

Influence of metal loading on morphology and performance of oxide supported cobalt electrocatalysts

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This work presents a research on the synthesis of composite nanosized Co-based materials deposited by sol-gel method on Magnelli phase titanium oxide (MPT) and their investigation as anode catalysts for alkaline water electrolysis. The chemical composition, surface structure and morphology are characterized by EDX, SEM, and XRD analysis. The activity toward the partial electrode reaction of oxygen evolution (OER) is assessed in aqueous alkaline media at room temperature. Cyclic voltammetry and steady state polarization curves are used to obtain information about the reactions proceeding on the catalysts surface, to determine the potentials of oxygen offset and the corresponding current densities and thus, to assess the OER catalytic efficiency. The results obtained showed that the Co-based MPT-supported catalysts are stable at the aggressive conditions of the alkaline water electrolysis. The metal content influences the structure and morphology. Among the tested samples the one with 30 wt.% metal content (Co30) demonstrates superior performance and best catalyst utilization. The OER starts at 0,64V (vs. Ag/AgCl) and reaches current density of about 55 mA cm⁻² already at 0,75V. This is explained with size effects (smallest Co particles) ensuring largest electrochemically active surface area.

Keywords: hydrogen generation, alkaline water electrolysis, non-precious catalysts, oxide support

INTRODUCTION

Since the first observation of water electrolysis by van Trostwijk and Deiman in 1789 [1,2] this method for hydrogen generation has been investigated in depth by many authors [3-7]. It is characterized with flexibility, almost zero detrimental emissions, and high purity of the produced gases. However, in order to become an economically attractive, the technology still needs to be improved in terms of efficiency and durability. The main classification of water electrolysis is based on the type of the used electrolyte (aqueous solution or solid polymer membrane) and the operating temperature. The classical water electrolysis which is a well-established technological process for decades is carried out in aqueous alkaline electrolytes. This type of electrolysis has the advantage of using cheap non-noble metal catalysts, while the main drawbacks are the decrease of process efficiency at high loads and potential risk of environment pollution due to leakage of the aggressive electrolyte. The electrolysis of water in cells with a

solid polymer electrolyte is a relatively new technology. In advanced stage of development are the electrolyzers using proton exchange membranes (PEMWE). Such systems with capacity of up to 10 Nm³/h are already available on the market. They offer number of advantages compared to the classical alkaline electrolysis: efficiency reaching 95% at current density of 1-2 A cm⁻², very high purity of the produced gases, compatibility with renewable energy sources, environmentally friendly [8-10]. The main problem in regard to this technology is the fact that hydrogen produced in PEMWE is still rather expensive due to the high price of the used polymer membranes and the rare noble metal catalysts [11,12]. Recently there is an increasing interest in development of electrolyte membranes with anion (OH⁻) conductivity. The usage of anion exchange membrane (AEM) would prevent the deposition of solid carbonaceous residue on the electrode / electrolyte interface, which in the conventional aqueous alkaline electrolyzers often leads to problems during the start-ups of the system. Another major advantage of this type of hydrogen generators is the possibility to use inexpensive and broadly available catalysts (mainly non-precious transition metals from the

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iron group and their alloys). In summary, AEMWE are supposed to combine the advantages of the classical aqueous alkaline and the acidic PEM systems - cheaper base metal catalysts, high efficiency, none risk for environment pollution.

Common to both PEMWE and AEMWE is the significant overpotential at the anode side where the oxygen evolution reaction (OER) takes place [13]. The OER is studied intensively for decades in order to elucidate the reaction mechanism. Various anode catalysts are employed in effort to minimize the energy loss during water electrolysis. The investigations are aimed to development of catalysts combining high efficiency with corrosion stability and performance durability. The establishment and elucidation of the correlation between catalyst activity and catalyst corrosion mechanisms is another important objective. Such an analysis allows for better understanding of the advanced catalysts design principles and definition of best trade-off between activity and stability.

One way to reduce the cost of the catalysts is to disperse the active component on catalytic support with high surface area and thus, to increase the catalyst utilization [14,15]. Thus obtained composite catalysts often show higher activity compared to the non-supported metals due to realization of electronic interactions with the support. The effect is known as strong metal-support interaction (SMSI-effect) [16]. It is related to redistribution of the electron density of the active surface sites which influences the adsorption strength of the intermediates and facilitates the mechanism of the electrode reactions. As a result, the catalytic loading can be drastically reduced preserving the efficiency of the electrolysis. The main advantage of the most broadly used carbon supports is their high surface area (over $200 \text{ m}^2 \text{ g}^{-1}$) combined with excellent electro-conductivity. Unfortunately, the carbon is not suitable for electrolysis applications since the high operative potentials cause its oxidation, followed by gradual electrode degradation and consequent failure of the system. Therefore, recently there is an increased interest in application of non-carbon supporting materials such as carbides, nitrides, and oxides which in addition to the required high surface area and good electrical conductivity offer increased chemical and electrochemical stability.

It is known that the metals from the iron group (Fe, Ni, Co, etc.) have high catalytic activity and corrosion stability in alkaline solutions, and that some of their composite and alloy systems demonstrate even superior performance compared to the pure metals [17-19]. This is due to increased

surface roughness as well as to changes in the electronic structure of the mixed catalysts leading to synergism. The catalytic activity of these systems can be further enhanced if they are dispersed on properly chosen catalytic support ensuring SMSI-effect. Such approach is applied and proven to be favourable in PEMWE [20], while in alkaline electrolysis there is a lack of systematic research and publications on the topic.

The main objective of this work is the preparation of advanced corrosion resistant composite catalysts based on cobalt nano-particles deposited on Magnelli phase titanium oxide and investigation of the influence of embedded metal content on the catalysts structure, morphology, and OER efficiency in alkaline water electrolysis. Another important aspect of the research is to elucidate the expected metal/support interactions and the resulting effects on electrode performance and durability.

EXPERIMENTAL

The catalysts under study are prepared by sol-gel method using acetylacetonate precursor $\text{Co}[\text{C}_5\text{H}_7\text{O}_2]_2$ (Alfa Acer). The cobalt nanoparticles are supported on Magnelli phases titanium oxide with general formula $\text{Ti}_n\text{O}_{2n-1}$ (MPT, Ti-dynamics Co. Ltd). The metal content is varied in the range 20-40 wt.% and the test samples are denoted accordingly (Co20, Co30, and Co40). The preparation procedure includes two steps: i) pretreatment of the support and the metal precursor using magnetic stirrer and ultrasonic bath, their mixing, and heating at 60°C under constant stirring until a fine gel is obtained; ii) thermal treatment of the obtained mixture at 240°C in reducing H_2 -atmosphere for 2 hours and gradual cooling to room temperature. The obtained powder is homogenized in a mortar and stored in dry oxygen-free atmosphere. To prepare the test electrodes the catalysts are mixed with propanol, spread as a thin film on the top of commercial gas diffusion layer (Freudenberg, Germany), and left to dry at room temperature.

The surface area of the support is measured by BET analysis. The composition, surface structure and morphology of the synthesized composite catalysts are studied by energy dispersion elemental analysis (EDX), scanning electron microscopy (SEM), and X-Ray diffraction (XRD) methods. SEM and EDX analysis are obtained by JEOL JSM 6390 electron microscope (images in secondary and back-scattered electrons), equipped with INCA Oxford elemental detector. XRD analysis is

performed by X-ray diffractometer Philips APD15. The diffraction data were collected at a constant rate of $0.02^\circ \text{ s}^{-1}$ over an angle range of $2\theta = 10\text{--}90^\circ$. The size of Co crystallites is determined by Scherrer equation [21].

The electrochemical performance and catalytic activity toward the oxygen evolution reaction are investigated applying the common experimental techniques of cyclic voltammetry and steady state polarization. The experiments are carried out in aqueous alkaline media (25% KOH) at room temperature using a standard three-electrode electrochemical cell with Ag/AgCl reference electrode and Pt wire as a counter electrode. The working electrode has geometric area of 0.5 cm^2 and contains $0.5 \text{ mg}_{\text{Co}}\text{cm}^{-2}$. All electrochemical measurements are carried out with a commercial Galvanostat/Potentiostat POS 2 (Bank Elektronik, Germany).

RESULTS AND DISCUSSION

According the technical specification of the producer the chosen support, MPT, has surface area of $7\text{--}8 \text{ m}^2\text{g}^{-1}$, very good electrical conductivity and corrosion stability both in acidic and in alkaline media. The performed BET analysis verified a surface area of $8 \text{ m}^2\text{g}^{-1}$.

The MPT electrochemical performance in aqueous alkaline electrolyte is shown in figure 1. As expected the support is very stable at high anodic potentials where the oxygen evolution takes place. The measured low current is of pseudo-capacitive nature and does not change with time indicating lack of catalytic activity.

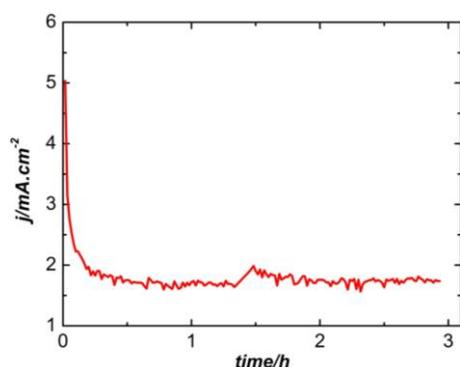


Fig. 1. Potentiostatic polarisation curve of MPT in 25% KOH at 1.8V.

To investigate the morphology and surface structure, XRD and SEM analysis were performed. The results obtained (figure 2 a,b) show that MPT consists of two well recognized crystalline phases -

(Ti_4O_7 and $\text{K}_x\text{Ti}_8\text{O}_{16}$) having homogeneously distributed particles with size in the range $100\text{--}150 \text{ nm}$.

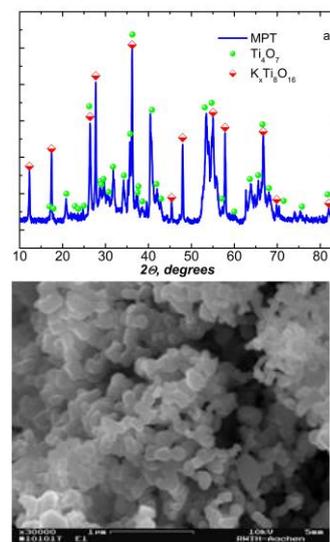


Fig. 2. X-ray diffraction patterns (a) and SEM image (b) of the MPT support.

Samples of the synthesized composite Co/MPT catalysts with target Co content 20, 30, and 40 wt.% (Co20, Co30, and Co40, respectively) are studied by energy dispersive X-ray diffraction to determine the exact metal content. The results obtained are presented in **Table 1**. They show that the amount of the detected cobalt correlates well with that introduced by the acetylacetonate precursor during the synthesis, except for Co20 in which case the deviation is relatively high.

Table 1. Cobalt content in the test samples determined by EDX analysis.

Sample	Co wt. %	
	target	obtained
Co20	20	15
Co30	30	29
Co40	40	40

According the SEM images (figure 3) the metal particles (white spots) of all three samples are homogeneously dispersed on the substrate, forming cauliflower-type aggregates.

The XRD spectra of the catalysts under study (figure 4) show the presence of metallic cobalt in all test samples. In Co20 the metal exists only in a hexagonal crystallographic state, while in Co30 and Co40 both hexagonal and cubic forms are detected. The values of the crystallite size determined by Sherrer equation using the half width of the full maximum (HWFm) of the peaks for all registered crystallographic planes are summarized in **Table 2**. They show that the synthesized catalysts have

relatively large cobalt crystallites with size varying in the range 30-50 nm. The smallest are the crystallites of the test sample having moderate cobalt content, Co30.

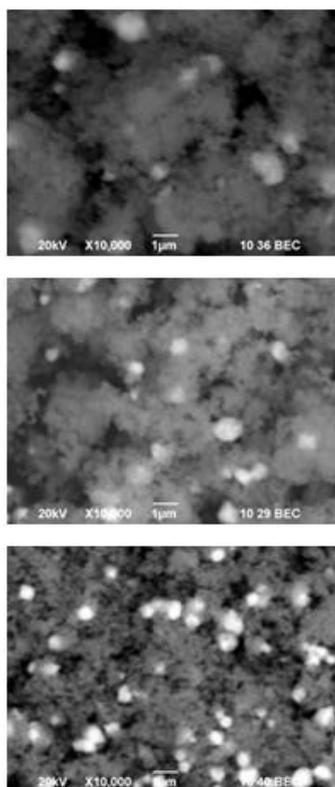


Fig. 3. SEM images (in back-scattered electrons) of the synthesized Co/MPT catalysts; a) Co20; b) Co30; c) Co40

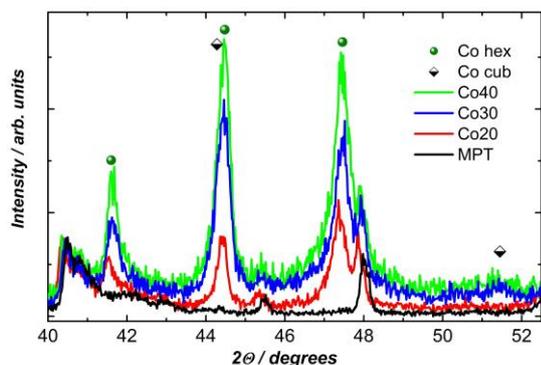


Fig. 4. X-ray diffraction patterns of the synthesized Co/MPT catalysts

The cyclic voltammograms in figure 5 show two well defined anodic current peaks related to changes in the oxidation state of Co (Co to Co^{2+} and Co^{2+} to Co^{3+}), followed by intensive oxygen evolution above 0,65V. The process starts earlier and is most intensive for the catalyst with 30 wt.% metal content. During the cathodic scan reduction current peaks can be seen on the curves of Co30 and Co40, while for the sample with lowest metal

content the cathodic branch of the curve is rather shapeless. The CVs do not change at long term cycling, demonstrating durability of the catalyst performance.

Table 2. Crystallite size of Co/MPT catalysts

Sample	hcp			fcc	
	41.6	44.5	47.7	44.5	51.5
	(100)	(001)	(101)	(111)	(200)
	nm	nm	nm	nm	nm
Co20	40	35	26	-	
Co30	26	30	20	20-	<10*
Co40	38	33	20	14	<10*

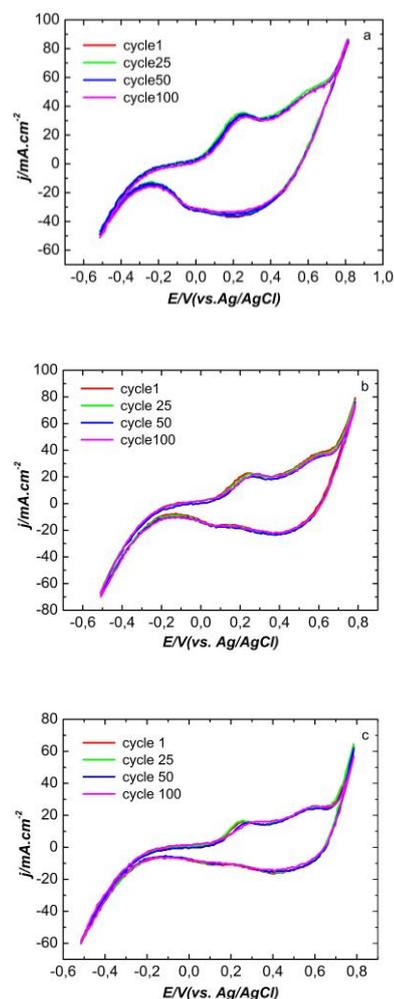


Fig. 5. Cyclic voltammograms of Co/MPT catalysts in 25% KOH at room temperature; a) Co20; b) Co30; c) Co40; potential scan rate 100 mV s^{-1}

The anodic polarisation curves are presented in figure 6. The intensity of the oxygen evolution reaction is nearly equal for Co30 and Co40, while the reaction proceeds slower on Co20.

In order to obtain information about the catalyst utilization, the morphology factor, f , is determined following the method of Da Silva [22]. The procedure is illustrated in figure 7.

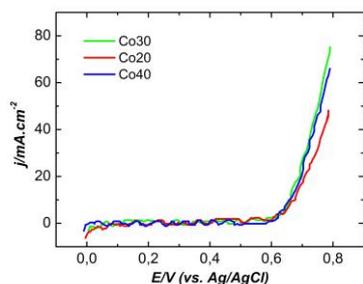


Fig. 6. Anodic polarisation curves of the Co/MPT in 25% KOH; room temperature; potential scan rate 1 mV s⁻¹

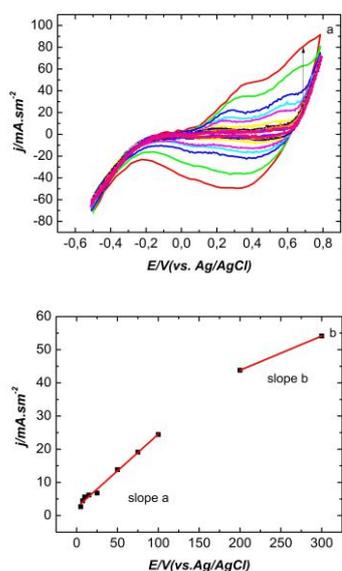


Fig. 7. Graphical illustration of DaSilva method for evaluation of catalyst utilization in OER porous electrodes

It includes recording of cyclic voltammograms at different scan rates and plotting the current at defined potential where the OER starts as a function of the scan rate. The slope of the obtained linear part of the curve at low scan rates (*slope a*) is a measure for the total capacity of the electrode surface C_T . The slope at high scanning rates (*slope b*) represents the capacity of the "external" easily accessible electrode surface, C_{EXT} . The difference $C_{INT} = C_T - C_{EXT}$ gives the capacity of the "internal" difficult to access surface. The ratio $f = C_{INT} / C_T$ gives the value of the morphology factor, which is a measure for the unused part of the catalyst. The calculated values of the morphology factor and the corresponding catalyst utilization are presented in Table 3. It is seen that for the catalysts under study the lowest f value is obtained for the sample Co30, meaning that for this catalyst the utilization is superior. The result correlates well with the data in Table 2 according which this sample has smallest

particles size which in turn, ensures the highest surface area available for the proceeding electrode reaction.

Table 3. Morphology factor and utilization of the Co/MPT catalysts

Sample	Co 20% wt	Co 30% wt	Co 40% wt
f	0.55	0.43	0.55

Finally, the stability of catalytic performance at long service was investigated, recording potentiostatic polarisation curves at high anodic potential of 1,8 V where an intensive oxygen evolution takes place. Figure 8 presents the results obtained in 48-hour experiment on the best performing electrode containing 0.5 mg cm⁻² Co30. It is seen that the intensity of the OER sustains for the whole duration of the experiment without any indications for decrease in catalyst performance and degradation of the electrode.

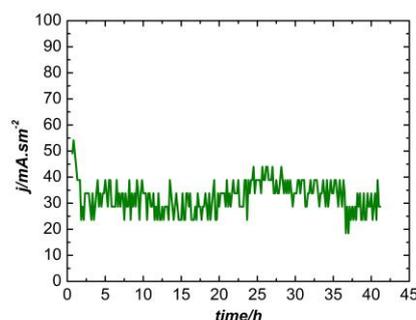


Fig. 8. Potentiostatic polarisation curve of Co30/MPT in 25% KOH.

CONCLUSION

The research performed verified that Magnelli phases titanium oxide is a promising catalytic support for application in alkaline water electrolysis. The synthesized Co/MPT catalysts possess high efficiency toward OER combined with good durability and corrosion resistance. The optimal metal loading of 30 wt. % Co ensures superior performance combined with best catalyst utilization, resulting from the most developed active surface of this sample. Further research is in progress focused on the influence of the electronic metal-support interactions on catalysts performance.

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ВЛИЯНИЕ НА КАТАЛИТИЧНОТО НАТОВАРВАНЕ ВЪРХУ МОРФОЛОГИЯТА И РАБОТНИТЕ ХАРАКТЕРИСТИКИ НА КОБАЛТОВИ ЕЛЕКТРОКАТАЛИЗАТОРИ, ОТЛОЖЕНИ ВЪРХУ ОКСИДЕН НОСИТЕЛ

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(Резюме)

Статията представя изследване върху синтеза на композитни наноразмерни материали на базата на кобалт, отложени по зол-гел метод върху Магнели фази титанов оксид и тяхното приложение като анодни катализатори за алкална електролиза на вода. Химичният състав, структурата на повърхността и морфологията са охарактеризирани с методите на сканираща електронна микроскопия (SEM), рентгеноструктурен анализ (XRD) и дисперсен елементарен анализ (EDX). Активността по отношение на реакцията на отделяне на кислород (OER) е определена във водна алкална среда при стайна температура. Методите на циклична волтаметрия и поляризационни криви са използвани за получаване на информация относно реакциите, които протичат на повърхността на катализаторите, за определяне на потенциалите, при които протича реакцията на отделяне на кислород при съответните токови плътности и на каталитичната активност. Получените резултати показват, че катализаторите на базата на кобалт, отложени върху оксиден носител са стабилни при агресивните условия на алкална електролиза на вода. Съдържанието на метал в катализаторите оказва влияние върху морфологията и структурата. От изследваните проби, тази с 30 тегловни процента съдържание на кобалт, показва отлична възпроизводимост и най-висока каталитична използваемост. Реакцията на отделяне на кислород (OER) започва при 0,64 V спрямо сравнителен електрод сребро/сребърен хлорид (Ag/AgCl), а при 0,75 V достига токова плътност от 55 mA.cm⁻². Това се обяснява с ефекта на размера на каталитичните частици - катализаторът с най-малки кобалтови частици, осигурява най-голяма активна повърхност.