Int. J. Electrochem. Sci., 17 **(2022)** Article Number: 221154, doi: 10.20964/2022.11.48

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Dependence Study of Peukert's Statistical Equation Parameters on Temperature for Nickel-Cadmium Batteries

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Received: 10 August 2022 / *Accepted:* 11 September 2022 / *Published:* 10 October 2022

In this paper, the Peukert statistical equation $C=C_m\mathrm{erfc}((i/i_k-1)/n)/\mathrm{erfc}(-1/n)$ is investigated. It is shown that this equation has the clear both physical and statistical meaning as it describes the phase transition of the electrodes active substance from the phases relevant to the battery complete charge to the phases relevant to the battery full depletion. Also the parameters of this equation have the clear both physical and statistical meaning unlike the classical Peukert equation, in which the parameters are just empirical constants. In addition, it has been experimentally proved that in the statistical Peukert equation, all the parameters (C_m, i_k and n) depend on a battery temperature; so when using the Peukert equation in any models, it is necessary to take into account the dependence of all the parameters of this equation on the battery temperature. Here the equations are proposed describing the dependence of the parameters (C_m, i_k and n) on the battery temperature. Unlike the classical Peukert equation, the statistical Peukert equation under study is true at any discharge currents and at any battery temperatures.

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

1. INTRODUCTION

Nowadays, batteries are important part of many technical devices. That is why there is the need in reliable battery models for any optimization of these devices operation and design.

The most accurate electrochemical models of batteries are developed based on the fundamental laws of the physics and the electrochemistry [1-5]. However these models are very sophisticated, which is unacceptable often from the point of view of their practical use [6]. Particularly, this is so because of their complexity: the electrochemical models are impossible to be calculated by on-board computers, for example, by ones installed on airplanes, electric vehicles, etc.

In addition, often, the battery models used in various technical devices should satisfy the requirement that the parameters values for these models could be found without the batteries disassembling.

These requirements are met only by either analytical models [7-10] built based on empirical equations or by nonlinear structural models [11,12]. It should be noted that also these analytical models are used as part of electrochemical models in the case that it is necessary to simulate some poorly studied processes such as the thermal runaway [13,14], or the hydrogen accumulation in battery electrodes [15,16], etc.

Many analytical models [6,17-21] use the Peukert equation [22], which is written in many papers [6,17] in the following form:

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

where i is the discharge current; C is the battery discharge capacity and A and n are empirical constants. But the Peukert equation does not take into account the battery temperature, while the latter affects strongly the battery released capacity [23-26] and especially so in the case of a battery significant decrease in temperature [27].

This study is aimed at development of the generalized Peukert equation able to take into account the effect of the battery temperature on the battery released capacity.

2. THEORY

The most useful analytical models for electric vehicles are ones able to determine the battery remaining capacity. This is so because the batteries remaining capacity determines the working time of the electric vehicles. In our opinion, the most promising analytical model for the batteries remaining capacity calculation is the Hausmann model [6]. In this model, the entire battery discharge time is divided into small time intervals Δt=1s. In every small time interval Δt, the current and the temperature can be considered to be constant. Hence in order to determine the released capacity in the time interval Δt, it is possible to use the empirical equations describing the dependence of the released capacity on the discharge current and the temperature, obtained at constant currents and temperatures. It was proved in [17] that the Peukert equation was used in the Hausmann model [6] in the following form: .

$$C(i,T) = \frac{C_{mref} K}{\gamma i^n} \left(\frac{T}{T_{ref}} \right)^{\beta} \quad , \qquad (2)$$

where T_{ref} is reference temperature for the tested battery (293°K); C_{mref} is top battery capacity at temperature T_{ref}; i is battery discharge current; and n, β, K, γ are empiric constants.

The second factor in the equation (2) determines the dependence of the battery released capacity on the temperature:

$$C_m(T) = C_{mref} \left(\frac{T}{T_{ref}} \right)^{\beta} \quad , \qquad (3)$$

where $C_m(T)$ is battery top capacity.

The first factor in the equation (2) (at A=K/γ) is just the classical Peukert equation (1).

The equation (3) cannot be used in a wide range of battery temperature changes. Firstly, in the equation (3), $C(T)\to 0$ at $T\to 0$. But in the batteries, $C(T)\to 0$ at $T\to T_k$, where T_k is temperature near the electrolyte freezing point. Secondly, in the equation (3), if $T\to\infty$, also $C(T)\to\infty$. However, in batteries, $C(T)$ value cannot be more than the capacity received by the batteries during charging.

These contradictions are not contained in the equation [17]:

$$C_m(T)=C_{mref}K\frac{\left(\frac{T-T_k}{T_{ref}-T_k}\right)^{\beta}}{(K-1)+\left(\frac{T-T_k}{T_{ref}-T_k}\right)^{\beta}}\quad, \qquad (4)$$

In the equation (4), $C(T_k)=0$ and $C(T)\to C_{mref}K$ at $T\to\infty$. Thus, the parameter K indicates how many times (theoretically) the battery released capacity can increase along with a temperature growth.

As it was shown in the papers [17,28], also the classical Peukert equation (1) contains a number of disadvantages. Firstly, in the equation (1), if $i\to 0$, then $C(i)\to\infty$. However, in practice, in batteries, $C(i)\to C_m$ at $i\to 0$, where C_m is the battery top capacity. Secondly, in the equation (1), always the function $C(i)$ is concave, at any discharge currents ($n>0$). However, in reality, on the curve of the function $C(i)$ of alkaline and lithium-ion batteries, there are both concave and convex parts [17,28].

In the papers [17,28-30], the Peukert generalized equations have been proposed free of these shortages. These equations look like as follows:

$$C(i)=\frac{C_m}{1+\left(\frac{i}{i_0}\right)^n}\quad, \qquad (5)$$

$$C(i)=\frac{0.522\ C_m}{\left(\frac{i}{i_0}\right)^n}\tanh\left(\left(\frac{i}{i_0}\right)^n\frac{1}{0.522}\right), \qquad (6)$$

$$C(i)=\frac{C_m}{\operatorname{erfc}\left(-\frac{1}{n}\right)}\cdot\operatorname{erfc}\left(\frac{i/i_k-1}{n}\right)\quad. \qquad (7)$$

In the equations (5-7), if $i\to 0$, then $C(i)\to C_m$ (at $n>0$), which corresponds well to the experimental data for alkaline and lithium-ion batteries. In the equations (5,6), $C(i_0)=C_m/2$; *i.e.* i_0 is the current, at which the battery released capacity is twice less than the top released capacity C_m. In the equation (7), $C(i_k)=C_m/\operatorname{erfc}(-1/n)$; i.e. i_k is the current, at which the battery released capacity is erfc(-1/n) times less than the top released capacity.

The equations (5-7) correspond well to the experimental data for alkaline and lithium-ion batteries at any discharge currents [28,30], while the classical Peukert equation is applicable only within the limited discharge currents range [29].

It should be noted that the equation (7) has a number of advantages over the equations (5,6). Firstly, the equation (7) has the smallest error of the experimental data approximation for alkaline and lithium-ion batteries as compared to the equations (5,6) [28,30]. Thus, the equation (7) corresponds best to the processes occurring in the batteries, when they are discharged. Secondly, the equation (7) has the statistical basis, while the equations (5,6) are just empirical equations. Indeed, equation (7) can be rewritten in the following form:

$$C(i) = \frac{A}{2} \cdot erfc\left(\frac{i - i_k}{\sqrt{2}\sigma}\right), \quad A = \frac{2C_m}{\mathrm{erfc}(-1/n)}, \quad \sigma = \frac{i_k n}{\sqrt{2}}, \qquad (8)$$

where σ is standard deviation of the statistical variable i; and i_k is average of the statistical variable i.

So the equation (7) is described by the complementary error function (8) governed by the normal distribution law. The batteries discharging process is the phase transition of the electrodes active substance from the phases relevant to the state of the electrodes complete charge to the phases relevant to the electrodes full depletion state. But in the paper [31], it is shown that often the phase transitions are described by the complementary error function (8). Undoubtedly, at the level of molecules and ions, any phase transition is a statistical process. Indeed, a process occurring at the boundary between the electrodes active substance and an electrolyte is determined by the Butler-Volmer statistical function with the exchange current j_0. Hence, it seems logical that the dependence of the released capacity on the discharge current (7) is described perfectly by the statistical function (namely by the complementary error function (8)).

The physical meaning of the parameter n in the equation (7) is clear from the following equation:

$$\lim_{i \to i_k} \frac{d(C(i)/C_m)}{d(i/i_k)} = -\frac{2}{n\,\mathrm{erfc}(-1/n)\sqrt{\pi}} \approx \frac{-1}{n\sqrt{\pi}}, \qquad 0.3<n<0.8. \qquad (9)$$

For the batteries being studied in this paper, the parameter n changes within the range 0.3<n<0.8. In this case, the function $\mathrm{fun1}(n) = -2/\left(n\,\mathrm{erfc}(-1/n)\sqrt{\pi}\right)$ is equivalent very accurately to the function $\mathrm{fun2}(n) = -1/\left(n\sqrt{\pi}\right)$, (Fig. 1).

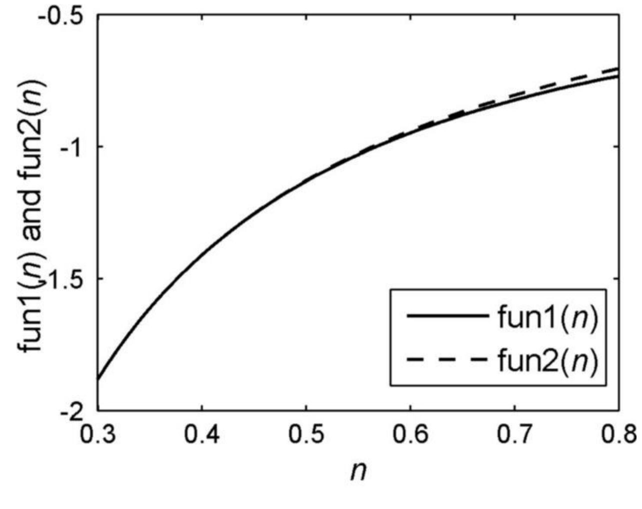

Figure 1. Comparison between curves for functions fun1(n) and fun2(n).

Thus, from the equation (9), it is seen that the parameter n determines the rate of decrease of the released capacity in the coordinates (C/C_m, i/i_k) at the current $i=i_k$.

The statistical meaning of the parameter n in the equation (7) can be established if to make a comparison between the equation (7) and the equation (8). It is seen in the equation (8) that the standard deviation Σ for the variable $x=i/i_k$ is equal to $\Sigma=\sigma/i_k$. In the equation (7), the same standard deviation is equal to $\Sigma=n/\sqrt{2}$. Therefore, for the standard deviation Σ of the variable $x=i/i_k$, we obtain the following equation:

$$\Sigma=\frac{\sigma}{i_k}=\frac{n}{\sqrt{2}} \qquad (10)$$

Thus within the accuracy up to a constant, the parameter n in the equation (7) is equal to the standard deviation Σ of the variable $x=i/i_k$ from its average value x=1.

The influence of the parameter n on the battery released capacity is properly seen in Fig. 2.

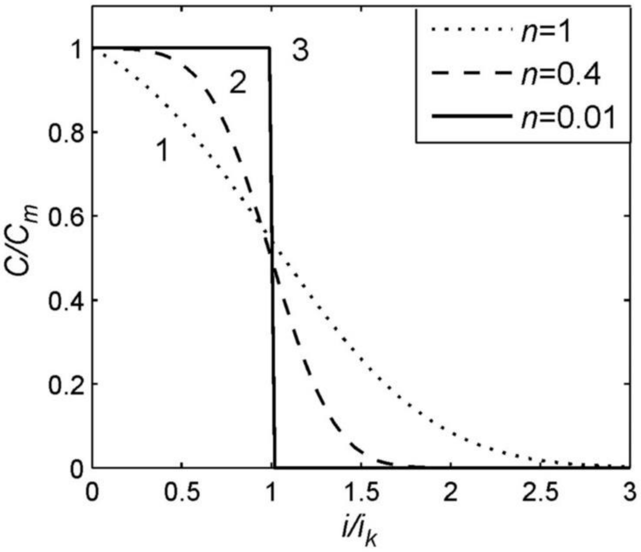

Figure 2. Dependence described by statistical Peukert equation (7) in standardized coordinates at different values of parameter n.

Thus, from Fig. 2, it is seen that at decrease of the standard deviation Σ (i.e. of the parameter n (10)) of the variable $x=i/i_k$ from its average value x=1, the released capacity decrease rate in the point $x=i/i_k$=1 grows (9).

From the analysis conducted, a number of conclusions can be drawn. Firstly, the statistical Peukert equation (7) has a clear both physical and statistical meaning. It describes the phase transitions of the electrodes active substance during batteries discharge. Secondly, also all the parameters (C_m, i_k, n) of the equation (7) have clear both physical and statistical meaning.

In our researches, we'll use the equation (7) as this equation corresponds best to the experimental data for alkaline and lithium-ion batteries [28,30]. Moreover, in the Hausmann model [6], it is considered that in the Peukert equation (2), only the parameter C_m (3) depends on temperature, while the parameter *n* does not.

In this paper with use of the equation (7), we'll investigate dependences of all its parameters (C_m, i_k, and *n*) on temperature changes in the case of the nickel-cadmium batteries.

3. EXPERIMENTAL

For experimental studies, the nickel-cadmium batteries made of SAFT, the company, were used. The cycling parameters of these batteries are presented in Table 1.

Table 1. Parameters of nickel-cadmium batteries used in experiments

Model	**SRX 720**	SRX 1200	**SRX 1900**
Type of positive electrode	sintered	sintered	sintered
Type of negative electrode	plastic bonded	plastic bonded	plastic bonded
Nominal capacity (Ah)	73	115	195
Charge current (A)	14.6	23	39
Charging time	8	8	8
Lower cutoff (V)	1	1	1
Discharge current (for training cycles) (A)	14.6	23	39

The batteries were charged in the direct current mode according to the parameters presented in Table 1. For charging, the electrochemical workstation ZENNIUM was used together with the potentiostat PP242 (with the top operating current 40A).

The batteries were discharged down to the voltage 1V at currents from $0.2C_n$ to about $6C_n$ (C_n is the battery rated capacity). For discharging, the electronic load ITECH IT8945-150-2500 was used (with the top operating current 2500A).

In our experiments, the batteries were discharged at the following temperature values: -30°C, -20°C, -10°C, 0°C, 10°C, 20°C, and 30°C. At each temperature, the parameters of the statistical Peukert equation (7) were found. For batteries cycling, the climatic chamber Binder MK240 (BINDER GmbH, Germany) was used. The batteries were kept in the climatic chamber during five hours before a measurement session. This precaution let the entire mass of the battery to take the temperature needed for the measurement. In order to control the battery temperature, six temperature sensors were fixed in different spots of the battery surface. Moreover, from all sides to the batteries, heat sinks were attached with use of a heat-conducting paste and special clips. The use of the heat sinks made it possible to increase the heat exchange and to stabilize the temperature of the batteries, when they were discharged by large currents.

The batteries cycling included the following stages.

Firstly, three training charge-discharge cycles were conducted according to the parameters given in the Table 1. This was done for five batteries of the same type at the temperature 20°C. If the obtained battery capacities differed by more than 5% from each other, the defective batteries were replaced with new more stable batteries.

Secondly, the discharge of batteries was performed at different currents and different temperatures for five batteries of the same type, which allowed to obtain more statistical data.

Thirdly, before each change in battery temperature and each change in discharge current, four training cycles were carried out in accordance with the parameters presented in Table 1. This method made it possible to exclude a mutual impact of different measured discharge cycles on other discharge cycles. However, if in these training cycles, the capacities of the five studied batteries differed by more than 5%, in this case, some additional training cycles were carried out – or the unstable batteries were replaced with new batteries.

Fourthly, in all the Figures, the experimental value of the capacity is presented being the average value of the five measurements for the five batteries of each type at a certain temperature and a certain discharge current. This enabled to reduce the random spread of the values obtained and to determine the battery capacity more reliably at each temperature and each discharge current and, besides, to evaluate statistically the experimental error of each measurement.

4. RESULTS AND DISCUSSION

The value of the measured battery capacity is influenced by many random factors related to both the processes of battery manufacturing and the process of their discharge. That is why in order to reduce the impact of those random factors, it is better to represent the experimental curves in the coordinates (C/C_m, i/i_k) instead of the ordinary coordinates (C, i). In this case, the mentioned random factors will be largely eliminated because for each specific battery, the parameters C_m and i_k will be measured experimentally, too. The experimental data obtained for the studied batteries are shown in Fig. 3.

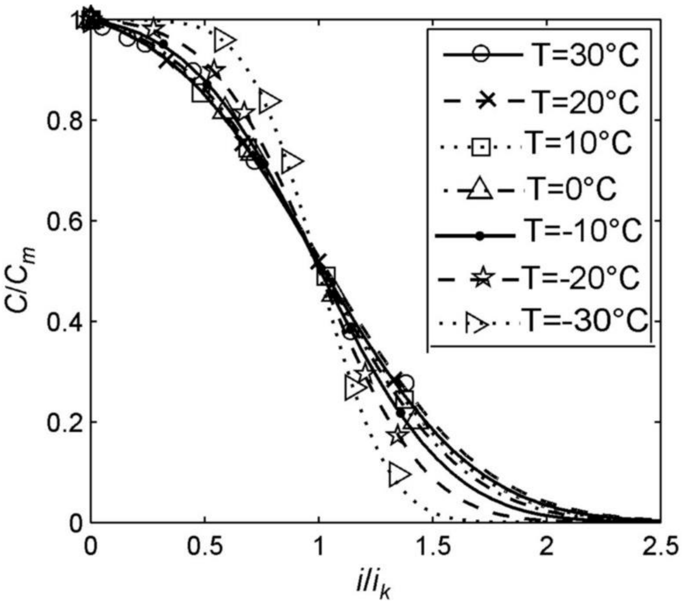

Figure 3. Comparison between equation (7) and experimental data obtained at different currents and temperature values. C_m and i_k are taken from Table 2 (SRX 720 batteries).

It should be noted that in the standardized coordinates (C/C_m, i/i_k), the curves for the batteries SRX 1200 and SRX 1900 coincide with the curves for the batteries SRX 720 (Fig. 3) within the statistical accuracy. This experimental result follows from the fact that in all the batteries (SRX 720, SRX 1200 and SRX 1900), the same electrodes are used. The difference is only in the electrodes working area and number. That is why in the standardized coordinates, the curves coincide for batteries of different capacities. This is typical for alkaline batteries of the same producer with the same type of electrodes [9,32].

The optimal parameters of the statistical Peukert equation (7) were obtained using the experimental data (Fig. 3), the least square method and the Levenberg–Marquardt optimization procedure. The obtained optimal parameters of the equation (7) are presented in Table 2.

Table 2. Optimal values for equation (7) parameters at different temperatures

Temperature (°C)	+30	+20	+10	0	-10	-20	-30
Parameters	Battery SRX 720						
C_m (Ah)	74.932	74.065	72.691	70.402	66.373	58.949	45.295
i_k (A)	300.331	296.594	290.656	280.738	263.295	231.362	173.875
n	0.782	0.767	0.744	0.704	0.637	0.521	0.343
δ^a (%)	2.3	2.4	2.1	1.6	1.1	0.9	1.0
Parameters	Battery SRX 1200						
C_m (Ah)	117.646	116.412	114.282	110.728	104.467	92.907	71.565
i_k (A)	477.716	471.539	461.755	445.439	416.845	366.828	277.219
n	0.761	0.748	0.727	0.692	0.621	0.513	0.340
δ^a (%)	2.1	2.3	2.2	1.8	1.6	1.0	1.2
Parameters	Battery SRX 1900						
C_m (Ah)	200.657	198.258	194.473	188.171	177.214	157.833	121.701
i_k (A)	776.199	767.374	753.354	729.819	685.011	603.522	454.024
n	0.759	0.743	0.718	0.681	0.611	0.499	0.334
δ^a (%)	2.0	2.4	2.1	1.7	1.5	1.1	1.1

[a] δ is relative error of experimental data approximation by equation (7) in Fig. 3.

The analysis of the data obtained in the experimental studies (Table 2) shows that all the parameters (C_m, i_k, n) of the statistical Peukert equation (7) depend on the temperature. Hence, the assumption given in [6,17] that only the parameter C depends on a temperature in the Peukert equation (2) and in its generalization (5) is incorrect. So in framework of analytical modeling, it is necessary to take into account the dependence of all the parameters of the equation (7) on the temperature.

Fig. 4 shows the dependencies of all the parameters (C_m, i_k, n) presented in Table 2 on the temperature. These dependencies were obtained for the statistical Peukert equation (7) in the standardized coordinates.

It should be noted that for all the studied batteries (of different capacities) in the standardized coordinates, the experimental data (Table 2) coincide with each other within the experimental error. This statement follows from the fact that all the batteries under study use the same electrodes (as mentioned above). That is why Fig. 4 shows the data only for the batteries SRX 720.

For the experimental data approximation, we'll use the equations in the form (4). We introduce the vector of parameters:

$$P=(C_m, i_k, n)\ . \qquad (11)$$

Now the dependence of the parameters on the temperature can be rewritten as follows:

$$P_i(T) = (P_{ref})_i K_i \frac{\left(\dfrac{T-(T_k)_i}{T_{ref}-(T_k)_i}\right)^{\beta_i}}{(K_i-1)+\left(\dfrac{T-(T_k)_i}{T_{ref}-(T_k)_i}\right)^{\beta_i}}\ ,\quad P_{ref}=(C_{mref}, i_{kref}, n_{ref}), \qquad (12)$$

where P_{ref} are vector of parameters P at reference temperature T_{ref}=293°K.

The optimal parameters of the equations (12) were obtained using the experimental data (Table 2), the least square method and the Levenberg–Marquardt optimization procedure. The obtained optimal parameters of the equations (12) are presented in Table 3.

Table 3. Optimal values of parameters for equations (12)

Parameters	C_m	i_k	n
K	1.041	1.044	1.064
T_k (°K)	211.899	211.88	211.896
β	2.954	3.001	3.201
δ^a	0.6	0.7	0.6

$^a\delta$ is relative error of experimental data approximation by equations (12) in Fig. 4.

From Table 3, it is seen that the relative error of the experimental data approximation by the equations (12) (Fig. 4) is less than 1%. Thus, the equations (12) describe very well the dependence of the statistical Peukert equation (7) parameters on the temperature.

It should be noted that in our previous paper [33], we studied the dependence of all parameters (C_m, i_0, n) of the equation (5) on temperature. It was also experimentally proved in [33] that all parameters of equation (5) depend on temperature, as do the parameters of equation (7). However, Peukert's statistical equation (7) (supplemented by the equations (12)) has a number of significant advantages over the classical Peukert equation (2) and generalized Peukert equations (5, 6).

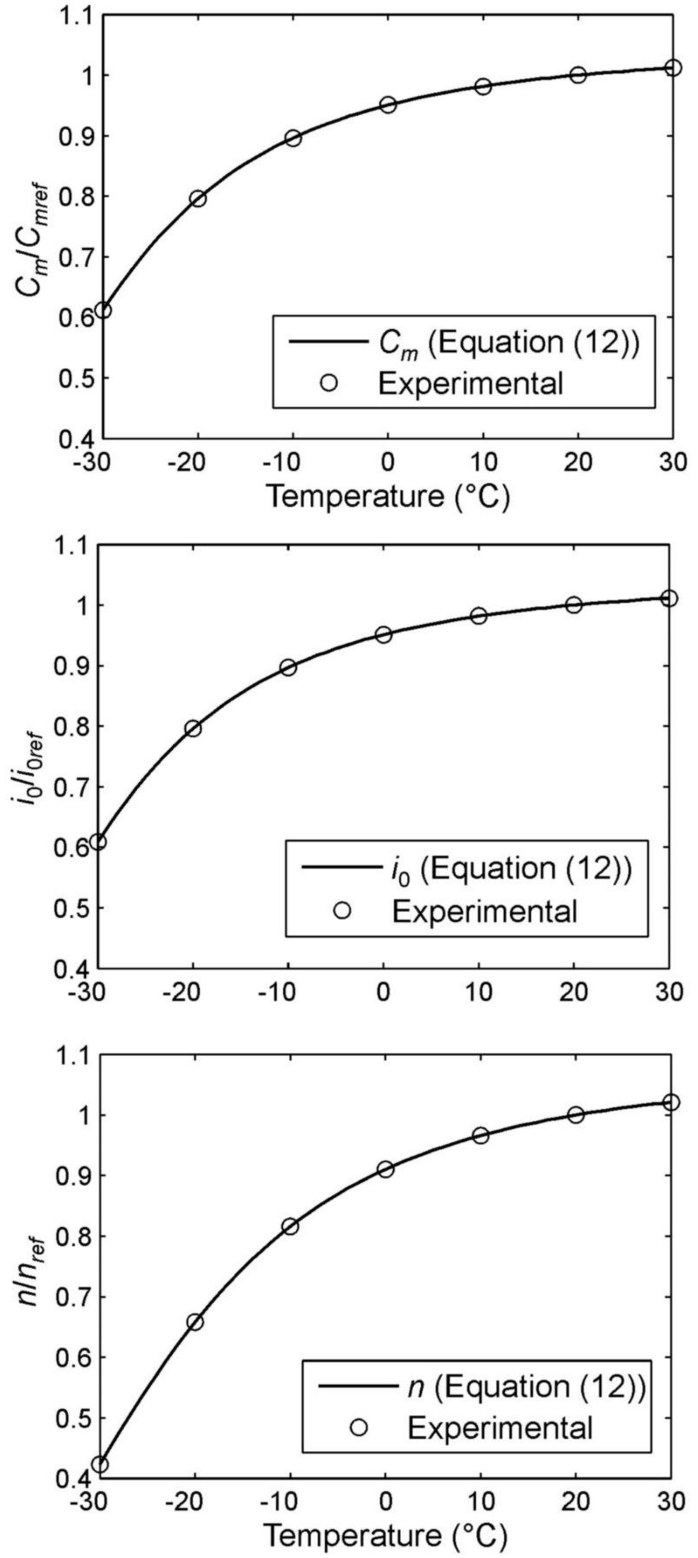

Figure 4. Comparison between equations (12) and experimental data for parameters (C_m, i_k, n), obtained at different temperature values (Tab. 2) (a, b and c, respectively). C_{mref}, i_{kref}, and n_{ref} are values of parameters C_m, i_k, and n, taken from Table 2 at reference temperature T_{ref}=293°K (SRX 720 batteries).

Firstly, the statistical Peukert equation (7) has the clear both physical and statistical meaning. It describes the phase transitions of the electrodes active substance from the phases relevant to the batteries full charge to the phases relevant to the batteries full depletion. But often, phase transitions are described [31] by a complementary error function (8). Here, this function is the statistical Peukert equation (7) and nothing else. Meanwhile, the classical Peukert equation (2) and its generalizations (5,6) are just empirical equations.

Secondly, all the parameters (C_m, i_k, n) in the statistical Peukert equation (7) have the clear both physical and statistical meaning, too. Unlike this, in the classical Peukert equation (1), all the parameters (A, n) are just empirical constants. It should be noted that in [33], the physical meaning of the parameters of equation (5) was not analyzed at all.

Thirdly, the Peukert equation (2) cannot be used at very low discharge currents because for this equation, $C(i)\rightarrow\infty$ at $i\rightarrow 0$. However this is not possible for any batteries. Meanwhile, the statistical Peukert equation (7) and equations (5,6) are applicable at any discharge currents [9,32].

Fourthly, the proposed in [6] classical Peukert equation taking the temperature into account (2) can be used only near the reference temperature T_{ref}, i.e. within the temperature limited range. Besides, in this paper, it was proved that if to take into account the temperature impact on the released capacity only regarding the parameter C_m dependence on the temperature (3,4) (as it was proposed in the papers [6,17]), also it will be incorrect. All the parameters of both the classical Peukert equation (1) and the statistical Peukert equation (7) depend significantly on the temperature. However, the statistical Peukert equation (7) supplemented by the equations (12) is true at any batteries temperatures.

Fifthly, it should be especially noted that in all our numerous experiments [28, 30], Peikert's statistical equation (7) had the smallest error in the approximation of experimental data for alkaline and lithium-ion batteries compared to equations (5, 6). Thus, the statistical Peukert equation (7) best describes the processes that occur in batteries when they are discharged. Therefore, it is preferable to use equation (7) in analytical models of batteries, and not equations (5,6).

In our experiments, batteries of the same type as in [33] were used to demonstrate the difference between equations (5) and (7). In this case, it is clearly seen that equations (5) and (7) differ from each other not only according to their physical meaning, but also according to the numerical values of their parameters ((i_0, n) and (i_k, n) respectively) at different temperatures.

5. CONCLUSIONS

Currently, many analytical models of batteries [6,17-21] use the Peukert equation or its generalizations (5-7). However often in these papers, the influence of the temperature is not taken into account [5,20,34] or is considered in a very rough approximation [6,17]. That is why the correct accounting of the temperature as well as the correct understanding of the occurring in batteries electrochemical and physical processes reflected by the Peukert equation have great both practical and theoretical importance.

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