Bulgarian Chemical Communications, Volume 43, Number 1 (pp. 74 – 80) 2011

Non-platinum electrode materials for hydrogen evolution: effect of catalyst support and metallic phase

P. Paunović[1*], D. Stoevska Gogovska[1], O. Popovski[2], I. Radev[3], E. Lefterova[3], E. Slavcheva[3], A. T. Dimitrov[1] and S. Hadži Jordanov[1]

[1]*Faculty of Technology and Metallurgy, University of Ss Cyril and Methodius, Skopje*
[1] *Faculty of Technology and Metallurgy, University of Ss Cyril and Methodius, 16 Ruger Bošković St, 1000 Skopje*
[2] *Military Academy, Mihajlo Apostolski Str., b.b., 1000 Skopje*
[3] *Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, Acad.G.Bonchev St., Building 10, 1113 Sofia, Bulgaria*

Received: June 17, 2010; accepted September 11, 2010

This work is concerned with the preparation and the characterization of nano-structured composite electrocatalytic material for hydrogen evolution based on Co as a hyper d-metallic phase and anatase (TiO_2) as a hypo d-phase, both deposited on a carbon substrate. The main goal is to replace the Pt as an electrocatalytic material, partially or completely. Two types of support material were used: Vulcan XC-72 and multiwalled carbon nanotubes (MWCNTs). Also two non-platinum metals were used as a hyper d-metallic phase: Ni and Co. The best performances were shown by the Co electrocatalyst, deposited on activated MWCNTs. This one approaches and even slightly exceeds the catalytic activity of the traditional Pt electrocatalyst, deposited on Vulcan XC-72. To improve the disadvantages of this electrocatalyst (instability in acid media and passivation in alkaline media) a precious metal (Pt or Ru) was added into the metallic phase. Only 20 % of the precious metal in the metallic phase considerably improves the electrocatalytic activity for the hydrogen evolution.

Co was shown to promote decreasing platinum particle size. From 12 nm in the catalyst with pure platinum as the metallic phase, the size of Pt particles decreases to 3-4 nm in the catalyst with mixed metallic phase (80% Co + 20% Pt).

Key words: hydrogen evolution, hypo-hyper d-electrocatalysts, Vulcan XC-72, multiwalled carbon nanotubes MWCNTs, metallic phase: Co, Ni, Pt, and Ru.

INTRODUCTION

The innovation of non-platinum electrode materials for water electrolysers/fuel cells is a very important issue, within the hydrogen economy, related to the most promising energy system in the future. The commercial application of Pt, still the leading electrode material, is limited due to its high cost and limited reserves. It was estimated that current Pt resources can cover only part of the automotive needs [1]. Electricity demands are not included in this estimation.

Therefore, the main goal of the modern electrocatalysis and material science, employed in the 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 (e.g., Jakšić hypo-hyper d-concept [2]) and ii) replacement of the traditional carbon support materials (e.g., Vulcan XC-72) with carbon nanotubes [1, 3].

According to Jaksić's interpretation [4-6] of Brewer valence-bond theory [7], significant synergetic effect of the catalytic activity can be achieved by alloying metal on the right side of transition series (good catalyst as an individual metal) with metal on the left side (bad catalyst as an individual metal). Bonding occurs between the metal with more electrons on the outer shell (the hyper d-component) and the metal with less valence electrons, i.e. more vacant orbitals – hypo d-component. 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 the hyper d-components, we can divide these electrocatalysts into five main groups: i) intermetallic catalysts, ii) metal-sulfides/ phosphides, iii) catalysts based on Raney Ni, mixed oxides, and v) hypo oxide – hyper metal [8]. These

---

* To whom all correspondence should be sent.
E-mail: pericap@tmf.ukim.edu.mk

catalysts can be used with the same effectiveness for both, the hydrogen evolution and the fuel cells.

The other approach to enhance the performance of the electrode materials is the improvement of the support materials. The support materials have to possess several very important characteristics such as the: *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*) strong metal-support interaction (SMSI) to improve intrinsic catalytic activity of the active catalytic phase. In this context, the carbon nanostructured materials, such as the carbon blacks, are commercially the most used support material [9, 10] due to their high surface area, conductivity and compositional homogeneity. Recently, the production of carbon nanotubes (CNTs) as catalyst support became a subject of intensive research [1, 3, 11]. CNTs show superior surface characteristics (high surface area and pore size distribution), electronic conductivity, mechanical and thermal properties, etc. These characteristics offer a great potential for electrocatalyst support materials aimed to serve both hydrogen electrolysers/fuel cells. CNTs electronic conductivity is in the range between 10^3 and 10^4 $\mathrm{S\cdot cm^{-1}}$. In comparison, the Vulcan XC-72 electronic conductivity is of 4 $\mathrm{S\cdot cm^{-1}}$. Furthermore, the specific surface area of Vulcan XC-72 is 250 $\mathrm{m^2\cdot g^{-1}}$, while that of the CNT is 200-900 $\mathrm{m^2\cdot g^{-1}}$. Also, the pores in Vulcan XC-72 are smaller than 2 nm, while CNTs have not pores smaller than 2 nm. So, the metallic phase may sink into pores that reduce active reactive sites over the catalytic surface [3].

Pathways for obtaining of non-platinum electrocatalysts or electrocatalysts with reduced amount of Pt are shown in this work. In this context, TiO_2 (anatase) was added to the carbon support, Vulcan XC-72 was replaced with MWCNTs, and finally MWCNTs were activated before metallic phase deposition. Co, Ni, and metallic mixtures of Co-Pt and Co-Ru were used as catalytic metallic phase.

EXPERIMENTAL

The studied catalysts contain 10 % hyper d-metallic phase, 18% TiO_2 as a hypo d-component, and the rest is carbon substrate. For comparison, Ni, Co, and Pt electrocatalysts were prepared only on the Vulcan XC-72 catalyst support (10 % Me and the rest is a carbon phase). Organometallics were used as precursors to obtain a metallic phase, Me-2,4-pentaedionate (Alfa Aesar, Johnson Matthey, GmbH, Me = Co, Ni, Pt, Ru). TiO_2 was produced from Ti-isopropoxide (Aldrich, 97%). Vulcan XC-72 (Cabot Corp. Boston, Mass.) or multiwalled carbon nanotubes (MWCNTs, *Guangzhou Yorkpoint Energy Company, China*) were used as a carbon substrate. The catalysts were produced by sol-gel procedure, simplified in some steps by the authors of this work [12, 13]. Firstly, TiO_2 was deposited on carbon substrate, and further, the modified support was thermally treated at 480^o for 1 h in the $H_2 + N_2$ atmosphere. In the next step, the metallic phase was grafted on the support and the obtained mixture was thermally treated at 250ºC for 2 h.

Activation/purification of the so-prepared MWCNTs was performed in a 28% (mass.) HNO_3. The process was carried out at a room temperature for 4 h. MWCNTs were stirred into the solution by magnetic stirrer. After filtering and washing, the activated MWCNTs were dried at 90ºC for 24 h. Table 1 shows the composition of the studied electrocatalysts.

Table 1. Composition of the studied electrocatalysts

Sample No	Catalysts composition
0	10% Pt + Vulcan XC-72
1	10% Ni + Vulcan XC-72
2	10% Co + Vulcan XC-72
3	10% Co + 18% TiO2 + Vulcan XC-72
4	10% Co + 18% TiO2 + MWCNTs
5	10% Co + 18% TiO2 + MWCNTs(a)
6	10% CoPt (4:1 wt.) + 18% TiO2 + MWCNTs(a)
7	10% CoPt (1:1 wt.) + 18% TiO2 + MWCNTs(a)
8	10% Pt + 18% TiO2 + MWCNTs(a)
9	10% CoRu (4:1 wt.) + 18% TiO2 + MWCNTs(a)
10	10% CoRu (1:1 wt.) + 18% TiO2 + MWCNTs(a)
11	10% Ru + 18% TiO2 + MWCNTs(a)
12	10% CoRuPt (4:0,5:0,5 wt.) + 18% TiO2 + MWCNTs(a)

To identify the intrinsic changes, caused by the modifications, spectroscopic and structural techniques were employed. XRD and SEM techniques were used for structural characterization. XRD measurements were carried out by Philips APD 15 X-Ray diffractometer, with CuK_α radiation, while SEM observations were carried out by JEOL Scanning Electron Microscope, 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.

Catalyst surface area was determined trough double layer capacity, measured by cyclic voltammetry [14, 15]. The ratio of real versus geometric surface area of the electrodes was determined as a quotient of catalyst double layer capacity C_{dl} versus double layer capacity C_{dlo} of a pure oxide surface.

Further, the produced catalysts were electrochemically tested for hydrogen evolution reaction. 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 a low amount of PTFE, and *ii*) gas-difussion layer facing the gas side, consisted of Vulcan XC-72 (or MWCNTs) bonded with PTFE. The procedure of electrode preparation is described elsewhere [16]. Electrochemical investigations were performed using AMEL equipment (AMEL 568 Function Generator, Potentiostate/Galvanostate 2053 and a SOFTASSIST 2.0 software package). The counter electrode was of platinum wire and the reference electrode of Hg/HgO. The electrolyte comprised an aqueous solution of 3.5 M KOH (p.a., Merck) at a room temperature.

RESULTS AND DISCUSSION

The first step of the study was the preparation and testing of non-platinum electrocatalysts, deposited on the most used support material, the Vulcan XC-72. Ni and Co were used as metallic phase. Why Co and Ni? Ni is a non-noble metal of platinum group, while Co is near the Ni in the periodic table, having similar properties. It was expected that both catalysts will show close catalytic activity for the hydrogen evolution. But, the Ni-based catalysts (sample 1) showed very inferior activity related to that of the Co-based one (sample 2, see Table 2). The difference in the overpotentials for hydrogen evolution at a reference current density of 60 mA·cm^{-2}, was 150 mV. This is due to the much higher size of the Ni particles, compared to those of the Co. It was determined by the XRD analysis (see Fig. 1) that Ni is crystalline with particle size of 15-20 nm. There are no pronounced peaks in the Co XRD spectra, which is a characteristic for amorphous phases with particle size less than 2 nm. Thus, the real surface area of the active catalytic centers, dispersed over the catalyst surface, is considerably higher in the case of a Co-based electrocatalyst. Compared to the corresponding Pt-based catalysts (sample 0), the activity of both non-platinum samples is considerably lower. The improvement of the Co-based electrocatalyst is discussed further down.

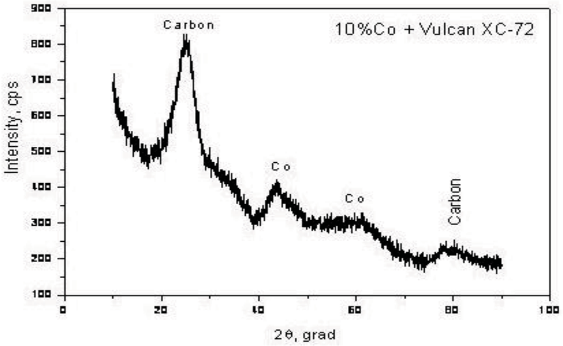


Fig. 1. XRD spectra of the a) Ni- and b) Co-based electrocatalysts deposited on Vulcan XC-72.

Table 2.

Sample No	Catalysts composition	η_{60}, mV
0	10% Pt + Vulcan XC-72	220
1	10% Ni + Vulcan XC-72	530
2	10% Co + Vulcan XC-72	380
3	10% Co + 18% TiO2 + Vulcan XC-72	265
4	10% Co + 18% TiO2 + MWCNTs	235
5	10% Co + 18% TiO2 + MWCNTs(a)	215
6	10% CoPt (4:1 wt.) + 18% TiO2 + MWCNTs(a)	135
7	10% CoPt (1:1 wt.) + 18% TiO2 + MWCNTs(a)	115
8	10% Pt + 18% TiO2 + MWCNTs(a)	125
9	10% CoRu (4:1 wt.) + 18% TiO2 + MWCNTs(a)	145
10	10% CoRu (1:1 wt.) + 18% TiO2 + MWCNTs(a)	135
11	10% Ru + 18% TiO2 + MWCNTs(a)	90
12	10% CoRuPt (4:0,5:0,5 wt.) + 18% TiO2 + MWCNTs(a)	125

Addition of anatase

First modification step of the new Co-based electrocatalyst was the addition of hypo *d*-phase TiO_2 (anatase). Hypo *d*- component has a bifunctional role, as a catalyst support (with carbon phase) and it contributes to the catalyst overall synergetic effect by the so called Strong Metal-Support Interaction (SMSI). The unique role of the anatase form of titania in the improvement of the catalytic activity in both, the heterogeneous chemical catalysis and the electrocatalysis, has been noticed by other authors [17, 18]. The addition of anatase in the catalyst support, contributes to the reduction of the overpotential for the hydrogen evolution even down to 115 mV (see Table 2). This considerable rise of the catalytic activity of the modified Co-based electrocatalyst (sample 3) is resulted by the strong hypo-hyper d-interaction between Co and TiO_2. This consequently increases the intrinsic catalytic activity. The above is illustrated by the FTIR spectra, shown in Fig. 2.

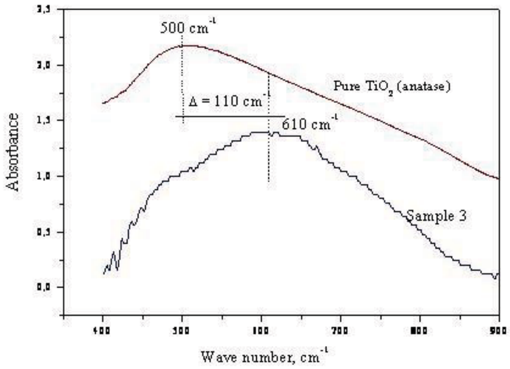


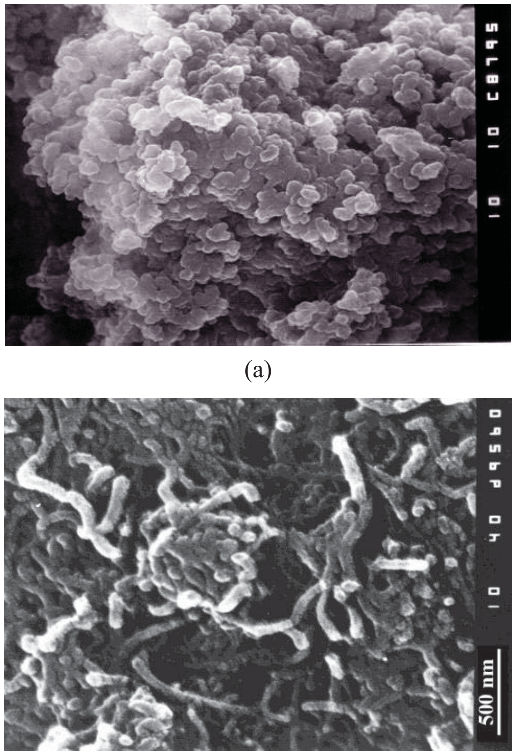
Fig. 2. FTIR spectra of the Co hypo-hyper d-electrocatalyst containing 10% Co + 18% TiO_2 + Vulcan XC-72 (sample 3) and pure TiO_2 (anatase).

The maximum of TiO_2 band, originated from the Co-based electrocatalyst, is shifted for a higher value of the wave number (110 cm^{-1}) compared to the maximum of band which originated from the pure anatase. This shift is a result from the interaction between TiO_2 and Co atoms [19]. The higher the wave number shift is, the shorter is the bond between TiO_2 and hyper *d*-metallic phase, i.e. the higher the hypo-hyper *d*-interaction is.

Replacement of Vulcan XC-72 with MWCNTs

Instead of the conventional Vulcan XC-72 carbon substrate, multiwalled carbon nanotubes (MWCNTs) were involved in the next modification step. Fig. 3 shows the SEM images of Co-based electrocatalysts, deposited on both, the Vulcan XC-72 and the MWCNTs.

The catalyst particles, deposited on Vulcan X-72 are of a spherical shape (Fig. 3a.). There is a grouping of the particles in clusters (150 – 200 nm), whereat good adherence between particles is achieved. The particles are not uniformly distributed, and a number of holes appear between the aggregates. This contributes to the higher specific surface area, and consequently, to a higher electrocatalytic activity. Catalyst deposited on MWCNTs shows completely different morphology (Fig. 3b.). The particles of oxide and metallic phases, grafted on MWCNTs, are grouped in smaller clusters than those on Vulcan XC-72. Their inner structure, geometry, surface area, and conductive characteristics are favourable for use as a carbon substrate of the nano-scaled electrocatalysts. Their high developed surface area enables better dispersion of active catalytic centres across the catalyst surface. On the other hand, MWCNT's high **inter-** and **trans-particle nano porosity** as well as its geometry (empty cylinders) do facilitate the escape of hydrogen molecules from catalyst surface [20]. Extra-conductive properties enable easier electron exchange with the hydrogen protons, which intensifies the formation of adsorbed hydrogen atoms and further hydrogen molecules. Estimation of real surface area by the value of double layer capacity (C_{dl}), measured by cyclic voltammetry, showed that MWCNTs have twice higher developed surface area than Vulcan XC-72 [21]. The decrease of hydrogen overpotential in this modified catalyst (sample 4), compared with the previous modified one (sample 3), is of 30 mV.



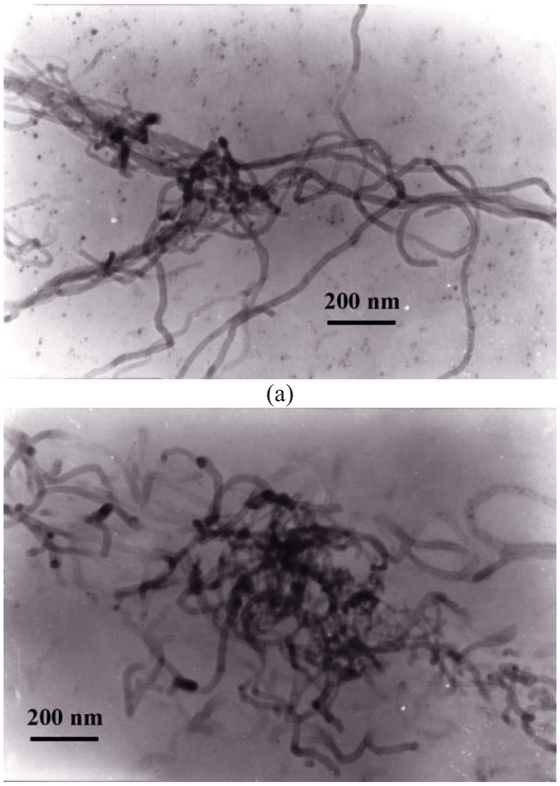
(a)

(b)

Fig. 3. SEM images of Co hypo-hyper d-electrocatalysts deposited on a) Vulcan XC-72 (sample 3) and b) MWCNTs (sample 4).

Activation of MWCNTs

Further, purification/activation of MWCNTs was made. During this operation, three main processes occur: (i) removing of other carbonaceous phases such as the amorphous carbon, and (ii) rise of defect sites as a result of



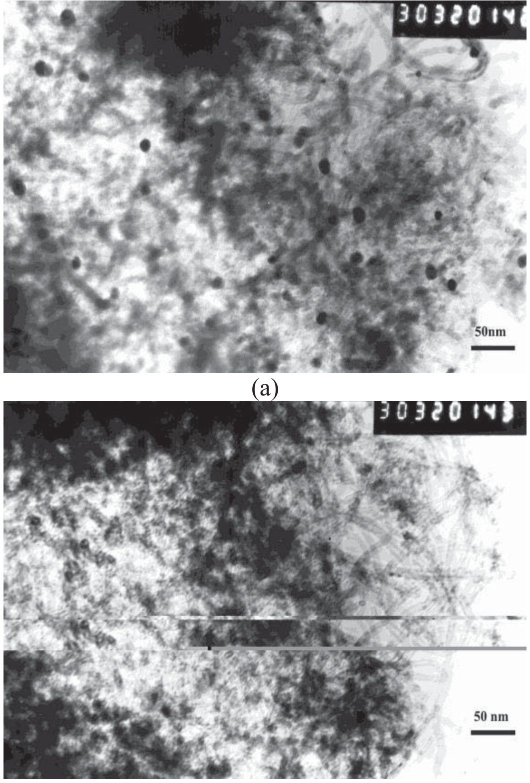
(a)

(b)

Fig. 4. TEM images of a) as-prepared and b) activated MWCNTs

shortening, thinning, and opening of the MWCNTs, and iii) functionalization of MWCNTs with oxide groups. The opening and shortening of the MWCNTs, and the increased number of the defective sites, results in the increase of their real surface area and reactivity, which are suitable for carbon substrates, used as electrocatalysts. This is illustrated by the TEM images of MWCNTs, before and after activation, in Fig. 4.

These changes in the support material contribute to a higher catalytic activity for the hydrogen evolution of the Co-based hypo-hyper d-electrocatalyst. In this case (sample 5) the hydrogen overpotential decreases to 20 mV in relation to the previous Co-catalyst (sample 4). This activity is very close to that of the traditional Pt electrocatalyst (Pt/Vulcan XC-72, sample 0). Thus, the maximal activity of the non-platinum Co-based catalyst approaches the Pt-based one, and slightly exceeds it. The performance of these electrocatalysts in the proton exchange membrane (PEM) electrolyte at lower cathodic overpotentials, however, was not so impressive, while at higher overpotentials, their activity approaches the performance of the traditional Pt catalyst [20].



(a)

(b)

Fig. 5. TEM images of hypo-hyper d-electrocatalysts containing a) 10% Pt + 18% TiO_2 + MWCNTs(a) (sample 8)and b) 10% CoPt (1:1 wt.) 18% TiO_2 + MWCNTs(a) (sample 7).

Addition of Pt in the metallic phase

Therefore, catalysts with mixed metallic phase were prepared in the next phase of the investigations. They contained 10 % CoPt (Co:Pt = 4:1, wt., sample 6 and Co:Pt = 1:1, wt., sample 7), and a Pt-based catalyst (sample 8) with analogous composition, produced under the same conditions. These catalysts showed impressive catalytic activity which considerably exceeded the activity of the conventional platinum (sample 0). The catalysts with mixed metallic phase, Co:Pt = 1:1, wt., (sample 7), showed the best catalytic activity while the catalysts with mixed metallic phase, Co:Pt = 4:1, wt. (sample 6), are less active but still very close to the activity of the pure Pt-based catalyst (sample 8). It sounds as a paradox, at first sight, when a catalyst with a double amount of Pt (sample 4) is less active. There is a logical explanation, however, for such order of the catalytic activity. Let's assume that the catalytic activity depends on the hypo-hyper d-interaction as well as on the surface area (particle size) of the metallic catalytic centres, dispersed over the catalyst surface. 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 MWCNTs usage as catalyst support as well. Thus, the improved activity of the catalyst with less amount of platinum, is obviously related to the considerably lower size of the Pt crystallites in the mixed systems. As it was shown from the XRD analysis [22], the size of the Pt crystallites in sample 8 is near to 12 nm, while in the mixed systems (samples 6 and 7), Co promotes considerably lower (up to 3-4 times) size of the Pt particles. These results were confirmed by the TEM analysis (see Fig. 5). The lower amount of Pt is compensated by the highly developed surface of the Pt-phase in the mixed systems.

Addition of Ru in the metallic phase

The catalyst with pure Ru metallic phase (sample 11) has shown the best catalytic activity for hydrogen evolution. The overpotential is 35 mV (at reference current density of 60 $mA \cdot cm^{-2}$) lower than that of the corresponding catalyst with pure Pt as a metallic phase (sample 8, see Table 2). Pt and Ru have very close intrinsic catalytic activity for hydrogen evolution. Also, the increase of intrinsic activity as a result of hypo-hyper *d*-interaction with TiO_2 is the same. Thus, the higher activity of Ru in this case, is a result of smaller particles (near 6 times) than that of the Pt. This means more developed surface area of the metallic active catalytic centres on the catalyst surface. In the catalysts with mixed CoRu metallic phase (4:1 and 1:1 wt., sample 9 and 10), catalytic activity decrease to 55 and 45 mV respectively, compared to the catalyst with pure Ru (sample 11). In this case addition of Co (non-precious metal) with particles almost equal with that of Ru, results in corresponding decrease of catalytic activity. The last studied electrocatalyst (sample 12, containing 20% precious metal mixture of Ru and Pt, and Co in the metallic phase) shows better catalytic activity than the previous electrocatalysts, containing CoRu metallic phase (sample 9 and 19) for 20 and 10 mV, respectively. Due to the presence of Co, the Pt particles are very small (3-4 nm) and the catalytic activity increases.

It is obvious that hypo-hyper *d*-electrocatalysts (hypo-oxides + hyper-metals) are very promising in the reduction of platinum in the electrocatalysts, aimed for hydrogen evolution. In this context, MWCNTs have considerable contribution as an extraordinary carbon support.

CONCLUSION

The investigations, presented in this paper, were motivated by the idea for reduction or even replacement of Pt in self-developed electrode material for hydrogen evolution. According to the presented results, the following conclusions could be done:

1) The catalytic activity for hydrogen evolution of a Co-based electrocatalyst is considerably higher than that of the Ni-based due to the smaller Co particles (2 nm) vs. the Ni particles (15 – 20 nm), and consequently the higher surface area of the active catalytic phase;

2) Catalytic activity of electrocatalysts, deposited on MWCNTs, is higher than that of the deposited on Vulcan XC-72 due to better surface characteristics (surface area > for twice, better inter-particle and trans-particle porosity). Further activation of the MWCNTs contributes to the improvement of the catalytic activity due to the shortening and opening of nanotubes, and consequently, the rise of real surface area [4];

3) Co electrocatalyst, deposited on activated MWCNTs, approaches, even exceeds the catalytic activity of the traditional Pt electrocatalyst, deposited on Vulcan XC-72;

4) Further addition of precious metals (Pt or Ru) in the metallic phase (only 20%) considerably improves the catalytic activity for hydrogen evolution, considerably exceeding the activity of the traditional Pt electrocatalyst, deposited on Vulcan XC-72;

5) In CoPt-based systems, the electrocatalyst with only 20% Pt in the metallic phase (sample 6) shows activity close to that of the corresponding catalyst with pure Pt metallic system (sample 8), while CoPt electrocatalyst with Co:Pt = 1:1 (sample 7) exceeds the activity of sample 8. This is due to the smaller particle size (higher surface area) of Pt in mixed metallic systems (3-4 nm) than that in the pure Pt system, where the size of the Pt particles is 12 nm [5];

6) The best performances for hydrogen evolution showed the Ru-based catalyst. Its better performances, related to the corresponding Pt-electrocatalyst, are due to the smaller particles of Ru (2 nm) than that of the Pt (12 nm). Further addition of Co in the Ru metallic phase linearly decreases the catalytic activity.

Acknowledgement: *This work has been supported by and carried out within the PROMETHEAS PL ICA2-2001–10037 EU Project, and the 13–1650/4–02 Project of the Ministry of Education and Science of the Republic of Macedonia.*

REFERENCES

1. K. Lee, J. Zhang, H. Wang and D. P. Wilkinson, *J. Appl. Electrochem*., **36**, 507 (2002).
2. M. M. Jakšić, *Electrochimica Acta*, **29**, 1539 (1984).
3. P. Serp, M. Corrias, P. Kalck, *Appl. Catal. A: General*, **253**, 337 (2003).
4. M. M. Jakšić, *Int. J. Hydr. Ener.*, **12**, 727 (1987).
5. M. M. Jakšić, *J. New Mater. Electrochem. Sys*., **3**, 153 (2000).
6. M. M. Jakšić, *Solid State Ionics*, **136-137**, 733 (2000).
7. L. Brewer, *Science*, **161**, 115 (1968).
8. P. Paunović in Nanostructured Materials for Advanced Technological Applications, J.P. Reithmaier et al. (eds.), © Springer Science + Business Media B.V. (2009), p. 391.
9. K. Kinoshita, Carbon, electrochemical and physicochemical properties, John Wiley & Sons, New York, 1988).
10. E. Budevski, *J. Optoelec. Adv. Mater*., **5**, 1319 (2003).
11. P. Paunović, A.T. Dimitrov, O. Popovski, E. Slavcheva, A. Grozdanov, E. Lefterova, Dj. Petruševski and S. Hadži Jordanov, *Mat. Res. Bull*., **44**, 1816 (2009).
12. S. Hadži Jordanov, P. Paunović, O. Popovski, A. Dimitrov and D. Slavkov, *Bull. Chem Technol. Macedonia*, **23**, 101 (2004).
13. P. Paunović, O. Popovski, A.T. Dimitrov, D. Slavkov, E. Lefterova and S. Hadži Jordanov, *Electrochimica Acta*, **52**, 1610 (2006).
14. B. Marsan, N. Fradette, G. Beaudoin, *J. Electrochem. Soc*., **139**, 1889 (1992).
15. L.M. Da Silva, L.A. De Faria, J.F.C. Boodts, *Electrochimica Acta*, **47**, 395 (2001).
16. BG patent Appl. N^{o} 38581.
17. S. J. Tauster, S.C. Fung, *J. Catal*., **55**, 29 (1978).
18. S.G. Neophytides, S. Zaferiatos, G. D. Papakonstantnou, J. M. Jakšić, F. E. Paloukis and M. M. Jakšić, *Int. J. Hydr. Energy*, **30**, 393 (2005).
19. P. Paunović, O. Popovski, A. T. Dimitrov, D. Slavkov, E. Lefterova and S. Hadži Jordanov, *Electrochimica Acta*, **52**, 4640 (2007).
20. P. Paunović, O. Popovski and I. Radev, *Bull. Chem. Technol. Macedonia*, **24**, 133 (2005).
21. P. Paunović, A. T. Dimitrov, O. Popovski, D. Slavkov and S. Hadži Jordanov, *Maced. J. Chem. Chem. Eng.*, **26**, 87 (2007).
22. P. Paunović, I. Radev, A.T. Dimitrov, O. Popovski, E. Lefterova, E. Slavcheva, S. Hadži Jordanov, *Int. J. Hydr. Energy*, **34**, 2866 (2009).

Не-платинови електродни материали за добиване на водород: ефект на подложката на катализатора и на металната фаза

П. Паунович[1*], Д. Стоевска-Госовска[1], О. Поповски[2], И. Радев[3], Е. Кефтерова[3], Е. Славчева[3],
А.Т. Димитров[1], С. ХаджиЙорданов[1]

[1]*Факултет за технология и металургия, Университет “Св. Кирил и Методий”,ул. Ругер*
Бошкович16, Скопие ,Република Македония16 Ruger Bošković St, 1000 Skopje
[2] *Военна академия, ул. Михайло Апостолски, 1000 Скопие, Република Македония*
[3] *Институт по електрохимия и енергийни системи, БАН, ул. Акад. Г. Бончев, бл. 10, 1113 София*

Постъпила на 17 юни, 2010 г.; приета на 11 септември, 2010 г.

(Резюме)

Работата разглежда приготвянето и охарактеризирането на нано-структурирани композити като електро-каталитичен материал за добиването на водород, основан на кобалт като хипер d-метална фаза и анатаз (TiO$_2$) като хипо d-фаза, и двете отложени върху въглероден носител. Главната цел е да се замени платината като електро-каталитичен материал, отчасти или напълно. Използвани са два типа носители: Vulcan XC-72 и многостенни въглеродни нано-тръби (MWCNT). Освен това като хипер d-метална фаза са използвани два не-платинови метала: никел и кобалт. Най-добри показатели са показани от Co-електрокатализатор, отложен върху активирани MWCNT. Той се доближава и дори леко превъзхожда каталитичната активност на традиционния платинов катализатор, отложен върху Vulcan XC-72. За преодоляването на недостатъците на този електро-катализатор (нестабилност в кисела среда и пасивиране в алкална) в металната фаза се добавя благороден метал ((Pt или Ru). Само 20 % от благородния метал в металната фаза подобряват значително електро-каталитичната активност за отделянето на водород..

Оказва се, че кобалтът промотира намаляването на размера на платиновите частици – от 12 nm при катализатор от чиста платина, размерът им се намалява до 3-4 nm в катализатор със състав (80% Co + 20% Pt).