Agronomy Research **16**(S1), 1178–1189, 2018
https://doi.org/10.15159/AR.18.026

Battery capacity drop during operation

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Abstract. A lithium-iron-phosphate ($LiFePO_4$) battery is nowadays considered one of the best types of batteries. The paper deals with the evaluation of the drop in their capacity during operation. Based on the physical analysis of charging and discharging processes, a mathematical model of the battery capacity has been developed during its lifetime. The decrease in capacity during battery operation is evaluated according to the loss of active material, which gradually diminishes due to a number of different processes. The analysis of the loss of the active material is carried out, in particular, according to the depth of discharge, battery temperature, charging and discharging time, including the time when the battery is out of service. The tests were performed on the Winston Battery, Calb, Thunder Sky and Sinopoly batteries by cyclic discharging and charging at the 50%, 90% or 100% depth of discharge. Their real parameters were determined, compared to the model parameters and the parameters specified by the manufacturers and suppliers. Two automated systems were used for testing. During the test, in the tested battery with several cells, charging and discharging by a constant current were carried out automatically. Operating parameters of the tested battery were continuously scanned, recorded and evaluated by the control computer. The capacity curves during the battery operation, determined by the type of models, were compared with the results of long-term real battery tests.

Key words: $LiFePO_4$ battery, lifespan, capacity drop, depth of discharge.

INTRODUCTION

A lithium-iron-phosphate ($LiFePO_4$) battery is now considered one of the best battery types. Although their purchase price is several times higher than that of other types of batteries, manufacturers and suppliers report that the $LiFePO_4$ battery has much longer lifetime and shows much lower cost of electrical energy storage than other batteries. For example, when comparing the cost of the accumulators for a standard stationary battery for cyclical energy storage of several kWh, the lowest purchase price can be found at the Pb battery of a traction type (Trojan, 2018). Approximately twice higher purchase price is at a NiCd battery (Saft-Ferak, 2018) and a $LiFePO_4$ battery (Winston, 2018). To ensure reliable operation, the $LiFePO_4$ battery needs to be supplemented with the battery management system, which increases the cost of the

$LiFePO_4$ system to approximately three times in comparison to the Pb battery price. If battery maintenance costs and the price of energy, dissipated due to the efficiency of the charging and discharging processes, is neglected the cost of electrical energy storage in the battery is decisively determined by its lifetime. Since the lifetime of NiCd battery is approximately the same as the lifetime of the traction Pb battery under the same operating conditions, its cost of electrical energy storage is approximately twice than that of the Pb battery. The $LiFePO_4$ battery, if its lifetime is, at minimum, three times higher than the Pb battery, shows even lower costs of electrical energy storage.

Determining a specific lifetime of $LiFePO_4$ batteries is very problematic. Whereas the values of the other batteries reported by most manufacturers are nearly the same; i.e., 600–800 cycles for the capacity drop to 80% of the nominal value for Pb and NiCd batteries with the capacity of several hundred Ah and with 80% discharge depth (DOD), the $LiFePO_4$ battery capacity reported by different manufacturers often differ more than three times. The stated capacities of the same products reported by the manufacturers and distributors differ by up to twofold; see Fig. 1. The unreliable determination of the battery lifetimes then becomes one of the barriers to their wide-range use in practice.

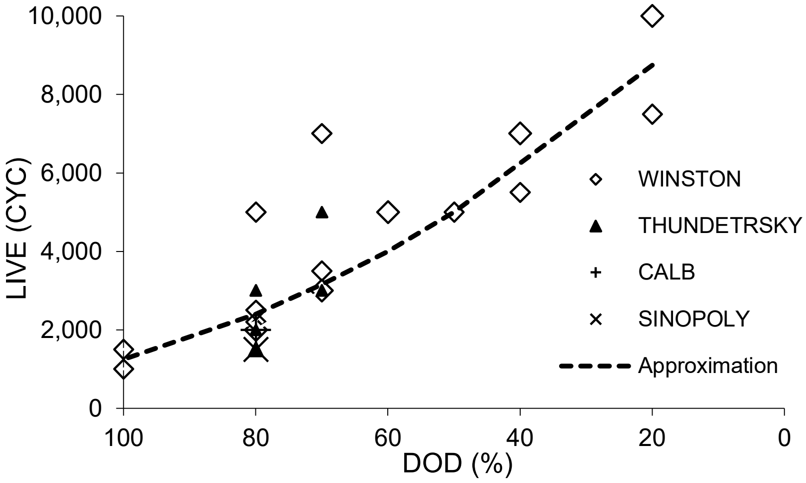


Figure 1. Dependence of the lifetime of the batteries from different manufacturers on DOD (Calb, 2018; Instruction, 2018; Lithium, 2018; Sinopoly, 2018).

The problem can then be solved only by the experimental verification of the real lifetime of the batteries and by providing at least an approximate description of the drop in the battery capacity during its operation. The lifetime also depends on other operating parameters, especially on the depth of battery discharge, its temperature, the charging and discharging currents with respect to time, including the time when the battery is out of service.

MATERIALS AND METHODS

The capacity exploitable in the battery operation is determined by the amount of active material on the battery electrodes that can react in electrochemical reactions in the process of discharging and charging.

The capacity drop during the battery operation is caused by the loss of active material that gradually diminishes due to a number of different processes. In general, these phenomena can be described as discrete cyclic and continuous processes. A discrete process is based on a defined initial state that proceeds according to a given algorithm and results in a final state. Individual cyclical processes of the same type take place one after another, whereas the final state of the n^{th} process is the initial state of the n+1 process.

To maintain a long battery lifetime, it is necessary to minimize the degradation of the battery structure during the cyclic process, i.e., to minimize the loss of active material between the initial and final states of the process. Continuous degradation processes are characterized by the rate of the loss of active material in the structure. For a known rate, it is possible to determine the loss of the active material over arbitrary time. It is also possible to express the result of the process over selected time and evaluate the continuous degradation process as a sequence of corresponding discrete processes.

A typical cyclic degradation process in the battery is the process of its discharging and recharging. By discharging, an active material is converted to another that is converted by charging back to the initial constituent. Since the reverse conversion efficiency is always less than 1, an active material on the battery electrodes is gradually diminishing and the capacity of the battery decreases. The loss of an active material, and thus the battery capacity during one cycle (discharge and subsequent charge) can be described by (1)

$$Q_{n+1} = Q_n(1 - \mathit{\Delta}) \tag{1}$$

where Q_n – the capacity of the battery in cycle n, proportional to the amount of active material; Δ – degeneration factor; (1-Δ) – the efficiency of an active material regeneration during the cycle.

The process of an active material loss during the sequence m of the identical cyclic degradation processes can be then described by a geometric progression, whose quotient is (1-Δ), as

$$Q_{n+m} = Q_n(1 - \mathit{\Delta})^m \tag{2}$$

Eq. (2) can be written in the form

$$Q_{n+m} \approx Q_n e^{-\mathit{\Delta} m} \tag{3}$$

This form of approximation is often used to describe the battery lifetime parameters. An argument of the function may be also continuous, which is usually time. This approach leads to modeling battery lifetime parameters by means of an analogy to the electrical signals during transient processes in RC circuits (Dalal, 2011)

$$Q(t) = Q(0)\, e^{-\frac{t}{\tau}} \tag{4}$$

where $Q(t)$ – an instantaneous value of the battery capacity at time t; $\tau = RC$ is a time constant of a simple RC circuit.

The problem with the models is to determine the relation of the model parameters (time constants) to the physical reality of the battery operation. Mathematical methods can determine very accurate values of the model parameters, valid for the set of measurements without specifying a more general dependence of these values on the battery operation parameters.

Analysis of the loss of an active material due to spontaneous discharges

A typical continuous degradation process of the battery is the process its aging, which can be, in the extreme case, approximated by the degradation of an active material of the battery when stored in a charged state in the store.

To approximate the process, the Arrhenius approximation of the rate of the active material degradation using an exponential function (Hu et al., 2016) is currently applied. The approximation is based on the idea that in order to initiate the degradation reaction, the particle must be supplied with a certain activation energy required to the transfer of chemical bonds. The probability that this condition will occur grows exponentially with the temperature.

$$k(T) = Ae^{-\frac{E_a}{RT}}, \tag{5}$$

here *k(T)* – represents a product degradation rate; A – the frequency factor; E_a – the activation energy; R – denotes the ideal gas constant (8.314 J $\text{mol}^{-1}.\text{K}^{-1}$); T – absolute temperature with the unit of K.

According to the above mentioned approximations, the process of losing both an active material and capacity during the battery operation, when it is degraded by N-cyclic degradation processes at time t, can be expressed by

$$Q(N,t) = Q_0 e^{-\Delta N}\left(1 - t.k_{ef}(T)\right). \tag{6}$$

The change in the battery capacity in the order of units of percent can also be expressed in the form of (7).

$$Q(N,t) = Q_0 e^{-\Delta N - \frac{t}{\tau_{ef}}}, \tag{7}$$

where k_{ef} (T) – the effective value of the product degradation rate; $\tau_{ef}(T)$ – the time constant of the thermal battery degradation (8).

$$\tau_{ef}(T) = \frac{1}{k_{ef}(T)} = \hat{A}e^{\frac{E_a}{RT}} \tag{8}$$

The constants Δ and τ_{ef} (T) primarily depend on the quality of the monitored products, and for one sample on the battery operating parameters.

Analysis of an active material loss of the battery due to DOD

The efficiency of an active material regeneration (1 - Δ) depends primarily on the depth of discharge (DOD) in the cycle. For a deeply discharged cell, the efficiency of an active material regeneration is significantly less than that of the cell that has been discharged with a small value of DOD only.

This phenomenon is caused by the dependence of a relative amount of active material, which is regenerated in the discharging and charging processes, on the depth inside the body with an active material, where the active material is being regenerated. For a simple approximation, it can be assumed that the ratio between the amount of m_l of the active material, non-regenerated at a certain depth, to the amount of an active material m_0, entering the regeneration, can be approximated by a linear function

$$\frac{m_l}{m_0} = a + bx \tag{9}$$

where x – the depth from the surface of the body with an active material; a, b – constants. Then the total amount of non-regenerated material from the surface to the maximum regeneration depth x_{max} can be expressed by the integral (10)

$$m_L = m_0 \int_0^{x_{\max}} (a + bx)dx = m_0 (a.x_{\max} + \frac{b}{2} x_{\max}^2) \,. \tag{10}$$

Considering the stoichiometric conception of electrochemical reactions in the battery, the amount of charge being regenerated is proportional to the amount of a regenerated active material. Since, for one sample of the battery, the size of the regenerated charge is proportional to the discharge depth (DOD), and the maximum depth of regeneration is again proportional to the amount of a regenerated active material, the amount of non-regenerated material, depending on DOD, can be expressed as

$$\frac{m_L}{m_0} = \Delta = a'(DOD) + b'(DOD)^2 \,. \tag{11}$$

Analysis of the loss of an active material due to thermal cell degradation

The time constant of a spontaneous thermal cell degradation $\tau_e f(T)$ depends both on the cell temperature and on the activation energy of the degradation processes in the cell. Searching for a time constant is complicated by the fact that the number of degradation processes can be higher, and the experimental monitoring of the cell ageing is highly time-consuming.

A normal aging of the cells at a normal temperature, which is reflected by a 4–8% drop of capacity per year, corresponds to the activation energy E_a of the most significant degradation process in the range of 45,000–51,000 J mol^{-1} that corresponds to the values 36,000–53,000 J mol^{-1} reported by Smith et al. (2014).

The temperature of the cell, however, need not be determined by the ambient temperature itself. The temperature increases due to the power losses in the cell at high currents, especially during the cell installation into the batteries or in poor cell cooling.

The power dissipated in the cell, when current I passes through, is determined by the equivalent cell DC internal resistance R_i

$$P_D = I^2 (R_i) \,. \tag{12}$$

The equivalent cell DC internal resistance R_i depends on the cell capacity. The cells with large capacity have an equivalent DC resistance significantly lower than the cells with low capacity. The dependence of the resistance on the cell capacity Q can be approximated, e.g., by Eq. (13). The approximation deviation, e.g., for cell series with capacity 40–1,000 AH is less than 10%.

$$R_i = \frac{0.02}{|Q|^{2/3}} . \tag{13}$$

The dissipated power for the cell capacity Q can then be approximated by (14). If the cell is loaded with a commonly considered current, whose size corresponds to the ampere-hour cell capacity, the dissipated power can be expressed by (15).

$$P_D = \frac{0.02\, I^2}{|Q|^{2/3}} , \tag{14}$$

$$P_D = 0.02\, |Q|^{4/3} . \tag{15}$$

For the known dissipated power, the resulting temperature rise ΔT in a steady state of the cell is determined by its thermal resistance R_{th} in the process of cooling. This can be determined for a free-standing cell as a reciprocal of the product of its surface S and a heat transfer coefficient α on its surface (16).

$$\Delta T = P_D . R_{th} = \frac{P_D}{\alpha\, S} . \tag{16}$$

The dependence of the stabilized temperature rise on the passing current for the cells with the capacity of 40–1,000 AH is shown in Fig. 2.

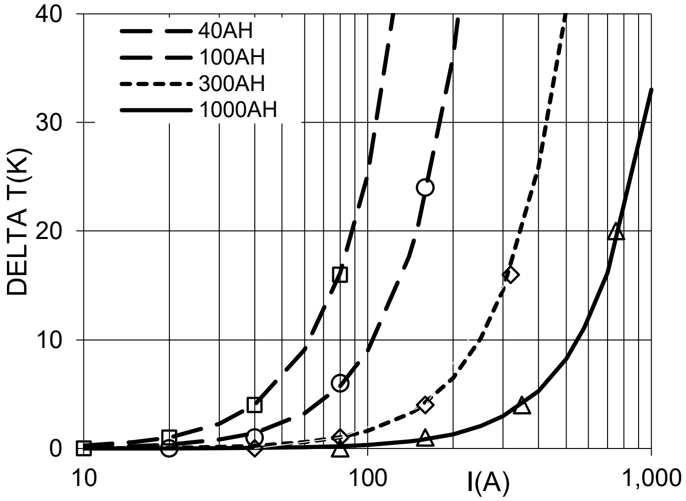


Figure 2. Dependence of the temperature rise of the cells with different capacity on the passing current.

The current, whose size corresponds to the ampere-hour cell capacity, will cause the temperature rise from 4 to 33 K. Minor temperature rise is exhibited by the cells with low capacity, because they have a larger surface area, with regard to the capacity, and hence a lower thermal resistance.

In case the cell is cyclically discharged and charged with the identical current during the test, the power dissipation of this level will be dissipated in the cell practically permanently and will cause the same cell temperature rise both during charging and discharging. This can lead to a significant reduction in the cell lifetime in long-term processes. The phenomenon is manifested, e.g., by the decrease in the cell lifetime during charging and discharging by large currents comparable with the numerical value of the ampere-hour cell capacity. As an example can serve the change in the battery WB-LYP 1000 AHA lifetime caused by the operation under high current 0.5 C or C; see Fig. 3.

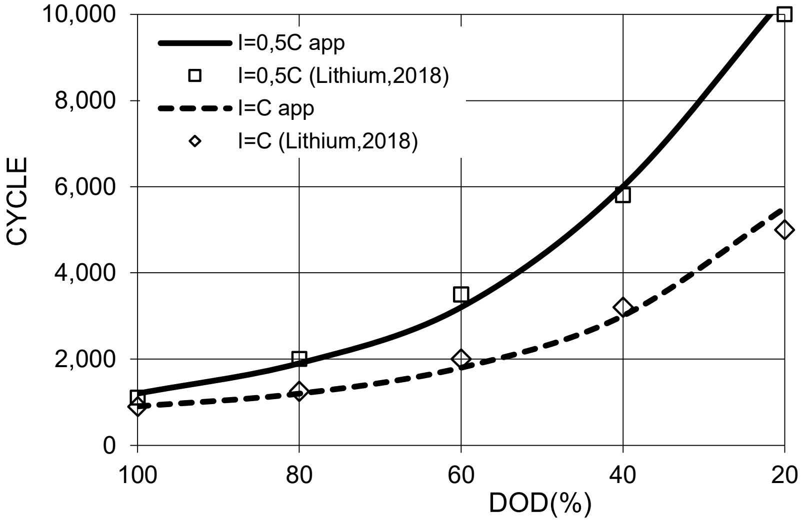
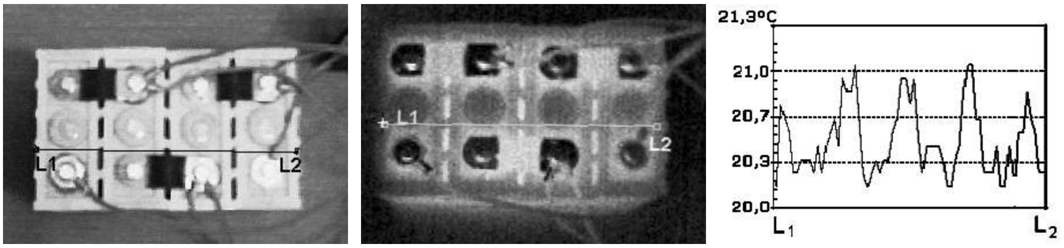


Figure 3. Comparison of the cell lifetime approximation with stated values (Lithium, 2018).

The temperature of the cell, which is charging or discharging by the current corresponding to the C-rate, is 25 to 30 K higher than the temperature of the cell, which is charging or discharging with a 0.5 C-rate current. Increasing the temperature causes about five times the increase in cell aging rate. Since the time corresponding to the time of charge and discharge of the cell is also inversely proportional to the load current, the time corresponding to the lifetime of the cell is also inversely proportional to the load current.

Effect of increasing the speed of the aging of the article is consequently smaller than would correspond to its absolute value; a double increase in the load current will cause cell life to decrease (for DOD < 80%) by approximately half.

The cell temperature rise sharply drops when the current passing through the cell decreases because the power dissipated in the cell, when the current passes through, is proportional to the square root of this current. For the current, corresponding to one quarter of the ampere-hour cell capacity, the influence of this charging and discharging current level on the lifetime of a well-cooled cell can usually be neglected. Another situation occurs when the cells are stacked into batteries. Such a composed body will have several times higher dissipated power related to its surface than the free-standing cell, hence it will have multiple times higher temperature rise. Typically, for a 4-cell battery (12 V $LiFePO_4$), the temperature rise on the surface of the external cells is about 2.5 times higher and 4 times higher at the central cells in comparison to the situation if they were placed separately. A state of a 4-cell battery with 40 Ah capacity, operated at a 10 A current is shown in Fig. 4 (Papezova & Papez, 2017).



a) b) c)

Figure 4. Temperature of the cells; a) real photo, b) infra photo, c) a distribution of temperature on the cells.

To solve the battery temperature rise in a dynamic mode, it is possible to simply connect thermal capacity and thermal resistance in parallel. The time constant of this integration network is 2,000–3,000 s for small cells and 4,000–5,000 s for large cells. The battery thermal response to fast current changes, too short for these time constants, can be solved according to the current RMS value. For slow current changes, the temperature rise must be solved as the integrator response to the pulse excitation signal.

Further increase in the rate of spontaneous degradation may also be caused by a number of other effects, e.g., by electrolyte contamination or by mechanical interaction in the cell electrode system.

RESULTS AND DISCUSSION

The initial analysis was performed for 8 batteries compiled from Winston Battery, Calb, Thunder Sky, and Sinopoly. The batteries have been tested continuously for almost 4 years by cyclic discharging and charging at a depth of the discharge 30–100%, as well as maintained at rest without operation. On the basis of the experiments, the parameters of the above mentioned model were determined to be the parameters for the batteries of individual manufacturers.

Two automatic systems (Papezova & Papez, 2017) were used for testing. In the tested 4-cell battery, the charging and discharging processes under the selected constant current were run automatically. Individual cells were equipped with balancing and protective circuits that prevented from exceeding the maximum voltage during charging, as well as the voltage drop under the minimum level during the discharge. The operating parameters of the tested battery were continuously scanned, recorded and evaluated by the control computer.

Examples of the measured values are given in Tables 1 and 2.

Table 1. Test results of 4 cellsWB-LYP40AHA Winston Battery with DOD = 100%

After	Time (h)	Dischar. voltage (V)	Charg. voltage (V)	Full dischar. (Ah)	Full dischar. (%)	Full charge (Ah)	Charg. Effic. (%)	Capac. drop (Ah)
0 c.	0	11.94	15.8	45.	112.5	45.6	97.7	
100 c.	900	11.94	15.9	43.7	109.3	44	99.4	1.3
200 c.	1,900	11.93	15.86	42.33	105.8	42.8	98.9	2.7
300 c.	2,800	11.87	15.85	41.3	103.3	41.7	99.1	3.7
400 c.	5,800	11.88	15.83	39.6	99.0	40	99.0	5.4
500 c.	10,000	11.89	15.8	37.2	93.0	37.9	98.1	7.8
600 c.	10,900	11.88	15.9	35.8	89.5	36.2	98.9	9.2
700 c.	11,800	11.87	15.86	35.	87.5	35.4	98.9	10
800 c.	12,700	11.87	15.85	33.8	84.5	34.3	98.5	11.2
900 c.	13,600	11.86	15.85	32.6	82.5	33.3	98.8	12.1
1,000 c.	14,500	11.86	15.84	32.1	80.25	32.5	98.8	12.9

Table2. Test results of 4 cellsWB-LYP40AHA Winston Battery with DOD = 50%

After	Time (h)	Dischar. voltage (V)	Charg. voltage (V)	Full dischar. (Ah)	Full dischar. (%)	Full charge (Ah)	Charg. Effic. (%)	Capac. drop (Ah)
0 c.	0	12.87	15.24	45.00	112.5	45.5	98.90	
200 c.	435	12.87	15.28	44.1	110.25	44.6	98.81	0.9
400 c.	870	12.86	15.26	43.3	108.25	43.7	98.98	1.7
600 c.	1,305	12.85	15.13	42.5	106.25	42.9	99	2.5
800 c.	1,740	12.86	15.20	41.7	104.25	42.0	99.3	3.3
1,000 c.	2,175	12.86	15.18	41	102.5	41.3	99.3	4
1,200 c.	2,610	12.87	15.22	40.4	101	40.7	99	4.6
1,400 c.	3,045	12.87	15.15	39.8	99.5	40.2	99.0	5.2
1,600 c.	3,480	12.86	15.15	39.2	98	39.6	98.72	5.8
1,800 c.	3,915	12.87	15.09	38.5	96.75	39.0	98.7	6.5
2,000 c.	4,350	12.86	15.10	37.9	94.75	38.4	98.7	7.1
2,200 c.	4,785	12.86	15.13	37.1	92.75	37.5	98.93	7.9
2,400 c.	5,220	12.87	15.15	36.3	90.75	36.8	98.64	8.7
2,600 c.	5,622	12.86	15.18	35.6	89	36	98.9	9.4
2,800 c.	5,655	12.86	15.19	35	87.5	35.4	98.87	10
3,000 c.	6,090	12.87	15.15	34.5	86.25	35	98.6	10.5
3,200 c.	6,525	12.86	15.2	33.9	84.75	34.4	98.5	11.1
3,400 c.	6,960	12.86	15.14	33.3	83.25	33.7	98.8	11.7
3,600 c.	7,395	12.86	15.16	32.7	81.75	33.1	98.8	12.3
3,800 c.	7,830	12.87	15.18	32	80	32.3	99.1	13
4,000 c.	8,265	12.86	15.18	31.6	79	32	98.8	13.4

CONCLUSIONS

The curves approximated by the model were further compared with the real measured values of the batteries from individual manufacturers. The parameters of the batteries from various manufacturers were also compared mutually. Dependences of the cell capacity of different manufacturers on the number of working cycles are displayed in Fig. 5.

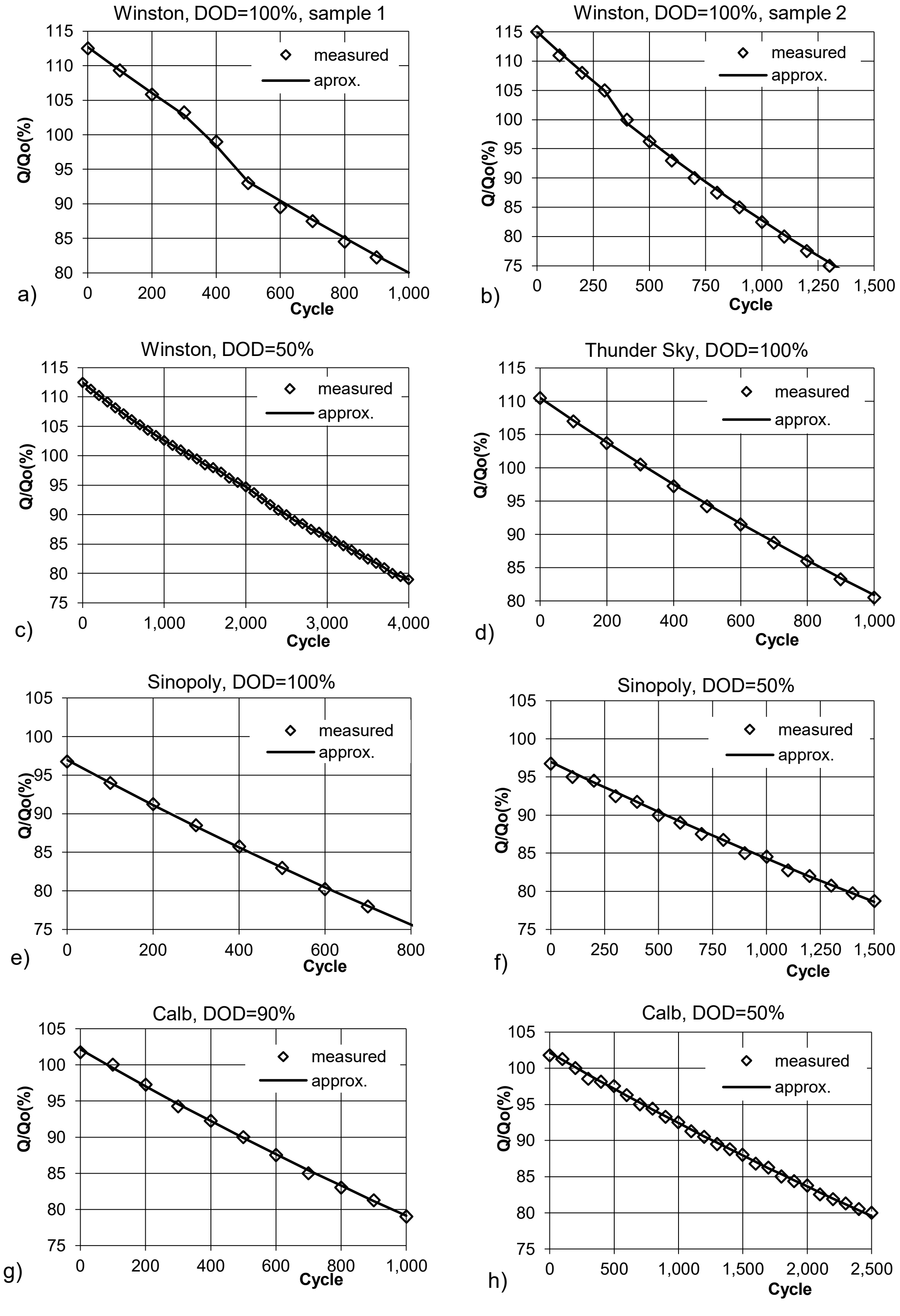


Figure 5. Dependence of the cell capacity of different manufacturers on the number of working cycles.

Mean square deviation approximations, optimized for all batteries, are 0.2–0.3%. The deviation can be reduced to a maximum value of 0.15% by fitting to individual manufacturers. The lifetime of the tested batteries of all manufacturers is approximately 1,000 cycles (for the drop in capacity to 80% of the nominal value), for the deep discharge with 90–100% DOD and the test lasting approximately 1 year.

The smallest lifetime, with only 800 cycles, was set for the Sinopoly batteries, which also had the largest capacity drop during storage. For the discharge with 50% DOD and for the test lasting approximately 2 years, the highest lifetime of approximately 4,000 cycles was set for Winston batteries. The lifetime is less than that stated by the manufacturer. The deviation is probably caused by the aging of the battery during the test. For the test lasting approximately 1 year, the battery lifetime would be by 1,000 cycles higher.

The lifetime of Calb batteries was approximately 2,500 cycles and the lifetime of Sinopoly batteries was only about 1,500 cycles in this mode; among others, due to the highest capacity drop in time, approximately 8% per year. The indicated time constant of the battery aging ranged from 10^5 hours (Sinopoly) to 1.7×10^5 hours (Thunder Sky). The cyclic degradation constant for DOD = 50% ranged from 5×10^{-5} (Calb) to 7×10^{-5} (Sinopoly); for DOD = 100% ranged from 22×10^{-5} (Sinopoly) to 26×10^{-5} (Thunder Sky).

To ensure the claimed lifetime, the manufacturers, mostly probably, assemble the cells with a larger initial capacity than they declare on the labels, e.g., at the Winston batteries by about 15%, at the Thunder Sky batteries even by 20%.

ACKNOWLEDGEMENTS. Thanks for cooperation belong to Laboratory of Photovoltaic Systems Diagnostics, Faculty of Electrical Engineering, Czech Technical University in Prague and Department of Electrical Engineering and Automation, Faculty of Engineering, Czech University of Life Sciences in Prague.

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