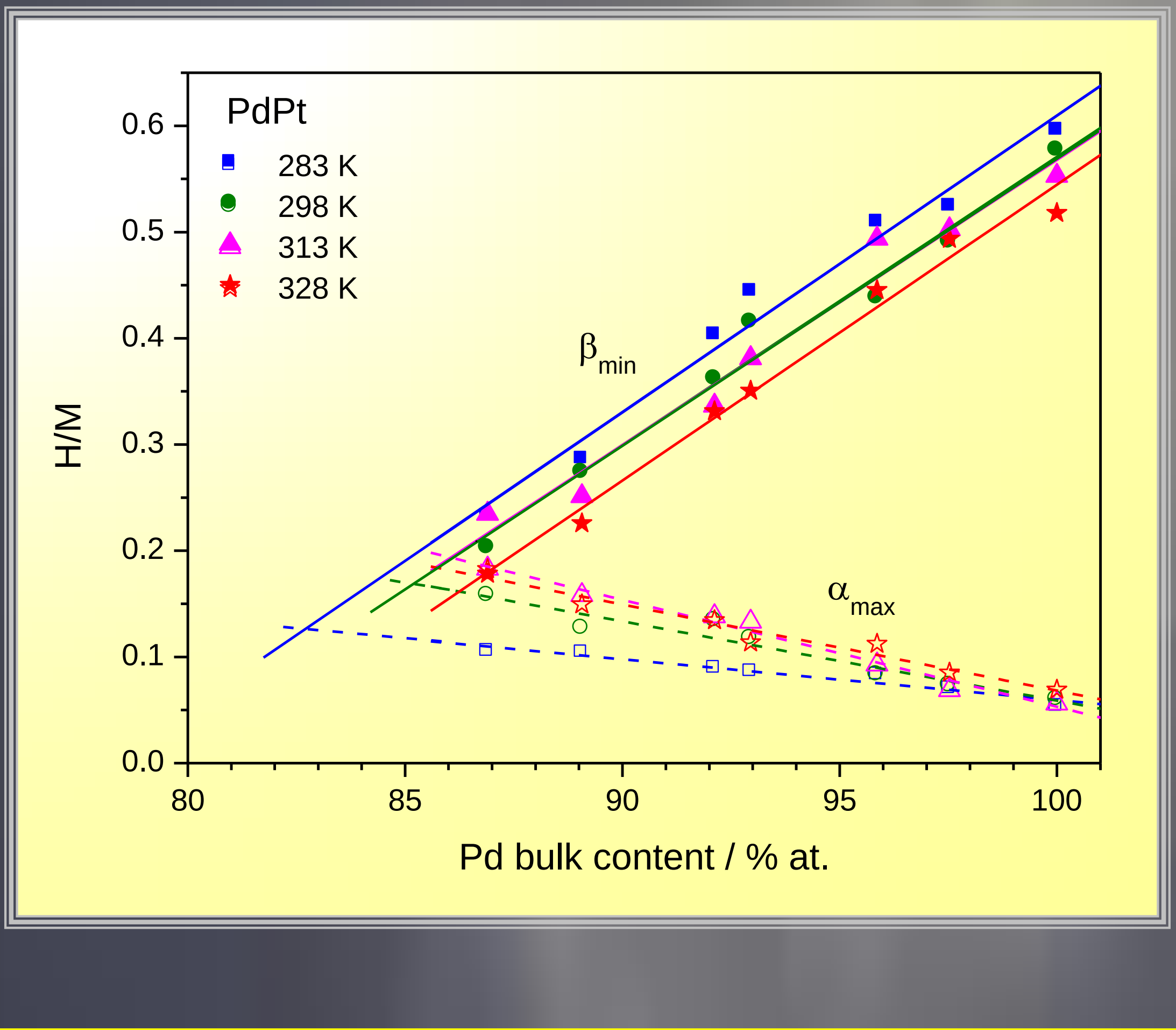

***Fig. 4.** The amount of electrosorbed hydrogen for the α- and β-phase boundaries in Pd-Pt alloys determined from chronoamperograms recorded during hydrogen absorption at -0.01 V and desorption at 0.50 V in different temperatures.*

EXPERIMENTAL

All the experiments were performed at room temperature (298 K) and some of them also in the range of 283-313 K (Pd alloys with Au, Pt and Rh) in 0.5 M H_2SO_4 solution, which was deoxygenated with an argon stream. Platinum gauze and $Hg|Hg_2SO_4|0.5$ M H_2SO_4 were used as the auxiliary and reference electrodes, respectively. Thin films (≈1μm) 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 1 M HCl and H_2PtCl_6, $HAuCl_2$, $RhCl_3$ or $RuCl_3$. All alloy compositions are bulk compositions expressed in atomic percentages determined using atomic absorption spectroscopy.

RESULTS & CONCLUSIONS

*Examined alloys can be divided into two systems: expanded: Pd-Au, Pd-Pt, and contracted: Pd-Rh, Pd-Ru. Expanded alloys are characterized by increased lattice parameters and contracted alloys by decreased lattice parameter as compared to pure Pd. This tendency is revealed by change of α↔β phase transition potentials (**Fig.1, Fig.2**) Rh or Ru addition to Pd entails a decrease in the potential of the α↔β phase transition while Pd alloying with Au leads to increase in the potential of the α↔β phase transition. Pd-Pt remains an exception to that rule. Despite the fact that Pd-Pt alloys are expanded, the potential of α↔β phase transition decrease with addition of Pt to pure Pd. The latter effect can be explained by the alteration of electronic or elastic properties, which are here more important factors than the geometric effect alone.*

Referring to described changes in the potential of the α↔β phase transition, Pt, Rh or Ru addition to Pd results in decrease in the thermodynamic stability of the β-phase, while Pd alloying with Au leads to increase in the thermodynamic stability of the β-phase.

*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 (**Fig.3**) hydrogen absorption and desorption times (with the exception of Pd-Ru alloys in the region of anomalously high hydrogen absorption).*

*Pd alloying with Pt and Au decreases maximum hydrogen solubility in β-phase, whereas in case of adding Ru or Rh to Pd in some range of compositions maximum hydrogen solubility in β-phase is higher than in pure Pd (**Fig.1**). This anomalous behavior can be explained taking into account changes in electronic and geometric factors during alloy formation.*

*Increase of the alloying metals bulk content entails the decrease of two-phase region in comparison with pure Pd. Thus, at a given temperature for a certain alloy bulk composition the miscibility gap in the alloy–hydrogen system disappears (i.e. $\beta_{min} = a_{max}$) and the b-phase can no longer be formed (for Pd-Pt alloys see **Fig. 4**)*

*Temperature increase in Pd alloys with Au, Pt [2] and Rh [3] facilitates the kinetics of hydrogen sorption and diminishes the alloy absorption capacity (**Fig.4** – Pd-Pt), making the formation of the β-phase thermodynamically less favorable.*

ACKNOWLEDGMENTS

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