

Determination of the Entropic Heat Coefficient of Lithium-Ion Batteries Based on a Continuous Measurement Method

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A comprehensive understanding of thermal battery behavior and, consequently, the design of efficient thermal management systems are crucial for optimal performance, a high safety level, and the prolonged lifetime of batteries in automotive applications. In this context, knowledge of the heat release within the battery is a key parameter. In this work, a methodology is investigated for determining the reversible heat release based on continuous quasi-open-circuit-voltage (qOCV) measurements, which is not yet fully established in the literature. Three key factors influencing the evaluation of the entropic heat coefficient are presented and it is discussed in detail how these should be taken

into account for the first time. The entropic coefficients derived from the continuous approach are compared with values obtained from potentiometric measurements of the same pouch cell and show a high level of accuracy for the continuous qOCV method. The standard battery cycler is used, with a measuring uncertainty of 1 mV, yields results that are in very good agreement with the broad spectrum of literature values, obtained using different methodologies and uncertainties. The validity and robustness of the approach are further demonstrated by applying the continuous method to data from a different automotive prismatic cell with a significantly different testing procedure.

1. Introduction

The transport and reaction processes within lithium-ion batteries are highly temperature-dependent, which means that the thermal behavior of lithium-ion batteries is of central importance for their performance, lifetime, and safety, especially in automotive applications. In order to achieve high performance and lifetime by minimizing internal losses and degradation processes, as well as ensuring the safety needed in terms of thermal runaway and propagation, thermal management systems are used in automotive applications to keep batteries within their individual optimum temperature range under the various operating conditions.^[1–13]

A profound understanding of thermal behavior is crucial for the development and optimization of thermal management systems, and numerical simulation models are a proven tool to gain insights into the processes within batteries and predict their thermal behavior. The quality of thermal simulation models depends decisively on their parameterization regarding the thermal material properties and the internal heat release of the battery cells.^[1,11,12,14]

The internal heat release of lithium-ion batteries can be described by the sum of two main heat source terms (Equation 1), the irreversible (Equation 2), and reversible (Equation 3) heat source, neglecting additional minor heat sources from side reactions or the heat of mixing.^[1,15–18]

$$\dot{Q} = \dot{Q}_{\text{irr}} + \dot{Q}_{\text{rev}} \quad (1)$$

$$\dot{Q}_{\text{irr}} = I^2 \cdot R_i \quad (2)$$

$$\dot{Q}_{\text{rev}} = I \cdot T \cdot \frac{dU_{\text{OCV}}}{dT} \quad (3)$$

The irreversible heat source term is based on the losses associated with the overpotential as a result of various processes, such as ohmic losses, charge transfer, and mass transfer limitations, summed up to the internal resistance and always represents a heat release (Equation 2).^[1,15–18] The reversible heat source term results from the entropy change of the electrochemical reaction and can act both as a heat source and a heat sink depending on the state-of-charge (SoC) and the current direction (charge or discharge) (Equation 3). The entropy changes are directly connected to the changes of the open-circuit-voltage (OCV) with the temperature (dU_{OCV}/dT or, for the purpose of this work only, dU/dT). This term is a material specific parameter and often referred to as the entropic heat coefficient or entropic coefficient.^[1,11,15–21]

Depending on the battery materials and specific operational conditions given, the reversible heat source can have a significant impact on the overall heat release of a lithium-ion battery.^[22–25] The impact of the reversible heat on the total heat source term is of increased importance, especially for cells with increasingly

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lower internal resistances (e.g., large-format automotive cells) and applications at higher temperatures.^[19] The irreversible heat source term always acts as a heat release and does not depend on the current direction; therefore, SoC-dependent phenomena in the thermal cell behavior, as well as differences in the charge and discharge, can only be accurately described by exact knowledge of the reversible heat source term.

The entropic coefficient is an important parameter for describing the thermal cell behavior; thus, numerous experimental studies can be found in the literature, most on the cell^[17,19–22,24–38] and some on the electrode^[23,27,39] level. There are three main categories of measurement methods: potentiometric,^[19,22,24–29,31,38] calorimetric,^[25,30,32–36] and special (such as electrothermal impedance spectroscopy^[17,37]).

The potentiometric method is based on the measurement of the OCV for different temperatures in the currentless state and is, therefore, a discontinuous method. The individual SoCs are approached in sequence and the temperature is changed in the currentless state according to the sampling points selected; after a sufficient relaxation time, the OCV and its change with temperature are recorded. The potentiometric method has the highest accuracy when used correctly and is often used as a reference method for the determination of entropic coefficients. The disadvantages of this method are the very time-consuming characterization, the need for elaborate measurement equipment with high accuracy (as is often mentioned in the literature) and possible interferences, such as self-discharge, which must be considered.^[17,19–22,24–29,31]

The main focus of further developments in the field of potentiometric methods, therefore, is on accelerating the characterization process with as little loss of accuracy as possible. In addition, background or baseline corrections to compensate for voltage drifts and the selection of the temperature sampling points used in the measurements are discussed in recent literature.^[19,20,22,24,26,29,31] An advanced potentiometric method is introduced in the work of Hu et al.^[38] using a sinusoidal temperature excitation to derive the entropic coefficient via hybridized time–frequency domain analysis to compensate for voltage drifts with a background correction and significantly reduce the measurement time.

The calorimetric methods are based on measuring the heat release of the battery cells during discharging and charging using different types of calorimeters. Assuming that the loss processes for discharging and charging are the same, the reversible heat release and the resulting entropic coefficient can finally be derived from the calorimetrically measured values. The advantages of calorimetric methods over the potentiometric method are the high time efficiency and the continuous measurement over the entire SoC range instead of individual discrete sampling points. At the same time, however, additional complex measuring devices or test setups are often required for characterization and the accuracy of potentiometric measurements cannot often be achieved. In addition, the test setup or the measuring device used depends on the battery cell size and must be matched to it.^[17,19,21,22,25,32–35]

Several further developments of the calorimetric method can be found in the literature pursuing, different advancements

strategies to increase accuracy or simplify the measurement method: Damay et al.^[33] used a combination of thermal models for the inverse determination of heat release. Murashko et al.^[36] utilized gradient heat flux sensors in their measurement setup, and Ahmad et al.^[35] showed the application of constant current pulses from a galvanostatic intermittent titration technique in their calorimetric approach to determine the entropic coefficients. A calorimetric method was developed in the work of Hu and Choe^[34] incorporating time–frequency domain analysis by a wavelet transform technique.

Within the category of special methods, the electrothermal impedance spectroscopy developed by Schmidt et al.^[17] allows the determination of entropy changes based on impedance and temperature measurements. The comparisons against conventional potentiometric measurements show that good accuracy and significantly faster measurement times can be achieved. However, a so-called thermal transfer function must be determined correctly and a sufficient excitation of the surface temperature measured is necessary. The method was recently further developed by Jung et al.^[37] using harmonic-dual-frequency electrothermal impedance spectroscopy, addressing the challenges given.^[17,22,37]

Inverse heat transfer analysis is used in the work of Han et al.^[21] to determine the entropic coefficient based on a combination of experimental measurements and modeling of the thermal cell behavior. Their approach provided good accuracy and time-efficiency compared to conventional potentiometric measurements. The approach requires precise knowledge of the thermal material properties and the irreversible losses and can be influenced by possible thermal gradients, inter alia.

Caposciutti et al.^[20] show an approach based on continuous quasi-OCV (qOCV) measurements in their work, incorporating a low constant current charge and discharge cycles for different temperatures to determine the entropic coefficient of a lithium-ion battery cell. They perform an averaging of the qOCV of the charge and discharge for the evaluation of the entropic coefficient and compare their results against data from potentiometric measurements showing the potential of fast determination via the continuous qOCV-based approach.^[20]

The goal of our work is to further investigate and systematically discuss an approach based on continuous qOCV measurements at different temperatures, similar to Caposciutti et al.,^[20] for the determination of the entropic coefficient without additional elaborate measuring equipment using only a standard battery cyclor with a measurement uncertainty of 1 mV. The entropic coefficients we determined using the continuous qOCV method are compared with the results of our own potentiometric measurements on both electrode level (using experimental test cells) and automotive cell level, as well as literature data for comparable cell chemistries to provide proof of the validity of the continuous qOCV approach.

It is of central importance for the continuous qOCV approach to understand the different main influence factors on the quality of the determination of entropic coefficients. In this work, we will show the impact of the following influence factors and how these

need to be considered in the evaluation of the entropic coefficient: a) The influence of the correct SoC assignment based on the analysis of the underlying testing procedure. b) The influence of the current direction (charge/discharge). c) The influence of the temperatures evaluated.

Our results enable us to show that the determination of the entropic coefficient via a continuous qOCV measurement can be an alternative to the accurate but time-consuming potentiometric methods without any significant loss of accuracy, considering the parameterization of thermal battery models. This is in agreement with the results of Caposciutti et al.^[20] which to the best of the authors' knowledge, is the only other work in literature that utilizes continuous qOCV measurements for the determination of entropic coefficients. Beyond the results of Caposciutti et al., which only consider the averaging of the charge and discharge measurements, we provide a thorough investigation of the main influence factors for the continuous qOCV approach that should be considered during data processing to achieve good accuracies and are the basis for a meaningful evaluation of the entropic coefficient. By taking into account the key influencing factors presented in our work, a higher agreement can be achieved between the entropic coefficients determined from the continuous method and the potentiometric measurements, as well as a broad spectrum of literature values of nickel manganese cobalt (NMC)-graphite cells based on different measurement methods and uncertainties. This shows that the entropy coefficient can be determined in good agreement with the values specified in the literature for NMC-graphite cells using a comparatively simple measurement method and setup. In addition, we verify the robustness and feasibility of the continuous qOCV method by applying our approach to two different automotive cells (pouch and prismatic) that were measured under different test routines and only share a similar cell chemistry. This also demonstrates that there is not necessarily one optimal test protocol, but that different testing procedures can be used to achieve a good approximation of the entropy coefficient if the influencing factors are systematically considered in the data processing. As part of our comparative potentiometric measurements, we also

investigated a combined and simultaneous determination of entropic coefficients of the full cell and both individual electrodes (anode and cathode) at the same time on a material level using experimental test cells. Our results show that the entropic coefficients derived from the experimental cells are in good agreement with the full cell measurement of the automotive pouch cell from which the electrodes were extracted. This shows that upscaling from material to the cell level is feasible for entropic coefficients and a profound characterization at the material level can be used to parameterize thermal models at the cell level based on the individual electrodes.

2. Results and Discussion

2.1. Potentiometric Method

The potentiometric measurements performed at four temperature sampling points (10, 25, 35, and 45 °C) are compared to each other and verified with typical values in literature to confirm the measurements of the pouch and the experimental test cells. It should be mentioned here that a standard battery cycler with a measurement accuracy of 1 mV was used for our measurements, although the literature often states that a significantly higher measurement accuracy is required. The comparison between the value from our pouch cell measurements calculated and different literature values for NMC-graphite cells is shown in **Figure 1a**. The literature values generally show a wide scatter within the entire SoC range. Our calculated values follow the trend of the literature values, deviating slightly only for a SoC of 100% and 10%, but still within the scatter range of literature data. Overall, however, we determined a very good agreement of the entropic coefficient values with the entropic coefficients of various NMC-graphite cells based on different measurement methods from the literature. This verifies that a moderate measurement accuracy of a standard battery cycler of ≈ 1 mV can be sufficient for the determination of entropic coefficients of lithium-ion batteries.

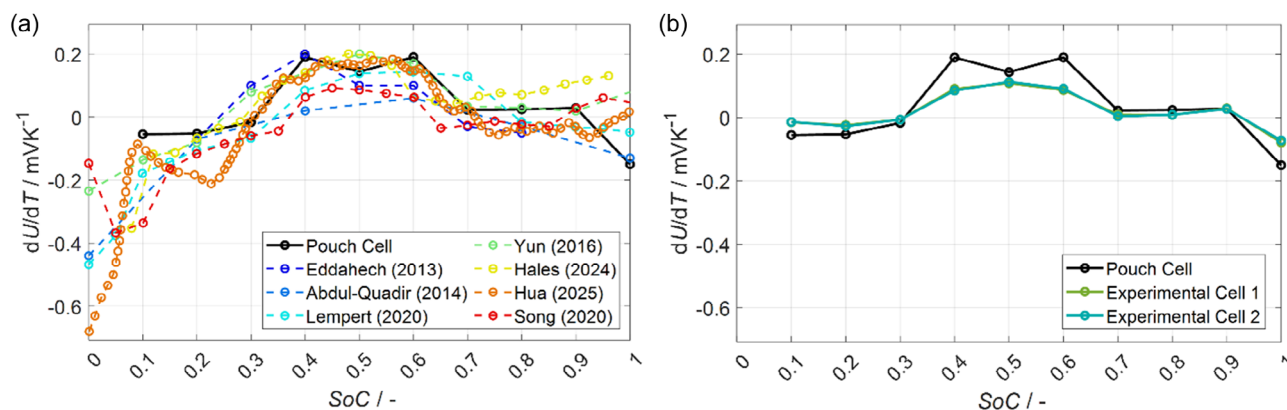


Figure 1. Comparison of the entropic heat coefficient calculated from the potentiometric measurements. a) Resulting entropic coefficient of the pouch cell measurements compared to literature values for NMC-graphite cells (Eddahech et al.^[25] Abdul-Quadir et al.^[40] Lempert et al.^[24] Yun et al.^[28] Hales et al.^[19] Hua et al.^[41] and Song et al.^[30]) b) Comparison of the calculated entropic coefficient of the pouch cell measurements and two different experimental test cell measurements.

The entropic coefficient based on the measurement of the pouch cell is compared to two different measurements with experimental test cells in Figure 1b. Both experimental cells are almost identical, so that reproducible assembly of the cells can be assumed. A deviation can be observed between the experimental and the pouch cell, mainly in the area of SoCs between 40% and 60%. The trend is the same, but the values of the test cells are lower than those of the pouch cell measurements in this area. Potential impact factors for the deviation between the entropic coefficient values from pouch and experimental cells could be slight differences in the electrode configurations (cell-to-cell variations of the pouch cells used) and minor changes of the electrodes during the experimental cell assembly (washing with solvent and renewed formation). However, the values derived from the experimental cells are still within the scatter range found in the literature and show a good agreement.

In addition to the full cell measurements, the experimental cells enabled us to measure the voltages of both the anode and the cathode. We showed the accordance between the experimental test cell and pouch cell measurements for C-rates below C/4 in our previous article.^[42] This offers the opportunity to calculate the entropic coefficient not only of the full cell but also of both electrodes. Hereby, the full cell voltage correlates to the sum of the cathode and anode voltage.

The resulting values for the a) graphite anode and b) the NMC cathode can be seen in Figure 2. Regarding the anodes, the calculated values are multiplied by -1 only for display in Figure 2a, which corresponds to a given display procedure in the literature for better comparability of anode and cathode.^[23,27] Both electrodes correlate very well with the data found in the literature, which shows a great potential to determine the values for anode and cathode directly in combination with the full cell values with the experimental test cells. Thus, the test cells are a comparably easy way to derive the entropic coefficient of the full cell and the individual electrodes, and is, therefore, a suitable method for the determination of the overall system characteristics. The entropic coefficient of the full cell can also be calculated, in the same way as the voltage, out of the sum of the electrode values.

2.2. Continuous Method

Potentiometric measurements are very time-consuming. A trade-off between the time, effort, and accuracy of the SoC points used should always be made. A method using qOCV measurements, comparable to Caposciutti et al.^[20] was thoroughly investigated to avoid this time-consuming measurement technique and obtain continuous data over the SoC. The calculation of the entropic heat coefficient based on the data of qOCV measurements at different temperatures is explained in the experimental section.

Different impact factors on the results of the entropic coefficients derived were identified and are presented in the following. The main influence factors are the specific testing procedure for the correct SoC assignment, depending on the specific test routine, the consideration of the charge and discharge direction, and the temperatures used.

2.3. Correct SoC Assignment Based on the Analysis of the Underlying Testing Procedure

The first thing that needs to be considered is the underlying measurement routine for the qOCV curves. It is important to consider whether the measurements at different temperatures were carried out in the same testing procedure or if there were different initial conditions, such as relaxation times for the curves at different temperatures.

There was always a discharge followed by a relaxation pause and a charge at the chosen temperature in our measurements of the pouch cell. This procedure leads to the important determination that the SoC of the discharge endpoint, which may, for example, be 0.5% in relation to the standard capacity of the cell at 25 °C, is the exact start SoC of the charge cycle and not 0% as usually assigned. Therefore, the specific history of the testing procedure must be known and taken into account in order to find the correct voltage values for the appropriate SoCs.

The specific SoC assignment is the basis for the correct calculation of the entropic coefficient as the comparison of the temperature-induced changes in voltage needs to be performed on the same SoC. Small inaccuracies or offsets due to

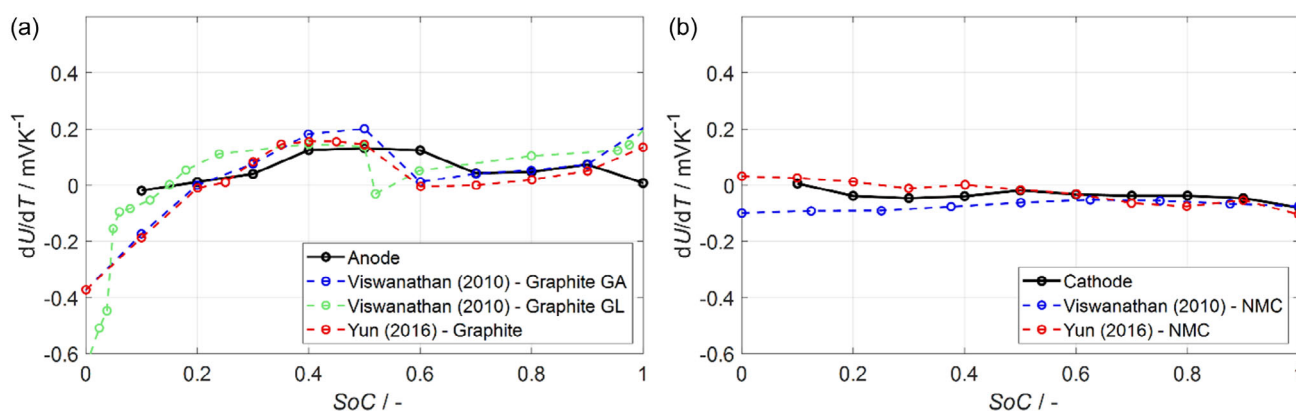


Figure 2. Comparison of the calculated entropic heat coefficient of the individual electrodes from experimental cell measurements with literature values (Viswanathan et al.^[23] and Yun et al.^[27]). a) graphite anode and b) NMC cathodes.

an inaccurate SoC assignment may lead to significant errors in the determination of the entropic coefficient from continuous qOCV measurements.

2.4. Consideration of Current Direction

A charge and discharge measurement exists for each temperature; they exhibit different trends in the entropic coefficient. An exemplary comparison of the dU/dT values calculated at SoC 10% for a) charge, b) discharge, and c) the averaged voltages is shown in Figure 3. This SoC value was chosen to demonstrate that the entropic coefficients based on charge and discharge measurements can show a significantly different behavior, in which not only different values but even different signs in the resulting coefficient can be seen.

In contrast to the potentiometric measurement technique, three different values for each SoC can be calculated from the continuous qOCV measurements.

Figure 4 shows the comparison of the calculated entropic coefficient for charge, discharge, and the averaged values. It is obvious that the charge values have a lower level than the potentiometric values and the discharge values have a higher level. The averaged curve of charge and discharge qOCV lies in between

these and correlates very well with the reference values of the potentiometric measurements. In order to obtain the averaged entropic coefficient, it is of no importance if the underlying voltage values of the qOCV or the derived entropic coefficient values from charge and discharge are averaged.

The cell is currentless and no voltage losses occur in the potentiometric measurements. Therefore, only one value for the entropic coefficient can be derived at each SoC. We assume a very low influence of the losses on the cell performance at low C-rates, such as C/40, but as these results show, there is still a significant influence on the calculation of the entropic coefficient from continuous qOCV measurements. This leads to the important fact that only the averaged values from qOCV measurements should be used for the NMC-graphite cells investigated, because the losses are still too dominant even at C/40 and the averaging of charge and discharge can negate these distorting influences on the calculation of the entropic coefficient. The method of averaging the qOCV measurements was also shown by Caposciutti et al.^[20] and is in good agreement with our investigation.

The values at very low (<10%) and very high (>90%) SoCs deviate more strongly from the potentiometric values and the values reach very high, especially for nearly 0%. The increased deviations for these low and high SoCs cannot be correlated

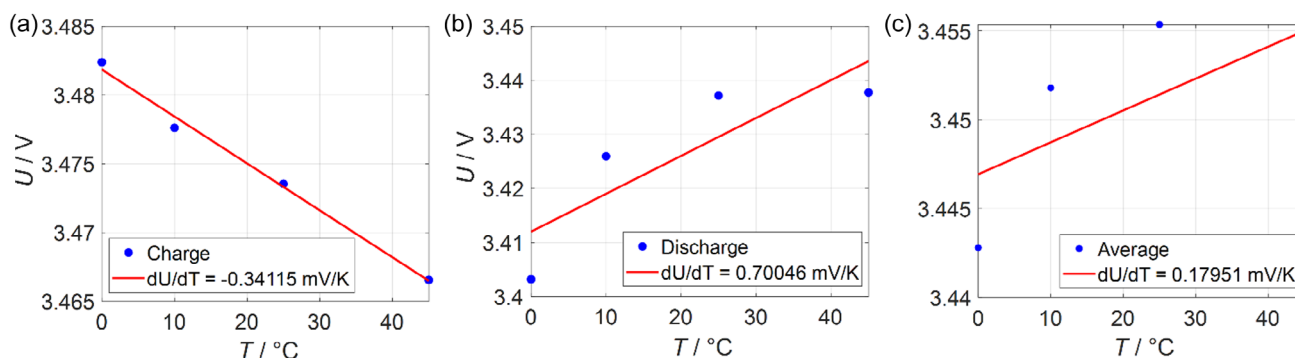


Figure 3. Comparison of calculated entropic coefficients at SoC 10% for a) charge, b) discharge, and c) the averaged values.

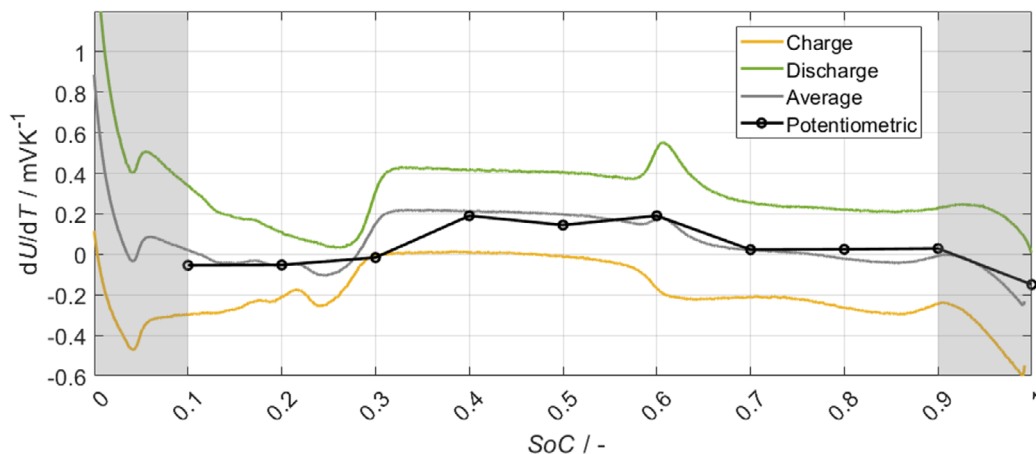


Figure 4. Comparison of entropic coefficient from charge, discharge and averaged values of the qOCV and the calculated values from the potentiometric measurement.

to the behavior of the cell. We assume them to be caused by increasing voltage losses, especially for lower temperatures, and the fact that these SoCs are not reached for all temperatures causes the calculation to fail. Very good results for the entropic coefficient can be reached by the calculation based on averaged qOCV measurements in a resulting SoC range from 10%–90%.

2.5. Choice of the Temperatures Evaluated

As described previously, the qOCV measurements are not free of losses and, thus, the temperatures evaluated play an important role, because the losses increase with decreasing temperature. In addition, depending on the cell investigated, too high temperature may trigger unwanted effects distorting the voltage measurement, which may impact the quality of the entropic coefficients derived. In order to reduce the measurement time necessary, the question arises regarding how many temperature sampling points are needed for a profound calculation of the entropic coefficient. Investigations into potentiometric methods concerning this question can be found in the literature, showing that only a few temperature sampling points with a quite large temperature change can be sufficient for the derivation of the entropic heat coefficients and a fine resolution of sampling points over a broad temperature range is not necessarily required.^[19,20,22,24,29] We use our data to add to that discussion in the following paragraph.

Regarding the pouch cell, the qOCV was measured for four different temperatures (0, 10, 25, and 45 °C). The entropic coefficients calculated for six different evaluated temperature combinations can be seen in **Figure 5a–f**. The qOCVs at different temperature sampling points, which are each listed in the legend, were used and averaged for each curve of the entropic coefficient. Additionally, the entropic coefficient based on the potentiometric method of the pouch cell is shown as a reference in black. Blue shades were selected for the lower temperatures (b and d) and red shades for the higher temperatures (c, e, and f). The gray curve (a) was calculated based on all four temperatures measured; three different temperatures were used for the

medium red (c) and light blue (b) curve, and the highest (light blue, b) and the lowest (light red, c) temperature were excluded. Only the two highest temperatures were used for the red curve (f), only the two lowest temperatures for the blue curve (d) and only the middle temperatures were used for the light red curve (e). Taking these constellations, the influence of the temperatures evaluated and especially the influence of very high and low temperatures on the calculation will be examined.

The general course of all entropic coefficient values is identical, independent of the temperatures used. The temperatures chosen only show a very small influence on the result, especially for SoCs between 10% and 40% as well as between 60% and 70%. The blue curve (d), in which only the two lowest temperatures were used, generally deviates the most. The gray curve (a) with all temperatures is, as expected, mainly in the middle of all other curves. The comparison with the potentiometric values shows that the red curves correlate very well, whereby the curves including the highest temperature fit best.

The results provide a few insights into the impact of the temperatures chosen on the calculation of entropic coefficients based on continuous qOCV measurements, which we want to discuss in the following. As expected, the lowest temperature with 0 °C has an especially noticeable influence on the entropic coefficient value calculated. The losses in the cell for lower temperatures occur severely, and, therefore, the voltage measured with the comparatively low current of C/40 is actually too affected by the losses to be used as a reliable qOCV. Regardless of that fact, the values calculated do not differ significantly from the others and the general trend is the same.

There is only the measurement at 45 °C for the gray curve (a) added for the calculation, in contrast to the light blue curve (b). Even though the 0 °C measurement is included, the additional qOCV at 45 °C seems to negate some of the stronger deviations, which leads to a slight convergence to the potentiometric measurement in comparison to the curve without this qOCV at the highest temperature. Nevertheless, the entropic coefficient calculated deviates more strongly than the red curves (c and f) with

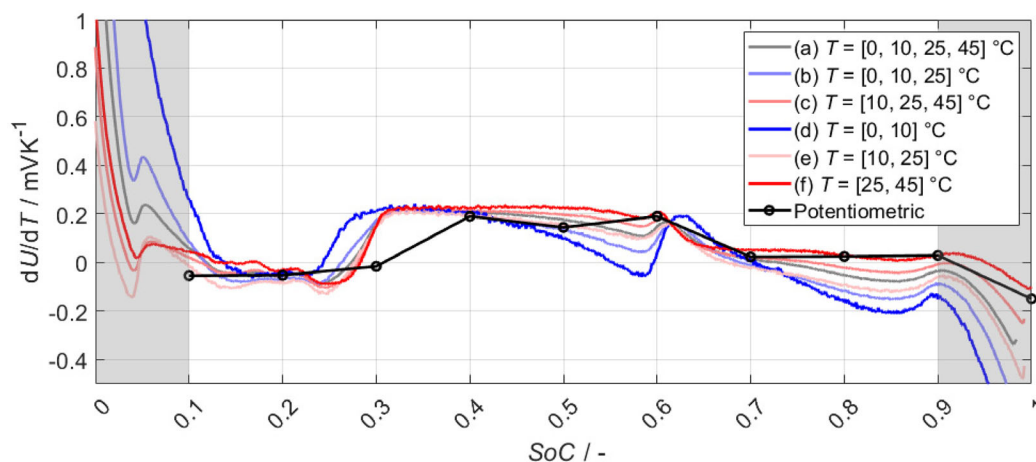


Figure 5. Comparison of the calculated entropic coefficient for different temperature combinations of the evaluated averaged qOCV-measurements as well as the potentiometric measurement.

45 °C and without the 0 °C measurement included. These curves only differ marginally, which shows that the losses at 10 °C are very low. Furthermore, this leads to the conclusion that the value calculated for two temperature sampling points corresponds to those with three and, therefore, the quality of the calculation is not directly dependent on the number of values used and the temperature difference between the sampling points. However, this only applies if the corresponding measurements are of good quality and do not deviate too much from the OCV due to excessive losses.

All in all, the observations above show that it is of more importance to choose the right temperature sampling points with a good quality than to use a high quantity of different temperatures for the calculation of the entropic coefficient. Nevertheless, even imperfect qOCV measurements of moderate quality can be used to calculate the entropic coefficients and still provide a good approximation of the more accurate values. It is important for the assessment to consider the intended use of the entropic coefficient determined. This method may not be well suited for highly precise material characteristics, while the precision is sufficient for most applications, such as the parameterization of thermal battery simulation, and the method can be applied. A decisive advantage of the continuous method is that the entropic coefficient is calculated continuously over a wide SoC range and not only for a few individual SoC points, as is the case with the potentiometric measurement.

2.6. Application to Different Cell and Testing Routine–Robustness of the Continuous Method

We applied the method described to the qOCV measurement dataset of a different automotive cell with similar NMC-graphite cell chemistry for further investigation and to test the reliability and robustness of the continuous qOCV method. This cell was investigated using a deviating test routine compared to the pouch cell. The test procedure for the prismatic cell is explained in detail in the experimental section. The main differences to the procedure used for the pouch cell are the higher C-rate of C/20

and the noncontinuous measurement of the discharge and charge cycles for different temperatures.

Following the steps of the qOCV method described, the analysis of the specific testing procedure enables the correct SoC assignment, which is the basis for the accurate calculation of the entropic coefficient. The qOCV measurements of charge and discharge of the prismatic cell are also averaged to take the current direction into account. Finally, the averaged qOCV datasets for the different temperatures measured are checked concerning their quality and the potential impact of voltage losses or other disturbances of the voltage signal. As described previously in the results of the pouch cell, the course of the entropic coefficients over the SoC is only slightly dependent on the temperature selected. This is also the case for the prismatic cell dataset, but the individual datasets should be checked to avoid interfering losses or other deviations, which may reduce the quality when using the continuous qOCV method.

Regarding the prismatic cell dataset, in addition to low temperature, some high temperature (higher than 40 °C) measurements exhibit insufficient quality of the voltage data and the entropic coefficients derived, including these temperature datasets, deviate the most from the potentiometric reference. A moderately elevated temperature range from 15 to 35 °C is identified for the best accuracy of the entropic coefficients calculated of the prismatic cell. This is in agreement with the previous observations of the temperature influence on the qOCV measurements of the pouch cell. The most suitable selection of temperature sampling points depends on the individual measurement setup, testing procedure (especially the C-rate chosen for the qOCV) and cell behavior defining the overall quality of the qOCV data. Nevertheless, this moderately elevated temperature range may be preferable as a general orientation to avoid interfering losses or other deviations of the voltage signals.

As the sum of these steps, the entropic coefficient for the prismatic cell derived from averaged qOCV measurements (C/20) based on temperature sampling points of 15 to 35 °C is shown in Figure 6 and compared to the entropic coefficients of the pouch cell from the potentiometric and the qOCV (Figure 5 curve c) method.

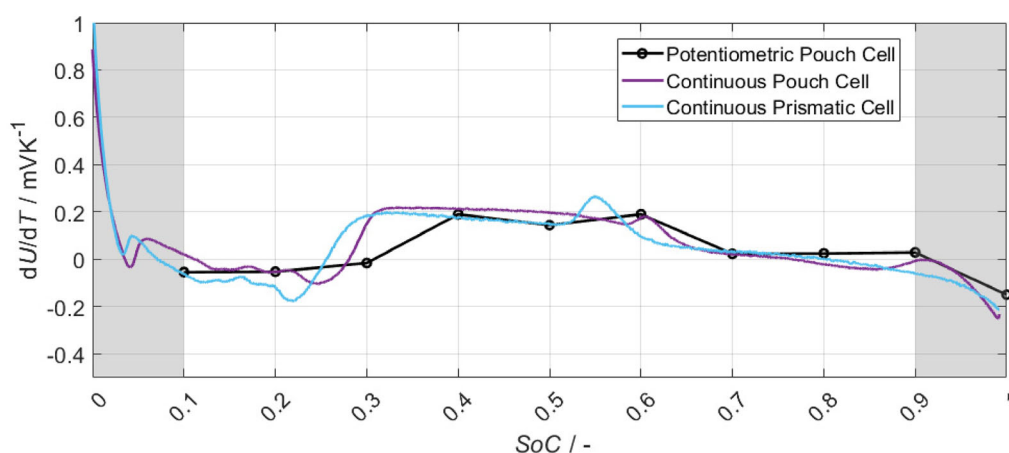


Figure 6. Comparison of the potentiometric and continuous measurement result of the pouch cell with the continuous measurement of the prismatic cell.

It can be seen that, although many parameters of the measurement data and testing routines of the prismatic and pouch cell differ significantly, the resulting entropic coefficient values derived via the continuous qOCV method are very close to each other and are in good agreement with the reference values of the potentiometric method. In addition to the robustness of the approach presented, this also demonstrates the potential to use existing constant low current qOCV datasets for the determination of the entropic coefficient without the need for one's own elaborate measurements, with the help of the systematic data processing shown in accordance with the three main influencing factors.

3. Conclusion

The determination of the entropic coefficient of lithium-ion batteries using a continuous qOCV method, along with the identification of three key factors that influence the quality of the evaluation of the entropic coefficient and how to account for them, was presented and discussed. We used discharge and charge voltage curves measured with low constant currents (for example C/20 or C/40) in the continuous approach to derive the qOCV at different temperatures for the automotive pouch cell (60 Ah) investigated. We compared our results from the continuous method with the derived entropic coefficient obtained from potentiometric measurements of the same pouch cell as well as with established literature data of similar NMC-graphite cells and showed a good accuracy of our results and, therefore, the validity of the continuous method. As part of our potentiometric reference measurements, we also investigated a combined determination of entropic coefficients of the full cell and both half-cells (anode and cathode) at the same time on a material level using experimental test cells. We showed a good agreement between the entropic coefficients determined at the material level via experimental cells and those of the automotive pouch cell. This demonstrates that a characterization at the material level can be used to parameterize thermal models at the cell level based on the individual electrodes.

The main influencing factors of the continuous method presented that need to be considered for the evaluation of the entropic coefficients are the analysis of the underlying testing procedure for a correct SoC assignment, the current direction (charge/discharge), and the temperatures evaluated. As the first step in data processing, based on the analysis of the underlying testing procedure, it is essential to ensure the correct assignment of the SoC to avoid even small inaccuracies or offsets, which could otherwise lead to significant errors in the entropic coefficients derived from continuous qOCV datasets. Second, the influence of the current direction needs to be considered via the averaging of discharge and charge values. The temperatures evaluated need to be examined as the last impact factor for the data processing. We compared the entropic coefficients calculated for different temperature combinations of the qOCV data and demonstrated that a large number of temperature sampling points or a high resolution over a broad temperature range are not

required to achieve good accuracy in the entropic coefficient. Instead, the quality of the individual qOCV dataset must be considered because insufficient quality at certain measurement temperatures (e.g., due to significant voltage losses at low temperature) may effect the entropic coefficients calculated.

Finally, we verified the robustness and feasibility of the approach presented by applying our method, taking into account the main influence factors in the data processing, to a qOCV dataset of an additional automotive cell. This prismatic 120 Ah cell, with similar NMC-graphite cell chemistry, was investigated using a significantly different testing procedure compared to the pouch cell. Despite the strong differences in the measurement procedure of both cells and, thus, the resulting datasets of the qOCV, the entropic coefficient could also be determined accurately for the prismatic cell by applying the steps mentioned. This shows that the approach presented provides the opportunity to use existing or provided datasets to determine the entropic coefficient with sufficient accuracy for thermal modeling, without the need for one's own extensive measurement studies. Furthermore, the datasets do not have to be measured using a specific, fixed testing procedure. It only requires the systematic processing of the datasets available and the consideration of the influencing factors mentioned in this work.

We were able to show that, compared to conventional potentiometric measurements, the determination of the entropic coefficient via a continuous method can be a time-efficient alternative without any significant loss of accuracy for the parameterization of thermal battery models. In contrast to the discrete values at selected SoCs from the potentiometric method, a continuous curve over the SoC is received from the continuous method. Additionally, only a standard battery cycler with a moderate voltage resolution and no complex measurement equipment or setup is needed to gain sufficiently accurate entropic coefficients.

However, the continuous method presented exhibits limitations at very high (>90%) and very low (<10%) SoCs and requires further refinement to provide a more accurate approximation in this range compared to the potentiometric method. Furthermore, the continuous method should be applied to other cell chemistries in the future to assess its applicability and identify potential modifications to the methodology presented, especially for cell chemistries that exhibit hysteresis between charging and discharging.

4. Experimental Section

Cells

The pouch cell investigated is a commercial automotive pouch cell with 60 Ah capacity, graphite anode and NMC cathode. The experimental test cells with a capacity of 7.49 mAh were built out of the electrodes extracted from the pouch cell. Accordingly, a pouch cell was discharged with C/10 to the minimum voltage of 2.5 V and subsequently opened inside an argon glovebox. The electrode sheets were extracted, washed in dimethyl carbonate, and the active material on one side was removed using N-methyl-2-pyrrolidone. The preparation steps are explained in more detail in our previous

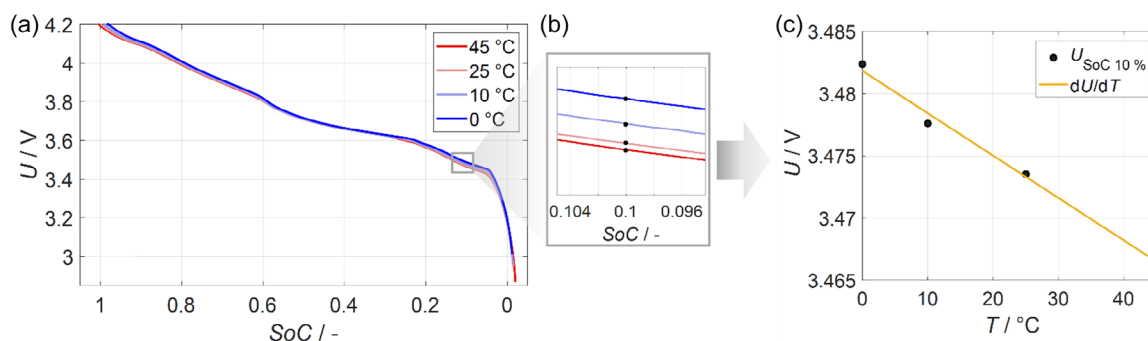


Figure 7. Example of the calculation method of the entropic coefficient. a) Charge qOCVs for different temperatures plotted over SoC. b) Zoom of the curves for an exemplary SoC of 10%. c) Plotted OCV values for SoC 10% over the temperatures and the linear fit which corresponds to the dU/dT .

article.^[42] The same pouch cell type, but not the same pouch cell, was used for the measurements with the pouch cell and the experimental test cells.

The experimental setup consists of the PAT-Cell housing from EL-Cell GmbH^[43] with a 220 μm PP fiber/PE membrane separator and lithium reference ring and standard 1 M lithium hexafluorophosphate (LiPF₆) dissolved in DMC (LP30, Sigma-Aldrich) as an electrolyte. Due to the lithium reference additional to the full cell voltage, the single electrode voltages can be measured in the experimental test cell set-up. The prismatic cell investigated was a commercial automotive prismatic cell with 120 Ah capacity, graphite anode, and NMC cathode.

The voltage range of all cells is 2.5 to 4.2 V.

Measurement Techniques

All cells were placed in individually designed, fluid-flow, and temperature control plates. These plates are connected to a cryostat (RE1050, LAUDA Dr R. WOBSE GMBH & CO. KG) to be able to set the temperature precisely directly on the cell surface.

Low constant current measurements at different temperatures were performed to obtain the qOCV. Accordingly, the pouch cells were charged at 25 °C with constant current constant voltage charging (CCCV) to 4.2 V (100% SoC). The temperature was then changed and after relaxation lasting 2 h, they were discharged with C/40 to 2.5 V and then, after relaxation lasting ten hours, charged with C/40 to 4.2 V. The next temperature was then set and the steps described were repeated. The following temperature sampling points were investigated: 0, 10, 25, and 45 °C.

Regarding the prismatic cell, C/20 measurements were performed in another independent study. The cell was charged at 25 °C with 10 A using CCCV to the upper voltage limit of 4.2 V (100% SoC). This was followed by the temperature change and a C/20 discharge, relaxation for two hours and subsequent C/20 charging. This was performed for the temperatures (10, 15, 20, 25, 30, 35, 40, and 45 °C). The pouch and prismatic cells were cycled using a CTS (BaSyTec GmbH, Asselfingen, Germany) cell test device with a measurement accuracy of 1 mV. The experimental test cells were cycled using a CTS LAB (BaSyTec GmbH, Asselfingen, Germany) cell test device with a measurement accuracy of 1 mV.

Regarding the potentiometric measurements, different SoCs of the cells were approached and the temperature was changed at each SoC in the following order: 25 to 10 to 35 and to 45 °C. Hereby, each temperature was held for at least two and a maximum of five hours before the next temperature was set.

Data Analysis

The calculation method for the entropic heat coefficient based on the charging qOCVs for different temperatures is shown exemplarily in Figure 7.

In order to calculate the entropic coefficient out of the qOCVs, the qOCV values for each SoC are compared between the different temperatures and a linear fit is made, whereby the slope of the fit corresponds to the entropic heat coefficient of the corresponding SoC. This calculation is performed for each SoC, resulting in the entropic coefficient values for the SoC range. However, this method has a weakness in the edge areas (SoCs higher than 90% and lower than 10%) where the calculation is unreliable. This is due to the fact that the qOCV does not cover the full SoC range for every temperature, which was defined by the 25 °C measurement and that at some temperatures the losses are not negligible. This must be taken into account when applying the coefficient calculated and comparing it with literature values.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: entropic coefficient · lithium-ion batteries · quasi-open-circuit-voltage · reversible heat · thermal behavior

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