



# Influence of operational condition on lithium plating for commercial lithium-ion batteries – Electrochemical experiments and post-mortem-analysis



Madeleine Ecker<sup>a,b,\*</sup>, Pouyan Shafiei Sabet<sup>a,b</sup>, Dirk Uwe Sauer<sup>a,b,c</sup>

<sup>a</sup> Chair for Electrochemical Energy Conversion and Storage Systems, Institute for Power Electronics and Electrical Drives (ISEA), RWTH Aachen University, Jägerstrasse 17-19, 52066 Aachen, Germany

<sup>b</sup> Juelich Aachen Research Alliance, JARA-Energy, Germany

<sup>c</sup> Institute for Power Generation and Storage Systems (PGS) @ E.ON ERC, RWTH Aachen University, Germany

## HIGHLIGHTS

- Investigation of lithium plating to support reliable system integration.
- Influence of operational conditions at low temperature on lithium plating.
- Comparison of different lithium-ion battery technologies.
- Large differences in low-temperature behaviour for different technologies.
- Post-mortem analysis reveals inhomogeneous deposition of metallic lithium.

## ARTICLE INFO

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## ABSTRACT

The lifetime and safety of lithium-ion batteries are key requirements for successful market introduction of electro mobility. Especially charging at low temperature and fast charging, known to provoke lithium plating, is an important issue for automotive engineers. Lithium plating, leading both to ageing as well as safety risks, is known to play a crucial role in system design of the application. To gain knowledge of different influence factors on lithium plating, low-temperature ageing tests are performed in this work. Commercial lithium-ion batteries of various types are tested under various operational conditions such as temperature, current, state of charge, charging strategy as well as state of health. To analyse the ageing behaviour, capacity fade and resistance increase are tracked over lifetime. The results of this large experimental survey on lithium plating provide support for the design of operation strategies for the implementation in battery management systems. To further investigate the underlying degradation mechanisms, differential voltage curves and impedance spectra are analysed and a post-mortem analysis of anode degradation is performed for a selected technology. The results confirm the deposition of metallic lithium or lithium compounds in the porous structure and suggest a strongly inhomogeneous deposition over the electrode thickness with a dense deposition layer close to the separator for the considered cell. It is shown that this inhomogeneous deposition can even lead to loss of active material. The plurality of the investigated technologies demonstrates large differences between different technologies concerning low-temperature behaviour and gives insight to the impact of cell properties. For the sample of cells considered in this work, cells rated to provide high power are found to be subject to faster degradation at low temperatures compared to high-energy cells, probably due to little self-heating. For application this result shows that cells designed for high current rates are not necessarily providing a good low-temperature performance.

## 1. Introduction

To enhance the consumer acceptance of battery-powered vehicles,

charging at all conditions as well as fast charging are issues frequently addressed by car manufactures. Lately, automotive industry announced the aim to charge the battery to 80% state of charge in only 15 min.

\* Corresponding author at: Chair for Electrochemical Energy Conversion and Storage Systems, Institute for Power Electronics and Electrical Drives (ISEA), RWTH Aachen University, Jägerstrasse 17-19, 52066 Aachen, Germany.

E-mail address: [batteries@isea.rwth-aachen.de](mailto:batteries@isea.rwth-aachen.de) (M. Ecker).

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However, certain charging conditions are known to provoke lithium plating. Lithium plating is an effect that strongly determines the ageing and the safety of lithium-ion batteries. To ensure reliable system integration and charging operation, the different influence factors on lithium plating have to be singled out for commercial lithium-ion batteries to be able to implement battery management strategies.

Much effort has been undertaken to provide an understanding of the mechanisms of lithium plating. It is widely accepted that lithium plating is an undesired side reaction on the anode side of lithium-ion batteries. Lithium ions are reduced to metallic lithium and build up dendrites instead of intercalating into the anode crystal structure. This occurs on places where the local anode potential drops down to 0 V vs. Li/Li<sup>+</sup>. However, due to inhomogeneity over the electrode, lithium plating can occur locally, as shown by [1,2]. Lithium plating can be induced by slow intercalation kinetics and high surface film resistances [3–5] as well as by limited diffusion processes [6,7] in the anode, for example due to low temperatures or high current rates. A poorly balanced cell or overcharge of ill-connected particles, however, may also cause lithium plating. The choice of anode material influences lithium plating due to the difference in equilibrium potential. Hard carbon, for example, is a safer material compared to graphite, and lithium titanate is hardly affected by lithium plating at all [8,4]. The impact of electrolyte composition on the low-temperature performance of lithium-ion batteries was extensively investigated by [3,9–12].

In general, the deposited metallic lithium is reversible. However, during oxidation, lithium dendrites can lose contact with the active material, leading to dead lithium in the cell [13]. Furthermore, the plated metallic lithium is highly reactive and reacts directly with the electrolyte to build an irreversible solid electrolyte interphase (SEI) [13–15]. Both, the dead lithium as well as the additionally formed SEI, lead to a fast capacity fade of the battery. Therefore, measurement of cell capacity and resistance is the most direct way to detect lithium plating. Different studies suggest that metallic lithium deposited on a graphite electrode is partly reversible. [16,6] showed that deposited lithium can re-intercalate into the graphite during relaxation of the electrode. Furthermore, oxidation ('stripping') of metallic lithium was observed during discharge processes [3,9]. Both processes of lithium recovery (re-intercalation as well as stripping) can be directly observed in the cell potential and have been used in literature for detection of lithium plating [3,17–19]. Other in-situ methods to detect lithium plating are neutron diffraction [20], thickness measurements [21] as well as calorimetric heat flow measurements [22] and high precision coulometry [23]. Conducting post-mortem analysis on aged cells is yet another method in order to investigate the mechanisms of lithium plating. [24,25,23,26–28]

For further mechanism elucidation, physico-chemical model approaches were applied to simulate lithium plating. [29] developed a model simulating diffusion and migration processes as well as the charge transfer kinetics of the intercalation reaction and the kinetics of the lithium plating reaction. [30] followed a more simple approach to investigate pulse charging strategies to reduce the charging time without increasing the risk of lithium deposition. Simulations of 2-D effects were conducted by [31,32]. Attempts to simulate the onset of lithium plating at different operational conditions including a comparison with experimental ageing data were published by [33,34].

Operational conditions play a crucial role for lithium plating. However, there are still only few publications investigating the influence of different factors such as temperature, current rate, state of charge (SOC) or state of health (SOH) on lithium plating experimentally. Different investigations were performed on laboratory cell systems [4,15,23,35–37]. Using reference electrodes in a laboratory full cell arrangement, [4] tested different anode materials at different temperatures applying charge pulses of 5 C. [35,36] used reference electrode measurements to study the effect of different charging protocols. The influence of different charging rates at different temperatures using high precision coulometry on lab-scale pouch cells was

investigated by [23]. Finally a large survey of the influence of temperature, current rate and end of charge voltage was performed by [37] using a reference electrode in a reconstructed pouch cell, resulting in a detailed mapping of critical conditions.

The results obtained by laboratory cells and simulations are important to understand the basic principles of lithium plating. There seems to be a widely accepted consensus on the influence of different operational conditions on lithium plating and the occurring mechanisms as described above. However, results obtained by laboratory cells and simulations can hardly be transferred quantitatively to commercial products, and the observed correlations have therefore to be confirmed by experiments on commercial cells. Only few publications are available investigating lithium plating in commercial cells. The influence of different charging rates [26,38] as well as different charging protocols to prevent lithium plating [6,39–41] has been investigated for different 18650 cells at moderate temperatures. Furthermore, [17] used the stripping of metallic lithium observable in the discharge curve as an indicator for lithium plating to investigate the impact of temperature, SOC and current rate for a commercial graphite LiFePO<sub>4</sub> battery. However, long-term stability was not considered in this work. [24] used the same cells to investigate long-term stability for three conditions. [25] also analysed the long-term stability at different temperatures, but neglected the influence of current and SOC.

No comprehensive study of the influence of different operational conditions on long-term stability for commercially available technologies has been conducted so far even though it is badly needed to ensure a reliable integration into application. Especially the long-term durability of cells subject to lithium plating at low temperatures needs to be investigated to provide guidelines for automotive engineers for the implementation of the battery management system. In this work the influence of temperature, current, SOC, charging strategy as well as SOH are examined for lithium-ion batteries of various types at low-temperature conditions. Section 2 summarises the experimental setup of this work. Section 3 displays the results of a comprehensive test matrix for a commercial cell investigating the different influence factors on lithium plating. In Section 4 an electrochemical investigation and a post-mortem analysis of anode degradation was conducted on selected cells in order to provide evidence of the deposited metallic lithium and to detect the changes inside the battery due to lithium plating. The latter two sections focus on the analysis of a 40 Ah high-power cell. Finally, Section 5 provides a comparison of the behaviour of different commercially available technologies. The plurality of the different technologies gives insight into the impact of cell properties such as size, material combination or whether the cell is designed to provide high-power (HP) or high-energy (HE) densities.

## 2. Experimental

### 2.1. Considered cell systems

To investigate the influence of different cell properties and operational conditions on lithium plating, different commercial lithium-ion batteries are investigated.

The cell used to investigate the influence of different operational conditions on lithium plating in detail is a 40 Ah high-power cell, labelled SLPB 100216216H. It is a pouch polymer battery produced by Kokam with a nominal voltage of 3.7 V. A voltage range of 2.7–4.2 V is allowed by the manufacturer. Charging with 3 C in a temperature range of 0–40 °C, as well as discharging with 5 C between –30 and 60 °C is approved for the cell. According to the manufacturer, this cell comprises carbon on the negative electrode, lithium nickel manganese cobalt oxide (NMC) on the positive electrode and an EC/EMC mixture with LiPF<sub>6</sub> as electrolyte.

Additionally, batteries of two other manufacturers, of different sizes and with two different cathode materials are investigated. All cells considered in this work comprise carbon as anode active material and

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