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Evolution of the safety behavior of Li-ion cells after aging

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Executive Summary

Lithium ion battery technology is more and more widespread due to its high energy density and good cyclability. Today electric vehicles runs with Lithium ion technologies. Despite Lithium ion technology has numerous advantages, it has been proved that lithium ion battery are the cause of many accidental car fires. Thereby battery safety is a key issue to continue to develop more performant and enduring vehicle, but also to ensure the user's safety. Depending on the condition of use, different aging mechanisms inside the cell could be activated and induce physical and chemical modifications of the internal components. So, aging of a cell has a strong influence on its safety behavior. One reference of commercial 18650-type lithium ion cell is investigated using BEV (Battery Electric Vehicle) representative aging at various temperatures (-20°C, 0°C, 25°C, 45°C) according to the international standard IEC 62-660. Ante-mortem and post-mortem analyses (half coin cell at the electrode level, SEM, EDX, XRD, GCMS, DSC, FTIR) are realized on internal components in order to identify clearly which aging mechanism occurs in accordance to the electrical profile of the cell. Then ARC test will be performed. By comparing safety behavior of fresh cell *vs.* aged cells, it will be possible to understand the impact of each aging mechanism on cell safety behavior.

Keywords: battery ageing, BEV , battery SoH (State of Health), internal resistance, safety

1 Introduction

Lithium ion battery became the most important energy-storage system for portable consumer electronics device and advance to a key technology to enable the broad commercial launch of electric vehicles. Today electric vehicles run with Lithium ion technologies and one of the most popular format is the 18650 cylindrical cell. In this work we will study three different 18650 commercial cells with two different high energy density technologies NCA/Graphite-Si and Ni-rich NMC/Graphite-Si.

Some research groups have already studied the impact of low temperature cycling on safety behavior [1], the correlation of aging with the thermal stability of batteries [2] or the thermal runaways during external heating abuse of commercial cells at different levels of aging [3]. But none of this studies accomplish a work with several aging mechanisms identified by post mortem analysis and several abuse tests for each aged batch in order to compare them together.

2 Cell aging and aging mechanism

Battery is an unstable system which will evolute according to usage and time. Battery component will be the support of physical and chemical degradation reactions which are summarized in the figure 1.

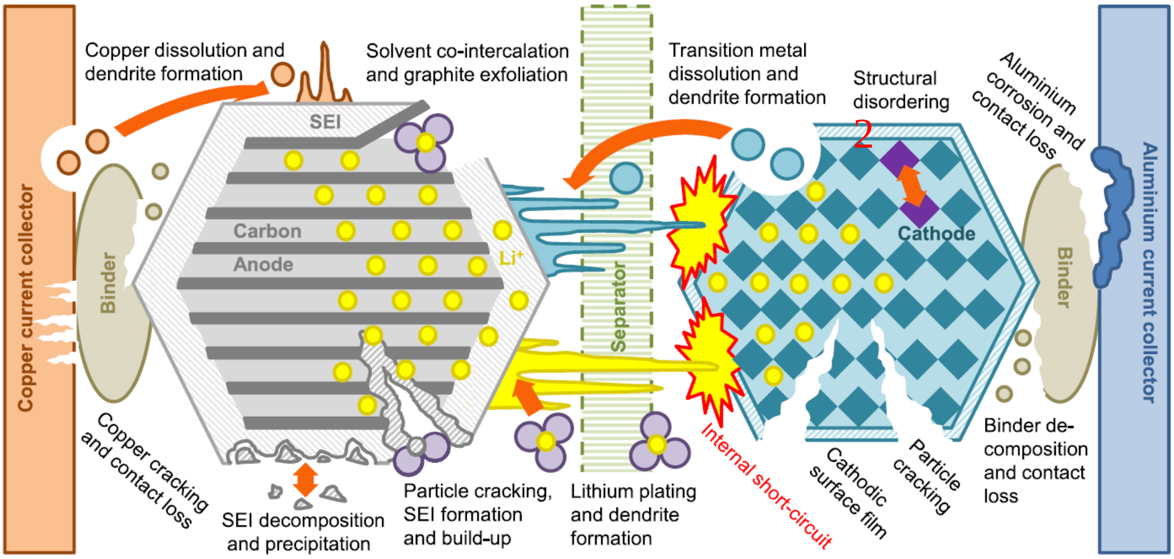

Figure 1: Degradation mechanisms of Lithium-ion cell [4]

Depending on the condition of use, different aging mechanisms inside the cell could be activated and induce physical and chemical modifications of the cell components. Current knowledge of literature allows to identify aging conditions which promote specific degradation mechanism (figure 2).

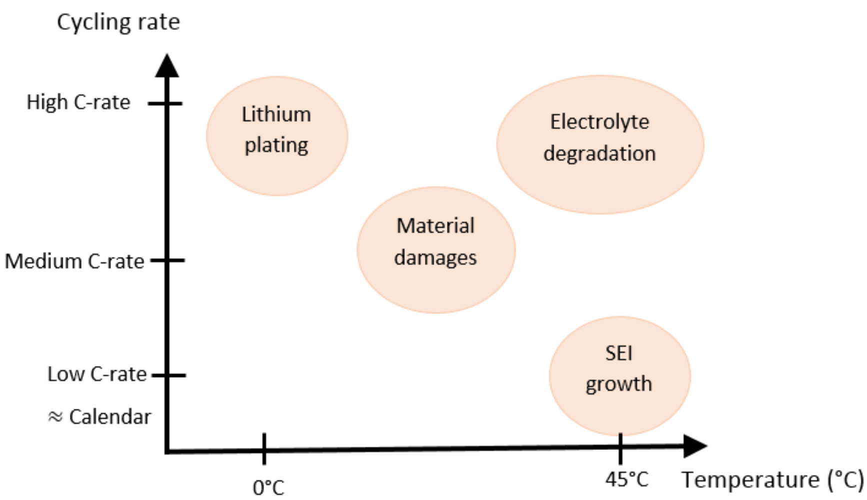

Figure 2: Scheme of the different aging mechanisms and their condition of occurrence

The aim of this work is to use cell in differents aging conditions in order to promote some degradation mechanisms. In particular, we will age several batches of cells to obtain lithium plating, material damages and SEI growth.

3 Ante-Mortem Analyses

One reference of commercial 18650-type lithium ion cell has already been investigated using BEV (Battery Electric Vehicle) representative aging at various temperatures (-20°C, 0°C, 25°C, 45°C) according to international standard IEC 62-660. This cell is dedicated to power application.

The results of this study are described below.

First of all, ante-mortem analyses and electrical tests were carried out in order to clearly define all the characteristics of the cell. Figure 3 explains the available characterization techniques performed on each internal component of the cell.

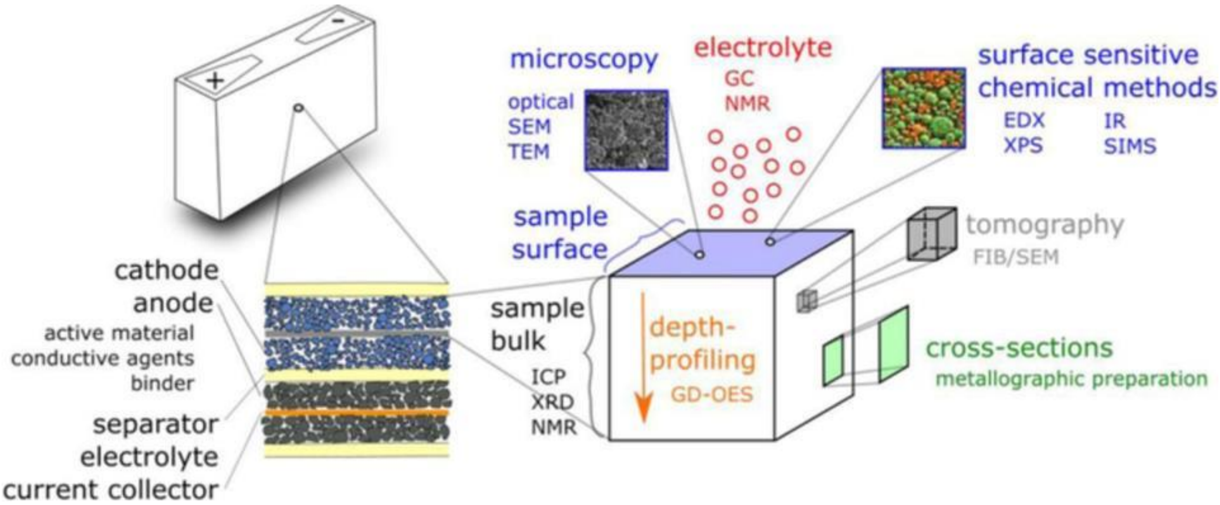

Figure 3: Diagram of all characterisation techniques used for cell ante-mortem and post-mortem studies [5]

We realized some of those tests on the fresh cell and all the characteristics of the cell are summerized in the Table 1. Results will be compared with aged cells.

Characteristics of the cell			Techniques
Electrical properties		Cell type: Power Voltage : 2.5-4.2V Capacity (C/3) : 3000 mAh Energy density : 237 Wh/kg Internal Resistance Hioki 1KHz, 50% SOC: 13.73 mΩ Internal résistance Pulse 10s, I max : 20,63 mΩ	Electrical cycling and check up
Positive electrodes	Active material	Blend NCA/NC NCA : Ni 88,5 at%, Co 10,0 at% et Al 1,5 at% NCO: Ni 78,0 at%, Co 22,0 at%	MEB and EDX quantification
	Coating thickness	45 ± 1 µm	Micrometer
	capacity	2.25 mAh/cm²	Button cell cycling vs metallic Li
Electrolyte		EC 40%, DMC 30%, FEC 30%	GCMS
Separator	material	PE	DSC
	coating	AlOOH coating on one face	FTIR
Negative electrodes	Active material	Blend Graphite/Silicon	MEB +EDX
	Coating thickness	44 ± 1 µm	Micrometer
	capacity	2.39 mAh/cm²	Button cell cycling vs metallic Li

Table 1: Characteristics of the fresh cell obtained after ante-mortem analyses

4 Post-Mortem Analyses

Cells were aged using BEV representative aging at various temperatures (-20°C, 0°C, 25°C, 45°C) and calendar aging (45°C at 4.2V and 45°C, 100% SOC, undefined potential). State of health via electrical performance measurement were realized at 25°C every 28 days for cycling aging. This electrical test allows us to track the evolution of some relevant characteristics of the cell: Capacity, Internal resistance, Energy density and Nominal Voltage.

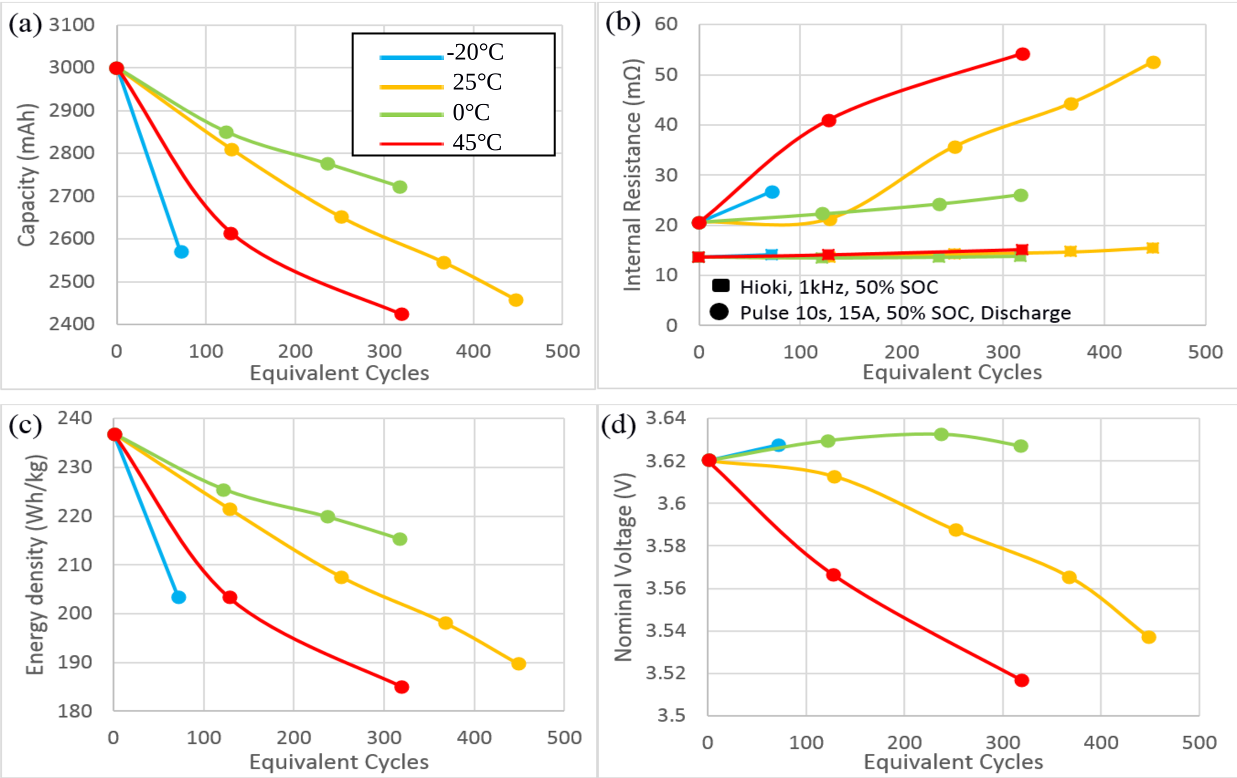

Figure 4: 25°C Check up results (a) capacity at C/3, (b) internal resistance, (c) energy density at C/3 and (d) nominal voltage at C/3 during cycle aging at different temperature

In terms of capacity, figure 4 (a) shows that aging at very low temperature (-20°C) is very harmful for cell. We note that during aging at -20°C, after a few days of cycling, the cell capacity falls down to ~70 mAh.Voltage thresholds in charge and discharge, were reached very quickly when a current was applied to the cell. However, when the cells were put at 25°C, it was possible to reach reasonable capacity. We guess the presence of Li plating for this cycling conditions. At high temperature (45°C) the cell performance decrease as well quite quickly: the effective capacity has decreased by ~20% after 300 equivalent cycles. At this temperature, electrode material damage should be responsible for capacity fading. Between 0°C and 25 °C, the evolution of cell capacity is less pronounced: capacity fading is approximately ~10% at 0°C and ~15% at 25°C after 300 equivalent cycles. All those results are in agreement with cell manufacturer datasheet: lifetime of cell should be equal to 250 cycles (with charging conditions between 0°C and 50 °C).

One significant indicator used for cell State Of Health (SOH) estimation is internal resistance [6,7]. In this study, internal resistance has been evaluatedd by two methods: Current Pulse method (10s, I discharge max=15A) and impedance measurement (AC,1 kHz, HIOKI equipment). Both technics allow to evaluate two aspects of electrochemical behavior of the cell (capacitive or resistive behavior), considering the corresponding time constant (respectively 10s or 1ms). Based on these results, we can conclude that impedance data at 1 kHz does not vary significantely during aging (few percent growth after a few months of cycling). It means that electrical contact between electrodes particles and/or collector should not have changed significantly after aging. Global impedance spectra study is currently led to understand the impact of aging on cell performance.

In regards to pulse measurements, we can already assume that aging impacts internal resistance, especially at high temperature. Aging mechanism which could be responsible for the internal resistance enhancement is the passivation layer growth due to chemical reactions (ex: SEI Growth on negative electrodes at high temperature).

Figure 4 (d) represents variations of nominal voltage during aging: two different trends are visible. For aging at low temperature (0°C and -20°C) the nominal voltage has increased after aging. For aging at ambient and high temperature the nominal voltage has decreased after aging. This observation seems to be the results of a non equiponderant aging of both positive and negative electrodes.

Post-mortem analysis will help us to identify the degradation mechanisms which take place for each conditions of aging [5]. Main post-mortem results obtained during this work are described below.

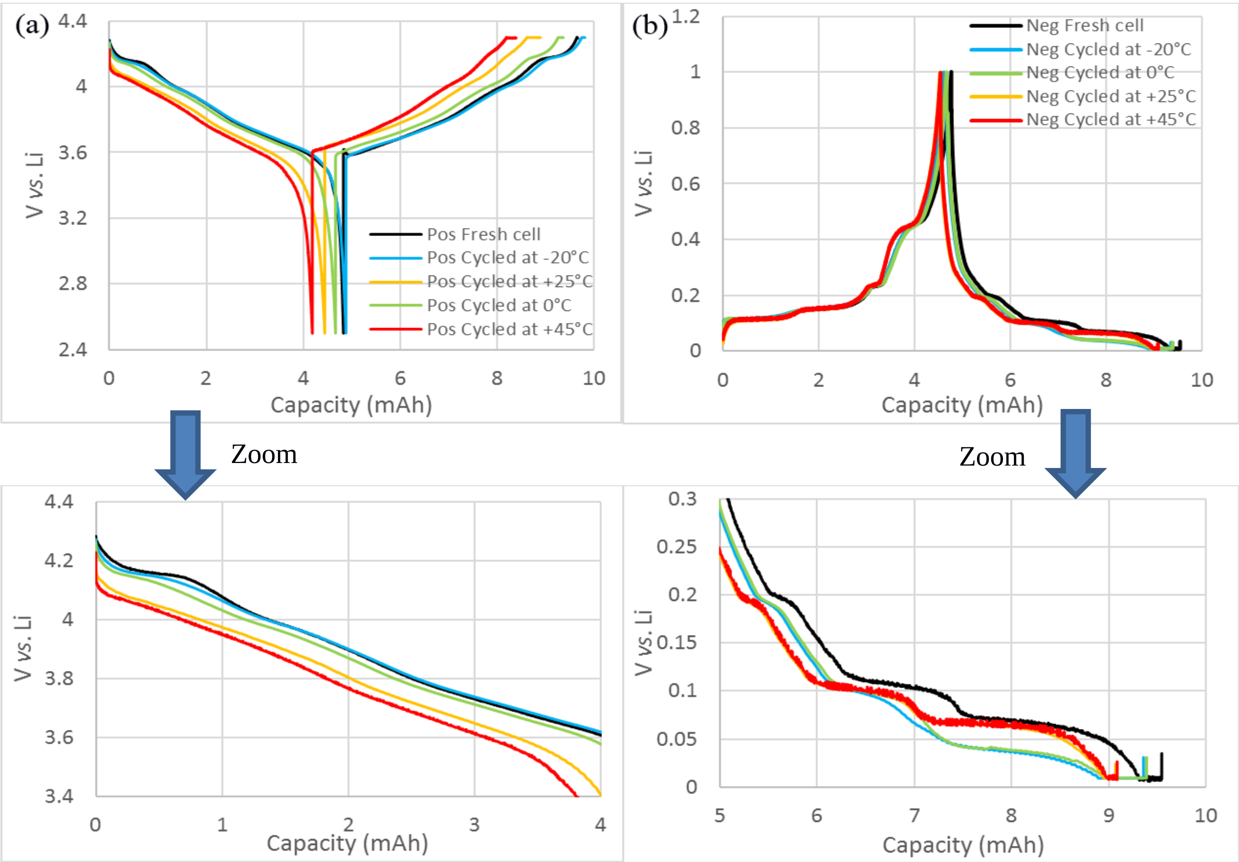

Figure 5: Cycling curves of (a) positive and (b) negative cycled electrodes vs. metal Li

In Figure 5, samples have been taken from both electrodes of aged cells (for each aging) and have been reintroduced in half coin cell. Towards the positive electrodes (Figure 5 (a)), the cycling profiles reveal that during discharge, the potential of positive electrode vs Li is lower for high temperature aging cells than for fresh or low temperature aged cells. The potential fall is about 0.1V *vs*. Li. So we can assume that in high temperature the main damages take place on the positive electrodes. By comparing the cycling curves of positive eletrodes from fresh cell and low temperature cycled cells, we can also assume that positive electrode did not demonstrate significant damages.

Toward negative electrodes(Figure 5 (b)), the cycling profiles reveal that during discharge, the potential of the negative electrode vs Li is lower for low temperature aging cells than for fresh or high temperature aged cells. The potential fall is about 0.03V *vs*. Li. So we can assume that in low temperature major damages take place on the negative electrodes. By comparing the cycling curves of negative eletrodes from fresh cell and high temperature cycled cells, we can also assume that the negative electrode did not demonstrate significant damages.

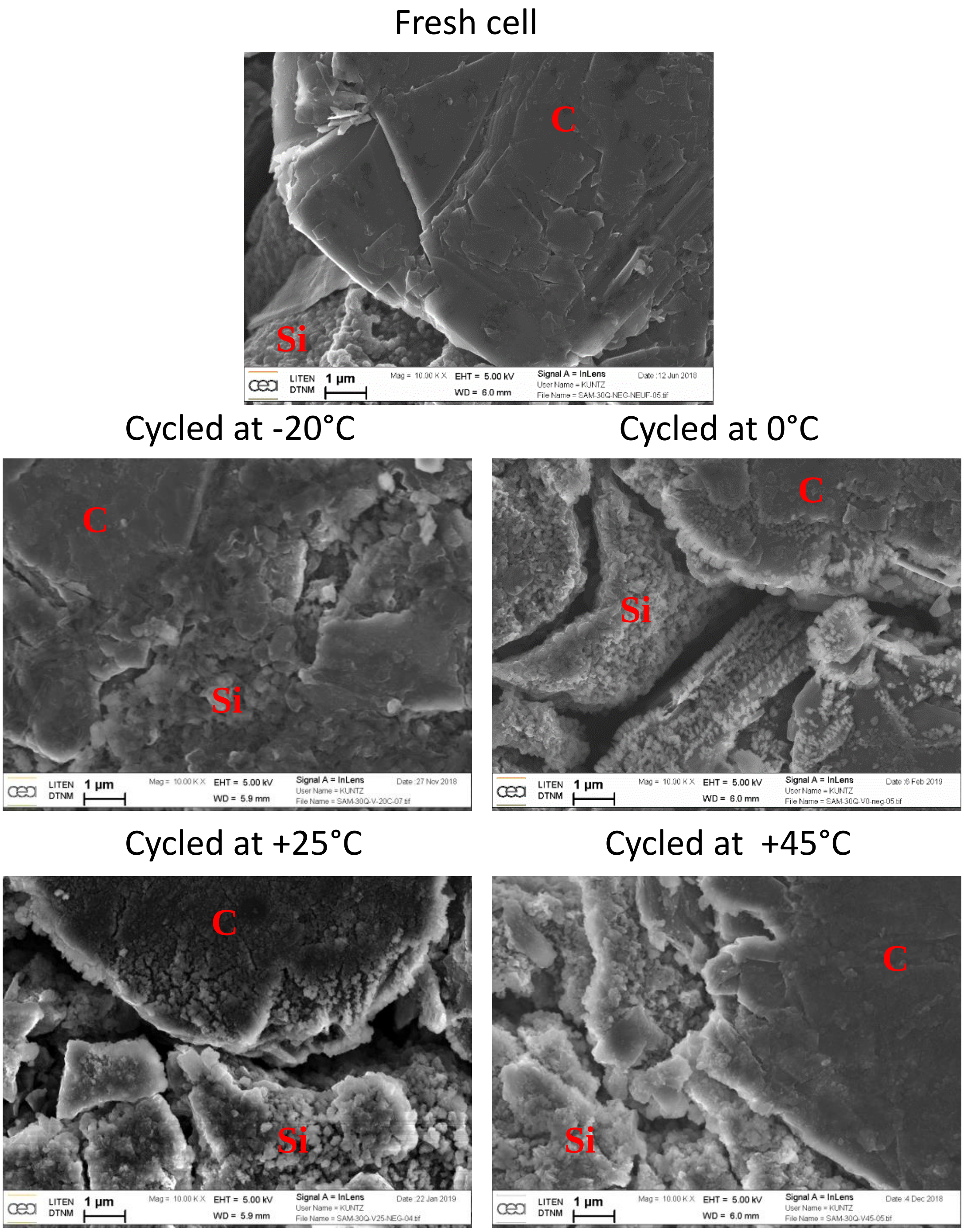

Figure 6: SEM Images of fresh and cycled negatives electrodes

SEM images of cycled negative electrodes show surface evolutions. Particles identification has been performed by EDX analysis. At -20°C we clearly see that silicon particles have been totaly destroyed but graphite particles did not demonstrate significant evolution. At 0°C and 25°C, cracks appear in silicone particles and the particles surface becomes locally coated. At 45°C cracks of silicone particles appear and the coating seems to be more homogeneous. To complete these visual observations and to determine more precisely the nature of the coating, XRF analyses will be performed on fresh and cycled electrodes.

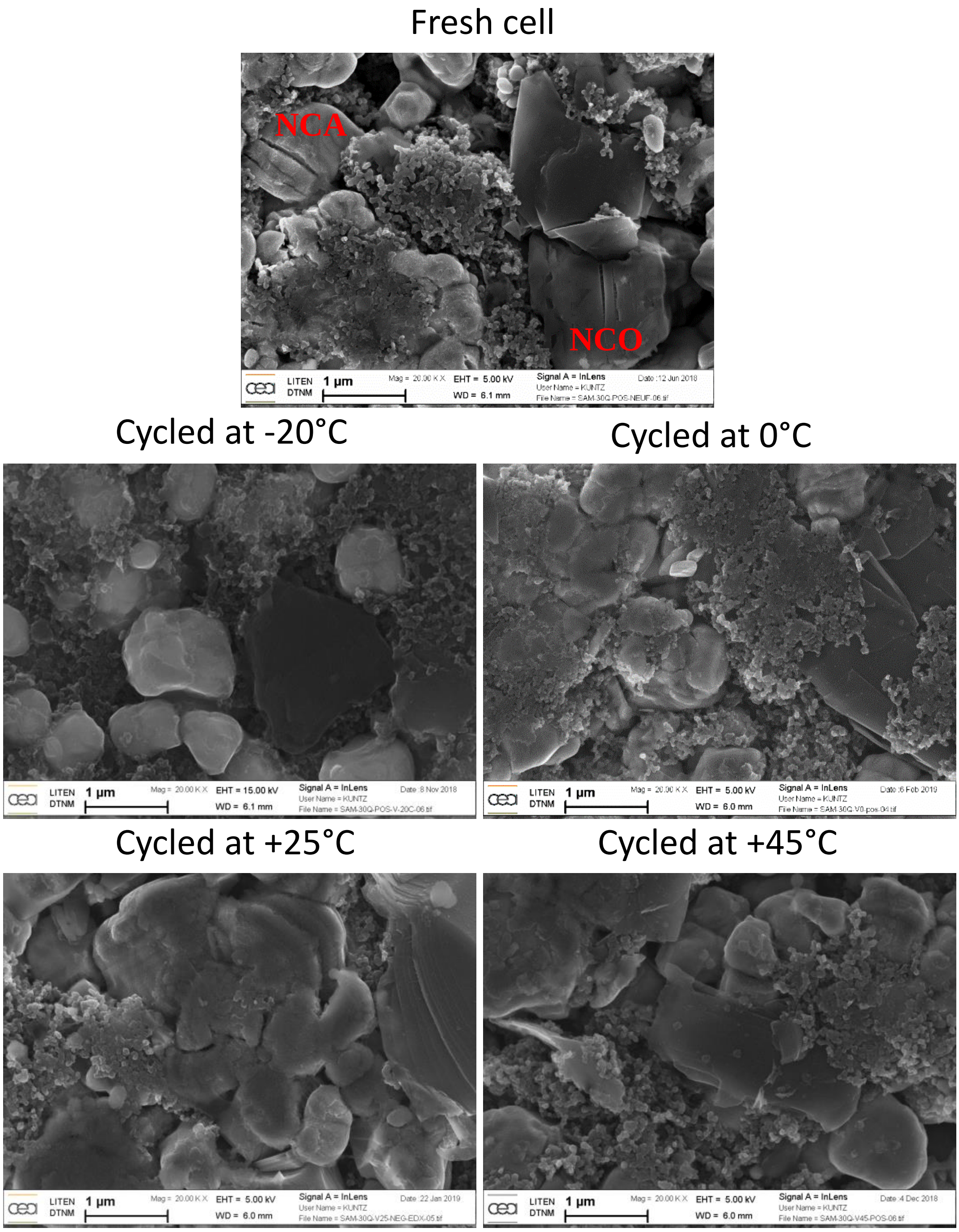

Figure 7: SEM Images of fresh and aged positive electrodes

SEM images of cycled positive electrodes did not show significant visual evolution. To complete these visual observations and to determine if modification happened or not, XRF analyses will be performed also on fresh and cycled electrodes.

5 Abuse Testing

To understand the impact of degradation mechanisms on safety behavior of cells, abuse tests are in progress on fresh and cycled cells. We presents here, the cell thermal stability behavior according to the Accelerating rate calorimetry (ARC) test (figure 8).

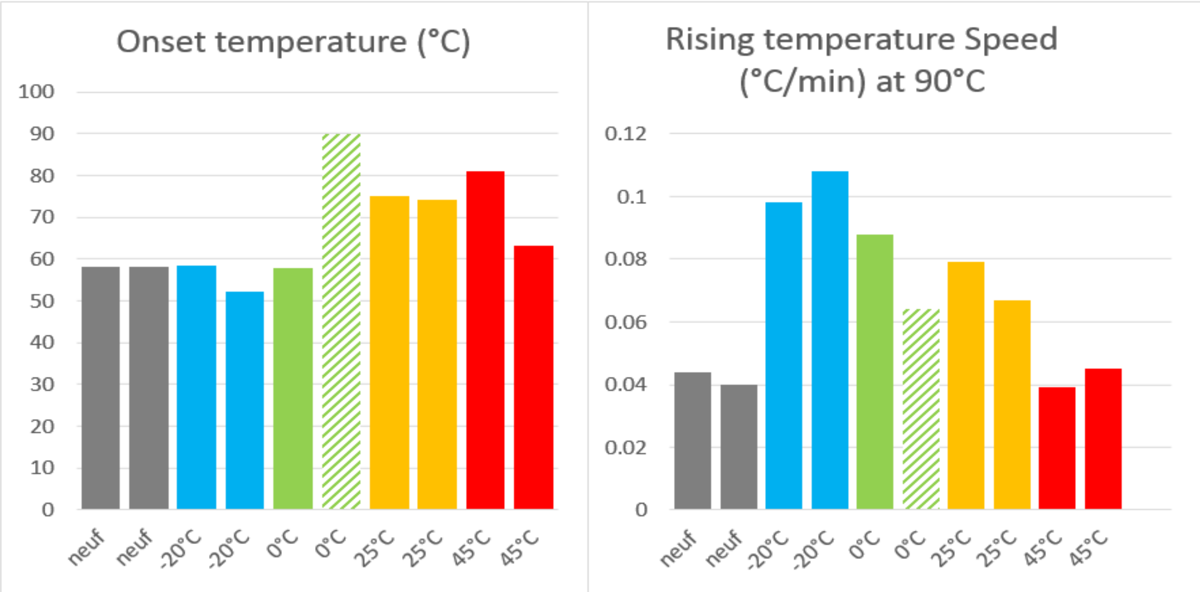

Figure 8: Results of ARC Abuse test for fresh and cycling aged cells

The results of ARC test (figure 8), highlight that "onset temperature" of cells aged at low temperatures (0°C and -20°C) did not change significantly compared to fresh cells (~55-58°C). In contrary, the cells aged at ambient and high temperatures (25°C and 45°C) for which onset temperature has increased by more than 10 degres (~70-75°C). In other terms we can assume that degradation mechanisms which occur at ambient and high temperatures improved the range of thermal safety behaviour of cell.

Once the thermal runaway started, we focused on the rising temperature speed at 90°C. We observe that temperature elevating speed is faster for the cycling at low temperature (~0.1 °C/min) and decreases gradually when temperature of aging is increased. For example the rising temperature speed is 2.5 times faster for aged cell at -20°C compare to fresh cell and aged cell at 45°C.

This experiment shows that cells aged at low temperature is much more reactive than cells aged at high temperature and than fresh cells. In other terms, physical-chemical changes due to cycling at low temperature causes a more violent thermal runaway. So cells having suffered from low temperature aging is more dangerous.

To complete this study, other abuse tests are planned i.e. Short-circuit, Overcharge and Overdischarge. By comparing all results, it will be possible to better understand the impact of each aging conditions and degradation mechanisms on the safety behavior of the cell. It is noteworthy that ARC has been voluntary stopped before the triggering of the cell event in order to proceed to a post abusive study of the internal components.

6 Conclusion

Post-mortem analyses helped us to identify the degradation mechanisms which take place for each conditions of aging. Performed analyses allowed us to understand that high temperature cycling involved mainly damages on positive electrode. In other terms it is plausible that at high temperature the positive electrode endured crystalline damages that can promote SEI growth on negative electrode [8] and/or passivation layer formation. Low temperature cycling caused main damages on negative electrodes material with possible Li plating [9]. To cleary identify which mechanism occurs and the exact nature of damage, some complementary analyses will be performed.

After ARC testing, some trends have been determined. Aging at high temperatures (positive material damage and SEI growth) enhance thermal stability of the cell because the onset temperature has increased. Aging at low temperatures (negative material damage and Li plating) makes the cell more reactive because the rising temperature speed during thermal runaway is significantly faster.

To complete this study, other abuse tests will be performed on fresh and aged cells. In addition, the same study will be carred out on two other references of commercial 18650 Li-ion cells for energy application.

7 References

[1] F. Alex, H. Fabian, M. Xaver, B. Gunther, K. Roman, B. Markus, R. Tim, W. Martin, S. Falko M., Impact of cycling at low temperatures on the safety behavior of 18650-type lithium ion cells: Combined study of mechanical and thermal abuse testing accompanied by post-mortem analysis, J. Power Sources. (2016) 1–11.

[2] M. Börner, A. Friesen, M. Grützke, Y.P. Stenzel, G. Brunklaus, J. Haetge, S. Nowak, F.M. Schappacher, M. Winter, Correlation of aging and thermal stability of commercial 18650-type lithium ion batteries, J. Power Sources. 342 (2017) 382–392.

[3] L. Fredrik, B. Simon, F. Maurizio, A. Ingvar, M. Bengt-Erik, Gas explosion and thermal runaways during external heating abuse of commercial lithium-ion graphite-LiCoO2 cells at differents levels of ageing, J. Power Sources. (2018) 220–231.

[4] C.R. Birkl, M.R. Roberts, E. McTurk, P.G. Bruce, D.A. Howey, Degradation diagnostics for lithium ion cells, J. Power Sources. 341 (2017) 373–386.

[5] T. Waldmann, A. Iturrondobeita, M. Kasper, N. Ghanbari, F. Aguesse, E. Bekaert, L. Daniel, S. Genies, I. Jiménez Gordon, M. W.Löble, E. De Vito, M. Wohlfahrt-Mehrens, Review- Post-Mortem Analysis of Aged Lithium-Ion Batteries: Disassembly Methodology and Physico-Chemical Analysis Techniques, J. Electrochem. Soc. 163 (2016) A2149–A2164. doi:10.1149.

[6] H.-G. Schweiger, O. Obeidi, O. Komesker, A. Raschke, M. Schiemann, C. Zehner, M. Gehnen, M. Keller, P. Birke, Comparison of Several Methods for Determining the Internal Resistance of Lithium Ion Cells, Sensors. (2010) 5604–5625.

[7] A. Brai, K. Uddin, M. Dubarry, L. Somerville, A. McGordon, P. Jennings, I. Bloom, A comparison of methodologies for the non-invasive characterisation of commercial Li-ion cells, Prog. Energy Combust. Sci. 72 (2019) 1–31.

[8] B. Stiaszny, J.C. Ziegler, E.E. Krauß, J.P. Schmidt, E. Ivers-Tiffée, Electrochimical characterization and post-mortem analysis of aged LiMn2O4-Li(Ni0.5Mn0.3Co0.2)/graphite lithium ion batteries. Part I: cycle aging, J. Power Sources. (2013) 439–450.

[9] M. Ecker, P. Shafiei Sabet, D.U. Sauer, Influence of operational condition on lithum plating for commercial lithium-ion batteries - Electrochimical experiments and post-mortem-analysis, Appl. Energy. 206 (2017) 934–946.

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Authors

Pierre Kuntz, born in 1994, grow up in a village near Strasbourg. Since I was attracted by science, my studies were quickly oriented towards physical and chemical qualifications. First of all I obtain a scientific baccalauréat in 2012. Then I continue my studies with a University Technologic Diploma named “Mesures Physiques”. It Allowed me to enter in PHELMA-INPG engineering school in Grenoble and I specialize me in Material Science. My interests for research and development leds me to begin a thesis work in 2018 in the CEA Grenoble. During my thesis research, I am working on the evolution of safety behaviour of lithium-ion battery after aging in order to understand how aging conditions could impact the safety behavior of battery.