# **CYCLIC VOLTAMMETRIC BEHAVIOR OF PALLADIUM ALLOYS**

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The studies on the electrochemistry of noble metal alloys are devoted mainly to their electrocatalytic properties. Most of such investigations were carried out for binary noble metal systems but the increasing number of reports provides similar data for alloys containing more than two elements, e.g. ternary alloys.

Although noble metals are neighboring elements in the periodic table, their electrochemical properties are markedly different. Pd, Pt and Rh can adsorb hydrogen at potentials positive to the reversible hydrogen potential, but only Pd can also absorb hydrogen. On the other hand, Au is completely inactive in hydrogen electrosorption reaction. All the elements also differ between each other in their electrochemical behavior at sufficiently high potentials where oxidation processes take

place, involving the formation of surface oxides and the electrochemical dissolution. The processes of surface oxides generation and reduction on Rh electrode proceed at potentials markedly lower than on Pd, Pt and Au. Pt and Au are much more inert in the process of electrochemical dissolution than Pd and Rh. Thus, Pd alloying with such elements as Pt, Rh or Au leads to alloys possessing various electrochemical properties.

In this work we present data on general electrochemical behavior of Pd alloys with other noble metals studied by cyclic voltammetry. The alloys were prepared by electrochemical codeposition on Au wires at constant potential from baths containing PdCl<sub>2</sub>, RhCl<sub>3</sub>, H<sub>2</sub>PtCl<sub>6</sub>, HAuCl<sub>4</sub> and HCl. All experiments were performed at room temperature in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. All potentials are recalculated with respect to the SHE. All alloy compositions are expressed in atomic percentages.

### **Cyclic voltammetry of noble metals**

In the investigations of electrochemical behavior of noble metals and their alloys cyclic voltammetry has been established as a powerful in situ technique. It has been demonstrated that for electrodes of this type the voltammogram recorded under given experimental conditions is an electrochemical fingerprint of the sample studied (Fig. 1). The voltammograms for pure noble metal electrodes differ markedly from each other in respect of the region of hydrogen electrosorption (1) as well as the region of surface oxide formation and reduction (2).





# Potential cycling of noble metal alloys



Fig. 3. Cyclic voltammograms for a Pd-Pt-Rh alloy (initial bulk composition: 57% Pd, 8% Pt, 35% Rh) subjected to continuous cycling in the hydrogen-oxygen potential range; scan rate 0.1 V/s.



— initial state

Fig. 4. Cyclic voltammograms for a Pd-Au alloy (initial bulk composition: 73% Pd, 27% Au) subjected to continuous cycling in the hydrogen-oxygen potential range; scan rate 0.05 V/s.

Long potential cycling of noble metal alloys involving polarization to the oxygen region causes significant changes in the surface state of the electrode, resulting from electrochemical dissolution of metals. These changes are reflected in the voltammogram course and are observed for both hydrogen and oxygen signals (Figs. 3 and 4). In particular, a positive shift of the potential of surface oxides reduction peak indicates alloy enrichment with more noble components. In the case of Pd-Au alloy a new surface phase rich in Au is formed (an additional surface oxide





Fig. 1. Cyclic voltammograms for noble metals in 0.5  $M H_2SO_4$ ; scan rate 0.1 V/s.

## Cyclic voltammetry of noble metal alloys

The shapes of voltammograms for homogeneous noble metal alloys are intermediate between those characteristic of pure metals (Fig. 2). Thus, we can draw qualitative and quantitative conclusions about the surface state of the alloys on the basis of the voltammogram course by utilizing the distinctive features associated with each component. In particular, the potential of the surface oxide reduction peak is a measure of alloy surface composition. The number of surface oxide reduction peaks provides the number of distinct surface phases.





reduction peak appears), while for Pd-Pt-Rh alloy the surface remains homogeneous (a single peak is observed).





Fig. 5. Scanning electron microscope images taken for: (a) a fresh Pd-



Detector= SE1

Fig. 6. Scanning electron microscope images taken for: (a) a fresh

Fig. 2. Cyclic voltammograms for noble metal alloys in 0.5 M H<sub>2</sub>SO<sub>4</sub>; scan rate 0.01 V/s (Pd-Au) or 0.1 V/s (Pd-Pt, Pd-Rh, Pd-Pt-Rh). Alloy bulk compositions: Pd-Au - 74% Pd, 26% Au; Pd-Pt - 70% Pd, 30% Pt; Pd-Rh - 60% Pd, 40% Rh; Pd-Pt-Rh - 81% Pd, 6% Pt, 13% Rh.

Pt-Rh alloy containing in the bulk 84% Pd, 7% Pt, 9% Rh and (b) after cycling in the hydrogen-oxygen potential range.

Pd-Au alloy containing in the bulk 71% Pd, 29% Au and (b) after cycling in the hydrogen-oxygen potential range.

Scanning electron microscope observations (Figs. 5 and 6) confirm the alteration of the alloy surface morphology after continuous cycling in the hydrogen-oxygen potential range, as a result of the successive surface oxide formation/reduction processes accompanied by metal dissolution and subsequent partial redeposition In particular, since for Pd and Pd alloys the 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.

#### **Summary**

Cyclic voltammograms for Pd-noble metal alloys are generally similar to the curves characteristic of pure metals, with the easily distinguishable regions of hydrogen sorption/desorption and surface oxidation/oxides reduction. Different alloy compositions lead to current-potential responses varying in respect of the shape and potential of particular current signals. During continuous cycling in the hydrogen-oxygen potential range electrochemical dissolution of metals takes place, causing the alloy enrichment with more noble components. Selective removal of less noble metals allows for in situ preparation of alloy electrodes possessing a variety of properties towards hydrogen and oxygen electrosorption.