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Review article

Li plating as unwanted side reaction in commercial Li-ion cells – A review

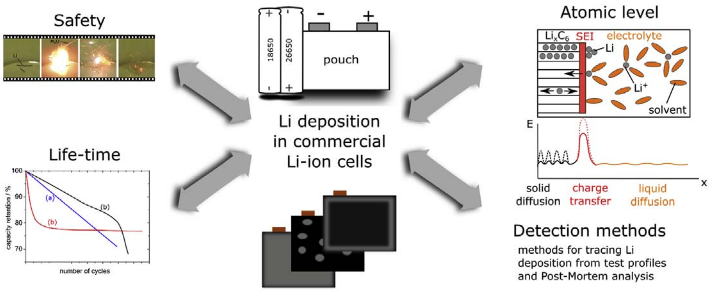
Thomas Waldmann, Björn-Ingo Hogg[1], Margret Wohlfahrt-Mehrens*

ZSW – Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg, Helmholtzstrasse 8, D-89081 Ulm, Germany

HIGHLIGHTS

- Literature on Li deposition in commercial Li-ion cells is reviewed.
- Aging and safety mechanisms are discussed.
- Macroscopic and microscopic points of view are taken into account.
- Methods giving hints and proofs of Li deposition are discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

Deposition of Lithium metal on anodes contributes significantly to ageing of Li-ion cells. Lithium deposition is connected not only to a drastic limitation of life-time, but also to fast-charging capability and safety issues. Lithium deposition in commercial Li-ion cells is not limited to operation conditions at low temperatures. In recent publications various types of commercial cells were investigated using complimentary analysis methods. Five cell types studied in literature (18650, 26650, pouch) serve as a basis for comparison when and why Li deposition happens in commercial Li-ion cells. In the present paper, we reviewed literature on (i) causes, (ii) hints and evidences for Li deposition, (iii) macroscopic morphology of Li deposition/plating, (iv) ageing mechanisms and shapes of capacity fade curves involving Li deposition, and (v) influences of Li deposition on safety. Although often discussed, safety issues regarding Li deposition are not only limited to dendrite growth and internal short circuits, but also to exothermic reactions in the presence of Lithium metal. Furthermore, we tried to connect knowledge from different length scales including the macroscopic level (Li-ion cells, operating conditions, gradients in cells, electrochemical tests, safety tests), the microscopic level (electrodes, particles, microstructure), and the atomic level (atoms, ions, molecules, energy barriers).

1. Introduction

Driven by the demand for higher energy and power density for mobile devices, Li-ion batteries were developed in the 1980s [1,2]. Nowadays, Li-ion technology is well established for energy storage in a large variety of applications such as smartphones, smartwatches, activity trackers, tablet/laptop computers, e-bikes, as well as garden and power tools. These devices typically use small sized pouch cells or standardized Li-ion cells such as 18650-type or 26650-type cells, which are currently produced in very large numbers.

On the other hand, limited fossil fuel resources and climate change call for alternatives like electrified transport (EV, HEV, PHEV) and decentralized energy storage in combination with renewable energy sources [3,4]. The challenging requirements for further improvement of Li-ion technology are longer life-time (> 10 years for automotive applications), fast-charging (< 20min for 80% SOC), low temperature

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* Corresponding author.
E-mail address: margret.wohlfahrt-mehrens@zsw-bw.de (M. Wohlfahrt-Mehrens).

[1] Current address: BMW AG, D-80788 München, Germany.

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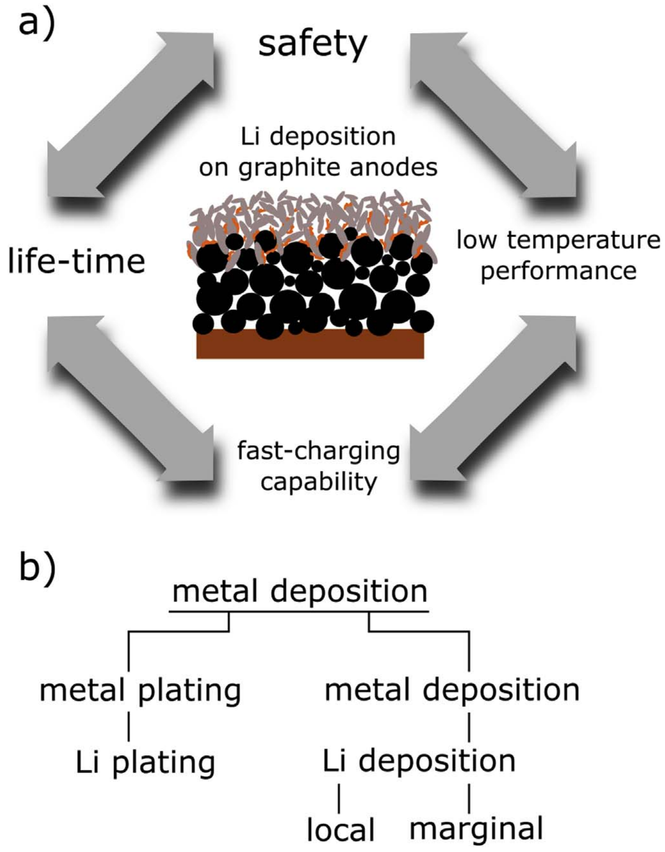

Fig. 1. a) Interaction of different topics with Li deposition on graphite anodes of Li-ion cells. b) Terminology for metal deposition.

charging, and recuperation capability. At the same time, the safety performance has to be excellent in all situations, i.e. during the whole life-time including all weather and abuse conditions. Interestingly, literature research shows that these four factors (life-time, low-temperature performance, fast-charging, and safety) are connected by the ageing mechanism of Li deposition/plating and anode kinetics [5–10] (see Fig. 1a).

The term 'metal plating' originates from homogeneous metals coatings, which were first reported around 1800 [11–13]. Back then, Cruickshank had deposited metallic needles on a silver wire [11,13] and Brugnatelli plated silver medals with gold [12,13]. Nowadays, metal plating is often used to form closed films on surfaces for protection and giving them new properties [14]. In contrast, Li deposition/plating on anodes of Li-ion cells leads to fast degradation/corrosion and safety issues and is therefore to be avoided. In order to suppress Li deposition/plating detailed knowledge about the underlying processes is very important.

The term 'metal plating' stands for a homogeneous film covering a surface and is often used in literature on Li-ion cells [15–26], although it is often not known if the deposited Li film is homogeneous or not. However, recent studies have revealed that Li metal can be deposited in different macroscopic morphologies [5,15,22,23,27–30]. This has motivated us to define the terms 'Li plating' and 'Li deposition' based on the morphologies found in commercial Li-ion cells. Fig. 1b shows an overview on the terminology. The term 'Li deposition' is the hypernym and may be used for all kinds of morphologies including 'Li plating' and other forms of deposition such as 'local deposition' or 'marginal deposition'. It is noted that the difference between plating and deposition is not the dendritic growth. Examples from literature will be discussed in section 3.2.

Li et al. had reviewed literature focusing on Li deposition, dendrite growth and charging protocols in Li-ion cells and in Li metal secondary cells [31]. Liu et al. covered the topics of in-situ and ex-situ characterization and operational parameters leading to Li plating [16]. However, some other very interesting and technically relevant aspects regarding commercial cells were revealed recently and have not been put into larger context, yet. This is the aim of the present review.

During our extensive review of literature, it turned out that various papers from different groups investigated the same five types of commercial Li-ion cell types cycled under different conditions leading to Li deposition [5–8,18–22,27,28,30,32–37]. Additional publications reported findings from other cell types with capacities up to 50Ah [9,15,23,24,38,39,39,40]; this opens up the opportunity to find common trends.

Furthermore, we tried to connect phenomena from different length scales including the macroscopic level (Li-ion cells, operating conditions, gradients in cells, electrochemical tests, safety tests), the microscopic level (electrodes, particles, microstructure), and the atomic level (atoms, ions, molecules, energy barriers) to gain a deeper understanding. In this review we focus on state-of-the-art commercial cells, including cells which are suitable for automotive applications.

Firstly, it is explained why Li deposition on graphite anodes in Li-ion cells happens and which parameters influence it. Secondly, commercial cells and their analysis by different groups and methods are reviewed, taking into account (i) hints, (ii) evidences, (iii) macroscopic morphologies of Li deposition/plating, as well as (iv) details in ageing mechanisms (including an analysis of the shapes of capacity fade curves), and (v) influences on safety when Li deposition is involved (including detection of dendrite growth and exothermic reactions of Li). Finally, we summarize the results and conclude on possibilities to suppress Li deposition in commercial Li-ion cells.

2. Parameters influencing deposition

During charging of Li-ion cells, Li is de-intercalated from the cathode and Li^+ ions are transferred through the electrolyte to the anode (see Fig. 2d). On the anode side, intercalation of Li ions into the graphite particles is the preferred reaction path. The insertion potential of Li in graphite is in the range of 200 to 65 mV vs. Li/Li^+ [41]. For potentials below 0 V vs. Li/Li^+, Li deposition on the graphite anodes becomes thermodynamically allowed [41]. However, the intercalation potential is usually more positive than the deposition potential of Li. Therefore, thermodynamically, Li deposition is not a competitive reaction to Li insertion [42]. Here one has to consider that charging of a Li-ion cell is a dynamic process and not in equilibrium, especially at high C-rates. In thermodynamic equilibrium, the cell voltage can be determined by the Nernst equation, however, a deviation is observed experimentally which is the polarisation [43]. The main causes for polarisation are Ohmic drop, charge transfer overpotential, and diffusion overpotential which are the kinetic cause for Li deposition. However, it is difficult to separate these overpotentials experimentally [10]. In simulations, the overpotential can be calculated [44–46] and is used as the kinetic condition for Li deposition: Li deposition happens when the sum of the equilibrium potential and the overpotential get negative vs. Li/Li^+ [46], which is essentially the same as a negative anode potential measured vs. Li/Li^+ in a 3-electrode cell with a reference electrode.

Experimentally it is observed that Li deposition happens as a reaction in parallel to intercalation [44]. Therefore, as depicted in Fig. 2c, charging can lead to intercalation (amount: x) and additionally to Li deposition (amount: y), while discharging leads to de-intercalation and stripping of deposited Li. Arora et al. described the charging process by dividing the total charging current into a part for the intercalation and another for the deposition [44]. During the stripping process a part of the Li can lose electrical contact to the anode, which is then called 'dead Li'. Dead Li in combination with Li that has reacted with electrolyte are often the main sources for capacity loss when Li deposition is involved in the ageing mechanism.