

COMBINED CATHODE PROCESSES IN THE ELECTROCHEMICAL SYNTHESIS OF SODIUM HYPOCHLORITE

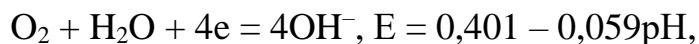
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Electrochemical synthesis of sodium hypochlorite is limited by the content of NaClO within 10...14 g·dm⁻³. Sodium hypochlorite can be reduced at the cathode of an electrolytic cell without diaphragm.

Application of gas diffusion cathode, obtained by the electrolysis of aqueous solution of NaCl without diaphragm is a promising way of increasing the concentration of sodium hypochlorite [1].

Aims and scope of research. Electrochemical reduction of molecular oxygen proceeds by the following reaction:



and is an alternative to the hydrogen reaction:

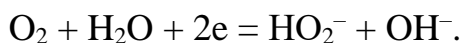


To intensify the electrochemical reduction of molecular oxygen, it is necessary to select electrode materials with low oxygen overvoltage and high hydrogen overvoltage.

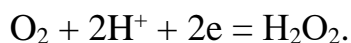
Electrochemical reduction of molecular oxygen may be proceeded through the following parallel-sequential mechanisms [2]: through the intermediate formation of hydrogen peroxide, immediately to the formation of water. That's why according to the references [2], a large attention should

be paid to research of staging of the electrochemical reduction of molecular oxygen on various types of electrode materials.

Analysis of stationary potential, which is set on electrodes during the depolarization of the cathode process by oxygen, allows us to estimate the thermodynamic possibility of various mechanisms realization. In [3] it has been shown the equilibrium in alkaline solutions on graphite, pyrographite, soot and activated carbon electrodes for the following reactions:



In acidic solutions, equilibrium has been set for the reaction:

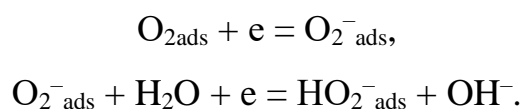


The reactions presented above indicate that the electrochemical reduction of molecular oxygen proceeds through an intermediate formation of hydrogen peroxide. The decomposition of hydrogen peroxide is the second stage.

The polarization curves on the pyrographite electrode in alkaline solution have well-defined areas of current limits that corresponds to the adherence of two and four electrons.

Using the method of a rotating disk electrode has made it possible set that in the region of the first wave molecular oxygen is reduced without breaking the O – O bond to hydrogen peroxide, which is a stable product of reaction in a wide range of potentials. Reduction of hydrogen peroxide begins in the range of second wave. Thus, the process of electrochemical reduction of molecular oxygen proceeds only through the intermediate formation of hydrogen peroxide.

On porous carbon activated by metal oxides [4], the rate of catalytic decomposition of hydrogen peroxide is much higher than on graphite. So the stage of hydrogen peroxide formation is the limiting stage on these types of electrodes. Therefore, on porous carbon activated by metal oxides, it is possible to implement a kinetic mechanism of oxygen reduction without the concentration polarization. For the most carbon materials, in neutral and slightly alkaline solutions, the reaction rate of electrochemical reduction of molecular oxygen does not depend on pH and the slope of the field with electrochemical kinetics is $2b_0$. That indicates that the process is limited by the transition of the first electron to an oxygen molecule adsorbed on the cathode surface:



It is necessary to use a gas diffusion electrode with an equally accessible surface for research the kinetic parameters of the electrochemical reduction of molecular oxygen. The equal distribution of activator materials over the surface of the gas diffusion electrode is an important factor. The most equal distribution can be achieved by impregnating the gas diffusion electrode with solutions containing activator metal salts, followed by the decomposition of the salts to the corresponding oxides..

1. Experimental technique

A gas diffusion cathode with a special current lead has been used for the cathodic oxygen reduction. This electrode has a well-developed surface for increasing the efficiency of the electrolysis process, as well as a high catalytic activity of the main process. [5].

Graphite PG-50 has been applied as a porous base. The gas diffusion cathode consists of a titanium current and gas lead and a graphite electrode fixed in a lead. The cylindrical graphite electrode has a diameter 15 mm and thickness 5 mm. The oxygen has been supplied from the air compressor from the back of the graphite electrode[4].

Voltage-current curves were obtained with a pulse potentiostat PI-50-1. The potential sweep rate is 10 mV/s. Polarization research has been performed in an electrochemical cell at 293 K. Porous graphite has been used as a cathode, anode has been made titanium with oxide ruthenium and titanium coating (ORTA). The graphite electrode has been activated by treatment in oxidizing solutions to create a layer of active carbon compounds on its surface. Nickel oxides were obtained by thermal decomposition of nickel nitrate [1].

The reference electrode is silver chloride. All potential have been recalculated according to the hydrogen electrode.

Electrochemical synthesis of sodium hypochlorite has been performed in a electrolyzer without diaphragm at 290 K in $3 \text{ mol}\cdot\text{dm}^{-3}$ NaCl on an activated cathode, and also using air supply through a gas diffusion cathode.

The determination of the NaClO content has been carried out using an iodometric method based on the oxidation of potassium iodide. The released iodine has been titrated with sodium thiosulfate solution.

2. Results and discussion

The influence of the electrode material on the cathode polarization dependences has been studied in aqueous solution of NaCl on porous graphite and graphite activated by nickel. It has been found out hat the air

supply to the gas diffusion electrode changes the character of current-voltage curves.

The current-voltage dependence for all studied cathode materials has two sections. The first section is located in the range from equilibrium potential to $-0.3\dots-0.4$ V. The second section is located at more negative potentials. Equilibrium potentials for the studied graphite electrode without coating and with an activating coating in an aqueous solution of $3\text{ mol}\cdot\text{dm}^{-3}$ NaCl at 290 K were 0.07 V and 0.314 V respectively.

The standard potential of the oxygen reaction for described conditions is about 1.01 V. A significant shift of the equilibrium potential into the negative direction indicates the effect of adsorption processes during the formation of an electrical double layer at the electrode-electrolyte boundary.

The standard potential of the hydrogen reaction at the described conditions is about 0.42 V. Therefore, the realization of the oxygen reaction is possible for the first potential range. Current density of oxygen reduction increases with cathode polarization. A transitional region of combined oxygen and hydrogen reduction appears. Graphite activated by nickel oxides presents great catalytic activity in the oxygen reduction reaction.

However, nickel oxides have had a catalytic effect not only in the oxygen reduction reaction, but also in the hydrogen reduction reaction.

The shift from the first to the second potential ranges has been most clearly observed at current-voltage curves for the process performed without air supply. In this case oxygen dissolved in an aqueous solution has been reduced. The abrupt change shift of the current-voltage curve has been associated with the displacement of adsorbed oxygen from the surface of a

graphite cathode by water molecules at potentials more negative than 1.1 V.

The amount of oxygen increases when air is supplied through a gas diffusion cathode. The gas diffusion construction of cathode complicates the adsorption of water molecules onto the cathode surface. The oxygen reduction current increases in 2...2.5 times.

Activation of the PG-50 surface by nickel oxides contributes to an increase of the rate of cathode processes. In the first potential range, the current of oxygen reduction (without air supply) increased by 3 times. The current of oxygen reduction on the activated gas diffusion cathode increases by 2 times, compared to the non-activated cathode.

An electrochemical synthesis of sodium hypochlorite has been carried out with an activated cathode with air supply through a gas diffusion cathode.

Table 1. Concentration and current efficiency of NaClO at $j = 0,2 \text{ A/sm}^2$;
 $T = 290 \text{ K}$; $3 \text{ mol}\cdot\text{dm}^{-3}$ of NaCl

Duration of electrolysis, hours	Without depolarization		With depolarization	
	C_{NaClO} , $\text{g}\cdot\text{dm}^{-3}$	Current efficiency, %	C_{NaClO} , $\text{g}\cdot\text{dm}^{-3}$	Current efficiency, %
1	7,9	56,1	10,1	62,2
2	11,9	42,2	15,8	55,8
4	14,7	25,9	20,1	55,5
6	14,7	17,2	23,2	51,8
8	14,7	12,8	26,4	38,2
10	14,7	10,2	27,2	27,3

In the first case, the current efficiency of sodium hypochlorite gradually decreases down to a maximum concentration of NaClO $14 \text{ g}\cdot\text{dm}^{-3}$. When air is supplied to the gas diffusion electrode, the concentration of sodium hypochlorite exceeds the amount of this concentration in the first case. The limiting concentration of NaClO was about $27 \text{ g}\cdot\text{dm}^{-3}$, with the gas diffusion mode.

The obtained results have shown the inhibition of supply of ClO^- ions to the cathode surface which helped to reduce the loss of ClO^- due to their cathode reduction.

3. Conclusion

The application of a gas diffusion cathode makes it possible to slow down the process of cathode reduction of hypochlorite ions. In 3 hours the current efficiency increased from 29 % to 55 %. This obstacle had a positive impact on the specific electricity consumption.

The oxygen reduction current in the gas diffusion mode, increases by 2 times due to the using of a porous graphite cathode PG-50 activated by nickel.

Changing the air supply modes in the gas diffusion cathode allows to control the combined cathode processes. The limiting concentration of NaClO raised up from 14 to $27 \text{ g}\cdot\text{dm}^{-3}$ due to the activation of the surface of graphite gas diffusion cathode.

Thus, the balance electrochemical synthesis of sodium hypochlorite has proved the effectiveness of the proposed technical solution.

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