Electrochemical oxidation of methanol on the surface of nanostructured Pd-Au

Oksana Dobrovetska

Department of Chemistry and Technology of Inorganic Substances, Lviv Polytechnic National University, UKRAINE, Lviv, S. Bandery street 12,
E-mail: oksana_dobrovetska@ukr.net

Abstract – The method of cyclic voltammetry researched the catalytic activity of nanostructured Pd-Au in electrooxidation of methanol in an alkaline environment. It was found, that during the anodic oxidation of methanol on the surface of the Pd-Au/GC electrode is manifested sequential catalytic action of components palladium and gold.

Keywords – nanostructure, Pd-Au, electrocatalys, methanol.

I. Introduction

In the last decade against the background of intensive development of nanotechnology is growing interest in the use of nanoscale materials in heterogeneous catalysis [1]. Catalysis on the nanoscale particles apparently can be seen as a manifestation of chemical dimensional effect. The especially is concern to metal nanoscale catalysts. It was found [2], that the use of nanoscale catalysts could affect the kinetics, yield of product and thermodynamics of catalytic reactions.

Due to the high energy capacity on today perspective is direct methanol fuel cells, as a power source for portable electronic devices and means of transportation [3]. In these fuel cells use electrodes, on which deposited the catalyst bed – usually metals or alloys of platinum group.

In recent years, started extensive research of processes obtaining of nanostructured Pd-Au catalyst, the components of them have a high catalytic activity in the oxidation reaction of alcohols [4-5]. It is known [6-7] that catalysts on based of nanosystems Pd-Au have higher activity than those which on based monometallic. The aim of this work was to research of the catalytic activity obtained by us nanostructured Pd-Au/GC electrode [8-9], in electrochemical oxidation of methanol in alkaline solutions.

II. Experimental

The main method research of catalytic properties of nanoparticles Pd-Au, obtained electrochemically on the surface glassy carbon was method of one and many cyclic voltammetry. Cyclic voltammogramms registered by using potentiostate Bipotentiostat (Model AFCBP1).

Research was carried out in aqueous solutions methanol composition: 0.5M NaOH + (0.5 ... 2.0)M CH_3OH, at room temperature, in the range of potentials -0.8 ... +0.5 V. By means of program VAM-9 was fixed change in current over time, which flowed through the studied system by overlay on her potential. The direction of potential sweep was originally anode, then automatically changed to the reverse (cathode) and returned is practically to the original value potential. The scanning speed of potential was 50 $mV \cdot s^{-1}$ for all the systems.

Polarization studies were performed in a standard three-electrode cell volume of 50 cm^3. The potential was measured by relative to a standard silver chloride reference electrode. The auxiliary electrode was a platinum plate area of 2 cm^2. The working electrode was a glassy carbon coated with a layer of nanostructured Pd-Au.

III. Results and discussion

Cyclic voltammogramms showed that anodic oxidation of methanol on the surface of the nano-Pd-Au (the exact thickness of 30 nm) is bifunctional and stage (fig. 1). Proof of this is the presence of two peaks of densities currents. The first peak corresponds to oxidation by the direct of scanning, the second – by reverse. For E = -0.11 V, ie in the area of first peak, catalytic action more measure shows palladium, as confirmed by coincidence maximums of current densities nano-Pd-Au (fig. 1, curve 3) and nano-Pd (fig. 1, curve 2). In the area of second peak (E = -0.25 V) catalytic action, preferably, manifests gold. For a potential first peak occurs oxidation of methanol to form the intermediate. The second peak density of the anode current responsible, preferably, pre-oxidation intermediates to the end product CO_2.

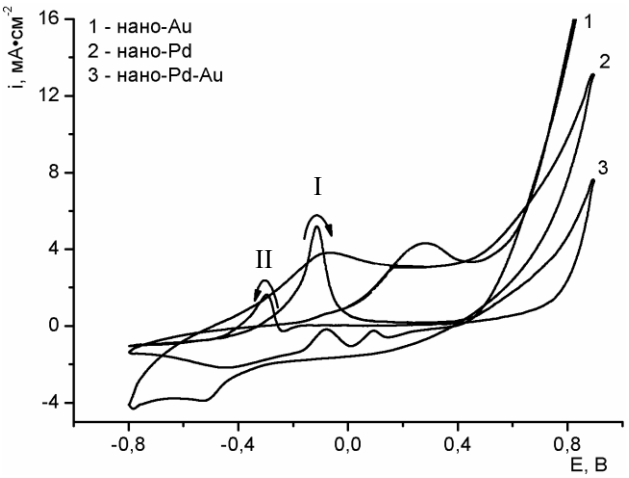

Fig. 1. Cyclic voltammogramms oxidation of methanol on the surface of the nanostructured Pd, Au and Pd-Au in composition of the solution: 0.5M NaOH + 2.0M CH_3OH

Comparing the characteristics of the electrochemical oxidation of methanol by using nanostructured catalyst Pd-Au/GC with nano-Pd/GC and nano-Au/GC are seeing: higher catalytic activity of nano-Pd-Au/GC, shift of potentials oxidation to less positive values, lack processes of renewal by reverse scanning. If using nano-Pd-Au/GC rate of oxidation of alcohol is 1.5 times greater than the rate of oxidation on nano-Pd / GC and nano-Au/GC, that indicates the catalytic effectiveness of nano-Pd-Au/GC catalyst.

The defined of regularities the impact of the concentration of methanol (0.5 ... 2.0M) on the catalytic activity of nanostructured Pd-Au/GC. According to increase of concentration methanol from 0.5 to 2.0M in 0.5M NaOH solution observed slight shift of potential maximums density current both peaks in positive direction (ΔE = 0.01V за ΔC_{CH3OH} = 0.5M) (fig. 2, table 1), which can be explained the adsorption factor of methanol molecules.

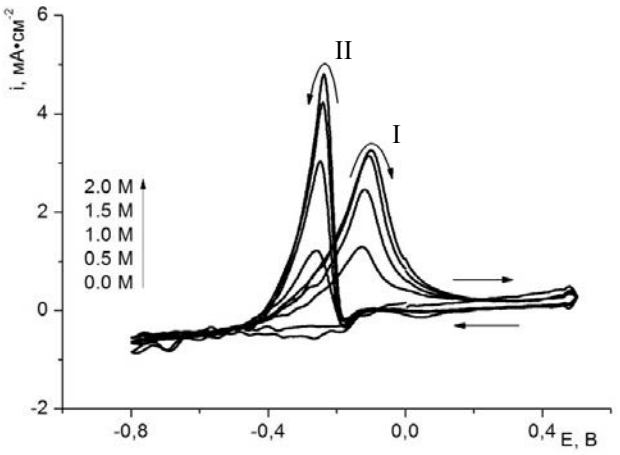

Fig. 2. Cyclic voltammogramms oxidation of methanol on the surface of the nanostructured Pd-Au/GC. The solution of 0.5M NaOH with concentrations of CH_3OH 0.5…2.0M

At the same time increasing the content of alcohol increases the density of anodic current. However, such increase is disproportionate in a wide range of concentrations of methanol. So, by increasing the content of latest from 0.5 to 1.0M maximum density current of oxidation increases almost twice. By further increasing of the concentration of methanol from 1.0 to 2.0M increment density current decreases, and for an increase to 3.0M, growth rate of alcohol oxidation almost no observed, which can be explained a kind of "saturation" surface of nanostructured Pd-Au/GC electrode adsorbed molecules of methanol.

TABLE 1

ELECTROCHEMICAL CHARACTERISTICS (E, i) OXIDATION OF METHANOL ON THE SURFACE OF THE NANOSTRUCTURED PD-AU ELECTRODE DEPENDING ON THE CONCENTRATION OF ALCOHOL IN THE SOLUTION

№	C_{CH3OH}	I peak		II peak	
		E, V	i, мА·cm^{-2}	E, В	i, мА·cm^{-2}
1.	0.5	-0.12	1.30	-0.25	1.21
2.	1.0	-0.12	2.44	-0.25	3.02
3.	1.5	-0.11	3.12	-0.25	4.18
4.	2.0	-0.10	3.23	-0.24	4.81

Conclusion

Electrooxidation of methanol on the surface of nanostructured Pd-Au happens with sequential catalytic action of palladium and gold. By increasing the methanol concentration from 0.5 to 2.0M in 0.5M NaOH solution occur shift of potential maximums of current density anodic oxidation in a positive direction, which is associated with adsorption factor of alcohol molecules.

The catalytic activity nanostructured Pd-Au/GC of catalyst is 1.5 times greater than comparison with activity on nano-Pd / GC and nano-Au/GC, that indicates the catalytic effectiveness of nano-Pd-Au/GC electrode.

References

[1] Volkov S.V, Kovalchuk E.P, Ohnenko V.M Reshetnyak E.V "Nanchimia, nanosystemy, nanomaterialy", Kyiv: Naukova Dumka, 2008, 423 p.

[2] Guzman J., Gates B.C. “Catalysis by supported gold: correlation between catalytic activity for CO oxidation and oxidation states of gold” J. Amer. Chem. Soc, vol 126, pp. 2672–2673, 2004.

[3] Hacquard A. “Improving and understanding direct methanol fuel cell (DMFC) performance” MS thesis – Worcester,. 107 p. 2005

[4] Shim J.H., Kim J., Lee C., Lee Y.”Porous pd layer-coated au nanoparticles supported on carbon: synthesis and electrocatalytic activity for oxygen reduction in acid media” Chem. Mater., vol. 23, pp. 4694-4700, 2011.

[5] Song H.M., Moosa B.A., Khashab N.M. “Water-dispersable hybrid Au–Pd nanoparticles as catalysts in ethanoloxidation, aqueous phase Suzuki–Miyaura and Heck reactions” J.Mater. Chem., vol. 22, pp. 15953-15959, 2012.

[6] You H., Yang S., Ding B., Yang H. “Synthesis of colloidal metal and metal alloy nanoparticles for electrochemical energy applications” Chem. Soc. Rev., vol. 42, pp. 2880-2904, 2013.

[7] Li H., Chen G.X., Yang H.Y. “Shape-Controlled Synthesis of Surface-Clean Ultrathin Palladium Nanosheets by Simply Mixing a Dinuclear Pd^{I} Carbonyl Chloride Complex with H_2O” Angew. Chem. Int. Ed., vol. 52, pp. 8368-8372, 2013.

[8] Dobrovetska O., Kuntyi O., Saldan I., Korniy S., Okhremchuk Ye., Reshetnyak O. “Nanostructured gold–palladium electrodeposited in dimethyl sulfoxide solutions” Mater. Lett., vol. 158, pp. 317-321, 2015.

[9] Dobrovetska O., Fratini E., Saldan I. and etc. “Nucleation and growth of Au and Au–Pd nanoparticles at the beginning of electrochemical deposition” Mater. Lett., vol. 161, pp. 263-266, 2015.