

Electrochemical quartz crystal microbalance study on carbon oxides adsorption in the presence of electrosorbed hydrogen on Pd alloys with Pt and Rh

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Abstract

CO₂ and CO adsorption on Pd–Pt and Pd–Rh alloys has been studied by cyclic voltammetry (CV) and the electrochemical quartz crystal microbalance (EQCM). Adsorbed CO₂ inhibits partially hydrogen adsorption on Pt and Rh surface atoms but does not block significantly hydrogen absorption into alloy bulk. In the presence of adsorbed CO both hydrogen adsorption and absorption are strongly suppressed. On electrodes covered with adsorbed CO the oxidation of previously adsorbed hydrogen is significantly shifted into higher potentials. The EQCM response in CO₂/CO adsorption experiments is affected by both the effects connected with the changes in mass attached to the resonator and the non-mass effects including changes in metal–solution interactions and variation of solution density and viscosity in the vicinity of the electrode. Differences in the EQCM behavior suggest that the products of CO₂ and CO adsorption on the alloys studied are not totally identical.

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1. Introduction

The processes of electrosorption of CO₂ [1–33] and CO [7,10,31,34–55] on platinum group metals and their alloys have been a subject of numerous investigations carried out electrochemically as well as using electrochemistry combined with an additional technique such as IR spectroscopy, mass spectrometry, radiochemistry, gas chromatography and quartz crystal microbalance. Most research has been carried out in the aspect of electrocatalysis, in particular of studies concerning methanol fuel cells (DMFC), where CO₂ and CO are the products of fuel oxidation.

The behavior of CO₂ and CO towards noble metals is markedly different. CO₂ can be adsorbed only on Pt and Rh electrodes at potentials positive to the reversible hydrogen potential. During CO₂ adsorption a reaction between CO₂ molecules and atoms of underpotentially deposited hydrogen takes place. Under conditions of a cyclic voltammetric experiment the pres-

ence of the CO₂ adsorption product can be observed as an effect of partial blocking hydrogen adsorption and desorption signals, while the adsorbate removal gives an oxidation peak placed at potentials in the double layer or at the beginning of the oxygen region. The process of CO₂ adsorption on Pt and Rh atoms occurs also in the case of alloys of these elements [10,11,31–33]. However, despite the strong ability to adsorb and absorb hydrogen Pd is totally inactive in CO₂ adsorption reaction at potentials positive to the reversible hydrogen potential [21,35,56,57].

Recent studies on the process of CO₂ adsorption on Pd alloys with Pt and Rh [11,31–33] have shown that the adsorption properties of Pt, Rh and Pd atoms towards CO₂ are retained in the alloy. Thus in a CO₂ adsorption experiment it is possible to block hydrogen bonded to Pt or Rh surface atoms, not causing simultaneously any significant effect on hydrogen bonded to Pd atoms. Hydrogen atoms bonded to Pd atoms do not participate in CO₂ adsorption reaction. From the fact that the presence of adsorbed CO₂ does not influence the processes of hydrogen insertion/removal into/from Pd alloys it has been stated that only Pd surface atoms are active in these processes.

CO is a much stronger surface poison than CO₂. In particular, the presence of CO has a great blocking effect on the process of

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hydrogen electroadsorption on all platinum metals. In contrast to CO₂ behavior CO adsorption takes place at potentials from both hydrogen and double layer regions [42,50]. The experiments performed on Pd electrode [34,35,40] have revealed that the product of CO adsorption strongly blocks hydrogen insertion as well as its removal into/from the metal. The presence of adsorbed CO influences the kinetics of hydrogen sorption/desorption processes due to inhibition of surface reactions involving atoms of adsorbed hydrogen. Similar effects have been reported for CO adsorption on Pd–Au [41] and Pd–Pt–Rh alloys [31,45].

In general the product of CO₂ or CO adsorption can be a mixture of various compounds, including linearly and bridge bonded CO molecules [3,6,7,14,15,19,20,24–27,29,30,34–39,46,47,50,51,53], COOH [2,5–9,16,17,25,37,50] and CHO [22,42] radicals and other species (CH₂ [18], CH [42], COH [6,20,21,23,42], or even C radicals [4,42,52]). Some authors support the opinion stated by Breiter [14] that the products of CO₂ and CO adsorption are the same. However, there are also claims that the products of CO₂ adsorption are not totally identical with the products of CO adsorption [1,6,7,12,42,52]. The process of CO₂/CO electroadsorption depends on such factors as electrode material (a pure metal or alloy of a given surface composition as well as plane orientation for single crystal electrodes), adsorption potential, adsorption time, electrode surface morphology, method of electrode pretreatment and solution composition.

In this work we continue our interest in the phenomenon of carbon oxides adsorption on noble metals and their alloys. We present preliminary results of the EQCM experiments performed on Pd alloys with Pt and Rh. The aim of our paper is to compare the EQCM response obtained in the presence of adsorbed CO₂ and CO as well as during the adsorbate oxidation on selected noble metal alloys. We want to verify the possibility of the application of this technique in studies on similarities and differences in the behavior of CO₂ and CO adsorption products. Such a comparative examination of both carbon oxides adsorption with the use of the EQCM method has not been performed yet.

2. Experimental

All experiments were performed at room temperature in 0.5 M H₂SO₄ solutions deoxygenated using an Ar stream. A Hg|Hg₂SO₄|0.5 M H₂SO₄ was used as the reference electrode. A Pt gauze was used as the auxiliary electrode. All potentials are recalculated with respect to the SHE.

The electrochemical quartz crystal microbalance (EQCM) M105 made by UELKO (Poland) was used together with AUTO-LAB potentiostat. In the EQCM experiments 10 MHz AT-cut Au-plated crystals (produced by International Crystal Manufacturing) were employed. The calibration constant determined by Ag and Pd deposition was 1.2 ng Hz⁻¹, very close to the theoretical value based on Sauerbrey equation [58]. Pd alloys were deposited electrochemically on the Au surfaces according to the procedures described earlier [11,33,59]. The thickness of the alloy layers was 0.2–0.3 μm. The roughness factor, as estimated from surface oxides reduction charge [60,61], was ca. 70–130 and remained constant during the experiments.

All alloy compositions given in this work are expressed in atomic percentages. The bulk compositions were obtained using EDAX analyzer (EDR-286) coupled with a LEO 435VP scanning electron microscope. Surface compositions were determined from the potential of the peak of surface oxide reduction [11,33,59–63].

In the experiments with CO₂ and CO gases with 99.9% purity were used. CO₂ (CO) adsorption was performed for 45 min (20 min) at 0.07 V, i.e. a potential low enough to obtain high surface coverage with adsorbed hydrogen but higher than the potential of the hydrogen evolution reaction. After completing CO₂/CO adsorption and before recording cyclic voltammograms the gases were always removed from the solution with Ar.

3. Results and discussion

3.1. General cyclic voltammetric behavior of Pd–Pt and Pd–Rh EQCM electrodes

Fig. 1a and b present cyclic voltammograms together with frequency–potential responses recorded in the full hydrogen–oxygen potential range (–0.03 to 1.37 V) for Pd–Pt (70% Pd in the bulk, 60% Pd on the surface) and Pd–Rh (52% Pd in the bulk, 14% Pd on the surface) alloys. The CV curves are similar to those reported previously in the literature [11,33,59,62,63]. 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 – 3), followed by surface oxide generation (4) and reduction (4′) currents (the oxygen region). In the case of Pd–Pt electrodes split hydrogen signals resemble two peaks attributed to strongly and weakly adsorbed hydrogen, typical of pure polycrystalline Pt [60]. Pd alloys cannot only adsorb but also absorb hydrogen [64], which is mirrored by the presence of additional current signals due to electrochemical hydrogen insertion (2) and removal (2′).

In general, the EQCM response for noble metals and their alloys under conditions of an cyclic voltammetric experiment can be affected by several factors [46–49,65–82]: (a) mass changes connected with electroadsorption 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 changes in the electrode roughness.

Except the lowest potentials in the hydrogen region for a Pd–Pt alloy, where the frequency increase occurs, a monotonic frequency decrease is observed during an anodic voltammetric scan. The frequency lowering in the hydrogen region probably results from stresses connected with hydrogen absorption [72,82]. However, it is also possible that this behavior reflects changes in hydrophilicity of the electrode surface caused by the presence of weakly adsorbed hydrogen (strongly interacting

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