# Aging test protocol for Lithium-ion cells

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***Abstract*— The paper describes a test protocol developed in order to build the aging model of electrochemical accumulators and estimate the expected lifetime with different operating conditions. The test protocol has been verified performing aging tests on three lithium-ion cells. The paper presents and comments the results and provides suggestions for further ageing tests on batteries. .**

***Keywords—Aging test, Lithium-ion battery, State of Health***

## I. Introduction

In recent years the number of requests for electrochemical storage systems with a high power and energy is keeping growing thanks to the growth of Electric Vehicle market as well as the Battery Energy Storage System market for residential, commercial and utility applications. Even if there are many different types of batteries, the best results in terms of energy density and power density have been obtained with lithium-based batteries. The wide diffusion of lithium-ion batteries (LiB) has required the development of new reliable diagnostic tools. Thus, an intensive modelling activity is requested to understand the behaviour of the complex system of a LiB [1].

The diagnostic of a LiB can be split into two classes. One is the diagnostic related to the up-to-dated status of the LiB, mainly focus on the State of Charge (SoC) estimation [2, 3, 4, 5]. The other class is associated to the evolution of the LiB performances over its lifetime. This second class is strictly linked to the State of Health (SoH) estimation [6, 7, 8].

The activity addressed by this paper is focused on the second class. The estimation of the lifetime and aging trend of a LiB is very important during the design phase of an energy storage system but also during its operation. A good knowledge about the aging mechanisms of a LiB is necessary for properly managing it, avoiding to put it to working conditions that can determine a significant reduction of its service life. Besides, it is important to predict the possibility of out-of-services of an energy storage system that can be caused by the degradation of its performances due to its aging. The LiB lifetime estimation requires a great amount of testing and modelling efforts to validate the results, because there are multiple stress factors that can accelerate battery aging, such as the working temperature, the typical depth-of-discharge of the working cycle, the characteristics of the load profile, the average SoC, etc. [9, 10]. In addition, these stress factors often act simultaneously, multiplying their effects.

Nowadays the aging test performed by the LiB manufacturers are not harmonized due to several reasons: lack of standardization, different application fields, different markets, difference of behaviour among the existing technologies, immaturity of some technologies. Hence, it is very difficult to compare the aging test results of different LiB. Since there is a lack of standardized aging test protocols for LiB technologies, the development of a simple but complete protocol, allowing to measure and compare the effect of aging and the SoH trends of different LiB technologies, is a need.

With the aim to determine the curves representing the degradation of SoH of a LiB due to cycling and calendar aging in correspondence of different stress factors, a specific aging test protocol has been developed. This test protocol would be a basic manual for aging tests, that can be adapted to accumulators of different sizes (single cells, modules of a few cells and complete battery packs) and also to different technologies.

This paper aims to provide an easy to implement protocol to test LiB and evaluate its performance over its lifetime. This procedure would cover the main variables which affect the aging of the LiB. Moreover, some earlier results of aging tests executed on three lithium-ion cells are presented and discussed.

The paper is structured as following. In Section II there is a description of the model used to depict its behaviour. Section III shows the procedure proposed for the aging test. Then, in the section IV the system under test is presented and, in the end, the section IV shows and comments the results of the aging test performed.

## II. Cell Model and Aging Indicators

This section shows the equivalent electrical model of a cell that was used to represent the electrical behaviour at any moment of its life. In particular the parameters affected by the aging phenomena has been highlighted and discussed. The focus is now on a single cell but all the consideration can easily be extended to modules and batteries.

### *A. Cell model*

According to the scope of the paper, the model presented does not aim to estimate the SoC of the LiB but to identify the parameters that change over the aging test. Analysing the evolution of these parameters, a prediction of the SoH, of the LiB can be done.

In a model-based control system, the precision and complexity of the model are very important. In [11], the commonly used electrical models for batteries are collected. The model accuracy and number of RC networks are strictly related, and a second-order RC model has the highest precision and is more suitable for the estimating the voltage of LiB cells [12, 13]. The time response for batteries used in grid-support is greater than 1 s [14]. Thus, it is possible to neglect the RC branch, with dynamic behaviour at high frequencies, integrating it in an equivalent series resistance, and obtaining the first order RC model indicated in Fig. 1.

The electrical behaviour of the proposed model can be expressed as follows:

$$\begin{cases} V(t) = V_{OC}(SoC) - R_0(SoC,T) \cdot I(t) - V_1(t) \\ \dot{V}_1(t) = \dfrac{I(t)}{C_1(SoC,T)} - \dfrac{V_1(t)}{C_1(SoC,T) \cdot R_1(SoC,T)} \end{cases} \quad (1)$$

where $V_{OC}$ is the open circuit voltage, I is the battery current (assumed positive for discharge), $V_{cell}$ is the output voltage, and $R_0$ is the equivalent resistance evaluated at 1 s (that represents the resistance of the electrolyte and the charge transfer phenomena, due to the solid electrolyte interphase). $R_1$ and $C_1$ are the resistance and capacitance of the RC group fed by voltage $V_1$; they represent the slow dynamic of the cell due to the ions diffusion. During operation, these parameters are not constant, but are dependent on the SoC and temperature of the cell. This means that to find out the trend of the parameters over the lifetime, in order to use them as aging indicators, is very important to refer the parameters to the same working conditions (SoC and temperature).

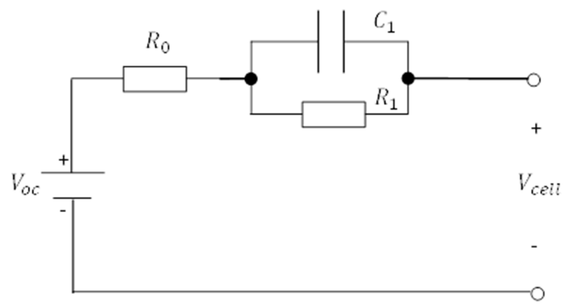


Fig. 1. First order electrical model of the cell

## B. *Aging indicators*

Aging mechanisms can result in a decrease of the performances of the cell (capacity fade, increase of internal resistance, etc), so it is possible to monitor the SoH of the accumulator measuring during lifetime the up-to-date value of some performance parameters. LiB manufacturers usually define the aging of a cell as function of its capacity measured at nominal conditions. Indeed the most common indicator for the $SoH_C$ is defined as:

$$SoH_C = \left(1 - \frac{C(0) - C(k)}{0.2 \cdot C(0)}\right) \cdot 100 \quad (2)$$

where C(0) is the capacity at the beginning of the cell lifetime and C(k) is the capacity at a certain time of the lifetime. The $SoH_C$ is 100% at the beginning of the cell lifetime and achieve 0% when the capacity drops to 80% of the C(0). It is possible to refer the $SoH_C$ to the *useful capacity* or to the *maximum capacity* of the cell. Both parameters can be measured through a full discharge test of the cell, including a constant current (CC) discharge phase from full charge until the minimum operating voltage of the cell and a constant voltage (CV) discharge phase, at the minimum operating voltage, in which the current supplied by the cell gradually decreases until a minimum value, indicating the achievement of the complete discharged state of the cell. The useful capacity can be calculated from the integration of the battery current during the CC discharge phase of the test, the maximum capacity from the integration of the battery current during the CC and CV discharge phase.

The maximum capacity is more reliable as aging indicator, because its fade is directly correlated to a reduction of active material, while the useful capacity depends also by the working conditions such as the cell current. On the other hand, it is not always possible to measure this parameter because the CV discharge phase is not always allowed for complete battery packs.

This indicator is useful for energy applications, where the power request is very low. However, since there are also many power applications with high power request, this indicator needs some refinements. In this second case it is possible to calculate the $SoH_R$, based on the increasing of the internal resistance instead of the maximum capacity, using the following formula [15]:

$$SoH_R = \left(1 - \frac{R(k) - R(0)}{R(0)}\right) \cdot 100 \quad (3)$$

where R(0) is the equivalent resistance $R_0$ of the electrical model of the cell (see Fig.1) at the beginning of its lifetime and R(k) is the capacity at a certain time of the lifetime. The $SoH_R$ is 100% at the beginning of the cell lifetime and achieve 0% when the resistance increase to 100% of the R(0).

Alternatively, for combined applications a mixed SoH indicator, that considers both the maximum capacity and the internal resistance, could be used. Taking into account all these considerations and the aging test results provided by manufactures and research centres, the main aging indicators identified are the maximum capacity and the internal resistance $R_0$ of the cell. The other model parameters, at least for the LiB technologies analysed, do not show any relevant changing as function of the SoH. Moreover the main variables that affect the SoH is the temperature, the mean SoC, the Depth of Discharge (DoD), the current and the number of changing working mode (charge to discharge and vice versa).

# III. AGING TEST PROTOCOL

The final goal of the aging tests defined by the test protocol is to find out the main parameters affecting the aging of the electrochemical technology under test. In order to reach this goal a muscular approach has been adopted, based on the execution in parallel of many different aging cycles on groups of identical elementary cells, changing the operating conditions. The developed test protocol [16] includes also some general prescriptions about the design of the testing station (climatic chamber, cyclers, data acquisition system, etc.) and safety aspects of the different technologies that can be tested, and a section describing some specific aging tests to be performed on commercial modules and battery packs including battery management systems.

Aging test protocol for elementary cells includes the following phases, that can be repeated until a specific sequence until the End-of-Life (EoL) conditions are reached.

- Preconditioning tests are performed in order to obtain the conditioning of the cell, i.e. a stabilization of its performance parameters (capacity, internal resistance, etc.) that can be altered by a long rest period. The preconditioning generally consists in a sequence of charge/discharge profiles of the cell.
- Aging cycling test sequence executed in order to age each technology under test in a controlled way.
- Standard check-up phase, i.e. a sequence of tests executed with the aim to evaluate the performances of each technology under test through the measurement or estimation of a series of performance parameters, that can be used as aging indicators. The standard check-up is executed after each aging cycling test sequence and includes a limited number of tests performed in order to measure the up-to-date values of the aging indicators of each cell in order to highlight the SoH trend of the cell.
- Extended check-up phase, including a greater number of tests able to measure the performances of the cell in a wide range of working conditions. This phase can be executed at the beginning of the aging test, after the preconditioning and can be useful for the choice of the aging indicators.

The table I summarized the sequence of execution of the different phases of the aging test protocol.

TABLE I. AGING TEST PROTOCOL TEST SEQUENCE

| Phase N. | Phase description |
|---|---|
| 1 | Initial inspection |
| 2 | Selection of cells to be tested |
| 3 | Preconditioning cycles of each cell |
| 4 | Execution of the extended check-up and choice of the aging indicators |
| 5 | Execution of the aging cycles in accordance to the test matrix (the number of repetitions depends on the type of aging test) |
| 6 | Adaptation to the check-up reference temperature (typically 20 °C) |
| 7 | Full charge of each cell |
| 8 | Execution of the standard check-up |
| 9 | Iteration of phases 5÷9 until reaching the EOL condition |
| 10 | Execution of extended check-up |

## A. *Cycling test sequence*

The cycling test sequence is based on the iteration of a basic load profile with the aim to age the cell in a controlled working condition. Before the beginning of the aging test is necessary to design a matrix of tests to be executed in parallel on groups of cells. The test matrix is built starting from the identification of the main stress factors for the technology under test. Each test of the matrix is in fact characterized by specific test conditions (load profile, temperature, etc.) in which one stress factor value is higher than in the other ones. Each cell under test (or better group of cells) works in accordance to the test conditions defined in each test of the matrix in order to be aged in a controlled way and periodically subjected to a standard check-up for monitoring the aging indicators. In this way it is possible to determine and compare the effects of some possible stress factors on the SoH degradation though the building of bundles of curves representing the SoH vs number of charge/discharge cycles of the accumulator at different stress factors (corresponding to different working conditions). Each stress factor in the test matrix can have a high or low value, in order to determine some aging acceleration factors useful to set-up accelerated aging tests. Most common and important stress factors can be ( [17] and references inside):

- Operating temperature, influencing the lifetime of the accumulator in according to the Arrhenius law [10] [15];
- typical DoD of the load profile;
- average SoC of the load profile;
- RMS current;
- presence of peaks of current during charge or discharge;
- number of current reversals per hour.

In order to minimize the number of cells that must be cycled in parallel is necessary to choose the really significant stress factors for each technology, on the basis of experimental data collected on similar technologies, the analysis of the scientific literature and the expected operating condition and application for the technology. The test matrix size can be adapted from time to time in function of the specific needs, eliminating some tests when it is already known that a specific stress factor has no influence on the technology under test and adding other tests more suitable.

The following table shows an example of aging protocol test matrix, for a lithium-ion accumulator technology.

TABLE II. EXAMPLE OF TEST MATRIX

| Test | Operating temperature range [°C] | Average SOC [%] | DOD [%] | $I_{peak}/I_{DC}$ rate | Number of current reversal per hour |
|---|---|---|---|---|---|
| 1 | 20÷30 | 50 | 0 | 0 | 10 |
| 2 | 40÷50 | 50 | 0 | 0 | 10 |
| 3 | 20÷30 | 80 | 0 | 0 | 10 |
| 4 | 20÷30 | 50 | 40 | 110% | 10 |
| 5 | 40÷50 | 50 | 40 | 110% | 10 |
| 6 | 20÷30 | 70 | 40 | 110% | 10 |
| 7 | 20÷30 | 50 | 80 | 110% | 10 |
| 8 | 20÷30 | 50 | 40 | Max limit | 10 |
| 9 | 20÷30 | 50 | <5 | 100% | 750 |

## B. *Extended check-up*

The extended check-up includes a wide type of tests able to evaluate the performances of each cell under test through the measurement or estimation of a series of characteristic performance parameters in a wide range of working conditions, such as:

- Discharged capacity [Ah] and energy [Wh] and at different temperatures and current rates
- Coulombic roundtrip efficiency [%]

- Energetic roundtrip efficiency [%]
- Energy density and specific energy [Wh/m$^3$]-[Wh/kg]
- Power density and specific power [W/m$^3$]-[W/kg]
- Self-discharge
- Electrical model parameter values at different SOC/temperatures/current rates
- Power peak [W]

The extended check-up can include for example the tests listed below.

- Constant current discharge tests at 20 °C and different current rates
- Constant current discharge tests at different temperatures
- Electrical model parameter estimation test
- Peak power estimation test
- Self-discharge test

Since the execution of this type of test is expensive and could influence the aging trend (some tests require stressful operating and environmental conditions) must not be repeated frequently. It is advisable to carry out an extended check-up before starting the aging test sequence and after reaching the EoL condition.

### *C. Standard check-up*

The standard check-up phase collects a series of tests executed periodically at the end of a sequence of aging cycling test, in order to measure the performances of the cells under test, hence the measure of the selected aging indicators. The selected tests can be different from each technology under test, but generally include:

- Full discharge test, including both constant current (CC) and constant voltage (CV) discharge phases of the cells, that allows to measure the up-to-date useful capacity (through the integration of the battery current during the CC discharge phase) and maximum capacity (through the integration of the battery current during the CC+CV discharge phase) of the cell, and the corresponding $SoH_C$.
- Electrical model parameter estimation test, useful to determine the values of the parameters of the first order electrical model (see Fig.1), in particular the electrical series resistance $R_0$, and the corresponding $SoH_R$, and the RC group parameters at different SoC values.

## IV. Results of aging tests on Lithium-ion cells

The aging test protocol has been experimented on three lithium-ion Nickel Cobalt Manganese - NMC cells. The aging tests have been carried on for about two years, until the achievement of one of the two predetermined EoL condition by two of the two cells.

### *A. Cells under test*

The three cells under test were 3.7 V – 40 Ah NMC polymeric LiB cells. The cells are characterized by a pouch geometry (see Fig.2). The technical specifications of the cells under tests are summarized in the following table.

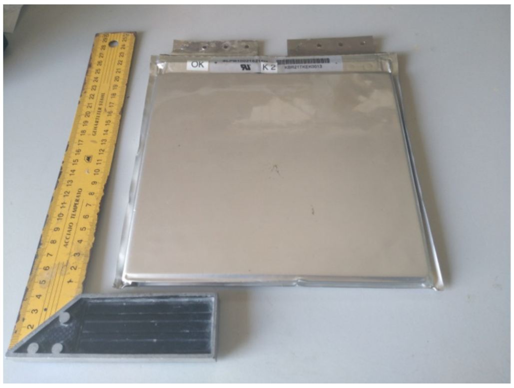

Fig. 1. Cell under test

TABLE III. CELL UNDER TEST SPECIFICATIONS

| | |
|---|---|
| Nominal Capacity | 40 Ah |
| Nominal Voltage | 3.6 V |
| Maximum current in charge | 120 A |
| Maximum current in discharge | 200 A |
| Size | 10.7 x 215 x 220 mm3 |
| wieght | 1100 g |
| Cathode | Nickel-manganese-cobalt on aluminium foil |
| Anode | Graphite on copper foil |
| Electrolyte | Polymeric |

### *B. Test set-up*

The cells have been subjected to an aging cycled characterized by an average SoC of 50%, a DoD of 60% and a constant current of 1C both in charge and discharge.

Cell 1 and cell 2 have been tested with a temperature of 20 °C, cell 3 with 40 °C.

Cell 2 and cell 3 have been cycled always with the aging cycle profile, while cell 1 has been tested according to very stressful profiles during its previous service life at the beginning of the aging tests.

Every 200 iterations of the basic aging test cycle (about every 10 days) the performances of the cells have been measured using a standard check-up of the aging indicators, consisting of the tests described in the section III C.

Two possible EoL conditions have been established at the beginning of the test, i.e. the degradation of the capacity down to 80% of its starting value and the increase of internal resistance $R_0$ up to 100% of its starting value, both determining the reset of the corresponding $SoH_C$ and $SoH_R$ of the cell.

The cells covered 4990 charge/discharge cycles until the end of the aging tests, supplying about 120 kAh of total capacity.

Table IV summarizes the results of the tests performed on the three cells.

TABLE IV. CELL UNDER TEST SPECIFICATIONS

| | CELL 1 | CELL 2 | CELL 3 |
|---|---|---|---|
| Working mode | T 20 °C, Very stress profiles during its previous service life | T 20 °C New cell | T 40 °C New cell |
| Useful capacity fade [%] | -7 | -1.1 | -7.5 |
| Maximum capacity fade [%] | -6.5 | -7.6 | -11.9 |
| Internal resistance $R_0$ increase [% ] | **+106** | +40 | **+226** |

The following graphs show the $SOH_C$ and $SOH_R$ of the three cells during the whole aging tests.

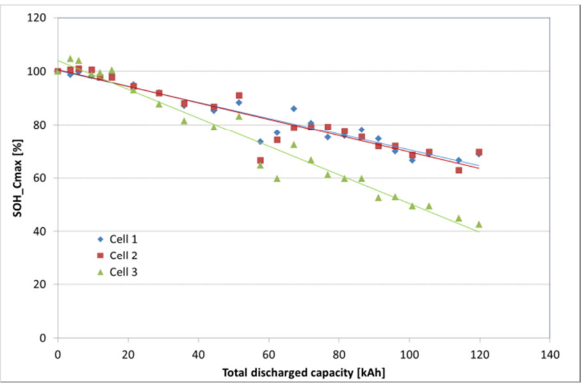


Fig. 2. $SOH_C$ vs total discharged capacity

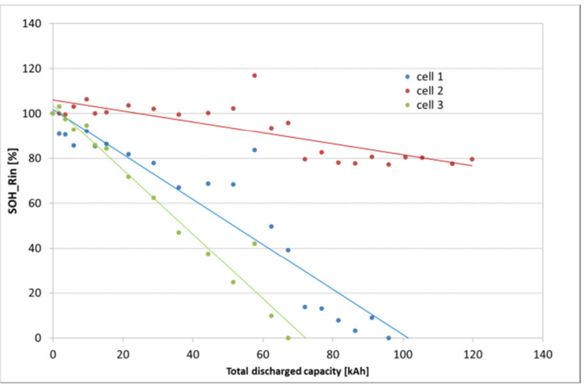


Fig. 3. $SOH_R$ vs total discharged capacity

At the end of aging tests the three cells have reached a different aging level:

- Cell 1 and cell 3 have reached the EoL condition, in fact their internal resistance $R_0$ (the resistance responsible of the instantaneous voltage dip) is increased more than 100% from the initial value.
- Cell 3, which has been cycled at 40°C, is by far the most aged cell, confirming the influence of temperature on the aging trend.
- Cell 2 has not yet reached the end of life condition and does not show a significant performance degradation, highlighted by a clear increase of internal resistance or decrease of useful capacity. The maximum capacity of the cell, however, has decreased to a value equal to cell 1, which has worked in similar environmental conditions and this can be determined by a reduction of the active material and a degradation of the electrode materials.

## V. CONCLUSIONS

The paper presents an aging test protocol that can be implemented by the cells manufacturers, and all the other stakeholders in field of the energy storage systems, in order to evaluate the aging phenomena of the electrochemical technology. The procedure proposed has been applied to three lithium-ion cells. The result shows that the temperature has a great impact on the aging of the cells.

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