Aging and shelf life capacity of Li-ion batteries for e-mobility

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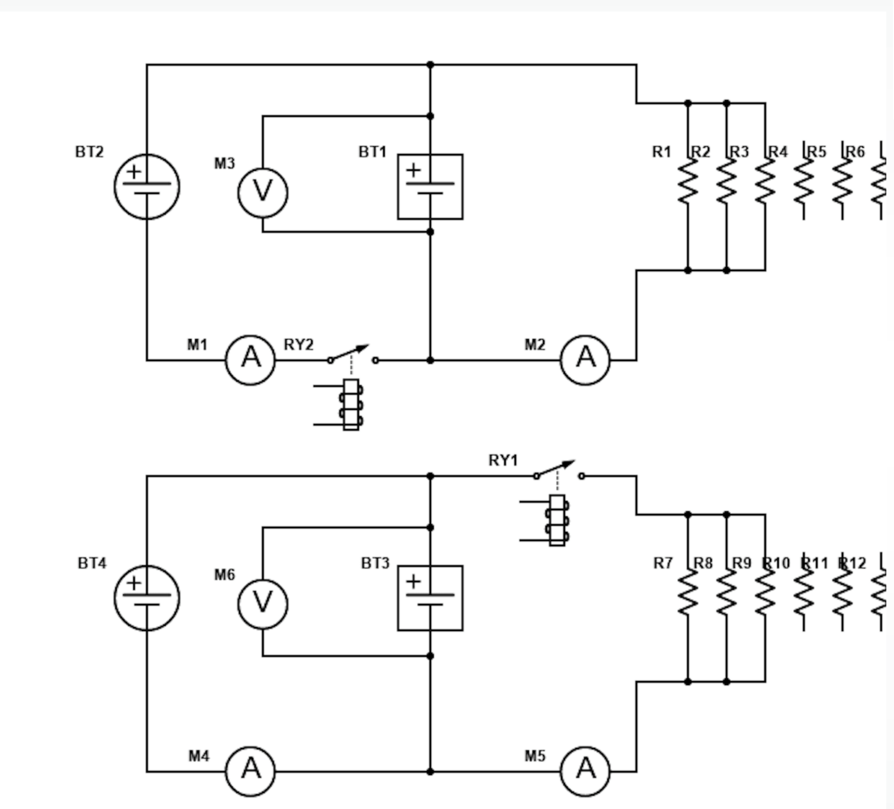
Introduction

In this poster we present the case study of NCM lithium ion cells that sat unused for more than three years. In this context of development we moved on double tracks: 1) we analyzed 25 aged cells undergoing charge/discharge cycles with the company cycler (monitoring: potential, current intensity, resistance, open circuit voltage, time, ambient temperature, CC and CV modes of charge). We performed by python: the calculations of some quantities of interest (during the charge/discharge cycles) and the statistical analysis of the data; 2) open voltage measures on 230 shelf-aged lithium cells finalized to evaluate and understand the self-discharge performing a statistic and plotting the data.

Methodology

Cycler Scheme

In Figure below the top (bottom) part represents the discharge (charge) phase: the lithium cell BT1 (BT3) is connected to a fixed resistance (power supply). An ammeter M2 (M4) is used to sample the current intensity and a voltmeter M3 (M6) applied to the electrodes of the cell is used to sample the voltage. A kissling relay RY2 (RY1) disconnects the cell from the charge circuit.



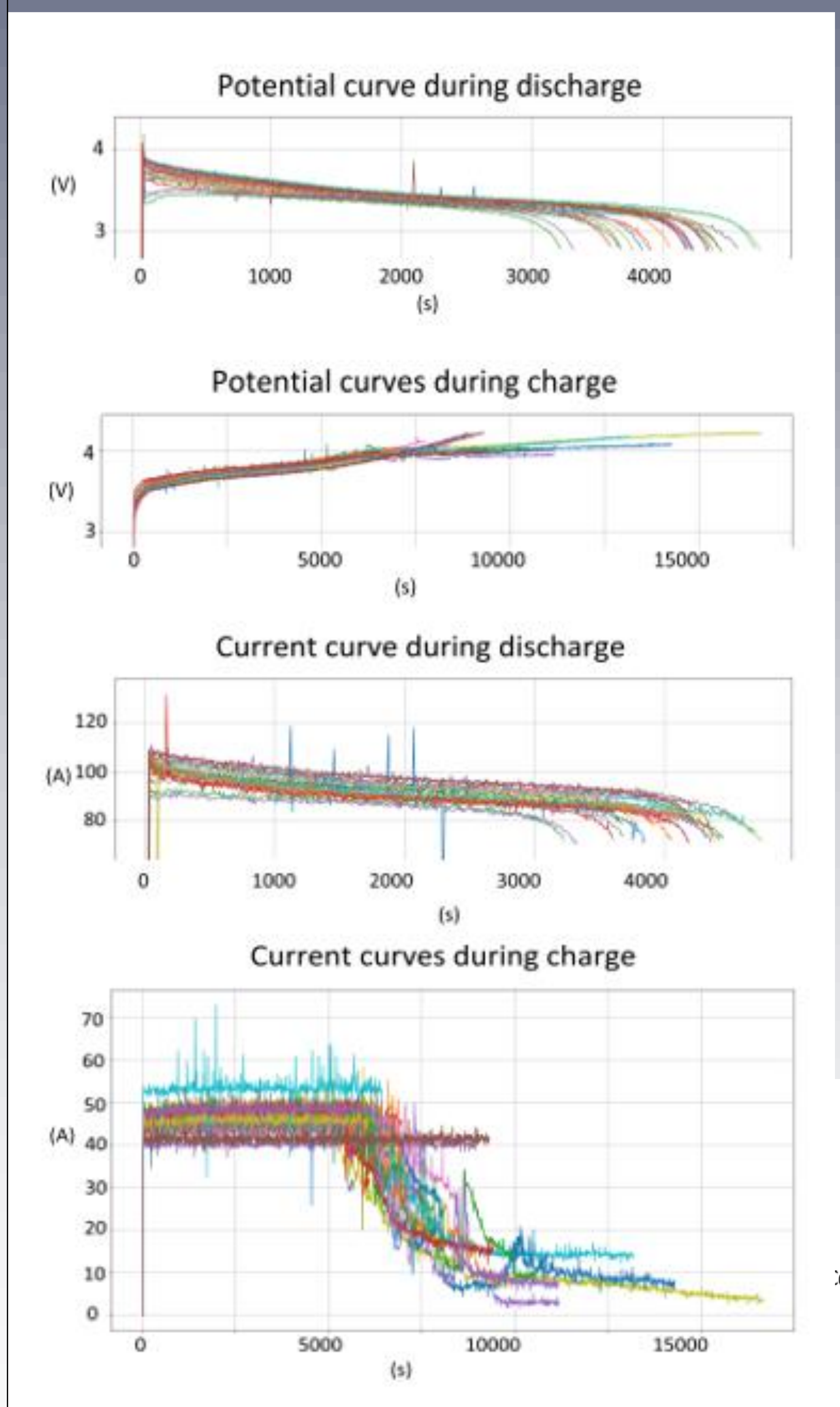
Li+ ion battery Data Sheet

Charge voltage	DC 4.2 V @ 220 Wh/kg
Nominal voltage	3.65 V
Minimal capacity	120 Ah @ 0.2C discharge
Charge current	Standard charge: 0.2C
Standard charghing method	0.2C CC charge to 4.2 V, then CV charge till charge current decline to $\leq$ 0.03C
Charging time	Standard charge: 5 hours
Max. charge current	0.5C
Max. discharge current	Max continual discharge 2C
Temperature increase	$\leq$ 15°C in 2C discharging
Discharge cut-off voltage	2.75 V
Operating temperature	Charging: 0°C ~ +45°C. Discharging: -20°C ~ +55°C
Storage temperature	-20°C ~ +45°C
Battery weight	Approx. 2.02 Kg
Thickness and material of tabs	Cathode: 0.2mm, Aluminium Anode: 0.2mm, Copper coated woth Nickel
Cycle Life	> 1500 cycles (with charge/discharge at 0.2C)
Self-discharge	Remaining capacity > 95% (after the standard charging, the battery was stored for 30 days under standard environmental test conditions: temperature 23±5°C, humidity 65±20% RH)
Initial impedance	$\leq 2m\Omega$ (internal resistance measured at AC 1 KHz after 50% charge)

Open Circuit Voltage measures

We took the open circuit voltage measured in 2018 before storing the cells on the shelf and measured again the open circuit voltage in 2021. In Figure on right we present the distribution of the variation of the open circuit voltage ΔOCV, and in next Figure we calculated the difference estimating the variation ΔOCV and performed a linear regression.

Measurements



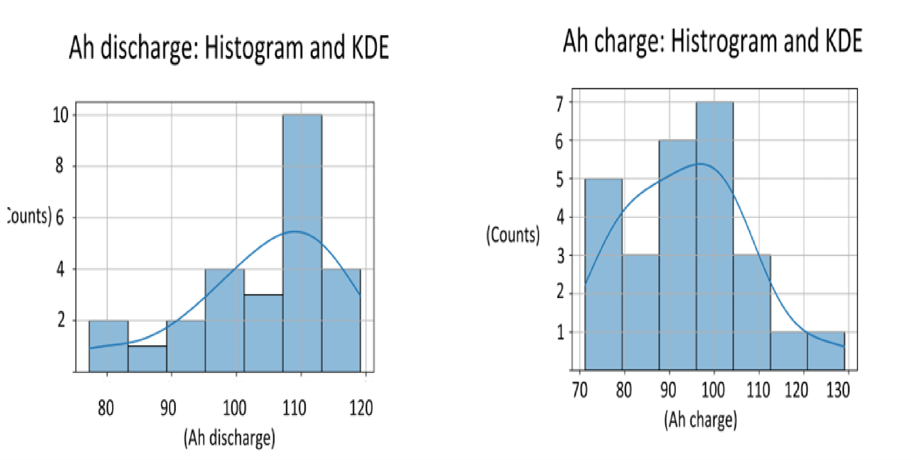
Charge/discharge

The lithium cells have been undergone in 2017/2018 to some partial charge/discharge cycles after some months that they sat on a shelf. Then the cells sat untouched till 2021. Cells were stored at a temperature around (25°±7° C). We cycled 25 cells once using this protocol:

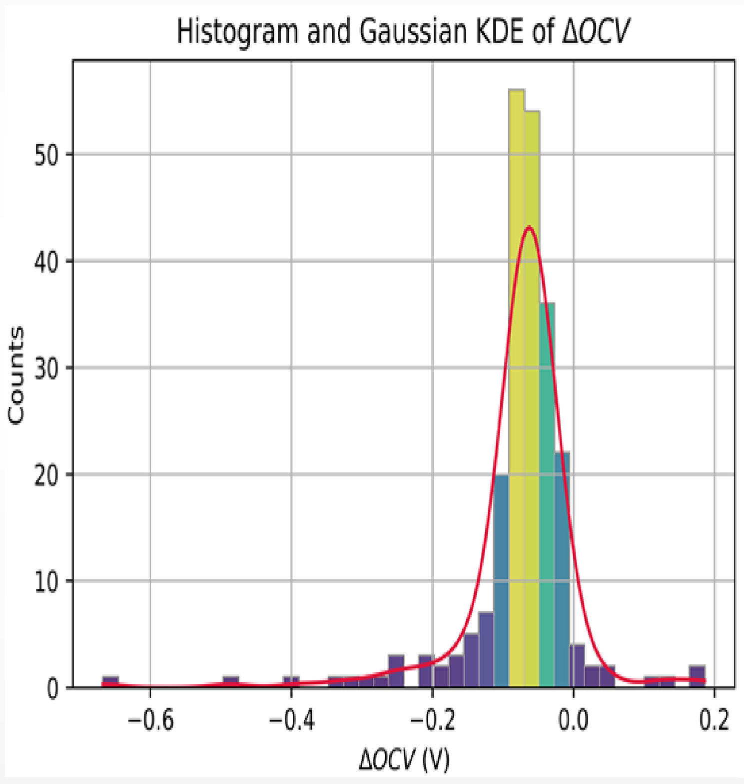
-regardless of the SoC (state of charge), charge the cell up to 4.2V: during the CC mode we set a current of 45A (≈0.375C), during the CV mode we set a voltage of 4.2V;

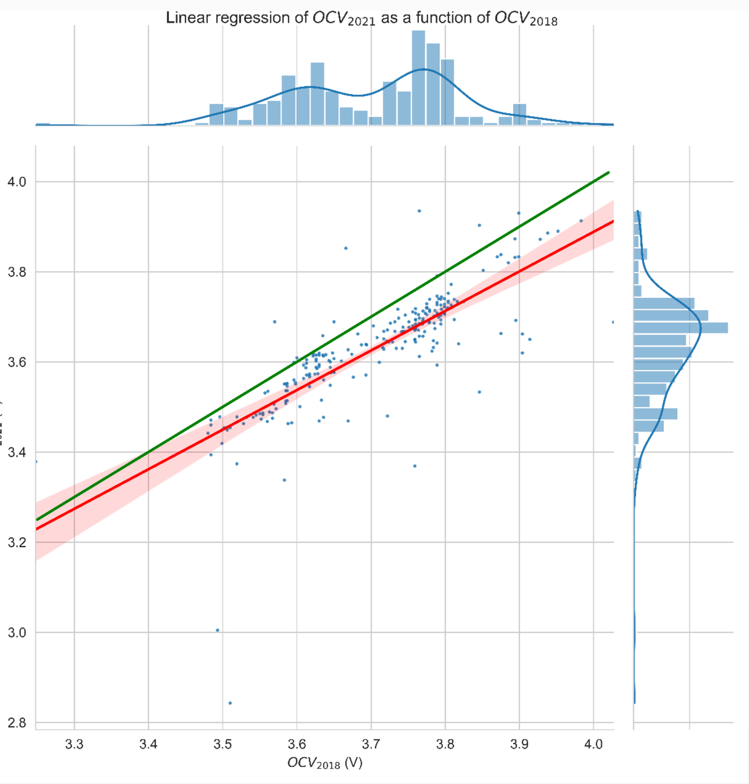
-full discharge: discharge the cell down to 2.75V through a constant resistance load;

-full charge: charge the cell up to 4.2V as at step 1. For every cell we measured the open circuit voltage before and after every step. In Figure we present the statistical analysis of the data. In Figure below we show the histograms and KDEs of the discharge (left) and charge (right) capacity.



Open Circuit Voltage





Conclusions

In 2018 the cells which undergone to a complete charge/discharge cycle with the same voltage cut-off parameters and current intensity have shown a capacity of 94 Ah. Since we discharged the cells around 0.4C we can expect a less capacity release then the stated nominal 120 Ah at 0.2C. The mean value of 104 Ah for discharge and 94 Ah for charge, combined with the fact that not all the times we were able to charge the cells in a potentiostatic way and combined to an experimental setup that give us some margin of error estimated in 10%, it makes us believe that the cells are still good for high power applications.

Also the open circuit voltage measures supports us believing that no shelf-damage occurred. A mean variation of 75 mV from 3.700 V to 3.625 V correspond to about 1 Ah loss (0,83% of the nominal capacity).

Bibliography

Yousef Firouz et al, (2018), *Evaluation of international standards for lithium-ion batteries*, Obelics.eu

Shenzen Auto-Energy Technology (Datasheet), auto-energy.cn

Peter Keil et al. (2016), *Calendar Aging of Lithium-Ion Batteries*, J. Eletrochem. Soc., 163 A1872.

Anthony Barré et al., (2016), *A review on lithium-ion battery ageing mechanisms and estimations for automotive applications*. Journal of Power Sources, Elsevier, volume 241, pp.680 - 689.

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