



# Low-temperature charging of lithium-ion cells part I: Electrochemical modeling and experimental investigation of degradation behavior



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## HIGHLIGHTS

- Parameterization and validation of an electrochemical model over a wide temperature range.
- Obtainment of model parameters via piecewise investigation of electrochemical impedance spectroscopy (EIS) data.
- Experimental data of low temperature degradation behavior of full cells.
- Correlation of electrochemical model and experimental data regarding low temperature degradation behavior (Li-plating).
- Introduction of a semi-quantitative degradation factor related to the local anode potential.

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## ABSTRACT

Fast charge of Li-ion cells is one of the main challenges in automotive battery application. As a particular problem at low temperatures and high charging rates, lithium deposits as metal on the anode surface (so-called lithium plating) instead of intercalation. Electrochemical models help to understand internal processes and predict aging effects, which finally lead to optimized charging strategies. In this work, a 1D + 1D (pseudo-2D) electrochemical model is developed, applied over a wide range of temperature ( $T = -25\text{ °C}$  to  $40\text{ °C}$ ) and current ( $I = 0.1\text{ C}$  to  $6\text{ C}$ ), and coupled with a 0D thermal model. The model is parameterized with measurement data in frequency domain using electrochemical impedance spectroscopy (EIS) and validated with time-domain data. In experiments cells are charged under different operating conditions. Capacity fade is measured after a significant number of cycles and compared to the simulated anode potential. A qualitative correlation is found between the degradation in experiment and the anode potential dropping below  $0\text{ V}$  vs.  $\text{Li/Li}^+$  at the separator-anode boundary in the simulation. Furthermore a semi-quantitative expression for degradation is introduced. The transformation of the model into an on-board applicable form is presented in the companion contribution (part II).

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## 1. Introduction

Li-ion batteries have been extensively studied in the past years, both in experiment and modeling. For previous applications like consumer electronics, thermal behavior has been sufficiently considered around room temperature. Therefore, also the focus of modeling activities has been between  $25\text{ °C}$  and  $40\text{ °C}$ . As Li-ion chemistry recently became the favorite technology for use in traction batteries for electrical and hybrid vehicles, operation of cells has to be ensured in a wide temperature range and simultaneously has to meet the lifetime requirements for automotive purposes under these environmental conditions. Understanding

the limiting factors for operation at low temperatures in terms of power and energy capability, e.g., cold cranking power, becomes one target for cell and battery suppliers and has been recently addressed in simulations by Ji et al. [1].

Not only the electrical performance has to be taken into account, also aging behavior at extreme thermal conditions has to be understood well to extend lifetime and performance to a maximum. Rapid charging is one of the main challenges in battery research and gets even more challenging at subzero temperatures due to the limited kinetics of electrochemical systems. Under these conditions lithium deposits in an unwanted side reaction on the anode surface instead of intercalating in the anode particles. This so-called lithium plating leads to capacity loss, which affects lifetime dramatically. Metallic lithium is highly reactive and is assumed to react quickly with the electrolyte components to form insoluble products leading to an increase of the passivation layer on the

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anode surface and electrolyte depletion. Dendritic growth of metallic lithium has also been reported [2]. Dendrites are a potential safety hazard by penetrating the separator and causing an internal short-circuiting of the cell. This is also why lithium metal anodes are avoided in consumer cells despite their promising potential in power and energy density [3].

Electrochemical models are crucial in understanding internal processes, e.g., degradation effects. The design process of batteries can be supported as well as derivation of optimized operation conditions. Concentrated solution and porous electrode theory introduced by pioneers Newman and coworkers [4–6] have become the widely used principles and acclaimed theory in literature [7] which also found their way into commercial tools like COMSOL Multiphysics which is used in this study.

The parameterization of electrochemical models is one of the problematic key factors of building up a reliable model because of the large number and sensitivity of parameters as well as their frequently unknown dependencies on temperature and Li-concentration. Literature values often strongly vary for the same materials due to different measurement techniques. Few papers have been published presenting a full set of characterized material properties. Hence, there are several different mathematical parameterization methods presented by obtaining material parameters of electrical measurements from the full cell instead of directly measure material properties. Physical model reduction, namely single-particle model (SP-model), allows for time-efficient calculations as well as parameterization techniques and has recently also been extended by a thermal energy balance [8,9]. By neglecting local current distribution in this approach such a model can only be used for low C-rates and small electrode thickness. A promising reformulated mathematical model is presented in Ref. [10] for real-time parameter estimation but has only been validated for rates up to 2 C and few input parameters. Experiment-driven parameterization of electrochemical models combined with fitting algorithms is presented in Refs. [11,12] by incorporating time domain data, respectively discharge–charge profiles. A more sophisticated but also more complex approach is the support of 1D models by extracting effective parameters of 3D structure resolved models as presented in Ref. [13].

First modeling approaches of Li-plating have been made by Arora et al. [14] resulting in an understanding of the lithium deposition reaction by extension of an electrochemical model. In that work lithium plating has been assumed as overcharge reaction which is likely to happen outside the defined voltage limits only not taking into account any temperature dependencies. Lithium deposition is often observed taking place at electrode edges due to non-uniformity of current and temperature distribution and design parameters. A 2D-modeling approach for studying edge effects is presented in Ref. [15]. Modeling the complexity of the solid electrolyte interphase (SEI) [16] growth which is clearly linked to Li-deposition reaction has been addressed by several research groups [17–20]. Experimental work on micro-structure level and visualization of lithium dendrite growth are presented by Harris [2]. Experimental work on the influence of electrolyte properties with regard to lithium plating is described in Ref. [21].

Given this situation this contribution presents a fully parameterized electrochemical model over a wide temperature and current range for a large-format high-energy automotive lithium-ion cell. The model has been linked with a thermal model which is essential for operation at low temperatures due to strong heating under load. Parameterization has been conducted via piecewise investigation of electrochemical impedance spectroscopy (EIS) measurement data of the full cell. Different operation parameters like charging current, cut-off voltage, temperature, and initial SOC are studied on a wide range in order to detect increased aging

effects due to Li-plating. The validated model is used for predicting the lithium deposition reaction at low temperature charging and compared to experimental degradation measurements. A semi-qualitative approach is introduced for expressing the level of degradation. Part II [22] of the paper presents a novel transformation of the model into an online-applicable form which can easily be integrated into a battery management system (BMS) while allowing to control internal cell parameters.

## 2. Methodology

### 2.1. Studied cells

In this work a high-energy Li-ion cell consisting of a graphite anode and NMC cathode was studied. Design parameters and electrochemical properties are listed in Table 1. Electrochemical performance parameters of the full cell are determined by an experiment-driven parameterization technique which is introduced in Section 4.2.

### 2.2. Experiments

Electrical tests were performed within the limits of 3.0 V for the lower and 4.2 V for the upper cut-off-voltage. Charging was performed with a constant current (CC) until reaching the upper voltage and is followed by a constant voltage (CV) phase until the current drops below a specific value. As break criteria for the CV phase  $I < C/20$  has been chosen. For discharging only CC was used until reaching the end voltage. Experiments were done in Vötsch climate chambers and tests were controlled by BaSyTec systems and measurement data recorded in BaSyTec software. GAMRY instruments were used for measuring electrochemical impedance spectroscopy (EIS) in galvanostatic mode.

Temperature profiles were measured with PT100 sensors. For low discharge rates ( $I < 1$  C) one sensor was placed in the middle of the cell area. For higher rates also temperature gradient was determined by six sensors on the cell area. When plotting temperature rise, a mean value is shown.

For degradation measurements, 1 C constant current discharge was performed for determining capacity of the cells before and

**Table 1**  
Design adjustable parameters and electrochemical properties for the investigated Li-ion cell.

Parameter	Anode	Separator	Cathode
Thickness $L$ [ $\mu\text{m}$ ]	65 <sup>a</sup>	28 <sup>a</sup>	54 <sup>a</sup>
Porosity $\epsilon_s$	0.62 <sup>a</sup>	0.52 <sup>a</sup>	0.49 <sup>a</sup>
Particle radius $r$ [ $\mu\text{m}$ ]	10 <sup>a</sup>	–	10 <sup>a</sup>
Electrolyte concentration $c_l$ [ $\text{mol m}^{-3}$ ]	–	1100 <sup>a</sup>	–
Maximum theoretical concentration $c_s^{\text{max}}$ [ $\text{mol m}^{-3}$ ]	31,363 <sup>b</sup>	–	51,385 <sup>b</sup>
Electric conductivity $\sigma_{\text{cond}}$ [ $\text{S m}^{-1}$ ]	0.4 <sup>b</sup>	–	100 <sup>b</sup>
Ionic conductivity $\kappa_l$ [ $\text{S m}^{-1}$ ]	–	Table 3 <sup>c</sup>	–
Reaction rate $k$ [ $\text{m s}^{-1}$ ]	Table 3 <sup>c</sup>	–	Table 3 <sup>c</sup>
Charge transfer coefficient $\alpha$	0.5 <sup>b</sup>	–	0.5 <sup>b</sup>
Thermodynamic factor $\nu_l$	–	Table 3 <sup>c</sup>	–
Transference number $t_+$	–	0.363 <sup>b</sup>	–
Diffusion coefficient $D$ [ $\text{m}^2 \text{s}^{-1}$ ]	Table 3 <sup>c</sup>	Table 3 <sup>c</sup>	$4 \times 10^{-11}$
Double layer capacity $C^{\text{dl}}$ [ $\text{F m}^{-2}$ ]	Table 3 <sup>c</sup>	–	Table 3 <sup>c</sup>
Cell density $\rho_{\text{cell}}$ [ $\text{kg m}^{-3}$ ]	2976 <sup>a</sup>	–	–
Heat capacity $c_p$ [ $\text{J kg}^{-1} \text{K}^{-1}$ ]	1090 <sup>a</sup>	–	–
Emissivity factor $\epsilon$	0.96 <sup>b</sup>	–	–
Convective heat transfer coefficient $h$ [ $\text{W m}^{-2} \text{K}^{-1}$ ]	8.7 <sup>b</sup>	–	–

<sup>a</sup> Measured.

<sup>b</sup> Assumed.

<sup>c</sup> Fitted.

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