



Data-driven approaches for the fast formation of lithium-ion pouch cells using operando gassing analysis

Sandro Stock^{a,*}, Jonas Böhm^a, Manuel Ank^b, Philipp Rath^a, Markus Lienkamp^b, Rüdiger Daub^{a,c}

^a Technical University of Munich (TUM), TUM School of Engineering & Design, Department of Mechanical Engineering, Institute for Machine Tools and Industrial Management, Boltzmannstr. 15, Garching, 85748, Germany

^b Technical University of Munich (TUM), TUM School of Engineering & Design, Department of Mobility Systems Engineering, Institute of Automotive Technology, Boltzmannstr. 15, Garching, 85748, Germany

^c Fraunhofer Institute for Casting, Composite and Processing Technology (IGCV), Am Technologiezentrum 10, Augsburg, 86159, Germany

HIGHLIGHTS

- Concurrent analysis of gas evolution and impedance change in single-layer pouch cells.
- Development of fast formation approaches using operando gassing analysis.
- Reduction of formation time to 2.4 h for NMC622/graphite cells.
- Comprehensive quality assurance using EIS, DCIR, DVA, and cycle life testing.
- Implementation of a data-driven approach for cycle life prediction with test errors <10 %.

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ABSTRACT

Formation is among the most time-intensive process steps during lithium-ion battery production due to complex electrochemical reactions. To reduce production costs, fast formation strategies are required that do not diminish the solid electrolyte interphase (SEI) and thus the cell quality. In this work, a novel approach to optimize formation based on inline gas analysis is presented. Critical potential ranges for SEI formation are revealed by coupling impedance analysis with gas volume measurement using a pouch cell with a gold wire reference electrode and a cell expansion bracket. Based on the gas evolution profile of 4 Ah NMC/graphite pouch cells, two formation strategies were derived that reduce the processing time from approx. 53.3 h to 5.3 h and 2.4 h. A comprehensive end-of-line (EOL) test, which included a 72 h calendar aging, C/3 capacity determination as well as EIS and DCIR measurements at 80%, 50%, and 20% SOC, showed no significant decrease in cell quality. The subsequent cycle life test revealed an 11.5% reduced mean cycle life for the 5.3 h formation protocol, and a 6.6% increased cycle life for the 2.4 h formation protocol, in relation to a common three-cycle reference protocol. Finally, early cycle life prediction was performed to enable a rapid evaluation of the cell quality using the first 50 cycles from cycle life testing only. A mean test accuracy of 7.4% was achieved when using multiple input features from the EOL test and early cycling. The results highlight the great potential of data-driven approaches to optimize formation strategies and accelerate process development in battery production.

* Corresponding author.

E-mail address: sandro.stock@tum.de (S. Stock).

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1. Introduction

The transition from fossil fuels towards a sustainable mobility sector promotes the application of lithium-ion batteries (LIBs) due to their high efficiency, energy density, and lifetime [1]. However, high production costs and safety hazards inhibit a wide-spread market penetration [2]. Both costs and cell quality are strongly determined by battery production, which is characterized by a time-intensive and complex production chain [3]. Formation is one of the most time-intensive and quality-determining process steps due to the cell-internal electrochemical processes [4]. The assembled cell is charged for the first time in the formation, whereby passivation layers are formed on the surface of the electrode particles. At the anode, the solid electrolyte interphase (SEI) is formed by reduction and decomposition reactions of the solvents as well as additives of the electrolyte [5]. A similar oxidation reaction triggers the formation of the cathode electrolyte interphase (CEI) at the cathode. In particular, the SEI has been reported to have a great influence on the resulting cell quality and the aging behavior. Thus, the central aim of the formation is the generation of a homogeneous and high-quality SEI. [6]

1.1. Gas evolution during SEI formation

The SEI composition, stability, and thickness are influenced by several factors such as the electrode materials, electrolyte solvents, electrolyte additives, ambient temperature, and formation protocol [5]. During SEI formation, gas is generated from reduction reactions of electrolyte solvents. Several gases can be formed such as carbon monoxide (CO), ethylene, and alkanes [7]. Ethylene is hereby emitted by the reduction of ethylene carbonate (EC) and alkanes arise from linear carbonates such as dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) [8]. The EC reduction at the anode starts at approx. 1 V vs. Li/Li⁺ and peaks at 0.5 V vs. Li/Li⁺, whereas linear carbonates are typically reduced below 0.9 V vs. Li/Li⁺. At the cathode, carbon dioxide (CO₂) can arise from the decomposition of lithium carbonate surface contaminants at potentials from 3.8 V vs. Li/Li⁺ to 4.5 V vs. Li/Li⁺ [9,10]. Oxygen release can occur in nickel manganese cobalt (NMC) oxide cathodes at potentials above 4.3 V vs. Li/Li⁺ [11–13]. Furthermore, water residues within the cell can trigger hydrogen and oxygen evolution at anode potentials of approx. 1.3 V vs. Li/Li⁺ [14,15]. An in-depth review of gassing mechanisms in LIB with primary and secondary sources is provided by Salomez et al. [7]. The formation of the SEI causes a change in the impedance of the cell [16,17]. Using a step-wise formation protocol in three-electrode cells and blocking conditions, Solchenbach et al. [18] were capable of extracting the SEI resistance and determining the respective potential ranges for SEI formation. The SEI resistance increase was tracked by performing subsequent EIS measurements and applying an equivalent circuit model (ECM). However, the potential ranges differed when an additive was introduced to the electrolyte, as some additives (such as vinylene carbonate (VC)) are reduced at higher anode half-cell potentials.

Tracking the gas evolution and impedance change that accompanies the SEI formation can help in understanding the formation process and identifying the relevant potential ranges. From a production perspective, the complete evolution and subsequent removal of gases has to be ensured during the formation to avoid safety hazards during operation [3]. The formation is considered to be completed when no more gas is produced and the passivation layers are sufficiently formed. This leads to high process times since low formation currents are often applied, and frequently multiple charge and discharge cycles are performed [4]. Hence, the formation process is among the most time-intensive process steps in battery production, and multiple approaches have been proposed to reduce the overall formation time.

1.2. Fast formation strategies

Among the first, Lee et al. [19] examined approaches to reduce the formation time for lithium cobalt oxide (LCO)/graphite cells without compromising the cell quality. Based on the potential ranges in which EC is reduced, a major SEI formation period at anode half cell potentials above 0.3 V vs. Li/Li⁺, and a minor SEI formation period, in which intercalation is predominant, was identified. By a step-wise reduction of formation time in the intercalation phase, a sufficient cut-off voltage of 3.7 V was identified. The formation protocol adjustment resulted in a total formation time of approx. 5 h without diminishing the cycle life. In contrast to the low-voltage profile, a high-voltage formation was proposed, in which multiple cycles at potentials above 3.9 V were applied for NMC/graphite cells [20]. By comparing the optimized formation protocol to a five-cycle baseline protocol, a significant time reduction was achieved, resulting in a minimum formation time of approx. 21 h. In a similar study by Mao et al. [21], a formation time of 26 h to 30 h was found to be ideal for minimal impedance rise. Shorter formation protocols with a C-rate of C/2 resulted in lithium plating, even at elevated temperatures.

The influence of pressure and temperature has also been studied for NMC/graphite cells. Higher external mechanical loads resulted in a capacity increase after formation of up to 2% [22]. Moreover, the pressure and temperature were adjusted to reduce the formation time and costs [23]. High temperatures (60 °C) were reported to cause severe side reactions during SEI formation, and low temperatures (−10 °C) reduced the ionic conductivity [24]. Thus, an optimum ambient temperature of 25 °C was concluded. Drees et al. [25] applied an electrode ECM to optimize the formation protocols based on the anode potential. By comparing different high-current formation protocols, a 45 min single cycle formation showed no reduced cycle life in comparison to the references. A subsequent study showed that no lithium-plating was detected in three-electrode coin cells using formation protocols that lasted 1.68 h [26]. However, the effects on the SEI composition when quickly reducing the anode potential below 0.3 V vs. Li/Li⁺ have not been evaluated, and a direct transfer of laboratory cells to large-format, industrial cells is challenging.

1.3. Quality assurance using machine learning

All formation optimization efforts have in common that time-intensive cycle life testing has to be performed to ensure that the changes in the formation protocol or environment do not diminish the SEI quality and thus the cell performance. While the cell capacity, the cell resistance, and rate capability can be checked immediately, cycle life analysis requires several months of testing [5]. This is because SEI quality is difficult to assess and an inferior SEI may only be detected by a reduced cycle life [27]. As a result, resources are tied and further process development is slowed down due to the time-consuming quality assurance in between improvement measures. Recently, multiple data-driven methods were proposed to predict the remaining useful life or cycle life of the LIBs [28,29]. Most approaches utilize features from electrical or thermal data, which are collected with battery test systems [30]. These features are then used to build models based on machine learning (ML) or artificial intelligence [31,32]. By using 124 commercial LIBs and 100 cycles as input data, Severson et al. [33] demonstrated that a test error of 9.1% for quantitative cycle life prediction is achievable. Similar studies achieved even lower prediction errors when utilizing more complex models or different data sets [34–42]. Furthermore, production data was used to extract features and to reduce the required number of testing cycles. By using impedance and formation data in combination with testing data, Stock et al. [43] showed that linear regression as well as artificial neural networks are suitable for early cycle life prediction and classification into quality groups. However, these approaches have not been utilized to accelerate process optimization in production and ensure the cell quality when altering formation protocols.

1.4. Structure of the article

In this work, a novel approach to optimize formation protocols based on operando gas analysis is presented. Section 2 provides information on the applied material systems, the building procedures for SLPs with GWRE [44], and MLPs, as well as the measurement devices. Section 3 summarizes the methods that were used to detect the critical potential ranges for SEI formation, and to evaluate the quality of the MLPs. Furthermore, a support-vector regression method to perform cycle life prediction is presented. Results are presented and discussed in Section 4, which is separated in the relation of SEI formation and gas evolution, the optimization of the formation protocol, a comprehensive quality assurance approach, and the early cycle life prediction using machine learning. Finally, the results are summarized in Section 5, and implications for research as well as the industry are discussed.

2. Experimental

2.1. Multi-layer pouch cells

For all cells, a state-of-the-art NMC622 cathode (CustomCells, Germany) and a natural graphite anode (CustomCells, Germany) were used as material systems (cf. Table 1) due to their representativity and frequent application. The MLP assembly was conducted inside a dry room at a dew point below -45°C at the Institute for Machine Tools and Industrial Management (iwb) of the Technical University of Munich (TUM). First, single electrodes were cut from the coil using a nanosecond-pulsed fiber laser (YLP-HP-0.2-30-500-100-LT, IPG Photonics, USA) to a size of 104 mm by 76 mm for the anode sheets, and 101 mm by 73 mm for the cathode sheets. An uncoated part of the substrate foil of 67 mm by 15 mm remained as current collectors at each sheet for the contacting. All MLPs were stacked in a z-folding process (z-folder, Manz, Germany) to a 10/11 cathode/anode stack using a Celgard 2500 separator [45]. The foils were contacted to a conductor tab using an ultrasonic welding process (L20, Branson Ultraweld), and the cell stack was packed into a deep-drawn pouch foil (D-EL408PH(3), DNP, Japan). After assembly, the MLPs were dried under constant evacuation (approx. 1 mbar) at 80°C for at least 12 h inside the lock of the filling glove box (ELFi, Mbraun, Germany). The electrolyte (LP572, E-Lyte innovations, Germany) consisted of 1 M lithium hexafluorophosphate (LiPF_6) solved in a mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with a mass fraction of 3:7, and 2 wt% vinylene carbonate (VC) as additive. The MLPs were manually filled with 11.6 mL electrolyte and sealed at a pressure of 200 mbar. Subsequently, the cells rested for approx. 4 h to ensure complete wetting. The formation was conducted at a defined pressure of 2 bar in a custom-made cell fixture (cf. Section 2.3) that was located inside a climate chamber (TempEvent T/340/40/3-S, Vötsch Industrietechnik, Germany), set at a constant temperature of 25°C . Three different formation protocols (see Section 4.2) were applied using a battery cell test system (BCS-815, Bio-Logic SAS, France).

2.2. Single-layer pouch cells with gold wire reference electrode

The electrodes for the SLPs were prepared analogously as described for the MLPs. Subsequently, SLPs with an incorporated GWRE were assembled that had the same dimension as the MLP electrodes. The schematic structure of the SLP is shown in Fig. A.2 in the appendix. The tip of the otherwise isolated GWRE (point-like reference) was centered between the anode and cathode using two separators. The electrochemically active tip was placed in the center of the coating surface of the anode, as far away from the electrode edges as possible. To ensure a leak-free transition of the GWRE out of the cell, a thin polypropylene foil piece was placed underneath and on top of the GWRE at the position where the pouch was later sealed. The insulation of the GWRE, which was used for the contacting to the potentiostat,

Table 1

Characteristics of the coated electrodes of the SLPs and MLPs.

Attribute	Cathode	Anode
Active material	NMC622	Graphite
Active material content	93.5 wt%	96.0 wt%
Conductive additive	CB	CB
Conductive content	3.5 wt%	2 wt%
Binder additive	PVDF	CMC & SBR
Conductive content	3 wt%	2 wt%
Specific capacity	160 mAh g ⁻¹	350 mAh g ⁻¹
Areal capacity	3.0 mAh cm ⁻²	3.5 mAh cm ⁻²
Areal mass loading	40.50 mg cm ⁻²	20.84 mg cm ⁻²
Coating thickness	66 μm	70 μm
Porosity	36%	33%
Current collector (CC)	Aluminum	Copper
CC thickness	15 μm	14 μm

was then carefully removed with a scalpel. Afterward, the pouch foil was sealed on three sides in such a way that the anode and cathode conductor tabs as well as the reference protruded from the pouch. The GWRE was sufficiently thin so that its outlet was tightened by the sealing of the surrounding pouch foil. The subsequent drying, filling, and sealing steps were carried out according to the previously described procedure for the MLPs except that the electrolyte amount was reduced to 6.9 mL.

2.3. Cell expansion bracket

To evaluate the gas evolution during formation, a cell expansion bracket (CEB) was utilized, which is described in detail in a previous study [46]. A depiction of the CEB with key elements is provided in Fig. A.1 in the appendix. The main functions of the CEB include the electrical connection of the pouch cell to the battery test system, the application of normal stress onto the cell stack, and tracking of the cell expansion as well as the expansion of the gas bag of the pouch. To assess the expansion of the gas bag, a lightweight aluminum plate is placed on top of the gas bag and the displacement of a vertically attached contact distance sensor is tracked (GT2 series, Keysight, Japan). Using area-dependent calibration curves, a conversion from the vertical expansion to the gas volume is then possible [46]. This enables a high-precision measurement of the volume change with resolutions of approx. 1 μL . However, initial absolute gas quantities are difficult to detect due to void volumes between the cell stack and the pouch foil. The expansion of the cell stacks is measured by a contact distance sensor, which is placed on top of the cell pressure plate. By using a screw-spring combination, a defined normal stress was applied to the cell throughout the formation.

3. Methods

3.1. SEI formation protocol

In the following, a method from Solchenbach et al. [18] is described that enables tracing the course of SEI built up during the formation via a step-wise formation procedure. In this work, the procedure was slightly adapted since a different cell type and material system were used. The CE half-cell potential (U_{CE}) controlled formation protocol is visualized in Fig. 1.

After a first potentiostatic electrochemical impedance spectroscopy (PEIS) measurement at open-circuit voltage (OCV) (100 kHz to 100 mHz, 20 points per decade in logarithmic spacing, 10 mV excitation amplitude, 5 average measures per frequency, activated drift correction), U_{CE} was reduced to a potential $U_{\text{CE,block}} = 1.81 \text{ V vs. Li/Li}^+$. At this potential, blocking conditions are approximately reached. This was ensured experimentally by a step-wise constant current constant voltage (CC-CV) discharge of a SLP with PEIS measurements at different U_{CE} after each constant voltage (CV)-phase. Furthermore, all following

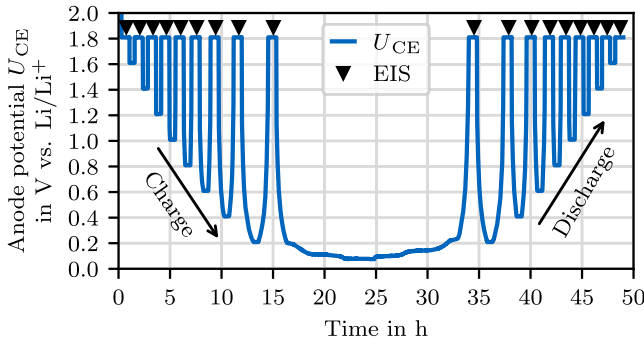


Fig. 1. Visualization of the anode half-cell potential controlled formation procedure measured in the three-electrode SLPs with GWRE, which was adapted from Solchenbach et al. [18]. The blue line represents the CE half-cell potential and the black triangles mark the EIS measurements. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

PEIS measurements at $U_{CE,block} = 1.81$ V vs. Li/Li⁺ further verify this approximation. After the initial partial charge, the potential was held for 0.5 h at blocking conditions before a PEIS measurement was conducted. Subsequently, U_{CE} was reduced by ΔU_{CE} , and held constant for 0.5 h before it was increased until blocking conditions were reached again. This procedure was repeated with increasing ΔU_{CE} until the cell was approximately fully charged at $U_{CE} = 0.07$ V vs. Li/Li⁺. Then the procedure was repeated in reverse and the cell was discharged. Taking the first PEIS at blocking conditions in Fig. 1 as a reference, each of the subsequent PEIS measurements can provide insights into irreversible processes of the CE half-cell that occurred in the potential range between blocking conditions and minimal half-cell potential of the previous discharge step. Hence, correlating a change in the blocking conditions SEI resistance ($R_{SEI,block}$) between two PEIS measurements in the formation procedure to an irreversible change of the SEI which took place in the respective potential interval is possible, i.e., the tracking of the SEI formation.

To quantify the results of the PEIS measurements, the obtained impedance spectra were fitted to a model that represents the physical processes of the system in the corresponding frequency range. This is frequently performed using an ECM. However, to model the mid-frequency region of a porous electrode, transition line models (TLMs) are often utilized to replace classical circuit elements. As introduced in Solchenbach et al. the resistance caused by the pore structure significantly impacts the overall impedance of the electrodes when containing high loadings (>2 mAh cm⁻²) [18]. The effect is noticeable in the Nyquist plot as a distinct 45° feature in the high-to-mid frequency range [47–51]. This behavior is most accurately described by TLMs [52], which reproduce the impedance contribution of the porous electrode soaked with electrolyte under the assumptions that the pores are of uniform cross-section, semi-infinite length, homogeneously filled with electrolyte, and without cross-links [53]. To obtain $R_{SEI,block}$, the spectra were fitted to a monorail transmission line model [44,48], which is shown in Fig. A.3 in the appendix. To account for the high-frequency response of the system, a single high-frequency resistance R_{HFR} is added in series. In the TLM, each of the infinite incremental interface fractions is modeled by two RQ-elements. One represents the SEI/graphite interface (index “CT”) and the other the electrolyte/SEI interface (index “SEI”). r_{SEI} and q_{SEI} are incremental elements of the SEI resistance R_{SEI} and the SEI capacitance Q_{SEI} . The corresponding half-cell impedance $Z_{half-cell}$ can be calculated with Eq. (1) using the impedance definition Z_I from Eq. (2) [48].

$$Z_{half-cell} = R_{HFR} + \sqrt{R_p Z_I} \cdot \coth \sqrt{\frac{R_p}{Z_I}} \quad (1)$$

$$Z_I = \frac{R_{CT}}{R_{CT} Q_{CT}(j\omega)^{\alpha_{CT}} + 1} + \frac{R_{SEI}}{R_{SEI} Q_{SEI}(j\omega)^{\alpha_{SEI}} + 1} \quad (2)$$

The model has originally eight free parameters, the pore resistance R_p , high-frequency resistance R_{HFR} , charge transfer resistance R_{CT} , SEI resistance R_{SEI} , charge transfer capacitance Q_{CT} , SEI capacitance Q_{SEI} , empirical constants α_{CT} and α_{SEI} . To reduce this number, the difference between α_{CT} and α_{SEI} is neglected: $\alpha = \alpha_{CT} = \alpha_{SEI}$ [18]. Furthermore, R_{SEI} and R_p dominate the mid-frequency region of the blocking condition spectrum. Hence, R_{SEI} can only be reliably isolated if the change of R_p during formation is negligible. However, an conservative estimation of the pore volume fraction occupied by the SEI results in 27% (assuming a BET surface of 3 m² g⁻¹ and a SEI thickness of 20 nm). This implies that the change in R_p during formation cannot be neglected. Hence, the porosity and average pore size decreases due to SEI formation and it can be expected that the R_p in blocking conditions will increase with the thickness of the SEI (for the relationship of porosity and pore resistance or ionic resistance) [47].

Since a physically meaningful fitting in blocking conditions with R_p and R_{SEI} as free parameters could not be obtained, R_p was determined via a fit of the impedance data at OCV with R_{SEI} set to zero and R_{CT} set to infinity in Eq. (2). For the fits of the subsequent impedance spectra obtained during the formation, the previously fitted R_p was then assumed to be constant (in analogy to [44]). With this procedure, a resistance R_{SEI}^* can be obtained which represents the actual R_{SEI} in blocking conditions increased by ΔR to compensate the in simultaneously growing pore resistance. It should be mentioned that the compensation will also influence other fit parameters which are not in the focus of this work. Since the variation of R_p in blocking conditions is mainly caused by porosity reduction due to SEI formation and can be considered small compared to the increase in SEI resistance [18], it is still possible to qualitatively correlate a positive change in R_{SEI}^* between two PEIS measurements in Fig. 1 to ongoing SEI formation during the correlated potential interval.

3.2. Quality evaluation

An in-depth end-of-line (EOL) test was designed to assess multiple quality parameters after formation and degassing. First, a 72 h calendar aging phase at medium SOC (at 3.4 V) with hourly PEIS from 10 kHz to 1 Hz (10 points per decade in logarithmic spacing, 10 mV excitation amplitude, 3 average measures per frequency, activated drift correction) was applied to observe the cell behavior after formation. The specific cell condition was finally determined as part of a detailed EOL test by carrying out a C/3 discharge capacity determination, pulse testing in both charge and discharge directions (1C charge for 18 s, 1C discharge for 10 s) and further potentiostatic EIS measurements (identical setup) at SOC levels of 80%, 50% and 20%, as well as a C/20 pOCV in charge and discharge directions. The entire EOL characterization protocol used is shown in Table B.1 in the appendix for ease of reference.

To assess the lifetime of the cells, a cycle life test at a C-rate of 1 C for charging and discharging with a check-up every 50 cycles was performed. The check-up contained a charging and discharging cycle at C/3 to determine the capacity of the cell. Based on the measured capacity, EIS and DC-IR measurements were performed at 80% SOC, 50% SOC, and 20% SOC, similar to the EOL test. The complete testing protocol is shown in Table B.1 in the appendix. A high-precision cyclor of the type BCS-815 (Bio-Logic SAS, France) was used to perform the EOL and cycle life test of the cells, which were secured in the custom-made cell fixture. The temperature in the test chambers (KB400, BINDER GmbH, Germany; TempEvent T/340/40/3-S, Vötsch Industrietechnik GmbH, Germany) was kept at a constant temperature of (25.0 ± 0.2) °C throughout the entire test.

3.3. Cycle life prediction

For the cycle life prediction of the MLPs, a feature-based approach based on previous work was chosen [43]. Input features for the prediction models were extracted from the EOL test, and the first 50 cycles

from the cycle life testing. The complete feature list is provided in Table A.2 in the appendix. A feature selection is required to reduce the dimensionality and the risk of over-fitting since a high number of features are available in the data set [54]. Recursive feature elimination (RFE) was selected due to its capability to detect interactions between different features. The RFE applies a regression algorithm to identify the ranking of each feature according to their linear correlation [55]. Support vector regression (SVR) with cross-validation was used as the prediction model, and a radial basis function (RBF) kernel was applied due to its advantage with non-linear data sets. Furthermore, grid search was used for hyperparameter tuning. Detailed information regarding early cycle life prediction can be found in previous work [43] and detailed information on SVR in Joshi et al. [55].

4. Results and discussion

The aim of this work is to provide a novel approach to reduce the formation time based on operando gas evolution. To show that the gas evolution for NMC622/graphite cells was primarily influenced by the SEI formation and that the measurement setup was sensitive enough to detect the gassing, a connection between the gas evolution and SEI formation was conducted by employing SLPs. Subsequently, two formation strategies were derived for MLPs that aimed at reducing the overall formation time using gas evolution tracking only. The cell quality was ensured by an in-depth EOL and subsequent cycle life test. Finally, a machine learning approach for early cycle life prediction was utilized to accelerate the time-intensive quality assurance.

4.1. Relation of gas evolution and SEI formation

Seven SLPs were built and analyzed in the CEB using the step-wise SEI formation protocol to assess the relevant potential ranges for SEI formation and to concatenate the gas evolution. One exemplary result of the measured impedance spectra, model fits, and residues for a SLP with GWRE is depicted in Fig. A.3 in the appendix. Fig. 2a shows the results of the modified SEI resistance R_{SEI}^* from the PEIS measurement (cf. Section 3.1) and the according gas volume, measured in blocking condition after each potential step. The R_{SEI}^* built-up takes place at a similar potential of approx. 1.0 V vs. Li/Li⁺ as the gas evolution. Moreover, the magnitude of gas evolution also correlates well between 1.0 V vs. Li/Li⁺ and 0.6 V vs. Li/Li⁺. The gas evolution then converges at approx. 0.6 V vs. Li/Li⁺, whereas R_{SEI}^* continuous to increase until 0.4 V vs. Li/Li⁺. This indicates a further formation of the SEI after the primary gaseous reduction reactions. Afterward, R_{SEI}^* decreases before converging when fully charged. The decrease in R_{SEI}^* between $U_{CE} = 0.2$ V vs. Li/Li⁺ and 0.08 V vs. Li/Li⁺ could be attributed to structural changes in the SEI that occur at high cell voltages [5]. Fig. 2b shows the relevant cell voltages for SEI formation and gas evolution that can be derived from the three-electrode SLPs as well. Here, the peak for R_{SEI}^* can be located at approx. 3.25 V. Considering the overshooting of R_{SEI}^* , the gas evolution can be used as a meaningful indicator for the start and magnitude of SEI formation.

4.2. Optimization of formation protocol

The connection of the gas evolution with R_{SEI}^* allows to determine the state of the SEI formation by simply measuring the gas evolution. This approach is utilized in the following to create gassing-dependent formation protocols that aim to reduce the formation time while assuring a high-quality SEI. To analyze the operando gas evolution in MLPs, the CEB presented in Section 2.3 is applied during formation. Eight reference cells (Ref1–Ref8) were built to identify the potential ranges for SEI formation. A three-cycle C/10 reference protocol (cf. Table 2a) was used, which is frequently applied in the literature.

The formation results of the reference cells are shown in Fig. 3a. For all cells, a high similarity in the voltage profiles is present, which

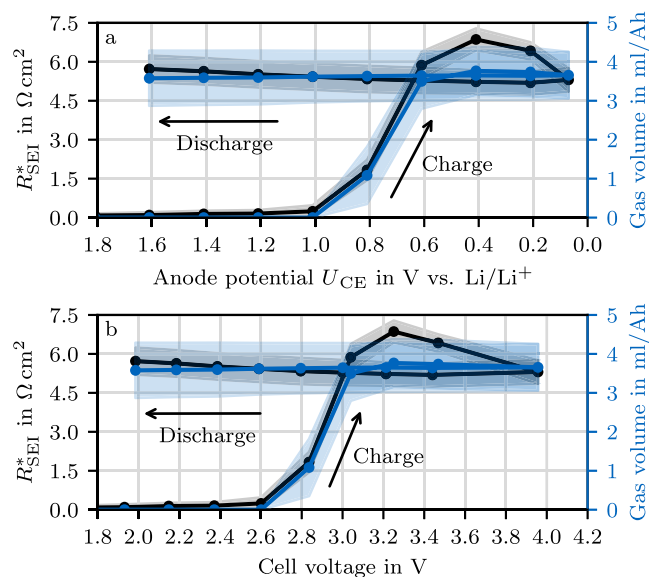


Fig. 2. Comparison between gas evolution (blue) and R_{SEI}^* built up (black) in the SLPs with GWRE during the formation procedure shown (a) against the minimal half cell potential of the prior (dis)charging step U_{CE} , and (b) against the full cell potential. The mean value and standard deviation of seven cells are depicted. The linear interpolation is for illustrative purposes only as well as the arrows, which indicate the charge and discharge directions from the step-wise formation protocol shown in Fig. 1.

Table 2

Formation procedures for the reference and derived current variation and voltage variation strategies.

(a) Reference formation procedure.			
State	Parameter	Termination	Repetitions
CC Charge	$I = C/10$	$U = 4.2\text{ V}$	3
CV Charge	$U = 4.2\text{ V}$	$I = C/20$	
CC Discharge	$I = C/10$	$U = 2.9\text{ V}$	
(b) Current variation formation procedure.			
State	Parameter	Termination	Repetitions
CC Charge	$I = C/10$	$U = 3.55\text{ V}$	–
CC Charge	$I = C/2$	$U = 4.2\text{ V}$	
CV Charge	$U = 4.2\text{ V}$	$I = C/20$	
CC Discharge	$I = C/2$	$U = 2.9\text{ V}$	
(c) Voltage variation formation procedure.			
State	Parameter	Termination	Repetitions
CC Charge	$I = C/10$	$U = 3.55\text{ V}$	–
CV Charge	$U = 3.55\text{ V}$	$I = C/20$	
CC Discharge	$I = C/2$	$U = 2.9\text{ V}$	

indicates a homogeneous charging behavior. The capacities in the last formation cycle deviated by less than 1%, resulting in a mean cell capacity of $(4.456 \pm 0.012) \text{ Ah}$. Fig. 3d shows the cell dilation that was measured using a contact distance sensor on the cell pressure plate. A maximum initial cell expansion of the reference cells of $(160 \pm 6) \mu\text{m}$ and an irreversible thickness increase of approx. $90 \mu\text{m}$ were measured in the first cycle. The thickness continued to increase over the subsequent second and third formation cycle. For all reference cells, a strong initial gas evolution was measured (cf. Fig. 3g) with the maximum reached in the first charging cycle. In the further formation, a continuous decrease in overall gas volume is present.

A detailed analysis of the first formation cycle is shown in Fig. 4. The gas volume peaks for each cell were detected at similar voltages ranging from 3.44 V to 3.47 V, as indicated by the black crosses in

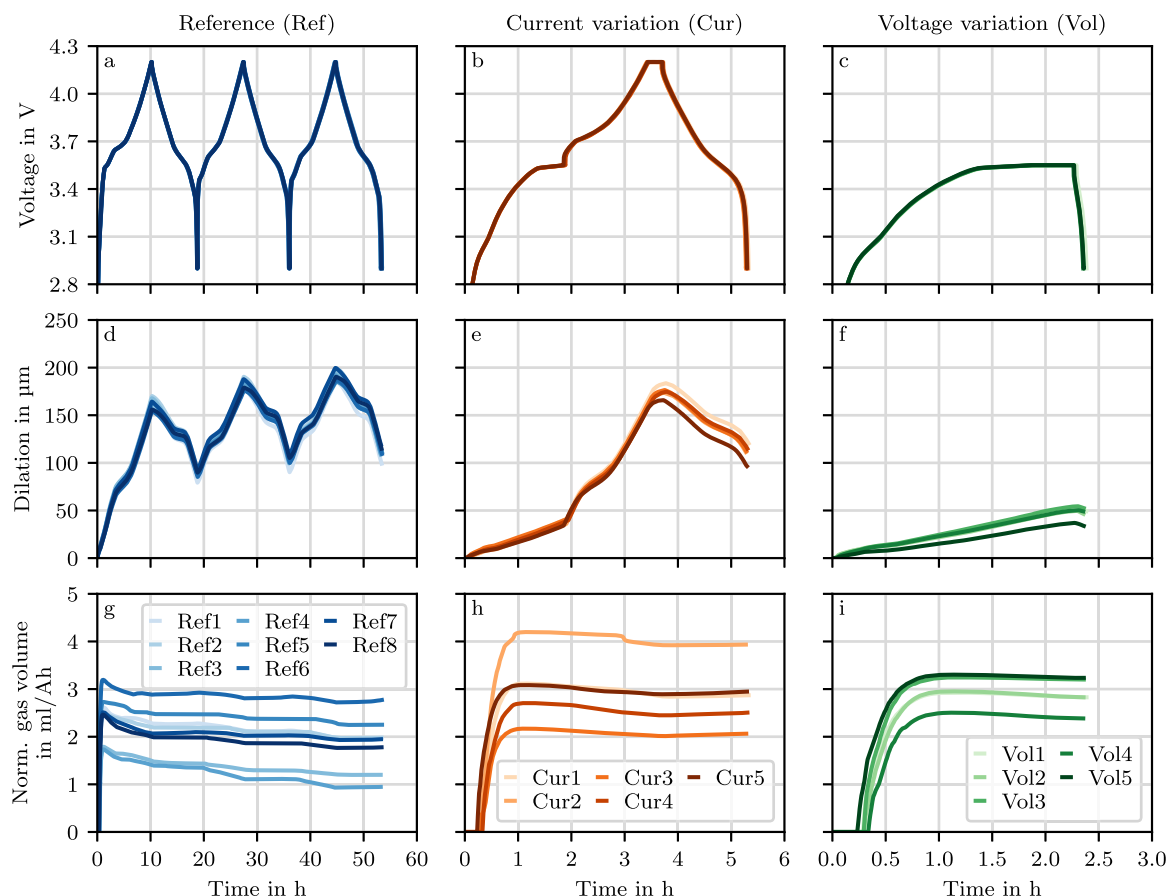


Fig. 3. Formation analysis of all cells using different procedures. Note that the abscissa are scaled differently for the reference, the current variation, and the voltage variation for better display. (a–c) Voltage course against formation time. (d–f) Cell dilation against formation time, measured with the tactile distance sensor in the cell expansion bracket. (g–i) Gas volume against formation time, determined by the displacement of the gas bag plate in the cell expansion bracket and normalized to the theoretical cell capacity. The conversion of the displacement to the gas volume was performed using the calibration measurement.

Fig. 4a. However, the magnitude differed in between 1.7 mL Ah^{-1} and 3.2 mL Ah^{-1} . In particular, two cells (Ref3 and Ref4) showed significantly lower maxima, which were caused by a slight misplacement of the dilation sensor. The sensors were probably placed not directly on the gas bag plate but slightly above, resulting in a measurement offset within the initial expansion of the gas bag. This assumption is supported by the similar, but slightly shifted, gas evolution course measured over the SOC, shown in **Fig. 4b**. Compared to the SLPs, the gas evolution peaked at a higher potential (cf. **Fig. 2**). This can be attributed to the continuous CC charging, since SEI formation also occurred during the CV steps and during discharging in the step-wise formation of the SLPs.

Fig. 4c shows the cell dilation against the cell voltage, revealing a sharp increase in dilation starting at approx. 3.54 V . This indicates that SEI formation starts prior to the graphite expansion resulting from lithium intercalation as reported by Lee et al. [19]. The typical expansion behavior of graphite is shown in **Fig. 4d**, exhibiting a clear plateau at medium SOC due to the final intercalation state of graphite (i.e., the transition from LiC_{12} to LiC_6 with small volume extension). During intercalation, fewer reduction reactions occur and predominantly structural changes are triggered due to the acquisition of inorganic components in the SEI [5]. Furthermore, reactions of the produced gas forming liquid or solid products have been reported, leading to a decrease in the absolute gas quantity [56]. Since the electrode expands during lithiation, gaseous products might get in the porous electrode structure, thus providing the possibility for further reactions of the gas and electrolyte. This effect causes a decrease in the absolute gas quantity and has also been reported by Aiken et al. and the authors [46,57]. In summary, degassing should ideally be performed

within or after the first formation cycle in order to prevent further (potentially detrimental) side reactions. From an economic perspective, time in the formation should also be kept as short as possible to reduce production costs [4]. This is because of high energy costs, space costs, and deprivation costs since the formation chambers are equipped with expensive safety features.

Based on the results of the reference cells, two fast formation strategies are derived. A starting current of $C/10$ is chosen in both variations to ensure a homogeneous formation of the SEI during the initial reduction potential range. The respective formation protocols of the reference and both variations are shown in **Table 2**. In the first variation (current variation), the current is increased from $C/10$ to $C/2$ upon reaching 3.55 V , which marks the point of strong dilation increase and end of gas generation. At the cut-off voltage of 4.2 V , a CV phase is added and the cell is subsequently discharged at a current of $C/2$ (cf. **Table 2b**). In the second variation (voltage variation), CC charging at $C/10$ is performed until 3.55 V is reached with a subsequent CV-phase (cf. **Table 2c**). The cell is immediately discharged afterward at a current of $C/2$. The discharging was performed to ensure a minimal safety hazard during degassing.

The results of the adapted formation strategies are shown in **Fig. 3**. In **Fig. 3b**, a voltage leap is visible at approx. 1.9 h , indicating the current increase from $C/10$ to $C/2$, and the accompanying overpotentials. Comparable to the references, high similarity in the voltage profiles is present, indicating homogeneous charging behavior over the approx. 5.3 h formation. The cell dilation, shown in **Fig. 3e**, showed an approx. $15 \mu\text{m}$ increased maximum cell dilation of $(175 \pm 7) \mu\text{m}$ compared to the references. The dilations after discharging were also higher due to the elevated C-rate of $C/2$ and the absence of a CV phase

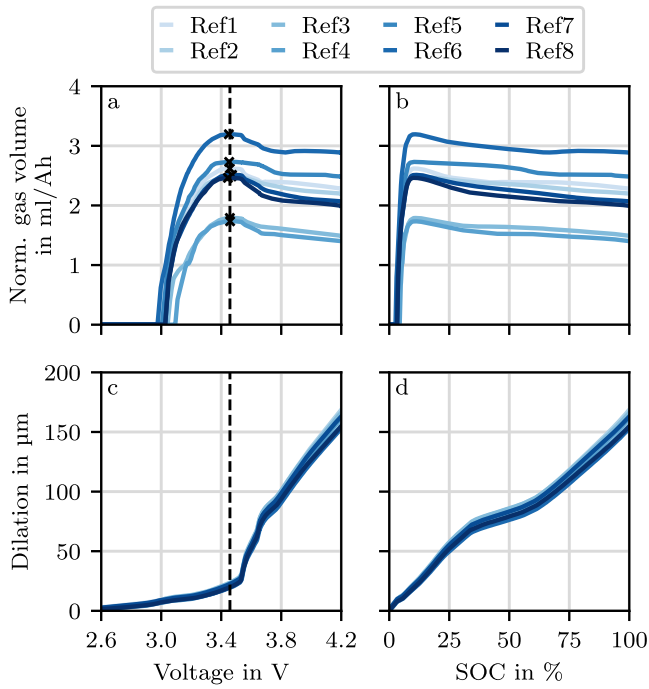


Fig. 4. First charging cycle analysis for the reference cells. (a) Gas volume against the voltage, normalized by the cell capacity. The black crosses mark the maxima of the gas volumes and the vertical black lines mark the mean voltage of the maxima. (b) Gas volume against the SOC, normalized by the cell capacity. (c, d) Cell dilation against voltage and SOC, respectively.

during discharging. This is again due to increased overpotentials when applying a higher C-rate. Fig. 3h shows the normalized gas volumes with a clear outlier (Cur2), which exhibits a maximum volume that is at least 1 mL Ah^{-1} above the other cells. This can either be explained by a measurement error, a deviation in the size of the gas bag, or side reactions due to contaminations. A check for possible contaminations, and thus a reduced cell quality, will be conducted in the subsequent section. Except for the outlier, all cells from the current variation exhibited similar gassing behavior to the reference cells.

Fig. 3c shows the voltage profile for the five cells of the voltage variation strategy. Again, a high similarity is visible, and a mean formation time of approx. 2.4 h. As expected, the cell dilation remained small as the major part of the intercalation stage starts at voltages above 3.55 V (cf. Fig. 3f). The dilation at the end of the formation is only slightly below the respective maximum due to the fast discharging at C/2. In Fig. 3i, a similar course of gas evolution is present, with a maximum normalized volume of $(3.0 \pm 0.3) \text{ mL Ah}^{-1}$. Due to the short formation, only a small decline in gas volume was detectable. Using the voltage variation strategy, the formation time could be decreased significantly to approx. 2.4 h, while assuring the generation of equivalent gas volumes during SEI formation. However, the SEI resistance examined in the SLP analysis showed a continuing variation upon reaching the end of the gas evolution period. This indicates a further restructuring or densification of the SEI that influences parameters like the SEI density, porosity, and permeability [5]. Nevertheless, no reduction reaction occur and reaching higher potentials might not be necessarily ensured during formation but can be shifted to a later stage in production or to the application. This increases the throughput of battery production and reduces production costs. A detailed cost analysis targeting the influence of the formation time on the investment costs for a gigafactory is presented in Heimes et al. [23]. For a 4 GWh production plant, investment costs of approx. 41.7 Mio. € per hour of formation were calculated. This highlights the significant cost lever

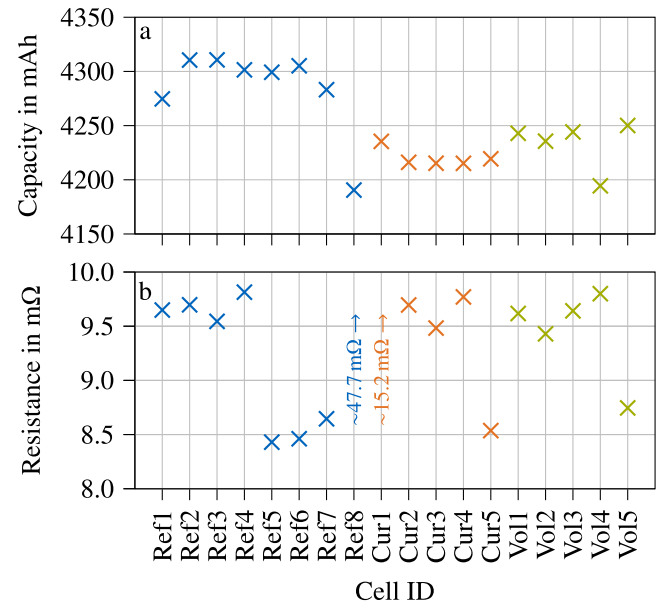


Fig. 5. (a) Measured C/3 discharge capacity after formation and (b) internal resistance (calculated as a 1C discharge 0.2 s DC-IR resistance at 80% SOC) of all cells in the EOL test. The outlier cells (Ref8 and Cur1) were not included in the calculation of the resistance statistics.

of reducing formation time during battery production. However, in-depth quality assurance is required to prove that the adapted formation strategies do not diminish the cell quality.

4.3. Quality assurance

In the following, the measurements of the EOL and cycle life test are evaluated and analyzed to quantify the quality of the tested cells and to assess the impact of the formation strategies. The respective testing procedures can be found in Section 3.2. Fig. 5a displays the variation of the measured C/3 discharge capacities over the 18 cells. A comparatively homogeneous distribution of capacities with at standard deviation $\sigma = 41.08 \text{ mAh}$ at a mean capacity $\mu = 4252.45 \text{ mAh}$ with a variation coefficient $\kappa = \sigma/\mu = 0.009$ can be observed.

However, the cells from both formation variations had slightly smaller capacities between 1% and 1.5% that might result from the adapted formation protocols or storage times. The analysis of the SLPs revealed an increase in SEI resistance at higher potentials. While this process is not producing gas, lithium ions can be consumed. Since the higher potential range was shortened for the current variation and completely neglected for the voltage variation, lithium is potentially consumed during the C/3 capacity check, resulting in a reduced discharge capacity. When evaluating the internal resistances at 80% SOC and 0.2 s evaluation time (Fig. 5b), a comparable picture of all tests emerges, although the cells Ref8 and Cur1 represent strong outliers with values up to 5 times the mean value of the remaining cells. These cells also show a similar trend for other evaluation times (e.g., 0.02 s or 1 s) as well as for the additionally measured SOC levels. Since the variation within the reference cells was greater than the variation to the optimized formation strategies, no influence of the formation strategy on the resistance was obtained.

The averaged C/20 pOCV curve of the charging and discharging direction of all cells is presented in Fig. 6a, while Fig. 6b depicts the corresponding DVA. The peaks of the differential voltage curves are associated with phases of the electrode materials and indicated in Fig. 6b based on literature [58–60]. Since all cells are pristine cells, the M-phase of the cathode is superimposed by the graphite stage 2 peak. When examining the DVA, slight differences in the characteristics

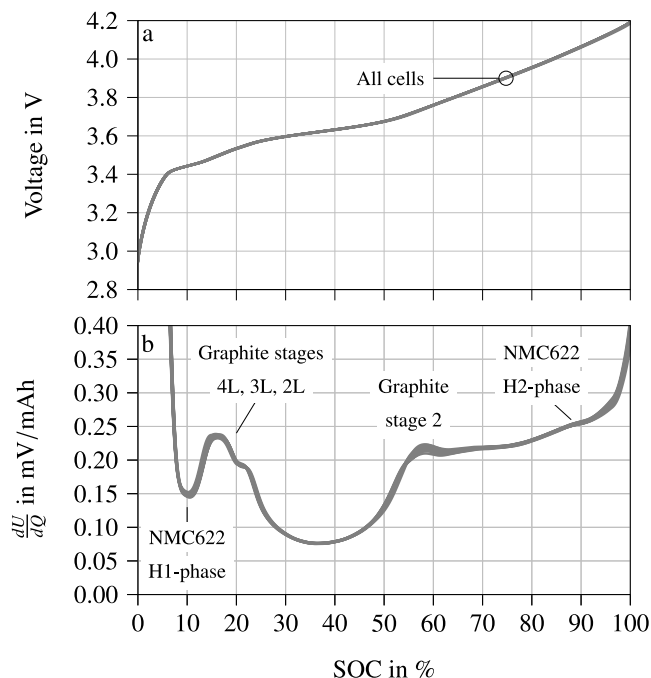


Fig. 6. (a) pOCV and (b) DVA investigations of all cells in the EOL test. In the DVA, the phases of the electrode materials are indicated according to literature.

of the peaks can be seen (e.g. graphite stage 2), which suggests minor variations in the material composition. No outliers are discernible when evaluating the pOCV data.

The impedance spectra measured in the EOL test at three SOC levels are shown in Fig. 7. In accordance with the DC-IR measurements, the cells Cur1 and Ref8 (the latter not shown in the plot) stand out as clear outliers. In both cases, the spectrum is strongly shifted in the positive $\text{Re}(Z)$ direction, which indicates an increased (ohmic) resistance. This may be due to improper assembly, e.g., due to the contacting of the current collector foils in the ultrasonic welding process, or a contacting issue in the measurement setup. Furthermore, two clusters are evident, which match the production batches of four cells each, ignoring the two outlier cells. In accordance with Fig. 5b, the first four reference cells (Ref1–Ref4) and batches 3 (Cur1–Cur4) and 4 (Vol1–Vol4) appear to be similar in their internal ohmic resistance values, as do batches 2 (Ref4–Ref8) and 5 (Cur5 & Vol5). Due to randomly assigned measurement channels, a varying channel calibration could be eliminated as the cause of these effects. Otherwise, the impedance characteristics, such as the shape of the distinctive semicircle and the local minima between the charge transfer region and the diffusion region, are consistent across all cells. Considering the differences between the Nyquist plots presented in Fig. 7a–c, the investigated cells reveal an SOC dependence of the impedance characteristics typical for lithium-ion batteries [61–64].

In summary, all measurement methods carried out in the EOL test indicate that homogeneous characteristics of the lithium-ion cells were achieved. Only the cells Ref8 and Cur1 should be regarded with caution in further evaluations due to the observed irregularities.

Finally, all cells were analyzed in a cycle life test at a C-rate of 1 C for charging and discharging, with a check-up test every 50 cycles. Fig. 8 depicts the mean relative discharge capacities at 1 C for all configurations and standard deviations until the end-of-life capacity is reached. End-of-life capacity is defined at 80% of the initial capacity, and the corresponding number of cycles up to this point is defined as the cycle life. The reference cells had a mean cycle life of 574 cycles with a relatively high standard deviation due to one cell (Ref2), which had a cycle life of 388 cycles only. Spikes every 50 cycles are

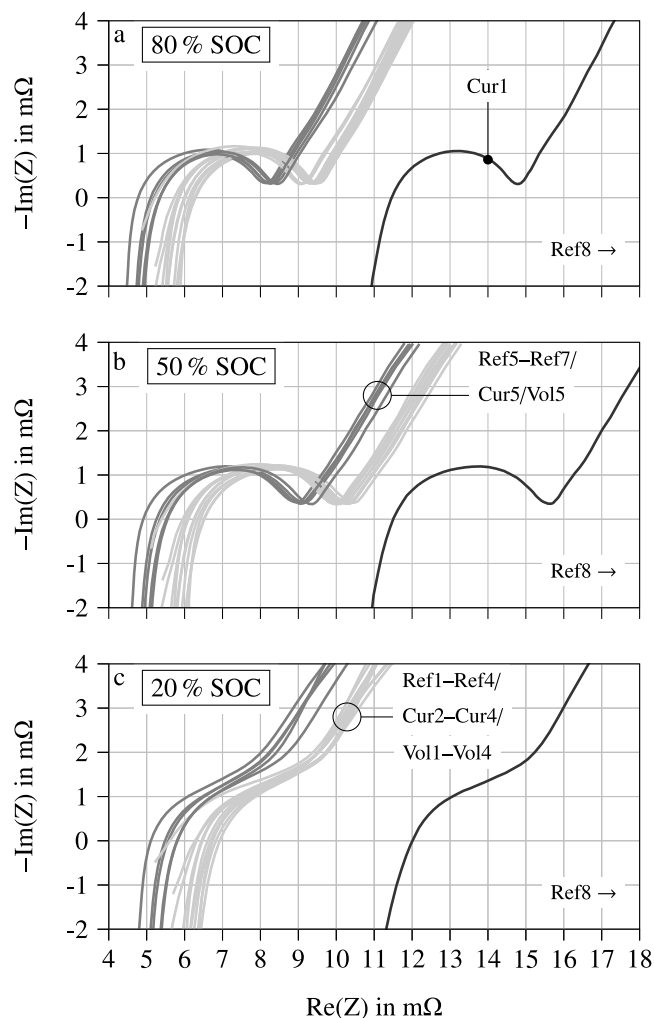


Fig. 7. Nyquist plots of all cells in the EOL test at (a) 80% SOC, (b) 50% SOC and (c) 20% SOC.

likely due to the reactivation of reversible lithium plating during the check-up [65].

The current variation strategy showed a higher mean capacity retention at the start of the cycle life testing, but a faster decrease when surpassing approx. 300 cycles. Consequently, a mean cycle life was 508 cycles with a standard deviation of 25 cycles. This is still within the standard deviation of the reference cell, however, the mean indicates an inferior cycling performance. This might be attributed to the more stressful formation procedure with a C-rate of C/2 and a potential deviation in the SEI formation. This either indicates that C/2 could be too high for the formation or that the switch to a higher C-rate happened too early. The spikes within the mean discharge capacities are caused by a single cell (Cur2), which was not conspicuous in the EOL test. The fluctuation therefore might be attributed to insufficient electrical contacting within the cell bracket.

For the voltage variation strategy, a higher mean cycle life of 612 cycles was achieved with a high standard deviation, similar to the reference cells. The initial capacity increase (cf. inset of Fig. 8) was even more profound than for the current variation strategy. This phenomenon is described for graphite anode in the literature and results from a high depth of discharge (DOD) [66]. The high DOD increases the probability of lithium-ion insertion within the graphene layers, thus providing a higher storage capacity that cannot be measured in the battery tester. Furthermore, reversibly bound lithium attributed to the adapted formation protocol could be released during the initial cycling.

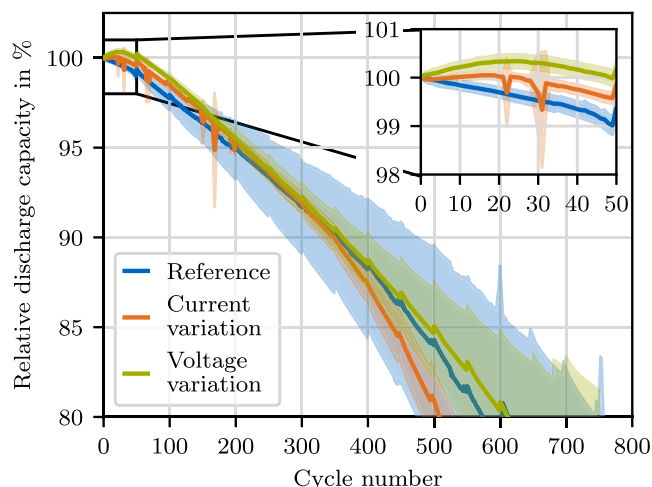


Fig. 8. Cycle life testing of the three configurations: reference, current variation, and voltage variation. The figure shows the mean relative discharge capacity and the respective standard deviations over sequential cycles at 1 C. The EOL is defined as the cycle number at which the capacity drops below 80% of the initial capacity. The inset displays the first 50 cycles that were examined in detail in this work and used to the later cycle life prediction.

Shorter formation protocols provide less time for parasitic reactions (e.g., with gaseous products) to occur that possibly cause irreversible lithium consumption [21]. Due to this suppressed parasitic reactions, a higher lithium reservoir is present which extends the cycle life. A shorter formation time might also result in a thinner SEI and thus to a lower internal resistance [67], which in turn leads to a higher cycle life. However, the course of the mean discharge capacity indicates a similar degradation for the reference and voltage variation. Consequently, the shorter formation protocol does not significantly influence the cycle life of the cells. In combination with the results from the EOL test, no negative effects of the voltage variation strategy on the cell quality were detected. The quality preservation enables the application of gassing-dependent formation protocols to reduce the formation time to the minimum required process time, which is needed for a complete degassing. From a production perspective, this equals the value-adding process time, since further charging does not improve the cell quality.

Comparing the current and voltage variation strategies revealed that applying a current of C/2 during formation results in a diminished cell quality. For the voltage variation strategy, a current of C/3 was applied in the subsequent aging and capacity check, resulting in a slightly improved capacity retention. This leads to the conclusion that a potential stabilization or restructuring of the SEI can be performed after formation. Furthermore, a maximum current of C/3 should be selected during formation to avoid deterioration of the cell quality. However, further studies targeting the influence of the aging process on SEI stabilization should be examined.

4.4. Cycle life prediction

The conventional step-wise optimization of formation protocols is time-intensive and costly since a complete cycle life testing has to be performed that requires several months of analysis. To reduce this effort and enable faster improvements, early cycle life prediction was performed. The prediction approach presented in Section 3.3 was applied and the eight reference cells, along with 16 similar cells from a previous production campaign, were used to train the SVR model. A minimum training error of (12.2 ± 1.0) cycles and a minimum validation error of (15.9 ± 4.0) cycles was achieved in the training. The results of the subsequent cycle life prediction of the two test groups (i.e., the cells from the current variation and voltage variation formation protocol)

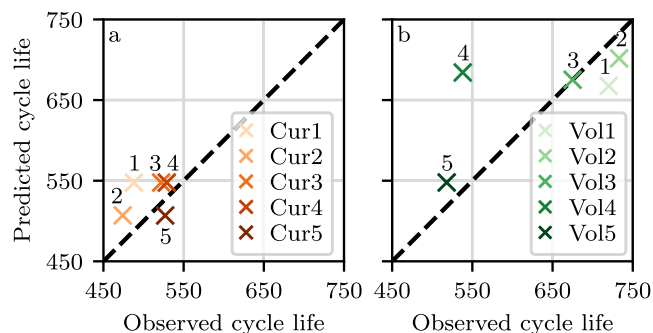


Fig. 9. Predicted cycle life against observed cycle life for the cells of (a) the current variation and (b) the voltage variation. The training was conducted using the reference cells and 16 similar NMC622/graphite cells from a previous production campaign. The diagonal dashed line displays the ideal prediction case.

are shown in Fig. 9. For the current variation (cf. Fig. 9a), a test error of 31 cycles was achieved which equaled a relative error of approx. 6.1% with respect to the mean cycle life. All cells were correctly predicted to have a cycle life of less than 550 cycles. Fig. 9b shows the prediction results for the voltage variation cells with a clear outlier in the top left corner (Vol4). Thus, a higher test error of 52 cycles was present, which equaled a relative error of approx. 8.6% with respect to the mean cycle life. Three cells (Vol1–Vol3) were correctly predicted to have a cycle life greater than 650 cycles, while one cell (Vol5) was predicted to have a cycle life below 550 cycles. The outlier can be explained by an accelerated degradation that started beyond 250 cycles. However, the cell Vol5 also showed an accelerated degradation but was predicted far more precisely. This may be attributed to a relative small number of training cells. The obtained prediction errors in both cases are comparable with a previous study [43], in which a 10.1% test error was achieved, and align closely with Severson et al. [33], who reported a 9.1% test error.

These findings show the great potential of using early cycle life prediction in battery testing since a clear divergence between both variations was evident in the prediction using 10% of cycling data only. The testing effort required to obtain an initial basis for decision-making is thus reduced from several months to one week, allowing faster adaptation and optimization of production processes. Nevertheless, the number of training cells was not sufficient to utilize the full potential of machine learning, and future studies should focus on scaling up these approaches to industrially relevant cell numbers.

5. Conclusion

This paper presents a novel approach for the efficient improvement of formation procedures using operando gas evolution analysis. First, the relation between gas evolution and SEI formation was analyzed using SLPs with GWRE inside a CEB. An anode potential controlled formation procedure was then applied to perform a step-wise (dis)charging of the SLPs, and to conduct EIS measurements in blocking conditions. This was done to determine the SEI resistance change from the impedance data by using an ECM. An initial strong gas evolution was detected at approx. 0.8 V vs. Li/Li⁺ that correlated strongly with the modified SEI resistance increase. The modified SEI resistance in blocking condition peaked at a prior anode half cell potential approx. 0.4 V vs. Li/Li⁺ and decreased afterward, which may be attributed to structural changes within the SEI at higher cell voltages. The analysis of 4 Ah MLPs showed that gas evolution occurred only during the first charging cycle until a voltage of approx. 3.46 V. Subsequently, two variations of the reference formation protocol were derived that had adaptations in the applied current (current variation) and voltage range (voltage variation). As a result, the formation time could be reduced from 53.3 h to 5.3 h for the current variation and to 2.4 h for the voltage variation. To

ensure that the cell quality was not diminished, a comprehensive EOL test was conducted that included a 72 h calendar aging, C/3 capacity determination as well as EIS and DCIR measurements at 80%, 50%, and 20% SOC. No significant deviations in the various quality parameters were detected in the EOL test, except for a slightly decreased cell capacity. The subsequent cycle life test revealed an accelerated mean discharge capacity decrease and reduced mean cycle life of approx. 12.5%, for the current variation strategy. However, the voltage variation showed a slightly increased mean cycle life and better capacity retention compared to the reference. The shorter formation protocol therefore does not diminish the cycle life of the cells and should be applied to reduce production costs. This leads to the conclusion that the voltage variation (Vol) is the preferred formation strategy to minimize the necessary formation time. Since cycle life testing is time-intensive and costly, a feature-based ML model was applied to predict the cycle life of the cells with adapted formation protocols. Based on features extracted from the EOL test and the first 50 testing cycles, a combined mean test error of 7.4% was achieved, indicating the great potential of data-driven models to accelerate cell development. In summary, the operando gas analysis offers great potential to determine time and cost-efficient formation strategies.

CRedit authorship contribution statement

Sandro Stock: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Jonas Böhm:** Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Manuel Ank:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis. **Philipp Rath:** Writing – review & editing, Investigation, Formal analysis, Data curation. **Markus Lienkamp:** Writing – review & editing, Supervision, Resources. **Rüdiger Daub:** Writing – review & editing, Supervision, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A

Calculation of the fit’s residuals $\Delta(\omega)$ with indices f or m standing for fitted or measured value in Table A.1:

$$\Delta(\omega) = \sqrt{\frac{[\operatorname{Re}(\underline{Z}_f) - \operatorname{Re}(\underline{Z}_m)]^2 + [\operatorname{Im}(\underline{Z}_f) - \operatorname{Im}(\underline{Z}_m)]^2}{\operatorname{Re}(\underline{Z}_m)^2 + \operatorname{Im}(\underline{Z}_m)^2}} \quad (\text{A.1})$$

Table A.1

Features extracted from the EOL and cycle life test. Q_{Ch} : Charge capacity; Q_{DCh} : Discharge capacity; ΔQ_{Ch} : Difference in charge capacity; ΔQ_{DCh} : Difference in discharge capacity; Q_{Loss} : Capacity loss; ΔQ_{Loss} : Difference in capacity loss.

ID	Feature
Features extracted from the end-of-line (EOL) test	
EOL_QCh1	Q_{Ch} first cycle
EOL_QCh2	Q_{Ch} second cycle
EOL_QCh2-1	ΔQ_{Ch} first and second cycle
EOL_QDCh1	Q_{DCh} first cycle
EOL_QDCh1	Q_{DCh} second cycle
EOL_QDCh2-1	ΔQ_{DCh} first and second cycle
EOL_dQCh1	Q_{Loss} first formation cycle
EOL_dQCh2	Q_{Loss} in second formation cycle
EOL_dQCh2-1	ΔQ_{Loss} first and second cycle
Single features extracted from cycle life testing (CLT)	
CLT_dQCh20-1	ΔQ_{Ch} first and 20th cycle
CLT_VarQCh20-1	Variance Q_{Ch} first 20 cycles
CLT_SkewQCh20-1	Skewness Q_{Ch} first 20 cycles
CLT_KurtQCh20-1	Kurtosis Q_{Ch} first 20 cycles
CLT_dQDCh20-1	ΔQ_{DCh} first and 20th cycle
CLT_VarQDCh20-1	Variance Q_{DCh} first 20 cycles
CLT_SkewQDCh20-1	Skewness Q_{DCh} first 20 cycles
CLT_KurtQDCh20-1	Kurtosis Q_{DCh} first 20 cycles
Multiple features extracted from cycle life testing (CLT)	
CLT_QCh(1–50)	Q_{Ch} cycle n
CLT_QDCh(1–50)	Q_{DCh} cycle n
CLT_tCVCh(1–50)	Length CV phase charge cycle n

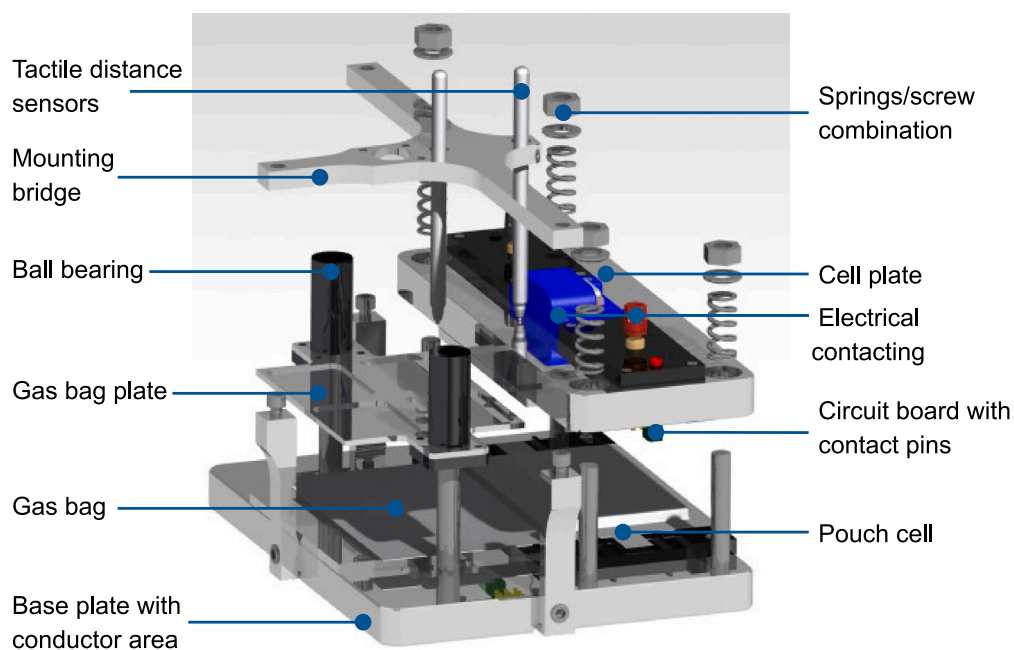


Fig. A.1. The depiction of the cell expansion bracket, employed for analyzing operando gas evolution and cell dilation through dual 1D dilatometry.
Source: Adapted from Stock et al. [46].

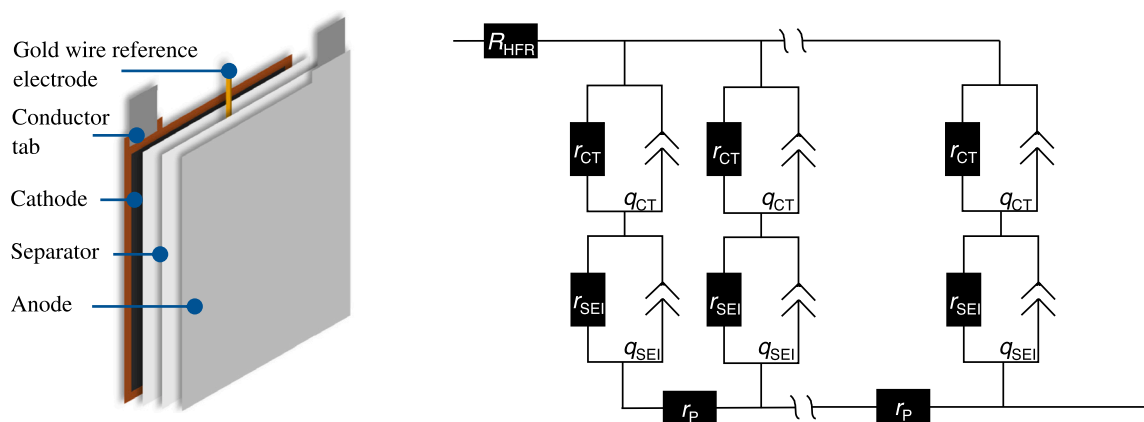


Fig. A.2. Left: Schematic structure of the single layer pouch cell with gold wire reference electrode. Right: Transmission line model for determining the SEI resistance.

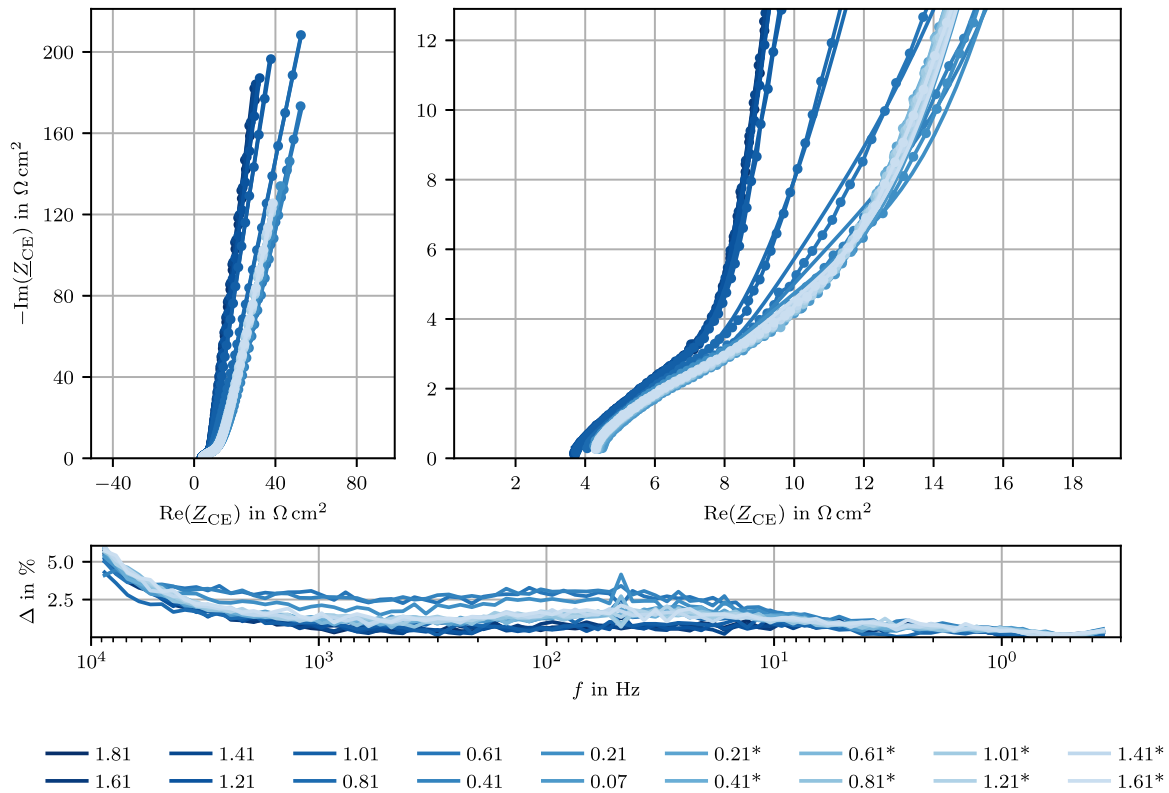


Fig. A.3. Impedance spectra (squares) and model fits (lines) of all impedance measurements during the step-wise formation for one SLP. The fit interval was chosen by the linear Kramers–Kronigmethod [68]. The subplot in the upper left-hand corner depicts the whole frequency area (10 kHz–300 mHz) while the subplot to its right shows the high- and mid-frequency area of the same spectra. Each spectrum is named after the minimum anode half-cell potential of the previous discharge step (cf. Fig. 1 value with a star in the second part of the protocol with rising minimum anode half-cell potential). The spectra were fitted to the model in Eq. (2). The residuals of the fits ($\Delta(\omega)$) were calculated using Eq. (A.1).

Appendix B

Table B.1

Test procedures for the EOL test (left) and the cycle life test (right). ΔT : Temperature change is less than 2 K in 1 h; ΔU : Voltage change is less than 2 mV in 10 min; EIS_{1Hz} : EIS from 10 kHz to 1 Hz with 10 points per decade in logarithmic spacing, 10 mV excitation amplitude, 3 average measures per frequency and activated drift correction; EIS_{10mHz} : EIS from 10 kHz to 0.01 Hz with 10 points per decade in logarithmic spacing, 10 mV excitation amplitude, 3 average measures per frequency and activated drift correction; Q_{Loss} : Capacity lost in discharge pulse.

EOL test				Cycle life test			
State	Parameter	Termination	Repetitions	State	Parameter	Termination	Repetitions / iterations
Aging				Initializing			
Pause	–	ΔT	72	Pause	–	ΔT	
CC Charge	I=C/3	U=3.4 V		CC Discharge	I=C/3	U=2.9 V	
CV Charge	U=3.4 V	I=C/20		Pause	–	t=30 min/ΔU	
Pause	–	t=1 h		CC Charge	I=C/3	U=4.2 V	
EIS	EIS _{1Hz}	–		CV Charge	U=4.2 V	I=C/20	
Capacity check				Check-up			
Pause	–	ΔT		Pause	–	t=30 min/ΔU	
CC Discharge	I=C/3	U=2.9 V		CC Charge	I=C/3	U=4.2 V	
Pause	–	t=30 min/ΔU		CV Charge	U=4.2 V	I=C/20	
CC Charge	I=C/3	U=4.2 V		Pause	–	t=30 min/ΔU	
CV Charge	U=4.2 V	I=C/20		CC Discharge	I=C/3	U=2.9 V	
Pause	–	t=30 min/ΔU		Pause	–	t=30 min/ΔU	
CC Discharge	I=C/3	U=2.9 V		CC Charge	I=C/3	U=4.2 V	
Pause	–	t=30 min/ΔU		CV Charge	U=4.2 V	I=C/20	
CC Charge	I=C/3	U=4.2 V		Pause	–	t=30 min/ΔU	
CV Charge	U=4.2 V	I=C/20		CC Discharge	I=C/3	U=2.9 V	
Pause	–	t=30 min/ΔU		Pause	–	t=30 min/ΔU	
CC Discharge	I=C/3	U=2.9 V		CC Charge	I=C/3	U=4.2 V	
Pause	–	t=30 min/ΔU		CV Charge	U=4.2 V	I=C/20	
CC Charge	I=C/3	U=4.2 V		Pause	–	t=30 min/ΔU	
CV Charge	U=4.2 V	I=C/20		CC Discharge	I=C/3	U=2.9 V	
Pause	–	t=30 min/ΔU		Pause	–	t=30 min/ΔU	1/20
CC Discharge	I=C/3	U=2.9 V		CC Charge	I=C/3	U=4.2 V	
Pause	–	t=30 min/ΔU		CV Charge	U=4.2 V	I=C/20	
CC Charge	I=C/3	U=4.2 V		Pause	–	t=30 min/ΔU	
CV Charge	U=4.2 V	I=C/20		EIS	EIS _{10mHz}	–	
Pause	–	t=30 min/ΔU		Pause	–	t=30 min/ΔU	
CC Discharge	I=C/3	U=2.9 V		CC Discharge	I=C/3	t=18 s	
Pause	–	t=30 min/ΔU		Pause	–	t=40 s	
CC Charge	I=C/3	U=4.2 V		CC Charge	I=C/3	Q=Q _{Loss}	
CV Charge	U=4.2 V	I=C/20		Pause	–	t=40 s	
Pause	–	t=30 min/ΔU		CC Charge	I=C/3	t=10 s	
CC Discharge	I=C/3	U=2.9 V		Pause	–	t=40 s	
Pause	–	t=30 min/ΔU		Pause	–	t=10 min	
CC Charge	I=C/3	U=4.2 V		CC Charge	I=C/3	U=4.2 V	
CV Charge	U=4.2 V	I=C/20		CV Charge	U=4.2 V	I=C/20	
Pause	–	t=30 min/ΔU		Pause	–	t=10 min	
CC Discharge	I=C/3	U=2.9 V		CC Discharge	I=C/3	Q=0.5 C	
Pause	–	t=30 min/ΔU		Pause	–	t=30 min/ΔU	
EIS	EIS _{10mHz}	–		EIS	EIS _{10mHz}	–	
Pause	–	t=30 min/ΔU		Pause	–	t=30 min/ΔU	
CC Discharge	I=C/3	t=18 s		CC Discharge	I=C/3	t=18 s	
Pause	–	t=40 s		Pause	–	t=40 s	
CC Charge	I=C/3	Q=Q _{Loss}		CC Charge	I=C/3	Q=Q _{Loss}	
Pause	–	t=40 s		Pause	–	t=40 s	
CC Charge	I=C/3	t=10 s		CC Charge	I=C/3	t=10 s	
Pause	–	t=40 s		Pause	–	t=40 s	
CC Charge	I=C/3	t=10 s		Pause	–	t=10 min	
Pause	–	t=40 s		CC Charge	I=C/3	U=4.2 V	
CC Charge	I=C/3	U=4.2 V		CV Charge	U=4.2 V	I=C/20	
CV Charge	U=4.2 V	I=C/20		Pause	–	t=10 min	
Pause	–	t=10 min		CC Discharge	I=C/3	Q=0.8 C	
CC Discharge	I=C/3	Q=0.8 C		Pause	–	t=30 min/ΔU	
Pause	–	t=30 min/ΔU		EIS	EIS _{10mHz}	–	
EIS	EIS _{10mHz}	–		Pause	–	t=30 min/ΔU	
Pause	–	t=30 min/ΔU		CC Discharge	I=C/3	t=18 s	
CC Discharge	I=C/3	t=18 s		Pause	–	t=40 s	
Pause	–	t=40 s		CC Charge	I=C/3	Q=Q _{Loss}	
CC Charge	I=C/3	Q=Q _{Loss}		Pause	–	t=40 s	
Pause	–	t=40 s		CC Charge	I=C/3	t=10 s	
CC Charge	I=C/3	t=10 s		Pause	–	t=40 s	
Pause	–	t=40 s		CC Charge	I=C/3	t=10 s	
CC Charge	I=C/3	t=10 s		Pause	–	t=40 s	
Pause	–	t=40 s		Pause	–	t=10 min	
CC Charge	I=C/3	t=10 s		CC Charge	I=C/3	U=4.2 V	
CV Charge	U=4.2 V	I=C/20		CV Charge	U=4.2 V	I=C/20	
Pause	–	t=10 min		Pause	–	t=10 min	
CC Discharge	I=C/3	Q=0.8 C		CC Discharge	I=C/3	Q=0.8 C	
Pause	–	t=30 min/ΔU		Pause	–	t=30 min/ΔU	
EIS	EIS _{10mHz}	–		EIS	EIS _{10mHz}	–	
Pause	–	t=30 min/ΔU		Pause	–	t=30 min/ΔU	
CC Discharge	I=C/3	t=18 s		CC Discharge	I=C/3	t=18 s	
Pause	–	t=40 s		Pause	–	t=40 s	
CC Charge	I=C/3	Q=Q _{Loss}		CC Charge	I=C/3	Q=Q _{Loss}	
Pause	–	t=40 s		Pause	–	t=40 s	
CC Charge	I=C/3	t=10 s		CC Charge	I=C/3	t=10 s	
Pause	–	t=40 s		Pause	–	t=40 s	
CC Charge	I=C/3	t=10 s		Pause	–	t=10 min	
Pause	–	t=40 s		CC Charge	I=C/3	U=4.2 V	
CC Charge	I=C/3	t=10 s		CV Charge	U=4.2 V	I=C/20	
CV Charge	U=4.2 V	I=C/20		Pause	–	t=10 min	
Pause	–	t=10 min		CC Discharge	I=C/3	Q=0.8 C	
CC Discharge	I=C/3	Q=0.8 C		Pause	–	t=30 min/ΔU	
Pause	–	t=30 min/ΔU		EIS	EIS _{10mHz}	–	
EIS	EIS _{10mHz}	–		Pause	–	t=30 min/ΔU	
Pause	–	t=30 min/ΔU		CC Discharge	I=C/3	t=18 s	
CC Discharge	I=C/3	t=18 s		Pause	–	t=40 s	
Pause	–	t=40 s		CC Charge	I=C/3	Q=Q _{Loss}	
CC Charge	I=C/3	Q=Q _{Loss}		Pause	–	t=40 s	
Pause	–	t=40 s		CC Charge	I=C/3	t=10 s	
CC Charge	I=C/3	t=10 s		Pause	–	t=40 s	
Pause	–	t=40 s		CC Charge	I=C/3	t=10 s	
CC Charge	I=C/3	t=10 s		Pause	–	t=40 s	
Pause	–	t=40 s		Pause	–	t=10 min	
CC Charge	I=C/3	t=10 s		CC Charge	I=C/3	U=4.2 V	
CV Charge	U=4.2 V	I=C/20		CV Charge	U=4.2 V	I=C/20	
Pause	–	t=10 min		Pause	–	t=10 min	
CC Discharge	I=C/3	Q=0.8 C		CC Discharge	I=C/3	Q=0.8 C	
Pause	–	t=30 min/ΔU		Pause	–	t=30 min/ΔU	
EIS	EIS _{10mHz}	–		EIS	EIS _{10mHz}	–	
Pause	–	t=30 min/ΔU		Pause	–	t=30 min/ΔU	
CC Discharge	I=C/3	t=18 s		CC Discharge	I=C/3	t=18 s	
Pause	–	t=40 s		Pause	–	t=40 s	
CC Charge	I=C/3	Q=Q _{Loss}		CC Charge	I=C/3	Q=Q _{Loss}	
Pause	–	t=40 s		Pause	–	t=40 s	
CC Charge	I=C/3	t=10 s		CC Charge	I=C/3	t=10 s	
Pause	–	t=40 s		Pause	–	t=40 s	
CC Charge	I=C/3	t=10 s		Pause	–	t=10 min	
Pause	–	t=40 s		CC Charge	I=C/3	U=4.2 V	
CC Charge	I=C/3	t=10 s		CV Charge	U=4.2 V	I=C/20	
CV Charge	U=4.2 V	I=C/20		Pause	–	t=10 min	
Pause	–	t=10 min		CC Discharge	I=C/3	Q=0.8 C	
CC Discharge	I=C/3	Q=0.8 C		Pause	–	t=30 min/ΔU	
Pause	–	t=30 min/ΔU		EIS	EIS _{10mHz}	–	
EIS	EIS _{10mHz}	–		Pause	–	t=30 min/ΔU	
Pause	–	t=30 min/ΔU		CC Discharge	I=C/3	t=18 s	
CC Discharge	I=C/3	t=18 s		Pause	–	t=40 s	
Pause	–	t=40 s		CC Charge	I=C/3	Q=Q _{Loss}	
CC Charge	I=C/3	Q=Q _{Loss}		Pause	–	t=40 s	
Pause	–	t=40 s		CC Charge	I=C/3	t=10 s	
CC Charge	I=C/3	t=10 s		Pause	–	t=40 s	
Pause	–	t=40 s		CC Charge	I=C/3	t=10 s	
CC Charge	I=C/3	t=10 s		Pause	–	t=40 s	
Pause	–	t=40 s		Pause	–	t=10 min	
CC Charge	I=C/3	t=10 s		CC Charge	I=C/3	U=4.2 V	
CV Charge	U=4.2 V	I=C/20		CV Charge	U=4.2 V	I=C/20	
Pause	–	t=10 min		Pause	–	t=10 min	
CC Discharge	I=C/3	Q=0.8 C		CC Discharge	I=C/3	Q=0.8 C	
Pause	–	t=30 min/ΔU		Pause	–	t=30 min/ΔU	
EIS	EIS _{10mHz}	–		EIS	EIS _{10mHz}	–	
Pause	–	t=30 min/ΔU		Pause	–	t=30 min/ΔU	
CC Discharge	I=C/3	t=18 s		CC Discharge	I=C/3	t=18 s	
Pause	–	t=40 s		Pause	–	t=40 s	
CC Charge	I=C/3	Q=Q _{Loss}		CC Charge	I=C/3	Q=Q _{Loss}	
Pause	–	t=40 s		Pause	–	t=40 s	
CC Charge	I=C/3	t=10 s		CC Charge	I=C/3	t=10 s	
Pause	–	t=40 s		Pause	–	t=40 s	
CC Charge	I=C/3	t=10 s		Pause	–	t=10 min	
Pause	–	t=40 s		CC Charge	I=C/3	U=4.2 V	
CC Charge	I=C/3	t=10 s		CV Charge	U=4.2 V	I=C/20	
CV Charge	U=4.2 V	I=C/20		Pause	–	t=10 min	
Pause	–	t=10 min		CC Discharge	I=C/3	Q=0.8 C	
CC Discharge	I=C/3	Q=0.8 C		Pause	–	t=30 min/ΔU	
Pause	–	t=30 min/ΔU		EIS	EIS _{10mHz}	–	
EIS	EIS _{10mHz}	–		Pause	–	t=30 min/ΔU	
Pause	–	t=30 min/ΔU		CC Discharge	I=C/3	t=18 s	
CC Discharge	I=C/3	t=18 s		Pause	–	t=40 s	
Pause	–	t=40 s		CC Charge	I=C/3	Q=Q _{Loss}	
CC Charge	I=C/3	Q=Q _{Loss}		Pause	–	t=40 s	
Pause	–	t=40 s		CC Charge	I=C/3	t=10 s	
CC Charge	I=C/3	t=10 s		Pause	–	t=40 s	
Pause	–	t=40 s		CC Charge	I=C/3	t=10 s	
CC Charge	I=C/3	t=10 s		Pause	–	t=40 s	
Pause	–	t=40 s		Pause	–	t=10 min	
CC Charge	I=C/3	t=10 s		CC Charge	I=C/3	U=4.2 V	
CV Charge	U=4.2 V	I=C/20		CV Charge	U=4.2 V	I=C/20	
Pause	–	t=10 min		Pause	–	t=10 min	
CC Discharge	I=C/3	Q=0.8 C		CC Discharge	I=C/3	Q=0.8 C	
Pause	–	t=30 min/ΔU		Pause	–	t=30 min/ΔU	
EIS	EIS _{10mHz}	–		EIS	EIS _{10mHz}	–	
Pause	–	t=30 min/ΔU		Pause	–	t=30 min/ΔU	
CC Discharge	I=C/3	t=18 s		CC Discharge	I=C/3	t=18 s	
Pause	–	t=40 s		Pause	–	t=40 s	
CC Charge	I=C/3	Q=Q _{Loss}		CC Charge	I=C/3	Q=Q _{Loss}	
Pause	–	t=40 s		Pause	–	t=40 s	
CC Charge	I=C/3	t=10 s		CC Charge	I=C/3	t=10 s	
Pause	–	t=40 s		Pause	–	t=40 s	
CC Charge	I=C/3	t=10 s		Pause	–	t=10 min	
Pause	–	t=40 s		CC Charge	I=C/3	U=4.2 V	
CC Charge	I=C/3	t=10 s		CV Charge	U=4.2 V	I=C/20	
CV Charge	U=4.2 V	I=C/20		Pause	–	t=10 min	
Pause	–	t=10 min		CC Discharge	I=C/3	Q=0.8 C	
CC Discharge	I=C/3	Q=0.8 C		Pause	–	t=30 min/ΔU	
Pause	–	t=30 min/ΔU		EIS	EIS _{10mHz}	–	
EIS	EIS _{10mHz}	–		Pause	–	t=30 min/ΔU	
Pause	–	t=30 min/ΔU		CC Discharge	I=C/3	t=18 s	
CC Discharge	I=C/3	t=18 s		Pause	–	t=40 s	
Pause	–	t=40 s		CC Charge	I=C/3	Q=Q _{Loss}	
CC Charge	I=C/3	Q=Q _{Loss}		Pause	–	t=40 s	
Pause	–	t=40 s		CC Charge	I=C/3	t=10 s	
CC Charge	I=C/3	t=10 s		Pause	–	t=40 s	
Pause	–	t=40 s		CC Charge	I=C/3	t=10 s	
CC Charge	I=C/3	t=10 s		Pause	–	t=40 s	
Pause	–	t=40 s		Pause	–	t=10 min	
CC Charge	I=C/3	t=10 s		CC Charge	I=C/3	U=4.2 V	
CV Charge	U=4.2 V	I=C/20		CV Charge	U=4.2 V	I=C/20	
Pause	–	t=10 min		Pause	–	t=10 min	
CC Discharge	I=C/3	Q=0.8 C		CC Discharge	I=C/3	Q=0.8 C	
Pause	–	t=30 min/ΔU		Pause	–	t=30 min/ΔU	
EIS	EIS _{10mHz}	–		EIS	EIS _{10mHz}	–	
Pause	–	t=30 min/ΔU		Pause	–	t=30 min/ΔU	
CC Discharge	I=C/3	t=18 s		CC Discharge	I=C/3	t=18 s	
Pause	–	t=40 s		Pause	–	t=40 s	
CC Charge	I=C/3	Q=Q _{Loss}		CC Charge	I=C/3	Q=Q _{Loss}	
Pause	–	t=40 s		Pause	–	t=40 s	
CC Charge	I=C/3	t=10 s		CC Charge	I=C/3	t=10 s	
Pause	–	t=40 s		Pause	–	t=40 s	
CC Charge	I=C/3	t=10 s		Pause	–	t=10 min	
Pause	–	t=40 s		CC Charge	I=C/3	U=4.2 V	
CC Charge	I=C/3	t=10 s		CV Charge	U=4.2 V	I=C/20	
CV Charge	U=4.2 V	I=C/20		Pause	–	t=10 min	
Pause	–	t=10 min		CC Discharge	I=C/3	Q=0.8 C	
CC Discharge	I=C/3	Q=0.8 C		Pause	–	t=30 min/ΔU	
Pause	–	t=30 min/ΔU		EIS	EIS _{10mHz}	–	
EIS	EIS _{10mHz}	–		Pause	–	t=30 min/ΔU	
Pause	–	t=30 min/ΔU		CC Discharge	I=C/3	t=18 s	
CC Discharge	I=C/3	t=18 s		Pause	–	t=40 s	
Pause	–	t=40 s		CC Charge	I=C/3	Q=Q _{Loss}	
CC Charge	I=C/3	Q=Q _{Loss}		Pause	–	t=40 s	
Pause	–	t=40 s		CC Charge	I=C/3	t=10 s	
CC Charge	I=C/3	t=10 s		Pause	–	t=40 s	
Pause	–	t=40 s		CC Charge	I=C/3	t=10 s	
CC Charge	I=C/3	t=10 s		Pause	–	t=40 s	
Pause	–	t=40 s		Pause	–	t=10 min	
CC Charge	I=C/3	t=10 s		CC Charge	I=C/3	U=4.2 V	
CV Charge	U=4.2 V	I=C/20		CV Charge	U=4.2 V	I=C/20	
Pause	–	t=10 min		Pause	–	t=10 min	
CC Discharge	I=C/3	Q=0.8 C		CC Discharge	I=C/3	Q=0.8 C	
Pause	–	t=30 min/ΔU		Pause	–	t=30 min/ΔU	
EIS	EIS _{10mHz}	–		EIS	EIS _{10mHz}	–	
Pause	–	t=30 min/ΔU		Pause	–	t=30 min/ΔU	
CC Discharge	I=C/3	t=18 s		CC Discharge	I=C/3	t=18 s	
Pause	–	t=40 s		Pause			

Table B.1 (continued).

EOL test				Cycle life test			
State	Parameter	Termination	Repetitions	State	Parameter	Termination	Repetitions / iterations
pOCV check				CC Charge	I=C/3	U=4.2 V	
Pause	–	t=10 min		CV Charge	U=4.2 V	I=C/20	
CC Charge	I=C/3	U=4.2 V		Pause	–	t=30 min/ Δ U	
CV Charge	U=4.2 V	I=C/20		CC Discharge	I=C/20	U=2.9 V	
Pause	–	t=30 min/ Δ U		Pause	–	t=30 min/ Δ U	
CC Discharge	I=C/20	U=2.9 V		CC Charge	I=C/20	U=4.2 V	
Pause	–	t=30 min/ Δ U		Pause	–	t=30 min/ Δ U	
CC Charge	I=C/20	U=4.2 V		CC Discharge	I=C/3	U=2.9 V	
Pause	–	t=30 min/ Δ U		CV Discharge	U=2.9 V	I=C/20	
CC Discharge	I=C/3	U=2.9 V		Pause	–	t=10 min	
CV Discharge	U=2.9 V	I=C/20		Cycling			
Pause	–	t=10 min		CC Charge	1C	U=4.2 V	
CC Charge	I=C/3	U=3.5 V		CV Charge	U=4.2 V	I=C/20	
				Pause	–	t=10 min	50/20
				CC Discharge	1C	U=2.9 V	
				Pause	–	t=10 min	

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