ELECTROSORPTION OF HYDROGEN INTO PALLADIUM-PLATINUM-RHODIUM ALLOYS

M. Łukaszewski^a, M. Grdeń^a, A. Czerwiński^{a, b}

^a Warsaw University, Department of Chemistry, Pasteura 1, 02-093 Warsaw, Poland ^b Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warsaw, Poland

INTRODUCTION

We present here the results of cyclic voltammetric and chronoamperometric studies on hydrogen electrosorption in Pd-Pt-Rh ternary alloys.

Pd-Pt-Rh alloys (thickness 0.20-0.60 μ m) were deposited on Au wires (diameter 0.5 mm) at a constant potential from a bath containing PdCl₂, H₂PtCl₆, RhCl₃ and HCl. Bulk compositions (expressed in atomic percentages) of the alloys were determined using EDAX analyzer (EDR-286) coupled with a LEO 435VP scanning electron microscope.

All cyclic voltammetric and chronoamperometric experiments were performed at room temperature in $0.5 \text{ M H}_2\text{SO}_4$ solution deoxygenated with Ar. All potentials are recalculated with respect to the SHE.

RESULTS AND DISCUSSION



0 004 -		
0.00-		0.003
	oxidation of hydrogen	A hydrogen desorption
	mainly absorbed Λ	njurogen uesorprion

Chronoamperometry of fresh alloys



Fig. 3. Chronoamperograms recorded for hydrogen electrosorption in a Pd-Pt-Rh alloy at various potentials after pretreatment at 0.36 V. Insert: hydrogen oxidation at various potentials after electrosorption at -0.09 V.

• The hysteresis between absorption and desorption is observed in chronoamperometric experiments. This effect is smaller for the Pd-Pt-Rh system than for Pd.

• Maximum time needed for hydrogen absorption/desorption is observed for potentials corresponding to the α - β transition region. The slow process of phase transition seems to control the rate of hydrogen absorption/desorption into/from thin Pd-based electrodes. • Due to electrochemical dissolution of Rh and Pd during potential cycling in the oxygen region the composition of both alloy surface and bulk is altered, modifying hydrogen electrosorption properties.

• A new bulk phase is generated possessing absorption characteristics different from those typical of a fresh alloy. The existence of two separate phases is reflected in two pairs of hydrogen absorption/desorption signals, two transition regions on the hydrogen absorption capacity vs. potential dependence and two maxima of time needed for hydrogen absorption/desorption.





Fig. 1. Hydrogen oxidation currents recorded after hydrogen electrosorption at various potentials in a Pd-Pt-Rh alloy containing in the bulk 81% Pd, 6% Pt and 13% Rh; scan rate 0.01 V s⁻¹. Insert: cyclic voltammogram in the full hydrogen-oxygen potential range; scan rate 0.01 V s⁻¹.

• Voltammograms for Pd-Pt-Rh alloys resemble CV curves typical of other noble metal/alloy electrodes. The potential regions of hydrogen sorption/desorption, double layer charging and surface oxidation/oxides reduction can be distinguished.

• The amount of hydrogen absorbed in Pd-Pt-Rh alloys is lower than for pure Pd and decreases with the increase in the bulk content of both Pt and Rh.

• In the case of Pd-Pt-Rh alloys the region of α - β transition is



Fig. 4. Hydrogen absorption capacities, H/(Pd+Pt+Rh) vs. potential for Pd and a Pd-Pt-Rh alloy obtained in chronoamperometric absorption and desorption experiments. Insert: time needed for a steady-state saturation of the electrode with hydrogen and time needed for the oxidation of hydrogen electrosorbed at -0.09 V vs. potential of absorption and desorption, respectively. Fig. 6. Hydrogen oxidation currents recorded after hydrogen electrosorption at various potentials in an electrochemically aged Pd-Pt-Rh alloy (subjected to 165 cycles in the oxygen region) containing in the bulk 82% Pd, 11% Pt and 7% Rh; scan rate 0.01 V s⁻¹. Insert: cyclic voltammogram in the full hydrogen-oxygen potential range; scan rate 0.01 V s⁻¹.



Fig. 7. Hydrogen charges normalized to maximum values (Q/Q_{max}) vs. potential for an electrochemically aged Pd-Pt-Rh alloy obtained in chronoamperometric absorption and desorption experiments. For comparison data for a fresh alloy and Pd are shown. Insert: time needed for a steady-state saturation of the electrochemically aged Pd-Pt-Rh alloy with hydrogen and time needed for the oxidation of hydrogen electrosorbed at -0.09 V vs. potential of absorption and desorption, respectively.

shifted negatively in comparison with Pd indicating lower stability of the β -phase.



Fig. 2. Hydrogen absorption capacities, H/(Pd+Pt+Rh) vs. potential for Pd and Pd-Pt-Rh alloys of different bulk compositions. The amount of electrosorbed hydrogen was calculated from the charge of hydrogen oxidation peaks on voltammograms recorded after electrode polarization at a given potential; scan rate 0.01 V s⁻¹. Insert: maximum absorption capacities vs. global bulk content of Pt and Rh. Influence of potential cycling on hydrogen electrosorption in Pd-Pt-Rh alloys



Fig. 5. Cyclic voltammograms for a Pd-Pt-Rh alloy containing in the bulk 81% Pd, 6% Pt and 13% Rh recorded in the hydrogen region (0.01 V s^{-1}) after indicated number of potential cycles in the oxygen region (0.1 V s^{-1}) . Insert: cyclic voltammograms recorded in the oxygen region (0.1 V s^{-1}) before and after the procedure of potential cycling. Arrows indicate changes in currents observed during potential cycling.

SUMMARY

Hydrogen electrosorption in thin Pd-Pt-Rh alloys has been studied in acidic solution using cyclic voltammetry and chronoamperometry. The influence of electrode potential on the amount of electrosorbed hydrogen has been examined. Three potential regions are distinguished corresponding to the existence of α - and β phases as well as the α - β phase transition. The maximum amount of absorbed hydrogen depends on the bulk composition being relatively high for Pd-rich alloys, although smaller than for Pd. The β -phase in the Pd-Pt-Rh system is less stable than in Pd, which is reflected in a lower potential of the α - β transition. The phase transition seems to control the rate of the processes of hydrogen absorption/desorption into/from thin Pd-based electrodes. The hysteresis effect is observed in chronoamperometric absorption and desorption experiments. Potential cycling of Pd-Pt-Rh alloys through the oxygen region leads to significant changes in hydrogen absorption properties including the appearance of an additional bulk phase.