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Short Communication

Statistical Models of Alkaline Batteries Discharge

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In this study, there was proved by experiments that the way, in which the activation-ohmic addend in Shepherd's and Tremblay's empiric equations and their generalizations describes activation-ohmic processes during a battery discharge by direct current, is wrong. The new addend has been proposed for the description of the activation-ohmic processes corresponding to all experimental data.

Keywords: battery, modeling, statistical model, nickel–cadmium, lead-acid

1. INTRODUCTION

Despite of an existence of a lot of battery models, there exist only three methods of such models construction, namely: electrochemical method (when transport of all components is taken into account), statistical method and structural method (in impedance theory). The electrochemical method is the most fundamental one. As a rule, practicians using the batteries electrochemical models in real electrochemical systems point out two disadvantages of those models [1]; Firstly, the electrochemical models contain very many parameters describing a lot of local processes and phenomena. As a rule in actual practice for a specific battery, these parameters are impossible or very hard to be measured. For example, it is impossible to measure directly the parameters of the Butler-Volmer function and other local parameters inside of the porous electrode (which are used in the models). These local parameters are found from experimental studies conducted on an electrode surface. Though it is not obvious at all that the found local parameters are equivalent to corresponding parameters inside of the porous electrode. Secondly, those models are very cumbersome and complicated for a practical use. This is why for modeling of batteries work being a part of, for example, hybrid vehicles, most commonly, the statistical models are used [2,3]. So at the present time, the batteries statistical models are of great practical importance.

This paper is geared to analyzing and improving of the most important empiric relations used for a battery discharge description and constituting a basis of the statistical models. This work is a continuation of the works [4-8] devoted to statistical and structural modeling of different batteries work modes.

2. ANALYSIS OF EMPIRICAL RELATIONS DESCRIBING THE BATTERIES' DISCHARGE AT DIRECT CURRENT

It is highly possible that among the most examined empirical relations describing voltage change at the battery terminals during their discharge by direct current shall be following relations:

- Shepherd [9]

$$U = E - Ri - K\left(\frac{q}{C-q}\right)i + A\left[\exp\left(-B\frac{q}{C}\right) - 1\right], \qquad (1)$$

- Tremblay [2]

$$U = E - Ri - K\left(\frac{q}{C-q}\right) + A\left[\exp\left(-B\frac{q}{C}\right) - 1\right], \qquad (2)$$

- generalized empirical relation (GER) [3,10,11],

$$U = E - Ri - \left(\frac{Dq + Kqi}{C-q}\right) + A\left[\exp\left(-B\frac{q}{C}\right) - 1\right], \qquad (3)$$

where E–battery EMF (electromotive force); R–internal activation-ohmic battery resistance; C–full battery capacitance; i–discharge current; K, A, and B–experimental constants and q–quantity of electricity, released by the battery, for the moment of voltage U measurement.

The Shepherd's equation (1) follows from the equation (3) at $D = 0$, and Tremblay's equation (2) at $K = 0$.

In addition to the earlier dependencies, there are many relations [12-15]. However, these relations, as a rule, are simplifications of the relations (1–3) or their possible approximations.

Equations (1–3) are obtained by the study of different types of batteries. For example, initially obtained Shepherd's equation (1) was applied to acid batteries, but currently, it is also used for the NiCd, Li-Ion, and NiMH batteries' categories [3,16].

The first element in equations (1-3) represents the ideal source of continuous EMF. The second element describes the activation-ohmic part in battery operation. The third element is transformed into zero at $q = 0$ and grows along the absolute value, as the battery discharges; that is, this element describes the change of voltage related to the degree of battery discharge. Therefore, we have conditionally named this voltage change *battery discharge polarization*. The final element describes transitional processes developing in the battery at its closure to discharge. Hence, we have conditionally named the change of voltage corresponding to this element *relaxation polarization*. Empirical relations describing the fourth element operation have a similar view in all equations (1–3).

In the equations (1-3), the activation-ohmic addend looks like

$$U_o=Ri, \tag{4}$$

that is, it is purely ohmic one.

In alkaline batteries, there are both a purely ohmic resistance connected with a resistance of an electrolyte & electrodes and an activation resistance connected with the main electrochemical reaction running. For instance, for nickel-cadmium batteries, this is the following reaction

$$\frac{1}{2}\mathrm{Cd}+\mathrm{NiOOH}+\mathrm{H_2O}\rightarrow\frac{1}{2}\mathrm{Cd(OH)_2}+\mathrm{Ni(OH)_2} \tag{5}$$

In electrochemistry, the activation processes are described with Butler-Volmer function:

$$i(u)=I_0\left\{\exp\left(\frac{\alpha zF\eta}{RT}\right)-\exp\left(-\frac{(1-\alpha)zF\eta}{RT}\right)\right\} \tag{6}$$

where I_0 - exchange current; F - Faraday constant; R - gas constant; T - absolute temperature; η - polarization potential, α - constant.

Therefore in any equations describing voltage variation on battery terminals during their discharge at direct current, an addend must necessarily be describing the activation polarization. However in the empiric equations (1-3), there is no such addend.

This addend must have a form of a function inverse to the function (6). In common case from the function (6), it is impossible to find an inverse analytical function

$$\eta=F(i). \tag{7}$$

However for use in the empiric equations (1-3), the function (7) can be simplified to a large extent. As the function (7) would be used only in a case of positive current direction ($\eta>0$), the function for a negative current direction $\eta<0$ can be any one. Besides, all the constants in the equation (7) will be empiric ones and therefore so far they would not have a direct physical meaning. In connection with this in the function (6), it is convenient to take the parameter α being either $\alpha=1$ or $\alpha=0.5$. In this case from the equation (7) for the activation (empiric) addend, we'll obtain two possible relations:

$$U_a=A\cdot ln(Bi+1) \tag{8}$$

$$U_a=A\cdot arcsh(Bi) \tag{9}$$

The relations (8,9) are empiric ones, so at positive current direction, they are equivalent, as on any large enough interval of change causing by discharge current, they can be approximated by each other with an accuracy sufficient for practical purposes [17]. In future, we shall use the relation (8).

Thus, the activation-ohmic addend in the equations (1-3) in common case must take a form

$$U_{oa}=Ri+A\cdot ln(Bi+1) \tag{10}$$

The function (10) sets Volt-Ampere characteristic of a battery in the case of the positive current direction.

3. EXPERIMENTAL

For our experimental studies, the following batteries were used: KL-13, KM-28, KM-125, KSX-6, KCSH-8, KCSL-13. The measures were conducted on completely charged batteries. In this case, the relations (1-3) reduce down to the function (4). A comparison of the functions (4,10) with the obtained experimental data will allow assessing a deposit of activation resistance into general voltage drop taking place at battery discharge.

The Volt-Ampere characteristic for the studied batteries was taken with use of rectangular current impulses. Values of discharge current impulses for each battery were chosen consistently equal: 0.01C; 0.1C; 0.5C; 1C (C- nominal battery capacity). Duration of a discharge impulse *t* under discharge current 1C was chosen to be equal to 0.1 second. At other discharge currents, durations of discharge impulses were determined on the basis of the requirement $i \cdot t$=const. This requirement ensured the same conditions at any discharge current values. The pulse current use allowed measuring Volt-Ampere characteristic of a battery without its essential discharge as per one current impulse, a battery discharged only by the fraction 0.000028 from its rated capacity. The resulted voltage change was measured on battery terminals. Via analog-to-digital converter, all data were delivered to computer. The measuring results of the Volt-Ampere function for the battery KL-13 are represented in Fig.1.

4. RESULTS AND DISCUSSION

The optimal parameters for the equations (4,10) were found from the requirement of an optimal coincidence of these equations with experimental data. With this purpose in mind, there were used the method of least squares and Levenberg-Marquardt's optimization procedure. The results are represented in the Table 1.

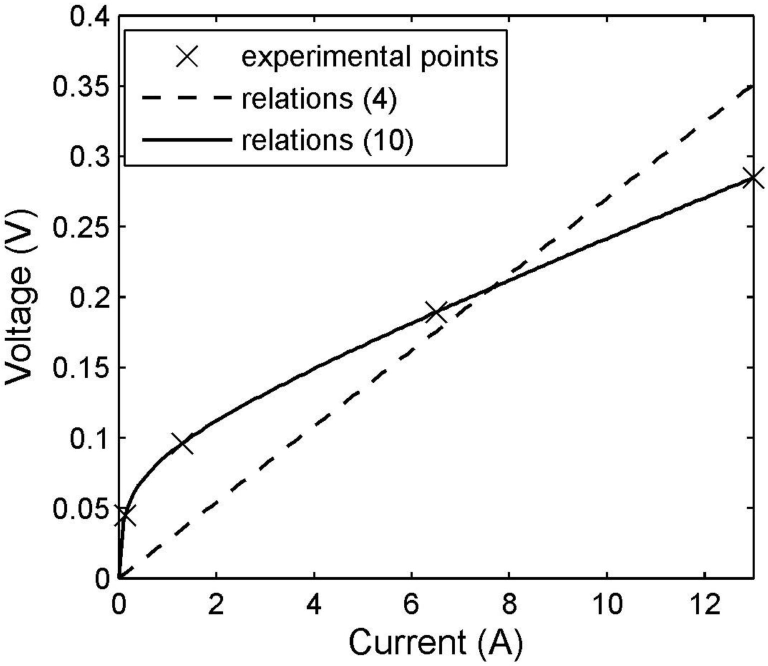

Figure 1. The Volt-Ampere function for the battery KL-13

On the Fig. 1 it is seen that an initial change of the activation-ohmic addend is typical for the activation component of the voltage change (8), while at high current values, the curve changes practically in a linear way, which is typical for the ohmic component of the voltage change (4). Thus, from the experimental results, it follows that the both components of the activation-ohmic voltage change are significant for a voltage change description on battery terminals during their discharge at direct current.

Table 1. Optimal parameters of activation-ohmic addends of empiric equations (1-3) for the battery KL-13

Empiric relations	R (Ом)	A (В)	B (A^{-1})	δ (%)
Relation (4)	0.028	-	-	38
Relation (10)	0.012	0.016	106	1.2

δ - relative error of approximation of experimental points in percents.

The similar calculation was performed also for nickel-cadmium batteries KM-28, KM-125, KSX-6, KCSH-8, KCSL-13. The optimal parameters of the equation (10) for these batteries are represented in the Table 2.

Table 2. Optimal parameters of the relation (10) for different kinds of nickel-cadmium batteries

Batteries	R (Ом)	A (В)	B (A^{-1})	δ (%)
KM-28	0.0027	0.010	106	1.2
KM-125	0.0020	0.010	106	1.3
KSX-6	0.0028	0.0031	105	1.1
KCSH-8	0.0083	0.0041	106	1.2
KCSL-13	0.0047	0.0036	106	1.3

In the Table 2, the approximation relative error of the experimental data is approximately the same that in the Table 1.

5. CONCLUSIONS

So approximation error of the experimental data for the relation (4) is very big (Table 1). That is, this relation cannot describe precisely enough the activation-ohmic processes in batteries during their discharge at direct current (Fig.1). This is why for improving of description quality of battery discharge with use of relations (1-3), it is necessary in them to replace the activation-ohmic addend (4) with the addend (10), which corresponds to the experimental data very well. Undoubtedly, this replacement will lead to considerable improvement of the process description of alkaline batteries discharge with aid of the empiric equations (1-3).

In the relation (10), there are more empiric parameters than in the relation (4). Nevertheless by virtue of the fact that they can be found independently from other parameters of the equations (1-3), the introduction of the addend (10) into the equations (1-3) does not complicate their use.

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