

ELECTROCATALYSTS FOR DIRECT METHANOL AND ETHANOL FUEL CELLS PREPARED WITH USE OF ION BEAM ASSISTED DEPOSITION TECHNIQUE

V.V. Poplavsky, A.V. Dorozhko, V.G. Matys

Belarusian State Technological University, Minsk, Belarus, vasily.poplav@tut.by

The prospects of developing alternative hydrogen energy are linked to production of hydrogen and its used for obtaining energy with the us of fuel cells. In a fuel cell energy, which is being emitted by electrochemical oxidation of fuel, is converted directly to electrical power. Fuel cells offer the promise of high efficiency and low emissions when compared to conventional technologies. The most developed are hydrogen-oxygen (or hydrogen-air) fuel cells. Intensive research is held on development of DMFC – direct methanol fuel cells, as well as DEFC – direct ethanol fuel cells. In a direct alcohol fuel cell (DMFC, DEFC) system, methanol or ethanol are converted directly to hydrogen. At the same time this approach helps resolve the problems of obtaining, storage and distribution of hydrogen.

A catalyst is needed for effective operation of fuel cell. An obstacle for the development of fuel cells is their high cost which is caused, first of all, by the cost of catalysts. That is why one of the main tasks is development of efficient catalysts for fuel oxidation with lowest possible content of platinum metals. On other hand ion-beam modification of the materials whose service properties are mainly controlled by the surface composition is of particular interest. These materials include catalysts for chemical reactions, in particular, electrocatalysts, namely, electrodes in electrochemical devices (electrolyzers and fuel cells) [1, 2].

We have introduced a method for preparation of methanol and ethanol oxidation catalysts by vacuum-based deposition of active metals. Active layers of the electrocatalysts were prepared by ion beam assisted deposition (IBAD) of catalytic metals onto carbon (AVCarb[®] Carbon Fiber Paper P50 (Ballard Material Products Inc.)) and valve metal (Al, Ti, Ta) supports [3–7]. Metal deposition and mixing between the precipitable layer and surface substrate atoms by accelerated ions of the same metal were carried out on the experimental unit from a neutral vapor fraction and the vacuum-arc discharge plasma of a pulsed electric arc ion source, respectively. The ions of the deposited metal have an effect of ions assisting to the process. Ion accelerating voltage is 10–20 kV; vacuum – 10^{-2} Pa.

The activity of prepared electrocatalysts has been measured during the electrochemical oxidation of methanol and ethanol via cyclic voltammetry [8]. Measurements were carried out in solutions of methanol and ethanol and sulfuric acid (1M CH₃OH + 0.5M H₂SO₄ and 1M C₂H₅OH + 0.5M H₂SO₄) at 20°C. The solutions were prepared from pure grade reagents using distilled water. As a working electrode, we used a sample; as an auxiliary electrode, we used a platinum electrode; and a saturated chlorine-silver electrode served as a reference electrode. For comparison, the voltammetry characteristics of a platinum electrode were measured under similar conditions.

Cyclic voltammograms characterizing the activity of prepared electrocatalysts on metal (tantalum) and carbon fiber paper substrates in the oxidation of methanol and ethanol processes are presented in Figs. 1, 2. The electrochemical oxidation of alcohol in a sulfuric acid solution appears, according to the cyclic voltammograms, in the form of specific current peaks when the electrode potential changes in both the anode and cathode directions. The anode parts of the voltammograms have current peaks, which arise from the multistage process of methanol or ethanol oxidation involving the electrochemical adsorption and decomposition of alcohol molecules and the formation

of adsorbed carbon monoxide (CO_{ads}) molecules. Thereafter, the latter are removed due to interaction with chemisorbed water molecules or OH_{ads} groups, followed by the generation of hydrogen ions and CO_2 [9]. The following current reduction can be explained by the decreased rate of electrochemical oxidation of alcohol because the catalyst surface is covered by electrochemically adsorbed water. During subsequent scanning of the potential in the cathode direction, the current peaks of the voltammograms are observed due to the renewal of alcohol oxidation. An oxidation reaction becomes possible only if the catalyst surface is reconstructed and adsorbate-free platinum atoms ensuring the electrochemical oxidation of alcohol are generated.

Comparison of cyclic voltammograms of prepared electrocatalysts and Pt electrode indicates that the processes of methanol and ethanol electrochemical oxidation on all electrodes are similar. However, the maximum current densities of alcohol oxidation on the test specimens are substantially higher than those on a platinum electrode, which indicates high electrocatalytic activity of prepared layers.

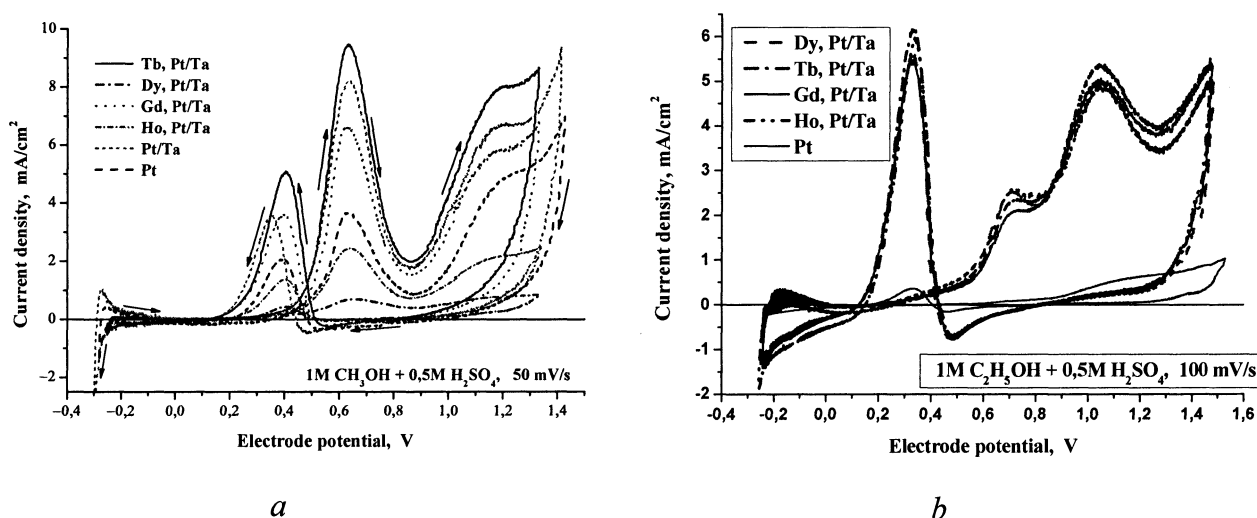


Fig. 1. Cyclic voltammograms of Ta-based electrocatalysts prepared with use rare earth metals and platinum IBAD in methanol (a) and ethanol (b) comprising ($1\text{M CH}_3\text{OH} + 0,5\text{M H}_2\text{SO}_4$; $1\text{M C}_2\text{H}_5\text{OH} + 0,5\text{M H}_2\text{SO}_4$) solutions (vs Pt-electrode) [5]

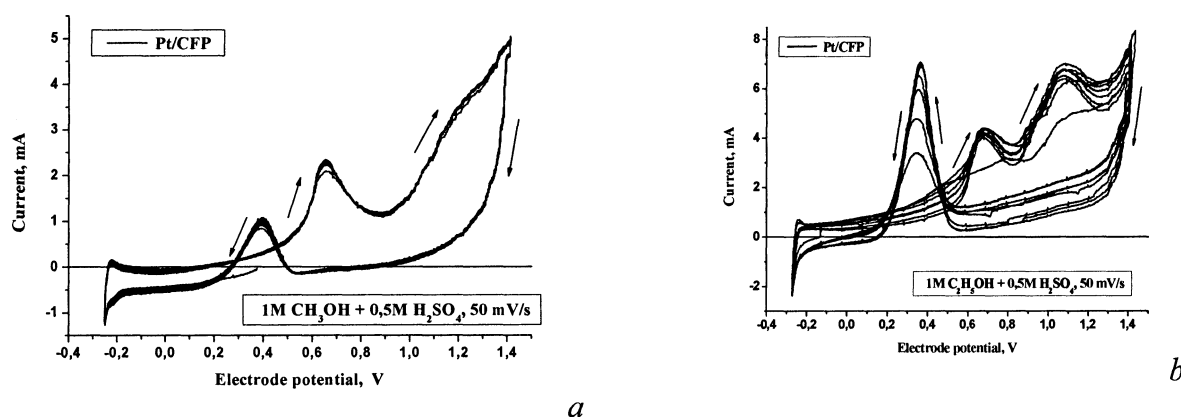


Fig. 2. Cyclic voltammograms of electrocatalysts prepared with use platinum IBAD on carbon fiber paper (CFP), which were obtained in the $1\text{M CH}_3\text{OH} + 0.5\text{M H}_2\text{SO}_4$ (a) and $1\text{M C}_2\text{H}_5\text{OH} + 0.5\text{M H}_2\text{SO}_4$ (b) solutions

Investigation of the composition and microstructure of layers was carried out by RBS (^4He ; $E_0 = 1.0 - 2.0$ MeV; AN-2500 High Voltage accelerator, SEM and EPMA (JEOL JSM-5610 LV electron microscope; 20 keV), and EBSD (HKL Channel 5 Premium EBSD phase analysis system and the LEO 1455 VP microscope; 20 keV; 70°) methods.

It has been established that the obtained catalytic layers are characterized by amorphous atomic structure and contain the atoms of deposited metals, substrate material, as well as impurities of oxygen, carbon and hydrogen; their thickness reaches $\sim 30-100$ nm. Atoms of the elements entering into the layers composition are uniformly distributed over the surface. According to RBS-data (see, for example, Fig. 3) the content of platinum atoms in the layers is $\sim (2-3) \cdot 10^{16} \text{ cm}^{-2}$, concentration of platinum atoms in the deposition maximum equals about a few at.%.

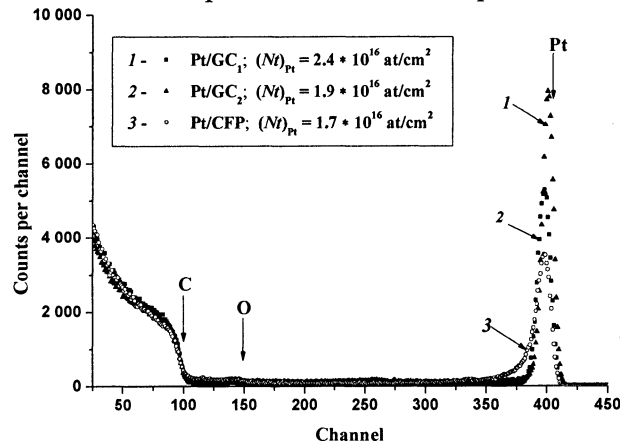


Fig. 3. RBS spectra of ^4He ions ($E_0 = 1.3$ MeV) scattered from a glasslike carbon (GC) and carbon fiber paper (CFP) surfaces with a layers prepared by platinum deposition

The activity of prepared electrocatalysts in the reactions of electrochemical oxidation of methanol and ethanol, which form the basis for the principle of operation of low temperature fuel cells (DMFC and DEFC), are significantly higher than the activity of a platinum electrode. The content of platinum in the prepared layers is less than 0.01 mg/cm^2 , whereas the platinum content in electrocatalysts for DMFC and DEFC, which are used at present, is $1-5 \text{ mg/cm}^2$.

In comparison with the traditional methods of preparation the deposited catalysts, proposed one stage IBAD method appear to be promising and often more preferable. They allow the introduction of microamounts of a doping impurity in the near-surface layer of a substrate under nonequilibrium conditions and the formation of cohesive catalytic layers at ultra-low platinum consumption.

Along with the investigations we have started developing devices for electrocatalysts testing. Some experimental samples of electrocatalysts and membrane electrode assemblies

(Sn, Pt / AVCarb® Carbon Fiber Paper | DuPont™ Nafion® N 115 | Pt / AVCarb® Carbon Fiber Paper),

5 cm^2 PEM testing fuel cell, air bath, and cell testing bench have been created. Initial results of membrane electrode assemblies' properties investigation have been obtained.

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