

EFFECT OF CARBON NANOTUBES SUPPORT IN IMPROVING THE PERFORMANCE OF MIXED ELECTROCATALYSTS FOR HYDROGEN EVOLUTION

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The effect of using multiwalled carbon nanotubes (MWCNTs) vs. traditional carbon materials (as e.g., Vulcan XC-72) as supports for mixed non-platinum catalysts for hydrogen evolution was studied. Intrinsic changes in catalyst's structure, surface and activity for hydrogen evolution were registered. It was found that MWCNTs significantly improve the activity of the catalysts as a result of (i) increase of the real surface area of the catalyst, (ii) improving the electrical conductivity of the electrode, (iii) better dispersion of active catalytic centers over the electrode surface and (iv) geometric nature of the nanotubes. This effect is most pronounced in the case of Ni-based catalyst, where the overpotential for hydrogen evolution was lowered by as much as 85 mV at a current density of 60 mA·cm⁻² in alkaline electrolyte. The corresponding lowering of overpotential in the Co-based system was 35 mV.

Key words: hydrogen evolution; mixed electrocatalysts; carbon black; multiwalled carbon nanotubes (MWCNTs)

ЕФЕКТ НА ЈАГЛЕРОДНИТЕ НАНОЦЕВЧИЊА ВРЗ ПОДОБРУВАЊЕТО НА АКТИВНОСТА НА ПОВЕЌЕКОМПОНЕНТНИ ЕЛЕКТРОКАТАЛИЗАТОРИ ЗА РАЗВИВАЊЕ ВОДОРОД

Во трудот е испитуван ефектот на примена на повеќесидни јаглеродни наноцевчиња како носачи на повеќеконпонентни неплатински електрокатализатори наменети за развивање водород, наспроти традиционалните активни јаглеродни материјали, на пример Vulcan XC-72. Следени се промените во структурата и електрохемиската активност за развивање водород, т.е. поларизациските карактеристики при референтна густина на струја. Показано е дека повеќесидните јаглеродни наноцевчиња значително ја подобруваат активноста на електродите за развивање водород, како резултат на 1) зголемената активна површина на електродите, 2) подобрување на електричната спроводливост и 3) подобрување на дисперзијата на активните каталитички центри врз целата електродна површина. Ефектот на подобрување е многу поизразен кај никелните катализатори, каде што пренапонот за развивање водород е намален за 85 mV при референтна густина на струја од 60 mA·cm⁻² во алкална средина.

Клучни зборови: развивање водород; повеќеконпонентни електрокатализатори; активен јаглен; повеќесидни јаглеродни наноцевчиња

INTRODUCTION

New electrode materials for hydrogen evolution are of crucial importance for the energy supply in the future. A term "hydrogen economy" was

coined to cover the complex of hydrogen evolution, storage and use/conversion back to electricity. One of the most important segment of the "hydrogen economy" is the choice of electrode material, because the lower the overpotential on the

electrode the higher the cost-effectiveness of the electrochemical processes. But, the choice of the electrode material is not an easy task because the criteria that it should satisfy are very strict. Electrode materials should be *i*) catalytically active, *ii*) chemically and mechanically stable and *iii*) inexpensive. In this context, Pt satisfies the former two criteria (active and stable material), but high cost and low abundance limits its commercial application. On the other side, non-platinum active metals, as e.g. Ni or Co are considerably cheaper, but suffer of corrosion, passivation and similar difficulties.

So, one of the most important tasks of modern electrocatalysis is to reduce or even completely replace Pt. There are two approaches to obtain cheaper and active catalytic material: *i*) develop multicomponent catalysts with catalytic activity comparable or even higher than that of Pt (chemical approach) and *ii*) increase the real surface area by lowering grain size of the catalytic phase to nano-scale, as well as reducing catalyst loading on the electrodes (physical approach).

The “hypo-hyper *d*-concept” is the most important for the development of multicomponent electrocatalysts. The composite materials based on a mixture of metal from the right side of the transition series (hyper *d*) and metal (or its compound) from the left side of transition series (hypo *d*) do satisfy the above criteria. A fundamental background of the hypo-hyper *d*-electrocatalysts was given by Brewer’s valence-bond theory [1], electrochemically interpreted by Jakšić [2].

Performances of the electrode materials can be improved by increasing their real surface area. In this context, modern electrocatalysis is moving toward nanostructured electrode materials. The most used conductive support materials for electrocatalysts are carbon blacks, for e.g. Vulcan XC-72 with high developed surface area of $250 \text{ m}^2 \cdot \text{g}^{-1}$ [3].

Iijima’s discovery in 1991 [4] has initiated intensive research on carbon nanotubes (CNTs). Their unique and superior physical, mechanical and electrical properties allow wide range of applications and use in the field of hydrogen or energy storage, as electrode materials in electrochemical capacitors, field emission electron sources, fillers in polymer composites etc. [5]. The extraordinary conductivity, mechanical stability and inner geometry also make the CNTs promising materials as catalyst supports, replacing tradition-

ally carbon blacks. In comparison with Vulcan XC-72 that has an electronic conductivity of $4 \text{ S} \cdot \text{cm}^{-1}$, the corresponding value for CNTs is significantly higher at $10^4 \text{ S} \cdot \text{cm}^{-1}$ [6].

The aim of this work was to produce and characterize non-platinum hypo-hyper *d*-electrocatalysts for hydrogen evolution, whit activity close to that of Pt. The catalysts contain TiO_2 (anatase) as a hypo *d*-phase, and Ni, or Co as a hyper *d*-metallic phase. As carbon substrate, traditional Vulcan XC-72 was used. In order to demonstrate performances of other carbon substrates, multiwalled carbon nanotubes (MWCNTs) were employed instead of Vulcan XC-72. Both the structural and electrochemical changes caused by introducing MWCNTs were studied.

EXPERIMENTAL

Electrocatalysts were prepared by sol-gel procedure as described elsewhere [7]. They consist of 10% (mass.) metallic phase (Ni or Co), and 18% oxide phase (TiO_2) deposited on carbon substrate – Vulcan XC-72 (*Cabot Corp. Boston Mass.*) or MWCNTs (*Guangzhou Yorkpoint Energy Company, China*). As precursors of the catalyst’s components, organometallics were used (Me 2,4-pentanedionat, $\text{Me}(\text{CH}_3\text{COCHCOCH}_3)_2$, *Alfa Aesar, Johnson Matthey, GmbH* and Ti-isopropoxide, $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$, *Aldrich, 97%*).

In order to identify the changes resulting from the introduction of MWCNTs as a catalyst support, several methods for determination of structural and surface changes were employed. Intrinsic characteristics of the catalysts were investigated by SEM microscopy and infrared spectroscopy. SEM observation of the electrocatalyst’s microstructure was performed by Scanning Electron Microscope JEOL, 6340F.

The ratio of real versus geometric surface area, i.e. roughness 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 [8, 9]. The electrochemical cell and electrodes were same as those used for determination of the electrochemical characteristics.

Electrochemical investigations were performed in alkaline solution using AMEL equipment (Function Generator AMEL 568, Potentio-

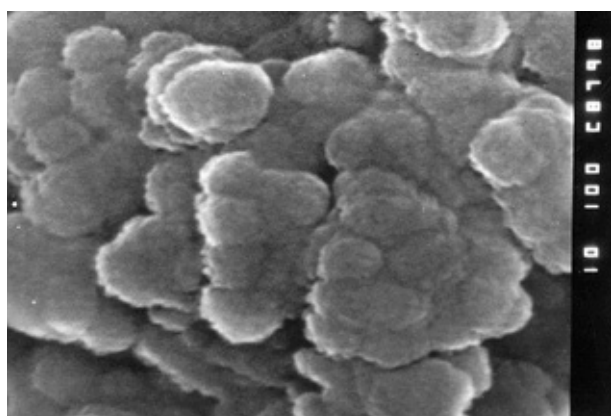
state/Galvanostat 2053 and software package SOFTASSIST 2.0). Gas-diffusion electrodes were prepared out of produced catalyst's powder by hot pressing at 300°C with the back layer of carbon black acetylene + PTFE, and the front layer of the catalyst + PTFE [10]. The counter electrode was a platinum wire, the reference was Hg/HgO, while the electrolyte was a solution of 3.5 M KOH (p.a., Merck) in deionized ultrapurified water. During the electrochemical testing, the solution in the cathodic area was purged with hydrogen.

RESULTS AND DISCUSSION

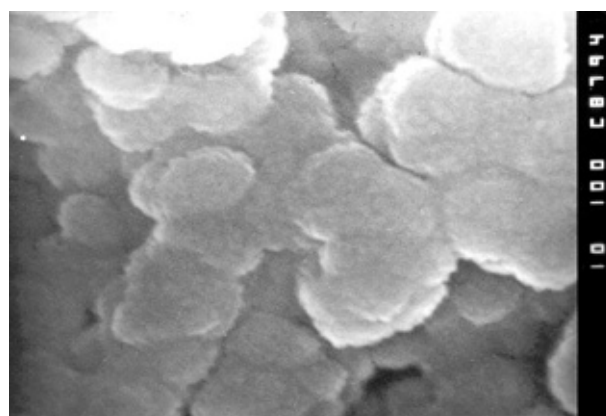
SEM images of catalysts deposited on both multiwalled carbon nanotubes (MWCNTs) and carbon black (Vulcan XC-72) are shown in Fig. 1. The spherical shape of the catalyst's particles deposited on carbon black is apparent (Fig.1 a–b). The particles of the catalysts as a whole are

grouped into aggregates of ca. 150÷200 nm, wherein good adherence is achieved. Based on XRD measurements [7], the size of individual Ni metallic grains is 15÷20 nm, the size of Co grains is less than 2 nm, and that of TiO₂ 7÷8 nm. Also, the presence of holes between the aggregates is evident. This contributes to higher real surface area of the catalysts, and consequently higher activity for hydrogen evolution reaction.

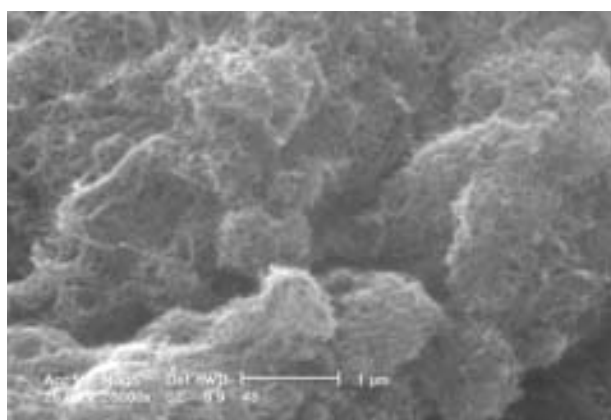
Catalysts particles deposited on MWCNTs (Fig. 1 c–d), are also spherical but form smaller aggregates than in the previous case, thus causing holes to be formed. This improves the **inter-particle porosity** of the catalytic material. Due to their intrinsic geometrical shape (empty cylinders with highly developed surface area), MWCNTs possess high inner porosity, i.e. **trans-particle porosity**. This provides better dispersion of metallic phase (active catalytic component) over the catalyst's surface.



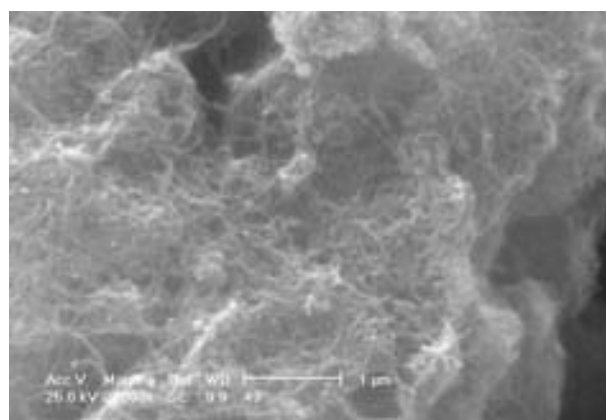
a)



b)



c)



d)

Fig. 1. SEM images of composite electrocatalysts: a) 10 % Ni + 18 % TiO₂* + Vulcan XC-72, (mag. × 100000); b) 10 % Co + 18 % TiO₂ + Vulcan XC-72 (mag. × 100000); c) 10 % Ni + 18 % TiO₂ + MWCNTs, (mag. × 20000); d) 10 % Co + 18 % TiO₂ + MWCNTs (mag. × 20000). * TiO₂ in all samples is in anatase crystalline form

To assign the surface roughness (the ratio of real vs. geometrical surface area, S_R/S_G), the double layer capacity (C_{dl}) of the catalysts was determined by cyclic voltammetry. The measurements were performed in the region of potentials where only charging of the double layer occurs with scanning rate from 1 to 10 $\text{mV}\cdot\text{s}^{-1}$. The cyclic voltammograms for MWCNTs are shown in Fig. 2.

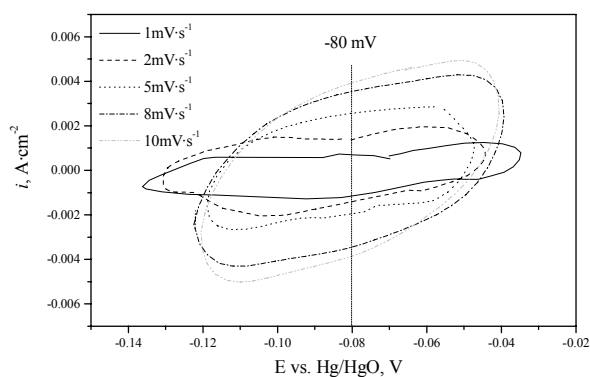


Fig. 2. Cyclic voltammograms scanned in the region of double layer charging for pure MWCNTs

The current density of double layer charging i_{cap} was adopted to be the average value of anodic and cathodic current densities at potential at middle of the scanned interval [8]. The change of i_{cap} as a function of scanning rate shows straight-line dependence (Fig. 3). The slope of this line is equal to the value of double layer capacity of the electrode surface:

$$C_{dl} = \frac{di_{cap}}{d\left(\frac{\partial E}{\partial t}\right)} \quad (1)$$

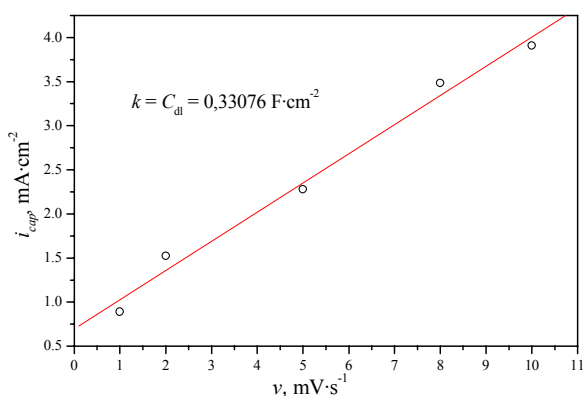


Fig. 3. i_{cap} – v_{scan} dependence of electrode of pure MWCNTs

The quotient of C_{dl} and double layer capacity of corresponding smooth surface (C_{dl0}) is defined

as surface roughness (S_R/S_G). In this case C_{dl0} was taken to be equal to the value of smooth oxide surface ($60 \mu\text{F}\cdot\text{cm}^{-2}$), because in the region of potential of double layer charging, all components of the catalyst are in oxide state.

The values of double layer capacity for the catalysts as well as for pure carbon substrates – Vulcan XC-72 and MWCNTs, are shown in Table 1. The C_{dl} values of pure MWCNTs are almost two times higher than that of Vulcan XC-72. This means that the real surface area of carbon nanotubes is 2 times more developed, implying twice as high real surface area of the catalysts deposited on MWCNTs (see Table 1). In the case of Co-based catalysts this ratio is somewhat lower due to the lower size of Co particles ($< 2 \text{ nm}$ [11]) as active catalytic centres, and consequently their high surface area.

Table 1

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

Sample	$C_{dl} / \text{mF}\cdot\text{cm}^{-2}$	S_R/S_G
Vulcan XC-72	331	–
MWCNTs	179	–
Ni/TiO ₂ /Vulcan XC-72	169	2820
Co/TiO ₂ /Vulcan XC-72	207	3450
Ni/TiO ₂ /Vulcan MWCNTs	325	5425
Co/TiO ₂ /Vulcan MWCNTs	306	5100

Shown in Fig. 4 are the cyclic voltammograms of both metallic systems. In the Ni-based system (Fig. 4a) there are no well shaped peaks of non-faradic surface processes, due to heterogeneity of the oxidation state of Ni in alkaline solutions [12], and the porous character of the electrode. One could regard the gas-diffusion electrode as a complex, composed of number of individual nano-scaled electrodes. Electrical contact between separate grains is not always with zero resistance, so that the existence of IR drop is possible component for some grains. Consequently, the real electrochemical potential of individual grains varies over a span of values. This causes the peak potential, as well as the whole position of peak, to vary, thus causing the overall peak to appear less shaped and irregular. It is evident that non-faradic processes as well as electrode processes – hydrogen (A) and oxygen (B) evolution are more intensive on the catalyst deposited on MWCNTs.

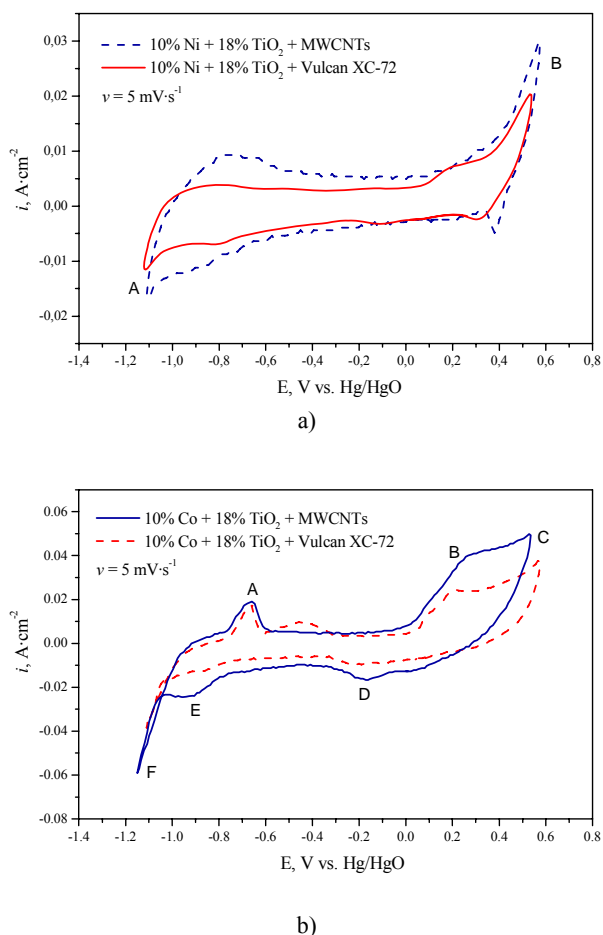


Fig. 4. Cyclic voltammograms of a) Ni-based and b) Co-based catalysts

The voltammograms of Co-based catalysts are more structured [13] (Fig. 4b). The peak A at $-0,6$ V corresponds to transformation of Co(0) to Co(II). Its asymmetric shape is result of heterogeneous forming of $\text{Co}(\text{OH})_2$ and CoO into so called sandwich-structure $\text{Co}/\text{CoO}/\text{Co}(\text{OH})_2$ [14]. Transformation of Co(II) to Co(III) is shown by peak B. There is also a sandwich-structure $\text{CoO}/\text{Co}(\text{OH})_2/\text{Co}_3\text{O}_4$ [15], that implies asymmetry of the peak. Peak D near $-0,17$ V, denotes the opposite transformation. It is obvious that the reaction $\text{Co}(\text{II}) \rightleftharpoons \text{Co}(\text{III})$ is irreversible. The stretched peak E in the potential region of $-0,8$ to -1 V denotes mainly Co(II) to Co(0) reduction. The shifted potential related to the peak A indicates irreversibility of this transformation too. The anomalous shape of the hydrogen evolution reaction (F) is due to the simultaneous occurrence of hydrogen evolution and transformation of backward amount of Co(II) to Co(0). Also, as in the previous case, the processes on electrodes made of catalyst deposited on MWCNTs

are more pronounced and occur in narrower potential region. Hydrogen/oxygen evolution occurs at more positive/negative potential and is considerably more intensive on MWCNTs based electrodes.

Due to the different conductivity of support materials, there will be a difference in the span of real scanning interval, even if the assigned one is the same. So, in Fig. 4 the span of the catalysts deposited on MWCNTs is shorter than those deposited on Vulcan XC-72, due to better conductivity of carbon nanotubes.

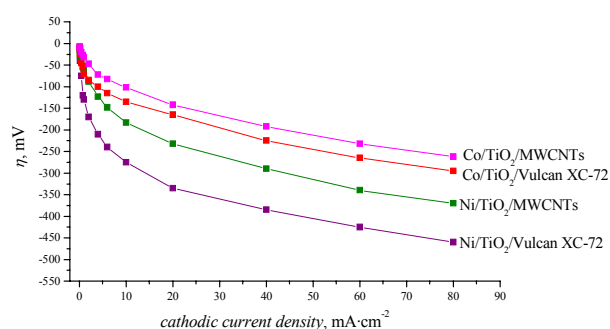


Fig. 5. Polarization curves of investigated catalysts

By analyzing the polarization characteristics (Fig. 5), it is obvious that considerable improvement of catalytic activity is achieved by using MWCNTs. The overpotential for hydrogen evolution at $60 \text{ mA}\cdot\text{cm}^{-1}$ is decreased for 35 mV in the case of Co-based catalysts, and for as much as 85 mV in the case of Ni-based ones. According to IR measurements presented elsewhere [7, 16], the intrinsic interaction between the metallic and oxide phases is almost the same in all investigated catalysts. On the other side, the S_R/S_G ratio is even two times higher for catalysts deposited on MWCNTs than those deposited on Vulcan XC-72. Thus, higher activity of electrodes containing MWCNTs is caused purely by the physical factor of more developed surface area. As mentioned above, carbon nanotubes provide *i)* rise of real surface area of the catalyst as a whole, *ii)* better dispersion of catalyst's particles over the surface, *iii)* extra-conductive properties, and *iv)* superior geometric nature.

Another feature of the polarization curves is that Co-based systems are considerably more active than Ni-based ones, although the intrinsic activity of both metallic systems are similar and Co-based systems have lower surface area. This behavior can be explained by the results of XRD

analysis, presented elsewhere, [17]. Co is amorphous, with particle size lower than 2 nm. So, involving Co as metallic phase considerably increases the real surface area of the active catalytic centers. Also, there is better dispersion of metallic catalytic centers, which means that the whole catalyst's surface is available for hydrogen evolution reaction. However, although the basic catalyst has a higher surface area, its crystalline particles are bigger (10–20 nm) [17], so the real surface area of the active catalytic centers is considerably lower. Dispersion of these larger particles is less uniform which means that only a part of the whole catalyst's surface is available for hydrogen evolution. These facts can also explain the slight rise of catalytic activity for Co-containing catalyst by involving MWCNTs (only 35 mV decreasing of overpotential at 60 mA·cm⁻²). The activity has already achieved its maximum because of the very small particles of Co phase. In the Ni-based system, the rise of activity as a result of involving MWCNTs is much higher (as much as 85 mV decrease of overpotential at 60 mA·cm⁻²). MWCNTs considerably improve dispersion of active metallic catalytic centers and make them available for hydrogen evolution over the whole catalyst's surface.

CONCLUSION

MWCNTs can successfully replace traditional carbon black as a catalyst support. Involving MWCNTs into catalytic systems provides (i) increase of real surface area, (ii) higher conductivity of the whole catalytic system and (iii) higher dispersion of active catalytic centers over the catalyst's surface. As a result, considerable rise of catalytic activity for hydrogen evolution is achieved.

Co-based systems have shown much higher catalytic behavior for hydrogen evolution than Ni-ones, due to the considerably smaller size of Co metallic particles – active catalytic centers, which are more uniformly dispersed over the catalyst's surface.

These complex non-platinum systems deposited on MWCNTs promise successful applications for economical hydrogen evolution as well as oxidation of hydrogen into fuel cells.

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