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ELECTROCHEMICAL BEHAVIOR OF PALLADIUM-GOLD ALLOYS

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INTRODUCTION

The electrochemical properties of noble metals and their alloys are still in the center of modern research mainly due to a constant search for new materials for electrocatalysis, electrosynthesis and, in particular, for chemical current sources. Palladium and palladium alloys have been studied extensively also because of their high ability to absorb hydrogen. However, electrochemical aspects of this process are still not well known, therefore further investigations are needed.

EXPERIMENTAL

All the experiments were performed at room temperature in 1 M H_2SO_4 aqueous solutions. All potentials in the text and on figures are referred to RHE.

Pd-Au alloys were deposited potentiostatically on a gold substrate in the form of a thin layer (limited volume electrodes - LVEs). The bulk compositions of the alloys were obtained from the EDAX analysis (Rontec M1 analyzer coupled with LEO 435VP scanning electron microscope).

RESULTS AND DISCUSSION

1. Influence of electrode potential and alloy composition on the ability to absorb hydrogen

In general, the potential range of hydrogen sorption into Pd-Au alloys is similar to the case of pure palladium. For Pd-rich alloys the H/(Pd+Au) vs. potential curves have a characteristic shape with a sharp increase of the amount of sorbed hydrogen between 0,050 V and 0,015 V, which corresponds to the $\alpha \rightarrow \beta$ transition (***Fig. 1***).

The dependence of the alloy composition on the maximum H/(Pd+Au) ratios is monotonic and alloys containing more than *ca.* 70 % at. of gold do not absorb hydrogen, which is consistent with data reported in the literature (***Fig. 2***).

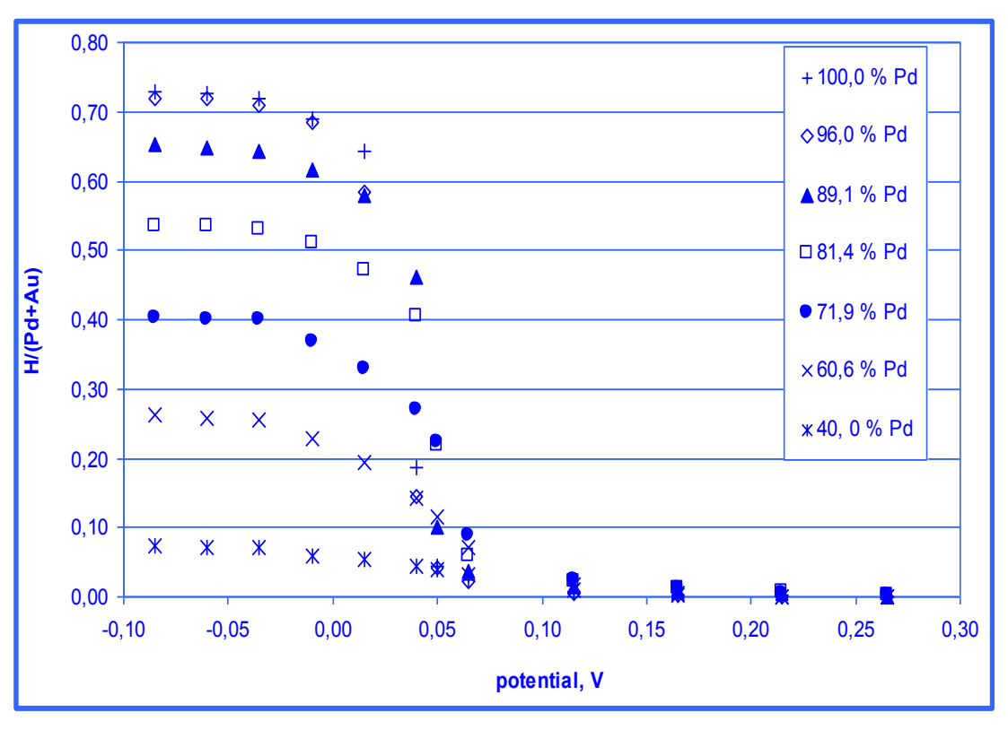

Fig. 1. Dependence of H/(Pd+Au) ratios on electrode potential for Pd-Au alloys of various bulk compositions. Time of hydrogen absorption 300 s; scan rate during hydrogen electrooxidation 0,01 V/s.

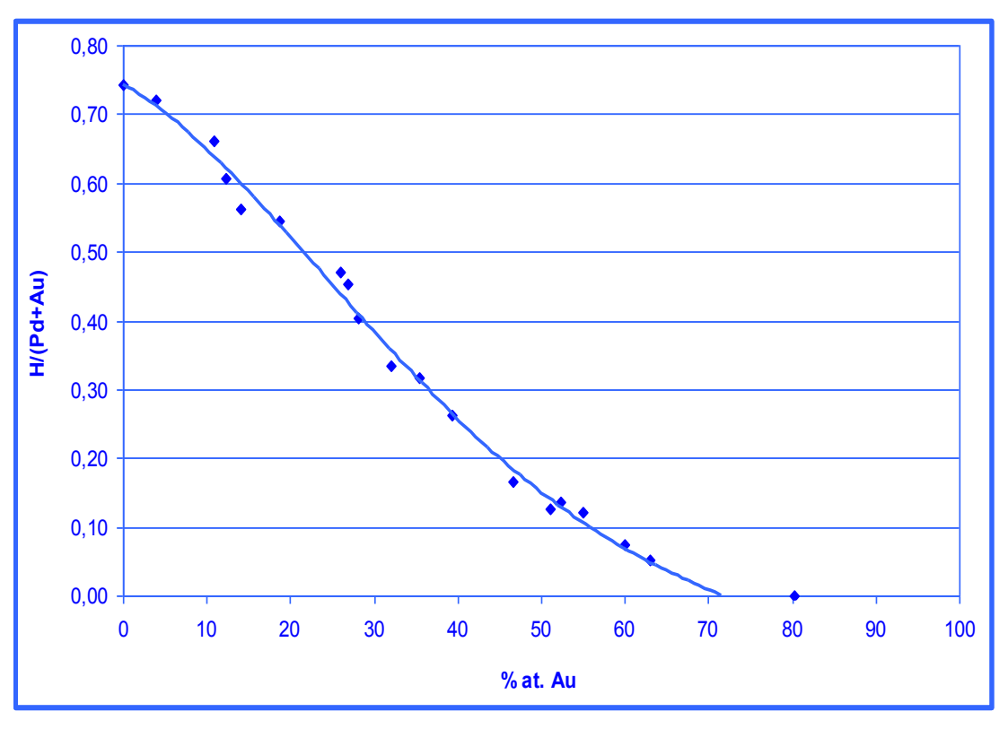

Fig. 2. Influence of bulk gold content on maximum H/(Pd+Au) ratios. Time of hydrogen absorption 300 s; scan rate during hydrogen electrooxidation 0,01 V/s.

2. Voltammetry of Pd-Au limited volume electrodes

Fig. 3 demonstrates some advantages of using of limited volume electrodes in the investigations of palladium-based alloys. This approach allows the amount of absorbed hydrogen to be limited and hydrogen peaks to be separated from the currents of various surface processes.

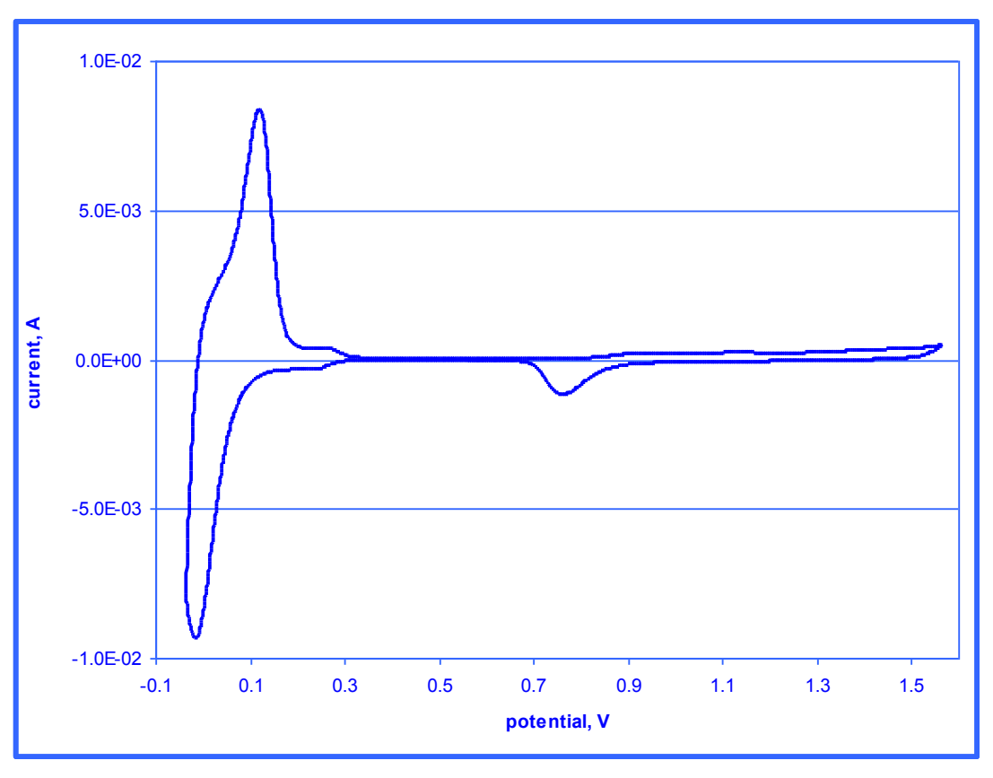

Fig. 3. Voltammogram of 74,0 % Pd-Au alloy at scan rate 0,01 V/s.

Two peaks in the hydrogen region, corresponding to two types of sorbed hydrogen, were observed on the voltammograms for alloys rich in Pd (***Fig. 4a***). Analogously to palladium the larger peak (I) can be attributed to hydrogen mainly absorbed as the β-phase and the smaller peak (II) can result from hydrogen absorbed as the α-phase and partly from the adsorbed hydrogen. The smaller peak did not appear on voltammograms for electrodes containing less than *ca.* 65 % at. Pd (***Fig. 4b***).

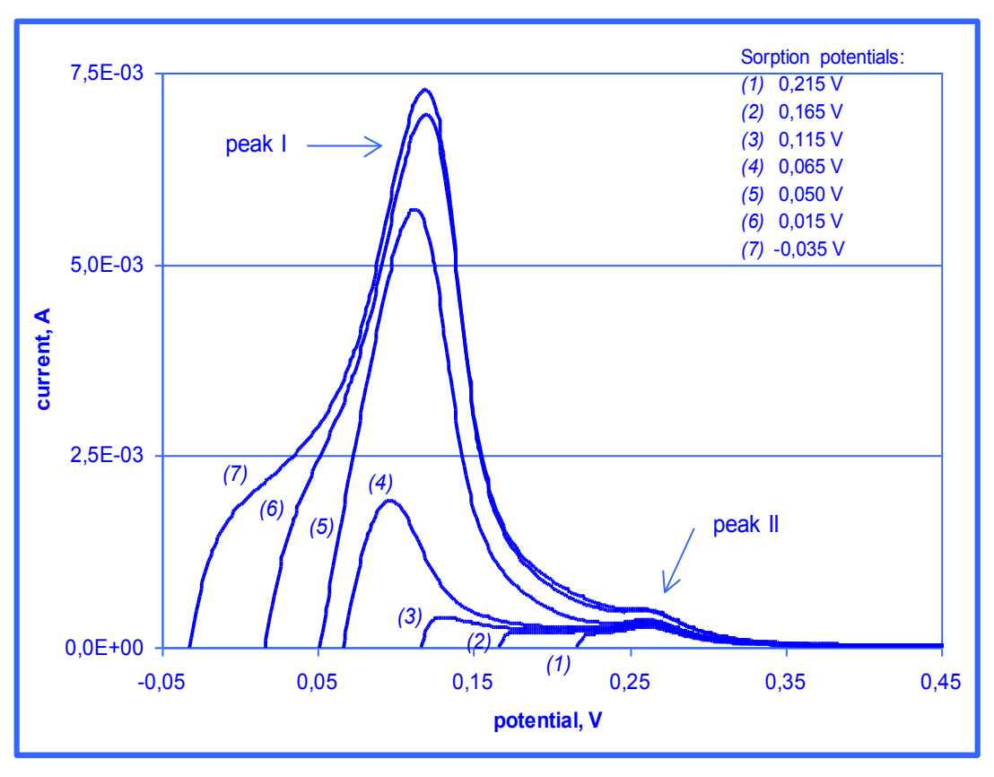

Fig. 4a. Oxidation peaks recorded after hydrogen sorption (300 s) at different potentials for 72,3 % Pd-Au alloy; scan rate 0,01 Vs.

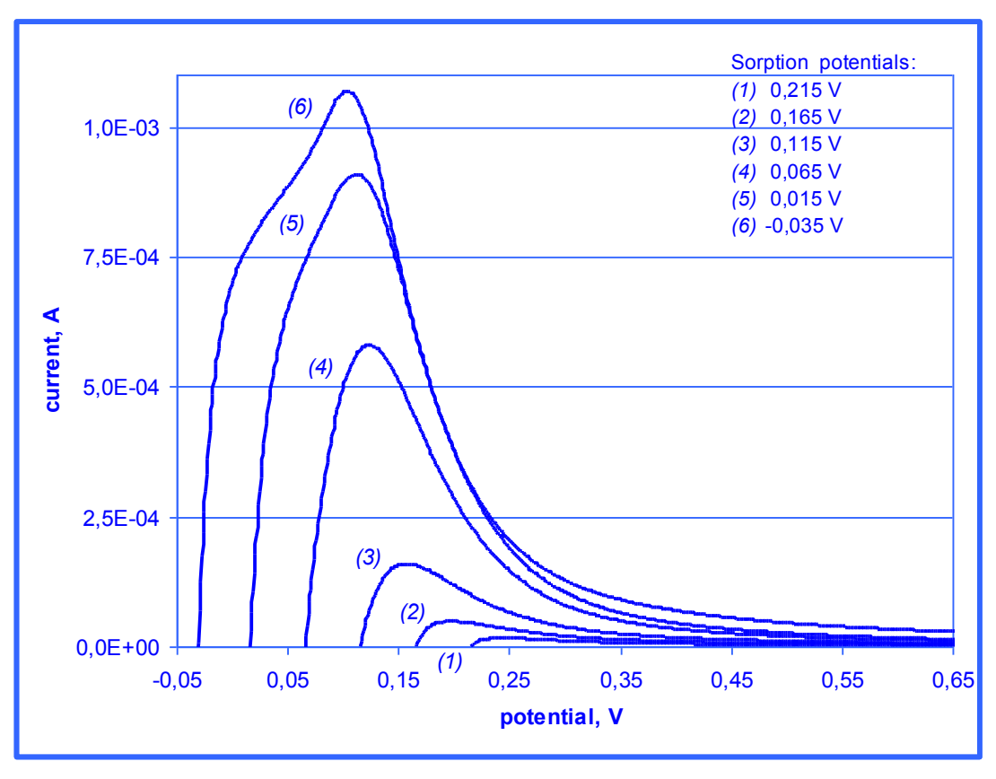

Fig. 4b. Oxidation peaks recorded after hydrogen sorption (300 s) at different potentials for 53,4 % Pd-Au alloy; scan rate 0,01 Vs.

3. Mechanism of hydrogen desorption from Pd-Au alloys

The amount of hydrogen absorbed into Pd-Au alloys, calculated from the charge of the hydrogen oxidation peaks, has been found to be dependent on the scan rate in cyclic voltammetry experiments.

A maximum of the hydrogen oxidation charge at scan rates between 5-10 mV/s (***Fig. 5***) suggests that (similarly to the case of Pd-LVEs) the absorbed hydrogen (H_{abs}) removal from the Pd-Au alloy follows two pathways:

1) the electrochemical oxidation:

$$H_{abs} \rightarrow H_{ads} \rightarrow H^+ + e^-$$

2) the non-electrochemical recombination process:

$$2\,H_{abs} \rightarrow 2\,H_{ads} \rightarrow H_2$$

Hydrogen atoms adsorbed on the electrode surface (H_{ads}) are involved in this model.

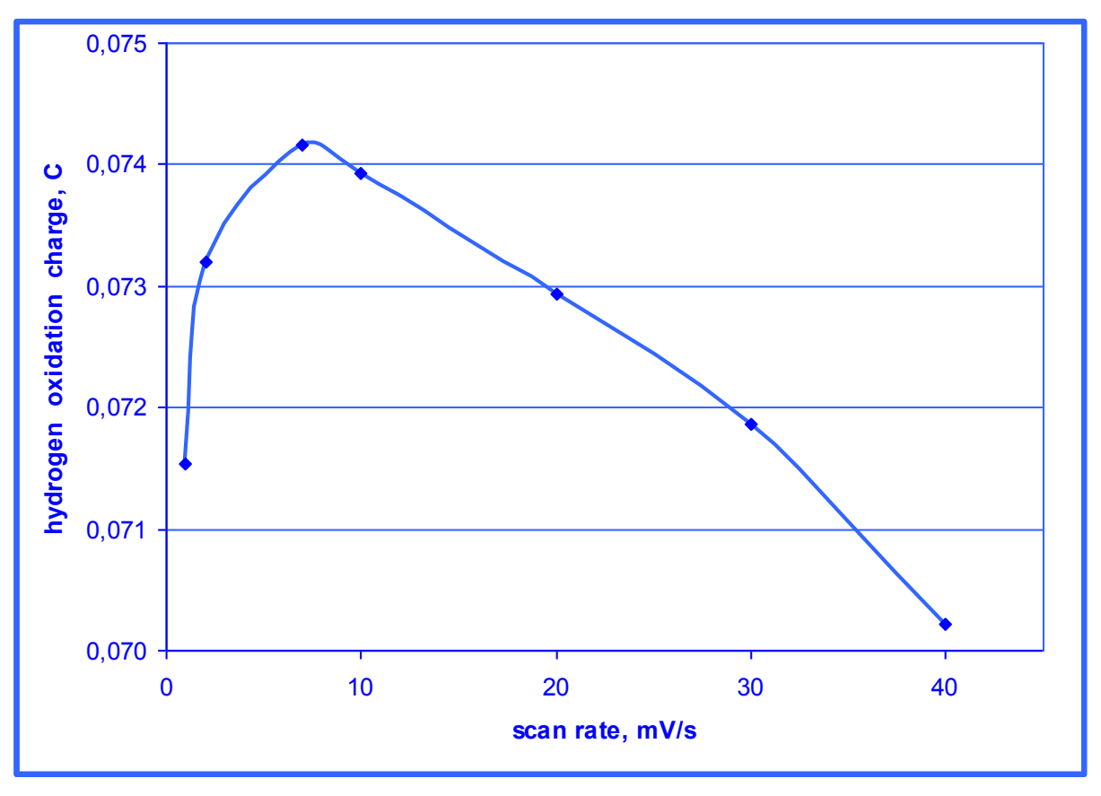

Fig. 5. Dependence of hydrogen oxidation charge on scan rate for 79,3 % Pd-Au alloy. Potential of hydrogen absorption -0,035 V; absorption time 300 s. Alloy layer thickness 2,9 mm.

4. Influence of potential cycling on the electrochemical behavior of Pd-Au alloys

Voltammograms of Pd-Au alloys change significantly during continuous potential cycling in the oxygen region in acid media due to the selective dissolution of palladium. In the hydrogen region the changes are less dramatic (***Fig. 6***), especially in the case of alloys initially relatively rich in Pd (above 60 % at.), when the amount of absorbed hydrogen remains significant after the strong depletion of palladium from the surface (***Fig. 7***).

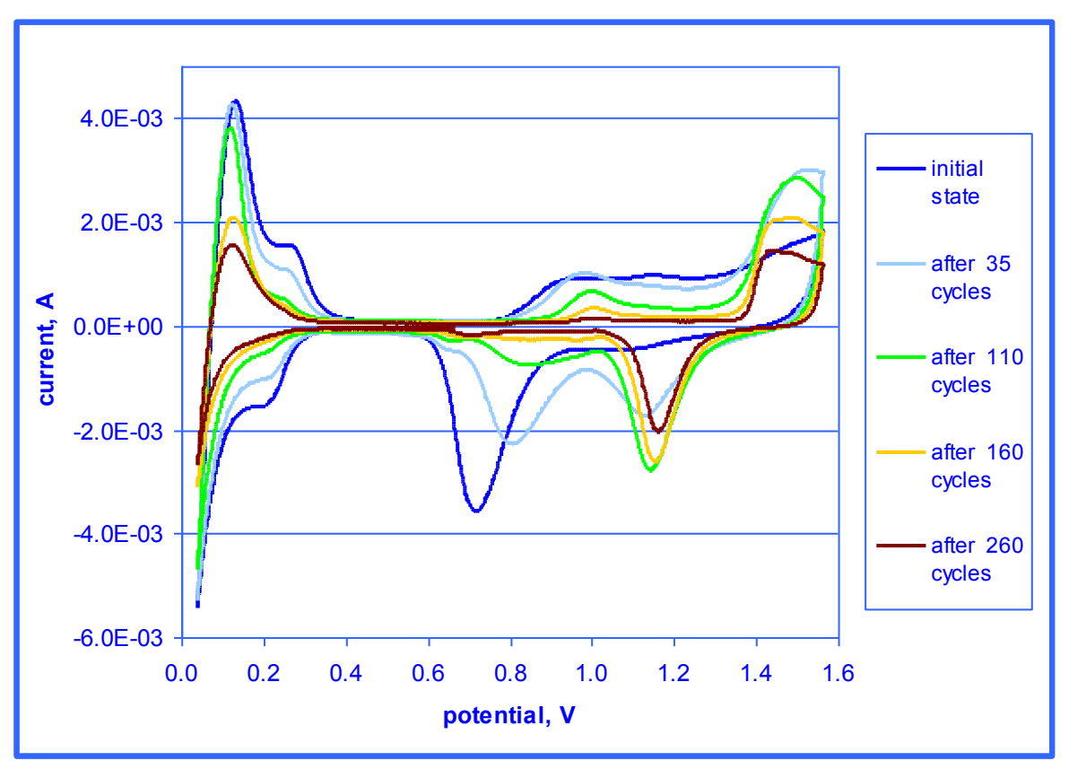

Fig. 6. Voltammograms of Pd-Au electrode (0,05 V/s) recorded after successive cycling in the potential range from 0,365 to 1,565 V at scan rate 0,1 V/s. Initial bulk palladium content 73,2 %.

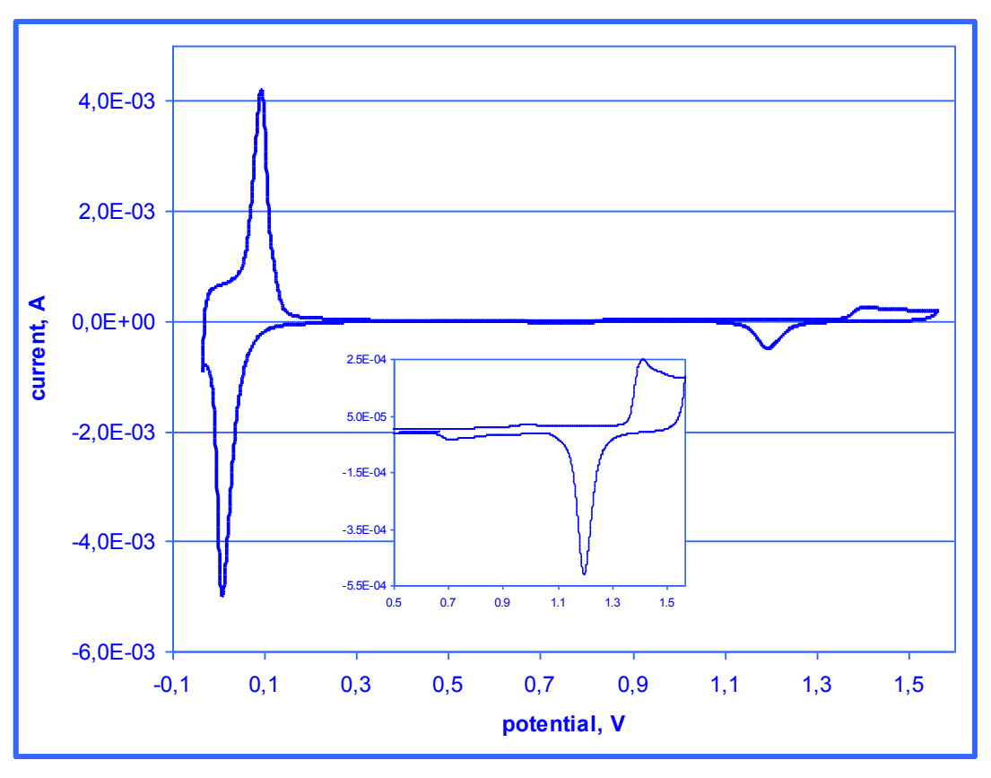

Fig. 7. Voltammogram of Pd-Au electrode (0,01 V/s), impoverished in Pd during electrochemical treatment. The region of oxygen adsorption/desorption is shown separately.

5. Adsorption of carbon monoxide on Pd-Au alloy of high gold surface concentration

The procedure of surface poisoning using CO has been applied to a Pd-Au alloy electrode, impoverished in palladium during electrochemical treatment. Two types of experiments were carried out: with hydrogen absorption performed after CO adsorption and *vice versa* (***Figs 8a*** and ***8b***). The voltammograms demonstrate a blocking effect of absorbed hydrogen by adsorbed CO. Hydrogen desorption is much more difficult than in the absence of CO – the oxidation wave is strongly shifted to positive potentials. It indicates that carbon monoxide and hydrogen compete for the same surface sites. *i.e.* palladium atoms, because CO adsorption on gold is negligible. It is noteworthy that in spite of the saturation of the electrode surface with CO adsorption products a certain amount of hydrogen can still be absorbed. The fact that not all palladium atoms are covered with the adsorbed CO could explain this observation. However, one cannot exclude the possibility that a simultaneous mechanism of the direct hydrogen absorption/ desorption, not involving an adsorption step, is also operative.

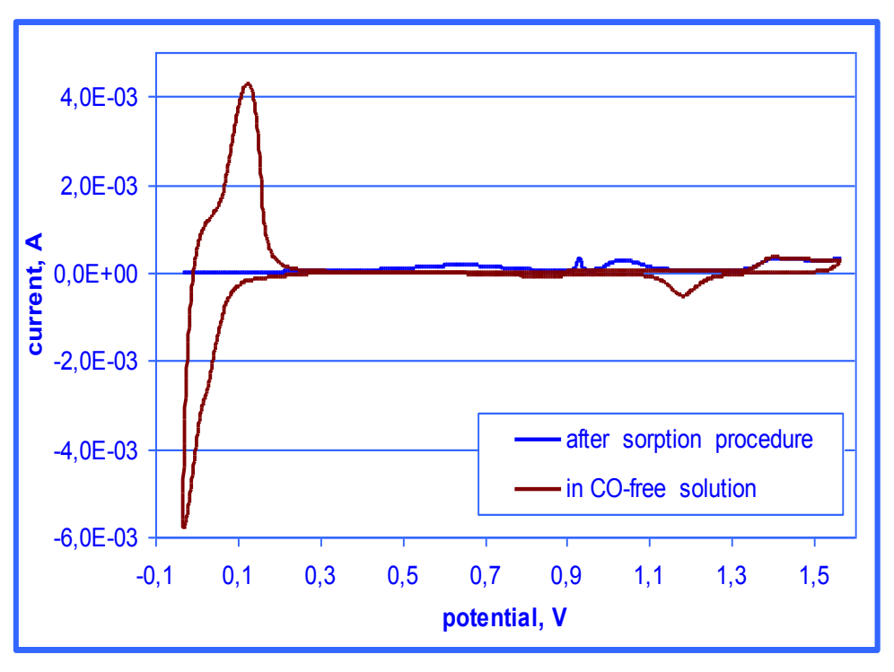

Fig. 8a. Voltammograms for Pd-Au alloy (rich in gold on the surface); scan rate 0,01 V/s.
Sorption procedure: 600 s - CO adsorption at 0,415 V;
300 s - CO removal with Ar; 300 s - hydrogen absorption at -0,035 V.

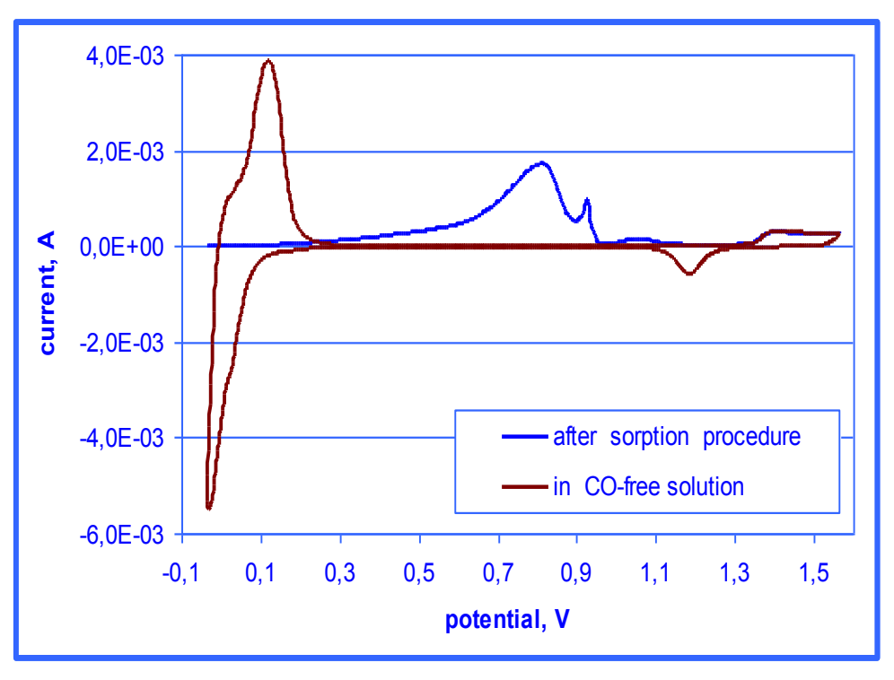

Fig. 8b. Voltammograms for Pd-Au alloy (rich in gold on the surface); scan rate 0,01 V/s.
Sorption procedure: 300 s - hydrogen absorption at -0,035 V;
600 s - CO adsorption at -0,035 V; 300 s - CO removal with Ar.

6. Influence of hydrogen sorption on electrochemical properties of surface oxides

We have observed that after electrode polarization into the hydrogen region, surface oxides are formed and reduced at potentials lower than before applying the hydrogen sorption procedure (***Fig. 9***). It indicates that surface oxides become electrochemically more stable. The shift of oxide reduction peaks into cathodic direction exceeded 100 mV in some cases. This effect probably results from changes of electrode surface properties caused by hydrogen penetration into alloy lattice. SEM images taken after hydrogen absorption/desorption show that there are a lot of cracks on the alloy surface (***Fig. 10***).

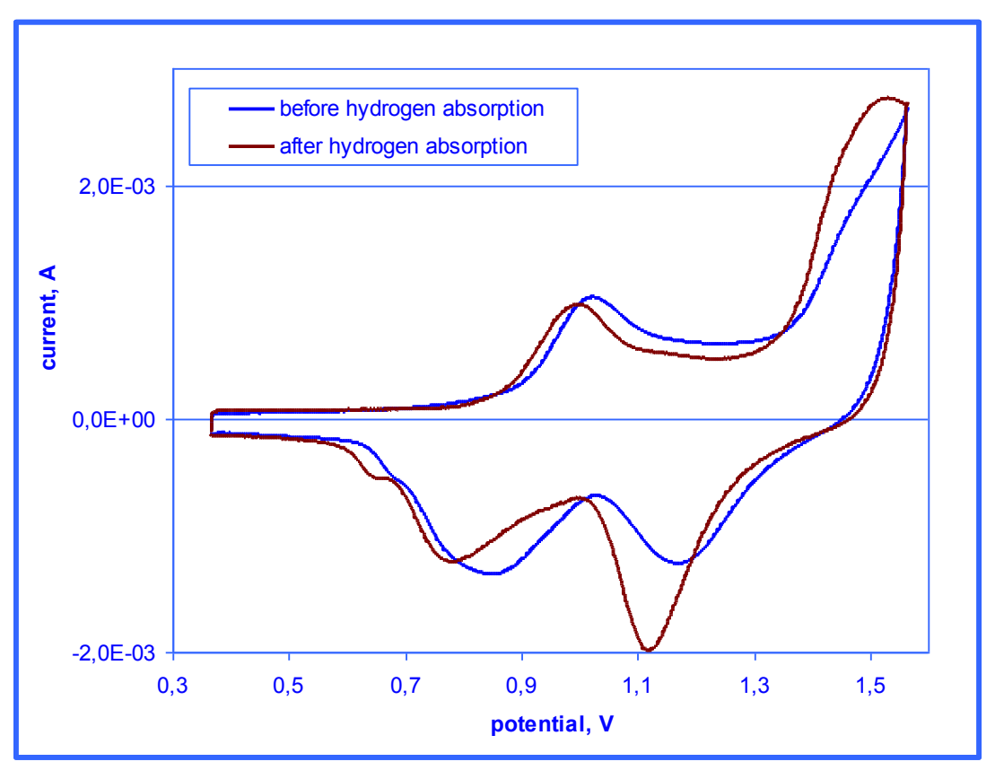

Fig. 9. Influence of hydrogen absorption/desorption experiments on the shape of voltammogram of Pd-Au alloy; scan rate 0,1 V/s.

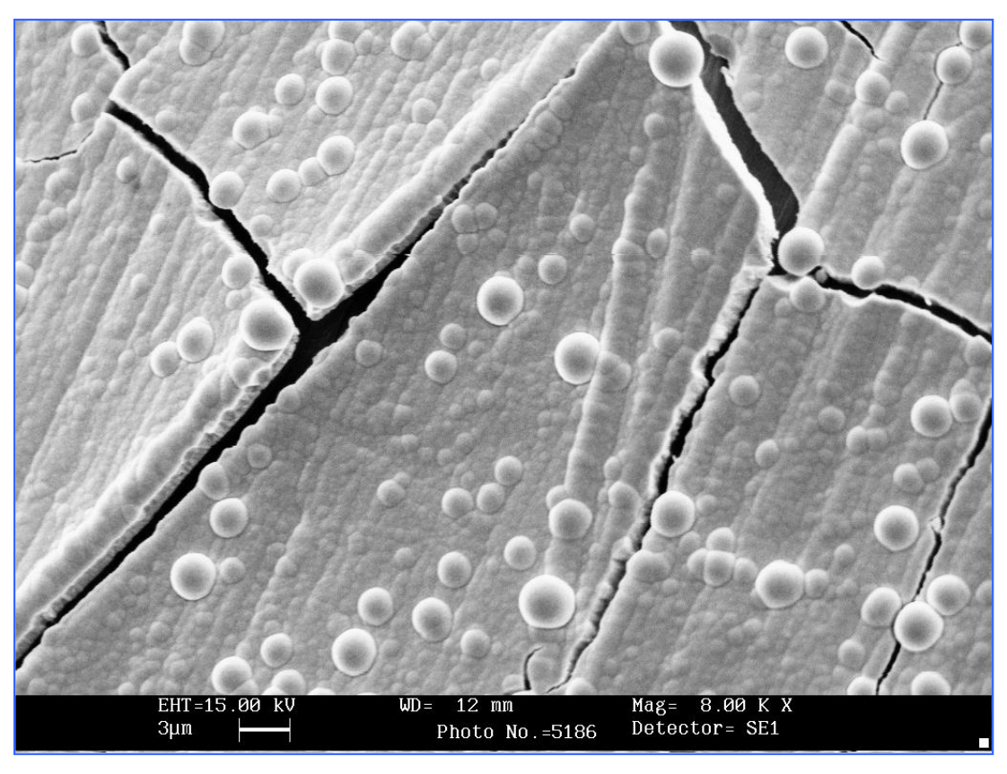

Fig. 10. SEM image of Pd-Au alloy surface taken after hydrogen absorption/desorption procedure.

SUMMARY

1. The maximum H/(Pd+Au) ratios decrease monotonically with increasing gold content and reach zero when it exceeds *ca.* 70 % at.
2. Two peaks in the hydrogen region, corresponding to two types of sorbed hydrogen, are observed on the voltammograms for alloys containing more than *ca.* 65 % at. Pd.
3. The hydrogen capacity, H/(Pd+Au), measured electrochemically, depends on the scan rate in the cyclic voltammetry experiments, which suggests that two different mechanisms of hydrogen desorption from the Pd-Au alloy (electrochemical oxidation and non-electrochemical recombination reaction) are possible.
4. In the case of Pd-rich alloys (above 60 % at. Pd) the amount of absorbed hydrogen remains significant after the strong depletion of palladium from the surface caused by long cyclic polarization to sufficiently anodic potentials.
5. Adsorbed CO inhibits the hydrogen absorption and desorption processes into/from the Pd-Au electrode. A "trapping" effect of hydrogen absorbed in the electrode by adsorbed CO is also observed. The obtained results indicate that gold atoms are inactive in the hydrogen absorption/desorption process.
6. Applying the hydrogen sorption procedure increases the electrochemical stability of surface oxides, which is reflected in the shift of oxide reduction peaks into lower potentials.