



Fast charging of lithium-ion cells: Identification of aging-minimal current profiles using a design of experiment approach and a mechanistic degradation analysis

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ABSTRACT

In this work, we present a novel approach to identify aging-minimal fast charging profiles for commercial lithium-ion cells by a design of experiment (DOE) methodology and a mechanistic degradation analysis of the obtained capacity retention figures. The DOE is based on the competitive comparison of specific current profiles under repeated application to the tested cell format. The current profiles are obtained from the linear superposition of a constant current profile and four independent, charge-neutral profiles modulating the shape of the base profile. The charge-neutral profiles rely on physically meaningful assumptions about their beneficial effects for the charging procedure, e.g. that a superimposed alternating current (AC) profile reduces unwanted polarization by its intrinsic heat generation. The aging minimal profiles are identified by multiple regression analysis. Mechanistic degradation analysis is applied to study the root cause of the observed capacity roll-over of the cells after a specific cycle number. This roll-over is attributed to the occurrence of lithium plating which itself is driven by active material losses in the initial stages of the cycle life. The onset of the roll-over can be considerably delayed by a suitable choice of the current trajectory, resulting in a more than doubled life expectancy.

1. Introduction

In the last decade, lithium-ion technology has made significant progress on both material as well as on system level, making its way to novel fields of application such as stationary energy storage systems and electric mobility. However, a widespread commercialization of electrical vehicles (EV) is currently not yet observed due to insufficient customer acceptance. Besides the price of an EV compared to a car equipped with an internal combustion engine, range anxiety and the reduced comfort with respect to the “fueling” process are among the most prominent reasons for the hesitant dissemination of battery powered EVs. To overcome these limitations, EVs either have to be supplied with battery packs of higher energy density and the available technologies have to be rigorously optimized towards a significant reduction of charging time. For this reason, the interest in the identification of fast charging capabilities of lithium-ion materials and cells has tremendously grown over the last years [1–4]. In literature, a variety of different approaches has been presented to identify optimal charging

profiles under different constraints [1,4–29]. Many authors make use of model structures of various complexity to derive time-, energy-, temperature- or loss-optimized profiles, based on either equivalent circuit models [6,9,16,30] or pseudo two dimensional modeling approaches [1,8,10,22,26], respectively single particle models [20,21] derived from porous electrode theory. Other authors consider identifying optimal profiles according to the observed degradation characteristics [5,7,12,13,17–19,24,28,29]. Lastly, few studies address the optimization issue by statistical methods [14,15,27]. It can generally be noticed that there is still a lot of disagreement about the required characteristics of charging profiles suitable for rapid charging of commercially available lithium-ion cells. For instance, some authors claim superimposed alternating current to be beneficial for the charging process [5,13,31,32] while others did not observe any positive effect [12,23], or only if specific preconditions on the waveform were met [11]. We believe that most of this discrepancy is caused by a lack of physical motivation for the application of a specific waveform, and particularly a lack of knowledge how the combination of different charging modes

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(direct/alternating current, multistage constant current, pulse charging) may support or impede time- and aging-minimal fast charging. Further, model-based identification intrinsically involves the risk not to cover all kinetic information to properly predict the evolution of critical state variables such as lithium concentrations in solid and electrolyte phase, especially if the used model structures have to be significantly reduced in their complexity to meet the conditions of real-time applicability. With respect to the increased susceptibility of lithium-ion cells to aging during fast charging, optimal charging profiles have to be designed to prevent or at least inhibit the following degradation mechanisms:

- **Lithium plating:** Lithium plating (LiP) preferably occurs during charging at low temperatures, high states of charge (SOC) and/or large current amplitudes and entails the growth of metallic lithium spots on top of the negative electrode (NE) [33–40]. Driven by high polarization forcing the potential difference between electrolyte and solid phase of the NE below 0 V, lithium ions arriving at the electrode/electrolyte interface cannot reversibly intercalate into the host structure of the electrode anymore [41]. Due to its high reactivity, the metallic lithium instantly reacts with the surrounding electrolyte to form passivating layers and dead lithium agglomerates [42–46]. Thus, in the long run LiP leads to an extensive loss of cyclable lithium which is not available any more for being stored in the electrodes [7,19,36,47,48]. LiP can be counteracted by active or passive control of the anodic polarization to keep the anode potential > 0 V vs. Li/Li⁺ for the entire charging process. Active control implicates an intelligent choice of the charging current depending on SOC and temperature whereas passive control could be realized by a sufficient NE capacity excess.
- **Electrolyte decomposition:** Electrolyte decomposition is a degradation process preferably occurring if the electrochemical potential in the electrolyte domain exceeds the stability limit of a given electrolyte system [49] and can lead to the formation of surface films on both cathode [50,51] and anode [52] or to formation of gaseous reaction products [53]. If triggered, electrolyte decomposition is accelerated by increased temperatures [54]. Therefore, the decomposition reactions may be slowed down by either keeping the electrolyte potentials or temperature within a predefined range.
- **Particle cracking/transition metal dissolution:** Particle cracking implicates a mechanical disintegration of the active material and results in a loss of surface sites taking place in the intercalation reaction [55–57]. Particularly for Manganese spinel or layered oxide materials, particle cracking can be accompanied by the dissolution of transition metals at the cathode/electrolyte interface [58–60]. The dissolved transition metals may diffuse through the separator layer and react with the organic compounds of the anodic solid electrolyte interface (SEI) [57,61–63]. These reaction products can decrease the protective effect of SEI towards further reduction. Since the probability of particle fracture is directly related to the applied charging load [64], the negative effects of particle cracking and transition metal dissolution may be circumvented by a careful selection of the charging current depending on the active material and electrode structure. Moreover, since metal dissolution is a temperature activated process [65], the cell's susceptibility to degradation due to metal dissolution may be decreased by proper temperature control.

Based on the explanations above, the charging current and voltage are the most critical parameters to take care of in the profile generation process. In this work, we propose a refined methodology for the identification of optimal (fast) charging profiles by designing profiles according to physically meaningful assumptions on their beneficial effects

to prevent the introduced degradation processes. This is done in a design of experiment (DOE) approach to clarify the influence and mutual interaction of different charging modes on the cycle life of a typical high-energy 18650 cell. In the DOE, different charging profiles compete against each other with respect to the capacity retention observed during prolonged cycling. The charging profiles themselves are designed as a superposition of a constant current base profile and up to four charge-neutral profiles to tune the shape of the current trajectory according to the assumed effects of the superposed profiles on the charging process. As each of the charge neutral profiles is applied in a range of three different amplitude levels, an extensive test matrix is generated to support a statistically meaningful assessment of the optimal charging profile. The latter is identified by multiple linear regression analysis of a cost function obtained by cross-correlation analysis of base and superposed profiles. Additionally, the observed degradation characteristics (capacity loss, impedance increase) are examined by mechanistic analysis introduced in [66,67]. The combination of the above mentioned approaches leads us to the identification of profile combinations which maximize cycle life and helps to understand the underlying mechanisms promoting or delaying cell degradation due to fast-charging of lithium-ion cells. Section 2 introduces the examined superposed profiles and the DOE approach followed in this study along with the experimental setup and test conditions. In Section 3, the cycle life of the tested configurations is assessed in a behavioral fashion. Therefore, a two-stage capacity loss function is set up and matched with the capacity roll-over behavior consistently observed for all cells. Section 4 presents the concept and results of the statistical assessment of the obtained capacity retention plots. Therein, a statistically meaningful life function is defined and evaluated versus the measured lifetimes. Finally, Section 5, presents the mechanistic study of the cell's degradation paths. As one major result, the unwanted capacity roll-over is assigned to the deterioration of the graphite anode which itself greatly depends on the applied charging profile (Table 1).

Table 1

List of abbreviations and symbols used in this manuscript (sorted in alphabetical order).

<i>a-d</i>	profile amplitudes/a.u.	LAM	loss of active material
AC	alternating current	LiP	lithium plating
BOL	begin of life	LLI	loss of lithium inventory
CC	constant current	NE	negative electrode
CCCV	constant current constant voltage	NMC	Nickel-Cobalt-Mangan oxide
CD	cold derating	OPR	overpotential reserve
CV	constant voltage	PE	positive electrode
C_{nom}	nominal capacity/Ah	pOCV	pseudo open-circuit voltage
CI	current interrupt	<i>p</i> -value	asymptotic significance
CP	center point	RPT	reference performance test
C_{rel}	(remaining) relative capacity/%	SEI	solid electrolyte interphase
DOE	design of experiment	SOC	state of charge/%
EIS	electrochemical impedance spectroscopy	<i>T</i>	duration of the charging phase/s
EOL	end of life	x_{C80}	cycle number at 80% cap. retention
EV	electric vehicle	x_{crit}	roll-over onset cycle
f_1-f_4	superposed profiles in terms of C-Rate	VIF	variance inflation factor
FC	full cell	η_{int}^{NE}	overpotential of interaction reaction/V
f_{life}	life function	Φ_0^{NE}	anode equilibrium potential/V

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