

Improvement of performances of complex non-platinum electrode materials for hydrogen evolution

P. Paunović^{a,*}, O. Popovski^b, A. Dimitrov^a, D. Slavkov^a,
E. Lefterova^c, S. Hadži Jordanov^a

^a Faculty of Technology and Metallurgy, University “Sts. Cyril and Methodius” Skopje,
Rudjer Boskovic 16, 1000 Skopje, The Former Yugoslav Republic of Macedonia

^b Military Academy “Gen. Mihailo Apostolski”, Skopje, The Former Yugoslav Republic of Macedonia

^c Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Science, Sofia, Bulgaria

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Abstract

Structural and electrochemical characteristics of hypo–hyper d-electrocatalytic materials aimed for preparation of electrodes for hydrogen evolution were studied and modified in order to improve their performances. All studied materials were of general composition 10% Ni + 18% TiO₂ + C.

All materials were prepared of amorphous or crystalline TiO₂, crystalline Ni or NiCo (10–20 nm) and Vulcan XC-72, by sol–gel procedure.

Both, material's intrinsic catalytic activity and surface area were affected by applied modifications. As a result, the electrocatalytic activity was improved, e.g. transformation of TiO₂ into anatase form lowers the HER overpotential for 60 mV. Introduction of MWCNTs was even more effective, lowering η for 120 mV. Co addition to metallic phase lowers η for utmost 195 mV.

Combined modification of TiO₂ and carbon substrate lowers η for 145 mV, while the complete modification of all three catalyst's components was the most effective with 230 mV decrease of overpotential.

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1. Introduction

Selection of electrode materials for industrial electrocatalytic 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, and resulted in development of multi-component catalysts. It started with combining the most active precious metals, as Pt–Pd or Ir–Re [1], but the resulting synergetic effect did not satisfy the expectations. Latter on, based on theoretical analysis given by Brewer [2], Jakšić et al. [3], the efforts were oriented towards combining nonprecious met-

als. 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 [4]. 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) become subject of scientific and technical interest. A “new era” of modern electrocatalysis was opened.

The partners in these multicomponent systems could be in both, elemental or valence state as oxides, sulphides and phosphides being the most frequent compounds. A number of combinations of metals in elemental or valence state were used in the multicomponent systems, as grouped in Table 1.

In cases when both components are in metallic state (group 1), intermetallic compound of the general composition A_xB_y are formed. In some cases solid-state solutions or mixtures do

* Corresponding author. Tel.: +389 2 3034 392; fax: +389 2 3034 392.
E-mail address: pericap@ian.tmf.ukim.edu.mk (P. Paunović).

Table 1
Typical hypo–hyper d-intermetallic electrocatalysts

Type of hypo–hyper d-electrocatalyst	Examples
(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.
(II) Sulfides, Phosphides	Ni–W–S, Ni–W–P, Fe–Ni–P, etc.
(III) Catalysts based on Raney–Ni	Ni–Al–Ti, Ni–Al–Mo, Ni–Al–Cr, Ni–Zn–Ti, Ni–Zn–Mo, etc.
(IV) Mixed oxides	TiO ₂ –RuO ₂ , TiO ₂ –IrO ₂ , Ru _x Ti _{1-x} O ₂ , RuO ₂ –IrO ₂ , etc.
(V) Hypo oxide–hyper metal	Pt–TiO ₂ , Pt–Ru–WO ₃ , Ni–V ₂ O ₅ , etc.

exist. The most representative examples of this group are systems that contain titanium and nickel, Ti_{1-x}Ni_x (“Tiney–Ni” electrodes) possessing both high surface area and high catalytic activity [5]. In opposite case, when both components are in combined state, usually sulphides or phosphides of hypo and hyper d-metals are present (group II). They are of amorphous character, with well-developed surface area, thus adsorbing/absorbing more hydrogen than pure Ni does. As a consequence, their activity is up to 10 times than corresponding of activated Pt and even 250 times than corresponding of metallic nickel [6]. In group III the 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). After leaching is completed, catalysts with surface area 1000–12,000 times than in case of pure Ni were referred to form [7]. A special case when both components are present as oxides (usually TiO₂ in combination with RuO₂, or RuO₂ combined with IrO₂ and nonstoichiometric Ru_xTi_{1-x}O₂, group IV) [8–11]. In group V d-component is metallic state (as metal or alloy, e.g. Ni, Pt, Co, Co–Ni, Pt–Ru, etc.), while the hypo d-component is an oxide, e.g. TiO₂, WO₃, TiO₂–WO₃, etc. [12–14].

Multicomponent catalysts of group V were subject of interest in this study. Ni and NiCo, respectively, were used as hyper d-phase, while TiO₂ was used as hypo d-phase.

2. Experimental

The specified catalysts were prepared by sol–gel procedure simplified in some parts by the present authors. In the first stage, in order to deposit (TiO₂) onto carbon substrate, Ti-isopropoxide (Aldrich, 97%) was added into dispersed Vulcan XC-72 (Cabot Corp., Boston, MA, USA) in anhydrous ethanol. To provide hydrolysis to Ti(OH)₄, small amount of 1 M HNO₃ was added. This mixture was evaporated at 60 °C with continuous intensive stirring until fine nano-structured powder of catalyst support was obtained. Further, individual or mixed Me-2,4-pentaedionate (Alfa Aesar, Johnson Matthey, GmbH, Me=Co or Ni) was dissolved in absolute ethanol. This solution was added into 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 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 + N₂. The produced basic catalyst is of composition: 10% Ni + 18% TiO₂ + Vulcan XC-72. To determine synergetic effect of this hypo–hyper d-combination,

corresponding Ni catalyst was deposited only on Vulcan XC-72.

In order to improve catalytic activity of basic catalyst, all components were modified separately: (i) hypo d-phase—TiO₂ was thermally treated at 480 °C, (ii) multiwall carbon nanotubes (MWCNTs, Guangzhou Yorkpoint Energy Company, China) were used instead of Vulcan XC-72 and (iii) Co was added into hyper d-metallic phase. Further, the basic catalyst was modified on the whole. The composition of investigated electrocatalysts is given in Table 2.

Produced catalyst powders were further used for preparing porous electrodes for hydrogen evolution reaction. Electrodes aimed for three-phase operation (solid electrode, liquid electrolyte and H₂ gas as product) were prepared by hot pressing at 300 °C with the back layer of carbon black acetylene + PTFE and the front layer of the catalyst + PTFE [15]. Electrochemical investigations were performed using AMEL equipment (Function Generator AMEL 568, Potentiostat/Galvanostat 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.

In order to identify the changes produced by the applied modifications, several spectroscopic and structural methods for determination of structural and surface changes were employed. XRD and SEM techniques were used for determining structural characteristics of the catalysts. XRD measurement was carried out on X-Ray diffractometer Philips APD 15, with Cu K α radiation, while SEM observation was on Scanning Electron Microscope JEOL, model JEM 200 CX. To determine the level of hypo–hyper d-interaction (TiO₂/Ni) infrared spectroscopy was employed, using FT-IR spectrometer, model Bruker Vector 22. A presence of surface valence-state phases of the catalyst’s components was determined by XPS spectroscopy, ESCALAB MK II, VG Scientific, England, using Al K α radiation. The ratio

Table 2
Composition of electrocatalysts prepared in this study

Sample no.	Hypo oxide d-phase (18%)	Carbon substrate (72%)	Hyper metal d-phase (10%)
1	TiO ₂ (250 °C)	Vulcan XC-72	Ni
2	–	Vulcan XC-72 ^a	Ni
3	TiO ₂ (480 °C)	Vulcan XC-72	Ni
4	TiO ₂ (250 °C)	MWCNTs	Ni
6	TiO ₂ (480 °C)	MWCNTs	Ni
5	TiO ₂ (250 °C)	Vulcan XC-72	NiCo
7	TiO ₂ (480 °C)	MWCNTs	NiCo

^a In this sample there is not TiO₂, so the content of Vulcan XC-72 is 90%.

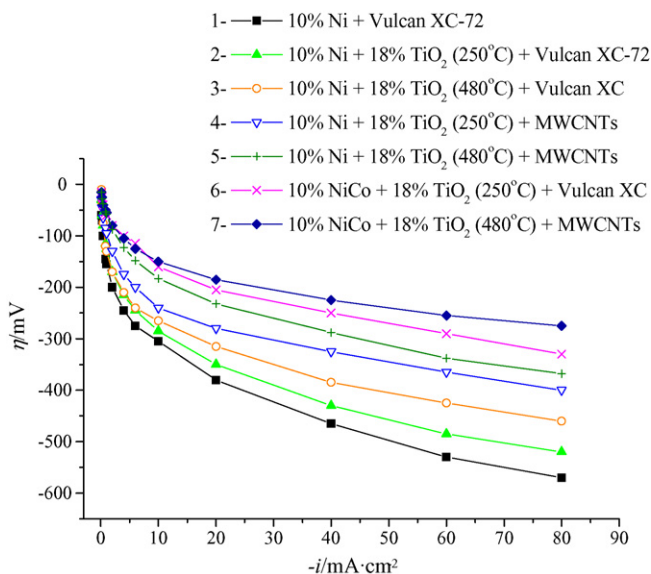


Fig. 1. Polarization curves of investigated hypo-hyper d-electrocatalysts.

of real versus geometric surface area of the electrodes was determined as a quotient of catalyst's double layer capacity C_{dl} versus double layer capacity C_{dl0} of pure oxide surface. The double layer capacity was measured by cyclic voltammetry [16,17].

3. Results

3.1. Polarization characteristics

Polarization curves for hydrogen evolution reaction taken on progressively improved electrocatalysts are shown in Fig. 1.

The beneficial effect of the addition of TiO_2 to the Ni solely-containing catalyst is visible from comparison of curves 1 and 2 (without and with TiO_2 , respectively). It accounts for 50 mV lower hydrogen evolution overpotential at 60 mA cm^{-2} (adopted as reference c.d.). Further modifications applied to the catalyst's components, as e.g. thermal treatment of TiO_2 at higher temperature, substitution of Vulcan XC-72 with MWCNTs and addition of cobalt into hyper d-phase (see Fig. 1. caption and Table 3) continually lower HER overpotential.

The system where all three components are substituted by modified ones (sample 7) appeared to show the most pronounced synergetic effect—with HER overpotential lower for 230 mV as compared to the basic system (sample 2) or even 280 mV with regard to the starting Ni-only catalyst (sample 1).

Table 3
Polarization characteristics of investigated electrocatalysts

Sample no. (see Table 2)	η_{60} (mV)	$\Delta\eta$ (vs. basic catalyst)
1	-535	-50
2	-485	0
3	-425	60
4	-365	120
6	-290	195
5	-340	145
7	-255	230

In order to produce sound explanation of the registered improvements in catalytic activity (Table 3, samples 1 toward 7) comprehensive structural and surface characterization has been made and is presented bellow.

3.2. Structural characteristics

XRD characteristics of the catalysts were presented elsewhere [18,19]. These catalysts contain a hyper d-metallic phase (Ni) of crystalline structure, the size of grains being 10–20 nm. In the mixed metallic system solid Ni–Co solution was detected too, what means that part of the Co substitutes Ni atoms in Ni crystal lattice. Co “impurity” atoms substitute Ni host atoms in local Ni crystalline environment and simultaneously structural phase transition of Co from amorphous to crystalline (as a solid-state solution) occurs [20]. The rest amount of Co continues to be amorphous with size of grains lower than 2 nm. Hypo d-oxide phase (TiO_2) treated at 250°C was not detected by XRD, what means that TiO_2 is amorphous. Rising the temperature of thermal treatment up to 480°C contributes to transformation of TiO_2 hypo d-oxide phase from amorphous to anatase crystalline structure with grain size of 7–8 nm [19].

3.3. SEM analysis

In Fig. 2 SEM microphotographies of four catalysts are shown. One can see, the catalyst's particles deposited on Vulcan are of a spherical shape. There is a grouping of the particles in clusters, whereat good adherence between particles is achieved. Presence of a numbers of holes between the aggregates is evident, thus contributing to the higher specific surface area, and consequently to a higher electrocatalytic activity. The size of clusters formed by deposition of TiO_2 on Vulcan XC-72 is approximately 50–100 nm (Fig. 2a). The clusters of Ni deposited directly on Vulcan XC-72 (sample 1) are bigger, 100–150 nm (Fig. 2b), what means that Ni crystals of size 10–20 nm are larger than particles of TiO_2 . Due to amorphous character of TiO_2 its size could not determine by XRD method. The clusters formed by deposition of Ni on support of Vulcan XC-72 + TiO_2 become larger than previous ones, with size of 150–200 nm (Fig. 2c). Catalysts deposited on MWCNTs are with oriented structure (Fig. 2d). The particles of hypo d-oxide and hyper d-metallic phases grafted on MWCNTs are grouped in smaller clusters than those on Vulcan XC-72. This causes holes between particles to appear. Due to intrinsic geometrical features of MWCNTs (empty cylinders with higher developed surface area as compared to the spherical particles of Vulcan XC-72), they possess inner holes and the inner porosity of MWCNTs is considerably higher than that of Vulcan XC-72. This is important for better dispersion of other components of the catalysts on the surface, especially active catalytic centers.

SEM analysis is not able to give any information on the nature of bonding (mechanical or chemical) of different particles into the catalyst's clusters. This information can be obtained by further spectroscopic investigation, by e.g. infrared spectroscopy or X-ray photoelectron spectroscopy (XPS), as shown bellow.

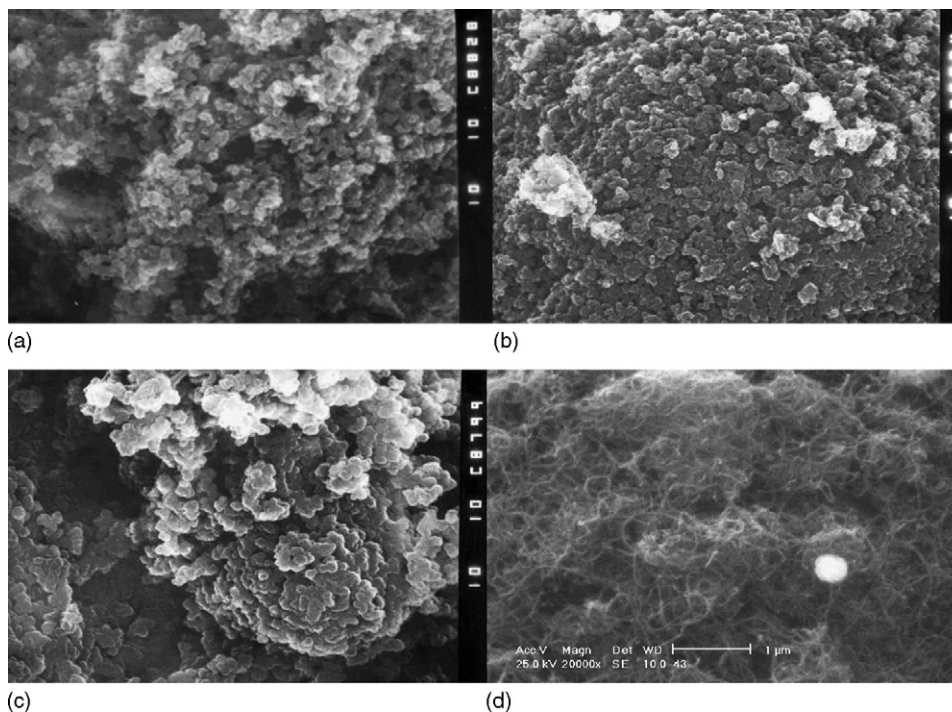


Fig. 2. SEM photographs of: (a) catalyst's support (TiO_2 (250 °C) on Vulcan XC-72), 10,000 \times ; (b) pure Ni deposited on Vulcan XC-72 (sample 1), 10,000 \times ; (c) basic hypo-hyper d-electrocatalyst (sample 2), 10,000 \times ; (d) modified carbon substrate (sample 4), 20,000 \times .

3.4. Infrared analysis

On the FT-IR spectra of investigated catalysts the only band of interest originates by TiO_2 [21]. 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 (Fig. 3). The band 1 in Fig. 3a originates from pure TiO_2 obtained at 250 °C, while bands 2 and 5 from TiO_2 in electrocatalysts (samples 2 and 5). The peaks of the bands 2 and 5 are shifted to higher wave number related to the peak of pure TiO_2 . The higher the shift of wave number, the shorter the bond between TiO_2 and hyper d-metallic phase, i.e. the higher the hypo-hyper d-interaction. This shift is about 50 cm^{-1} for both systems. This is an evidence for existence of hypo-hyper d-interaction what causes changes in adsorption characteristics of the electrode materials and synergistic electrocatalytic effect of for hydrogen evolution. Ni- TiO_2 and NiCo- TiO_2 interactions (Fig. 3a) are almost the same due to similar size of Ni and Co atoms. The band of TiO_2 originated by modified electrocatalyst (sample 3) and corresponding band of pure TiO_2 thermally treated at 480 °C and shown in Fig. 3b. The shift of peak of TiO_2 in the catalyst is 120 cm^{-1} related to the peak of pure TiO_2 . This means that hypo-hyper d-interaction Ni- TiO_2 (anatase) is more than twice stronger than interaction Ni- TiO_2 (amorphous). It is expected the adsorption and catalytic characteristics for hydrogen evolution to be higher related to basic hypo-hyper d-electrocatalyst (sample 2). The shifts of TiO_2 peaks for all catalysts, shown in Table 4, show that (a) intensity of hypo-hyper d-interaction depends on the thermal treatment of TiO_2 and (b) the shifts are the same for catalysts with identical TiO_2 treatment. These facts are important

for further explanation of the changes produced by the studied modifications.

3.5. XPS analysis

In order to identify valence state of surface phases of the catalysts, XPS measurements were done. Analyzing the values of binding energy of Ti-spectra (Fig. 4a) one can conclude that peaks originated from $\text{Ti}2p_{3/2}$ and $\text{Ti}2p_{1/2}$ correspond to valence state Ti^{4+} . The peaks are wide and non-symmetric, what means that they are produced by superposition of several elemental ones. This is due to the interaction between hypo d-oxide and hyper d-metallic phases. The values of binding energy of peaks of $\text{Ti}2p_{1/2}$ (465.0 eV) and $\text{Ti}2p_{3/2}$ (459.3 eV) correspond to table values of TiO_2 (464.7 eV for $\text{Ti}2p_{1/2}$ and 459.2 eV for $\text{Ti}2p_{3/2}$) [22]. The table value of TiO_2/TiNi phase (459.0 eV for $\text{Ti}2p_{3/2}$) imply a presence of some amount of this phase, what is reasonable due to the interaction TiO_2 -Ni detected by IR and XPS spectra.

Table 4

Differences of maximum values of wave number of TiO_2 bands originated by electrocatalysts vs. corresponding ones of pure TiO_2

Sample no.	Δ wave number (cm^{-1})
1	–
2	50
3	120
4	50
6	50
5	120
7	120

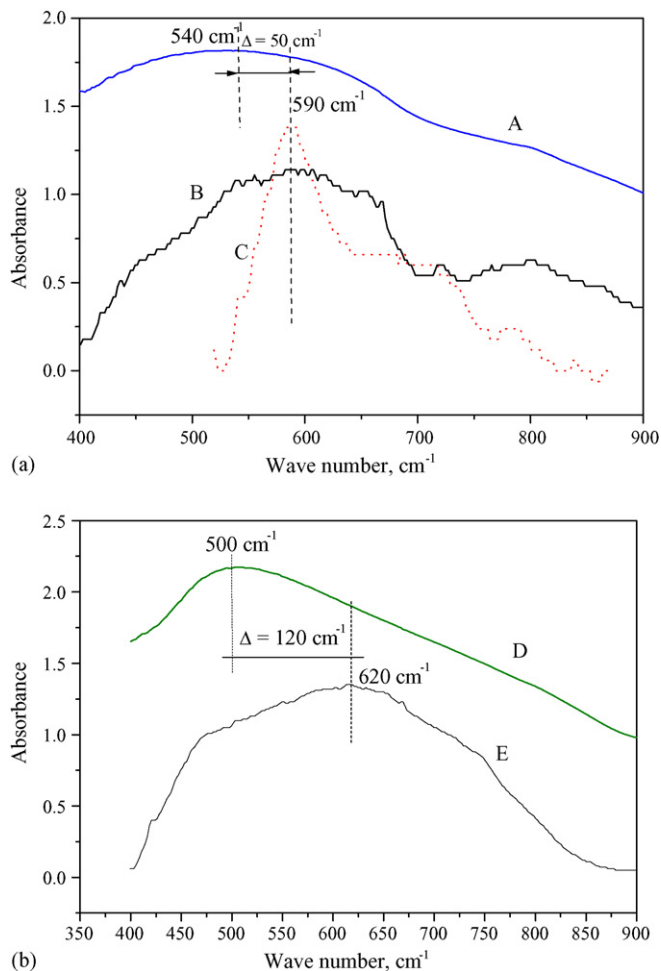


Fig. 3. Infrared spectra of TiO_2 thermally treated at: (a) 250°C and (b) 480°C . (A) Pure TiO_2 treated at 250°C ; (B) TiO_2 incorporated in the basic catalyst (sample 2); (C) TiO_2 incorporated in the modified catalyst (sample 5); (D) pure TiO_2 treated at 480°C ; (E) TiO_2 incorporated in the modified catalyst (sample 3).

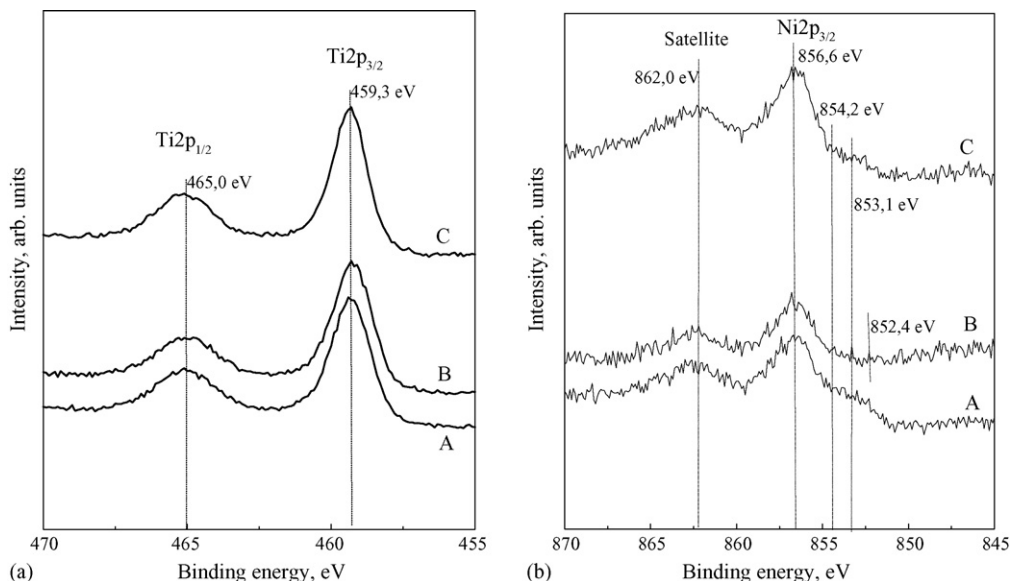


Fig. 4. XPS spectra originated by Ti^{4+} and Ni^{2+} . (A) basic hypo–hyper d -electrocatalysts (sample 2); (B) modified hyper d -phase (sample 5); (C) modified hypo d -phase (sample 3).

The peak of $\text{Ni}2p_{3/2}$ spectra on position of binding energy of 856.6 eV and satellite peak $\text{Ni}2p_{3/2}(\text{sat})$ on 862 eV suggest an existence of $\text{Ni}(\text{OH})_2$ phase. This means that the main amount of Ni on the surface layer up to depth of several Å exists as $\text{Ni}(\text{OH})_2$. The small peak on position of 854.2 eV indicates a presence of small amount of NiO with the same table value as the measured one, while the peak on position 853.1 eV corresponds to presence of NiTi phase (table value of 853.15 eV). This is in accordance with the previous spectra of TiO_2 phase as well as the IR spectra. The peak on position 852.4 eV for the catalyst modified with adding of Co (sample 5) implies a presence of small amount of NiCo (table value 852.7 eV).

All these results suggest on hypo–hyper d -interaction as the considerable factor in improvement of catalytic characteristics of the investigated electrocatalysts.

3.6. Real versus geometrical surface area

To compare the level of surface roughness (the ratio of real versus geometrical surface area, S_R/S_G), the capacity of double layer (C_{dl}) of the catalysts was determined by cyclic voltammetry in the potential region where only charging of double layer occurs. Scan rates of $1\text{--}10\text{ mV s}^{-1}$ were applied. Current density of double layer charging i_{cap} was adopted to be as an average value of anodic and cathodic current densities at potential at middle of the scanned interval. The plot of i_{cap} as a function of scan rate shows straight-line dependence with a slope equal to the value of double layer capacity of the electrode surface:

$$C_{dl} = \frac{di_{\text{cap}}}{d(\partial E/\partial t)}. \quad (1)$$

The values of double layer capacity and the ratio of real versus geometrical surface area of investigated catalysts are shown in Table 5. As can see, the surface area of all catalysts is highly developed, especially of those deposited on MWCNTs

Table 5
Double layer capacity, C_{dl} and ratio of real vs. geometrical surface area, S_R/S_G

Sample no.	C_{dl} (mF cm ⁻²)	S_R/S_G
1	16230	2705
2	16000	2670
3	16940	2820
4	32551	5425
6	15648	2610
5	32663	5443
7	30260	5043

as a substrate. C_{dl} value of MWCNTs are almost twice higher than that of Vulcan XC-72 ($C_{dl(MWCNT)} = 331 \text{ mF cm}^{-2}$ versus $C_{dl(Vulc XC-72)} = 179 \text{ mF cm}^{-2}$), what means that real surface area of MWCNTs is twice then the surface of Vulcan XC-72 [19]. The surface area of the catalysts deposited on MWCNTs is as well twice higher than those on Vulcan XC-72 (see Table 5). All catalysts deposited on Vulcan XC-72 (pure Ni (sample 1), basic hypo–hyper d-electrocatalyst (sample 2) and modified ones (samples 3 and 5) have approximately similarly developed surface area. NiCo-based catalysts (samples 5 and 7) in both cases deposited on Vulcan XC-72 and MWCNTs show some lower surface area than corresponding ones of Ni-based catalysts (samples 2, 4 and 6). Thermal treatment of TiO₂ to 480 °C also contributes to slight increase of surface area.

4. Discussion

4.1. Basic hypo–hyper d-electrocatalyst

Adding hypo d-oxide phase, TiO₂, into hyper d-metal, Ni, results in appearance of synergetic effect of electrocatalytic activity for hydrogen evolution reaction. This was confirmed with the analysis and discussion of the polarization curves shown in Fig. 1. Other proof that the improved activity is result of hypo–hyper d-interaction only was produced with IR spectroscopy (Fig. 3). Presence of TiO₂/TiNi and Ni phase indicated by XPS analysis supports this conclusion. The ratio of real versus geometric surface area is almost the same for samples 1 and 2 (Table 5), what means that surface area effect is negligible, and that only an increase of intrinsic catalytic activity was achieved due to Ni–TiO₂ interaction. In this case hypo d-oxide phase TiO₂ has bifunctional role, as a catalyst's support and as a participant in the overall synergetic effect, due to the "strong metal–support interaction" (SMSI). SMSI has been termed by Tauster et al. [23] to account for the changes in catalytic activity when metals of VIII group are supported on TiO₂ in heterogeneous catalysis. Hypo d-phase changes electronic structure of hyper d-metal. These changes of electron structure and mutual sharing of d-orbitals provides electronic configuration suitable for H⁺ adherence and transference [4]. The electron density near hyper d-metal is higher in the alloy than in a pure state, due to electron transfer from the surrounding atoms of hyper d-phase [24,25]. In this case, hydrogen evolution near the metal atoms should be favored in the composite catalyst rather than in pure hyper d-metal.

4.2. Modification of hypo d-oxide phase

Transformation of amorphous titania in anatase crystalline form at 480 °C contributes to higher activity of catalyst where this TiO₂ is used. The overpotential for HER on the modified catalyst (sample 3) is for 60 mV lower than on the basic catalyst and even 110 mV lower than on pure Ni (see Table 3). Comparing S_R/S_G values, one can see that modified catalyst has negligible higher surface area (only 5%). IR analysis provides evidence that after heating at 480 °C absorbance band maximum of TiO₂ incorporated into the modified catalyst (sample 3) is shifted for 120 cm⁻¹ as compared to the reference, pure TiO₂ treated at the same temperature (see Fig. 3b). This shift is to be compared with a shift of only 50 cm⁻¹ measured in the basic catalyst (Fig. 3a). This difference indicates that the measured increase of electrode's activity is a result of pure hypo–hyper d-interaction between Ni and anatase, which is 2.4 times higher than in the basic catalysts. Thus, the SMSI is much stronger when anatase is used as a hypo d-oxide phase. The unique role of anatase form of titania in improvement of catalytic activity in both heterogeneous chemical catalysis and electrocatalysis has been noticed by other authors [26,27].

4.3. Modification of carbon substrate

Substitution of Vulcan XC-72 with MWCNTs as carbon substrate results in a decrease of HER overpotential for as much as 120 mV. This increase of the catalytic activity is of different character than the previous ones. Data presented in the Table 4 show that the mentioned carbon substitution does not change the level of hypo–hyper d-interaction. On the other side, the surface area of MWCNTs (sample 4) is almost twice higher than the one with Vulcan XC-72. This indicates that the increased activity of MWCNTs based catalysts is caused not by the rise of intrinsic electrocatalytic activity, but by increase of the electrode's real surface area.

The higher activity for hydrogen evolution is a result first of all of the nature of carbon nanotubes. Their inner structure, surface area and conductive characteristics are favorable for used MWCNTs as a carbon substrate for the nanostructured electrocatalysts. Their high developed surface area enables better dispersion of active catalytic centers across the catalyst's surface. Also, extra-conductive properties enable easier electron exchange with hydrogen protons, what intensifies formation of adsorbed hydrogen atoms and further hydrogen molecules. On the other side, its high inter- and trans-particle porosity as well as its geometry (empty cylinders), do facilitate the escape of hydrogen molecules from catalyst's surface.

4.4. Modification of hyper d-metallic phase

Addition of cobalt into metallic phase in atomic ratio Ni:Co = 1:1, shows remarkable increase of catalytic activity for HER. This is surprising because: (a) according to the IR results the hypo–hyper d-interaction is not affected by addition of Co (Fig. 3a), (b) the real surface area of the modified catalyst is even lower than the referent one (See Table 5). The same is

situation with the ratio of BET surfaces (basic versus modified catalyst = 108:96 m² g⁻¹), (c) Ni and Co, as individual metals, exhibit similar activity for HER [28]. So, the question arises on what is the reason why addition of Co into Ni causes such a remarkable activity increase?

The answer lays in the similarity of NiCo-based catalyst with the systems that contain Co only [29].

The XRD analysis, as well as the results presented elsewhere [18,20] indicates that Co in this case exists in two different phases. A minor part of it forms a Ni–Co solid-state solution, while the rest continues to exist as pure (amorphous) Co with size of particles lower than 2 nm. So, involving Co into metallic phase considerably increases the real surface area of active catalytic centers. Also, there is better dispersion of metallic catalytic centers, what means that whole catalyst's surface is available for hydrogen evolution reaction. Instead of that, although basic catalyst has a higher surface area, its crystalline particles are bigger (10–20 nm), so the real surface area of active catalytic centers is considerably lower. Dispersion of these larger particles is less uniform what means that no whole catalyst's surface is available for hydrogen evolution.

4.5. Complete modification

Ni-based catalyst with completely modified support (sample 6) shows high decrease of overpotential for HER, i.e. 145 mV as compared to the basic electrocatalyst. The improved activity for hydrogen evolution is a result of both intrinsic hypo–hyper d-interaction between Ni and anatase and increasing of the real surface area. As discussed above, the higher contribution in the total effect has the increase of surface area caused by introduction of MWCNTs.

The completely modified catalyst (sample 7) was shown to perform the best one of all investigated series. Overpotential for hydrogen evolution is even 230 mV lower than that of basic electrocatalyst. The ratio of hydrogen evolution current densities at $\eta = -250$ mV is 6 mA cm⁻² versus 60 mA cm⁻², indicating that completely modified catalyst performs 10 times faster hydrogen evolution. This remarkable activity improvement is result of three phenomena: hypo–hyper d-interaction, increase of surface area of the catalyst as a whole and high surface area of hyper d-metallic phase as an active catalytic center. The order of their contribution has an opposite order: the most effective is the involving of Co into hyper d-metallic phase.

On the end, one should mention that three-dimensional gas-diffusion electrodes could possibly acquire lower activity at higher current densities (as compared to, e.g. Raney–Ni or Raney–Ni activated electrodes) due to the nature of their structure. If evolved hydrogen could not escape out of the subcritically sized pores, then the operating surface area (of such 3D electrodes) is lower than the real one. Similar phenomenon was found and discussed by Wendt and co-workers [30,31]. According to them even as much as 90% of the surface area available for hydrogen evolution could be blocked and become inactive. Probably the similar is situation with our electrodes. Engineering aspects of the electrodes are planned to be subject of study in

some further stages, and are not included in this paper. The aim of this research is to improve catalytic behavior of the investigated composite material.

5. Conclusion

The investigations in this study were motivated by the idea to obtain nanostructured composite non-platinum electrocatalysts for hydrogen evolution. So, hypo–hyper d-electrocatalysts based on Ni were prepared and tested. The basic hypo–hyper d-electrocatalyst has shown a synergetic effect, i.e. higher activity than that of pure Ni obtained in the same conditions.

Further modifications consist of: (i) transformation of amorphous TiO₂ into anatase crystalline form, (ii) substitution of carbon substrate (Vulcan XC-72) with carbon nanotubes and (iii) introducing of Co into metallic phase. The very choice of these modifications is not at all occasional, but is rather based on some previous experiences and results achieved by such and/or similar options. This is why all three modifications appeared to be successful.

The effect of converting TiO₂ from amorphous into crystalline one results in decreasing of the overpotential for 60 mV.

The effect of use of MWCNTs instead of Vulcan XC-72, was very successful. The overpotential decreases for 120 mV as compared to the basic electrocatalyst.

Finally, the addition of Co in atomic ratio Ni:Co = 1:1 lowers the overpotential even for 195 mV.

Completely modified catalyst performed the best for HER, lowering overpotential for remarkable 230 mV compared with the basic hypo–hyper d-electrocatalyst.

The highest contribution in improvement of catalytic behavior for HER was attributed to the addition of Co into metallic phase, the resulting rise of the active catalytic centers surface area, next was the effect of MWCNTs as a carbon substrate, due to increase of real surface area of the catalyst as a whole and finally is intrinsic hypo–hyper d-interaction.

Finally, one could conclude that the investigated catalytic systems are rather complex and one could practically never state that the best of their performance is achieved. Modifications like this (or other) will probably be further visioned and applied, just contributing to further, steep or slow, but no matter continuous increase of the catalytic activity for the HER.

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