Nano-structured Electrode Materials with Reduced Amount of Platinum Aimed for Hydrogen Evolution. Part I: Effect of cobalt

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Abstract: *The subject of this study is electrochemical and structural characterization of nano-dimenzioned composite electrode materials for hydrogen evolution consisted of Co, Pt or CoPt metallic phase and TiO_2, both grafted on multiwalled carbon nanotubes (MWCNTs) as a support material. The main idea was to replace platinum entirely or to some extent as an electrode material. The electrode materials with different The common composition of the studied electrode materials was 10%Me + 18%TiO_2 + MWCNTs, where Me = Pt, CoPt (1:1, wt.), CoPt (4:1, wt.) and Pt. The structural and surface changes, as well as their influence on electrocatalytic activity were analyzed by means of XRD, TEM, SEM and FTIR. It was found that Co considerably reduces Pt particle size, from 11 nm (in pure Pt metallic system) to 3–4 nm (in mixed CoPt systems). This is a reason for better activity of the electrode material with CoPt (1:1) metallic phase than that with pure Pt, while the CoPt (4:1) with very low quantity of Pt approaches the acitivity of the electrode material with pure Pt.*

Keywords: HYDROGEN EVOLUTION, ELECTRODE MATERIALS, COBALT, PLATINUM, ANATASE

1. Introduction

One of the most important issue of the hydrogen economy as the most promising alternative energy system, is the choice of active and effective electrode materials as a site for taking place of the electrode reactions in the hydrogen electrolysers and fuel cells [1]. Platinum has the largest commercial application as the most active catalytic material. But, the use of Pt will be limited, due to its high cost and low abundance [2]. The situation of limited Pt resources and a high energy needs, the price of Pt will be incredibly increased. Therefore, the crucial challenge of the hydrogen economy is to reduce the amount of Pt in the electrode materials or totally replace by some non-noble materials with activity close or even better than Pt. According to the physical approach, increasing of real surface area of the electrode material, i.e. smaller particle size lead to increasing of the catalytic activity [3]. This is the concept for involving of nanomaterials in electrode materials. The chemical approach suggests increase of the intrinsic catalytic activity through mixing the catalytic metal with other metals or its compounds [4]. Strong synergetic effect can be achieved by mixing of metals/compounds with opposite electronic character. According to Jakšić's hypo-hyper d-concept [5,6] based on the the Brewer resonance bond-valence theory for intermetallic compounds [7], the mixing of hyper d- electronic transition metals (with more electrons in the outer d-shell and good individual catalysts) with hypo d- electronic transition metals (with less electrons in the outer d-shell and poor individual catalysts) shows a pronounced synergetic effect for hydrogen evolution (HE). TiO_2 as an anatase has shown the highest interaction with metals considered as good catalysts [8, 9]. Hypo and hyper d-components may be not only in the elemental state, but also in higher oxidation states. Depending on the valence state of the hypo and hyper d-components, these electrode materials can be distinguished into 5 types [10]: *i*) intermetallic compounds ($MoPt_3$, $MoNi_3$, $MoFe_3$, $Ti_{1-x}Ni_x$, etc.) [11], *ii*) mixed sulphides/phosphides (Ni-W-S, Ni-W-P, Fe-Ni-P etc.) [12,13], *iii*) Reny-Ni based electrocatalysts (Ni-W-S, Ni-W-P, Fe-Ni-P etc.) [14,15], *iv*) mixed oxydes (TiO_2-RuO_2, TiO_2-IrO_2, $Ru_xTi_{1-x}O_2$ etc.) [16] and v) hypo metal + hypo oxyde Pt-TiO_2, Co-TiO_2, Ni-TiO_2 etc.) [1].

The aim of this research is electrochemical and structural study of the electrode materials with reduced quantity or without Pt, aimed for (HE). Mixed Co-Pt and pure Co and Pt nanoparticles deposited on nano-scaled catalyst support consisted of multiwalled carbon nanotubes (MWCNTs) and TiO_2 (anatase), were prepared for studying.

2. Materials and Methods

The studied electrode materials were consisted of 10 wt.% metallic phase (Co, CoPt or Pt, see Table 1), 18 wt. % TiO_2 as anatase and MWCNTs. Precursors for metallic and oxide phase were orgnometallics (Me-2,4-acac, Me = Co or Pt, Alfa Aesar, Johnson Matthey, GmbH and Ti-isopropoxide, Aldrich, 97%). As a carbon substrate, MWCNTs (*Guangzhou Yorkpoint Energy Company, China*) were used. The studied electrode materials were prepared by sol-gel procedure, elsewhere [17].

Table 1: *Composition of the studied electrode materials.*

Sample N°	Metallic phase (10%wt.)	Oxide phase (18%wt.)	Support material (72%wt.)
1	Pt	TiO_2	MWCNTs
2	CoPt (1:1,wt.)	TiO_2	MWCNTs
3	CoPt (4:1,wt.)	TiO_2	MWCNTs
4	Co	TiO_2	MWCNTs

Porous gas-diffusion electrodes (GDE) of the studied samples were prepared and tested for hydrogen evolution in both, alkaline and acid electrolytes (aqueous solutions of 3.5 M NaOH and 0.5 M H_2SO_4, p.a., Merck). The procedure for GDE preparation is described elsewhere [18]. Electrochemical measurements using steady-state galvanostatic method, were performed using AMEL equipment (Function Generator AMEL 568, Potentiostate/Galvanostate AMEL 2053 and software package SOFTASSIST 2.0). Pt wire was used as a counter electrode and Hg/HgO as s reference electrode. The electrochemical line for testing the studied electrodes is shown in Fig.1.

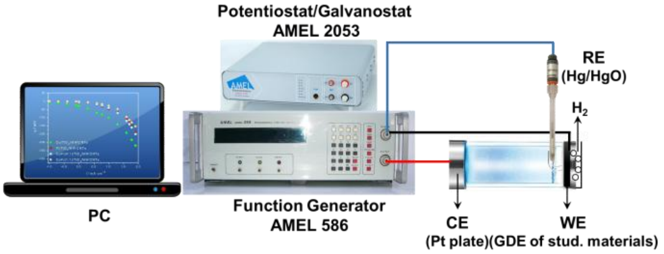

Fig. 1 *Electrochemical instrumentation line for testing the studied electrodes*

The structural characterisation was performed by means of FTIR, XRD, TEM and SEM analysis. FTIR spectra were recorded using KBr pellets at room temperature with Perkin-Elmer System 2000 interferometer. XRD measurements were carried out by X-Ray diffractometer Philips APD 15, with CuK_α radiation. The crystallite size was calculated using the Scherrer equation [19]. Transmission electron Microscope JEOL JEM - 200 CX was used in scanning and transmission regime. SEM observation was carried out on Scanning Electron Microscope JEOL, model JEM 200 CX.

3. Results and Discussions

In Figures 2 and 3 are shown polarization curves of the studied electrode materials for hydrogen evolution reaction in alkaline and acid electrolyte, respectively. In Figures 4 and 5 are shown derived Tafel plots from polarization curves shown in Figures 2 and 3 for platinum based electrode, Pt/TiO_2/MWCNTs. The values of Tafel plots and overpotentials at reference current density of 60 $mA\cdot cm^{-2}$

for all studied electrode materials, are summarized in Tables 2 and 3. These curves and parameters express the eletrocatalytic activity for HE of the studied electrode materials. The lower the overpotential, the higher the electrocatalytic activity for HE.

The first conclusion that can be drawn from the polarization curves (Fig. 2 and 3) is that the catalytic activity of all electrode materials is considerably higher in alkaline electrolyte than that in acid one. The reason for this is the weak chemical stability of cobalt and its tendency to dissolve in an acid environment. So, the difference in the activity of catalyst with pure Co (more than twice) and Co with 20% in metallic phase (even triple), is the most remarkable. In the case of catalyst with equal content of Co and Pt, this difference is lower (1.5 times), while in case of pure platinum system is the lowest (1.3 times).

A second observation is the order of electrocatalytic activity of the different metal systems. In the equal quantity of the whole metallic phase, it is expected the most active to be pure Pt electrode. But, according to the presented results, in both electrolyte, better activity has shown the electrode with mixed metallic phase in the equal amount ratio (Co:Pt = 1:1). Also, the activity of the other mixed electrode material with considerable reduced amount of platinum (Co:Pt = 1:1) is not so lower than that of pure Pt electrode. The order of the electrocatalytic activity expressed through the overpotential at reference current density of 60 mA·cm^{-2}, in alkaline electrolyte is the follow: CoPt(1:1)[–130mV] > Pt[–145 mV] > CoPt(1:1)[–160mV]. The pure Co electrode has shown far lower electrocataltyc activity, i.e. much higher overpotential of 235 mV at 60 mA·cm^{-2}.

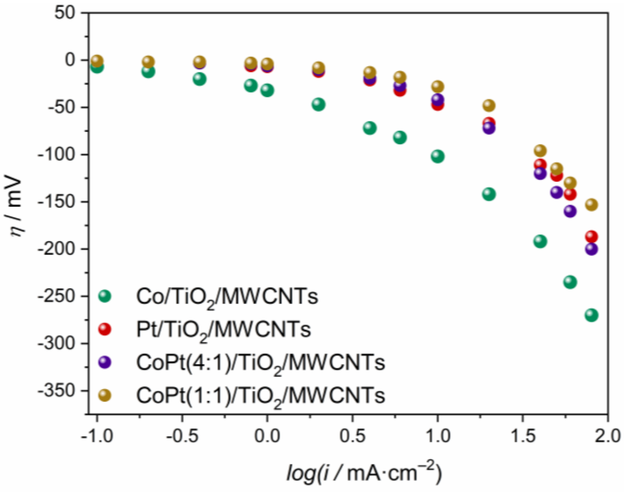

Fig. 2 *Polarization curves in the plot logi–η for the studied electrode materials in 3.5 M KOH.*

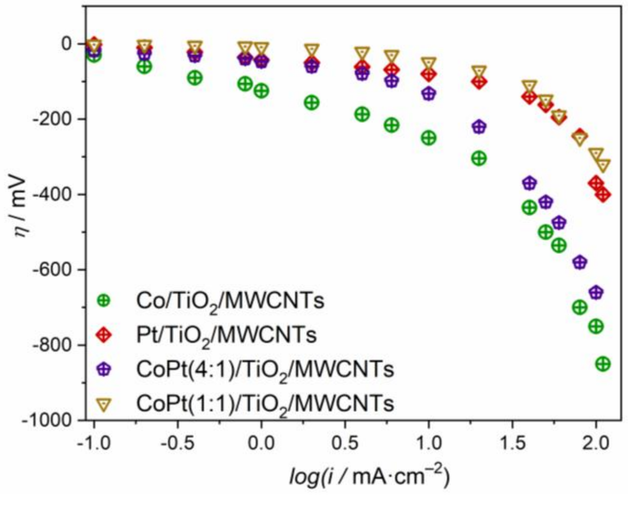

Fig. 3 *Polarization curves in the plot logi–η for the studied electrode materials in 0.5 M H_2SO_4.*

In acid electrolyte the order of activity is the same, but the ratio between the activities is different. The electrodes with pure Pt and mixed metallic phase CoPt(1:1) show very close overpotentials at reference current density (–195 and –190 mV, respectively), while the activity of electrode with mixed metallic phase CoPt(4:1) is so far from those of the previous two (–475 mV). The reason of its poor activity is very low stability of cobalt in acid solutions. As in previous case, the electrode with pure Co phase was shown as the poorest catalyst for HE with overpotential of –535 mV at reference current density of 60 mA·cm^{-2}.

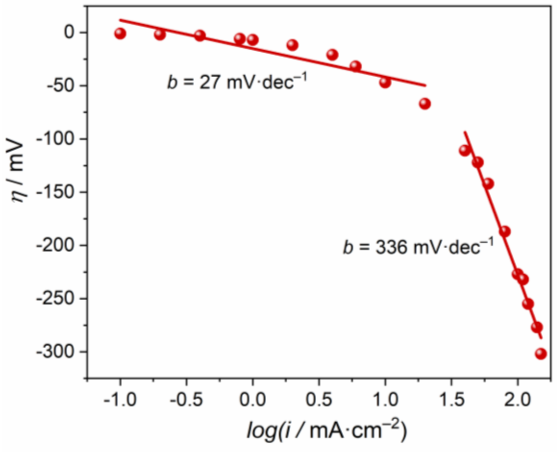

Fig. 4 *Tafel slopes in the plot logi–η for the Pt/TiO_2/MWCNTs electrode material in 3.5 M KOH.*

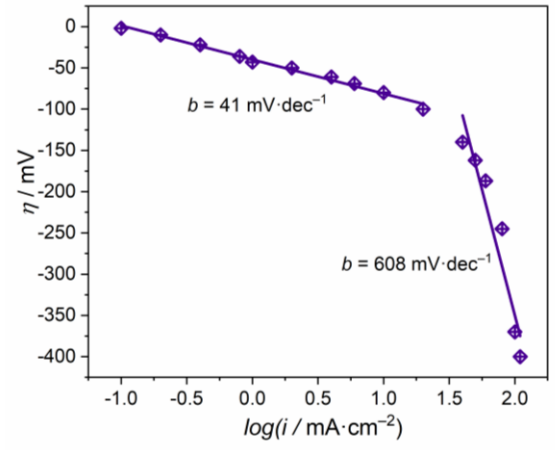

Fig. 5 *Tafel slopes in the plot logi–η for the Pt/TiO_2/MWCNTs electrode material in 0.5 M H_2SO_4.*

Table 2: *Tafel slopes and overpotential at the reference current density of 60 mA·cm^{-2} for HE of the studied electrode materials in 3.5 M KOH.*

Sample N^{o}	Met. phase (10%wt.)	b_1	b_2	b	η_{60}
1	Pt	27	336	57	–145
2	CoPt (1:1,wt.)	17	357	49	–130
3	CoPt (4:1,wt.)	26	374	62	–160
4	Co	47	391	87	–235

Table 3: *Tafel slopes [mV·dec^{-1}] and overpotential [mV] at the reference current density of 60 mA·cm^{-2} for HE of the studied electrode materials in 0.5 M H_2SO_4.*

Sample N^{o}	Met. phase (10%wt.)	b_1	b_2	b	η_{60}
1	Pt	41	608	101	–195
2	CoPt (1:1,wt.)	26	474	92	–190
3	CoPt (4:1,wt.)	73	743	197	–475
4	Co	114	920	236	–535

The third inference is that the studied electrode materials show two different Tafel slopes, one in lower current range and the second in the higher current range (Fig. 4 and 5). The Tafel slopes are also an indicator for catalytic activity. The slighter the Tafel slope, the higher the electrocatalytic activity or the steeper the Tafel slope, the lower the electrocatalytic activity. According to the values of Tafel slopes shown in Tables 2 and 3 (in the low current region, b_1, in high current region, b_2 or value for whole scanned current region) for both electrolytes (alkaline and acid) one can see the same order of the catalaytic activities of the studied electrode materials.

These results obtained in aqueous electrochemical cell are in agreement with the results obtained in Proton Exchange Membrane (PEM) electrochemical cell, so called “Easy Test Cell”, for the same electrode systems [17]. Equivalent metallic systems deposited on non-stoichiometric titanium oxides “Magneli phase” were tested for oxygen reduction reaction (ORR) in a real (two-electrode) PEM alkaline hydrogen fuel cell (AHFC) and similar order of the electrocatalytic activity was registered [20].

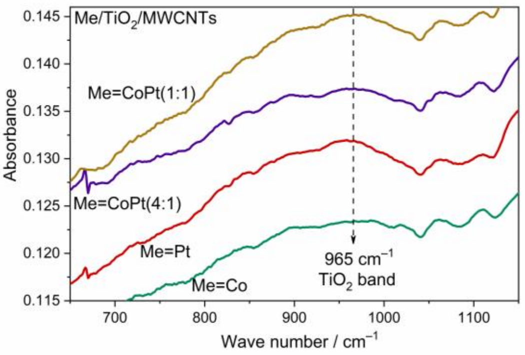

Fig. 6 *FTIR spectra of the studied electrocatalysts.*

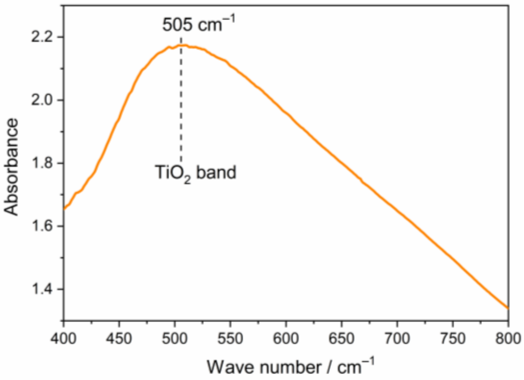

Fig. 7 *FTIR spectrum of pure anatase TiO_2.*

Electrocatalytic activity of electrode materials is a sum of intrinsic and surface activity. The intrinsic activity means the ability of the electrode material to exchange electrons with the reactive ions, to adsorb discharged atoms at the electrode surface and to desorb hydrogen gas from the surface. Surface activity is mainly connected with the real surface area of the electrode material. The higher real surface means that the electrode reaction takes place faster. In order to determine whether the enhancement of the electrocatalytic activity is result of the improvement of intrinsic or surface activity, as well as to explain the unexpected better activity of electrode material with mixed metallic phase CoPt(1:1) related to electrode with pure Pt metallic phase, structural investigations were done by means of FTIR spectroscopy, X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM).

Using FTIR analysis, the hypo-hyper d-interaction between the metallic phases and TiO_2 can be determined. Within the d-metals/compounds d-bonds are predominant, which are responsible for adsorption/desorption processes [21] – very important part of the hydrogen evolution reaction. Therefore, the higher the interaction, the higher the electrocatalytic activity of the electrode. FTIR spectra of the studied catalysts are shown in Fig. 6. The only band of interest within the FTIR spectra is that of anatase titania. For all studied electrode materials, the maximum of this band is at 965 cm^{-1}. In Fig. 7 is shown FTIR spectrum of pure anatase TiO_2 obtained by identical procedure as the studied electrode materials. The maximum of the band originated from anatase is at 505 cm^{-1}. It is evident a shift of the TiO_2 band maximum for even 460 cm^{-1}. This shift is result of shortening of the bands in TiO_2 as result of interaction with metallic phase. This points out that in studied electrode materials there is strong hypo-hyper d-interaction and all of them possess improved intrinsic activity related to the activity of the electrode material with only metallic phase. But, the level of interaction in all materials is the same, thus it cannot be an explanation of better activity of the electrode materials with mixed metallic phase related to that with pure Pt.

We could find an explanation of this question with XRD and TEM analysis.

XRD spectra of the studied electrode material are shown in Fig. 8. In all studied materials TiO_2 was detected as crystalline anatase with crystallite size of ~4 nm. It was not observed peaks typical for cobalt, due to its very small particles. It was shown for other Co-based electrode materials in our previous studies [22,23]. Only the sample with pure Co as metallic phase has shown very weak and less pronounced peak at 44.22°, corresponding to (111) crystalline plane of cubic Co. In the spectrum of electrode material with pure Pt as metallic phase, a sharp and fine pronounced peaks of crystalline Pt were observed, with crystallite size of ~11 nm. These peaks in the spectra of electrode materials with mixed CoPt metallic phases are wider and less pronounced. Their positions are the same as those in the sample with pure Pt metallic system, pointing out that in the mixed CoPt electrode materials there is not CoPt intermetallic phase, but only a mixture of Co and Pt particles exists.

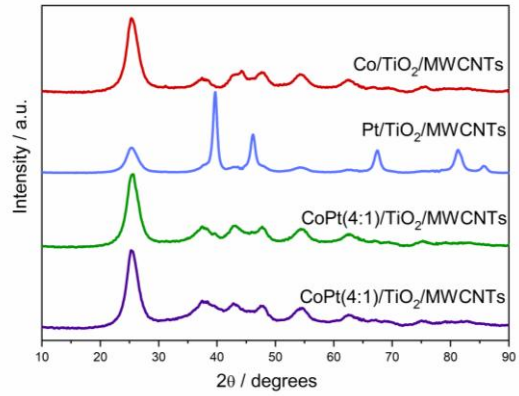

Fig. 8 *XRD spectra of the studied electrode materials.*

An assessment of the metallic particle size and observation of their dispersion over the electrode material surface, was carried out by means of TEM analysis (Fig. 9). The black spots are the metallic particles on the electrode material surface. The diameter of these black spots is 10÷12 nm for the sample containing pure Pt. Very close value was calculated by the Sherrer equation using XRD data. The metallic particle size of the electrode materials with mixed metallic phase are considerably smaller (d < 4 nm). It is evident that results of XRD and TEM analysis are in good agreement. For all studied samples, the active catalytic phase – metallic particles are uniformly and good dispersed over the electrode material’s surface.

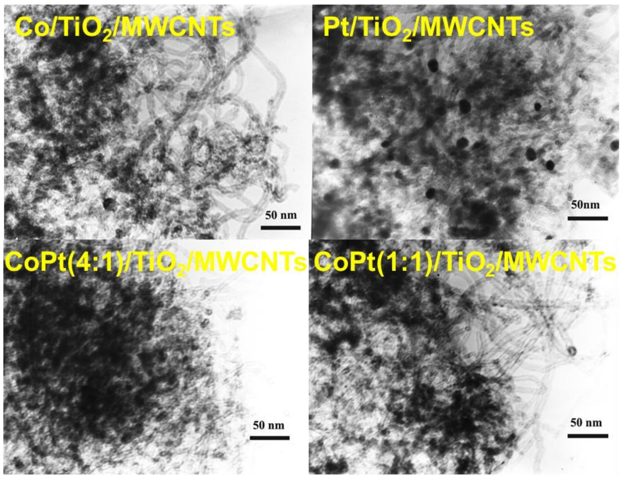

Fig. 9 *TEM images of the studied electrode materials.*

The main inference from XRD and TEM analysis is that the Pt particles in the presence of Co are much smaller (~3–4 times). This points out that cobalt behaves as a promoter for decrease of the Pt particles size. This was noticed also by other authors [24,25]. The smaller the metallic particles size, the higher the surface area of the active catalytic phase and the greater the number of active catalytic centers which are better dispersed over the surface of electrode material. Therefore, the electrocatalytic activity toward hydrogen evolution is higher.

In Fig. 10, the SEM images of the CoPt(1:1)/TiO_2/MWCNTs is shown. The intertwined tube-like morphology can be seen as a result of MWCNTs. This morphology is more suitable than that of electrode materials deposited on carbon blacks [26]. The electrode's components are arranged into smaller clusters, creating more holes between them. This contributes to better inter-particle porosity of the catalysts, appropriate for passing trough of the gas phase. Due to the geometric shape of MWCNTs, they have inner holes, causing trans-particle porosity of the electrode material. Both types of porosity have a favorable effect on the electrocatalytic activity. All other studied materials have shown similar morphology.

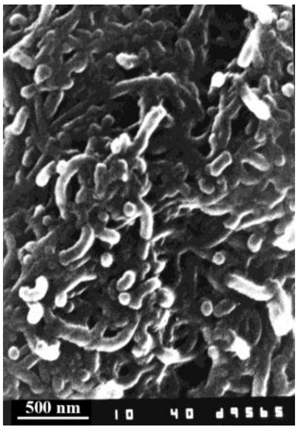

Fig. 10 *SEM image of the CoPt(1:1)/TiO_2/MWCNTs sample.*

4. Conclusions

The main goal of this research was to reduce or even replace Pt in the electrode material for HE. Platinum was replaced with cobalt, so the series of the studied electrode materials consisted of samples with pure metallic phase – Pt or Co and mixed metallic phase – CoPt, 4:1 and 1:1, wt. The electrode materials were composed of 10% metallic phase, 18% TiO2 and the rest the catalyst support – MWCNTs. deposited on catalyst support consisted of TiO_2 and activated (MWCNTs) were prepared and studied. The main conclusion points derived from the presented results, are the follow:

- All studied electrode materials have shown improved intrinsic electrocatalytitc activity detected through the pronounced hypo-hyper d-interaction between metallic phase and TiO_2, proven by the FTIR analysis.
- According to the XRD and TEM analysis, cobalt has been shown to be a promoter for decrease of platinum particle size, reducing them for 3-4 times.
- Reduction of the Pt particles size, causes increase of the real surface area of the metallic phase as the main catalytic centers, which compensates the less amount of Pt in the electrode material. So, the activity of the electrode material with only 20% Pt in metallic phase is close to that of pure Pt containing electrode material, while the electrode material with 50% Pt in metallic phase exceeds its activity.

5. References

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