

### Electrodeposition Assisted by Organic and Inorganic Polymers: Quasitemplated Nanostructured Electrocatalysts

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One of the most important goals of electrochemical nanotechnology consists in the development of the strategies to design the catalysts with desired properties. The original results on electrodeposition and characterization of two types of materials are reported:

- platinum metals electrodispersed from solutions of polyethylene glycol (PEG) and polyvinyl pyrrolidone (PVP) of various molecular weights (we denote these catalysts "quasitemplate" [1]);
- nanostructured platinum modified with inorganic polymeric molecules (polyoxometalates, POM) [2].

To characterize quasitemplated metals, STM, SEM, XRD, DTA and electrochemical techniques are involved. Among the latter the most important tools are cyclic voltammetry with subsequent coulometric analysis and deposition current transients. Special efforts are applied to construct a self-consistent approach to the treatment of these data in terms of nanoparticles size and degree of coalescence.

Quasitemplate deposition exploits the recognition phenomenon in the system 'growing crystal/polymer molecule'. Basically the interaction of these key constituents is determined by adsorption or complex formation. It gives a possibility to stop the growth of crystal at a certain critical size, and also contributes to directional growth (Fig.1). Main effects of polymer length/conformation and chemical nature on the nanostructural features of deposited metal are discussed. In particular, the role of edge fragments in adsorption behavior of PEGs is considered.

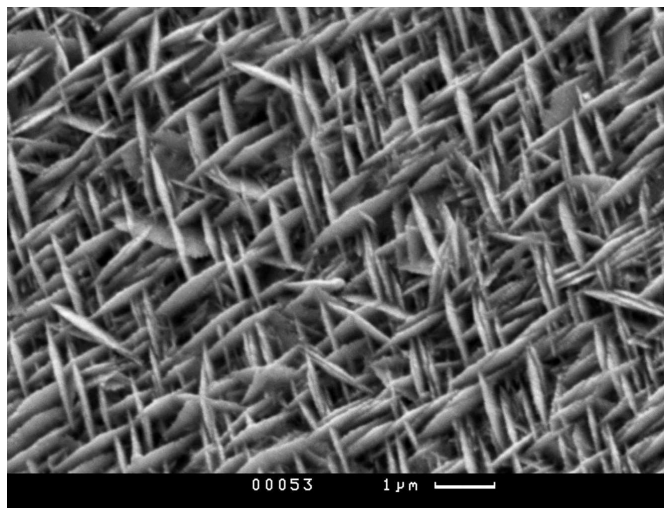


Fig.1. SEM image of quasitemplated Pd formed in the presence of PEG, molecular weight 1000, in  $\text{PdCl}_2 + \text{HCl}$  solution on Pt foil support. Deposition potential 0.2 V (RHE).

PEG- and especially PVP-templated deposits are demonstrated to contain the residual organic molecules which are probably responsible for stabilization of nanos-

tructures, and also can affect the adsorption/electrocatalysis phenomenon. Specific types of surface modification with foreign metal adatoms is already found, which can become an additional tool to control catalytic activity. Deposition modes are found to form catalysts of high surface area and increased catalytic activity, consisting of the ordered arrays of nanoparticles. (Fig.2).

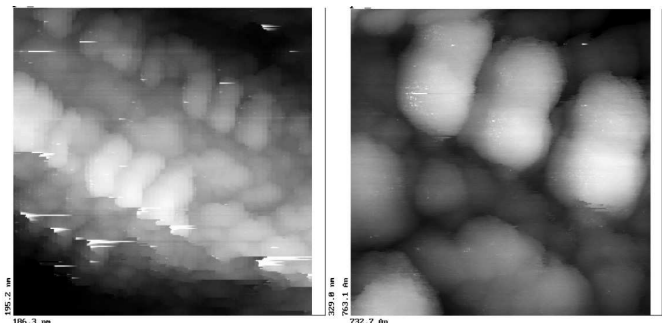


Fig.2. Typical STM image of quasitemplated Pd formed in the presence of PEG in  $\text{PdCl}_2 + \text{HCl}$  solution on Pt foil support. Deposition potential 0.2 V. Scales: 186 nm (left), 73 nm (right).

Inorganic polymeric molecules have an important advantage because they do not induce any poisoning of catalysts. Moreover, these molecules immobilized at the electrode surfaces can induce additional catalytic effects, for example to decrease self-poisoning effects in the course of oxidation of organic fuels [3]. Correspondingly, possibility to increase the surface area of electrodeposited Pt by adding Keggin type heteropolyoxometalates [2] makes templating with these compounds bifunctional. In this context the studies of POM adsorption on Pt and their coadsorption with various species is discussed.

Another aspect of POM application in the studies of platinum metal electrocatalysis appears from data on 3D oxometalate films [4]. Their effect on nitrate electroreduction on dispersed Pt [5] demonstrates unambiguously that nm-size pores of dispersed catalyst are permeable for these large species, and overall surface can be easily modified. We consider POMs as a tool to study nanoporous electrocatalysts.

Joint consideration of usual and quasitemplated dispersed electrocatalysts broadens the experimentally available basis for further understanding of size, site and other nanostructural effects in electrocatalysis, in addition to providing new types of highly active catalysts.

The study is supported by RFBR N 02-03-33285a and Grant of RF President for leading Russian scientific schools N 2089.2003.

#### References

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