

ELECTROCATALYSTS IN THE LAST 30 YEARS – FROM PRECIOUS METALS TO CHEAPER BUT SOPHISTICATED COMPLEX SYSTEMS

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The paper is concerned with the advance and diversification of materials used as electrodes for evolution of chlorine, hydrogen and oxygen. In the first part a survey is given of our research in the field of electrocatalysis 30 years ago, when Ru and other precious metals were the exclusive electrocatalyst materials. A brief scope of the achievements of electrocatalysis in that period is given as well. The second part deals with our recent research on formulation and characterization of a new class of electrocatalysts, based on a combination of non-precious metals, but still exhibiting an ability to promote hydrogen evolution reaction as successful as platinum and other precious metals are.

Among the produced (non-platinum) catalysts the best performance for the hydrogen evolution reaction was measured at the electrocatalyst containing Co or CoNi as hyper *d* phase and TiO₂ as hypo *d* phase. A typical formulation of the electrodes is, e.g.: 18% (TiO₂) alloyed with 10% Co and applied on a substrat of carbon powder (Vulcan XC-72). At this electrocatalyst hydrogen evolution overpotential at 10 mA·cm⁻² was 40 mV higher than that on a corresponding electrode containing platinum as hyper *d* phase.

For both electrocatalyst systems of interest analysis is made and aimed to recognize the sources that cause the electrocatalytic activity. This is the proper way how to use the acquired knowledge for further improvement of the existing materials or/and to discover new ones.

Key words: electrocatalysis; hydrogen evolution; hypo-hyper *d*-electrocatalysts

INTRODUCTION

Electrocatalysis is one of the most actual fields of contemporary electrochemistry. Practically, electrocatalysis was initiated in the 1920s by Bowden and Rideal, who made a series of measurements of hydrogen evolution overpotential as a function of *j* for a number of metals [1]. The term electrocatalysis was coined in 1936 by Kobozev [2], but in the next 30 years little attention was paid to this phenomenon.

For many years hydrogen evolution reaction was mainly the only one where the effect of the electrode material on the rate of hydrogen evolution was studied in details. Platinum was found to be the electrode material on top of which hydrogen

evolves with minimum overpotential. From purely academic, the problem how to lower the overpotential (thus lowering the product price) gets on importance with the growth of technical processes of electrolysis. Performed on a large scale, their economy depends greatly on the electricity consumption per unit product, i.e. on the value of cell voltage. As shown in Fig. 1 bellow, some components of the cell voltage could be lowered, thus making the product cheaper.

Overpotentials related to the charge transfer processes at the anode or cathode are the ones that could be lowered by the proper selection of electrode's material. This is the issue of the electrocata-

lysis. Summarized, the goal of the applied electrocatalysis is to improve the electrode activity for the wanted reaction, but at the same time to prevent (or slow down) side reactions. Technical reasons request the selected electrode material to be stable (without corrosion and wear), economical reasons favor cheaper materials, while environmental concern is in favor of nonpolluting electrode materials. (Overpotentials related to the Ohmic drop are lowered by proper cell design.)

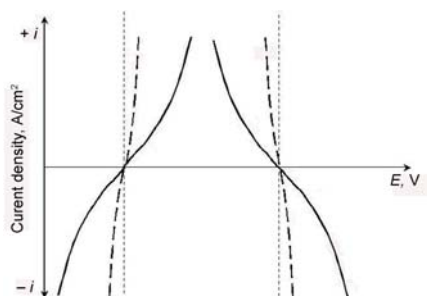


Fig. 1. Polarization curves for poor and good electrocatalysts (lowering of η_a and η_c values at good catalysts is shown)

Applied electrocatalysis advanced over the fundamental research with the extraordinary performances of anodes for chlorine evolution patented by Beer [3] in the mid 1960s. RuO_2 was the active component in these catalysts. For the first time platinum was not in the focus of the material choice and the result was more than excellent [4].

Traditionally, for laboratory and small-scale plants, platinum was the first choice as electrode material for both cathodic and anodic processes [5]. Platinum metal in a shape of bars, foils (continuous and latter perforated) or gauze, was used over a long period. Nevertheless, platinum was not accustomed in commercial use, due to its disadvantages (too expensive, extensive corrosion when used for Cl_2 production, etc.).

Later the surface area was enlarged by a factor of $10^2 - 10^3$ by plating Pt on top of Pt ('Pt-black') or by applying tiny quantities of finely dispersed Pt on a proper substrate. It was demonstrated that even immeasurable traces of Pt (remained on crucible walls after its thorough cleaning) enhance the electrocatalytic activity of oxide catalysts calcinated in that crucible. A number of paints were developed containing platinum only, and then platinum/iridium in the ratio 70/30. This was the pioneering step in the field of synergism, due to the fact that the alloy was superior to pure platinum. Later these coatings for titanium electrodes were replaced by ones containing ruthenium dioxide [6]. The field of porous electrocatalysts

with the roughness factor reaching even over 10^3 was opened.

Next to the efforts to increase the electrode's activity by purely 'mechanical' means (as the increase of the surface is), other efforts were made and aimed to change the polarization characteristics of the electrode material. This could be considered as true electrocatalysis, because achieving higher exchange current density and/or lowering the slope of polarization curve (i.e. parameter b in the Tafel equation $\eta = a + b \log j$) is the real task of the electrocatalysis (Fig. 2).

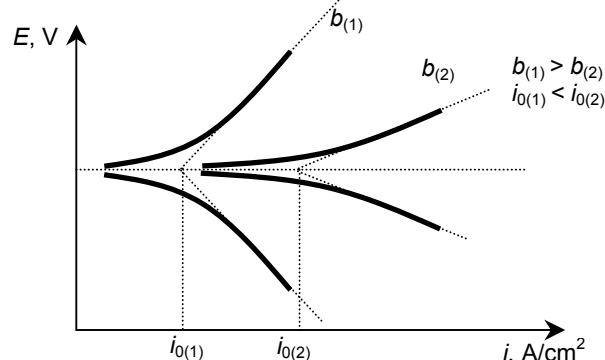


Fig. 2. Polarization curves showing the increase of i_0 and decrease of the slope parameter b at good catalysts

The transition from one-metal-only electrocatalyst to a two or more metal (or their compounds) catalysts was not at all easy. It took almost 30 years from the first rhodium electrodeposited on titanium electrocatalyst till the first titanium-based anodes in the cathodic protection of rebar in concrete (see Table 1). Development of electrocatalysts without precious metals started in the middle 1970's and then extended over a long period.

Table 1

Chronology of the new era of non-single metal electrocatalysts

Year	Electrocatalyst	Author
1958	Rhodium electrodeposited on titanium	H. B. Beer
1958	Platinum electrodeposited on titanium	J. B. Cotton
1960	Paint/thermal decomposition coatings	C. H. Angell
1965	First mixed metal oxide coatings	H. B. Beer
1968	First titanium based electrodes (70/30 Pt/Ir coated)	/
1974	First nonprecious metal alloys (Co-Mo)	M. M. Jakšić
1984	Titanium-based anodes in electrogalvanizing	/
1986	Titanium-based anodes in the cathodic protection application	/

The strategy laying behind this important switch from one type of electrocatalysts, made out of rather expensive and limited in quantities pre-

vious metals, to the new type of compound (?) catalysts engineered trivial components, but promising unrestricted possibilities was fully correct.

A. PRECIOUS METAL ELECTROCATALYSTS

Depicturing the ruthenium oxide electrodes

Over a span of 30 years* the Electrochemistry group at the Faculty of Technology and Metallurgy in Skopje experienced an almost identical development of the subject of interest in electrocatalysis. Starting with noble metal electrocatalysts we switched to systems without precious metals. The former research was mainly concerned with ruthenium, while the latter one comprised systems of hypo-hyper *d* electronic metals, such as Ni, Co, Mo, W etc.

As described in [7–9], in order to elucidate the behavior of RuO₂ as corrosion-resistant electrode material having low overpotential for anodic Cl₂ evolution, characterization of oxidized Ru-electrodes was done. Four different types of Ru-electrodes were prepared and tested, e.g. bulk Ru-electrode, ruthenized Pt- and Ru-electrode and a Ru-electrode chemically formed by painting a strong solution of Ru-red on a cleaned glass tube and firing it in air at 700–750 K. In all cases electrode surfaces were produced that were used to resolve the states of surface oxide formation and reduction as well as of H-adsorption at Ru, as a step inevitable for further depicting of the complex TiO₂ + RuO₂ systems (see Fig. 3).

At that time, there were a few studies on the stability of ruthenium under anodic polarization in acidic and alkaline solution [10]. As far as RuO₂ is concerned, the electrochemical behavior of chemically prepared RuO₂ was compared with that of electrochemically grown one on a ruthenium electrode by Trasatti [11] and Galizzioli [12]. The cyclic voltammograms for those two kinds of electrodes are presented in Fig. 4. It is shown that formation of RuO₂ on ruthenium occurs at approximately 1.0 V, following the onset of metal surface oxidation at 0.55 V. The main feature of the voltammogram taken at Ru-electrode (Fig. 4) is that no definite separation between the hydrogen adsorption and the oxide reduction regions is observed, as it is at Pt (see, e.g. [13]). Performing similar study at the University of Ottawa with B.

E. Conway's group, one of us was able to show more clearly the hydrogen adsorption peaks on electroplated ruthenium [8, 9]. Some adsorption of hydrogen in Ru was detected as well [14, 15].

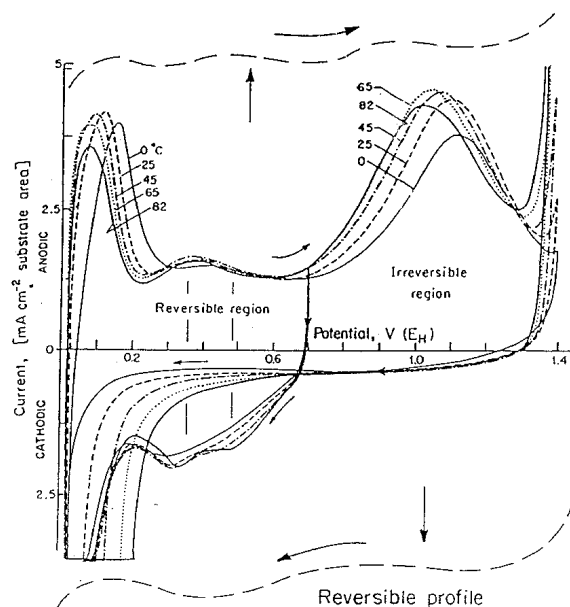


Fig. 3. Cyclic voltammograms for three different types of Ru-electrocatalysts. Ruthenized Pt and Ru thermally deposited on glass

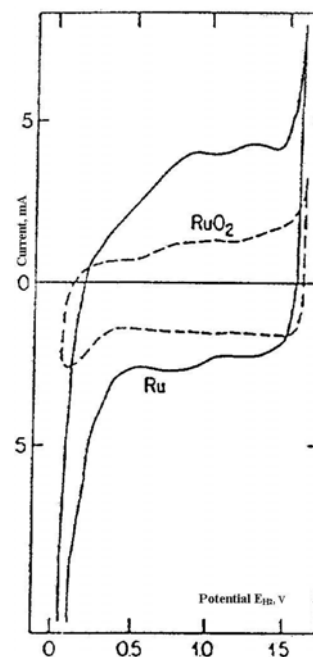


Fig. 4. Cyclic-voltammograms at a ruthenium and RuO₂ electrode

* The period that coincides with the Jubilee of the Bull. Chem. Technol. Maced.

Studies on the formation and reduction of surface oxide on Ru (see Fig. 5) led to conclusion that:

– initial stages of reversible oxidation arise at low potentials (0.2–0.4 V E_H), where ionization of hydrogen also occurs;

– higher state of oxidation, progressively more irreversible, occurs beyond 0.8 V;

– oxidation that occurs at 1.3–1.4 V gives rise to a film that is only slow reducible in the hydrogen region;

– repetitive cycling to 1.3 V causes an irreversible transformation of surface oxide film to a state that undergoes red-ox process over a wider range of potentials. Consequently, reduction back to metallic state becomes less complete;

– as the potential scan rate increases, the cyclic voltammetric curves become less structured.

More complete explanation of the electrocatalytic effect of oxide electrodes was given later (see, e.g. S. Trasatti's review [16], or L. D. Burke [17]).

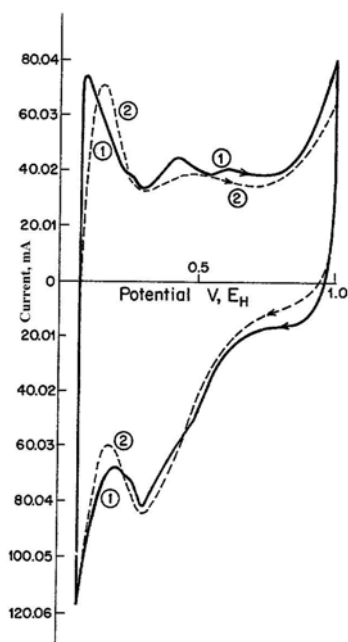


Fig. 5. Cyclic voltammograms for Ru metal in aqueous $1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ showing behavior of initial cycles where monolayer oxide formation arises

Among the issues important for the electrocatalytic activity of oxide electrodes one should refer to (i) chemical composition (bulk, surface and profile) of the active layer; (ii) properties of the active layer as e.g. electrical conductivity, structure, etc.; (iii) the size of the electrochemically ac-

tive surface area; (iv) the nature of the layers support; (v) hydration and proton exchange between oxide and the electrolyte, which could have a decisive role in switching the mechanism of electrode reaction to a slope of 40 mV/decade (instead of unfavorable 120 ones), thus producing the electrocatalysis' main effect.

The surface structure of the electrode in solution is the feature that distinguishes the oxide electrodes. Their surface is with high energy content and with strong hydrophilic character, so that it attracts water molecules and gives a layer of OH groups on top of the oxide. This layer mediates the action of the oxide's surface with the solution species. The OH groups are responsible for the exhibited electrocatalytic activity. The mechanism of surface charging of oxidized catalysts is quite different from that of bare metal surfaces, since it is governed by the pH-dependent acid-base dissociation of the surface OH-groups. Behaving as weak acids or basis, these groups exchange protons with the solution. This is the basis of the mechanism by which the inner sites can be active in reactions involving water molecules. (Water molecules can penetrate into the oxide layer, thus producing an 'inner' interface).

Cyclic voltammetry can produce informative characterization of oxide layers if taken in conditions where no Faradaic process occurs and the solvent is not electrochemically decomposed. The shape of the voltammograms provides evidence of intermediate species, surface red-ox transitions or phase formations. So, when repetitive cycling of a Ru metal electrode was done in the potential range of 0.05 – 1.42 V (E_H), progressive growth of oxide film occurs since the oxide is not reduced to Ru metal at the least positive potential of the sweeps (see Fig. 6).

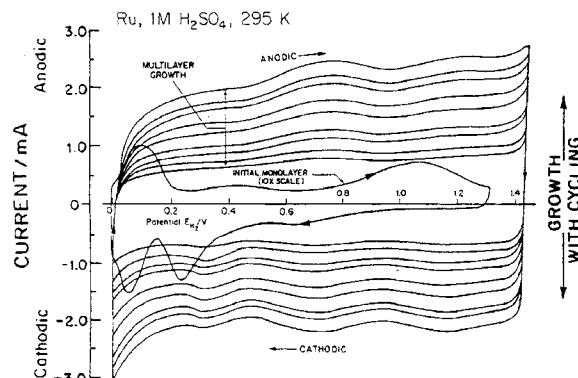


Fig. 6. Progressive increase of oxide film growth with potential cycling at Ru, exhibiting increase of capacitive reversible current response

Peaks on the voltammetric curves in Fig. 5 are associated with red-ox transition of surface sites. Therefore, the voltammetric charge is proportional to the number of active sites. It is a measure

how large is the active surface area and is valuable in determining the real catalytic activity as opposed to the one resulting from purely geometric factors only (large roughness factor).

B. ELECTROCATALYSTS BASED ON NONPRECIOUS METALS ($2\text{H}^+ \rightleftharpoons \text{H}_2$) COMBINING HYPO-HYPER *d*-METALS

Brief history

Selection of electrode materials for industrial electrocatalysis processes is not at all an easy task. The conflict of technical and economical issues is evident: the best performing electrocatalysts as, e.g. Pt, Pd, Ru are expensive, while the cheaper substituents using less noble metals as, e.g. Ni, Co etc. suffer of corrosion, passivation or similar problems.

The need for active, stable and cheaper electrocatalysts motivated intensive research, resulting in development of multicomponent catalysts. It was normal to start with combining the most active precious metals. So, electrocatalysts as Pt-Pd or Ir-Re [18,19] were prepared, but the resulting synergetic effect did not satisfy the expectations. Later on, based on theoretical analysis of bonding in metals and intermetallic phases given by Brewer [20], Jakšić et al., [21], the efforts were oriented towards combining nonprecious metals. In the early stages of this research, intermetallic Mo-Co alloys were prepared with activity even superior to that of the individual metals of the platinum group. For hydrogen evolution/reduction reaction it was predicted and proved that combination of *d*-metals with dissimilar electronic character exhibits pronounced synergetic effect [22]. As a result, combination of hyper *d*-electronic transition metals (having proper individual catalytic activity) with hypo *d*-electronic transition metals (poor catalysts as individual metals) becomes subject of scientific and technical interest. A “new era” of modern electrocatalysis was opened.

There is an analogy between the stability and the electrocatalytic activity of this group of intermetallic compounds. The existence of Laves phases of high symmetry and extra stability is associated with the highest electrocatalytic activity, in some cases even exceeding that of the most active precious metals. This is the case with hypo-hyper *d* combinations as MoFe₃, WFe₃ [22], LaCo₅, LaNi₅ [23] etc.

The partners in these polycomponent systems could be in both elemental or combined state, ox-

ides, sulfides and phosphides being the most frequent compounds. Also, their crystallinity could vary from crystalline to amorphous, depending on the preparation procedure.

Depending on the state of hypo and hyper *d* components, these catalysts can be distinguished into 5 groups as it is shown in Table 2.

Table 2

Distinguishing hypo-hyper d-intermetallic electrocatalysts

	Type of hypo-hyper <i>d</i> -electrocatalyst	Examples	References
I	Intermetallic catalysts	Mo-Co, MoPt ₃ , MoNi ₃ , MoFe ₃ , LaCo ₅ , Ti _{1-x} Ni _x (Tiney Ni), Ni-Co-Mo, Ni-Zr, Co-Zr, etc.	[22–27]
II	Sulfides, Phosphides	Ni-W-S, Ni-W-P, Fe-Ni-P etc.	[28–30]
III	Catalysts based on Raney-Ni	Ni-Al-Ti, Ni-Al-Mo, Ni-Al-Cr, Ni-Zn-Ti, Ni-Zn-Mo etc.	[31–35]
IV	Mixed oxides	TiO ₂ -RuO ₂ , TiO ₂ -IrO ₂ , Ru _x Ti _{1-x} O ₂ , RuO ₂ -IrO ₂ etc.	[36–41]
V	Hypo oxide – hyper metal	Pt-TiO ₂ , Pt-Ru-WO ₃ , Ni-V ₂ O ₅ etc.	[42–44]

I. Both components are in *metallic state*, crystalline or amorphous. Usually, an intermetallic compound (A_xB_y) is formed, although there are some cases where solid-state solutions or mixtures exist.

The most representative catalysts of this group are systems containing titanium and nickel, (Ti_{1-x}Ni_x), also called “Tiney-Ni” electrodes. They are produced by mechanical alloying and are characterized with both high surface area and a high catalytic activity [24].

II. Both components are in *combined state*, usually (both or only hyper component) as *sulfides* or *phosphides*. Due to their amorphous character, these electrodes could adsorb and absorb more hy-

drogen than pure Ni does. Their activity could exceed by a factor of 10 the one of activated Pt or even by a factor of 250 the one of nickel [29].

III. Hyper *d*-component is in *combined state*, while the *hypo* one is in *metallic state*. The hyper *d*-component is a Raney-Ni alloy (alloy of Ni with a metal that is easily leachable in alkaline solution, as e.g. Al or Zn). The real surface area of this group of catalysts could reach 1000 to 12000 times the surface area of pure Ni [35].

IV. Both components are in *oxide state*. Traditionally RuO₂ or Co₃O₄ were (co)deposited on Ni, thus giving improved activity for hydrogen evolution reaction and long-term stability too [38, 39]. Oxide phase concentrated at the surface implies development of high surface area. Latter, mixtures of oxides were applied instead one-metal oxide hypo *d*-phase. TiO₂-RuO₂, Ru_xTi_{1-x}O₂, TiO₂-IrO₂ etc. were successfully prepared [38–41].

V. Hyper *d*-component is individual *metal* or *alloy*, while the *hypo d*-component is a *metal oxide*. The former is, e.g. Ni, Pt, Co, Co-Ni, Pt-Ru etc, while the latter is e.g. TiO₂, WO₃, TiO₂-WO₃ etc. [42–44].

This is a subject of a recent investigation. It is also a subject of our interest in this paper. We do use pure nonprecious metals (as e.g. Co or Ni) or their mixture (CoNi) as hyper *d*-phase and TiO₂ as hypo *d*-phase.

Preparation

The investigated catalysts were prepared by the sol-gel procedure described elsewhere [45], but simplified in some parts by the present authors. In the first stage, the hypo *d*-electronic oxide phase (TiO₂) was deposited on carbon substrate. Ti-isopropoxide (Aldrich, 97 %) was added into dispersed Vulcan XC-72 (Cabot Corp. Boston Mass.) in anhydrous ethanol. To provide hydrolysis of Ti-isopropoxide to Ti(OH)₄, a small amount of 1M HNO₃ in the ratio of 10:1 was added. This mixture was evaporated at 60 °C with continuous stirring with 600 ÷ 900 min⁻¹ until fine nano-structured powder of catalyst support was obtained. Further, individual or mixed Me-2,4-pentaedionate (Alfa Aesar, Johnson Matthey, GmbH) was dissolved in absolute ethanol or acetone. This solution was added into a dispersed catalyst support in anhydrous ethanol. The evaporation was carried out under the same conditions as above. The aim of this operation is to graft the metal-hyper phase

onto a catalyst support. To decompose both Ti(OH)₄ to TiO₂ and the residual amount of organometallics, the powder was heated for 2 h at 250 °C in the atmosphere of H₂ and N₂. Catalysts were prepared having the following composition: 18 % TiO₂ + 10 % Ni + Carbon and 18 % TiO₂ + 10 % CoNi + Carbon. Also the platinum/TiO₂ catalyst was prepared as a reference catalyst.

The produced catalyst powders were further used for preparing porous electrodes for hydrogen evolution reaction. Electrodes where three phases (solid electrode, liquid electrolyte and H₂ gas as product) are in contact were prepared by hot pressing at 300°C with the back layer being of carbon black acetylene + PTFE and the front layer is the catalyst + PTFE [46]. The cross section of electrodes is shown in Fig. 7.

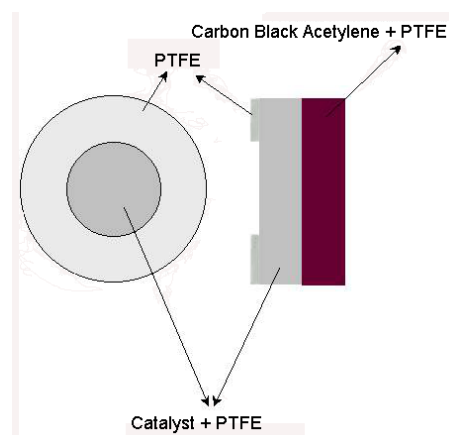
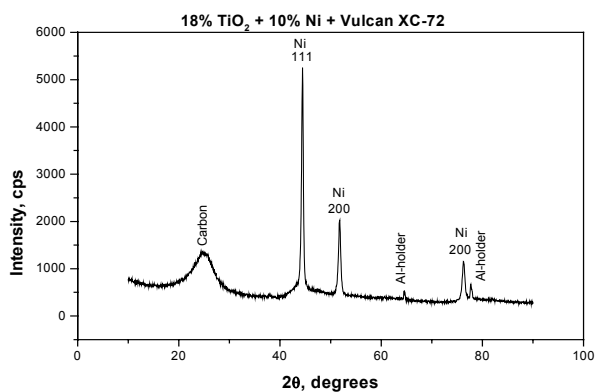


Fig. 7. Cross section of three phase gas-diffusion porous electrode

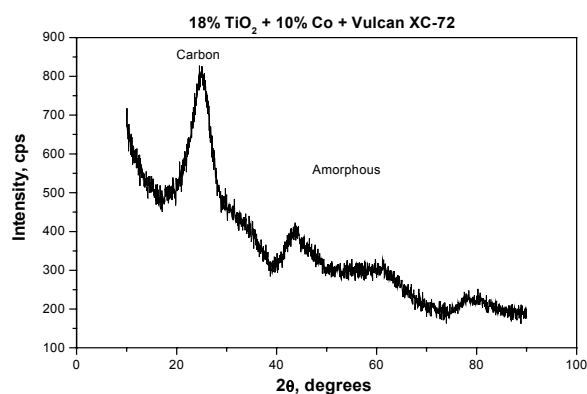
Structural characterization

XRD and SEM techniques were used for determining structural characteristics of the catalysts. XRD measurement was carried out on XRD diffractometer Philips APD 15, with CuK_α radiation. XRD spectra are shown in the Fig. 8. In the first XRD pattern (Fig. 1a), there are characteristic peaks corresponding to Ni crystalline f.c.c. structure. This pattern corresponds to pure Ni with a cell parameter $a = 3,524 \text{ \AA}$. There is no peak corresponding to the crystalline phase of TiO₂ (anatase or rutile), what means that TiO₂ is amorphous. XRD-spectra of the Co/TiO₂ catalyst show a very wide range of peaks, corresponding to the amorphous state of all components with the particles size less than 2 nm (Fig. 8b). For the CoNi/TiO₂ catalyst, the present peaks correspond to crystalline Ni, but with lower intensity (Fig. 8c). The determined value of the cell parameter of the metal

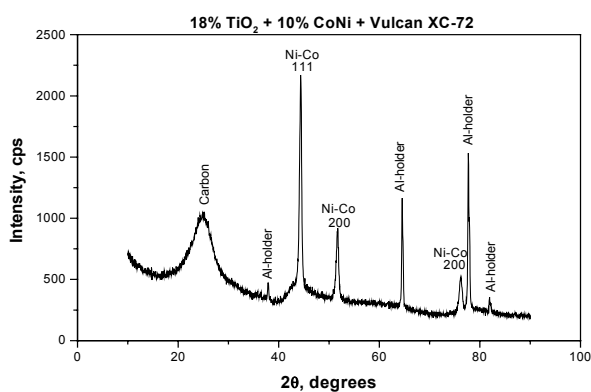
phase ($a = 3,5318 \text{ \AA}$) is between the values of pure Ni ($a = 3,524 \text{ \AA}$) and pure Co ($a = 3,544 \text{ \AA}$). This reveals a presence of a solid-state solution of Co and Ni. It means that Co atoms substitute Ni in the crystalline Ni local environment through a structural phase transition where the host component Co changes from amorphous to crystalline. The crystal size of hyper-metallic d components in the Ni/TiO₂ and the CoNi/TiO₂ catalysts is 10 to 20 nm.



a)



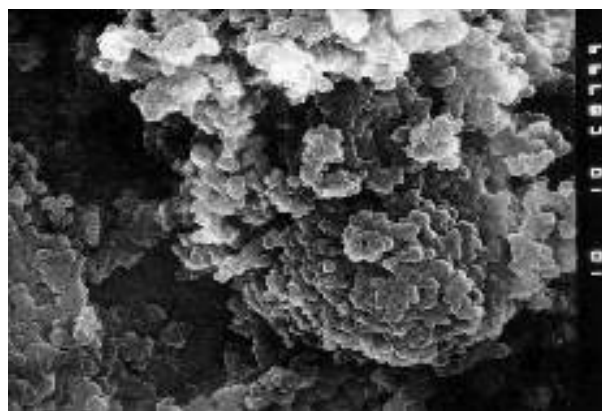
b)



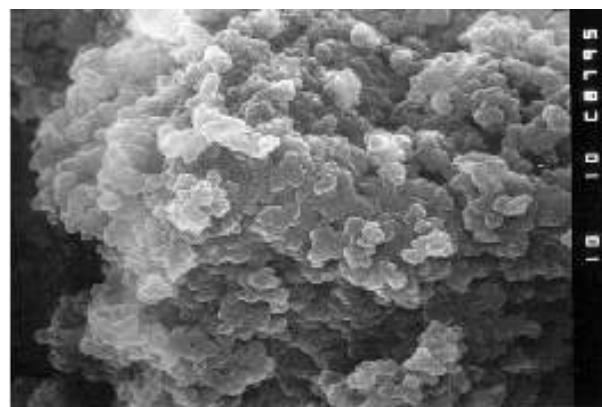
c)

Fig. 8. XRD spectra of a) Ni/TiO₂, b) Co/TiO₂ and c) CoNi/TiO₂ catalysts

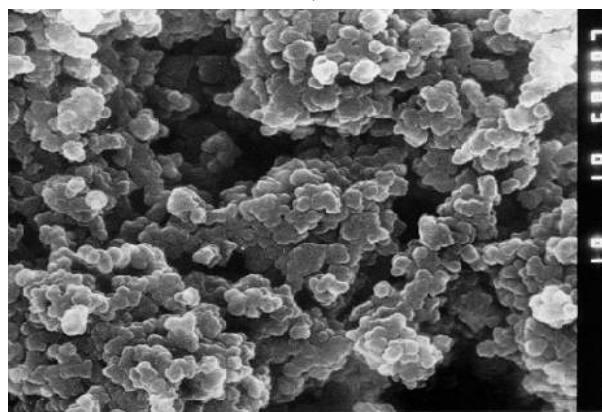
SEM observation was carried out on the Scanning Electron Microscope (JEOL, model JEM 200 CX). The SEM photographs shown in the Fig. 9 are similar for all types catalysts. All particles are of a spherical shape. They consist of hypo-phase deposited on carbon substrate and hyper-phase grafted on the hypo-component. The particles are grouped in clusters of around 100 nm and there is a good adherence between them. Presence of holes, that contributes to the increased active surface area, is evident between aggregates.



a)



b)



c)

Fig. 9. SEM pictures of the a) Ni/TiO₂, b) Co/TiO₂ and c) CoNi/TiO₂ catalysts

BET-analysis has shown that the Ni/TiO₂ catalyst has a specific surface area of 110 m²/g, CoNi/TiO₂ – 95 m²/g and Co/TiO₂ – 70 m²/g. Adding the oxide and metallic hypo-hyper *d* components contributes to decreasing of a specific surface area of the carbon substrate – Vulcan XC-72 which is around 250 m²/g. The level of decreasing the surface area depends on the condition of evaporation of the hypo-hyper *d* organic solution. If evaporation occurs under normal condition, the decreasing of the surface area is higher due to the rising of capillary pressure that causes shrinkage of the gel (called xerogel). If evaporation occurs in autoclave under supercritical condition, there is no capillary pressure that causes obtaining non-shrunked gel named aerogel. In this case, the decreasing of the surface area of the catalyst is lower.

Testing the electrochemical activity for the HER

Cyclic voltammetry with a scan rate of 5 mV/s was used in order to obtain the electrochemical spectra with a characteristic surface and electrode reaction. Polarization characteristics i.e. catalytic activity for the hydrogen evolution reaction was measured by means of the potentiodynamic method with the scan rate of 0.1 mV/s. Electrochemical investigations were performed by the AMEL equipment (Function Generator AMEL 568, Potentiostat/Galvanostat 2053 and software package SOFTASSIST 2.0). Porous gas-diffusion

electrodes were used as the working electrode. The counter electrode was a spiral shaped platinum wire and the reference electrode – Hg/HgO. The electrolyte was an aqueous solution of 3,5 M KOH (p.a., Merck) at room temperature.

The cyclic voltammograms are shown in Fig. 10. A common characteristic for all electrodes is that there is no pronounced peak of surface processes. Such behaviour is typical for porous electrodes. Every small particle of the catalyst behaves as a microelectrode and their peaks of surface reaction do overlap. For Co and CoNi based catalysts, the presence of a peak in the anodic region is evident which implies oxidation of the metallic phase to higher valence state, typical for Co-species, because a similar peak was not detected at the voltammogram of Ni.

More informations on the achieved catalytic activity are found in the polarization curves (Fig. 11). They were scanned with 0.1 mV/s, i.e. in quasi-steady-state conditions. As seen from Fig. 11 the catalytic activity increases by the order: Co ≥ CoNi > Ni. Taking the overpotential of HER at $j = 20 \text{ mA/cm}^2$ of the respective platinum electrode (18% TiO₂ + 10% Pt + Carbon) as a reference level, it can be seen that the HER overpotential on the Co electrode is only 50 mV higher than that of Pt, while for CoNi this difference is 65 mV and for Ni 250 mV. Activities of Co and CoNi electrodes at higher current densities are almost the same, while at 20 mA/cm² Co is more active for ca. 15 mV.

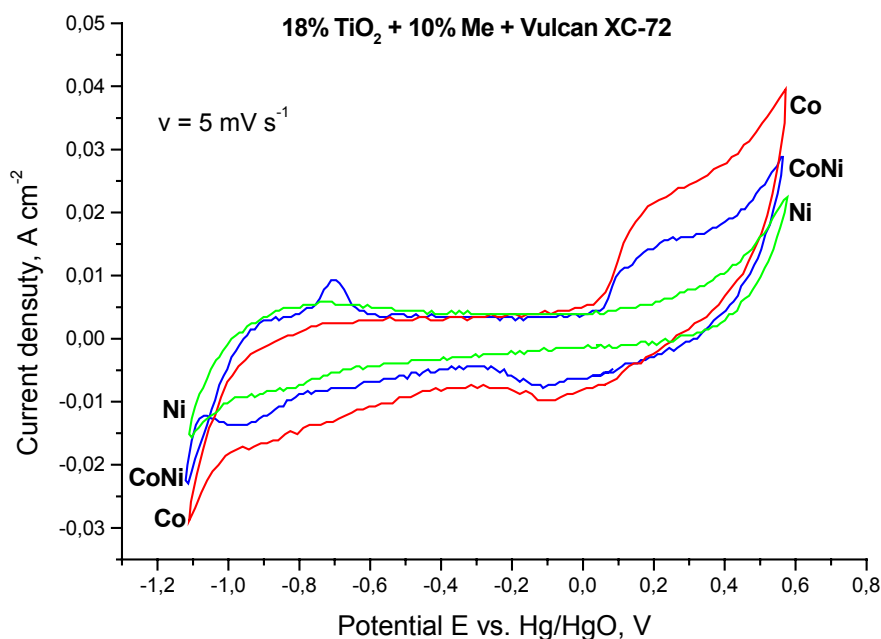


Fig. 10. Cyclic voltammograms of Ni/TiO₂, Co/TiO₂ and CoNi/TiO₂ catalysts

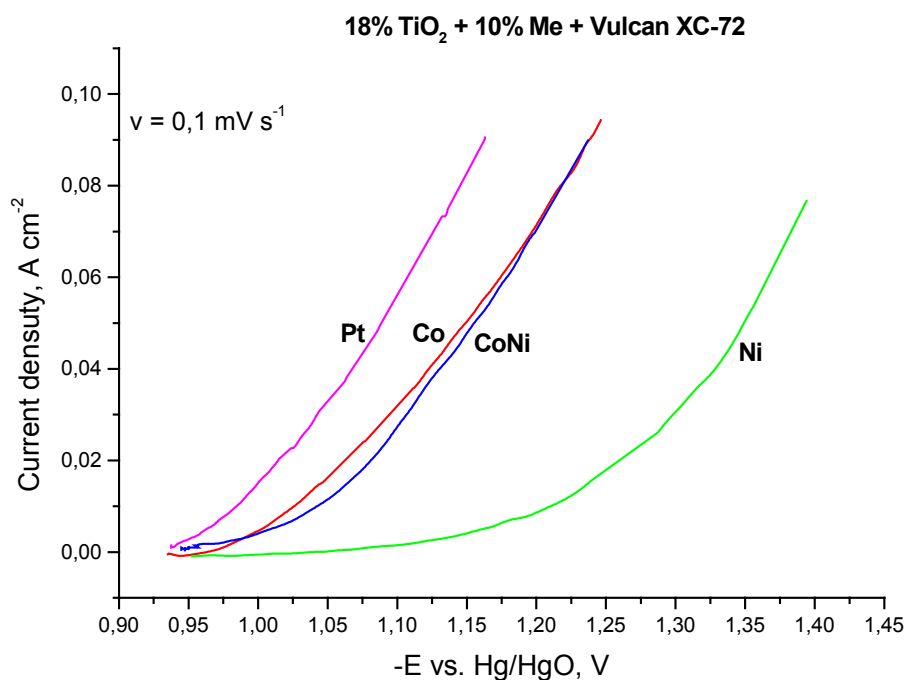
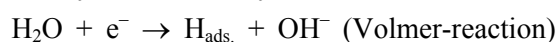


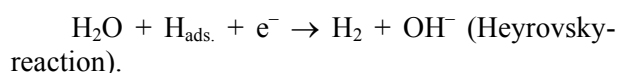
Fig. 11. Polarization curves of Ni/TiO₂, Co/TiO₂ and CoNi/TiO₂ and Pt/TiO₂ catalysts (n.b.: the negative sign of potential values is inserted in the sign –E)

Tafel slopes were determined by steady state galvanostatic measurements. The measured Tafel slope for Ni catalysts of 125 mV/decade could be interpreted as the theoretical one of 120 mV/decade, thus indicating that HER is of Heyrovski type. Tafel slopes for other two catalysts (70 mV/decade for Co and 100 mV/decade for CoNi) being lower

than 120 mV/decade according to [47] indicate applicability of Volmer-Heyrovski mechanism, i.e.:



and



CONCLUSIONS

Properties of electrocatalysts of two different generations and two different types are subject of analysis, thus giving a short survey of the progress of electrocatalysis in the past 30 years.

The first group of electrocatalysts are of classical type, based on the use of precious metals (Ru and Pt), while the second one are of contemporary complex systems that use non-precious metals or their alloys, but nevertheless perform the hydrogen evolution reaction as well as the former generation did. In principle, they are based on the proper combination of transition metals of hypo and hyper *d*-electron nature in either elemental or combined state. Technically, their preparation contains a number of consequent procedures and the usage of at least three different types of materials (hypo, hyper and substrate) in order to achieve:

- good catalytic activity,
- high surface area,

- ability to operate in 3 phase (solid, liquid and gas) environment,
- stability, selectivity, etc.

The former catalysts, especially the ones containing RuO₂ were studied with a primary goal to elucidate the origin of electrocatalytic properties of these materials and, further to explain their already proved excellent performance in technical electrolysis, such as chlorine evolution.

The latter catalysts are an example that fundamental knowledge could be later transformed in practical innovations. The behavior of hypo, hyper *d*-systems was forecasted in advance, after a deep insight in the electronic structure of potential catalysts was achieved and later confirmed as correct. This raises hope that further improvement of the theory of electrocatalysis could be a realistic basis for engineering of even better electrocatalysts in

future. In other words, electrocatalysis is on its best way to bridge the global energy supply between the present era of fossil fuels and the future era based on hydrogen economy. It is only needed to prepare electrocatalysts that will evolve hydrogen with the lowest possible energy consumption and later to use that hydrogen in fuel cells with minor voltage losses.

Acknowledgement: This paper has been supported by and carried out within the EU Project "PROMETHEAS" PL ICA2-2001-10037.

The authors are grateful and indebted to Professor Milan Jakšić, University of Belgrade, for his bountiful and extensive help in the literature supply and valuable advices for both theoretical consideration and practical aspects of catalysts preparation.

Great thank to the staff of "Institute of Electrochemistry and Energy Systems", Bulgarian Academy of Science, Sofia for the fruitful collaboration and the hospitality in their labs during structural analysis and electrode preparation. Special thank to Academician Evgeny Budevski, Dr. Evelina Slavcheva and Dr. Tamara Petkova.

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Резиме

ЕЛЕКТРОКАТАЛИЗАТА ВО ПОСЛЕДНИТЕ 30 ГОДИНИ – ОД БЛАГОРОДНИ МЕТАЛИ ДО ПОЕВТИНИ НО СОФИСТИЦИРАНИ КОМПЛЕКСНИ СИСТЕМИ

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Клучни зборови: електрокатализа; развивање водород; хипо-хипер d-електрокатализатори

Предмет на трудот се разновидноста и напредокот на електродните материјали кои се користат за издвојување хлор, водород и кислород. Во првиот дел

е даден преглед на сопствените истражувања во областа на електрокатализата во последните 30 години, кога рутениумот и другите благородни метали беа екс-

клизивни електрокаталитички материјали. Даден е и краток осврт на постигнувањата на електрокатализатората во тој период. Во вториот дел се прикажани резултати од нашите тековни истражувања во областа на синтезата и карактеризацијата на нови типови неплатински композитни катализатори, чија електрокаталитичка активност е многу блиска до онаа на благородните метали.

Од синтетизираните неплатински катализатори најдобри електрокаталитички карактеристики за издвојување водород покажа катализаторот кој содржи Co или CoNi како хипер-*d*-фаза и TiO₂ како хипо-*d*-

фаза. Типичен состав на ваквиот катализатор е: 18 % TiO₂ помешан со 10 % Co нанесени на јаглероден супстрат (Vulcan XC-72). При густина на струја од 10 mA/cm² овој пренапон на издвојување водород на овој катализатор е само за 40 mV повисок од соодветниот врз катализатор со платина како хипер-*d*-фаза.

Направена е и структурна анализа на испитуваните катализатори со цел да се утврдат причините за таквата електрокаталитичка активност. Врз основа на анализите и литературните сознанија, предвидени се натамошни подобрувања на електрокаталитичката активност на ваквите типови катализатори.