



Electrocatalytic properties of Au electrodes decorated with Pt submonolayers by galvanic displacement of copper adatoms



B.I. Podlovchenko*, Yu. M. Maksimov, K.I. Maslakov

Department of Chemistry, Moscow State University, Moscow 119992, Leninskie Gory, Russia

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ABSTRACT

Submonolayer Pt⁰ coatings are synthesized by the displacement of copper adatoms (Cu_{ad}) on polycrystalline (pc) Au in PtCl₄²⁻ solutions (supporting electrolyte 0.5 M H₂SO₄). Cyclic voltammograms (CVA) measured on Pt⁰Au demonstrate that for initial surface coverages $\theta_{\text{Cu}} < 0.5$, the Pt⁰ adatoms that have displaced Cu_{ad} are mainly deposited in the first layer. At large surface coverages, the agglomeration of Pt⁰ and its partial deposition into the second layer take place; ~30% of Au surface remains free. SEM, XPS and Auger-spectroscopic data confirm the absence of multilayer Pt⁰ agglomerates. The specific rates of CH₃OH electrooxidation (per cm² of Pt) on Pt⁰Au turn out to be much lower than on pc Pt⁰. This is explained by the fact that dehydrogenation of CH₃OH requires the presence of «areas» formed by a large number of platinum atoms (> 3). For HCOOH, the strong increase (more than by one order of magnitude) in both non-steady-state and steady-state specific electrooxidation currents is observed. It is assumed that new active sites are formed for the current-determining reaction that proceeds through the one-site adsorption of HCOOH molecules.

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1. Introduction

Platinum is the best catalyst for many chemical and electrochemical reactions including reactions taking place in fuel cells. However, the high cost and shortage of platinum make scientists seek new ways for reducing the platinum content in catalysts (electrocatalysts) and this problem was always challenging [1–3]. One of the ways to solve it is to synthesize bi- and multicomponent catalysts that in addition to platinum include the cheaper and/or less deficient metals. Such bi- and polymetallic structures make it possible to reduce the consumption of platinum and often also exhibit the higher catalytic activity in reactions important for fuel cells such as, e.g., electrooxidation of HCO compounds (including CO).

To date, the main regularities of electrooxidation of CH₃OH and HCOOH in acidic solutions on Pt electrodes are already elucidated [4–15]. The HCOOH electrooxidation in the low potential range which is of interest for fuel cells (<0.5 V vs. reversible hydrogen electrode in the same solution) is mainly limited by the rate of dehydrogenation HCOOH molecules. This process is inhibited by accumulation of strongly chemisorbed species (first of all, CO_{ads}) on the electrode surface. The current-determining reactions of CH₃OH electrooxidation are as follows: (i) at low potentials, the

interaction of relatively weakly surface-bound intermediate species with adsorbed oxygen (probably in the form of OH_{ads}), (ii) at high potentials, dehydrogenation of CH₃OH molecules. Methanol oxidation is also characterized by self-inhibition which is associated with the formation of almost near-monolayer coverages with strongly chemisorbed species such as CO_{ads} and/or HCO_{ads}. According to the literature data [15–22] on binary systems, certain acceleration of electrooxidation of HCO compounds can be achieved due to bifunctional catalysts, the «ensemble effect», and also due to changes in the electronic structure of Pt, i.e., the «electronic effect».

The system of gold (single-crystal and polycrystalline) decorated with Pt submono- and monolayers and Pt clusters appears to be convenient as a model system for developing further the principles of synthesis of optimal platinum-containing electrocatalysts [22–35]. Different decoration methods were proposed, both chemical [26–28,31,32] and electrochemical [22–25,29,30,33–35]. A lot of such systems demonstrated high activity in reactions of oxygen electroreduction [24,25,33] and HCOOH electrooxidation [22,26–32]. The pronounced (by a factor of several tens) acceleration of HCOOH electrooxidation was observed [22,28] for submonolayer Pt coatings synthesized by pulsed electrodeposition on polycrystalline (pc) Au [22] and chemical deposition on Au nanoparticles [28].

Adzic et al. [23,24] proposed a highly efficient method for deposition of Pt submono and monolayers on gold. The method is based

* Corresponding author. Tel.: +7 495 939 4027; fax: +7 495 932 8846.
E-mail address: podlov@elch.chem.msu.ru (B.I. Podlovchenko).

on galvanic displacement of adsorbed atoms of a non-noble metal (M_1) by Pt atoms due to a redox reaction with solution ions containing Pt(IV) or Pt(II) (in the literature several names are used for this process: galvanic displacement (GD), galvanic replacement (GR), spontaneous deposition (SD), surface limited redox replacement (SLRR)). Later, this method of gold decoration was employed in several studies [25,30,33–35]. Virtually all these studies used PtCl_6^{2-} anions as the displacing agent. The higher specific activity (calculated per Pt surface or Pt mass) of thus obtained electrodes in oxygen reduction and HCOOH oxidation reactions as compared with individual platinum electrodes was mentioned. However, certain problems associated with the structure of formed Pt deposits, its dependence on the formation conditions and also with the stability of both the structure and the activity of the Pt–Au system synthesized by the GD method require additional studies to be carried out.

The goal of this study was (i) to prepare Pt deposits on polycrystalline Au by the galvanic displacement of submono- and monolayers of copper adatoms (Cu_{ad}); (ii) elucidate the structure of thus prepared Pt coatings and its dependence on the preparation conditions; (iii) assess their electrocatalytic activity in CH_3OH and HCOOH electrooxidation reactions as a function of the surface coverage with platinum. When solving problem (i) and carrying out the GD process, the primary attention was drawn to eliminating the contact with air when passing from $\text{Cu}_{\text{ad}}/\text{Au}$ to Pt/Au [33]. The PtCl_4^{2-} anions were used as the displacing agent because, in contrast to PtCl_6^{2-} , they provide displacement of copper by platinum in the 1:1 ratio and rule out the possibility of partial ionization of Cu_{ad} due to the reaction $\text{PtCl}_6^{2-} \rightarrow \text{PtCl}_4^{2-}$. The comparison of data on the electrooxidation of CH_3OH and HCOOH carried out under the same conditions on platinum-decorated gold is of interest for elucidation the effect of the second component in binary Pt–M systems (where M is the catalytically inactive metal) on the catalytic activity of platinum.

2. Experimental Section.

2.1. Materials and Apparatus

All electrochemical measurements were carried out in a three-electrode cell with separate anodic and cathodic compartments. Working solution was stirred with a magnetic stirrer. Electrochemical experiments were carried out by means of an IPC-pro potentiostat-galvanostat developed at the A. N. Frumkin Institute of Physical Chemistry and Electrochemistry (Moscow). All potentials refer to the reversible hydrogen electrode in the same solution. We used Au (99.99%); all results were obtained in solutions prepared from sulfuric acid (Merck Suprapur), twice crystallized copper sulfate (reagent grade), K_2PtCl_4 (Aldrich), methanol and formic acid (both of analytical-grade purity (Fluka)). Water was cleaned in the Milli-Q unit (Millipore, USA). For solution deaeration, argon (special grade) was used. The working electrodes represented plates of pc Au and pc Pt ($S_{\text{geom}} = 1.0 \text{ cm}^2$). Counter electrodes represented gold or platinum wires.

The surface morphology of samples was examined on a scanning electron microscope JEOL JSM-6490 LV at the accelerating voltage of 30 kV. Samples surface was analyzed by X-ray photoelectron (XPS) and Auger (AES) spectroscopy using Axis Ultra DLD spectrometer (Kratos Analytical Ltd, UK) with hemispherical analyzer. XPS and Auger spectra were excited with monochromatic Al K_{α} (1486.6 eV) radiation source and 10 kV electron gun, respectively. The binding energy scale of the instrument was calibrated with Au $4f_{7/2}$ (83.96 eV) and Cu $2p_{3/2}$ (932.62 eV) peaks of sputter cleaned gold and copper metals. XPS spectra were acquired in the constant analyzer energy mode with 160 eV pass energy for

survey spectra and 40 eV for narrow scans. Electron gun excited Auger spectra were recorded in the constant retard ratio mode.

2.2. Preparation of Pt^0Au Electrodes and Electrochemical Measurements

Prior to experiments, the potentials of Au and Pt electrodes were cycled at $\nu = 50 \text{ mV/s}$ in 0.5 M H_2SO_4 in intervals of 50–1700 mV (Au) and 50–1450 mV (Pt) until steady-state voltammograms were obtained. Figure 1a shows typical CVA for Pt and Au electrodes. The true surface of Au electrodes (S_{tr}) was determined from the charge consumed in the oxygen electrodesorption under an assumption that at $E = 1.70 \text{ V}$, the layer of O_{ads} corresponds to the charge of $420 \mu\text{C cm}^{-2}$ [36,37]. The surface of pc Pt was assessed from the hydrogen adsorption ($210 \mu\text{C cm}^{-2}$) [38]. The electrode roughness factors were 4.6 ± 0.2 for Au and 4.5 ± 0.2 for Pt.

The procedure of measuring transients of open-circuit potential observed upon bringing PtCl_4^{2-} anions into contact with the Pt electrode both in the absence and in the presence of Cu_{ad} on its surface was described in sufficient detail elsewhere [39]. The measurements on Au electrodes were carried out by the similar procedure. Here, we describe the main experimental stages. As for pc Pt [39], the Cu_{ad} monolayer (ML) on pc Au was formed in the solution of 2 mM $\text{CuSO}_4 + 0.5 \text{ M H}_2\text{SO}_4$ at $E = 290 \text{ mV}$. The circuit was opened and immediately after this (in $< 2 \text{ s}$) the deaerated solution of 0.5 M $\text{H}_2\text{SO}_4 + 10^{-3} \text{ M PtCl}_4$ was added to the solution in contact with the working electrode under the pressure of argon. After its addition, the PtCl_4^{2-} concentration became 10^{-4} M . A transient of open-circuit potential was recorded until the establishment of the steady-state potential E_{st} (the steady-state criterion was $dE/d\tau < 4 \text{ mV/min}$). The working part of the cell was washed with background solution 0.5 M H_2SO_4 . The charge corresponding to MLCu_{ad} (Q_{MLCu}) was $400 \pm 10 \mu\text{C/cm}^2$ (when S_{tr} was determined from O_{ads}). The resulting Q_{MLCu} values were close to that calculated in [37] based on the crystallographic structure of pcAu, which pointed to sufficient reliability of the S_{tr} determination based on oxygen adsorption. The Q_{MLCu} value was later used in determination of the gold surface coverage by Cu_{ad} (θ_{Cu}).

Figure 1b shows CVA measured on pc Au after the copper adsorption (adsorption time 60 s) in 2 mM $\text{CuSO}_4 + 0.5 \text{ M H}_2\text{SO}_4$ (curve 2). By setting the potential of copper adsorption in this solution, the θ_{Cu} vs. E dependence was obtained (Fig. 1b, insert). By changing the initial potentials E^{in} at which PtCl_4^{2-} anions were added to solution (i.e., at different θ_{Cu}), the amount of deposited Pt was varied. The stationarity criterion for the potentials established in solutions 0.5 M $\text{H}_2\text{SO}_4 + 10^{-4} \text{ M PtCl}_4$ and 0.5 M $\text{H}_2\text{SO}_4 + 2 \text{ mM CuSO}_4 + 10^{-4} \text{ M PtCl}_4$ (E_{st}) was their variation by less than 0.4 mV min^{-1} . After the attainment of a steady-state potential, the Au electrode was thoroughly washed with supporting electrolyte solution (0.5 M H_2SO_4) after which CVA were measured in this solution in order to determine the adsorption characteristics of the Pt^0Au surface formed and the degree of occupation of the Au electrode surface with the Pt deposit.

Figure 1c shows a CVA measured of the Pt^0Au electrode immediately after the displacement of a copper monolayer (curve 1) with the upper potential scan limit of 1700 mV. The curve demonstrates the hydrogen adsorption and desorption waves on platinum particles ($E \sim 50\text{--}300 \text{ mV}$) and also the waves of oxygen adsorption and desorption on both platinum particles (desorption peak at $\sim 780 \text{ mV}$) and the free gold surface (desorption peak at $\sim 1200 \text{ mV}$). The repeated cycling of electrode potential up to such high potentials leads to the reconstruction of Pt islets and/or partial dissolution of deposited platinum. According to Fig. 1c (curve 2), after 10 cycles, the adsorption of hydrogen and oxygen on the platinum deposit falls down but the amount of oxygen adsorbed on the gold surface increases. This is why, to preserve the characteristics of Pt^0Au

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