

Investigation of electrode reactions in hydrogen peroxide alkaline medium onto Pt and Au electrodes by cyclic voltammetry - Part I

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In the present paper, the effect of electrolyte convection on the electrode reactions taking place on Pt and Au electrodes in alkaline H₂O₂ solution is investigated by cyclic voltammetry (CV). The electrochemical behavior of H₂O₂ obtained by hydrolysis of calcium peroxide (CaO₂) in the presence of potassium hydrogen carbonate (KHCO₃) is also studied with a view to its use as a reagent (fuel and oxidant) for hydrogen peroxide fuel cells (HPFC).

The first cathodic reaction taking place on a Pt electrode is the reduction of the perhydroxyl ion (HO₂⁻). At more negative potentials current oscillations are observed. Based on the analogy to acidic medium it is supposed that the reaction continues with formation of a hydroxide passive film and only after that by recombination of the hydrogen atoms to the evolution of hydrogen. The electrode processes take place in conditions of stationary diffusion and the reaction rate is determined solely by the concentration of reagent.

On solid gold, as well as on an electrodeposited gold coating onto a nickel substrate, the reactions of reduction, as well as of oxidation take place with high catalytic activity. The morphology of the gold coating onto nickel foam does not disintegrate after the electrochemical treatment in alkaline H₂O₂ solution. The trends of CV curves (respectively, the electrode reactions) of synthesized and stabilized alkaline solution of H₂O₂ are analogous. This result leads to the conclusion that hydrogen peroxide obtained by hydrolysis of CaO₂ can be used directly as a reagent (fuel or oxidant) for HPFC.

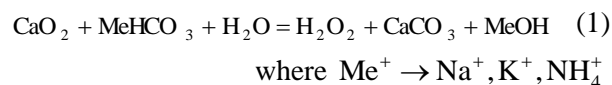
Keywords: cyclic voltammetry, platinum, gold, electrode, hydrogen peroxide, calcium peroxide

INTRODUCTION

The search for energy sources alternative to the traditional carbon-based fuels is a task of primary importance nowadays. The use of hydrogen peroxide in the fuel cells (HPFC) is determined by the chemical nature of this reagent to be both oxidant and reducer. The feasibility of transforming its chemical energy into electrical through electrochemical reactions makes it competitive to other ecological energy sources such as hydrogen, methanol, etc., especially where oxygen is not easily available [1, 2]. Some of the main problems that still hinder the wide use of H₂O₂ for HPFC are difficulties related to its storage, low stability, and generation of large quantities of water upon decomposition. One of the possible solutions is production of H₂O₂ by hydrolysis of peroxides of alkaline and alkali earth metals (BaO₂, SrO₂, CaO₂ etc.) [3]. Of these, CaO₂ is considered the most promising due to its low price, non-toxicity and

affordability.

In the course of our previous research [4] a new method was developed for obtaining H₂O₂ by hydrolysis of CaO₂ in the presence of sodium (potassium or ammonium) hydrogen carbonate, the chemistry of which can be described by the following summary reaction:



It was found that the process runs at a high rate, while the concentration of H₂O₂ in the solution can be controlled by variation of the pH, temperature, density of the pulp and manner of mixing the reagents.

According to [5–7] the electrode processes taking place on Pt and Au electrodes in neutral and alkaline hydrogen peroxide solutions are comparatively well studied. It is known that both precious metals are good catalysts of the electrode reactions taking place in alkaline hydrogen peroxide solution. There is lack of information in the literature about the effect of H₂O₂ concentration on the course of the electrode reactions, as well as

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the influence of the natural and forced convection on them. Both parameters are of great significance for improving the efficiency of HPFC operation.

At the same time, taking into account that platinum and gold electrodes can be considered as model ones in terms of catalytic capabilities with respect to the electrode reactions taking place in alkaline solution of H_2O_2 , it would be interesting to compare the run of electrode reactions of hydrogen peroxide obtained by hydrolysis of CaO_2 in the presence of KHCO_3 (called briefly „non-stabilized”) with data about stabilized hydrogen peroxide in analogous conditions.

The objectives of this paper are: to determine the influence of convection on the electrode processes taking place on Pt and Au electrodes in alkaline hydrogen peroxide medium (a vertical electrode for determination of the natural convection and a rotating disc electrode (RDE) providing forced convection in conditions of stationary diffusion) and to assess the behavior of synthesized H_2O_2 on platinum and gold, with a view to its direct use as a reagent (fuel and oxidant) for hydrogen peroxide fuel cells.

EXPERIMENT

The following solutions were prepared for the CV 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; solution C - 0.4 ± 0.45 M H_2O_2 in 1M KOH. Solutions A, B and C were prepared using a 30% solution of H_2O_2 , potassium hydroxide with purity *pro analysis* and distilled water. Solution D was prepared before each experiment by hydrolysis of CaO_2 in the following conditions: temperature 298K, 50% excess of KHCO_3 , solid:liquid ratio = 1:10, contact time 5 min. The variations in the molar concentration of H_2O_2 in the examined solutions are due to low stability of the peroxide. Its concentration in the solution was determined before and after each experiment by a method proposed by Solvay [8].

The method of cyclic voltammetry that permits comparatively easy determination of the thermodynamic (reaction potential) and kinetic (current density) parameters of reactions taking place in the system [9] was used to investigate the efficiency of electrode reactions taking place on platinum and gold electrodes.

The experiments were carried out in a glass three-electrode Gamry cell with volume of 200 cm^3 at room temperature. The working electrodes made of solid platinum and gold had areas between 1 and

2 cm^2 . The area of the rotary disc electrode was 0.0707 cm^2 . A platinum counter-electrode with area $\sim 2 \text{ cm}^2$ was used in all experiments. A calomel reference electrode ($\text{Hg}/\text{Hg}_2\text{Cl}_2$) was used. Its potential, compared to a normal hydrogen electrode, is $E_{\text{SCE}} = 0.244 \text{ V}$. During the experiment it was placed in a separate cell filled up with 3M solution of KCl. Its connection to the electrolytic cell was made by a Haber-Lugin capillary through an electrolyte bridge filled with 3M KCl on one side, and with the working electrolyte on the other side. The experiments were carried out with a computer-controlled potentiostat-galvanostat Model G 300/ZRA made by GAMRY Instruments. GAMRY FRAMEWORK PHE 200 software was used for processing the experimental data.

The scan rate during cyclic voltammetry experiments was 0.1 V s^{-1} . In most cases scanning started from 0 V compared to the potential of the comparator calomel electrode and continued up to -2.0 V , a potential sufficiently negative to trigger the reaction of hydrogen release. After that the scanning direction was reversed and scanning was carried out up to a potential of $+1.2 \text{ V}$ in the anode region. Before each experiment, the cathode surface was cleaned and pickled.

RESULTS AND DISCUSSION

Effect of convection on the electrode processes

Figures 1a to 1d present cyclic voltammetry curves obtained in solutions A, B and C onto a Pt working electrode. As mentioned above, platinum is one of the best catalysts for cathodic reduction of hydrogen peroxide [10]. One major drawback of using platinum is the occurrence of a random reaction of destruction manifested by covering the electrode surface with bubbles of oxygen immediately after its immersion in hydrogen peroxide solution.

The CV curves obtained with a working rotating disc electrode (RDE) without rotation are presented in Fig.1a. In this case the natural convection is severely suppressed. The difficulties met by the electrolyte flow in ascending are due to absence of microconvection along the electrode/solution interface. In consequence, the new reagent flow is not delivered uniformly to the electrode surface, in case of non reacted hydrogen peroxide. During the experiments, a gas bubble occupying a large part of the electrode can be observed, which grows with scanning to more negative potentials. According to Littauer and Tsai [11], in strongly alkaline solution,

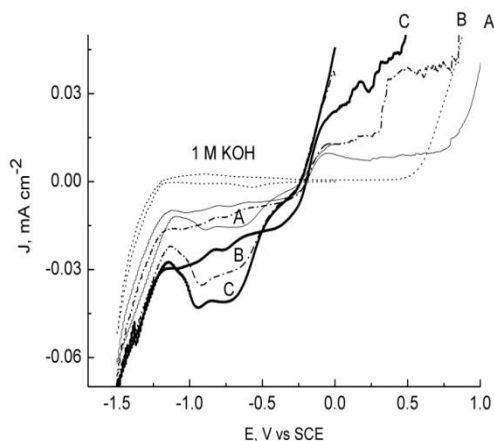


Fig.1a. Cyclic voltammograms of Pt RDE electrode, rpm = 0. Solutions: A,B and C, T = 298K, scan rate 0.1V s⁻¹

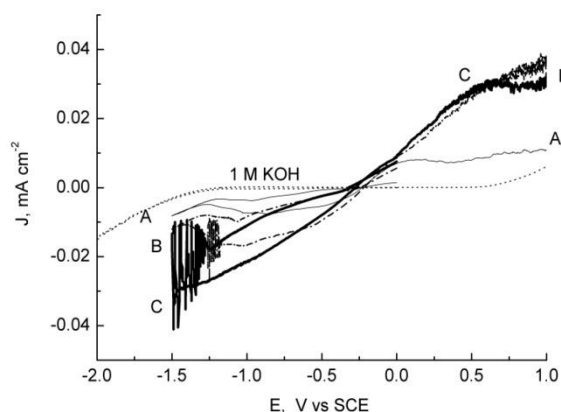


Fig.1b. Cyclic voltammograms of Pt RDE electrode, rpm = 1000. Solutions: A,B and C, T = 298 K, scan rate 0.1V s⁻¹

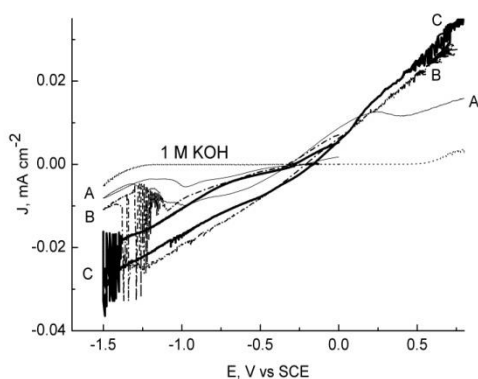


Fig.1c. Cyclic voltammograms onto Pt RDE electrode, rpm = 2000. Solutions: A, B and C, T = 298K, scan rate 0.1V s⁻¹

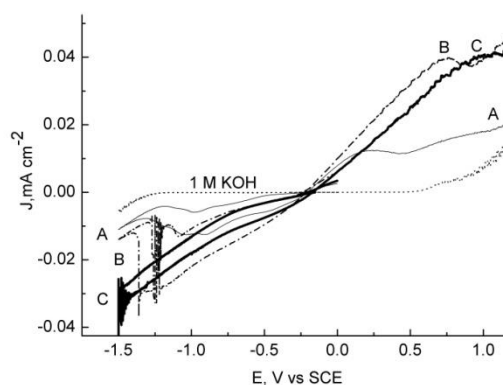
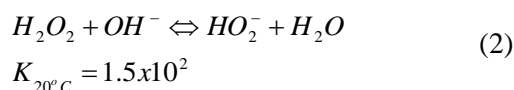
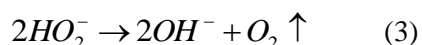


Fig.1d. Cyclic voltammograms onto Pt RDE electrode, rpm = 3000. Solutions: A, B and C, T = 298K, scan rate 0.1V s⁻¹

H₂O₂ is transformed almost completely into perhydroxyl ion (HO₂⁻)



and subsequently within bulk solution and especially at catalytic surface:



The reaction of reduction of an HO₂⁻ ion starts at potentials about -0.2V and reaches its maximum rate at potentials -0.6V for all three investigated concentrations. The hydrogen evolution reaction (HER) starts at potentials after -1.2V, such as in 1M solution of KOH. In the case of scanning in the reverse direction an anode current is observed

immediately after reaching 0 V. This fact indicates that the oxidation reaction taking place at the anode is highly catalyzed by the platinum substrate [7]. It can be seen that in 1M solution of KOH without hydrogen peroxide, the oxidation reaction starts only after +0.6 V.

With a higher H₂O₂ concentration in the alkaline solution, higher limiting currents of the cathodic, as well as of the anodic reactions are reached (i.e., the rates of the reactions of both reduction and oxidation are increased).

The influence of forced convection on the electrode processes taking place on platinum RDE at rotation speed of the electrode – 1000, 2000 and 3000 rpm is shown in Fig.1b÷d. The start of the cathodic reaction (4) can be determined at potentials about -0.2 V. According to the main theoretical principle of the rotating disc electrode, its rotation creates conditions for occurrence of the electrochemical processes in conditions of

stationary diffusion [12]. The higher the rotation speed, the thinner is the boundary layer, where there is a uniform layer with constant reagent concentration, i.e., there are conditions of stationary diffusion. Critically, if the limiting current density depends on the rotation speed, then diffusion is the limiting stage. Analysis of the CV curves indicates that at all three rotation speeds the limiting currents were: for electrolyte A $\sim 0.008 \text{ mA cm}^{-2}$, for electrolyte B 0.01 mA cm^{-2} and for electrolyte C 0.02 mA cm^{-2} . Therefore, the rotation speed at the same concentration of the investigated solution does not affect the boundary current, i.e. the reaction speed. It is obvious that the limiting current density is determined solely by the hydrogen peroxide concentration. Therefore, the charge transfer is most probably the limiting stage and the reaction speed will be determined only by the reagent concentration [13].

An occurrence of current oscillations (with amplitude reaching $\sim 0.10 \text{ mA cm}^{-2}$) could be observed using an RDE. This phenomenon is observed upon reduction of hydrogen peroxide on a platinum electrode, but in acidic medium [6, 14] and is accounted for by the formation/disintegration of a passive hydride layer on the platinum surface. Probably, the reason of oscillations in the alkaline medium is also the formation of a passive film of hydroxides generated at more negative potentials. The thorough clarification of this phenomenon is beyond the frame of the present study. However, it is significant enough for clarification of the possible reactions of hydrogen peroxide destruction in alkaline medium and could be the subject of another study.

The anode behavior of electrode processes indicates a clear dependence of the reaction speed (current density, respectively) only from the hydrogen peroxide concentration.

Fig.2 presents cyclic voltammetric curves obtained by the use of a platinum vertical electrode (platinum lamella) in the investigated solutions. Here, a significant difference is observed in the cathodic part of the curves compared to CV curves obtained on a horizontal platinum electrode (Fig.1a). In all three investigated electrolytes the cathodic reactions pass through a clearly marked maximum, unlike the flat observed at the horizontally positioned platinum lamella. The cause of such trend of the curve is that with a vertical electrode the natural convection, as a result of the Archimedian force, is not suppressed and the released bubbles „stir” the electrode surface, thus continuously providing a fresh reagent flow.

Analysis of the electrode reactions of hydrogen peroxide synthesized from CaO_2

It is a fact that cyclic voltammetric curves obtained on Pt and Au can be considered as a model for the electrode processes. For this reason these electrodes were chosen to determine the electrochemical activity of hydrogen peroxide (solution D) obtained by hydrolysis of $\text{CaO}_2 \times \text{H}_2\text{O}_2$ in the presence of KHCO_3 .

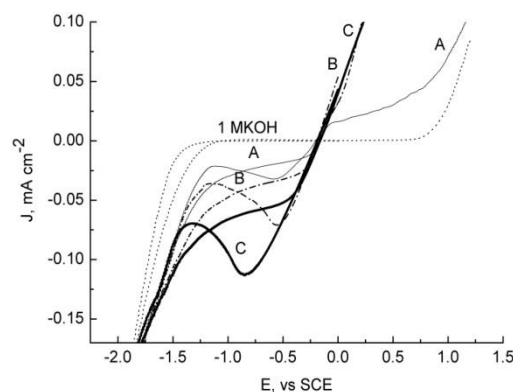


Fig.2. Cyclic voltammograms onto vertical Pt electrode Solutions: A, B, C and D, $T = 298\text{K}$, scan rate 0.1 V s^{-1}

Figure 2 presents a comparison between CV curves obtained on a platinum electrode in alkaline solution of stabilized H_2O_2 and the cyclic voltammetric curve obtained in synthesized medium of hydrogen peroxide electrolyte (solution D). It can be seen that the curve trend (respectively, the nature of electrode processes taking place) is identical to that obtained by investigation of stabilized H_2O_2 solutions. This fact is of great significance for the future development of the peroxide fuel cell, since it shows the feasibility of using CaO_2 for producing hydrogen peroxide for fuel cells.

The cyclic voltammetric curves obtained in the investigated solutions (A, B, C and D) on a vertical gold electrode are presented in Figure 3. Gold demonstrates its catalytic activity in the manner defined by other authors as well [7, 14]. The cathodic reactions start almost immediately after initial scanning of the potential in negative direction (after 0V) and reach the maximum rate of reaction at -1.3V . Hydrogen evolution reaction starts after -2.0V .

The anodic reactions are also visibly catalyzed because they start as soon as a potential of 0 V is reached. The rates of both cathodic and anodic reactions in solutions depend on the concentration of hydrogen peroxide.

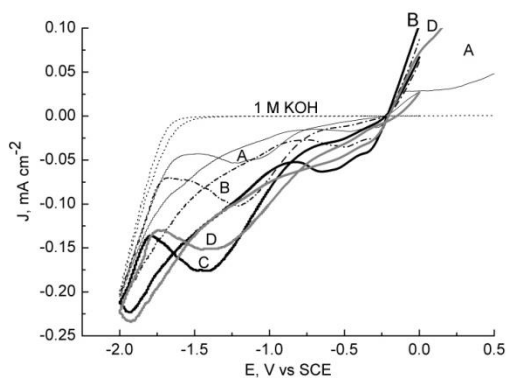


Fig.3. Cyclic voltammograms onto vertical Au electrode. Solutions: A, B, C and D, T = 298K, scan rate 0.1V s⁻¹

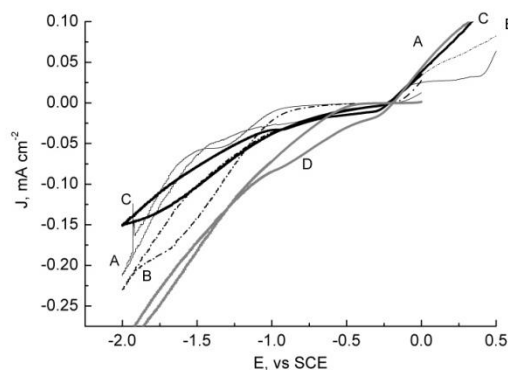
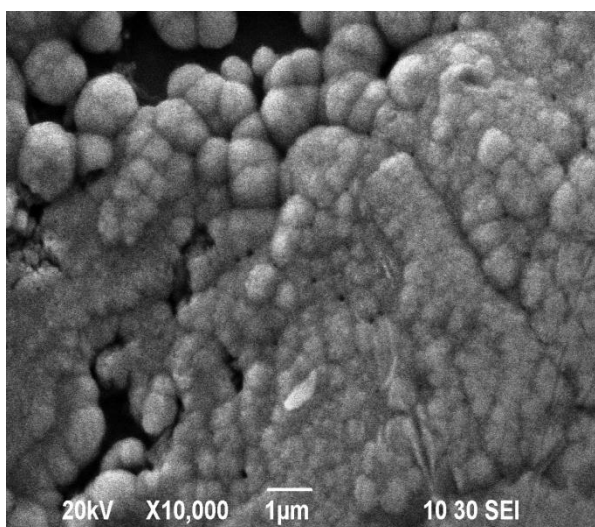
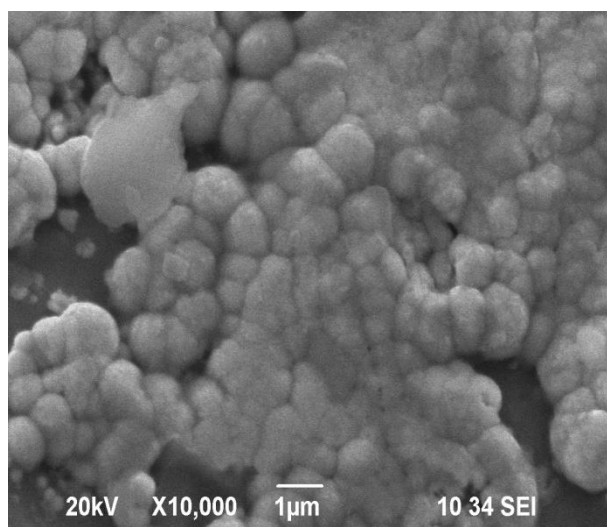


Fig.4. Cyclic voltammograms obtained onto electrodeposited gold coating (thickness 2 μm) on substrate Ni foam. Solutions: A, B, C and D, T = 298K, scan rate 0.1V s⁻¹



(a)



(b)

Fig.5. SEM images of electrodeposited coating Au onto Ni foam before (a) and after (b) electrochemical treatment in 0.42M H₂O₂ alkaline solution.

Fig.4 presents the CV curves obtained on an electrodeposited gold film. The results could be interpreted as similar to those obtained using a solid gold electrode.

The trend of a CV curve obtained in solution D (synthesized hydrogen peroxide) is analogous to the curve obtained at the same concentration in stabilized hydrogen peroxide (solution C). Therefore, the electrode reactions of synthesized hydrogen peroxide with scanning of the potential in cathode and anode direction are similar to those taking place in an alkaline solution of stabilized H₂O₂. This result once again corroborates the conclusions drawn here for the platinum electrode and shows the feasibility of using CaO₂ as a reagent in the production of H₂O₂ for HPFC.

Having in mind the high price of precious metals (platinum and gold), a further step was done

in the present work – study of the catalytic activity of a gold electrodeposited film onto a lighter and less expensive material - nickel foam.

The morphology of the gold coating before and after electrochemical treatment in alkaline solution of hydrogen peroxide is presented in Figs. 5a and b. It is obvious that the gold coating deposited on nickel foam does not disintegrate. This fact, as well as the trend of the electrode processes allow to proceed to a further study – the use of nickel foam with electrodeposited films.

CONCLUSIONS

On the basis of the experiments made the following conclusions can be drawn:

The first cathodic reaction on a platinum electrode is a reduction of the peroxide ion (HO₂⁻).

At more negative potentials current oscillations are observed. Based on the analogy to acidic medium, formation of a passive hydroxide film is supposed and only after that - recombination of the hydrogen atoms and evolution of hydrogen. The process of peroxide ion reduction does not occur under diffusion control.

It was found that on both solid gold and electrodeposited gold coating on nickel substrate, the reduction and oxidation reactions take place with high catalytic activity. The coat morphology does not change after electrochemical treatment in alkaline solution of hydrogen peroxide. The trends of the CVA curves (respectively, the chemistry of electrode processes) observed during working with an electrode with electrodeposited gold coating on nickel foam indicate the feasibility of using less

expensive and scarce materials with electrodeposited films.

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

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ИЗСЛЕДВАНЕ НА ЕЛЕКТРОДНИ РЕАКЦИИ НА ВОДОРОДЕН ПЕРОКСИД В АЛАКАЛНА СРЕДА ВЪРХУ Pt И Au ЕЛЕКТРОДИ ЧРЕЗ ЦИКЛИЧНА ВОЛТАМПЕРОМЕТРИЯ – ЧАСТ I

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(Резюме)

В настоящата статия, с помощта на циклична волтаперометрия (ЦВ), е изследвано влиянието на конвекция на електролита върху електродни реакции протичащи върху Pt и Au електрод в алкален разтвор на H_2O_2 . Анализирано е също електрохимичното поведение на H_2O_2 , получен чрез хидролиза на калциев пероксид CaO_2 в присъствие на калиев водороден-карбонат ($KHCO_3$) с цел използването му като реагент (гориво и окислител) за водородни пероксидни горивни клетки (ВПК).

Установено е, че първата катодна реакция протичаща върху Pt електрод е редукция на перхидроксидов йон (HO_2^-). Тя е последвана от образуване на хидрооксиден пасивен слой и последваща рекомбинация на водородните атоми до образуването на водород. Електродните процеси протичат в условията на стационарна дифузия и скоростта на реакцията се определя единствено от концентрацията на реагента.

Върху масивно злато, а също така върху златно покритие, електроотложено върху никелова пяна, реакциите на редукция, а също така и на окисление протичат с висока каталитична активност. Морфологията на златното покритие върху никелова пяна не се разрушава след електрохимичното третиране в алкален разтвор на H_2O_2 . Ходът на ЦВ криви (съответно, на електродните реакции) на синтезиран и стабилизиран алкален разтвор на H_2O_2 е аналогичен. Този резултат води до извода, че водороден пероксид получен чрез хидролиза на CaO_2 може да бъде използван като реагент (гориво или окислител) за ВПК.