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Short Communication

Models for Evaluation of Capacitance of Batteries

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In this study, it is proved that for batteries, the following empiric equations: generalized Peukert's equations, porous electrode equation, and probability integral describe the changes in the batteries' capacitance in the case of a complete range of change in discharge current with the same parameters, regardless of the capacitance of the batteries under study. Meanwhile, Peukert's equation is true only from the point of inflexion of the experimental curve C(*i*) infinitely.

Keywords: battery; empiric equations; capacitance; discharge current.

1. INTRODUCTION

Extensive experimental material has been accumulated by the cycling of batteries as of today. A multitude of empiric correlations describing discharge of the given batteries at a constant current was proposed. Nevertheless, the correlations just cited greatly differ from one another. This is the reason that it is very important to perform a comparative analysis of these correlations. A comparative analysis will allow the revelation of common fundamental features of all empiric correlations, reflecting the actual electro-chemical processes of discharge, which will form a good basis for the future development of a unified generalized equation of discharge, and probably the basis of development of the adequate general battery model in the long term. This study continues the study [1], based on the above program.

In all probability, the following correlations may be attributed to the most frequently used and verified empiric correlations for the calculation of capacitance, which is released by a battery at different discharge currents:

- Peukert's [2]

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

- Liebenow's [3]

$$C = \frac{A}{1 + B \cdot i} \quad , \qquad (2)$$

- generalized Peukert's equations [4]

$$C = a0 + \frac{a1}{i} + \frac{a2}{i^2} + \frac{a3}{i^3} + ... \quad , \qquad (3)$$

$$C = \frac{A}{i^n} th\left(\frac{i^n}{B}\right) \qquad (4),$$

where C is the released capacitance; i is the discharge current; A, B, n, $a0$, $a1$ and $a2$ are empiric constants. Peukert's equations (1,3) were obtained in an application to acid batteries, but currently, they are used to determine the capacitance of batteries and other electrochemical systems [5]. The correlations (1,3) are inapplicable at very low discharge currents, as at $i \to 0$, $C \to \infty$, which is devoid of physical sense. The formulas (1-4) are most frequently used to determine the capacitance released by batteries, though there are many other formulas and methods of calculation of released capacitance that are less frequently used [6, 7]. An analysis of the methods just mentioned shows that they are either special cases of correlations (1-4) or their combinations. Let us generalize Peukert's equation in such a way that it does not lead to a contradiction at small discharge currents. We will obtain the correlation

$$C = \frac{A}{1 + B \cdot i^n} \quad , \qquad (5)$$

It is possible to derive the equations (1,2) from correlation (5) at different meanings of constants B, n. Empiric equation (4) is also one of the generalizations of Peukert's equation, as at high discharge currents, it is transformed into Peukert's equation; whereas at low currents, it tends to remain a constant. Hence, generalized Peukert's equation (4), similar to equation (5), is one of the generalizations of Peukert's equation onto the interval of low discharge currents.

The process of batteries discharge is a phase transition, and phase transitions are often described by the probability integral [8]:

$$C(i) = \frac{A}{2} \cdot erfc\left(\frac{i - i_0}{\sigma}\right) \qquad (6)$$

Hence, we will also analyze this dependency. In these articles [9-10], during the process of studying the distribution of current in the depth of a porous electrode, it was demonstrated that one of the reasons for the decrease in the capacitance released by a battery at an increase of discharge current is the decrease of depth of electrochemical process penetration into the depth of a porous electrode. Thus, the higher the discharge current, the steeper is the decline of discharge current along the depth of a porous electrode, and the smaller portion of active substance of the electrode takes part in the process of discharge. It means that the electrochemical process of discharge is concentrated more and more in the surface layers of the electrode. The capacitance released by a battery decreases according to the following law:

$$C = \frac{C_m(1 - Ai^n)}{1 + B \cdot H(i)}, \quad (7)$$

$$H(i) = exp\left(-\frac{D}{i}\right) + \sqrt{\frac{\pi i}{D}} erfc\left(\frac{D}{i}\right),$$

where *A, B, D* and n are empiric constants, and C_m is the maximal battery capacitance. It should be noted that in all equations (1-7) all empiric constants are considered as being greater than zero.

2. EXPERIMENTAL

The batteries made by the SAFT company with stationary application and a high rate of discharge were used in the experiments.

Battery discharge was performed up to the voltage of 1 V, as peripheral devices connected to a battery do not function at lower voltages; that is why the released capacitance at these lower values of voltage has no practical meaning. The charging of batteries was performed according to their operational manual.

In order to exclude the cross-impact of one charge-discharge cycle to another (through all types of residual effects, memory effect, etc.), one to three training cycles were performed before changing the discharge current. The battery capacitance obtained after every training cycle was compared with initial capacitance. If the obtained capacitance differed by more than 10%, additional training cycles were performed. Thus, equal initial conditions were provided for all the charge-discharge cycles. The training cycles were performed according to the operating manual of the batteries under study.

Three charge-discharge cycles were performed at each discharge current. If the discharge capacitance did not differ greatly in these cycles (not more than 5%), then the average value at the discharge current under study was considered the experimental discharge capacitance. Otherwise, the training cycles were repeated according to the method just mentioned, and the experiment was repeated over again. Discharge was performed at constant discharge currents from $0.1C_n$ (C_n – nominal battery capacitance) up to discharge currents, when the capacitance released by the battery was close to zero. For results of experimental research, see Fig. 1.

3. RESULTS AND DISCUSSION

Experimental data shown in Fig. 1 are normalised to the maximal capacitance of a particular battery. The maximal capacitance of a battery is usually obtained at discharge currents of $0.1C_n$. It is convenient to normalise experimental data on the maximal capacitance of a battery, and not on the nominal capacitance for the following reasons. First, at one and the same nominal capacitance, there is a difference between the maximal capacitance of batteries of different manufacturers and of different battery types. Second, even with one and the same manufacturer, the maximal capacitance of a battery depends on the type of electrodes, their thickness, design features and so on.

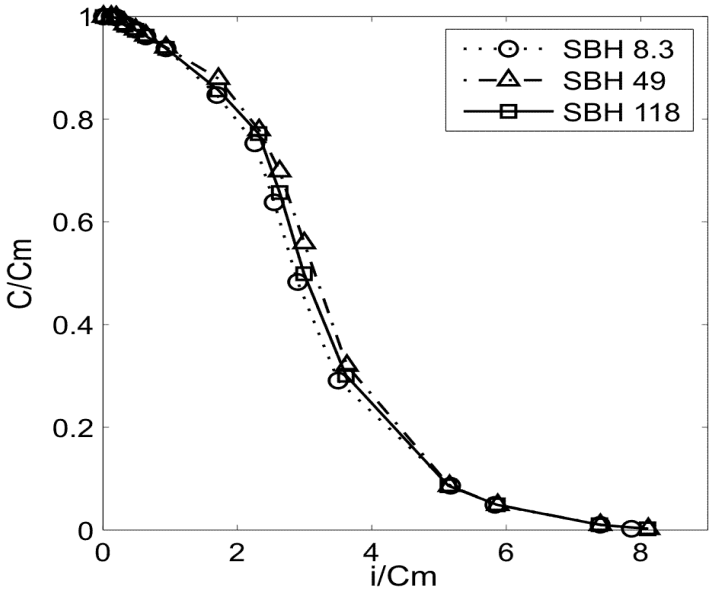

Figure 1. Dependencies of battery capacitance from discharge currents. C_m – maximal capacitance of batteries

Third, the maximal capacitance of a particular battery out of the same batch of batteries of one and the same type and one and the same manufacturer depends on the following aspects: statistical dispersion of battery parameters during the process of their manufacturing, battery operation time, mode of battery operation and so on. Practical experience of different types of Ni-Cd batteries' cycling shows that during the cycling of a batch of batteries of one and the same type and one and the same capacitance, the obtained experimental curves differ from one another by 4–6% and sometimes even more. This is true for batteries of any electrochemical system, and not only for nickel-cadmium. Thus, if one normalises the experimental data on the maximal capacitance of the battery under study (obtained experimentally), it is possible to exclude the random factors just mentioned from the parameters of correlations (1-7).

The curves coincide for the obtained experimental data of Fig. 1 within the limits of statistical error, as their confidence intervals overlap, that is, these curves are identical.

This experimental fact has a rigorous theoretical substantiation beneath it. All the batteries of SBH type with a high rate of discharge are made of one and the same electrodes of pocket construction design and are of an equal thickness. They differ only in the area of electrodes and in their amount. Hence, the parameters of any battery in the normalized coordinates should be equivalent to the parameters of a battery of a unit capacitance having the same electrodes; consequently, all the curves of the type of Fig. 1, within the limits of statistical error, should coincide, which is exactly what is observed in experiments. It has just been mentioned in the case of dividing battery characteristics by their maximal capacitance (obtained experimentally) that the scatter of experimental data related to battery manufacturing is smooth in many instances.

The correlations (1-3) cannot describe the experimental curves of Fig. 1 along all the intervals of the changing of discharge currents. First, experimental curves are convex close to zero, and the correlations (1-3) give only concave curves (at positive values of all constants). Second, we obtain $C \to \infty$ at $i \to 0$, which is devoid of physical sense. This is why we should first research the

applicability of correlations (4-7) for the description of dependency of batteries' capacitance from discharge currents.

The optimal parameters for correlations (4-7), corresponding to the indicated experimental data, were obtained using the least square method with the Levenberg–Marquardt optimization algorithm, and are presented in Table 1.

One can see from Table 1 that the parameters of correlations (4-7) change very little for different types of batteries, in spite of the fact that the capacitance of batteries changes more than tenfold. It is related to the fact that normalised experimental curves of the SBH 8.3, SBH 49 and SBH 118 batteries practically coincide, as observed in Fig. 1. Hence, let us obtain average optimal parameters for every correlation (4-7) by applying the least square method, using experimental data for all the SBH 8.3, SBH 49 and SBH 118 batteries at once, as depicted in Fig. 1. See the last column of Table 1 for the result.

Table 1. Optimal parameters of empiric correlations (4-7) for SAFT batteries with a high rate of discharge

Equation Parameters	SBH 8.3	SBH 49	SBH 118	Mean Values
Generalised Peukert's equation (4)				
A	10.033	13.196	13.022	11.757
B	10.317	13.576	13.417	12.1
n	2.831	2.958	2.955	2.897
S^a	0.026	0.027	0.027	0.029
δ [b]	4.2	4.2	4.3	4.5
Generalised Peukert's equation (5)				
A	0.979	0.978	0.976	0.978
B	0.011	7.058E-3	7.177E-3	8.429E-3
n	4.25	4.443	4.441	4.35
S	0.02	0.02	0.02	0.022
δ	3.1	3.1	3.1	3.5
Probability integral (6)				
A	1.002	0.999	0.998	1.001
i_0	1.697	1.743	1.737	1.748
σ	2.929	3.086	3.074	3.03
S	0.024	0.022	0.022	0.025
δ	3.8	3.5	3.5	3.9
Equation of porous electrode (7)				
A	0.067	0.063	0.065	0.065
B	95.428	125.243	131.732	110.029
D	15.506	17.14	17.252	16.505
n	1.206	1.226	1.201	1.219
S	8.564E-3	8.002E-3	7.343E-3	0.014
δ	1.3	1.2	1.2	2.1

[a] Standard deviation of experimental points of relatively optimal curve. [b] Relative error in percent.

One can see from Table 1 that equations (4-7) show experimental data correctly at any discharge currents with a relative error of less than 4.5%, regardless of the capacitance of the batteries used, which is quite sufficient for practical purposes.

Generalized Peukert's equation (5) and the equation of porous electrode (7), which correspond to experimental data with a relative error of 3% and 1.5%, respectively, should be particularly noted. These correlations undeniably are of global character, as they are applicable to all the studied range of changing of discharge currents from zero to $i = 8C_n$, and theoretically to infinity. This means that the data of equation correspond to the nature of the electrochemical process of Ni-Cd batteries discharge, and, consequently, are the most fundamental among all of the investigated.

Equation (7) was obtained from an analysis of distribution of current in the depth of a porous electrode at the discharge of batteries [9-10]. The decrease in capacity, released by a battery in this equation, is related to a decrease in the depth of penetration of the electrochemical process into the depth of a porous electrode at the increase of discharge current, and, consequently, with a decrease in active material of the electrode taking part in the process of discharge. Since the equation is extremely well confirmed by the experiment, it is possible to consider this as one of the proofs, which exactly decreases the depth of penetration of the electrochemical process into the depth of a porous electrode with an increase in the discharge current, and this serves as one of the main reasons of battery capacitance decrease.

Thus, empiric generalized Peukert's equations (4,5), porous electrode equation (7) and probability integral (6) for SAFT batteries with stationary application and a high rate of discharge describe the changes in batteries' capacitance at different discharge currents with one and the same parameters, regardless of the capacitance of the studied batteries.

Let us now investigate the applicability of Peukert's (1,3) and Liebenow's (2) equations for the given batteries. Due to the inverse relationship between battery capacitance and the discharge current in the equations (1-3), they can only be used starting from the point of function inflexion C(i), as seen in Fig. 1, to infinity. The point of inflexion of the C(i) curve for SBH batteries is approximately at the discharge current of $i = 3C_n$. In this relation, let us check the applicability of "Peukert's (1,3) and Liebenow's equations for the batteries under study within the range of discharge currents from $i = 3C_n$ to $i = 8C_n$ ($8C_n$ – highest currents in our experimental studies). Let us find the optimal parameters for these equations using the experimental data, as seen in Fig. 1. See Table 2 for the results.

One can see from Table 2 that Peukert's equations (1,3) correspond well to the experimental data within the given interval of discharge currents; the relative error is less than 3% and 2%, correspondingly, which is quite sufficient for practical purposes. Hence, Peukert's equations (1,3) can be used for practical calculations of the capacitance released by SBH alkali batteries within the range of discharge currents from $i = 3C_n$ to infinity. Liebenow's equation within the given range of discharge currents corresponds poorly to the experimental data, and the relative error is 7.5%; see Table 2. In this regard, we note that in the article [11], Peukert's equation significantly is generalized. This equation takes into account the influence of temperature, and change of a current on the capacitance released by battery. However and in this case it is not suitable for small currents of discharge in accordance with the above study.

Let us evaluate the place of Liebenow's equation among the other empiric equations (1-7) in greater detail. Liebenow's equation was proposed for the calculation of released capacitance at low discharge currents [3].

Table 2. Optimal parameters of Peukert's and Liebenow's empiric correlations for discharge currents from $i = 3C_n$ and to $i = 8C_n$

Equation Parameters	SBH 8.3	SBH 49	SBH 118	Mean Values
Peukert's equation (1)				
A	13.396	17.296	17.433	14.937
n	3.107	3.21	3.225	3.129
S	0.015	0.018	0.017	0.022
δ	2.4	2.8	2.7	3.5
Generalised 'Peukerts equation (3)				
*a*0	-0.118	5.334E-3	0.042	4.087E-3
*a*1	0.366	-0.974	-1.334	-0.907
*a*2	3.873	7.367	8.113	6.972
S	0.012	5.384E-3	4.387E-3	0.014
δ	1.9	0.8	0.7	2.3
Liebenow's equation (2)				
A	-0.115	-0.115	-0.114	-0.124
B	-0.426	-0.409	-0.409	-0.423
S	0.041	0.045	0.044	0.046
δ	6.5	7.1	7.1	7.3

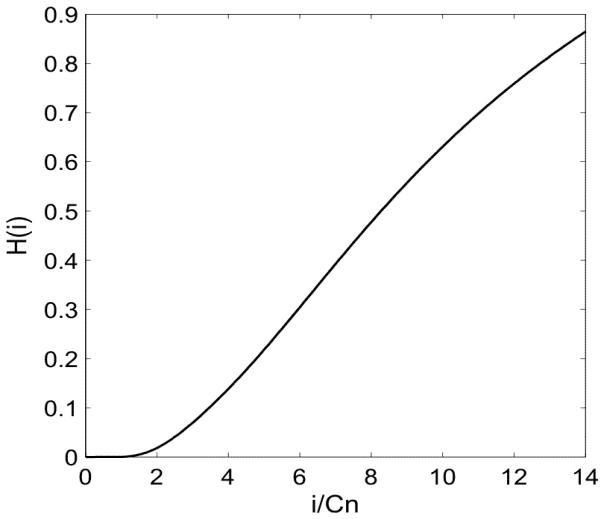

Figure 2. Dependency of function H(*i*) from discharge current

However, at low discharge currents, the curve corresponding to Liebenow's equation is concave, whereas the experimental curve C(*i*) is convex, as seen in Fig. 1. Thus, at low discharge currents, Liebenow's equation in even a qualitative approach does not accurately show the type of change of released capacitance, depending on discharge currents. Liebenow's equation (2) is close in its appearance to equation (7), which describes the C(*i*) experimental curve most fundamentally and correctly. At low discharge currents Ai^n summand in the numerator of equation (7) can be neglected in comparison to a unit, as the *A* parameter is small (see Table 1). In this case, the difference between equation (2) and equation (7) is made by the function H(*i*). The given function has the following type: See Fig. 2. One can see from the figure that function H(*i*) in the vicinity of the point of inflexion varies approximately linearly along the large segment of variation of discharge currents, that is, it has a type that is similar to Liebenow's function. Hence, only this segment can be considered the area of application of Liebenow's equation (2), but not the low discharge currents as was considered earlier.

Function *H*(*i*) for SBH batteries is approximately linear within the interval from $i = 4C_n$ and to $i = 8C_n$. In this regard, let us find the optimal parameters of Liebenow's equation (2) within the given interval (see Table 3).

One can see from Table 3 that within the given interval of the changing of discharge currents, Liebenow's equation corresponds to the experimental data with a relative error of 1.5%. Thus, Liebenow's equation can be used for practical calculations of the capacitance released by alkali batteries within the interval of discharge currents from $i = 4C_n$ to $8C_n$.

Table 3. Optimal parameters of empiric Liebenow's equation for discharge currents from $i = 4C_n$ to $8C_n$

Equation Parameters	SBH 8.3	SBH 49	SBH 118	Mean Values
A	-9.707E-3	-0.01	-0.011	-0.01
B	-0.215	-0.217	-0.218	-0.217
S	7.708E-3	7.811E-3	7.875E-3	9.193E-3
δ	1.2	1.2	1.2	1.5

4. CONCLUSIONS

Thus, the following empiric correlations can be used to evaluate capacitance released by battery at all possible discharge currents:

Generalized Peukert's equation (4),

$$C(i) = C_m \frac{A}{(i/C_m)^n} th\left(\frac{(i/C_m)^n}{B}\right), \quad \text{A=11.757, B=12.1, n=2.897,} \quad (8)$$

Generalized Peukert's equation (5)

$$C(i) = \frac{C_m A}{1 + B \cdot (i/C_m)^n}, \quad \text{A=0.978, B=0.0084, n=4.35.} \quad (9)$$

Probability integral (6),

$$C(i) = C_m \frac{A}{2} \cdot erfc\left(\frac{(i/C_m - i_0)}{\sigma}\right), \qquad A=1, \quad \sigma=3.03, \quad i_0 = 1.748, \qquad (10)$$

Porous electrode equation (7),

$$C(i) = \frac{C_m(1 - A(i/C_m)^n)}{1 + B \cdot H(i/C_m)}, \quad A=0.065, \quad B=110.029, \quad D=16.505, \quad n=1.219, \quad (11)$$

where $$H(i) = exp\left(-\frac{D}{i}\right) + \sqrt{\frac{\pi i}{D}} erfc\left(\frac{D}{i}\right)$$

The above equations are applicable for the Ni-Cd batteries with a high rate of discharge of any capacitance. For practical application of the above equations, it would suffice to know only one parameter of a particular battery: C_m. It is possible to obtain the maximal capacitance of a battery by discharging the battery with small currents, normally $i = 0.1C_n$. The relative error at capacitance evaluation using the correlations (8–11) equals 1.5–4.5%, which is quite sufficient for practical purposes.

Generalized Peukert's equation (11) is the most preferable among correlations (8–11) for practical purposes. On one hand, it is the simplest correlation in terms of structure and the number of parameters used. On the other hand, it gives the smallest relative error among all the correlations (8–10). Thus, this correlation is the best to reflect electrochemical processes taking place at discharge of nickel-cadmium batteries.

Peukert's equations (1,3) can only be used starting from the point of function inflexion C(i), as seen in Fig. 1, to infinity. Liebenow's equation (2) can be used for practical calculations of the capacitance alkali batteries nearby of the point of function inflexion C(i).

Since the relations (8-11) are determined by electrochemical process, they are likely to not have to depend neither on firm of the manufacturer of batteries nor from type of electrodes. However, this assumption, of course, requires additional experimental and theoretical checking.

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