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Peukert's Generalized Equation Taking into Account the Temperature for Nickel-Cadmium Batteries

Nikolay E. Galushkin[*], *Nataliya N. Yazvinskaya, Dmitriy N. Galushkin*

Don State Technical University, Laboratory of electrochemical and hydrogen energy, 147 Shevchenko Street, Town of Shakhty, Rostov Region, Russia, 346500.
[*]E-mail: galushkinne@mail.ru

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In this paper, batteries' temperature influence was analyzed on parameters of Peukert's generalized equation $C=C_m/(1+(i/i_0)^n)$. It was proved by experiments that all the parameters (C_m, i_0 and n) of Peukert's generalized equation depend heavily on battery temperature. So when assessing battery released capacity, it is absolutely necessary to consider battery temperature. Empiric equations have been proposed describing parameter changes (C_m, i_0 and n) depending on temperature. These equations are correct at any battery temperature values widely used in practice. Thus, experimentally it was proved that the proposed Peukert's generalized equation is correct at any discharge currents and at any battery temperatures, unlike the classical Peukert's equation.

Keywords: Peukert's equation, battery, nickel–cadmium, lithium-ion, temperature

1. INTRODUCTION

In connection with the wide battery use in diverse technical devices, the necessity arose to develop reliable models of batteries. Notably, often by companies using these or those battery models, a number of requirements are put forward that newly developed models must meet. Firstly, for battery models used in onboard systems (airplanes, electromobiles, etc.), it is necessary that such battery models should be immediately computed by onboard computers, so the models should be quite simple. Secondly, it is often required that all parameters of a model would be possible to find with the aid of experiments with a whole battery, without dismantling it.

The most fundamental electrochemical batteries models [1-5] were built based on the kinetic laws of ion and molecule transportation and other fundamental laws of electrochemistry. That is why these models contain a lot of local parameters, which are impossible to be determined without dismantling a battery. Besides, these models are very sophisticated and require great computational power for their solving. Hence, these models do not meet the abovementioned requirements.

A practical battery model meeting the above-specified requirements can be built only within the frame of the statistical method [6-9] or the non-linear structural method of modeling [10-12]. Also, these methods are often used when modeling such poorly studied phenomena in batteries as thermal runaway [13,14] or hydrogen accumulation in battery electrodes during their cycling [15,16].

For batteries statistical models development often, Peukert's equation is used, or various generalizations of this equation [17,18]. However, in no way does Peukert's equation take into consideration an ambient temperature or the effects of battery self-heating [19,20]. although any temperature change results in a great change of a battery's released capacity [21-24]. In particular, at a temperature fall, a battery's released capacity decreases due to the deceleration of chemical reactions [25].

This paper is aimed at the development of a generalized Peukert's equation taking influence into account of both a discharge current and battery temperature.

2. GENERALIZATION OF PEUKERT'S EQUATION

In the paper [17], a statistical model was built for the batteries' remaining capacity evaluation, which took into account both a discharge current change and battery temperature. This model was built based on the following generalization of Peukert's equation:

$$C = \frac{C_m}{\left(\dfrac{i}{I_{ref}}\right)^n}\left(\frac{T}{T_{ref}}\right)^{\beta} \quad . \tag{1}$$

where C_m is the absolute capacity of a fully charged battery or top capacity, I_{ref} and T_{ref} are reference current and temperature for a battery under investigation. In the paper [17], the following values were used: I_{ref}=1 A, T_{ref}=298K and n, β are empiric constants.

Equation (1) has a number of shortages. Firstly, Peukert's equation

$$C = \frac{C_m}{\left(i/I_{ref}\right)^n} \tag{2}$$

is inapplicable at small discharge currents, as from the equation (2) it follows that at a decrease of a discharge current i, a battery released capacity tends to infinity. However, such function is devoid of physical sense. In a similar paper [18], instead of the Peukert's equation (2), the Peukert's generalized equation was used:

$$C(i) = \frac{C_m}{1+\left(i/i_0\right)^n} \quad . \tag{3}$$

The equation (3) corresponds well to all experimental data at any discharge currents [26,27]. Here, i_0 is a discharge current, at which a battery's released capacity is twice less than their top capacity.

Secondly, in the equation (1), the temperature dependence of a battery's released capacity is not optimal. It can be used only for a narrow range of temperatures. Indeed, from the equation (1), it follows that capacity C becomes zero at T=0. However, from the electrochemical conception of discharge processes, it is clear that a battery's released capacity C becomes zero much earlier. It must become zero at temperatures close to that of electrolyte freeze-up [28]. Besides, from the equation (1), it follows that the capacity C grows constantly along with battery temperature growth. But this is impossible, as a battery's released capacity is limited from above by an active matter mass in electrodes. Hence, a battery maximum released capacity must exist, beyond which the battery's released capacity can not grow any longer. In the paper [18], these two shortages were corrected, and for a battery's released capacity evaluation, the following form of Peukert's generalized equation was used:

$$C = \frac{C_{mref}}{\left(1+\left(\frac{i}{i_0}\right)^n\right)} K \frac{\left(\frac{T-T_L}{T_{ref}-T_L}\right)^\beta}{(K-1)+\left(\frac{T-T_L}{T_{ref}-T_L}\right)^\beta} \qquad (4)$$

where C_{mref} is the top capacity released by a battery at temperature T_{ref}, T_L is a temperature at which C=0, and T_{ref} is a reference temperature for studied type of batteries. From the equation (4), it follows that at $T=T_{ref}$, the temperature-related multiplier is equal to 1, i.e. it does not make any impact on a battery's capacity. Nevertheless, in a case that $T\to\infty$, the temperature-related multiplier in the equation (4) will tend to the parameter K. So, the parameter K shows how many times (theoretically) the capacity C_m in the equation (3) can be increased with a battery's temperature growth in comparison of the capacity C_{mref}.

The use of the equation (4) in the batteries' statistical model in the paper [18] (instead of the equation (1) in the paper [17]) allowed improving much the evaluation of batteries's remaining capacity. The equation (4) is the generalization of the equation (3), at which the parameter C_m of the equation (3) depends on a temperature in line with the law:

$$C_m = C_{mref} K \frac{\left(\frac{T-T_L}{T_{ref}-T_L}\right)^\beta}{(K-1)+\left(\frac{T-T_L}{T_{ref}-T_L}\right)^\beta} \qquad (5)$$

Thus, in the papers [17,18], the authors think that in the Peukert's equations (2) and (3) on the temperature, only one empiric parameter C_m depends, while the other two empiric parameters (i_0 and n) do not depend on a temperature.

In the present paper, we experimentally study a dependence of all the empiric parameters (C_m, i_0, and n) of the equation (3) on a temperature.

3. EXPERIMENTAL

For our experimental studies, the following batteries made by the company SAFT were used: SRX 720, SRX 1200, and SRX 2200 with their nominal capacities of 72, 120, and 220Ah, respectively. In these batteries, positive electrodes are sintered, while negative ones are plastic bonded.

In the experiments, there were found the parameters of the Peukert's generalized equation (3) at the following temperature values: -30°C, -20°C, -10°C, 0°C, 10°C, 20°C, and 30°C. The batteries were cycled in the climatic chamber Binder MK240 (BINDER GmbH, Germany).

The batteries' cycling was performed in the following modes. Their charging was performed according to the operation manual of the studied batteries during 8 hours with use of the current 0.2C_5 A (C_5 is a battery's released capacity observed at a five-hour discharge mode). The batteries' discharge was done (down to the voltage 1 V) by constant currents in the range from 0.1C_5 A up to the currents, at which the released capacity of batteries was close to zero.

Before each change of a discharge current or of a battery temperature, training cycles were performed. The use of training cycles allows avoiding a cross-impact of different cycles of charge-discharge (via various remaining phenomena, in particular the memory effect, etc.) The training cycles were performed until the moment, when in three consequent cycles the released capacity would differ by less than 5%. The training cycles were performed according to the studied batteries' operation manuals. Charging was implemented by the current 0.2 C_5 A, applied for 8 hours, while discharging was made by the current 0.2 C_5 A down to the voltage 1 V on battery terminals.

In order to decrease a random spread for the obtained values of the batteries' capacities, the following procedure was used. As an experimental value of the released capacity (at a certain discharge current and temperature of a battery) the average value of the capacity was taken in three consequent cycles of charge-discharge. However, if in these three cycles a released capacity differed by more than 5%, additional training cycles were performed and the experiments repeated again. The found experimental data are represented in Figure 1.

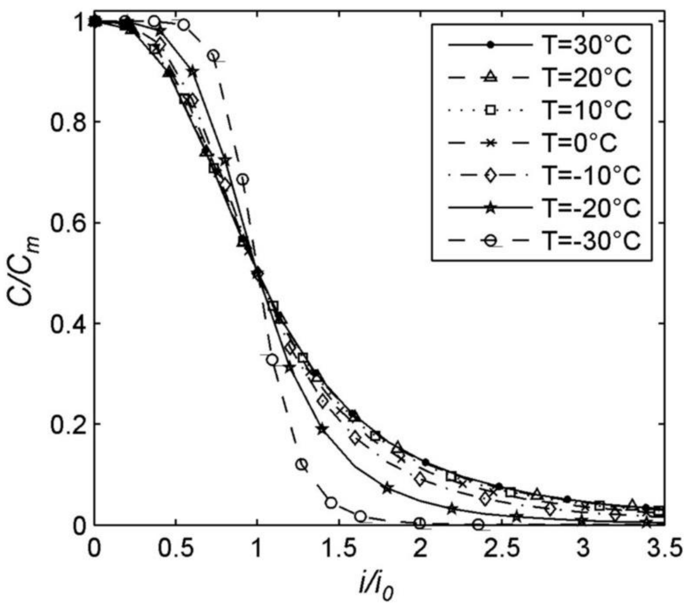

Figure 1. Experimental values of a battery's released capacity at different discharge currents and temperatures. C_m is the top capacity, and i_0 is the current at which a battery's released capacity is twice as low as its top capacity. C_m and i_0 are taken from Table 1 (SRX 720 batteries).

4. RESULTS AND DISCUSSION

In Figure 1, there are represented only experimental data for the SRX 720 batteries. However, the curves (in normalized coordinates) for the SRX 1200 and SRX 2200 batteries coincide with the curves shown in Figure 1 in limits of the statistical error. That is why we do not give the similar curves of SRX 1200 and SRX 2200 batteries here. From this experimental fact, it follows that a curve of a battery's released capacity at different discharge currents (in normalized coordinates) does not depend on the capacity of batteries under investigation. Repeatedly, this fact has been confirmed by us in our previous papers [26,27] for alkaline batteries of various types.

Using the obtained experimental data (Fig. 1), the optimal parameters were found of Peukert's generalized equation (3) for the studied batteries. For this, we used the least square method and the Levenberg–Marquardt optimization procedure. The obtained optimal parameters are represented in Table 1.

Table 1. Optimal values of parameters in equation (3) at various temperatures.

Temperature (°C)	+30	+20	+10	0	-10	-20	-30
Parameters	Battery SRX 720						
C_m (Ah)	73.377	72.528	71.193	68.999	65.190	58.174	45.548
i_0 (A)	288.355	285.161	280.008	271.265	255.590	226.048	171.456
n	2.753	2.785	2.848	2.986	3.324	4.33	8.281
δ^a (%)	2.2	2.3	2.1	1.8	1.6	1.3	1.5
Parameters	Battery SRX 1200						
C_m (Ah)	115.56	114.224	112.122	108.666	102.667	91.827	71.733
i_0 (A)	454.066	449.037	440.923	427.155	402.472	356.388	269.988
n	2.746	2.778	2.841	2.978	3.316	4.189	8.260
δ^a (%)	2.0	2.2	2.3	2.0	1.8	1.6	1.9
Parameters	Battery SRX 2200						
C_m (Ah)	220.786	218.233	214.218	207.614	196.152	175.248	137.050
i_0 (A)	852.627	843.183	827.947	802.095	755.745	673.006	506.972
n	2.829	2.862	2.927	3.068	3.416	4.632	8.510
δ^a (%)	2.2	1.9	2.0	1.8	1.9	1.7	2.1

[a] δ is relative error of experimental data approximation by the equation (3) in Fig. 1.

From the analysis of Table 1, it follows that all the parameters (C_m, i_0, and n) of Peukert's generalized equation (3) depend on a temperature. Hence, the supposition presented in the papers [17,18] in the equations (2) and (3) – that only parameter C_m depends on a temperature – is wrong. That is why the equations (1) and (4) can be used only in a limited range of temperatures.

Let us check the applicability of equation (5) for parameter C_m finding in the studied temperatures range. In Figure 2(a), values C_m are given from Table 1 in the normalized coordinates (C_m/C_{mref}, T). As a reference top capacity C_{mref}, we took the capacity value from Table 1 at T_{ref}=20°C. It should be observed that in the normalized coordinates (C_m/C_{mref}, T), the experimental data in Table 1 (for batteries of various capacities) coincide in limits of the experimental error.

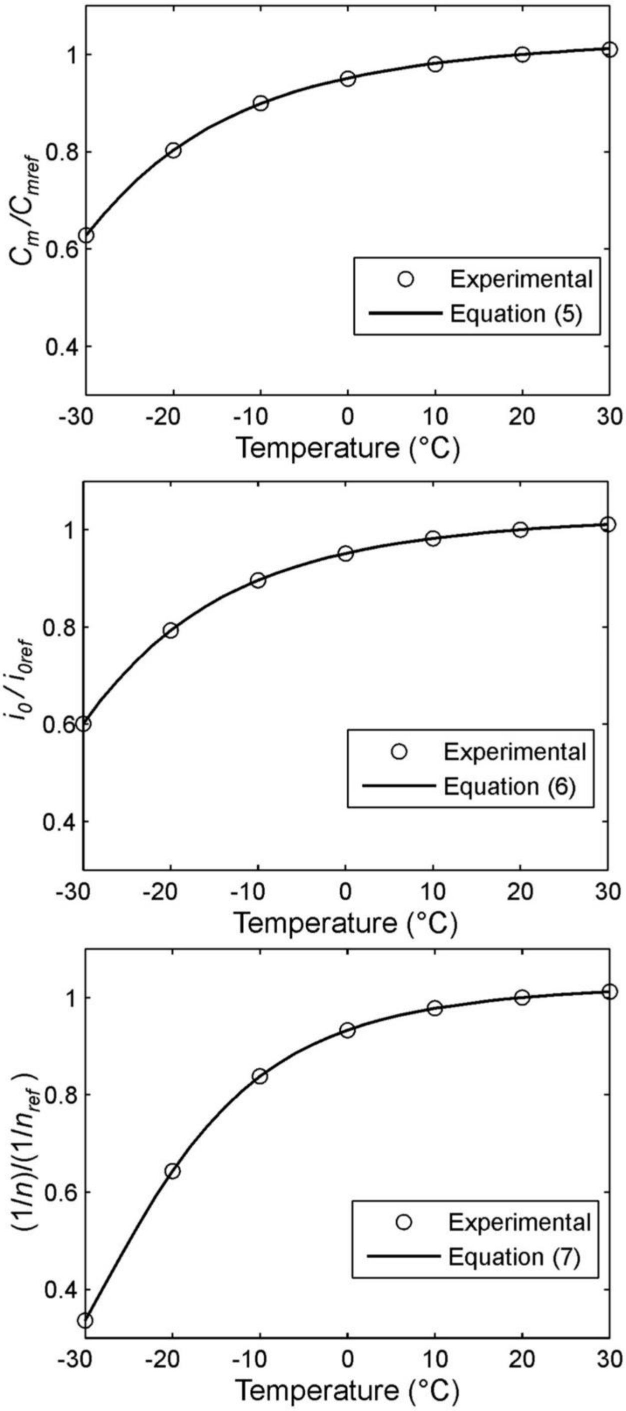

Figure 2. Parameters (C_m, i_0 and $1/n$) of Peukert's generalized equation (3) depending on battery temperatures (a, b and c, respectively). C_{mref}, i_{0ref}, and n_{ref} are values of parameters C_m, i_0, and n_r, respectively, taken from Table 1 at T_{ref}=20°C (SRX 720 batteries).

It follows just from the coincidence of the experimental curves in Figure 1 (in limits of the experimental error) for batteries of various capacities in the normalized coordinates, which was said above. That is why the data given in Figure 2(a) are fair for all the batteries under investigation. With use of the obtained data (Fig. 2(a)), the optimal parameters for equation (5) were found. For this, the least square method and the Levenberg–Marquardt optimization procedure were used. The obtained optimal parameters are represented in Table 2.

Table 2. Optimal values of parameters for equations (5-7).

Parameters	Equation (5)	Equation (6)	Equation (7)
K	1.043	1.038	1.03
T_L (°C)	-61.268	-61.432	-61.29
β	2.865	3.091	4.447

From the Figures 2(b,c), it is seen that qualitatively (in the normalized coordinates), the dependence of the parameters (i_0 and $1/n$) on temperature is the same as that for the parameter C_m. Hence, one can suppose that the dependence of the parameters (i_0 and $1/n$) on a temperature is described by equations similar to the equation (5), i.e.

$$i_0 = i_{0ref} K \frac{\left(\frac{T - T_L}{T_{ref} - T_L}\right)^{\beta}}{(K-1) + \left(\frac{T - T_L}{T_{ref} - T_L}\right)^{\beta}} \qquad (6)$$

$$1/n = 1/n_{ref} K \frac{\left(\frac{T - T_L}{T_{ref} - T_L}\right)^{\beta}}{(K-1) + \left(\frac{T - T_L}{T_{ref} - T_L}\right)^{\beta}} \qquad (7)$$

Let's check the applicability of the equations (6) and (7) by using the data for the parameters i_0 and $1/n$ from Table 1. It should be observed that the experimental data for these parameters (in the normalized coordinates) for batteries of diverse capacity also coincide (as for parameter C_m) in limits of the experimental error. That is why the data in Figures 2(b,c) are fair for all the studied batteries.

As reference parameters i_{0ref} and n_{ref} (Fig. 2(b,c)), the values of these parameters were taken from Table 1 at T_{ref}=20°C. Using the obtained data (Fig. 2(b,c)), the optimal values were found for the parameters in the equations (6) and (7). The parameters' obtained values are shown in Table 2.

The relative error of approximation of the experimental data in Figure 2 by the equations (5-7) is less than 1%. Hence, the proposed equations (5-7) describe very well the dependence of the parameters of the Peukert's generalized equation (3) on a temperature.

The dependence of a battery's released top capacity on a battery's temperature (Fig. 2 (a)) was checked by us with the aid of direct experiments. With this purpose, the SRX 720 batteries were cycled in line with the above-described procedure (Section 3) at the following temperatures: -30°C, -20°C, -10°C, 0°C, 10°C, 20°C, and 30°C. The top capacity was found at the discharge current 0.1 C_5 A. The obtained direct experimental data coincided with the data from Table 1 with a relative error less than 4%.

The found in this paper Peukert's generalized equation (3) (with due account for the equations (5-7)) has a number of advantages in comparison with the classical Peukert's equation (2).

Firstly, the classical Peukert's equation (2) is inapplicable at small discharge currents, as according to the equation (2) at a decrease of a discharge current, the battery's released capacity tends to infinity. However such function is devoid of a physical sense. Meanwhile, the Peukert's generalized equation (3) is applicable at any discharge currents [26,27].

Secondly, as for the Peukert's equation (1) with due consideration of a temperature impact on a battery's released capacity (proposed in the paper [17]), it is correct only in a limited temperatures range close to a reference temperature T_{ref}. Also, the equation (4) proposed in the paper [18] has a limited area of applicability as it does not take into account the dependence of the parameters (i_0,n) of the Peukert's generalized equation (3) on temperatures. However, the experimental data (Fig. 2(b,c)) show that this dependence is very significant. The proposed Peukert's generalized equation (3) (with due consideration for equations (5-7)) is correct at any battery temperatures usually used in practice.

Thirdly, the direct calculations show that the use of the proposed Peukert's generalized equation 3 (with due account of the equations (5-7)) instead of the equation (4) improves further an evaluation of lithium-ion batteries remaining capacity by 10-15% as compared to the evaluation made in the papers [17,18].

5. CONCLUSIONS

The Peukert's equation is widely used in different models of batteries [17,18]. Notably, as shown in the paper [17] and Table 1, a battery temperature influences heavily a battery released capacity. However, in many papers, where the Peukert's equation is used, the temperature impact either is not taken into consideration [19,20,29] or is taken in a rough approximation [17,18]. That is why, undoubtedly, the improvement of the Peukert's equation (as well as the possibility of the precise computation of the temperature impact) is going to enhance the quality of battery models.

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