A VOLTAMMETRIC STUDY ON THE ELECTROCATALYTIC ACTIVITY OF A Pt OVERLAYER CHEMICALLY DEPOSITED ON Au SUBSTRATES

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ABSTRACT

A chemical modification of Au substrates by electroless deposition of Pt is achieved. The procedure used is based on the classical one comprising chemical reduction from a complex alkaline Pt(IV) hydroxide solution by hydrazine and subsequent heating of the electrode material at 393.2 K for at least 3 hours. Pt deposits corresponding to Pt surface content ranging from 0.20 to 0.60 are obtained aiming comparison with Pt+Au alloys electrocatalytic activity. The latter is well outlined in this particular composition range. The enhanced catalytic properties of the electrode materials obtained are investigated in the electrooxidation of 1,3-propanediol in KOH medium. The apparent activation energy of the process is found dependent on Pt surface content. The plot obtained is juxtaposed to that derived from the study of the same process but on Pt+Au alloys. It is shown that the apparent activation energy of the alcohol's electrooxidation is lower when Pt+Au alloys of Au surface content less than 0.70 are used. The most plausible explanation discussed refers to the interaction between the adsorbate valence states and the metal surface resulting from the deposition although the effect of Pt clusters' size and the type of the substrate can not be excluded.

Keywords: electroless deposition, electroless deposition of Pt upon Au, electrooxidation, Pt+Au alloys

INTRODUCTION

Bimetallic and alloys materials are well known to have unique catalytic properties for many important chemical transformations [1]. They have been a particularly active area of research in electrocatalysis [2]. Bi- or even tri-metallic anodic materials are used to improve the CO tolerance of hydrogen and methanol oxidation in low-temperature fuel cells [3-6]. It is well known that alloying changes the adsorption [7,8] and reaction [9] properties of the metals used. Changes in the interaction between the adsorbate valence states and the metal surface can be also achieved by deposition of a monolayer or overlayers of another metal [10-12], i.e. by shifting the d-state of the substrate. More stable adsorbate states and hence lower activation energies are usually expected to result.

Innovative recent research has suggested that Au-based catalysts are potentially capable of being effectively employed in fuel cells and related hydrogen fuel processing. The justification for developing the Au catalyst technologies described, is not only based on their promising technical performance, but also on the relatively low stable price and greater availability of Au when compared with the Pt group metals [13]. Au, contrary to Pt is considered as a poor catalyst towards methanol oxidation especially in acidic solutions, but poisoning intermediates are not formed [14]. The electrocatalytic properties of the metal can be improved by selecting appropriate medium for the reaction [14],
alloying with Pt [15-18] or other metals, modifying the electrode surface structure by perturbation [19,20] or by forming overlayers [12].

A recent study [17] on the electroabsorption of a model alcohol at a Pt+Au-alloy reports an energetically more favorable process when compared to that at Pt and Au. The enhanced adsorption of reactants and intermediates on the alloy and the resulting increased rate of the overall process of oxidation [18] are ascribed to the electronic effect in alloys electrocatalysis. The investigation of the effect of alloys bulk composition [18] shows that the lowest apparent activation energy of electrooxidation refers to an alloy containing ca 55 at. % of Au. The latter value is very close to that for which the d-band vacancies of Pt are filled [21]. The aim of the present study is to study the electrocatalytic activity of Au electrodes modified by electroless deposition of Pt, to outline the effect of the surface composition of these anode materials and to compare the results obtained to those referring to Pt+Au -alloy electrodes.

**EXPERIMENTAL**

Electroless deposition of Pt on Au substrates (the roughness factor was above 2.0) was carried out in accordance with the procedure described in [22]. The bath was prepared by boiling water solution of chloroplatinic acid with an excess of NaOH. The end point of the reaction was marked by solution color change from blood red of chloroplatinic acid to an orange characteristic of the aqueous solution of Na₂Pt(OH)₄. The content of the latter was 10 gl⁻¹. The bath pH was maintained on the alkaline side to prevent undesired hydrolysis of the solution. This was achieved by introducing 1.0 M KOH. The reduction was carried out with N₂H₄ which was added to the bath continuously as N₂H₄.H₂SO₄ dissolved in H₂O. Its content in the bath was 1 gl⁻¹. The temperature was maintained at 298.2 K. The deposition time varied to reach different surface content of Pt. After the deposition the electrodes were kept at 393.2 K for at least 3 hours. This was found of crucial importance for the coating stabilization. Thus Pt deposits of finely divided structure and enhanced catalytic properties were obtained. The surface composition and the true electrode surface of the materials prepared was checked prior to and after each experiment carried out in 0.1 M 1,3-propanediol in 1.0 M KOH. The procedure [23,24] is identical with that applied to Pt+Au alloys as the response of the modified Au electrodes in 1.0 M KOH is similar to that of the alloys. It is based on the determination of charges required for O-coverage reduction at Au and H-coverage formation at Pt.

Cyclic voltammetry (CV) was applied in the potential range 0.05 V-1.55 V with a scan rate of 0.10 Vs⁻¹ at five temperature values varying from 293.2 K to 313.5 K. The accuracy was ± 0.2 K. Doubly distilled water, Fluka (purum) 1,3-propanediol and Merck (p.a.) KOH were used to prepare the solution investigated. It was purged with nitrogen. The gas inflow was interrupted prior to the CV profiles recording. The latter continued until reproducibility of the electrode response was achieved at the temperature value set in advance. The gradual increase of the current density observed during the cycling was considered as an additional criterion for a stable surface coverage of Pt.

The experiments were carried out in two identical three-compartment cells and conventional electrochemical equipment described elsewhere [17,18]. The electrode set consisted of an Au plate electrode used as a substrate for Pt deposition, an Au counter electrode and an Hg/HgO/1MKOH reference electrode. All potentials are reported against the reversible hydrogen electrode (RHE).

**RESULTS AND DISCUSSION**

Prior to the discussion of the experimental data it is important to visualize the respond of the working electrode which followed the electroless deposition of Pt. Fig. 1 presents CV profiles recorded in 0.1 M 1,3-propanediol after the stabilization of the Pt coverage. The effect of temperature increase is demonstrated as well. It is seen that in both cases illustrated the Au substrate surface is modified by Pt, as the first anodic peak at ca 0.8 V is well outlined, i.e. the response is analogous to that of Pt+Au alloys. The CV profiles presented show that the current density (iₜ) of the first anodic maximum grows, while its peak potential shifts towards higher positive potentials with temperature increase. It can be concluded that in this respect too the electrodes behavior is identical with that of Pt+Au al-
The further comparison shows that the peak current densities obtained are very close in values for the both electrode systems but the temperature effect on the anodic process discussed is more pronounced at the modified Au substrates. Therefore it seems reasonable to expect higher apparent activation energies of the overall anodic process taking place at the modified Au electrodes when compared to those found for the process at the alloys irrespective of the fact that the catalytic activity of the Pt deposit is obviously enhanced.

The validity of this statement can be verified by estimating the apparent activation energy of the alcohol’s electrooxidation at ca 0.8 V and studying its dependence on Pt content on the substrates surface and by comparing the results obtained with those referring to the same process but taking place at Pt+Au alloys of varying composition. Thus, the Arrhenius plots in the form of ln i_p vs. 1/T were studied. Some of the linear graphs obtained are presented in Fig. 2. The values of the apparent activation energy derived were found dependent on the surface content of Pt. This is visualized in Fig. 3. It is seen that the Pt deposits obtained refer to a definite range of surface compositions which is of interest when comparing the electrocatalytic activity of the electrodes studied and that of Pt+Au alloys [18]. It is important to note that the points corresponding to the apparent activation energy of the process taking place at Au and at Pt are shown in Fig. 3 as well. It is seen that the plot discussed goes through a minimum (the minimal value is of 21.06 kJ mol^{-1}) at Au surface content of ca 0.75, i.e. the apparent activation energy for the process on the modified electrodes is lower than those determined for Pt and Au. The study on the bulk composition effect of Pt+Au alloys on the electrooxidation kinetics of 1,3-propanediol in KOH medium [18] provides data on the standard rate constant of the process and its dependence of the electrode composition and the temperature of the electrolyte. The information reported was used to derive...
the dependence of the apparent activation energy of the alcohol’s electrooxidation on the surface composition of the alloy electrocatalysts. The graph obtained, presented in the same figure (Fig. 3) goes through a minimum as well but it is outlined at Au surface content of 0.55 and the value of the corresponding apparent activation energy is 13.37 kJ mol\(^{-1}\). The results just reported are in full correspondence with the findings discussed in ref. [18]. This is worth mentioning because there is no data in the literature on the effect of the surface composition of Pt+Au alloys on their electrocatalytic activity. The juxtaposition of both plots shows that in the range of higher surface content of Pt, i.e. at Au surface content less than 0.70 the anodic process studied proceeds with a lower apparent activation energy at the alloy electrodes. A few explanations can be considered. One of these can be attributed to the fact that the apparent activation energy of the process taking place at the modified Au substrates was estimated on the ground of the temperature dependence of the peak current density. Therefore, some slight changes can be expected if the standard rate constant of the process is determined and its dependence on the electrode’s surface composition and the electrolyte temperature is studied. It seems plausible to explain the difference discussed with the interaction [10-12] between the surface sites occupied by Pt and the neighboring Au sites, i.e. to the interaction between the adsorbate valence states and the metal surface resulting from the deposition. This interaction can be enhanced by increasing the temperature and the duration of the deposits stabilization procedure. The Pt clusters’ size as well as the type of the substrate used can change dramatically the kinetics of the alcohol’s electrooxidation. The studies [25] which are in progress will provide knowledge for better understanding of these factors.

CONCLUSIONS

A chemical modification of Au substrates by electroless deposition of Pt is achieved. The procedure used is based on the classical one comprising chemical reduction from a complex alkaline Pt(IV) hydroxide solution by hydrazine and subsequent heating of the electrode material at 393.2 K for at least 3 hours. The electrocatalytic activity of the modified Au substrates was studied in the process of electrooxidation of 1,3-propanediol in KOH medium. The apparent activation energy of the process investigated was found dependent on Pt surface content. The comparative consideration of the results obtained and those derived from the study of the same process but on Pt+Au alloy electrode materials shows that the latter are better electrocatalysts than the modified Au substrates if the surface content of Au is less than 0.70. The plausible explanations discussed refer mainly to the procedure of apparent activation energy estimation, to the interaction between the adsorbate valence states and the metal surface resulting from the deposition, to the effect of Pt clusters’ size and the type of the substrate.

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REFERENCES