

Preparation and investigation  
of yttrium-hexacyanoferrate and  
ruthenium(III)-trichloride - polypyrrole nanocomposite  
surface thin layers  
by electrochemical piezoelectric nanogravimetry

Thesis of doctoral dissertation

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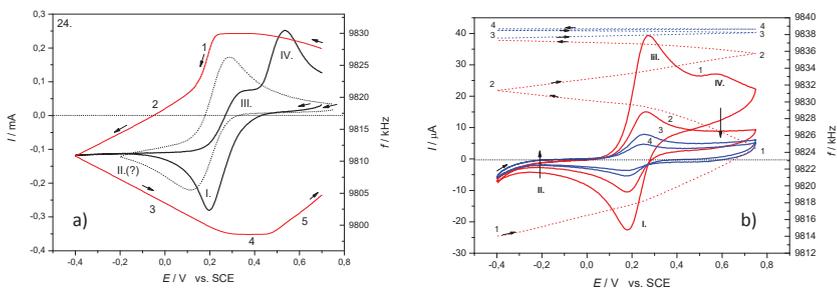
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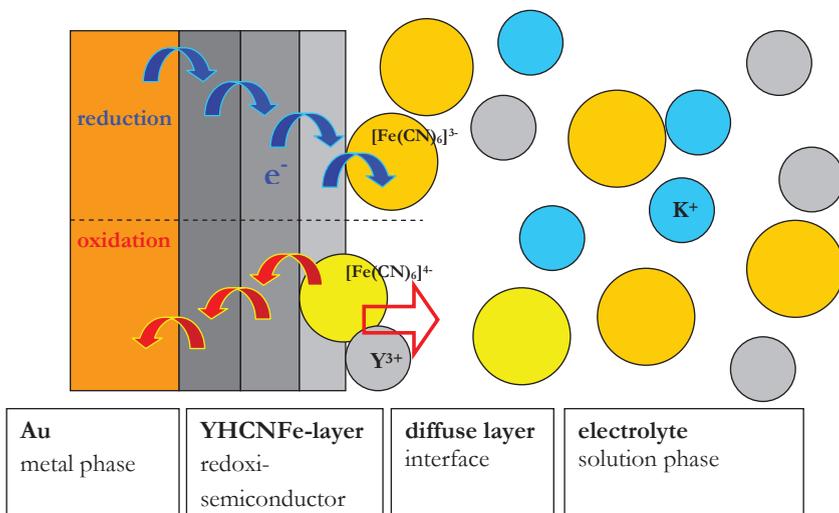
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- a) The cyclic voltammogram of electrodeposition of YHCNFe-layer (black line) and the simultaneously obtained frequency changes (red line) on gold surface. Solution:  $0,0675 \text{ mol dm}^{-3} \text{ Y}(\text{NO}_3)_3$  and  $0,01 \text{ mol dm}^{-3} \text{ K}_3[\text{Fe}^{\text{III}}(\text{CN})_6]$ . Scan rate  $10 \text{ mV s}^{-1}$ .
- b) Dissolution of YHCNFe-layer from the surface of gold electrode, in the  $0,5 \text{ mol dm}^{-3} \text{ K}_2\text{SO}_4$  solution. Scan rate  $10 \text{ mV s}^{-1}$ . Cyclic voltammograms (continuous lines, 1-2 cycle red, 3-4 cycle blue), and the simultaneously obtained frequency changes dotted lines (1-2 cycle, red, 3-4 cycle blue).



Model of deposition and dissolution of YHCNFe-layer.

## Introduction

In the course of my doctoral research I have prepared electrochemically active materials that attached to the electrode surface spontaneously during electrodeposition or by applying different methods. The redox transformations of these surface layers and the simultaneously occurring ion exchange processes have been studied by several techniques. In the present thesis the results obtained regarding the preparation and characterization of yttrium-hexacyanoferrate (YHCNFe), ruthenium-trichloride ( $\text{RuCl}_3$ ) and ruthenium-trichloride – polypyrrole nanocomposite  $((\text{PP})_x(\text{RuCl}_3)_y)$  are presented.

## Antecedents

During the last decades intense research has been directed towards the preparation, characterization and application of electrochemically active surface layers in the Electrochemical and Electroanalytical Laboratory of the Chemistry Institute of the Eötvös Loránd University led by Professor György Inzelt. Among these systems metal hexacyanoferrates and layered polynuclear complexes including their nanocomposites have been in the foreground of the studies.

In metal hexacyanoferrates hexacyanoferrates anions become ligands, and consequently a complex polymeric material is formed, which bounded together with dative bonds. In many cases the electrodeposition of these polynuclear complexes occur spontaneously, they display electroactivity in a wide potential range, mostly due to the redox reaction of the  $\text{Fe}^{2+} / \text{Fe}^{3+}$  couple. The complex ions in the rigid polynuclear structure are highly stable, and the variations of their charge are accompanied by the transport of cations.

The layered, lamellar nanocomposites consist of lamellar inorganic compounds having a similar structure to graphite, and the conducting polymers forming within the layers. Albeit the components of these composites themselves possess very interesting properties, due to synergic effects based on interactions on molecular level, a novel material with useful properties can be obtained. Owing to the high oxidation power of  $\text{RuCl}_3$  and its layered structure the formation of polypyrrole from pyrrole molecules within the layers is a spontaneous process. This induced topotactic polymerization results in a semiconductor nanocomposite material having redox properties.

## Aims

As continuation of previous efforts my aims are to gain a deeper understanding on redox properties / processes of yttrium-hexacyanoferrate (YHCNFe) and  $(PP)_x(RuCl_3)_y$  nanocomposite, furthermore in the case of nanocomposite electrochemical tuning of conduction with exploration of ion transport processes in different redox states.

## Applied electrochemical methods

Electrodeposition and ion exchange processes have been studied by cyclic voltammetry and chronoamperometric methods combined with piezoelectric nanogravimetry by using electrochemical quartz crystal nanobalance (EQCN).

In the case of YHCNFe-layer the deposition and the properties of deposited layer were investigated on gold and PIGE surfaces from solutions of  $Y(NO_3)_3$  and  $K_3[Fe^{III}(CN)_6]$  of different concentrations and concentration ratios. The  $(PP)_x(RuCl_3)_y$  nanocomposite crystals, as well as ruthenium(III)-trichloride crystals and polypyrrole were attached to gold and PIGE surfaces.

The YHCNFe-layers were formed at high enough concentrations and adequate concentration ratios of reactants by electrodeposition in the course of reduction of  $K_3[Fe^{III}(CN)_6]$ . The  $(PP)_x(RuCl_3)_y$  nanocomposite was prepared by chemical (redox) reaction of pyrrole and  $\alpha$ - $RuCl_3$ .

An Elektrofex 453 potentiostat (Szeged, Hungary) and Universal Frequency Counter TR 5288 (Philips) with home-made quartz crystal nanobalance connected with an IBM personal computer were used for the control of the measurements and for the acquisition of the data. The Sauerbrey equation with an integral sensitivity of the crystals was used to calculate the mass change ( $\Delta m$ ) from the frequency change ( $\Delta f$ ). The integral sensitivity was determined by electrodeposition of Ag from 0.5 M  $AgClO_4 + 0.5$  M  $HClO_4$  solution.  $C_f(10\text{ MHz}) = 2,05 \pm 0,2 \times 10^8\text{ Hz cm}^2\text{ g}^{-1}$ ,  $C_f(6\text{ MHz}) = 8,5 \pm 0,2 \times 10^7\text{ Hz cm}^2\text{ g}^{-1}$ .

## Collateral analytical examinations

The yttrium-hexacyanoferrate samples precipitated were investigated by total reflection X-ray fluorescence spectrometry. A TXRF spectrometer (Atomika Instruments EXTRA IIA, Germany) was used to determine the element

concentrations. The line-focused Mo-tube was operated at 50 kV (38 mA). A 200  $\mu\text{m}$  Mo cut-off filter was applied. An energy dispersive Si(Li)-detector (QX 2000 (Oxford Instruments, England) was used. The integration time was 1000 s. The sensitivity factors:  $\varphi(\text{K}) = 11,25$  at line  $\text{K}_\alpha(\text{K}) = 3,31$  eV,  $\varphi(\text{Fe}) = 1,25$  at line  $\text{K}_\alpha(\text{Fe}) = 6,40$  eV and  $\varphi(\text{Y}) = 0,266$  at line  $\text{K}_\alpha(\text{Y}) = 14,93$  eV.

$(\text{PP})_x(\text{RuCl}_3)_y$  nanocomposites as pressed KBr pellets were investigated by infrared (FTIR) transmission spectroscopy by using Bruker IFS-55 Fourier transform spectrometer, at 2000 – 400  $\text{cm}^{-1}$  wavenumber range.

### ***Summary of results of study on YHCNFe-layers***

1. It has been shown that during the electroreduction of  $\text{Fe}^{\text{III}}(\text{CN})_6$  in the presence of  $\text{Y}^{3+}$  sparingly soluble YHCNFe(II) layers are formed on the gold surface used as a cathode if the concentrations of the  $\text{K}_3[\text{Fe}^{\text{III}}(\text{CN})_6]$  and  $\text{Y}(\text{NO}_3)_3$  is high enough, i.e.,  $c(\text{K}_3[\text{Fe}^{\text{III}}(\text{CN})_6]) \times c(\text{Y}(\text{NO}_3)_3) > 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$ .
2. The results of both cyclic voltammetric and chronoamperometric piezoelectric nanogravimetry at an EQCN reveal a nucleation and growth kinetics. The rate of formation of nuclei is smaller than that of the layer growth. Both rates depend on the concentration and the molar ratio of the reacting species.
3. According to the TXRF analysis the atomic ratios of K, Y and Fe is equal to 0.46 : 1.18 : 1. A comparison of this values with the apparent molar masses obtained by EQCN experiments the following formula can be given for the composition of YHCNFe(II) precipitate:  $\text{K}_{0,46}\text{Y}_{1,18}[\text{Fe}^{\text{II}}(\text{CN})_6] \cdot 2 \text{ H}_2\text{O}$ . The solubility of this compound is  $5 \times 10^{-5} \text{ mol dm}^{-3}$ .
4. At high concentrations of the reactants a spontaneous deposition of YHCNFe(III) occurs. Its composition is  $\text{Y}[\text{Fe}^{\text{III}}(\text{CN})_6]$ , and its solubility is  $10^{-2} \text{ mol dm}^{-3}$ .
5. The deposited YHCNFe(II) layer is unstable at higher positive potentials due to its oxidation, and the fast dissolution of YHCNFe(III).
6. There are also practical aspects of the electrodeposition and electrodisolution of YHCNFe. It seems to be a rather straightforward way to collect and regenerate yttrium isotopes which are formed in the course of nuclear fission in nuclear power plants.

### ***Summary of results of study on $(PP)_x(RuCl_3)_y$ nanocomposites***

7. Solid  $RuCl_3$  microcrystals can be immobilized on gold surface, and their redox transformations can be investigated in the presence of aqueous solutions. The combined voltammetric and piezoelectric nanogravimetric techniques revealed that in the potential range from 0.8 V to  $-0.15$  V several redox processes occur, which are accompanied with the incorporation of cations and the simultaneous desorption of water molecules during reduction and the opposite transport of these species during reoxidation. The electrochemical reactions involve the formation of complexes and solid-state phase transitions. The results can be elucidated by the formation of complexes or intercalation compounds which contain mixed valence  $Ru^{III/II}$  – centers,  $Cl^-$  ions, univalent metal ions ( $M^+$ ) or  $H^+$  ions and water molecules, the ratio of which depends on the potential and the solution composition. During reduction  $M^+$  ions enter the layer. The highly hydrated small ions transport their hydrate sphere, while the insertion of large size ions causes a desorption of water molecules. The exchange of chloride ions is also likely at high electrolyte concentrations. The redox transformations are accompanied with structural changes of the microcrystals.
8. The results of the electrochemical nanogravimetry indicates that pyrrole molecules can be intercalated in the lamellar structure of  $\alpha$ - $RuCl_3$ .  $Ru^{3+}$  ions oxidise pyrrole molecules which reaction results in the formation of polypyrrole monolayers within the gallery space of  $RuCl_3$ . The formation of polypyrrole has been proven by infrared spectra.
9. The electrochemical responses of  $(PP)_x(RuCl_3)_y$  nanocomposites clearly show the redox responses of both the redox reactions of PP and  $Ru^{3+} \rightleftharpoons Ru^{2+}$  transitions. The results of electrochemical nanogravimetric studies can be explained by the sorption / desorption of ionic species and water molecules. The nanocomposite behaves as a self-doped conducting polymeric system where  $RuCl_3^{x-}$  sites act as counterions, however, sorption / desorption of cations is inevitable when PP becomes fully reduced in order to compensate the negative charge of  $(RuCl_3)_y^{z-}$ . At positive potentials in a smaller extent anion transport also takes place.
10. The properties of the nanocomposites can be tuned electrochemically, which gives an opportunity to prepare catalysts and supercapacitors that can be used for special purposes.

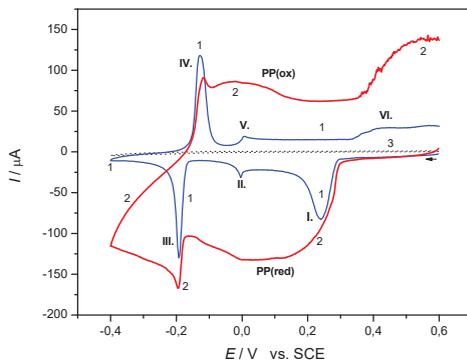
## **Publications**

### ***Publications connected with dissertation***

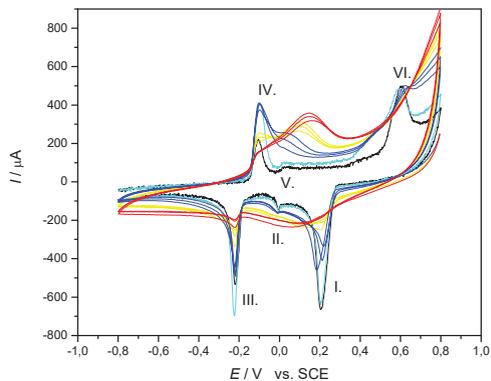
1. A. Róka, I. Varga, G. Inzelt:  
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Electrochimica Acta 51, 6243-6250 (2006).
2. G. Inzelt, A. Róka:  
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Electrochimica Acta 53, 3932-3941 (2008).
3. G. Inzelt, A. Róka:  
Electrochemical nanogravimetric studies of ruthenium(III)trichloride microcrystals  
Israel Journal of Chemistry 48, 185-197 (2008).
4. G. Inzelt, A. Róka:  
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### ***Other publications***

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Electrochemical quartz crystal microbalance study of redox transformations of TCNQ microcrystals in concentrated LiCl solutions  
Electrochimica Acta 52, 4015-4023 (2007).
6. E. Bura-Nakic, A. Róka, I. Ciglenceki, G. Inzelt:  
Electrochemical nanogravimetric studies of sulfur/sulfide redox processes on gold surface  
J. Solid State Electrochemistry 13, 1935-1944 (2009).
7. E. Bura-Nakic, A. Róka, I. Ciglenceki, G. Inzelt:  
Electrochemical quartz crystal microbalance study of FeS particles attached to Au surface  
Electroanalysis 21 (15), 1699-1708 (2009).



The comparison of cyclic voltammograms of  $\alpha$ -RuCl<sub>3</sub> (1, blue line) and (PP)<sub>2</sub>(RuCl<sub>3</sub>)<sub>7</sub> nanocomposite (2, red line) attached to PIGE in the presence of 0,5 mol dm<sup>-3</sup> NaCl. Scan rate 20 mV s<sup>-1</sup>. (Base-line 3, dotted black line).



Formation of polypyrrole overlayers on  $\alpha$ -RuCl<sub>3</sub>-layer attached to PIGE by electropolymerization of pyrrole. Solution in the first cycle (black line): 50 cm<sup>3</sup> 0,5 mol dm<sup>-3</sup> NaCl. Scan rate: 50 mV s<sup>-1</sup>. From the second to the tenth cycles + 100 μl pyrrol. Order of colour lines of the consecutive cycles are black, pale blue, blue, yellow, red.