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Summary of Scientific Achievements Providing an Overview of Monothematic Series of Scientific Publications

Appendix 3

as attachment for the habilitation procedure proposal

Faculty of Chemistry, University of Warsaw

Warsaw 2016

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1. Name and surname

Iwona Rutkowska

2. Information about diplomas and academic degrees

2006r.	**The degree of PhD** in the field of Chemical Sciences, Doctoral Thesis title: "Analysis of processes accompanying redox reactions at electrodes modified with selected metal hexacyanoferrate films"; Doctoral Dissertation supervisor (research director): Prof. Zbigniew Galus (Faculty of Chemistry, University of Warsaw)
2000r	**The degree of M.Sc.** with Highest Honors in Chemistry (Analytical & Inorganic). The thesis title: "Application of electrochemical methods and quartz crystal microbalance to study electrode processes of copper hexacyanoferrate"; Major Professor: Zbigniew Galus (Faculty of Chemistry, University of Warsaw)

3. Information on employment

From February **15th, 2007** till now as **Adjunct** in the Laboratory of Electroanalysis Chemistry, Division of Inorganic and Analytical Chemistry, **Faculty of Chemistry University of Warsaw**

Iwona Rutkowska

4. Indication of the achievements resulting from Article 16, paragraph 2 of the Act of 14 March 2003 on Academic Degrees and Title in Art (Journal of Laws No. 65, item. 595, as amended.)

4A. Type of scientific achievement

The monothematic series of publications which are the scientific achievement submitted for the habilitation procedure:

„Nanostructured electrocatalytic systems of defined functionality, reactivity and capability of fast charge propagation"

4B. Publications included in the scientific achievement

Author(s), date of issue, title, journal or publishing house, volume, pages		IF
H1	Zoladek S., **Rutkowska I.A.**, Kulesza P.J., *Enhancement of activity of platinum towards oxidation of ethanol by supporting on titanium dioxide containing phosphomolybdate-modified gold nanoparticles*, Applied Surface Science 257 (2011) 8205-8210	$\mathrm{IF}_{(2011)}=2.103$ $\mathrm{IF}_{(2014)}=2.711$
H2	**Rutkowska I.A.**, Andrearczyk A., Zoladek S., Goral M., Darowicki K., Kulesza P.J., *Electrochemical characterization of Prussian blue type nickel hexacyanoferrate redox mediator for potential application as charge relay in dye-sensitized solar cells*, Journal of Solid State Electrochemistry 15 (2011) 2545- 2552	$\mathrm{IF}_{(2011)}=2.131$ $\mathrm{IF}_{(2014)}=2.446$
H3	**Rutkowska I.A.**, Marks D., Perruchot C., Jouini M., Kulesza P.J., *Admixing palladium nanoparticles with tungsten oxide nanorods toward more efficient electrocatalytic oxidation of formic acid*, Colloids and Surfaces A: Physicochemical and Engineering Aspects 439 (2013) 200-206	$\mathrm{IF}_{(2013)}=2.354$ $\mathrm{IF}_{(2014)}=2.752$
H4	**Rutkowska I.A.**, Koster M., Blanchard G.J., Kulesza P.J., *Nanoporous Platinum Electrodes as Substrates for Metal Oxide-Supported Noble Metal Electrocatalytic Nanoparticles: Synergistic Effects During Electrooxidation of Ethanol*, Australian Journal of Chemistry 67 (2014) 1414–1421	$\mathrm{IF}_{(2014)}=1.558$
H5	**Rutkowska I.A.**, Koster M., Blanchard G.J., Kulesza P.J., *Enhancement of ethanol oxidation at Pt and PtRu nanoparticles dispersed over hybrid zirconia-rhodium supports*, Journal of Power Sources 272 (2014) 681-688	$\mathrm{IF}_{(2014)}=6.217$

H6	**Rutkowska I.A.**, Kulesza P.J.,*Electrocatalytic oxidation of ethanol in acid medium: enhancement of activity of vulcan-supported Platinum-based nanoparticles upon immobilization within nanostructured zirconia matrices*, Functional Materials Letters 7 (2014) 1440005	$IF_{(2014)}$=1.606
H7	**Rutkowska I.A.**, Sek J.P., Mehdi B.L., Kulesza P.J., Cox J.A., *Assembly of crosslinked oxo-cyanoruthenate and zirconium oxide bilayers: Application in electrocatalytic films based on organically modified silica with templated pores*, Electrochimica Acta 122 (2014) 197-203	$IF_{(2014)}$=4.504
H8	**Rutkowska I.A.**, Zoladek S., Kulesza P.J., *Polyoxometallate-assisted integration of nanostructures of Au and ZrO_2 to form supports for electrocatalytic PtRu nanoparticles: enhancement of their activity toward oxidation of ethanol*, Electrochimica Acta 162 (2015) 215–223	$IF_{(2014)}$=4.504
H9	**Rutkowska I.A.**, Marszalek M., Orlowska J., Ozimek W., Zakeeruddin S.M., Kulesza P.J., Grätzel M., *Nanocomposite Semi-Solid Redox Ionic Liquid Electrolytes with Enhanced Charge-Transport Capabilities for Dye-Sensitized Solar Cells*, ChemSusChem 8 (2015) 2560-2568	$IF_{(2014)}$=7.657
H10	**Rutkowska I.A**., Kulesza P.J., *Electroanalysis of Ethanol Oxidation and Reactivity of Platinum-Ruthenium Catalysts Supported onto Nanostructured Titanium Dioxide Matrices*, Journal of Electrochemical Society, 163 (4) (2016) H1-H9	$IF_{(2014)}$=3.266
H11	**Rutkowska I.A.,** *Enhancement of Oxidation of Formic Acid in Acid Medium on Zirconia-Supported Phosphotungstate-Decorated Noble Metal (Pd, Pt) Nanoparticles*, Australian Journal of Chemistry 69 (2016) 394-402	$IF_{(2014)}$=1.558
H12	**Rutkowska I.A.**, Wadas A., Kulesza P.J., *Enhancement of Oxidative Electrocatalytic Properties of Platinum Nanoparticles by Supporting onto Mixed WO_3/ZrO_2 Matrix*, Applied Surface Science – in press (online: http://dx.doi.org/10.1016/j.apsusc.2016.02.241)	$IF_{(2014)}$=2.711

4C. Discussion of scientific goals and the series of publications mentioned above (including their potential utility)

Preliminary information

My monothematic series entitled: “Nanostructured electrocatalytic systems of difined functionality, reactivity and capability of fast charge propagation” consists of twelve publications based on research published in 2011-2015 in the following international journals indexed in the *Journal Citation Report* (JCR) database: two publications (H7,H8) in *Electrochimica Acta* (*Elsevier*), two publications (H4,H11) in the *Australian Journal of Chemistry (CSIRO Publishing)*, two publications (H1, H12) in *Applied Surface Science (Elsevier)*, one publication (H2) in the *Journal of Solid State Electrochemistry (Springer)*, one publication (H3) in *Colloids and Surfaces A: Physicochemical and Engineering Aspects (Elsevier)*, one publication (H5) in the *Journal of Power Sources (Elsevier)*, one publication (H6) in *Functional Materials Letters (World Scientific)*, one publication (H9) in *ChemSusChem (Wiley)* and one publication (H10) in the *Journal of Electrochemical Society (The Electrochemical Society)*. Most of publications have co-authors, but I am the first author in ten of them as well as a sole in one publication. During discussion of the scientific problems in the series of publications mentioned above, I refer to other research conducted in the course of my academic career and included on the list of additional publications (D2). I also mention the work (W1) I and co-author by me have submitted to *Electrochimica Acta (Elsevier)* and to the review articles (D5, D13) published in the *Journal of Materials Chemistry (Royal Society of Chemistry)* and in *Electrochimica Acta (Elsevier)*, respectively.

Introduction

After obtaining a doctoral degree, my research activities have focused on **the search for new catalytic systems, as well as on the optimization of their activities and on better understanding of their mechanisms of operation with the ultimate goal of fabrication of systems (materials) of potential importance to the development of the low-temperature fuel cell technology (oxidation of small organic molecules such as ethanol or formic acid), amperometric sensors of defined specificity or selectivity, and mediators, or charge relays, for dye solar cells.**

Electrocatalytic processes are special cases of chemical catalysis they can be described in terms of rate constants or other kinetic parameters that are activation-energy dependent. Unlike the conventional catalytic processes, rates of the catalyzed electrochemical processes are also dependent on the electrode potential. Of course, raising the temperature results in accelerating the reaction; but electrochemical reactions at temperatures much higher than room temperature are often difficult to perform. Since the **current signal** serves as a measure the electrode process rate, **electrocatalytic systems characterized by rapid (reversible) electron transfers are of practical significance, especially in electrochemical energy accumulation and conversion technology** (including low-temperature fuel cells and photoelectrochemical cells)**, and in electroanalysis, e.g. in amperometric sensors.**

Both in practical systems and in diagnostic measurements, it is desirable to place a catalyst on the electrode surface, i.e. to establish the so-called modified electrode. Durable are multilayer (three-dimensional), rather than monolayer, catalytic coatings that are in contact with the electrolyte's liquid phase; they can be viewed as the systems at the borderline between heterogeneous and homogeneous electrocatalysis. It is crucial for an expensive catalyst (for example, a catalyst composed of noble metal nanoparticles) be active on the surface of the electrode where electron transfer involving a reactant takes place.

During the electrocatalytic processes, electron transfers are accelerated. Consequently, we observe higher current values (maximum to mass transport-controlled value rather than to kinetic controlled value) which are usually accompanied by shifts in potentials: toward the less positive potentials in the case of oxidation, and in the direction of less negative potentials in the case of reduction. Quite often, electrochemical catalytic reactions can be described in terms of the electrode process characterized by pseudo-first-order chemical reaction. **Upon introduction of a redox system** (i.e. a coordination compound present at two different oxidation states) capable of rapid outer-sphere charge transfer (which is not accompanied by breaking existing and creating new bonds in the system), into the catalytic layer we are dealing with the specific case of electrochemical catalysis: **mediation processes leading to the elctrocatalytic effect**. The direct function of outer-sphere redox centers is, in principle, to enable "non-specific" mediation of charge transfer between the electrode and the reagent. For instance, in a case of the mediator-based oxidation, the formal potential of the redox pair (mediator) must be more positive than the reversible (thermodynamic) redox potential of the induced process. **Electrocatalytic mediation plays a huge role in dye sensitized solar cells** [1-3] during charge transfer between the dye (adsorbed on a photo-anode of titanium oxide) and the redox system (mediator) located between the photo-anode and the counter-electrode. In this respect, my interests have centered on **preparation and characterization (also under**

conditions of the operation of dye sensitized solar cells) of new mediating system in the form of solid redox electrolytes, namely nickel(II) hexacyanoferrate (III, II) present in the mixed oxidation state [H2]. Efficient charge transfer has proved to be dependent on the morphology of the layers, on the concentration of redox centers and on the distance between them required for electron hopping, as well as on the dynamics of counterion (potassium ion) transport that ensures electroneutrality in the system. **In another work [H9] the electrocatalytic mediation, I have proposed the use of platinum nanoparticles ("three-dimensional") distributed in a semi-solid ionic liquid containing a iodine/iodide redox couple capable of inducing chemical step (breaking the iodine-iodine bond in I_3^-) that limits electron transfers in the system.** This concept has been demonstrated (together with measurement methodology of solid-state electrochemistry) to be practical for dye sensitized solar cell measurements [H9].

In chemical catalysis, systems supported onto carriers are often used, especially metal nanoparticles or coordination nanostructures deposited on layers of metal oxides of high surface area. In **electrocatalysis**, the use of a carrier should preclude agglomeration of catalytic sites and their degradation, as well as its use should lead to better distribution of charge (electron, ion) at the interface: electrode - electrolyte solution (with reactant). An ideal support should also interact in a specific way with centers of the catalyst or reactant, or with intermediate products that appear during the reaction. In the case of noble metal nanoparticle interactions with transition metal oxides, a change in the catalytic metal reactivity and selectivity is expected. **My research has encompassed the design, preparation and use of catalytic systems consisting of nanoparticles of platinum, palladium, rhodium or alloys of platinum with ruthenium (or in combination) deposited on the selected oxide support (matrix) during the electrooxidation of such small organic molecules (fuels) as ethanol, methanol or formic acid** [H1, H3, H4, H5, H6, H8, H10, H11, H12]. In particular, in the case of ethanol oxidation, it is necessary to develop multi-functional electrocatalytic systems with the ability to induce C-C bond breaking (in the C_2H_5OH molecule) and the oxidative removal of toxic intermediate adsorbates (typically CO) [4-16,D13]. The problem of deactivation of the catalytic material (noble metal nanoparticles) by poisoning with carbon monoxide is a broader issue and is also an issue in the processes of electrooxidations of methanol and formic acid. Therefore, mono-carbon organic molecules have also been considered, mainly for the purposes of comparative (to the oxidation of ethanol) diagnostic measurements.

The analysis of literature data described in a review article (which I am a co-author) of [D13] has indicated that nanoparticles or sub-microparticles of metal oxides (for example such as WO_3, MoO_3, TiO_2 or CeO_2 have the ability to get covered with hydroxyl groups capable of interacting with the metal centers (e.g. nanoparticles platinum) and inducing oxidation of CO-type poisoning adsorbates. The X-ray photoelectron spectroscopic (XPS) studies show that surface of catalytic platinum become richer in electrons (in other words, they are more metallic) in the presence of metal oxides such as tungsten oxide or titanium oxide [17]. **My interest has centered on very promising (but less understood) zirconium oxide**. In acidic medium (usually considered in research on oxidation of organic fuels for low-temperature fuel cells), ZrO_2 gets covered with the "network" oxo cations characterized by a large population of hydroxyl groups. In view of similarities between the titania and the zirconia, interactions with ruthenium oxo species (responsible for the oxidative removal of poisoning CO adsorbates) originating from bimetallic nanoparticles of PtRu are expected. It is apparent from my studies [H5, H6, H8, H11, H12] that **both nanoparticles of Pt and PtRu exhibit higher electrocatalytic activity in the presence of ZrO_2 matrices during electrooxidation of ethanol, methanol and formic acid**. In order to improve the distribution of charge on the electrocatalytic interface using ZrO_2 or TiO_2, additional carriers in the form of nanostructures (carbon nanoparticles or multi-walled carbon nanotubes) [H6, H10] or gold nanoparticles [H1, H8] should be considered. By controlled combining of nanoporous Pt substrates [H4] or Rh nanoparticles [H5], together with PtRu catalyst and ZrO_2 matrices, it has also been possible to produce **multifunctional electrocatalytic systems (nanoreactors)**, where platinum or rhodium have tended to induce the covalent carbon-carbon bond breaking in the ethanol molecule, whereas centers of bimetallic PtRu have catalyzed (in the presence of ZrO_2) electrooxidation of ethanol and the intermediate products of the reaction. In this context, **the use of super-acidic mixed oxides ZrO_2-WO_3** [18,19] showing a very good mobility of the proton and the good electronic conductivity appears to be particularly **promising with respect to their use as carriers for catalytic Pt or PtRu** [H12, W1]. Some of my observations have been supported with mechanistic and kinetic considerations [H4, H8, H10, H11, H12], that include development of a methodology permitting elucidation of dynamics of processes in a manner analogous to Michelis-Menten approaches known in bioelectrochemistry [H10].

Electrocatalytic processes are also of primary importance to electroanalysis. Modification of surfaces of electrode substrates with an appropriate catalyst allows the use of electrochemical techniques for the determination of substances at the conventional electrode materials (e.g., glassy carbon or graphite) that are otherwise inert during oxidation or reduction. Under the latter conditions, electron transfer is so slow that it leads to low currents associated with the analyte redox processes and precludes determinations with desired sensitivity. The use of an appropriate electrocatalytic material should improve the selectivity the electroanalytical approach or it may permit enhancement of signal originating from the redox reaction relative to those coming from the interfering substances. In addition, the catalyst may be active in the potential range free from common interferences. **In my research, I emphasize the desired properties of the oxide matrix (a layer of ZrO_2 nanoparticles) and its ability to increase activity of oxo-cyanoruthenate toward electrooxidation of L-cysteine** [H7]. It is expected that in the presence of hydroxyl groups covering the zirconia nanostructures the oxidative activity of oxo-ruthenium centers is increased. Consequently, the observed higher oxidation currents of L-cysteine make the electrocatalytic approach of bioanalytical importance (possibility of voltammetric or chronoamperometric determinations).

New concepts of increasing charge transport in redox mediators

During the work on the design, preparation, physicochemical characterization and potential application of electrode layers exhibiting electrocatalytic properties, **I have paid some attention to research aiming at developing redox mediators capable of rapid charge propagation**. Such systems can be used in bioelectrochemistry, as well as charge relays in dye sensitized solar cells. In this context, I have referred my experience (gained during my stay in the laboratory of Prof. J. Augustyński at the University of Geneva) on the preparation and characterization of the semiconductor type electrode materials utilizing nano-TiO_2 layers having thicknesses of 50 microns and consisting of nanoparticles at the level of 25-30 nm in diameter [D2, D5]. The relevant properties of nanostructured TiO_2 are related to the presence of the electrolyte in the pores of the electrode. Application of nanostructured TiO_2 photoanodes coated with ultra-thin layers of the macromolecular complexes of ruthenium (II) allowed absorption of visible light. Here, the commonly used dye (N3) of cis-Ru $(SCN)_2L_2$, where L = 2,2'-bipyridyl-4,4'-dicarboxylate, has been explored. The study has concentrated on new systems as potential redox mediators capable of efficient charge transport in dye sensitized solar cells. Instead of a conventional redox couple (I_3^-/I^-) **we have proposed a mediator layer in a form of film of compressed (solid) inorganic compound at mixed**

oxidation state, namely nickel (II) hexacyanoferrate(II,III), [H2]. From a thermodynamic point of view, a significant **advantage of the cyanometallate as mediator has been in its redox potential system, being not only more positive than the potential corresponding to the level of the ground state of the N3 dye, but also being more positive with respect to the commonly used I_3^-/I^- redox couples**. In other words, the photo-induced potential difference between the photoanode and the counter electrode **could be enlarged**. During preparation of nickel(II) hexacyanoferrate(III,II) layers, care has been exercised to keep **concertation of redox centers on the level higher** than 0.5 mol dm^{-3} and **to assure high rates** (larger than 10^{-1} cm s^{-1} in heterogeneous units) of **electron transfers and of charge propagation** (close to 10^{-7} cm^2 s^{-1}). During incorporation of the mediating system into the pores of dye modified TiO_2, special attention has been paid **obtain dense but porous morphology of the material**. It should be remembered, that electron transfers between iron sites in the cyanometallate mediator must be accompanied by the unimpeded counterion (K^+) displacements. The resulting photocell has been characterized by the following parameters: current density, 8 mA cm^{-2} upon illumination (100 mW cm^{-2} or 1 sun; open-circuit potential, 785 mV, fill-factor, 0.8; and efficiency co-efficient higher than 4%. The diagnostic experiments have also indicated the reproducible behavior during consecutive photoelectrochemical experiments. The system has produced comparable currents (within 20%) over the period of 3 days. Although the efficiency is not impressive relative to the recent reports, it should be remembered that the **obtained results refer to the solid system and therefore are promising**.

Because the usefulness of the redox electrolyte in dye sensitized solar cells depends on the dynamics of charge propagation (both within the electrolyte layer and at the interfaces), I have initiated systematic studies aiming at coupling the catalytic effect with the redox phenomena responsible for electron self-exchange (hopping mechanism) within the redox couple. The triiodide/iodide redox system has been the most commonly and most successfully used charge relay (mediator) in dye sensitized solar cells. Although photoelectric conversion efficiencies as high as 13% have recently been obtained for porphyrin-sensitized solar cells utilizing organic liquid electrolytes containing cobalt(III/II) complexes [20] triiodide/iodide-based systems have provided the most promising results in the area of practical dye sensitized solar cells. There has also been growing interest in **room temperature ionic liquids**, especially those with **1,3-dialkylimidazolium cations** owing to their advantages such as negligible vapor pressure, high ionic conductivity and thermal stability, fairly wide electrochemical window, and ability to dissolve organic and inorganic solutes [21,22]. **The triiodide/iodide redox couple has been considered together with ionic liquids** [23,24]. Both interfacial and bulk (self-exchange) electron transfers involving the triiodide/iodide redox system are somewhat complicated and appear slower than one would expect. Among **the kinetic limitations there is a need to break the I-I bond in the I_3^- or I_2 molecule**; it has also been well-established that Pt (e.g., deposited on the counter electrode) induces electron transfer within the iodine/iodide redox system. Strong interactions of Pt with iodide or iodine have been described [25,26]. Here **I have explored the interfacial (electrocatalytic) phenomena of nanostructured Pt (namely, Pt nanoparticles three-dimensionally distributed in the electrolyte phase at 2% weight level) and utilized them to enhance triiodide/iodide electron transfers to develop more efficient charge relays**. Finally, to make the electrolyte more solid (nonfluid) and to improve the overall electron distribution within the redox-conducting electrolyte, I have also introduce multi-walled carbon nanotubes into the nanocomposite system at 10% weight level as supports for the dispersed iodine-modified Pt nanoparticles. By using the microelectrode-based and sandwich-type electroanalytical methodologies of solid-state electrochemistry, **I have addressed the charge-transport dynamics within the semisolid triiodide/iodide ionic liquid electrolyte admixed with Pt nanostructures and commented on the reasonably high power conversion efficiencies of dye sensitized solar cells utilizing such electrolytes** [H9]. It is noteworthy that the fundamental electrocatalytic investigations have been performed at the University of Warsaw whereas the practical tests with photocells have been done in prof. Grätzel's laboratory in Lausanne. **By applying the solid-state electrochemical methodology (both microelectrode-based and sandwich-type systems), it has been determined that the charge transport coefficients have reached values on the level of $1*10^{-6}$ cm^2 s^{-1} for the Pt-containing electrolytes**. The fact that **the most promising results were obtained with the iodine-modified Pt nanoparticles supported on a network of multi-walled carbon nanotubes reflects the improved electron distribution under such conditions**, as it was found previously for carbon nanotubes in electrode films of importance to electrocatalysis, bioelectrocatalysis, and charge storage (electrochemical capacitors, lithium-ion batteries). Consequently, the limitation originating from the chemical step (accompanying the electrode reaction) practically disappears, and the iodine/iodide redox couple behaves like a reversible electrochemical system. By applying the optimum semisolid redox electrolyte, we obtained

7.9% power conversion efficiency in a dye sensitized solar cell under standard recording conditions.

Multifunctional electrocatalytic systems utilizing metal oxide carriers

There are many reasons for applying metal oxide nanostructures as active matrices in electrocatalytical reactions. In electrocatalysis, the reactivity of surfaces is of particular importance. Redox reactions of metal oxides involve both ion and electron transfer processes. The electron transfer reactions, which could be outer-sphere (less specific) or inner-sphere (more specific) are influenced by the distribution of electronic states in the electrolyte and within the oxide. When oxides are in contact with aqueous solutions, their surfaces are covered with –OH groups; their actual population depends on the nature of the oxide and its specific crystal face [27]. Obviously some metal oxides are more hydrous than the others. The hydrous behavior, which favor proton mobility and affect overall reactivity, reflects not only chemical structure but the oxide texture as well. Recently, there has been growing interest in the utilization of certain non-noble metals, such as W, Mo, Mn, V, Zr and Co, and their oxides.

The respective systems offer a large variety of oxidation states, the potential for mixed electronic/ionic conduction, and the possibility of generation of highly functionalized oxy-species. There also have been attempts to utilize such metal oxides as CeO_2, MgO, Pt–MoOx, WO_3, ZrO_2 and TiO_2 in the preparation of catalysts for direct alcohol oxidation [D13]. Consequently, significant improvement in electrode performance for alcohol oxidation, both in terms of an enhanced reaction activity and of diminution of poisoning has been observed. In the presence of these oxides, both platinum- and palladium-based catalysts were found to be more active than the bare metals alone; that is, the onset potentials for oxidation of alcohols were moved to less positive values.

Metal oxide supports are known to interact with noble metal catalytic centers to affect their morphology, dispersion as well as chemisorptive and catalytic properties [28]. It has apparent from the present study that ZrO_2 surfaces in acid media are also characterized by high population of hydroxyl groups facilitating mobility of protons and oxidative removal of poisoning (e.g. CO) intermediates. **Application of selected metal oxide as carriers for noble metal nanoparticles as catalysts of electrooxidation processes such as formic acid, methanol or ethanol has been explored here**. In particular, oxidation of ethanol is the most determining because, on mechanistic grounds, it does require the C-C bond splitting in the C_2H_5OH molecule.

In a series of my publications, **I have considered the oxide matrices fabricated from WO_3** [H3,H4,H12], **TiO_2** [H1,H4,H10] **and ZrO_2** [H5,H6,H8,H11,H12] **nanostructures**. They tend to stabilized catalytic centers of noble metal nanoparticles (by preventing their agglomeration), provide hydroxyl groups at the electrocatalytic interface, or they can induce formation of oxo species at noble metal (Pt, Pd) and bimetallic (PtRu) surfaces.

I have demonstrated that **the electrocatalytic oxidation of ethanol in acidic medium can be enhanced significantly by supporting bimetallic PtRu nanoparticles on hybrid nanostructured supports composed of zirconia nanostructures and dispersed within rhodium centers** [H5]. The ability of rhodium to induce C-C bond breaking in ethanol is important to this work. It is apparent from diagnostic (voltammetric, chronoamperometric) experiments with two-component (Pt, Rh) catalysts that **the incorporation of rhodium to the catalytic system tends to enhance the electrocatalytic activity of Pt toward the oxidation of ethanol at low potentials (0.25-0.5 V)**. Previously, it was found that bimetallic PtRh nanoparticles exhibited high activity during the oxidation of methanol and ethanol [29-32]. The introduction of **nanostructured and porous ZrO_2** (while being in contact with acid electrolyte) **facilitates proton mobility and provides a large population of –OH groups at the electrocatalytic interface**. Under such conditions, the PtRu system is well-behaved and has been found particularly reactive toward the oxidation of a small organic molecule as methanol. Zirconia behaves in a manner analogous to tungsten oxide or ceria, except that it is likely to provide a larger population of active hydroxyl groups at the electrocatalytic interface. Another important issue is **the presence of oxygen vacancies in zirconia**. Finally, at the proposed to electrocatalytic interface, all components are in close vicinity.

With respect to **oxidation of formic acid, I have demonstrated** [H11] **that modification of noble metal (such as palladium and platinum) catalytic nanoparticles with sub-monolayers of phosphotungstates (in addition to supporting them onto nanostructured zirconia ZrO_2) has led to enhancement effects resulting in increases in the formic acid electrocatalytic currents**. Regarding differences in mechanisms for the oxidation of formic acid at Pd and Pt sites, and remembering that larger amounts of CO adsorbate intermediates are formed on platinum when compared with those formed on palladium, it is reasonable to attribute the enhancement effects to the well-known ability of hydroxyl groups (existing on zirconia in the vicinity of the catalytic metal sites) to promote the oxidative removal of CO-poisoning adsorbates. Polyoxometallates are also likely to compete with CO for noble metal catalytic sites and facilitated their removal according to so-called ‘third-body’ mechanism. On the whole, the most pronounced current increases were observed when both phosphotungstate and zirconia nanostructures have been introduced together into the Pd- or Pt-based electrocatalytic interfaces.

During my internship at the Department of Chemistry, Michigan State University, East Lansing in the USA in the group of prof. G. Blanchard I have also used also **nanostructured platinum plates as electrode substrate**, which were prepared by Stöber method, and they contained Pt nanopores of size of about 200-300 nm. This nanoporous platinum electrode substrate has been **modified with titanium dioxide or tungsten oxide and, subsequently, combined with catalytic bimetallic platinum–ruthenium nanoparticles** [H4]. **Enhancement of electrocatalytic currents in the presence of nanostructured TiO_2 and WO_3 originates most likely from the large surface area and the presence of a large population of hydroxyl groups on the surfaces of those oxides and possible interactions between platinum substrate and the respective nanostructured oxide**. Hydroxyl groups are likely to induce oxidation of CO, passivating intermediates (on Pt), according to a so-called bifunctional mechanism as well as to increase the activity of Ru component (particularly in the presence of TiO_2). **Large populations of hydroxyl groups facilitate high mobility of protons (their displacements are of importance in the ethanol oxidation mechanism).** Contrary to WO_3, which is electroactive and undergoes fast and reversible redox transitions (reversible formation of non-stoichiometric hydrogen tungsten oxide bronzes of the H_xWO_3 type or sub-stoichiometric WO_{3-y} oxides), TiO_2 is inert and non-electroactive. Therefore, the observed current density for electrooxidation of ethanol is higher for PtRu nanoparticles deposited onto platinized nanoporous substrate modified with WO_3 rather than TiO_2. **Thus titania requires admixing with carbon nanostructures (carbon nanotubes)** to improve the overall conductivity at the electrocatalytic interface.

During collaboration with prof. Mohamed Jouini from *Université Paris 7 Denis Diderot, Interfaces, Traitements, Organisation Dynamique des Systèmes in France*, I used a nanostructured WO_3 in a form of **anhydrous WO_3 nanowires as carriers for dispersed nanoparticles of palladium for the electrooxidation of formic acid** [H3]. Nanowires have been prepared according to the procedures developed by the French side through the hydrothermal method and had hexagonal structure. Their diameter have ranged from 50 to 70 nm and the length has been 5 μm. I have showed that **the catalyst system consisting of the**

tungsten oxide nanorods (together with dispersed Pd nanoparticles) has exhibited the enhancement effect during oxidation of formic acid at the potential as low as 0.04 V. It can be expected that, in addition to the presence of the specific interactions between the metal catalytic sites (Pd) and OH groups on tungsten oxide surfaces, the formation of partially reduced WO_{3-y}, or H_xWO_3 (coexisting with the oxidized WO_3 nanostructures) facilitates adsorptive/desorptive phenomena or interfacial oxygen transfers leading to the oxidative removal of CO adsorbates from the catalytic palladium. Utilization of WO_3 nanorods together with Pd nanoparticles may be of importance to the development of the catalytic anode materials for oxidation of simple organic molecules.

I have also considered the **hybrid system consisting of gold nanoparticles** (sizes, 30-40nm) **modified with a heteropolyacid of molybdenum together with platinum nanoparticles** (7-8 nm) **dispersed over the matrix of nanostructured titanium oxide for the electrocatalytic oxidation of ethanol process** [H1]. Due to the high active surface area and the possibility of a specific interaction with the catalytic centers of platinum, nanostructured TiO_2 (which is composed of anatase (80%) and rutile (20%)) in form of particles (20-25 nm) has been used. **The use of nanostructured TiO_2 matrix for platinum nanoparticles has improved the efficiency of the catalyst (during the electrooxidation of alcohol) Pt nanoparticles**. Among important issue are the presence of hydroxyl groups, good conductivity (due to the presence of gold nanoparticles) and the existence of specific interactions with the centers of platinum. Immobilization of nanometric carriers of gold (stabilized with phosphomolybdates) onto the porous matrix oxide (TiO_2), followed by introduction of nanoparticles of platinum, has resulted in the improvement of the performance during electrocatalytic oxidation of ethanol, as determined from both the voltammetric and chronoamperometric responses. The activating effect of TiO_2 on platinum catalyst can be facilitated by the presence of specific interactions between nanoparticles of gold and platinum.

The most promising and truly novel results related to the electrooxidation of ethanol on platinum catalysts refer to the use of the matrix utilized in the form of the mixed metal oxide WO_3/ZrO_2 [H12,W1]. An important feature of **the mixed oxide of tungsten and zirconium is its high Broensted acidity**, for example well-established during the hydrocarbon conversion or selective catalytic reduction of NO_x to N_2. In the course of my studies **I have proposed methodology for the preparation of the nanostructured matrix composed of the mixed metal oxide (WO_3/ZrO_2) in the form of interpenetrating thin**

layers of both oxides deposited on the inert glassy carbon electrode (here the internal layer is tungsten oxide, and zirconium oxide serves as outer layer). Electrooxidation of ethanol is a complex process, because it requires the C-C bond breaking in the molecule of ethanol. The overall process of electrooxidation of ethanol (in an acidic medium) involves 12 electrons leading to carbon dioxide. In practice, intermediate products such as acetaldehyde, acetic acid and carbon monoxide tend to predominate. Platinum itself is characterized by the highest activity toward the dissociative adsorption of ethanol molecules, but its surface is rapidly poisoned by strong adsorption of the intermediate products of the electrooxidation process (mainly carbon monoxide). The activating role of WO_3/ZrO_2 is to weaken the CO-Pt bond or to induce removal of CO type adsorbates from Pt. **I clearly demonstrate that the electrooxidation of ethanol, methanol and acetaldehyde in acid medium is enhanced by deposition of Pt nanoparticles onto the matrix consisting of a thin layer of the mixed metal (W, Zr) oxide.** Indeed significant increases catalytic currents measured have been observed at room temperature both under the voltammetric and chronoamperometric conditions. This effect is due to the fact that **the matrix (a mixed oxide of tungsten and zirconium) is characterized by high porosity and high population of hydroxyl groups (due to the presence of ZrO_2) in addition to high Broensted acidity of mixed WO_3/ZrO_2, rapid electron transfers coupled to proton mobility** (e.g., in partially reduced hydrogen tungsten oxide bronzes, H_xWO_3) **occurring in the vicinity of the platinum catalyst in addition to the possibility of strong interaction between metal oxides and Pt nanostructures.** The fact that the mixed metal oxide WO_3/ZrO_2 nanostructures are in direct contact with catalytic sites of the Pt **leads to the competitive effects ("third body effect")** [33-35] through hydroxyl groups competing on the surface with adsorbed CO. Therefore, these features facilitate desorption and the oxidative removal (eg. CO to CO_2). Partially reduced tungsten oxide (H_xWO_3) component characterized by fast propagation of electrons and protons and tends to improve charge distribution at the electrocatalytic interface. Furthermore, mixed oxide (WO_3/ZrO_2) exhibits increased stability due to electrostatic interactions between the positively charged surface of the zirconium oxide and negatively charged anion of tungsten.

An important observation coming from our further research on **the electrooxidation of ethanol refers to the use of mixed tungsten oxide/zirconium oxide as matrix for bimetallic PtRu**. Indeed, **the observed electrocatalytic currents have been higher and electrooxidatin of ethanol has started at less positive potentials (relative to the behavior**

at bare PtRu) [W1]. Because the electrooxidation of the ethanol PtRu-based catalysts proceeds through a simple dehydrogenation to acetaldehyde [36], there is a need to induce C-C bonds breaking in the molecule of ethanol. Consequently methanol is formed, and it further oxidized to CO_2. Knowing that Rh metal and its alloys have the ability to break of C-C bond, and to improve the selectivity of the oxidation of ethanol toward the formation of CO_2 [31,32,37-39], **rhodium nanoparticles have been introduced in a controlled manner to the electrocatalytic interface**. Thus electrocatalytic system has consisted of two types of particles: **rhodium nanoparticles deposited on WO_3 (inner layer), and bimetallic platinum-ruthenium nanoparticles, placed on ZrO_2 (outer layer). Both Rh nanoparticles and PtRu nanostructures are separated by ZrO_2 (in WO_3/ZrO_2)**. This situation leads to the significant increase in catalytic currents. In other words, **it is reasonable to expect formation of "nanoreactor" where Rh catalyzes the C-C bond breaking (chemical step) in the C_2H_5OH.** Consequently, CH_x/CH_4 and CO-typeadsorbates [40], or even the methanol-type intermediates, are formed [D13]; they can be further oxidized (electrochemical step) over the bimetallic PtRu .

Electrocatalytic processes in systems of analytical importance

Hexacyanoruthenate (III,II) ruthenium (II,III,IV) can be considered as ruthenium analogue of Prussian Blue, namely iron (III,II) hexacyanoferrate (III, II). Unlike the latter arrangement, **ruthenium cyanide complexes**, can be oxidized to higher oxidation states which leads to the generation oxo-ruthenium centers within cyanoruthenate network (hence it can be called system oxo-cyanoruthenate) with high catalytic activity in the processes of **electrooxidation of inert organic compounds** [41]. It is believed that oxo-cyanoruthenate layer consists of ruthenium oxide forms of oxidation states higher than the third, and consists of two kinds of active sites $-Ru^{IV}-O-Ru^{III}-OH_{ads}$ and $-Ru^{IV}-O-Ru^{IV}-O-$, which are formed with increasing time electrode potential. These centers result from oxidation of the Ru (III) layer, and the oxygen comes from the electrochemical decomposition of water (O_{ads} and OH_{ads}). They differ in their abilities and catalytic specificity during electrooxidation processes in which there is transfer of the oxygen atom to the molecule reagent. Hexacyanoruthenate (III) are transformed into dual-core complex of ruthenium $(CN)_5-Ru^{II}-CN-Ru^{III}-(CN)_5^{6-}$. The deposits have low ohmic resistance as a result of the effective electron transport between the ruthenium ions on mixed oxidation states.

My research has centered on utilization of oxo-cyanoruthenate as the analogue of Prussian blue as the electrocatalytic system for the detection of L-cysteine. Although the simple layer oxo-cyanoruthenate exhibits some catalytic properties toward the electrooxidation of L-cysteine, its reactivity is insufficient and leads to very low currents (during both amperometric and voltammetric measurements) impractical for analytical purposes. In work [H7], **I have proposed a composite layer composed of zirconium oxide and oxo-cyanoruthenate through application of the layer-by-layer type method to the substrate of glassy carbon modified with an ormosil film** with pores templated to have 10-50-nm diameters. Consequently, a **new stable composite system of controlled composition and morphology containing oxo-cyanoruthenate centers adjacent to zirconia nanostructures has been obtained**. In this context, the electrostatic interactions between the positively charged zirconia (ZrO^{2+}, $ZrOH^{3+}$ $[Zr_3(OH)_4]^{3+}$) oxo cations and oxo-cyanoruthenate polyanion should also mentioned. Nanostructured ZrO_2 has been chosen here because the oxide is characterized by high population of hydroxyl groups and high mobility of protons on the surface, in addition to high degree of porosity and physicochemical stability. Furthermore the activating interactions between zirconium oxides and oxo compounds of ruthenium can be envisioned. In this context, ZrO_2 has properties similar to the TiO_2 [27]. **The proposed multi-layer composite system has exhibited significant electrocatalytic effect resulting in the increase of L-cysteine oxidation current.** The catalytic current has increased along with the number of multilayers although the electrode processes are diffusion limited. It seems that the ZrO_2 increases the number of active sites originating from oxo-cyanoruthenate. Also easier access of protons to catalytic sites is expected in the presence of hydroxyl groups on zirconia promoting their mobility. This study emphasizes once more the activating role of nanostructures ZrO_2, not only with respect to nanoparticles of noble metals, but also toward the catalytic oxo-ruthenium centers. **The proposed electrocatalytic system can be used to study the oxidation of biological compounds and to prepare electrocatalytic amperometric sensors of practical analytical importance**.

Conclusions

During my studies, I have proposed and developed the concept of the preparation of new nanostructured electrocatalytic systems of defined composition and morphology, specific reactivity, as well as the defined functionality. In particular, the subject of my interest has been to develop systems operating according to simple or induced electrocatalytic mediation, namely with use of polynuclear layers of nickel hexacyanoferrate with mixed oxidation states ($Fe^{III,II}$) and good conductivity of the potassium ion or by considering ionic liquids containing the iodine/iodide redox couple together with a finely dispersed catalytic platinum nanoparticles. These solid or semi-solid mediation systems are capable of facilitating rapid charge propagation in dye sensitized solar cells. Consequently, the performance parameters of these cells have been competitive with respect to those cited in literature. Much attention I have been paid to designing and physicochemical characterization (in particular, electrochemical) of systems exhibiting specific properties in electrocatalytic (namely, during oxidation of simple organic fuels: formic acid, methanol, and particularly ethanol). The proposed systems have utilized nanoparticles of noble metals (Pt, Pd, and bimetallic PtRu) deposited on the selected oxides of transition metals (ZrO_2, TiO_2, WO_3 and mixed WO_3/ZrO_2). Special attention has been paid to the determination of desirable physicochemical parameters of nanostructured oxide matrices, including their ability to generate active hydroxyl groups, their acidity and the proton mobility, as well as good electron conductivity at the electrocatalytic interface. In the case of electrooxidation of ethanol, the use of systems consisting of two types of catalytic nanoparticles (Rh and PtRu separated by the nanostructured oxide) or utilizing the platinized sub-microporous substrate electrode modified with the metal oxide with finely dispersed PtRu nanoparticles have resulted in the formation of multifunctional electrocatalytic "nanoreactor", in which rhodium has catalyzed the C-C bonds breaking in the C_2H_5OH molecule and PtRu has induced further oxidation of both reactant and the reaction intermediates (carbon monoxide, methanol, or acetaldehyde). Because of oxidation of simple organic molecules is normally accompanied by the formation of the passivating -CO type adsorbates, the specific interaction between metal oxide with the hydroxyl groups existing on its surface and noble metal nanostructures is also of primary importance. The results summarized here point on promising properties of matrices consisting of ZrO_2 nanoparticles or strongly acidic mixed oxides, WO_3/ZrO_2. Certain metal oxides, in particular the zirconia nanostructures, can also be act as active matrices for more complex catalysts, such as cyanide crosslinked ruthenium oxide nanocenters (oxo-cyanoruthenates). Such systems may be useful in electroanalysis because they can catalyze oxidation of electrochemically inert reactants (e.g. L-cysteine) they are of general bioanalytical importance. In the latter case, interactions between activating zirconia nanostructures and ruthenium oxo-compound, similar to those postulated for the mixed oxides of the type TiO_2-RuOx can be envisioned. In my research, much attention has also been paid to mechanisms and dynamics of charge transport in both the catalytic layers having redox properties, and at the electrocatalytic interfaces.

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