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Exploring the Impact of State of Charge and Aging on the Entropy Coefficient of Silicon–Carbon Anodes

Kevin Böhm ^{1,2} , Simon Zintel ¹ , Philipp Ganninger ¹ , Jonas Jäger ¹ , Torsten Markus ¹ and David Henriques ^{1,*}¹ Institute for Materials Science and Engineering (IMaSE), Mannheim University of Applied Sciences, Paul-Wittsack-Straße 10, 68163 Mannheim, Germany; k.boehm@doktoranden.hs-mannheim.de (K.B.)² Netzsch-Gerätebau GmbH, Wittelsbacherstraße 42, 95100 Selb, Germany

* Correspondence: d.henriques@hs-mannheim.de

Abstract: Due to its improved capacity compared to graphite, silicon is a promising candidate to handle the demands of high-energy batteries. With the introduction of new materials, further aspects of the battery system must be reconsidered. One of those aspects is the heat generation during the charging and discharging of a cell, which delivers important information for the development of cooling systems, the battery management system and the overall performance of the cell. Since the reversible heat presents an important contribution to the overall heat generation during cycling, the entropy coefficient is the main value that needs to be determined. This study evaluates the entropy coefficient of custom-produced 2032 coin half-cells with lithium counter electrodes, containing 45 wt% nanosilicon and 45 wt% carbon black. The potentiometric method, utilizing VR and self-discharge curves, produced reliable results, yielding entropy coefficient values between 95% SoC and 10% SoC during delithiation. These values of the entropy coefficient are consistently negative. Furthermore, ICA measurements identified two phase transitions during delithiation, with these transitions shifting to lower SoC as SoH decreases, impacting the slope of the entropy coefficient.

Keywords: entropy; silicon; anodes; heat generation; thermodynamics; incremental capacity analysis



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1. Introduction

The increase in electric vehicles has reinforced the demand for batteries with higher energy density [1]. Nowadays common graphite anodes are limited by a theoretical gravimetric capacity of 372 mAh g^{−1} (LiC₆) [2–4]. Silicon offers a theoretical gravimetric capacity of 4200 mAh g^{−1} (Li₂₂Si₅) [2,4,5], but it is reported that at room temperature the maximum gravimetric capacity is 3579 mAh g^{−1} (Li₁₅Si₄) [3,6–8]. However, this is still about 10 times the capacity of graphite. Moreover, silicon is non-toxic and available in large quantities. These parameters make silicon an attractive candidate for the upcoming generations of lithium-ion batteries.

The main issue for the commercialization of anodes with a high content of silicon is its volumetric expansion of over 280% [8–10] during lithiation, leading to degradation mechanisms like pulverization, delamination or the continuous formation of the solid electrolyte interphase (SEI). As a result, silicon anodes suffer from poor cycle stability and rapid capacity fades. Nevertheless, solutions have been proposed to minimize these negative effects [4,5,11], such as the mixture of nanosized silicon with graphite or carbon black. Liu et al. [10] reported that the critical size for silicon particles is about 150 nm, below which no cracking of the particles was observed.

The introduction of a new electrode material offers new possibilities for optimization of the overall battery system. The battery temperature turns out to be a parameter of particular importance, as it significantly influences the aging [8,12–15], efficiency [8,12,16,17] and capacity [12,14,16] of batteries. As a result, well fitted cooling and battery management systems allow handling of the generated heat. Therefore, the batteries can be operated at the optimal temperature.

The overall heat flux exhibited by a battery during charging and discharging $\dot{Q}_{tot}$ can be separated into four main heat sources [18].

$$\dot{Q}_{tot} = \dot{Q}_{irrev} + \dot{Q}_{rev} + \dot{Q}_{mix} + \dot{Q}_{par} \quad (1)$$

However, the heat flux caused by mixing $\dot{Q}_{mix}$ and parasitic side reactions $\dot{Q}_{par}$ are often neglected [16,19–21], leading to the simplified description of $\dot{Q}_{tot}$ with the irreversible heat flux $\dot{Q}_{irrev}$ and reversible heat flux $\dot{Q}_{rev}$.

$$\dot{Q}_{tot} \approx \dot{Q}_{irrev} + \dot{Q}_{rev} \quad (2)$$

The irreversible heat flux is caused by the internal ohmic resistance and polarization. The internal resistance is the sum of the charge transfer resistances towards the electrons and lithium ions. During cycling the electrode/electrolyte interface forms an activation energy barrier that needs to be overcome to start the chemical reactions. Moreover, due to the limitation of diffusion, a concentration gradient in the anode can form. These three mechanisms hinder the ion transport in the battery, which is reflected in the formation of an overpotential. The overpotential causes a decrease in the voltage U during charge or a decrease in U during discharge, while the current I is applied relative to the open circuit voltage U_{OCV} . As a result, the irreversible always exothermic heat flux $\dot{Q}_{irrev}$ can be calculated as follows [22]:

$$\dot{Q}_{irrev} = I(U - U_{OCV}) \quad (3)$$

Through the insertion of lithium, the structure of the silicon anode is changed, leading to a change in entropy ΔS , which generates a reversible heat flux $\dot{Q}_{rev}$. With the current I , the cell temperature T , the number of exchanged electrons n and the Faraday constant F , the mathematical description is as follows [23]:

$$\dot{Q}_{rev} = IT \frac{\Delta S}{nF} = IT \frac{dU_{OCV}}{dT} \quad (4)$$

A common way to calculate $\dot{Q}_{rev}$ is to determine the entropy coefficient $\frac{dU_{OCV}}{dT}$. The potentiometric method measures the change in the relaxation voltage dU_{OCV} over a change in temperature dT and has been demonstrated for cells with graphite anodes in several publications [13,24,25].

For graphite, it has been observed that the amount of intercalated lithium has a significant impact on the system's entropy coefficient [24–29], ranging from $250 \mu\text{V K}^{-1}$ to a minimum of $-100 \mu\text{V K}^{-1}$ during discharge [30]. The characteristic changes in the entropy coefficient can be correlated with the intercalation steps of graphite [31]. Due to this state of charge (SoC) dependency, thermal management and cooling systems must account for the additional reversible heat generation of graphite, particularly between 0% and 10% SoC during discharge [24]. In contrast, the entropy coefficient of other anode materials, such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$, shows little variation with SoC [32], leading to a simplification of the thermal management system.

Since the open circuit voltage (OCV) of a cell [33] is impacted by the state of health (SoH), the influence on the entropy of a battery can be assumed. This was demonstrated by Spitthof et al. [13] with pouch cells containing an LCO cathode and a graphite anode, where a change in the SoH led to a shift in entropy coefficient peaks regarding the SoC.

On the other hand, the information density of the entropy coefficient of anodes containing primarily silicon is very limited, since silicon is often mixed with graphite.

Mertin et al. [31] tested two different kinds of silicon–graphite half-cells. For both cells, the silicon content was given by the proportion of capacity, which was 70% for one cell and for 20% for the other. Independent of the silicon content the entropy was dominated by graphite.

Moreover, Wojtala et al. [34] determined the entropy coefficient of commercial cells containing about 10 wt% Si and 90 wt% graphite. They compared the impact of calendric aging at elevated temperatures and cyclic aging. Again the characteristic course of graphite

was identified, but the obtained flattening of the entropy coefficient was related to the aging mechanisms of the silicon.

So far Chevrier et al. [35] seem to be the only ones predicting the entropy mixing of a silicon anode containing 70 vol% silicon and 5 vol% carbon black. For lithiation, they qualitatively predicted one zero crossing for the predominantly negative coefficient.

The current research shows that a measurement of the entropy coefficient for a system without the influence of graphite has not been conducted. However, an increase in the use of silicon as an active material is expected [36]. To predict and simulate how this might impact the entropy coefficient of mixed anodes [31], it is necessary to determine the coefficient for silicon without the influence of graphite. By determining the entropy coefficient for silicon, it can also be forecasted whether additional heat peaks may arise with increasing silicon content, which would need to be considered by the thermal management system.

Consequently, the aim of our work is to determine the entropy coefficient of electrodes containing silicon as the only active material, thereby eliminating the influence of graphite. This allows for an accurate assessment of how phase transitions in silicon affect the entropy coefficient. Additionally, the tested cells undergo cyclic aging to evaluate the impact of the state of health (SoH) on the electrodes.

To the best of our knowledge, this study presents the first measurements of the entropy coefficient of silicon–carbon black anodes using a potentiometric method. We begin by detailing the preparation of three coin half-cells and the methodology applied in this study. The second section focuses on data analysis, including correction for the effects of voltage relaxation and self-discharge. Following this, the results are presented and discussed, highlighting the entropy coefficient as a function of both the state of charge (SoC) and SoH. To further investigate the influence of phase transitions, ICA measurements are conducted to determine the SoC positions of the phase transitions and correlate them with the behavior of the entropy coefficient.

Our results show that the entropy coefficient remains consistently negative within the SoC range of 95% to 10%, without the rapid changes seen in graphite. Moreover, cyclic aging leads to a reduction in the entropy coefficient, potentially due to initial side reactions such as the formation of the solid electrolyte interface (SEI). Finally, we demonstrate how phase transitions influence the behavior of the entropy coefficient.

2. Materials and Methods

2.1. Cell Preparation

In this study, self-made silicon–carbon anodes were examined. All raw materials for the anodes and half-cells were purchased from Nanografi Nano Technology (Ankara, Türkiye). The anodes contained nano-silicon (particle size: 100 nm) as the active material, carbon black (particle size: 20 nm) for the electrical conductivity and carboxymethylcellulose as the binder. The weight ratio of the three components was 45/45/10 wt%.

First, the materials were dry mixed together in a planetary centrifuge from NETZSCH (Selb, Germany). Afterward, completely desalinated water in a weight ratio of 1:5 (powders:water) was added. Once the second mixing was completed, the slurry was placed in an ultrasonic bath for 15 min and then mixed a third time in the centrifuge. The finished slurry was coated onto a 10 µm thick copper foil. The anodes were dried overnight in a vacuum drying oven from BINDER (Tuttlingen, Germany) at 70 °C.

From the dried sheets, three anodes with a diameter of 15 mm were cut. Three 2032 coin half-cells were assembled inside an argon-filled glovebox with O₂ and H₂O content below 0.5 ppm. The lithium counter electrode had a thickness of 0.5 mm and a diameter of 13 mm. As a separator, the double-layered FS-5P separator (Freudenberg Viledon FS 2226E + Lydall Solupor 5P09B), purchased from EL-CELL (Hamburg, Germany), was used. The polyethylene side faced the lithium; 100 µL of electrolyte for silicon anodes (MPGX-22-483_1) from E-LYTE Innovations (Kaiserslautern, Germany) was used.

2.2. Formation

Before the formation, an OCV measurement of 1 h was conducted. Then, the assembled coin cells were cycled three times at 25 °C with a constant current (CC) of 0.2 mA, which corresponds to a C-rate of about 0.05 C (or 0.05 h^{−1}). The voltage limits were set to 1 V as the upper limit and 0.06 V as the lower limit. The lower limit indicates the highest lithiated state of the anode. At both voltage limits, a constant voltage (CV) phase was applied with a cutoff current of 0.05 mA. After each charging and discharging step, an OCV of 30 min was conducted.

The capacities of the cells (Table 1) were determined during the last delithiation of the formation.

Table 1. Measured capacities during the last delithiation of formation from the examined cells.

Cells	Q ₀ in mAh
Cell 1	4.47
Cell 2	4.44
Cell 3	4.42

2.3. Potentiometry

After the formation, the cells were placed inside a climate chamber from Memmert (Schwabach, Germany). For charging and discharging the cells were put into a universal battery holder from Gamry Instruments (Warminster, PA, USA) and connected to a VMP-300 potentiostat from BioLogic (Seyssinet-Pariset, France).

To determine the entropy coefficient, the potentiometric method was chosen, as it has been successfully demonstrated in several studies on graphite [13,24,25,37] and does not require specialized equipment, unlike calorimetric methods [38,39].

For this purpose, the climate chamber was heated to 40 °C. Then, the cells were lithiated with 0.1 C, following a CV phase with a cutoff current of 0.01 mA. When 0.06 V was reached, the potentiostat switched to CV with a cut-off current of 0.01 mA. After the lithiation was finished, the cell was relaxed for 12 h. Next, the temperature program was initiated. The temperature of the climate chamber was reduced for 10 min at a cooling rate of 0.5 K min^{−1}, resulting in a temperature reduction of 5 K. Then the temperature was held constant for 2 h. The cooling and constant temperature steps were repeated until the temperature of the climate chamber reached 10 °C. When the measurement of the OCV at 10 °C was finished, the climate chamber was heated to 40 °C with 0.5 K min^{−1}.

Subsequently, the cell was delithiated with a constant current of 0.05 C for 1 h and relaxed for 12 h. The delithiation and temperature programs were repeated until the cell voltage surpassed the upper voltage limit of 1 V; the temperature program was repeated one last time. Figure 1 shows an excerpt from the measurement program for a single SoC step.

2.4. Incremental Capacity Analysis

The incremental capacity analysis (ICA) is a method to visualize voltage plateaus of a phase transition during lithiation or delithiation [40,41]. This technique enables the identification of the specific positions of phase transitions as a function of the SoC, which can then be compared to variations in the entropy coefficient. A constant current of 0.05 C is applied for lithiation and delithiation. For the visualization, the mathematical description of the ICA curve is the ratio of the increments of charge Q and the cell voltage U [40].

$$\frac{dQ}{dU} \approx \frac{\Delta Q}{\Delta U} \quad (5)$$

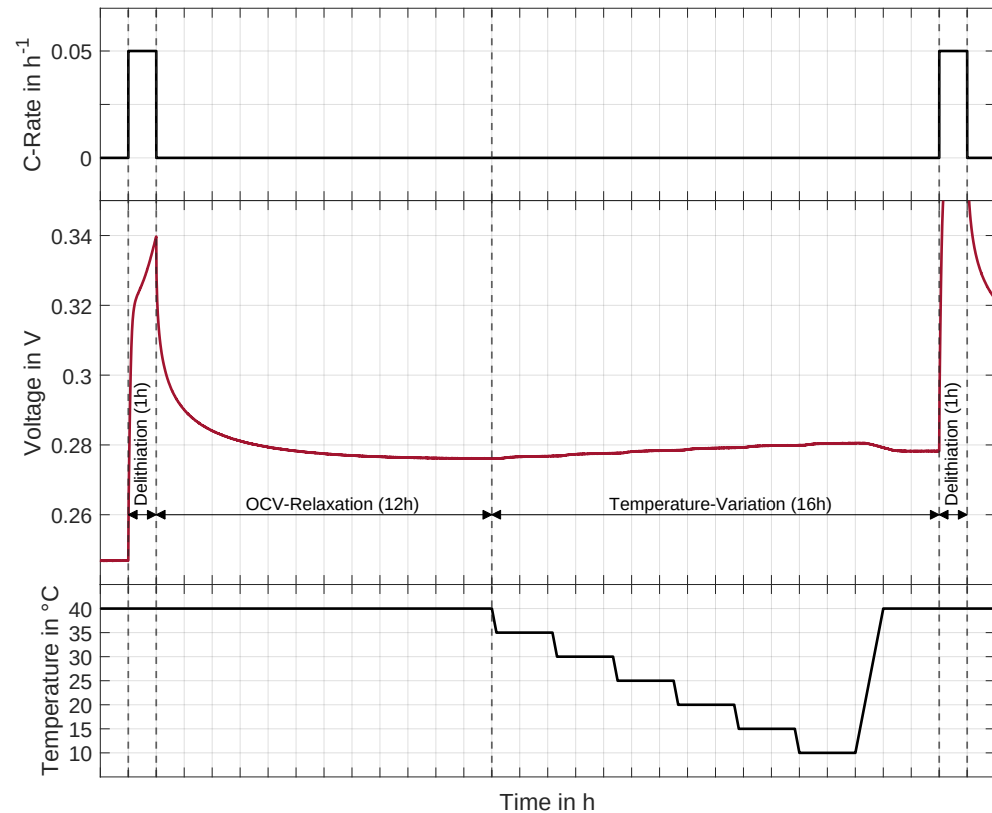


Figure 1. One step of the potentiometric measurement, starting with a delithiation pulse followed by the OCV relaxation. When 12 h had passed, the temperature variation for the determination of the entropy coefficient starts. The red line represents the cell's voltage response to the current pulses and temperature changes, shown by the black lines.

2.5. Cyclic Aging and Capacity Check

For cyclic aging, all three cells were charged and discharged 25 times with a constant current of 2.73 mA. This corresponds to an initial C-Rate of 1.63 ± 0.01 C. To determine SoH, before starting the next potentiometric measurements, a CC charge and discharge was conducted with a current of 0.2 mA. Like the formation, at the upper and lower voltage limit, there were CV phases with a cutoff current of 0.05 mA. The SoHs of the cells were calculated via the initial capacity Q_0 and the discharge capacity Q_{dis} of the current check-up.

$$SoH = \frac{Q_{dis}}{Q_0} \cdot 100\% \quad (6)$$

The determined capacities and calculated SoHs are presented in Table 2. The capacity values were used to calculate the currents for the entropy measurement.

Table 2. Determined capacities and SoHs before the potentiometric measurement.

Cells	Q_0 in mAh Initial	Q_{dis} in mAh Checkup 1	Q_{dis} in mAh Checkup 2
Cell 1	4.47	3.50	3.03
Cell 2	4.44	3.60	3.22
Cell 3	4.42	3.58	3.18
SoH	100%	$80.7 \pm 2.3\%$	$71.0 \pm 2.6\%$

2.6. Methodological Approach: Visualizing the Measurement Process

For clarity, Figure 2 illustrates the sequence of the previously described measurements. After formation, a loop comprising potentiometry, ICA, cyclic aging, and a capacity check is repeated three times. The third loop concludes with the ICA step.

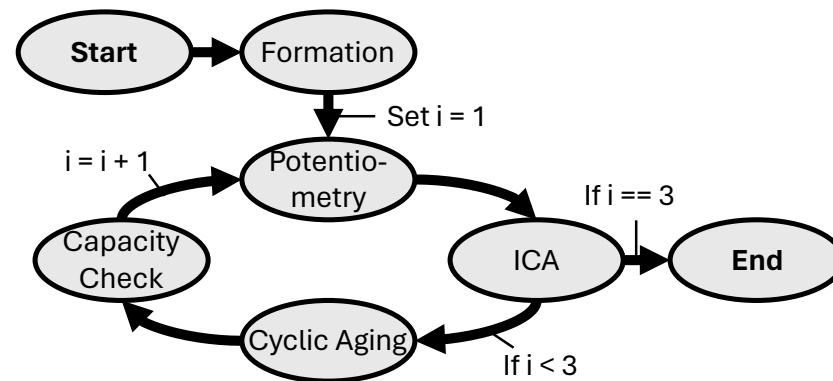


Figure 2. Schematic representation of the measurement process, showing a loop comprising potentiometry, ICA, cyclic aging, and capacity check, repeated three times. The third loop concludes with the ICA step.

3. Data Analysis

The analysis of the data previously obtained by potentiometry must consider different mechanisms influencing the voltage data used to determine the entropy coefficient. Here, specifically, voltage relaxation (VR) was examined further.

Since the entropy coefficient is defined as the voltage response to the variation in temperature, all other influencing factors, including VR, need to be eliminated before determining the entropy coefficient. To facilitate their elimination from the data, the influence of these mechanisms needs to be quantified.

3.1. Voltage Relaxation

VR is shown as a red curve in Figure 3 and describes the change in voltage towards the steady state open circuit voltage (SS-OCV) after a current is interrupted and the initial drop in voltage, caused by internal resistance (IR), has occurred. In this process, the voltage changes in the direction opposite the preceding voltage change by charge or discharge (shown in blue). The change in voltage is caused by the gradient of lithium ions present in the electrode as a result of charging or discharging, which leads to the movement of lithium ions toward homogenization when the current is interrupted. Since the voltage of the cell is determined at the surface layer of the electrodes, the redistribution of lithium ions affects the cell voltage.

Theuerkauf et al. [42] use a theoretical approach by predicting the VR curve using an equivalent circuit model. This assumes that all the data necessary to predict the VR curve are present in the voltage data preceding the voltage response to temperature variation. The equivalent circuit used in this approach is shown in Figure 4 and described by Equation (7).

$$U_{OCV}(t) = U_s + \sum_{i=1}^n U_{RC,i} \cdot (1 - e^{-\frac{t}{\tau_i}}) \quad (7)$$

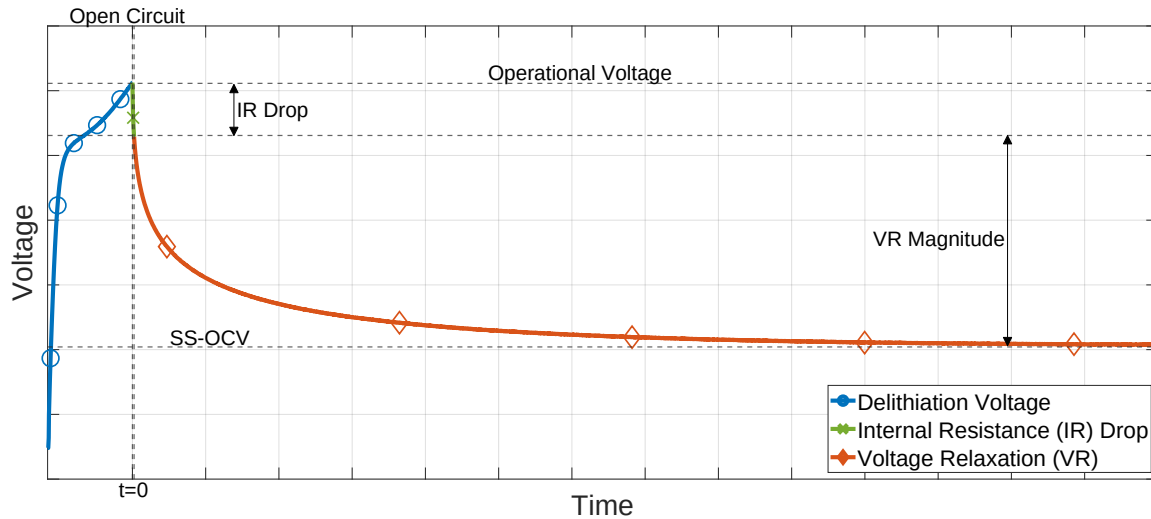


Figure 3. The typical shape of voltage relaxation (VR) of a cell after an initial current pulse. First, the immediate internal resistance (IR) drop is observable. Afterward, the decline of the voltage reduces until it reaches the steady state open circuit voltage (SS-OCV) (cf. [42]).

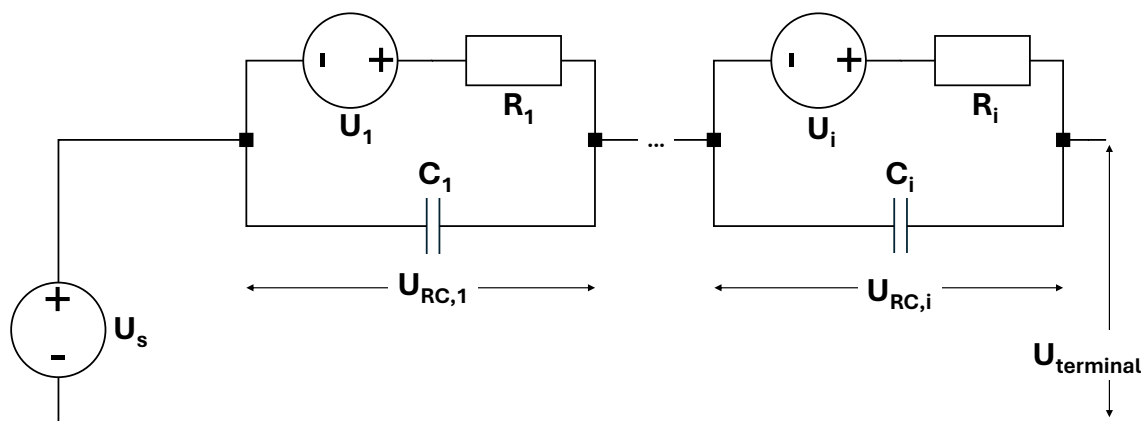


Figure 4. Equivalent circuit model for prediction of voltage relaxation according to [42].

Here, U_s describes the voltage at the beginning of VR after the IR drop. The term $U_{RC,i} \cdot (1 - e^{-\frac{t}{\tau_i}})$ describes the voltage drop resulting from each RC pair, and these contributions are summed over the number of pairs used n . Equation (7) is solved by iteration of the coefficients τ_i and $U_{RC,i}$. Corresponding to Theuerkauf et al. [42] the Levenberg–Marquardt algorithm was selected to solve the equation and produce a curve fit in an accurate and time-efficient manner. To balance computational effort and accuracy, the number of used RC elements was set to three. The initial value of each $U_{RC,i}$ was set to represent half of U_s and the time constant τ_i was given the initial value of 500 s, 5000 s and 50,000 s, for the first, second and third term, respectively. Additionally, $t = 0$ is determined to occur as soon as the ohmic polarization and the corresponding IR drop have been completed, leading to the exclusion of the first six data points or the first minute of data after the current is interrupted; 20 to 30 iterations of the Levenberg–Marquardt algorithm resulted in a coefficient of determination of ~ 1 (>0.9999) and a measurement uncertainty of 0.1 mV to 0.8 mV. Thereby, high accuracy and low computational effort were achieved.

3.2. Voltage Increase

Additionally, an increase in voltage during the temperature variation was observed, which cannot be explained by VR.

Under the assumption that solely the temperature variation produces the voltage change relevant for the determination of the entropy coefficient, equal temperatures must

result in equal voltage. Yet even after a theoretical subtraction of the modeled VR curve the 40 °C areas did not show equal voltages, leading to the assumption of more mechanisms being present.

House et al. [9] attribute their change in voltage, although only present in lithiation as opposed to delithiation, to parasitic reactions. Additionally, these parasitic reactions are more pronounced at low voltages, in accordance with the data presented by Sethuraman et al. [43].

This possibility is further explained by the renewal of the SEI. In this scenario, the temperature variation induces mechanical stress, leading to local cracking and subsequent renewal of the SEI. This process consumes lithium previously bound in the electrode, therefore, changing the voltage.

Irrespective of the specific mechanisms at play, a straight line between singular, corresponding voltage data points at each 40 °C area can be assumed to characterize the correlation. This assumption of a linear correlation is supported by the linear appearance of the voltage plateaus for each temperature. In addition, the linear correlation corresponds to the correction used by House et al. [9]. The straight line and the modeled VR curve determined in the aforementioned step were used to project the data onto the modeled VR curve. This process is shown in Figure 5.

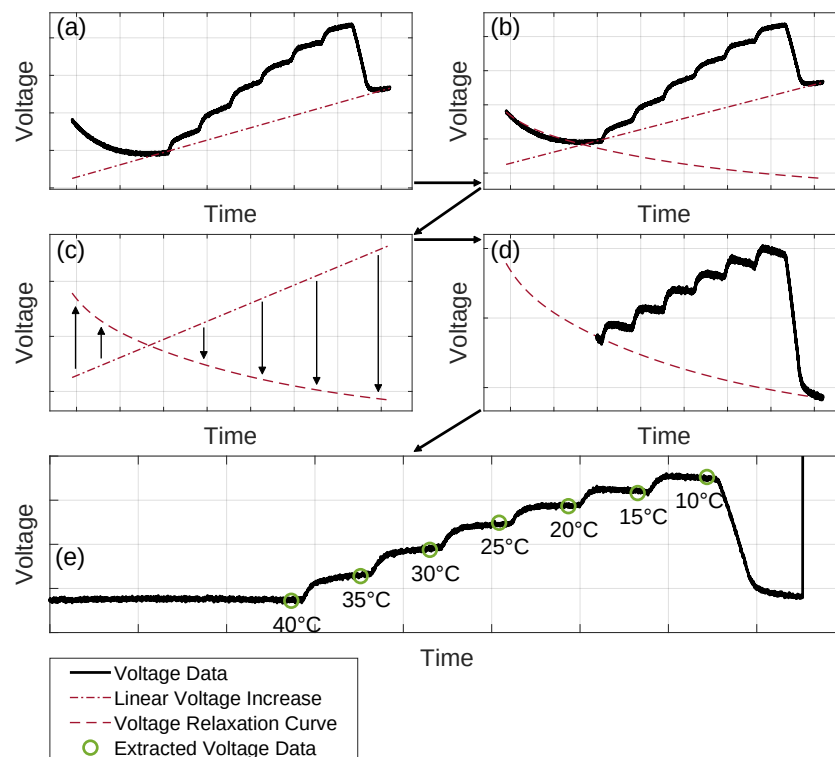


Figure 5. Presentation of the steps conducted for the data analysis. The sequence of steps is indicated by the black arrows. (a) Linear Fit through the measurement points at 40 °C used as a new baseline. (b) Calculation of the voltage relaxation (VR) via the equivalent circuit model (Figure 4). (c) Transformation of the linear baseline to the calculated VR leads to (d) a projection of the measurement data on the VR. (e) Through subtraction of the VR from the projection in (d) the final form of the measurement data is achieved. In (e) the voltage-points for the entropy coefficient are determined.

In the first steps, visible in Figure 5a,b, the linear increase in voltage, as well as the VR curve are determined. Figure 5c depicts the process of projecting the linear increase in voltage onto the modeled VR curve. The resulting voltage data, identically projected onto the VR curve, is seen in Figure 5d. The modeled VR curve is then subtracted from the projected data. The resulting voltage data, visible in Figure 5e, are now usable in the general determination of the entropy coefficient.

3.3. Determining the Entropy Coefficient

To determine the entropy coefficient, voltage data were extracted for each temperature and subsequently plotted against the corresponding temperatures, as seen in Figure 5e. Linear regression was used on these data points. The slope of the line is equal to the entropy coefficient, as shown in Figure 6. This process was repeated for all measured SoC, resulting in an entropy coefficient profile, plotted over SoC.

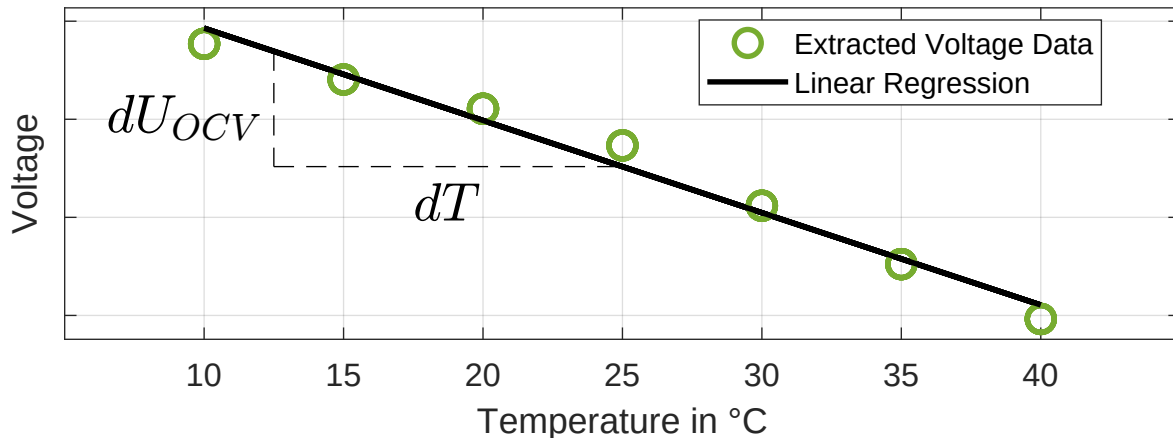


Figure 6. Linear fit for the determination of the entropy coefficient.

4. Results and Discussion

4.1. Entropy Coefficient

The entropy coefficient for all three cells was determined at three different SoH (Table 2). Figure 7 shows the course of the entropy coefficient depending on the SoC between 10% and 95% SoC. Due to poor linear fits of the voltage values ($R^2 < 0.8$) (Figure 6) the values of the entropy coefficient above 95% SoC and below 10% SoC are uncertain.

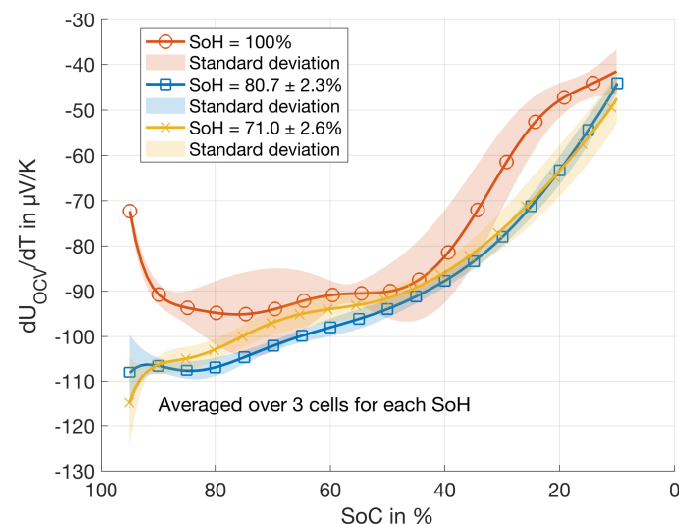


Figure 7. Curve fits of the entropy coefficient with confidence intervals for the delithiation at an SoH of 100%, $80.7 \pm 2.3\%$ and $71.0 \pm 2.6\%$

As can be seen in Figure 8, which shows the voltage profiles of cell 2 during delithiation, the areas of poor linear fit correspond to the regions of significant voltage change. In these regions, steep VR curves were obtained, which at the time of the temperature program had not yet flattened sufficiently to allow for a proper fit of the VR curve and self-discharge. The poor fit of the voltage response, in turn, leads to a non-linear distribution of the voltage

responses with respect to the temperature change. Therefore, as a possible solution, the relaxation time before the temperature program might be increased for these SoCs.

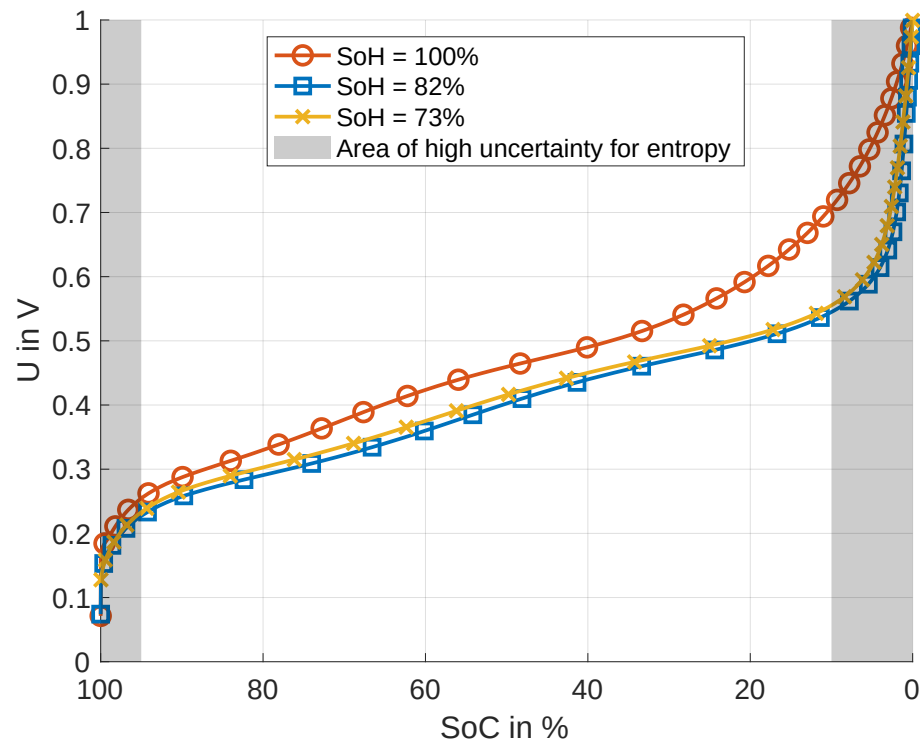


Figure 8. Impact of the SoH on the cell voltage during delithiation of cell 2. The grey area of high uncertainty for the entropy coefficient is displayed. In these areas, the change in voltage is the greatest. Between 100% and 82% the voltage during the whole delithiation process decreases.

Consequently, the entropy coefficient was evaluated between 95% SoC and 10% SoC (Figure 7), where sufficient fits ($R^2 > 0.8$) were achieved. Data outside this range are excluded from further evaluation and are not included in the following discussion.

The entropy coefficient at 100% SoH shows a rapid decrease from about $\sim -70 \mu\text{V K}^{-1}$ at 95% SoC to $\sim -95 \mu\text{V K}^{-1}$ at $\sim 90\%$ SoC. Afterward, the entropy coefficient remains relatively constant with a value of $\sim -95 \mu\text{V K}^{-1}$ until it reaches an SoC of $\sim 45\%$, followed by a steady increase to $\sim -40 \mu\text{V K}^{-1}$ at $\sim 10\%$ SoC.

In comparison, the aged cells show an initial increase between 95% SoC and $\sim 90\%$ SoC. With the further decrease in SoC, a constant increase in the entropy coefficient is observed, starting with $\sim -105 \mu\text{V K}^{-1}$ at 90% SoC. The slope increases from $\sim 30\%$ SoC until it reaches a value of $\sim -45 \mu\text{V K}^{-1}$ at 10% SoC.

When comparing the entropy coefficient at approximately 80% SoH and 71% SoH with that at 100% SoH, a consistent reduction in the coefficient is observed. However, the distinction between 80% SoH and 71% SoH is less pronounced, with a slight increase in the coefficient between 90% and 35% SoC for the 71% SoH condition. After 40% SoC, the coefficients for both states of health align closely. Another noticeable change after aging occurs between 95% and 90% SoC. While an increase in the entropy coefficient is observed for 100% SoH, both aged measurements show a reduction in the coefficient. Furthermore, for the 100% SoH cells, a change in the slope is seen at approximately 45% SoC. This slope change shifts to a lower SoC of around 30% after the first aging cycle and remains at that level.

The significant deviation in the entropy coefficient at 100% SoH suggests that the measurement may be influenced by side reactions. Since the current used during the measurement was higher than that used during the formation process, it is possible that additional SEI formation occurred. As the formation of the SEI involves the rearrangement of lithium ions, this process also affects entropy. This change in entropy overlaps with

the entropy changes caused by delithiation, thereby distorting the measurement results. Another indicator of initial SEI formation is the capacity loss during the first set of aging, which is approximately twice as high as the capacity loss observed during the second set of aging.

Furthermore, the entropy coefficient remains below zero for all three SoHs. When these negative values are used in Equation 4, the negative entropy coefficient and a positive current for delithiation lead to a negative (endothermic) heat flux. Since silicon forms alloys with lithium during lithiation, these alloys must be dissolved, which is an endothermic reaction.

This is also reflected in calculations using the Hess's law theorem, which states that the reaction enthalpy ΔH_r is represented by the difference in the enthalpy of formation from the products $\Delta_f H_{products}$ and reactants $\Delta_f H_{reactants}$.

$$\Delta H_r = \sum(\Delta_f H_{products}) - \sum(\Delta_f H_{reactants}) \quad (8)$$

According to the literature [44,45], the formation enthalpy of $\text{Li}_{3.5}\text{Si}$ is smaller than Li_2Si . As a result, the delithiation ΔH_r is positive, which indicates an endothermic reaction.

Consequently, the reversible nature of entropic heat leads to an exothermic heat flux during lithiation. Since the irreversible heat flux, due to the internal resistance and polarizations is always exothermic, the overall exothermic heat flux during lithiation must be higher compared to that during delithiation.

This is in agreement with the measurements from Li et al. [46] and Housel et al. [9], both of whom analyzed the heat flux in silicon half-cells during the first two cycles. Since the heat flux in the first cycle was heavily influenced by the formation reaction, the second cycle is of more interest. In both studies, the assumption of a lower heat flux during delithiation was confirmed. On the other hand, a study by Arnot et al. [8] found no significant difference in the heat flux between lithiation and delithiation. Nevertheless, current research supports the notion that the negative entropy coefficient for silicon during delithiation is accurate.

Despite this, the heat flux remains consistently exothermic during delithiation, indicating that the irreversible heat flux is dominant in the coin cell systems.

4.2. Impact of Phase Changes on the Entropy Coefficient

A peak in ICA indicates a phase transition in the electrode of interest and is well-suited for the analysis of half-cells. The determined ICA curve for the delithiation of the cells at three SoHs is shown in Figure 9. Two peaks (D1 and D2) were observed. D1 is correlated to the phase change from $\text{a-Li}_{3.5}\text{Si}$ to $\text{a-Li}_2\text{Si}$ and D2 to $\text{a-Li}_2\text{Si}$ to a-Si [47].

Two changes in the shape of the ICA curves are noticeable. First, both peaks of D1 and D2 are shifted for all cells to lower SoC after the first set of aging cycles. This could be caused by a resistance increase due to the formation of SEI [41]. This supports the assumption that the first cycles experience more side reactions influencing the delithiation. Moreover, Cells 1 and 3 show only peak D2 after the second set of aging. This is again caused by the internal resistance of the cells [47]. Since the ICA measurement was conducted without a CV-phase during lithiation, $\text{a-Li}_{3.5}\text{Si}$ is not formed due to reaching the lower voltage limit early. As a result, during delithiation no peak D1 is observable. However, the lithiation for the potentiometric measurement contained a CV-phase which leads to the formation of $\text{a-Li}_{3.5}\text{Si}$, despite the increased internal resistance. In consequence, for a comparison between the ICA and the entropy coefficient at a SoH of ~70% only cell 2 can be used.

The second effect deals with the decrease in the peak intensities. Since the first measurement might be influenced by side reactions, the two measurements at the lower SoH align well with the observations from Casino et al. [47], who referred to the decrease in D1 and D2 as a loss of active material.

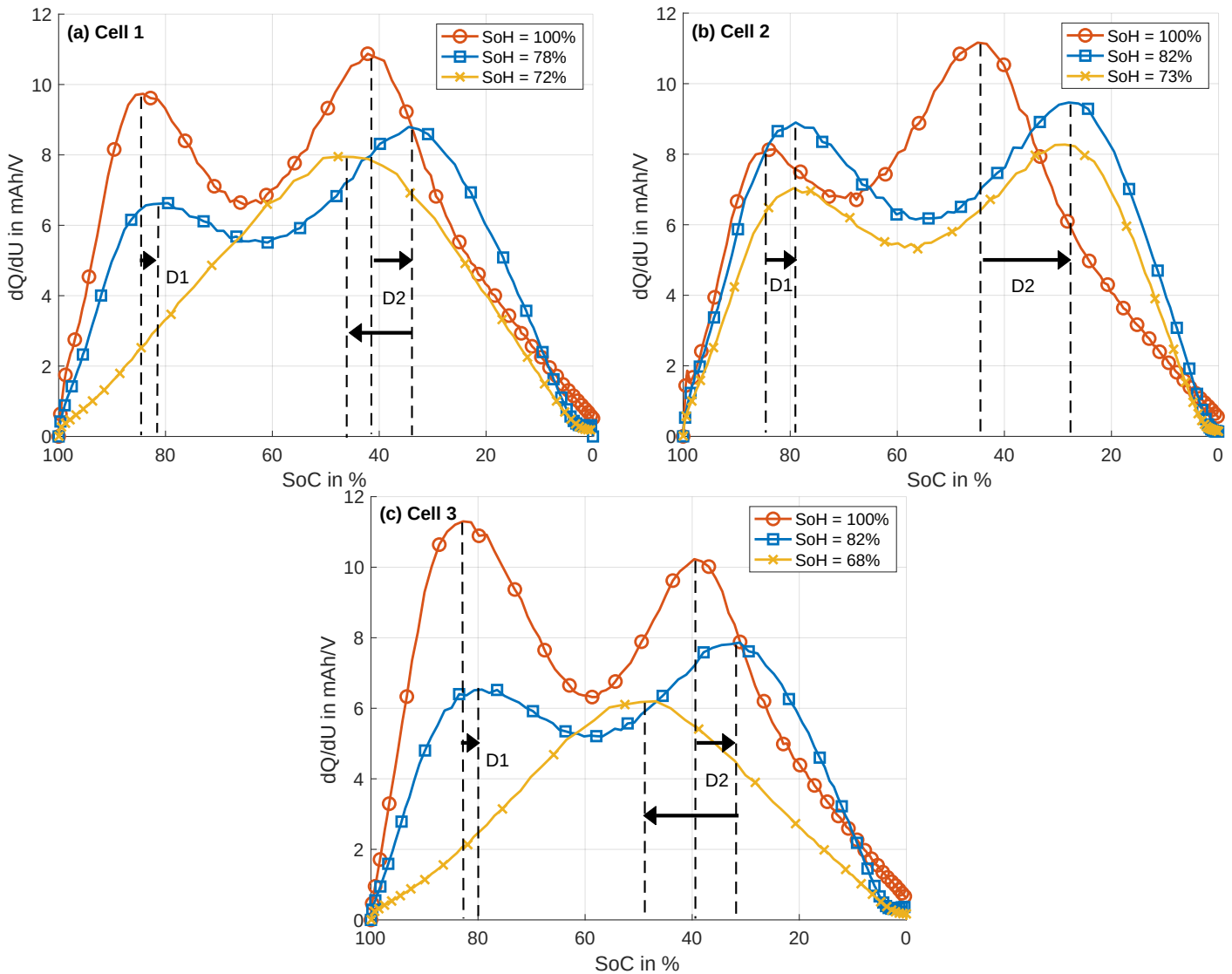


Figure 9. ICA signals for all the cells (a–c) at three different SoH show two peaks (D1 and D2), which shift with SoC (indicated by arrows) and are reduced in peak intensity with decreasing SoH. Note that for cells 1 and 3 at SoH ~70% there is one peak only.

The position of the peaks of D1 and D2 contain the information when the phase transitions occur during delithiation. The numerical SoC values of peaks D1 and D2 are listed in Table 3. Given that only cell 2 provides positions of D1 and D2 for all three SoH, the standard deviation for ~70% SoH cannot be calculated. Instead, the standard deviation for ~70% SoH is estimated.

Figure 10 displays the comparison between the peak positions of the ICAs and the entropy coefficient. For better visibility of the incline of the entropy coefficient, two dotted lines are inserted into the diagram. The intersection of the two lines falls within the area of the phase transition D2 for all SoH. This indicates that the phase change from α - Li_2Si to α -Si leads to a change in the slope of the coefficient.

Table 3. SoC values from the peaks of the phase transitions D1 and D2 for all three cells depending on SoH. The standard deviation for the SoH at ~70% is estimated, as only cell 2 shows both peaks, D1 and D2.

Cells	D1 SoH = 100%	D2 SoH = 100%	D1 SoH = ~80%	D2 SoH = ~80%	D1 SoH = ~70%	D2 SoH = ~70%
Cell 1	83.98%	45.00%	78.97%	37.98%	-	50.32%
Cell 2	82.77%	39.61%	80.72%	31.11%	79.35%	28.67%
Cell 3	84.19%	42.16%	80.90%	34.48%	-	52.32%
Mean	$83.65 \pm 0.77\%$	$42.26 \pm 2.70\%$	$80.20 \pm 1.07\%$	$34.52 \pm 3.44\%$	$79.35 \pm 2.00\%$	$28.67 \pm 4.00\%$

For all SoH, the initial slope is smaller than after the phase change D2, corroborating the assumption that the entropy for a-Si is overall smaller than for other lithiation states.

For D1 such an effect cannot be determined from the current data.

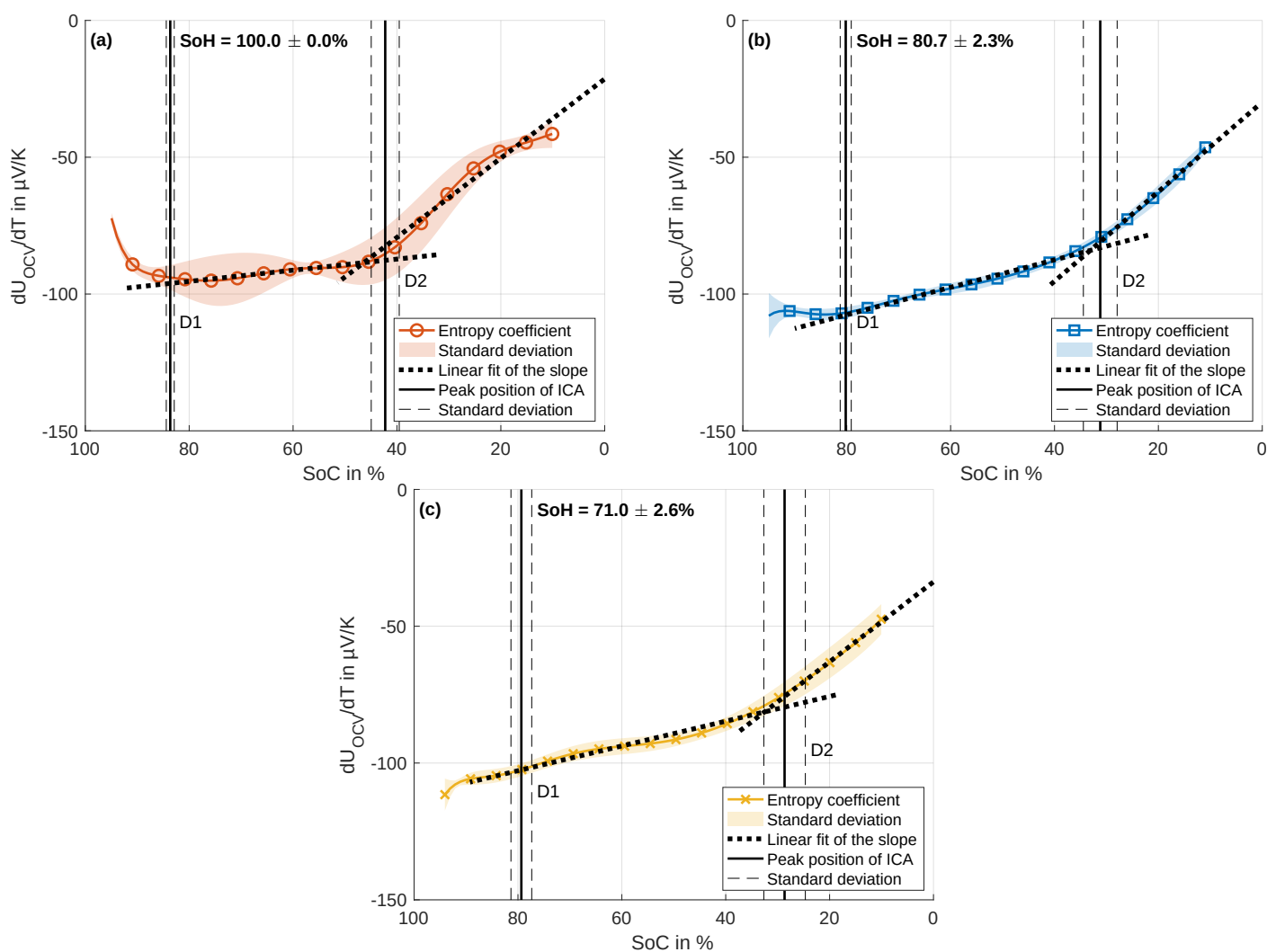


Figure 10. Comparative visualization of the entropy coefficient and the SoC values from the peaks of the ICA plots (Table 3) at various SoH levels as follows: (a) 100% SoH, (b) $80.7 \pm 2.3\%$ SoH, (c) $71.0 \pm 2.6\%$ SoH. Two straight lines characterize the slope of the entropy coefficient. The intersection of this line corresponds to the phase transition D2 for all SoH.

5. Conclusions

In this study, the entropy coefficient of silicon anodes containing 45 wt% nanosilicon and 45 wt% carbon black was evaluated, with silicon serving as the sole active material. The VR curve and self-discharge curve were used to obtain accurate voltage signals from the

potentiometric method to determine the entropy coefficient. This method yielded reliable results for the entropy coefficient between 95% SoC and 10% SoC during delithiation. Additionally, the entropy coefficient was measured at three different SoHs. The results show a consistently negative entropy coefficient, ranging from $\sim -40 \mu\text{V K}^{-1}$ to $\sim -95 \mu\text{V K}^{-1}$ at 100% SoH, increasing with the SoC. This range shifts to lower values after cycling, leading to values between $\sim -45 \mu\text{V K}^{-1}$ and $\sim -105 \mu\text{V K}^{-1}$ at $80.7 \pm 2.3\%$ SoH and $71.0 \pm 2.6\%$ SoH. Furthermore, two phase transitions during silicon delithiation were identified using ICA measurements. The positions of these phase transitions shift to lower SoC values as SoH decreases. Moreover, it is shown that the phase transition from a- Li_2Si to a-Si affects the entropy coefficient, resulting in an increase in the slope of the entropy coefficient at lower SoC values.

For practical applications, especially in thermal management systems, the results indicate that increasing the silicon content in anodes leads to a more consistent entropic heat flux compared to graphite [24]. This suggests that cooling and battery management systems could potentially be simplified, as no abrupt changes in heat generation due to entropy variation, as observed with graphite, occur with silicon. Additionally, thermal management systems may find it easier to predict and maintain a stable cell temperature, thereby enhancing both the safety and performance of the cells.

However, for a comprehensive understanding of entropy changes in silicon anodes, further studies must investigate the lithiation process. Additionally, precise entropy coefficient measurements at the extremities of SoC are necessary to establish the full range of its variability.

This study underscores the complex interplay between material composition, aging, and electrochemical behavior, highlighting the need for continued research to optimize cooling, battery management systems or simulations of silicon-based anodes in lithium-ion batteries.

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