

Electrocatalysts with reduced noble metals aimed for hydrogen/oxygen evolution supported on Magneli phases. Part II: Electrochemical characterization

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This study is concerned with electrochemical testing of nano-scaled electrocatalysts consisted of Magneli phases as a support and different metallic phases (Co, Pt, Ru, CoPt (Co:Pt = 1:1 wt.), CoRu (Co:Ru = 1:1 wt.) and CoPtRu (Co:Pt:Ru = 1:0,5:0,5 wt.)). Electrocatalytic materials were prepared by sol-gel procedure using organometallic precursors (Me-acetylacetonate) deposited on dispersed Magneli phases in wt. ratio 10% Me and 90% Magneli phases. Electrochemical testing of the studied electrocatalysts was performed in aqueous alkaline electrolyte. The order of activity for hydrogen evolution was the following: CoPt > CoPtRu > CoRu, while for oxygen evolution: CoRu > CoPtRu > CoPt. Co has been shown as promoter for reducing Pt particles (the most active monometallic phase), so reduction of Pt quantity in the metallic phase was compensated with smaller particles. Also, mutual interaction between metallic phases (shifting the centre of d-band to values close to Fermi level) increases the intrinsic catalytic activity for both hydrogen and oxygen evolution. Due to large particle of Magneli phases, the catalytic activity is lower compared with corresponding electrocatalysts deposited on carbon nanomaterials. But, they are very good catalysts for oxygen evolution, because Magneli phases in this case, behave not only as support material, but also, as an active oxide electrode.

Key words: Magneli phases, Co, Pt, Ru, hydrogen evolution, oxygen evolution.

INTRODUCTION

One of the most challenging issues within the hydrogen economy as the most promising alternative energy system is finding out catalytically active electrode materials for water electrolysis/fuel cells with reduced amount or without platinum. The exploitation of platinum as a leading electrode material in the hydrogen economy is limited due to high price and low abundance [1]. There are two main approaches to enhance the catalytic activity of the metals: physical and chemical. The first approach is based on the reduction of the particles size, which implies increase of the real surface area (size-effect) [2]. So, this approach leads to nano-scaled electrocatalytic materials in hydrogen economy. The second one is based on alloying of the catalytic metal phase or interaction of metallic phase with the support material (intrinsic effect). According to Jakšić's hypo-hyper d-concept [3,4], the mixture of hyper d- electronic transition metals (having more electrons in the outer shell and good individual catalysts) with hypo d- electronic transition metals (having less electrons in the outer shell and poor catalysts as individual metals) exhibits pronounced synergetic effect of electrocatalytic activity. In this context, TiO₂ has shown unique hypo-hyper d-interaction with the metallic phase [5,6]. TiO₂ as an oxide material have

high chemical stability, but it is non-conductive. Thus, it is used most commonly accompanied with carbon nanostructures as support material. Non-stoichiometric titanium oxides with high electrical conductivity could be potential substitution for carbon support within the electrode materials. Besides supportive role, Magneli phases behave as hypo d-phase, which interact with hyper d-metallic phase and contribute to the strong metal-support interaction (SMSI) [7,8]. As was mentioned in our previous work [9], the main disadvantage of Magneli phases as support material is the low specific surface area. The maximal achievement of the mechanical techniques for preparation of Magneli phases was the specific surface area in the range of 1.6–3.0 m²g⁻¹ [10], instead of more than 250 m²g⁻¹ in the case of carbon nanostructures [11].

The aim of this work is firstly, to examine a possibility of usage of Magneli phases as an electrocatalysts support material and secondly, to determine the effects of addition of non-noble metal – Co in the platinum or ruthenium metallic phase of electrocatalysts aimed for both hydrogen and oxygen evolution.

EXPERIMENTAL

As a catalyst support commercial The procedure for mechanical activation of Magneli phases, as well as the procedure for sol-gel

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preparation of the studied electrocatalysts is given in our previous work [9].

The composition of the prepared electrocatalysts is shown in Table 1.

Table 1. Composition of the studied electrocatalysts

	Metallic phase (hyper d-phase)	Support (hypo-phase)
	10%, wt.	90%, wt.
E-1	Co	Ebonex
E-2	Pt	Ebonex
E-3	Ru	Ebonex
E-4	CoPt, 1:1, wt.	Ebonex
E-5	CoRu, 1:1, wt.	Ebonex
E-6	CoPtRu, 1:0.5:0.5, wt.	Ebonex

Electrocatalytic activity of the studied electrocatalysts was tested by means of steady-state galvanostatic method. The measurements were performed using AMEL equipment (Function Generator AMEL 568, Potentiostat/Galvanostat 2053 and software package SOFTASSIST 2.0). As working electrodes three-phase gas-diffusion electrodes were used, prepared by hot pressing at 300 °C and pressure of 300 kgcm⁻² [12]. It consists of two layers: i) the electrolyte-side layer, covered by catalyst with low amount of PTFE, and ii) the gas-side layer consisted of carbon black bonded with PTFE. The counter electrode was of platinum wire, while Hg/HgO was used as a reference electrode. The electrolyte was an aqueous solution of 3.5 M KOH (p.a., Merck) at room temperature.

RESULTS AND DISCUSSION

Electrochemical characterization for HER

Electrocatalytic activity for both hydrogen and oxygen evolution was observed by steady-state galvanostatic measurements of overpotentials at different current densities. The results of $i \div \eta$ measurements for hydrogen evolution are summarized in Fig. 1. Also, Tafel slopes and corresponding exchange current densities (i_0) were determined in the region of low current densities. This is illustrated in Fig. 2, for sample E-1. Determined values of Tafel slopes and current densities are summarized in Table 2, where also, the corresponding overpotentials for hydrogen evolution at a reference current density of 80 mAcm⁻² (η_{80}) are given.

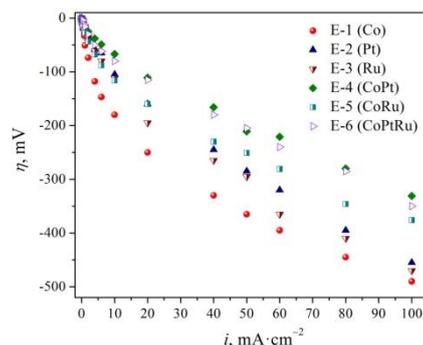


Fig. 1. Polarization curves of the studied electrocatalysts for HER in the plot $i \div \eta$.

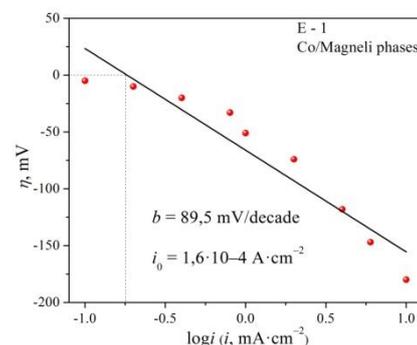


Fig. 2. Polarization curves of the studied electrocatalysts for HER in the plot $\log i \div \eta$, in region of low current densities

Generally, the monometallic electrocatalysts have shown lower activity for HER than the multimetallic ones, wherein the order of activity is as follows: E-2 (Pt) > E-3 (Ru) > E-1 (Co). This is the expected order according to the intrinsic activity of the studied metallic systems [13] as well as to the determined values of i_0 shown in Table 2. Considering that the sample E-2 (pure Pt as metallic phase) has the lowest specific surface area (almost 3 times than Ru, E-3 and 1.5 times than Co, E-1), one can notice that in monometallic systems, the intrinsic effect of electrocatalytic activity is more pronounced than the size effect.

Multimetallic electrocatalysts have shown considerably better activity for HER than monometallic ones. According to TEM and BET analysis (see ref. [9] in this issue), as well as to electrochemical results (Table 2), the improved activity in different electrocatalysts is result of size and/or intrinsic effect. The impact of size and intrinsic effect will be analyzed separately for each multimetallic system.

Table 2 Electrochemical indicators for electrocatalytic activity of the studied catalytic materials for HER and OER, BET surface area presented in [9]

Sample	10% metallic phase + 90% Ebonex	BET s. a., m ² ·g ⁻¹	<i>b</i> , mV·dec ⁻¹	<i>i</i> ₀ , A·cm ⁻²	η ₈₀ , mV	
					HER	OER
E-1	Co	6.1	90	1.60·10 ⁻⁴	-445	475
E-2	Pt	4.3	46	1.80·10 ⁻⁴	-395	490
E-3	Ru	11.0	52	1.68·10 ⁻⁴	-410	450
E-4	CoPt, 1:1, wt.	7.6	31	1.90·10 ⁻⁴	-280	455
E-5	CoRu, 1:1, wt.	9.4	54	1.79·10 ⁻⁴	-345	400
E-6	CoPtRu, 1:0.5:0.5, wt.	6.4	40	2.20·10 ⁻⁴	-285	430

Firstly, to see how addition of non-noble metal – cobalt affects the electrocatalytic activity of platinum, comparing the results for sample E-4 (CoPt) and E-2 (Pt). The quantity of Pt in the bimetallic sample E-4 is twice lower than that of monometallic platinum based sample E-2, while the catalytic activity is considerably higher (-280 mV for E-4 vs. -395 mV for E-2, See Tab. 2). According to the values of particle size (TEM and XRD analysis [9]), BET surface area and exchange current densities, one can conclude that improvement of catalytic activity with addition of Co in Pt is result of both, size and intrinsic effect. The size effect is reflected in the considerably smaller (near 4 times) platinum particles in the bimetallic CoPt system E-4 (2 to 3 nm), compared with the pure Pt system E-2 (5 to 15 nm). It was already shown that Co behaves as promoter to reduce the size of platinum particles [14–16]. The smaller metallic particles affect on the increasing of the specific BET surface area of the catalyst as a whole (4.3 m²g⁻¹ for E-2 vs. 7.6 m²g⁻¹ for E-4) and consequently on better catalytic activity. Therefore, the size effect can be seen in the smaller metallic particles as an active catalytic centers over the catalyst's surface as well as in the higher BET surface area of the bimetallic catalyst as a whole. According to the values of exchange current densities (1.8·10⁻⁴ Acm⁻² for E-2 vs. 1.9·10⁻⁴ Acm⁻² for E-4), there is also an enhancement of intrinsic electrocatalytic activity. This means that there is a synergetic interaction between metallic phases in the bimetallic electrocatalysts E-4 (PtCo). This interaction comprises modification of electronic properties (electronic density and average electron configuration) of certain metallic phase in presence of the other one [17]. For better understanding of the synergetic interaction, so-called “d-band center theory” can be used, explained elsewhere [17–20]. The position of d-band has leading role in determining the affinity of d-metals to adsorption of variety of adsorbates, such as H, O, CO etc. The higher the d-band center lies regarding the Fermi

level, the better is the interaction metal–adsorbate. The metals with larger atomic radius and electronegativity up-shift d-band center of Pt, thus improving its adsorptive ability and consequently, accelerate the overall electrode reaction. Theoretically, this does not occur in the case of addition of Co to Pt, because Co has smaller atomic radius than Pt. But, Nørskov and collaborators [18,19] have shown that as the Pt particles are smaller, the d-band center is approaching to Fermi level, achieving better adsorption of adsorbates. So, Co can not affect this synergism, but indirectly, through reduction of Pt nanoparticles causes the same synergetic effect.

Improvement of the catalytic activity of sample E-6 (CoRuPt) can be explained similarly. The catalytic activity is slightly lower (only 5 mV) than that of sample E-4 (CoPt), but in this case the quantity of platinum in the metallic phase is only 25 %.

Now to see how the addition of Co in the Ru improves electrocatalytic activity, comparing the results for samples E-5 (CoRu) and E-3 (Ru), where the overpotential for HER was decreased from -410 mV for monometallic catalyst (E-3) to -345 mV for bimetallic catalyst (E-5). Firstly, the size effect is considered. Specific BET surface area [9] of the sample E-5 (9.4 m²g⁻¹) is lower than that of monometallic sample E-3 (11 m²g⁻¹). Also, the average size of particle of bimetallic sample is slightly higher (2 to 4 nm for sample E-5 vs. 2 to 3 nm for sample E-3). These results highlight that there is not a size effect. On the other hand, the values of exchange current densities (1.68·10⁻⁴ Acm⁻² for E-3 and 1.79·10⁻⁴ Acm⁻² for E-5) point out that improvement of catalytic activity of bimetallic electrocatalysts E-5 is result only of intrinsic effect, i.e. of synergetic interaction between the present metals.

Generally, the activity of the studied electrocatalysts for HER is not so high compared with electrocatalysts deposited on nano-scaled carbon support material [15,21], mainly due to large

particles of the Magneli phases (180-200 nm) and consequently low specific surface area (4.2 vs. 250 m^2g^{-1} and more for nanoscaled carbon materials). Also, one should mention that the amount of metallic phase in the electrocatalysts is low, only 10 %.

Electrochemical characterization for OER

Polarization curves for oxygen evolution are shown in Fig. 3.

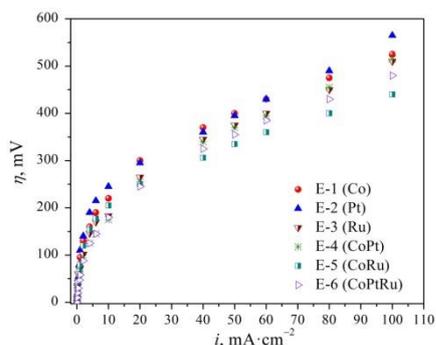


Fig. 3. Polarization curves of the studied electrocatalysts for OER

The order of activity of the monometallic samples is the follow: E-3 (Ru) > E-1 (Co) > E-2 (Pt). According XRD analysis [9], Ru surface structure was in oxidized state (oxides and/or hydroxides), and it is known that oxidized Ru is one of the most active electrodes for oxygen evolution [22]. The better activity of Co than that of Pt is result of higher specific surface area (6.1 vs. 4.3 m^2g^{-1}), but also, due to early transition of Co to Co(II) and then to Co(III) [21]. This oxidized surface is covered with hydroxyl groups, in so-called sandwich-structure Co/CoO/ Co(OH)₂ during Co(0) to Co(II) transformation [23] and sandwich-structure CoO/Co(OH)₂/Co₃O₄ during Co(II) to Co(III) transformation [24], which is an appropriate to accelerate oxygen evolution.

Similarly to HER, multimetallic electrocatalysts have shown better catalytic activity and for OER than the corresponding monometallic systems. Improvement of the catalytic activity for OER can be explained on the same way as was explained that for HER above. As the most active catalyst for OER sample E-5 based on CoRu has been shown. As was already shown, the improvement of catalytic activity in this system is result only of intrinsic effect, i.e. of synergetic interaction between Ru as the most active individual catalyst for OER and Co which has shown good individual catalytic activity for OER.

In contrast to the poor activity for hydrogen evolution, these catalytic systems have shown good activity for oxygen evolution, compared to other

electrocatalysts [14, 25-27]. Besides the electrode surface composition of the metallic phase (Co and Ru are in oxidized state at potentials close to oxygen evolution region), in this case, Magneli phases behave not only as support material, but also, as an active oxidized electrode. The surface structure in the electrolyte is a characteristic that distinguishes the oxide electrodes [28]. Their surface is characterized with high energy content and strong hydrophobicity, making it easier to interact with water molecules and to cover the top of oxide with layer of OH⁻ ions. This layer mediates the action of the oxide's surface with the electrolyte species. The OH⁻ groups are responsible for the exhibited electrocatalytic activity. The mechanism of surface charging of oxidized catalysts is quite different from that of bare metal surfaces, since it is governed by the pH-dependent acid–base dissociation of the surface OH⁻ ions. Behaving as weak acids or basis, these groups exchange protons with the electrolyte. This is the basis of the mechanism by which the inner sites can be active in reactions involving water molecules [29].

CONCLUSIONS

This research was motivated by the idea to reduce the amount of noble metals in the electrocatalysts, studying the addition of non-noble metal Co in platinum or ruthenium metallic phase. According to the presented results the following conclusions can be drawn:

1. Addition of cobalt in platinum or in ruthenium considerably increases the catalytic activity of pure Pt or Ru for both hydrogen and oxygen evolution. In the Pt based systems this is due to both size and intrinsic effect, while in the case of Ru, this is result only of intrinsic effect. Co has shown as promoter for reducing of Pt particles (size effect), while smaller Pt particles cause the d-band center to approach to Fermi level, achieving better adsorption of adsorbates. As a total effect, considerably higher catalytic activity was achieved with double lower amount of platinum in the multimetallic systems than that of pure metallic catalysts.

2. The studied electrocatalytic systems have shown poor activity for hydrogen evolution due to large particles (180-200 nm) and low specific surface area (4.2 m^2g^{-1}) of the catalyst support – Magneli phases. One should be considered and the low amount of the metallic phase in the electrocatalysts of only 10 %. Contrary to the inferior activity for hydrogen evolution, the studied electrocatalysts have shown very satisfactory activity for oxygen evolution. In this case, Magneli

phases behave not only as support material, but also, as an active oxidized electrode.

Therefore, an appropriate “bottom-up” technique for preparation of Magneli phases should be applied to obtain support material in nanodimensions (20 to 50 nm) instead of the presented mechanical treatment. This would improve considerably the catalytic activity for hydrogen evolution, while extra-ordinary catalytic activity for oxygen evolution should be expected.

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REFERENCES

- 1.K. Lee, J. Zhang, H. Wang, D. P. Wilkinson, *J. Appl. Electrochem.*, **36**, 507 (2006).
- 2.P. Paunović, O. Popovski, A. T. Dimitrov, in: Nanotechnological Basis for Advanced Sensors, J.P. Reithmaier, P.Paunović, W. Kulish, C. Popov, P. Petkov (eds), Springer Science+Business Media B.V., p. 545. (2011).
- 3.M. M. Jakšić, *Mater. Chem. Phys.*, **22**, 1 (1989).
- 4.M. M. Jakšić, *J. Mol. Catal.*, **38**, 161 (1986).
- 5.S. J. Tauster, S. C. Fung, R. L. Garten, *J. Am. Chem. Soc.*, **100**, 170 (1978).
- 6.S. G. Neophytides, S. Zaferiatos, G. D. Papakonstantinou, J. M. Jakšić, F. E. Paloukis, M. M. Jakšić, *Int. J. Hydrogen Energy*, **30**, 131 (2005).
- 7.J. M. Jakšić, N. V. Krstajić, Lj. M. Vračar, S. G. Neophytides, D. Labou, P. Falaras, M. M. Jakšić, *Electrochim. Acta*, **53**, 349 (2007).
- 8.M. M. Jakšić, *J. New Mater. Electrochem. Syst.*, **3**, 153 (2000).
- 9.P. Paunović, O. Popovski, G. Načevski, E. Lefterova, A. Grozdanov, A. T. Dimitrov, *Bulg. Chem. Com.*, this issue.
- 10.E. Antolini, E. R. Gonzales, *Solid State Ionics*, **180**, 746 (2009).
- 11.P. Serp, M. Corrias, P. Kalck, *Appl. Catal.*, **A**, **253**, 337 (2003).
- 12.BG patent appl. no 38581; 1978.
- 13.H. Kita, *J. Electrochem. Soc.*, **113**, 1095 (1966).
- 14.E. Slavcheva, V. Nikolova, T. Petkova, E. Lefterova, I. Dragieva, T. Vitanov, E. Budevski, *Electrochim. Acta*, **50**, 5444 (2005).
- 15.P. Paunović, I. Radev, A. T. Dimitrov, O. Popovski, E. Lefterova, E. Slavcheva, S. HadžiJordanov, *Int. J. Hydrogen Energy*, **34**, 2866 (2009).
- 16.A. E. Stoyanova, E. D. Lefterova, V. I. Nikolova, P. T. Iliev, I. D. Dragieva, E. P. Slavcheva, *Bulg. Chem. Com.*, **42**, 167 (2010).
- 17.S. Papadimitriou, A. Tegou, E. Pavlidou, S. Armanyanov, E. Valova, G. Kokkinidis, S. Sotiropoulos, *Electrochim. Acta.*, **53**, 6559 (2008).
- 18.P. Norlander, J. K. Nørskov, F. Besenbacher, *J. Phys. F: Met. Phys.*, **16**, 1161 (1986).
- 19.J. K. Nørskov, T. Bligaard, A. Logadottir, S. Bahn, L. B. Hansen, M. Bollinger, H. Bengaard, B. Hammer, Z. Sljivancanin, M. Mavrikakis, Y. Xu, S. Dahl, C. Jacobsen, *J. Catal.*, **209**, 275 (2002).
- 20.R. Ojani, J. BakhshRaoof, E. Hasheminejad, *Int. J. Hydrogen Energy*, **38**, 92 (2013).
- 21.P. Paunović, D. StoevskaGogovska, O. Popovski, A. Stoyanova, E. Slavcheva, E. Lefterova, P. Iliev, A. T. Dimitrov, S. HadžiJordanov, *Int. J. Hydrogen Energy*, **36**, 9405 (2011).
- 22.S. Trasatti, *Electrochim. Acta*, **29**, 1503 (1984).
- 23.N. Sato, T. Ohtsuka, *J. Electrochem. Soc.*, **125**, 1735 (1978).
- 24.L. D. Burke, O. J. Murphy, *J. Electroanal. Chem.*, **109**, 373 (1980).
- 25.S. Siracusanu, V. Baglio, C. D’Urso, V. Antonucci, A. S. Aricò, *Electrochim. Acta*, **54**, 6292 (2009).
- 26.M. García-Mota, A. Vojvodić, H. Metiu, I.C. Man, H-Y. Su, J. Rossmeisl, J. K. Nørskov, *Chem. Cat. Chem.*, **3**, 1607 (2011).
- 27.A. Stoyanova, G. Borisov, E. Lefterova, E. Slavcheva, *Int. J. Hydrogen Energy*, **37**, 16515 (2012).
- 28.S. HadžiJordanov, *Bull. Chem. Technol. Macedonia*, **16**, 75 (1997).
- 29.J. C. F. Boodts, S. Trsatti, *J. Appl. Electrochem.*, **19**, 255 (1989).

ЕЛЕКТРОКАТАЛИЗАТОРИ С НАМАЛЕНО СЪДЪРЖАНИЕ НА БЛАГОРОДНИ МЕТАЛИ ЗА ОТДЕЛЯНЕ НА ВОДОРОД/КИСЛОРОД С МАГНЕЛИ ФАЗИ КАТО КАТАЛИТИЧЕН НОСИТЕЛ. ЧАСТ II: ЕЛЕКТРОХИМИЧНО ОХАРАКТЕРИЗИРАНЕ

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(Резюме)

Предмет на това изследване е електрохимично тестване на наноразмерни електрокатализатори, състоящи се от Магнели фази като носител и различни метални фази (Co, Pt, Ru, CoPt (Co:Pt = 1:1 тегл.), CoRu (Co:Ru = 1:1 тегл.) и CoPtRu (Co: Pt: Ru = 1:0,5:0,5 тегл.)). Електрокаталитичните материали са синтезирани по зол-гел метода, като са използвани органометални прекурсори (Me-ацетилацетонат), нанесени върху диспергирани Магнели фази в тегловно съотношение 10% Me и 90% Магнели фази.

Електрохимичното тестване на изследваните електрокатализатори се извършва във воден алкален електролит. Редът на активността за отделяне на водорода е следният: CoPt > CoPtRu > CoRu, докато за отделянето на кислорода: CoRu > CoPtRu > CoPt. Co се проявява като промотор за намаляването на размера на Pt частиците (най-активната монометална фаза), така че намаляването на количеството Pt в металната фаза е компенсирано с по-малки частици. Също така взаимодействието между металните фази (преместването на центъра на d-ниво до стойности по-близки до нивото на Ферми) увеличава вътрешната каталитична активност, както за отделянето на водород, така и за кислорода. Поради големите частици на Магнели фазите, каталитичната активност е по-ниска в сравнение със съответните електрокатализатори, нанесени върху въглеродни наноматериали. Но те са много добри катализатори за отделянето на кислорода, тъй като Магнели фазите в този случай се държат не само като субстрат, но и като активен оксиден електрод.

Ключови думи: Магнели фази, Co, Pt, Ru, отделяне на водород, отделяне на кислород.