

Role of Ionic Transport in the Electrochemical Activation of Water Solutions

Abstract. The change in electrical conductivity of water solutions during electrochemical activation in a stationary diaphragm cell was studied. It is shown that the chemical composition of solutions and processing time have an important influence on the activation process. Method of operational control of the electrochemical activation process based on an analysis of the value of the current passing through the cell at a constant voltage on the electrodes was proposed.

Streszczenie. Zbadano zmianę przewodności elektrycznej wodnych roztworów podczas elektrochemicznej aktywacji w stacjonarnym diafragmowym elektrolizerze. Pokazano, że przy aktywacji ważną rolę odgrywa początkowy skład roztworu i trwałość procesu aktywacji. Zaproponowano metodę kontroli procesu elektrochemicznej aktywacji na podstawie analizy wielkości prądu, który przepływa przez elektrolizer, przy stałym napięciu na jego elektrodach. **Rola transportu jonów podczas elektrochemicznej aktywacji roztworów wodnych**

Keywords: water, conductivity, electrochemical activation.

Słowa kluczowe: woda, konduktywność, elektrochemiczna aktywacja.

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Introduction

Significant growth rates of environmental pollution require decisive and systematic public action towards the implementation of "green" technologies and protection of people against the negative factors. Over the last thirty years, scientists have developed, patented and implemented in production a lot of devices that are based on the method of electrochemical activation (ECA) of water solutions. Under the ECA process of water solutions is understood the process of transferring them to a metastable state caused by structure-energy and electrochemical changes in the electric field, which resulted in solutions for a period of relaxation show anomalous properties in the physical and chemical transformations. ECA is carried out in dilute solutions (generally at a concentration less than 0.01 M) at a high value of the external polarizing electromotive force. In such solutions, along with the products of electrolysis of dissolved solids, grow up the role of a solvent electrolysis, occur an intermediate states of the reacting particles - ions of different oxidation states, radicals and molecules [1-3]. If this process is carried out in a stationary two-chamber electrolytic cell with a separating diaphragm, then in the cathode chamber is obtained the activated solution – the catholyte and in the anode chamber – the anolyte.

The main constraining factors for the development of technologies based on ECA of water solutions are the metastability of its characteristics and the absence of a complete theoretical description of the process. As a result, there are still many unanswered questions, especially the concept of structural ordering of the activated water solution. Besides, the absence of standardized terminology and the holistic theory within the different scientific schools hinder systematization and synthesis of knowledge, significantly slowing down the progress of research. Therefore, the problem of fundamental physics research to identify the basic mechanisms of electrochemical activation is still relevant.

The electrochemical activation process of water solution depends on various factors – beginning from the solution composition and ending with the design features of the electrolysis cell. However, the current density has a defining influence – with its increasing electrode processes are intensified. [2] Power consumption of process is calculated from Faraday's laws, in which the amount of substance reacted on the electrodes, is directly proportional to the current strength and the processing time.

In practice, the electrochemical treatment is performed at a controlled current density [4-7], and at a constant voltage on the electrodes of the electrolysis cell [8-12]. The last option is most often used for stationary (stagnant) electrolysis cells. The density of the current passing through the cell is varied depending on the conditions and time of activation, which is caused by changes in electrical conductivity of water solutions in the chambers of the electrolysis cell. Processes responsible for these changes has not been fully investigated. The aim of this study was to investigate the role of ionic transport in the ECA process and determine the causes of the current density changes during the electrochemical treatment of water and water solutions at a constant voltage on the electrodes.

Experimental technique

Electrochemical treatment of the water was carried out in a stationary cell with two graphite electrodes and separating diaphragm made of nonwoven polypropylene of mark FS 2226-14E (pore volume 55%, the predominant pore radius of 10 μm). Electrode voltage was 600 V during treatment with distilled water and 220 V in all other cases. For studies was used tap water and distilled water degassed by prolonged boiling, as well as 0.001 M solutions of NaCl , NaHCO_3 , Na_2CO_3 .

Digital ammeter Pro'sKit MT-1820 was used to determine the density of the current passing through the cell. Measurement of the specific electrical conductivity of anolyte and catholyte was conducted using combimeter COM-100 with platinized electrodes. Measurements of the hydrogen ion concentration pH were carried out using a pH meter pH-301 with a combined glass electrode ESK-10601/7 and automatic temperature compensator DT-1000-1.

Experimental results and discussion

Degassed distilled water as a weak electrolyte is exposed in a small degree to dissociation with the occurrence of ion-molecule complexes formed by stable ions OH^- and H_3O^+ . The product of the molar concentrations of these ions determines the ionic product of water. At 25 °C it is equal to 10^{-14} , indicating a low concentration of current carriers, and therefore the distilled water had a specific electrical conductivity of less than 5 $\mu\text{S}/\text{sm}$. Therefore, for research of the electrochemical activation processes of such water, we used a large voltage values on the electrodes of the cell.

Consider the results of measurements of the current density in the cell during the electrochemical activation of distilled water (Fig. 1). As seen from the figure, the current density decreases in dependence nearly exponential. Such dependence can be described by the Ligan equation [13] for normal electrolysis, accompanied by the transport of ions through the diaphragm. Reducing the number of ions transported through it, should reduce the current density. Deviations from the exponent can be explained by additional ionization of the water molecules by the electric field.

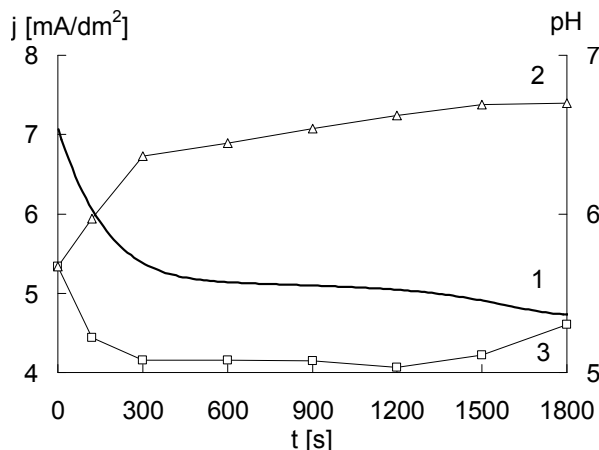


Fig.1. The dependence of the current density, flowing through the electrolytic cell (1) and the hydrogen index value of pH of the catholyte (2) and anolyte (3) from the time of electrochemical treatment for distilled water

Electrical conductivity and ionization of water is explained by three types of transport mechanisms of electric charge in an electric field: convective, relay-race and croquet [14].

According to [15], the formation of strong hydrogen bonds in complexes $(A...H...B)^{\pm}$ represents a fundamental property of a proton (in the hydronium ion H_3O^+), and hydroxyl ion OH^- . The experimental and estimated data [16-18] indicate that the electrical current in ice and water has a protonic nature.

Model of proton conduction in chains of molecules of H_2O , held by hydrogen bonds, based on the fact that the proton can be transported (Fig. 2) along the chain in the form of ion defects H_3O^+ or OH^- , which are formed by the dissociation of water molecules.



Fig.2. A simplified model of H_3O^+ and OH^- ion migration in the H_2O molecules chain [17]

Along with the movement of a proton is possible movement of orientational positive (D) and negative (L) Bjerrum defects (Fig. 3), formed at the rotation of molecules of H_2O [19].

According to estimates [20], each of these processes transports only a portion of the charge. At the first mechanism through the chain is transported 0.64 share of positive charge, and at the second – 0.36. Despite the great simplicity of such model, it is well explains why proton mobility almost twice as high mobility of hydroxyl ion OH^- and almost 5 times of most other ions.

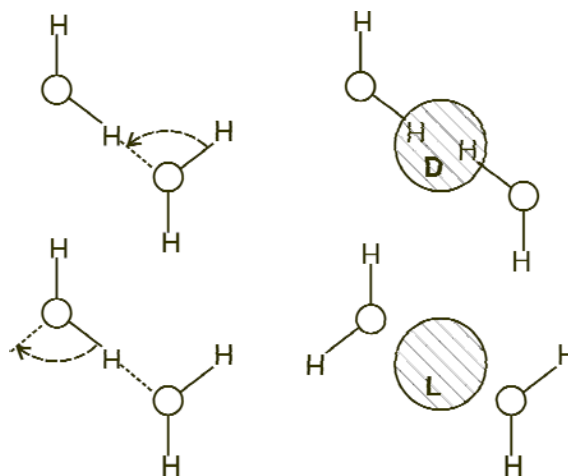
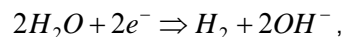


Fig.3. Scheme of the positive and negative Bjerrum defects [17]

At passing an electric current due to more rapid removal of protons compared with the influx of anions, negative space charge is formed in the anode space. Excess negative space charge is formed in the cathode space, since the cations discharge faster than the outflow of anions. Space charges can temporarily contribute substantially in the increasing of the pH in the cathode chamber and in the reduction of the pH in the anodic chamber. Calculations carried out in [21] shows that in the electrode zones during passing a current through the cell, the pH is changed in a greater degree than is obtained from the current consumption on the reaction:



flowing in the cathode chamber of the electrolyzer. This confirms the assumption of a substantial effect on the ECA processes of mobility difference of the proton and the hydroxyl ion.

Since the practice of the ECA solutions of various substances are used, for many problems in the solvent tap water is used. ECA also carry natural waters [2]. While ECA of tap water the current density and pH in electrolyzer chambers, vary during electrolysis as shown in Fig. 4. Consider the possible reasons for the change.

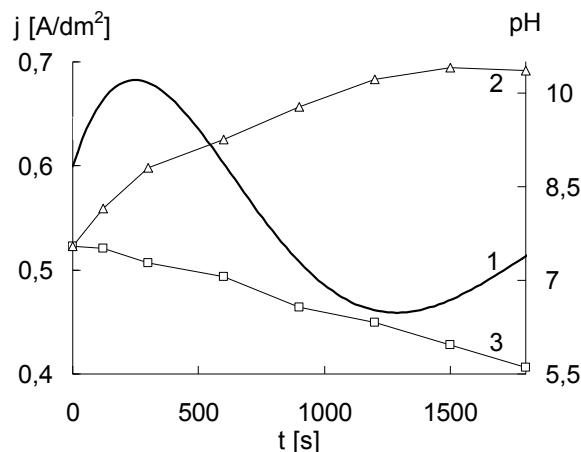
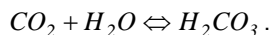


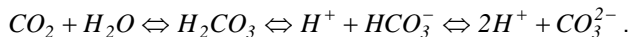
Fig.4. The dependence of the current density, flowing through the electrolytic cell (1) and the hydrogen index value of pH of the catholyte (2) and anolyte (3) from the time of electrochemical treatment for tap water

Tap, as well as natural, water is a multi-dynamic system, which includes gas, mineral and organic matter. The most

important of compounds that alter the pH of the water due to hydrolysis is carbon dioxide [15]. When it is dissolved in water, it partially reacts with the molecules forming carbonic acid:



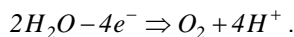
Various forms of carbonic acid in water solutions are bounded by carbon-dioxide balance [22]:



The quantitative relations between H_2CO_3 , CO_2 , HCO_3^- and CO_3^{2-} are determined by pH values of water [15, 22].

As seen from Fig. 4, curve 2, the catholyte has an alkaline reaction, which leads to the softening of water, since the tap water has a hardness salts [21]. At $\text{pH} > 8$, almost all the carbon dioxide passes into hydrocarbonate, then ($\text{pH} > 12$) – in the carbonate forms [22]. If the production of activities of Ca^{2+} and CO_3^{2-} in water is higher than the solubility production of calcium carbonate, this process is accompanied by the formation of a solid phase of calcium carbonate [21].

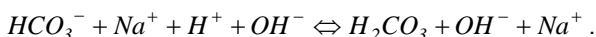
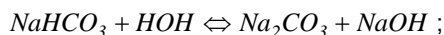
There is decreasing of the pH for the anolyte from the reaction of:



With decreasing pH hydrogen ions are gradually converted to the free carbonic acid, which is defined as the amount of $\text{H}_2\text{CO}_3 + \text{CO}_2$, and when $\text{pH} = 4$ – completely disappear [22].

These processes, especially those related to changes of the carbon dioxide balance in the anolyte, and the redistribution of oppositely charged ions in the cells of the electrolyzer and cause observed changes in the current density in the electrolysis with a constant voltage at the electrodes in the first stage – before reaching a minimum current density. Increasing of the current density at further electrolysis, most likely due to the use as a diaphragm a well-permeable material, thereby entering from the anode chamber acidic solution dissolves CaCO_3 in cathode chamber [2]. At concentrations of dissolved salts over 10^{-5} M, typical for natural and tap water, the influence of associates of water molecules according to [23] can be neglected.

To confirm the influence of changes in the carbon dioxide balance on the current density in the electrolysis a series of experiments was performed with solutions with a controlled chemical composition. Selection of NaCl and NaHCO_3 salt solutions due to various anions and different processes at their hydrolysis. In aqueous NaCl hydrolysis hardly occurs and NaHCO_3 is hydrolyzed by anion:



Concentrations of 0.001 M solutions are selected with the aim to reduce the influence of gas generation at the electrodes, because this process can also affect the flow of electric current in the cell [24].

As shown at Fig. 5, when ECA of Na_2CO_3 solutions (curve 2) a pronounced peak of current density at the initial stage of electrochemical treatment is observed, similar to the peak of current density in tap water. When processing of NaCl solution there are no a peak at all. The observed effect can be explained by the formation of sparingly soluble free carbonic acid, produced in the process of changes of the carbon dioxide balance in NaHCO_3 solution at pH

decrease in the anode chamber of the cell. This is confirmed by direct measurement of the electrical conductivity of water, collected from the chambers of the cell, while ECA.

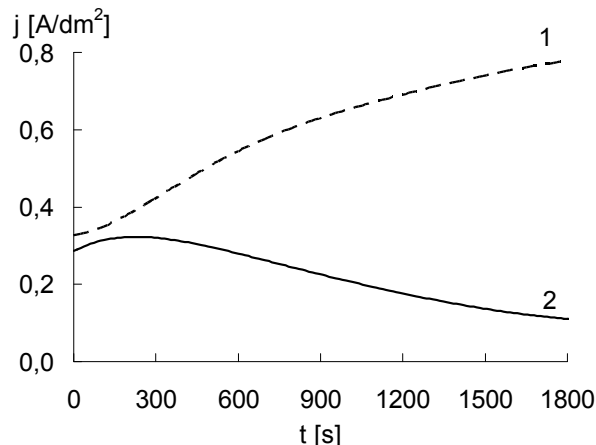


Fig.5. The dependence of the current density, flowing through the electrolytic cell, from the time of electrochemical treatment of 0.001 M solutions of 1 – NaCl , 2 – Na_2CO_3

Conductivity of catholyte and anolyte resulting ECA solution of NaCl , increased with time (Fig. 6, curves 1 and 2), wherein the electrical conductivity of the anolyte is higher than catholyte. This may be due, primarily, twice higher mobility of ions H^+ compared with the OH^- ions on a background of low mobility differences of the ions Na^+ and Cl^- . At the same time, at the ECA of NaHCO_3 conductivity of the anolyte decreases (Fig. 6, curve 3). This is due to the carbon dioxide balance offset while decreasing pH towards the formation of free carbonic acid, which reduces the amount of ions capable to participate in the transfer of electric charge.

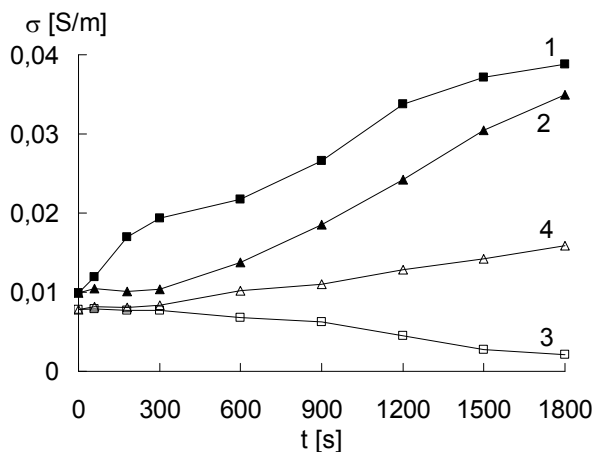


Fig.6. The dependence of electrical conductivity of anolyte (1, 3) and catholyte (2, 3), obtained from the 0.001 M solution of NaCl (1, 2) and NaHCO_3 (3, 4) from the ECA time

This analysis allows to conclude that selected in different time of ECA water solution should have a different composition and properties. Especially it concerns contained therein metastable electrolysis products capable to decay during storage of the activated solution.

For selected at different stages of ECA by pH values catholyte and anolyte had been calculated H_3O^+ and OH^- ion concentration. It was found that the concentration of hydroxyl ions in the catholyte is almost in two orders greater

than concentration of H_3O^+ ions in the anolyte. Thus, the relaxation changes in catholyte should be more than the relaxation changes in anolyte. The catholyte was placed in closed darkened glass vials. Relaxation changes of pH during the storage time are shown at Fig. 7.

As shown at Fig. 7, the relaxation curves depend on the activation time, and the longer the time of activation is, the less relaxation. Because for catholyte, selected after the minimum current density at ECA, relaxation changes are minor, it can be concluded that it is a measure of the completion of electrolysis at ECA. This is because the volatile products of electrolysis conversion is terminated and are formed the more stable products of electrolysis only.

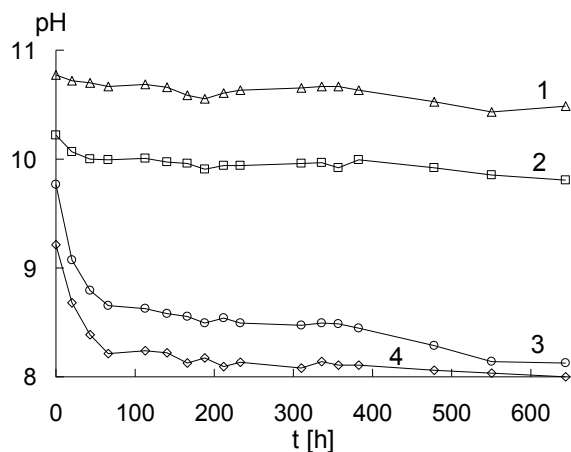


Fig.7. Relaxation of pH samples of catholyte collected at 1800 (1), 1200 (2), 600 (3), 300 (4) seconds of electrochemical activation

Conclusion

Based on the foregoing it can be concluded that the variation of the current density is determined in the stationary electrolytic cell by the content and type of ions in the source solution. Because tap water contains a certain amount of dissolved salts and gases, including carbon dioxide, during its ECA characteristic peak of current density is observed. Changing the current density during electrochemical treatment is correlated with the change of pH value and conductivity of solutions. This indicates a significant effect of ion transport through the diaphragm and changes the carbon dioxide balance on the rate of passage and the nature of ECA. Analyzing the dependence of the current density from the electrolysis time may be, for example, estimated the rate of the electrochemical reaction [25], as well as its completeness. [26] For water and water solutions ECA in a stationary cell, this approach allows to determine the depth (completeness) of the electrochemical treatment [27].

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