Limited volume electrodes (LVEs).
Study of hydrogen sorption in palladium alloys

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Abstract

One of the important problems in studing hydrogen electrosorption process in Pd and Pd alloys is the generation of absorption/desorption currents which are a few orders of magnitude higher than those originating from surface processes. This problem has been eliminated by the use of a thin metal layer deposited on a neutral matrix. Electrodes of this type, called limited volume electrodes (LVEs), have been successfully applied in the investigations of hydrogen absorption in pure Pd [1-3] and some its binary alloys [4, 5]. Such an approach allows for the limitation and control of the amount of sorbed hydrogen. In cyclic voltammetric experiments performed on LVEs hydrogen oxidation peaks can be easily separated from the currents of various surface reactions (Fig. 1). Using this kind of Pd electrodes it is possible to examine the process of hydrogen sorption in the full potential range, in particular at potentials where the rate of hydrogen removal is determined by the rate of its diffusion in the bulk of metal. These experiments, easy to perform on LVEs, cannot be carried out in the case of bulk Pd electrodes, made from wires or foils.

In this communication we present new results concerning hydrogen absorption and desorption into/from Pd-based noble metal alloys. The processes were studied in acid solutions (0.5 M H_2SO_4) using cyclic voltammetry technique. Pd-Pt binary alloys and Pd-Pt-Rh ternary alloys, less than 1 μm in thickness, were prepared by electrodeposition of the metals on a gold substrate. The hydrogen absorption capacities were obtained by integration of anodic peaks in cyclic voltammetric experiments on the voltammograms recorded after potentiostatic saturation of the electrodes with hydrogen. The influence of a scan rate (v) on hydrogen oxidation charge (Q_H) was also examined. The results obtained for Pd-based alloys have been compared with the data for Pd-LVEs. It has been found that the mechanism of hydrogen desorption from Pd-Pt and Pd-Pt-Rh alloys, evaluated on the basis of the Q_H -v dependence, seems to be similar to that proposed for pure Pd, involving two independent pathways of hydrogen removal, *i.e* electrochemical oxidation and a non-electrochemical recombination of H atoms. Additionally, carbon oxides electrosorption experiments were applied in order to examine the nature of various current signals occurring on the voltammograms in the hydrogen region. The results suggest that only Pd atoms are active in the processes of hydrogen absorption and desorption into/from Pd-based noble metal alloys.

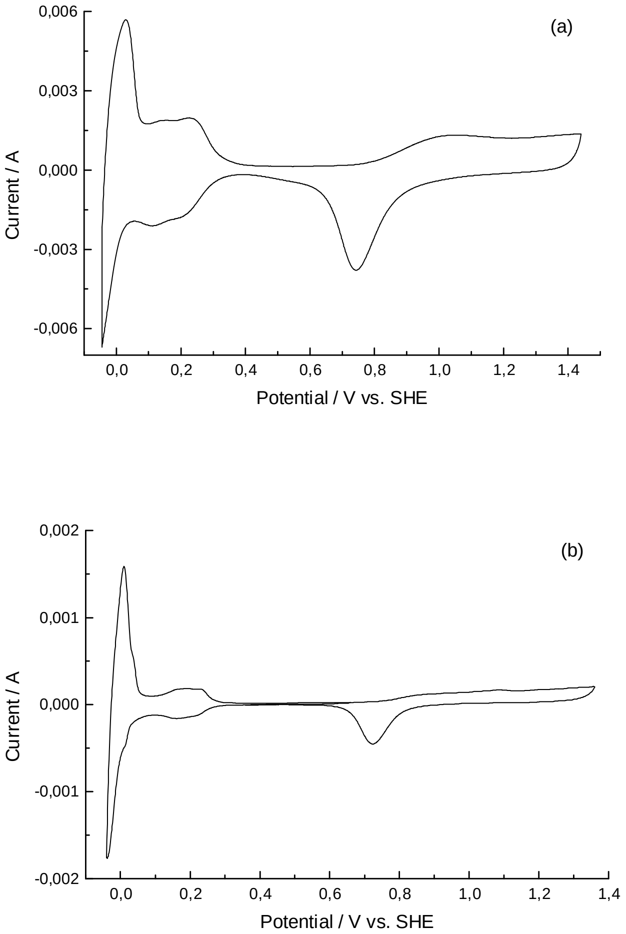

Fig. 1. Cyclic voltammograms recorded in 0.5 M H_2SO_4 for limited volume electrodes: (a) Pd-Pt alloy with 86%Pd and 14%Pt in the bulk, scan rate 0.05 Vs^{-1}; (b) Pd-Pt-Rh alloy with 84%Pd, 7%Pt and 9%Rh in the bulk, scan rate 0.01 Vs^{-1}. Both of the alloys were *ca.* 0.5μm in thickness.

References

[1] A.Czerwiński, R. Marassi, S. Zamponi, J. Electroanal. Chem., 316 (1991) 211.
[2] A. Czerwiński, Polish J. Chem. 69 (1995) 699.
[3] A. Czerwiński, I. Kiersztyn, M. Grdeń, J. Czapla, J. Electroanal. Chem., 471 (1999) 190.
[4] M. Grdeń, A. Piaścik, Z. Koczorowski, A. Czerwiński, J. Electroanal. Chem. 532 (2002) 35.
[5] M. Łukaszewski, K. Kuśmierczyk, J. Kotowski, H. Siwek, A. Czerwiński, J. Solid State Electrochem. on line