Nonlinearity of the heterogeneous process of zinc release in flow Batteries

Violetta Chebakova, Maksim Dmitriev, Nail Kashapov and Konstantin Kormushin

1 Kazan Federal University, Kazan, Russia
2 Institute of Mechanics and Engineering - Subdivision of the Federal State Budgetary Institution of Science “Kazan Scientific Center of the Russian Academy of Sciences”, Kazan, Russia
3 Kazan National Research Technical University named after A. N. Tupolev - KAI, Kazan, Russia

Abstract. Currently, there is a worldwide search for technologies allowing to use alternative (renewable) energy sources. It is related to both the environmental degradation and the growing demand for electricity. In recent times, concerning the transition to “alternative” types of energy, there was a great interest in flow hybrid-type batteries, specifically, based on the following pairs: zinc-nickel, zinc-silver, zinc-manganese, zinc-cobalt and zinc-air.

1 Introduction

Currently, there is a worldwide search for technologies allowing to use alternative (renewable) energy sources. It is related to both the environmental degradation and the growing demand for electricity. In recent times, concerning the transition to “alternative” types of energy, there was a great interest in flow hybrid-type batteries, specifically, based on the following pairs: zinc-nickel, zinc-silver, zinc-manganese, zinc-cobalt and zinc-air.
batteries. Hybrid flow battery uses one or more electrically conducting components deposited as a solid layer. In this way galvanic cell contains one battery electrode and one fuel cell electrode. This type is limited in energy production over the matter of the surface area of electrode where the deposit forms. When it comes to zinc flow batteries, zinc metal is released from the electrolyte solution on the surface of negative electrodes during charging. During discharging, it occurs the reverse process: zinc metal applied on the negative electrodes dissolves in the electrolyte.

Thus, in [1], it is proposed a new method to create hybrids of zinc nitride as high-performance multifunctional electrocatalysts for electrocatalysis and energy storage in Zn-air batteries. Furthermore, in [2,3] there are considered hybrid batteries based on zinc deposition processes.

Depending on electrolyte, zinc batteries are divided into aqueous (alkaline, neutral and acid), organic and gel electrolytes. Thus, in the review [4], each type of zinc batteries is placed in the history of the development of flow redox batteries, it is given a comparative analysis of strengths and shortcomings. In [5], there are given more than 30 versions of cathode composition using soft aqueous electrolytes for zinc anode and acid electrolyte, as well as general reactions for manganese and cobalt batteries, the operating principle of which is considered in more detail.

In [6], it is given a review of alkaline zinc batteries. It was noted that they have high energy density, there are shown comparative characteristics of Zn-air, Zn-silver, Zn-manganese, Zn-nickel and Zn-cobalt batteries, as well as complex reactions.

In [7], it is given a review of zinc batteries, there are considered composition options for deposited product (zinc, zinc oxide and tetrohydroxozincate ion) in accordance with acidity (pH) of aqueous solution. Moreover, in [7], it is highlighted that anodic issues, such as dendrite growth caused by the inherently limited diffusion of zinc ions, hydrogen release and corrosion caused by water splitting, are closely interrelated and mutually reinforcing. There are given recommendations for the zinc batteries development process: firstly, pay attention to quantitative characteristics of zinc batteries when testing them, since it is associated with undershoot of some critical parameters subject to reasonable quantitative determination, such as Zn reversibility, amount of hydrogen released, quantity, test temperature, current density and depth of discharge; secondly, use additives allowing to limit nucleation; thirdly, develop multifunctional separators, since suitable separators can improve the performance of cathode and anode simultaneously; fourthly, deepen studies of fundamental mechanisms of both the deposition and dissolution processes. One way to explore fundamental processes of zinc deposition and dissolution is modelling.

When developing new technologies and optimizing already known ones, mathematical modeling reduces the number of experiments by tying external and internal parameter together. Models consist-ing of kinetic equations allow to carry out primary analysis on electrolyzer efficiency. If the values of rate constants of near-electrode processes are known, then the problem of predicting the yield of de-posited substance is not particularly difficult and can be solved numerically using Runge-Kutta method used for solving system consisting of Cauchy problems [8]. With unknown rate constants, it often occurs inverse problems which can be reduced to optimization problems sometimes, for example, for chemical reactors and in problems of chemical kinetics in gases [9]. Electrochemical processes of solution electrolysis refer to heterogeneous processes. Their most intensive development and course occur at the interface between metal electrode and liquid electrolyte, and it’s common for them to have actual and apparent reaction order. Electrolysis can be referred to zero-order reactions directly. In these reactions, the concentration depends on time linearly, and it is observed the linear dependency of substance release, but since the experiment conditions have a significant impact, the dependence ceases to be linear. When modelling electrochemical processes occurring at the
interface of different phase media, in particular, metal electrode – liquid electrolyte, there is an issue associated with collection and searching of rate constants of stepwise electrochemical reactions. This issue stems from the fact that rate constants of processes depend on parameters of heterogeneous system researched, such as electrode material, electrolyte composition, surface roughness, rate of removal of reaction products, etc. The difficulty of experimentally search for constants is that the rate of overall release reaction, calculated using yield data, depends on rate of the slowest limiting reaction which can be any of step-wise reactions. However, stepwise reactions can refer to different orders and, subsequently, can have both the linear character defined by zero-order reactions and the character expressed by Arrhenius equation, that is having exponential dependence. Thus, the expression for calculating the limiting rate depends on the definition of limiting process which is also far from being a trivial task. In this work, it presents a solution to solve the problem of predicting the yield of zinc deposit based on the method to solve the optimization problem of finding parameters, in particular, rate constants of stepwise processes and implicit Runge-Kutta method for direct solving kinetic equation system.

2 Statement of a problem of studying cathode processes of zinc release

\[
\begin{align*}
\frac{\partial G_{[Zn(OH)₄]^{2-}}}{\partial t} &= D\left(G_0 - G_{[Zn(OH)₄]^{2-}}\right)L/\sqrt{2Kt} - R_1 G_{[Zn(OH)₄]^{2-}} \\
\frac{\partial G_{Zn^+}}{\partial t} &= R_1 G_{[Zn(OH)₄]^{2-}} - R_2 G_{Zn^+} \\
\frac{\partial G_{Zn}}{\partial t} &= R_2 G_{Zn^+}
\end{align*}
\]

In [10], it is shown that, in dependence to electrolyte nature, zinc batteries can be divided into two categories: alkaline and neutral Zn-batteries. In terms of electrolyte acidity, near-electrode processes will not occur in the same way over the matter of different electrochemical behaviour of Zn anodes in alkaline and neutral electrolytes. Thus, in alkaline electrolytes, it is shown that reactions proceed by the process of formation and decomposition of tetrohydroxozincate ion \([Zn(OH)_4]^{2-}\). Alongside with zinc deposition, it is noted the release of hydrogen, and it is proposed a theory about spontaneous release of hydrogen during the interaction between zinc metal and electrolyte. This assumption is based on the fact that in theory the deposition potential of zinc metal is lower than the hydrogen release potential.

Disengagement of zinc from alkaline electrolytes is widely used in production of zinc using electroextraction. In virtue of similarity of the processes, authors studied the cathodic electrodeposition of zinc from sodium hydroxide solution containing tetrohydroxozincate. This electrolyte was obtained by the process of leaching zinc ore. Electroextraction of metal powder from alkaline electrolyte is of great relevance since it allows to obtain rare metals from depleted ores and dispose metal mining waste. In [11], it is shown a technology of processing powder waste from steel founding to produce zinc.
$G_{\left[Zn(OH)_4\right]^{2-}} \geq 0, G_{Zn^{2+}} \geq 0, G_{Zn} \geq 0, R_1 \geq 0, R_2 \geq 0, L \geq 0$.

We also introduce $K$ is the constant of proportionality between the thickness of deposit porous film and the time from Yander equation, and $L$ is the coefficient of proportionality of diffusion flow through the porous layer.

This mathematical model is based on the assumption that the deposit is porous, which is generally confirmed when studying the formation of dendrites [14,15]. In the case of porous film, it is considered that it offers no resistance to reactants approaching the interface and has no impact on reaction rate. In the case of non-porous film, the resistance of boundary layer can be neglected considering the resistance of product released layer as main one. This despite the fact that the process is controlled by diffusion through the boundary layer. But if there are additives that reduce dendrite formation the model must be changed.

In order to calculate the mass of zinc deposit, it uses the relation binding mass and concentration of zinc and film volume:

$$M_{Zn} = G_{Zn} S \sqrt{2KT} \times 65.38$$

3 Solution procedure
The solution procedure of system (2) is iterative. The initial approximation is taken from Kutta method, considering that system

\[ U(t) = (G_{[Zn(OH)_4]^2-}, G_{Zn^{2+}}, G_{Zn^{3+}})^T \]

\[ K = (R_1, L, R_2, K) \]

\[ F(t, K, U) = (f_1(t, K, U), f_2(t, K, U), f_3(t, K, U), f_4(t, K, U))^T \]

Here, \( f_1(t, K, U) \), \( f_2(t, K, U) \), and \( f_3(t, K, U) \) are defined as follows:

\[ f_1(t, K, U) = D\left(G_0 - G_{[Zn(OH)_4]^2-}\right)L/\sqrt{2Kt} - R_1 G_{[Zn(OH)_4]^2-} \]

\[ f_2(t, K, U) = R_1 G_{[Zn(OH)_4]^2-} - R_2 G_{Zn^{3+}} \]

\[ f_3(t, K, U) = R_2 G_{Zn^{3+}} \]

Here, \( t \) is the time coordinate, \( K \) is a vector of parameters, and \( f(t, K, U) \) are functions of time and parameters.

Consider the explicit Runge-Kutta method. Let \( h \) be the step size. Then, the error at each step is estimated as follows:

\[ \frac{d\delta(t)}{dt} = \vec{F}(t, K, U), \text{ where } t_0 < t \leq T \]

\[ h = t_{i+1} - t_i = const \]

\[ \omega_n = \{t_0, t_1, t_2, ..., t_i = t_0 + ih, ..., t_n = T\} \]

\[ \bar{U}_{i+1} = \bar{U}_i + h\bar{d}_i \]

\[ \bar{d}_i = (d_i^{(1)} + 2d_i^{(2)} + 2d_i^{(3)} + d_i^{(4)}) \]

\[ d_i^{(1)} = F_i(t_i, K, U_i) \]

\[ d_i^{(2)} = F_i(t_{i+\frac{1}{2}}, K, U_i + h*\bar{d}_i^{(1)}/2) \]

\[ d_i^{(3)} = F_i(t_{i+\frac{1}{2}}, K, U_i + h*\bar{d}_i^{(2)}/2) \]

\[ d_i^{(4)} = F_i(t_{i+1}, K, U_i + h*\bar{d}_i^{(3)}) \]

\[ \bar{U}^{n+1} = \bar{U}^n + h\bar{S} \]
\[ S = (\sum_{i=1}^{4} b_i k_{1i}, \sum_{i=1}^{4} b_i k_{2i}, \sum_{i=1}^{4} b_i k_{3i})^T \]

\[ k_{ji} = f_j(t_n + c_i h, K, U_j^n + h S_j), \quad j = 1, 2, 3 \text{ in } S_j = \sum_{i=1}^{4} a_{i,j} k_{ji} \]

The coefficients \( k_{ji}, a_{i,j}, c_i \) are obtained from the system of nonlinear equations:

\[ k_{ji} = F_j(t_n + c_i h, K, U_j^n + h S_j) \]

The coefficients \( a_{i,j}, b_i, c_i \) are obtained from the corresponding places in the Butcher matrix:

\[ \begin{array}{cccc}
  c_1 & a_{1,1} & a_{1,2} & a_{1,3} & a_{1,4} & 1/4 & 1/4 & 0 & 0 & 0 \\
  c_2 & a_{2,1} & a_{2,2} & a_{2,3} & a_{2,4} & 0 & -1/4 & 1/4 & 0 & 0 \\
  c_3 & a_{3,1} & a_{3,2} & a_{3,3} & a_{3,4} & 1/2 & 1/8 & 1/8 & 1/4 & 0 \\
  c_4 & a_{4,1} & a_{4,2} & a_{4,3} & a_{4,4} & 1 & 3/2 & 3/4 & 3/2 & 1/4 \\
  b_1 & b_2 & b_3 & b_4 & 1/6 & 2/3 & -1/12 & \\
\end{array} \]

The initial approximation is \( k_{j0} \)

If \( \max_i |k_{pj+1}^p - k_{pj}^p| \leq \varepsilon \) (where \( \varepsilon \) is the accuracy of the solution), the algorithm stops.

\[ k_{pj+1}^p = \Phi(k_p) \]

Fig. 1 Algorithm of the method.
The results of numerical simulation

The mathematical model of deposited substance yield was verified with experiment described in [18]. In it, it is investigated the impact of voltage applied on near electrode processes of zinc electrodeposition in sodium hydroxide solutions on stainless steel cathode. It was calcined zinc-containing ore at 400 °C for 2 hours in it, further, it was comminuted to an approximate size of 150 μm and subjected to leaching with 20% sodium hydroxide solution at 100 °C for 4 hours. Then, it was injected sodium sulfide into the solution to deposit the lead contained in solution obtained. The electrolyte prepared will be ready for use after separating the liquid phase from solid one. The concentration of zinc ions $\mathbf{Zn}^{2+}$ in prepared solution is 10 g/l. The working electrode was made from stainless steel and has an area of 1 cm$^2$.

In [19], it is shown that 20% concentration of sodium hydroxide solution was enough to provide the molar ratio of hydroxyl group $\mathbf{OH}^-$ to zinc contained that is sufficient for existence of $\mathbf{[Zn(OH)_4]}^{2-}$. Moreover, if the concentration of hydroxyl group ions is low, then the compound $\mathbf{[Zn(OH)_4]}^{2-}$ transforms into $\mathbf{ZnO}$. Thus, process of leaching zinc-containing ore in 20% NaOH solution can be described using a general dissolution reaction:

$$2\mathbf{NaOH} + \mathbf{Zn} + 2\mathbf{H}_2\mathbf{O} \rightarrow \mathbf{Na}_2[\mathbf{Zn(OH)}_4] + \mathbf{H}_2$$

There are different opinions concerning the proceeding of near electrode reactions of zinc release. Thus, in [19], relying on [20], it is given that the compound $\mathbf{[Zn(OH)_4]}^{2-}$ is subject to modification into hydrogenated $\mathbf{Zn(OH)}_2$ during zinc electrodeposition. At the same time, zinc hydroxide is an insoluble base and, as a result, its presence should be observed in deposit obtained, but this is not observed in most studies.

The results of work were compared with the experimental results from [18], with current density of 125 А/m$^2$. Initial conditions for calculations were set in view of experiment conditions until the electric current was supplied.

The concentration of zinc ions $\mathbf{Zn}^{2+}$ in prepared solution is 10 g/l. The working electrode was made of stainless steel and has an area of 1 cm$^2$. In the wake of recalculation, initial conditions for concentrations were taken as $G_8|t=0 \approx 0,153 \text{ mol/l}$, $G_2|t=0 \approx 0,168^{-14}\text{ mol/l}$, $G_6|t=0 \approx 0$, $G_7|t=0 = 0$, $G_1|t=0 \approx 41,7 \text{ mol/l}$, $G_4|t=0 \approx 0$, $G_5|t=0 \approx 4,29 \times 10^{-7}\text{ mol/l}$, $G_9|t=0 \approx 4,29 \times 10^{-7}\text{ mol/l}$, $G_{10}|t=0 = 0$, $G_{11}|t=0 = 0$, $G_{12}|t=0 = 0$.

<table>
<thead>
<tr>
<th>Time step, min</th>
<th>Experiment [18], yield g</th>
<th>Calculation, yield g</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.467 - 0.49</td>
<td>0.30</td>
</tr>
<tr>
<td>40</td>
<td>0.976 - 1.03</td>
<td>0.56</td>
</tr>
<tr>
<td>60</td>
<td>1.4945 - 1.60</td>
<td>1.55</td>
</tr>
</tbody>
</table>

Table 1. Data comparison with current density of 125 A/m$^2$. 

4 The results of numerical simulation
5 Conclusion

Currently, there is a worldwide search for technologies allowing to use alternative (renewable) energy sources. It is related to both the environmental degradation and the growing demand for electricity. In recent times, concerning the transition to “alternative” types of energy, there was a great interest in flow hybrid-type zinc batteries due to their efficiency and environmental safety. However, this type of flow batteries has a number of problems, such as growth of dendrites caused by inherently limited diffusion of zinc ions, hydrogen release and corrosion recoiling on the opportunity of long-term use. Investigations aimed at eliminating these problems are complex to date: this includes system modification and adding additives bearing on uniformity of filling the electrode area with deposit. Mathematical modelling is one of the methods for studying fundamental processes occurring at the interface in heterogeneous systems. In this article, it is proposed a numerical algorithm that allows to find rate constants of near-electrode processes, predict the yield and study the influence of separate processes.

The algorithm proposed allows to consider electrochemical processes on each electrode individually. As an example, it is taken the electroextraction of zinc. The results of calculation showed that it is necessary to consider hydrogen release processes in spite of apparent independence of parallel reactions. Thus, in [21], it is proposed that electron exchange is possible between zinc ions and hydrogen atoms, as well as zinc and hydrogen ions, so there are charge exchange reactions, as well as establishing linearity of the process over time. At the initial phase during the formation of zinc nucleus on steel electrode it is observed a delinearity of process, since the processes of hydrogen release and zinc accretion occur with different rates. In [22], for acid electrolyte in zinc ions battery, it was studied the dependence between nucleation density, current density and capacity, and it was shown that the higher current density means the higher nuclear density and its smaller size. With alkaline electrolytes, it can be assumed the existence of similar dependencies. In [23], it is noted that dendrite formation hampers the use of zinc batteries, and it has been proposed to use additives with base electrolyte as a solution. In this article, it is explored
the L-tartrate (Na-L) additive to provide more uniform deposition. However, investigators noted in many cases that the presence of catalysts for more uniform zinc deposition leads to challenges in dissolving of zinc back. Thus, in [24], it is noted that the problem of deposit uniform has not yet been solved, and its solution should be complex and lies in modifying surface of electrode itself and finding easily accessible additives to electrolyte.

Since rate constants depend on factors inherent in systems researched directly, such as heterogeneity and roughness of electrode surface, coefficient of charged particle transfer, electrolyte concentration, it is impractical to verify algorithm by the way of comparing rates of processes determined for other systems. At the same time, the rate constants found can be used for calculation using higher-dimensional models when calculating the spatial characteristics of electrothermal system.

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References


