Electrochemical formation of functional materials of new generation: nanostructured coatings with pre-set properties (for electronics and energy)

O. L. Bersirova, V. S. Kublanovsky
V.I. Vernadskii Institute of General and Inorganic Chemistry NAS of Ukraine, Kiev, Ukraine
e-mail bersibol@ukr.net

Proposed work deals with the fundamental problem of the modern electrochemistry: synthesis of materials with tailor-made structure and properties in a controlled and repeatable way for various practical applications, as well as with materials science as its methodologies will be used for chemical and structural characterization of obtained materials as well as for determination of functionality.

Concept of the study is to develop a theory and practice of controlling the electrodeposition of functional films of alloy with tailor-made nanostructure and properties. Now such a general theory does not exist in the world, there are only scattered data concerned each particular case. The efficiency of transformation of chemical energy in electric one in fuel cells (FC) is determining the constant of rate of electrochemical electrode reaction, reversibility of electrochemical process and electrochemical resistance of the system. A tendency in creation of electrocatalysts is a transition from monometallic constructions to multi-component with a certain structure and functionalization. The idea of the work consists in the use of bifunctional electrocatalysis, which is conditioned by the action of different in nature catalytic centers included in one structure at a certain spatial arrangement of them. These centers have to be of nucleophilic and of electrophilic nature, that creates conditions for the selectivity and electrocatalysts efficiency.

The problem of the catalytic activity of *d*-metal alloys in the hydrogen evolution reaction (HER) is discussed in the literature. Hydrogen overvoltage reaction significantly affects the number of vacant *d*-orbitals in the electronic structure of the metal or alloy, the nature of this influence depends on the limiting step of the process of hydrogen evolution. Based on the analysis of the electronic configuration of metals belonging to the binary alloys it was found that the greatest catalytic effect on the HER should be observed in case when one of the metals has d^4–d^5, and another d^6–d^8 electron configuration. From this viewpoint, the alloys of tungsten and molybdenum with metals of the iron subgroup are important for practical applications. These properties have to be inherent to the alloys of metals belonging to iron subgroup with tungsten, and molybdenum (CoW, CoMo, NiW, NiMo, FeW, FeMo) that is necessary for their electrocatalytic activity in hydrogen/oxygen reduction processes and ethanol oxidation.

Since the availability of direct correlation between corrosion and electrocatalytic characteristics of the surface layer of nanostructure catalysts FC (as "core-shell"), the study of corrosion and nanocorrosion properties of catalysts is important and sometimes crucial. The advantage of researches of FC based on ethanol with proton-conductive polymeric electrolyte lays in the possibility of application of the catalytic systems which do not contain platinum. The main trends of this study are 1) to develop the electrochemical deposition of alloys containing nucleophilic and electrophilic component; 2) to create electrocatalysts of ethanol oxidization or hydrogen reduction-oxidization. The ideas of spillover and synergistic effects are also used, which can be realized using bifunctional electrocatalysts on the carbon surface and nanostructure compositions.

Acknowledgement. Publications are based on the research provided by the grant support of the State Fund for Fundamental Research (project N Ф50/017).