Numerical modelling of spatial distributions of the pH value and electric field in a liquid electrode

R M Askhatov, N F Kashapov, R N Kashapov and V Yu Chebakova*
Kazan Federal University, 18 Kremlin street, Kazan, 420008, Russia

*vchebakova@mail.ru

Abstract. This paper presents a mathematical model of sodium hydroxide electrolysis with inert electrodes, which allows calculate the amount of gas released, as well as the spatial distribution of the electric field and the pH value.

1. Introduction
Discharges with liquid electrodes are widely used in practical activities water purification tasks and hydrogen production [1-3]. Both experimental methods and mathematical modelling are used to study it [4-7]. When modelling discharges with liquid electrodes, the kinetics of plasma chemical processes at the water surface plays an important role, since even a small percentage of radicals coming from electrolyte or water solutions used as an electrode has a significant effect on the distribution functions of charged particles, and, consequently, affects the characteristics and formation of the discharge. One of possible ways out of radicals from an electrolyte is electrolysis [8]. In this work, we propose a mathematical model of the process of electrolysis of sodium hydroxide with inert electrodes, which allows you calculate the amount of gas released, as well as the spatial distribution of the electric field and the hydrogen index.

2. Statement of theorems.
In alkaline solutions due to the very low concentration of hydrogen ions and the activity of hydroxonium ions $H_3O^+$ current transfer is performed by sodium $Na^+$ ions and hydroxyl $OH^-$. Since the water dissociation constant is very low, the concentration of water can be considered constant. When calculating the concentration of hydroxyl [$OH^-$], we will consider diffusion $D_{OH^-} \nabla \cdot (\nabla C_{OH^-})$ and migration $\pm U_{OH^-} C_{OH^-} \nabla \varphi$ flows, where $D_{OH^-}$ is the diffusion coefficient of hydroxide ions, $C_{OH^-}$ is hydroxyl concentration, $U_{OH^-}$ is hydroxyl mobility. The mobility of hydroxyl here is understood as the average speed of its movement at the electric field strength equal to 1V/m. Further, considering that the equivalent ionic conductivity $\Lambda_{OH^-}$ is equal $U_{OH^-} F$, we write the migration flux in the form $\pm \Lambda_{OH^-} C_{OH^-} \nabla \varphi / F$. Then the equation for the concentration of sodium ions is supplemented by the equation

$$\frac{\partial C_{OH^-}}{\partial t} = \nabla \cdot \left( D_{OH^-} \nabla C_{OH^-} + \frac{\Lambda_{OH^-} C_{OH^-} \nabla \varphi}{F} \right)$$  (1)
Sodium hydroxide \( \text{NaOH} \) is a strong base, therefore, neglecting the imperfection solutions, we assume that it completely dissociates into ions \( \text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^- \). To describe the movement of ions \( \text{Na}^+ \) in the electrolyte due to diffusion and migration, we use the following equation:

\[
\frac{\partial C_{\text{Na}^+}}{\partial t} = \nabla \cdot \left( D_{\text{Na}^+} \nabla C_{\text{Na}^+} - \frac{Z_{\text{Na}^+} C_{\text{Na}^+} \nabla \phi}{F} \right)
\]

(2)

Where \( D_{\text{Na}^+} \) is the diffusion coefficient of sodium ions, \( Z_{\text{Na}^+} \) is the valence number of sodium ion, \( F \) is Faraday constant, \( R \) is universal constant, \( T \) is temperature, \( C_{\text{Na}^+} \) is the concentration of sodium ions, \( \phi \) is the potential of the electric field. In \( \text{NaOH} \) solutions at moderate current densities, the concentration of hydrogen ions in the volume is small. Therefore, to calculate the concentration of hydrogen ions, we use the constancy of the ionic product of water \( K_w = C_{\text{OH}^-} C_{\text{H}^+} \).

At constant current the electric field is potentially. The equations for the potential of the electric field can be represented as

\[
\varepsilon \varepsilon_0 \nabla \cdot \nabla \phi = F \sum_{a=\text{Na}^+, \text{H}^+, \text{OH}^-} Z_a C_a
\]

(3)

Here \( \varepsilon = 1 + \chi \) is the dielectric constant of the medium, taking into account the polarization of the medium, \( \chi \) is the electrical susceptibility of the medium.

3. Boundary and initial conditions.

We give the lemma used in the proof of the theorem. We denote \( \chi, (n) \) as the semi-invariant of the

When setting the boundary conditions, we assume that electrode is inert. Hydrogen evolution during electrolysis of water occurs as a result of the discharge of hydroxyl ions or water molecules. In \( \text{NaOH} \) solutions with moderate current densities the reagent is water, since the activity of hydroxonium ions is extremely low. Therefore, the electrochemical stage consists in the restoration of water molecules, the concentration of which at the electrode surface is always high: \( 4\text{H}_2\text{O} + 4e \rightarrow 2\text{H}_2 + 4\text{OH}^- \).

Oxygen is released as a result of the following reaction: \( 4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4e \). Thus, the hydroxide transfer equation is supplemented by the following boundary conditions: for a positive charge electrode, the hydroxide ion flux \( G_{\text{OH}^-} \) on the electrode cancels out at the reaction rate \( K_a \), and for negative charge electrode \( G_{\text{OH}^-} = K \).

The rate constants of the anodic \( K_a \) and cathodic \( K_k \) processes are derived from Butler-Volmer equation [9]

\[
i = FZ_a S K_a \left( \exp \left( \frac{\alpha F \eta_i}{RT} \right) - \exp \left( \frac{(1-\alpha)F \eta_i}{RT} \right) \right)
\]

(4)

where \( i \) is the current density, \( \eta_i = \phi_i - E_{0ij} \) is the overvoltage of the electrode reaction on the electrode \( l \), \( E_{0ij} \) is the decomposition voltage at the electrode \( l \), \( \phi_i \) is the electrode potential, \( S \) is the electrode area, \( Z_a \) is valence number.

Sodium ions \( \text{Na}^+ \) on the electrodes do not discharge, over time accumulating concentration in the cathode space and decreasing it in the anode. The initial-boundary problem for the concentration of ions \( \text{Na}^+ \) will have the following boundary conditions: on the positive electrode \( C_{\text{Na}^+} = 0 \), and on the negative electrode \( \frac{\partial C_{\text{Na}^+}}{\partial x} = 0 \).
The current density is related to the potential of the electrodes \( \varphi \) by the equation of anode-cathode wave [10,11]

\[
\varphi = E_0 - \frac{RT}{Z_nF} \ln \left( \frac{i_{d,a}}{i_{d,c} - i} \right) \sqrt{\frac{D_o}{D_r}}
\]

where \( D_o, \) \( D_r \) are diffusion coefficients of oxidized and reduced forms, \( i_{d,a} = Z_n F D_g G \cdot C_g \) is diffusion anodic or cathodic currents. Neumann condition is set on the side walls. When setting the initial conditions, we assume that sodium hydroxide completely dissociates into ions. The initial concentration of hydrogen ions is expressed through the ionic product of water.

To solve the problem under consideration a numerical algorithm is proposed based on finite-dimensional approximation of the problem using difference schemes with the subsequent application of an iterative process proposed in the paper [12-16] and generalized to the two-dimensional case for its implementation.

4. Solving a model problem.
The system consists of rectangular electrodes of size 10x30 mm and interelectrode distance 10. The electrolyte is a solution of sodium hydroxide NaOH in which one liter is 0.1g NaOH. The molar concentration of this solution will be equal to 0.0025 mol/l. Sodium hydroxide refers to strong bases and aqueous solutions completely dissociates according to the equation \( \text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^- \). Therefore, the molar concentration of hydroxide ions \( C_{\text{OH}}^- \) and sodium ions \( C_{\text{Na}}^+ \) is equal the molar concentration of the solution, \( C_{\text{H}^+} = 4 \cdot 10^{-12} \text{[mol/l]} \) and pH solution is equal to \( -\log_{10}(C_{\text{H}^+}) = 11.4 \). The calculations were carried out at a constant temperature \( T \) equal to 210 C and at a current strength of \( i = 0.35 \text{ A} \), the constants for the calculations were taken from [9,17]. Overvoltage taken from platinum electrodes for low currents of [17]. Numerical calculations showed a change in the value of the pH value in the near-electrode zones even at low currents, however, no significant changes occurred in the interelectrode space.

5. Conclusion
This paper presents a mathematical model of sodium hydroxide electrolysis processes in a two-dimensional formulation with inert electrodes, which takes into account electrochemical processes and the model problem is solved. To solve the problem under consideration a numerical algorithm is proposed based on finite-dimensional approximation of the problem using difference schemes with the subsequent application of an iterative process. Authors obtained first results showinga change in the value of the pH value in the near-electrode zones even at low currents, however, no significant changes occurred in the interelectrode space.

Acknowledgments
The work was supported by the Russian Science Foundation (project 16-11-10299)

References
[1] Kashapov R N, Kashapov L N and Kashapov N F 2019 Investigation of parameters of low-temperature gas discharge plasma with liquid electrodes upon receipt of metal powder Journal of Physics: Conference Series 1328 012104
[2] Bespalko Sergii 2014 Recent advances in hydrogen generation by contact glow discharge electrolysis: review Materials, Methods and Technologies 8 355-63,
[3] Chaffin John H; Bobbio Stephen M; Inyang Hilary I and Kaanagbara Life 2006 Hydrogen Production by Plasma Electrolysis Journal of Energy Engineering 132(3)
[4] Gaisin Al F., Kashapov N F, Akhatova G Sh and Gaisina A I 2019 Electrophysical and thermal characteristics of gas-vapor discharge with liquid electrodes Journal of Physics: Conference
[5] Sirotkin N A, Khlyustova A V and Titov V A 2020 Chemical Composition and Processes in the DC Discharge Plasma of Atmospheric Pressure with a Liquid Electrolyte Cathode Plasma Chemistry and Plasma Processing 40(1) 187-205

[6] Bobkova E S, Ivanov E V, Gushchin P A and Tatarinov A V 2018 Hydrogen peroxide formation in boiling water plasma of electrolyte-cathode discharge High energy chemistry 52(2) 171-82

[7] Takeuchi N, Ishii Y and Yasuoka K 2012 Modelling chemical reactions in dc plasma inside oxygen bubbles in water Plasma Sources Sci. Technol 21 015006

[8] Bruggeman P.J. et al. 2016 Plasma-liquid interactions: a review and roadmap Plasma Sources Science and Technology 25 053002

[9] Yakimenko L M, Modylevskaya I D and Tkachek Z A 1970 Electrolysis of water (Moscow: Chemistry) p 264.

[10] Zherin I I, Amelina G N, Strashko A N and Voroshilov F A 2015 Fundamentals of electrochemical analysis methods (Tomsk: Tomsk Polytechnic University Publishing) p 175.

[11] Serebrennikova N V and Ivanova N V 2007 Voltammetry (Kemerovo: Kuzbassizdat) p 81

[12] Zheltukhin V S, Fadeeva M S and Chebakova V Yu 2017 Modification of the Scharfetter-Gummel method for calculating the flux of charged particles for simulation of a radio-frequency capacitive coupled discharge Uchenye Zapiski Kazanskogo Universiteta-Serija Fiziko-Matematicheskie Nauki 159 (4) 444-57

[13] Chebakova V Y 2017 Modeling of radio-frequency capacitive discharge under atmospheric pressure in Argon Lobachevskii Journal of Mathematics 38(6) 1165-78

[14] Badriev I B, Golovanov K S and Gnedenkova V L 2019 Numerical methods for determination the boundaries of unrecovered visco-plastic oil Journal of Physics: Conference Series 1158(2) 022017

[15] Badriev I B, Zadvornov O A and Saddek A M 2001 Convergence Analysis of Iterative Methods for Some Variational Inequalities with Pseudomonotone Operators Differential Equations, 37(7) 934-42

[16] Badriev I B and Karchevskii M M 1994 Convergence of an iterative process in a Banach space Journal of Mathematical Sciences 71 (6) 2727-35

[17] Haran B S, Popov B N, Zheng G and White R E 1993 Mathematical modelling of hexavalent chromium decontamination from low surface charged soils Journal of Hazardous Materials 56 93-107