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Analysis of Generalized Peukert's Equations for determining the capacity of nickel-cadmium batteries

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In this paper, we analysed the use possibility of the generalized Peukert's equations $C=C_m/(1+(i/i_0)^n)$, $C=0.522C_m\tanh((i/i_0)^n/0.522)/(i/i_0)^n$, and $C=C_m\mathrm{erfc}((i/i_k-1)/n)/\mathrm{erfc}(-1/n)$ to compute the released capacity of nickel-cadmium batteries at different discharge currents. It was proven that these equations correspond well to the experimental data throughout the entire variation interval of discharge currents. It was shown that the parameter *n* does not depend on the nominal capacity of the batteries under examination; however, it possesses various values for batteries of different modes of discharge (Long, Medium, High). Further, it was shown that the functional dependence of a battery's released capacity with a discharge current is determined by the statistical phase transition subjected to the normal distribution law. The proposed statistical mechanism allows us to explain the variation in parameter *n* depending on the types of batteries under examination.

Keywords: Peukert's equation, modeling, battery, nickel-cadmium, capacity

1. INTRODUCTION

Virtually all contemporary technical devices contain batteries in their structure. Hence, for these devices' design engineering and work optimization, highly reliable models of batteries are needed.

The Peukert's equation was one of the first analytic equations describing the processes in batteries [1]

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

where C is the capacity released by a battery at the discharge current *i*, while *A* and *n* are empiric constants. However even now, the Peukert's equation is widely used in various models. For

example, in the papers [2,3], the Peukert's equation was used as a component part of the statistical models for the evaluation of the remaining capacity in lithium-ion batteries.

Further, the Peukert's equation is often used as a possible criterion for the validation of the fundamental electrochemical models of batteries [4-8] and non-linear structural models [9-11]. It should be observed that electrochemical models of batteries are not always acceptable for practical use [2]. Using this kind of models requires knowledge of a lot number of local parameters, which – at any system changes – must be corrected. Further, they are very sophisticated. Consequently, for their solutions require high computation-intensive power, which is not acceptable for the on-board computers of aeroplanes and electromobiles [12,13]. That is why often at building of practical models of batteries, statistical models are used [2,3,12-15]. In addition, the statistical models are used, when there is a need in modeling of poorly studied phenomena in batteries, such as the thermal runaway [16,17] or the hydrogen accumulation in electrodes [18,19].

This study analyses the parameters variation in the generalized Peukert's equations for batteries of various modes of discharge, as these equations are often used in different models of batteries [2,3].

2. GENERALIZED PEUKERT'S EQUATIONS

According to the Peukert's equation (1), a battery's released capacity tends to infinity as the discharge current decreases. Hence, the Peukert's equation is not applicable at small discharge currents. At present, there exist a lot of Peukert's equation generalizations to address this problem [20-22]

$$C = \frac{A}{1 + Bi^n} \quad , \tag{2}$$

$$C = \frac{A}{i^n} tanh\left(\frac{i^n}{B}\right) . \tag{3}$$

The process of battery discharge is a phase transition, with phase transitions often described by the complementary error function [22,23]

$$C = \frac{A}{2} \cdot erfc\left(\frac{i - i_k}{\sqrt{2}\sigma}\right), \tag{4}$$

where σ is the standard deviation and i_k is the mean value of the statistical variable i.

There also exist other equations and methods for computing a battery's released capacity at different discharge currents [20,24-26]. However, in the papers [21,22], it was shown that the empiric equations (2-4) are the most appropriate for experimental data throughout the entire interval of discharge current variation including at small discharge currents. That is why in this paper, we study only these equations.

For the sake of analytical convenience, we rewrite equation (2) in the following form:

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

Then, C_m is a battery's top capacity (obtained at small discharge currents because $C(0)= C_m$), while i_0 is the current at which the battery releases half the capacity than its top capacity because $C(i_0)= C_m/2$. Hence, in equation (5), the constants have a clear electrochemical sense unlike in equation (2), where *A* and *B* are just empiric constants.

Let us also rewrite equations (3) and (4) in the following form:

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

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

In equation (6), we added the constants 0.522 in order that the parameters C_m and i_0 had the same electrochemical sense as in equation (5). For equation (7), the conditions $C(0)=C_m$ and $C(i_k)=C_m/erfc(-1/n)$ are fulfilled. Hence, for equation (7), C_m is also the top capacity of a battery, whereas i_k is the current value at which the battery releases a capacity $erfc(-1/n)$ times less than its top capacity. In the following, it is shown that – as a rule – n≤1; in this case $1.85 \le erfc(-1/n) \le 2$.

It should be observed that the parameters i_k and σ in equation (4) have a well-known statistical sense. From a comparison between equations (4) and (7), it follows that $\sqrt{2}\sigma = i_k n$. Hence, in the rewritten equations (5-7), all the constants have a clear electrochemical or statistical sense unlike the initial empiric equations (2-4).

Moreover, upon the parameters of equations (5-7), we must impose restrictions following from the boundary conditions. Indeed, based on the accumulated experimental data [20,27,28], it is fair to say that with a rise in the discharge current, a battery's released capacity falls and tends to zero, i.e.

$$\lim_{i\to\infty} C(i) = 0 \quad (8)$$

Restriction (8) is fulfilled by equations (5-7) under the condition n>0. The second boundary condition can be obtained at small discharge currents.

Batteries of any electrochemical system release their top capacity at small discharge currents. With a rise in the discharge current, batteries' released capacity falls insignificantly to some current value I_k. The range of discharge currents from zero to I_k determines a working range of discharge currents for a specific battery. Hence, at small discharge currents, one more boundary condition must be fulfilled:

$$\lim_{i\to 0} \frac{dC(i)}{di} = -a \ . \quad (9)$$

Notably, the parameter *a* should be either very small or equal to zero.

Later, we analyse equations (5-7) not in the coordinates (*C*, *i*) but instead in the standardized coordinates (C/C_m, i/i_0 (or i/i_k)). That is why we also write boundary condition (9) for equations (5-7) in the standardized coordinates.

For equation (5), boundary condition (9) takes the form:

$$\lim_{i\to 0}\frac{d(C(i)/C_m)}{d(i/i_0)}=\lim_{i\to 0}-\frac{i^{n-1}n}{(i^n+1)^2}=\begin{cases}0, & \text{when } n>1\\ -\infty, & \text{when } 0<n<1\\ -1, & \text{when } n=1\end{cases}. \qquad (10)$$

Consequently, at n>1, equation (5) can be used for the evaluation of a battery's released capacity throughout the range of discharge currents variation.

For equation (6), boundary condition (9) takes the form:

$$\lim_{i\to 0}\frac{d(C(i)/C_m)}{d(i/i_0)}=\lim_{i\to 0}-\frac{i^{2n-1}n}{(0.522)^2}=\begin{cases}0, & \text{when } n>0.5\\ -\infty, & \text{when } 0<n<0.5\\ -1.835, & \text{when } n=0.5\end{cases}. \qquad (11)$$

Consequently, at n>0.5, equation (6) can be used for the evaluation of a battery's released capacity throughout the range of discharge currents variation.

For equation (7), boundary condition (9) takes the form:

$$\lim_{i\to 0}\frac{d(C(i)/C_m)}{d(i/i_k)}=-\frac{2\exp(-1/n)}{\sqrt{\pi}n\cdot\operatorname{erfc}(-1/n)}=\mathrm{f}(n) \qquad (12)$$

The function f(*n*) is presented in Figure 1. Figure 1 shows that the function f(*n*) changes within the interval from -0.3 to zero. Hence, the slope factor of the curve for equation (7) (at *i*=0) is negative and always less than 16.7 degrees, i.e. it is very small. Hence, at *n*>0, equation (7) can be used for the evaluation of a battery's released capacity throughout the range of discharge currents variation.

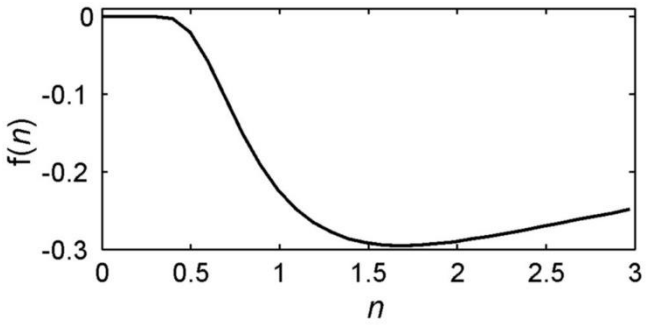

Figure 1. Dependence of the slope factor of the curve (at *i*=0) for equation (7) on the parameter *n*.

3. EXPERIMENTAL

To evaluate the parameters of equations (5-7), batteries made by SAFT were used with different discharge modes: SBLE, SBM, and SBH (of stationary use) with pocket electrodes.

Batteries' discharging was performed down to the voltage 1V. In the experiments, we used discharge currents from $0.1C_N$ (where C_N is a battery's nominal capacity) up to the currents at which the battery discharge capacity was close to zero. Batteries' charging was performed according to batteries' operation manuals.

To avoid the mutual influence of charge/discharge cycles (via various remaining phenomena, in particular, the memory effect), before each discharge current change, training cycles were fulfilled. These training cycles were performed until in three cycles without interruption, the released capacity started differing by less than by 5%. The training cycles were performed according to the operation manuals of the batteries under examination.

As the released capacity value at a specific discharge current, an average capacity value was taken in three charge/discharge cycles in succession. However, if in these three cycles the released capacity differed by more than by 5%, additional training cycles were performed and the experiment was repeated again.

It should be observed that for batteries of the same nominal capacity, their released capacity depends on a lot of random factors such as the statistical dispersion of batteries' parameters in their manufacturing, their operation life, their operation modes, etc. Our experience with batteries cycling showed that in a lot of batteries of the same kind, under the same discharge current, their released capacity can differ by 4-5 % or more. This relates to batteries of any electrochemical system and is due to the above-mentioned random factors. Hence, by standardizing the obtained experimental data for batteries' capacity by their top capacity – found in experiments for a specific battery – the above-mentioned random factors were obviated to a large extent. This method allows us to find empiric experimental curves more reliably.

4. RESULTS AND DISCUSSION

In the experiments, we used batteries produced by SAFT of stationary use with pocket electrodes and with different modes of discharge: SBLE 15, SBLE 95, and SBLE 230 (with the capacities 15, 95, and 230Ah respectively, long discharge mode); SBM 56, SBM 84, and SBM 208 (with the capacities 56, 84, 208Ah respectively, medium discharge mode); and SBH 49, SBH 98, and SBH 236 (with the capacities 49, 98, and 236Ah respectively high discharge mode).

The obtained experimental data (in the standardized coordinates) for the batteries under examination are presented in Figures 2-4. As the parameter C_m in Figures 2-4, the experimental values were taken from batteries' released capacities found at the discharge current $0.1C_N$. As a result of such a calibration, the locations of the experimental points in Figures 2-4 are the same regardless of the studied equations. The parameters i_0 and i_k in Figures 2-4 were taken from Tables 1-3 for each of the generalized Peukert's equations (5-7) respectively.

For the generalized Peukert's equations (5-7), the optimal parameters were found with the use of the least squares method and Levenberg–Marquardt optimization procedure. The obtained optimal parameters are presented in Tables 1-3.

From Figures 2-4, it is seen that for batteries of different capacities (in the standardized coordinates), the optimal experimental curves coincide in limits of the standard error. That is why in Figures 2-4 for each of equations (5-7), only one curve is presented, corresponding to the average capacity of the batteries under investigation.

Based on the results in Tables 1-3, one can come to the following conclusions.

Firstly, all the studied generalized Peukert's equations (5-7) can be used for the evaluation of a battery's released capacity, as the relative error of the experimental data approximation is less than 6%. As a rule, this error is acceptable for the practical evaluation of the remaining capacity in a battery [2]. However, it should be observed that equations (5,7) correspond to the experimental data best as they have the lowest error of approximation.

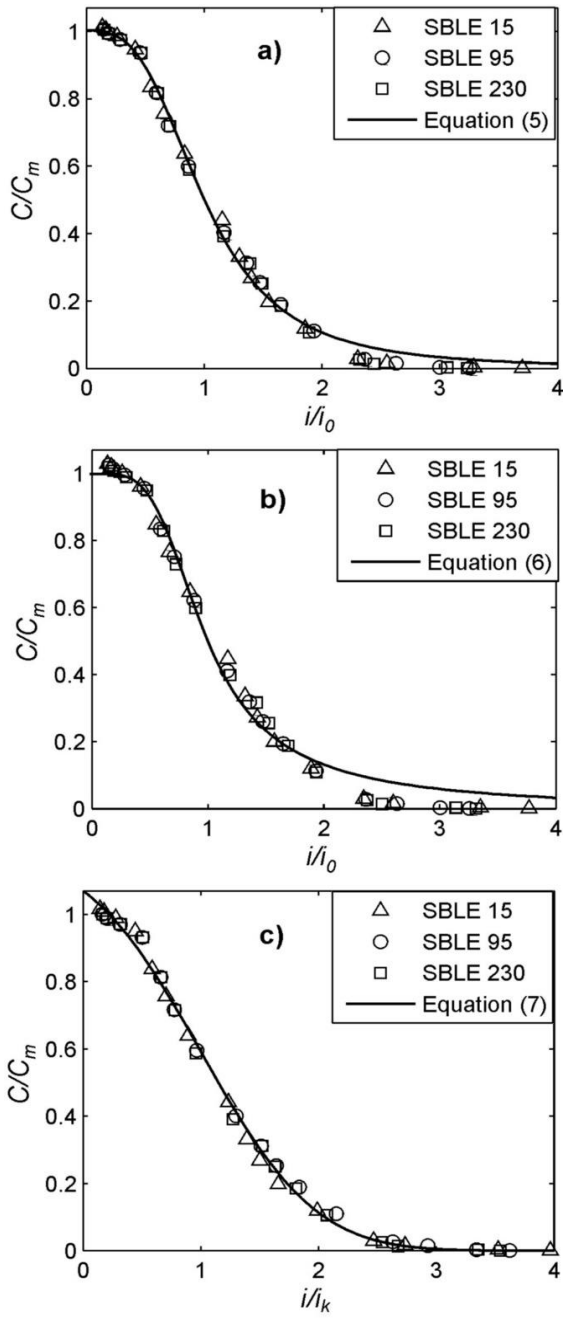

Figure 2. Experimental data for the batteries of the long discharge mode with pocket electrodes and the generalized Peukert's equations (5-7) (a, b, and c respectively). Cm is the top capacity of batteries found at the discharge current $0.1C_N$. i_0 is the current at which batteries release a capacity half that of their top capacity. i_k is the current at which batteries release capacity $erfc(-1/n)$ times less than their top capacity. The values of the parameters i_0 and i_k were taken from the Table 1 for each of the generalized Peukert's equations (5-7) respectively.

Table 1. Optimal parameters of the generalized Peukert's equations (5-7) for batteries with pocket electrodes and a long discharge mode

Equation Parameters	batteries		
	SBLE 15	SBLE 95	SBLE 230
Уравнение (5)			
C_m (Ah)	15.207	97.139	235.846
Standard error for C_m (Ah)	0.230	1.343	3.885
i_0 (A)	11.644	67.963	159.272
Standard error for i_0 (A)	0.258	1.341	3.693
n	3.071	3.082	3.095
Standard error for n	0.159	0.137	0.160
Mean n		3.083	
SD[a]	0.266	1.562	4.17
δ^b (%)	3.691	3.472	3.861
Уравнение (6)			
C_m (Ah)	14.984	95.708	232.568
Standard error for C_m (Ah)	0.344	2.046	5.279
i_0 (A)	11.434	66.521	155.515
Standard error for i_0 (A)	0.393	2.043	4.964
n	1.988	2.019	2.032
Standard error for n	0.161	0.144	0.150
Mean n		2.013	
SD	0.420	2.398	5.951
δ	5.833	5.33	5.950
Уравнение (7)			
C_m (Ah)	16.212	104.313	253.400
Standard error for C_m (Ah)	0.204	1.793	5.219
i_k (A)	10.862	62.057	145.430
Standard error for i_k (A)	0.370	3.174	8.906
n	1.032	1.074	1.081
Standard error for n	0.077	0.115	0.136
Mean n		1.062	
SD	0.206	1.307	3.287
δ	2.859	2.914	3.044

[a]Standard deviation of experimental points of relatively optimal curve. [b]Relative error of experimental data approximation by the Equations (5-7) in Figure 2.

Secondly, the parameter n in the generalized Peukert's equations (5-7) does not depend on a battery's capacity, as the found values coincide in the limits of the standard error (Table 1-3). This is because in the standardized coordinates, equations (5-7) depend only on one parameter, namely n. Hence, in the case of the coincidence of the experimental data (Figures 2–4), this parameter is also expected to concur. The parameters C_m, i_0, and i_k depend on batteries' capacity (Tables 1-3).

Thirdly, the parameter n in the generalized Peukert's equations (5-7) takes a different value for batteries of different modes of discharge (Long, Medium, High). Notably, for equations (5) and (6), the parameter n rises with a discharge mode change (in the succession from L through M to H), while for equation (7) it falls.

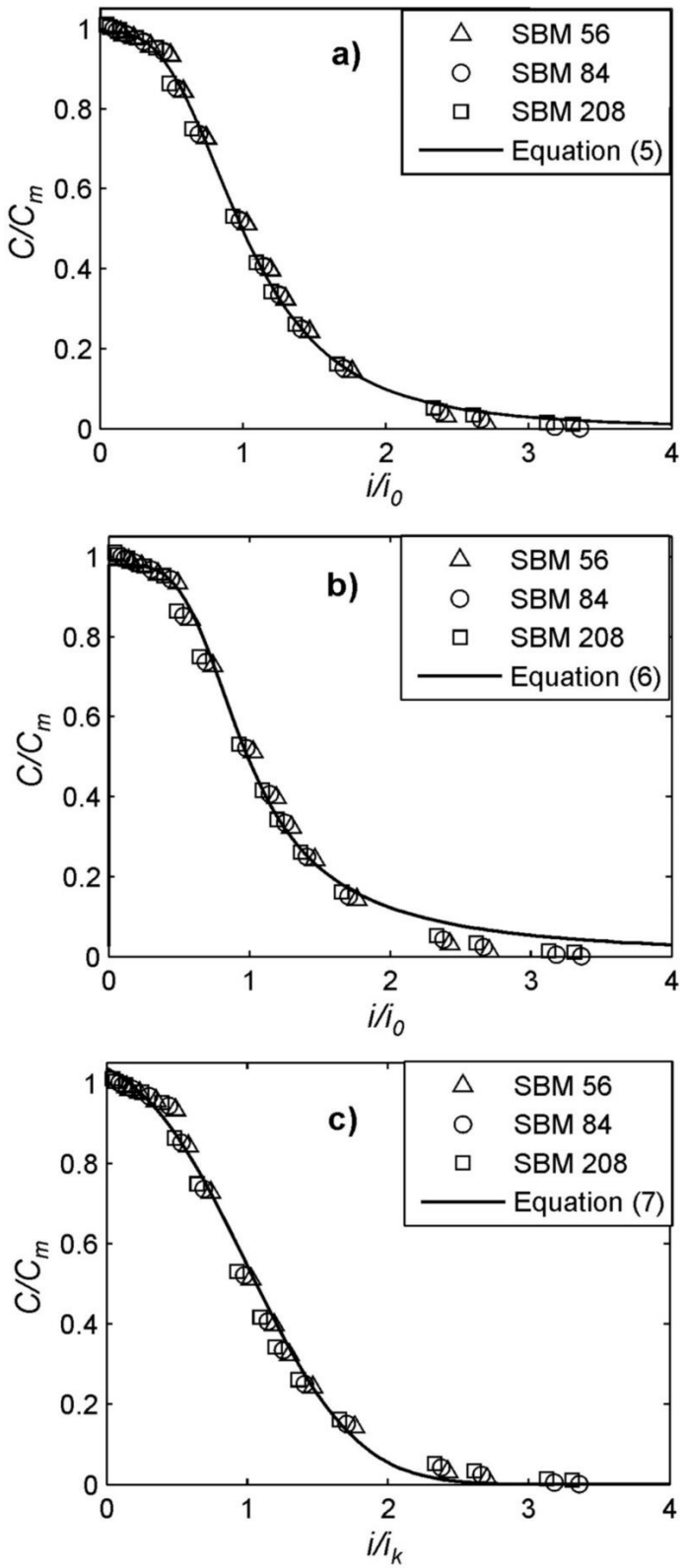

Figure 3. Experimental data for the batteries of the medium discharge mode with pocket electrodes and the generalized Peukert's equations (5-7) (a, b, and c respectively). Cm is the top capacity of batteries found at the discharge current $0.1C_N$. i_0 is the current at which batteries release a capacity half that of their top capacity. i_k is the current at which batteries release capacity *erfc(-1/n)* times less than their top capacity. The values of the parameters i_0 and i_k were taken from the Table 2 for each of the generalized Peukert's equations (5-7) respectively

Table 2. Optimal parameters of the generalized Peukert's equations (5-7) for batteries with pocket electrodes and a medium discharge mode.

Equation Parameters	batteries		
	SBM 56	SBM 84	SBM 208
Уравнение (5)			
C_m (Ah)	56.371	84.611	209.283
Standard error for C_m (Ah)	0.453	0.693	1.586
i_0 (A)	60.668	90.835	225.108
Standard error for i_0 (A)	0.750	1.144	2.611
n	3.169	3.173	3.190
Standard error for n	0.106	0.109	0.102
Mean n		3.177	
SD[a]	0.826	1.262	2.897
δ^b	2.831	2.883	2.674
Уравнение (6)			
C_m (Ah)	55.611	83.476	206.464
Standard error for C_m (Ah)	0.852	1.296	3.087
i_0 (A)	59.949	89.754	222.531
Standard error for i_0 (A)	1.452	2.205	5.231
n	2.060	2.059	2.074
Standard error for n	0.138	0.140	0.137
Mean n		2.064	
SD	1.671	2.539	6.066
δ	5.727	5.801	5.599
Уравнение (7)			
C_m (Ah)	58.98	88.464	218.756
Standard error for C_m (Ah)	0.991	1.439	3.586
i_k (A)	58.974	88.491	219.489
Standard error for i_k (A)	2.139	3.053	7.523
n	0.859	0.851	0.845
Standard error for n	0.087	0.083	0.082
Mean n		0.852	
SD	0.923	1.879	3.507
δ	3.164	3.110	3.237

[a]Standard deviation of experimental points of relatively optimal curve. [b]Relative error of experimental data approximation by the Equations (5-7) in Figure 3.

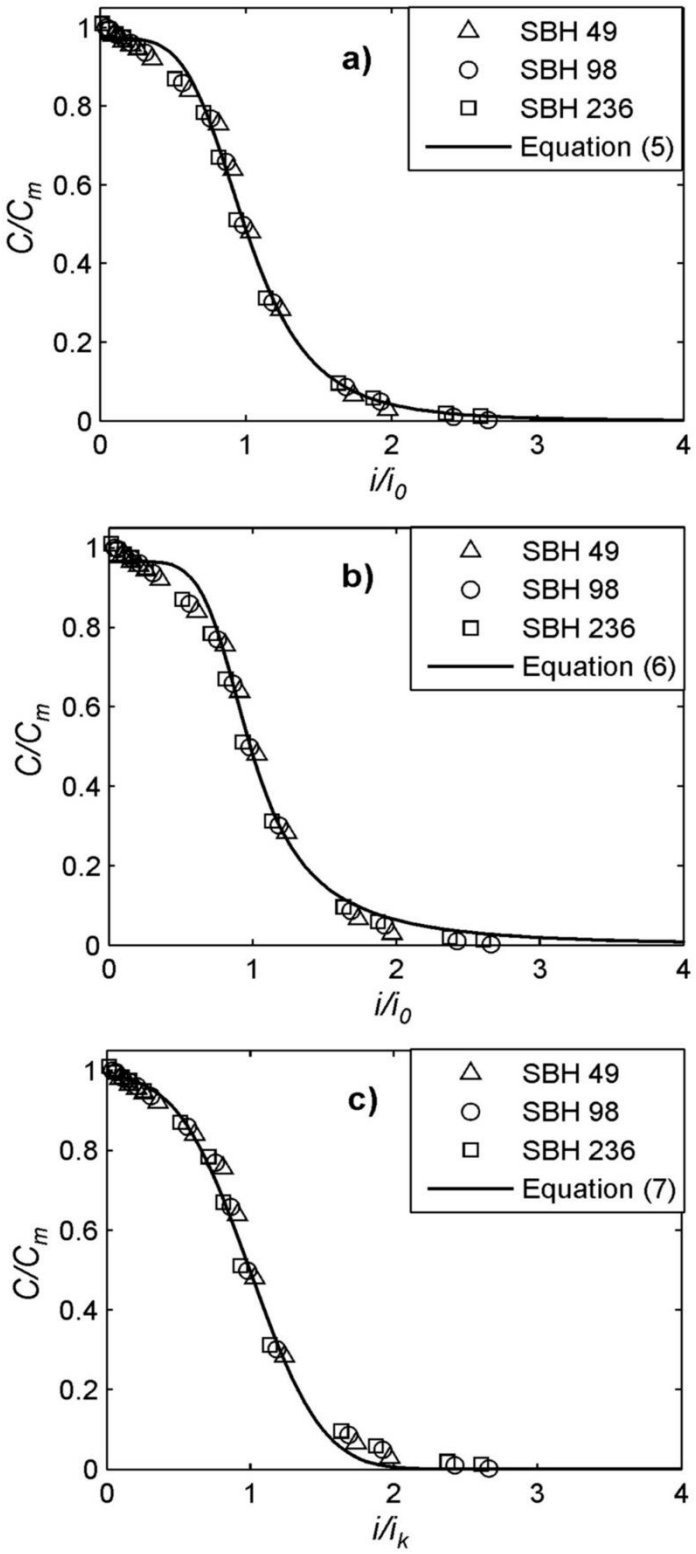

Figure 4. Experimental data for the batteries of the high discharge mode with pocket electrodes and the generalized Peukert's equations (5-7) (a, b, and c respectively). Cm is the top capacity of batteries found at the discharge current $0.1C_N$. i_0 is the current at which batteries release a capacity half that of their top capacity. i_k is the current at which batteries release capacity *erfc(-1/n)* times less than their top capacity. The values of the parameters i_0 and i_k were taken from the Table 3 for each of the generalized Peukert's equations (5-7) respectively

Table 3. Optimal parameters of the generalized Peukert's equations (5-7) for batteries with pocket electrodes and a high discharge mode.

Equation Parameters	batteries		
	SBH 49	SBH 98	SBH 236
Уравнение (5)			
C_m (Ah)	47.776	95.593	230.076
Standard error for C_m (Ah)	0.417	0.833	2.002
i_0 (A)	149.857	299.460	721.926
Standard error for i_0 (A)	1.787	3.556	8.551
n	4.475	4.488	4.495
Standard error for n	0.235	0.236	0.236
Mean n		4.486	
SD[a]	0.928	1.856	4.461
δ^b	3.326	3.324	3.319
Уравнение (6)			
C_m (Ah)	47.452	94.940	228.500
Standard error for C_m (Ah)	0.553	1.113	2.674
i_0 (A)	147.923	295.738	712.960
Standard error for i_0 (A)	2.242	4.496	10.809
n	2.978	2.982	2.989
Standard error for n	0.213	0.215	0.216
Mean n		2.983	
SD	1.265	2.545	6.117
δ	4.533	4.559	4.551
Уравнение (7)			
C_m (Ah)	48.626	97.275	234.096
Standard error for C_m (Ah)	0.580	1.151	2.760
i_k (A)	151.478	302.584	729.454
Standard error for i_k (A)	2.358	4.648	11.154
n	0.561	0.557	0.556
Standard error for n	0.042	0.041	0.041
Mean n		0.558	
SD	1.093	2.172	5.217
δ	3.916	3.892	3.882

[a]Standard deviation of experimental points of relatively optimal curve. [b]Relative error of experimental data approximation by the Equations (5-7) in Figure 4.

From a theoretical point of view, the most interesting equation is equation (7). Equation (7) has a statistical fundament unlike equations (5,6), which are purely empiric equations.

The battery discharge process is a phase transition. For example, for positive electrodes during discharge, the phase transition goes from more oxidized phases of active matter to less oxidized phases, whereas for negative electrodes it is the opposite:

$$NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^- \quad \text{(cathode)} \qquad (13)$$

$$Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^- \quad \text{(anode)} \qquad (14)$$

In physics [22,23], phase transitions are often described by complementary error function (4). Complementary error function (4) is based on the normal distribution law. It is beyond doubt that at

the level of molecules and ions, the discharge process is a statistical process. Hence, owing to the good coincidence of the experimental data with equation (7) (Figures 2-4), it is possible to conclude that the battery discharge process is a statistical process subject to the normal distribution law. In our opinion, this experimental fact is very significant for the theoretical substantiation of the charge/discharge processes in batteries.

In particular, starting from this concept of a statistical mechanism of the battery discharge process, the decrease becomes understandable for the parameter *n* in equation (7) in the succession (L, M, H) of batteries of different discharge mode. In this succession for the studied batteries, the thickness of electrodes decreases but their active mass stays the same. When batteries discharge, the electrochemical process decreases exponentially in relation to the depth of a porous electrode [9,28]. That is why as the electrodes thickness decrease, the statistical dispersion also decrease for a discharge extent of active matter in relation to the depth of a porous electrode. Hence, shrinking will also be observed in the statistical dispersion for the whole battery discharge process. However, as it is seen from equations (4,7), the parameter *n* in equation (7) determines the statistical dispersion for the battery discharge process in the standardized coordinates. In this case, the curves in Figures 2-4 for equation (7) (at a decrease in the statistical dispersion, i.e. *n*) will be subjected to more drastic changes. However, for equations (5,6), the decrease in the statistical dispersion is connected with the rise in the parameter *n*.

Hence, the proposed statistical mechanism of the battery discharge process has a clear physical and electrochemical sense and this allows us to explain the variation in the parameters in equations (5-7) depending on the type of batteries in use.

5. CONCLUSION

There are a number of advantages of the proposed generalized Peukert's equation (7) compared with both the classical Peukert's equation (1) and the equations (5) and (6).

Firstly, the generalized Peukert's equation (7) has a clear statistical and electrochemical sense unlike equations (1), (5), and (6), which are purely empiric equations. This statistical mechanism of the battery discharge process allows us to explain the parameters variation of equation (7) depending on the types of batteries used.

Secondly, both equation (7) and equation (5) have the lowest error of approximation of the experimental data (less than 4%), which is quite enough for the practical evaluation of a battery's released capacity.

As different generalizations of the Peukert's equation are widely used in various evaluations and models [2,3,28], the correction of those equations and understanding of the physical and electrochemical mechanisms on which they are based have great practical and theoretical significance.

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