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THE KINETICS OF WATER TRANSFER THROUGH CATION EXCHANGE MEMBRANES

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The purpose of this work is to research the kinetics transfer of proton water through the membrane and to evaluate the influence of technological options of electrolysis on this process.

The values of the ions streams through the membrane were determined by measuring the quantity of substance in electrode cameras, separated from each other by membrane, after putting the known quantity of electricity through.

In order to simplify the technological scheme of membrane electrolysis to get the NaClO «A», the conditions of electrolysis which exclude the circulation of electrolyte were proposed. High concentration of NaCl in anolit will be provided by transfer of proton water through the membrane from the anode camera to the catode camera.

Experimental measurements of transfer numbers were carried out by the Hittorf method.

The results of calculations according to the Breslau and Miller model, for the Nafion 125 – solute NaCl system shows that with decreasing NaCl concentration the numbers of proton water transfer grows from $t_w = 4,3$ mol·F^{-1} with $c = 5$ mol·dm^{-3} to degree $t_w = 7,8$ mol·F^{-1} with $c = 2$ mol·dm^{-3}.

It was found that with increasing amperage density more 100 A·m^{-2} influence on electrolysis chloride solutes make the ohmic component of amperage decreasing. Increasing of ohmic amperage leads to local increasing of temperature of anode and negatively affect the solutes stability of NaClO. So, if the main purpose is to get the NaClO, it's important to foresee the possibility of decreasing temperature of anode.

Decreasing of anode potential is possible at the expense of decreasing of Ph of electrolite solute. However decreasing of Ph lower than 2,5 leads to excess of critical anode potential, decreasing the persistence RuO_2 – catalycity active component of low vanishing anode.

Achieving of critical potential DSA with low temperatures (288 K and lower) reflects the decreasing of electrode activity DSA when electrochemical getting of Cl_2.

Last years a lot of researches are aiming on developing of membrane way of electrolyses of water chlorides solutes. Technological process of production of NaClO with using of membrane technologies composed in getting Cl_2 and NaOH in cameras of membrane electroliser, their cooling and the next cooperation in reactor with next getting of NaClO [1 – 3].

Research Methodology

With electrochemical synthesis of concentrated solutes "active chlore" as a membrane we used МФ-4СК, Nafion-125.

For tests the membrane setting was investigated, which helps to get concentrated solutes "active Cl_2".

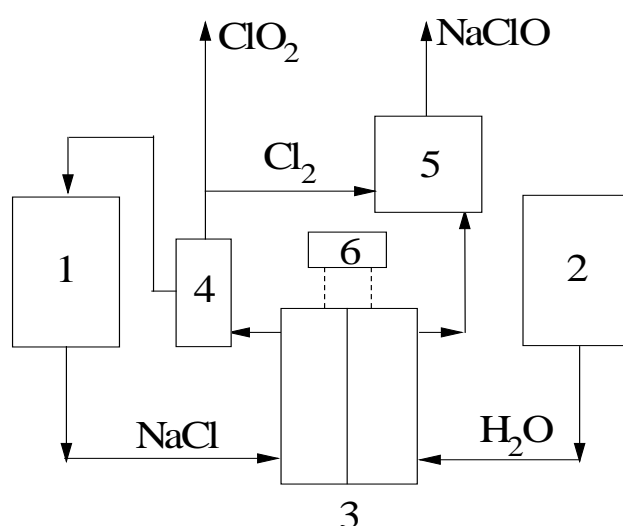Common view on the setting is on picture 1.

Fig. 1. *Scheme of electrolyses membrane setting work*

Solute of Chloride Na given pH from streaming tank 1 goes to the lowest part of anode camera of **e**lectrolyses 3. Using of streaming tank lets us use the expend calculator, which provides smooth, self flowing transmission of electrolyte to electroliser with set speed and keeps in this cameras concentration of **e**lectrolyte in exact determined interval $280 \ldots 310$ g·dm^{-3}. Self flowing transmission of $NaCl_2$ solute to electroliser and flowing mode heads to installing stationary more of electrolyze.

To catode camera the flow of distilled water was organized from flowing tank 2 through union in the lower part. Before start of electroliser catode camera was filled $1,5$ mol·dm^{-3} of NaOH solute.

The speed of flows in catode and anode cameras was determined by expend calculator and was regulated by crane.

Exiting the electroliser anode products of electroliser were headed to gas bleeder 4. In which Cl_2 separated from NaCl solute. Depleted on Cl$^-$

solute of NaCl was headed to additional saturation and then goes back to electrolyze. Thus, this way let us to realize wasteless technology of getting solutes of "active Cl". Also to gas bleeder mercury thermometer was put, which helped to watch the temperature of formatted in electrochemical generator products.

Catode products of electrolise in form of NaOH and carbon was headed to reactor of blending. 5. In reactor of blending worked catolite with gas Cl in result of Chemical reaction forming the concentrate solute of NaClO. Presence of reactor of electrolise product blending levels the danger of blowout of Cl_2 to the atmosphere, because it combines with alkali which increases the level of installation work in general.

With a view to simplify the technological scheme of membrane electrolyses for getting NaClO "A" we proposed such conditions of electrolise when the circulation of anolite will be absent. High concentration of NaCl in anolit**e** will be provided by transfer of protone water through membrane from anode camera to catode.

Set the dependency of coefficients of ions diffusion in cations from the temperature. With increasing of temperature (with decreasing of 1/T) the effective energy of activation decreases. This fact can be explained by changing the mechanism of water replacement. With increasing of water temperature increases the level of ions dissociation and increases the role of solvation mechanism in ions transfer. Worth noting that energy of activation decreases with increasing of electrolyte solute concentration (4).

Adding the electric field the charged water moves in direction of anions move, at that working on it force is proportional to charge of matrix and the voltage of electric field, and force of movement resistance – versus proportional to hydraulic penetration of membrane.

Results and Discussion

The experimental results of membrane electrolise work without of electrolyte flow in anode camera are shown on pic. 2 like dotted line and changed from t_w = 4,3 mol·F^{-1} при c = 5,13 mol·dm^{-3} to point t_w = 9,6 mol·F^{-1} with c = 2 mol·dm^{-3}. Comparison of experimental and calculation results shows that model proposed by authors (4), adequately describes the process of transfer of hidrate water in investigated by ours field of concentration NaCl (4 … 5 mol·dm^{-3}). Differences of experimental and calculative data with concentration NaCl less than 4 mol·dm^{-3} related to part hydratation of ions in membrane with decreasing of pH anolite in electrolise process.

But for investigated, and moreover for working range concentration of NaCl using of model is permissible. Using in quality of anolite water solute of NaCl with concentration 280 g·dm^{-3} through the surface of

membrane 0,05 m^2 when flows 100 A·hour of electricity will be transferred 300±0,5 g H_2O.

With chosen concentration 280 g·dm^{-3} (ρ = 1,178 g·sm^{-3}) in 900 sm^3 will be 254 g NaCl and 806 g H_2O.

In accordance to Faraday law when flows 100 A·hour voltage mass NaCl will decrease on 206 g (BT ≈ 95 %). After one hour of electrolyze with voltage density 2000 A·m^{-2} in anode camera of membrane electroliser will still be 254 – 206 = 48 g NaCl. During the same time in accordance with investigated numbers of water transfer from outputing 806 g H_2O through membrane wil be transferred 302 g H_2O, another words, there will be only 504 g H_2O left. Thus in the result of electrolise anolite contain only 8 % solute NaCl, that match the concentration of NaCl 85 g·dm^{-3}.
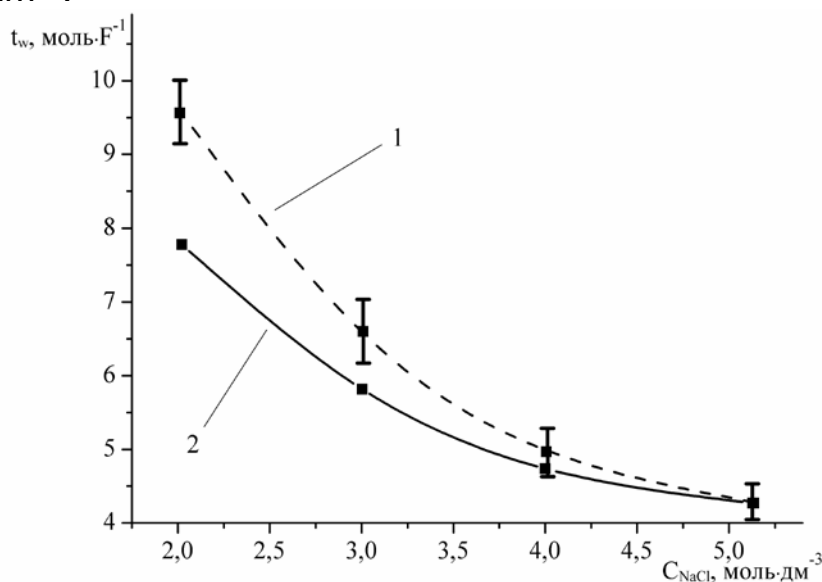

Fig. 2. *Dependence of numbers of transfer water from concentration of solute NaCl, which is in contact with membrane: 1 – experimental. 2 – calculative*

Made calculation was confirmed with the results of recourse tests of laboratory setting, which confirmed the hypothesis about possibility of technical scheme of membrane electrolyses without of using the stage of analite additional saturation of solid NaCl qualification.

Based on made investigations of the different factor's influence on kinetics of anode process, we can make the next conclusions:

- increasing of thickness of voltage more than 100 A·m^{-2} great influence on Cl solute electrolise makes the Ohm component of the voltage falling. Increasing of Ohm component makes the local heat up of anode surface and makes the negative influence on stability of NaClO. That's why if the final product foresees getting of NaClO, in the construction of electroliser is important to foresee the possibility of cooling anode.

- decreasing of anode potential is possible through decreasing of pH of electrolite solute. However decreasing lower than 2,5 leads to excess of critical anode potential, decreasing of RuO_2 resistance – katolit active component low damaging anode.

- gaining the critical of potential OPTA with decreasing temperatures (288 K and lower) reflects the decreasing of electrode DSA activity with electrochemical getting of Cl.

- Oxide ruthenium-titanium anode cover holds katalit activity in electrochemical synthesis of Cl and dioxid Cl. However in the conditions of low temperatures in order to increase the working thicknesses of voltage was proposed the using of more stable anode material – IrO_2.

- Comparing of experimental and calculative results shows that used model describes adequately the process of transfer proton water through membrane in range of working (4 … 5 $mol \cdot dm^{-3}$) concentration of NaCl.

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