ELECTROCHEMICAL BEHAVIOR OF PALLADIUM ALLOY LIMITED VOLUME ELECTRODES (LVEs)

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One of the important problems in studying hydrogen electroadsorption process in Pd and Pd alloys made of wires or foils is the generation of absorption/desorption currents, which are much higher than those originating from surface processes (Fig. 1). This problem can be eliminated by the use of a thin (of the order of micron) metalalloy layer electrodeposited on a neutral matrix (e.g., Au). Electrodes of this type, called limited volume electrodes (LVEs), allow for the limitation and control of the amount of absorbed hydrogen. In cyclic voltammetric experiments such an approach results in hydrogen absorption signals and surface currents of comparable magnitude, well separated from each other (Figs. 2 and 3).

LVEs have been applied in the investigations of numerous aspects of hydrogen electroadsorption in Pd and Pd metal alloys (1-5):

- The mechanism of hydrogen desorption from Pd, Pd-Pt and Pd-Pt-Rh alloys (Figs. 4 and 5).
- The influence of temperature on the process of hydrogen desorption from Pd (Fig. 6).
- The influence of alkaline cations on the process of hydrogen insertion into Pd (Fig. 7).
- The processes of hydrogen insertion/removal into/from Pd-Pt and Pd-Pt-Rh alloys in the presence of adsorbed carbon oxides (Figs. 8 and 9).

Conclusions:

- There are two independent pathways of hydrogen removal from Pd and its alloys - electrochemical oxidation and non-electrochemical recombination of H atoms.
- The rate constants of electrochemical and non-electrochemical desorption are affected by the temperature in a different manner.
- The amount of hydrogen or deuterium electroadsorbed in Pd from basic solutions depends significantly on the presence of alkaline cations, while in acidic solutions this effect is negligible.
- Adsorbed CO does not block hydrogen absorption/desorption into/from Pd alloys, while adsorbed CO inhibits strongly both hydrogen absorption and adsorption as well as its desorption.
- Only Pd atoms seem to be active in the processes of hydrogen insertion/removal into/from Pd alloys.

All the effects observed in experiments with the use of LVEs would be very difficult to study in the case of bulk Pd and Pd-based alloy electrodes made from wires or foils. Therefore, LVEs create new possibilities for electrochemical examination of hydrogen-absorbing materials.

References