# ELECTROCATALYTIC ACTIVITY OF HYPO–HYPER-*d*-ELECTROCATALYSTS (Me/TiO₂/MWCNTs) BASED ON Co-Ru IN ALKALINE HYDROGEN ELECTROLYSER [*]

**Perica Paunović[1], Orce Popovski[2], Dafinka Stoevska Gogovska[1],
Elefteria Lefterova[3], Evelina Slavcheva[3], Aleksandar T. Dimitrov[1]**

[1]*Faculty of Technology and Metallurgy, Ss. Cyril and Methodius University Skopje
Republic of Macedonia*
[2]*Military Academy "General Mihailo Apostolski"*
*Vasko Karangeleski bb, MK-1001 Skopje, Republic of Macedonia*
[3] *Institute of Electrochemistry and Energy Systems,*
*Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl.11, 1113 Sofia*
pericap@tmf.ukim.edu.mk

This study is concerned with preparation and characterization of Co-Ru based hypo-hyper *d*-electrocatalysts aimed for water electrolysis. The composition of the studied electrocatalysts was: 10 % mixed metallic phase (Co : Ru = 1 : 1 wt., Co:Ru = 4 : 1 wt. and Co : Ru : Pt = 4 : 0.5 : 0.5), 18 % TiO₂ as a crystalline anatase deposited on activated multiwalled carbon nanotubes (MWCNTs). For comparison, corresponding electrocatalysts with pure hyper *d*-metallic phase (Co and Ru) were prepared. The structural characterization of the studied electrocatalysts was performed by means of XRD, SEM and FTIR analysis. The prepared hypo-hyper *d*-electrocatalysts were electrochemically studied by cyclic voltammetry and potentiodynamic method in the alkaline hydrogen electrolyser. The order of the catalytic activity for hydrogen evolution of studied electrocatalysts was the following: Ru > CoRuPt (4 : 0.5 : 0.5, wt.) > CoRu (1 : 1 wt.) > CoRu (4 : 1 wt.) > Co. The electrocatalyst with only 20 % precious metals (Pt and Ru) in the metallic phase (the rest being Co-metal) exhibited excellent performance approaching that of the electrocatalyst with 100 % precious metallic phase (Ru).

**Key words:** hyper-hypo *d*-electrocatalysts; water electrolysis; hydrogen evolution; Co; Ru; anatase; MWCNTs

## ЕЛЕКТРОКАТАЛИТИЧКА АКТИВНОСТ НА ХИПО-ХИПЕР *d*-ЕЛЕКТРОКАТАЛИЗАТОРИ (Me/TiO₂/MWCNTs) БАЗИРАНИ НА Co-Ru ВО АЛКАЛНИ ВОДОРОДНИ ЕЛЕКТРОЛИЗЕРИ

Предмет на трудот е подготовка и карактеризација на хипо-хипер-d-електрокатализатори со намалено количество благородни метали, наменети за електролиза на водата. Испитуваните електрокатализатори содржат 10 % мешана метална фаза (Co : Ru = 1 : 1 мас., Co : Ru = 4 : 1 мас. and Co : Ru:Pt = 4 : 0,5 : 0,5 мас.), 18 % TiO₂ (анатаз), нанесени врз активирани повеќесидни јаглеродни

---

наноцевчиња (MWCNTs). За споредба, изработени се соодветни електрокатализатори со чиста хипер d-метална фаза (Co и Ru).Карактеризација на структурата на испитуваните електрокатализатори беше извршена со помош на рентгенска дифракциона метода (XRD), скенирачка електронска микроскопија (SEM) и инфрацрвена спектроскопија (FTIR). Електрохемиската карактеризација беше изведена со помош на циклична волтаметрија и потенциодинамичка метода, во алкална електрохемиска ќелија за електролиза на вода. Редоследот на каталитичката активност за развивање водород е следен: најдобар Ru > CoRuPt (4:0,5:0,5, мас.) > CoRu (1:1 мас.) > CoRu (4:1 мас.) > Co. Електрокатализаторот со метална фаза која содржи само 20 % благородни метали (Pt и Ru, а остатокот Co) покажува висока електрокаталитичка активност за развивање водород, блиска до онаа на електрокатализаторот со 100 % благороден метал – Ru.

**Клучни зборови:** хипо-хипер d-електрокатализатори, електролиза на вода, Co, Ru, анатаз, MWC-NTs.

## 1. INTRODUCTION

In recent years, the interest for hydrogen as a fuel and for hydrogen economy as the most perspective energy system of the future has been increasing. There are several reasons for that, such as: *i*) increased price of the fossil fuels, *ii*) their exhaustion will happen soon and *iii*) serious damaging of the Earth as result of their exploitation (green house effect, global warming, climate change, photochemical smog, acid rain etc.). Electrochemical hydrogen production in electrolysers and its conversion to electricity in fuel cells is a closed loop in which the water is source for hydrogen production and product in the conversion to electricity. Thus, hydrogen economy is ***environmental friendly*** energy system which produces ***the most calorific fuel*** – hydrogen. There are many other advantages of hydrogen as fuel, such as production from/to electricity with ***high efficiency*** (50÷60 %), ***conversion to energy by different ways*** (combustion, electrochemical conversion, hydriding), ***storage and transport possible in all aggregate states*** (gas, liquid and metal/chemical hydrides) [1].

One of the most important issues for technically and economically efficient hydrogen production/conversion is the electrode material. The higher catalytic activity of the electrode material, the lower overpotential for hydrogen evolution/oxidation, and consequently the lower energy consumption of the process and finally more cost-effective production/conversion of hydrogen. Platinum is the leading electrode material in the hydrogen economy. But its exploitation in the future is limited due to high price and low abundance. According to some estimates [2], the present platinum resources will be enough to satisfy only 20 % of the automotive needs. The rest of these needs and the needs for electricity will not be covered. So, especially important issue in the field of hydrogen economy is the invention of new non-platinum electrode materials with activity close or better than that of Pt.

There are two approaches to overcome this problem. The first one is mixing of metals (or their compounds) to obtain synergetic electrocatalysts for hydrogen evolution/oxidation. Jakšić's hypo-hyper *d*-concept has been shown as very promising for this goal [3]. According to this concept, combination of *d*-metals with dissimilar electronic character exhibits pronounced synergetic effect for hydrogen evolution reaction. Namely, the mixture of hyper-*d*-electronic transition metals (having more electrons in the outer shell and good individual catalysts) with hypo-*d*-electronic transition metals (having less electrons in the outer shell and poor catalysts as individual metals) shows electrocatalytic activity close to or even better than Pt. After Jakšić's successful attempt тo obtain Co-Mo hypo-hyper-*d*-electrocatalyst with catalytic activity comparable with that of Pt [4], a "new era" of modern electrocatalysis was opened.

The second approach is replacement of the traditional support material – carbon blacks (e.g.Vulcan XC-72) with carbon nanotubes (CNTs) [2, 5–8]. Generally, the support material has to possess several very important characteristics, such as: *i*) highly developed surface area to provide better dispersion of the nano-scaled catalytic particles; *ii*) high electric conductivity to allow efficient electron transfer to ions involved in the electrochemical reactions, *iii*) mechanical and chemical stability and *iv*) to improve intrinsic catalytic activity of the active catalytic phase through the strong metal-support interaction (SMSI) [9, 10]. Carbon nanotubes show superior characteristics over the carbon blacks. CNTs have considerably higher electronic conductivity (104 S×cm$^{-1}$) [2] than that of Vulcan XC-72 (4 S×cm$^{-1}$), while the specific surface area is in range of 200÷900 m$^2$×g$^{-1}$ [5] vs. Vulcan XC-72 of 250 m$^2$×g$^{-1}$. Also, Vulcan XC-72 has micropores smaller than 2 nm, while this is not case with CNTs [2]. This is important for electrocatalytic behaviour, because small nano-structured metallic phase can sink into the micropore, reducing the three-boundary reaction sites. Other advantage of CNTs vs. Vulcan XC-72 is higher chemical, i.e. corrosion stability. Namely, electrochemical degradation of carbon materials is slowed considerably by carbon graphitization [11]. This is explained by considering that electrochemical corrosion takes place at the edge planes of graphite, whereas the basal planes are relatively inert. Thus, a considerable better corrosion resistance was detected in materials such as Pt/CNTs which are rolls-up of graphene sheets and present long-range order, related to Pt supported on the carbon blacks which have turbostratic structure [12].

The previous papers of the present authors were focused on preparation and characterization of hypo-hyper-*d*-electrocatalysts based on non-platinum metals. It was found out that Co-based electrocatalysts deposited on carbon nanotubes and anatase in alkaline electrolysers are superior compared to Ni-based ones [13–16]. Activation of carbon nanotubes in 28 % HNO$_3$ improves

catalytic activity for hydrogen evolution and exceeds that of traditional Pt electrocatalyst deposited on Vulcan XC-72 [17]. But, the performance of these electrocatalysts in proton exchange membrane (PEM) electrolyser at lower cathodic overpotentials was poor due to instability of Co and Ni in acid medium, while at higher overpotentials their activity approaches the performance of a traditional Pt catalyst [18]. For this reason, further investigations were directed towards producing electrocatalysts with mixed metallic phase containing Co and Pt [19]. Cobalt behaves as a promoter of reducing Pt particle size during sol-gel synthesis of electrocatalysts. So, electrocatalyst with only 20 % Pt wt. in metallic phase has shown close activity to that with pure Pt metallic phase, while the activity of electrocatalyst with 50 % Pt wt., is considerably higher than that of pure Pt based electrocatalyst.

The main goal of this paper is to study structural and electrochemical characteristics of hypo-hyper-*d*-electrocatalysts with Co-Ru mixed metallic phase.

## 2. EXPERIMENTAL

The studied electrocatalysts contain 10 % hyper-*d*-metallic phase, 18 % hypo-*d*-component (TiO$_2$) and the rest, carbonaceous substrate – activated multiwalled carbon nanotubes (MWCNTs). As precursors to obtain metallic phase, organometallics were used: Me-2,4-pentanedionate (Alfa Aesar, Johnson Matthey, GmbH, Me = Co, Ru, Pt). TiO$_2$ was produced from titanium isopropoxide (Aldrich, 97 %). As a carbon substrate activated MWCNTs (Guangzhou Yorkpoint Energy Company, China) were used. Activation/purification of the manufactured MWCNTs was performed in 28 % (mass.) HNO$_3$. The process was performed at room temperature for 4 h. MWCNTs were stirred into solution by magnetic stirrer. After filtering and washing, activated MWCNTs were dried at 90 ºC for 24 h.

The catalysts were produced by sol-gel procedure. First, TiO$_2$ was deposited on carbon

substrate and further, the modified support was thermally treated at 480 ºC for 1 h in the $H_2 + N_2$ atmosphere. In the next step, metallic phase was grafted on the support material and the obtained mixture was thermally treated at 250 ºC for 2 h.

The composition of the metallic phase of the studied electrocatalysts is Co : Ru = 1 : 1 wt., Co : Ru = 4 : 1 wt. and Co : Ru : Pt = 4 : 0.5 : 0.5. For comparison, corresponding electrocatalysts with pure hyper-*d*-metallic phase (Co and Ru) were prepared. In Table 1 the composition of the studied electrocatalysts is shown.

To identify the intrinsic changes caused by the modifications, spectroscopic and structural techniques were employed. So, XRD, SEM techniques were used. XRD measurements were carried out by X-Ray diffractometer Philips APD 15, with CuKα radiation, while SEM observations were performed by Scanning Electron Microscope JEOL, model JEM 200 CX. Infrared spectroscopy was employed to determine the strength of hypo-hyper-*d*- interaction (TiO$_2$/Ni), using FTIR spectrometer, model Bruker Vector 22.

Further, the produced catalysts were electrochemically tested by means of cyclic voltammetry and potentiodynamic method. Porous electrodes aimed for three phase operation (solid electrode, liquid electrolyte and H$_2$ gas as a product) were prepared. They consist of two layers: *i*) catalytic layer facing the electrolyte, covered by catalyst with low amount of

PTFE and *ii*) gas-diffusion layer facing the gas side consisted of Vulcan XC-72 (or MWCNTs) bonded with PTFE.

The procedure of electrode preparation is described elsewhere [20]. Electrochemical investigations were performed using AMEL equipment (Function Generator AMEL 568, Potentiostate/Galvanostate 2053 and software package SOFTASSIST 2.0). The counter electrode was of 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.

## 3. RESULTS AND DISCUSSIONS

### 3.1. *XRD analysis*

In order to identify the phases present in the prepared samples as well as to estimate their particle size, XRD analysis was performed. XRD spectra of the studied electrocatalysts are shown in Figure 1. The presence of characteristic peaks of Ru, Co or Pt was not detected. This means that the particle size of the present metallic components is very small (< 2 nm). The murmur-like shape of the diffractograms points out on the amorphous character of the present metals. The amorphous character of Co in the corresponding electrocatalysts produced by the same procedure, and its particles of 2 nm were detected in the previous works of the present authors [13–16]. Also, it was detected that Pt particles in presence of Co showed consider-

T a b l e 1

*Composition of the studied hypo-hyper-d-electrocatalysts*

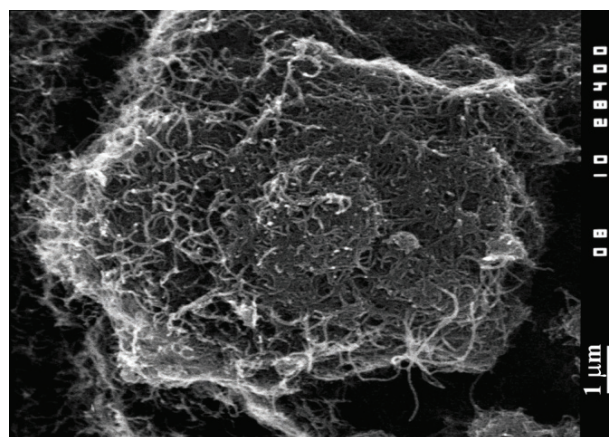| Sample No | Composition |
|---|---|
| 1 | 10 % Co + 18 % TiO$_2$ + MWCNTs |
| 2 | 10 % CoRu + 18 % TiO$_2$ + MWCNTs (Co : Ru = 4 : 1, wt.) |
| 3 | 10 % CoRuPt + 18 % TiO$_2$ + MWCNTs (Co : Ru : Pt = 4 : 0,5 : 0,5, wt.) |
| 4 | 10 % CoRu + 18 % TiO$_2$ + MWCNTs (Co : Ru = 1 : 1, wt.) |
| 5 | 10 % Ru + 18 % TiO$_2$ + MWCNTs |
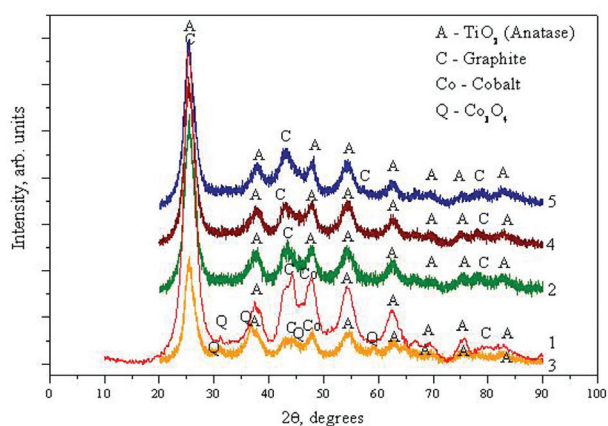
**Fig. 1**. XRD spectra of the studied electrocatalysts. 1) 10 % Co + 18 % TiO$_2$ + MWCNTs; 2) 10 % CoRu + 18 % TiO$_2$ + MWCNTs (Co:Ru = 4:1, wt.); 3) 10 % CoRuPt + 18 % TiO$_2$ + MWCNTs (Co:Ru:Pt = 4:0.5:0.5, wt.); 4) 10 % CoRu + 18 % TiO$_2$ + MWCNTs (Co:Ru = 1:1, wt.); 5) 10 % Ru + 18 % TiO$_2$ + MWCNTs

ably reduced size [19]. In the electrocatalyst with pure Pt as metallic phase, particle size of Pt were 12 nm, while in the electrocatalyst with mixed metallic phase CoPt (Co : Pt = 4 : 1, wt.), they were reduced to 3÷4 nm. In this study, the size of Pt particles in electrocatalyst containing mixed metallic phase CoRuPt (Co : Ru : Pt = 4 : 0.5 : 0.5, wt., sample 3), are ≈2 nm. Due the higher Co : Pt ratio, the reduction of the Pt particle size is higher than in previous study [19]. The possibility that and Ru behaves as promoter for reduction of Pt particle size is not excluded. In all studied samples, characteristic peaks for TiO$_2$ were detected at $2Q$ = 25.46º; 37.8º; 48.09º; 54.44º, 62.51º, 69.57º; 75.22º and 82.98º. According to literature values, these peaks correspond to the anatase crystalline structure of TiO$_2$. It was estimated that
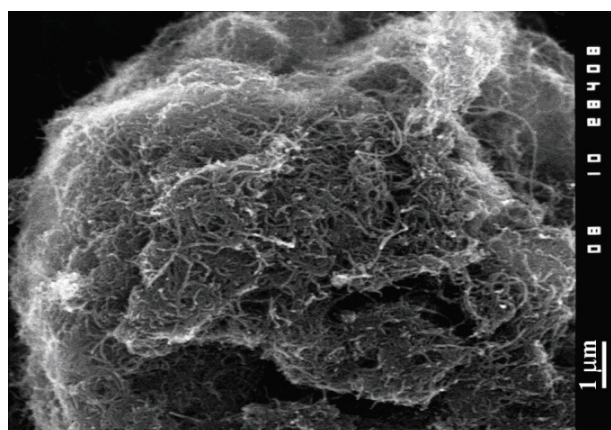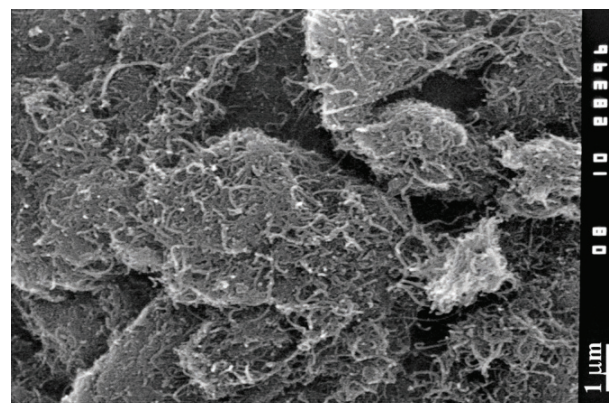


a)



c)
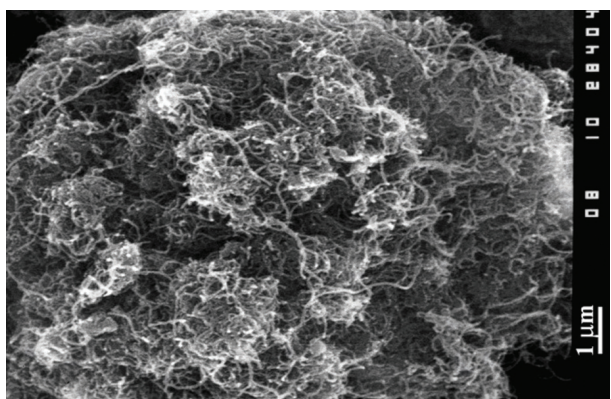


b)



d)

**Fig. 2**. SEM images of the studied electrocatalysts.

**a)** 10 % CoRu + 18 % TiO$_2$ + MWCNTs (Co:Ru = 4:1, wt.); **b)** 10 % CoRuPt + 18 % TiO$_2$ + MWCNTs (Co:Ru:Pt = 4:0.5:0.5, wt.); **c)** 10 % CoRu + 18 % TiO$_2$ + MWCNTs (Co:Ru = 1:1, wt.); **d)** 10 % Ru + 18 % TiO$_2$ + MWCNTs.

the size of anatase particles is 4 nm. For values of $2Q$ of 25.46°; 43.21° and 57.2°, characteristic peaks for graphite were detected, originated by the carbonaceous support material – MWCNTs.

### 3.2. *SEM analysis*

The SEM images of the studied hypo-hyper-*d*-electrocatalysts are shown in Figure 2. They have intertwined threa *d*-like morphology, as a result of presence of the MWCNTs. This morphology is more appropriate than that of electrocatalysts deposited on Vulcan XC-72 [15, 16]. Here, the catalyst's components are grouped into smaller clusters; there are more holes between them which lead to better inter-particle porosity of the catalyst. Due to the intrinsic geometric shape of MWCNTs, empty cylinders ordered one over the other; they possess inner holes, so the inner or trans-particle porosity of electrocatalysts deposited on MWCNTs is considerably higher.

### 3.3. *FTIR Analysis*

According to Jakšić's hypo-hyper-*d*-theory for electrocatalysts, as result of interaction between hypo and hyper-*d*-components, i.e. $TiO_2$ and metallic phase (Co, CoRu, CoRuPt or Ru) the intrinsic catalytic activity increases. The intensity of this hypo-hyper-*d*-interaction can be determined by infrared spectroscopy. Shown in Figure 3a are the FTIR spectra of the studied electrocatalysts. The only band of interest within the spectra originates by $TiO_2$ [21]. This band is denoted by the circle B in Figure 3b. In the Figure 3a only the region within the circle is shown for each sample. To determine hypo-hyper *d*-interaction one has to compare $TiO_2$ band from electrocatalyst and band from pure $TiO_2$ obtained in identical conditions as that in electrocatalyst. The maximum of this band is located at wave number value of 495 cm$^{-1}$. The maximum of $TiO_2$ bands from the electrocatalysts is shifted at higher values of wave number. The higher the shift of the wave number, the shorter the bond between
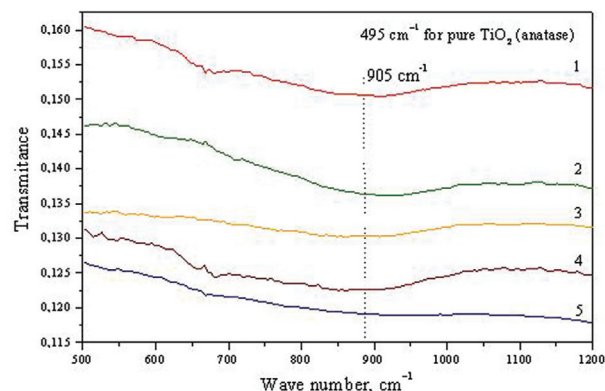


a)
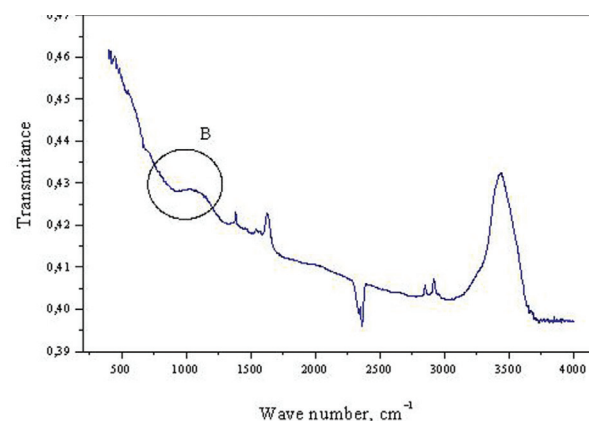


b)

**Fig.3.** FTIR spectra of the a) studied electrocatalysts in the wave number region of 500–1200 cm$^{-1}$:
1) 10 % Co + 18 % $TiO_2$ + MWCNTs; 2) 10 % CoRu + 18 % $TiO_2$ + MWCNTs (Co:Ru = 4:1, wt.);
3) 10 % CoRuPt + 18 % $TiO_2$ + MWCNTs (Co:Ru:Pt = 4:0.5:0.5, wt.);
4) 10 % CoRu + 18 % $TiO_2$ + MWCNTs (Co:Ru = 1:1, wt.);
5) 10 % Ru + 18 % $TiO_2$ + MWCNTs,
b) electrocatalyst 5 (10 % Ru + 18 % $TiO_2$ + MWCNTs) in the whole wave number region.

the $TiO_2$ and the hyper-*d*-metallic phase, i.e. the higher the hypo-hyper-*d*-interaction. All investigated samples show almost the same shift of the wave number value of bands maximum, near 905 cm$^{-1}$. This means that the intensity of hypo-hyper *d*-interaction in all samples is the same. Therefore, in all samples there is an increase of the intrinsic catalytic activity and this rise is equal for all studied electrocatalysts.

### 3.4. *Cyclic voltammetry*

In Figure 4 cyclic voltammograms of the studied electrocatalysts in alkaline electrolyser (3.5 M KOH) with scan rate of 5 mV×s$^{-1}$ are shown. The value of the potential is described versus Hg/HgO reference electrode. First, the cyclic voltammograms of the electrocatalysts with pure metallic phase were analyzed. The voltammogram of the electrocatalyst with Co as metallic phase (sample 1), shown in Figure 4a, is more structured than the other ones. At potential of –0.6 V, there is a peak I, which corresponds to transition of cobalt to higher valence state, Co(0) → Co(II) [22]. Its asymmetric shape is result of the heterogeneous forming of Co(OH)$_2$ and CoO into so called sandwich-structure Co/

CoO/Co(OH)$_2$ [23]. Transformation of Co(II) to Co(III) is shown by peak II. There is also a sandwich-structure CoO/Co(OH)$_2$/Co$_3$O$_4$ [24], what implies asymmetry of the peak. The peak II' near –0.14 V, denotes the opposite transformation. It is obvious that the reaction Co(II) ⇆ Co(III) is irreversible. The oxygen evolution reaction (OER) is denoted by the peak III. The broadened peak I' in the potential region of –0.75 to –1 V denotes Co(II) → Co(0) transformation as well as adsorption of the H ad-atoms over the electrode surface. The peak IV denotes hydrogen evolution reaction (HER). The anomalous shape of this peak is due to simultaneously occurrence of hydrogen evolution and transformation of backward amount of Co(II) to Co(0).



a)

b)

c)

d)
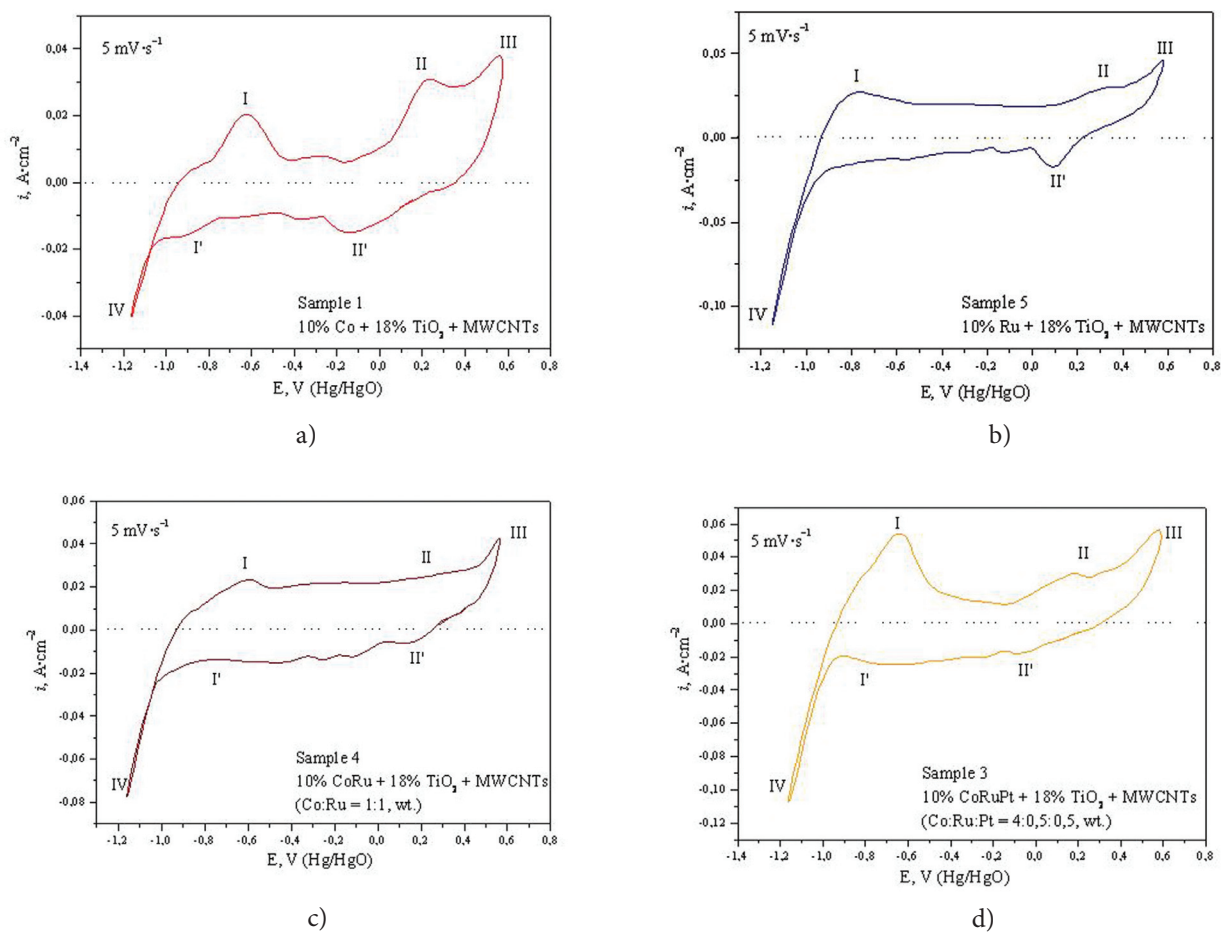
**Fig.4.** Cyclic voltammograms of the studied electrocatalysts.
a) 10 % Co + 18 % TiO$_2$ + MWCNTs; b) 10 % Ru + 18 % TiO$_2$ + MWCNTs; c) 10 % CoRu + 18 % TiO$_2$ + MWC-NTs (Co:Ru = 1:1, wt.); d) 10 % CoRuPt + 18 % TiO$_2$ + MWCNTs (Co:Ru:Pt = 4:0.5:0.5, wt.).

The voltammogram of the Ru-based electrocatalyst (sample 5) is shown in Figure 4b. Initial stages of oxidation arise at low potentials ($-0.85 \div -0.7$ V), where ionization of hydrogen also occurs. The higher state of oxidation, more irreversible, occurs beyond 0.15 V. The opposite reaction is denoted by the peak II' at 0.09 V, which implies its irreversibility. The opposite peak of the initial oxidation (peak I) is not shaped. This means that the reduction back to metallic state becomes incomplete [25]. The peaks III and IV denote oxygen evolution and hydrogen evolution reactions respectively.

The additional voltammograms show the electrochemical behaviour of the mixed metallic systems. The electrocatalyst containing mixed metallic system CoRu (1:1, wt., sample 4) show less structured voltammogram (Figure 4c) than the corresponding ones containing pure Co or Ru. Due to overlapping of more surface processes occurring over the Ru and Co surface some characteristic peaks have anomalous shape or have disappeared. So, the peak I is resultant one of the initial oxidation of Co which occurs at $-0.6$ V and initial oxidation of Ru which occurs in the range of $-0.85 \div -0.7$ V. The resulting peak is non-symmetric and it is stretched in the potential interval of $-0.85 \div -0.5$ V. Furthermore, the corresponding peak for transition to higher oxidation state is less shaped and stretch in the potential region of 0.06 to 0.4 V. Also, and the opposite peak of this reaction denoted by II' (0.17 V) is less shaped than in case of pure metallic systems. The opposite peak of the initial oxidation and hydrogen adsorption (peak I') has disappeared. The voltammogram of the electrocatalyst with CoRu (4:1, wt., sample 2) is very similar to this one with less pronounced peaks.

The voltammogram of the electrocatalyst with mixed metallic phase CoRuPt (sample 3) is similar with the previous one. The first peak of initial oxidation I is stretched from $-0.8$ to $-0.5$ V with pronounced maximum at $-0.65$ V. This well shaped peak is a result of the presence of Pt. Namely, there are two processes occurring simultaneously: the initial surface

oxidation of the metallic phases, characteristic for all metals present in the electrocatalyst and oxidation of hydrogen characteristic for Pt. The opposite peak I' is noticeable stretched from $-0.5$ to $-0.9$ V which denote adsorption of H ad-atoms over the electrode surface. The peaks II denote oxidation of metallic phases at higher oxidation state ($-0.1$ to $-0.3$ V) and corresponding opposite peak II' ($-0.07$ V) are similar as in previous case.

### 3.5. *Polarization Curves*

The polarization curves which put across the electrocatalytic activity of the studied hypo-hyper-*d*-electrocatalysts for hydrogen evolution are shown in Figure 5. In Table 2 the overpotentials at reference current density of 60 mA×cm$^{-2}$ are given. The order of the catalytic activity is the following: Ru > CoRuPt (4 : 0.5 : 0.5) > CoRu (1:1) > CoRu (4:1) > Co. One should consider that all electrocatalyst are deposited on the same carbon support – activated MWCNTs with $TiO_2$ – anatase with the same size of particles. Also, according to the XRD characterization, all metallic components have the similar size of particles. FTIR analysis has shown that the rise of the intrinsic activity of all studied electrocatalysts as result of the hypo-hyper-*d*-interaction is the same. Therefore, one could state that the
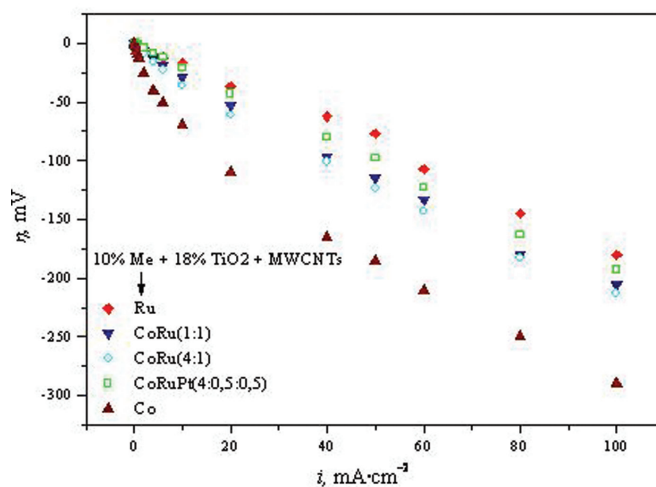


**Fig. 5.** Polarization curves of the studied electrocatalysts

T a b l e 2

*Overpotential for hydrogen evolution at referent current density of 60 mA·cm$^{-2}$*
*for the studied electrocatalysts*

| Sample No | Metallic phase within the general composition of the catalyst 10% Me + 18% TiO$_2$ + MWCNTs | $\eta_{60}$, mV |
|:---:|:---|:---:|
| 1 | Co | -210 |
| 2 | CoRu (Co : Ru = 4 : 1, wt.) | -145 |
| 3 | CoRuPt (Co : Ru : Pt = 4 : 0,5 : 0,5, wt.) | -120 |
| 4 | CoRu (Co : Ru = 1 : 1, wt.) | -135 |
| 5 | Ru | -110 |

difference in electrocatalytic activity is a result of the intrinsic activity of the catalytic metallic phase into the studied samples. One can see that as the content of Ru decreases from pure Ru to pure Co (the content of Co increases), the catalytic activity for hydrogen evolution decreases. Exception is the catalytic activity of the sample containing CoRuPt as metallic phase (sample 3). This catalyst containing only 10 % Ru and 10 % Pt wt. in the metallic phase (the rest 80 % is Co) showed catalytic activity close to that of the electrocatalyst containing pure Ru. The high catalytic activity of this sample comes from the presence of Pt, which has higher intrinsic activity than those of Ru and Co. As was shown in the previous paper [19], Co behaves as promoter for reduction of Pt particle size. So, the size of Pt particles in electrocatalyst with pure Pt metallic phase was 12 nm, while in the presence of Co (Co : Pt = 4 : 1 wt.), the size was reduced to 4 nm (3 times). The catalytic activity of these catalysts was very close. The lower amount of Pt was compensated by the highly developed surface of Pt-phase in the mixed systems. In this study, the ratio of Co:Pt is higher (8 : 1 wt.) and the size of Pt particles reaches 2 nm. The surface area of the Pt catalytic centers in this case is more developed, thus contributing to higher catalytic activity.

## 4. CONCLUSION

The main goal of this study was to produce mixed nano-structured electrocatalysts for hydrogen evolution with reduced load of noble metals. Metallic phase with mixture of Co and Ru with various Co : Ru ratios (from pure Ru to pure Co) was deposited on catalyst support consisted of MWCNTs activated in HNO$_3$ and anatase titania with particle size of 4 nm as promoter of hypo-hyper-$d$-interaction. According to presented results the following conclusions can be drawn:

All studied electrocatalysts contain nano-sized components. So, the size of Co, Ru and Pt particles (hyper-$d$-metallic phase) was near 2 nm, while the size of TiO$_2$ particles (hypo-$d$-phase) was near 4 nm.

The level of hypo-hyper-$d$-interaction between metallic phase and TiO$_2$ was the same for all studied electrocatalysts.

The equality of hypo-hyper-$d$-interaction indicates that there is some other phenomenon that causes differences in the electrocatalytic activity between the studied electrocatalysts. In fact, it is result of the intrinsic activity of metallic phase into the studied samples. So, as the content of Ru decreases, i.e. the content of Co increases, the catalytic activity for hydrogen evolution decreases, except for the sample that contains CoRuPt as metallic phase (Co : Ru : Pt = 4 : 0.5 : 0.5).

The exclusively high catalytic activity of the electrocatalyst containing CoRuPt as metallic phase (Co : Ru : Pt = 4 : 0.5 : 0.5) is ascribed to the presence of Pt (Pt has higher intrinsic activity than Ru and Co) as well as to the higher surface area of the Pt catalytic centers (particles of near 2 nm).

## REFERENCES

[1]   F. Barbir, Fuel cells and hydrogen economy, *Chem. Ind. & Chem. Eng. Quuart.*, **11** (2005), 105–13.

[2]   K. Lee, J. Zhang, H. Wang and D. P. Wilkinson, Progress in the synthesis of carbon nanotube- and nanofiber-supported Pt electrocatalysts for PEM fuel cell catalysis, *J. Appl. Electrchem.*, **36** (2006), 507–522.

[3]   M. M. Jakšić, Brewer intermetallic phases as synergetic electrocatalysts for hydrogen evolution, Materials Chemistry and Physics, **22** (1989), 1–26.

[4]   М. Јакшич, В. Комненич, Р. Атанасоски, Р. Аджич, Електрокатализ при виделении водорода на титане, его сплавах и графите, *Елекȶрохима*, **13** (1977), 1355.

[5]   P. Serp, M. Corrias and P. Kalck, Carbon nanotubes and nanofibers in catalysis, *Appl. Catal. A: Gen.*, **253** (2003), 337–358.

[6]   U. Sahaym and M. Grant Norton, Advances in the application of nanotechnology in enabling a 'hydrogen economy', *J. Mater. Sci.*, **43** (2008), 5395–5429.

[7]   P. Paunović, A. T. Dimitrov, O. Popovski, D. Slavkov, S. Hadži Jordanov, Use of multiwalled carbon nanotubes (MWCNT$_S$) as a support material in complex electrocatalysts for hydrogen evolution, *Maced. J. Chem. Chem. Eng.*, **26** (2007), 87–93.

[8]   P. Paunović, A. T. Dimitrov, O. Popovski, E. Slavcheva, A. Grozdanov, E. Lefterova, Dj. Petruševski and S. Hadži Jordanov, Effect of Activation/Purification of Multiwalled Carbon Nanotubes (MWCNTs) on Activity of Non-platinum Based Hypo-Hyper *d*-Electrocatalysts for Hydrogen Evolution, *Mat. Res. Bull.*, **44** (2009), 1816–1821.

[9]   S. J. Tauster, S. C. Fung, R. L. Garten, Strong metal-support interactions. Group 8 noble metals supported on titanium dioxide, *J. Am. Chem. Soc.*, **100** (1978), 170–75.

[10]  S. G. Neophytides, S. Zaferiatos, G. D. Papakonstantinou, J. M. Jakšić, F. E. Paloukis and M. M. Jakšić,

Extended Brewer hypo-hyper-*d*-interionic bonding theory, I. Theoretical considerations and examples for its experimental confirmation, *Int. J. Hydr. Ener.*, **30** (2005), 131–147.

[11]  F. Maillard, P. A. Simonov and E. R Savinova, in P. Serp and J. L. Figueiredo, *Carbon Materials as Supports for Fuel Cell Electrocatalysts*, John Wiley & Sons (2009), 429.

[12]  Y. Shao, G. Yin, J. Zhang, Y. Gao, Comparative investigation of the resistance to electrochemical oxidation of carbon black and carbon nanotubes in aqueous sulfuric acid solution, *Electrochim. Acta*, **51** (2006), 5853–5857.

[13]  S. Hadži Jordanov, P. Paunović, O. Popovski, A. Dimitrov and D. Slavkov, Electrocatalysts in the last 30 years – from precious metals to cheaper but sophisticated complex systems, *Bull. Chem. Technol. Macedonia*, **23** (2004), 101–112.

[14]  P. Paunović, O. Popovski, S. Hadži Jordanov, A. Dimitrov and D. Slavkov, Modification for improvement of catalysts materials for hydrogen evolution, *J. Serb. Chem. Soc.*, **71** (2006), 149–165.

[15]  P. Paunović, O. Popovski, A. T. Dimitrov, D. Slavkov, E. Lefterova and S. Hadži Jordanov, Improvement of performances of complex non-platinum electrode materials for hydrogen evolution, *Electrochim. Acta*, **52** (2006), 1610–1618.

[16]  P. Paunović, O. Popovski, A. T. Dimitrov, D. Slavkov, E. Lefterova and S. Hadži Jordanov, Study of structural and electrochemical characteristics of Co-based hypo-hyper *d*-electrocatalysts for hydrogen evolution, *Electrochimica Acta*, **52** (2006), 4640–4648.

[17]  P. Paunović, A. T. Dimitrov, O. Popovski, E. Slavcheva, A. Grozdanov, E. Lefterova, Dj. Petruševski and S. Hadži Jordanov, Effect of activation/purification of multiwalled carbon nanotubes (MWCNTs) on activity of non-platinum based hypo-hyper *d*-electrocatalysts for hydrogen evolution, *Material Research Bulletin*, **44** (2009), 1816–1821.

[18]  P. Paunović, O. Popovski and I. Radev, Investigation of cell assemblies prepared out of electrocatalysts aimed for hydrogen evolution, *Bull. Chem Technol. Macedonia*, **24** (2005), 133–141.

[19]  P. Paunović, I. Radev, A. T. Dimitrov, O. Popovski, E. Lefterova, E. Slavcheva, and S. Hadži Jordanov, New nano-structured and interactive supported composite electrocatalysts for hydrogen evolution with partially replaced platinum loading, *Int. J. of Hyd. Ener.*, **34** (2009), 2866–2873.

[20] BG patent Appl. No 38581.

[21] Y. Jin, G. Li, Yo. Zhang, Yu. Zhang, L. Zhang, Photoluminescence of anatase TiO$_2$ thin films achieved by the addition of ZnFe$_2$O$_4$, *J. Phys.: Condens. Matter.*, **13** (2001), L913-L918.

[22] W. K. Behl and J. E. Toni, Anodic oxidation of cobalt in potassium hydroxide electrolytes, *J. Electroanal. Chem.,* **31** (1971), 63–75.

[23] N. Sato and T. Ohtsuka, Anodic Oxidation of Cobalt in Neutral and Basic Solution, *J. Electrochem. Soc.*, **125** (1978), 1735–1740.

[24] L. D. Burke and O. J. Murphy, Electrochromic behaviour of oxide films grown on cobalt and manganese in base, *J. Electroanal. Chem*., **109** (1980), 373–377.

[25] S. Hadži Jordanov, Towards the year 2000: Some aspects of the electrochemistry in the last decades of twentieth century, *Bull. Chem. Technol. Macedonia*, **16** (1997), 75–88.