

INVESTIGATION OF CELL ASSEMBLIES PREPARED OUT OF ELECTROCATALYSTS AIMED FOR HYDROGEN EVOLUTION

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Electrode materials, electrodes, and cell assemblies aimed for hydrogen evolution were prepared, characterized, and tested for their performance.

Instead of Pt-group metals, non-precious metals such as Co and Ni were used to prepare complex hypo-hyper *d*-electrocatalysts grafted on TiO₂ + Carbon. The catalyst composition was 10% Me + 18% TiO₂ + Carbon. BET, XRD and SEM were used to determine the structural and surface characteristics of the catalysts.

The polarization characteristics for the hydrogen evolution reaction (HER) of the basic catalyst's series were further improved by changing the crystallinity and/or the morphology of their components. As a result, the overpotentials of hydrogen evolution on these electrocatalysts approach the corresponding ones exhibited on Pt-based electrode materials. The catalysts deposited on support containing anatase titania grafted on multi-walled carbon nanotubes (MWCNTs) have shown the best performance. Testing was done in aqueous alkaline cells used as gas-diffusion electrodes (GDE) for hydrogen evolution.

Nafion[®] PTFA membranes were used to prepare membrane electrode assembly (MEA) with the above electrocatalysts. It was shown that the use of a proton exchange membrane (PEM) in the electrochemical cell for hydrogen evolution has a number of advantages.

An unusual shape of the MEA's polarization curves was registered. The curves steepened their slope after reaching given overpotential (–590 mV for Ni based catalyst, –450 mV for CoNi, and –420 mV for Co ones). Such behavior is in contrast to the Pt-based catalysts whose slope remains practically constant over the whole region of the tested overpotentials. It is important to stress that at higher overpotentials the latter's activity is very close to that of non-precious metal catalysts, especially the Co-containing ones. Increasing of the temperature contributed to considerable rise of catalytic activity.

Key words: hypo-hyper *d*-electrocatalysts; gas-diffusion electrodes (GDE); membrane electrode assembly (MEA); proton exchange membrane (PEM); multi-wall carbon nanotubes (MWCNTs)

INTRODUCTION

Research and development in the field of hydrogen production is one of the most challenging and intriguing topics today in electrochemistry and science in general. Increased global demand for energy and the need for imminent substitution of fossil fuels with renewable ones are the two major driving forces behind this high priority research.

Hydrogen production at a competitive price is very challenging. The electrochemical approach in attacking this problem consists of, at least, two steps. The first one is preparation of electrode material with proper catalytic activity for cathodic evolution of hydrogen. Such material is often termed as “electrocatalyst”. The second step is of

engineering nature: one should design an electrolysis cell in which the prepared electrocatalyst will be incorporated in such a way that it will perform its best for the hydrogen evolution process. (Similar is the situation with development of fuel cells that reverses the same cell reaction, with a difference being that the engineering aspect in this case is even more important).

Recent development in the field of conductive membranes (polyfluorosulfonic acid/PTFE copolymer – Nafion[®] PFSA, copolymer of polybenzimidazole (PBI) [1]), and in the preparation and application of nano-sized catalyst powders on such membrane's walls, did create a possibility to prepare extremely thin cell assemblies. MEAs (Membrane Electrodes Assemblies) aimed for both hydrogen electrolysis or fuel cell operation, are compact tiny cells, with as low as 25 μm thickness, where the membrane serves both as an electrolyte and separator [1–3]. This gives an opportunity to produce as well performing electrochemical cells, if all the other characteristics (e.g. electrode material's activity, stability, acceptable price, etc.) are satisfied.

In this work results are presented on our research on (i) preparation of hyper-hypo-*d*-electron based electrocatalysts, (ii) testing of gas-diffusion electrodes prepared out of these catalysts in aqueous alkaline cell, and (iii) testing of MEAs assembled with these materials in proton exchange membrane (PEM) electrolyser for hydrogen evolution. Full details of the former part of our research were reported elsewhere [4–8]; provided here is only a short description of the preparation procedure. Much wider attention is paid on testing of materials that provided the best results during the preliminary electrolysis. The investigations in this study were performed in aqueous alkaline cell and PEM hydrogen electrolyser.

Electrocatalysts for hydrogen evolution based on hypo-hyper d-non-precious metals

The choice of catalytic material for hydrogen evolution is very important. The higher the catalytic activity of the material the lower the overpotential for HER, and the lower the specific energy consumption of the process. The most active metals are precious metals such as Pt, Re, Rh and Ir, which are electrode materials on top of which hydrogen evolves with minimum overpotential. Un-

fortunately, precious metals are expensive. The alternative, non-precious metals such as Ni, Co etc. are cheaper, but suffer of corrosion, passivation, and similar problems. Hence, the optimal electrode material has to satisfy both technical and economical criteria, i.e. to be active for HER, stable, and cheap. To avoid or reduce contribution of platinum, new composite electrode materials with high intrinsic catalytic activity and/or increased real surface area are being developed. Significant synergetic effect has been achieved by combining transition metals having proper individual catalytic activity (hyper *d*-metals, Co, Ni, Pt, Pd etc.) with transition metals which are poor catalysts as individual metals (hypo *d*-metals, Ti, W, Zr etc.) [9].

Hypo-hyper *d*-electrocatalysts are complex systems that consist of support and active phase. Catalyst's support contains high conductive and porous carbon and hypo *d*-metal oxide phase, while nano particles of non-precious hyper *d*-metal serve as active catalytic centers. Thus, the catalysts contain *i*) carbon black – Vulcan XC-72, *ii*) hypo *d*-phase (TiO_2) and *iii*) hyper *d*-metallic phase (Ni, Co or CoNi).

The hypo *d*-electronic phase in hyper *d*-metallic part is like a central atom of either trigonal or tetragonal structure unit. Metallic atoms occupy the outer position in the hypo-hyper structural units, thus being the active places where the HER occurs. The main catalytic activity originates in the hyper *d*-metallic phase, which prevails on the catalyst's surface, while the hypo *d*-phase contributes to the catalyst's overall synergetic effect by so called Strong Metal-Support Interaction (SMSI). The SMSI gives rise to both the electrocatalytic activity of the hyper *d*-electronic phase (by reinforcing it), and to the catalyst's stability (due to stronger adherence between the catalyst's components). SMSI as a basic idea in contemporary catalysis has been termed by Tauster to account for the changes in catalytic activity when metals of VIII group are supported on TiO_2 in heterogeneous catalysis [10]. Nanostructured catalysts require much stronger bonding supports, for both long-term stability, and higher activity. In this respect titania has a unique role [11].

The aim of this work was to apply nanostructured non-precious hypo-hyper *d*-electrocatalysts in MEAs for PEM-type cells for hydrogen production. We start with a short description of the characterization of these materials as electrocatalysts for HER in aqueous alkaline media.

PREPARATION AND CHARACTERIZATION OF BASIC CATALYSTS

A modified sol-gel procedure for synthesis of the catalysts was applied, as described in [5, 8]. The final thermal treatment was performed at 250 °C. The composition of the produced catalysts was 10 % Me, 18 % TiO₂ and the rest Vulcan XC-72 (Me = Ni, Co or CoNi).

Surface structure characterization was done by XRD, SEM and BET methods of analysis [4–8]. Ni metallic phase appeared crystalline with grain size of 10÷20 nm, while Co showed XRD spectra characteristic for amorphous state (grain size lower than 2 nm). In Co-Ni systems some Co atoms are incorporated into Ni crystalline lattices forming solid-state solution, but the prevailing amount of Co still remains as amorphous phase.

Crystalline structure of the TiO₂ hypo *d*-phase was not detected. SEM investigations showed that the catalyst's spherical particles are grouped in clusters sized 100÷200 nm with good mutual adherence. The order of electrocatalytic activity [8] was shown to be: Co ≥ CoNi > Ni, despite of the fact that the order of BET-determined specific surface area of the catalysts as a whole was quite opposite (Co:CoNi:Ni = 70:96:108 m²·g⁻¹). This means that the catalysts with higher specific surface area does not necessarily have higher activity [12]. Co particles are smaller than Ni (2 nm of Co particles vs. 10–20 nm of Ni) and more evenly dispersed on the catalytic surface, contributing to considerably higher activity.

IMPROVEMENT OF CATALYSTS PERFORMANCE

Further research was concerned with improving the catalyst's activity for HER. For this purpose, all components of the catalysts were modified separately, i.e. *i*) molybdenum was added into hyper *d*-metallic phase, *ii*) hypo *d*-oxide phase was transformed into crystalline anatase form, and *iii*) multi-walled carbon nanotubes (MWCNT) were used as carbon substrate instead of Vulcan XC-72. The effects of the modifications were discussed elsewhere [13]. Generally, any modification contributes to higher catalytic activity for HER, especially the introduction of MWCNT as a carbon substrate.

To confirm these findings as well as to determine the integral effect of all modifications, catalysts containing MWCNT and anatase form of TiO₂ were prepared for Co, Ni and CoNi systems by the same preparation procedure and identical conditions.

The structural characteristics of the hyper *d*-metallic components were the same as in the previous basic series, while XRD spectra showed anatase structure of TiO₂. Also, the parameter of Ni crystalline lattice showed different value than that of pure Ni, indicating that some interaction occurred between crystalline lattices of TiO₂ and Ni.

Electrochemical measurements were performed in alkaline cell (Fig. 1) containing gas-diffusion electrodes (GDE). Gas-diffusion electrode separates the three phase gas-liquid-solid system on its surface (Fig. 2). The structure of GDE provides several functions: *i*) serves as a car-

rier catalyst, *ii*) ensures highly-developed three phase boundary where the electron exchange reaction takes place, and *iii*) separates the liquid reactants from the gaseous products (hydrogen and oxygen), and provides fast transportation of liquid reactants/gaseous products to/from the three phase boundary. It consists of two layers (Fig. 3). The electrolyte-side layer is covered by catalyst with low amount of PTFE, while the gas-side layer consists of carbon black (Vulcan XC-72 or carbon black acetylene) bonded with PTFE. A metal grid serving as a current collector is in contact with the gas side layer. The composition of the catalytic layer of the investigated GDEs is 10 % Me + 18 % anatase + MWCNT (Me = Co, Ni or CoNi).

The electrocatalytic activity was measured by means of electrochemical steady-state galvanostatic method. The polarization curves are shown in Fig. 4.

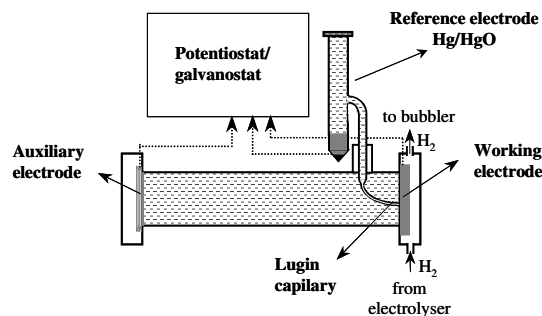


Fig. 1. Arrangement of a cell for electrochemical measurements in aqueous alkaline electrolyte

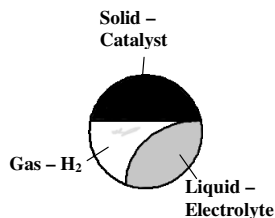


Fig. 2. Three phase gas-liquid-solid boundary in the gas-diffusion electrode (GDE)

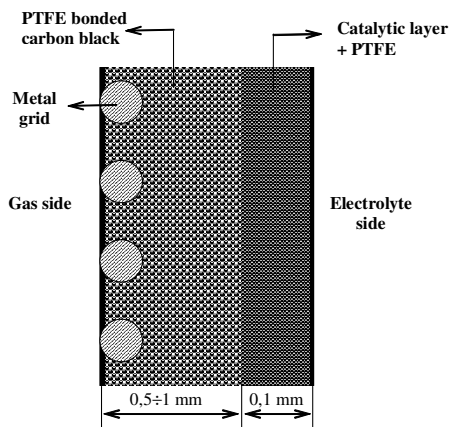


Fig. 3. Cross section of three phase gas-diffusion electrode (GDE)

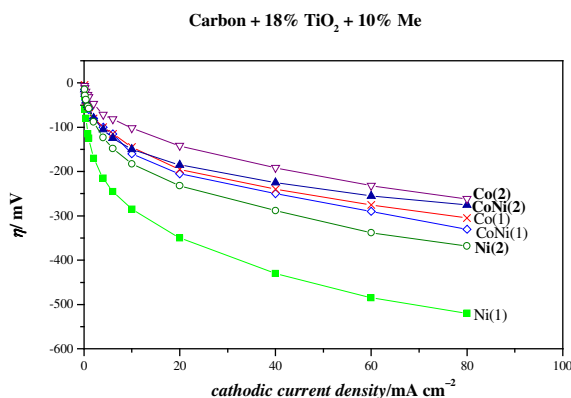


Fig. 4. Polarization curves taken at gas-diffusion electrodes containing 10 % Me + 18 % TiO₂ + carbon (Me = Co, Ni or CoNi) in 3M aqueous solution of KOH at 25 °C.

- (1) – electrodes made with amorphous TiO₂ and Vulcan XC-72,
 (2) – electrodes made with TiO₂ as anatase and MWCNTs

It was found that the order of the catalytic activity of the new series of catalysts is the same as the basic series. Modifications of the catalyst's support by means of using MWCNTs and anatase titania contributed to considerable increase of the activity for HER. This is very pronounced in the

case of Ni containing catalysts. Taking current density of 60 mA·cm⁻² as a reference level (Table 1), the overpotential for HER of the Ni based catalyst is -485 mV, while after the modification, the overpotential is decreased to -335 mV, i.e. for 150 mV. In the case of Co and CoNi systems, the decrease of the overpotential was only 45 and 35 mV, respectively (Table 1). Applied modifications did not produce more pronounced rise of the Co and CoNi activity, probably due to the fact that it has already achieved its best performance due to the small particles of Co phase, thus maximizing the surface area and the better dispersion of active centers over the catalyst's surface.

Table 1

Overpotentials taken at GDE prepared of catalysts containing 10% Me + 18% TiO₂ + carbon in 3M aqueous solution of KOH, at current density of 60 mA·cm⁻²

	Support	
	TiO ₂ (250 °C) + Vulcan XC-72 (mV)	TiO ₂ (anatase) + MWCNTs (mV)
Co	-275	-230
CoNi	-290	-255
Ni	-485	-335

Improvement of the electrocatalytic characteristics is caused by both better conductive and surface characteristics of MWCNTs vs. Vulcan XC-72, and higher hypo-hyper *d*-interaction between the metallic phase and anatase titania. Hypo-hyper *d*-interaction where anatase TiO₂ participates as hypo *d*-component is the strongest in both heterogeneous chemical catalysis [10] and electrocatalysis [11]. For example, interaction between anatase and gold, which is a poor individual catalyst, contributes to striking catalytic effect for many catalytic reactions [14].

However, carbon nanotubes have shown higher contribution in the resulting increase of the catalytic activity [15]. They possess extraordinary conductive properties [15]. On the other side, their structure and surface characteristics are proper for its application in catalytic systems. Previous SEM investigations [6, 8] have shown that spherical particles of oxide and metallic phases are grafted onto carbon nanotubes and grouped in smaller clusters than those grafted onto Vulcan XC-72. This causes holes between particles to appear and conse-

quently results in an increase of the inter-particle porosity. The intrinsic geometrical shape (empty cylinder) of carbon nanotubes itself is characterized with high trans-particle nano porosity. This is favorable for better dispersion of the active catalytic centers (hyper *d*-metallic particles) through the whole surface of the catalyst. To compare the level of surface roughness (the ratio of real vs. geometrical surface area), the capacity of the double layer (C_{dl}) in MWCNTs and Vulcan XC-72 was determined by cyclic voltammetry in the potential region of 0÷100 mV vs. Hg/HgO, where only charging of the double layer occurs. The C_{dl} value of MWCNTs were almost double than that of Vulcan XC-72 ($C_{dl(MWCNT)} = 331 \text{ mF}\cdot\text{cm}^{-2}$ versus $C_{dl(Vulc.XC-72)} = 179 \text{ mF}\cdot\text{cm}^{-2}$).

Also, separation of the three-phase system in GDE is improved. As it can be seen in Fig. 5, catalyst's particles or clusters are grafted on the outer side of the tube, while transportation of the gas-phase occurs into the tube. Reacting ions (liquid

phase) surround the tube. The situation is simpler with the two-phase (solid and gas) electrolysis, which occurs in PEM electrolyzers. For this reason, the catalysts deposited on MWCNTs were selected for further investigation of membrane electrode assembly (MEA) in PEM-type cells for hydrogen evolution.

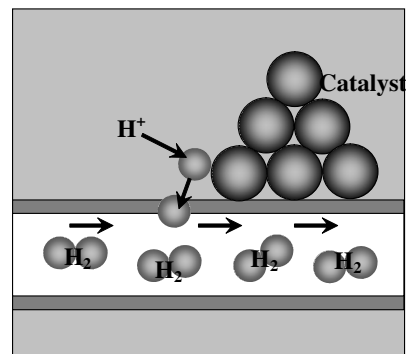


Fig. 5. Sketch of a solid/gas boundary in case when hydrogen passes through a carbon nanotube

TESTING THE ASSEMBLY OF A PROTON EXCHANGE MEMBRANE (PEM) CELL

The operation of PEM electrochemical cells (for both hydrogen evolution or fuel cell) is based on use of gas reaction electrodes, where the two-phase (gas-solid) boundary appears. The polymer membrane material has a bifunctional role: as a separator of the cathodic and anodic area, and as a solid electrolyte which can selectively transport cations across the cell junction. The use of polymer membrane alleviates the concerns connected with liquid electrolytes (e.g. corrosion, watertight compartment and safety issues). Also, the membrane is chemically resistant and stable on long-term. The most used membranes are those based on polyfluoro-sulfonic acid/PTFE copolymer, commercially named Nafion® PFSA. The operating temperature region of Nafion® PTFA is below 100 °C, and the thickness is in the range of 50÷250 μm . Before use these membranes should be activated with sulfuric acid.

Both sides of the membrane are coated with the catalytic layers in the so-called membrane electrode assembly (MEA) (Fig. 6). This is a very simple system that enables straightforward operating regime for both industrial or investigation purposes. For better adherence between the catalytic layers and the membrane, carbon phase (carbon black Vulcan XC-72, carbon fibers or carbon nanotubes) was used.

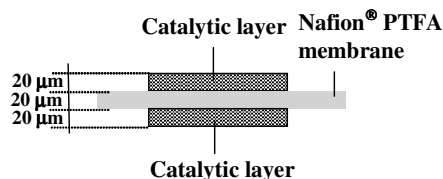


Fig. 6. Cross section of membrane electrode assembly (MEA)

The PEM electrochemical test cell used in this work is composed of three-electrode system: working (WE), auxiliary (AE) and reference (RE) electrodes. The working and auxiliary electrodes are two catalytic layers grafted on the Nafion® PTFA membrane (Fig. 7 [2]). The reference electrode is usually of the same catalytic material as the working electrode. It is placed on the membrane near the working and auxiliary electrodes. An advantage of this cell is that the electrode reaction that occurs on the auxiliary electrode is the same as that on the working electrode, but proceeds in opposite direction. Thus, the reactants/products transformed/produced on the working electrode are entirely restored on the auxiliary electrode. In this way, the electrode environment is not changed during operation. This type of cell is able to work as both hydrogen electrolyser and

fuel cell simultaneously. As it can be seen from Fig. 7, when the working electrode functions as cathode for hydrogen evolution, the auxiliary electrode works as anode for hydrogen oxidation, as in a fuel cell. So, the hydrogen gas environment will not be changed during operation because the hydrogen used on the one electrode will be restored on the other one. The hydrogen supply into the test cell is provided by alkaline hydrogen electrolyser.

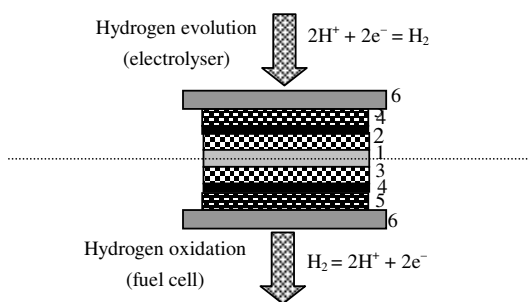


Fig. 7. Cross section of MEA into "easy test" cell: 1) Nafion® PTFA membrane, 2) working electrode, 3) auxiliary electrode, 4) graphitized paper, 5) metal carrier of assembly, and 6) upper and lower terminal

The small surface area of MEA (1 cm²) keeps the preparation procedure very simple and saves the expensive materials, primarily the Nafion® PTFA membrane. The membrane was produced by evaporation of Nafion® PTFA solution (Aldrich, 5 % solution), resulting in a very thin membrane of 20 μm. The catalytic layer containing 10 % Me + 18 % anatase + MWCNT (Me = Co, Ni or CoNi) was grafted onto both sides of the membrane using the Nafion® PTFA solution. Simultaneously, very small amount of Pt E-Tek was deposited on the side of the membrane as a reference electrode, as shown in Fig. 8 [2, 3]. After that, MEA was slightly pressed and was ready for incorporation into the test cell. For comparing the activity of the non-precious hypo-hyper *d*-electrocatalysts, MEAs of Pt (E-Tek and Ion-Power) were prepared.

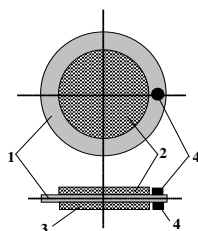


Fig. 8. The position of reference electrode in the membrane electrode assembly (MEA), 1) Nafion membrane, 2) working electrode, 3) auxiliary electrode, and 4) reference electrode

Shown in Fig. 9 are the polarization curves of the investigated catalysts. As it can be seen, the order of catalytic activity of the non-precious hypo-hyper *d*-electrocatalysts is the same as that in the aqueous alkaline cell, but the trend of curves is quite different. In this series, the curves show two slopes: slight and steep rise of overpotential with increase of the current density. The turning points, where the steep increase of hydrogen evolution starts, are at -590 mV (RHE) for the Ni based catalyst, -450 mV for the CoNi based catalyst, and -420 mV for the Co based catalyst. The Pt catalysts show approximately linear rise of the current density, but at higher overpotentials the activity is very close with that of non-precious catalysts, especially the Co-containing ones. Pt (E-Tek) shows higher activity than Pt (Ion-Power Inc., IP), but at overpotentials near -650 mV its activity was saturated and lower than that of Pt (IP), and even lower than that of the Co based catalyst. This anomalous catalytic behavior of the non-precious hypo-hyper *d*-electrocatalysts is due to the acid character of Nafion® PTFA membrane, which is activated with sulfuric acid. As a matter of fact, the metallic phases Co and Ni are not stable in acidic media (i.e., some dissolving occurs), thus decreasing the number of active catalytic centers. But, at higher overpotentials, after cathodic reduction of the dissolved Me-ions, the catalytic activity for HER considerably increases. At overpotential near 650 mV Co based catalyst exceeds the activity of Pt (E-Tek) and is very close to that of Pt (Ion-Power).

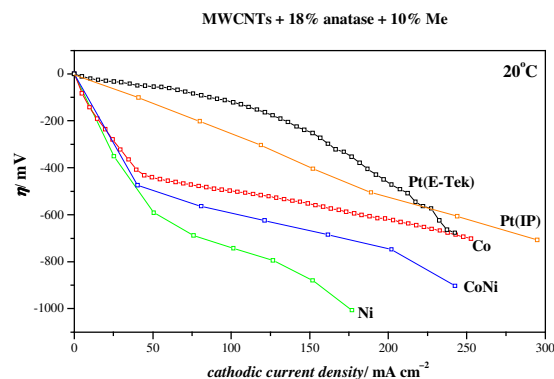


Fig. 9. Polarization curves of MEAs of non-precious hypo-hyper *d*-electrocatalysts, containing 10 % Me + 18% anatase + MWCNTs (Me = Ni, Co or CoNi) and Pt (E-Tek and Ion-Power) in PEM easy test cell at 20 °C

Shown in Fig. 10 are the polarization curves of all non-precious catalytic systems at higher temperatures (50 and 80 °C). Increasing of the temperature contributes to considerable rise of

catalytic activity. At 50 °C almost maximum activity is achieved, because further rise of the temperature to 80 °C only slightly increases the catalytic activity. For example, for the Ni based catalyst (as the less active of all), the rise of temperature from 20 to 50 °C causes the overpotential for HER at 150 mA·cm⁻² to decrease from -945 to -670 mV, respectively. In the CoNi and Co based systems, these changes of overpotential at 200 mA·cm⁻² are -750, -680 and -645 mV, and -615, 500, and -465, for 20, 50 and 80 °C, respectively. The turning points are moved at lower overpotential, as it is shown in Table 2, so that there is a not difference between turning points on 50 and 80 °C.

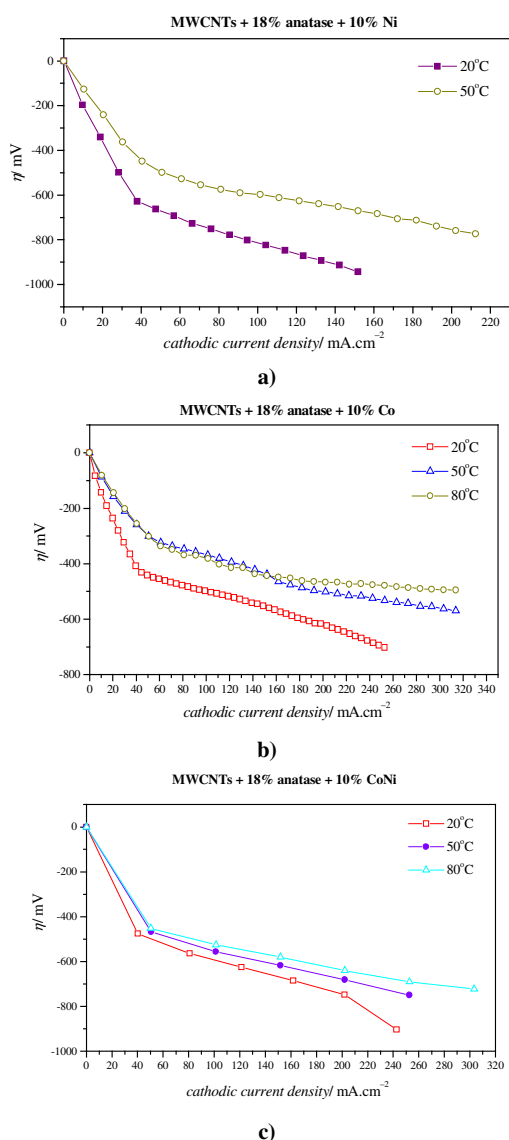


Fig. 10. Polarization curves of MEAs of non-precious hypo-hyper *d*-electrocatalysts, containing 10 % Me + 18 % anatase + MWCNTs in PEM easy test cell at 20, 50 and 80 °C. Me = a) Ni, b) CoNi and c) CoNi.

Table 2

Turning Values of overpotentials at which change of slope occurs in polarization curves of catalysts containing 10% Me + 18% anatase + MWCNTs in PEM “easy test” cell at different temperatures

	20 °C (mV)	50 °C (mV)	80 °C (mV)
Co	-420	-300	-300
CoNi	-470	-450	-450
Ni	-590	-490	-

There are two approaches to overcoming the inferior catalytic behavior of hypo-hyper *d*-electrocatalysts at lower values of overpotentials: to replace Nafion® PTFA membrane with another having lower acid character, or adding some amount of Pt in the catalyst.

An alternative membrane could be a copolymer of polybenzimidazole (PBI), which is activated with phosphoric acid. This material has been under intensive research in the last decade [1]. It is stable up to 350 °C, its mechanical strength is comparable with that of steel, and it has lower acidic character than Nafion® PTFA.

In this work the results for catalytic activities of two opposite cases, pure platinum and entirely non-platinum catalysts, were shown. At higher overpotentials these activities are very close but the problem with non-platinum catalysts is at lower overpotentials, which are of practical interest. So, Pt could not be entirely avoided. By reducing Pt in account of these types of catalysts, especially the Co based one, one could expect to obtain good results, even better than those obtained for pure Pt E-Tek. This expectation is encouraged by the fact that Co itself forms small, very active catalytic particles [8], but also in mixture with Pt contributes to smaller Pt particles than that of pure Pt [16]. For example, pure Pt has particles of 4.2 nm, while Pt particles in Pt-Co mixed catalyst are lower than 2 nm [16].

The results of this study direct further research activity toward determining the minimum amount of Pt in mixture with this type of non-platinum catalysts, and determining the performance of the non-platinum hypo-hyper *d*-electrocatalysts grafted on PBI membrane.

CONCLUSION

Preparation, characterization and improvement of electrode materials aimed for hydrogen evolution reaction was achieved. Complex catalysts systems based on use of non-precious metals were prepared by grafting Co, Ni and CoNi on top of a nanosized TiO₂ applied on carbonaceous substrate. Electrodes were of constant composition, i.e.: 10 % Me (Co, Ni or CoNi), 18 % TiO₂, the rest being carbon.

Crystallinity, grain size, surface area, and structure were determined, and further characterization was done by measuring the polarization characteristics of the electrodes prepared out of these materials.

It was found out that Co based electrocatalysts exhibit lower overpotential for HER than the CoNi and Ni based ones.

Applying modifications such as transformation of TiO₂ into crystalline form (anatase) and/or introduction of carbon nanotubes as a substrate material, the electrocatalytic characteristics of these materials were improved and made closer to the ones exhibited by platinum based electrodes. So, at catalysts prepared with Co, hydrogen was evolved with an overpotential of -230 mV at current density of $60 \text{ mA}\cdot\text{cm}^{-2}$.

Electrodes that were determined to be most successful were further used to assemble an PEM cell. The performance and polarization characteristics of such cell were tested.

It was concluded that PEM cell containing Co based catalyst at overpotentials higher than -650 mV behaves similarly to a cell with Pt based catalysts. The similarity in behavior between the compared electrode systems occurs at lower overpotentials.

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REFERENCES

- [1] E. Budevski, Structural aspects of fuel cell electrodes, *J. Optoelectronics and Advanced Materials*, **5**, 5, 1319–1325 (2003).
- [2] E. Budevski, The ultra thin MEA concept and the easy test technology, Invited lecture of the 6th National Workshop – Nanoscience & Nanomaterials 2004, November 24–27, 2004, Sofia, Bulgaria.
- [3] E. Budevski, I. Radev, E. Slavcheva, The Easy Test Cell – An enhanced MEA investigation and optimization technique, *Proceedings International Hydrogen Energy Congress and Exhibition IHEC 2005*, Istanbul, Turkey, 13-15 July, p. 37 (1–7), (2005).
- [4] P. Paunović, O. Popovski, S. Hadži Jordanov, A. Dimitrov, D. Slavkov, Modification for improvement catalyst materials for hydrogen evolution, *J. Serb. Chem. Soc.* (in press).
- [5] P. Paunović, O. Popovski, V. Nikolova, P. Iliev, M. Tasev, E. Lefterova, Ni-Me/TiO₂ electrocatalysts for hydrogen evolution reaction (HER), XVIIIth Congress of the Chemists and Technologists of Macedonia, *Extended abstracts*, [ECH-1], Ohrid, September 23–25 (2004).
- [6] P. Paunović, O. Popovski, A. Dimitrov, M. Tasev, S. Hadži Jordanov, Influence of the support on electrocatalytic activity of Ni-TiO₂ hypo-hyper *d*-catalysts for hydrogen evolution reaction (HER), XVIIIth Congress of the Chemists and Technologists of Macedonia, *Extended abstracts*, [ECH-2], Ohrid, September 23–25 (2004).
- [7] P. Paunović, O. Popovski, A. Dimitrov, D. Slavkov, M. Tasev, S. Hadži Jordanov, Co/TiO₂ hypo-hyper *d*-catalyst for hydrogen evolution reaction (HER), XVIIIth Congress of the Chemists and Technologists of Macedonia, *Extended abstracts*, [ECH-3], Ohrid, September 23–25 (2004).
- [8] S. Hadži Jordanov, P. Paunović, O. Popovski, A. Dimitrov, D. Slavkov, Electrocatalysts in the last 30 years – from precious metals to cheaper but sophisticated complex systems, *Bull. Chem. Technol. Macedonia*, **23**, 2, 101–112 (2004).
- [9] M. M. Jakšić, Advances in Electrocatalysis for Hydrogen Evolution in the Light of the Brewer-Engel Valence-Bond Theory, *Int. J. Hydr. Energy*, **12**, 727–752 (1987).
- [10] S. J. Tauster, S. C. Fung, R. L. Garten, Strong metal-support interactions. Group 8 noble metals supported on titanium dioxide, *J. Am. Chem. Soc.*, **100**, 1, 170–175 (1978).
- [11] S. G. Neophytides, S. Zafiriatis, G. D. Papakonstantinou, J. M. Jakšić, F. E. Paloukis, M. M. Jakšić, *Extended*

- Brewer hypo-hyper-*d*-interionic bonding theory II. Strong metal-support interaction grafting of composite electrocatalysts, *Int. J. Hydr. Energy*, **30**, 2, 131–147 (2005).
- [12] A. D. S. Tantram, A. C. C. Tseung, *Nature*, **222**, 556–558 (1969).
- [13] S. Hadži Jordanov, P. Paunović, O. Popovski, A. Dimitrov, D. Slavkov, Progress report N°4 of EU Project “PROMETHEAS” – ICA2-CT-2002-10001, November (2004).
- [14] Tsubota S, Cunningham DAH, Bando Y, Haruta M. In: Poncelet G., ed., Preparation of catalysts VI. Amsterdam: Elsevier; (1995), p. 227.
- [15] A. Dimitrov, P. Paunović, Carbon nanotubes as a possible material for catalyst carrier, Invited lecture of the 6th National Workshop – Nanoscience & Nanomaterials 2004, November 24–27 (2004), Sofia, Bulgaria.
- [16] E. Slavcheva, V. Nikolova, T. Petkova, E. Lefterova, I. Dragieva, E. Budevski, On the role of Magneli phase Ti_nO_{2n-1} support in the electrocatalytic activity of Pt and CoPt synthesized by BH reduction, 55th Annual Meeting of the International Society of Electrochemistry, *Book of Abstracts II*, p. 716, September 19–24, (2004) Thessaloniki, Greece.

Резиме

ИСПИТУВАЊЕ НА ЕЛЕКТРОХЕМИСКИ КЕЛИИ ИЗГОТВЕНИ СО ЕЛЕКТРОКАТАЛИЗАТОРИ НАМЕНЕТИ ЗА РАЗВИВАЊЕ ВОДОРОД

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Клучни зборови: хипо-хипер *d*-електрокатализатори; гас-дифузиони електроди (GDE); комплекти анода-мембрана-катада (MEA); протоноразменувачки мембрани (PEM); повеќесидни јаглеродни наноцевчиња (MWCNTs)

Беа подготвени и карактеризирани, односно тестирани материјали за изготвување електрокатализатори, електроди и на крајот комплетни ќелии, сите наменети за развивање водород.

Комплексни хипо-хипер *d*-електрокатализатори беа изготвени со употреба на Co и Ni, наместо традиционалните, но скапи метали од групата на платината. Ваквите метали се нанесуваат врз TiO_2 на јаглероден носач, така што конечно се добива материјал со состав 10 % Me + 18 % TiO_2 + јаглерод.

Структурните и површинските карактеристики на добиените катализатори беа определени со помош на методите BET, XRD и SEM.

Поларизациските карактеристики за водородната реакција на основната серија катализатори беа понатаму подобрувани со модифицирање на кристалната состојба и/или морфологијата на нивните компоненти. Со тоа се постигна да се добијат електрокатализатори врз кои водородот се издвојува со пренапони приближно исти како и врз материјалите изработени со употреба

ба на платина. Најдобри својства се постигнати кај катализаторите што во својата формулација содржат анатаз (TiO_2) и јаглеродни наноцевчиња со повеќеслојни сидови (MWCNTs). Изготвените гас-дифузиони електроди (GDE) беа испитувани при електролиза на водород во алкални електролити.

Мембраните Nafion[®] PFSA беа користени за изготвување на комплекти анода-мембрана-катада од вака подготвените материјали. Се потврди дека протоноразменувачките мембрани имаат повеќе предности при вградувањето во вакви електрохемиски ќелии.

Поларизациските криви на испитуваните комплекти при дадена вредност на потенцијалот го менуваат наклонот (590 mV; 450 mV и 420 mV). Споредуваните криви за материјалите што содржат платина не го менуваат наклонот во испитуваниот интервал на густини на струја. Со зголемување на температурата на електролиза на 50 °C односно 80 °C се зголемува и активноста на добиените катализатори.