

PALLADIUM BINARY ALLOYS WITH HIGH HYDROGEN CAPACITY

U. Koss, K. Hubkowska-Kosińska, M. Łukaszewski, A. Czerwiński

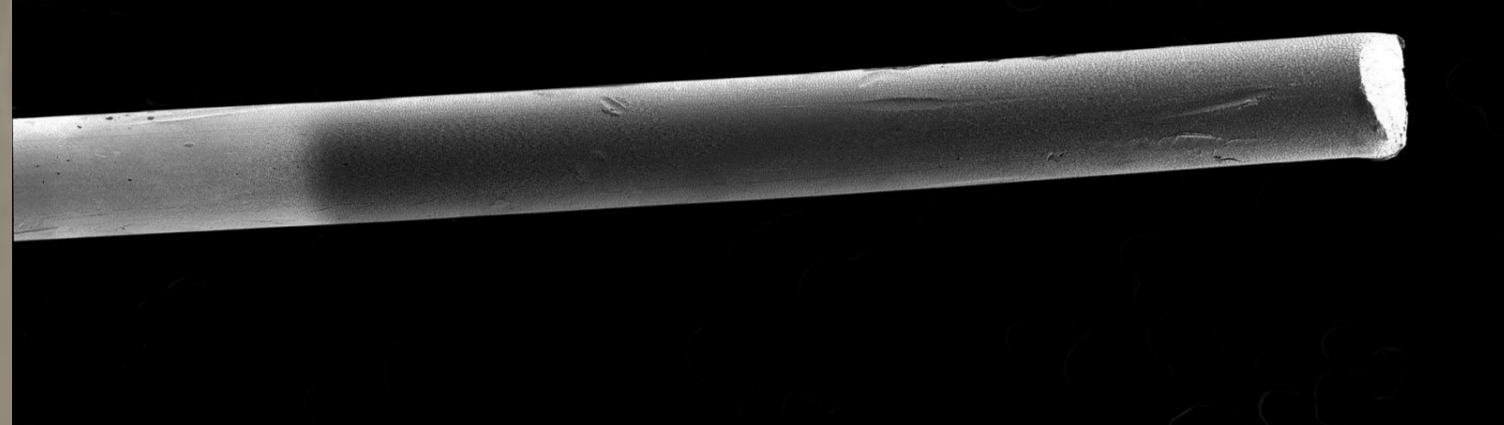
University of Warsaw, Faculty of Chemistry, Pasteura 1, 02-093 Warsaw, Poland, urszula.koss@gmail.com

introduction

Palladium alloys with noble metals are important model systems for understanding the process of hydrogen sorption in metallic systems. It is known that the addition of a second metal to palladium changes hydrogen absorption properties of the system. It is a consequence of the alteration of crystal lattice structure, electronic and elastic properties. Pd-Rh and Pd-Ru alloys are exceptional systems because the amount of absorbed hydrogen in Pd-rich Pd-Rh and Pd-Ru alloys is larger than in case of pure Pd. This behavior is in contrast to a general rule that Pd alloys with a non-absorbing metal are characterized by a smaller hydrogen absorption capacity. Thus an accurate examination of Pd-Rh and Pd-Ru systems is very important considering alloys application for the hydrogen storage.

experimental

Fig. 1. Limited volume electrode – LVE.

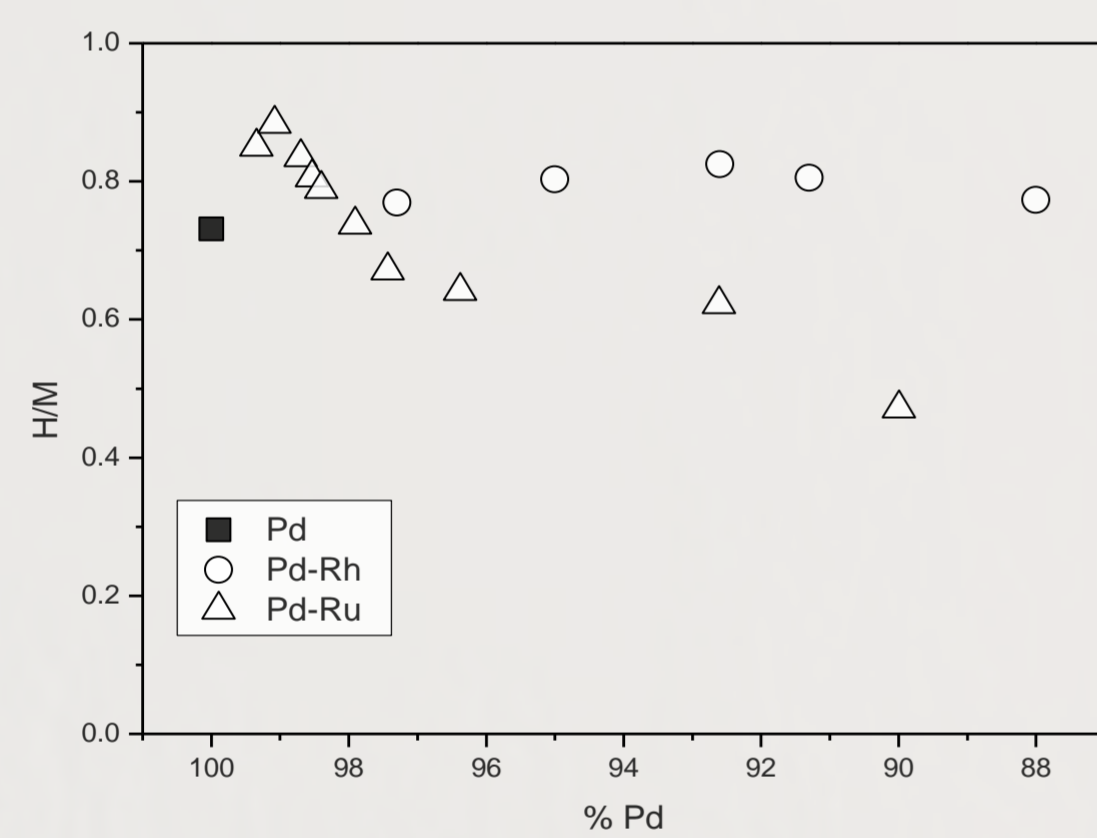


Au wire
99.9%
d = 0.5 mm

Pd alloy layer
h = 5 mm
L = 1 μm

Hydrogen electrosorption into Pd-Rh and Pd-Ru alloys was studied in acidic solution (0.5 M H₂SO₄) using cyclic voltammetry and chronoamperometry. Platinum gauze was used as the auxiliary electrode and Hg|Hg₂SO₄|0.5 M H₂SO₄ was used as the reference electrode. Alloys were obtained by electrodeposition from baths containing PdCl₂, RhCl₃, RuCl₃ and HCl. Thin films (≈ 1 μm) of Pd and its alloys were deposited as limited volume electrodes (LVEs) on a gold wire (Fig. 1). Alloys with various content were prepared by changing i) the potential of the deposition and ii) concentrations of the chlorides in baths.

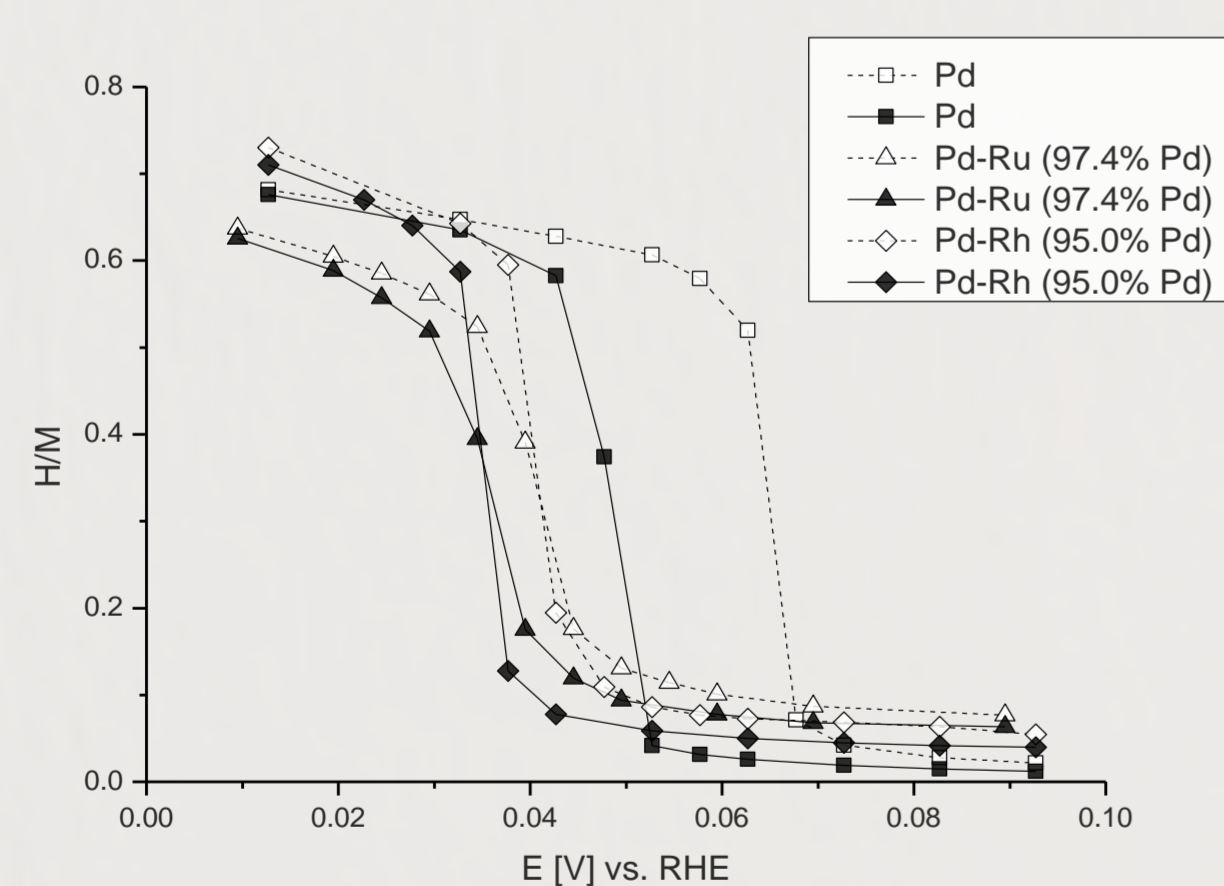
results and discussion



high hydrogen capacity

In general, Pd alloying with noble metals decreases maximum hydrogen solubility in β -phase. The decrease in the amount of absorbed hydrogen in most of Pd most alloys is explained by the electronic effect, i.e. by filling the gaps in the Pd d-band by electrons originating from the alloying metal. On the other hand, in case of Pd-Rh and Pd-Ru alloys with small Rh/Ru content there is an increase in the number of gaps in the Pd d-band [1], which is manifested by an increase in the maximum amount of hydrogen absorbed [2,3]. Pd-Rh and Pd-Ru ability to absorb high amounts of hydrogen gives new opportunities to construct future hydrogen storage devices.

Fig. 2. Influence of noble metal additive (Rh or Ru) on the amount of hydrogen absorbed at -0.05 V vs. RHE.



hysteresis effect

Pd-Ru and Pd-Rh alloys are contracted systems which means that they are characterized by decreased lattice parameter as compared to pure Pd. This tendency results in change of $\alpha \leftrightarrow \beta$ phase transitions potentials. Rh or Ru addition to Pd entails a decrease in the potential of the $\alpha \leftrightarrow \beta$ phase transitions. In addition, the transition potentials for the $\beta \rightarrow \alpha$ phase transition are always higher than those for the $\alpha \rightarrow \beta$ phase transition and this phenomenon is called as hysteresis effect. The hysteresis decreases with Rh or Ru additive which is very important taking into account an alloy application as an anode in cells. This is connected with the fact that waste of energy in repeating absorption/ desorption cycles is smaller than in case of pure Pd.

Fig. 3. Hysteresis effect in Pd, a Pd-Rh alloy and a Pd-Ru alloy. Solid lines – absorption course; dashed lines – desorption course.

conclusions

Pd-Rh and Pd-Ru alloys are exceptional systems of Pd alloys because the amount of absorbed hydrogen in Pd-rich Pd-Rh and Pd-Ru alloys is larger than in case of pure Pd. Pd-Rh and Pd-Ru ability to absorb high amounts of hydrogen gives new opportunities to construct future hydrogen storage devices.

Pd-Ru and Pd-Rh alloys are contracted systems. It results in change of $\alpha \leftrightarrow \beta$ phase transitions potentials. Rh or Ru addition to Pd entails a decrease in the potential of the $\alpha \leftrightarrow \beta$ phase transitions as well as a decrease of hysteresis effect. It is very important taking into account an alloy application as an anode in cells. This is connected with the fact that waste of energy in repeating absorption/ desorption cycles is smaller than in case of pure Pd.

references

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2. U. Koss, M. Łukaszewski, K. Hubkowska, A. Czerwiński, *J. Solid State Electrochem.* 15 (2011) 2477.
3. K. Hubkowska, M. Łukaszewski, A. Czerwiński, *Electrochem. Commun.* 20 (2012) 175.