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# Chronicle

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## Habilitation works on chemistry (03 P) maintained in 2002

**Dr. Gintaras Baltrūnas**

### **Influence of Ligand Chemisorption on Electroreduction of Silver and Gold Complex Compounds**

(Maintained at the Committee of Faculty of Chemistry of Vilnius University on 31 May 2002).

The electrochemical systems in which the chemisorption of ligand occurs in parallel to the electroreduction of complex ions were studied in this work. The main purpose was to evaluate the character of adsorption of  $\text{CN}^-$  and  $\text{SO}_3^{2-}$  ions and the possible influence of this adsorption on the determination of kinetic parameters of electrochemical reactions.

It was demonstrated that adsorption of cyanide ions at the surface of silver electrode occurs in two stages. The first stage (reversible) starts in the region of low concentrations and increases the capacity of the double-electric layer, as is customary for adsorption. With a further increase in concentration and in degree of surface coverage, the distance between adsorbed ions is shortened inasmuch as the formation of covalent bounds between them is possible. Then the oxidation process might start, yielding an electroneutral surface compound, which is chemically and electrochemically inert. This second stage of adsorption is irreversible and, furthermore, decreases the capacity of the double-electric layer.

The surface compound formed in the course of irreversible absorption of cyanide ions insulate the part of the electrode surface in the region of the equilibrium potential, and practically no silver dissolution-deposition process is observed under these conditions. The degree of surface blocking depends on the concentration of free (not bound in complex compounds) cyanide ions and temperature, and can reach *ca.* 90% of the electrode surface.

Silver electrocrystallization at high concentrations of free cyanide ions and at low electrode polarisation occurs only on localized active sites of the surface. The upraises of a couple hundreds of nanometers height increase the real surface area of the electrode up to threefold. The maximum surface roughness is

obtained after passing through the electrode the electricity charge equal to *ca.* 100 mC/cm<sup>2</sup>, irrespective of the concentration of complex compounds and of the polarisation of the electrode. The longer electrolysis leads to a smooth surface.

The small cathodic polarisation practically does not change the degree of surface blocking in comparison with the equilibrium conditions, but decreases *ca.* tenfold the dimensions of the active islands of the surface.

The complicated voltammetric dependence of electroreduction of silver(I)–cyanide complexes can be accounted for both the different values of exchange current and transition coefficient in active and inactive sites of the electrode.

$\text{Ag}(\text{CN})_2^-$  ions directly participate in the charge transfer stage:  $\text{Ag}(\text{CN})_2^- + e \leftrightarrow \text{Ag} + 2\text{CN}^-$  irrespective of the concentration of free cyanide ions and of the composition of silver(I)–cyanide complex compounds predominating in the bulk solution. At higher cyanide concentrations, when the  $\text{Ag}(\text{CN})_3^{2-}$  complex predominates in the solution, the first chemical reaction, which does not change the rate of the overall process, should occur before the charge transfer:  $\text{Ag}(\text{CN})_3^{2-} \leftrightarrow \text{Ag}(\text{CN})_2^- + \text{CN}^-$ .

The stable complex ions of  $\text{Au}(\text{SO}_3)_2^{3-}$  are predominant ( $\log\beta_2 \approx 27.4$ ) in the bulk of the gold(I)–sulphite electrolyte. The gold electrode surface is partially passivated by adsorbed sulphite ions. The degree of surface blocking depends on the potential of the electrode and reaches the maximum value at  $E_H = -0.4$  V. For this reason, the impedance spectra obtained are rather complicated. In the region of infra-low frequencies the imaginary part becomes positive, but the real part becomes negative when the surface blocking increases (at potentials from  $-0.3$  to  $-0.4$  V). When a mathematical simulation of the electrochemical system is made, the inductance element RL, which is parallel to charge transfer resistance, appears in the equivalent circuit.

The comparable amounts of silver–sulphite complex compounds of  $\text{Ag}(\text{SO}_3)_2^{3-}$  ( $\log\beta_2 \approx 7,9$ ) and  $\text{Ag}(\text{SO}_3)_3^{5-}$  ( $\log\beta_1 \approx 8.5$ ) can exist simultaneously in

the electrochemical system containing sulphite and silver–sulphite complexes. The density of the cathodic limiting current is defined by diffusion of silver–sulphite complexes. When extrapolating the values of the limiting current density towards the infinite rotation speed of a disc electrode, the voltammetric dependence (which is defined solely by the kinetic parameters of the process) of the electrochemical reaction can be found. The shape of this voltammetric dependence is typical for the slow crystallization stage, whose investigation is complicated due to adsorption of sulphite ions occurring in parallel.

The work is written in Lithuanian on 106 pages with 66 figures, 2 tables and 107 references with an extended abstract in English.

### Dr. Arūnas Ramanavičius

#### Design of Catalytic and Affinity Biosensors

(Maintained at the Committee of Faculty of Chemistry of Vilnius University on 31 May 2002)

The main purposes of this habilitation work were (1) to design new biosensors employing PQQ-dependent enzymes and various redox mediators; (2) to apply the viral protein of bovine leukemia in sensors of *gp51* and *p24* affinity; (3) to employ polypyrrolle for immobilization of some biologically active substances; (4) to define the advantages and disadvantages of different methods of immobilization, above all of those using polypyrrolle.

It was defined that an electrochemically synthesized layer of polypyrrolle reduces considerably the effect of electrochemically active anions (*e.g.*, ascorbic acid) on the electrode, therefore it can be applied as a selective permeable matrix of immobilization of biologically active substances.

PQQ-dependent alcohol dehydrogenase, PQQ-dependent glucose dehydrogenase and the viral proteins of bovine leukemia can be immobilized into the layer of electrochemically synthesized polypyrrolle. Such polymers exhibit the properties of biological recognition of inserted substances and can be used in designing biosensors.

An analysis of experimental data of this work showed that polypyrrolle exhibits many features that can be useful for designing affinity sensors assigned for direct detection of analyte: polypyrrolle synthesis on the electroconductive surface can be readily checked; it is easy to immobilize biologically active substances into it; characteristics of recognition of the biologically active substances immobilized into polypyrrolle remain undisturbed; polypyrrolle protects the electrodes from surface-contaminating substances and the effect of hindered compounds; polypyrrolle

can participate also in the process of transformation of a biological indication signal (*e.g.*, formation of antigen–antibody complex) to the electrochemical signal.

The work is written in English on 95 pages with 40 figures, 3 tables and 174 references.

### Dr. Gediminas Niaura

#### The Structure of Molecules and Ions at Surfaces as Studied by Raman Spectroscopy

(Maintained at the Committee of the Institute of Chemistry (Vilnius) on 7 June 2002)

Raman spectroscopy and surface-enhanced Raman spectroscopy (SERS) have been employed to investigate the structure and bonding of inorganic ions, heterocyclic and redox active organic molecules, and biomolecules at the surface of solid electrodes, as well as the structure of model membrane systems. The main goal of the work was molecular-level characterization of the adsorbed molecules and ions at electrode surfaces. The *in situ* vibrational spectroscopic technique was addressed to the following main problems at the interface: 1) bonding and structure of inorganic anions at electrodes; 2) formation of contact and water-separated ion pairs at the interface; 3) the state and integrity of adsorbed biomolecules as well as structural transformations induced by the potential and solution pH; 4) formation and structure of model membrane systems as well as interaction of solution components with lipids.

Combination of SERS and labeling by stable isotopes allowed to identify: 1) two different states of adsorbed OH<sup>-</sup> ions at Cu electrodes, and 2) chemisorbed SO<sub>4</sub><sup>2-</sup> ions at copper surface in acidic solutions. The interpretation of the SERS spectra of adsorbed phosphate species on Au, Ag, and Cu electrodes based on the frequency shifts upon solution H<sub>2</sub>O/D<sub>2</sub>O exchange were performed. Monodentate surface coordination of PO<sub>4</sub><sup>3-</sup> and HPO<sub>4</sub><sup>2-</sup> ions was proposed. SERS study provided evidence phosphate adsorption in the Au/Ag UPD system induced by Ag adatoms. The frequency of the metal–oxygen vibration has indicated that the anions are coordinated to the Ag adatoms rather than to the substrate Au atoms. The adsorbed phosphate anions were spectroscopically observed at potentials 0.9 V more negative compared with bare Au electrodes. Formation of surface ion pair between the acridinium cation and the chemisorbed chloride ion has been detected at Cu electrode surface. Different adsorption states of amino acid, histidine, on Cu electrode have been observed spectroscopically depending on the solution pH, potential, and presence of the SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> ions. SER spectra from cyt c adsorbed on Ag

electrodes have been obtained with 632.8 nm excitation for the first time. Formation of the hybrid bilayer membrane consisting of a lipid monolayer covering a self-assembled alkanethiol monolayer on the metal surface has been evident when the SERS technique was used *in situ*.

The habilitation work is written in English on 116 pages with 70 figures, 19 tables and 237 references.

### **Dr. Audrius Sigitas Maruška**

#### **Stationary Phases and Techniques for Liquid Chromatography and Electrochromatography: Towards Microseparations.**

(Maintained at the Habilitation Committee of Vytautas Magnus University, Kaunas on 20 December 2002)

Development and characterization of polymer-based stationary phases for different format liquid phases separation techniques was the main object of this work. The methods extensively used in the work include column liquid chromatography, classical high-performance liquid chromatography, capillary electrochromatography, capillary liquid chromatography, inverse size-exclusion chromatography, atomic force microscopy, scanning electron microscopy, high resolution optical microscopy.

Many original stationary phases and separation methods developed are described. New characterization methodologies for the stationary phases are also proposed. The theoretical and practical importance of the results is summarized.

The work is written in English on 123 pages with 32 figures, 19 tables and 147 references.