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SIMCAL Project: calendar aging results obtained on a panel of 6 commercial Li-ion cells

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Introduction

Battery performances degrade over time, not only due to their charge/discharge profile, commonly called 'cycling aging', but also at rest, commonly called 'calendar aging' [1–4]. This second type of aging is much less studied than the first one, probably due to the fact that the purpose of a battery is precisely to be charged / discharged. Many efforts have thus been made by battery manufacturers to improve aging in cycling. Moreover, we intuitively expect a greater impact on aging of cycling compared to rest time. However, time spent at rest can be prominent in many applications. This is the case of vehicles (including electric vehicles) which stay at rest approximately 90% of their time (in parking mode). This is why the SIMCAL Project, conducted by 14 French partners, focused on the study of calendar aging during 3 years.

This communication establishes a synthesis of performances obtained, and describes the main aging mechanism understood thanks to post-mortem analyses.

Experimental

The SIMCAL study focused on a panel of 7 commercial battery technologies, including 1 NiMH and 6 Li-ion cells references, among which 1 C/NCA, 1 C/NMC, 1 C/LMO-NMC, and 3 C/LFP. Only results obtained on Li-ion cells are discussed in this communication, the case of the NiMH being too specific to be compared to Li-ion results. The table below gives the general characteristics of the 6 Li-ion cells tested.

Tab. 1: characteristics of the studied cells

Cell #	1	2	3	4	5	6
Cell chemistry	C/NCA	C/NMC	C/LMO-NMC	C/LFP	C/LFP	C/LFP
Nominal capacity (Ah)	7.0	12.0	5.3	8.0	15.0	2.3
Post-mortem analyses (Y/N)	N	Y	N	Y	Y	Y

9 storage conditions including 3 temperatures (30°C, 45°C, and 60°C respectively) and 3 SOC (30%, 65%, and 100% respectively) have been applied to the cells stayed at rest and disconnected up to 2 years and half (shorter test durations for more severe storage conditions). Aging was punctuated by periodical electrical tests performed at 25°C, including a residual discharge followed by 2 complete cycles at 1C in charge and discharge to assess the State-of-Health (SOH).

For each condition, 3 cells were tested to verify the reproducibility of the results, and allow the sample of 2 cells during aging for autopsies, including SEM, XRD, and electrochemical measurements on half-cells [5].

Results and discussion

The Fig. 1 presents the calendar aging results obtained on 6 commercial Li-ion cells (Tab. 1) according to the 9 conditions previously mentioned (3T × 3 SOC).

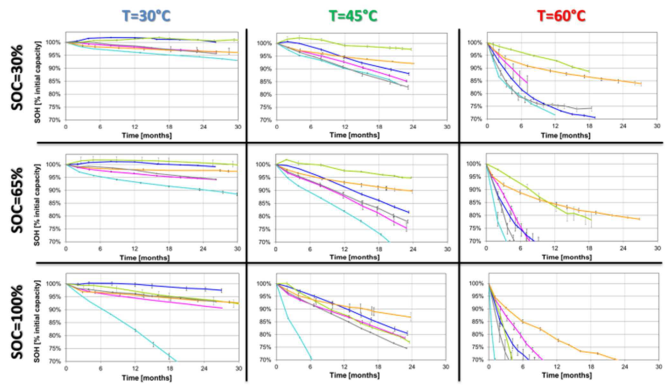

Fig. 1: Calendar aging measured on 6 Li-ion commercial cells according to 9 aging conditions *(measured data)*

Generally speaking, results obtained confirm that the calendar aging increases for all Li-ion technologies with the temperature, and in a lesser extent with the SOC. However, as also indicated by the figure above, each technology follows its own aging laws.

On the other hand, post-mortem analyses realized on 4 cells (Tab. 1) have shown that a same main mechanism is involved in the calendar aging of these cells, namely the loss of cyclable lithium. As shown by the Fig. 2, the maximum lithium stoichiometry of cathodes collected from cells decreases with the capacity fade; results were obtained both from XRD and electrochemical titration.

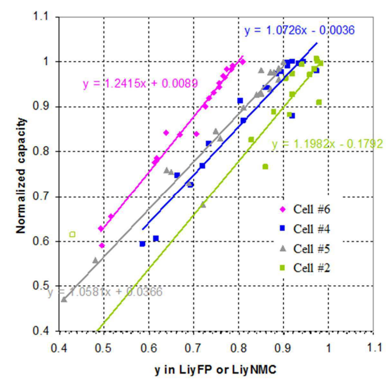

Fig. 2: Cells capacity fade vs. cathodes maximum Li stoichiometry

These results are interpreted as the consequence of the Solid Electrolyte Interphase (SEI) growth at the negative electrode particle / electrolyte interface, that consumes Li ions and leads consequently to an increase of the imbalance between the electrodes, and so to the diminution of cyclable Li.

Conclusion

Results obtained in the SIMCAL Project confirm the necessity to address the calendar aging when one wishes to forecast the lifetime of batteries. This type of aging may even become the dominant aging factor depending on the temperature and the SOC usage profile. Moreover, this aging mode is not representative of one application and its study is hence useful for virtually all applications. This type of aging is also particularly interesting since it can be partially contained by a thermal and/or a SOC range management strategies. Finally, post-mortem analyses have helped to better understand the aging mechanisms involved in calendar aging, mainly ruled by the loss of cyclable Li considering the autopsied cells.

Acknowledgments

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