

## Glassy carbon (GC) electrode modified with electrodeposited $ZrO_2$ and $ZrO_2 + Ce_2O_3 + Y_2O_3$ nanostructures as a cathode in the obtaining of active chlorine

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The experiments onto glassy carbon (GC), modified by electrodeposited oxide layers from zirconium, cerium and yttrium with sizes 30-100 nm are performed. The morphology and structure of deposits is characterised by SEM and elemental composition is investigated by XPS. Electrochemical activity of the modified glassy carbon is investigated by cyclic voltammetry as well by potentiodynamic method and tested with respect to the electrolysis of sodium chloride in order to obtain active chlorine. It is established, that the thin film of  $ZrO_2$  onto glassy carbon with intermediate layer of copper obtained in the regime of the reversible current increase the current efficiency of the process as a result of catalytic effect onto hydrogen evolution reaction.

**Keywords:** cyclic voltammetry, hypochlorite, modified cathode, nanostructures, oxides Ni-P plating; Zirconium dioxide ( $ZrO_2$ ), Metal-matrix composites; Flexible materials; Metal dispersion coatings.

### 1. INTRODUCTION

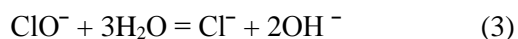
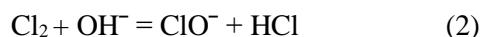
The modification of the electrode surface with deposits by organic and inorganic compounds, metals, metallic oxides, polymers, etc. favoured the widening of their application for the electrocatalytic and analytical properties, corrosion protection, improvement of magnetic and semiconducting properties and others. Especially the modification of the glassy carbon has important aspects. Some papers depict explanations of the obtaining of catalytic active thin films from the mixtures of  $RuCl_3 + K_4Ru(CN)_2$  [1] и  $OsO_4 + K_4Ru(CN)_6$  [2] onto glassy carbon. It has been proved, that rhuthenium film furthers the catalytic oxidation of  $As^{3+}$  [1] (also by mixed Os-Ru – thin film) methanol [3] and dythiocianat [4]. The coatings from  $Ag^{+1}$  and  $Mo(CN)_8^{-4}$  onto glassy carbon could also be used for the determination of the nonelectroactive ions [5].

In the last decade there has been a tendency in the modification of the surface of glassy carbon by films with the nuclei under 100 nm or shortly named nanostructures. The modification of the surface done this way gave the possibility for the wide application of the GS (mostly in the analytical chemistry) as an electrode with the increased sensitivity and selectivity for the determination of the different compounds as ascorbic acids [6], hydrazine [7], acetaminofenol [8], tyramine [9]

,  $Cr^{6+}$  [10], methylene blue [11], 2-4-6 trinitrotoluene [12], dopamine [13].

The method of obtaining electrochemically produced nanostructures is widely applied due to its advantages - ability to regulate the content of the coatings – the form and size of the particles, small expense, and easy control [14]. From this point of view the „template synthesis”, where the different materials – metals, oxides, semiconductors and other could be deposited onto porous substrate - polycarbonate „foams”, glassy carbon. By this way the process of the deposition ensures forming of nanotubes, nanorods and nanowires which dimensions could be easily controlled by changing the geometry of pores and the conditions of the electrodeposition [15-18].

It is well known that at by electrolysis of water solution of NaCl in the cell without diaphragm the follows processes proceed:



The reaction (3) occurs to be a secondary reaction which leads to a decrease of the yield of the active chlorine –  $ClO^-$ . In order to suppress this reaction some amount of  $Cr^{6+}$  is added which could be reduced onto the cathode to the  $Cr^{3+}$  and three valence chromium forms passive  $Cr(OH)_3$  film, which embarrass the access to the ions of  $ClO^-$  to the cathodic surface and thus, the rate of their reduction. This method is ineffective from an ecological point of view. Its alternative is a

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obtaining of suitable material with selective properties which allow the hydrogen evolution reaction and also embarrass the speed of cathodic reaction. Some appropriate material, investigated at the process of obtaining of active chlorine is  $ZrO_2$ , where the oxide is obtained by thermal and anodic oxidation of zirconium at the respected defined conditions [19].

The aim of the presented work is two-fold: modified glassy carbon electrode (500 pores  $inch^{-2}$ ) by nanosized layers of  $ZrO_2$  and  $ZrO_2 + Ce_2O_3 + Y_2O_3$  obtained electrochemically from organic (alcohol) solutions to be characterised by SEM, XPS, linear and cyclic voltammetry and moreover, by the method of cathodic efficiency the possibility to use this electrode as a cathodic material with mentioned selective properties to be proved.

## 2. EXPERIMENTAL

The experiments about modifying the electrode surface were performed onto samples from glassy carbon foam (500 pores  $inch^{-2}$ ) (with size 20x20 mm). Before electrolysis in the alcoholic solutions, containing Zr, Ce and Y onto carbon surface were deposited thin layer of copper (from sulfuric electrolyte) at different conditions (current density; time of deposition): sample 1 - 15  $mA\ cm^{-2}$ , 5 min; sample 2 - 1.5  $mA\ cm^{-2}$ , 2 - 5 min; sample 3 - reversive regime of deposition with cathodic period 240  $mA\ sec$  and anodic period - 15  $mA\ sec$  [20].

The samples has been deposited by  $ZrO_2$  in the solution of absolute ethyl alcohol, containing 60  $g\ dm^{-3}$  -  $ZrCl_3$  at the following conditions: for the sample 1 - at the temperature 15 °C, time of deposition - 1 hour, current density 250  $mA\ cm^{-2}$ , for the sample 2 - at the temperature 35 °C, time of deposition - 1 hour, current density 250  $mA\ cm^{-2}$ ; for the sample 3 - at the temperature 12 °C, time of deposition - 1 hour, current density 2000  $mA\ cm^{-2}$  [21].

The films of  $ZrO_2 + Ce_2O_3 + Y_2O_3$  was obtained onto glassy carbon with copper coatings, deposited during 50 sec - sample 4, 15 sec - for the sample 5 and the sample 6 was not deposited with sublayer of copper. The oxides were deposited in the solution of their respected salt in the absolute ethyl alcohol /  $ZrCl_3$  -3.2  $g\ dm^{-3}$ ,  $CeCl_3 \cdot 7H_2O$  -5.7  $g\ dm^{-3}$  и  $YCl_3 \cdot 6H_2O$  -3.5  $g\ dm^{-3}$  / at the potential 9 V, temperature 8-12 °C for 60 minutes/

The morphology, structure and the size of particles of the obtained  $ZrO_2$  and  $ZrO_2 + Ce_2O_3 + Y_2O_3$  thin films was studied by means of scanning electron microscopy (SEM) using a JEOL

200CX scanning microscope under conditions of secondary electron image (SEI).

The chemical states and composition of layers were investigated by XPS analysis. They were carried out by means of a VG Escalab Mk II spectrometer (England) using an Al  $K_{\alpha}$  excitation source (1486.6 eV) with a total instrumental resolution of ~1 eV, under a base pressure of  $1.10^{-8}$  Pa. The O 1s, Zr 3d, Ce 3d and Y 3d photoelectron lines were calibrated to the C 1s line. The surface composition of the mixed oxide layers was determined from the ratio of the corresponding peak areas, corrected with the photoionization cross sections [22].

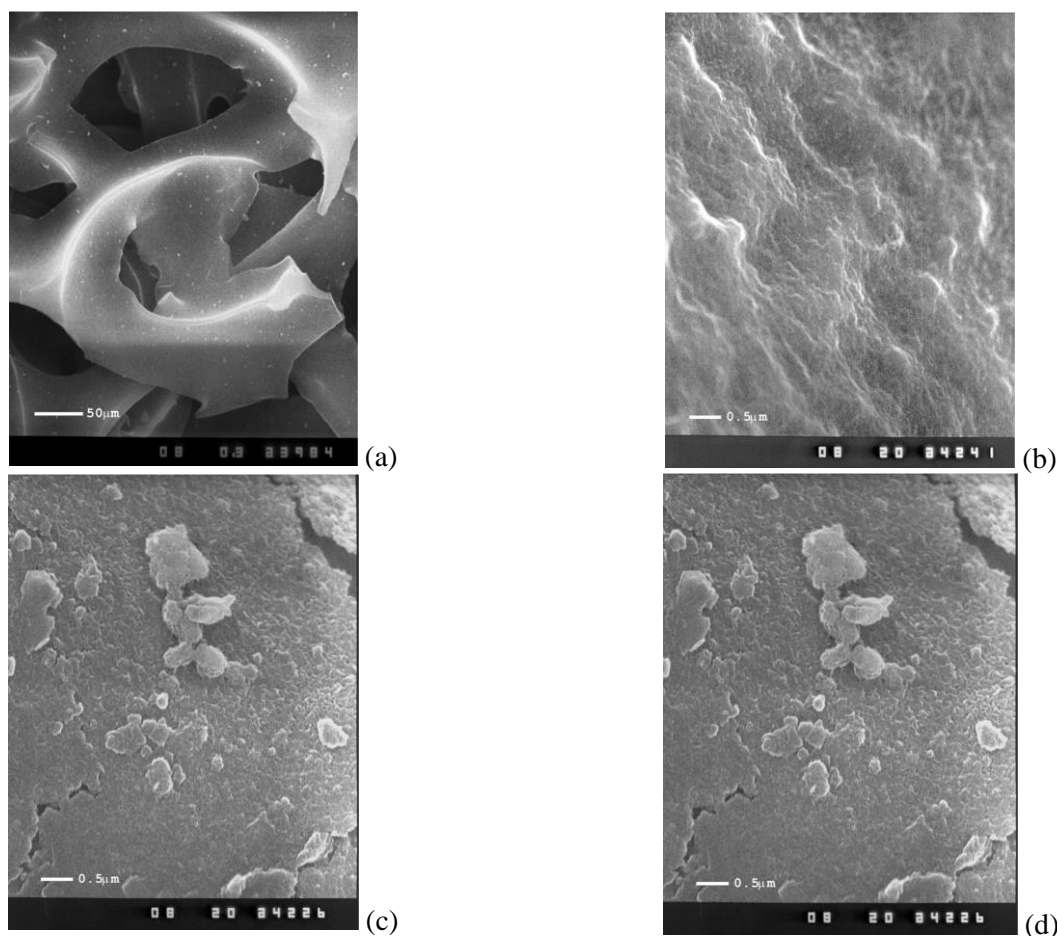
Electrochemical characterisation was performed by cyclic voltammetry and potentiodynamic polarisation technique in the three electrode cell with volume 100  $cm^3$ . The counter electrode was platinum rode and reference electrode was Ag/AgCl with potential +0.197 V vs SHE. The experiments were performed onto potentiostat-galvanostat GAMRY FRAMEWORK PHE 200 with scan rate 25  $mV\ sec^{-1}$ . The concentration of the solutions was as follows: NaCl - 100  $g\ dm^{-3}$ ; NaOH - 40  $g\ dm^{-3}$ , NaCl 100  $g\ dm^{-3}$  + NaClO - 5.52  $g\ dm^{-3}$ .

Catalytic activities of the samples were investigated volumetric, by comparative analysis of the quantities of evolved from the cathode hydrogen. The experiments were performed at the cathodic current density -0.05  $A\ cm^{-2}$ , temperature -22° C and measuring time - 6 minutes. At this experiments the solutions of NaCl (100  $g\ dm^{-3}$ ), was used -100  $g\ dm^{-3}$  and NaCl - 100  $g\ dm^{-2}$ , containing NaClO - 5.52  $g\ dm^{-3}$  (obtained at the electrolysis of the solution of NaCl with ORTA) at the current density - 0.05  $A\ cm^{-2}$  and time - 4 hours.

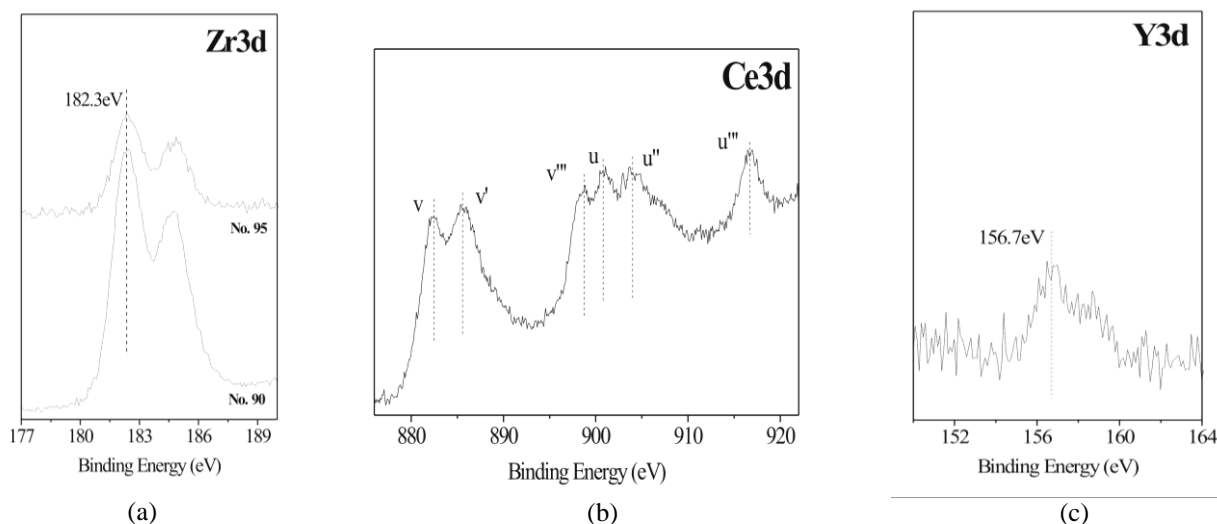
## 3. RESULTS AND DISCUSSION

### *Morphology of the coatings*

The investigations of the structure and morphology of the modified glassy carbon with electrodeposited oxides of Zr, Ce and Y were performed by scanning electron microscopy. The systematic electron-microscopic investigation of the macro and microstructure of the porous carbon substrates, performed in the wide range of microscopic magnifications (from 50x to 100 000x) established that they are characterized with the size of macropores 50 to 300  $\mu m$  (Figure 1a). The elementary structural elements, that build the microstructure of the carbon material have a size about 10-20 nm, which firms the agglomerates with



**Fig. 1.** Scanning electron images of glassy carbon: a) magnification 300x; b) modified with Cu (magnification 20 000x); c) modified with Cu and  $ZrO_2$  (20 000x) (sample 3) ; d) modified with Cu and  $ZrO_2-Ce_2O_3-Y_2O_3$  (20 000x) (sample 5).



**Figure 2.** Photoelectron spectra of  $ZrO_2$  and  $ZrO_2-Ce_2O_3-Y_2O_3$  films, electrodeposited onto porous carbon surface (sample 3 and 5); a)  $Zr3d$  ; b)  $Ce3d$ ; c)  $Y3d$ .

size 25-50 nm. These agglomerates as well the existing much bigger „defects” (with size 0.5-4  $\mu m$ ) onto the smooth surface of the carbon material, which construct the macropores of the investigated „carbon foam”, most probably represent the

energetically favourable places for the growth/deposition (electrochemical or chemical) of the „carrier” from copper film (Figure 1 b) and „catalytic active phase” from oxides ( $ZrO_2$  or  $ZrO_2-Ce_2O_3-Y_2O_3$ ) layers (Figure 1c, d). The presence of

the carried copper layer with very high specific surface would guarantee the requisite adhesion of the coated afterward catalytic-active layers. Together, the high specific area of the copper sublayer with combination of extremely high specific (working) surface of the glassy carbon will work for the increasing of the catalytic activity of the complex system „foam carbon substrate- copper sulayer –  $ZrO_2$  or  $ZrO_2-Ce_2O_3- Y_2O_3$ .

Figure 1c and d shows that the electrodeposited layers of the real catalytic phases of  $ZrO_2$  or  $ZrO_2-Ce_2O_3-Y_2O_3$  (Figure 1 c, d) characterise with higher developed specific (working) surface, consisted from nanoparticles with sizes 30-100 nm.

#### XPS characterisation of the coatings

Figure 2 shows the parts of XPS spectra that were used for the characterisation of the chemical state of the elements in the electrodeposited oxide layers on the basis of Zr and Zr-Ce-Y onto deposited with a thin copper layer porous carbon substrates.

The binding energy of  $Zr3d_{5/2}$  peak in the spectrum of the electrodeposited thin film of  $ZrO_2$  at 182,3 eV (Fig.2a) for both samples (C/Cu/ $Zr_{Oxide}$  and C/Cu/ $Zr_{Oxide}-Ce_{Oxide}-Y_{Oxide}$ ) is characteristic for  $ZrO_2$  [23-26]. Also the obtained value of 2.4 eV for the peak separation between Zr  $3d_{3/2}$  and Zr  $3d_{5/2}$  is in accordance with other data for  $ZrO_2$ .

The Ce3d spectra (Figure 2b) are typical for Ce(III) and Ce (IV) oxidation state since the spectra contain two spin orbit doublets formed due to final state effects. Obviously,  $Ce_2O_3$  oxide is formed during the process of electrodeposition of ternary oxide system Zr –Ce –Y. The binding energy of the Y3d peak at 156.7 eV for electrodeposited mixed ternary system Zr –Ce –Y (Fig.3,c) corresponds to yttrium in  $Y_2O_3$  [27].

#### Cyclic voltammetry

Figure 3 presents the cyclic voltammetry curves, obtained onto glassy carbon with and without  $ZrO_2$  deposits - samples 1, 2 and 3 in the solution of NaCl . From the figures it can be seen that at the samples with oxide layer the depolarizing effect onto cathodic process - in this case, the hydrogen evolution reaction. The observed effect is about 400 mV and is not affected from the type of the sample.

The same effect of depolarisation of the cathodic process is observed at the relationships, recorded in 1M NaOH – Figure 4. In this case the depolarisation effect is smaller- about 200 mV. Moreover, the sharp increasing of the current density (second part of the polarisation curves) in

the samples 2 and 4 starts at the more positive, about 100 mV potentials.

The addition in the solution of  $NaClO$  /5.5 g  $dm^{-2}$ / leads to the changes of the type of the investigation. The maximum of current onto sample 1 is observed at the potentials 0.6-0.8 V – Figure 5. The same correspond to the reduction of the  $NaClO$  and its height at the sample 1 is higher than those, observed

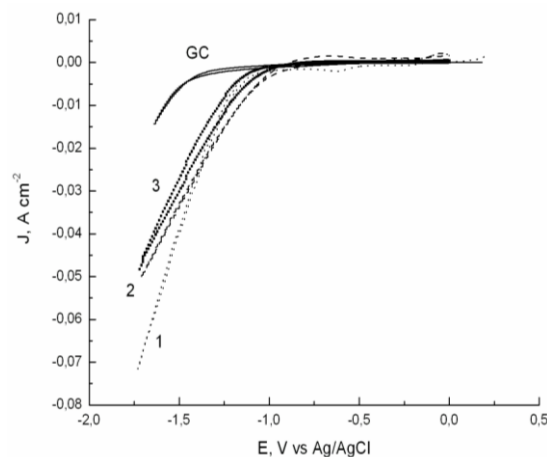


Fig. 3. Cyclic voltammetric curves in the solution of NaCl onto the glassy carbon, sample 1, 2 and 3.

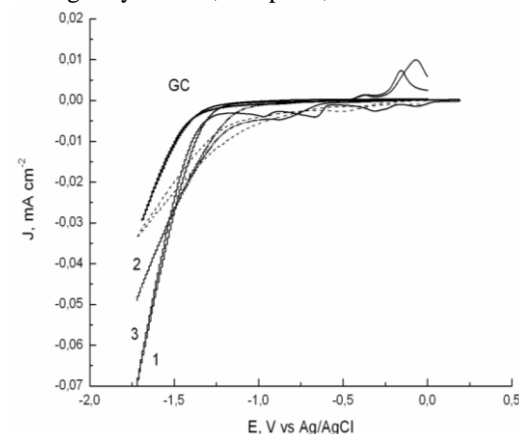


Fig. 4. Cyclic voltammetric curves in the solution of NaOH onto the glassy carbon, sample 2 and 3.

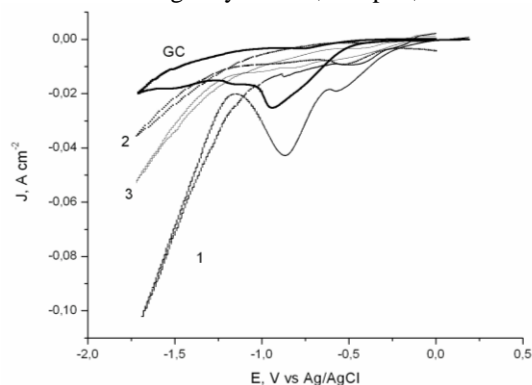
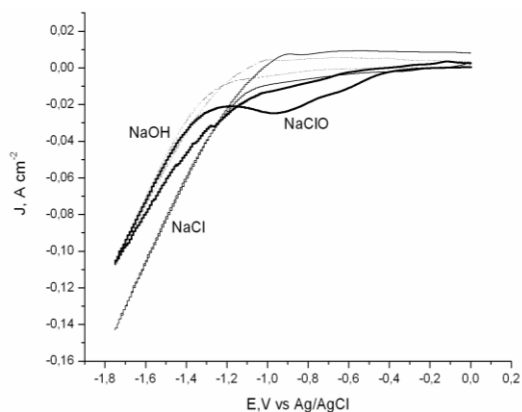


Fig. 5 . Cyclic voltammetric curves in the solution of NaCl+  $NaClO$  onto the glassy carbon, sample 1,2 and 3.



**Fig. 6.** Cyclic voltametric curves obtained onto sample 5 in three investigated solutions NaCl, NaOH and NaOH + NaClO.

onto the GC sample. As could be seen from the same figure onto the samples 2 and 3 the similar peak can not be observed (see Figure 5). Onto the samples from glassy carbon and the sample 1 the peak of current.

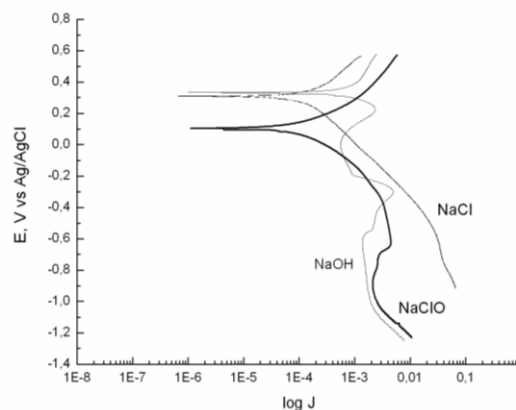
The maximum value of current density, respected to the reduction of NaClO also is observed at the samples from glassy carbon -  $ZrO_2 + Ce_2O_3 + Y_2O_3$  (samples 4, 5 and 6), but with smaller height in comparison with the sample 1 and the glassy carbon without oxide layer. Due to the similar behaviour of the run of the curves for all three above mentioned samples in Figure 6 the cyclic voltammetry curves for sample 5 are presented.

#### Potentiodynamic investigations

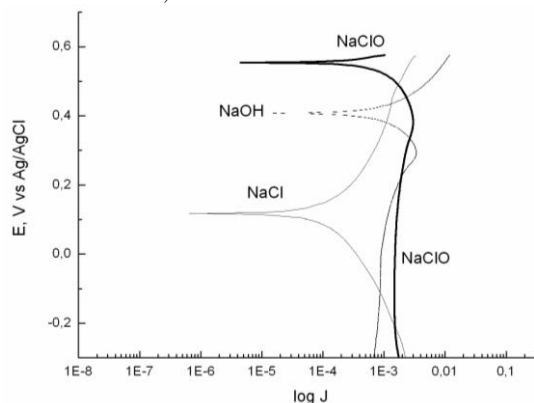
In Figures 7, 8 and 9 the potentiodynamic dependencies obtained in the solutions of NaCl, NaOH and NaCl + NaClO are depicted for samples 1, 2 and 3. From the obtained results it can be seen, that for all investigated solutions the dependencies have the same character. Some differences in the range of potentials for the cathodic parts of the sample 1 from one hand and samples 2 and 3 could be detected. Some conclusion about effect of depolarisation of the cathodic process which can be observed in sample 3 (and partially sample 2). Similar differences are not observed at the potentiodynamic dependencies for the samples with coatings from  $ZrO_2 + Ce_2O_3 + Y_2O_3$  - Figures 10 (due to the similarities the results for sample 5 only is given).

#### Volumetric determination of the catalytic activity

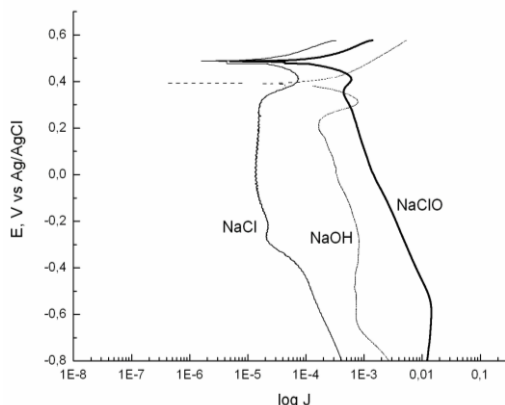
In order to determine the catalytic activity of the samples and their selectivity, experiments were conducted connected with the quantities of the evolved hydrogen from the solution of NaCl and



**Fig. 7.** Polarisation curves onto sample 1 – in the solutions NaCl, NaOH and NaCl + NaClO.



**Fig. 8.** Polarisation curves onto sample 2 – in the solutions NaCl, NaOH and NaCl + NaClO.



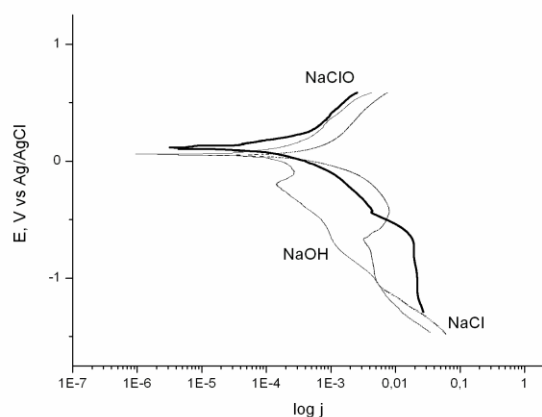
**Fig. 9.** Polarisation curves onto sample 3 – in the solutions NaCl, NaOH and NaCl + NaClO.

the solution of NaCl, containing NaClO ( $5.52 \text{ g} \cdot \text{dm}^{-3}$ ). The obtained results are presented in Table 1.

From the results, presented in Table 1 it can be seen, that the modifying of the surface of the glassy carbon with oxides of Zr and  $Zr+Ce + Y$  could lead to the increasing of the reaction rate of the hydrogen evolution reaction in comparison with the non-modified glassy carbon from the solution of NaCl.

The presence of NaClO leads to the decreasing of the quantity of the evolved hydrogen – results of the reduction onto the cathode. The slightest effect

is at probe 2 and just before probe 3 – at these samples the process of the reduction of the active chlorine  $Cl^+$  proceeds with smallest rate. The observed results correlate with the absence of the peak of current density onto the samples 2 and 3 onto the cyclic voltammetric curves, respected to the reduction of the



**Figure 10.** Polarisation curves onto sample 5 in the solution of NaCl, NaOH and NaCl +NaClO.

hypochlorite. It should be noted some depolarised effect of the process for sample 3, observed onto the potentiodynamic dependencies – Figure 8.

### CONCLUSIONS

1. The modification of the surface of the glassy carbon with nanosized  $ZrO_2$  и  $ZrO_2 + Ce_2O_3 + Y_2O_3$  leads to the increasing of deposition rate of the hydrogen evolution reaction in comparison with the cases of glassy carbon without coatings.

2. At the presence of the NaCl of the active chlorine /NaClO/ this effect is sliher due to the reduction of process of the reduction of active chlorine to chloride ions.

3. Deposition of sublayer onto the glassy carbon in the regime of reverse current effects positively onto the layer of  $ZrO_2$  in the relation of its selectivity of the hydrogen reaction and simultaneously the rate of reduction of  $Cl^+$  do not increase.

4. Modification of the surface of glassy carbon with a nanosized oxides of Zr and Zr + Ce + Y could be alternative to the compounds of  $Cr^{6+}$  related with suppressing of the process of reduction led to the decreasing of current efficiency of its electrochemical obtaining.

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**Table 1.** Quantity of evolved hydrogen in the solutions of NaCl and NaCl + NaClO.

Sample	$V_{H_2}/cm^{-3}$ NaCl, 100 g $dm^{-3}$	$V_{H_2}/cm^{-3}$ NaCl, 100 g $dm^{-3}$ + NaClO 5,52 g. $dm^{-3}$
Glassy carbon	6.4	3.0
1	8	3.6
2	8.4	5.0
3	7	6
4	7.8	4.4
5	7.8	4.6
6	8.2	4.4

As it was notes in the Experimentals the sample 3 presented the modified with  $ZrO_2$  glassy carbon, which should be coated with copper with the regime of reversive current. The obtained by these way coatings, characterized with high surface with comparison with copper coatings onto the other samples, obtained in the regime of direct current.

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## СТЪКЛОВИДЕН ВЪГЛЕРОД (СВ) МОДИФИЦИРАН С ЕЛЕКТРООТЛОЖЕНИ НАНОСТРУКТУРИ НА $ZrO_2$ И $ZrO_2+Ce_2O_3+Y_2O_3$ КАТО КАТОД ПРИ ПОЛУЧАВАНЕТО НА АКТИВЕН ХЛОР

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(Резюме)

Проведени са експерименти със стъкловиден въглерод (СВ), модифициран с електроотложени оксиди на цирконий, церий и итрий с размери 30 – 100 nm. Морфологията и структурата на покритията е охарактеризирана чрез SEM, а елементният състав е изучен чрез XPS. Електрохимичната активност на модифицирания стъкловиден въглерод е изследвана, както чрез циклична волтаперометрия, така и чрез потенциодинамичен метод и е тествана по отношение на електролизата на натриев хлорид с цел получаването на активен хлор. Установено е, че тънък филм от  $ZrO_2$  върху стъкловиден въглерод с междинен меден слой, получен в режим на импулсен ток, повишава токовата ефективност на процеса в резултат на каталитичен ефект върху реакцията на отделяне на водород.