Generalized Analytical Models of Batteries' Capacitance Dependence on Discharge Currents

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Global analytical correlation *C(i)* describing the dependency of released capacitance by the batteries at different discharge currents was suggested for nickel-cadmium batteries, which is true for batteries of any capacitance and any mode of discharge (H, M, L). The global correlation *C(i)* can be described by porous electrode equation, generalized Peukert's equations and probability integral with accuracy sufficient for practical application. This correlation is most easily described by the generalized Peukert's equation $C = C_m / (1 + (i / I_{C/2})^{3.6})$.

1. INTRODUCTION

Many empirical correlations have been obtained to describe the change of batteries' capacitance at different discharge currents. However, as a rule, empiric parameters included into these correlations depend upon many factors, such as battery capacitance, mode of its discharge, type of electrodes, etc. That is why it is necessary for calculation of batteries' capacitance to obtain all empiric parameters for each battery, which is extremely inconvenient in practice. Besides, these correlations 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 studies [1,2], based on the above program.

The goal of this manuscript was to obtain correlations that include only parameters with clear physical meaning or fundamental constants, which depend neither upon batteries' capacitance nor upon the modes of discharge. We review the most well-known empiric correlations for calculation of capacitance released by a battery at different discharge currents, particularly the following correlations:

Peukert's [3]

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

Liebenow's [4]

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

generalized Peukert's equations [5]

$$C = a0 + \frac{a1}{i} + \frac{a2}{i^2} + \frac{a3}{i^3} + \dots \quad , \tag{3}$$

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

where C is released capacitance and i is discharge current. Equations (1–3) were originally derived for lead-acid batteries, but presently they are also applied to determine the capacitance of other batteries [6]. Although many other formulas and methods to determine capacitance are available [7-9], they are either special cases of correlations (1–4) or their combinations.

Let us generalize Peukert's equation in such a way it shall not lead to a contradiction at small discharge currents. Hence we obtain the correlation

$$C = \frac{A}{1 + B \cdot i^n} \tag{5}$$

Empiric equation (4) is also one of the generalizations of Peukert's equation, because at large discharge currents it goes over to Peukert's equation, and at small currents it tends to be constant.

The process of battery discharge is a phase transition, and phase transitions are often described by a probability integral [10].

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

That is why we need to analyze this dependency also.

In [11-13], it was evidenced that one of the reasons for decrease in capacitance released by a battery at increasing discharge current is the decrease in electrochemical process penetration into porous electrode. The larger the discharge current, the steeper is the discharge current curve along the depth of a porous electrode, and the smaller portion of an electrode's active agent takes part in the process of discharge. At this case, the capacitance released by a battery decreases according to the following law.

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

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

In equations (1–7), *A, B, D, n, i_0, σ, a0, a1, a2*, etc., are empiric constants and C_m is maximal capacitance of a battery.

2. EXPERIMENTAL

Ni-Cd batteries (SAFT) of stationary application were used in the experiment. Discharging of batteries was performed up to the voltage of 1 V, because peripheral devices connected to the battery cannot function at lower voltages, and that is why the released capacitance at these lower values of voltage has no practical meaning. Charging of batteries was performed according to their operating manual.

In order to exclude the cross-impact of one charge-discharge cycle with another (through residual effects, memory effect, etc.), up to three training cycles were performed prior to changing discharge current. Battery capacitance obtained after every training cycle was compared to 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 batteries under study.

Three charge-discharge cycles were performed at each discharge current. If discharge capacitance did not differ greatly in those cycles (not more than 5%), the average value was taken as experimental discharge capacitance. Otherwise, training cycles were repeated as described above, and the experiment was repeated over again. Discharge was performed beginning with a constant discharge current of $0.1C_n$ (where C_n is nominal battery capacitance) to up to a point when the capacitance released by the battery was close to zero. For experimental results, see Figs. 1 to 3.
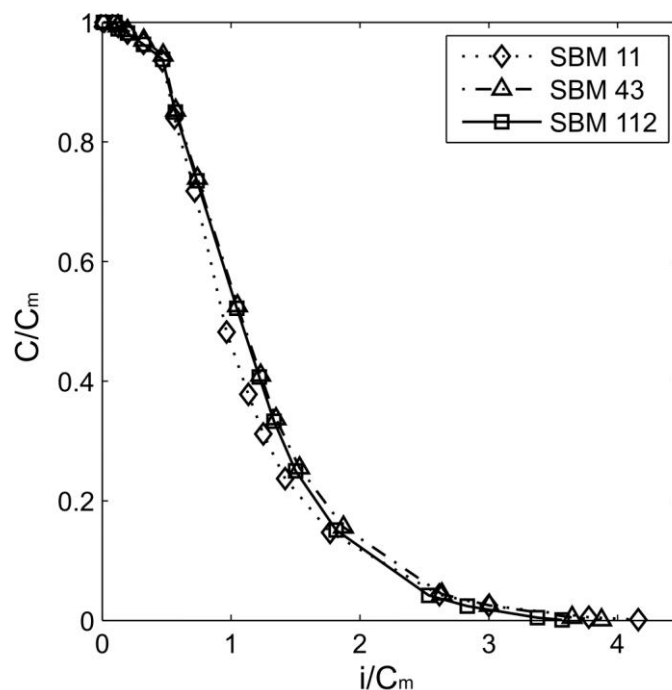
3. RESULTS AND DISCUSSION
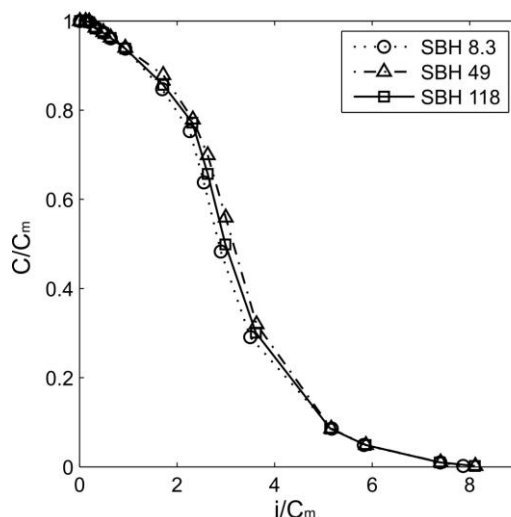
Figure 1. Dependencies of batteries capacitance of high discharge mode, from discharge currents. C_m – maximal capacitance of batteries
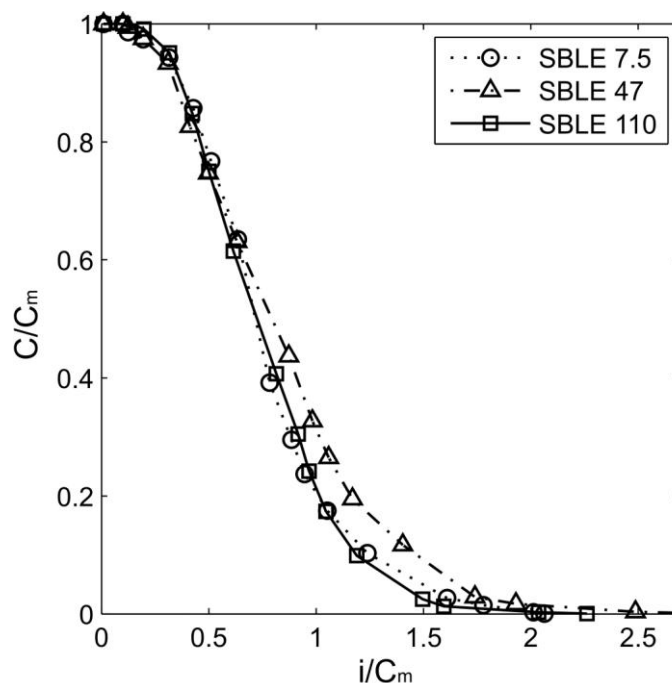
Figure 2. Dependencies of batteries capacitance of long discharge modes, from discharge currents. C_m – maximal capacitance of batteries

Figure 3. Dependencies of batteries capacitance of medium discharge modes, from discharge currents. C_m – maximal capacitance of batteries

Experimental data, shown in Figs. 1 – 3, are normalized on the maximal capacitance of batteries. The capacitance was obtained at discharge current of $0.1C_n$.

It was found that the cycling curves of a batch of nickel-cadmium batteries of the same type and of the same capacitance differed from one another by 4–6% and sometimes more. This is true for

batteries of any electrochemical system, and not only for nickel-cadmium. Thus, if the experimental data on maximal capacitance of the battery under study were normalized, it could be possible to exclude the above mentioned random factors from parameters of correlations (1-7) under study.

The curves (Figs. 1–3) coincide for the obtained experimental data within the limits of statistical error because their confidence intervals overlap, i.e. these curves are identical.

This fact unequivocally follows from the point that for all the batteries under study (of the same discharge mode) had same electrodes of pocket construction design and of a specific thickness. The difference among the batteries of different capacitance was only in the area and amount of electrodes. Hence, the parameters of any battery in the normalized coordinates shall be equivalent to the parameters of a battery of a unit capacitance having the same electrodes; consequently, all the curves of the type of Figs. 1–3 within the limits of statistical error shall coincide, as accurately in the experiment.

Table 1. Optimal parameters of empiric correlations (4–7)

Equation Parameters	batteries		
	SBH	SBM	SBLE
Generalized Peukert's equation (4)			
A	11.757	0.529	0.232
B	12.1	0.537	0.237
n	2.897	1.975	2.283
S^a	0.029	0.031	0.039
δ^b	4.573	5.672	7.94
Generalized Peukert's equation (5)			
A	0.978	0.997	0.993
B	8.429E-3	0.91	3.171
n	4.35	3.067	3.509
S	0.022	0.022	0.03
δ	3.568	4.169	6.14
Probability integral (6)			
A	1.001	1.08	1.056
i0	1.748	0.862	0.535
σ	3.03	1.019	0.722
S	0.025	0.033	0.032
δ	3.942	6.121	6.457
Equation of porous electrode (7)			
A	0.065	0.176	0.357
B	110.029	8.672	17.562
D	16.505	2.909	2.636
n	1.219	1.368	1.402
S	0.014	0.023	0.031
δ	2.168	4.193	6.236

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

Moreover, as pointed out earlier in the case of dividing battery characteristics by their maximal capacitance (obtained experimentally), the scatter with respect to battery manufacturing smoothes in many instances.

The correlations (1–3) cannot describe the experimental curves of Figs. 1–3 along the intervals of changing discharge currents. For correlations (1) and (3), the capacitance released by a battery tends to infinity at decreasing discharge current, which is devoid of physical sense. Besides, experimental curves are convex close to zero, but the correlations (1–3) give only concave curves (at positive values of all constants). That is why we shall first study the applicability of correlations (4–7) to describe the dependency of batteries' capacitance on discharge currents.

Since experimental curves for batteries of the same mode of discharge (in normalized coordinates) coincide (Figs. 1–3) within limits of statistical error, we shall find average optimal parameters for each of the correlations (4–7) using experimental data for all batteries of the same mode of discharge, according to the least square method with Levenberg–Marquardt optimization algorithm. The results are presented in Table 1.

It is evident from Table 1 that equations (4–7) show experimental data correctly at any discharge current with the relative error less than 7%, which is quite sufficient for practical purposes.

This is to say that the given equations correspond to the nature of discharge by electrochemical process in nickel-cadmium batteries and, consequently, are the most fundamental among all the considered correlations (1–7).

Thus, generalized Peukert's equations (4,5), porous electrode equation (7), and probability integral (6) for batteries of stationary application of the same mode of discharge describe the change of capacitance at different discharge currents with the same parameters.

However, empiric constants in correlations (4–7) differ for the batteries of different modes of discharge (Table 1). The electrodes of SBLE, SBM and SBH batteries with different modes of discharge differ primarily by thickness (active agents of pocket are the same for all batteries). Electrodes of SBLE batteries are the thickest, and of SBH batteries are the thinnest. Hence, it is possible to find the dependency of empirical constants of equations (4–7) on thickness of electrodes. However the resulting correlation shall be of little promise for practical use since it is not always simple to find electrode thickness or area of its surface for a particular battery in operation. It is much more promising to use the approach, which was originally applied for the generalization of empiric correlations (4–7), that is, to normalize discharge current by some value characteristic for SBLE, SBM, and SBH batteries. That is why we shall normalize discharge current by the current $I_{C/2}$ at which the batteries' capacitance is twice as small as their maximal capacity. This current is not difficult to obtain for practically any battery.

Normalization of released capacitance and discharge current of a battery by the maximal capacitance shall convert the study of a particular battery to the study of a battery with unit capacitance. Hence, in the normalized coordinates, all the batteries shall have the same function $C(i)$, under the condition that they have similar electrodes. If after that we normalize discharge current by the current $I_{C/2}$ at which the released capacitance is twice as small as the maximal capacitance, we shall convert the study of a particular battery to the study of a battery of unit capacitance, which releases capacitance equal to $C_m/2$ at the relative discharge current $I=i/I_{C/2} = 1$. In the coordinates normalized

in such a way for any SBLE, SBM, or SBH battery, the experimental curves *C(i)* shall coincide within the limits of statistical error of experiment, at least for the electrodes of one type and of the same manufacturing technology.

Let us verify the theoretical conclusions experimentally. The experimental data from Figs. 1–3 for SBLE, SBM, and SBH batteries in bi-normalized coordinates are shown in Fig. 4. In the figure, the curves coincide within the limits of statistical error, as their confidence intervals overlap, i.e. the curves are identical.
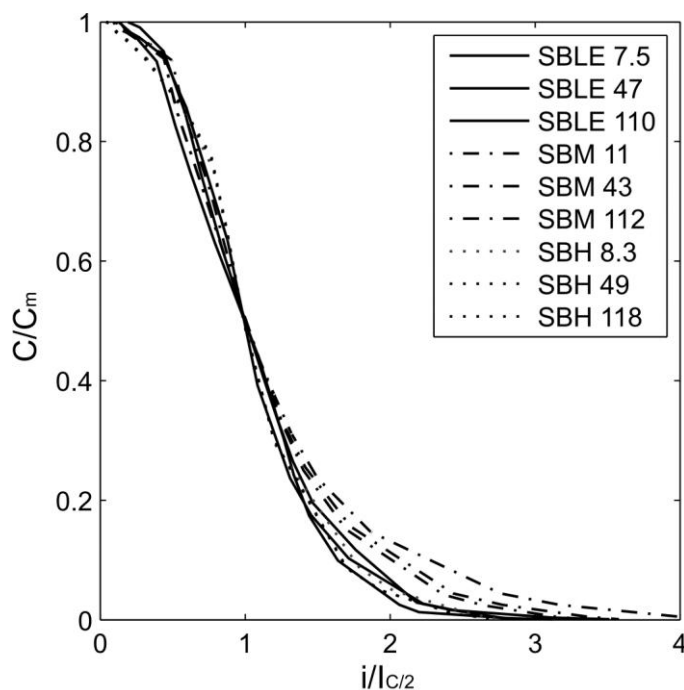
Figure 4. Dependencies of batteries capacitance from discharge currents. C_m − maximal capacitance of batteries; $I_{C/2}$ − discharge current at which the battery releases capacitance twice as small as the maximal capacitance of the battery

From Fig. 4, the biggest difference in experimental data at relative currents $I = i/I_{C/2}$ greater than unity is noted. At that, the data for SBH batteries with the thinnest electrodes and the data for SBLE batteries with the thickest electrodes coincide very well, and the data for batteries with electrodes of intermediary thickness are most different. It cannot be a regular tendency, as there are neither electrochemical nor physical reasons for extreme dependency. Such a discordance of experimental data can only be explained by statistical dispersion.

It is worth noting that data dispersion in cycling, as at Fig. 4, is typical even for a batch of batteries of one and the same type (e.g. SBM 43).

Let us identify the optimal parameters (according to least square method) for correlations (4–7) using experimental data in Fig. 4, separately for batteries of different discharge modes (H, M, L). See Table 2 for the results.

The last column of Table 2 shows the optimal parameters of correlations (4–7), using all experimental curves from Fig. 4 for the batteries of different discharge modes (H, M, L).

The correlations (4–7), obtained using experimental data for the batteries of any discharge mode (H, M, L) and any capacitance (see Table 2 last column), have the relative error of 5–7%. It is a typical relative error for any type of empiric curves of batteries obtained using experimental data.

Table 2. Optimal parameters of empiric correlations (4–7) (experimental data normalized by maximal capacitance of batteries, C_m, and discharge current, $I_{C/2}$)

Equation parameters	batteries			
	SBLE	SBM	SBH	Mean values
Generalized Peukert's equation (4)				
A	0.464	0.504	0.499	0.496
B	0.477	0.514	0.516	0.511
n	2.336	2.029	2.936	2.380
S	0.037	0.026	0.026	0.036
δ	8.047	5.045	4.305	6.77
Generalized Peukert's equation (5)				
A	0.987	0.994	0.974	0.982
B	1.093	0.985	0.964	0.991
n	3.581	3.133	4.411	3.636
S	0.026	0.015	0.019	0.027
δ	5.512	2.845	3.183	5.079
Probability integral (6)				
A	1.067	1.095	0.997	1.042
σ	0.724	0.844	0.575	0.715
i0	0.964	0.976	1.018	1
S	0.023	0.027	0.023	0.028
δ	4.876	5.233	3.825	5.398
Porous electrode equation (7)				
A	0.255	0.194	0.243	0.246
B	20.433	10.408	117.292	27.166
D	3.804	3.045	5.586	4.172
n	1.364	1.314	1.206	1.28
S	0.026	0.016	8.25E-3	0.026
δ	5.511	3.21	1.365	4.958

Thus, it is experimentally proved that for nickel-cadmium batteries there is a global empiric dependency *C(i)*, which is true for batteries of any capacitance and any mode of discharge. The simplest way to express this dependency is the generalized Peukert's equation (5)

$$C = \frac{C_m}{1 + \left(\dfrac{i}{I_{C/2}}\right)^{3.6}},$$

as $A \approx B \approx 1$ (Table 2), C_m is maximal capacitance of batteries, and $I_{C/2}$ is discharge current at which the battery releases capacitance twice as small as the maximal capacitance, C_m, of battery.

Now let us examine the applicability of Peukert's equations (1,3) and Liebenow's equation (2) for the given batteries. The correlations (1–3) give concave curves (at positive meanings of all constants). Experimental curves are concave only starting the point of inflexion of *C(i)* curve and up to infinity (Fig. 4). Let us examine the applicability of correlations (1–3) in the given area. The point of inflexion of *C(i)* curve is approximately at the value of discharge current $i = I_{C/2}$ (Fig. 4). The Peukert's equations (1,3) correspond well to experimental data; within the interval of discharge currents from $i = I_{C/2}$ and till the biggest currents used in our experiment, the relative error is 7% and 9%, correspondingly (Table 3). That is why only this area can be regarded as the domain of applicability of correlations (1) and (3). In this regard, we note that in the article [14], 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.

Table 3. Optimal parameters of empiric correlations (1–3) for discharge currents from $i = I_{C/2}$ and till the biggest currents used in our experiment

Equation parameters	batteries			
	SBLE	SBM	SBH	Mean values
Peukert's equation (1)				
A	0.709	0.598	0.494	0.532
n	3.278	2.613	3.18	2.772
S	0.017	0.018	0.016	0.022
δ	6.638	7.032	6.378	9.072
Liebenow's equation (2)				
A	-0.063	-0.146	-0.116	-0.169
B	-0.965	-1.172	-1.237	-1.318
S	0.03	0.035	0.041	0.05
δ	12.17	13.96	16.416	20.05
Generalized Peukert's equation (3)				
a0	0.067	0.003	0.024	0.007
a1	-0.564	-0.202	-0.372	-0.269
a2	1.065	0.775	0.837	0.784
S	0.014	0.012	0.006	0.020
δ	5.558	4.974	2.029	7.024

Liebenow's equation has the relative approximation error of 20% (Table 3). Thus, Liebenow's equation cannot be used for the evaluation of the capacity of alkaline batteries in the given area.

Liebenow's equation (2) was proposed for the calculation of released capacitance at low discharge currents [4]; however, in this area it does not correspond to experimental data even qualitatively. In the area of small discharge currents, the experimental curves are convex (Fig. 4), but the correlation (2) plots concave curves. Liebenow's equation can be used, only in a small range of discharge currents starting from the inflection point of the curve C (i) [2]

4. CONCLUSIONS

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

Generalized Peukert's equation (4),

$$C(i) = C_m \frac{A}{(i/I_{C/2})^n} th\left(\frac{(i/I_{C/2})^n}{B}\right), \quad A=0.464, \quad B=0.477, \quad n=2.336, \quad (8)$$

Probability integral (6),

$$C(i) = C_m \frac{A}{2} \cdot erfc\left(\frac{(i/I_{C/2} - i_0)}{\sigma}\right), \quad A \approx 1, \quad \sigma = 1, \quad i_0 = 0.715, \quad (9)$$

Porous electrode equation (7),

$$C(i) = \frac{C_m(1 - A(i/I_{C/2})^n)}{1 + B \cdot H(i/I_{C/2})}, \quad A=0.246, \quad B=27.166, \quad D=4.172, \quad n=1.28, \quad (10)$$

where

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

Generalized Peukert's equation (5)

$$C(i) = \frac{C_m A}{1 + B \cdot (i/I_{C/2})^n}, \quad A \approx 1, \quad B \approx 1, \quad n=3.636. \quad (11)$$

The above equations are applicable for the batteries of any capacitance and any discharge mode. For practical application of the above equations, it would suffice to know only two parameters of a particular battery: C_m and $I_{C/2}$. It is possible to obtain the maximal capacitance of a battery by discharging the battery with small currents, normally $i = 0.1C_n$. Current $I_{C/2}$ is possible to obtain by the results of yet another discharge (at quite large discharge currents), as there is only one unknown parameter $I_{C/2}$ in correlations (8–11). The relative error at capacitance evaluation using the correlations (8–11) equals 5–7%, 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 (8–11). Thus, this correlation is the best to reflect electrochemical processes taking place at discharge of nickel-cadmium batteries.

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.

References

1. N.E. Galushkin, N.N. Yazvinskaya, and D.N. Galushkin, *J. Electrochem. Soc*., 159, (2012) A1315
2. N.E. Galushkin, N.N. Yazvinskaya, and D.N. Galushkin, *Int. J. Electrochem. Sci.,* 9 (2014) 1911
3. H. Wenzl, in: J. Garche (Ed), *Encyclopedia of Electrochemical Power Sources, vol. 1*, Elsevier, Amsterdam (2009)
4. N.F. Compagnone, *J. Power Sources,* 35 (1991) 97
5. J. Garche (Ed), *Encyclopedia of Electrochemical Power Sources, Elsevier, Amsterdam* (2009)
6. M. Dubarry and B.Y. Liaw, *J. Power Sources,* 104 (2009) 541
7. L.H. Saw, K. Somasundaram, Y. Ye, A.A.O. Tay, *J. Power Sources*, 249 (2014) 231
8. S. M. Rezvanizaniani, Z. Liu, Y. Chen and J. Lee, *J. Power Sources*, 256 (2014) 110
9. G. Pilatowicz, H. Budde-Meiwes, D. Schulte, J. Kowal, Y. Zhang, X. Du, M. Salman, D. Gonzales, J. Alden, and D. U. Sauer, *J. Electrochem. Soc.,* 159 (2012) A1410
10. L.P. Pitaevskii, E.M. Lifshitz, *Physical Kinetics*. Vol. 10, Pergamon Press, Oxford, (1981) 522
11. N.E. Galushkin and Y.D. Kudryavtsev, *Russian journal of electrochemistry,* 30 (1994) 344
12. N.E. Galushkin and Y.D. Kudryavtsev, *Russian journal of electrochemistry,* 33 (1997) 559
13. N.E. Galushkin, *Portugaliae Electrochimica Acta*, 14 (1996) 279
14. A. Hausmann, C. Depcik, *J. Power Sources*, 235 (2013) 148