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Capacity fade of lithium-ion batteries upon mixed calendar/cycling aging protocol

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Abstract

Energy and power fade of lithium-ion batteries over time is a cause of complaints from Electric and Hybrid vehicles customers. Car manufacturers strive to improve accuracy of battery performance degradation predictions, in order to reduce warranty costs. Currently, these predictions are mainly based on accelerated aging tests in cycling mode or on calendar tests. However, testing protocols with combination of calendar and cycling modes representing the usage of a vehicle in real life application are not much used. In this paper, a mixed aging protocol combining cycling and calendar repetitive phases is elaborated. Experimental results obtained on a LIB technology are presented and discussed in comparison with conventional accelerated cycling tests at the same conditions.

Kewywords: battery calendar life, cycle life, lithium battery, reliability

1 Introduction

Lithium-ion battery (LIB) technology is a promising candidate for current and new generations of electric vehicles (EVs) and hybrid electric vehicles (HEVs) due to their significantly increased energetic and power densities compared to previous NiMH generations. Besides being more expensive, a major drawback of LIBs is their performances degradation over time and usage. Therefore, LIBs are nowadays substantially oversized to meet power and energy performance requirements at the end-of-life.

Aging of LIBs has been intensively studied in the literature as these vehicle applications require a long cell lifetime, typically between 5 and 10 years. In the literature, aging of LIBs is tested according to either one year calendar or accelerated cycling tests [1]–[4], serving to establish predictive aging rate based on empirical laws, which are used to extrapolate 10 years real-usage scenarios at design stage [5]–[7].

However, real automotive application differs significantly from repetitive laboratory tests in controlled environment. LIBs will experience the vehicle driving phases separated by long parking phases where the battery is either charged or unused under very variable environment conditions. Moreover, some cycle life study shows possible change in degradation mechanisms depending upon how frequently the battery is

cycled [8], [9]. Therefore, current prediction based on accelerated cycling results could potentially over-estimate life for real situations.

In order to tackle this issue, car manufacturers, suppliers and research centers have teamed their efforts into the French National collaborative program MOBICUS, whose purpose is to design and validate strategies to extend battery lifespan, depending on vehicle usage and charging patterns.

This program involves RENAULT, VALEO, EDF, SIEMENS, ERDF, as large companies, CONTROLSYS and DBT-CEV as small and medium companies, IFPEN, CEA, IFSTTAR, IMS, and EIGSI as research centers. PSA, SAFT, UTC, and LA POSTE are guest companies of this program. The program receives the financial support from BPI FRANCE, Conseil Général des Yvelines, and Conseil Régional Pas de Calais.

As part of this program, this study presents a specific aging protocol where cycling phases are interrupted by long rest period representing vehicle driving periods followed by parking phases. This aging protocol is considered by being much closer to the practical use of a LIB than conventional accelerated cycling aging tests. Influence of the last of rest periods have been explicitly taken into account by the proposed protocol. Results of these tests can be compared to more conventional accelerated storage and cycling tests in order to observe influence of alternating aging modes on cell lifetime.

2 Experimental

2.1 Tested cell technologies

Two LIB technologies dedicated to automotive application have been supplied for testing in 2014 from two different cell manufacturers. Cell nominal capacities are respectively 43 Ah (Tech #1) and 26 Ah (Tech #2). The cell ratings are summarized in Table 1. The nominal discharge rate value is referred as “C” in the following.

Table 1: cell ratings for both tested technologies

Parameters	Values of technology #1	Values of technology #2
Nominal capacity at 25°C (Ah)	43	26
End of discharge voltage, U_{min} (V)	3.00	2,80
End of charge voltage (Floating) (V)	4.20	4.15
End of charge current under floating voltage (A)	2.2 (~C/20)	1.5 (~C/20)

In the MOBICUS program, a wide set of tests have been performed on cells, including calendar, continuous cycling or mixed aging tests. In calendar tests, cells are disconnected and voltage is not maintained. Modules are made out of three cells in series for reproducibility. Three cells are submitted to similar conditions, and the performance degradation of each one is measured during Reference Performance Tests (RPTs) presented in details in 2.3. In continuous cycling tests, cycling is interrupted only to perform RPTs. In mixed aging tests, cells are submitted to alternating cycling and rest periods which durations are defined in **Erreur ! Source du renvoi introuvable.**.

Regarding continuous cycling and mixed aging tests, three series connected cells of the same technology are assigned to a specific aging test allowing using only one test channel for cycling three distinct cells at the same condition. Surface temperature of each cell is monitored and a thermal management is applied to keep the temperature difference between the cells surface and ambient below 10°C maximum.

Aging tests have been shared amongst all the experimenters of the MOBICUS program which are presented on Figure 1.

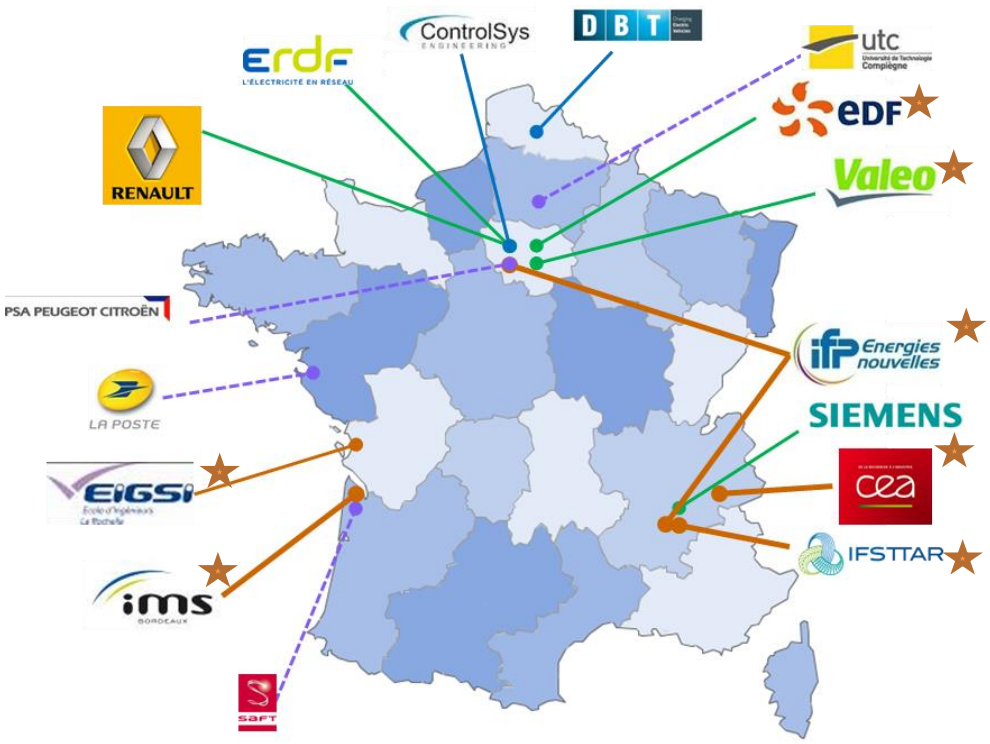

Figure 1 : Members of the MOBICUS program. Experimenters sharing aging tests are highlighted using ★. Renault is the program leader.

2.2 Calendar and continuous cycling aging protocol

2.2.1 Calendar tests

Amongst the different calendar tests, storage on fixed SoC and fixed temperature for both cell technologies have been started in March 2015 and shared by the MOBICUS experimenters.

Modules of three cells have been allocated to the different test conditions presented in the calendar test matrix presented in Table 2. These tests are distributed in 4 different temperatures (0, 25, 45 and 60°C) and 5 different SoCs (0, 30, 65, 80 and 100%). For cell technology #1, 10 storage tests have been carried out, whereas a more complete test has been planned for cell technology #2 (16 tests).

Table 2: calendar test matrix and cell allocations for both technologies

	SoC=100%	SoC=80%	SoC=65%	SoC=30%	SoC=0%
Temp. 60°C	#2	#1, #2	#2	#2	
Temp. 45°C	#1, #2	#1, #2	#1, #2	#1, #2	#1, #2
Temp. 25°C	#2	#1, #2	#2	#2	
Temp. 0°C	#2	#1, #2		#1, #2	

#1: Cell techno #1, #2: Cell techno #2

2.2.2 Continuous cycling tests

Furthermore, the vast experimental plan of the MOBICUS project contains accelerated cycling tests at different values of SoC. Influence of aging factors such as ambient temperature (3 values), SoC (4 values), charge current (2 values) and discharge current (2 values) are being investigated. Cycling is performed

around a mean SoC value in a +/- 5% SoC window. It is interrupted only during Reference Performance Tests.

A full factorial design of experiments (DoE) for these selected aging factors would have required 48 tests for each cell technology. Taking into account the available equipment for MOBICUS project, only 17 tests for each technology have been realized. A D-optimal design is thus chosen to answer these conditions, and the obtained DoE is decomposed on 3 test batches to be most adaptive as possible.

In this paper, we will focus only on results obtained at maximum charging current and discharge currents at 25°C and 45°C as they correspond to the same rates than those used for mixed aging tests. A detailed study of results of the cycling tests is carried out in a distinct dedicated paper [10].

Table 3: experimental plan of "continuous" cycling tests divided into three test batches and their status

Test batch 1 (finished)				
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

Test batch 2 (on-going)				
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**

Test batch 3 (planned)				
Test	**Temperature**	**SoC**	**I charge**	**I discharge**
14	0	65	min	MAX
15	25	90	min	MAX
16	45	90	MAX	MAX
17	45	90	min	MAX

2.2.3 Mixed calendar and cycling aging protocol

The mixed aging test protocol consists in a 12 hours aging basic pattern which is divided into a calendar part and a cycling part (Figure 2). The two investigated patterns differ only by the repartition of the aging parts: in the first pattern, the cycling part lasts only 2 hours over the 12 hours of the pattern (pattern = 2/12) whereas it last 6 hours for the second one (pattern = 6/12), meaning that the cell spends equal time in cycling and storage mode.

These specific tests have been shared between L3E (EIGSI) and IMS (Bordeaux University).

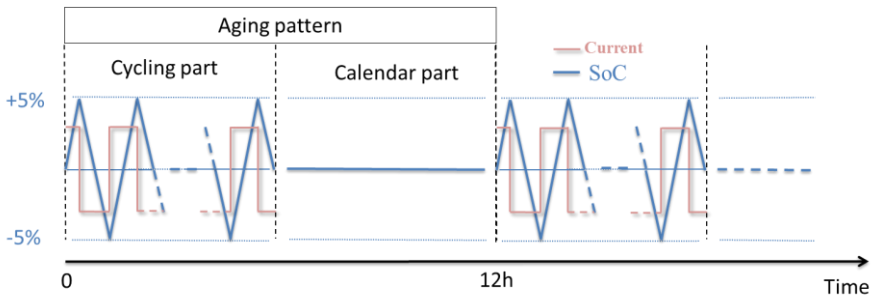

Figure 2: repeated basic aging pattern divided in a cycling part (I≠0) and a calendar part (I=0)

Table 4 : experimental plan of mixed aging protocol for the two tested cell technologies

Ambient temperature	Fraction of cycling time in aging pattern	SoC (%)	Charging & discharge current
25°C	2/12	80	1C (Tech #1) 3C (Tech #2)
	2/12	65	
	6/12	65	
45°C	2/12	80	
	2/12	65	
	6/12	65	

During the cycling phases, cells are successively discharged and charged at constant current without relaxation around a specified SoC according to a simple temporal profile presented on Figure 2. Ambient temperature is maintained constant whichever the part of the aging pattern.

Influences of aging factors such as the ambient temperature (25°C and 45°C) and SoC (65% and 80%) have been investigated as summarized by Table 2 for the two tested cell technologies. Choice of current value has been made in agreement with cell application (respectively EV for tech #1 and Plugin HEV for tech #2). Three cells of each technology are tested as a series module for each condition of the testing plan shown on Table 2, representing 18 tested cells per technology.

2.2.4 Technical implementation of the mixed aging protocol

The choice of the patterns enables to use only one test channel to test three distinct modules. Indeed, as shown in Figure 3, cycling phases of the three modules do not overlap each other if two of them are tested according to the aging pattern 2/12 (cycling only 2 hours over 12) whereas a third module is submitted to the second aging pattern 6/12 (cycling 6 hours over 12).

Therefore, a specific multiplexing system using command and power relays were specifically designed to disconnect automatically modules entering in the calendar phase and connect the module entering in the cycling phase to the channel. The multiplexing switch is directly managed by the cycling program in the test channel as illustrated on Figure 4. Surface temperature and voltage of all cells of the three modules are monitored and recorded during tests regardless of the aging mode (cycling or calendar).

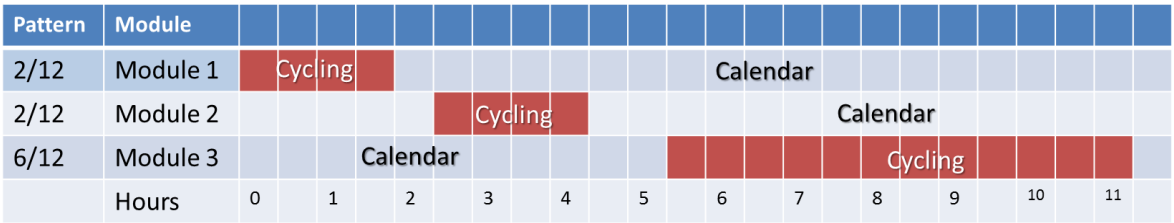

Figure 3 : time schedule highlighting cycling and calendar phases of 3 cell modules connected to a single test channel

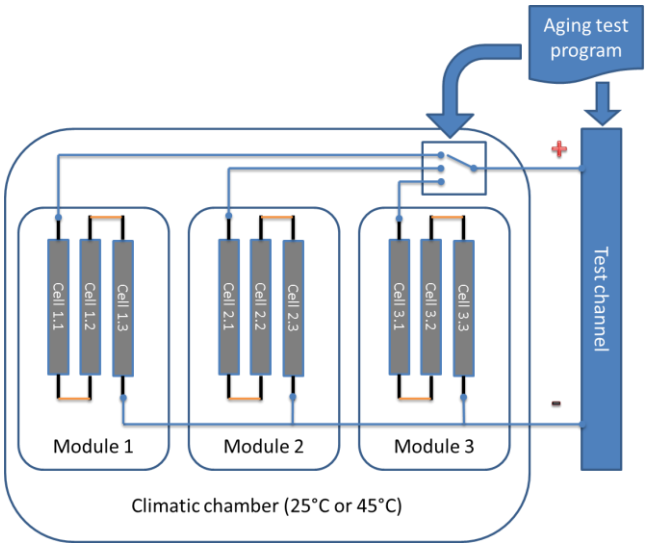

Figure 4 : Schematic representation of the multiplex system used to test 3 modules on a single test channel

2.3 Reference performance test

Periodically, cells of each module are taken individually and their performances are tested according to a Reference Performance Test (RPT). Capacities for each cell are measured using a CCCV discharge C/10 rate until U_{min} defined in Table 1. The choice of low C-rates enables to realise incremental capacity analysis on cells at different state-of-health.

Then, cells are reconnected in modules and fully charged. Cell resistance is then characterized using current pulses at every 15% SoCs for two values of current both in charge and discharge mode. Open Circuit Voltage of cells is also recorded at the end of pauses of 45 minutes between pulses. RPT are systematically performed at 25°C which serves a reference temperature for both cell technologies every 6 weeks for continuous cycling, every 8 weeks for mixed aging tests and every 12 weeks for calendar tests. For some test conditions, additional RPTs are conducted at 2 other temperatures, 10°C and 45°C, at the beginning and at the end of the aging tests.

Figure 5 presents capacity and discharge resistance evolutions for the two cell technologies measured during the first RPT with tested temperatures. Resistances are obtained from cell voltage evolution after 10 seconds during a C/2 discharge pulse at SoC=100%.

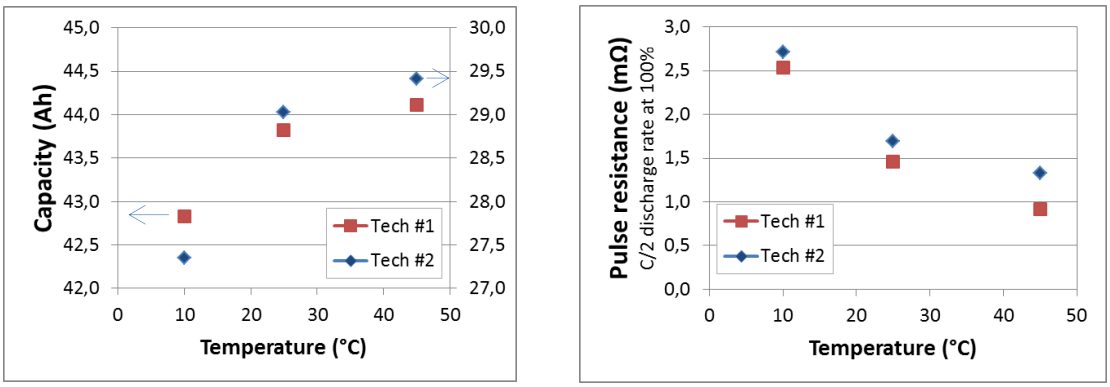

Figure 5 : capacity and resistance evolution with temperature for the two tested LIB technologies at fresh state

3 Preliminary aging results and analyses

3.1 Calendar and continuous cycling aging tests

This part presents aging results from calendar and accelerated cycling obtained for Tech. #1. Capacity retentions of continuous cycling at 1C/1C at 0°C, 25°C and 45°C are compared with results of calendar aging tests at similar test conditions (except for T=25°C where the SoC is slightly different) on Figure 6.

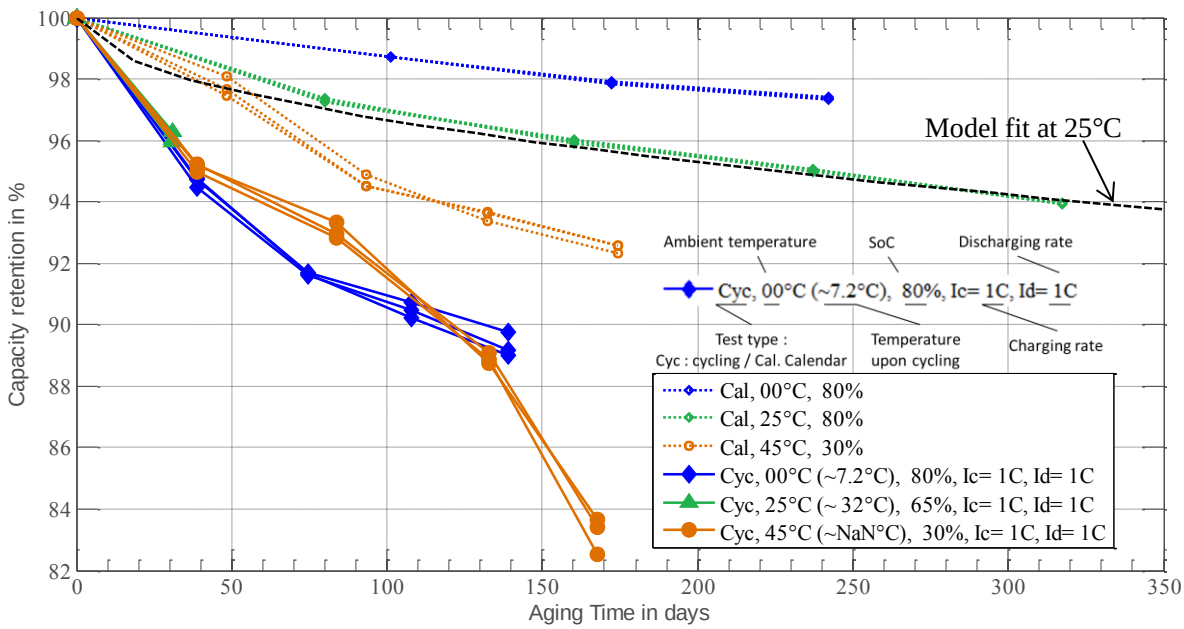

Figure 6 : capacity degradation versus aging time measured according to the calendar and "continuous" cycling aging protocol defined in 2.2. A model fit for calendar data at 25°C is also shown.

Predicting capacity loss requires a correct separation between calendar and cycling aging mechanisms.This graph allows estimating how the cycling affects global aging of cell by comparing them to data from cells stored in similar temperature and SoC conditions (calendar cells).

For all tested temperatures, impact of continuous cycling on aging is very significant at the presented C-rates on tech #1 Impact of continuous cycling is the most severe at 0°C as cycled cells experienced a sharp capacity loss and as the calendar aging is the most limited at this temperature. At 45°C, a very significant part of the global aging of continuous cycling can be attributed to the calendar aging. After 165 days of aging at 45°C, results suggest that calendar aging may be responsible of about the half of the measured capacity loss on continuous cycling.

Previous studies demonstrated that the main mechanism of LIBs in storage mode was growth of the Solid Electrolyte Interphase (SEI) on negative electrode which evolution follows classically a √t time dependency [1], [3], [11]. Here, a simple model for the relative capacity loss in % $Q_{loss,cal}$ has been derived from calendar aging data at 25°C using least-squares regression and will be used in the following of this document. In this paper, SoC dependence of $Q_{loss,cal}$ at 25°C has been neglected.

$$Q_{loss,cal}(25°C, t) = k_{cal} \cdot \sqrt{t} \approx 0.333 \cdot \sqrt{t} \qquad (1)$$

3.2 Mixed calendar and cycling aging tests

So far, only preliminary results at 25°C of the mixed aging protocol presented in **Erreur ! Source du renvoi introuvable.** on cell technology #1 were obtained at the time of writing this paper. All cells experienced approximately the same aging time but the number of microcycles depends on the aging protocol: naturally, cells submitted to continuously cycling achieved the highest number of microcycles and the highest Ah Throughput (cumulated discharged Ah) even if their aging time is the smallest. These aging results are then compared with results of calendar aging conditions and on Figure 7. Influence of aging pattern of mixed aging protocol (2h/12h) and (6h/12h) can be therefore estimated. Comparison of cell surface temperature evolutions have revealed a very small difference of surface temperature upon cycling whichever cells are submitted to continuous or mixed aging test for the presented tests.

As expected, cells cycling 6 hours over 12 (half time) deteriorate more rapidly than cells cycling only 2 hours. However, there is only a tiny difference in measured degradation rates (capacity loss versus aging time) between cells cycled half time and those submitted to continuous cycling for similar conditions after

about 40 days of cycling. Furthermore, preliminary results suggest that cells cycling only 2 hours over 12 around SoC=80% deteriorate faster than cells stored at 25°C at SoC=65%.

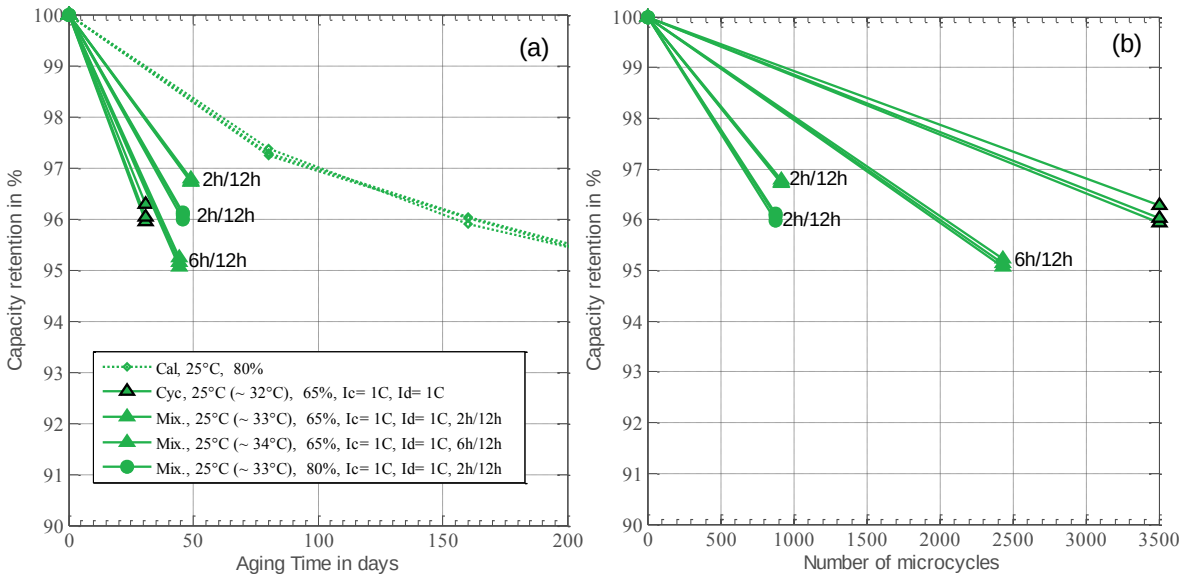

Figure 7: capacity degradation for calendar (Cal.), continuous cycling (Cyc.) and mixed aging patterns (Mix.) at 25°C for cell technology #1 versus aging time (a) and cycling number (b)

Table 5 summarizes the aging results of the different cycling conditions at 25°C obtained at the time of writing this paper. According to their respective aging time, an equivalent loss of capacity due to calendar aging $Q_{loss,cal}$ has been derived for each cycling condition using Eq. (1). As a first approach, the degradation induced by cycling $Q_{loss,cyc}$ is then approximated by subtracting the estimated calendar part to the measured capacity loss of the cells.

Table 5: summary of aging results for cell technology #1 for mixed protocol and continuous cycling at 25°C

Aging protocol	Aging time (days)	Accomplished number of cycling	Cumulated Ah throughput (Ah)	Experimental Q_{loss} (%) (Average value on the 3 cells)	Predicted $Q_{loss,cal}$ by Eq. (1) (%) "calendar loss"	$Q_{loss,cyc} = Q_{loss} - Q_{loss,cal}$ (%) "cycling loss"
SoC=65%, Mixed 2h/12h	49	920	4154	3.30	2.33	0.97
SoC=65%, Mixed 6h/12h	44	2435	10651	4.92	2.22	2.70
SoC=80%, Mixed 2h/12h	46	880	3973	3.99	2.25	1.74
SoC=65% Continous cycling	31	3500	15257	3.91	1.85	2.06

3.3 Degradation rates upon cycling

The aging protocol enables to study how degradation of cells is affected by the frequency at which the battery is cycled. In the present case, depending on the cycling protocol cell are cycled 2 over 12 hours, 6 over 12 hours or cycled continuously at same ambient temperature (25°C) and cycling C-rate (1C).

The bar graph shown in Figure 8 (a) presents the repartitions of capacity loss between calendar and cycling losses for each test conditions reported in Table 5. Capacity loss induced by cycling is then used to estimate the capacity loss degradation rate according to the number of microcycles accomplished by the cells which is plotted on Figure 8 (b) for every cycling condition.

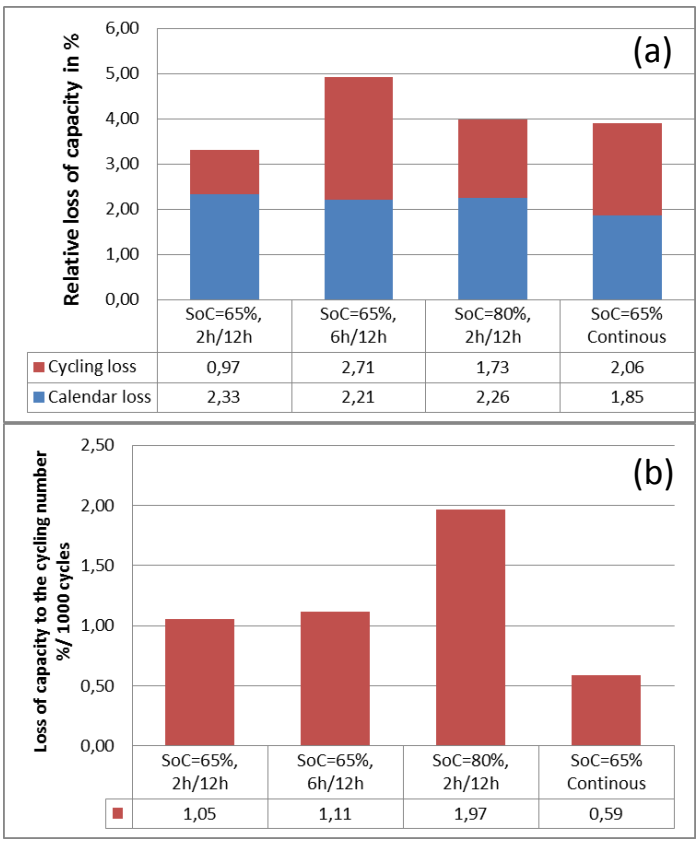

Figure 8: repartition between estimated calendar and cycling loss (a) and derived degradation rates upon cycling (b) for mixed and continuous cycling conditions at 25°C for cell technology #1

Figure 8 (b) shows that degradation rate of cells is significantly affected by the cycling protocol for presented aging tests. At same temperature and C-rate conditions, cycling the cells either 2 hours or 6 hours over 12 hours does not modify the degradation rate due to cycling. In our case, cells lose about 1.1% capacity per 1000 microcycles (+/- 5% SoC) when they are used either 2 hours or 6 hours over 12 hours at same C-rates, SoC levels and ambient temperature. The calculated degradation rates for the continuous cycling condition is however 40% lower than for other tests which tends to indicate that accelerated cycling leads to temper significantly the degradation rate and confirm previously presented results showing that degradation rate depends on how frequent LIBs are used [8], [9].

Furthermore, results suggest also that SoC of cycling has a significant influence on the capacity degradation induced by cycling for the considered cell technology. At same temperature, same C-rates and same cycling frequency, increasing only the SoC of cycling from 60% to 80% and contributes to almost double the degradation rate due to cycling at 25°C.

These results have been established on the basis of ongoing aging results and must be confirmed by future measurements at same conditions. Moreover, results of similar aging protocol but performed on LIB tech #2 will permit to consolidate or not present conclusions.

4 Conclusion

In a real automotive application, LIBs are submitted to a complex usage mixing calendar and cycling aging modes. Nevertheless, aging of LIBs is rarely tested according to such a mixed usage. As a consequence, aging predictive models are in the most cases built from calendar aging data on the first hand and accelerated cycling data on the other hand but there is still a lack of validation of these models according to complex usages. This paper tackles this issue by presenting two aging patterns that combine both calendar and cycling aging modes but differs in the repartition of the two modes. Two recent LIB technologies

dedicated to automotive application are tested according to an experimental plan investigating influences of ambient temperature and SoC and how frequent the battery is cycled.

Analysis of degradation upon cycling has been conducted by subtracting the part attributable to calendar aging at 25°C before deriving the cell capacity degradation rate (capacity loss versus cycling number) for each cycling test. By comparison with results obtained from a conventional 1C/1C continuous cycling aging test, analysis of preliminary results of mixed aging patterns tends to indicate that degradation rate is significantly affected by the aging pattern and therefore by the frequency of cycling. Accelerated cycling leads to temper significantly degradation rate due to cycling in comparison with more realistic aging pattern of automotive application where cells are cycled only 2 hours over 12. As a consequence, current prediction based on accelerated cycling results may potentially over-estimate life for real situations. Future results of similar aging protocol but performed on a different LIB technology will permit to generalise or not present conclusions.

Acknowledgments

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