

**ANALYSIS OF THE ELECTROCHEMICAL ACTIVITY OF VARIOUS TYPES
OF MATERIALS TOWARDS H_2O_2 DEPENDING ON THE MEDIUM PH LEVEL**

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Abstract

The current paper considers the electrochemical activity of electrode materials towards oxidation and reduction of hydrogen peroxide (H_2O_2) at different pH values of the electrolyte. The different types of electrode materials are discussed and eligible materials for anode and cathode are defined. The potential-pH equilibrium diagram of the system H_2O_2 - H_2O is analyzed and appropriate electrode potentials are specified.

Key words: hydrogen peroxide, electrode material, fuel cell

1. INTRODUCTION

The electrochemical activity of electrode materials is the main parameter determining the technical and cost indicators of fuel cells, since the maximum current density and efficiency depend on them. The studies cited in the literature address mainly determining of the material activity with respect to the processes of H_2O_2 reduction and oxidization. They can be provisionally classified in several groups:

- Metals: Zinc (Zn) [3], Tin (Sn) [3], Titanium (Ti) [3], Aluminum (Al) [7,11-13], Tantalum (Ta) [7], Zirconium (Zr) [7], Nickel (Ni), Platinum (Pt), Palladium Pd [2], [3], [5], Silver Ag [8,9,10,14], Gold Au [29];
- Metal alloys: *NiPdCd* [6,25], ruthenium-rhodium (Ru-Rh) [4];
- Metal oxides: Iridium oxide (IrO_2) [1], simple and spinel oxides of Ni and Co [15,16], *Rh₂TeO₆*, *Rh₂WO₆* or *Rh₂MoO₆* [17,23,24], Tl_2O_3 [20,22]
- Non-metals: pyrolytic graphite electrodes – [3,18].

The purpose of this paper is to define the electrochemical potential regions of electrode materials for achievement of the maximum electromotive force and to analyze the activity of various materials with respect to the processes of reduction, oxidization and spontaneous decomposition of the hydrogen peroxide depending on pH of the medium.

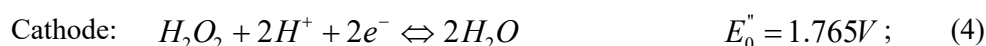
2. ELECTROCHEMICAL ACTIVITY ANALYSIS OF THE MATERIALS TOWARDS H_2O_2

In our previous work [19] we made a theoretical analysis of the direct conversion of chemical energy of H_2O_2 into electrical and the voltage generated by the reactions:

at $pH \geq pK = 11,63$:



at $pH < pK$:



where pK denotes the equilibrium electrolytic constant of hydrogen peroxide.

These reactions determine the chemical and electrochemical activity of substances towards the processes of H_2O_2 reduction and oxidization depending on their electrode potential.

The indicated electrode semireactions (1-4), in the Pourbaix diagram (Fig.1) three regions can be defined in the M.Pourbaix diagram (Fig.1) with respect to the electrochemical activity of electrode material and their electrode potential (E_0) towards the electrode potentials E''_0 (on the cathode) and E'_0 (on the anode).

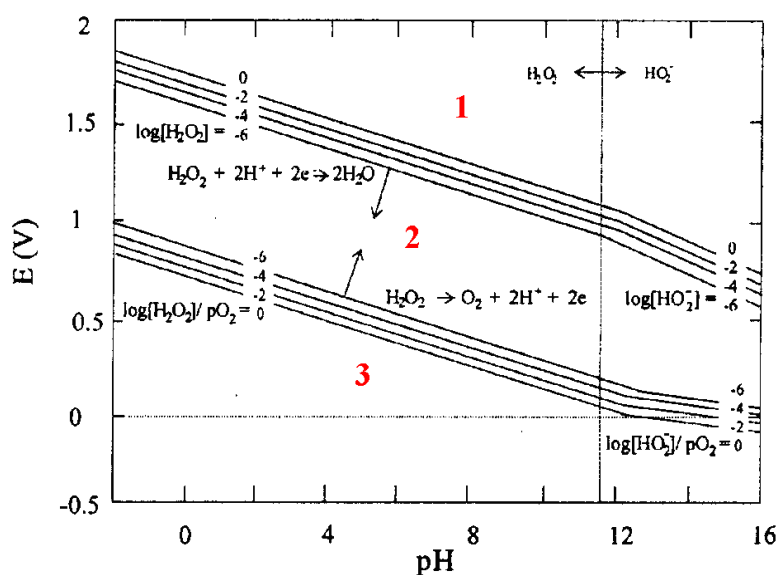


Fig.1. Pourbaix diagram for H_2O_2 at $T_0=298^\circ K$ ($pK=11.63$) [30]

The indicated electrode semireactions (1-4) define three regions in the Pourba diagram (Fig.1) with respect to the electrode potential of the analyzed material (E_0) and electrode potentials of the cathode (E''_0) and the anode (E'_0):

Region 1 - materials capable of oxidizing H_2O_2 to O_2 with potential $E_0 > E''$;

Region 2 – materials that can both oxidize and reduce H_2O_2 . Usually they are positive catalysts of the spontaneous decomposition of H_2O_2 . Their potential satisfies the inequality $E''_0 > E_0 > E'_0$;

Region 3 – materials capable of reducing H_2O_2 to H_2O with electrode potential $E_0 < E'_0$.

It should be noted that a material may belong to various regions of Fig.1 because the electrode potential is function of the medium pH [19]:

at $pH \leq pK = 11,63$

$$\begin{aligned} E' &= f_1(pH) = E'_0 - b^0 pH - \frac{b^0}{2} \lg \frac{a_{H_2O_2}}{P_{O_2}} \\ E'' &= g_1(pH) = E''_0 - b^0 pH - \frac{b^0}{2} \lg \frac{a_{H_2O}^2}{a_{H_2O_2}} \end{aligned} \quad (5)$$

at $pH \geq pK = 11,63$

$$\begin{aligned} E' &= f_2(pH) = E'_0 - \frac{b^0}{2}(pH - 14) - \frac{b^0}{2} \lg \frac{a_{HO_2^-}}{a_{H_2O} P_{O_2}} \\ E'' &= g_2(pH) = E''_0 - \frac{3b^0}{2}(pH - 14) + \frac{b^0}{2} \lg a_{H_2O} a_{HO_2^-} \end{aligned} \quad (6)$$

where: $b^0 = 2,3 \frac{RT_0}{F} = 0,0591V$ at $T_0 = 298^0 K$.

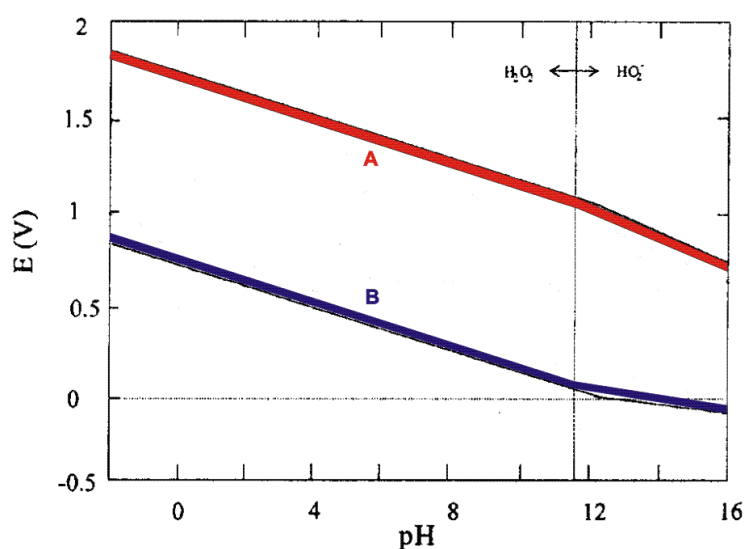


Fig.2. Electrode potential regions of the cathode and anode materials

Therefore, the material of which the cathode is made should possess an electrode potential as close as possible to, but less than E_0'' (region A of Fig.2), while the material of which the anode is made should possess an electrode potential as close as possible to, but more than E_0' (region in of Fig.2). Therefore, the electrode potentials of the materials for electrodes should lie within the above-defined region 2, respectively in its upper and lower part.

The width of zones A and B is defined as 0,1V in order to reduce electromotive force losses to 20%.

3. DISCUSSION

Beside an appropriate electrode potential value, the electrode materials for the peroxide fuel cells should also meet the following additional requirements:

- to oxidize (at the anode) and reduce (at the cathode) H_2O_2 at a high velocity rate;
- to be chemically inert with respect to the electrolyte, resp. with respect to pH of the medium;
- not to catalyze the self - decomposition process of H_2O_2 ;
- to be non-toxic with respect to the environment and non-carcinogenic;
- to be low-cost and affordable;
- to be non-corrosive.

Since some of the above-indicated requirements are conflicting, the main attention is devoted to the first three requirements, since they determine also the technical and cost parameters of the fuel cell.

In the region A defined in Fig.2 it can be seen that, in the event of work in highly acidic environments, the electrochemical potential value of the electrode materials should be very high, of an order of magnitude $1.6\div 1.7V$. A comparatively limited number of oxidizing–reduction pairs have such electrode potential, for example: Ce^{3+}/Ce^{4+} ($E_0=1,73V$), $PbO_2/PbSO_4$ ($E_0=1,685V$), etc. [28]. Taking into account the concentration of reaction substances, the potential of the first pair decreases to 1,25V in highly acidic solutions of H_2SO_4 , H_3PO_4 , etc. In the second pair, PbO_2 is a positive catalyst of the self - decomposition of H_2O_2 and is toxic to the environment. Therefore, both materials are unsuitable for electrodes.

According to [26] in a slightly acid, neutral and slightly alkali medium ($pH = 5\div 9$) the electric conductivity of the electrolyte is low: $7388\cdot 10^{-4} \Omega^{-1}\cdot cm^{-1}$ in 30% H_2SO_4 ; $5403\cdot 10^{-4} \Omega^{-1}\cdot cm^{-1}$ in 25% KOH and rises to $2677\cdot 10^{-4} \Omega^{-1}\cdot cm^{-1}$ in 20% KCl and $2222\cdot 10^{-4} \Omega^{-1}\cdot cm^{-1}$ in 30% K_2CO_3 . That severely limits the current density and results to increased ohmic losses. For this reason these media are not considered promising for fuel cell applications with high current density.

From our previous study [19], as well as from Fig.2 it follows that in a highly alkaline medium, theoretically, the electromotive force between the electrodes is significantly smaller than that in an acidic medium. Nevertheless, it is preferred for two reasons: the lower corrosive activity of the structural materials in alkaline solutions and the lower electrode potential values that shall be possessed by the electrode materials in peroxide fuel cells – about 0,75÷0,85V at the cathode and 0,0÷0,1V at the anode.

One of the serious drawbacks of a highly alkaline electrolyte is the potential for formation of soluble carbonates under the influence of CO_2 dissolved in the aqueous solutions of H_2O_2 . This drawback, however, can be avoided by direct production of the aqueous solutions of H_2O_2 through hydrolysis of

CaO₂.xH₂O [19]. In the event that the dissolved carbonates can be separated from the electrolyte in the form of non-soluble CaCO₃.

Table 1 presents various types of materials used in peroxide fuel cells and defines the region of pH within which they can be used as electrode materials. The relationships of $E_0 = f(\text{pH})$ were derived on the basis of potential-pH Pourbaix diagrams for the respective metals. The limits of applicability are defined for concentration of substances in the solution 10⁻⁴M.

The same Table presents the electrode potential values calculated for a highly alkaline medium. From the results indicated in Table 1 it follows that Gold and Platinum possess the widest regions of the pH values in which they can be used. At pH =14 the potential of the pair Au/Au₂O₃ still has an appropriate value (0,63V), but the ions of Gold (Au³⁺) pass into the solution in the form of soluble ion (H₂AuO₃⁻). The main disadvantages of Platinum are: in a highly alkaline medium it acts as positive catalyst of the spontaneous decomposition of H₂O₂ and its high price.

Table 1. Relationships of $E_0 = f(\text{pH})$ * for various types of materials

No.	Material	Electrode reaction	$E_0 = f(\text{pH})$ *	Region of pH	E ₀ at pH=14
1	Gold	$2\text{Au} + 3\text{H}_2\text{O} \rightarrow \text{Au}_2\text{O}_3 + 2\text{H}^+ + 2\text{e}^-$	$1.457 - 0.0591\text{pH}$	$0,5 \div 13,3$	0.63
2	Platinum	$\text{Pt} + 2\text{H}_2\text{O} \rightarrow \text{Pt}(\text{OH})_2 + 2\text{H}^+ + 2\text{e}^-$	$0.980 - 0.0591\text{pH}$	$-1.0 \div 16,0$	0.15
		$\text{Pt}(\text{OH})_2 \rightarrow \text{PtO}_2 + 2\text{H}^+ + 2\text{e}^-$	$1,045 - 0.0591\text{pH}$	$-1.0 \div 16,0$	0.21
3	Silver	$2\text{Ag} + \text{H}_2\text{O} \rightarrow \text{Ag}_2\text{O} + 2\text{H}^+ + 2\text{e}^-$	$1.173 - 0.0591\text{pH}$	$10,3 \div 13,7$	0.34
		$2\text{Ag}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{AgO} + 2\text{H}^+ + 2\text{e}^-$	$1.398 - 0.0591\text{pH}$	$10,3 \div 13,7$	0.57
4	Paladium	$\text{Pd} + \text{H}_2\text{O} \rightarrow \text{PdO} + 2\text{H}^+ + 2\text{e}^-$	$0.896 - 0.0591\text{pH}$	$2,35 \div 16,0$	0.07
		$\text{PdO} + \text{H}_2\text{O} \rightarrow \text{PdO}_2 + 2\text{H}^+ + 2\text{e}^-$	$1,283 - 0.0591\text{pH}$	$2,35 \div 16,0$	0.46
5	Nickel	$\text{Ni}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{NiO}_2 + 2\text{H}^+ + 2\text{e}^-$	$1.434 - 0.0591\text{pH}$	$5,2 \div 16,0$	0.61
		$2\text{Ni}_3\text{O}_4 + \text{H}_2\text{O} \rightarrow 3\text{Ni}_2\text{O}_3 + 2\text{H}^+ + 2\text{e}^-$	$1.305 - 0.0591\text{pH}$	$6,3 \div 16,0$	0.48
		$3\text{Ni}(\text{OH})_2 \rightarrow \text{Ni}_3\text{O}_4 + 2\text{H}_2\text{O} + 2\text{H}^+ + 2\text{e}^-$	$0,897 - 0.0591\text{pH}$	$9,0 \div 12,0$	-
6	Iridium (IV) oxide	$\text{Ir} + 2\text{H}_2\text{O} \rightarrow \text{IrO}_2 + 4\text{H}^+ + 4\text{e}^-$	$0,930 - 0.0591\text{pH}$	-	0.10
7	Cobalt (III) oxide	$\text{Co}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{CoO}_2 + 2\text{H}^+ + 2\text{e}^-$	$1.477 - 0.0591\text{pH}$	$5,2 \div 16,0$	0.65
8	Bismuth (III) oxide	$2\text{Bi}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{Bi}_4\text{O}_7 + 2\text{H}^+ + 2\text{e}^-$	$1.338 - 0.0591\text{pH}$	$8,6 \div 16,0$	0.51
		$\text{Bi}_4\text{O}_7 + \text{H}_2\text{O} \rightarrow 2\text{Bi}_2\text{O}_4 + 2\text{H}^+ + 2\text{e}^-$	$1.541 - 0.0591\text{pH}$	$8,6 \div 16,0$	0.71
		$\text{Bi}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow \text{Bi}_2\text{O}_5 + 2\text{H}^+ + 2\text{e}^-$	$1.607 - 0.0591\text{pH}$	$8,6 \div 16,0$	0.78
9	Tin	$\text{Sn} + 2\text{H}_2\text{O} \rightarrow \text{SnO}_2 + 4\text{H}^+ + 4\text{e}^-$	$-0,106 - 0.0591\text{pH}$	$3,6 \div 9,1$	-
10	Titanium	$\text{Ti}(\text{OH})_3 \rightarrow \text{TiO}_2 \cdot \text{H}_2\text{O} + \text{H}^+ + \text{e}^-$	$-0.091 - 0.0591\text{pH}$	$1,5 \div 13,9$	-0.92
11	Aluminium	$\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + 3\text{H}^+ + 3\text{e}^-$	$-1.471 - 0.0591\text{pH}$	$4,0 \div 8,8$	-
12	Zinc	$\text{Zn} + 2\text{H}_2\text{O} \rightarrow \text{Zn}(\text{OH})_2 + 3\text{H}^+ + 3\text{e}^-$	$-0,400 - 0.0591\text{pH}$	$7,5 \div 12,4$	-
13	Zirconium	$\text{Zr} + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 4\text{H}^+ + 4\text{e}^-$	$-1,553 - 0.0591\text{pH}$	$3,6 \div 14,8$	-2.38
14	Tantalum	$2\text{Ta} + 5\text{H}_2\text{O} \rightarrow \text{Ta}_2\text{O}_5 + 10\text{H}^+ + 10\text{e}^-$	$-0.750 - 0.0591\text{pH}$	$-2.0 \div 16,0$	-1.58
15	Thallium (III) oxide	$2\text{TlOH} + \text{H}_2\text{O} \rightarrow \text{Tl}_2\text{O}_3 + 4\text{H}^+ + 4\text{e}^-$	$0.777 - 0.0591\text{pH}$	$7.0 \div 16,0$	-0.05

*) Potential versus a standard hydrogen potential (SHE)

In the existing solutions for peroxide fuel elements [8,10,14], an Ag electrode is quite often proposed in the role of a cathode notwithstanding that its potential is too low ($E_0=0,345V$ at $pH=14$) and the expected generated electromotive force of the cell will be too low – of the order of magnitude 0,4V, which is unsatisfactory.

An electrochemical pair $Pd(OH)_4/Pd(OH)_2$ with electrode potential 0,46V at $pH=14$ can be used as activator of H_2O_2 reduction. According to the results published in [25] the applicability of this pair can be problematic, since in a highly alkaline medium PdO_2 is dissolved leading to reduced activity of the electrodes. This material, however, can be used as promoter in the composition of other skeletal catalysts such as *Ni-Cd*.

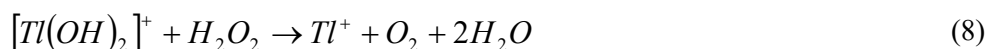
It is obvious that Nickel, the simple and spinel oxides of Ni and Co, Palladium and Bismuth (III) oxide can also be used as cathode material. The latter is of particular interest since in hot, highly alkaline mediums of KOH insoluble potassium bismuthate ($KBiO_3$) is formed under the influence of H_2O_2 . The latter is a strong oxidizer and its electrode potential lies in the region A (Table 2).

The electrode potential of IrO_2 at $pH=14$ is 0.1V, which determines it as a material suitable for making of the anode. An advantage of Iridium oxide is its high stability in a wide pH and temperature region [1], and its drawback – its relatively low chemical activity with respect to H_2O_2 .

Aluminum, zinc, tin and titanium cannot be used as electrode materials in peroxide fuel cells operated in an alkaline medium because they dissolve forming hydroxides and have a highly negative electrode potential which is outside the region B.

Zirconium and Tantalum have similar electrode potential values, however, unlike Al, Zn, Sn and Ti, in a highly alkaline medium they are passivated. Thanks to this fact they can be used as indifferent electrode materials since they are corrosion resistant and do not catalyze the spontaneous decomposition of H_2O_2 .

Thallium (III) oxide the electrode potential of which is within region B defined in Fig.2 can also be used as anode material. The studies carried out in [20-22] find that $Tl(OH)_3$ is a promising material for the anode. The pattern of interaction of Tl^+ with H_2O_2 proposed by the authors at 0.015-0.1125M concentration of sodium hydroxide is as follows:



i.e., the resultant reaction of the process is:



According to [20] the reaction rate (9) is in inverse proportion to temperature. The energy of process activation is -46,9kJ/mol, which is indicative of drastic reduction of the rate of H_2O_2 decomposition with increase of the temperature. On the basis of values of reaction rate constant (9) depending on the temperature of the medium (Table 2) cited in [22] the following conclusion can be drawn. The heat released upon spontaneous decomposition of H_2O_2 on the one hand will contribute to quick heating of the fuel cell and achievement of the rated operating conditions (70°C), while on the other hand it will

reduce the rate of peroxide decomposition and therefore will not have a negative effect on the fuel cell operation.

Table2. Values of the reaction rate constant [22]

Temperature, °C	Rate constant - $k \cdot 10^3$
35	15,65
45	9,85
55	6,50
65	2,83

One drawback of Tl_2O_3 is the high toxicity of Tl^+ -ions and its possible accumulation in the human organism. Another barrier to the use of $Tl(OH)_3$ as electrode material can be the high solubility of $TlOH$ in the electrolyte, thence decrease of the electrode activity and higher probability of the electrolyte pollution with highly poisonous Thallium ions.

4. CONCLUSION

The analysis of the electrochemical activity of electrode materials with respect to reduction and oxidization of H_2O_2 shows that there are currently comparatively few materials characterized by an appropriate electrode potential value. The following can be used as cathode material: Gold, simple oxides of Nickel and Cobalt and their spinels and bismuth (III) oxide. Anode materials possessing suitable electrode potentials are: iridium (IV) oxide and thallium (III) oxide.

It is obvious that the future work of the team shall address both research into the electrochemical activity of the electrode materials discussed, through their modification with metal compositions of Ni-Zn, Cd-Pd, $Co(II)PP/PG$ where PP is protoporphyrin-IX dimethyl ester, and PG - pyrolytic graphite electrode) etc.; organic substances: porphyrin or phthalocyanine complexes, Prussian blue $KFe[Fe(CN)_6]$ or other hexacyanoferrates, etc., as well as search for new electrode materials with suitable electrode potentials enabling achievement of the maximum electromotive force in peroxide fuel cells.

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