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Cell testing by calculated discharge curve method

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Abstract

The actual discharge curve of a primary or secondary cell is a set of measurements: voltage vs. time, from which the cell/battery characteristics may be determined as well as the family of Calculated Discharge Curves. In addition to the experimental measured discharge curve, the cell relaxation curve is needed. A Calculated Discharge Curve Method (CDCM) was developed to improve discharge curve monitoring and cell characterization. A Calculated Discharge Curve Algorithm (CDCA) was used to generate Calculated Discharge Curves. The Algorithm procedure is presented. Alkaline manganese cell LR 20-VARTA, load 10 Ω, was used for demonstration of the method. The mathematical calculations were conducted on an IBM personal computer using Symphony software.

Keywords: Galvanic cell; Discharge curve; Relaxation curve; Energy balance; Cell overvoltage

1. Introduction

Cell/battery testing is based on an extensive series of discharges of a large number of individual samples. The various discharges as well as cell/battery simulations are needed to provide for successful research and development, production and reliable exploitation of a cell type [7].

The goal of this work is to improve cell testing by treating the cell discharge as a change of cell state from the initial to the final one due to continuous partial or full discharge. Both the discharge curve, followed by the relaxation path of cell, determine the overall path of cell change. Data acquisition procedures may be simplified and more complete experimental data processing provided. This requires that cell voltage should be monitored during on-load as well as during off-load periods, and both of these two voltage paths are used to calculate cell extensive and intensive properties.

A discharge curve is the principal exploitation characteristic of a cell. It may be treated as the electrochemical system response to a passive or active (current or voltage) load. A constant resistive load was chosen as the most benign operating mode in this study.

During continuous discharge of a cell, the operating voltage (V_i) departs from the initial open-circuit voltage (U^{o}). This departure [1] is termed the cell discharge overvoltage: $\eta_i^{\mathrm{o}} = (U^{\mathrm{o}} - V_i)$. During the subsequent relaxation a cell recovery voltage (U_{r}) is observed above the cutoff voltage (V_{cutoff}). At the end of relaxation the maximum value of $U_{\mathrm{r},t \to \infty}$ should be achieved. The difference between this value and the discharge cutoff voltage is termed the cell overvoltage: $\eta_i = (U_{\mathrm{r},t \to \infty} - V_{\mathrm{cutoff}})$. Both of these overvoltages are experimental facts, and at any state of discharge there is a difference between the two values. Simultaneously, the energy delivered as the useful work is related to capacity withdrawn, and a departure of this value from the cell open-circuit voltage was named the cell energy to capacity overvoltage: $\eta_{E/C,i} = (U^{\mathrm{o}} - E_i/C_i)$, which is an experimental fact, too.

In this paper, the term ''cell'' denotes a standard type vessel, i.e., a designed monoblock container which contains cell structural components. The two electrical terminals connect the self-driving cell to an external load, usually by a switch, whose characteristics need to be known. A cell box may be defined as a physicochemical,

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thermodynamical, and electrochemical system as well as closed, but not a batch reactor. A cell being discharged generates electrical [3] work on load resistor as well as heat inside the system. The generated heat accumulates inside the box and, at thermal steady state, should be dissipated by the wall's surface heat flux to the environment. The useful electrical work is a measurable extensive property. If a cell being discharged is placed into an adiabatic or flux calorimeter, the energy loss as dissipated heat may be measured.

The dependence of discharge time (i.e., the cell service life, its principal exploitation characteristic) on discharge voltage has been investigated [8,9,11] using the ''power of cell discharge overvoltage'' [2,12] instead of discharge voltage. The set of discharge voltage values $V_i = U^o - i\Delta V = \Delta V(n-i)$, $U^o > V_i \geq V_{final}$, was formed by dividing the closed interval: $U^o - V_{final}$ into $i = 1 \dots n$ steps. The set of discharge voltage values is mapping the set of power of cell initial overvoltage: $P_i = (U^o - V_i)I_i$, $i = 1 \dots n$. The set $P^o > P_i > P_{final}$ depends on U^o value, instead of which the estimated U value should be used. This U value must be selected from the initial instantaneous voltage drop interval: $U^o - V_i$, i.e., $U^o \geq U > V_o$.

The use of a set of power of cell discharge overvoltage values as independent variable enables the formulation of a differential equation: $\mathrm{d}Y/Y = b\mathrm{d}P/P$. The differential equation was solved [9,11] by an iterative procedure using the known initial, boundary, and final conditions. The iterative procedure enables the voltage evolution of all the cell characteristics (denoted by Y), i.e., time, cell capacity, energy on load resistor, cell energy losses as well as cell overvoltages and their components, and was named the ''Calculated Discharge Curve Algorithm (CDCA)''. Cell characteristics which were generated by CDCA are termed ''Calculated Discharge Curves (CDC)''. CDCA entering data may be observed by cell standard, non-destructive, accelerated and by the other testing techniques, to meet a user's requirements.

In addition, the ''Calculated Discharge Curve Method (CDCM)'' may be performed as a cell simulation methodology, generating cell discharge curves from the known initial conditions and having regard to defined discharge time, capacity, energy on load resistor or energy losses. CDCM simulations may be an addition to the fundamental cell simulation [10,13] as well as to cell energy balance calculations [12].

2. Discharge and relaxation curve

The discharge of a cell may be represented by the discharge curve, i.e., operating voltage vs. time during on-load period, followed by an off-load relaxation of the cell system, i.e., the relaxation curve.

2.1. Discharge curve

The cell discharge curve is a set of pairs: measured voltage vs. time. The cell open-circuit voltage (U^o) is the highest cell voltage value, i.e.:

$$U^o > V_i \geq V_{cutoff} \geq V_{final} = V_n \qquad (1)$$

where V_{cutoff} is the discharge interrupted voltage, V_{final} is the lowest device operating voltage, and $i = 1 \dots n$ is the number of pairs.

A cell undergoing periodic discharge may be denoted by:

$$U^o > U_j^o > V_{j,i} \geq V_{j,cutoff} > V_{final} \geq V_n \qquad (2)$$

where $j = 1 \dots m$ is a number of discharge periods.

2.2. Relaxation curve

A cell discharging is accompanied by charge, mass, and heat transport, and is followed by a relaxation, i.e., mass and heat transport processes, which take place due to the fact that the system tends to a new equilibrium state. A cell relaxation voltage may be monitored and noted as a set:

$$V_{cutoff} < U_{r,o} < U_{r,t} < U_{r,t\to\infty} = U_n \qquad (3)$$

where $U_{r,o} - V_{cutoff}$ is the instantaneous voltage rise, $U_{r,t}$ are the measured relaxation voltages, and $(U_{r,t} - U_{r,t-1}) \to 0$ shows that a new open circuit state is achieved, i.e., U was denoted by U_n. During a continuous discharge, the initial (U^o) as well as the final (U_n) cell open-circuit voltage may be measured. The existence of a set: $U^o > U_i > U_n$ must be proposed due to the facts that (1) a reversible path between two states of the cell is one that connects a continuous series of equilibrium states and (2) a cell discharge interruption at any moment (t_i, V_i) during discharge will be finished by a relaxed new open-circuit state. There are experimental observations of the U_i values [6] as well as other experimental ways [9,10,12] to define the immeasurable [2] cell open-circuit set during continuous discharge of a cell under defined conditions. It is instructive to note that both the relaxation process and the open-circuit state depend on the previous discharging regime as well as on the overall cell history.

2.3. Capacity and energy on load resistor

The available, nominal or rated capacity of a cell is usually used as its exploitation characteristic. All of these capacities are related to the theoretical coulombic storage density, which can be calculated from the formula weight, the faradaic efficiency and cell volume. There may be assumed that the cell coulombic storage will not be withdrawn at all due to the transport limitations of reactants from the unreacted region of the porous electrode to the reaction zone. The capacity per cell actually withdrawn during discharge (calculated by summation) needs to be used to analyze the energy on load resistor and the energy losses for a particular cell characterization. The cell capacity and energies depend on the cell characteristics at the time of use, the applied discharge mode and the environment conditions such as ambient temperature, as well as other conditions.

The useful electrical work, which is available on a load resistor, may be calculated by summation using time or capacity steps:

$$E_i = \sum_1^n I_i V_i (t_i - t_{i-1}) = \sum_1^n V_i (C_i - C_{i-1}) \tag{4}$$

Eq. (4) may be rearranged and the actual discharge voltage may be expressed as a cell energy to capacity change relation:

$$V_i = (E_i - E_{i-1})/(C_i - C_{i-1}) \tag{5}$$

2.4. 3D discharge curve

Galvanic cells are characterized by their discharge voltage, current, and service life, all of which are interrelated. This interrelation may be represented by a 3D discharge curve in a volume:

time − current − voltage

3D discharge curve can be considered as a set of points produced by a continuous transformation of a closed interval: $\Delta V - \Delta I - \Delta t$, and alternatively, it can be regarded as the path of a moving point. The electrochemical methods can be classified by the parameter controlled (cell voltage: $V = f(t)$ or current, $I = f(t)$) and by the quantities actually measured or calculated. The considerations employed in bulk electrolysis methods [13] are applicable to self-driving cell continuous discharge across a constant resistive load due to the CDCM calculations of a cell's intensive and extensive characteristics.

3. Calculated discharge curve

If a cell voltage has been measured during four possible states of a galvanic cell:

–initial equilibrium state: open-circuit voltage (U^o),
–during discharge: initial voltage drop (V_o) followed by voltage delay (V_{vd}) and discharge voltage (V_i) to the cutoff voltage (V_{cutoff}),
–during relaxation: instantaneous voltage rise after switch-off, ($U_{r,o} - V_{cutoff}$) followed by relaxation voltage ($U_{r,t}$), to the new equilibrium state, and
–final equilibrium state: open-circuit voltage (U_n), a typical discharge profile would be completed:

$$U^o > V_o > V_{vd,i} > V_i > V_n = V_{cutoff} < V_{r,o} < V_{r,t} < U_n \tag{6}$$

which governs a cell from the initial to the final state. When a cell is considered in two different states, the difference in any property between the two (quasi)equilibrium states depends solely on those states themselves, and not in the way in which the cell may pass from one state to other.

3.1. Cell overvoltages

The complete cell discharge profile shows (1) the departure of the cell operating voltage (V_i) and (2) the departure of the energy on load resistor to capacity relation (E_i/C_i) from the initial open-circuit voltage (U^o), and (3) the departure of the cell open-circuit voltage (U_i) from the operating voltage (V_i), which is not measurable during the continuous cell discharge, while U^o and U_n are experimentally observed values.

3.1.1. Cell discharge overvoltage

The cell discharge overvoltage (η_i^o) represents the departure of the cell operating voltage (V_i) from the cell initial open-circuit voltage (U^o) due to continuous current flow:

$$\eta_i^o = U^o - V_i = \sum_1^i \Delta V_i \tag{7}$$

The discharge overvoltage (η_i^o) is equal to the sum of cell operating voltage drops. One can imagine that a cell's actual irreversible state as well as the corresponded new equilibrium state depend on both the cell initial state and the applied discharge mode. CDCM recognizes that at any moment during discharge the power of cell internal resistance $I_i \eta_i^o = I_i(U^o - V_i)$ is lower than the sum of cell power losses on load resistor: $\sum_1^i I_i \Delta V_i$, $i = 1 \dots i$. If a relaxed cell is discharged during a short period, the departure of a cell irreversible from the cell reversible state could be negligible.

3.1.2. Cell energy to capacity overvoltage

By substituting Eq. (5) into Eq. (7) we obtain:

$$\eta_i^o = U^o - (E_i - E_{i-1})/(C_i - C_{i-1}) \tag{8}$$

which express a cell energy balance during interval: $\Delta C_i = I_i \Delta t_i$.

The summation across the discharge interval ($i = 1 \dots i$) gives the cumulative cell energy balance: $E_i + E^o_{int,i}$, where $\eta_i^o(C_i - C_{i-1})$ is equal to ($E^o_{int,i} - E^o_{int,i-1}$), from which the cell energy to capacity overvoltage is defined:

$$\eta_{E/C,i} = U^o - E_i/C_i = E^o_{int,i}/C_i \tag{9}$$

The cell energy to capacity overvoltage ($\eta_{E/C,i}$) is the calculable value during a continuous discharge. In a cell during the continuous discharge through an infinite load resistor the discharge may be considered as reversible one. The cell voltage is therefore always the near equilibrium value, i.e., $I_i \to 0$ and $E^{o}_{\mathrm{int},i} \to 0$. Simultaneously, the cell energy to capacity relation may be defined as a function of discharge voltage, current, and time:

$$E_i/C_i = [E_{i-1} + (t_i - t_{i-1}) I_i V_i]/[C_{i-1} + (t_i - t_{i-1}) I_i] \tag{10}$$

Eq. (10) may be rearranged to express discharge time as a function of cell current, voltage, capacity and energy on load resistor:

$$t_i - t_{i-1} = [E_{i-1} - (E/C)_i C_{i-1}]/[(E/C)_i I_i - I_i V_i] \tag{11}$$

where the sequences: $V_i = U^{o} - i\Delta V$ and $I_i = V_i/R_1$, $i = 1 \dots n$, were determined across the discharge interval. In such a way, the set: $U^{o} > (E/C)_i \geq (E/C)_n > V_n$ appears as a discharge variable.

3.1.3. Cell relaxation overvoltage and cell overvoltage

The cell relaxation curve, $V_{\mathrm{cutoff}} < U_{\mathrm{r},t} \leq U_{\mathrm{r},t\to\infty} = U_n$, defines the cell recovery overvoltage:

$$\eta_t = U_{\mathrm{r},t} - V_{\mathrm{cutoff}} \tag{12}$$

where index t denotes relaxation time, and V_{cutoff} denotes the interrupted voltage. At the end of the relaxation, $\Delta\eta_t = 0$, the new cell open-circuit state is achieved, and $U_{\mathrm{r},t\to\infty} = U_n$ may be measured to obtain the cell overvoltage, η_n:

$$\eta_n = U_n - V_{\mathrm{cutoff}} \tag{13}$$

The existence of a set: $[\eta_{\mathrm{o}} = U^{o} - V_{\mathrm{o}}] < [\eta_i = U_i - V_i] < [\eta_n = U_n - V_{\mathrm{cutoff}}]$, i.e., a set of the actual immeasurable cell open-circuit voltage: $U^{o} > U_i > U_n$, should be attributed to theoretical consideration as well as to experimental facts. Eq. (8) may be rewritten using cell overvoltage: $\eta_i = U_i - V_i$ instead of cell discharge overvoltage: $\eta^{o}_i = U^{o} - V_i$, i.e.,

$$\eta_i = U_i - (E_i - E_{i-1})/(C_i - C_{i-1}) \tag{14}$$

The summation across the discharge interval $(i = 1 \dots i)$ gives the cumulative cell energy balance: $E_i + E_{\mathrm{int},i}$, where $\eta_i(C_i - C_{i-1})$ is equal to $(E_{\mathrm{int},i} - E_{\mathrm{int},i-1})$. A cell may be measured in the microcalorimeter $(E_{\mathrm{cal},i})$ while being discharge through a resistive load. In this way, there are tree sets: $E^{o}_{\mathrm{int},i}$, $E_{\mathrm{int},i}$, and $E_{\mathrm{cal},i}$ of a cell's energy losses, which may be analyzed.

3.1.4. Cell overvoltage components

There is a possibility to decompose a cell overvoltage into its components:

$$\eta_i = \sum_{1}^{x} \sum_{1}^{y} \eta_{y,i} \tag{15}$$

where x denotes the cell structural component (anode, separator, cathode, etc.), and y denotes the overvoltage's component (ohmic, reaction, diffusion, etc.). The power of cell overvoltage or its component is defined by:

$$P_{x,y,i} = \eta_{x,y,i} I_i \tag{16}$$

The CDC Algorithm may generate the sequence of $P_{x,i}$, $i = 1 \dots n$, starting from the known initial-value: $P_{x,y,\mathrm{o}} = \eta_{x,y,\mathrm{o}} I_{\mathrm{o}}$, through the discharge interval, to the final-value: $P_{x,y,n} = \eta_{x,y,n} I_n$.

3.2. Calculated discharge curve algorithm

An algebraic curve may be expressed symbolically as $Y = f(X)$. If the curve is a monotonic increasing one, a small enough segment of curve may be linearized:

$$Y_i - Y_{i-1} = (\Delta Y/\Delta X)(X_i - X_{i-1}) \tag{17}$$

where $\Delta Y = Y_i - Y_{i-1}$ and $\Delta X = X_i - X_{i-1}$. Eq. (17) may be divided by Y_{i-1} to obtain:

$$(Y_i - Y_{i-1})/Y_{i-1} = (\Delta Y X_{i-1}/\Delta X Y_{i-1})(X_i - X_{i-1})/X_{i-1} \tag{18}$$

If $\Delta X \to 0$ and $\Delta Y \to 0$ the next form should be obtained:

$$\mathrm{d}Y/Y_{i-1} = (\mathrm{d}Y/Y_{i-1})(\mathrm{d}X/X_{i-1})/(\mathrm{d}X/X_{i-1}) \tag{19}$$

Eq. (19) is a simple form of an ordinary differential equation.

Its solution is:

$$Y_i = Y_{i-1}(X_i/X_{i-1})^{b_{y,i}};$$
$$b_{y,i} = \ln(Y_i/Y_{i-1})/\ln(X_i/X_{i-1}) \tag{20}$$

The calculation of the unknown Y_i value from the known values to ith step was solved by introducing integration constant, k_y as follows:

$$b_{y,i} = \ln(Y_{i-2}/Y_{i-1})/\ln(k_y X_{i-2}/X_{i-1}) \tag{21}$$

The integration constant k_y is valid across the discharge voltage interval: $U^{o} > V_i \geq V_{\mathrm{cutoff}}$. The power of cell discharge overvoltage must be used as the independent variable:

$$X_i = P_i = (U - V_i) I_{ii} \tag{22}$$

where U-value must be selected from the interval: $U^{o} \geq U > V_{\mathrm{o}}$.

Eqs. (20)–(22) should be used to generate discharge time (t_i), cell capacity (C_i), energy on load resistor (E_i), cell energy losses $(E^{o}_{\mathrm{int},i})$, and power of cell's overvoltage $(P_{\mathrm{cell},i})$ or its components $(P_{x,i})$. The initial conditions $Y_{1,2}$ vs. $X_{1,2}$, must be known to initiate the CDCA iterative procedure.

3.3. Derived discharge curve

Derived discharge curve is a set of numerical differential:

$$(\Delta V/\Delta Y)_i = (V_i - V_{i-1})/(Y_i - Y_{i-1}) \tag{23}$$

where Y may be time, capacity, energy on load resistor or energy losses. One can find initial $(\Delta V/\Delta Y)_o$, boundary $(\Delta V/\Delta Y)_{max}$ and final $(\Delta V/\Delta Y)_{final}$ conditions for differential Eq. (20). If the several or more subsequent enough precise readings give the same value of discharge voltage: $V_{i\ldots(i+k)}$ vs. $t_{i\ldots(i+k)}$, $1 \leq k < n$, $\Delta t =$ constant, i.e.: $(\Delta V/\Delta t)_{i\ldots(i+k)} = 0$, the steady state discharge process of a galvanic cell as the closed or isolated electrochemical system, must be recognized. Since the cell state-of-charge is changed during the discharge it is more exact to recognize the transient or quasi steady state instead of steady state conditions. The CDC Algorithm is based on the conclusion that: (1) $(\Delta V/\Delta t)_i < 0$, $i = 2\ldots n$; (2) $(\Delta V/\Delta t) = (\Delta V/\Delta t)_{inflection\ point} = (\Delta V/\Delta t)_{max}$, i.e., the second derivative is equal to zero; and (3) a discharge voltage scale may be formed using $\Delta V =$ constant or $V_i = f[U, R_1, V_o, V_n, i, n]$.

3.4. Calculated discharge curve method

The CDCM is governed by both discharge and relaxation curves. The cell starts from the initial state and being discharged to cutoff voltage $(V_{cutoff} \geq V_{final})$ and than relaxed to the final state. The both states may be characterized by Complex Impedance Analysis [4–7] as well as by the electrochemical techniques [7] by which the change of a cell state-of-charge is negligible. It is the CDC Algorithm which generates the set of the immeasurable characteristics of the self-driving galvanic cell during a continuous discharge and across the closed discharge interval: $U^o > V_i > V_{cutoff}$. Also, it is instructive to express the power of a cell overvoltage in the form:

$$(\Delta G_{reaction}/nF - \Delta E_i/\Delta C_i)\Delta E_i/(\Delta C_i R_1) = P_{E/C,i-1}(P_i/P_{i-1})^{b_i} \quad (24)$$

where $b_i = \ln(P_{E/C,i-2}/P_{E/C,i-1})/\ln(k_y P_{i-2}/P_{i-1})$. The analogous equation may be formulated by both cell open-circuit and operating voltage set [2], page 40, $i = 1\ldots i$:

$$(U_i - V_i)I_i = P_{cell,i-1}(P_i/P_{i-1})^{b_i} \quad (25)$$

where $b_i = \ln(P_{cell,i-2}/P_{cell,i-1})/\ln(k_y P_{i-2}/P_{i-1})$ and the set of $U_{1\ldots n}$ is immeasurable, but calculable by CDCA. The basic of CDCM is that the cell enthalpy change is the driving force of a cell discharge, i.e., the bulk electrolysis occurs without the use of an external power supply. If a cell discharge is controlled either by voltage or current, Eqs. (20)–(22) become more simply. If the CIA should be used to determine the cell impedance characteristics at the both initial and final equilibrium states Eq. (25) gives the set: $\eta_o I_o < \eta_i I_i < \eta_n I_n$, $i = 1\ldots n$, where η_i is defined by Eq. (15). If there is a line-graph of a discharge curve, it may be discretized either by $\Delta t = t_{end}/n$ (and used to simulate the discharge curve: $V_i = f[t_{1\ldots i}, U, R_1, V_{1\ldots(i-1)}, i, n]$) or by $V_i = f[U, R_1, V_o, V_n, i, n]$ steps to obtain the sets of pairs voltage vs. time or time vs. voltage, respectively. Digital simulations of electrochemical problems [13] uses Δt step. CDC Algorithm uses ΔV_i steps to generate discharge time as well as the other extensive and intensive properties. Eqs. (24) and (25) are valid for an ideal galvanic cell being discharge. A real galvanic cell must be treated as the sum of elementary volumes in accordance to the cell model [12,13]. A calorimeter may be used to determine a cell energy losses and experimental data may be compared with the results of CDCA calculations. Since the purpose of this article is to demonstrate the CDCA generations of the discharge time, a further analysis of Eqs. (24) and (25) belong to the CDCM progress.

4. Experimental

The demonstration of CDC Method may be performed by monitoring cell operating voltage and heat generation during a cell continuous discharge as well as by determination of cell impedance characteristics at the initial state, during relaxation and at the final state. The demonstration in this article, is given to enable the reader to see how CDC Algorithm have been put into practice using any experimentally observed set of pairs: voltage vs. time. Alkaline manganese cell LR 20-VARTA [8] was discharged continuously through constant load 10 Ω at room temperature, to the cutoff voltage, $V_{cutoff} = 0.8$ V. An HP 3054 DL computer was used to determine and record discharge voltage as a function of time. The following pairs were recorded: (1) the short-time discharge, $1 < i <$

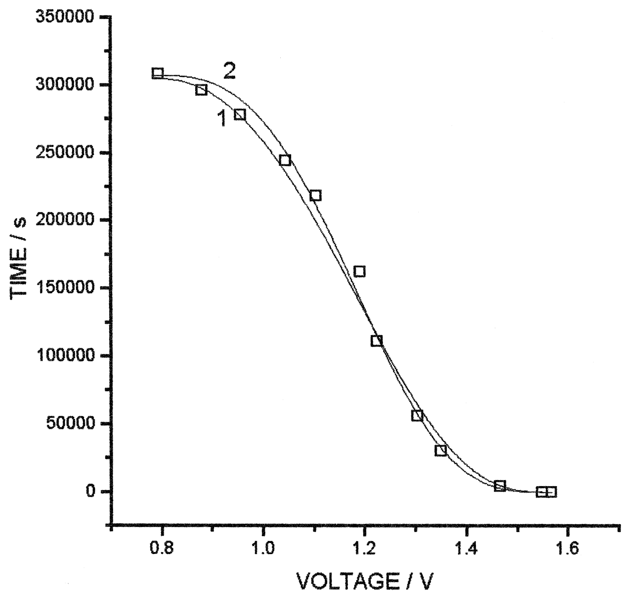

Fig. 1. Time vs. discharge voltage, V_i, LR 20-VARTA, $R_1 = 10$ Ω. $U^o = 1.5905$ V, Symbols, experimental discharge voltage, V_i, $i = 16$, 17, 49, 96, 114, 146, 159, 194, 218, 253, 283, 318, Curve 1-line, generated, t_g (s) by Eqs. (26) and (27), $k = 0.9999800$, $P_i = (1.5898 - V_i)I_i$, Curve 2-line, generated, t_c (s) by Eqs. (11) and (28), $k_{E/C} = 0.9999845$, $P_i = [1.5905 - V_i]I_i$.

20, $\Delta t = 1$ s, and (2) the period to the end of discharge, $21 < i < 150$, $\Delta t = 2160$ s. The derived discharge curve, calculated by the recorded data, is not a smooth curve due to (1) the imprecise voltage readings at very beginning because of the mercury relay was used to close the circuit over the period 0.1–0.3 s and across the discharge interval due to (2) the small resolution (5×10^{-5} V) of the voltage readings. One can note that the dimensions of the derived discharge curve (V/s) is identical to the dimensions of voltage reading resolution (V) multiplying by frequency of readings (1/s).

Both the precision of measurement for a voltage range and the frequency of readings (usually constant) are the technical characteristics of an automatic checking system for cells. The voltage reading resolution may be treated as the voltage step (by which the discharge interval may be divided) at which the discharge time may be determined. In this case the frequency of reading is changing in accordance to the profile of the discharge curve. In the vicinity of the discharge curve inflection point $(\Delta V/\Delta t)_{max}$, $(\Delta V/\Delta t)_i$ tends to zero. If the voltage reading resolution is greater then the cell voltage change is, the two subsequent readings should give $\Delta V/\Delta t = 0$. Eqs. (20) and (22) may be used if there is no $\Delta V/\Delta t = 0$. Because of that the twelve pairs were selected from the discharge curve [cf. Ref. [8], Fig. 1] to represent the overall discharge curve, see the symbols in Figs. 1 and 2. The random selection of the pairs: V_x vs. t_x, $1 < x \geq 6$, across

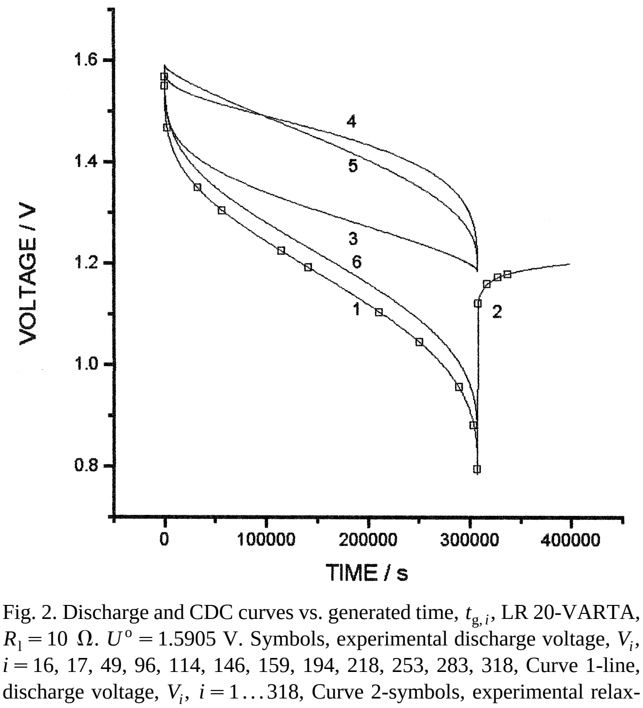

Fig. 2. Discharge and CDC curves vs. generated time, $t_{g,i}$, LR 20-VARTA, $R_l = 10\ \Omega$. $U^o = 1.5905$ V. Symbols, experimental discharge voltage, V_i, $i = 16$, 17, 49, 96, 114, 146, 159, 194, 218, 253, 283, 318, Curve 1-line, discharge voltage, V_i, $i = 1 \dots 318$, Curve 2-symbols, experimental relaxation voltage, $U_{r,t}$, Curve 2-line, relaxation voltage, $U_{r,t}$, $U_{r,t} = 1.011(t_r - 308160)^{0.015}$, Curve 3-line, energy to capacity relation: E_i/C_i set, $k_{E/C} = 0.9999845$, $P_i = [1.5905 - V_i]I_i$, Curve 4-line, $U_{E/C,i} = V_i + U^o - (E/C)_i$ set, Curve 5-line, $U_i = V_i + P_{cell,i}/I_i$ set, Eqs. (20)–(22), $k = 0.999905$, $P_i = (1.5905 - V_i)I_i$, Curve 6-line, $U_{ohmic,i} = V_i + P_{ohmic,i}/I_i$ set, Eqs. (20)–(22), $k = 0.997100$, $P_i = (1.5905 - V_i)I_i$.

the overall discharge interval may be treated as a manually discharge data acquisition. The cell relaxation was monitored ($V_{r,1-4}$ vs. $t_{r,1-4}$, symbols in Fig. 2). The new cell open-circuit state was not observed, because the relaxation was not monitoring long enough. The power function: $U_{r,t} = 1.011(t_r - 308\,160)^{0.015}$ was used to fit the curve-2 in Fig. 2, which shows that the relaxation leads to the new cell open-circuit state represented by the estimated: $U_{r,t \to \infty} = U_n = 1.1972$ V.

5. Results and discussion

The first step of CDCA procedure is to form the discharge voltage scale by constant step: $\Delta V = (U^o - V_n)/n$, $i = 1 \dots n$, to obtain the set: $U^o > V_i > V_n \geq V_{final}$. This set is mapping the set: $P_o^o > P_i^o > P_n^o \geq P_{final}^o$, where $P_i^o = (U^o - V_i)V_i/R_l$.

The generation of both the discharge curves: $t_{18 \to 318}$ vs. $V_{18 \to 318}$ and $t_{15 \to 1}$ vs. $V_{15 \to 1}$, starts from the pairs: $t_{\alpha,16} = 24.00$ [s] vs. $V_{16} = 1.5500$ [V], and $t_{\alpha,17} = 31.20$ [s] vs. $V_{17} = 1.5475$ [V], see the two first symbols in Fig. 1. The equations to be of use are:

$$t_i = t_{i-1}(P_i/P_{i-1})^{b_i},$$
$$b_i = \ln(t_{i-2}/t_{i-1})/\ln(k_t P_{i-2}/P_{i-1}), \quad (26)$$

$18 < i < 318$, and

$$t_{i-2} = t_{i-1}(kP_{i-2}/P_{i-1})^{b_{i-2}},$$
$$b_{i-2} = \ln(t_i/t_{i-1})/\ln(P_i/P_{i-1}) \quad (27)$$

$15 > i \geq 1$. The overall set $t_{1 \to 318}$ vs. $V_{1 \to 318}$ is shown in Figs. 1 and 2, curve 1-line. The generation of the discharge curve is one form of curve fitting in which we seek the k-value that best fit the pairs experimentally observed.

The time independent set: E_i/C_i, $i = 3 \dots 318$ was generated using:

$$P_{E/C,i} = P_{E/C,i-1}(P_i/P_{i-1})^{b_{E/C,i}} \quad (28)$$

where $b_{E/C,i} = \ln(P_{E/C,i-2}/P_{E/C,i-1})/\ln(k_{E/C} P_{i-2}/P_{i-1})$ and $P_{E/C,i} = [(1.5905 - E/C)(E/C)]_i/R_l$. Introducing this set into Eq. (11) the set $t_{o,i}$, $i = 3 \dots 318$ was calculated, which is shown in Fig. 1, curve 2-line. The calculated sets $(E/C)_i$ and $U_{E/C,i} = V_i + U^o - (E/C)_i$ are shown in Fig. 2, curve 3-line and 4-line, respectively.

The generation of the sets of the power of the cell internal resistance ($P_{cell,i}$) and the power of the cell ohmic resistance ($P_{omhic,i}$), start from the pairs: $P_{cell,1} = P_{ohmic,1} = P_1 = (1.5905–1.5850)0.1585$ and $P_{cell,2} = P_{ohmic,2} = P_2 = (1.5905–1.5825)0.15825$, using Eqs. (20)–(22). The results are presented in Fig. 2 in the forms: $U_{cell,i} = V_i + P_{cell,i}/I_i$, curve 5-line and $U_{ohmic,i} = V_i + P_{ohmic,i}/I_i$, curve 6-line. The final $U_n = 1.1979$ V value was estimated, while $U_{ohmic,n} = 0.8542$ V value is an arbitrary one.

The sequence of instructions in Symphony software are available by private communication.

6. Conclusions

1. Calculated Discharge Curve Method was described as a new approach to cell testing procedure and experimental data processing.

2. Calculated Discharge Curve Algorithm was presented, and the procedures of time, capacity, energy on load resistor, and energy losses generations were reported. The generated sets satisfy the experimentally observed pairs of time versus voltage. Simultaneously, these sets satisfy initial, discharge curve inflection point, and final conditions.

3. Calculated Discharge Curves as a family of discharge voltage set, cell open-circuit voltage (discharge voltage plus cell overvoltage) set, and cell recovery voltage (discharge voltage plus overvoltages of components) sets were generated as the time-independent relations.

4. An application of Calculated Discharge Curve Method need to be detailed due to cell type, discharge mode, testing purpose, and data acquisition procedure.

References

[1] K.S. Piter, L. Brewer, Thermodynamics, McGraw Hill, New York, 1974.
[2] B.V. Beljajev, Rabotosposobnost Kimiceskih Istocnikov Toka, Svjaz, Moscow, 1979.
[3] D.F. Untereker, J. Electrochem. Soc. 125 (1978) 1907.
[4] R. Barnard, L.M. Baugh, C.F. Randel, J. Appl. Electrochem. 17 (1987) 165–173.
[5] R. Barnard, L.M. Baugh, C.F. Randel, J. Appl. Electrochem. 17 (1987) 174–184.
[6] R. Barnard, L.M. Baugh, C.F. Randel, J. Appl. Electrochem. 17 (1987) 185–195.
[7] P. Bro, S.C. Levy, Quality and Reliability Methods for Primary Batteries, Wiley, 1990.
[8] A.B. Djordjevic, J. Power Sources 50 (1994) 97–108.
[9] A.B. Djordjevic, D.M. Karanovic, Electrochemical Power Sources 1–2 (1996) 5–20.
[10] M. Doyle, J. Newman, A.S. Gozdz, C.N. Schmutz, J.-M. Tarascon, J. Electrochem. Soc. 143 (1996) 1890.
[11] A.B. Djordjevic, 20th International Power Sources Symposium, J. Power Sources 65 (1997) 27.
[12] L. Rao, J. Newman, J. Electrochem. Soc. 144 (1997) 2697.
[13] A.J. Bard, L.R. Faulkner, Electrochemical Methods, Wiley, 1980.