New nano-structured and interactive supported composite electrocatalysts for hydrogen evolution with partially replaced platinum loading

Perica Paunović[a,*], Ivan Radev[b], Aleksandar T. Dimitrov[a], Orce Popovski[c], Elefteria Lefterova[b], Evelina Slavcheva[b], Svetomir Hadži Jordanov[a]

[a]Faculty of Technology and Metallurgy, University "Sts. Cyril and Methodius", Ruger Bošković Str., 16, 1000 Skopje, Republic of Macedonia
[b]Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl.10, 1113 Sofia, Bulgaria
[c]Military Academy, Mihajlo Apostolski Str., b.b., 1000 Skopje, Republic of Macedonia

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ABSTRACT

This work is concerned with preparation and characterization of nano-structured composite electrocatalytic material for hydrogen evolution based on CoPt hyper d-metallic phase and anatase (TiO_2) hypo d-phase, both deposited on multiwalled carbon nanotubes (MWCNTs) as a carbon substrate. The main goal is partially or completely to replace Pt as the electrocatalytic material. Four electrocatalytic systems were prepared with common composition 10% Me + 18% TiO_2 + MWCNTs, where Me = Co, CoPt (4:1, wt. ratio), CoPt (1:1, wt. ratio) and Pt. The structural changes and their influence on electrocatalytic activity were studied by means of XRD, TEM, SEM and FTIR. The electrocatalytic activity was assessed in aqueous alkaline and polymer acidic electrolytes by means of steady-state galvanostatic method. It was found that Co strongly affects the platinum particle size. The addition of Co reduces platinum particle's size from 11 nm (in pure Pt metallic system) to 4 nm (in both systems 4:1 and 1:1), i.e. almost by 3 times. The corresponding increase of the surface area and the number of the active catalytic centres improves the efficiency, despite the fact that the amount of used platinum was decreased up to 5 times. The catalyst based on CoPt (1:1) performed the best, while the activity of the pure platinum and CoPt (4:1) systems were very close. Generally, the studied electrocatalysts have shown good and stable performances for hydrogen evolution in PEM electrochemical cell. The influence of the hydrogen electrodes under investigation on the water electrolysis efficiency at current density of 0.3 A cm^{-2} was assessed, using previous data oxygen evolution on IrO_x electrode. Related to the performances of commercial Pt (ELAT) electrode, when hydrogen electrodes with the prepared mixed electrocatalysts were used, the water electrolysis efficiency was only 5% lower for CoPt (1:1), nearly 10% lower for CoPt (4:1) and 13% lower in the case of pure Co-based electrocatalyst.

1. Introduction

The membrane electrode assembly (MEA) as a structure of cathode–membrane (solid electrolyte)–anode, can be considered as a driving force of modern fuel cells/water electrolysers. It is a meeting place of three phases (ionic conductor–electronic conductor–gas) where electrochemical reactions occur. So, the power efficiency of MEA depends on the material characteristics of both the electrodes (electronic conductors) and membranes (ionic conductors) as well as on the architecture of the triple phase boundary [1–9].

Innovation of non-platinum electrode materials for water electrolysers/fuel cells is a very important issue within the hydrogen economy, which is considered as the most perspective energy system in the future. The commercial application of the still leading electrode material – Pt is limited due to its high cost and low abundance. About 50% of the modern fuel cell cost is attributed to MEA in which Pt cost is more than 70% [10,11]. On the other hand, according to some analysis [11–13], the present resources of Pt are enough to cover only 20% of the automotive industry needs. What about the remaining 80%? What about the future electricity needs that are considerably higher than in the automotive industry?

Considering the above facts, the main goal of the modern electrocatalysis and material science employed in hydrogen economy, is to reduce or even to replace platinum in the MEA, keeping the same level of efficiency. There are two main approaches to achieve this: i) exploration of synergetic mixture of non-platinum electrocatalytic materials (ex., Jakšić hypo–hyper d-concept [14–16]) and ii) replacement of the traditional carbon support materials (ex., Vulcan XC-72) with carbon nanotubes [17–19].

The previous works of the present authors were concerned with production and characterization of so-called hypo–hyper d-electrocatalysts, containing 10% Me + 18% TiO$_2$ + carbon substrate [20–22]. Different metallic phases were studied such as Ni, Co or CoNi, deposited on both traditional Vulcan XC-72 and multiwalled carbon nanotubes (MWCNTs). Hypo–hyper d-interaction between metallic phase and TiO$_2$ (anatase) contributes to the intrinsic activity of the electrocatalyst. The better electrical and surface characteristics of MWCNTs provide considerable increase of the electrocatalysts' real surface area as well as more uniform dispersion of the active catalytic centres over the whole catalyst's surface. The best activities were achieved when hypo–hyper d-mixture Co–TiO$_2$ was deposited on activated/purified MWCNTs in nitric acid [23], approaching performances of corresponding traditional Pt electrocatalyst deposited on Vulcan XC-72. The performance of these electrocatalysts in proton exchange membrane (PEM) electrolyte at lower cathodic overpotentials was not so impressing, while at higher overpotentials their activity approaches the performance of a traditional Pt catalyst [24].

The subject of this work is to study the catalytic activity of hypo–hyper d-Co–Pt based electrocatalysts deposited on activated/purified MWCNTs as carbon support. Hydrogen evolution reaction (HER) was tested in alkaline water electrolyser as well as in the so-called *EasyTest Cell* (ETC) using a proton exchange membrane as an electrolyte [25].

2. Experimental

The investigated electrocatalysts contain 10 wt.% metallic phase (Co, CoPt or Pt, see Table 1), 18 wt. % TiO$_2$ as anatase and activated/purified MWCNTs. As precursors for hyper d-metallic and hypo d-oxide phase orgnometallics were used (Me-2,4-pentanedionate, Me = Co or Pt, Alfa Aesar, Johnson Matthey, GmbH and Ti-isopropoxide, Aldrich, 97%). Multi-walled carbon nanotubes (MWCNTs, *Guangzhou Yorkpoint Energy Company, China*) were used as carbon substrate. The catalysts were produced by a sol–gel procedure [20]. In the first stage, in order to deposit TiO$_2$ onto carbon substrate, Ti-isopropoxide (Aldrich, 97%) was added into dispersed activated MWCNTs in anhydrous ethanol. To provide hydrolysis to Ti(OH)$_4$, small amount of 1 M HNO$_3$ 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-pentanedionate was dissolved in anhydrous 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 d-phase onto catalyst support. To decompose both Ti(OH)$_4$ to TiO$_2$ and the residual amount of oraganometallics, the powder was heated for 2 h at 480 °C in the atmosphere of H$_2$ + N$_2$. Before the sol–gel preparation of the catalysts, activation/purification of the as-prepared MWCNTs in 28 wt.% HNO$_3$ was performed.

Firstly, the produced electrocatalysts were electrochemically tested for hydrogen evolution in alkaline electrochemical cell. Porous electrodes aimed for three phase operation in alkaline cell (solid electrode, liquid electrolyte and H$_2$ gas as a product) were prepared. They consist of two layers: i) a catalytic layer facing the electrolyte, covered by catalyst with low amount of PTFE and ii) a gas-diffusion layer facing the gas side, consisting of Vulcan XC-72 bonded with PTFE. The electrode preparation procedure is described elsewhere [26]. Electrochemical investigations were performed using AMEL equipment (Function Generator AMEL 568, Potentiostate/Galvanostate 2053 and software package SOFTASSIST 2.0). The counter electrode was a 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 structural characteristics of the studied electrocatalysts were observed by means of XRD, TEM, SEM and FTIR

Table 1 – Composition of the studied electrocatalysts.			
Sample no.	Hyper-metal d-phase (10%)	Hypo-oxide d-phase (18%)	Carbon substrate (72%)
1	Co	TiO$_2$	MWCNTs
2	CoPt (4:1, wt. ratio)	TiO$_2$	MWCNTs
3	CoPt (1:1, wt. ratio)	TiO$_2$	MWCNTs
4	Pt	TiO$_2$	MWCNTs
5[a]	Pt	–	Vulcan XC-72

a In this sample there is no TiO$_2$, so the content of Vulcan XC-72 is 90%.

analysis. XRD was employed in order to identify the present phases in the catalysts and to determine their crystallite size. XRD measurement was carried out by X-ray diffractometer Philips APD 15, with Cu Kα radiation. The crystallite size was calculated using the Scherrer equation, $D = k\lambda/\beta \cos\theta$, where D is the crystallite size, $k = 0.9$ is a constant, λ is the X-ray wavelength, θ is the diffraction angle and β is the full width at half maximum (FWHM) of the diffraction peak at θ [27]. The morphology and the particle size of the electrocatalysts were investigated by scanning (SEM) and transmission (TEM) electron microscopy. Transmission electron microscope JEOL JEM – 200 CX was used in scanning and transmission regime. Infrared spectroscopy was employed to determine the strength of hypo–hyper d-interaction (Me–TiO_2). FTIR spectra were recorded using KBr pellets at room temperature with Perkin–Elmer System 2000 interferometer.

Further, performances for hydrogen evolution reaction of the prepared electrocatalysts were tested in ETC. The ETC design and its operational principle is described elsewhere [25]. MEA consisted of working electrode containing the studied electrocatalysts and a counter electrode of the commercial Pt ELAT, both grafted on a commercial Nafion 117 membrane (Alfa Aesar). A small piece of Pt electrode ELAT (ca. 0.1 cm^2) was used as a reference hydrogen electrode (RHE). All electrochemical measurements in ETC were carried out with a Galvanostat/Potentiosat POS 2, Bank Electronik, and CPCDA software, at 80 °C and relative humidity (RH) of 100%.

The MEAs under study were prepared by hot pressing of catalyzed gas-diffusion layers on both sides of the polymer membrane. The proton conductivity in the catalytic layers and the attachment of the prepared electrodes to the PEM were ensured by an optimized amount (15 μl cm^{-2}) of 5 wt.% Nafion solution (Alfa Aesar). Immediately, a hot pressing was performed gradually increasing the temperature and pressure starting at 50 °C and 50 kg cm^{-2} and ending at 120 °C and 120 kg cm^{-2}. The amount of the metallic phase in the electrodes under study was 1 mg cm^{-2}. All electrode potentials presented were measured versus RHE at the given testing conditions. For comparison, the polarisation curves of a commercial ELAT electrode (ELAT (R) V.21, Lot # MB030105-1, Pt loading 0.5 mg cm^{-2}, E-TEK) were also recorded.

3. Results and discussions

3.1. Structural characteristics

In Fig. 1 are shown XRD spectra of the studied electrocatalysts. In all samples TiO_2 was detected as crystalline anatase [28] with crystallite size about 4 nm. Characteristic peaks of Co cannot be seen due to its amorphous character and very small particles [20,21]. Only in spectrum 1 (sample with pure Co as metallic phase) a very weak peak was indicated at $2\theta = 44.22°$, corresponding to (111) reflection of cubic Co [29]. Within spectrum 4 (sample with pure Pt as metallic phase) well-pronounced peaks of crystalline Pt can be seen [30], with crystallite size about 11 nm. The corresponding Pt peaks in spectra 2 and 3 (samples with mixed Co and Pt metallic phases) are considerably weaker. The position of the Pt peak is the same as that in the pure Pt metallic system (sample 4)
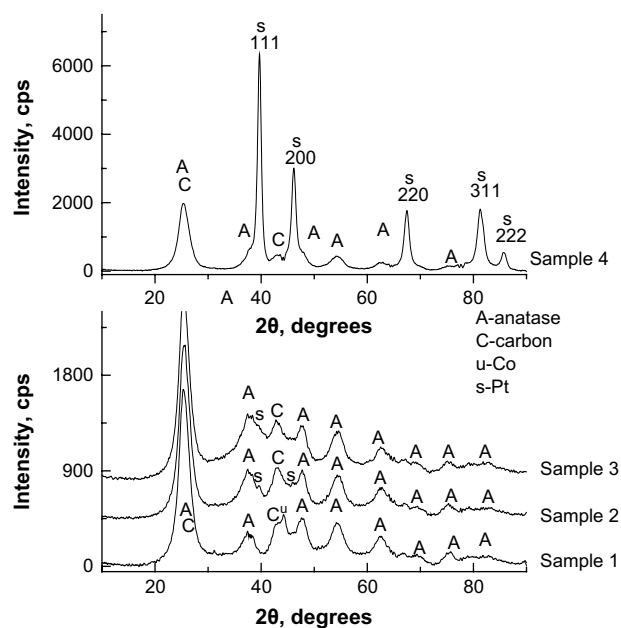

Fig. 1 – XRD analysis of the studied electrocatalysts.

suggesting that in the mixed CoPt systems there is no new CoPt intermetallic phase, but only a mixture of Co and Pt particles exists. This is confirmed by the fact that the Co phase spectrum of the bimetallic catalysts is the same as in the pure Co metallic system (sample 1).

In order to estimate particle size as well as to observe the dispersion of catalyst's components over the surface, TEM analysis was performed (Fig. 2). There is a strong correlation between XRD and TEM analyses related to the crystallite size and the particle size. The black spots represent the metallic phase particles over the catalyst's surface. In the case of pure Pt (Fig. 2b) the diameter of these black spots is 10–12 nm. The same value was determined by XRD analysis for the crystallite size. The black spots in the catalysts with mixed metallic phase are much smaller or very poorly visible (Fig. 2c and d) and their size is not greater than 4 nm. The diameter of the activated MWCNTs is about 8–10 nm. In all samples, the components are uniformly well dispersed over the catalyst's surface.

By both analyses it was shown that Pt particles in the presence of Co are considerably smaller (about 3–4 times). Thus, cobalt can be considered as a promoter for reduction of the platinum particle size which was observed also by other authors [31–33]. Smaller particles mean higher surface area of the metallic phase and greater number of active catalytic centres which are more uniformly dispersed over the catalyst's surface. This is favourable for the electrocatalytic activity toward hydrogen evolution.

The results of SEM analysis are shown in Fig. 3. The studied electrocatalysts show intertwined thread-like morphology, as a result of the presence of MWCNTs. This morphology is more appropriate than that of electrocatalysts deposited on carbon blacks [20,21]. In this case the catalyst's components are grouped into smaller clusters, there are more holes between them, which leads to better inter-particle porosity of the catalysts. Due to the intrinsic geometric shape of MWCNTs (empty cylinders ordered one over the other), they
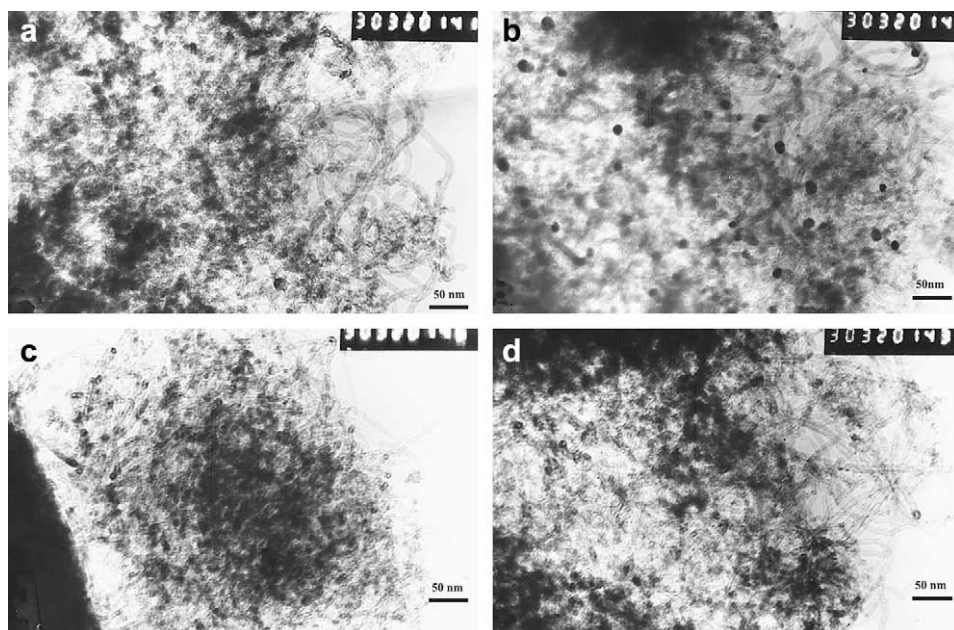
Fig. 2 – TEM images of the studied electrocatalysts. a) Sample 1, b) sample 2, c) sample 3 and d) sample 4.

possess inner holes, so the inner (trans-particle) porosity of MWCNTs is considerably higher. As can be seen, MWCNTs with thickness of 8–10 nm (see Fig. 2), stick on each other and their thickness increases to nearly 100 nm.

FTIR analysis was performed in order to determine hypo–hyper d-interaction between the metallic phases and TiO_2. In hypo–hyper d-interaction d-bonds are predominant. From the fact that d-bonding is responsible for adsorption/desorption processes [34,35] which are an important part of the hydrogen evolution reaction, it is clear that the higher level of interaction means higher activity of the material for hydrogen evolution. FTIR spectra of the studied catalysts are shown in Fig. 4. The only band of interest originates from TiO_2. To determine hypo–hyper d-interaction one has to compare TiO_2 band from the electrocatalyst and a band from pure TiO_2 obtained at identical conditions. The maximum of the pure TiO_2 band is about 495 cm^{-1}. 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 470 cm^{-1} for all samples (maximum of TiO_2 band is at 965 cm^{-1}) which evidences a considerable high hypo–hyper d-interaction. As a result of this an improved intrinsic activity for all electrocatalysts related to the corresponding pure metallic phases without TiO_2 was observed. But because the value of the hypo–hyper d-interaction is the same for all catalysts under study, the expected differences in their electrocatalytic activity cannot be attributed to the increase of the intrinsic activity.

3.2. Electrocatalytic activity for hydrogen evolution in the alkaline electrolyser

In Fig. 5 are shown polarisation characteristics of the studied electrocatalysts for hydrogen evolution reaction in alkaline electrolyte. For comparison, a polarisation curve of pure Pt electrocatalyst deposited on Vulcan XC-72 using the same procedure is shown. The overpotentials for hydrogen evolution at referent current density of 60 mA cm^{-2} are shown in Table 2. The activity of the Co-based hypo–hyper d-electrocatalyst (sample 1) is very close to that of the traditional Pt/Vulcan XC-72 one. This considerable improvement of catalytic activity of the Co-based catalyst is a result of several factors: i) intrinsic hypo–hyper d-interaction between Co and TiO_2; ii) use of activated MWCNTs as carbon substrate, improving the inter- and trans-particle porosity as well as dispersion of the active catalytic centres over the catalytic surface; and iii) very small particles of Co (about 2 nm), i.e. very high developed surface area of the metallic phase as the main catalytic centres.

These factors also explain why Pt-containing catalyst of this series (sample 4) is so superior to the traditional Pt catalyst. It has shown nearly 90 mV lower overpotential for hydrogen evolution related to Pt/Vulcan XC-72. As shown in our previous works, the corresponding difference in overpotentials of the Co-based systems (Co/Vulcan XC-72 vs. Co/TiO_2/MWCNTs) is about 130 mV [21], while for Ni-based catalysts (Ni/Vulcan XC-72 vs. Ni/TiO_2/MWCNTs) it is even 250 mV [20].

The best catalytic activity is shown by the catalysts with mixed metallic phase Co:Pt = 1:1, wt. ratio. (sample 3), while the catalyst with mixed metallic phase Co:Pt = 4:1, wt. ratio (sample 2) is less active but still very close to the activity of pure Pt-based catalyst (sample 4). At the first glance, it is a paradox that the catalyst with double the amount of Pt (sample 4) is less active. But, there is logical explanation for this order of catalytic activity. Let's consider the above factors having an influence on the catalytic activity. The intrinsic hypo–hyper d-interaction is the same in all catalysts. They all have better porosity and dispersion of the metallic phase as a result of MWCNT usage as catalyst support as well. Thus, the
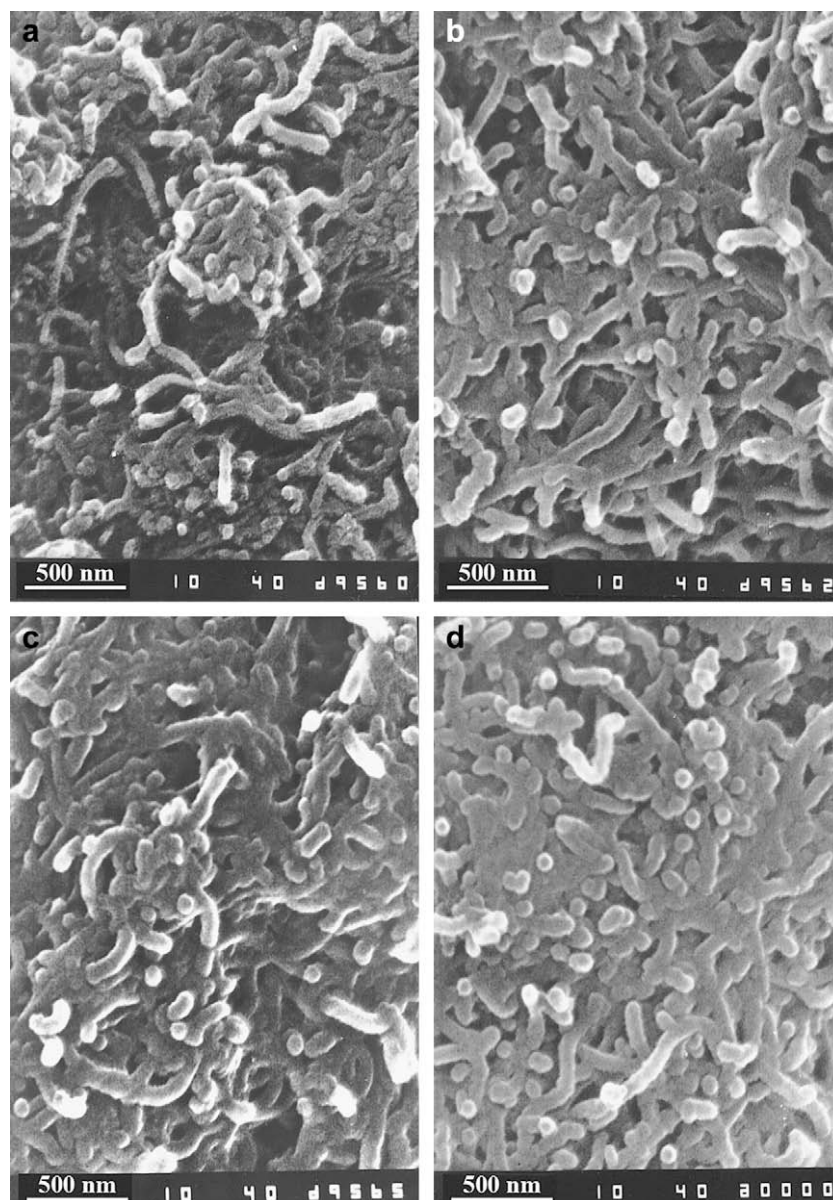
Fig. 3 – SEM images of the studied electrocatalysts. a) Sample 1, b) sample 2, c) sample 3 and d) sample 4.

improved activity of the catalyst with less amount of platinum obviously is related to the considerably lower size of Pt crystallites in the mixed systems. As it was shown from the XRD analysis, the size of Pt crystallites in sample 4 is about 12 nm, while in the mixed systems (samples 2 and 3), Co promotes considerably lower (up to 3–4 times) size of Pt particles. The lower amount of Pt is compensated by the highly developed surface of Pt-phase in the mixed systems.

3.3. Electrocatalytic activity for hydrogen evolution in the EasyTest Cell

A series of quasi-steady-state cathodic polarisation curves of the studied catalysts and the commercially available ELAT were obtained in the EasyTest Cell. A detailed description of this electrochemical test approach and cell has been

published elsewhere [25]. The experiments were carried out at a total pressure of 1.25×10^5 Pa, temperature of 80 °C with 100% RH, hydrogen partial pressure of 7.75×10^4 Pa and potential scan of 0.2 mV s^{-1}. As it can be seen from the curves obtained on freshly prepared MEAs (Fig. 6) at current densities below 0.2 A cm^{-2} the best electrode performance, identical to that of ELAT is shown by the electrode containing catalyst sample 3 (Co:Pt = 1:1, wt. ratio), while the partial or complete substitution of Pt by Co in sample 2 and sample 1 leads to voltage penalties.

All of the tested electrodes have shown a stable electrode performance during a 24 h galvanostatic test at current density of 0.3 A cm^{-2} (Fig. 7). The electrode polarisations at 0.3 A cm^{-2} taken before and after the galvanostatic test are summarized in Table 3. While the trend in the electrode performance is similar to that obtained during the short-term
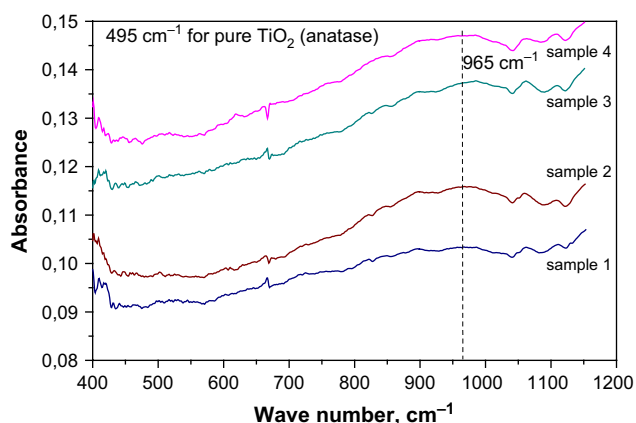
Fig. 4 – Infrared spectra of TiO₂ originated from the studied electrocatalysts.

Fig. 6 – Quasi-steady-state polarisation curves of the investigated electrocatalysts as cathode for hydrogen evolution in MEAs in *EasyTest Cell*, using Nafion 117 proton exchange membrane.

tests, higher voltage penalties of ca. 100 and 50 mV, were observed for the electrodes containing catalysts with mixed metallic phase (sample 3 and sample 2, respectively). On the contrary, the pure Co-based electrode enhanced its perfor-

cell performance of a single cell PEM water electrolyser the above data were combined with previous ETC results for oxygen evolution on IrO_x electrode [36,37]. The measured anode polarisation on the IrO_x electrode at current density of $0.3\,A\,cm^{-2}$ was 1.6 V [36,37]. In Table 4 are presented the calculated cell potentials and the corresponding cell efficiency values as ratio of the theoretical and determined cell voltages at $0.3\,A\,cm^{-2}$. Sample 3 has shown the best cell efficiency, only 5% lower than that of commercial Pt. The poorest efficiency, 13% lower related to commercial Pt, has been shown by sample 1. Taking into consideration the fact that this sample contains only Co as metallic phase (0% Pt), such efficiency can be considered as very satisfying.
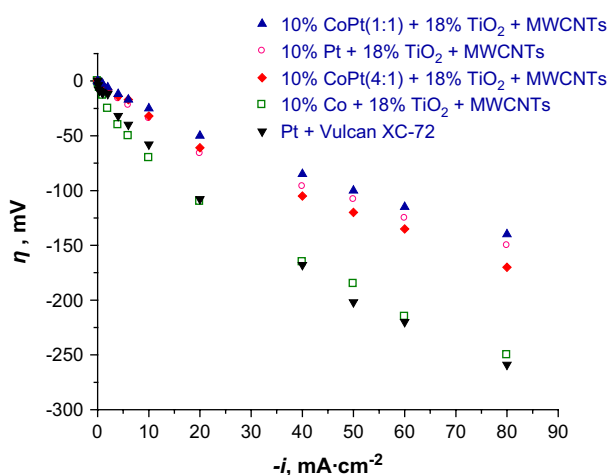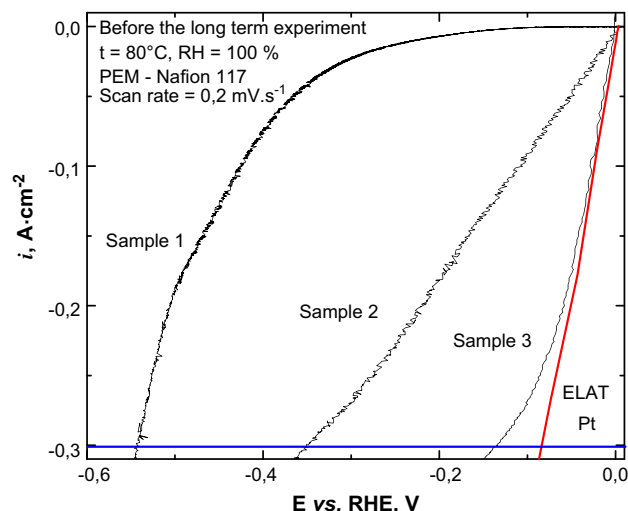

Fig. 5 – Steady-state polarisation curves of investigated electrocatalysts in alkaline cell.

mance gaining a decrease of 65 mV in the electrode polarisation.

In order to obtain information about the influence of the studied catalysts (as hydrogen evolution electrodes) on the
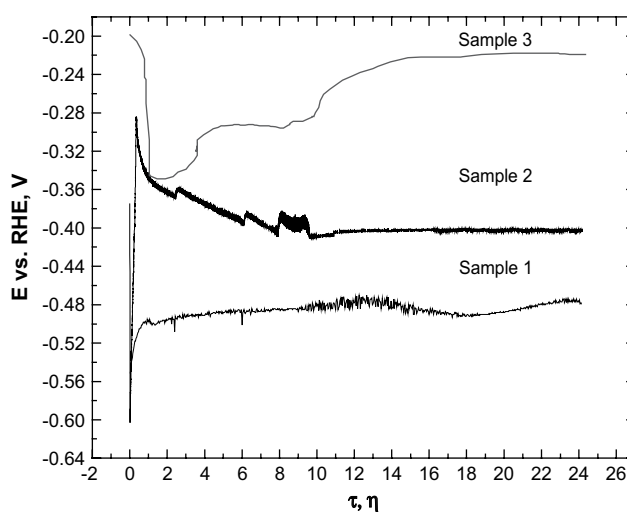

Fig. 7 – Long-term galvanostatic test of the studied electrode materials in *EasyTest Cell* at 0.3 A cm⁻² for 24 h.

Table 2 – Overpotentials at 60 mA cm⁻² for hydrogen evolution reaction of the studied electrocatalysts.	
Sample no. (see Table 1)	η_{60}/mV
1	−215
2	−135
3	−115
4	−125
5	−220

Table 3 – Electrode potentials (E) registered before and after long-term electrode performances.

Electrode prepared of the sample no.	E vs. RHE, mV at $i = 0.3$ A cm^{-2}	
	Before long-term experiment	After long-term experiment
ELAT (E-TEK)	−83	–
3	−133	−220
2	−350	−402
1	−543	−478

Table 4 – Cell voltage and efficiency of PEM water electrolyser (studied electrocatalysts as cathode and IrO$_x$ as anode) calculated at $i = 0.3$ A cm^{-2} (Nafion 117, 80 °C, RH = 100%).

Electrode prepared of the sample no.	Cell voltage, mV	Efficiency, %
ELAT (E-TEK)	1683	70.4
3	1820	65.1
2	2002	59.1
1	2078	57.0

4. Conclusions

The investigations presented in this paper were motivated by the idea to reduce or even replace Pt in self-developed electrode material for hydrogen evolution. Electrocatalysts with pure metallic phase (Co and Pt) and mixed metallic phase (CoPt, 4:1 and 1:1, wt. ratio) deposited on catalyst support consisting of TiO$_2$ and activated MWCNTs were prepared and studied. According to the achieved results the following conclusions can be drawn:

1. The addition of Co–acac during the sol–gel synthesis results in the decrease in the size of the Pt particles from 12 to 3–4 nm (XRD, TEM). Thus, Co has shown to be a promoter reducing considerably the size of the Pt crystallites.
2. As a result of the Pt particle size reduction, the surface area of the metallic phase increases, that compensates the less amount of Pt in the catalytic activity. The activity of the catalyst with only 20 wt.% Pt in metallic phase is close to that of pure Pt-containing catalyst, while the catalyst with 50% Pt in metallic phase exceeds its activity. It should be mentioned that improvement of the catalytic activity is a result of the rise of both hypo–hyper d-interaction and real surface area. Because the level of hypo–hyper d-interaction in all studied catalysts is almost the same, differences in catalytic activity are a result of corresponding differences of the 'size effect'.
3. The improved activity of all hypo–hyper d-Pt-containing catalysts deposited on activated MWCNTs compared to the traditional Pt/Vulcan XC-72 is a result of: i) intrinsic hypo–hyper d-interaction between hyper d-metallic phase and TiO$_2$, and ii) improved inter- and trans-particle porosity as well as dispersion of the active catalytic centres over the catalytic surface.

4. In comparison to the commercial Pt electrode (ELAT) in the PEM electrochemical cell, the efficiency penalty of the water electrolysis based on the best electrode of the studied series (catalyst with metallic phase CoPt, 1:1 wt. ratio, sample 3) is about 5%.
5. The complete substitution of Pt by Co in the hydrogen electrode (sample 1) results in efficiency penalty of ca. 13% compared to the commercial Pt electrode (ELAT).

The investigated catalytic systems are rather complex and one could practically never state that the best of their performance is achieved. Further modification of both the catalyst's components and preparation of the MEA can contribute to increase even more the catalytic activity for HER and eventually, to replace Pt completely in the electrode materials.

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