APPLICATION OF QUARTZ CRYSTAL MICROBALANCE TO STUDIES ON SELECTED ELECTROCHEMICAL PROPERTIES OF NOBLE METALS AND THEIR ALLOYS

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Fig. 1. Cyclic voltammograms and frequency-potential curves for Rh; scan rate 0.1 V/s.



Fig. 2. Cyclic voltammograms and frequency-potential curves for Pt; scan rate 0.1 V/s.







The electrochemical quartz crystal microbalance allows us to record in situ frequency changes accompanying electrode processes together with electrochemical signals like current or potential. Under specific conditions the frequency shift can be recalculated into mass changes according to Sauerbrey equation. However, in many situations the EQCM response is also determined by other factors. In the case of noble metals and their alloys these factors are: (a) mass changes connected with electrosorption of hydrogen (both adsorption and absorption) and oxygen (surface oxide formation), (b) mass changes connected with the electrochemical dissolution and subsequent redeposition of metals, (c) mass changes connected with specific adsorption of ions and adsorption of water molecules, (d) changes in density and viscosity of the solution layer adjacent to the electrode surface caused by non-specific adsorption of ions and changes in interactions between electrode surface and solution, (e) stresses in metal lattice during hydrogen absorption and surface oxide formation, (f) effects connected with the electrode roughness. 10 MHz AT-cut Au- or Pt-plated crystals were used in our EQCM experiments. The calibration constant (C) determined by Ag and Pd deposition was 1.2 ng Hz⁻¹, very close to the theoretical value based on Sauerbrey equation. Thin (0.2-0.3 µm) metal or alloy layers were deposited electrochemically on the resonator surface. The real surface area of Pt and Rh electrodes was calculated from adsorbed hydrogen oxidation charge, while in the case of Pd and Pd alloys surface oxide reduction charge was utilized. All experiments were performed at room temperature in 0.5 M H_2SO_4 solutions deoxygenated using an Ar stream. All potentials are recalculated with respect to the SHE. It is well known that the voltammogram recorded under given experimental conditions is characteristic of the individual noble metal and it is an electrochemical 'fingerprint' of the investigated sample (Figs. 1-3). One can distinguish hydrogen adsorption (1) and desorption signals (1'), then a potential range free from faradaic currents - double layer region (2), followed by surface oxidation (3) and surface oxide reduction signals (3'). Pd can additionally absorb hydrogen, which is reflected in large currents originating from hydrogen insertion (1a) and removal (1a'). Due to a greater number of factors affecting the EQCM response, the course of the frequency-potential relationship is less characteristic than a CV curve. The EQCM method is very suitable for studying the dissolution reactions, where the resonator response is dominated by electrode mass changes. The extent to which a given metal dissolves increases with an increase in electrode potential and a decrease in scan rate (Fig. 4). Under fixed experimental conditions Pd and Rh are much more sensitive to dissolution than Pt. At relatively low potentials Rh is the most soluble metal, while above a certain potential value (ca. 1 V) Pd dissolves the most rapidly. At a potential slightly lower than the oxygen evolution potential the amount of dissolved metal at scan rate 0.1 V s⁻¹ corresponds to ca. 15% of monolayer of surface atoms for Pd, 4% for Rh and 0.2% for Pt. The EQCM experiments indicate great metal dissolution during the procedure of continuous potential cycling of noble metal alloys through the oxygen region (Fig. 5).



Fig. 4. Dependence of the loss in electrode mass per unit of real surface area on upper potential limit in a cyclic voltammetric experiment; scan rate 0.1 V/s. Insert: influence of scan rate on the amount of dissolved metals.



Fig. 6. Apparent molar mass of electrosorbed hydrogen (M_a) as a function of its amount in Pd-based electrodes during chronoamperometric absorption (potential step from 0.37 to -0.03 V). Alloy bulk compositions: Pd-Pt - 88.5% Pd; Pd-Rh -91.5% Pd; Pd-Pt-Rh - 77% Pd, 12% Pt, 11% Rh.

The frequency shift connected with hydrogen electrosorption in Pd and its alloys exceeds the value predicted by Sauerbrey equation and can be attributed not only to the mass changes but also to the stresses generated inside the metal/alloy (Fig. 6). The influence of stresses on the EQCM response depends on the amount of electrosorbed hydrogen (Fig. 7) and the kind of the system (pure Pd or an alloy of a given bulk composition). EQCM experiments indicate that the magnitude and distribution of stresses are different for absorption and desorption processes, which seems to confirm the important role of the stress effect in the phenomenon of absorption/desorption hysteresis (Fig. 8). Fig. 5. The loss in electrode mass per the unit of real surface area (solid symbols) as a function of number of potential cycles in the range from -0.03 to 1.37 V; scan rate 0.1 V/s. The changes in the potential of surface oxide reduction peak are also shown (open symbols). Initial alloy compositions: Pd-Pt-Rh - 46% Pd in the bulk, 14% Pt in the bulk; Pd-Rh - 45% Pd in the bulk, 9% Pd on the surface; Pd-Pt - 70% Pd in the bulk, 71% Pd on the surface.



Fig. 7. Dependence of the frequency changes on the amount of electrosorbed hydrogen during voltammetric (0.01 V/s) desorption of hydrogen absorbed at different potentials in a Pd-Pt alloy (88.5% Pd in the bulk). Dotted line indicates response expected from Sauerbrey equation.



Fig. 8. Dependence of the stress-related frequency changes on the amount of electrosorbed hydrogen during chronoamperometric absorption and desorption (potential steps between 0.07 and -0.03 V) for Pd and Pd alloys: Pd-Pt (88.5% Pd in the bulk) and Pd-Pt-Rh (77% Pd, 12% Pt, 11% Rh in the bulk). Insert: hydrogen absorption capacities versus potential obtained in chronoamperometric absorption (solid symbols) and desorption (open symbols) experiments.

The EQCM response in CO_2/CO adsorption experiments (Fig. 9) is affected by both effects connected with the changes in mass attached to the resonator and non-mass effects including changes in metal-solution interactions and variation of solution density and viscosity in the vicinity of the electrode. Therefore, the analysis of the EQCM data is complicated and it is difficult to separate various contributions to the measured frequency shift. However, from the differences in the EQCM signal in the presence of the products of CO_2 and CO adsorption it can be concluded that these adsorbates are not totally identical.

Our papers devoted to the EQCM:

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Fig. 9. Cyclic voltammograms (scan rate 0.05 V/s) and frequency-potential curves recorded after CO_2 adsorption (45 min at 0.07 V) and CO adsorption (20 min at 0.07 V) on a Pd-Pt alloy (70% Pd in the bulk, 60% Pd on the surface).