Short communication

Research of the simplified model of lead-acid battery discharge

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Abstract

In the present work, it is considered a simplified model of the lead-acid battery discharge, based on simulation of electrolyte diffusion process in space between a positive and negative electrode. The correctness of model and influence of various boundary conditions are investigated.
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1. Introduction

The research of lead-acid cell discharge process is a very difficult problem, both from the point of view of calculations and owing to a plenty of factors that are necessary taking into account for the correct description of electrochemical reaction: heterogeneity of the porous environment during discharge, plugging electrode pores with discharge product, etc.

In [1] an attempt was made to construct the discharge model based on consideration of electrolyte diffusion process in space between a positive and negative electrode. Within the framework of the given model necessity to take into account electrochemical reaction in researched volume disappears, except for an electrode/electrolyte solution boundary. In [1] presented model was not investigated numerically and only qualitative conclusions about discharge process were made. Thus, dimensional densities of an overall discharge current were conditionally divided on "big" (the fast discharge) and "small" (the slow discharge), and electrolyte concentration distribution function in interelectrode space for the fast discharge a priori was considered as a broken line consisting of two pieces of various straight lines.

In the present work, detailed numerical researches above mentioned model with various boundary conditions at electrode/electrolyte solution are executed.

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2. The model description

The reaction–diffusion equations arise frequently at the description of the various physical and chemical processes. The mathematical formulation of such problems usually includes the partial derivatives equation of parabolic type and initial and boundary conditions. For example, a problem with the homogeneous diffusion equation and non-uniform boundary conditions has the form:

$$u_t(x, t) = Du_{xx}(x, t), \quad 0 \le x \le a, \quad 0 < t < t_{max}, \tag{1}$$

$$u(x, 0) = f(x), \quad 0 \le x \le l, \quad t = 0,$$

$$u_ч(0, t) = q_1, \quad x = 0, \quad 0 \le t \le t_{max}, \tag{1a}$$

$$u_ч(a, t) = q_2, \quad x = l, \quad 0 \le t \le t_{max}, \tag{1b}$$

or

$$u_t(x, t) = Du_{xx}(x, t), \quad 0 \le x \le a, \quad 0 < t < t_{max},$$

$$u(x, 0) = f(x), \quad 0 \le x \le l, \quad t = 0,$$

$$u_ч(0, t) = u_1, \quad x = 0, \quad 0 \le t \le t_{max}, \tag{1c}$$

$$u_ч(a, t) = u_2, \quad x = l, \quad 0 \le t \le t_{max}. \tag{1d}$$

Factors q_1 and q_2 are generally functions of time. Boundary conditions (1a) and (1b) mean that concentration flows as functions

of time are given and boundary conditions (1c) and (1d) mean that concentration as functions of time are given on boundary.

In [1] the depletion of an electrolyte solution (a sulfuric acid) owing to diffusion in space between a positive and negative electrode and electrochemical reaction on electrode/electrolyte solution is considered. Such process is described by the diffusion equation

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \tag{2}$$

with boundary conditions [1]

$$\frac{\partial c}{\partial x}(0) = q_1 = \frac{|I| \, G_+}{2DF} \tag{3}$$

on a surface of a positive electrode, and

$$\frac{\partial c}{\partial x}(L) = -q_2, \qquad q_2 = \frac{|I| \, G_-}{2DF} \tag{4}$$

on a surface of a negative electrode. Here, D is binary diffusion coefficient in electrolyte ($m^2 \, s^{-1}$), I the overall current density ($A \, m^{-2}$), F the Faraday constant ($A \, s \, kg \, equiv^{-1}$), and $G_+ = 3 - 2t_1$ and $G_- = 2t_1 - 1$, where $t_1 = 0.7$ is the transference number of hydrogen ion.

In [1] the equations for electrolyte concentration change at the boundary also were received:

$$c(t) = c_0(t) - 2j\sqrt{\frac{t}{\pi}}, \tag{5}$$

where

$$j = \frac{GI}{2F\sqrt{D}},$$

and $G = G_+$ for a positive electrode and $G = G_-$ for a negative electrode. With boundary conditions (4) we receive a problem with the homogeneous diffusion equation (2) and boundary conditions (4).

We solved a problem (3)–(5) using Crank–Nicolson scheme [2]. The fall of electrolyte concentration up to zero near to a surface for any electrode was considered as criterion discharge ending.

3. Results and discussion

Model researching was carried out for boundary condition (3)–(4) or (5).

Our calculations have shown qualitative conformity of the received results with the ones carried out within the framework of other models, for example, macrohomogenious discharge model for porous electrode [3]. As in [4] faster falling electrolyte concentration near to a positive electrode surface in comparison with a negative one was observed.

Also it was established that it is possible to achieve good conformity between experimental and calculated time of the discharge, for example, at values $I = 500 \, A \, m^{-2}$, $q_1 = 1.1 \times 10^{-2} \, mol \, m^{-4}$ and $q_2 = -2.72 \times 10^{-3} \, mol \, m^{-4}$ for boundary conditions (3)–(4) (theoretical time of the discharge—0.5 h, it is practically equal experimental [4]) and
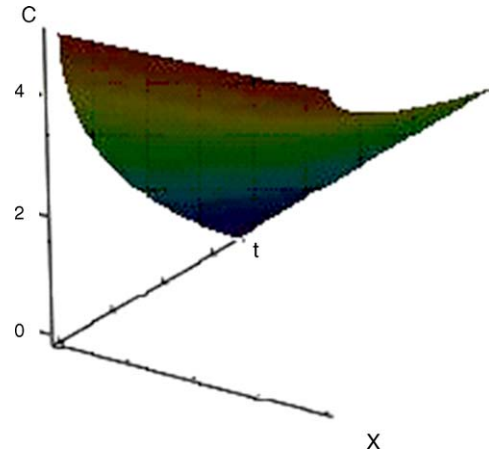

Fig. 1. The concentration distribution in space between electrodes with current of time.

$j_1 = 107.7 \, mol \, m^{-3} \, s^{-1/2}$, $j_2 = 0$ for boundary conditions (5) (theoretical time of discharge 30 min practically coincides with experimental [4]). However, boundary conditions (5) are represented to be more preferable for using because in this case final distribution of concentration in interelectrode space is better be in agreement with calculations [3,5]. With boundary conditions (3)–(4) practically homogeneous distribution of concentration decreasing eventually is observed. The concentration distribution in space between electrodes for boundary conditions (5) is shown in Fig. 1.

However, it is necessary to notice that the specified values of parameters are not be in accord with the values calculated with (3) and (4) as they correspond to values of diffusion coefficients up by some orders exceeding ones in [4] and similar works. We assume that this discrepancy is connected with pores plugging at the electrode/electrolyte solution interface. In [1] during the boundary conditions derivation the structural changes of electrodes near to boundary were not taken into account. The account of these conditions should to improve quality of considered model appreciably.

To achieve good conformity between theoretical and experimental time of the discharge the constants q_1 and q_2 (or, similarly, j_1 and j_2) considered as some fit parameters which change
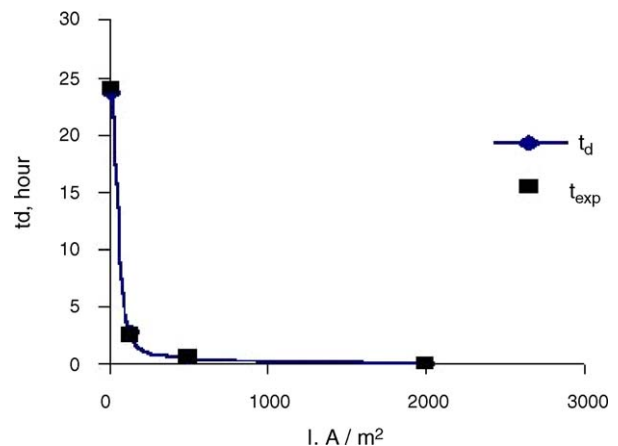

Fig. 2. The dependence of discharge time on overall discharge current density.

as overall discharge current density changes. The discharge time dependence on overall discharge current density is shown in Fig. 2.

4. Conclusions

In the given work the simplified model of the lead-acid battery discharge [1] based on consideration of electrolyte diffusion in interelectrode space was analysed. The Crank–Nicolson scheme application was analysed for a case of the fixed electrolyte flows near the electrode surfaces and when time dependence of acid concentration at electrode/electrolyte solution was given.

It is shown that within the framework of the given model it is possible to receive good conformity between theoretical and experimental discharge capacity if values of electrolyte flows near electrode surface consider as phenomenological parameters that change as overall discharge current density changes. To improve the model structural changes of electrodes near the electrode/electrolyte solution boundary should be taken into account.

Acknowledgments

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