# Overview of Aging Mechanism of Lithium-Ion Batteries

In this short blog, I will provide an overview of the various aging mechanisms occurring in lithium-ion batteries (LIBs). The topic of LIB aging and its prediction has been a hot topic in the battery community for many years. Due to the battery's complex nature and its critical importance for ensuring a long lifetime during battery operation, understanding and improving the ability to predict LIB aging behavior and lifetime is indispensable. Analyzing LIB aging behavior relies on the correct differentiation between irreversible and reversible capacity losses. In general, aging experiments of LIBs can be subdivided into calendar aging (where batteries are stored under various conditions for several months or years) and cyclic aging (where batteries are repeatedly charged and discharged, often replicating real-use case scenarios). These experiments rely on precise capacity measurements to correctly distinguish between irreversible effects, such as the loss of cyclable lithium and active materials, and reversible effects, such as temperature-dependent rate capability. Both are determined using two specific parameters measured in the lab, i.e., actual capacity and internal resistance. The main results of LIB aging include its impact on the ability to store energy and provide the required power.

The Main reasons for LIB aging and their results can be summarized as follows [1-2]:

- Solid-Electrolyte-Interface (SEI)
    - It cannot be avoided and is mainly caused on the anode (graphite) but can also occur on the cathode.
    - The SEI can be influenced by the electrolyte and is accelerated by high current rates and high cycle depth (DoD)
      →Results in an increase of cell impedance and power loss, respectively.
- Lithium plating on the anode
    - Occurs during charging at low temperatures and/or high current rates.
    - Occurs when a graphite anode is used. For LIBs using LTO anode, it does not occur (due to higher local potential of LTO).
    - An additional reason for lithium-plating occurrence is the cell over-charging.
      →In addition to the aging risk, it affects the safety issue
- Cracking on the anode
    - Is accelerated by over-charging of the cell (very high SoC)
      → Results in capacity loss (Loss of lithium and loss of active materials)
- Electrolyte decomposition / Binder decomposition
    - Is accelerated by high temperatures and high SoC
      →Leads to capacity loss and power loss
- Decrease of active surface (occurs due to continuous SEI increase)
    - Is accelerated by high temperatures and high SoC
      →Leads to impedance increase and power loss
- Contact loss of active mass particles due to volume change
    - Is accelerated by high current-rates and high depth-of-Discharge (DoD)
      →Leads to capacity loss
- Corrosion of the current collectors
    - Is accelerated by low SoC and deep discharge of the cell
      → Results in impedance increase and power loss

However, the main three aging modes commonly addressed in the literature are [1]:

1. Loss of lithium inventory
2. Loss of active negative electrode material
3. Loss of active positive electrode material

In addition, a schematic illustration of the overall interdependencies between the root cause, its effect, and the related aging mode is presented in Figure 1.

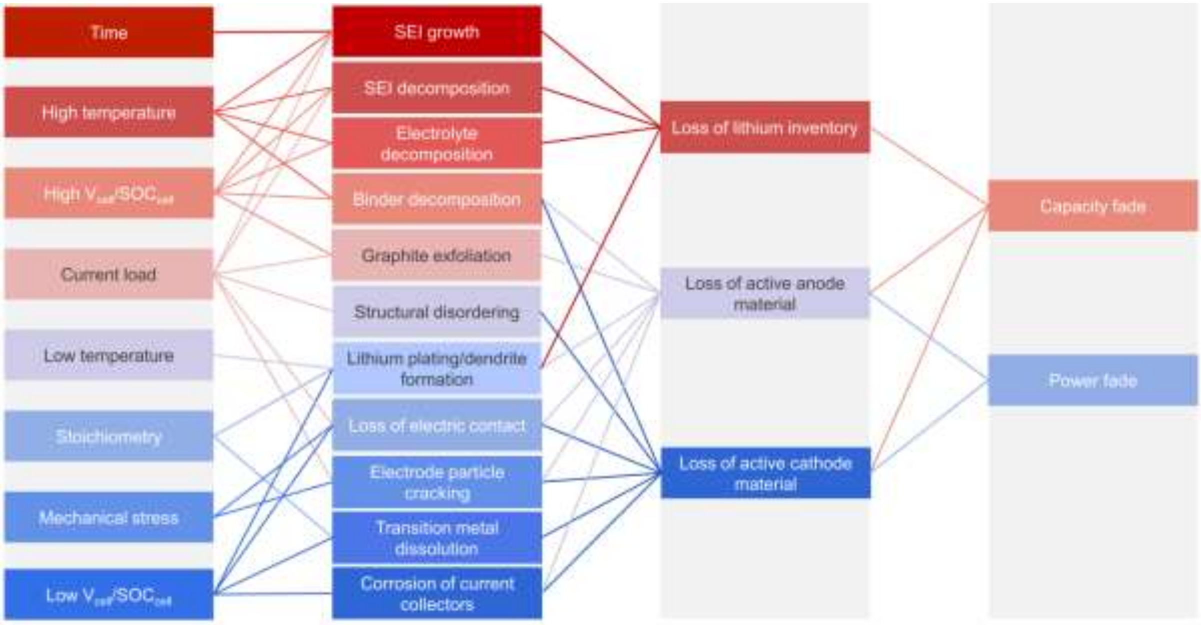

*Figure 1: Illustration of root-causes and battery aging mechanisms and their respective aging modes according to Ref. [3]*

In general, lithium-ion batteries exhibit three different aging trajectories: linear, sub-linear or superliner aging trajectories.

To obtain a higher degree of reliable test data, it is often recommended to conduct tests for every working point of the test matrix as a batch consisting of three or more similar LIBs in terms of capacity and resistance. Additionally, it is advisable to relate SoC and DoD to the nominal capacity of the investigated LIBs. Furthermore, it is crucial to maintain a constant temperature throughout the test period. Below a short description of essential factors to be considered during cell and module testing is provided:

## Measurement of Resistance

The determination of battery resistance is an essential aspect for accurately estimating the LIB's current aging state. Generally, resistance measurement can be primarily categorized into a.c. and d.c. resistance. It is important to note that a.c. resistance measurement is preferred at the cell level and not at the system level, primarily due to inconsistencies within the battery system. On the other hand, the test method for d.c. resistance measurement differs significantly from the a.c. measurement method. For d.c. resistance measurement, the LIB or the battery system at a certain SoC must be discharged or charged for a specific period of time, for example, 10 seconds or 30 seconds [2]. Furthermore, the respective current pulses are repeated for different current rates and various SoCs. The charging pulses can be performed directly after the discharging pulses following a short break, for example, 60 seconds. The determination methods for battery resistances are provided in Eqs. (1-2):

$$R_{\mathrm{a.c}}(f) = V_{\mathrm{rms}}(f)/I_{\mathrm{rms}}(f) \qquad [1]$$

$$R_{\mathrm{d.c}}[\Omega] = (V_2 - V_1)/(I_2 - I_1) \qquad [2]$$

Depending on the respective application, the End-of-Life (EoL) of the LIB is reached when the actual resistance of the LIB reaches 100% or is doubled in contrast to its nominal/initial resistance value at Begin-of-Life (BoL).

## Measurement of actual capacity

In contrast to resistance measurement, the determination of actual battery capacity is relatively straightforward. According to the cell or manufacturer data, the cell or system is initially fully charged and then discharged at 25°C using the specified discharge current rate until the End-of-Discharge voltage is reached. Typically, battery capacity is expressed in Ampere-seconds (As) or Ampere-hours (Ah) and is determined regularly after a specific number of cycles (e.g., 500 cycles). The aging trajectories, based on laboratory measurements, are often depicted as capacity versus cycle number (or equivalent full cycle number). Depending on the respective application, the EoL of the LIB is reached when the actual capacity of the LIB reaches 80% or 70% of its nominal/initial value at BoL.

## Summary

This blog underscores the importance of understanding the aging mechanisms of lithium-ion batteries. It recognizes the existing knowledge gaps and calls for comprehensive examination through high-fidelity tests, post-mortem analysis, and the use of extensive field-data from various applications, use-cases, and cell chemistries. The blog also acknowledges the awareness within the battery industry, research institutions, and other stakeholders regarding the significance of understanding and predicting battery aging for specific applications, noting the progress achieved thus far. However, it highlights the ongoing challenges and emphasizes the need for substantial efforts by stakeholders to make further improvements in this area.

## References

[1] A. Farmann et. al. Critical review of on capacity estimation techniques for lithium-ion batteries in electric hybrid electric vehicles, J. Power Sources 281 (0) (2015)

[2] A. Farmann, “Comparative study of reduced-order equivalent circuit models for state-of-available-power prediction of lithium-ion batteries in electric vehicles”, Ph.D. thesis, RWTH Aachen University, 2019, ISSN 1437-675X.

[3] C. Birkl et. al. Degradation diagnostics for lithium ion cells, J. Power Sources 341 (2017).