

Study of Discharge Process Final Voltage Influence on Parameters of Generalized Peukert's Equation for Nickel-Cadmium Batteries

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In this paper, the Peukert's generalized equation $C=C_m/(1+(i/i_0)^n)$ is proposed to describe the dependence between a battery's capacity and discharge current for nickel-cadmium batteries. It was proved by experiments that this equation is good for the description of batteries' capacity at any discharge currents unlike the classical Peukert's equation, which is inapplicable at small discharge currents. Further, all the parameters of this equation have a clear electrochemical sense. The dependence of the parameters of the Peukert's generalized equation was studied both: batteries' nominal capacity and their discharge process' final voltage. It was proved that the parameter n does not depend on a batteries nominal capacity but instead does depend on a final discharge voltage. The empiric dependences of the parameters C_m and i_0 were found on batteries' nominal capacity and final discharge voltage.

Keywords: model, battery, nickel–cadmium, capacity, discharge current

1. INTRODUCTION

At present, in connection with the wide spread of batteries in diverse machines and technical devices, reliable practical models of those batteries are needed. The models of batteries are necessary in the course of both projecting of various technical devices and their operation, in particular for evaluation of their remaining capacity. This problem is very important for both lithium-ion batteries used in electrical vehicles, aviation, and so on and nickel-cadmium or lead/acid batteries used in aviation, railway transport, and communication systems, etc. [1–3].

The most fundamental models of batteries are based on the electrochemical modelling method. Under this method, battery models are built based on fundamental physical and electrochemical laws [4–8]. Although these models describe all the processes in batteries with the highest exactness, their use in technical systems is not always possible. Hausmann [9] highlighted three of the shortcomings of these models. Firstly, they contain a lot of local parameters, which are very difficult or impossible to measure experimentally. For example, it is impossible to measure directly the various kinetic parameters inside a porous electrode, particularly the parameters of the Butler-Volmer function. Secondly, these models have a very sophisticated system of calibration. That is why if at projecting of technical systems containing batteries, it may become necessary to change batteries' requirements, in this case, all experimental studies must be redone from the very beginning. Thirdly, these models require considerable computational potency, which is unacceptable for the on-board computers of electrical vehicles and aeroplanes. All these factors restrict the applicability of these models [1,2].

Further, many companies require the development of such battery models, the parameters of which could be measured without disassembling a battery. It is principally impossible to build such models under the electrochemical method of modelling. These models can be developed only by using either the statistical method [1,2,10,11] or the non-linear structural method [12]. Under the non-linear structural method, the object or process under examination is considered as a system consisting of its subsystems or elements. The separation of the studied process into elements takes place by studying the process and differentiating its various stages. To every stage of the process, one or few structural elements are assigned. The structural elements are connected by linear links based on Kirchhoff's laws. Unfortunately, this modeling method is used extremely seldomly [13,14]. That is why in practice, statistical models of batteries are used very often [9,15-17]. These models are used where it is impossible or undesirable to use electrochemical models [9,15] or where the processes being modelled are studied poorly [18–21]. As a fundament of modern statistical models for evaluating a battery's remaining capacity, either the Peukert's equation [9] or various improvements of the Peukert's equation are used [15].

The purpose of this paper is to study the influence of the discharge process' final voltage on the parameters of the Peukert's generalized equation, as this equation is used very often in various statistical models.

2. PEUKERT'S GENERALIZED EQUATION

As a rule, in statistical models, to evaluate a battery's remaining capacity, the Peukert's equation is used [9]:

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

where C is the battery's capacity at discharge current i ; A and n are empiric constants.

However, at small discharge currents, the Peukert's equation is inapplicable because as the discharge current decreases, the battery's capacity tends to infinity (1), which is deprived of a physical

sense. In the paper [11] tested the best known empiric equations generalizing the Peukert's equation. It was proved that the equation

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

corresponds most perfectly to the experimental data within the entire interval of changes in the discharge current. Moreover, this equation, unlike the Peukert's equation (1), is also applicable at small discharge currents.

Let us rewrite equation (2) in the form:

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

Then, at $i=0$, we obtain $C=C_m$, i.e. C_m is the maximum possible capacity for a battery. At $i=i_0$, we obtain $C=C_m/2$, i.e. i_0 is the current at which the battery's capacity is half its maximum capacity. Hence, the constants in equation (3) have a clear electrochemical sense unlike equation (2), where A and B are just empiric constants.

Further, on the parameters of the Peukert's generalized equation (3), additional limitations must be imposed connected with boundary conditions.

Based on the accumulated experimental data [22,23], it is possible to state that for batteries of any electrochemical system, the higher the discharge current, the lower is the battery's capacity $C(i)$. At very big discharge currents, the capacity must be close to zero, i.e.

$$\lim_{i \rightarrow \infty} C(i) \approx 0. \quad (4)$$

Further, for batteries of most electrochemical systems at small discharge currents, the battery's capacity is at its maximum and virtually does not change with a discharge current growth up to some critical value I_k . Due to this property, batteries are used in various machines and devices, and the range of discharge currents from zero to I_k is the working range of batteries' discharge currents. The span of the working range of discharge currents depends on a battery's electrochemical system, constructive features, electrodes type, and so on. Thus, for any battery, the following boundary condition must be correct:

$$\lim_{i \rightarrow 0} \frac{dC(i)}{di} \approx 0. \quad (5)$$

Exceptions are provided only by a small number of batteries unable to discharge at very small currents for various reasons [22,23]. However, for these batteries, equation (3) is also correct if not to take – into consideration – currents less than some critical value $I_0 \ll I_k$. Consequently, any equations $C(i)$ being correct through the whole range of the discharge currents must fulfil the boundary conditions (4,5).

For the Peukert's generalized equation (3), the boundary condition (4) is fulfilled at $n > 0$. From the boundary condition (5), we obtain the following limitation on the parameters of equation (3).

$$\lim_{i \rightarrow 0} \frac{dC(i)}{di} = \lim_{i \rightarrow 0} \frac{-C_m n (i/i_0)^{n-1}}{i_0 (1 + (i/i_0)^n)^2} = \begin{cases} 0 & \text{at } n > 1 \\ -\infty & \text{at } 0 < n < 1 \\ -nC_m/i_0 & \text{at } n = 1 \end{cases}. \quad (6)$$

Hence, the parameter n in equation (3) must fulfil the inequation

$$n > 1 \quad (7)$$

3. EXPERIMENTAL

For studying the final discharge voltage's influence on the parameters of the Peukert's generalized equation (3), we used the nickel-cadmium batteries SBM 11, SBM 43 and SBM 112, with capacities 11, 43 and 112 Ah, respectively, made by the company SAFT of stationary application. In our various experiments, a battery's discharge was performed down to voltages 1.0, 1.05, 1.10 and 1.14 V. Batteries' charge was fulfilled according to their operation manuals.

Before every change of a discharge current or a final discharge voltage, three training cycles were performed. The training cycles were made in accordance with the operation manuals of the batteries under investigation. The battery's capacity obtained after every training cycle was compared with its initial capacity. If in the course of the training cycles, the obtained capacity differed by more than 10%, additional training cycles were performed. The training cycles allowed us to exclude the cross-impact of various charge/discharge cycles through residual effects, a memory effect and so on.

For every discharge current, three charge/discharge cycles were fulfilled. If the measured capacities differed by less than 5%, an average capacity value for these three cycles was taken to be the experimental discharge capacity at this current value. Otherwise, additional training cycles were performed and the experiment was repeated from the very beginning. In the experiments, discharge currents were used from $0.1C_N$ (where C_N is the nominal battery's capacity) to current values, at which the batteries' discharge capacity was close to zero.

To find the true functional dependence of a battery's capacity on discharge currents, it is preferable to exclude all random factors already in the experimental data. It should be noted that at the same batteries' nominal capacity, their maximum capacity, i.e. their capacity at small discharge currents, depends on the following random factors. The first factor is the producer of batteries, electrode type, thickness, constructive features and so on. Secondly, even in a consignment of batteries of the same type and from the same producer, the maximum capacity of a specific battery depends on the statistical dispersion of batteries' parameter values on their production, operation duration, operation mode and so on. On the basis of our experience of battery cycling, it is possible to affirm that even in the same consignment of batteries of the same type and the same capacity, the found maximum capacity values differ from each other, as a rule, by 4% to 6% and sometimes even more. This is true for batteries of all electrochemical systems and not only for nickel-cadmium ones. By taking the obtained experimental data for batteries' capacities and standardizing them by their maximum capacity found experimentally, all the above-mentioned random factors are excluded from the experimental data. Further, in accordance with the Peukert's generalized equation (3), it is convenient to standardize the discharge current on parameter i_0 . The obtained experimental data for batteries of various capacities and various final discharge voltages (1.0, 1.05, 1.10 and 1.14 V) in the standardized coordinates are given in Fig. 1 (a, b, c and d, respectively). The parameters C_m and i_0 in Fig. 1 are taken from Table 1. From Fig. 1, it is seen that for batteries of different capacities in the

standardized coordinates, the optimal experimental curves coincide at the limits of the standard error. That is why in Fig. 1, only one curve is presented, corresponding to the average capacity of the batteries under investigation.

In Fig. 1 (a–d), it is seen that despite the big difference in batteries’ capacities (11–112 Ah), their experimental data in the standardized coordinates coincide at the limits of the experimental statistical error.

4. RESULTS AND DISCUSSION

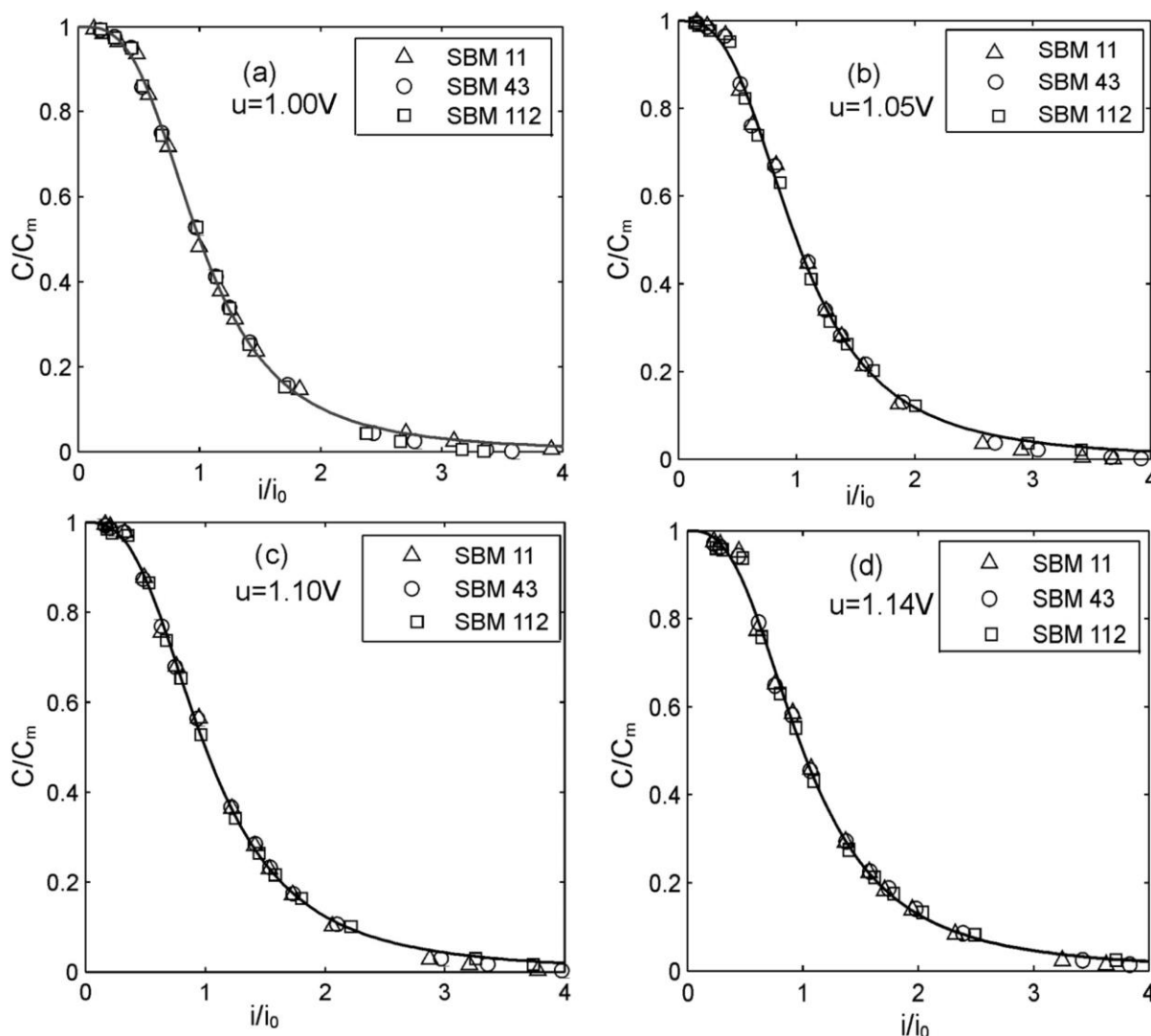


Figure 1. Batteries’ capacity dependence from the discharge current and final discharge voltage. C_m is the battery’s maximum capacity and i_0 is the current at which a battery’s capacity is half its maximum capacity.

The optimal parameters for the Peukert’s generalized equation (3) with the use of the obtained experimental data (Fig. 1) were found by the least squares method using the optimization procedure of Levenberg-Markquardt. The obtained parameters for the batteries of various capacities and various final discharge voltages are given in Table 1.

While analysing Table 1, it is seen that the parameter n of the Peukert’s generalized equation does not depend on a battery’s capacity as the found values coincide at the limits of the standard error. In addition, this fact is evident from Fig. 1, where all the experimental data coincide with the optimal curve in the standardized coordinates at the limits of the experimental statistical error regardless of a battery’s capacity.

Table 1. Optimal parameters of the Peukert’s generalized equation (3)

| Equation Parameters | batteries | | |
|------------------------------------|-----------|--------|---------|
| | SBM 11 | SBM 43 | SBM 112 |
| Discharge final voltage $u=1.00$ V | | | |
| C_m | 11.191 | 43.348 | 112.709 |
| i_0 | 10.831 | 47.21 | 121.575 |
| n | 3.124 | 3.113 | 3.176 |
| Standard error for n | 0.082 | 0.096 | 0.109 |
| Mean n | 3.138 | | |
| SD ^a | 0.127 | 0.542 | 1.687 |
| δ^b | 2.254 | 2.411 | 2.89 |
| Discharge final voltage $u=1.05$ V | | | |
| C_m | 11.159 | 43.216 | 112.231 |
| i_0 | 8.173 | 35.473 | 91.228 |
| n | 2.904 | 2.923 | 2.989 |
| Standard error for n | 0.093 | 0.129 | 0.138 |
| Mean n | 2.939 | | |
| SD | 0.162 | 0.781 | 2.356 |
| δ | 3.105 | 3.75 | 4.362 |
| Discharge final voltage $u=1.10$ V | | | |
| C_m | 11.067 | 42.886 | 111.452 |
| i_0 | 6.045 | 25.898 | 66.461 |
| n | 2.824 | 2.806 | 2.861 |
| Standard error for n | 0.058 | 0.091 | 0.097 |
| Mean n | 2.830 | | |
| SD | 0.103 | 0.515 | 1.749 |
| δ | 2.171 | 2.721 | 3.566 |
| Discharge final voltage $u=1.14$ V | | | |
| C_m | 11.039 | 42.873 | 110.79 |
| i_0 | 4.335 | 18.337 | 47.392 |
| n | 2.768 | 2.747 | 2.808 |
| Standard error for n | 0.109 | 0.106 | 0.118 |
| Mean n | 2.774 | | |
| SD | 0.185 | 0.667 | 2.065 |
| δ | 4.364 | 3.932 | 4.714 |

^aSD - standard deviation of experimental points of relatively optimal curve. ^b δ - relative error (in percent) of experimental data approximation by the Equation (3) in Figure 1.

It should be noted that the Peukert's generalized equation (in the standardized coordinates) depends only on one independent parameter n . Hence, in the case of the coincidence of the experimental data, this parameter must coincide, too. Therefore, let us find the average value n for each final discharge voltage with the use of all the experimental data for the batteries SBM 11, SBM 43 and SBM 112. The obtained average values are presented in Table 1.

With the use of the experimental data from Table 1, we can find the function of the parameter n from the final discharge voltage u :

$$n = 5.686 - 2.579u, \quad SD = 0.035, \quad \delta = 1.192, \quad (8)$$

In a similar way, we can find the functions of the parameters i_0 and C_m from batteries' nominal capacity C_N and final discharge voltage u :

$$i_0 = 11.974 + 1.078(C_N - 11) - 97.212(u - 1) + 346.986(u - 1)^2 - 4.750(C_N - 11)(u - 1), \\ SD = 0.816, \quad \delta = 2.03, \quad (9)$$

$$C_m = 6.897 + 0.996C_N - 6.263u, \quad SD = 0.308, \quad \delta = 0.556. \quad (10)$$

The obtained equations (8-10) correspond very well to the experimental data as the relative error of the experimental data approximation (in percent) by these equations is very small.

5. CONCLUSION

In conclusion, I would like to highlight a number of the advantages of the proposed Peukert's generalized equation (3) in comparison with the classical form of the Peukert's equation (1). Firstly, the Peukert's generalized equation (3) corresponds well to the experimental data at all discharge currents, while the classical Peukert's equation (1) is inapplicable at small discharge currents. Secondly, in equation (3), all the constants have a clear electrochemical sense, while in equation (1), they are just empiric constants. In connection with this, the constants of the equation (3) can be found based on far less number of experiments as for their finding, it is possible not to use the procedure of approximation of experimental data by this equation. Thirdly, the parameter n in the Peukert's generalized equation (3) does not depend on the capacity of the studied batteries, i.e. this parameter is universal unlike the same parameter in the classical Peukert's equation (1). Hence, this experimental fact sharply reduces the experiments needed to find the Peukert's generalized equation (3) for a number of batteries of various capacities.

By virtue of the fact that the Peukert's equation (1) is used in various practical models of batteries [9,15,23], the determination of the most exact function of a battery's capacity from a discharge current is very significant for practical needs.

References

1. O. Tremblay, L.A. Dessaint and A.I. Dekkiche, in: *Vehicle Power and Propulsion Conference, VPPC 2007. IEEE*, (2007) 284 Arlington, USA.
2. O. Tremblay and L. A. Dessaint, *World Electric Vehicle Journal*, 3 (2009) 1.
3. D. Rakhmatov, S. Vruthula and D. A. Wallach, *IEEE Transactions on Very Large Scale Integration (VLSI) Systems*, 11 (2003) 1019.

4. M. Cugnet, S. Laruelle, S. Grugeon, B. Sahut, J. Sabatier, J.M. Tarascon and A. Oustaloup, *J. Electrochem. Soc.*, 156 (2009) A974.
5. K. Siniard, M. Xiao and S. Y. Choe, *J. Power Sources*, 195 (2010) 7102.
6. M. Venkatraman and J. W. Van Zee, *J. Power Sources*, 166 (2007) 537.
7. T. G. Zavalis, M. Behm and G. Lindbergh, *J. Electrochem. Soc.*, 159 (2012) A848.
8. V. Boovaragavan, R. N. Methakar, V. Ramadesiga, and V. R. Subramanian, *J. Electrochem. Soc.*, 156 (2009) A854.
9. A. Hausmann and C. Depcik, *J. Power Sources*, 235 (2013) 148.
10. N. E. Galushkin, N. N. Yazvinskaya and D. N. Galushkin, *Int. J. Electrochem. Sci.*, 9 (2014) 1911.
11. N. E. Galushkin, N. N. Yazvinskaya, D. N. Galushkin and I. A. Galushkina, *Int. J. Electrochem. Sci.*, 9 (2014) 4429.
12. N. E. Galushkin, N. N. Yazvinskaya and D. N. Galushkin, *Int. J. Electrochem. Sci.*, 9 (2014) 6305.
13. N. E. Galushkin, N. N. Yazvinskaya and D. N. Galushkin, *J. Electrochem. Soc.*, 159 (2012) A1315.
14. N. E. Galushkin, N. N. Yazvinskaya and D. N. Galushkin, *ECS Electrochem. Lett.*, 4 (2015) A94.
15. N. E. Galushkin, N. N. Yazvinskaya and D. N. Galushkin, *J. Electrochem. Soc.*, 162 (2015) A308.
16. N. E. Galushkin, N. N. Yazvinskaya, D. N. Galushkin and I. A. Galushkina, *Int. J. Electrochem. Sci.*, 10 (2015) 5530.
17. N. E. Galushkin, N. N. Yazvinskaya and D. N. Galushkin, *Int. J. Electrochem. Sci.*, 13 (2018) 1275.
18. N. E. Galushkin, N. N. Yazvinskaya and D. N. Galushkin, *J. Electrochem. Soc.*, 162 (2015) A2044.
19. N. E. Galushkin, N. N. Yazvinskaya, D. N. Galushkin and I. A. Galushkina, *Int. J. Electrochem. Sci.*, 10 (2015) 6645.
20. N. E. Galushkin, N. N. Yazvinskaya and D. N. Galushkin, *J. Electrochem. Soc.*, 164 (2017) A2555.
21. N. E. Galushkin, N. N. Yazvinskaya and D. N. Galushkin, *Int. J. Hydrogen Energy*, 41 (2016) 14813.
22. C. A. Vincent and B. Scrosati, *Modern batteries*, Butterworth-Heinemann, (2003) Oxford, UK.
23. T. R. Crompton, *Battery Reference Book*, Newnes, (2000) Oxford, UK.

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