

# ELECTROSORPTION OF HYDROGEN INTO PALLADIUM-RHODIUM ALLOYS

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## INTRODUCTION

Hydrogen absorption in Pd and its alloys has been studied for more than 100 years in both fundamental and application aspects. Among the systems examined, the Pd-Rh system is of special interest owing to their increased hydrogen absorption capacity (higher than for pure Pd) in the  $\beta$ -phase observed for alloys containing several percent of Rh. The Pd-Rh system is an exception to the general rule that Pd alloying with a non-absorbing element results in a decrease in the amount of absorbed hydrogen.

In this work we studied hydrogen electro sorption in thin (0.50 – 0.85  $\mu\text{m}$ ) Pd-Rh alloy layers electrodeposited on Au wires at a constant potential from a bath containing  $\text{PdCl}_2$ ,  $\text{RhCl}_3$  and HCl. All experiments were performed at room temperature in 0.5 M  $\text{H}_2\text{SO}_4$  solutions deoxygenated using an Ar stream. All potentials are recalculated with respect to the SHE. All alloy compositions given in this work are bulk compositions expressed in atomic percentages, determined by EDAX and AAS methods.

## RESULTS AND DISCUSSION

On cyclic voltammograms recorded after hydrogen electro sorption (Fig. 1) two signals are observed. Peak (a), placed at lower potentials, can be attributed to the oxidation of mainly hydrogen absorbed as the  $\beta$ -phase. Signal (b), placed at higher potentials, is mainly due to oxidation of adsorbed hydrogen but includes also current due to oxidation of hydrogen absorbed as the  $\alpha$ -phase. By the integration of hydrogen oxidation currents the amount of hydrogen electro sorbed at various potentials could be obtained (Fig. 2). On  $\text{H}/(\text{Pd}+\text{Rh})$ -E plot one can distinguish the potential regions of  $\alpha$  and  $\beta$  phase existence as well as the  $\alpha$ - $\beta$  transition region. It has been found that the potential of the phase transition decreases linearly with the increase in bulk Rh content.

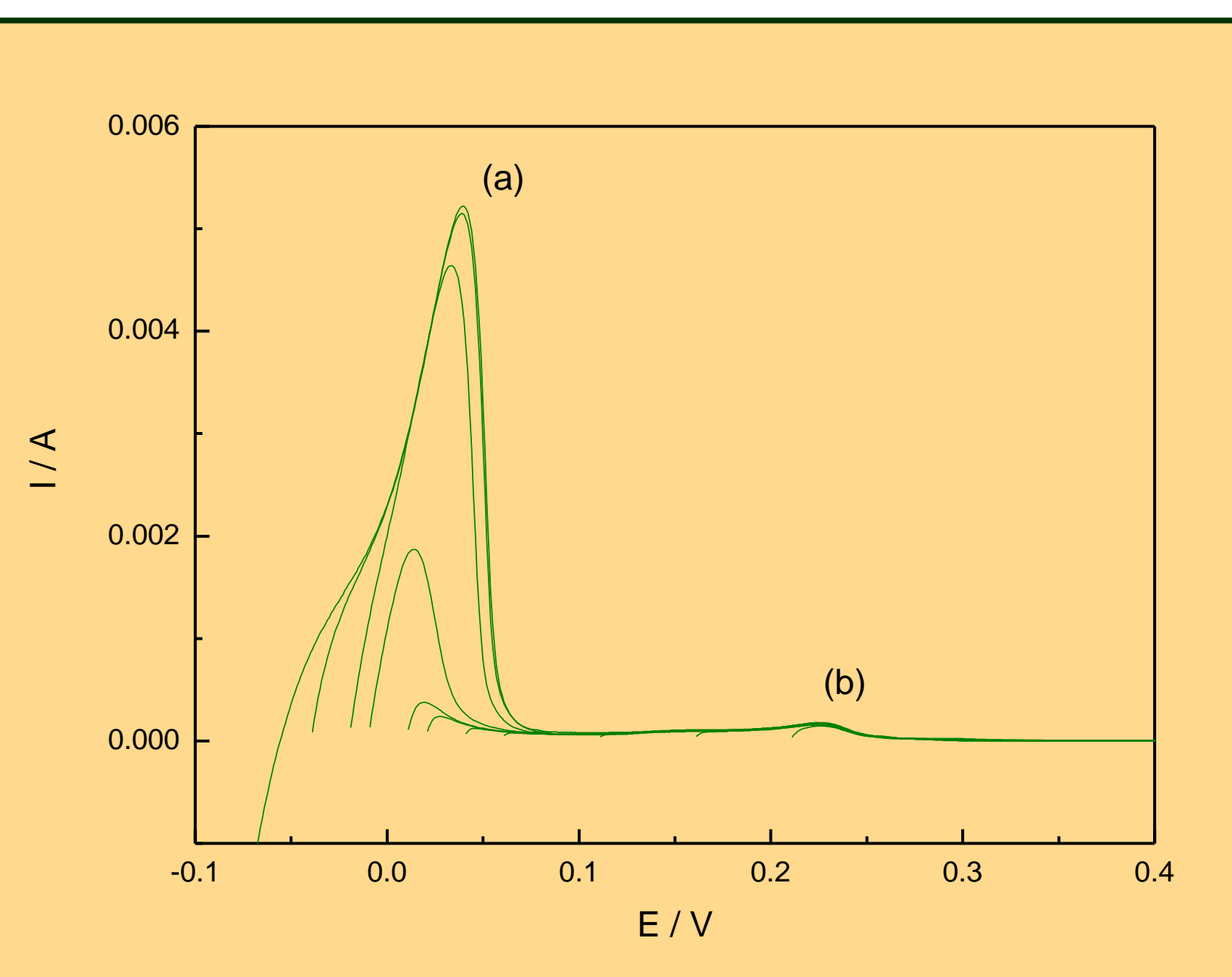


Fig. 1. Hydrogen oxidation currents recorded after hydrogen electro sorption at various potentials in a Pd-Rh alloy (85.6% Pd); scan rate 0.01 V/s.

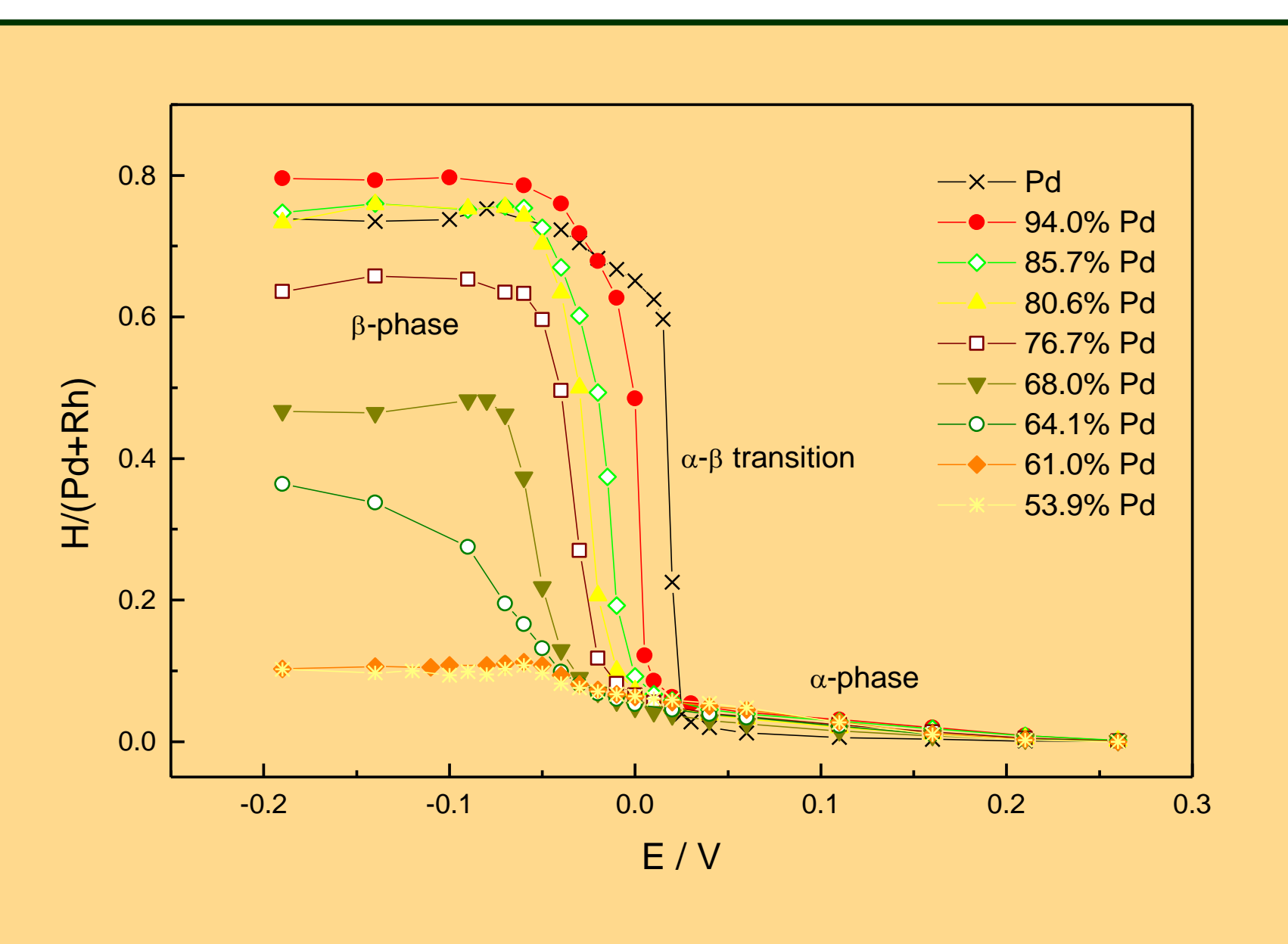


Fig. 2. Hydrogen absorption capacities versus potential for Pd and Pd-Rh alloys of different bulk compositions.

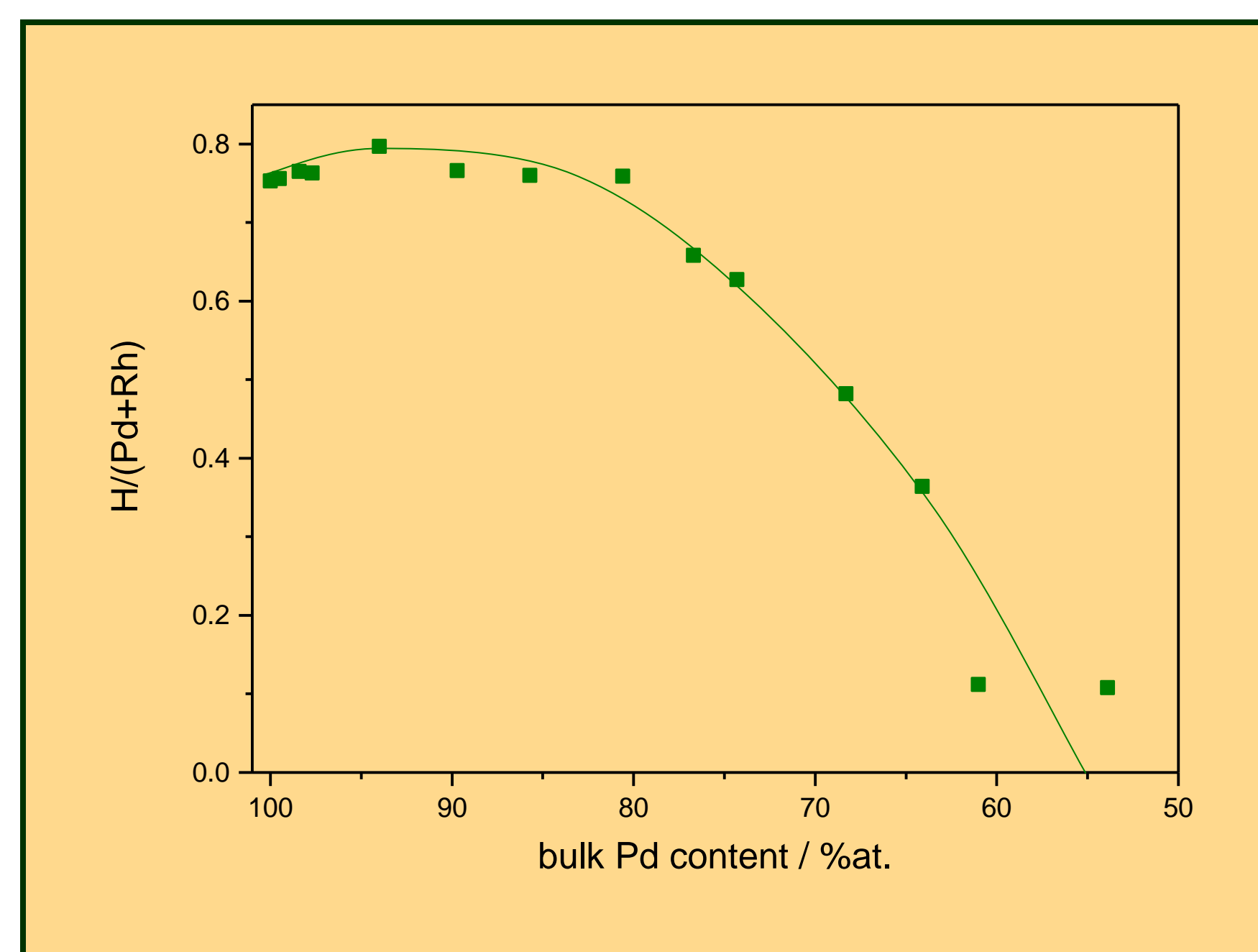


Fig. 3. Maximum hydrogen absorption capacities versus bulk Pd content in Pd-Rh alloys.

Fig. 3 shows the influence of the alloy bulk composition on the maximum  $\text{H}/(\text{Pd}+\text{Rh})$  ratios. For alloys containing more than 80 % Pd in the bulk the amount of electro sorbed hydrogen is higher than in Pd. The highest hydrogen absorption capacity,  $\text{H}/(\text{Pd}+\text{Rh}) = 0.80$ , is exhibited by an alloy containing 94% Pd. For bulk Pd content below 80% a gradual decrease in the amount of electro sorbed hydrogen is observed and alloys containing less than ca. 60 % Pd can only adsorb hydrogen.

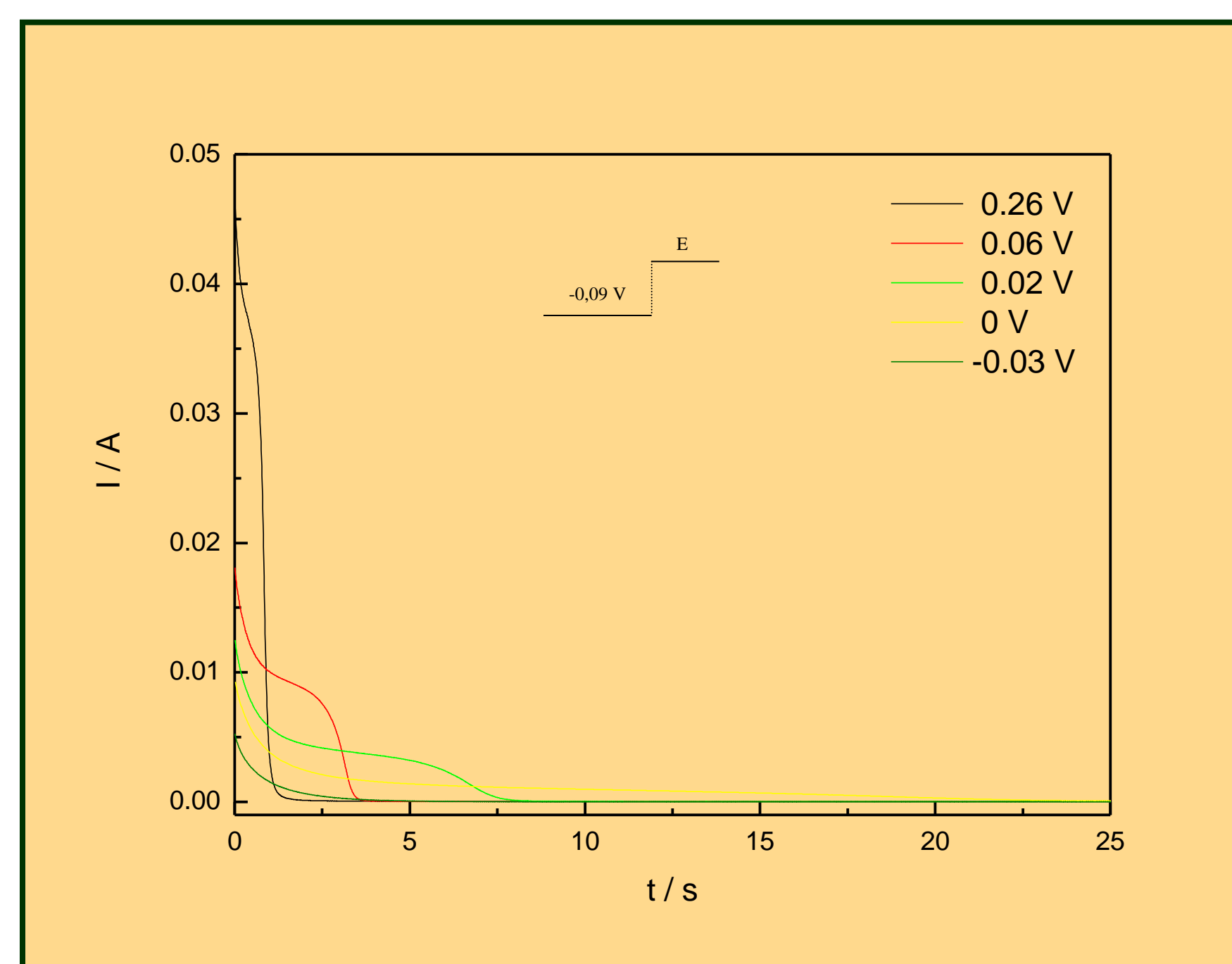
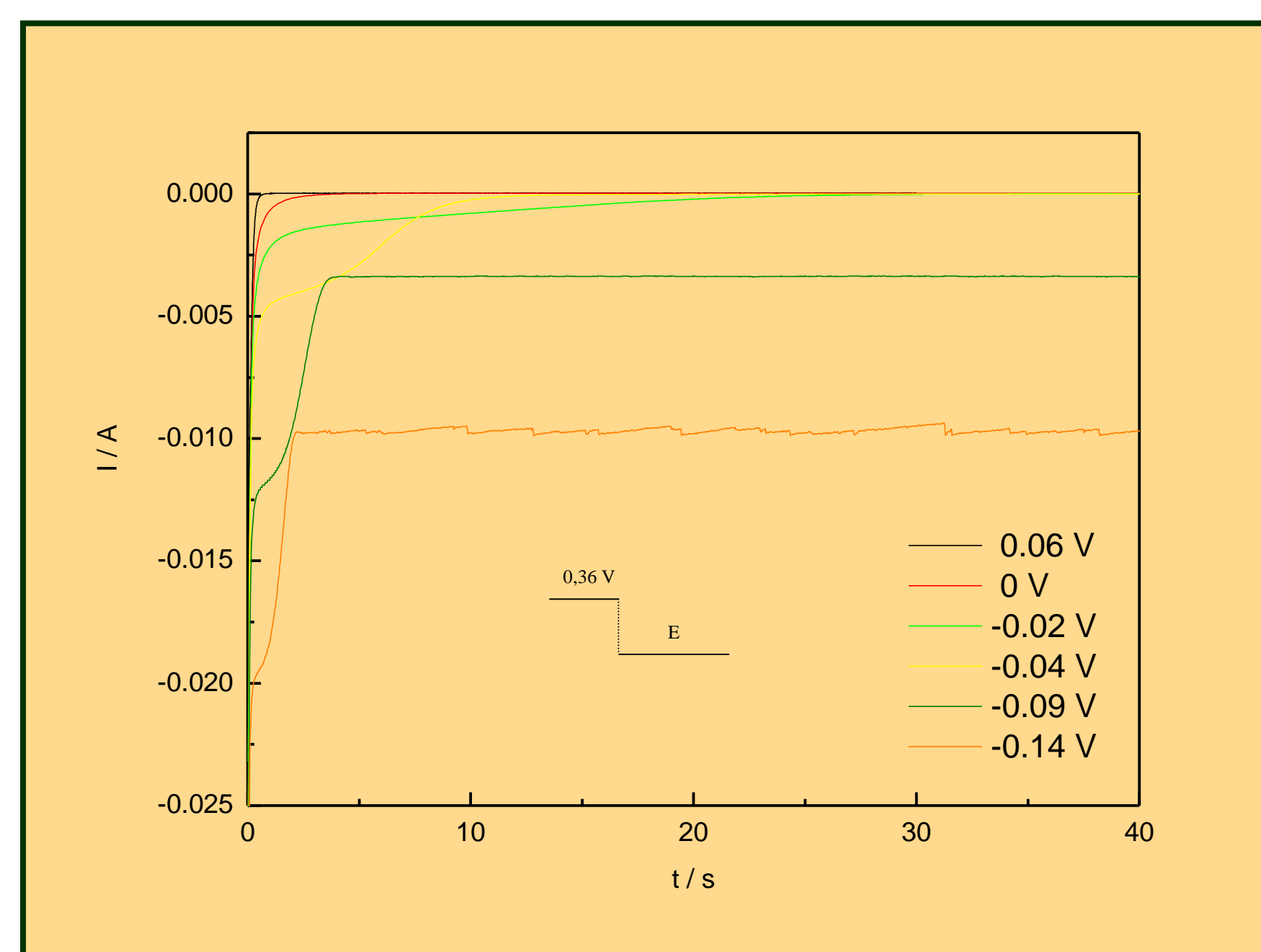


Fig. 4. Chronoamperograms recorded at various potentials for a Pd-Rh alloy (85.6% Pd); (a) cathodic steps - hydrogen electro sorption after pretreatment at 0.36 V, (b) anodic steps - oxidation of hydrogen electro sorbed at -0.09 V.

Hydrogen absorption into Pd-Rh alloys has also been studied chronoamperometrically (Fig. 4). After the negative potential step a current flows due to reduction of  $\text{H}^+$  ions to H atoms adsorbed on the surface, which subsequently enter the alloy lattice forming a bulk phase of absorbed hydrogen ( $\alpha$ - or  $\beta$ -phase, depending on potential and alloy composition). At sufficiently low potentials hydrogen evolution also occurs. After the positive potential step oxidative removal of electro sorbed hydrogen is observed, and the amount of oxidized hydrogen depends on the oxidation potential.

On the basis of chronoamperometric data  $\text{H}/(\text{Pd}+\text{Rh})$ -E plots were obtained for absorption and desorption. As can be seen in Fig. 5, a hysteresis is observed in the phase transition region, similarly to the gas-phase measurements where the hydrogen pressure connected with the  $\alpha$ - $\beta$  equilibrium during absorption is higher than during desorption. In the case of Pd-Rh alloys the hysteresis is smaller than for Pd and decreases with the increase in bulk Rh content.

From the chronoamperometric curves it is possible, for a given potential, to determine the time needed to obtain a steady-state electrode saturation with hydrogen as well as the time necessary for hydrogen oxidation (Fig. 6). It has been found that with a decrease in the electrode potential the absorption time initially increases, passes through a sharp maximum and then decreases. Similar dependence has been found for hydrogen desorption, but with the maximum placed at a slightly higher potential. A comparison of the potentials of time maxima with the respective  $\text{H}/(\text{Pd}+\text{Rh})$ -E plots for absorption and desorption reveals that the potentials are always within the phase transition region. It suggests that the slow process of  $\alpha$ - $\beta$  transition controls the overall rate of hydrogen absorption/desorption into/from thin Pd-Rh layers.

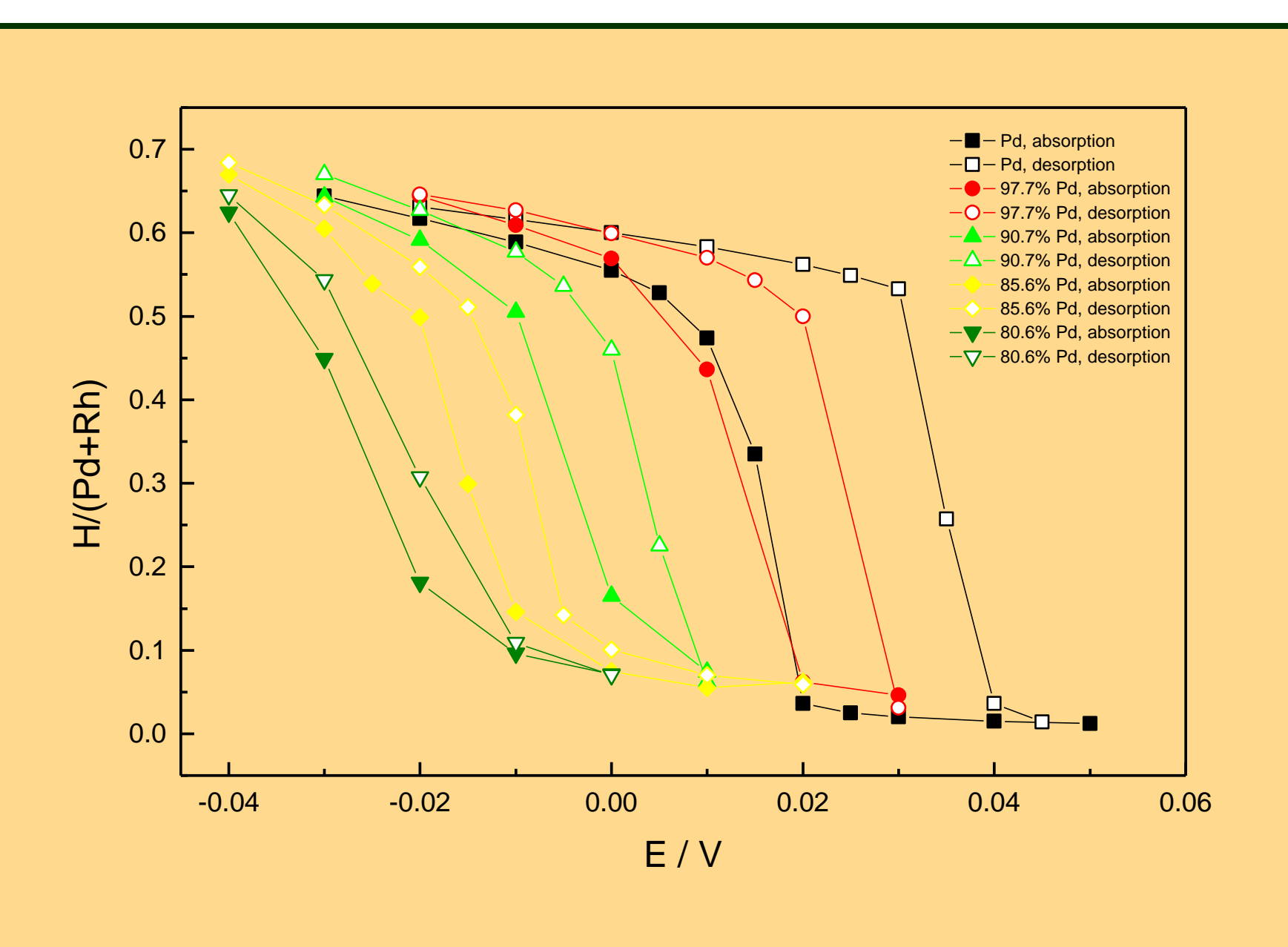


Fig. 5. Hydrogen absorption capacities versus potential in the phase transition region for Pd and Pd-Rh alloys obtained in chronoamperometric absorption and desorption experiments.

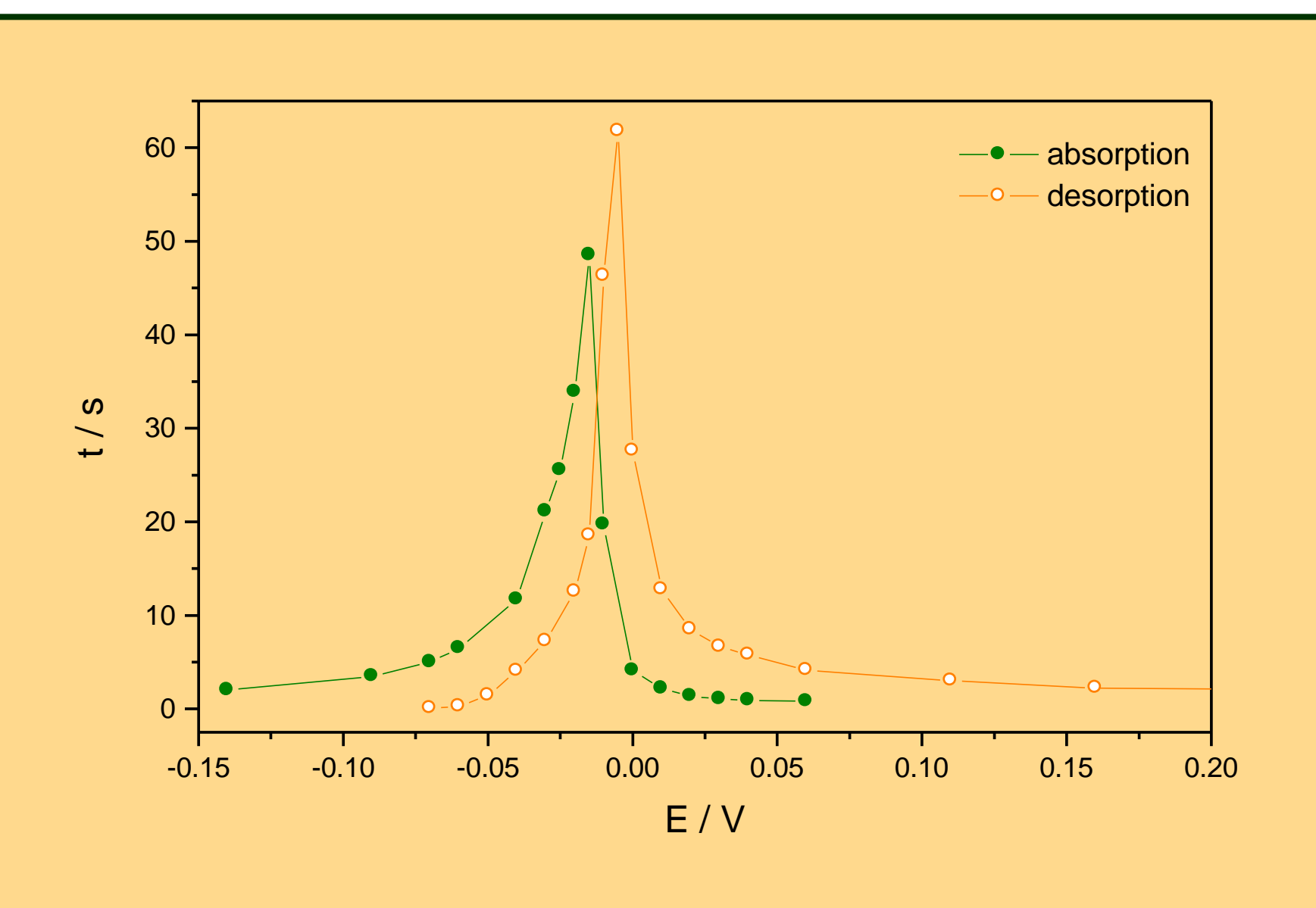


Fig. 6. Time needed for a steady-state saturation of the electrode with hydrogen and time needed for the oxidation of hydrogen electro sorbed at -0.09 V versus potential of absorption and desorption, respectively for a Pd-Rh alloy (85.6% Pd).

## SUMMARY

For alloys containing less than 20% Rh in the bulk the amount of electro sorbed hydrogen is greater than in pure Pd. The maximum value of the  $\text{H}/(\text{Pd}+\text{Rh})$  ratio is 0.80 for an alloy containing in the bulk 94 % Pd. For Pd-Rh alloys containing less than ca. 60% Pd only hydrogen adsorption is observed.

The  $\alpha$ - $\beta$  transition in Pd-Rh alloys occurs at potentials lower than in Pd. The potential of the phase transition depends linearly on the alloy bulk composition. The slow process of  $\alpha$ - $\beta$  transition controls the overall rate of hydrogen absorption and desorption into/from thin Pd-Rh layers.

The hysteresis is observed in chronoamperometric absorption and desorption experiments, the effect decreasing with the increase in bulk Rh content.