

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

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The subject of this study is preparation and physical characterization of nano-scaled electrocatalysts for water electrolysis, 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.)). Magneli phases were mechanically treated (top-down approach) to reduce their particles from micro to nano scale. 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. Pure Magneli phases and the studied electrocatalysts were characterized by means of TEM, XRD and BET analysis. The obtained results have shown that the size of the micro-scaled Magneli phases after the applied mechanical treatment, were reduced to 180÷200 nm. Specific surface area of 4.2 m²g⁻¹ was determined by BET analysis. After grafting of the metallic phase over the Magneli phase, good dispersion of the catalytic centers over the support surface was achieved, that is appropriate for catalytic purpose. Metallic particles are nano-scaled in the range of 2 to 15 nm, thus the BET surface area of the electrocatalysts is higher (4.3 to 11 m²g⁻¹) related to the BET surface area of pure Magneli phases.

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

INTRODUCTION

In the last decade, non-stoichiometric titanium oxides, so called Magneli phases (trade name Ebonex) have attracted great attention within the hydrogen economy, as potential support material for nano-scaled electrode materials for fuel cells and water electrolysis [1–3]. Generally, the support material should meet the following important characteristics, such as: i) highly developed surface area to provide better dispersion of the nano-scaled catalytic particles; ii) high electric conductivity to provide efficient electron transfer to ions involved in the electrochemical reactions, iii) mechanical and chemical stability and iv) to improve intrinsic catalytic activity of the active catalytic phase through the strong metal-support interaction (SMSI). In the electrocatalytic systems with metallic (catalytic phase), Magneli phases have bifunctional role: i) as a catalyst support and ii) 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 metal component as the main catalytic phase (by reinforcing it) and to the catalyst's stability (due to stronger adherence between catalyst's components) [4,5].

The main general formula of Magneli phase is Ti_nO_{2n-1} (4 < n < 10) [6]. It was observed that removing oxygen from the TiO₂ octahedra leads to shear planes in the crystal structure and forming of TiO octahedron. Depending of the ratio of TiO₂ vs. TiO octahedra within the crystal structure, different non-stoichiometric titanium oxides can appear [6,7]. Within this way formed crystal lattices, besides Ti⁴⁺ ions, also Ti³⁺ ions exist, which are responsible for increasing of electrical conductivity by three orders of magnitude, approaching the conductivity of graphite-like carbon nanomaterials [8,9]. Magneli phases show very similar physical properties to that of TiO₂, so they could be used for the same applications as that of TiO₂. The only difference in the properties of Magneli phases and TiO₂ is high electric conductivity, which make the Magneli phases applicable in more fields such as sensing [7], electrocatalysis [10,11] and energy storage [12–14]. The high electrical conductivity, chemical stability and possibility for interaction with the metallic catalytic phase, make them as an appropriate support material for electrocatalysts. The main disadvantage of Magneli phases as support material is the low specific surface area, compared with nano-scaled

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carbon materials with specific surface area of more than 250 m²g⁻¹. The maximal achievement of the “top-down” procedures for preparation of Magneli phases including mechanical reduction of the particle size (attrition and milling) was specific surface area to 1.6–3.0 m²g⁻¹ [11,15]. The “bottom up” approach employing high temperature reduction in atmosphere of hydrogen and inert gas (N₂ or Ar) has enabled specific surface area of 25.3 m²g⁻¹ [16] or 26.6 m²·g⁻¹ [10] so far. Maximal achievement of “bottom up” approach was 45 m²g⁻¹ [17], but with lower electrical conductivity of 4.7 Scm⁻¹.

The aim of this work is to prepare and characterized a electrocatalysts with reduced amount of noble metals, deposited on Magneli phases as a support material.

EXPERIMENTAL

As a catalyst support commercial micro-sized Magneli phases were used (Ebonex®, Altraverda, UK). To reduce their particle size, top-down approach was applied, using mechanical treatment by Fritsch Planetary Mill (Pulverisette 5) for 20 h with acceleration of balls of 200 rpm. The ball diameter was 1 cm, while the weight ratio of balls vs. treated material was 3:1.

The electrocatalytic materials were prepared using simplified sol-gel method proposed by the present authors [18]. Magneli phases were dispersed in organic solvent – anhydrous ethanol (Merck, p.a.), using magnetic stirrer with 600 to 900 rpm. Metallic phase as organometallic compound (Me-2,4-pentaedionate, Me = Co, Pt, Ru; Alfa Aesar, Johnson Matthey, GmbH) was added into the support’s suspension. The mixture was evaporated at temperature below 60 °C, with continuous stirring. The obtained fine catalyst’s powder was thermally treated for 1 h at 250 °C in inert (N₂) atmosphere in order to remove the residual organic groups from organometallics. The composition of the prepared electrocatalysts is shown in Table 1.

The catalyst support (mechanically treated Magneli phases) and the prepared electrocatalysts were observed by transmission electron microscope (TEM) FEI Tecnai G2 Spirit TWIN equipped with LaB6. XRD measurements were carried out by X-ray powder diffractometer Philips APD 15, with CuKα radiation. The diffraction data were collected at a constant rate of 0.02 deg over an angle range of 2θ from 20 deg to 80 deg. The average crystallite size was calculated from the broadening of the XRD peaks using the Scherrer’s equation [19]. Specific BET surface area of the samples was determined using measurements of isothermal nitrogen adsorption by Quantachrome NovaWin, Quantachrome Instruments version 11.0. Zeta

potential measurements of Magneli phases were performed using Zeta Meter System 4.0 – electrochemical cell which works on the principle of electrophoresis, at room temperature (23 °C) and pH = 7. As a surface active agent (anionic surfactant), sodium dodecyl sulfate was used.

Table 1. Composition of the studied electrocatalysts

Sample	Metallic phase 10%, wt.	Support 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
E-6	CoPtRu, 1:0.5:0.5,wt.	Ebonex

RESULTS AND DISCUSSION

Characterization of the catalysts support – Magneli phases

According to TEM images shown in Fig. 1, it was determined that the size of mechanically treated Magneli phases (Ebonex) is in submicron-scaled region, near 180 to 200 nm. Our previous research [3] has shown that this value of particle size is maximum achievement of the mechanical treatment of Magneli phases. The difference of the particle size of Magneli phases treated for 16 and 20 h is only 10-15 nm. Therefore, further mechanical treatment would exceed the critical value of the surface energy and the treated material would tend to reach the thermodynamic steady state through agglomeration of the particles.

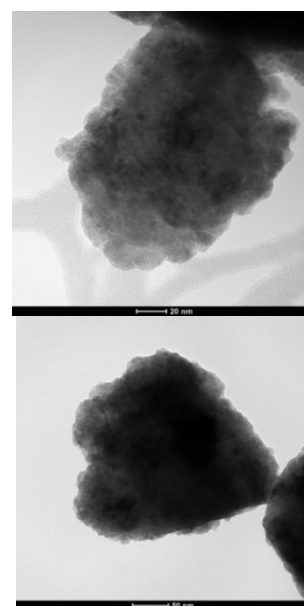


Fig. 1. TEM images of Magneli phases mechanically treated for 20 h

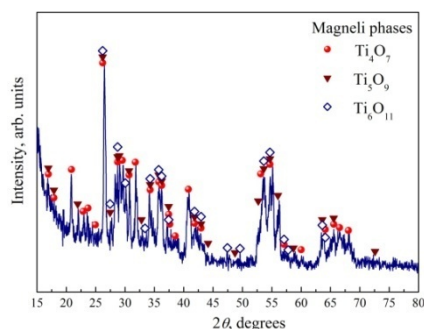
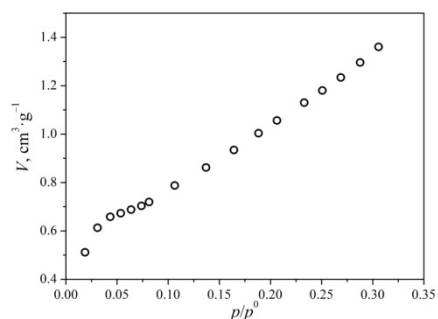
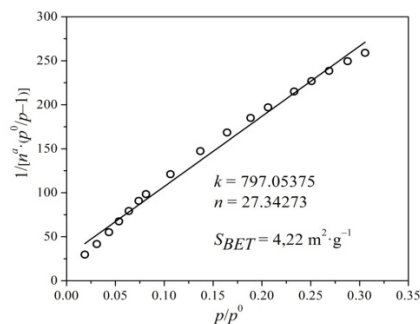


Fig. 2. XRD spectrum of Magneli phases mechanically treated for 20 h

Qualitative identification of Magneli phases was performed by means of XRD analysis. Characteristic peaks of the Magneli phase's constituents such as Ti_4O_7 , Ti_5O_9 and Ti_6O_{11} are on different positions



a)



b)

Fig. 3. Nitrogen adsorption curves of Magneli phases: a) as-measured in plot $V \div p/p^0$ and b) linearized adsorption curve in plot $1/[n^a \cdot (p^0/p - 1)] \div p/p^0$.

Specific surface area (m^2g^{-1}) of Magneli phases was determined by the nitrogen adsorption curve shown in Fig. 3a. After linearization of this curve (Fig. 3b), BET surface area of $4.2 \text{ m}^2\text{g}^{-1}$ was calculated. This is good achievement of the applied mechanical treatment, compared with the corresponding results of other studies, ranging from 1.6 to $3 \text{ m}^2\text{g}^{-1}$ [1,11].

Characterization of the electrocatalysts

The studied electrocatalysts were prepared by sol-gel route and contain only 10 %wt. metallic phase (see Table 1) deposited on mechanically treated Magneli phases as support material. Shown in Fig. 4 are their TEM images. Generally, one can say that metallic particles (active catalytic centers) are uniformly dispersed over the surface of catalyst support (Magneli phases), and there is no segregation on particular areas of the surface.

that correspond to peaks of the basic XRD peaks of rutile [20]. As the content of oxygen decreases within the rutile octahedra, TiO octahedron is forming. Due to the different ratio of TiO_2 and TiO in the different Magneli phases, different diffractions of X-rays occur than in rutile octahedral. As result, the XRD spectrum of Magneli phases contains larger number of less pronounced, widespread and less intensive peaks along whole range of 2θ [21] (Fig. 2). As result of presence of TiO , some of them are less shifted compared with the basic rutile peaks, but most of them are on quite different positions. The peaks of first three homologues Ti_4O_7 , Ti_5O_9 and Ti_6O_{11} can be seen, while the rest homologues are in small quantity and their peaks are very less intensive and cannot be detected within the spectra.

Uniform dispersion provides active participation of all catalytic centers (metallic particles) over the whole surface of the catalysts in adsorption/desorption processes with ionic/atomic participants in the electrochemical reactions. This intensifies the total electrochemical reaction, at constant intrinsic activity of the metallic phase. Good dispersion of the metallic particles was expected according to the Zeta potential value of the support material – Magneli phases. The measured value of -48.3 mV highlights on their good stability and dispersibility, while the negative sign points out that the particles of Magneli phases are surrounded by negatively charged ions within the suspension. This is suitable for better attracting the positive metallic ions over the whole surface of the support material. So, the result of Zeta potential measurements is in good agreement with TEM analysis.

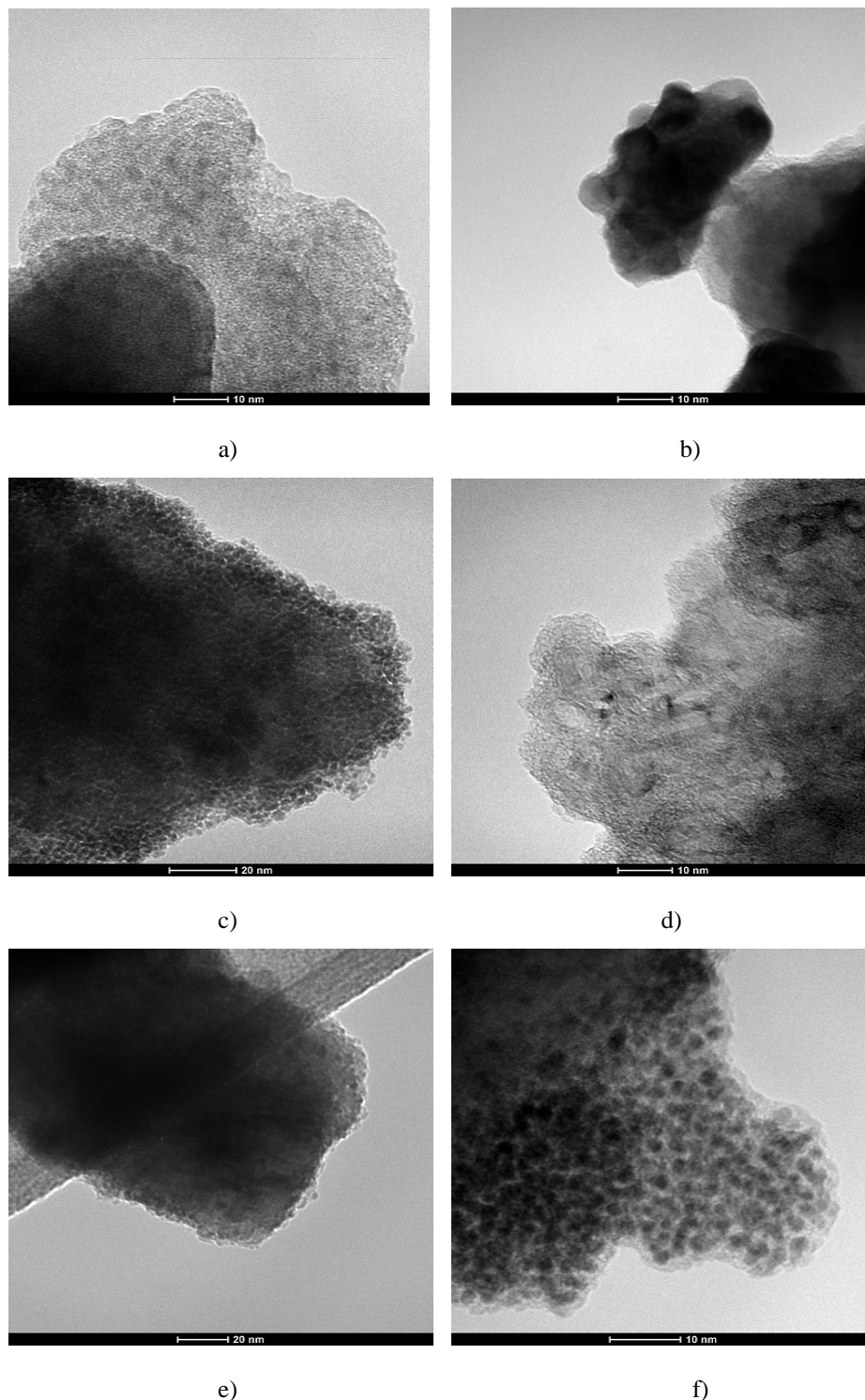


Fig. 4. TEM images of the studied electrocatalysts: a) E-1, b) E-2, c) E-3, d) E-4, e) E-5 and f) E-6

In sample E-1 (Fig. 4a) prevailing cobalt particles with an average size of 2 to 3 nm, and in the darker part of the image, particles with size of 10 to 15 nm can be seen. These larger particles are in very small amount. Sample E-2 (Fig. 4b) contains uniformly dispersed platinum particles with variation in size from 5 to 15 nm. Very fine dispersed particles of the metallic phase over the support surface, with size of 2 to 3 nm can be observed in the sample E-3 based

on Ru metallic phase (Fig. 4c). Also, the sample E-4 with mixed metallic phase, CoPt (Fig. 4d) has shown outstanding dispersion of the metallic particles with size of 2 to 3 nm, and less quantity with size of near 5 nm. The size of metallic particles in the sample E-5 containing CoRu (Fig. 4e) is 2 to 4 nm, while in the sample E-6 containing CoPtRu is 3 to 5 nm.

In order to detect the catalysts constituents, their crystalline state, possibility of formation the solid

solutions and/or intermetallic compounds in polymetallic phase, the presence of oxidized state, etc., XRD analysis was applied. The obtained XRD spectra of the studied electrocatalysts are shown in Fig. 5.

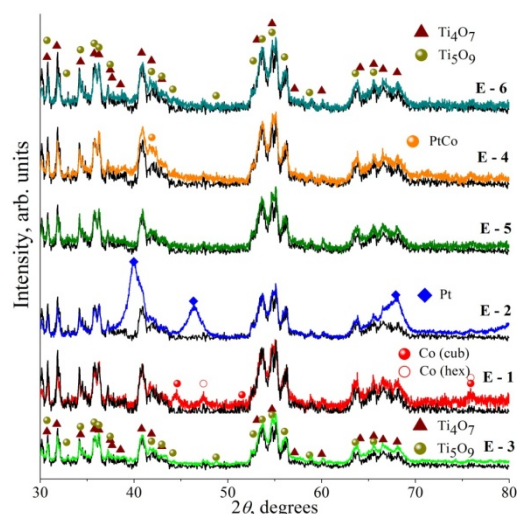


Fig. 5. XRD spectra of the studied electrocatalysts

In the electrocatalysts with pure Co and Pt (E-1 and E-2), crystalline metallic phase was detected. The crystallites size was determined using Scherrer equation [19] and fitting procedure was applied for determination of the FWHM (full width at half maximum). In the sample E-1 cubic and hexagonal crystalline metallic phase were detected with size of near 13 nm. The corresponding weak pronounced peaks, highlight on low amount of this phase within the electrocatalysts, while the size of the main part of the Co metallic phase is very small, near 2 nm, and in oxidized state. For the sample E-2, two strong, relatively broad platinum peaks were registered, corresponding to crystal orientation of 111 and 200. Average size of 111 crystallites is 8 nm, while that of 200 crystallites is 6 nm. In the spectrum of sample 4 with mixed metallic phase, CoPt, one can see weak and broad peak at position of $2\theta = 41.8^\circ$, corresponding to the solid state solution type of CoPt alloy. The size of these particles is 2 nm. According to the previous researches [22,23], and here was confirmed that in the presence of cobalt, platinum has smaller particles, which means that cobalt is a promoter to reduce the platinum nanoparticles. Therefore, one can expect that the catalytic activity of this electrocatalyst (E-4) could be close or even better than that of electrocatalysts containing pure Pt as metallic phase (E-2), although it contains less than half quantity of Pt. XRD spectra of the electrocatalysts containing Ru (E-3) and mixed CoRu (E-5) metallic phase, coincide with the spectrum of pure Magneli phases, which means that no metallic phase was detected. Hence, the metallic

phase in these catalysts is in amorphous or most probably in oxidized state (oxides and/or hydroxides).

Shown in Table 2 are the values of BET surface area of the studied electrocatalysts, calculated as was explained in previous section. Addition of the nanoscaled metallic phase more or less increases the BET surface area of the electrocatalysts related to the pure Magneli phases. In the monometallic systems, this effect is most pronounced in the case of addition of Ru, while Pt has shown the lowest effect. In the sample E-2, platinum insignificantly increased the surface area related to the pure Magneli phases (4.3 vs. 4.2 m^2g^{-1} , respectively). The increased BET surface area of the sample E-4 (CoPt) is result of addition of Co. Comparing the Ru based electrocatalysts, one can see that addition of Co in the Ru metallic phase (E-5) decreases the BET surface area (9.4 m^2g^{-1}) related to the monometallic Ru based electrocatalysts (E-3), which has shown the highest BET surface area (11 m^2g^{-1}). Also, in the sample E-6 based on CoPtRu, platinum and cobalt have decreased the BET surface area to 6.4 m^2g^{-1} . Generally, higher BET surface area means higher catalytic activity as result of larger available area for adsorption/desorption processes. But also, one should consider the intrinsic catalytic activity of the metallic phase. However, the values of BET surface area can be used for explanation of electrocatalytic activity of the studied catalysts.

Table 2. BET surface area of the studied catalytic materials

	10% metallic phase + 90% Ebonex	BET s. a., m^2g^{-1}
	Pure Magneli phases	4.2
E-1	Co	6.1
E-2	Pt	4.3
E-3	Ru	11.0
E-4	CoPt, 1:1, wt.	7.6
E-5	CoRu, 1:1, wt.	9.4
E-6	CoPtRu, 1:0.5:0.5, wt.	6.4

CONCLUSIONS

The study presented in this paper was motivated by the idea to use Magneli phase as support for electrocatalysts aimed for hydrogen/oxygen evolution, instead of nano-scaled carbon support materials, and to investigate 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. The size of the micro-scaled Magneli phases by the applied mechanical treatment were reduced to 180 to 200 nm, with specific surface area of 4.22 m^2g^{-1} and high stability and dispersibility in liquid

media. This is a good achievement for this type of treatment.

2. Metallic phase was uniformly dispersed over the support surface providing active participation of all catalytic centers in adsorption/desorption processes with ionic/atomic participants in the electrochemical reactions.

3. The size of different metallic particles within the studied electrocatalysts is in range of 2 to 15 nm, which points out that the support material successfully prevent the agglomeration and segregation of metallic phase over the catalyst surface.

4. The obtained results point out that the studied electrocatalysts could be used as an effective electrode material for water electrolysis.

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

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(Резюме)

Предмет на това изследване е синтез и физическо охарактеризиране на наноразмерни електрокатализатори за водна електролиза, 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.)). Магнели фазите са механично обработени за да се намалят техните частици от микро до наноразмери. 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. Чистите Магнели фази и изследваните електрокатализатори са охарактеризирани с помощта на ТЕМ, РД и БЕТ анализ. Получените резултати показват, че размерът на микроразмерните частици на Магнели фазите след приложеното механично третиране е намален до 180-200 nm. Специфичната повърхност, определена чрез БЕТ анализ е 4,2 m²g⁻¹. След нанасяне на металната фаза върху Магнели фазите се постига добра дисперсия на каталитичните центрове върху носещата повърхност, което е благоприятно за каталитичния процес. Металните частици са наноразмерни в диапазона от 2 до 15 nm и следователно специфичната повърхност на електрокатализаторите е по-висока (4.3 до 11 m²g⁻¹) спрямо тази на чистите Магнели фази.

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