

9th International Frumkin Symposium

“Electrochemical Technologies and Materials for 21st Century”

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Introduction

The 9th International Frumkin Symposium was held at the Conference Hall of the Russian Academy of Sciences in Moscow, Russia, between 24th–29th October 2010. The event was organised jointly by the A. N. Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences (IPCE RAS) and the Chemical Department of Lomonosov Moscow State University. The Symposium was sponsored by the Russian Academy of Sciences and the International Society of Electrochemistry. The first symposium of this series, held in 1979, was dedicated to the memory of Russian electrochemist Alexander Frumkin (1895–1976). Since then, the Symposia have been held every 3–5 years to discuss current understanding of fundamental electrochemistry and its applications.

The 9th Frumkin Symposium included 4 plenary lectures, 112 oral and 131 poster presentations. Scientists from the Russian Federation, Ukraine, Belarus, the USA, Canada, Austria, the UK, Germany, Spain, Denmark, Poland, Serbia, Switzerland, Finland, France, Italy, Iran and Taiwan took part in five ‘microsymposia’ which made up the conference, including ‘Electrical Double Layer and Electrochemical Kinetics’, ‘New Processes, Materials and Devices for Successful Electrochemical Transformation of Energy’, ‘Corrosion and Protection of Materials’, ‘Electroactive Composition Materials’ and ‘Bioelectrochemistry’.

Platinum group metals (pgms) are widely used by electrochemists as electrode materials for studies of adsorption, nucleation, electrodeposition, electrocatalytic reactions and many other electrochemical processes used in applications such as fuel cells. About 30 presentations focused on pgm studies at the Symposium. This short review highlights a selection of the work presented.

Electrochemistry of PGM Single Crystals

The Symposium was opened with a plenary lecture by Juan Feliu (University of Alicante, Spain). He discussed models for the estimation of potential zero

total charge (pztc) and potential zero free charge (pzfc), experimental results on anion adsorption and displacement of the adsorbed species by carbon monoxide and the thermodynamic analysis of the temperature dependence of interfacial properties of platinum single crystal electrodes (basal faces and stepped surfaces).

For the three basal planes of Pt, both the entropy of formation of the interface and the entropy of adsorbed hydrogen and hydroxyl species are structure sensitive magnitudes. These results can be analysed using statistical thermodynamic calculations, revealing that adsorbed hydrogen is rather mobile on Pt(111) and Pt(100), while adsorbed hydroxyl is rather immobile. Interestingly, adsorbed hydrogen on Pt(110) is rather immobile at low coverages but becomes very mobile at near saturation coverage. Using cyclic voltammetry (CV), it has also been shown that some anions are not adsorbed on Pt. For instance, trifluoromethanesulfonic acid and perchloric acid both show the same voltammetry on basal plane electrodes and no adsorbate bands were observed by spectroscopy (2).

The main problem in carbon monoxide displacement experiments (3) is oxygen interference. Without this, the pztc and the pzfc almost coincide at 0.37 V vs. reversible hydrogen electrode (RHE) for the Pt(111) electrode. The potential of the maximum entropy of double layer formation, obtained from laser pulsed experiments, also coincides with this value (4). The results of CO displacement experiments for stepped surfaces Pt(S)[$n(111) \times (111)$] (n atomic width (111) terraces separated by parallel steps of monoatomic height with (111) orientation) are shown in **Figure 1**. It can be seen that an increase in the step density leads to a negative shift in the pztc.

Several reports by Alexey Danilov and colleagues (IPCE RAS and University of Alicante) were devoted to the kinetics and mechanism of nitrate anion reduction on Pt single crystals and copper modified electrodes (5, 6). Modification of the Pt surface with Cu adatoms or a small amount of 3D Cu crystallites was performed using potential cycling in solutions with a low concentration of Cu^{2+} ions. This allowed the surface coverage of Cu, θ_{Cu} , to be varied smoothly. It was also found that nitrate reduction in sulfuric acid

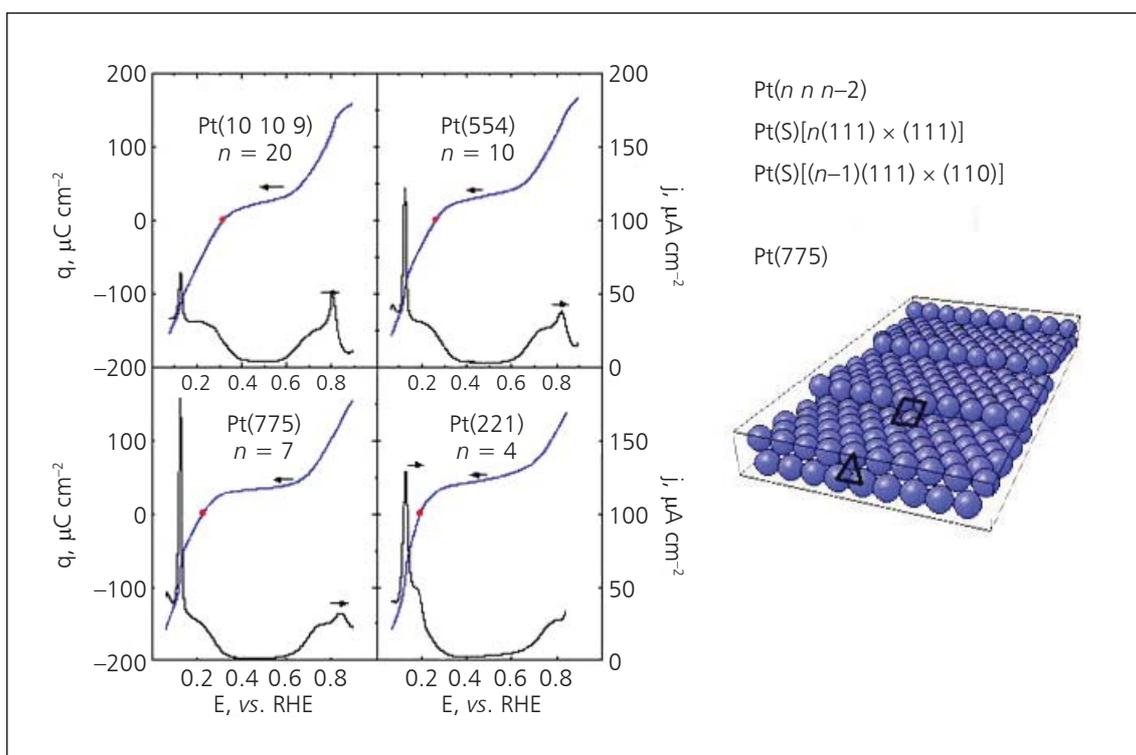


Fig. 1. Potential dependences of total charge and positive-going sweeps of cyclic voltammograms for stepped surfaces of platinum single crystals (Courtesy of Professor Juan Feliu)

solutions at $E > 0.05$ V on Cu modified electrodes was hindered due to enhanced adsorption of sulfate anions on a positively charged Cu adlayer. The effect was less pronounced for the Pt(100) surface where sulfate adsorption was weaker.

In perchloric acid solutions, a strong catalytic effect was observed at low potentials, due to induced adsorption of nitrate anions. Nitrate reduction on Cu modified electrodes was much faster as compared to pure Pt; the current density was higher by 2 to 4 orders of magnitude. Structure-sensitive competitive adsorption of background electrolyte and nitrate anions largely determined the kinetics of nitrate reduction both on the faces of Pt single crystals and on the epitaxial 2D and 3D deposits of Cu. The maximal rate of the process was observed for the Cu modified Pt(100) electrodes. The origin of intermediate products of the nitrate reduction was discussed on the basis of CV and Fourier transform infrared (FTIR) spectroscopy data.

Results of electrochemical and *in situ* scanning tunneling microscopy (STM) studies of the Pt(100) surface structure as dependent on the cooling atmosphere after flame annealing were presented by Alexander Rudnev (IPCE RAS) and Thomas Wandlowski (University of Bern, Switzerland). The following cooling conditions were applied: a mixture of hydrogen and argon (reducing atmosphere), argon (inert gas) and air (oxidising atmosphere). Previous *in situ* STM experiments revealed that a Pt(100) surface as prepared by flame annealing and subsequent slow cooling in a H_2 flow exhibits atomically flat terraces (7). Cooling in an Ar atmosphere led to a reconstructed Pt(100)-hex- $R0.7^\circ$ surface, where $R0.7^\circ$ means rotated by 0.7° . However, the reconstruction was lifted after electrosorption of H_2 and/or in the presence of traces of O_2 in the electrochemical system (8). Because of the excess of Pt surface atoms originating from the lifting of the hexagonally reconstructed Pt(100)-hex- $R0.7^\circ$ electrode, a (1×1) surface with many islands of monatomic height was generated (9). Cooling in air led to a disordered surface structure characterised by a large number of defects.

The influence of defect density and of long range surface order of the Pt(100) electrode on the kinetics of CO electrooxidation and Cu underpotential deposition (UPD) was demonstrated. A Pt(100) electrode cooled in Ar displayed a slightly higher activity with respect to the CO oxidation reaction than that cooled in an Ar and H_2 mixture. On the other hand, the Cu adsorption rate was higher for the 2D ordered Pt(100)

surface than for the disordered surface. This difference was attributed to the blocking of surface defect sites by (bi)sulfate anions. However, at a low Cu concentration in the solution (1.2×10^{-6} M), the adsorption of Cu adatoms occurred at lower potentials, where the interaction of anions with the Pt surface was weaker. In this case the defects act as the preferential adsorption sites for UPD Cu. The Cu UPD process seems to be more sensitive to crystalline defects in the Pt(100) surface than CO electrooxidation, and can be used as a monitoring reaction to estimate the degree of ordering of a Pt(100) surface.

PGMs as Electrocatalysts

Jean-Pol Dodelet (National Research Institute of Energy, Materials and Telecommunications, Varennes, Canada) in his plenary lecture compared the behaviour of platinum- and iron-based electrocatalysts for the reduction of oxygen in proton exchange membrane (PEM) fuel cells. The catalytic activity of new Fe/N/C electrocatalysts (Figure 2) was significantly improved by using a new synthesis procedure (10). Cell current densities were comparable to those of Pt catalysts in the kinetic region and in the mass transport region of the polarisation curve. However, all Fe/N/C catalysts produced thus still lack necessary stability. The catalyst should be stable at least for 5000 hours at the current density and potential practically used in fuel cells. Solving this problem is in progress.

A highly active catalyst based on organometallic clusters was designed and tested for low temperature fuel cells, as reported by Vitaly Grinberg and colleagues (IPCE RAS and Kurnakov Institute of General and Inorganic Chemistry, RAS, Moscow). A new approach to the synthesis of electrocatalysts has been suggested. Individual heterometallic clusters were subjected to thermal destruction on highly dispersed carbonaceous supports at the temperatures of 250–500°C. The distinguishing feature of these catalysts was their good reproducibility with respect to composition, as well as uniformity of the catalyst distribution over the support, which results in stability and reproducibility of the catalyst characteristics (11). A bimetallic platinum-tin catalyst (Pt:Sn atomic ratio in the surface layer 2:1) and fluoro-containing nickel-ruthenium catalyst (Ni:Ru atomic ratio in the surface layer 8.6:1) were synthesised by deposition on highly dispersed carbon black from clusters of the corresponding metals. These catalysts (Pt_3Sn and $Ni_{12}RuF_5$) were characterised by X-ray diffraction and energy dispersive X-ray (EDX) analysis, laser mass spectrometry and transmis-

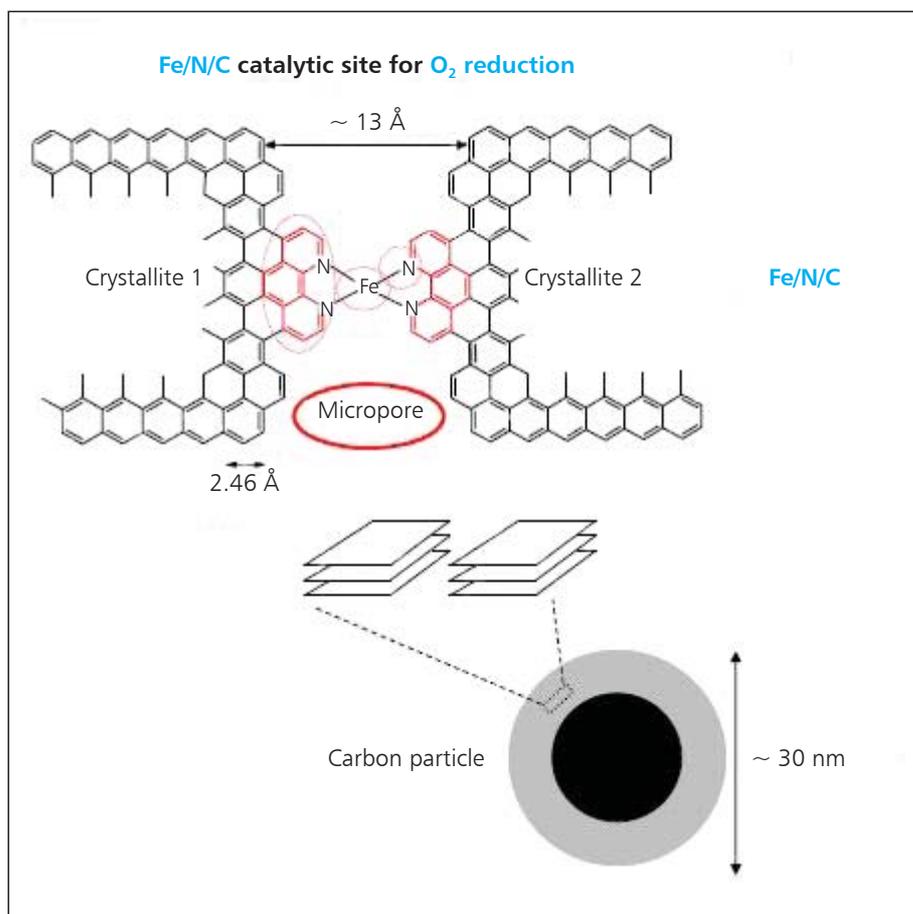


Fig. 2. Schematic presentation of new iron/nitrogen/carbon electrocatalysts (Courtesy of Professor Jean-Pol Dodelet)

sion electron microscopy (TEM). The mean size of these catalyst particles was in the range 1–12 nm. According to voltammetric data, the synthesised Pt₃Sn and Ni₁₂RuF₅ catalysts are superior to the Pt-Sn and Ni-Ru catalysts described in literature for ethanol oxidation and for sodium borohydride oxidation, respectively. It was also shown that the specific catalytic activity of these catalysts exceed those of Pt-Sn and Ni-Ru bimetallic systems prepared from simple salts by impregnation of carbon black.

Concluding Remarks

This Symposium made it very clear that the pgms remain very popular for electrochemical studies of the electric double layer structure and of electrocatalytic reactions. Although much research is being carried out to attempt to replace pgms by other materials for use in fuel cells and other electrocatalytic processes, the pgms currently provide the

best operating characteristics for many electrochemical applications.

The abstracts of oral and poster presentations given at this conference are available by contacting the organisers (1). The next Frumkin Symposium is planned to be held in October 2015 in Moscow, Russia.

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The Reviewer

Alexey I. Danilov completed his PhD studies in the field of electrochemical metal nucleation and growth at the Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences (IPCE RAS) of Moscow, Russia, in 1985. He obtained his Dr Sci (Physical Chemistry) in 2002. Most of his studies have been devoted to processes of adsorption, nucleation and electrocatalysis on pgms. He is currently the Head of the Laboratory of Surface Layer Structure at the IPCE RAS.