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Drop of Activity of the Oxygen Electrode on the Base of Ag Catalyst (Polytetrafluorethylene)*

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The article describes the determination of the effect of »impurities«, originating from dissolution of the cell components, upon the activity of the oxygen electrode Ag-catalyst in 7 *N* KOH. It was confirmed that the silver surface plays a more serious part in electrochemical processes than it had been assumed previously. It refers, above all, to the formation and solubility of silver oxides and further to eventual adsorption of ions $[Ag(OH)_2]^-$ on the active surface of the oxygen electrode silver catalyst, especially with positive potentials in unloaded conditions. For the determination of the total effect of events upon the activity of the oxygen electrode, methods comparing the changes of current density, in dependence on time, were applied. Current density was measured with electrode potential of — 300 mV *vs.* Hg/HgO. The experiments proved that the activity of the oxygen electrode on the base of Ag catalyst — PTFE in unloaded conditions and without oxygen pressure in 7 *N* KOH at the approximate temperature of 63° C, drops expressively with time. More we observed the influence of the collector material construction, effect of Zn, Ni, Cd and Fe, effect of amalgamation of the oxygen electrode and effect of CO_3^{2-} upon its activity. It was proved, on the basis of experimental results, that the oxygen electrode on the basis of Ag/PTFE is practically inapplicable. »Selfpoisoning« occurs here probably due to the effect of ions $[Ag(OH)_2]^-$. On the other hand, the formation of $[Ag(OH)_2]^-$ can be utilized in the production technology of electron conductive skeleton of the electrode by the application of a mixture of silver and electronegative metal, *e. g.* Zn.

INTRODUCTION

One of the significant problems of the contemporary applied electrochemistry consists in the design of such an oxygen electrode which would have minimum excess voltage at a sufficient current load. When evaluating all kinds of fuel cells the most important factor is the service life of the electrodes. In case of low-temperature fuel cells the drop of activity of the catalysts occurs frequently, which results in the short service life of the electrodes. According

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to Austin[1] the drop in power of fuel cells in comparison with time is caused by following general reasons:

a) by the drop of activity of the catalyst caused by impurities of the electrolyte;
b) by the drop of activity of the catalyst caused by impurities which arise by the dissolution of the fuel cell components;
c) by the desintegration of electrodes caused by the effect of slow corrosion;
d) by the loss of contact between the catalyst and the current collector;
e) by the recrystallization of the catalyst which results in the loss of the electrode active surface;
f) by the loss of electrode hydrophobicity.

Therefore, before it was possible to pass on to the application of the oxygen electrode made of Ag-catalyst—synthetic polymer (*e. g.* PTFE) solution in a source system, it was essential to find out what was the effect of »impurities« of the electrolyte and of »impurities« originating by the dissolution of the fuel cell components, upon the activity of the Ag-catalyst of the oxygen electrode in a strong alkaline electrolyte.

THEORETICAL PART

2.1 *Choice of Catalyst*

From the analyses of Schwartz and Wardem[2] resulted that for the oxygen electrodes of low-temperature systems of fuel cells it is necessary to apply nowadays Pt or Ag as catalysts. The economic suitability of Pt can be considered only in that case if the contents of this catalyst in the electrode is reduced to 1/10 of the amount applied nowadays. Thus, from the practical point of view, only Ag remains as a suitable catalyst for the oxygen reduction. Simultaneously, when selecting this kind of catalyst, the necessity of applying an alkaline electrolyte (6—7*N* KOH is the most suitable) is thus required.

Austin[1] and Bockris[3] have shown that Pt in acid medium reaches the potential of about 0.9 V, whilst the standard potential of the oxygen electrode is 1.23 V. This electrode is then thermodynamically unstable and can be dissolved. Since the standard potentials of all metals reach lower values than 1.23 V, no metal can fulfil the requirement of insolubility put upon the oxygen electrode. The metal washer of the oxygen electrode can dissolve by itself or by the effect of surface oxide films. Simultaneously it was proved that the setting of the reversible potential of oxygen reduction is strongly dependent upon the contents of »impurities« that are present in the electrolyte, either at the beginning of the oxygen electrode function, or are formed in the system during the function of the fuel cell. Analogically, it is possible to assume that similar phenomena will occur even in the alkaline electrolyte, above all with Ag in 7*N* KOH.

2.2 *Oxidation of Silver in Alkaline Electrolyte*

Anodic oxidation of silver in alkaline electrolytes represents a process of two stages.[4-7] First a layer of Ag_2O is formed on the surface, and after reaching a critical thickness, oxidation of Ag_2O to AgO begins. Further oxidation will result in the development of oxygen on the electrode. There are assumptions on formation of highly unstable »higher-order-oxides« during long-term anodic oxidation, especially with high current densities[8]. It is also well known that a great amount of further Ag_2O[9] is formed simultaneously during the second stage of oxidation.

The standard potential of Ag/Ag_2O system in alkaline solutions is $+ 0.342$ V[10], and standard potential of Ag_2O/AgO system is $+ 0.604$ V[11].

Giles *et al.*[12] studied the kinetics of oxidation of smooth silver and silver single crystals within the sphere where the first layer of Ag_2O was formed, with the help of impedance and potentiostatic measurements and with measurements of electronic diffraction. They proved that the dissolution of silver electrode comes about during the formation of $[Ag(OH)_2]^-$ after preceding formation of Ag_2O on the electrode. The oxidation of silver to the first stage, *i. e.* to Ag_2O occurs within two periods:

a) first the unimolecular layer of Ag_2O is formed according to equation

$$2\,Ag + 2\,OH^- \rightleftarrows Ag_2O + H_2O + 2\,e \qquad (1)$$

when the reversible potential of this layer is

$$E_M = -8 \pm 3 \text{ mV } (vs.\ Ag_2O/Ag)$$

b) unimolecular layer of Ag_2O deposits slowly onto the thicker layer.

The dissolution of silver, according to Giles *et al.*[12] takes place in accordance with the following dissolving reaction:

$$Ag + 2\,OH^- \rightleftarrows [Ag\,(OH)_2]^- + e \qquad (2)$$

and continues to a limited extent through the film of Ag_2O.

If the Ag electrode includes both metallic silver and AgO, the following chemical reactions with potential $+ 0.262$ V occur[13,14]:

$$2\,Ag + 2\,OH^- \rightleftarrows Ag_2O + H_2O + 2\,e \qquad E_0 = +\,0.342 \text{ V} \qquad (3)$$

$$Ag_2O + 2\,OH^- \rightleftarrows 2\,AgO + H_2O + 2\,e \qquad E_0 = +\,0.604 \text{ V} \qquad (4)$$

The resulting reaction is given by following equation:

$$Ag + AgO \rightarrow Ag_2O \qquad \Delta G = -\,6.05 \text{ kcal} \qquad (5)$$

The mechanism of formation and reduction of Ag_2O and AgO has always been a matter of dispute. Some conclusions were given by Wales and Burbank[15] which were based on X-ray pattern data. Extensive microscopic and X-ray pattern observations carried out by Wales and Simon[16] with a sintered Ag electrode within the course of long-term cyclic charging and discharging showed that the electrochemical formation and reduction of silver oxides is a fully reversible process and the comparison of examined electrodes with the structure of an unused silver electrode showed that in the examined electrodes only the size of Ag components is changing the result of which is the depreciation of the electrode structure uniformity.

2.3 Dissolubility of Silver Oxides in Alkaline Electrolytes

Very thorough measurements of solubility of Ag_2O in alkaline electrolytes were carried out by Johnston[17]. These measurements were done only up to the concentration of 6 N solution of OH^- ions. He supposed that Ag_2O in alkaline solution forms soluble anions according to

$$Ag_2O + 2\,OH^- \rightarrow AgO^- + H_2O \tag{6}$$

The existence of AgO^- ion was called in question in the work of Pleskov[18]. This author proved that Ag^I ions in alkaline solution form trinuclear univalent negative complexes in accordance with following equation

$$3\,Ag_2O + 2\,OH^- + H_2O \rightarrow 2\,[Ag_3O(OH)_2]^- \tag{7}$$

The existence of these trinuclear complexes was confirmed by Koba[19]. Koba determined the solubility of Ag_2O with various KOH concentrations and temperature of 25° C by means of radioactive isotope ^{110}Ag. The solubility of Ag_2O within the range of concentrations of 1 to 14 M KOH was studied by Amlie[6] as well. The values given by Amlie[6] coincide with those given by Johnston[17], but they differ from the values stated by Koba[19]. Nowadays, it is Giles *et al.*[12] who have verified these data again. They showed that in 1M concentration of OH^- ions, Ag_2O is dissolving in the form of ions $[Ag(OH)_2]^-$ in concentration of 1.5×10^{-4} M, which coincides well with the results of Amlie and Rüetschi[6].

The authors[12] proved that the main product of solubility of Ag_2O in KOH is the formation of ions of $[Ag(OH_2]^-$. With high concentration of OH^- ions some other particles may appear, as well. It is known that dissolved silver changes completely into form of $[Ag(OH)_2]^-$ if the concentration of OH^- ions does not fall below 0.5 M. With 0.5 M concentrations of OH^- ions and with lower ones even a small part of $[Ag(OH)_3]^{2-}$ is supposed to be present. Other particles of Ag^I which can be present like, *e. g.* Ag^+ or AgOH, are formed in 100 times lower concentrations (of 10^{-6} M order) with respect to concentration of $[Ag(OH)_2]^-$.

Amlie and Rüetschi[6] also state that all solutions which included dissolved Ag_2O produced a small Tyndall effect which points to the presence of colloidal particles of Ag_2O. Johnston[17] mentions this effect in his work, too.

Amlie and Rüetschi[6] were measuring also the solubility of Ag_2O in KOH solutions which contained zincate. They proved that the presence of zincate in KOH solutions had only a little influence upon the solubility of Ag_2O. Koba and Balasova[19] confirm too, that the presence of zincate ion has no effect upon the solubility of Ag_2O.

Cd in strong alkaline solutions shows an analogous behaviour, too. According to Visco and Sonner[20] the solubility of Cd^{II} in 7.1 M KOH is 1.05×10^{-4} M and Cd^{II} is supposed to form a complex in the form of $[Cd(OH)_3]^-$.

Solid AgO is unstable in alkaline solutions[4,6]. Decomposition of AgO is realized according to following reaction:

$$2\,AgO \rightarrow Ag_2O + {}^1\!/\!_2\,O_2 \qquad \Delta G = -9.360 \text{ kcal} \tag{8}$$

Nevertheless, the decomposition of AgO in alkaline electrolytes is very slow, in spite of its thermodynamic instability. Pleskov and Kabanov[18] studied the instability of Ag^{II} in alkaline electrolytes and found out that the amount of Ag^{II} which could penetrate into electrolyte is polarographically unmeasurable.

Amlie and Rüetschi[6] were dealing with a detailed analysis of AgO in alkaline electrolytes. They studied the effect of KOH concentration, light, presence of $[Zn(OH)_4]^{2-}$ and method of preparation of AgO. The conclusion of the achieved results is that the destructive reaction of AgO may *e. g.* significantly contribute to the self-discharge of Ag — Zn accumulator.

Nevertheless, according to some authors, the solubility of AgO in alkaline electrolytes coincides with the solubility of Ag_2O[19, 21] but according to the achieved results of Amlie and Rüetschi[6] as well as of Hammer and Craig[10] AgO is soluble in negligible concentrations and if silver can be found in alkaline electrolyte which is in contact with AgO, then it is Ag^I which origins by the decomposition of AgO.

2.4 *Catalyst Surface*

When studying the electrode reactions one should have corresponding knowledge on the substance of electrode surface and its changes in dependence with electrode potential. This requirement is of high importance especially when studying the reactions of oxygen reduction with silver in strong alkaline electrolyte since here complex compounds may form due to the dissolution of oxides which is produced within the potential limit of oxygen electrode function. The observation of oxygen reduction reactions is a wide and complex sphere which requires separate analysis and does not represent the subject matter of this article.

2.4.1 *Surface of Pt-Catalyst*

During all studies of electrode reactions of oxygen reduction we have been touching the problem consisting in the perfect lack of knowledge of the substance of electrode surface on which the reactions take place. The acquirement of this knowledge is not a simple matter. Bockris[3] observed the surface changes with Pt and gives us a general statement that it is possible to distinguish the following stages during oxygen reduction reactions:

a) oxygen or substances containing oxygen (*e. g.* — OH) are adsorbed on the surface,

b) oxides that can be two- or three-dimensional are formed on the surface.

It is rather difficult to acquire sound knowledge of the metal washer surface since suitable methods for its observation are not at our disposal. Bockris[3] gives us a survey of methods for observing platinum surface: X-ray diffraction, coulometry, ellipso-metric methods.

The ellipso-metric method in conjuction with coulometric data enabled to throw light upon changes that occur on Pt surface with various potentials in acid medium. It was proved that with potential values lower than about 1.0 V the oxygen particles on Pt surface should be adsorbed and with potentials higher than 1.0 V oxide phase is formed on Pt surface.

If knowledge of the substance of electrode surface as well as of its changes in dependence on electrode potential are at our disposal, then they serve us to create better facilities to clear up the reasons why some electrode reactions show great ranges in velocities at such electrode potentials at which oxides are formed on the surface of the catalyst (*e. g.* oxygen reduction, oxidation of ethylene and of other hydrocarbons *etc.*).

2.4.2 *Ag-Catalyst Surface*

The result of the previous part of this article is that the chemical substance of a metallic surface plays an important role when determining the reaction mechanisms of processes that take place on an electrode and simultaneously affect, in a decisive way, the properties of the electrode double layer. It is well known that only mercury acts as uncovered metal within wide potential range whilst platinum shows much narrower potential sphere within which it is not covered with adsorbed hydrogen or oxygen. Other metals have been much less investigated and it is impossible to say that their behaviour will be similar as in case of Hg or Pt especially in strong alkaline electrolytes.

In the case of silver the mechanism of oxygen reduction at the point of zero charge is much more complicated by the condition of electrode surface. In practice, it depends above all, upon so called »electrode pre-history«. The effect of the substance of silver surface upon electrochemical processes is much more serious than was assumed originally, especially in electrolytes which contain alkaline metal.

From the viewpoint of »pre-history« of the oxygen electrode containing silver catalyst, following conditions should be taken into account:

a) *Anodic limitation.* — This is given by the formation of $[Ag(OH)_2]^-$ and Ag_2O, as already mentioned in previous part of this article (see parts 2.2 and 2.3). Koryta *et al.*[22], Jantsa and Dousek[23] assume in their work the formation of thermodynamically stable thin layer of silver oxides on the surface of the electrode which can form a passivating film on the electrode which acts as inhibitor of the oxygen reduction. According to the work of Giles *et al.*[12] this statement is questionable since this monolayer of Ag_2O is stable only at a potential which is by about 8 mV more negative than the reversible potential of Ag/Ag_2O ($E_0 = + 0.342$ V).

b) *Cathodic limitation.* — This is given by the cathodic exclusion of alkaline metal and by the development of hydrogen while the reversibility degree of alkaline metal exclusion remains inexplicable for the time being. Kabanov *et al.*[24–27] have given us a proof that the alkaline metal becomes a part of some metal cathodes. They found that in case of silver especially, the hydrogen overvoltage in alkaline electrolytes is time-dependent and the gradient of Tafel line increases with cathodic polarisation, especially when this is more negative than — 1.75 V. With constant current density the final value for hydrogen overvoltage increases with the dimensions of alkaline metal ions in the following order: $Li < Na < K < Ca < N(CH_3)_4^+$. It was confirmed that the course of alkaline metal oxidation from the electrode surfaces is slowed down by gradual formation of intermetallic compounds of alkaline metal — silver type.

Zhutajeva *et al.*[28–30] confirmed that alkaline metal and hydrogen are simultaneously excluded during cathodic polarisation on the electrode, while alkaline metal and silver form intermetallic compounds. Giles and Harrison[31] observed the behaviour of $\langle 111 \rangle$ silver monocrystalline electrodes in alkaline solutions and demonstrated that with potential near to — 50 mV (*vs.* Ag_2O/Ag) either dissolving of silver occurs during the origin of $[Ag(OH)_2]^-$ or the metal is excluded again, which depends whether it refers to anodic or cathodic behaviour of the electrode, respectively. More the measurings proved that following Faraday's processes occur within the potential range of — 50 to — 1640 mV (*vs.* Ag_2O/Ag):

a) in case of cathodic connection with potential up to —1050 mV hydrogen atoms ($H^{\cdot}$) are probably excluded on the surface phase of silver — alkaline metal according to following equation:

$$H_2O + e \gtrless H^{\cdot}\,(MAg) + OH^- \tag{9}$$

where

M = atoms of all alkaline metals; and simultaneously exclusion of alkaline metals occurs on priority places of silver surface during the formation of M Ag surface phase according to equation:

$$M^+ + e \gtrless M\,Ag \tag{10}$$

together with the exclusion of hydrogen ions according to equation (9).

b) in case of more negative potential than — 1050 mV further exclusion of alkaline metal occurs on less preferential places and the condition is formed when the surface of Ag electrode is completely covered with alkaline metal; during longer periods of time, the atoms of alkaline metal (M) will diffuse slowly into silver.

The exclusion of alkaline metal on a solid Ag washer can be compared with the origin of alkaline metal amalgams in case of liquid mercury application. With electrode potential of — 1300 mV (*vs.* Ag_2O/Ag) and more negative, exclusion and simultaneously dissolution of alkaline metal from silver occurs during its longer action, which leads to surface recrystallization with corresponding increase of the number of places on which alkaline metals are excluded with high preference.

The result of experiments carried out is that the exclusion of alkaline metal and hydrogen reduces considerably the reduction rate of oxygen and hydrogen peroxide. The measurements proved that alkaline metal is excluded on the surface of monocrystalline silver electrodes with potential of — 1080 mV (*vs.* Ag_2O/Ag) and it cannot be easily reoxidized from the surface.

Kinetic measurements may be carried out only on an uncovered surface of the silver electrode, *i. e.* within the potential range of — 100 to — 900 mV (*vs.* Ag_2O/Ag) in 1*M* solutions of alkaline metals.

2.5 Adsorption of Ions

The electric double layer is of high importance in electrochemistry and observation, of the adsorption of ions in this layer is necessary. Only a limited number of suitable methods for the study of ion adsorption have been at our disposal until nowadays. None of them could be applied to measurements of ion adsorption on solid metals.

Therefore Bockris[32] modified in 1967 the newly developed ellipsometric method for the study of ion adsorption. It was applied first for studying ion adsorption on mercury and the results were compared with the values obtained by the electrocapillary method: the agreement was reasonable. Bockris[33, 34] continued developing a general method suitable for the study of ion adsorption in the electric double layer. Gold, silver, rhodium, nickel, lead and cadmium, were investigated. The results achieved by this method show that the degree of coverage of the surface of Pt electrodes with adsorbed anions is extremely dependent upon the electrode potential; with more positive potential the surface covering with adsorbed ions is more intensive.

2.6 Summary

We may expect that the function of oxygen electrode on the base of silver catalyst in strong alkaline electrolyte will considerably depend on the surface condition of Ag catalyst, *i. e.* on the oxygen electrode potential and on the amount and character of »impurities« contained in the electrolyte. We were extremely interested whether the »impurities« affect the activity of the silver catalyst in conditions when the electrode gains positive potential values, *i. e.* in the unloaded condition. It is evident that in these conditions the electrolyte contains dissolved silver in the form of ions $[Ag(OH)_2]^-$ and eventually it may contain »impurities« which originate by dissolving the cell components as mentioned in the work of Young[35], Wagner[36] and Klemm[37]. Knowledge of the influence of these »impurities« upon the activity of the silver catalyst in conditions of positive potential values is, according to our opinion, of high importance since even such a small quantity of »impurities« as 10^{-10} moles is capable to cover 1 cm^2 of electrode surface[12].

EXPERIMENTAL

3.1 Chemicals

Chemicals for the preparation of solutions: NaOH, KOH, Na_2CO_3, Ag_2O, ZnO and $HgCl_2$ were *p. a.* purity. Metals were applied in powder form: Zn (amalgamated with 14.5% Hg and not amalgamated), Fe, Ni, Cd; all were of *p. a.* purity.

Powdered Teflon Soreflone 5 (Société Ugine Kuhlmann) was applied for the preparation of the electrode. Ag_2CO_3 was supplied by Czechoslovak Company Vestec.

AgO was obtained by chemical oxidation of silver oxide prepared by precipitation from aqueous solutions of silver nitrate with alkali. Amorphous AgOH dehydrates immediately during the formation of Ag_2O and then oxidizes with potassium peroxidisulphate $K_2S_2O_8$ to AgO.

Preparation of AgO

AgO was prepared in a water bath at a temperature of 85° C in the following way: 0.28 mole of $K_2S_2O_8$ water suspension was added to 1.8 mole of KOH aqueous solution in 1 litre of water and at the end, during constant stirring, 0.3 mole of $AgNO_3$ dissolved in a minimum amount of water was added. Black AgO obtained was filtered through a Büchner funnel, then thoroughly washed in slightly alkalised water and dried in air. The oxide contained about 86.9% of Ag, as determined by the gravimetric chloride method after previous dissolution in HNO_3[38].

Preparation of NaOH Solution without CO_3^{2-}

It was prepared from 14.55 *N* solution of NaOH which was left in a refrigerator for 24 hours. Then the solution was filtered through S4 sintered disk without the access of air. The filtered solution was diluted with distilled water to 7 *N* NaOH concentration. Distilled water was scrubbed with nitrogen and was kept in a polyethylene bottle without access of air.

Preparation of 7N NaOH without CO_3^{2-} with Dissolved Ag^I

This solution was prepared by dissolution of 2 g AgO or Ag_2O in 500 ml of 7 *N* NaOH without CO_3^{2-} with constant stirring for 24 hours, and filtered through a S 4 sintered disk without access of air. This solution was then kept in dark because of its instability caused by the effect of light.

Preparation of 7N KOH with Dissolved Ag^I

This solution was prepared by dissolution of 2 g AgO or Ag_2O in 500 ml of 7 *N* KOH (with 1.5% of K_2CO_3 max.) in the same way as described above for the preparation of 7 *N* NaOH with dissolved Ag^I.

Preparation of K_2ZnO_2 Solution

Weighed quantity of ZnO is dissolved in warm solution of KOH of higher concentration (about 400 g KOH/100 g H_2O) and after being dissolved the solution is diluted with distilled water to the concentration required.

3.2 Preparation of Oxygen Electrode

As catalyst for electrochemical reduction of oxygen and as material for electronically conductive skeleton of the electrode we applied silver which was obtained by thermal decomposition of powdered silver carbonate (Ag_2CO_3) and/or silver monoxide (AgO) during sintering moulded electrode.

As binding agent we applied the above mentioned Soreflone 5, *i. e.* powdered polytetrafluorethylene (PTFE). A mixture of Ag_2CO_3-PTFE of 60 : 40% weight ratio was prepared from Ag_2CO_3 (and/or AgO) and PTFE by dry homogenization — shaking (about 20 minutes). Weighed quantity of thus produced mixture was poured in a press die and a tablet of ⌀ 36 mm and 1 to 1.2 mm thickness was pressed under pressure of 1,000 kp/cm^2. The electrode made in this way was inserted between silver plates and was sintered for 20 minutes in an electric furnace with air atmosphere at the temperature of about 390^0 C followed by quick cooling of the completely sintered electrode.

By the above mentioned production process we prepared the electrodes which were further applied for measurements of polarisation curves. In the same way the electrodes on the base of silver/PTFE were prepared by Brill[39].

Measuring Fixture

The tested electrode together with the current collector and sealing were put into a fixture made of polymethyl methacrylate and was clamped with screws. The whole fixture was inserted into a glass vessel. From the viewpoint of long-term measurements and/or in order to eliminate the effect of the environment (above all of CO_2) the vessel was provided with a ground joint neck, which was provided with sealing passages. When designing this fixture we followed the work of Jansta[40].

For clamping the fixture we applied screws of following material: Fe, Ni, Cd, Zn, polyamide, polyethylene, polypropylene and polyphenyleneoxide.

As collector we applied Ag annulus and later Pt gauze. The counter-electrode was made of Pt sheet or Pt gauze. Collector and counter-electrode outlets were of Ag wire and later of Pt wire. Silicon rubber was used for sealing the electrode into the fixture.

The measurements were carried out at the temperature of 63^0 C ± 3^0 C.

3.3 Measuring Method

For the verification of electrochemical qualities of the electrode we selected the measurement of polarisation curves. Measurements were carried out in a half-cell system the principal arrangement of which is described[41].

The potential of the tested electrode was measured with respect to reference **Hg/HgO** electrode which was connected to the surface of oxygen electrode by means of a Luggin capillary. An electronic voltmeter with 10^8 Ohms (Tesla BM 289 or BM 388 E) input resistance was used.

Since the equipment for ellipsometric method by means of which it is possible to follow the events that may occur on the surface of silver catalyst during unloaded condition of the oxygen electrode was not at our disposal, we selected the method of comparing the changes of current density in dependence on time for the determination of the total effect of these events.

The following procedure was adopted:

a) every tested oxygen electrode, was, before following the drop of activity, polarised minimum for 24 hours with such current in order the electrode potential could move within — 100 to 200 mV *vs.* Hg/HgO;
b) after reaching steady state of electrode potential a polarisation curve was sensed from every electrode tested of which the current density with — 300 mV *vs.* Hg/HgO potential was evaluated; the value achieved in this way was chosen as the initial value.
c) then every electrode tested was subjected to unloading condition either with oxygen operating pressure or without oxygen pressure *(flooded state)* during pre-determined time;
d) in further phase of measuring the activity change the electrode was subjected to the same conditions as in item a)
e) after steady state of electrode potential the electrode polarisation curve was measured again and current density with — 300 mV *vs.* Hg/HgO potential was evaluated; the resulting value was compared with the standard one.

We take due notice that it is not possible to apply this method for throwing light upon the substance of events that occur on the electrode under above mentioned conditions, but on the other hand, it is possible to find out the share of individual effects upon the whole function of the oxygen electrode and to presume the changes of activity of the oxygen electrode silver catalyst in strong alkaline electrolyte.

3.4 Evaluation of Results

The results of measurements given in following diagrams include the values of a minimum of 3 and a maximum of 10 samples. Current density of investigated electrodes with — 300 mV *vs.* Hg/HgO potential was within 40 to 140 mA/cm². Therefore the drop of oxygen electrode activity is evaluated as relative drop expressed in per cents of the initial value (see 3.3, it. b) of the electrode tested according to formula:

$$\delta A = \frac{b}{a} \cdot 100\% \tag{11}$$

where

δA = relative drop of electrode activity in %
a = initial activity of the electrode expressed in mA/cm² (initial value)
b = electrode activity in time t expressed in mA/cm²; with respect to speed up the events causing the drop of activity of oxygen electrode all measurements were carried out at the temperature of 63^0 C ± 3^0 C in unloaded condition of the electrode and without oxygen pressure, if not stated differently.

RESULTS

4.1 Drop of Oxygen Electrode Activity

Changes of current density in dependence upon time were followed on the basis of measuring the polarisation curves, and changes of oxygen electrode activity were evaluated from the relative change of current density.

All measurements showed that activity drops with time. This occurs both in loaded and in unloaded conditions. The results are given in Fig. 1 where it is evident that an expressive drop of activity during the same time interval occurs in an oxygen electrode in unloaded condition and without oxygen pressure. The current density during loading was selected so that oxygen electrode potential could move within the range of — 150 to — 200 mV *vs.* Hg/HgO while in unloaded condition the electrode reached positive potential values *vs.* Hg/HgO. This resulted in the fact that the activity drop of oxygen electrode on the base of Ag-PTFE depends above all upon the potential of this electrode; the more positive values the potential reaches the more expressive is the drop of activity.

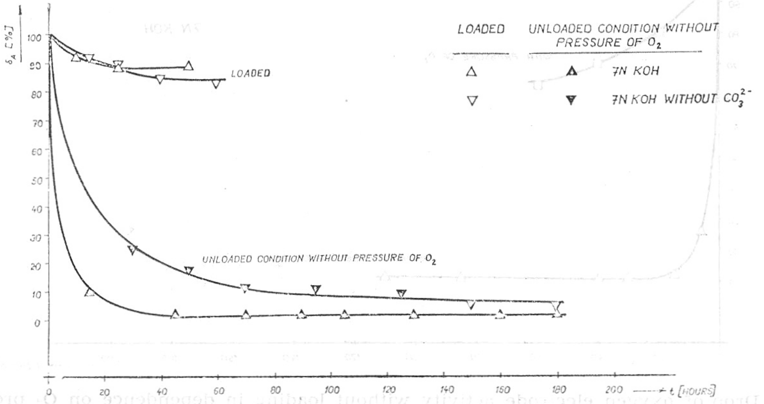

Fig. 1. Drop of oxygen electrode activity when loaded and in unloaded condition without pressure of O_2.

During measuring, no expressive difference in the application of 7*N* KOH or 7*N* NaOH was observed.

4.2 Effect of Oxygen Pressure upon Drop of Oxygen Electrode Activity

On the basis of preceding results the drop of oxygen electrode activity was observed in conditions of unloaded state. It was demonstrated that in these conditions, oxygen pressure supplied to the electrode has a substantial effect on the drop of activity. The results of measurements are given in Fig. 2 and clearly indicate that the electrolyte »impurities« play probably a decisive role.

4.3 Effect of Ag^I upon Drop of Oxygen Electrode Activity

The result of Chapter 2 is that oxygen electrode on the base of silver catalyst may »contaminate« strong alkaline electrolyte with $[Ag(OH)_2]^-$ anions in loaded conditions of the electrode during longer time periods. We carried out a series of experiments observing the drop of oxygen electrode activity in unloaded conditions without adding Ag^I at the beginning of the experiment and with Ag^I added at the beginning of the experiment. More we investigated what was the effect of oxygen pressure supplied to the electrode upon the drop of activity of oxygen electrode in above mentioned conditions. The

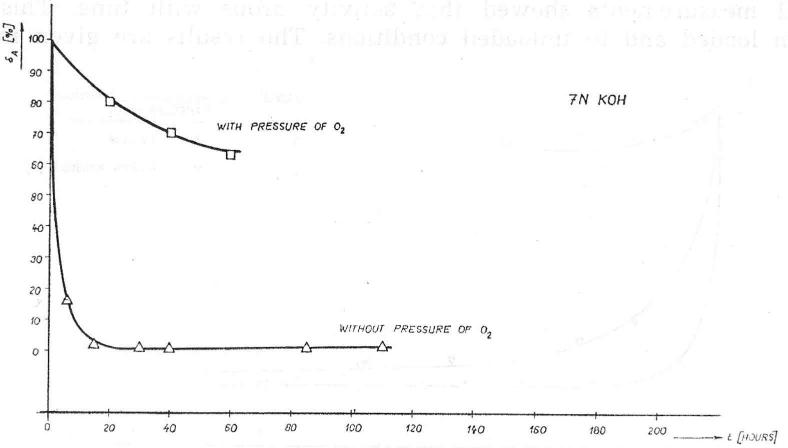

Fig. 2. Drop of oxygen electrode activity without loading in dependence on O_2 pressure

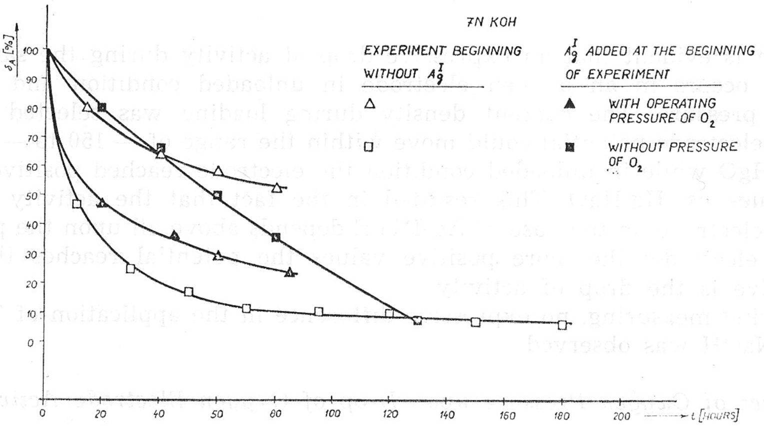

Fig. 3. Effect of Ag^I added into electrolyte at the beginning of experiment, upon drop of O_2 electrode activity without loading.

results are given in Fig. 3. The results obtained confirm that Ag^I has a great effect upon the drop of electrode activity if it is present at the beginning of the experiment in the form of anion $[Ag(OH)_2]^-$. In case Ag^I was added at the beginning of the experiment under conditions that the electrode was not loaded and without oxygen pressure an anomaly which we are not able to explain, appeared within the course of activity drop. But after about 120 hours the activity drop coincided with the activity drop without adding Ag^I at the beginning of the experiment under the same conditions.

4.4 Effect of Collector Material upon the Drop of Oxygen Electrode Activity

An Ag-annulus was applied as collector from the very beginning; this annulus was attached to the oxygen electrode from the side of electrolyte. Later a Pt gauze with Ag outlets was applied and after that, a Pt gauze

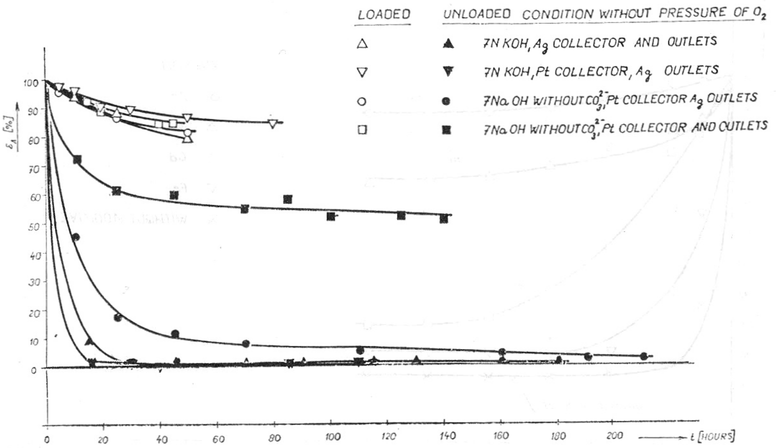

Fig. 4. Effect of various materials of collector construction upon drop of O_2 electrode activity

with Pt outlets. Comparison of the effects of these types of gauzes upon the drop of oxygen electrode activity is given in Fig. 4. Measurements showed that if the electrode is loaded, the type of collectors has no substantial effect upon the drop of activity. A substantial difference appeared, nevertheless, in unloaded condition without oxygen pressure. On the basis of the results obtained, all other experiments were carried out with collectors of Pt only.

4.5 Effect of Zn, Ni, Cd and Fe upon the Drop of Oxygen Electrode Activity

The results obtained when determining the effect of Zn, Ni, Cd and Fe upon the drop of oxygen electrode activity in dependence on time in the unloaded condition of the electrode and without oxygen pressure, are given in Table I and are graphically represented in Fig. 5. The above mentioned metals were added into the electrolyte in powder form and in 0.5 g quantity per one experiment. Obtained results show that these metals slow down the

TABLE I

Drop of Ag/PTFE Oxygen Electrode Activity after 120 hours of its Unloaded Condition without Oxygen Pressure in the Presence of Zn, Ni, Cd and Fe

Serial Number	Kind of additive	Drop of oxygen electrode activity δ_A (%)
1	Without additive (Ag/PTFE electrode)	99
2	Fe	96
3	Cd	90
4	Zn	22
5	Fe + Zn	77
6	Zn (amalgamated (14.5% Hg)	83

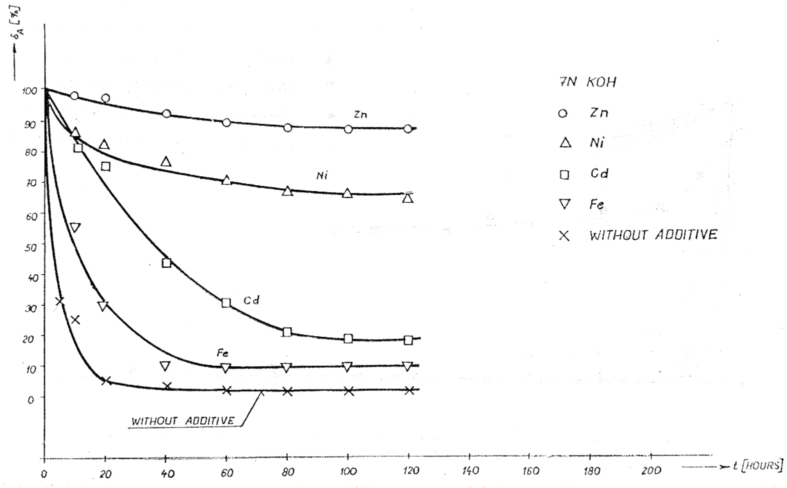

Fig. 5. Effect of Zn, Ni, Cd, and Fe upon drop of oxygen electrode activity in unloaded condition without pressure of O_2.

drop of activity of the oxygen electrode proper in the following sequence: Zn > Ni > Cd > Fe.

Zn has the strongest effect of all tested metals on slowing down the drop of activity of an unloaded oxygen electrode without oxygen pressure. It was added to the electrolyte in powder form too, but in the quantity of 5 g per one experiment. The reason of adding greater quantity of Zn consists in its substantially higher corrosion in applied electrolytes caused especially by the effect of higher operating temperature.

It was found out simultaneously that soluble anions of these metals do not affect substantially the function of the oxygen electrode.

Nevertheless, if we assume they affect unfavourably the activity of the oxygen electrode, made on the base of Ag/PTFE, then their effect should be much smaller than is the effect of anions $[Ag(OH)_2]^-$.

4.6 *Slowing down of the Drop of Oxygen Electrode Activity by the Effect of Zn*

Zn acts positively in slowing down the drop of oxygen electrode activity in unloaded condition without oxygen pressure in dependence on time. Simultaneously it was found out, that the presence of Zn only in the form of zincate has no effect upon slowing down the drop of oxygen electrode activity. We bestowed attention on following the conditions under which the positive effect of Zn appears expressively and the measured values are given in Figs. 6 and 7. It results from the curves that positive effect of Zn is lower if there are favourable conditions in the cell for the increased formation of $[Ag(OH)_2]^-$ (see material of the collector construction) and decreases substantially when zinc is applied in amalgam form (14.5% Hg) or if Fe is added into the electrolyte together with Zn.

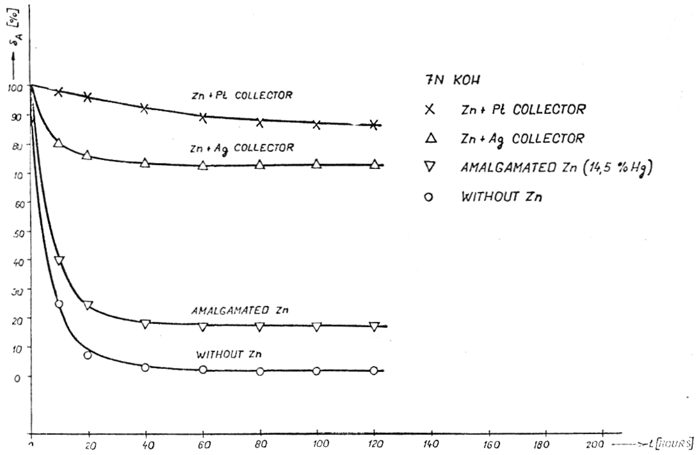

Fig. 6. Effect of Zn upon drop of oxygen electrode activity in unloaded condition without oxygen pressure.

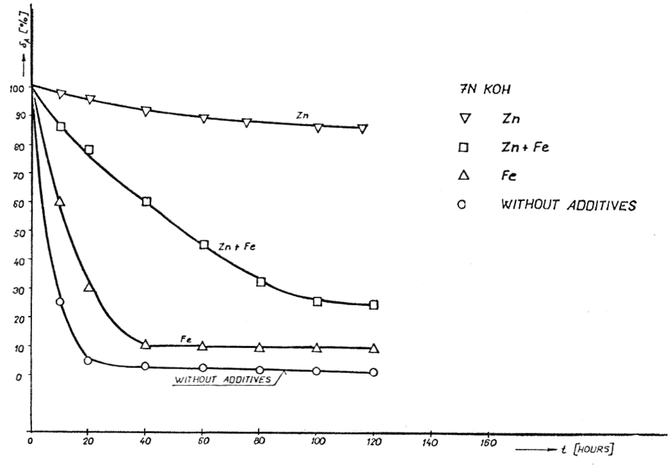

Fig. 7. Limiting of Zn effect upon drop of oxygen electrode activity in unloaded condition without oxygen pressure by action of Fe.

4.7 *Effect of Amalgamation of the Oxygen Electrode upon its Activity*

The amalgamation effect of the proper oxygen electrode (Ag/PTFE) by 2.5% solution of $HgCl_2$ upon the drop of its activity was followed in conditions of unloaded state without oxygen pressure, as well. Results given in Fig. 8 show that this amalgamation does not effect the activity of the oxygen electrode.

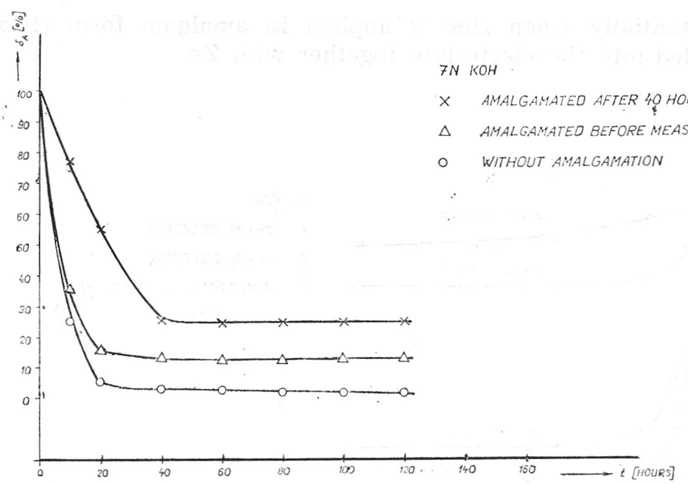

Fig. 8. Effect of amalgamation of oxygen electrode upon activity drop in unloaded condition without oxygen pressure.

4.8 *Effect of* CO_3^{2-} *upon the Oxygen Electrode Function*

The observation of the effect of CO_3^{2-} was carried out with 7 *N* NaOH. In loaded conditions the oxygen electrode, when increasing the concentration of carbonates in NaOH solution, decreases its total activity, as indicated in Fig. 9.

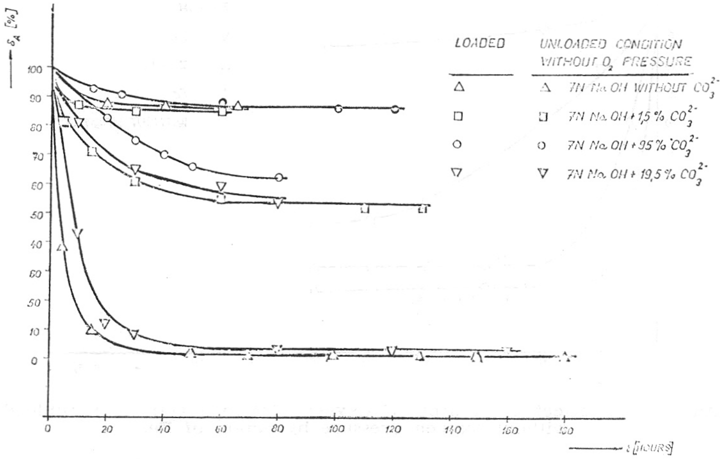

Fig. 9. Effect of CO_3^{2-} upon oxygen electrode activity.

On the other hand, in conditions of unloaded state of the oxygen electrode without oxygen pressure, a positive effect of the presence of carbonate to approximate concentration of 9.5% CO_3^{2-} is evident. But this positive effect was not evident in the presence of 19.5% CO_3^{2-}.

The result of above mentioned facts is that even if carbonates slow down the drop of activity of the unloaded oxygen electrode without oxygen pressure, their presence is generally undesirable since they reduce the output of the electrode in loaded conditions.

4.9 Oxygen Electrode Operating Pressure

It became evident during preparation and testing of the manufactured oxygen electrodes that the operating pressure of these electrodes, except for the size of particles of initial raw materials, is affected by the process of pressing. Our intention consisted in obtaining the electrodes operating with low-pressure working regime, *i. e.* up to pressure of about 50 cm of H_2O column. Pressing conditions were not optimalised but a good production reproducibility of electrodes that operated within the range of oxygen pressure of 14 ± 4 cm of H_2O column, as far as the production process mentioned in Chapter 3.2 was followed, was observed.

DISCUSSION

From the results given in Chapter 4 follows that the unloaded condition of the oxygen electrode on the base of Ag/PTFE with and without oxygen pressure causes, in dependence on time, the drop of activity of Ag catalyst up to such an extent that oxygen electrode of this composition is from the viewpoint of reached output practically inapplicable for electrochemical systems.

The question what actually causes such an expressive drop of Ag catalyst activity and what are the processes causing this drop of activity, remains open. Although the methods for giving a direct evidence are not at our disposal we believe that the drop of Ag catalyst activity is caused by the effect of Ag^I which is present in strong alkaline electrolyte in the form of complex anions, above all of $[Ag(OH)_2]^-$. Further on we assume that the »self-poisoning« of the catalyst occurs owing to adsorption of these ions on the conductive skeleton (silver) of the tested oxygen electrode on the base of Ag/PTFE, when this unloaded state of the electrode without oxygen pressure forms the most favourable conditions for this adsorption. The measuring proper showed that metallic Zn effects actively upon slowing down the drop of Ag catalyst activity, especially in those cases when its surface is not »blocked«. Achieved results coincide with the work of Arcand[42,43] who observed exclusion of silver on zinc from concentrated KOH solutions and proved that Ag^I will be excluded during 6 hours approximately from 90% of KOH solution on zinc sheet in form of silver coating.

The fact that 4.8×10^{-4} *N* concentration of Ag^I in 7 *N* KOH may cause expressive changes on the electrode surface was proved by our experiment when we prepared a porous electrode on the base of Zn/PTFE by the same technology as Ag/PTFE electrodes. This electrode was subjected to conditions of unloaded state without oxygen pressure for about 90 hours, when 7 *N* KOH was saturated at laboratory temperature with dissolved Ag^I in the form of $[Ag(OH)_2]^-$ anion.

Then oxygen at operating pressure was supplied to this electrode and within the course of 75 hours we measured its potential in unloaded condition,

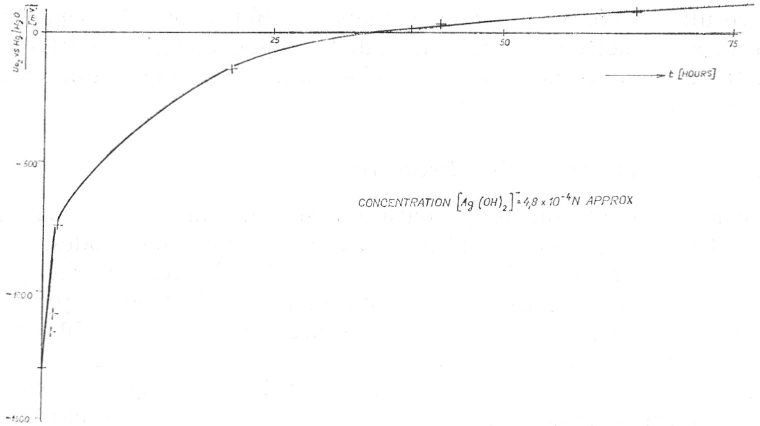

Fig. 10. Change of Zn-PTFE electrode system potential effected by Ag^I present in 7 *N* KOH in form of $[Ag(OH)_2]^-$.

the course of which is represented in Fig. 10. It is evident from the final potential values of this electrode that after this time it indicates the same potential as the electrode on the base of Ag/PTFE even when, at the beginning of the experiment, its potential indicates the potential of pure Zn electrode. Positive potential value was indicated by the electrode even in that case when it was subjected to conditions of unloaded state without oxygen pressure. Electrode on the base of zinc skeleton-PTFE subjected to above mentioned regime was tested from the viewpoint of oxygen electrode function as well, *i. e.* during polarisation. It was possible to load the electrode by current density of 1 to 2 mA/cm^2 with polarisation of — 300 mV *vs.* Hg/HgO. It was possible to load oxygen electrodes on the base of Ag/PTFE where drop of activity took place with time in conditions of unloaded state and without oxygen pressure by the same current density.

On the basis of all above mentioned facts we concluded that it is possible to consider the application of electronegative metals as components of electronically conductive skeleton of oxygen electrode, especially in case when silver is applied as catalyst in strong alkaline electrolyte. Our own experience in the experimental work made us to choose powdered Zn of 99.99% purity. After a series of tests and experiments we made an electrode of PTFE/Zn/Ag_2CO_3 composition in ratio of 40 : 40 : 20% by weight which contained 64 mg of Ag/cm^2 and which was made by nearly the same technology as the electrode on the base of Ag/PTFE. From the viewpoint of decreasing the corrosion of Zn in 7 *N* KOH the made electrode was amalgamated by 2.5% solution of $HgCl_2$ before application. This electrode indicates potential of Zn electrode at the beginning of the experiment. After supplying oxygen operating pressure in unloaded condition this potential changes with time and at the end the electrode obtains such potential values as the electrode on the base of Ag/PTFE. Values of polarisation curves and long-term operating activity of PTFE/Zn/Ag electrodes are given in Figs. 11 and 12.

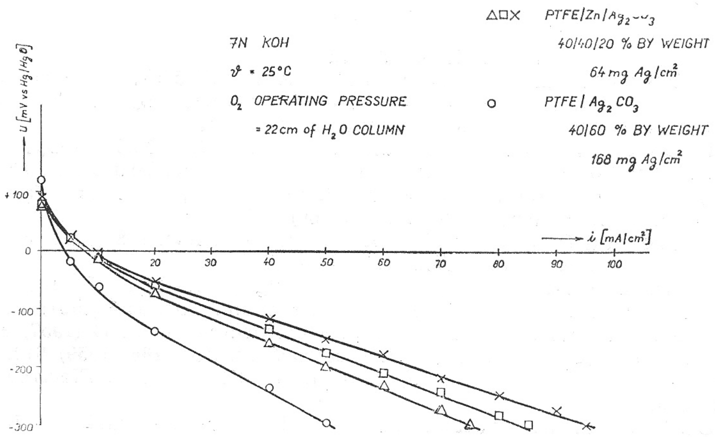

Fig. 11. Polarisation curves of oxygen electrodes on the base of PTFE | Zn | Ag and **PTFE—Ag.**

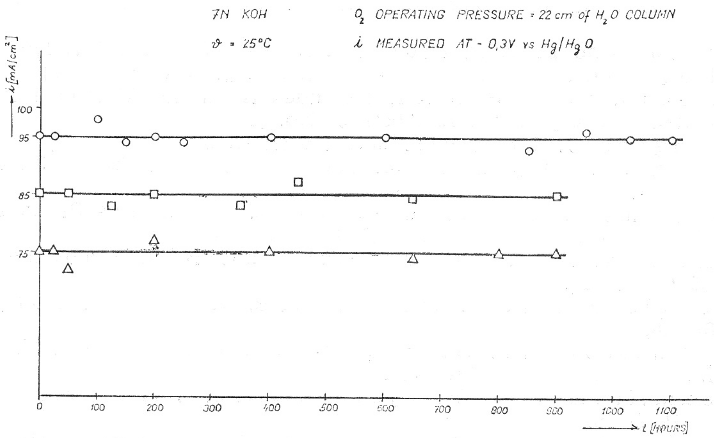

Fig. 12. Time dependence of current density of oxygen electrodes on the base of PTFE | Zn | Ag_2CO_3 (40 : 40 : 20%) by weight, 64 mg Ag/cm²).

CONCLUSION

On the basis of obtained experimental results we came to the conclusion that the oxygen electrode on the base of Ag/PTFE is practically inapplicable especially at high temperatures and in unloaded conditions in 7 *N* KOH. Its »self-poisoning« is probably caused by the effect of adsorption of $[Ag(OH)_2]^-$ anions. But this undesirable property of silver can be positively utilized when applying highly electronegative metal, *e. g.* zinc. At the same time the application of electronegative metal enables the assumption for the reduction of the quantity of silver and/or other catalysts in the electrode.

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IZVOD

Smanjivanje aktiviteta kisikove elektrode izrađene na osnovi srebrnog katalizatora u politetrafluoretilenu

M. Cenek, O. Kouřil, J. Šandera i J. Vaňáček

Proučavano je određivanje utjecaja nečistoća, koje potječu od otapanja dijelova ćelije, na smanjivanje aktiviteta kisikove elektrode od srebrnog katalizatora u 7 *N* KOH. Utjecaj površine srebra značajniji je, nego što se to pretpostavljalo. Od posebnog su značenja stvaranje i otapanje srebrnih oksida, te s time povezana naknadna adsorpcija iona $Ag(OH)_2^-$ na aktivnoj površini. Određivanje aktivnosti vršeno je mjerenjem gustoće struje kod —300 mV prema Hg/HgO referentnoj elektrodi, nakon standardne predobrade. Rezultati pokazuju da aktivitet elektrode opada s vremenom zbog utjecaja onečišćenja, kao što su to ioni Zn, Ni, Cd, Fe, Hg, kao i CO_3^{2-}. Utvrđen je i efekt samozatrovanja stvaranjem iona $Ag(OH)_2^-$. Iz svega slijedi da je elektroda Ag/PTFE neprikladna za praksu. Pozitivan rezultat ovih istraživanja je činjenica da se stvaranje $Ag(OH)_2^-$ može korisno upotrijebiti kao metoda proizvodnje vodljivog skeleta za elektrode primjenom smjese srebra i cinka u matrici PTFE.

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