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Experimental protocols and first results of calendar and/or cycling aging study of lithium-ion batteries – the MOBICUS project

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On behalf of MOBICUS project partners

Abstract

This paper presents the MOBICUS project experiment protocols with some first results. Twelve partners from companies and research labs have joined forces to conduct a large study on lithium-ion batteries (LIB) aging under real automotive conditions. Experiments include not only calendar or cycling aging tests, which a part of them was built using a D-optimal design, but also mixed sequences with calendar and cycling experiments. The collected data will enable to build rigorous aging laws taking into account combined calendar and cycling phases. Two different technologies of LIB are tested.

Keywords: lithium battery, battery SoH (State of Health), cycle life, battery calendar life, France

1 Introduction

With the growing market of electrified vehicles across the whole world, the need for long-life batteries becomes more and more essential for economic issues. The battery can cost up to several thousand of euros that's why the knowledge of the aging mechanisms is primordial to optimize its different using process. The study of aging laws for lithium-ion batteries (LIB) is a challenging plan. Many projects exist all-around the world [1]–[5]. Most of these works take into account either the calendar aging or the cycling aging although in real automotive applications LIBs usually experience the both aging in driving phases separate by parking phases.

The objectives of MOBICUS project (2014 - 2017) were the design and validation of strategies to extend batteries life-time depending on vehicle use and charging patterns, from experimental measures. MOBICUS gathers 12 partners (5 research labs and 7 industrial companies) and mobilizes 18 testing benches in order to conduct an ambitious and innovative aging test program combining cycling and calendar phases of aging. Most partners of MOBICUS have participated to two previous research projects: SIMTOCK (2007-2010) on the cycling aging [2] and SIMCAL (2009-2012) on calendar aging [3], [4]

The two different types of LIB technologies tested in MOBICUS are detailed in Table 1. The Techno#1 was tested in both SIMSTOCK and SIMCAL projects. Techno#2 is specific to MOBICUS.

Table 1: characteristics of the two technologies of LIB testes in MOBICUS

Technology	Composition	Capacity	Type	Application
#1	NMC-LMO	43 Ah	Energy	EV
#2	NMC-Ni rich	26 Ah	Power	PHEV

In this project 86 modules are in test (40 modules for Techno#1 and 46 for Techno#2). For each technology, each module represents a different test (different conditions: temperature, SoC, current of charge or discharge). For measurements quality, every module is composed of three cells. This means 258 cells are in test in MOBICUS

2 Experimental

In order to cover almost all the types of batteries aging in automotive application, three large categories of tests constitute the experimental plan: calendar aging, cycling aging and mixed calendar /cycling aging.

2.1 Calendar aging

This category of tests summarizes more than 90% of the vehicle life-time (personal car) which is the parking mode. That's why many scientists are studying batteries aging at this "rest" mode. From these studies [4], the aging here depends mainly on temperature and SoC factor. To study the simple and the combined effects of these two factors, three types of tests in this category were planned: storage on fixed SoC and fixed temperature, storage on fixed SoC and variable temperature and finally storage on variable SoC and fixed temperature.

2.1.1 Pure calendar (fixed SoC and temperature)

This type of tests is designed to validate and enrich the results obtained by SIMCAL project. Pure calendar aging tests consist on storing each module at a constant temperature and fixed SoC for almost 2 years. During this time a periodical characterisation is planned to check-up the evolution of batteries electrical properties.

The tests are distributed in 4 different temperatures (0, 25, 45 and 60°C) and 5 different SoCs (0, 30, 65, 80 and 100%). Since we have already some results from a former project (SIMCAL [3]) for the first technology, only complementary tests are scheduled (10 modules) whereas for the second one, a more complete test is planned (16 modules will be tested).

The figure below (Figure 1) represents the capacity loss in function of time at different temperatures at SoC 80.

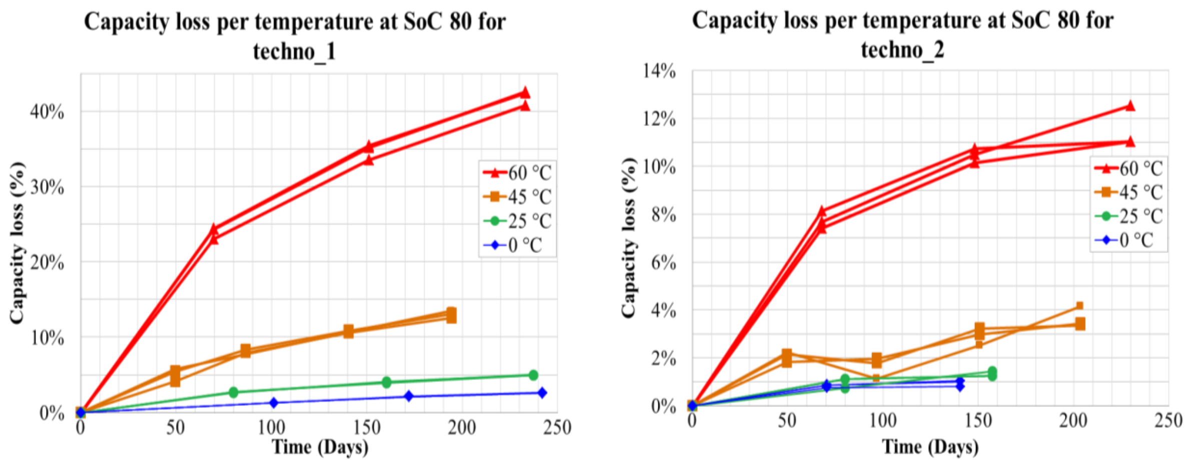

Figure 1 : Pure Calendar aging tests first results: Capacity loss for each technology at SoC 80

Our first results presented here confirm that the high temperature is a very degrading factor for the LIB. Although the curve's shape of capacity loss for Techno#1 and Techno#2 is approximately the same, the two technologies haven't the same capacity loss. The Techno#1 is more alterable against temperature than Techno#2. At the end of testing, more points will be obtained and then a better analysis and understanding of the calendar aging phenomena will be possible.

2.1.2 Thermal cycling calendar tests (fixed SoC and variable temperature)

In real aging conditions, the temperature is never constant; it varies depending on the season and the moment of the day. Following this principle, we've designed this type of tests. It consists on storing the cells at a fixed SoC and a variable temperature.

For each technology, we test the aging in 2 different SoCs (60 and 100%) and within 2 temperature ranges (0-30°C and 30-60°C).

A thermal cycling between the 2 values of each range is an iteration of a 24 hours loop. It is composed of 10 hours at temperature#1, 2 hours of ramp, then 10 hours at temperature#2 and another 2 hours of ramp (this can be related to the variation of temperature during the day). To optimize the use and availability of equipment, one test consists of 11 weeks of thermal cycling in the 0-30°C range, one check-up of cells performances, 11 weeks of thermal cycling in the 30-60°C, one check-up of cells performance, etc. as shown in Figure 2 (the variation of temperature depending on season)

CU-0	TC 0-30 °C 11 weeks	CU-1	TC 30-60 °C 11 weeks	CU-2	TC 0-30 °C 11 weeks	CU-3	TC 30-60 °C 11 weeks	...

Figure 2 : Planning of the test showing periodicity of Check-Up (CU) and Thermal Cycling (TC)

This type of tests helps us better understand the influence of the variable temperature on the calendar aging. The figure below (Figure 3) represents our first results.

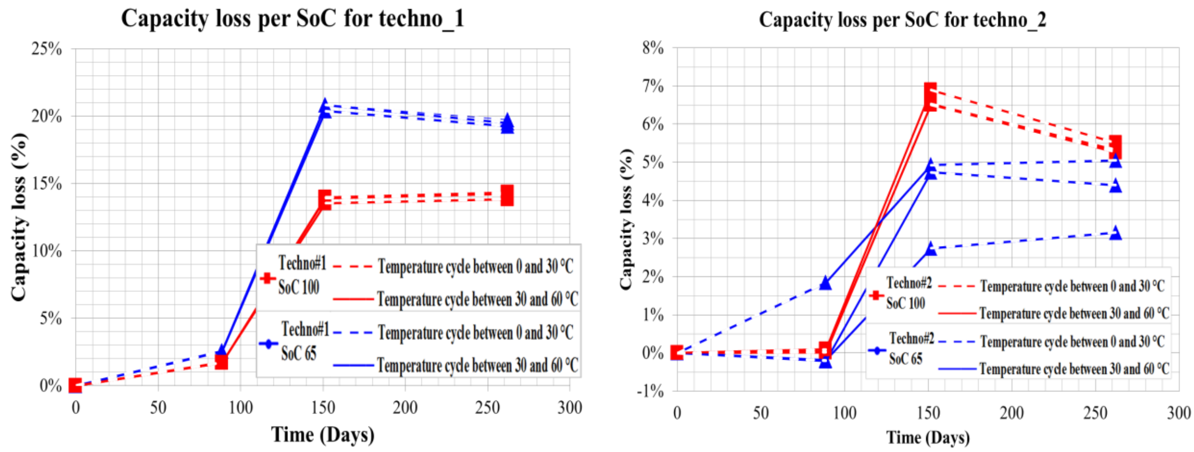

Figure 3 : Thermal cycling calendar tests first results: Capacity loss for each techno

The important influence of the high temperature is again visible by comparing the capacity loss rate in the range 0-30°C to 30-60°C range. It can be noted that after a phase of aging at high temperature (temperature cycle between 30 and 60 °C), there is a stabilisation of the capacity loss or even a regeneration phenomenon at the next phase (temperature cycle between 0 and 30 °C). This can be checked and understood better at a further stage of testing.

2.1.3 Variable SoC calendar tests

In real life automotive application and at parking phases, the level of SoC is never the same. So to study this effect and to validate the results that will be obtained from the previous types of test, this type of tests is designed. It combines the aging at a high and a low level of SoC.

This type of tests helps also to check the influence of SoC variation on calendar aging. So for each technology we test one module stored at only one temperature 45°C but at 2 alternating values of SoC (30 and 80%). The tests are composed of a series of calendar aging periods at each SoC level: 11 weeks at SoC

30 / 1 week characterization / 11 weeks at SoC 80 / 1 week characterization. An additional check-up is planned in the case of SoC80 as the aging is expected to be faster as shown in Figure 4

CU	45°C - SoC30 11 weeks	CU	45°C - SoC80 5 weeks	CU	45°C - SoC80 5 weeks	CU	45°C - SoC30 11 weeks	….

Figure 4 : Planning of the test showing periodicity of Check-Up (CU) and calendar storage at various SoC

The figure below is a representation of the first results obtained for the capacity loss at the same conditions for each technology (each line represents the mean value of three cells at the same conditions).

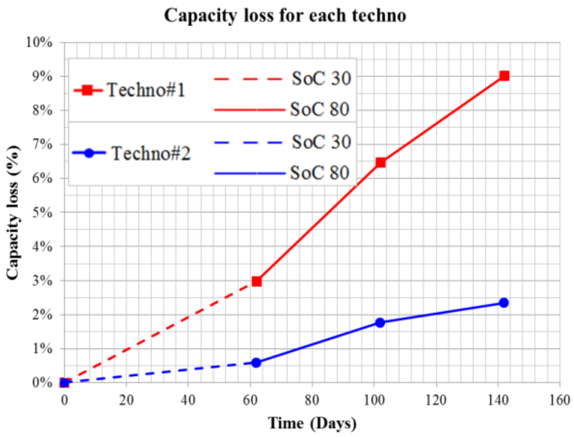

Figure 5 : Variable SoC calendar tests first results: Capacity loss for each techno

The variation of the capacity loss speed here confirm the results obtained from SIMCAL (the SoC have a big influence on the LIB aging). To quantify this influence, a combined analysis, of these tests and the pure calendar tests, is required (at the end of the tests).

2.2 Cycling aging

In order to discriminate the effect of SoC on the cycling aging mechanisms, experiments contain cycling tests at different values of SoC is needed (Cycling at fixed SoC). Then to measure the effect of SoC variation like in real life aging, some tests are designed for cycling in a specified range of SoC.

2.2.1 Cycling at fixed SoC

The treated factors here are temperature (3 values), SoC (4 values), charge current (2 values) and discharge current (2 values). For this category of test, there are 2 main values of charge or discharge current: “MAX” and “min”, they are defined differently for each technology. The “min” and “MAX” values for the charge current can define respectively a normal or a rapid charge whereas for the discharge current they describe the economic or the non-economic driving. For Techno#1 the “MAX” and “min” values are respectively 1C and C/3 however for Techno#2 they are 3C and 1C. The choice of current level is related mainly to the batteries application (Techno#1 EV and Techno#2 PHEV). The cycling at a fixed SoC consists in a cycling of +/- 5% around a SoC value.

To build a full factorial design of experiments (DoE) for these selected factors, we need 48 tests for each technology. Taking into account the available equipment for MOBICUS project and its duration, only 17 tests for each technology can be realized. A D-optimal design [6] is thus chosen to answer these conditions, and the obtained DoE is decomposed on three test waves to be the more adaptive as possible. These tests are distributed among three waves (Table 2). The first wave contains 9 tests, the second one 4 tests and the last 4 tests).

The first wave is a DoE subset with only 2 values of SoC designed to study the simple effect of factors and to get an overview of interaction between temperature and SoC. The second and third waves could be modified according to the first wave’s results in order to study more precisely the SoC effect (with 4 levels), and other factor interactions.

The first results of the wave#1 (e.g. Figure 6) showed that there is no much difference between on the one hand, tests at Icharge=”MAX” and Idischarge =”min” and on the other hand, tests at Icharge=”min” and Idischarge =”MAX”. That’s why all the tests susceptible to be changed are delayed to the wave#3 in order to properly analyse the results of the wave#1 and some first results of the second wave of tests.

Table 2: experiments plan for cycling around a SoC tests for one technology

Wave#1				
Test	Temperature	SoC	I charge	I discharge
1	0	30	MAX	min
2	0	80	min	MAX
3	0	80	MAX	MAX
4	25	30	min	MAX
5	25	30	MAX	min
6	25	80	MAX	min
7	45	30	min	min
8	45	30	MAX	MAX
9	45	80	min	MAX

Wave#2 (changed)				
Test	Temperature	SoC	I charge	I discharge
10	0	90	min	min
11	25	65	min	min
12	25	65	MAX	MAX
13	45	65	MAX	MAX

Wave 3#(changed and adaptable)				
Test	Temperature	SoC	I charge	I discharge
14	0	65	min	MAX
15	25	90	min	MAX
16	45	90	MAX	min
17	45	90	min	MAX

The figures below represent the first results of the first techno. The Figure 6 represents the capacity loss at 25°C for different SoCs however; the Figure 7 illustrates the capacity loss at the same SoC (SoC 30) at different temperatures (0, 25 and 45°C)

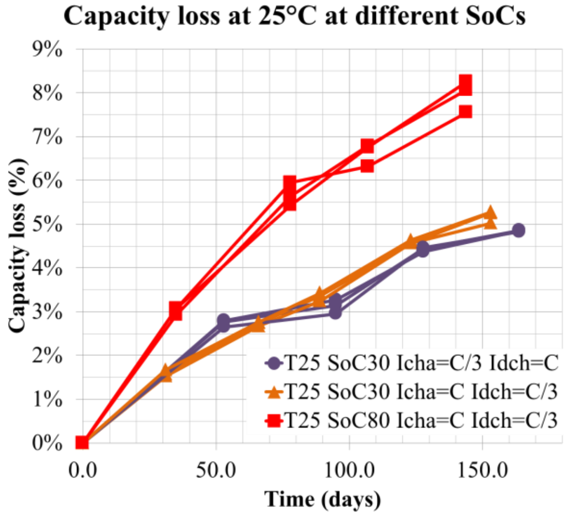

Figure 6 : Cycling at fixed SoC first results: Capacity loss at 25°C at different SoC for Techno#1

The figure above confirms what it is expected, that at the same current and temperature conditions, the capacity loss is more important at high level of SoC than at low SoC level.

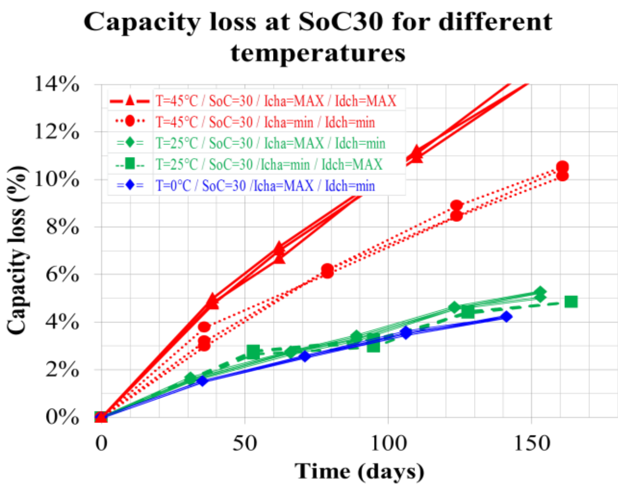

Figure 7 : Cycling at fixed SoC first results: Capacity loss at SoC 30 at different temperature for Techno#1

This latter figure shows that the high temperature is the most degrading factor for batteries life even at low level of current (*Icharge=Idischarge=min=C/3*). More results can be collected and analysed side by side at the end of the experimental part of the project. To build rigorous aging laws that takes into account all the tested factors.

2.2.2 Cycling in a range of SoC

The main objective of this type of tests is to validate the results of the previous tests. It can also contribute to study the batteries aging of professional automotive application (vehicle that travels long distances daily). This cycling aging is tested within two current profiles, a constant current profile and a Dynamic Stress Test (DST) profile [7], at 2 different temperatures (0 and 45°C) in a large range of SoC (between SoC 80% and SoC 30%). The figure below (**Erreur ! Source du renvoi introuvable.**) is a graphical representation of the difference between cycling at fixed SoC (part 2.2.1) and cycling in a range of SoC (part 2.2.2) for the same level of current (1C).

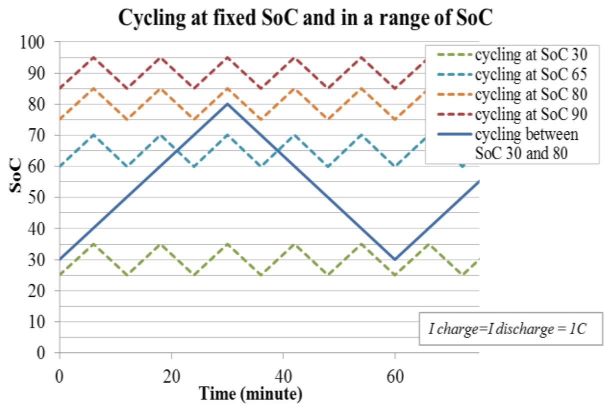

Figure 8 : Difference between cycling at fixed SoC and in a range of SoC

The current level of the cycling in a range of SoC at a constant current profile is the same as the "MAX" level of cycling at fixed SoC to simplify the comparison between these two tests types and also to have the same cells heating.

Current level:

Techno#1 *Icharge=Idischarge=1C*

Techno#2 *Icharge=Idischarge=3C*

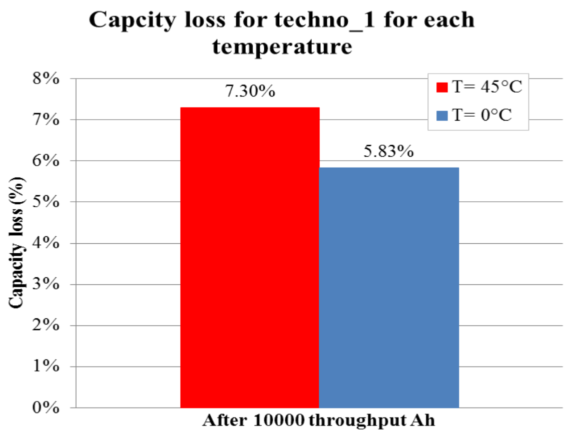

Figure 9 : Cycling in a range of SoC first results: Capacity loss after the first 10000 throughput Ah

Since we've just started this type of tests, the results above are extracted after only one check-up. At a further stage, these results will be combined and compared with the others of cycling at fixed SoC.

2.3 Mixed calendar/cycling aging

The third category of tests is the mixed aging tests. It consists on a combination of the calendar and cycling aging to approach the real life automotive application.

For each technology there are 3 modules per temperature (25 and 45°C) in three different patterns.

Each pattern is a repetition of a 12 hours loop containing an alternation between the cycling and calendar aging Table 3. The difference between the patterns is either the ratio cycling and calendar or the SoC level

Table 3 : cell ratings for both tested technologies

Pattern	Duration of the cycling part per 12 h	Duration of the calendar part per 12 h	SoC (%)
Pattern 1	2 hours	10 hours	80
Pattern 2	2 hours	10 hours	65
Pattern 3	6 hours	6 hours	65

The cycling part consists on cycling between (*SoC target + 5%*) and (*SoC target -5%)* at "MAX" current (*Techno#1=1C; Techno#2=3C*), just like the cycling at fixed SoC. The calendar part is like a rest stage at the chosen SoC.

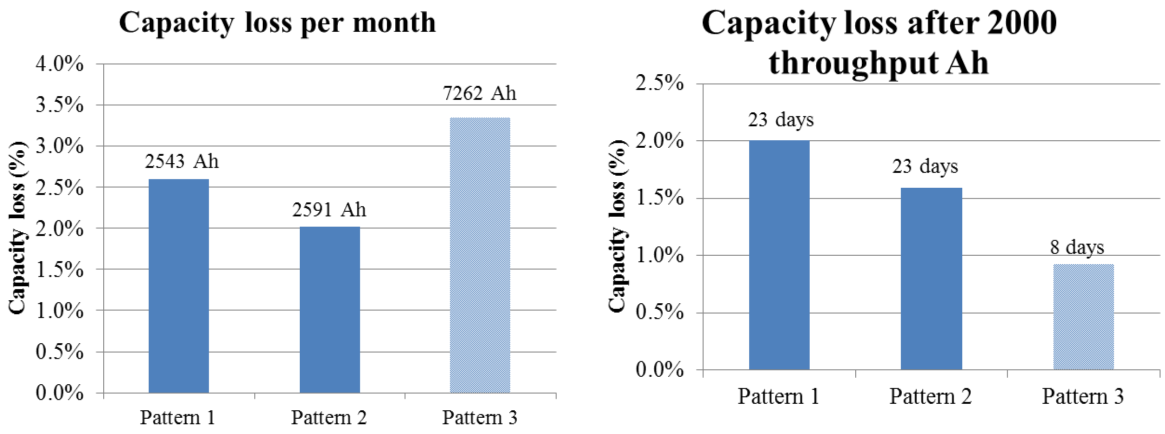

Figure 10 : Mixed calendar/cycling aging first results: Capacity loss per time and per Ah

More details about this category of tests and analysis are presented in a separate paper submitted also to EVS29 : "Capacity fade of lithium-ion batteries upon mixed calendar/cycling aging protocol"

2.4 Periodical characterisation

A check-up protocol is periodically applied to the tested cells in order to track their characteristics and status of aging. Firstly, a charge/discharge pattern at C/10 is individually applied on each cell which enables to measure cell capacity and observe voltage behaviour at low C-rate. Also, it enables to realise incremental capacity analysis (ICA) on cells at different state-of-health [8]–[10]. Particularly, a representation of ICA curves are realised for the both technologies summited to cycling at 0°C SOC80% at minimum C-rate (Figure 11). ICA profiles of both technologies presents three significant peaks located at 3.5, 3.9 and 4.05 V for Techno#1 and, at lower voltages for Techno#2, i.e. at 3.45, 3.65 and 3.75 V. These peaks have equivalent levels for Techno#1 despite of the 2nd technology which presents one predominant peaks around at 3.65 V. For both technologies, we can observe that aging occurs a decrease of peak level and a decay to high voltage. This effect could be due to cumulative effect of charge slippage and LAM (Loss of Active Material).

Secondly, a pulsed profile pattern is applied on the module each 5% of SOC during discharge and charge in order to measure open circuit voltage (OCV) and impedance of cells. In order to compare easily direct current resistance (DCR) measurements and ICA curves, resistances are represented versus OCV for both technologies in similar previous conditions (Figure 12). Resistances of the two tested technologies present similar behaviour with an important rise for low voltage under 3.6V for Techno#1 and 3.5 V for Techno#2. For both technologies, we can observe a cross of charge and discharge DCR curves. It happens one time for Techno#1 around 3.95 V and two times for Techno#2 at 3.7 V and 3.95 V. This phenomenon traduces

OCV plateau transition. For Techno#2, the cross observed at 3.7 V disappears for 79% of SOH which can be due to charge slippage.

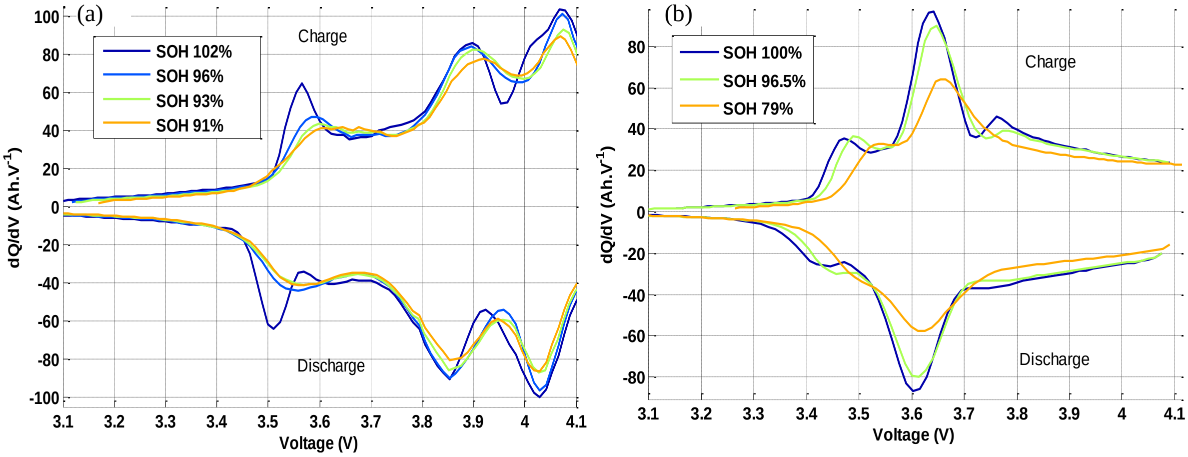

Figure 11 : Incremental capacity analysis at different state-of-health on (a) Techno#1 and (b) Techno#2 at different SOH attained after cycling at 0°C SOC80% with minimum C-rate.

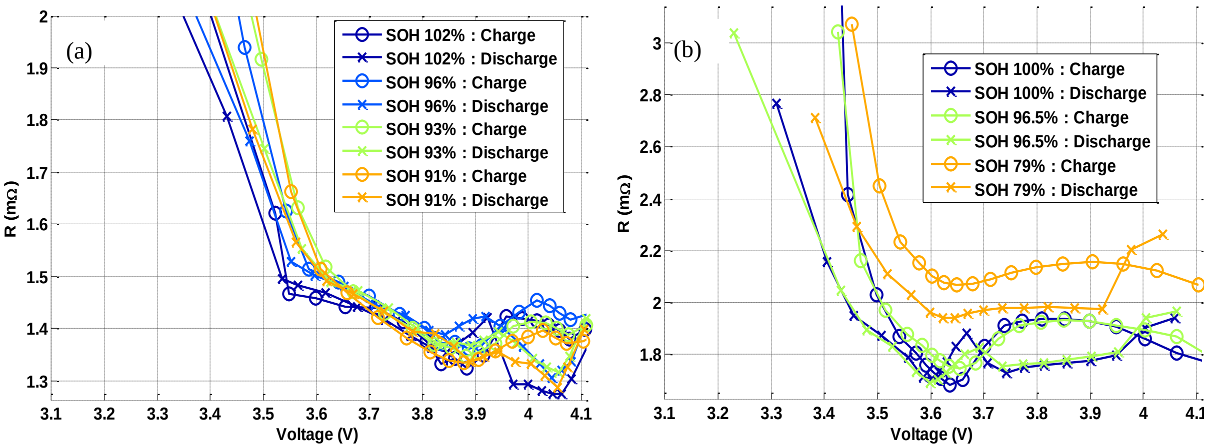

Figure 12 : 10s – DCR vs OCV measured on (a) Techno#1 and (b) Techno#2 at different SOH attained after cycling at 0°C SOC80% with minimum C-rate.

3 Conclusion

An ambitious and innovative experiment campaign is organized to study the aging of LIB under real use conditions. Calendar and cycling aging are studied in separate and mixed tests. The program mobilizes 12 partners and 18 experimental test benches. 258 cells from 2 technologies of LIB are tested. All the collected data will feed into aging laws and models at the end of the project.

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