Interdependencies of electrical and thermal early-life abuse on the performance of lithium-ion cells

BAM
Bundesanstalt für Materialforschung und -prüfung

R. Leonhardt[a,b], T. Tichter[a], P. Scharpmann[a,b], A. Schmidt[a], J. Kowal[b], and J. Krug von Nidda[a]
[a)] Bundesanstalt für Materialforschung und –prüfung (BAM), Berlin, Germany
[b)] Technische Universität Berlin, Fachgebiet Elektrische Energiespeichertechnik, Berlin, Germany

Abstract

Reusing aged lithium-ion cells holds great potential for increasing their overall sustainability. Likewise, their viability depends on accurate state of health (SOH) estimation, which, in fact, is a multifactorial problem. Significantly, SOH dynamics are influenced by exposure to overstressing conditions during the cell's early life [1,2].

The present study illuminates the intricate interplay of multiple overstressing conditions.

For this purpose, the combination of early-life overstresses on lithium-ion cells (LCO, pouch, 4.8 Wh) is tested by deliberately imposing abuse conditions (i.e., deep discharge and high temperatures) and monitoring the subsequent ageing performance (impedance and capacity). The findings reveal that the collective impact of different abuse modes cannot be represented as a sum of individual effects.

Instead, a specific abuse sequence leads to a unique degradation pathway, suggesting that SOH cannot be described as a state function dependent on early-life parameters.

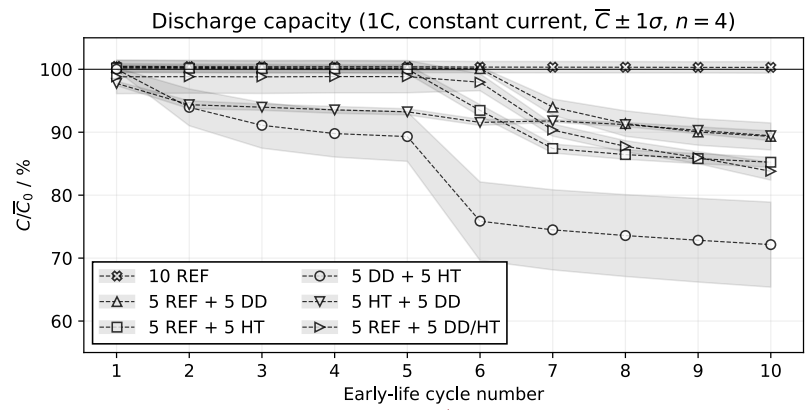
Test groups (defined by early-life cycles)

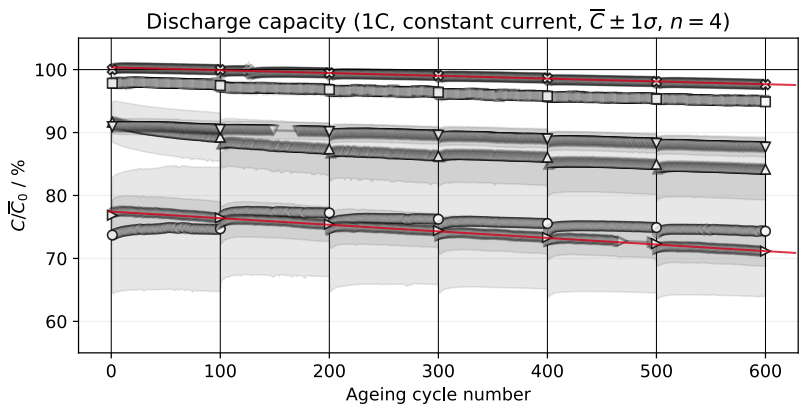
Each group consists of combinations of the following cycle types:

- **Non-abusive cycle (REF)**: 1 C, 20 °C
- **Deep-discharge cycle (DD)**: 0 V for 1800 s
- **High-temp cycle (HT)**: Cycling at T = 70 °C

The following combinations/groups are tested in this study:

10 REF | 5 REF + 5 DD | 5 REF + 5 HT | 5 DD + 5 HT | 5 HT + 5 DD | 5 REF + 5 DD/HT





-0.45 % per 100 cycles (10 REF)

The **capacity fading rate changed permanently** for overstressed samples

-1.02 % per 100 cycles (5 REF + 5 DD/HT)

Early-life phase (10 cycles)

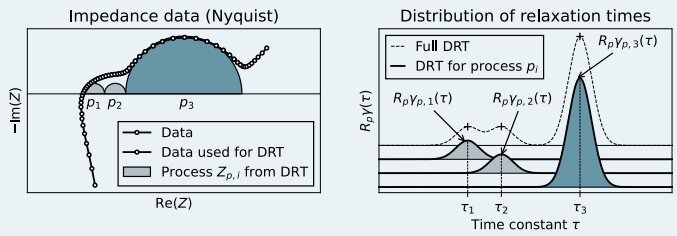
Electrochemical characterization → 5-10 abusive cycles (e.g., deep discharge) → Electrochemical characterization

How does early-live overstress impact the cell characteristics?

Cycle-ageing phase (600+ cycles)

n repetitions: 100 non-abusive cycles (1 C, 20 °C) → Electrochemical characterization

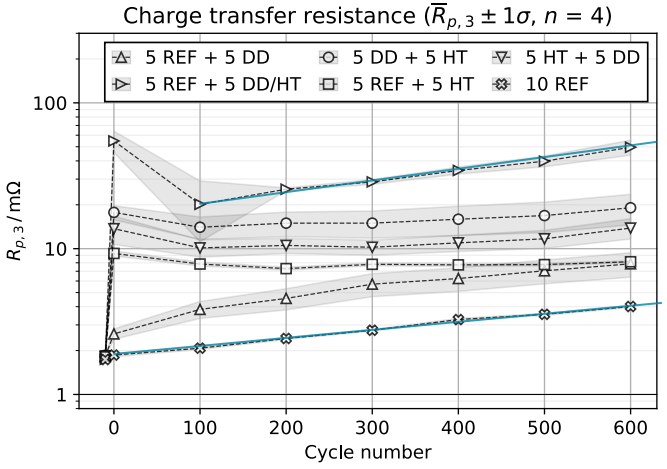
How does early-live overstress affect the long-term degradation behavior?



From the DRT, the process resistance $R_{p,i}$ is determined by:

$$R_{p,i} = R_p \int_{-\infty}^{\infty} \gamma_{p,i}(\tau)\, \mathrm{d} \ln \tau$$

$R_{p,3}$[3]



+4.78 mΩ per 100 cycles (5 REF + 5 DD/HT)

The **impedance growth rate was significantly affected** by early-life overstress

+0.36 mΩ per 100 cycles (10 REF)

Key findings

- **Early-life overstressing affects the immediate and long-term performance** of lithium-ion cells
- The effects of single abuse modes are not additive, implying that **SOH is not a state function**

Funding: The authors thank the Austrian Federal Ministry for Climate Action, Environment, Energy, Mobility, Innovation and Technology (BMK), the Bundesanstalt für Materialforschung und -prüfung (BAM), and the French National Institute for Industrial Environment and Risks (Ineris) for supporting the research project "SafeLiBatt" (FFG project no. 880683).

Sources:

1) Waldmann, T., et al., *Temperature dependent ageing mechanisms in Lithium-ion batteries – A Post-Mortem study*. Journal of Power Sources, 2014. 262: p. 129-135.
2) Langner, T., T. Sieber, and J. Acker, *Studies on the deposition of copper in lithium-ion batteries during the deep discharge process*. Sci Rep, 2021. 11(1): p. 6316.
3) Danzer, M. *Generalized Distribution of Relaxation Times Analysis for the Characterization of Impedance Spectra*. Batteries 2019, 5(3), 53. https://doi.org/10.3390/batteries5030053

Sicherheit in Technik und Chemie