ELECTROCHEMICAL BEHAVIOR OF Pd-Rh ALLOYS

M. Łukaszewski^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	

3.0x10 ⁻³	1.0x10 5.0x10		

5.0x10 ⁻³ -	blank curve	<u>5</u>	

The electrochemical behavior of binary alloys of noble metals has been widely investigated, mainly in the context of their electrocatalytic properties. Among the systems studied, including Pt-Rh, Pt-Ru, Pd-Pt, Pd-Au and Pt-Au alloys, the Pd-Rh system belongs to rather rarely examined ones. Most research of Pd-Rh alloys has been devoted to the phenomenon of hydrogen absorption. This system is particularly interesting in that aspect, since alloys containing small amounts of Rh can absorb more hydrogen than pure Pd. However, basic electrochemistry of Pd-Rh alloys has not been sufficiently explored and few such reports are available in the literature.

Pd-Rh alloys were prepared by potentiostatic deposition on gold wires (99.9 %, 0.5 mm diameter) from baths containing RhCl₃,PdCl₂ and HCl. Different alloy compositions were obtained applying different deposition potentials and bath compositions. Bulk compositions of the alloys were determined by EDAX analyzer (EDR-286) coupled with a LEO 435VP scanning electron microscope. Surface compositions were determined using the literature method based on a linear dependence of the potential of surface oxide reduction peak on the surface content of an alloy component.

All experiments were performed at room temperature in 0.5 M H_2SO_4 solution deoxygenated with Ar. All potentials are recalculated with respect to the SHE. In CO₂ and CO adsorption experiments the solution was saturated with 99.9 % purity gas at a potential from the hydrogen region. After completing the adsorption, which took 45 min for CO₂ and 20 min for CO, the gas was always removed from the solution with Ar and a voltammogram was recorded.



Fig. 2. Cyclic voltammograms for a Pd-Rh alloy (initial composition: 47% Rh in the bulk and 87% Rh on the surface) recorded during continuous potential cycling in the range from -0.04 to 1.36 V; scan rate 0.1 V/s (every 25th cycle is shown). Arrows indicate changes in current. Inserts: (a) cyclic voltammogram after 180 cycles, (b) cyclic voltammogram after 450 cycles.

Long potential cycling of Pd-Rh alloys through the oxygen region causes significant changes in the surface state of the electrode, resulting from electrochemical dissolution of the alloy components. These changes are reflected in the voltammogram course (Fig. 2) and are observed for both oxygen and hydrogen signals. At the beginning of cycling procedure the potential of the surface oxide reduction peak (3') is not altered suggesting constant surface composition. Such a steady state can be explained assuming that the ratio between the dissolution rates of Rh and Pd is similar to their relative surface content. However, long potential cycling causes the splitting of the surface oxide reduction peak into two signals (insert a in Fig. 2). It indicates that the surface of Pd-Rh alloys becomes heterogeneous, i.e. a separation occurs into two surface phases of different compositions, namely one rich in Rh and one rich in Pd. The mechanism of this segregation might involve a partial cathodic redeposition of previously dissolved metals in proportions different than for dissolution. During further potential cycling the initial peak disappears and the surface becomes again homogeneous, but strongly enriched with Pd, as can be concluded from the voltammogram shape (insert b in Fig. 2). The results of EDAX analysis confirmed alloy enrichment with Pd at the expense of Rh. The effect of composition changes occurs simultaneously with the decrease in the real surface area of the electrode indicated by the decrease in hydrogen adsorption/desorption (signal 1 and 1') as well as oxide formation and reduction currents (3 and 3').



Fig. 4. Anodic parts of cyclic voltammogramms (scan rate 0.05 V/s) recorded after CO₂ and CO adsorption at 0.06 V for a Pd-Rh alloy containing 39% Rh in the bulk and 72% Rh on the surface.

On the basis on the voltammetric signals it is possible to calculate eps (electron per site) value, i.e. a number of electrons taking part in the process of the adsorbate oxidation from one surface site. This quantity can be obtained from the ratio of the adsorbate oxidation charge (Q^{ox}_{COx}) to the difference between the charges of adsorbed hydrogen oxidation (calculated from the area under peak 1') in the absence and presence of the adsorbate $(\Delta Q^{\text{ox}}_{\text{Hads}})$:

 $eps = Q^{ox}_{COx} / \Delta Q^{ox}_{Hads}$

The obtained eps values are not integers indicating a mixed nature of the adsorbate, composed at least of two kinds of species of different eps values. In the case of eps values between 1 and 2 the products of CO_2 and CO adsorption can be linearly (eps = 2) and bridge bonded (eps = 1) CO molecules in various relative amounts. When eps is higher than 2, additional products might be proposed, such as multibonded C-H or C-OH species, suggested earlier for Rh electrodes. Fig. 5 demonstrates that the alloy surface composition affects the eps value and hence the nature of the adsorbate. The comparison of voltammogram shapes and eps values suggests that the products of CO₂ and CO adsorption on Pd-Rh alloys are similar but not totally identical.

RESULTS AND DISCUSSION

Cyclic voltammetry of Pd-Rh alloys







Pd-Rh: 32% Rh bulk

37% Rh surface

Scanning electron microscope (SEM) images (Fig. 3) show the alteration of the alloy surface during the potential cycling procedure. We can observe changes in crystallites size, and consequently, in the surface roughness as a result of the surface oxide formation/reduction processes accompanied by metal dissolution and subsequent partial redeposition. Since the alloy lattice parameter increases due to the formation of the hydride phase, hydrogen penetration into the bulk of the electrode causes an increase in sample volume leading to cracking.





Fig. 5. The influence of Rh surface concentration on the eps values calculated for CO₂ and CO adsorption on Pd-Rh alloys for two adsorption potentials; scan rate during adsorbate oxidation 0.05 V/s.

SUMMARY

Fig. 1. Cyclic voltammograms for Pd, Rh and Pd-Rh alloys recorded in the range from -0.04 to 1.36 V; scan rate 0.05 V/s.

Fig. 1 presents cyclic voltammograms recorded for Pd, Rh and Pd-Rh alloys of different bulk and surface compositions. One can distinguish hydrogen adsorption (1) and desorption (1') signals (the hydrogen region), then a potential range free from faradaic processes (the double layer region - 2), followed by surface oxide formation (3) and reduction (3') currents (the oxygen region). Due to the presence of Pd the alloys can also absorb hydrogen, which is mirrored by the presence of additional current signals due to electrochemical hydrogen insertion (1a) and removal (1a'). As it can be seen in Fig. 1, a single peak of surface oxide reduction (3') is observed for all freshly prepared Pd-Rh electrodes independently of bulk and surface composition indicating phase homogeneity of the alloy surface. Fig. 1 clearly demonstrates that with the change in alloy composition the voltammogram shape transforms from a CV curve typical of Rh into that characteristic of Pd.

Photo No.=2090 Detector= SE1

Fig. 3. SEM images taken for a fresh alloy containing 47% Rh in the bulk and 87% Rh on the surface (a) and after 450 cycles (b) in the range from -0.04 to 1.36 V, scan rate 0.1 V/s.

Carbon oxides adsorption on Pd-Rh alloys

Carbon oxides adsorption was performed on Pd-Rh alloys at potentials of hydrogen adsorption for a wide range of surface compositions. It was found that the decrease in Rh surface content markedly weakens the alloy affinity to CO₂, since hydrogen adsorbed on Pd atoms does not take part in the reaction with CO₂ molecules. For Pd-rich Pd-Rh alloys, containing less than ca. 20 % Rh on the surface, the amount of adsorbed CO_2 was negligible. On the other hand, CO can be adsorbed on both metals and therefore also on their alloy, regardless of its composition.

The main features of the voltammograms (Fig. 4) recorded in the presence of the carbon oxides adsorption product are: (a) a decrease in hydrogen oxidation currents reflecting blocking hydrogen electrosorption reaction on surface sites occupied by adsorbed CO₂ or CO and (b) a peak of the adsorbate oxidation, placed at potentials in the oxygen region.

• Cyclic voltammograms for Pd-Rh alloys are intermediate between CV curves for Pd and Rh with well-defined hydrogen electrosorption (adsorption, absorption and desorption) peaks as well as surface oxide formation and reduction signals.

• As a result of prolonged potential cycling of Pd-Rh alloys through the oxygen region both electrode surface and bulk are enriched with Pd. During the procedure of electrochemical ageing the surface can become temporarily heterogeneous.

• Adsorbed CO₂ causes diminution of currents originating from hydrogen adsorption on Pd-Rh alloys, but it has much less influence on signals connected with hydrogen absorption. In the presence of adsorbed CO both hydrogen adsorption and absorption currents are strongly suppressed.

• The number of electrons required for the oxidation of the adsorbate from one surface site (eps) depends on the alloy surface composition. The comparison of voltammogram shapes and eps values suggests that the products of CO₂ and CO adsorption on Pd-Rh alloys are similar but not totally identical.