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Electrosorption of hydrogen into palladium-gold alloys

Abstract Hydrogen electrosorption into Pd-Au alloys has been studied in acidic solutions (1 M H_2SO_4) using cyclic voltammetry. Pd-Au electrodes with limited volume were prepared by electrochemical co-deposition. It was found that the maximum $H/(Pd+Au)$ ratios decrease monotonically with increasing gold content and reach zero at ca. 70 at% Au. Similarly to the case of Pd limited volume electrodes, two peaks in the hydrogen region, corresponding to two types of sorbed hydrogen, are observed on voltammograms for Pd-rich alloys. The hydrogen capacity, $H/(Pd+Au)$, measured electrochemically, depends on the sweep rate in the cyclic voltammetry experiments, which suggests that two different mechanisms for hydrogen desorption from the Pd-Au alloy are possible. After a strong decrease of Pd concentration at the electrode surface, caused by long cyclic polarization to sufficiently anodic potentials, the amount of absorbed hydrogen is still significant for alloys initially rich in Pd. The results obtained from CO adsorption experiments suggest that only Pd atoms are active in the hydrogen absorption/desorption process.

Keywords Palladium-gold alloys · Hydrogen sorption · Carbon monoxide adsorption · Limited volume electrodes

Introduction

The electrochemical properties of noble metals and their alloys are still at the center of modern research, mainly

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due to a constant search for new materials for electrocatalysis, electrosynthesis and, in particular, for fuel cell applications. Palladium and palladium alloys have been studied extensively also because of their high ability to absorb hydrogen [1]. Together with other metals capable of forming hydrides, they are of special interest owing to the possibility of their application as hydrogen storage materials, e.g. in rechargeable Ni-MH batteries [2]. Palladium-hydrogen and palladium alloy-hydrogen systems can be treated as model systems and the knowledge of their electrochemical behavior allows us to understand better the hydrogen sorption/desorption processes occurring at the electrodes of this type.

Palladium and gold form a continuous series of f.c.c. solid solutions, homogeneous at normal conditions, with the lattice parameter varying almost linearly with the alloy composition [3, 4]. Although hydrogen absorption into Pd-Au alloys (performed from the gas phase or electrochemically) has been the subject of many investigations, electrochemical aspects of this process are still not well known.

According to the data reported in the literature [5, 6, 7, 8, 9], the ability to absorb hydrogen ceases when the gold content in Pd-Au alloys reaches 60–75 at%. Most results indicate that the hydrogen capacity decreases monotonically with increasing gold content. However, there were some reports about a maximum existing on the $H/(Pd+Au)$ vs. %Au dependence. There is also controversy about the amount of gold above which a second phase in Pd-Au-H ternary system is no longer formed [7, 10, 11, 12].

The results obtained in our laboratory [13, 14, 15] using palladium limited volume electrodes (Pd-LVEs) have clearly demonstrated that two mechanisms are involved in the hydrogen desorption process from palladium during anodic polarization, namely electrochemical oxidation and a non-electrochemical recombination reaction. The presence of subsurface hydrogen was also proven. Investigations are needed in order to establish whether similar phenomena occur at palladium-based alloys or whether they are unique features of the palladium electrode.

Experimental

All the experiments were performed at room temperature in 1 M H_2SO_4 solutions prepared from triply distilled water and analytical grade reagents. The solutions were deoxygenated with an argon stream for 25 min. A platinum gauze and $Hg|Hg_2SO_4|1$ M H_2SO_4 were used as the auxiliary and the reference electrodes, respectively. All potentials in the text and on the figures are referred to the RHE.

Pd-Au alloys with limited volume were deposited potentiostatically on a gold wire (0.5 mm diameter) from a bath containing $PdCl_2$ and $HAuCl_4$ in 1 M HCl, according to the method described by Woods [8]. The composition of the alloys was altered by employing different electrolyte compositions and deposition potentials. The thickness of the obtained electrodes was in the range 1.5–3.0 μm. This approach allowed the amount of absorbed hydrogen to be small as well as hydrogen oxidation peaks to be separated from the currents of various surface processes. LVEs have already been used for studying hydrogen electrosorption in palladium [13, 14, 15, 16, 17, 18, 19] and some palladium alloys, e.g. Pd-Ni [20] and Pd-Pt [21]. The bulk composition of the Pd-Au alloys was obtained from EDAX analysis (Rontec M1 analyzer coupled with a LEO 435VP scanning electron microscope). All alloy compositions are expressed in atomic percentages.

The roughness factor, as estimated from the double layer capacity and surface oxide reduction charge measurements, was in the range 100–500. The values of the double layer capacity were determined according to the method described in the literature (see e.g. [22, 23]). Voltammograms were recorded at various scan rates in the potential region which is free from faradaic processes (0.365–0.665 V). The values of the double layer charging current for 0.575 V were then plotted against the scan rate and the double layer capacity was determined from the slope of the linear dependence obtained. To determine the value of the capacity of 1 cm^2, necessary for the real surface area calculations, separate experiments were carried out for pure alloy components, i.e. palladium and gold, under identical experimental conditions (solution, temperature) as in the case of Pd-Au electrodes. Double layer capacity values were determined for Pd and Au electrodes using the method described above and their real surface areas were obtained from the charges of the surface oxide reduction, which is a well-established and generally accepted method [24]. A value 44.5 μF cm^{-2}, which was found for both Pd and Au, was then used to calculate the real surface area of the Pd-Au alloys. The method based on surface oxide reduction charge m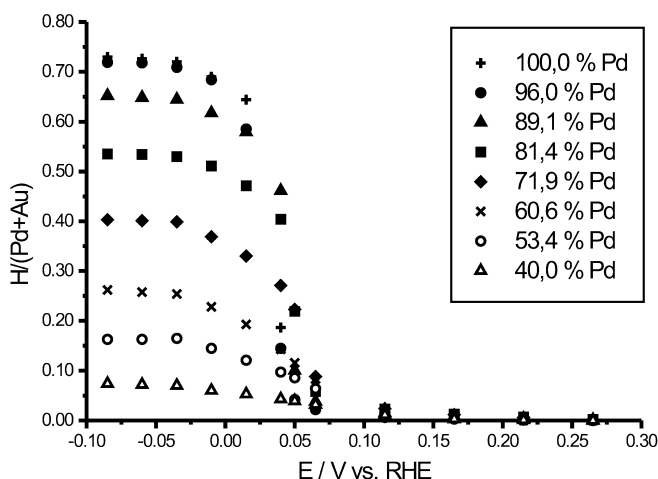easurements was also used independently to estimate the real surface area values of the alloys studied, although it seems less reliable than for pure noble metals. The differences between real surface areas obtained using both methods were within 30%.

At the beginning of each experiment the electrodeposited alloy electrode was cycled continuously in the potential range from –0.035 V to 0.665 V at 0.01 V/s until a steady state voltammogram was obtained. Then, the hydrogen sorption was performed by the electrode polarizing to a potential in the range 0.265 to –0.085 V. It was found that 300 s was a sufficient time for saturation of all the electrodes used. The amount of absorbed hydrogen was calculated from the charge obtained by integration of the anodic peak currents of a cyclic voltammogram taken after the saturation procedure.

Results and discussion

Figure 1 presents the dependence of the electrochemically measured hydrogen absorption capacity, expressed as the H/(Pd + Au) ratio, on the absorption potential for Pd-Au alloys of various compositions. In general, the

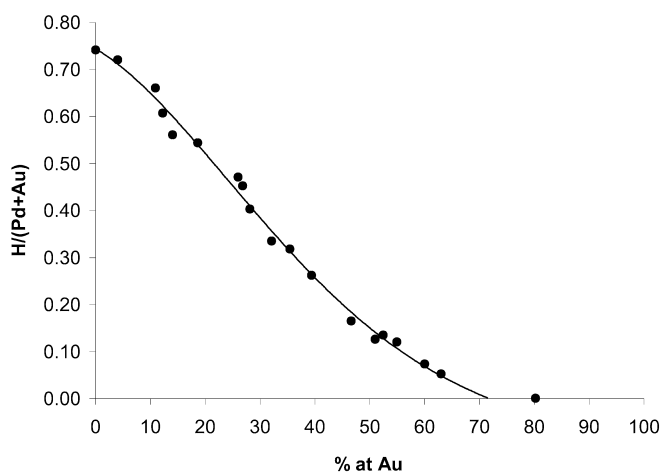**Fig. 2** Influence of bulk gold content on maximum H/(Pd + Au) ratios. Time of hydrogen absorption, 300 s; scan rate during hydrogen electrooxidation, 0.01 V/s; 1 M H_2SO_4 solution

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; 1 M H_2SO_4 solution
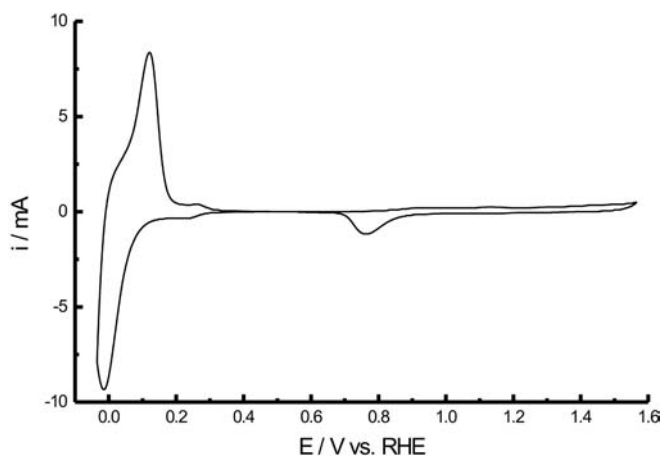

Fig. 3 Voltammogram of the 74.0% Pd-Au alloy in 1 M H_2SO_4; scan rate, 0.01 V/s
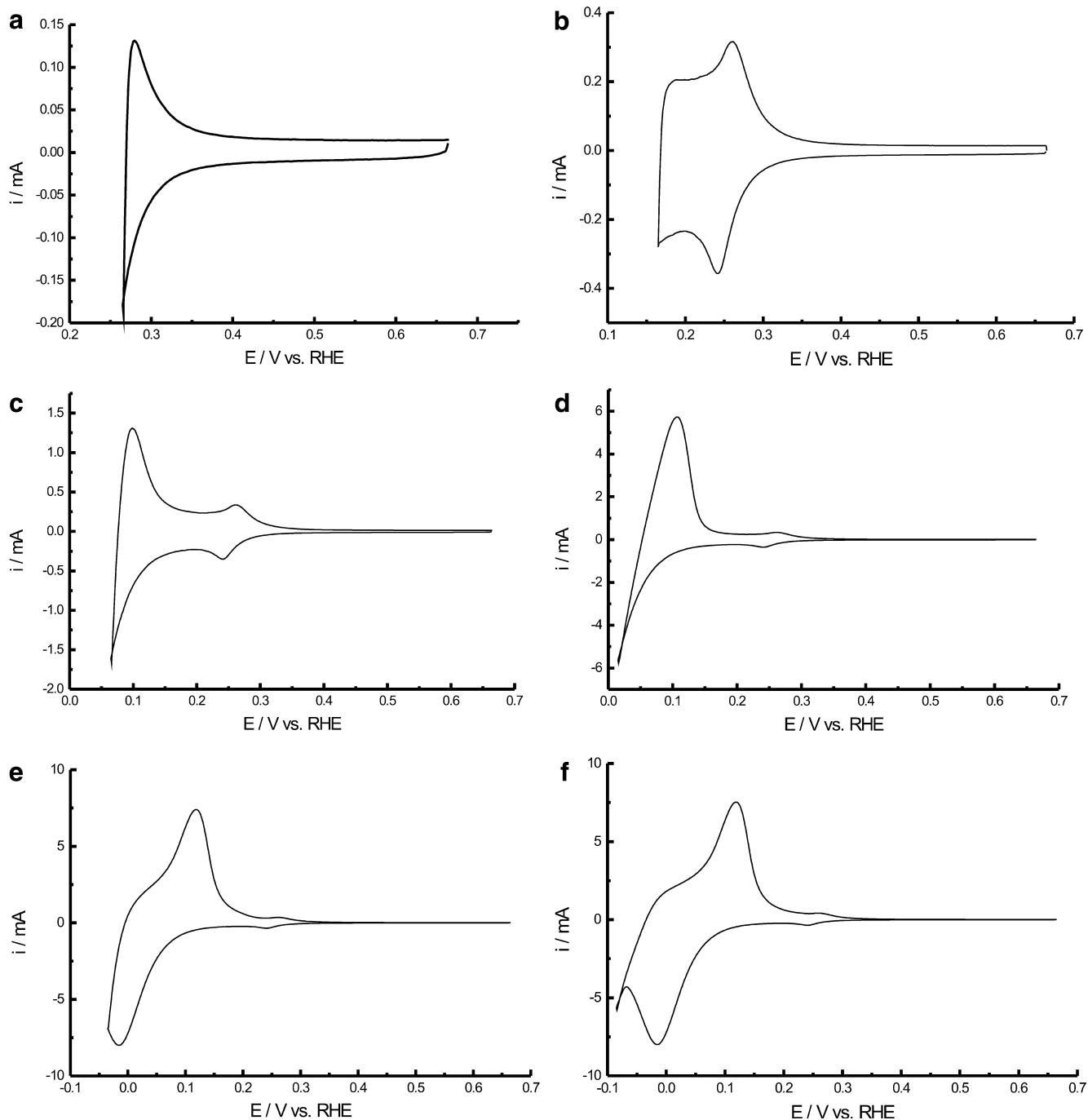
Fig. 4a–f Voltammograms of the 72.3% Pd-Au electrode, recorded in the hydrogen region to various cathodic vertex potentials; 1 M H_2SO_4; scan rate, 0.01 V/s

potential range of hydrogen sorption is similar to the case of pure palladium [16, 17]. For Pd-rich alloys the curves have a characteristic shape with a sharp increase in the amount of sorbed hydrogen between 0.050 V and 0.015 V, which corresponds to the $\alpha \rightarrow \beta$ transition. The plateau is shifted slightly in the positive direction as the amount of gold increases. This is probably the effect of increasing the lattice parameter in the Pd-Au alloys with

respect to palladium [25]. With a further increase of the gold content the plateau becomes less and less pronounced, which suggests that the second phase is no longer formed (below ca. 70 at% Pd).

Figure 2 shows the influence of the alloy composition on the maximum H/(Pd + Au) ratios. This is a monotonic dependence and alloys containing more than ca. 70 at% gold do not absorb hydrogen.

A typical i vs. E curve for a Pd-rich alloy (74.0 at% Pd) electrode in the full range of potentials is presented in Fig. 3. One can distinguish hydrogen sorption/desorption signals as well as surface oxidation/oxide
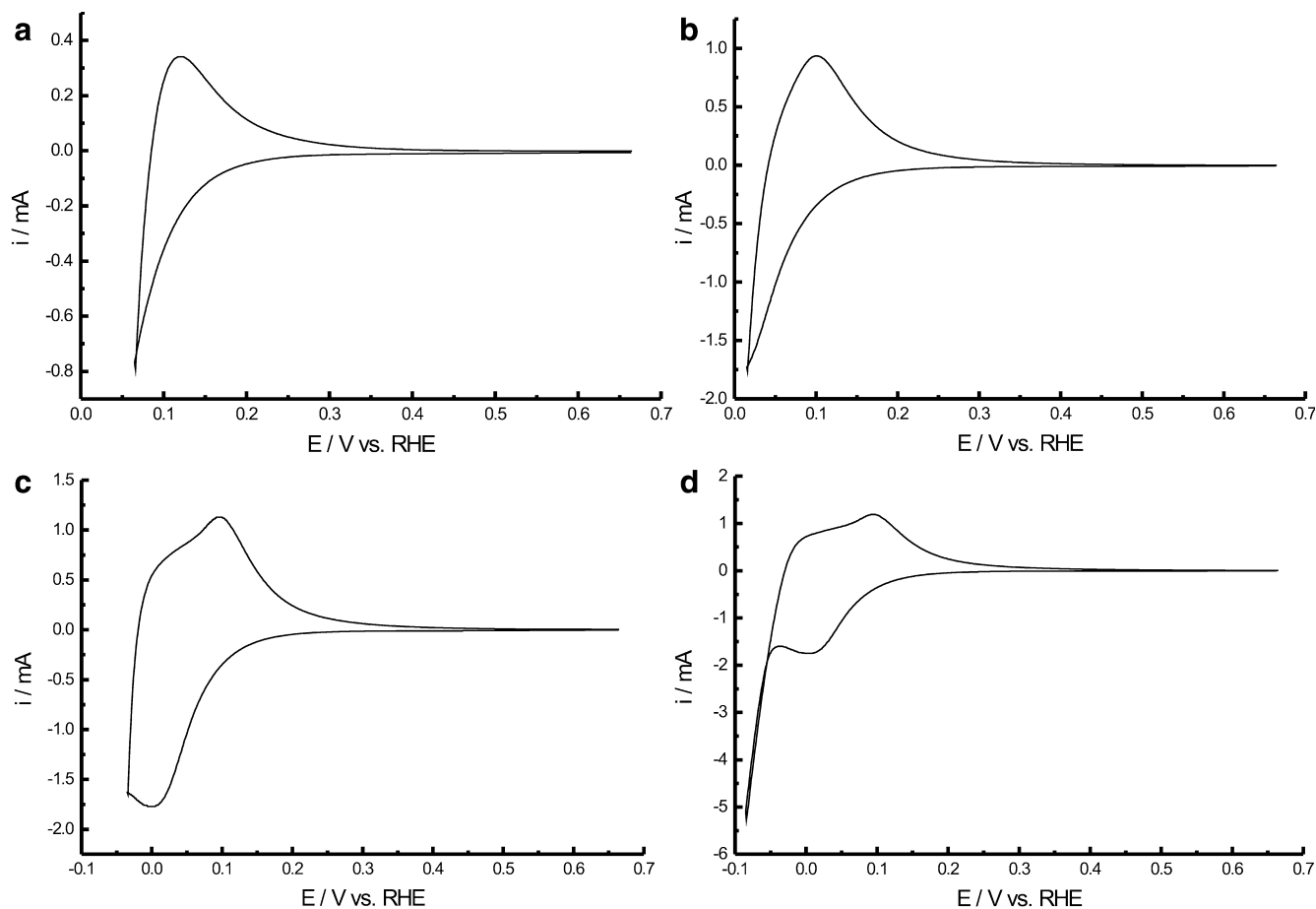
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Fig. 5a–d Voltammograms of the 53.4% Pd-Au electrode, recorded in the hydrogen region to vertex potentials; 1 M H_2SO_4; scan rate, 0.01 V/s

reduction currents. Voltammograms recorded in the hydrogen region to various cathodic vertex potentials are shown in Fig. 4. Their shapes, with two waves present, are very similar to the *i-E* curves characteristic of Pd-LVEs [16, 17, 26]. Analogously to palladium, the
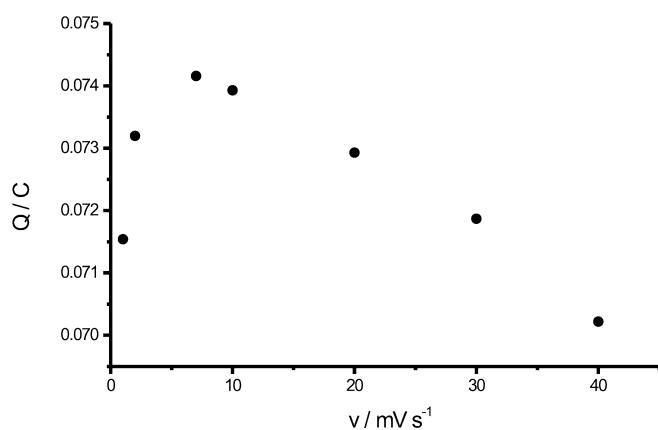
larger peak can be attributed to hydrogen mainly absorbed as the β-phase, and the smaller peak results from hydrogen absorbed as the α-phase and partly from the adsorbed hydrogen. This smaller peak did not appear on voltammograms for electrodes containing less than 65 at% Pd (Fig. 5). At sufficiently cathodic potentials, a current due to the hydrogen evolution reaction is

Fig. 6 Dependence of hydrogen oxidation charge on sweep rate for the 79.3% Pd-Au alloy in 1 M H_2SO_4 solution. Potential of hydrogen absorption, –0.035 V; absorption time, 300 s; alloy layer thickness, 2.9 μm
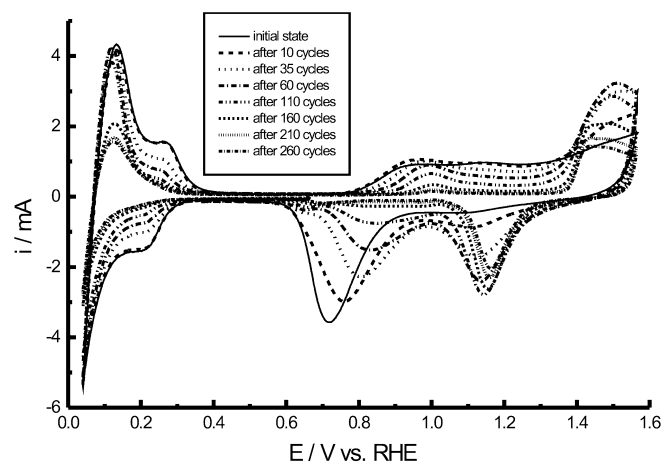

Fig. 7 Voltammograms of the Pd-Au electrode (1 M H_2SO_4; 0.05 V/s) recorded after successive cycling in the potential range from 0.365 to 1.565 V at sweep rate 0.1 V/s. Initial bulk palladium content, 73.2%
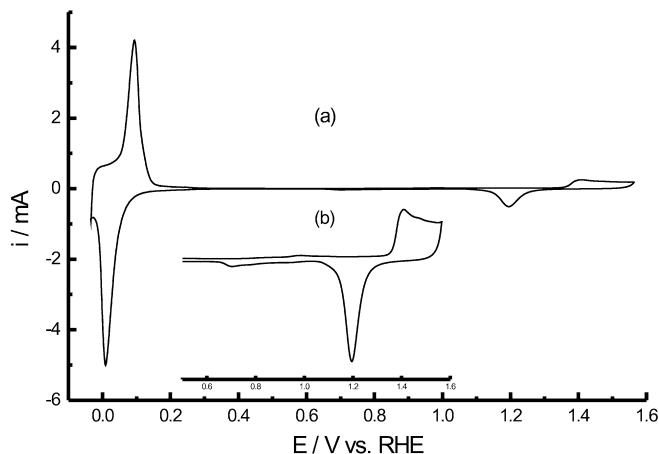
Fig. 8 Voltammogram of the Pd-Au electrode (1 M H$_2$SO$_4$; 0.01 V/s), impoverished in palladium after long cycling to anodic potentials (*a*). The region of oxygen adsorption/desorption is shown separately (*b*)

observed. In the case of the alloys not absorbing hydrogen, the hydrogen evolution current was the only signal recorded in this potential region. It should be noted that for the alloys incapable of absorbing hydrogen the oxidation current in the anodic scan was negligible. This indicates that the contribution of molecular hydrogen ionization to the hydrogen oxidation peaks should not be significant. As was stated for palladium [14, 27], the amount of sorbed hydrogen, calculated electrochemically, is not influenced by gas evolution.

The amount of hydrogen absorbed into Pd-Au alloys, calculated from the charge of the hydrogen oxidation peaks (it is, actually, the amount of hydrogen leaving the electrode through reactions involving a charge transfer process), has been found to be dependent on the sweep rate in the cyclic voltammetry experiments. This fact is illustrated in Fig. 6. A maximum of the hydrogen oxidation charge is visible at sweep rates of 5–10 mV/s.

A similar dependence was reported for Pd-LVEs [14, 15]. This effect could be observed only in the case of thin layers of palladium. When the thickness of the metal deposited increases, the hydrogen absorption properties of the system change towards those typical of bulk palladium electrodes (i.e. wires or foils), where the H/Pd ratios obtained in electrochemical experiments agree with the values found for absorption from the gas phase [28].

The behavior observed for Pd-Au alloys may be explained in the manner previously proposed for Pd-LVEs [14, 15], i.e. assuming that the absorbed hydrogen (H$_{abs}$) removal from the Pd-Au alloy follows two pathways:

1. Electrochemical oxidation: H$_{abs}$→H$_{ads}$→H$^+$ + e$^-$
2. A non-electrochemical recombination process: 2H$_{abs}$→2H$_{ads}$→H$_2$

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

As reported in the literature [8, 24, 29, 30, 31, 32, 33], the *i-E* curves for the Pd-Au alloys change significantly

during continuous potential cycling in the oxygen region in acid media owing to the selective dissolution of palladium. The evolution of the voltammograms reflects mainly the changes of electrosorption properties of the electrode surface towards oxygen adsorption. The alloy surface becomes enriched with gold, which results in a decrease of the oxide reduction peak and its shift into the anodic direction, along with a growth of a second cathodic peak in the position typical of the pure gold electrode. Thereby the alloy surface becomes heterogeneous [24]. In the hydrogen region the evolution of the voltammograms does not proceed as rapidly as in the oxygen region and during initial potential cycles the changes are less dramatic [8], as is easily seen in Fig. 7, presenting *i-E* curves recorded in the full potential range for an alloy subjected to this kind of electrochemical treatment.

At the beginning, only the smaller hydrogen peak diminishes and disappears but the second peak remains almost undisturbed even after a large number of cycles. (Earlier investigations of Pd-LVEs [15, 26] have shown that the first hydrogen peak is very sensitive to every change of the electrode surface.) However, the main peak finally starts to decrease but the amount of absorbed hydrogen is still significant, although the voltammogram shape in the oxygen region indicates a high surface concentration of gold (Fig. 8).

Such a behavior was observed in the case of alloys initially relatively rich in palladium (above 60 at% Pd). Alloys with a smaller palladium content, whose ability for hydrogen sorption is generally weaker, demonstrated higher sensitivity to potential cycling and their absorption capacities decreased rapidly (Fig. 9). According to the explanation given by Woods [8], palladium is preferentially removed from the surface, at least during a certain number of initial potential cycles; hence for Pd-rich alloys the bulk composition might remain unaltered for quite a long experimental time.

Since the hydrogen electrosorption process occurring on platinum metals is known to be easily influenced by the presence of impurities on the electrode surface, one can expect the investigations of carbon monoxide adsorption (one of the strongest poisons of the solid electrodes) to lead to a better understanding of the hydrogen absorption/desorption reaction on palladium alloys. In the case of palladium, recent studies [13, 26, 34] have shown that adsorbed CO inhibits the hydrogen absorption and desorption processes and a "trapping" effect of hydrogen absorbed in the electrode has been observed.

The procedure of surface poisoning using CO has been applied to a Pd-Au alloy electrode, impoverished in palladium in the manner described above. Figure 10 a presents the voltammogram obtained in an experiment where, after CO adsorption at 0.415 V (no hydrogen sorption takes place there), followed by the removal of CO from solution with argon, the hydrogen absorption was performed at –0.035 V. The *i-E* curve was then recorded. It shows that only a small amount of hydrogen
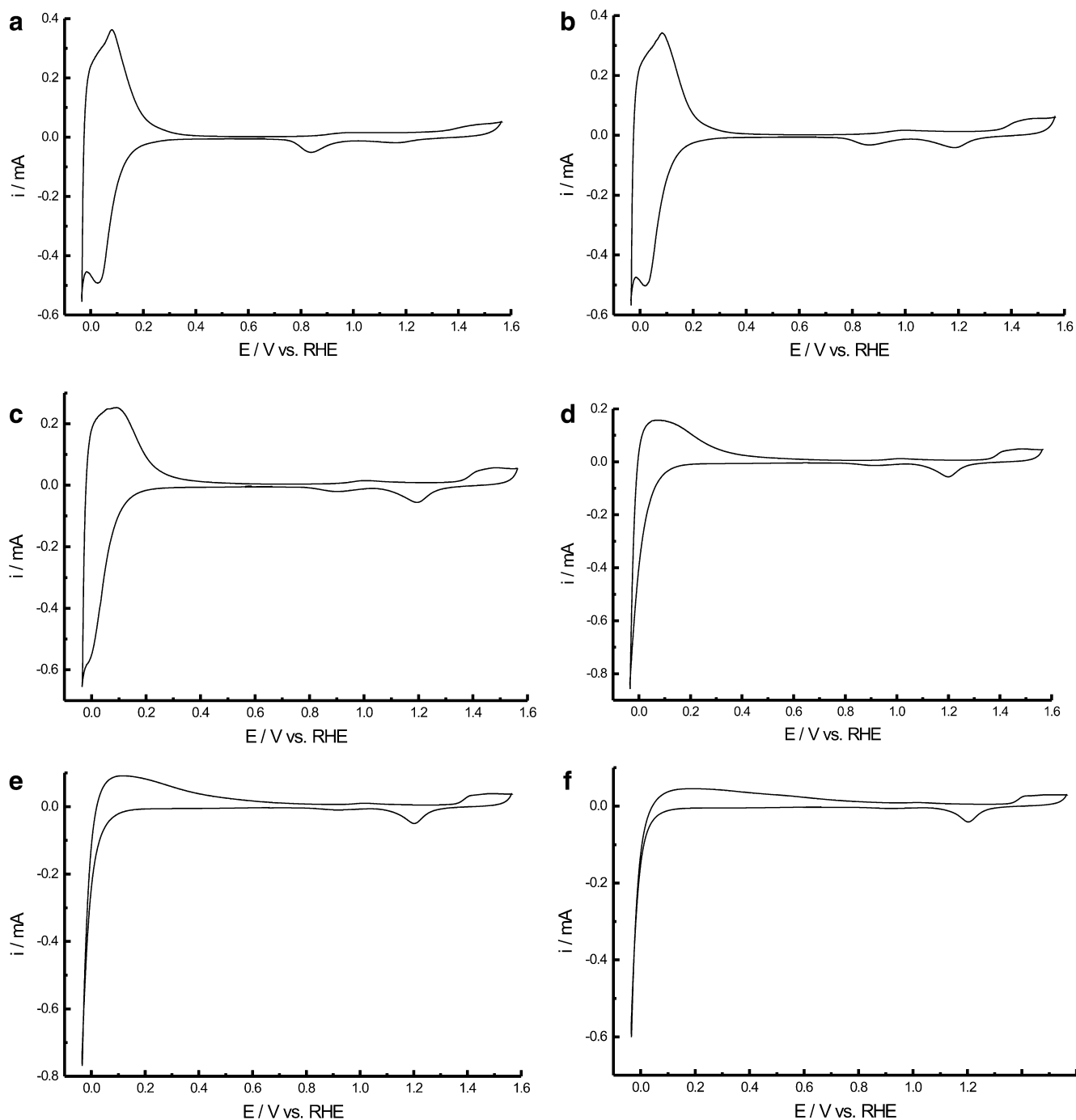
Fig. 9a–f Voltammograms of the Pd-Au electrode (1 M H$_2$SO$_4$; 0.01 V/s) recorded after successive cycling in the potential range from 0.365 to 1.565 V at sweep rate 0.5 V/s. Initial bulk palladium content 49.0%. **a** Initial state. **b–f** After 25, 75, 175, 325 and 575 cycles, respectively

is absorbed under these conditions and its oxidation is much more difficult than in the absence of CO. This fact is reflected in the appearance of the anodic hydrogen signal, which is diminished, flattened and shifted to positive potentials (a small wave at ca. 0.65 V). In a second experiment the same electrode was first kept at –0.035 V in the CO-free solution and then the solution was saturated with CO. This procedure allowed hydrogen to be absorbed into the alloy before surface poisoning by the CO adsorption products. The voltammogram obtained after stripping of the CO is presented in Fig. 10b. It shows a large wave strongly shifted to positive potentials (ca. 0.8 V), corresponding to oxidation of the hydrogen trapped inside the electrode by adsorbed CO. The amount of hydrogen is close to that absorbed without CO in solution. One should note a sharp peak overlapping with the descending part of the hydrogen wave. This peak, although smaller, appears at
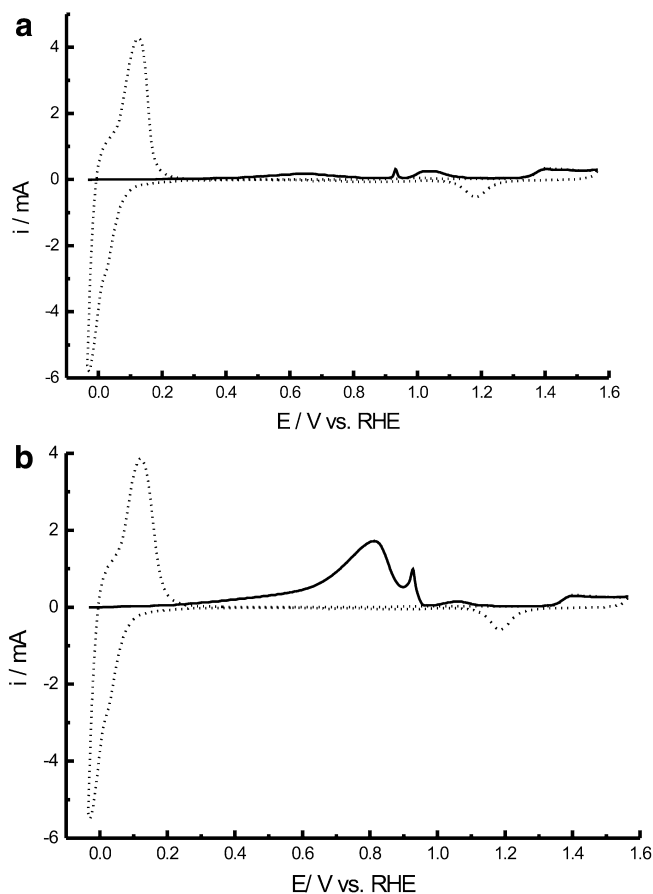
Fig. 10 a Voltammograms for the Pd-Au electrode (with high gold surface concentration) in 1 M H$_2$SO$_4$; sweep rate, 0.01 V/s. Sorption procedure: 600 s CO adsorption at 0.415 V; 300 s CO removal with Ar; 300 s hydrogen absorption at –0.035 V. *Full curve*: first anodic segment recorded after sorption procedure; *dashed curve*: next two segments. **b** Voltammograms for the Pd-Au electrode (with high gold surface concentration) in 1 M H$_2$SO$_4$; sweep 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. *Full curve*: first anodic segment recorded after sorption procedure; *dashed curve*: next two segments

absorbed. The fact that not all the palladium atoms are covered with the adsorbed CO could explain this observation. However, at this stage, one cannot exclude the possibility that a simultaneous mechanism for direct hydrogen absorption/desorption, not involving an adsorption step, is also operative.

It should be noted that CO effects are surface effects concerning the kinetics of hydrogen sorption. Adsorbed CO decreases sharply the rate of H-atom transfer into the subsurface layer. Since the electrodes investigated were rather thick, their bulk sorption properties could not be changed during CO adsorption experiments.

Conclusions

The following conclusions may be drawn:

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 sweep rate in the cyclic voltammetry experiments, which suggests that two different mechanisms of hydrogen desorption from the Pd-Au alloy (electrochemical oxidation and a 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.

the same potential (ca. 0.925 V) also on the voltammogram recorded in the previous experiment. It has not been observed for the pure palladium electrode [13, 26, 34]. From these preliminary results it is difficult to state whether the peak is due to the oxidation of one of the adsorbed CO forms or to the oxidation of the product of a reaction between adsorbed CO and hydrogen. Nevertheless, general conclusions in view of the data presented in Fig. 10a and b are as follows. First, a blocking effect of absorbed hydrogen by adsorbed CO is evident. It indicates that carbon monoxide and hydrogen compete for the same surface adsorption sites, i.e. palladium atoms, because CO adsorption on gold is negligible [35]. The situation seems to be similar to the case of Pd-Pt alloys, where only Pd atoms are active in the hydrogen absorption/desorption process [21]. Second, despite the saturation of the electrode surface with CO adsorption products, a certain amount of hydrogen can still be

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