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Investigation of electrode reactions in hydrogen peroxide alkaline medium onto Co, In and Ni by cyclic voltammetry – Part II

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The electrocatalytic activity of cobalt and indium (solid and electrodeposited), nickel and nickel foam towards the electrode reactions taking place in stabilized as well as synthesized (produced by calcium peroxide hydrolysis) hydrogen peroxide solutions was investigated. It was found that the cyclic voltammetry (CV) experiments carried out on electrodes of solid cobalt, indium and nickel indicated activity with respect to the anode reaction in alkaline hydrogen peroxide solution. The most probable reason for the observed behaviour is a formation of passive hydroxy-oxide layers on the surface of these metals. It was demonstrated that the nickel foam is a material suitable not only for anodes, but can also be used as substrate of various electrodeposited layers.

The cyclic voltammetry investigations, carried out on electrodeposited layers of Co and In indicate similar electrode activity compared to the results obtained with solid electrodes with respect to the anode reaction in alkaline hydrogen peroxide solution.

An important conclusion from performed experiments is that the data obtained by investigation of hydrogen peroxide medium synthesized through decomposition of CaO_2 are analogous to those obtained in stabilized hydrogen peroxide solution which renders this reagent suitable for use in fuel cells.

Keywords: Cyclic voltammetry, hydrogen peroxide, calcium peroxide, Co, In, Ni, electrode

INTRODUCTION

Increasing of the efficiency of fuel cell operation in an economic as well as in technological aspect is the main objective targeted by numerous research teams working in this area. Simplification of the fuel cell design, selection of the proper material for electrodes (which are at the same time catalysts of the respective cathodic and anodic reactions), and of electrolyte – these are the main parameters that directly influence the fuel cell efficiency [1, 2]. The team of Yamazaki et al. [3] established the feasibility of operation of a fuel cell without separation of the cathodic and anodic compartments, where an alkaline hydrogen peroxide medium can serve as a fuel as well as an electron acceptor during its operation. However, a suitable catalytic material shall be selected both for the cathodic, as well as the anodic reactions. A number of authors define some precious metals such as platinum, gold and silver as catalysts appropriate for the cathodic reaction, while nickel is found to be suitable for an anode [4]. A new material – nickel foam (polymer material with nickel coating), according to a number of authors, is also found to be a suitable material for operation of the anodes [4].

In our previous study, the electrode processes taking place on Pt and Au electrodes in alkaline hydrogen peroxide medium were examined [5]. The strong catalytic activity of the two metals for the cathodic and anodic reactions of H_2O_2 in 1M solution KOH was verified and it was found that hydrogen peroxide obtained through CaO_2 hydrolysis in the presence of $KHCO_3$ (non-stabilized) has the same electrochemical behavior as the stabilized H_2O_2.

The purpose of this investigation is to select materials suitable for catalysts of the electrode reactions taking place in stabilized, as well as in synthesized (obtained by hydrolysis of calcium peroxide) hydrogen peroxide among cobalt, indium (solid and electrodeposited), nickel and nickel foam.

EXPERIMENTAL

The following solutions were prepared for the experiments: basic electrolyte with concentration 1 M KOH, solution **A** – 0.1÷0.15 M H_2O_2 in 1M KOH; solution **B** – 0.2÷0.25 M H_2O_2 in 1M KOH;

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solution **C** – 0.4÷0.45 M H_2O_2 in 1M KOH. The solutions **A, B** and C were prepared from 30 % solution of H_2O_2 and potassium hydroxide with *pro analysis* purity and distilled water. Solution D was prepared before each experiment by hydrolysis of CaO_2 in the following conditions: temperature 298 K, 50% excess $KHCO_3$, solid:liquid ratio = 1:10, contact time 5 min. The variations in H_2O_2 molar concentration in the investigated solutions were due to the low stability of the peroxide. Its concentration in the solution was determined before and after each experiment by a methodology proposed by the firm Solvay [6].

The composition of the electrolytes for deposition of cobalt and indium coatings was as follows: for deposition of cobalt - 0.3 M Co as $CoSO_4$ $7H_2O$ and 0.2 M diammonium hydrogen citrate ($C_6H_{14}N_2O_7$); for deposition of indium – 0.1M In as $InCl_3$ and 0.2 M $C_6H_{14}N_2O_7$. The deposition was carried out at current densities 3 A dm^{-2} for Co and 1 A dm^{-2} for In, with the same electric charge –1.2 Ah dm^{-3}. Chemical substances with purity *pro analysis* and bidistilled water were used for preparation of the electrolytes.

The electrode processes were investigated by the cyclic voltammetry. The experiments were carried out in a Gamry cell with capacity 200 cm^3 at room temperature without stirring of the electrolyte. The working electrode area was 1 to 2 cm^2. In the case of nickel foam that area was only geometrical, not actual, due to the highly developed surface. Nickel Foam (supplier Good Fellow) has a specificiations as follows: thickness 1.6mm, bulk density 0.45g.cm^{-3}, 20 pores/cm^2. The counter electrode (~2 cм^2) was made of platinum. A calomel reference electrode (Hg/Hg_2Cl_2) was used. Its potential, compared to a normal hydrogen electrode, was E_{SCE}=0.244V. The experiments were carried out with a computer-controlled GAMRY potentiostat-galvanostat Model G 300ZRA. The GAMRY FRAMEWORK PHE 200 program was used.

The scan rate was 0,1 V s^{-1}. In most cases scanning started from the potential of the reference calomel electrode and was continued until a sufficiently negative potential was reached, at which the reaction of hydrogen release is assumed to start. After that the scanning direction was reversed and scanning was carried out up to the selected potential in the anode zone.

The surface morphology of the coatings was studied by means of JEOL 6390 scanning electron microscope (SEM).

RESULTS AND DISCUSSION

The initial experiments were carried out with working electrodes made of solid metals – cobalt, indium and nickel. It was found that the electrode processes in all four solutions (A, B, C and D) run in the same manner, and that is why, in order to facilitate the presentation, only the curves obtained at the highest concentration of hydrogen peroxide (solution C) were presented in graphic form (Fig.1–3).

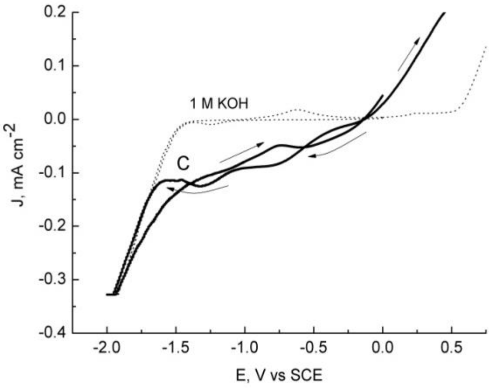


Fig. 1. Cyclic voltammograms of cobalt in 1 M KOH; solution C - 0.42 M H_2O_2 in 1 M KOH.

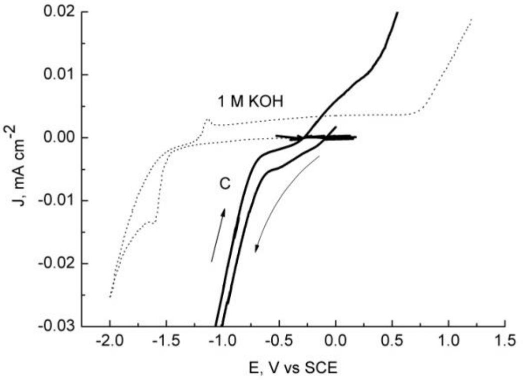


Fig. 2. Cyclic voltammograms of indium in 1 M KOH; solution C - 0.42 M H_2O_2 in 1 M KOH.

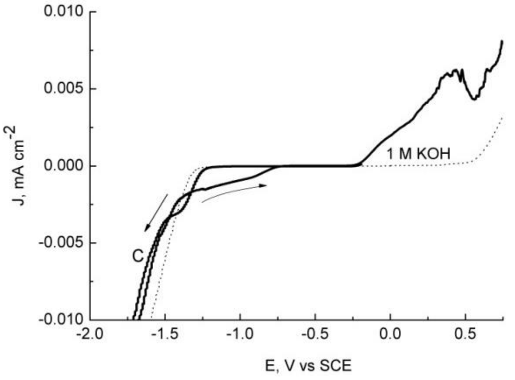


Fig. 3. Cyclic voltammograms of nickel in 1 M KOH; solution C - 0.42 M H_2O_2 in 1 M KOH

Cyclic voltammograms obtained on a Co working electrode – in basic solution (1 M KOH) and in solution C are presented in Fig.1. Activity of hydrogen peroxide can be observed in the cathodic zone, presented in two cathodic waves, at –0.8 V and after –1.2 V. Due to the high peroxide concentration, the first wave is most probably due to the reduction reaction of HO_2^- as follows:

$$HO_2^- + 2e^- + H_2O = 3OH^- \qquad (1)$$

Upon transition to more negative potentials, a horizontal sector can be observed, most probably due to the growth of a passive oxy-hydroxide layer on the cobalt working electrode. According to [7], passivation of the cobalt surface is the result of alkalization of the cathode-contiguous layer and its covering with cobalt hydroxides. At the potentials of the ”second wave” in the cathodic part of the cyclic curve some alkalization of the double layer takes place. This alkalization leads to the formation of hydroxide-oxyde layer.

The reaction of reduction of water and hydrogen evolution starts after potentials of –1.5 V, where it happens in aqueous solution 1 M KOH. The anode reaction taking place on the cobalt is marked. In the alkaline medium of hydrogen peroxide it is described by the equation [8]:

$$HO_2^- + OH^- \rightarrow O_2 + H_2O + 2e^- \qquad (2)$$

It starts immediately at the first positive potentials, beyond 0 V and evidences the fact that cobalt can be used as anode in the oxidation reaction of hydrogen peroxide. Here its activity coincides with that observed in gold and platinum [5].

A base cyclic voltammograms obtained onto indium in 1 M solution KOH (without hydrogen peroxide) is characterized by a cathode peak at potentials –1.5 V, which is related to the formation of a passive film of indium oxides and hydroxides (Fig.2). The formation of such passive film is confirmed by the investigations carried out in alkaline indium solution [7] and the high value of the stability constant of $In(OH)_3$ – 10^{-30} [9]. According to [10] formation of indium hydroxide starts at pH = 3.3 of the medium. In the working solution 1 M KOH the solution pH is more than 12, therefore the formation of a passive film is beyond doubt. In the reverse direction of the curve an anode peak is observed at potentials –1.1 V and corresponds to the dissolution of this passive film. Oxygen generation starts at potentials above 0.8 V.

In a hydrogen peroxide medium (curve C) - the beginning of the reduction reaction occurs at –0.4 V. At present it cannot be maintained whether this is a reduction reaction of the HO_2^- ion, or release of hydrogen on a passivated indium layer. The anode reaction on indium working electrode shows activity similar to that of a cobalt electrode (compared to Figure 1).

Fig.3 presents cyclic voltammograms obtained in 1 M solution KOH and in alkaline solution of hydrogen peroxide on a solid nickel electrode. A minor peak observed in H_2O_2 solution in the range about -1.5 V evidences the possibility of formation of nickel oxide before the hydrogen release reaction. The anodic reaction runs at a high rate, which corresponds to the information presented in the literature [4].

On the basis of the results presented here above it can be concluded that cobalt, indium and nickel can be used successfully as anodes in alkaline hydrogen peroxide solutions. Most probably reason of such catalytic behavior of the oxidation reaction is that it takes place on the passive films formed on the three metals. The catalytic activity of the cathodic processes on cobalt and indium could be assumed, however, the type of the catalyzed reaction should investigated in more details, because the quantitative analysis of shown CVs shows that the magnitude of recorded currents with Co, In and Ni - electrodes are different.

Considering that the steps to higher efficiency of fuel cells operation include lighter structure and, to be sure, reduction of the electrode material prices, further research was carried out using nickel foam and cobalt and indium layers electrodeposited on it. Fig. 4 presents the cyclic voltammograms obtained in aqueous solution 1 M KOH and in alkaline hydrogen peroxide solution (solution C) onto nickel foam.

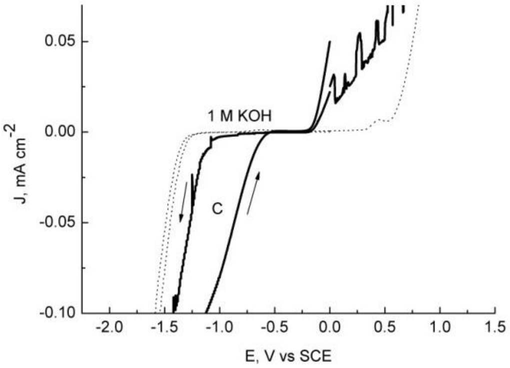
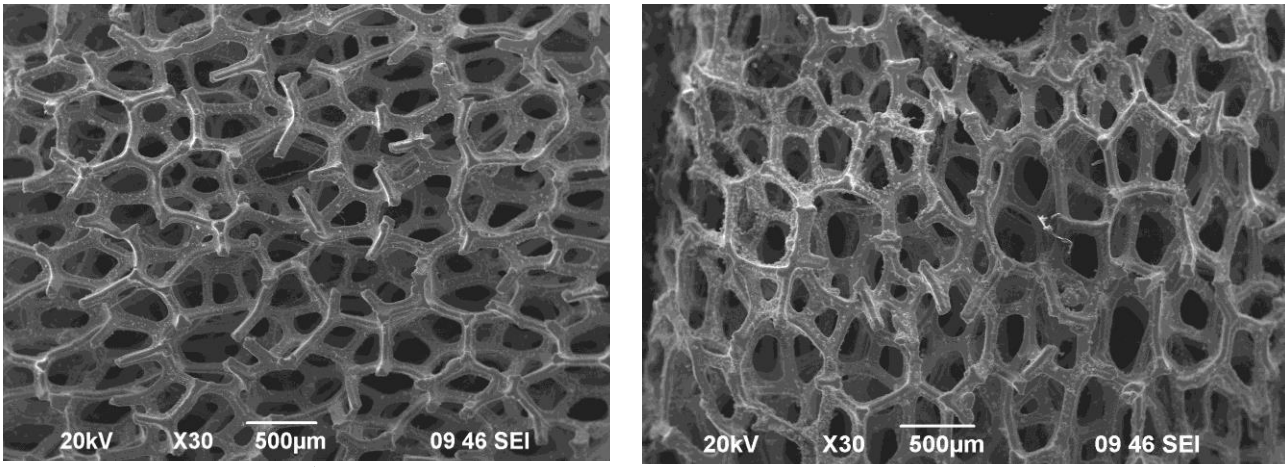


Fig. 4. Cyclic voltammograms of nickel foam in 1 M KOH and solution C - 0.42 M H_2O_2 in 1 M KOH

It can be said that the results are not different from those obtained with a solid nickel electrode – nickel foam demonstrates a high rate of the anodic reaction. The morphology of the nickel foam before and after the experiments is shown in Figure 5a and 5b.



(a) (b)

Fig. 5. SEM images of Ni foam before (a) and after (b) electrochemical treatment in 0.42 M H_2O_2 alkaline medium

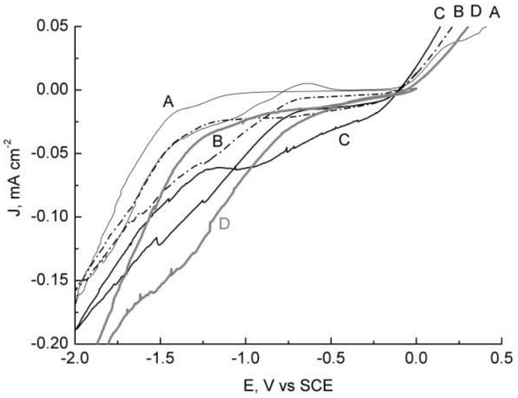
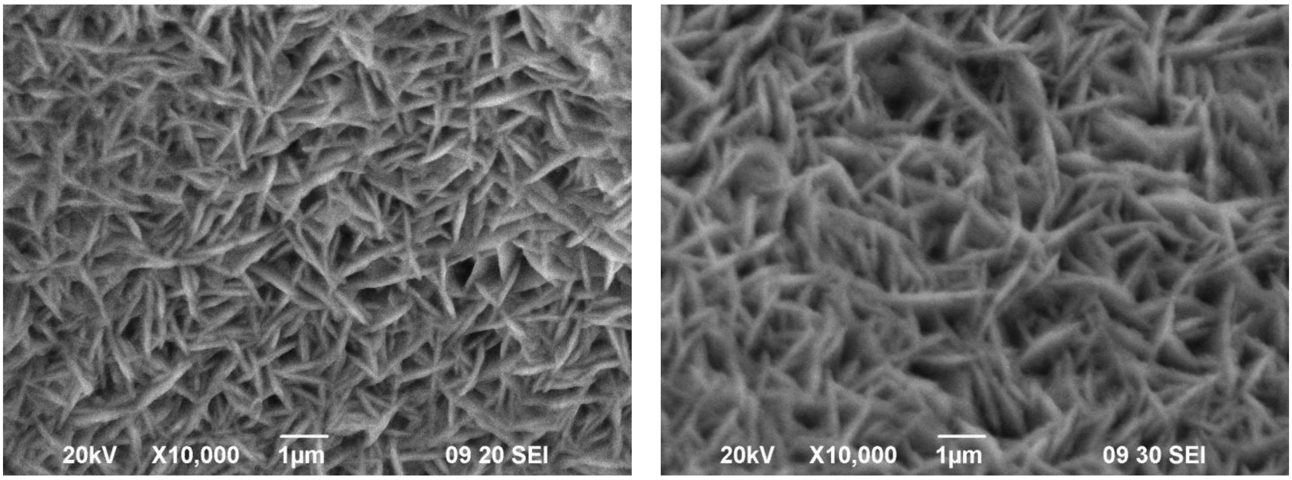


Fig. 6. Cyclic voltammograms obtained onto electrodeposed Co coating (thickness 3 μm) on substrate Ni foam Solutions: A, B, C and D, T = 298K, scan rate 0.1V s^{-1}

It can be seen that in a chemically active medium, with the potential applied over quite a wide range – from -2.0 to +1.0 V does not have a destructive effect on this material.

Cyclic voltammograms obtained in hydrogen peroxide solutions of different concentrations on electrodeposited cobalt layer with thickness 3 μm on a nickel foam substrate are presented in Fig.6. The trend reported in experiments on a solid cobalt electrode is observed here as well - the cathodic reaction starts after –0.4 V, reaching the maximum reduction rate at –1.2 V and high rate of the anode reaction at positive potentials immediately after 0 V. No concentration dependency during the electrode reactions can be reported. The electrode reactions in solutions of stabilized hydrogen peroxide (curves A, B, C) and of non-stabilized H_2O_2 obtained by



(a) (b)

Fig. 7. SEM images of electrodeposited cobalt coating on Ni foam before (a) and after (b) electrochemical treatment in 0.42 M H_2O_2 alkaline solution.

hydrolysis of calcium peroxide (curve D), have the similar behavior. Such conclusion was drawn also from another investigation carried out on working electrodes of gold and platinum [5].

The morphology of the cobalt coating before and after electrochemical treatment (investigated by cyclic voltammetry) is presented in Figure 7a and b. The typical crystallites of electrodeposited cobalt are unchanged after the investigations carried out, which confirm stability of the obtained coatings and further investigations of the nature of the electrode reactions on cobalt. Electrodeposition of indium is carried out with the same electric charge as cobalt. However, a layer of indium deposited on nickel foam is much thinner, ~1 µm. That is due to the fact that the electrolyte used for deposition of indium coatings has low cathodic current utilizability.

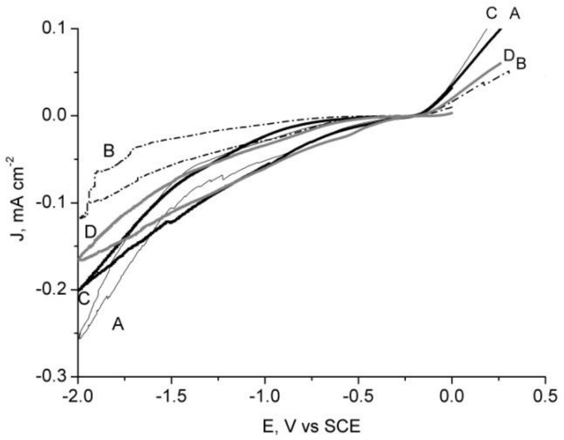
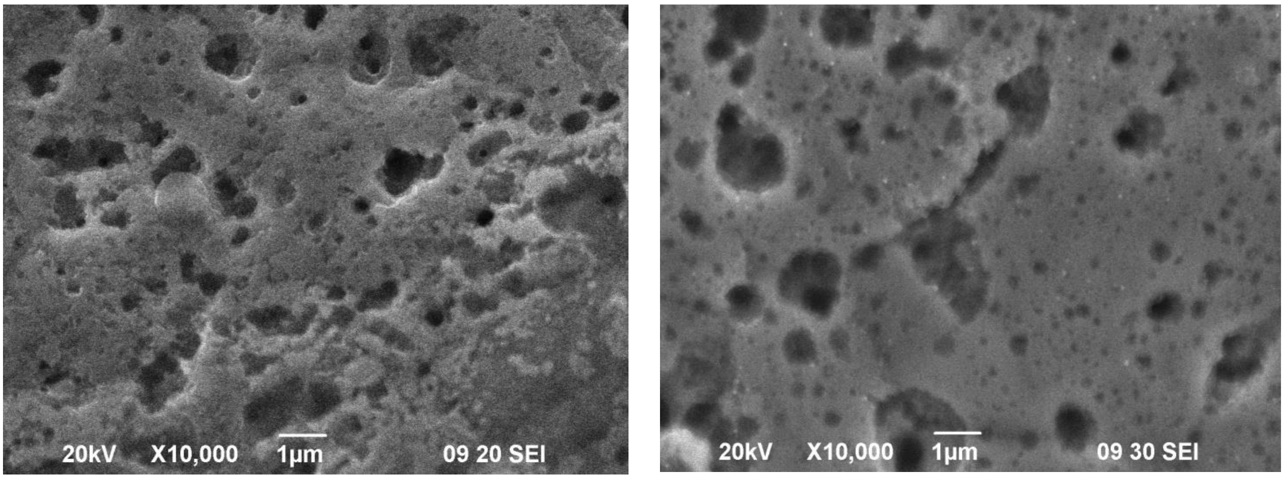


Fig. 8. Cyclic voltammograms obtained onto electrodeposed In coating (thickness 1 µm) on substrate Ni foam.
Solutions: A,, B, C and D, T = 298K, scan rate 0.1V s^{-1}

Analogous to that of cobalt, an investigation is carried out with solutions A, B, with and D. The obtained CV curves are presented in Figure 8. The analogy with the behavior of solid indium (compared to Figure 2) is obvious. Solution D (synthesized hydrogen peroxide) has a behavior similar to that of stabilized hydrogen peroxide. The morphologies of the indium coating before and after electrochemical investigations, presented in Figures 9a and b, prove the stability of the indium film. The pitting observed in the two photos can be accounted with the low thickness of the indium coating.

Even as a thin indium coating it can be stated that indium as a material is suitable for catalytic carrier of the anode reaction of hydrogen peroxide in alkaline solution.



(a) (b)

Fig. 9. SEM images of electrodeposited In coating on Ni foam before (a) and after (b) electrochemical treatment in 0.42 M H_2O_2 alkaline solution.

CONCLUSIONS

On the basis of the investigations carried out the following conclusions can be drawn:

The cyclic voltammetric investigations carried out on electrodes of solid cobalt, indium and nickel indicate activity with respect to the anode reaction in alkaline hydrogen peroxide medium. The most probable cause of such catalytic activity is the formation of passive hydroxy-oxide layers of the surface of these metals.

Nickel foam is a material suitable not only as anode in the anode reaction, but also as substrate for deposition of various electrodeposited layers.

The trends of CV curves obtained on cobalt and indium electrodeposited coating on nickel foam are similar to those obtained on solid Co and In electrodes. That indicates analogous activity with respect to the anode reaction in alkaline hydrogen peroxide medium and therefore - the feasibility of making the fuel cell lighter through replacement of the solid electrodes by a lighter material – nickel foam with electrodeposited films of cobalt or indium.

An important conclusion from the present investigation is that the electrode processes taking place in hydrogen peroxide synthesized by hydrolysis of calcium peroxide in the presence of $KHCO_3$ are similar to those in a stabilized, alkaline hydrogen peroxide medium. This result corroborates the thesis that synthesized hydrogen peroxide can be used directly as reagent in hydrogen peroxide fuel cells.

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ИЗСЛЕДВАНЕ НА ЕЛЕКТРОДНИ РЕАКЦИИ ВЪРХУ Co, In И Ni В АЛКАЛЕН РАЗТВОР НА ВОДОРОДЕН ПЕРОКСИД ЧРЕЗ ЦИКЛИЧНА ВОЛТАМПЕРОМЕТРИЯ – ЧАСТ II

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(Резюме)

Изследвана е електоро-каталитичната активност на кобалт и индий (масивен и електроотложен), никел и никелова пяна спрямо електродните реакции, протичащи в стабилизирани а също така и в синтезирани (получени чрез хидролиза на калциев пероксид) разтвори на водороден пероксид. Установено е, че циклични волтамперометрични експерименти проведени върху масивен кобалт, индий и никел показват активност по отношение на анодна реакция в алкален разтвор на водороден пероксид. Най-вероятна причина за наблюдаваното поведение е образуване на пасивни хидрокси-оксидни слоеве върху повърхността на тези метали. Доказано е, че никеловата пяна е материал, подходящ не само за анодите, но също може да бъде използван за подложка на различни електроотложени слоеве.

Циклични волтамперометрични изследвания, проведени върху електроотложени слоеве на Co и In, показват подобна електродна активност в сравнение с резултатите получени с масивни електроди по отношение на анодна реакция в алкален разтвор на водороден пероксид.

Важен извод от проведените експерименти е че резултатите, получени при изследване на водороден пероксид в синтезиран чрез разлагане на CaO_2 са аналогични на тези, получени в стабилизиран разтвор на водороден пероксид, което прави този реагент подходящ за използване в горивни клетки.