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Discrimination of degradation processes in lithium-ion cells based on the sensitivity of aging indicators towards capacity loss

Marius Bauer [a, *], Clemens Guenther [a], Michael Kasper [a], Mathias Petzl [b], Michael A. Danzer [a, b]

[a] Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW), 89081 Ulm, Germany
[b] Helmholtz-Institut Ulm, 89081 Ulm, Germany

HIGHLIGHTS

- 10 s resistance shows a different sensitivity towards low and high temperature aging.
- Trajectories in a $(\Delta c, \Delta p)$-plane spanned by capacity and power fade are analyzed.
- They allow discriminating between the effects of low and high temperature aging.
- The onset of lithium plating is more abrupt than expected from an Arrhenius law.
- There is a correlation between anode morphologies and trajectories in the $(\Delta c, \Delta p)$-plane.

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ABSTRACT

In typical applications of lithium-ion batteries, the cells are monitored in order to guarantee a safe and stable performance during operation. Therefore, methods to characterize aging processes in a non-destructive way are desired. In this work, internal resistance and power capability calculated from time domain measurements are investigated. Test cells (NMC/graphite) are cycled at the lowest temperature in the operational range ($T = 0\,^{\circ}C$) as well as under high temperature conditions ($T = 50\,^{\circ}C$) in order to characterize the aging behavior for extreme temperatures. For both internal resistance and power capability, an analysis of their sensitivities towards capacity loss induced by high or low temperature cycling is carried out. It is demonstrated how discrepancies in sensitivity can be used for the diagnostic purpose of discriminating between low and high temperature aging effects during cycling. A baseline diagnostic approach for constant operating conditions and an extended algorithm for varying conditions are presented. The extended approach is based on the evaluation of cell trajectories in a state space with capacity loss and polarization parameters. It provides measures which characterize the aging behavior and allow to identify the dominant aging mechanism.

1. Introduction

In recent years, one could see an incremental improvement of lithium-ion battery technology especially with respect to features relevant to automotive applications such as safety, energy density, and lifetime [1]. Nonetheless, battery lifetime still remains a critical obstacle for the market success of electric vehicles as customers will expect their car's lifetime to be in a similar range as the lifespan known from conventional cars. Triggered by the growing market for battery electric vehicles [2], there is an increasing interest in methods for on-board battery characterization. Aging-related information is needed in battery-management-systems (BMS) for multiple purposes [3]. For instance, aging related parameters such as impedance parameters or internal resistance values are used in *SOH* prediction and provide an input for BMS algorithms which guarantee safe and reliable operation [3].

During battery operation, different aging processes contribute to capacity loss $\Delta C := C_0 - C(t)$, where $C(t)$ is the remaining capacity and C_0 is the initial capacity at $t = t_0$ (begin of life) [4–6]. As discussed by Waldmann et al. [7] for a commercial NMC/graphite Li-ion cell, the relative aging rate $r := \Delta C/(C_0 t)$ during cycle aging (C-rate: $I = 1$ C) is approximately described by an Arrhenius-like approach

* Corresponding author.
E-mail address: marius.bauer@zsw-bw.de (M. Bauer).

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$$r = A_p \exp\{-E_{A,p}/(k_B T)\} + A_s \exp\{-E_{A,s}/(k_B T)\}. \quad (1)$$

Therefore, temperature behavior is divided into two major domains: A low temperature domain empirically described by a negative activation energy $E_{A,p} < 0$ and a high temperature domain characterized by $E_{A,s} > 0$. Obviously, the aging effects in cells cycled in the higher and lower temperature range are caused by distinct aging processes.

At low temperatures, lithium plating, i.e. metallic deposition of lithium on the negative electrode during charge is the dominant aging mechanism. Poor electrode kinetics are regarded as the major reason for the occurrence of lithium plating at low temperatures and high charge currents. Lithium intercalation is slowed down under such conditions because of limited solid state diffusion and slow charge transfer processes [8]. This leads to a drop of the surface potential of graphite particles below 0 V vs. Li/Li^+ favoring metallic deposition of lithium ions against the intercalation process [4,9–11]. Effects from lithium plating include capacity loss and additional polarization. Capacity loss from lithium plating is explained by the loss of electronic connection between metallic lithium and the electrode particles occurring primarily during discharge [8]. As a result, one can find agglomerates of *dead lithium* covered by a surface layer as discussed by Petzl et al. [8]. These agglomerates of dead lithium contribute to a loss of cyclable lithium resulting in loss of cell capacity [5,12]. Additional polarization, on the other hand, is explained by increased SEI growth due to cracks in the SEI induced by lithium deposited at the graphite surface or inside the SEI. Moreover, surface films on the metallic lithium will consume electrolyte species [8] and lead to increased polarization due to decreased ionic conductivity of the electrolyte (electrolyte dry-out).

During cycling at high temperatures, diffusion and charge transfer processes are much faster so that the rate of intercalation processes is sufficient to keep the potential well above the lithium plating criterion of 0 V vs. Li/Li^+ [9]. Therefore, capacity loss during high temperature cycling is driven by other processes. Firstly, there are lithium consuming side reactions like the reduction of electrolyte species leading to loss of cyclable lithium [12]. Secondly, there is capacity loss due to loss of active material. Possible causes for active material loss include dissolution and particle isolation [5,12]. Simultaneously, the aging mechanisms at high temperatures also lead to additional polarization. In accordance with the aging mechanisms, we can expect additional polarization to be caused by an increased SEI layer [4,13–15], electrolyte dry-out, contact deterioration, and reduced active surfaces in case of active material loss. It should be considered that additional SEI layer growth will be induced by particle cracks due to mechanic stress during rapid charging or discharging [16].

With regard to battery applications, easy-to-measure indicators allowing for the discrimination of high-temperature aging vs. lithium plating are desired. Existing approaches to decipher different aging effects in the course of aging include differential voltage based data analyses [5], model based methods for the investigation of voltage response and its derivatives [17–19] and methods based on changes in entropy and enthalpy [20]. In addition to that, also the analysis of the cell's impedance spectra allows to conclude about the aging mechanisms [4,21–23]. These approaches all require a significant amount of measurement time and equipment involved.

An easy-to-implement method for on-board applications is a voltage based measurement of resistance values after pulse excitation, for instance 10 s resistance or power capability as defined in the FreedomCar Standard [6,24]. Such measurements can give a good estimate for total polarization, but do not directly permit to separate distinct aging effects because all polarization effects occurring during the pulse are superposed in the 10 s resistance values.

Nonetheless it would be favorable to extract information about the occurrence of different aging processes under distinct conditions of operation from pulse response measurements rather than from electrochemical impedance spectroscopy or other more complex techniques. In the following sections, a diagnostic approach to separate high temperature aging effects from low temperature effects due to lithium plating is derived from experimental work using NMC/graphite cells. Being based on the measurement of 10 s resistance as an indicator of actual cell aging, this approach allows for the discrimination of different aging effects without the need of a mechanistic aging model.

As described in Section 2 (Experimental), aging behavior is investigated for low temperature cycling at $T = 0\,°C$ and high temperature cycling at $T = 50\,°C$. In Section 3 (Aging indicators), polarization based parameters are introduced. These parameters (10 s resistance and power capabilities) are further investigated in Section 4 with a focus on their sensitivity towards capacity loss from the different aging conditions. In Section 5, the different sensitivities are used to establish a diagnostic method able to conclude about the dominant aging mechanism under specified operating conditions. Finally, in Section 6, some results determined with the diagnostic approach are discussed.

2. Experimental

Kokam Pouch cells (SLPB75106205 16 Ah) are used to experimentally evaluate the effect of cycling at $I^{ch} = -I^{dc} = 16\,A =: 1\,C$ at high and low temperatures, where I^{ch} and I^{dc} denote charge and discharge currents, respectively. Cycling is applied according to a CCCV-scheme with $|I_{end}| = C/20$ for both charge and discharge. Before the actual aging test, all cells were cycled four times to ensure that formation related processes are completed. One cell (denoted by #1) is undergoing low temperature cycle aging for 18 cycles at $T = 0\,°C$, while another cell (denoted by #2) is cycled for 200 cycles under high temperature conditions at $T = 50\,°C$. The test conditions are chosen to comprise the most extreme low temperature load covered by the cell specification ($T_{min} = 0\,°C$), whereas a temperature of $T = 50\,°C$ exceeding the high temperature limit ($T_{max} = 40\,°C$ for charging) is applied on the other side of the temperature range in order to accelerate testing. Based on the results demonstrated with NMC/graphite cells in Ref. [7], we might assume that the aging mechanisms occurring at $T = 50\,°C$ are mostly equivalent to those occurring at $25\,°C < T < 70\,°C$, i. e. the processes are the same, but occur at higher rate for higher temperatures. Under this assumption, the results in this paper are applicable to the whole temperature range.

After cycling as described above, the cells' (#1 and #2) cycle conditions (high and low temperature) are exchanged in order to evaluate the effect of low (high) temperature aging with pre-existing degradation from high (low) temperature aging in Section 5 (Fig. A.5). For cell #1, another 20 cycles at $T = 50\,°C$ are applied after the first 18 cycles at $T = 0\,°C$, while cell #2 is subjected to another 9 cycles at $T = 0\,°C$ after the first 200 cycles at $T = 50\,°C$.

An additional set of four test cells were cycled with $I = 1\,C$ at temperatures of $T \in \{5\,°C, 12.5\,°C, 25\,°C, 40\,°C\}$ in order to apply the diagnostic approach for cells cycled at various temperatures in Section 6. With these cells, a number of 30 (5 °C), 115 (12.5 °C), 400 (25 °C), and 160 (40 °C) cycles were recorded. Another test cell stored at $T = 50\,°C$ was used to evaluate the effect of calendar aging. As a result, all aging related effects (capacity loss, shift of impedance spectra, resistance increase) are negligible, so calendar aging will not be regarded anymore in this work.