Journal of Electroanalytical Chemistry 756 (2015) 140–146

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jeac

Peculiarities in the electrocatalytic behavior of ultralow platinum deposits on gold synthesized by galvanic displacement

B.I. Podlovchenko [*],[1], Yu.M. Maksimov

Department of Chemistry, Moscow State University, Leninskie Gory, Moscow 119992, Russian Federation

A R T I C L E I N F O

Article history:
Received 14 May 2015
Received in revised form 29 July 2015
Accepted 2 August 2015
Available online 11 August 2015

Editor: J.M. Feliu

Keywords:
Au electrode
Galvanic displacement of Cu adatoms
Pt multilayers
MOR
FAOR

A B S T R A C T

Composites $Pt_n{}^0Au$ are synthesized in $PtCl_4^{2-}$ solutions by galvanic displacement of Cu_{ad} monolayers ($MLCu_{ad}$) from polycrystalline (pc) Au (to afford Pt_1^0Au), and also from Pt_1^0Au (Pt_2^0Au) and Pt_2^0Au (Pt_3^0Au). The data of open-circuit potential transients, CVA, SEM, and XPS studies indicate that the displacement of $MLCu_{ad}$ proceeds not layer-by-layer but to form Pt clusters. The degree of blocking of the Au surface by Pt is approximately (%): 65 (Pt_1^0Au), 80 (Pt_2^0Au), and 90 (Pt_3^0Au). These $Pt_n{}^0Au$ deposits simulate the gradual transition of Pt coatings close to monolayer to those formed by small Pt particles. The specific rates of methanol oxidation reaction (MOR) (per cm^2 of $EASA_{Pt}$) increase in the row: $Pt_1^0Au < Pt_2^0Au < Pt_3^0Au <$ pc Pt. For the formic acid oxidation (FAOR), the inverse dependence is observed: pc Pt $< Pt_3^0Au < Pt_2^0Au < Pt_1^0Au$. The difference is explained by the fact that the chemisorption of CH_3OH requires a larger area (≥3 Pt surface atoms), whereas its single-site adsorption results in formic acid oxidation by the direct path. It is assumed that the Pt/Au interface of particles plays the important role in the formation of active sites ("ensembles") for FAOR. The high specific mass activities (mA/mg Pt) of $Pt_n{}^0Au$ composites are observed not only in FAOR, but also in MOR, which is associated with the high degree of dispersion of these Pt deposits (~90–170 m^2 EASA/g Pt).

1. Introduction

Since the 60s of the last century up to nowadays, the electrooxidation of HCO compounds (small organic molecules) was always in the focus of attention of scientists [1–8]. First of all this is associated with the fuel cell problem. Fuels such as methanol and formic acid are the best alternative to hydrogen. Platinum is the best single-component catalyst for the methanol oxidation reaction (MOR) and Pd is the best catalyst for formic acid oxidation (FAOR). However, at present it is the nanostructurized catalysts built not of "pure" platinum metals but of their composites with the other *d*-metals that are the most popular. Their use allows one to decrease the consumption of the more expensive component and/or to enhance its activity.

The promising methods of enhancing the activity of a Pt catalyst consist in modifying its surface with ultralow amounts of another noble metal (Pd [9–11] and Au [12,13]) and also dispersing Pt microamounts over the surface of some other noble metal (Pd [14–16], Au [13,17–22]). Among numerous chemical and electrochemical methods proposed for modifying the Pt catalyst surface, the method of galvanic displacement (GD) (also called galvanic replacement, spontaneous deposition, surface-limited redox deposition) [17,21–26] shows the best promise. In this method, adatoms of the less electropositive non-noble metal (most often, Cu or Pb) serve as the mediators for the noble metal deposition. The modification of platinum can be described by formal equations

$$M_{1ad}/Pt + (n/z)M_2{}^{z+} \rightarrow (n/z)M_2{}^0/Pt + M_1{}^{n+},$$

$$M_{1ad}/M_2 + (n/z)Pt^{z+} \rightarrow nPt^0/M_2 + M_1{}^{n+},$$

where M_1 is the non-noble metal (M_{1ad} is its adatom) and M_2 is the noble metal.

The GP method is characterized by simplicity and easiness of dosing the deposited metals, because the deposit amount is determined by the amount of displaced metal M_1.

MOR and FAOR are the complex reactions which can proceed by several parallel routes [1–8,13,22,27–31]. Their common feature is that the current-determining route (the direct path) proceeds via adsorbed intermediate species weakly bound with the surface. The second route is the oxidation through strongly bound chemisorbed species (SCS), which is characterized by relatively low rates and inhibition of the direct-path oxidation by SCS. The main difference between the MOR and FAOR mechanisms falls to the region of low potentials (≤0.6 B vs. RHE), which is of greatest interest for fuel cells. The oxidation via the current-determining path is limited by the dehydrogenation stage for FAOR [3,6–8,28] and by the interaction by adsorbed species with adsorbed oxygen (probably, in the form of OH_{ads}) for MOR [1,2,5].

---

[*] Corresponding author.
E-mail address: podlov@elch.chem.msu.ru (B.I. Podlovchenko).

[1] ISE member.

http://dx.doi.org/10.1016/j.jelechem.2015.08.004
1572-6657/

There are also differences in the composition of adsorbed species both weakly bound and SCS [2,5–7,22]. According to the literature data, the acceleration of CH_3OH and HCOOH oxidation can be achieved by increasing their amount and/or by changing the binding energy of OH_{ads} (the bifunctional mechanism) [32,33], the geometric factor [6,22,34,35], the ensemble effect [36–38] and also by modifying the electronic state of the platinum surface [13,39,40].

The Pt–Au system turned out to be suitable for developing scientific concepts on the nature of electrocatalytic activity of Pt and the ways of its enhancement and also on the oxidation mechanisms of CH_3OH и HCOOH [12,13,17–22]. The studies on gold electrodes decorated with small amounts of Pt gained in importance for practice when it was shown that the specific activity of FAOR on Pt(Au) electrodes much exceeds the activity of monoplatinum catalysts. At the same time, no promoting effect of Au on the activity of Pt surface in MOR was observed [12,22,38].

In our previous study [22], we considered the electrocatalytic behavior of electrodes of polycrystalline (pc) gold decorated with submonolayers of Pt by the galvanic displacement of copper adatoms ($Pt_x{}^0Au$, $x \le 1$). It was shown that the displacement of a monolayer (ML)Cu_{ad} failed to afford a monolayer Pt coating. On $Pt_x{}^0Au$, the specific rates of MOR (per cm^2 of the electrochemically active Pt surface, i.e., $EASA_{Pt}$) were found to be lower than on compact pc Pt. At the same time, for FAOR the strong acceleration was observed. In [22], we also discussed the possible reasons for such a different effect of the Pt–Au contact on the platinum activity in MOR and FAOR.

In the present study, Pt was deposited on pc Au in amounts corresponding to the displacement of from one to three $MLCu_{ad}$ (the resulting deposit did not exceed 1.8 μg/cm^2 $EASA_{Au}$). We followed the changes in the adsorption properties and electrocatalytic activity of Pt (MOR and FAOR) in $Pt_n{}^0Au$ composites ($n = 1, 2, 3$) with the increase in n. These composites simulate the transition from Pt coatings close to a monolayer to the layers of Pt clusters. Analyzing the changes in the properties of $Pt_n{}^0Au$ observed with the increase in n is important as regards both the further development of fundamental concepts on the electrocatalysis by Pt–Au composites and the assessment of prospects for their practical application.

2. Experimental

The materials, the cell, the apparatus used and the procedure of Au electrode preparation to measurements were the same as in [22]. The roughness factors of electrodes were ~3.3 for Au and ~5.2 for Pt. The electrochemically active surface of gold $EASA_{Au}$ (the geometric surface was 1 cm^2) was determined based on the oxygen adsorption [41,42]; the $EASA_{Pt}$ was determined based on hydrogen adsorption [43]. The measurements were carried out at 19 ± 1 °C. The working electrode potentials are shown with respect to the reversible hydrogen electrode (RHE).

The monolayer of copper atoms ($MLCu_{ad}$) on the Au electrode was formed in a solution of 2 mM $CuSO_4$ + 0.5 M H_2SO_4 at $E = 290$ mV [22]. Immediately after opening the circuit, a portion of deaerated solution of 10^{-3} M K_2PtCl_4 + 0.5 M H_2SO_4 was added under argon pressure to the working compartment in order to reach the 10^{-4} M $PtCl_4^{2-}$ concentration. The transient of open-circuit potential was recorded to the point of establishment of its stationary value E_{st} (the stationarity criterion $dE/d\tau < 0.4$ mV/min). The working compartment of the cell was repeatedly washed with the supporting electrolyte solution, after which the measurements were carried out on the resulting electrode. The electrode corresponding to the first $MLCu_{ad}$ displacement was designated as Pt_1^0Au. Note that the subscript indicates not the coverage of the Au surface with platinum but the amount of displaced copper expressed in ML [22]. The platinum amount in the Pt^0Au composite was increased as follows. On the freshly synthesized Pt_1^0Au, CVA were recorded first in 0.5 M H_2SO_4 (in the E range of 0.05–1.45 V) and then in 2 mM $CuSO_4$ + 0.5 M H_2SO_4 (in the E range of 0.29–1.45 V). In the latter solution, a new $MLCu_{ad}$ was formed on Pt_1^0Au. After this the same operations as those undertaken when preparing Pt_1^0Au on Au were performed. As a result, the Pt_2^0Au electrode was prepared. The Pt_3^0Au electrode was formed by the same procedures from Pt_2^0Au.

The electrocatalytic activity of $Pt^0{}_nAu$ electrodes was tested in solutions of 0.5 M CH_3OH + 0.5 M H_2SO_4 and 0.5 M HCOOH + 0.5 M H_2SO_4. The CVA were recorded with 20-s exposure at the lower potential scan limit. In this paper, we show the steady-state CVA. Voltammetric curves of MOR and FAOR were recorded on $Pt_n{}^0Au$ electrodes formed from Pt_{n-1}^0Au and never before subjected to polarization measurements in CH_3OH and HCOOH solutions.

3. Results and discussion

3.1. Transients of open-circuit potential

Curves in Fig. 1 show the potential variation on $MLCu_{ad}Au$ (1), $MLCu_{ad}Pt_1^0$ (2), $MLCu_{ad}Pt_2^0Au$ (3) and $MLCu_{ad}Pt$ (4) electrodes after bringing them in contact with $PtCl_4^{2-}$ anions under open-circuit conditions. The delays observed in the potential region from 300 to ~750 mV correspond to the removal of Cu_{ad} according to the reaction

$$Cu_{ad} + PtCl_4{}^{2-} \rightarrow Cu^{2+} + Pt^0 + 4Cl^- . \tag{1}$$

The time required for the $MLCu_{ad}$ removal increased with the increase in the gold coverage with platinum (curves 1–3), which agrees with the high rates of Cu_{ad} displacement from pc Au as compared with pc Pt [44]. However, for the formation of Pt_3^0Au too, the time of $MLCu_{ad}$ displacement (curve 3) was still substantially lower than the time of $MLCu_{ad}$ displacement from pc Pt (curve 4). This allows us to assume the presence of Au areas free of Pt on the Pt_3^0Au surface and/or the acceleration of reaction (1) on the Pt atoms in contact with Au.

After the removal of $MLCu_{ad}$, the potential rise in curves of Fig. 1 was determined by the changes in the electrode total charge Q [43–45] as a result of reaction

$$PtCl_4{}^{2-} + 2e \rightarrow Pt^0 + 4Cl^- . \tag{2}$$

The stationary potential (E_{st}) on $Pt_n{}^0Au$ electrodes was established the higher the larger n, but did not exceed 900 mV. At these potentials, oxygen is not yet adsorbed on Au but is adsorbed in small amounts on Pt and its adsorption is reversible [43]. It can be assumed [44] that the reaction $Pt^0 + H_2O + e \leftrightarrow Pt^0OH_{ads} + H^+$ is potential determining. However, E_{st} is of the mixed nature, because the surface concentration of OH_{ads} is determined by compensation of rates of the reduction of

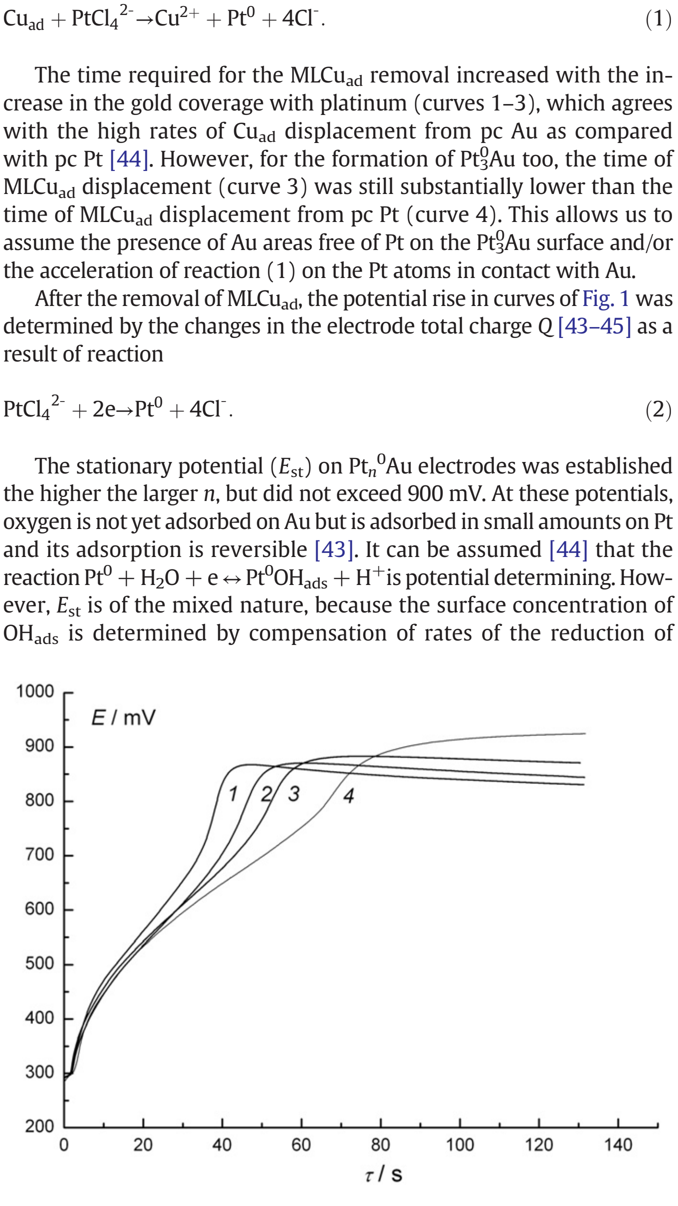

Fig. 1. Transients of open-circuit potential corresponding to displacement of $MLCu_{ad}$ from (1) Au, (2) Pt_1^0Au, (3) Pt_2^0Au and (4) Pt in 0.1 mM K_2PtCl_4 + 0.5 M H_2SO_4.