Sensor applications

Investigation of the Coulombic Efficiency and the Superior Differential Capacity Degradation Analysis

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Abstract—The Coulombic efficiency (CE) measurement is a promising method to quickly determine the potential lifetime of a battery cell. It will be demonstrated that high-precision measurements are required to determine the CE of modern cells. For this purpose, a comparison of our in-house developed precision hardware and two commercially available hardwares is performed. Furthermore, it is shown by means of a model that the CE can be misleading when it comes to the determination of cell aging. As a better alternative, the (conventional) differential capacity analysis (ΔC) is presented and the difference compared to the CE is demonstrated by a precision measurement.

Index Terms—Sensor applications, Ah-efficiency, battery aging, capacity degradation, Coulombic efficiency (CE), lithium-ion battery, precision measurement.

I. INTRODUCTION

In cell development of lithium-ion batteries, the problem is that due to their high cycling stability, the determination of the total lifetime turns out to be a time-consuming process. At normal operating temperatures and cycling currents, the cycling of the cells until their end-of-life (falling below a defined residual capacity or exceeding a maximum tolerable internal resistance) often takes several months to years [4], [8], [19], [21]. To accelerate this aging process, cells are cycled under increased load [1], [5], [12], [13]. However, lifetimes determined in this way are misleading, as rapidly aged cells have a different aging profile than slowly aged cells [4].

For this reason, the Coulombic efficiency (CE) measurement is proposed in the literature as a promising alternative to quickly determine the cell aging of normally operated cells. The CE is used to determine the amount of charge lost between charging and discharging. It is assumed that the missing charge quantity is a measure for the cell-internal parasitic reactions, which lead to a capacity loss or the increase of the internal resistance [3], [4], [6], [7], [10], [17], [18], [20].

However, two fundamental problems occur as follows.

1) As shown in Section II, commercial standard hardware is not able to measure the CE precisely enough to quickly make a meaningful statement regarding cell aging. Only specialized high-precision measurement systems allow these measurements to be performed adequately.
2) A detailed investigation of what the CE actually means in Section III shows that the measured charge loss of the CE is a mixed quantity of reversible and irreversible charge losses as also suggested in [14]. A possible correlation between achievable battery life and CE is, therefore, no longer quite clear.

In the course of this letter, we would like to discuss point 2 in more detail and propose an alternative method: the differential capacity degradation analysis (ΔC). In fact, looking at capacity degradation over cycles is already a well-known analysis. We simply extend this analysis by looking at the derivative of the capacity degradation and thus looking at the capacity loss from cycle to cycle. However, a cycle-to-cycle analysis can only be measured meaningfully with precise measuring equipment. With commercial standard hardware, this has not been possible so far due to the too-high measurement noise.

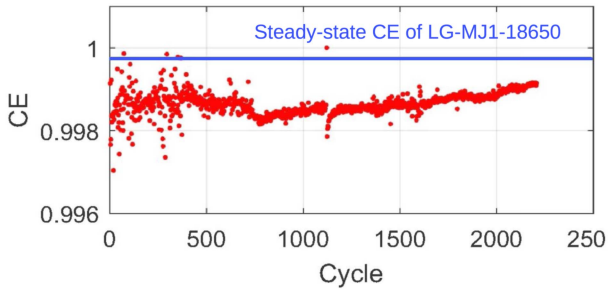

Fig. 1. Here, a 1-Ah LFP cell was cycled at 1 C using an Arbin BT2000. The temperature was kept constant at 45 °C [21]. The high noise level in the first 500 cycles prevents a quick determination of the CE. In comparison, the blue line represents the steady-state CE of a modern LG-MJ1-18650 cell, which obviously cannot be determined meaningfully with this measuring device.

II. STATE OF THE ART OF CE-MEASUREMENT

Since the cell damage per cycle of modern long-life cells is very low, it is necessary to measure the capacity loss during charging and discharging with high precision. In general, a meaningful determination of the CE is no longer possible with ordinary battery cyclers, as shown in Figs. 1 and 2. The blue line represents the steady-state CE of a state-of-the-art LG-MJ1-18650 cell. This cell has a minimum cycle life of 400 according to the data sheet [11]. In [9], a remaining capacity of 80% was reached at approximately 1000 cycles. The cell life is, thus, not exceptionally high, which is why it should be easy compared to

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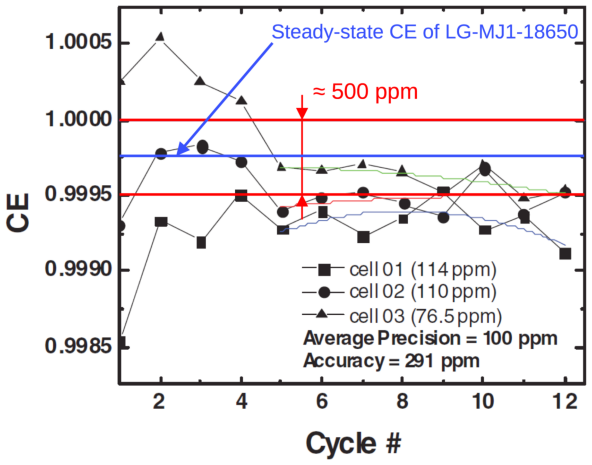

Fig. 2. Here, three identical Graphite/LCO cells were cycled with a state-of-the-art MACCOR 4000 cell tester [2]. The cells were kept at 40 °C with a deviation of ±0.05 °C. The cycling current was 4 mA and was measured with the 5-mA measuring range. Since the measuring range was almost completely utilized, the best possible measuring precision was achieved with this measuring device. The blue line represents the steady-state CE of a modern LG-MJ1-18650 cell in comparison. Although the measurement is better than Fig. 1 in terms of precision, it would still not be sufficient to quickly determine the CE of the LG cell due to the noise.

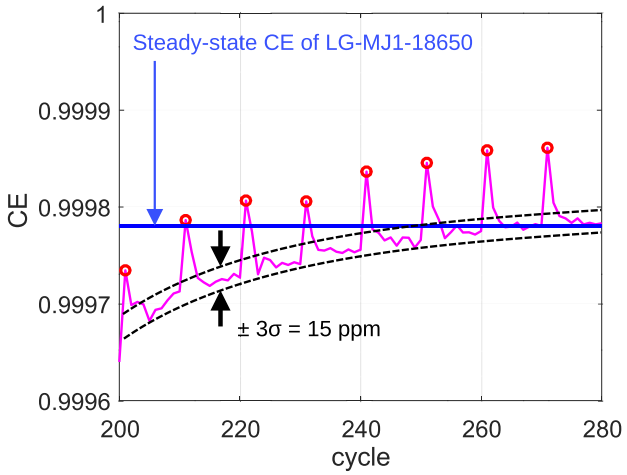

Fig. 3. Here, the CE of an LG-MJ1-18650 cell is shown (magenta curve). The nominal cell capacity is 3.5 Ah and the cycling rate was chosen with $C/8$. The temperature was kept constant at 40 °C (measurement deviation peak to peak: 1/10 °C). The red circles demonstrate when a new measurement cycle starts. At the end of each measurement cycle (10 CE-cycles), an impedance spectroscopy is performed at 70% state-of-charge. After that, the CE measurement takes about two cycles to settle back on the trend line. The $\pm 3\sigma$ measurement error between the black dashed lines is 15 ppm. For more details on the measurement uncertainty of the setup used, see [16].

long-life cells (with a life expectation of several thousand cycles) to measure the CE with low noise. Fig. 1 shows a CE measurement of a 1-Ah LFP cell (red measuring points). The noise of the red measuring points (measured with Arbin BT2000) indicates that the CE of the LG-MJ1-18650 cell can neither be determined quickly nor accurately with this device. Several hundred cycles would be necessary to detect a trend. This, however, would defeat the purpose of determining the capacity degradation quickly under normal operating conditions.

The measurements made with the MACCOR 4000 system from the work in [2], as shown in Fig. 2, perform better. However, although the measurements with the MACCOR 4000 were carried out under good temperature stability and the current measurement range is used optimally (best possible measurement precision), the noise is still too high to be able to determine the CE of the LG-MJ1-18650 cell sufficiently well in a short time.

In Fig. 3, a measurement with our precision measurement hardware is demonstrated. Here, an LG-MJ1-18650 cell is cycled at 40 °C with $C/8$. The measurement hardware was carefully designed to minimize temperature drift in both the cell and hardware, as well as to reduce measurement noise. This allows for determining the CE very fast and precisely from cycle to cycle. A more detailed description of the measurement setup can be taken from the work in [15] and extensive considerations on the resulting measurement uncertainties from the work in [16].

III. MEANING OF CE

CE is calculated from the quotient of the discharge quantity (Q_{OUT_n}) and the charge quantity (Q_{IN_n}) previously inserted into the battery as shown in Fig. 4:

$$\mathrm{CE} = \frac{Q_{\mathrm{OUT}_n}}{Q_{\mathrm{IN}_n}}. \tag{1}$$

The problem with the CE measurement is that it does not fully represent the irreversible capacity losses, as shown in Fig. 5.

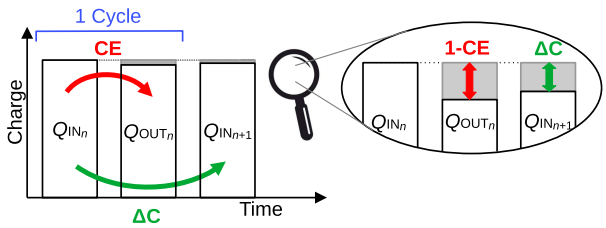

Fig. 4. Here, it is shown schematically that charge is lost during cycling. In order to calculate the CE, successive charge and discharge measurements are taken (red arrow). In comparison, one has to take solely successive charge (or discharge) measurements to observe the differential capacity degradation (ΔC) (green arrow). As shown in Fig. 5, the discharge capacity Q_{OUT_n} is usually lower than the charge capacity in the following cycle $Q_{\mathrm{IN}_{n+1}}$ because the charge is lost due to the leakage current.

Only irreversible discharge capacity loss and reversible self-discharge (leakage charge) are recorded but not irreversible charge capacity loss. Therefore, the CE is a mixture of irreversible and reversible effects and, in our opinion, does not allow a clear interpretation of whether something is really destroyed in the cell or not. As a thought experiment, one can imagine a cell in which no irreversible damage occurs but reversible charge losses due to leakage currents do arise: This results in CE < 1, although nothing is damaged. This shows that the CE does not necessarily have anything to do with cell aging.

On the contrary to CE, ΔC is calculated with successive charging capacities (or discharging capacities)

$$\Delta C = Q_{\mathrm{IN}_n} - Q_{\mathrm{IN}_{n+1}}. \tag{2}$$

ΔC is actually nothing other than the well-known derivative of the capacity degradation over cycles. In principle, this is possible with all measuring instruments. However, with high-precision measurements, there is the advantage that the measurement can be evaluated from cycle to cycle, and thus, the instantaneous aging rate can be determined very

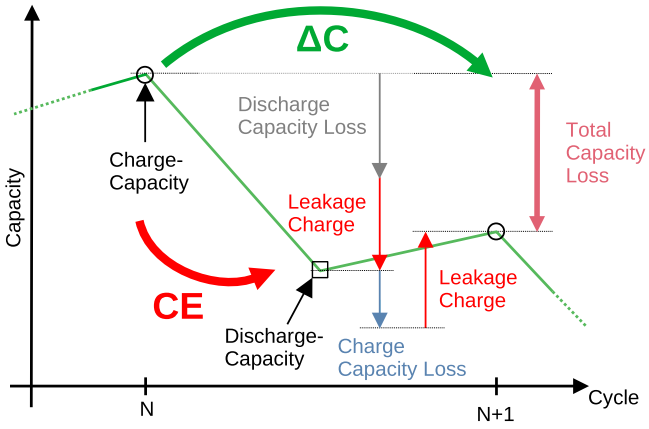

Fig. 5. This figure demonstrates at which point during cycling the different charge losses occur. Due to the constant cycling rate, it can be assumed that the amount of leakage charge during charging and discharging is the same. Differential capacity degradation (ΔC) captures the total capacity loss from cycle to cycle. The CE only ever captures a mixture of leakage charge and discharge capacity loss [15].

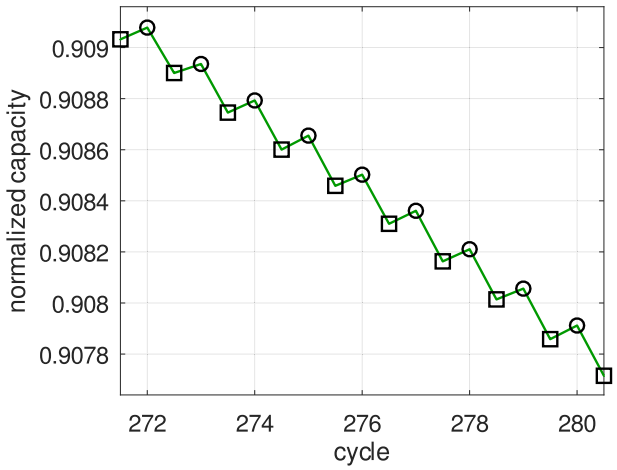

Fig. 6. In this figure, the conventionally used normalized capacity degradation is shown for a few cycles. Due to the high measurement precision, the capacity decrease can be read from cycle to cycle. As in Fig. 5, the discharge capacities are marked as squares and the charge capacities as circles. The increase in the capacity between the discharge process and the subsequent charge process indicates the presence of leakage currents.

quickly under normal operating conditions. ΔC records the sum of all capacity degrading processes (sum of discharge and charge capacity loss) without leakage currents. The leakage charges between charging and discharging cancel each other out with ΔC when the cycling current for charging and discharging is constant because then the cells are charged and discharged for almost the same time. Because the ΔC measurement fully describes the capacity decrease and is not a difficult-to-interpret mixed quantity, we claim that ΔC is better suited than CE for assessing cell aging.

To verify the difference between CE and ΔC by measurements, an LG-MJ1-18650 cell with 3.5 Ah (identical cell as in Fig. 3) was cycled at $C/8$ for several months with the self-developed measurement setup from the work in [15] and [16]. The temperature was kept constant at 40 °C (measurement deviation peak to peak 1/10 °C). After every

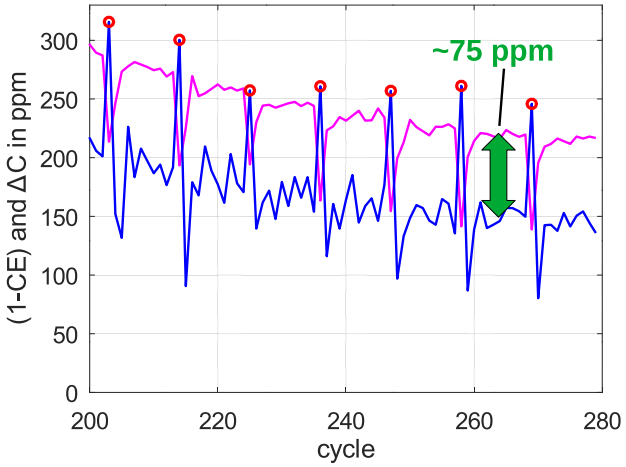

Fig. 7. Here, the $C/8$ measurement shows the difference between Coulombic inefficiency ($1-$CE, magenta curve) and differential capacity degradation (ΔC, blue curve). The red circles indicate when a new measurement routine begins. Here, both $1-$CE and ΔC need about two cycles to return to their original trend. The green arrow shows the difference between $1-$CE and ΔC.

10 cycles, an impedance spectroscopy was performed at 70% state-of-charge, which distorts the first two measurements of the following cycle due to a settling process.

In order to better illustrate the difference between CE and ΔC, the Coulombic inefficiency ($1-$CE) is compared with ΔC in Section IV.

IV. RESULTS AND DISCUSSION

As the measurement result from Fig. 6 shows, the measurement agrees with the model of Figs. 4 and 5. The discharge capacity is smaller than the subsequent charge capacity, which can be explained by leakage currents.

If we now compare $1-$CE and ΔC, we see that $1-$CE is about 75 ppm larger than ΔC over the displayed cycles from Fig. 7. This difference resulting from the systematic measurement error described in Section III can lead to wrong assumptions regarding capacity degradation of the cell, and one should be aware of it when using the CE value for any further calculations.

V. CONCLUSION

As shown in Section II, the measurement precision of standard battery cyclers is not sufficient to accurately determine the CE of modern cells. For this purpose, more precise battery cyclers—like our in-house built measuring system—are necessary. Furthermore, in Section III, it is claimed that the CE value is misleading with respect to the actual capacity degradation because it consists only of some part of the damaging effects but also includes the reversible charge loss due to leakage currents. Therefore, ΔC measured with high precision should be used for the fast assessment of the cell degradation. The measurement results to support this claim were shown in Section IV, where it could be demonstrated that the measured capacity degradation (see Fig. 6) is consistent with the model (see Fig. 5). In the course of further research, an attempt will be made to split the capacity degradation up into its separate components: Charge capacity loss, discharge capacity loss, and leakage current (which exist according to Fig. 6). This would be an important tool in cell development to check

more quickly under realistic conditions whether a measure to increase the cell lifetime was successful.

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