

Generalized Peukert's Equation for Nickel-Cadmium Batteries at High Discharge Currents

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In this paper both experimentally and theoretically, the dependence was analyzed of released capacity of nickel-cadmium batteries at diverse discharge currents. It was shown that the classical Peukert's equation is inapplicable at both small and high discharge currents. Meanwhile, the well-known generalized Peukert's equation $C=C_m/(1+(i/i_0)^n)$ corresponds well to the experimental data at small and medium discharge currents. However at high discharge currents, the capacity released by nickel-cadmium batteries is diminished much faster than this generalized Peukert's equation predicts. By experiments and theoretically, it was proved that the reason of the sharper descent of the batteries' released capacity at high discharge currents is the voltage loss escalation on battery internal resistance at a growth of discharge current. There was proposed the equation $C=C_m/(1+i^n/(i_0^n(1-i/i_1)))$ taking into account this effect; and this one corresponds well to the experimental data at any discharge currents.

Keywords: Peukert's equation, modeling, battery, nickel–cadmium, discharge current

1. INTRODUCTION

The Peukert's equation was one of the first empiric equations describing processes taking place in electrochemical batteries [1]. Nevertheless even now, it is widely used in analytical models of batteries (belonging to different electrochemical systems) [2,3]. Undoubtedly, most precise batteries models can be built only with use of fundamental electrochemical modeling methods taking all kinetic processes in batteries into account [4-8].

However, not every time, it is possible to build or use the fundamental electrochemical models. In this case, one use the analytical models [9-12] based on various empiric equations.

For example, it is impossible to build fundamental electrochemical models for such poorly studied processes taken place in batteries as the following ones: the thermal runaway [13-15], the hydrogen accumulation in batteries electrodes [16,17], the gases release at cycling of lithium-ion

batteries [18,19], etc.

It should be noted that the fundamental electrochemical models are not possible to be used in electric vehicles or airplanes as those models are very sophisticated and cannot be calculated by on-board computers of airplanes [3]. Besides, those models contain a lot of parameters that are often difficult or impossible to be measured (for example, parameters inside of a porous electrode). Notably, for measurement of kinetic parameters of batteries, the latter should be dismantled, which – quite often – is forbidden by an ordering customer.

So battery analytical models are widely used even at present time. The basis of the analytical models is made of various empiric equations. That is why at present time, a clarification and an improvement of empiric equations is an actual challenge.

In the paper [3], the analytical model is built for assessment of battery remaining capacity at different temperatures and discharge currents. This model was based on the classical Peukert's equation [1]

$$C = \frac{A}{i^n}, \quad (1)$$

where C is capacity released by a battery at discharge current i , while A and n are empiric constants. The Peukert's equation is inapplicable at small discharge currents as at descent of discharge current, the battery released capacity tends to infinity, which has no physical sense.

In the paper [2] for evaluation of battery remaining capacity at various temperatures and discharge currents, the analytical model was built based on the well-known generalized Peukert's equation

$$C = \frac{C_m}{1 + \left(\frac{i}{i_0}\right)^n}. \quad (2)$$

where C_m is the top capacity a battery is able to release. At $i=i_0$, we obtain $C=C_m/2$, i.e. i_0 is the current, at which the battery releases capacity twice less as compared to its top capacity. The equation (2) is applicable for both lithium-ion batteries [2] and alkaline ones [20-23].

However, the conducted by us investigations as well as the studies described in the paper [24] showed that at high discharge currents, the experimental data correspond poorly to the equations (1,2).

This work is aimed at construction of a generalized Peukert's equation corresponding well to the experimental data at any discharge currents.

2. PEUKERT'S EQUATION GENERALIZATION

In the Fig. 1, the experimental data is shown for nickel-cadmium battery SBM 84 (by capacity 84 Ah with pocket electrodes) made by the company SAFT. The experimental data is given in comparison with the predictions based on the equations (1,2).

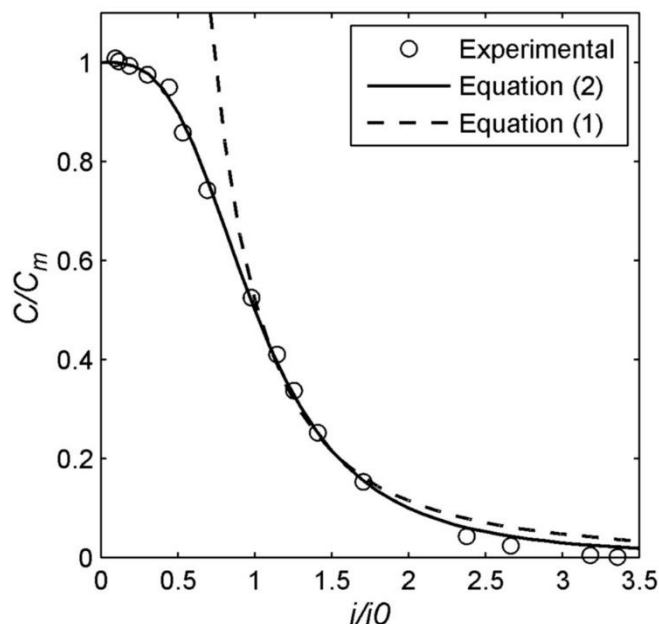


Figure 1. Comparison of Peukert’s equations (1,2) with experimental data for nickel-cadmium battery SBM 84. C_m is the top battery capacity, and i_0 is the current, at which a battery released capacity is twice as low as its top capacity.

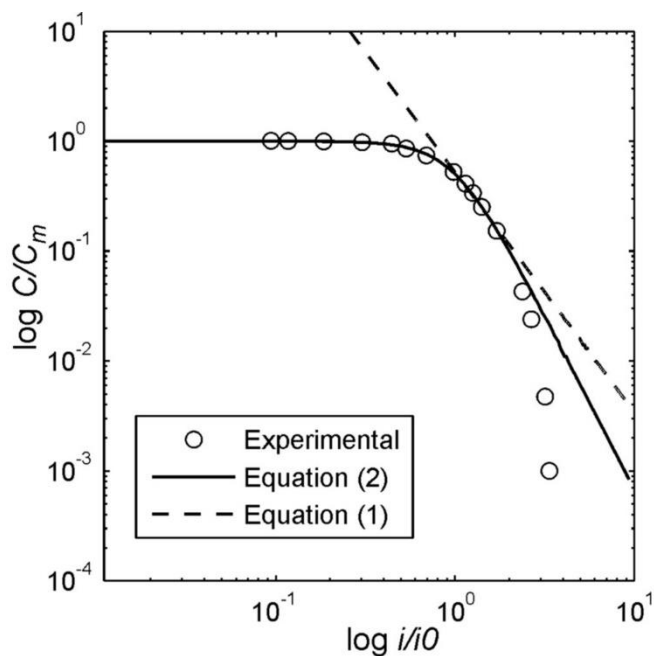


Figure 2. Comparison of Peukert’s equations (1,2) with experimental data for nickel-cadmium battery SBM 84 in logarithmic system of coordinates. C_m is the top battery capacity, and i_0 is the current, at which a battery released capacity is twice as low as its top capacity.

From the Fig. 1, it is seen that always the classical Peukert’s equation curve is concave. That is why, it can coincide with any experimental data only in some interval of discharge currents starting with point of inflection of an experimental curve. The generalized Peukert’s equation (2) corresponds

well to any experimental data at small and medium discharge currents. However at high discharge currents, the equation (2) differs much from the experimental data. Especially well it is seen in frame of logarithmic system of coordinates (Fig. 2).

For finding out of a reason, why the descent of batteries' released capacity at growth of discharge current is going on quicker than the equation (2) predicts it, let us study a connection between the empiric equations by Peukert and Shepherd.

The Shepherd's equation looks like as follows [25]

$$U = E - Ri - K \left(\frac{C}{C_m - C} \right) i + u_r \left[\exp \left(-B \frac{C}{C_m} \right) - 1 \right] \quad , \quad (3)$$

where U is voltage on battery terminals; i is discharge current; C is battery released capacity; E is EMF of fully charged battery; R , C_m is battery internal resistance and top capacity; u_r is voltage drop due to relaxation processes at start of discharge process; K and B are empiric constants.

At discharge under direct current down to the final voltage u_k (which usually is equal to 1 V for nickel-cadmium batteries), for parameters of the equation (3), we obtain the equations

$$u_r \left[\exp \left(-B \frac{C}{C_m} \right) - 1 \right] \approx -u_r \quad , \quad U = u_k \quad . \quad (4)$$

The first equation (4) follows from the evident fact that the closer to the battery discharge process end, the weaker are relaxation processes connected with discharge beginning until they would die completely.

Besides, if to discharge a battery with small currents, it is possible to neglect the voltage drop on its internal resistance, i.e. $Ri \approx 0$. In this case from the equation (3) (with due account of the equations (4)) for battery released capacity, we obtain the following equation:

$$C = \frac{C_m}{1 + Di} \quad , \quad \text{where} \quad D = \frac{K}{E - u_k - u_r} \quad (5)$$

Thus from the Shepherd's equation (3) at small discharge currents, the well-known Liebenow's equation (5) follows. The Liebenow's equation was obtained for lead-acid batteries in the case of their discharge by small currents, at which the Peukert's equation is inapplicable [26]. It should be noted that the Shepherd's equation (3) and Liebenow's one (5) were obtained for lead-acid batteries and that is why, their close interrelation is of no surprise.

At present time, the Shepherd's equation (3) is used also for analysis of discharge of batteries belonging to other electrochemical systems [27]. However, from the given above analysis, it follows that both the Shepherd's equation and Liebenow's one are true only at small discharge currents, which is also confirmed both experimentally and theoretically in the papers [12,26].

The classical Peukert's equation (1) is true for lead-acid batteries at medium discharge currents [1,27]. In our previous papers [2,20], by experiments, it was proved that for alkaline and lithium-ion batteries at small and medium discharge currents true is the generalized Peukert's equation (2).

In the paper [12], it was shown that for alkaline batteries at small and medium discharge currents, the equation, which better corresponds to the experimental data, is the generalized Shepherd's equation in the following form:

$$U = E - Ri - K \left(\frac{C}{C_m - C} \right) i^n + u_r \left[\exp \left(-B \frac{C}{C_m} \right) - 1 \right] \quad (6)$$

From the equation (6) at $n=1$, we obtain the classical Shepherd's equation (3).

If to use the equation (6) and the equations (4), for dependence of battery released capacity on discharge current we shall obtain the generalized Peukert's equation (2). If also in addition to take into account a battery internal resistance, we'll obtain the following equation:

$$C = \frac{C_m}{1 + \left(\frac{i}{i0} \right)^n \left(\frac{1}{1 - i/i1} \right)} \quad \text{where} \quad i0 = \sqrt[n]{\frac{E - u_k - u_r}{K}} \quad \text{and} \quad i1 = \frac{E - u_k - u_r}{R} \quad (7)$$

Unlike the equation (2), the additional co-factor in the denominator of the equation (7) takes into account the internal resistance of the battery. At $i=i1$, the battery released capacity will be equal to zero. Hence, the equation (7) means that at high discharge currents ($i \geq i1$) already in the launching instant of battery discharge on its terminals, the voltage will be less than the final voltage of the battery discharge (u_k). This situation is quite real for any battery. However, this real situation is taken into consideration neither by the Peukert's equations (1,2) nor by any other similar equations [20,21].

From the equation (7) at high discharge currents, it follows that with due account of the battery internal resistance, its released capacity will drop faster as compared to calculations based on the Peukert's equations (1,2).

3. EXPERIMENTAL

For comparative testing of the generalized Peukert's equations (2 and 7), there were used the batteries produced by the company SAFT with pocket electrodes. In the experiments, there were used batteries distinguished with different discharge modes: SBLE, SBM, SBH (Long, Medium, High).

The batteries were discharged down to the voltage 1 V by currents within the interval from $0.1C_N$ (where C_N is battery nominal capacity) and up to current values, at which the batteries' released capacity was close to zero. Batteries' charge was accomplished according to their operation manual.

Before every change of discharge current value, training cycles were conducted. The training cycles were implemented according to the operation manuals of the batteries under studying. The training cycles use allows excluding a mutual influence of discharge different modes on each other via various remaining phenomena (for example, via the memory effect, etc.) The training cycles were made not less than three times. Notably, if – upon that – the released capacity differed by more than 5% , three new training cycles were conducted; and so on.

At every discharge current value, three discharge cycles were conducted. Upon that as the released capacity, the capacity average value of the obtained values was taken. However if the capacity obtained values differed by more than 5%, additional training cycles were conducted and the experiments were repeated again from the very beginning.

It should be noted that the measured capacity of identical batteries can differ insignificantly because of statistical dispersion of batteries' parameters at their production and also because of

different modes and duration of their operation. That is why in order to obtain more stable experimental data, any experimental data for batteries' capacity should be standardized on their top capacity (found in experiments for a concrete battery). This method allows finding empiric curves more reliably.

4. RESULTS AND DISCUSSION

In our experiments the following batteries were used: SBLE 95, SBM 56, SBH 98 (with capacity values 95, 56, 98 Ah respectively).

The obtained experimental data (in the standardized coordinates) for batteries under studying are represented in the Figure 3. The standardizing parameters (C_m and i_0) in the Figure 3 are taken from the Table 2. In our previous papers (20-22), it was proved that the experimental curves of the dependence of batteries' released capacity on discharge currents (in the standardized coordinates) do not depend on capacity of studied batteries. That is why the shown in the Figure 3 experimental data is true for batteries of any capacity.

The optimal parameters for the generalized Peukert's equations (2,7) were found from the experimental data on the least square method with use of Levenberg–Marquardt optimization procedure. The found optimal parameters are represented in the Tables 1 and 2.

Table 1. Optimal values of parameters for generalized Peukert's equation (2)

Battery	SBLE 95	SBM 56	SBH 98
C_m (Ah)	97.328	56.371	95.593
i_0 (A)	67.325	60.668	299.461
n	3.029	3.17	4.488
δ^a (%)	3.507	2.831	3.324

^aRelative error of experimental data approximation by the Equations (2) in Figure 3.

Table 2. Optimal values of parameters for generalized Peukert's equation (7)

Battery	SBLE 95	SBM 56	SBH 98
C_m (Ah)	99.135	56.857	95.827
i_0 (A)	81.062	69.409	333.846
n	2.263	2.615	3.849
i_1 (A)	202.469	208.986	903.07
δ^a (%)	1.991	1.723	2.000
R (m Ω)	1.482	1.436	0.332

^aRelative error of experimental data approximation by the Equations (7) in Figure 3.

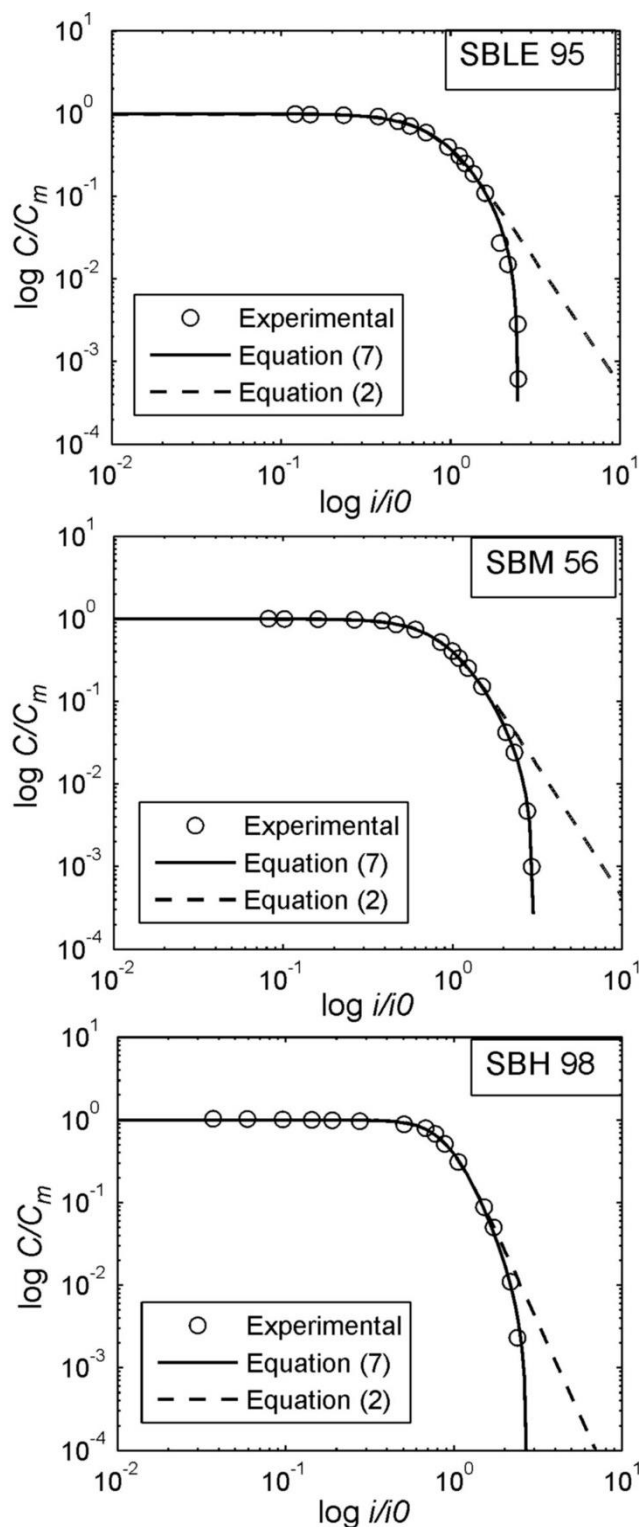


Figure 3. Comparison of generalized Peukert’s equations (2,7) with experimental data for capacity released by nickel-cadmium batteries (SBLE 95, SBM 56, SBH 98) at various discharge currents in logarithmic system of coordinates. (C_m and i_0 from Table 2).

From the analysis of the Figure 3, it follows that at high discharge currents, the generalized Peukert’s equation (7) corresponds to the experimental data much better than the equation (2). Upon that, the generalized Peukert’s equation (7) corresponds well to the experimental data through the

entire range of discharge current changes. The relative error of approximation of the experimental data by the equation (7) makes not more than 2%. Thus the conducted calculations prove positively that the reason of the sharp descent of the batteries' released capacity at high discharge currents is the voltage drop on batteries' internal resistance.

With use of the last ratio in the equations (7), it is possible to find the battery' internal resistance:

$$R = \frac{E - u_k - u_r}{i1} \quad (8)$$

In our experiments, the final voltage of batteries' discharge is equal to $u_k=1\text{V}$, while EMF of charged batteries is equal to $E\approx 1.36\text{ V}$ and the batteries' relaxation polarization is equal to $u_r\approx 0.06\text{ V}$. With use of this data as well as the data for the parameter $i1$ from the Table 2, from the equation (8), we shall find the internal resistance of the batteries under investigation. The found values of batteries' internal resistance are given in the Table 2.

Separate experiments showed that the values found based on the equation (8) coincide with direct changes of internal resistance of studied batteries with the relative error not more than 5%.

The fact that the Peukert's equation (1) is not applicable at high discharge currents was observed by other authors, too. For example, in the paper [24] the following improved Peukert's equation was proposed

$$C = \frac{A}{i^n} \sqrt{\frac{1}{s1^{(i/s2-1)} + 1}} \quad (9)$$

which describes correctly functioning of lithium-ion batteries at high discharge currents. In the equation (9), $s1$ and $s2$ are new empiric constants. The additional multiplier was entered into the equation (9) similarly with use of such multiplier in radiotechnics for determination of the cut-off frequency of low-pass filters. It can be said about the equation (9) that from formal point of view, it is correct in description of the dependence $C(i)$ at medium and high discharge currents. However in no way can this empiric equation explain a reason of such sharp fall of the batteries released capacity at high discharge currents.

5. CONCLUSIONS

The proposed generalized Peukert's equation (7) has a number of advantages as compared to the classical Peukert's equation (1).

Firstly, in the classical Peukert's equation (1), no constant has an electrochemical sense. Those constants are just empirical. In the proposed generalized Peukert's equation (7), the constants (C_m , $i0$ and $i1$) have the clear electrochemical sense.

Secondly, the classical Peukert's equation (1) is inapplicable at both small and high discharge currents (Fig.1,2). The curve of the classical Peukert's equation (1) is concave always; more to it, at decrease of the discharge current, it tends to infinity, which has no physical sense. The experimental curve of dependence of capacity released by nickel-cadmium batteries at small discharge currents is convex, while at high discharge currents it is concave. Hence, the classical Peukert's equation (1) can

describe the batteries' released capacity only in a certain interval of discharge currents starting from the point of inflection of an experimental curve (Fig. 1). Besides, as it was shown by investigations described in this paper, the equation (1) is inapplicable at high discharge currents, too.

Thirdly, the classical Peukert's equation (1) (like other similar empiric equations) does not take into consideration the voltage drop on a battery internal resistance. However, it is evident that a situation is possible at high discharge currents, when already at a battery discharge switching-on, the voltage on its terminals will be less than the final voltage of the battery discharge. For the first time, this very important factor is taken into account in the proposed generalized Peukert's equation (7). Thus, the generalized Peukert's equation (7) describes the capacity released by nickel-cadmium batteries correctly at any discharge currents.

Inasmuch as the different forms of the Peukert's equation are widely used in various analytical models [2,3], the refinement of these equations and the establishment of the electrochemical sense of the used in them parameters have great both practical and theoretical significance.

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