FOPRA - 101 Lithium-Ion Batteries (LIB)

Lösch Augustin, Matthias Quintern, Bauer Lukas

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Contents

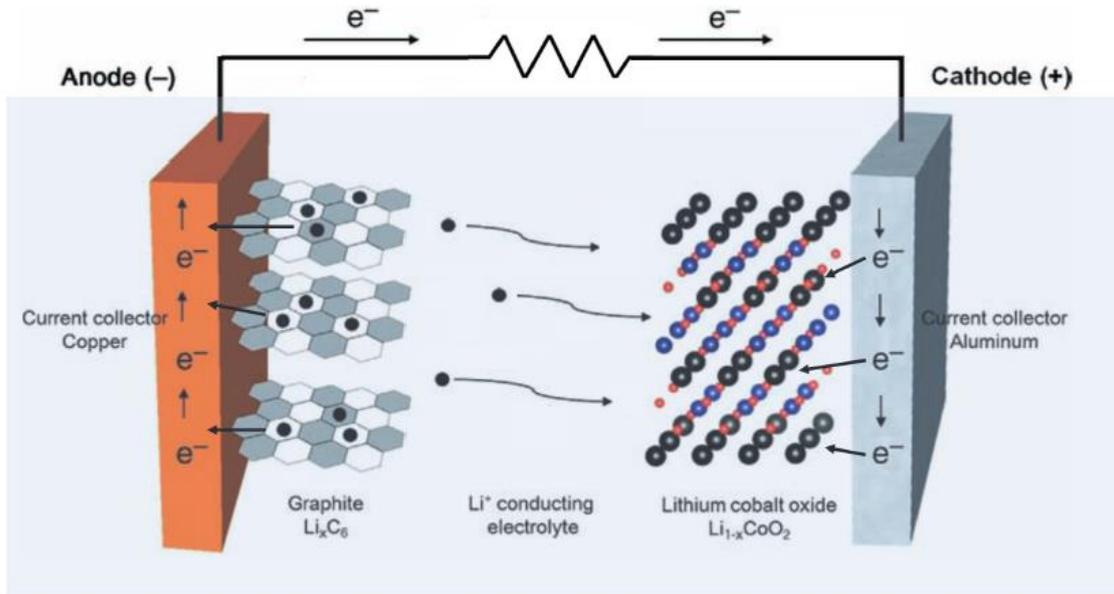# 1 Introduction

2 Theory

2.1 Fundamentals of a LIB

Figure 1: Schematic representation of a $LiCoO_2$/ graphite battery in discharge mode

Like most other Batteries a LIB consists of a cathode and an anode (the terms "anode" and "cathode" apply to the discharging process) soaked in an electrolyte with a separator (fig. (1)). In order for the battery to work well and safe the electrode active materials should have a high potential difference while also staying within the stability window. For the cathodes lithium-rich transition metals are used for which $LiCoO_2$ is common for example. The anode material is usually graphite as it is very cost-effective and increases the specific capacity of the cell. In order to make the usage of graphite possible, organic electrolytes have to be used which are non-aqueous to prevent an extreme reaction with lithium. Also a higher cell voltage can be obtained with non-aqueous electrolytes made from lithium-salts such as $LiPF_6$ dissolved in organic liquids like ethylene carbonate (EC) for example. In order for the battery to work well and safe the electrode active materials should have a high potential difference while also staying within the stability window and the electrolyte should only be permeable for the ions not the electrons. When charging and discharging the LIB, electrochemical reactions occur which are accompanied by a reversible (de)intercalation of lithium ions through the elektrolyte into the host electrode structures. As can be seen in figure (1) copper (anode) and aluminium (cathode) are used as current collectors because they provide better conductivity than the used active electrode materials and therefore ensure a higher and faster flow of electrons.

2.2 Charging and Discharging Process

The chemical process that takes place while charging and recharging is a redox reaction. A redox reaction is a sum of two reactions taking place at the same time and depend on each other. While charging the cathode is being oxidised. This means that electrons are removed from the electrode and travel through an external circuit towards the anode by an external circuit towards the anode. On the other hand the anode is being reduced. A reduction is more or less the counterpart of an oxidation, meaning the anode is taking up electrons. In the meanwhile the Lithium ions are wandering from the cathode through the separator of the battery to the anode where they are getting stored again. The process of storing the ions in the graphite is called intercalation. Which is the reversible inclusion or

insertion of a molecule (or ion) into layered materials with layered structures.

$$\text{Anode} \qquad\qquad\qquad\qquad \text{Cathode}$$

$$C_6 + x\,Li^+ + x\,e^- \rightleftharpoons Li_xC_6 \qquad\qquad LiCoO_2 \rightleftharpoons Li_{1-x}CoO_2 + x\,Li^+ + x\,e^- \qquad (1)$$

2.3 Coin-cell-type Electrochemical Half-Cell

In a battery both of the electrodes consist of active material. The performance of a battery is composed of the performance of various components. In order to find out the performance of a single electrode one uses the principal of a working and reference electrode (RE). The RE has the property that its potential is being constant throughout the experiment. This helps to get the electrochemical potential of the electrode, we try to examine, which we call from now on working electrode (WE). Such a configuration is called half cell. In order to achieve that one can either use a counter electrode (CE) to close the electric circuit or one could use an electrode with a very narrow potential for its electrochemical reactions both for RE and CE.
Usually coin cells are used for such kind of experiments.

3 Experimental Procedure

As this FoPra was held online, the experiment could not be done in person, but a video with the experimental procedure and excel files with the measured data were provided. In the video a calendered coin cell was built and later tested together with an uncalendered one. A short overview of the coin cell preparation that was shown in the video will be given in the following section.

3.1 Electrode Preparation

The Anode active material was prepared as a slurry using a mortar. For that a mixture of 95% graphite and 5% polyvinylidene fluoride (PVDF) which acts as a binding material was made. To turn it into a slurry n-methyl-2-pyrrolidone (NMP) with an approximate ratio of 5:4 (solid:liquid) was added and processed until the desired consistency was reached.
The slurry was then coated onto the current collector (copper foil) and dried on a hot plate in the fume hood to evaporate all the hazardous NMP solvent from the electrode.
After drying the electrode was punched into 12 mm circles in order to fit into the coin cell housing.

3.2 Coin Cell Assembly

The coin-cell assembly (2) was performed in a glove box because metallic lithium was used as counter and reference electrode and must be kept away from water and oxygen.
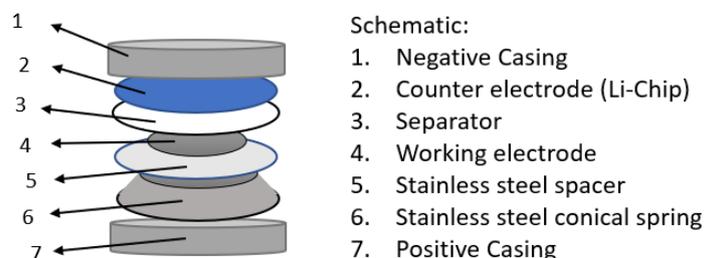

Figure 2: Schematic representation of the internal structure of a coin-cell

First a lithium chip that was scratched clean with a surgical blade was placed into the positive casing and a separator on top of it. Then the prepared working electrode was weighed in order to calculate the active material mass. Thereafter the electrolyte (120 µl 1 M LiPF$_6$ in EC:DEC (1:1)) was added

quickly as it evaporates fast and a spacer together with a conical spring was put on the electrode, followed by the positive casing to close the battery. After that the battery was put into the crimper and out of the glove box as it was ready for testing.

3.3 Testing Setup

The two coin-cells were tested by a potentiostat with a potential range of $0,05\,V - 1,40\,V$ vs Li. It was cycling the cells within the voltage range by constant-current techniques (galvanostatic mode). The current is set in terms of the so-called "C-rate", which is defined as C = current / capacity, [C] = 1/h. The following tests with different C-rates were made:

1. SEI formation: 3 cycles charge-discharge (C/10)

2. Stress preparation: 5 cycles charge-discharge (C/4)

3. Rate capability tests: 5 cycles charge-discharge by C/2, 1C, 2C, 4C and C/2 again (stability)

4 Data Evaluation and Results

Our task was it to generate some plots out of the given data. The generated plots are following:

- Charge-discharge curves for each setting

- Rate-capability plot

- Differential capacity (dQ/dE) vs potential for the different C-rates

Every plot was generated each for the calendered as well as the uncalendered halfcell.

4.1 Uncalendered Coin-Cell

First of all we began with looking into the data of the uncalendered battery.

4.1.1 Charge-discharge curves

All of the Charge-discharge curves (potential vs specific capacity) for each setting are shown in figure (3). In the SEI formation curves one can see that the first discharging cycle starts out at a potential of about $2,7\,V$ while the second discharging cycle already only starts at about $1,2\,V$. This is a clear indication of the SEI layer building up in the first (dis-)charging cycle. It is also clearly visible that the voltage drops a lot faster in the second discharging process and that after reaching a specific capacity of almost $500\,mAh/g$ on the fist discharge, the second second discharging process only reaches a specific capacity of almost $300\,mAh/g$.
The stress preparation curves (C/4) are quite similar to the last SEI formation cycle reaching a specific capacity of around $300\,mAh/g$ and a and a rapid drop in potential at the beginning.
Looking at the rate capability curves, one will notice that the higher the C-rate is set the lower the specific capacity gets. Going as far down as about $150\,mAh/g$ for a C-rate of 4C which is only half the capacity of that was reached in the the stress preparation cycles. The drop in potential is also getting more extreme as the C-rate increases.
When comparing the first C/2 cycle to the C/2 cycle after the three high C-rate cycles (C, 2C and 4C), one can see that the maximum capacity dropped a little in the second C/2 cycle.
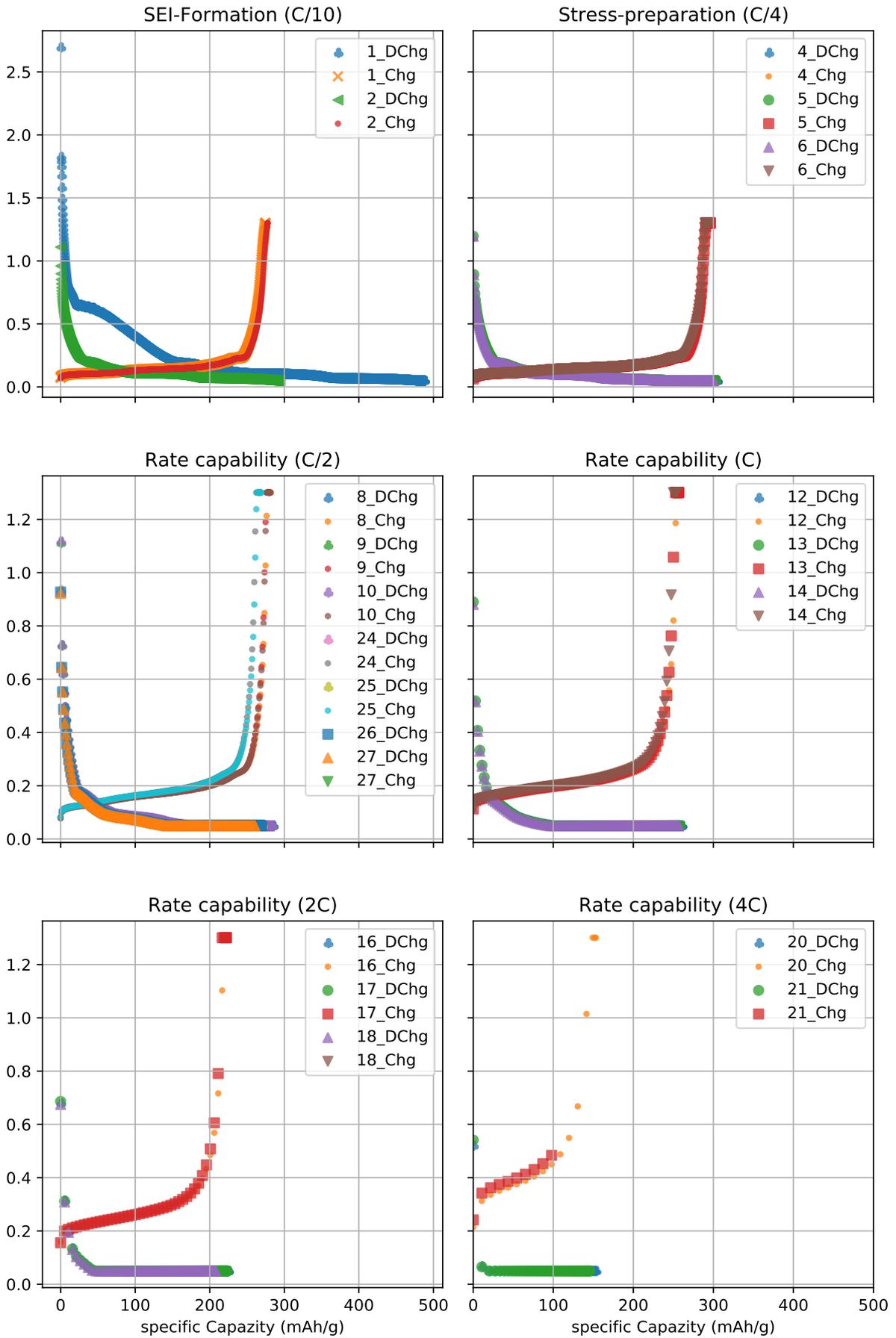
Figure 3: Charge-discharge curves (potential vs specific capacity) for each setting for the uncalendered cell

4.1.2 Rate capability

In figure (4) the specific capacity was plotted against the cycle showing the specific capacity for every C-rate and cycle that was run. After the SEI formation a clear trend is visible. The specific capacity drops with every cycle, even after consecutive cycles with the same C-rate. Thas means that even after SEI formation there are some processes in the battery either consuming Li^+ ions or hindering charge transport and (de-)intercalation. When the C-rates increases the specific capacity decreases depending on how great the increase in C-rate was. This indicates a direct dependency of the capacity on the C-rate.
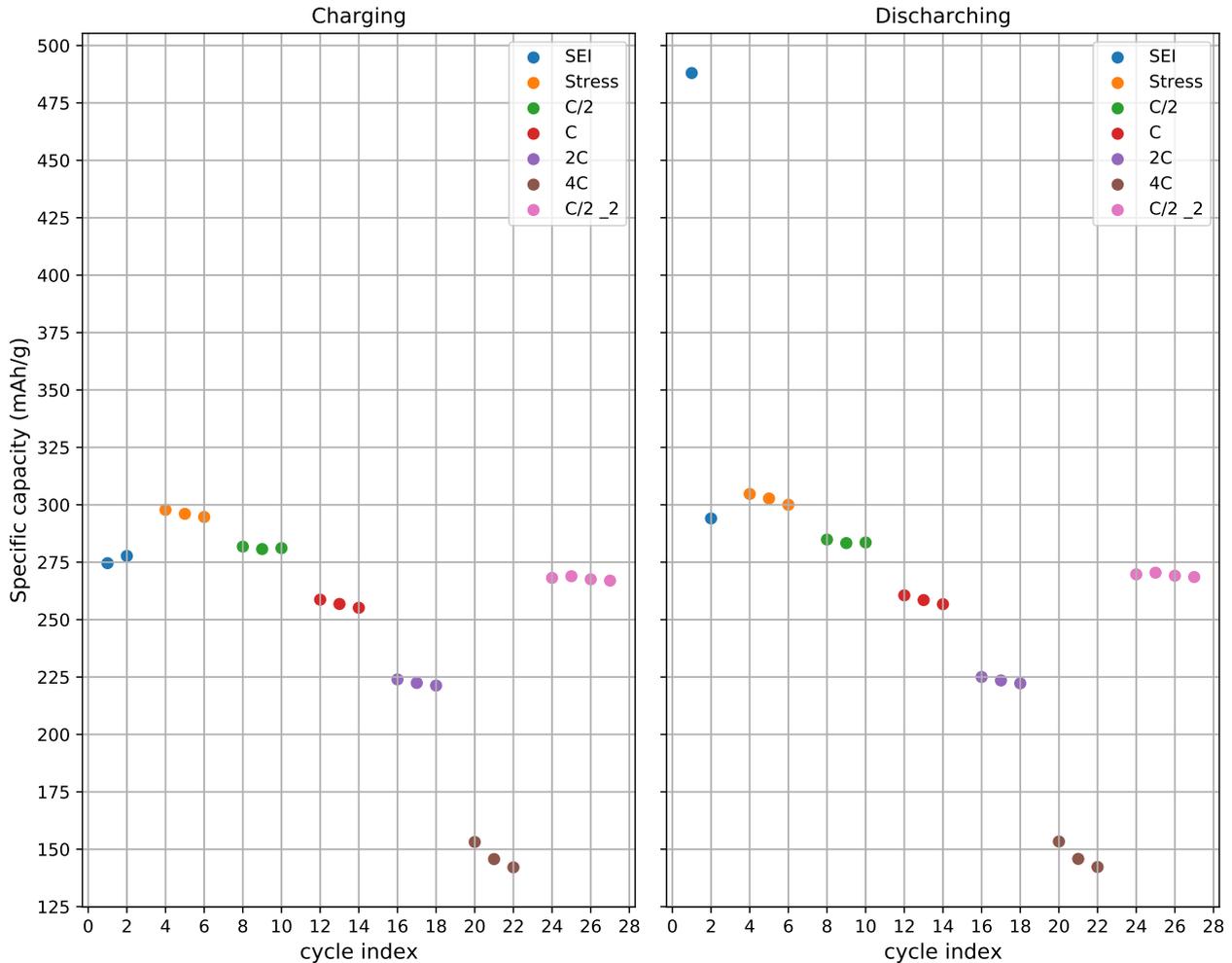

Figure 4: Specific capacity vs C-rate for the uncalendered cell

This diagram (figure 4) also confirms the previous observation that the specific capacity of the C/2 cycles after the high C-rate cylcles is quite a bit lower than the capacity of the C/2 cycles before the high C-rate cylcles.
Another interesting point is that the specific capacity of the stress preparation cycles is - except for the first discharging process - higher than the specific capacity of the SEI formation cycles although the C-rate is significantly higher in the stress preparation.

4.1.3 Differential capacity (dQ/dE)

The differential capacity is used to see how steady the dis-/charging processes proceed. To calculate the differential capacity the charge difference of cycle two to cycle one was calculated and divided by the difference of the Voltage of cycle two to cycle one. In figure (5) the differential capacity was plotted against the potential vs Li/Li$^+$ where only the area of interest is shown to make it more visible, because the differential capacity does not change anymore over the last section of the potential. In all the other differential capacity graphs the same focused area is shown out of the same reasons.
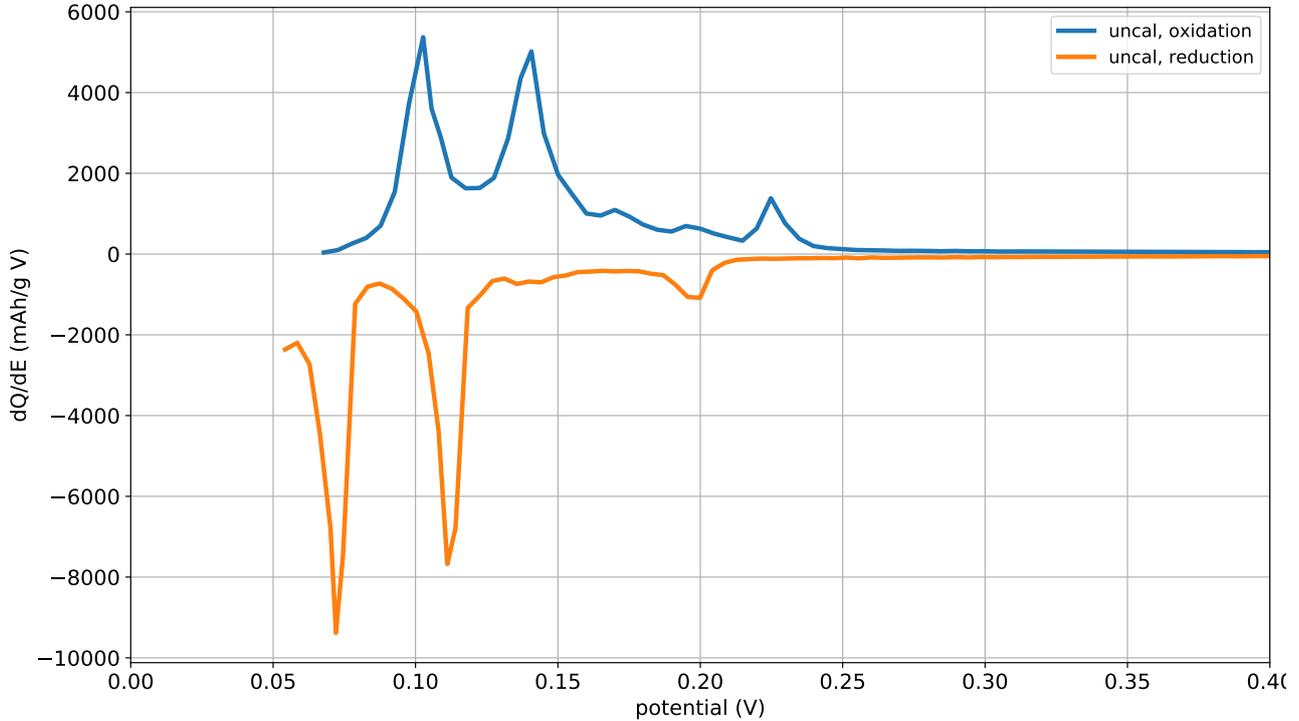

Figure 5: differential capacity (dQ/dE) vs potential for the uncalendered cell

As one can see in the plot, the differential capacity for both the oxidation and the reduction shows some irregularities that can be interpreted in a way that the oxidation process does not proceed very steady in the beginning.

4.2 Calendered Coin-Cell

With the calendererd halfcell we did the same analysis as before with the uncalendered one.

4.2.1 Charge-discharge curves

The course of the graphs does not change much, except that the differences of the respective cycles, in contrast to the uncalendered ones, are much smaller. The most obvious difference is to be seen in the rate capability of C/2. There one can observe that there is no visible difference in the specific capacity before and after the heavy load of 4C, whereas the uncalendered one had a significant change in the specific capacity. So one can say the specific capacity stays approximately same for this rate. The other major change is that in the SEI-formation from the 1st to the second discharge cycle, the difference in specific capacity is much smaller.
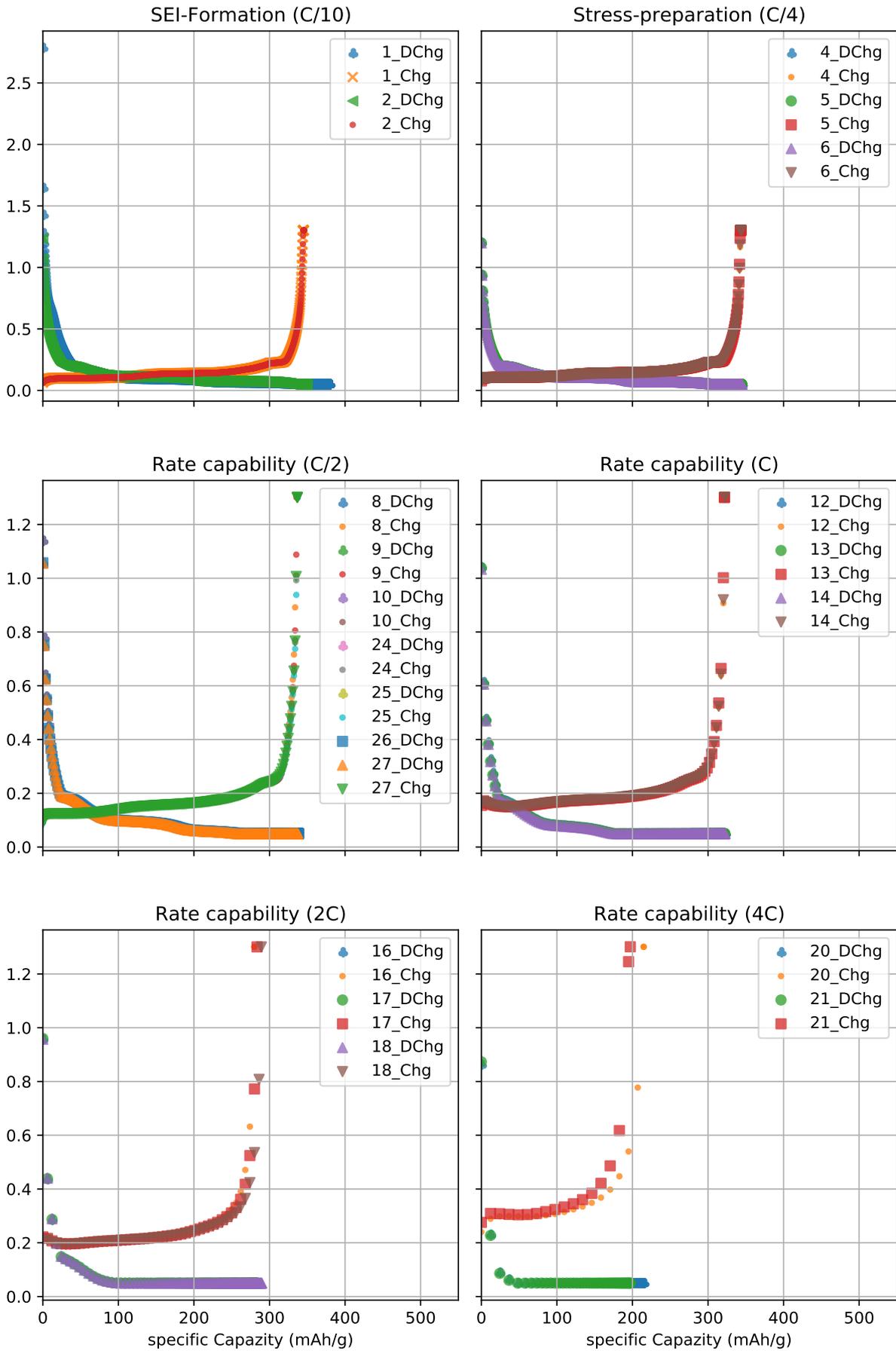
Figure 6: Charge-discharge curves (potential vs specific capacity) for each setting for the calendered cell

4.2.2 Rate capability

In figure 7 on sees a similar graph than for the uncalendered one before (see figure 4). Whereas the capacity decreases constantly for different C-rates on can observe that within the consecutive measurements of a certain C-rate the specific capacities start to increase.
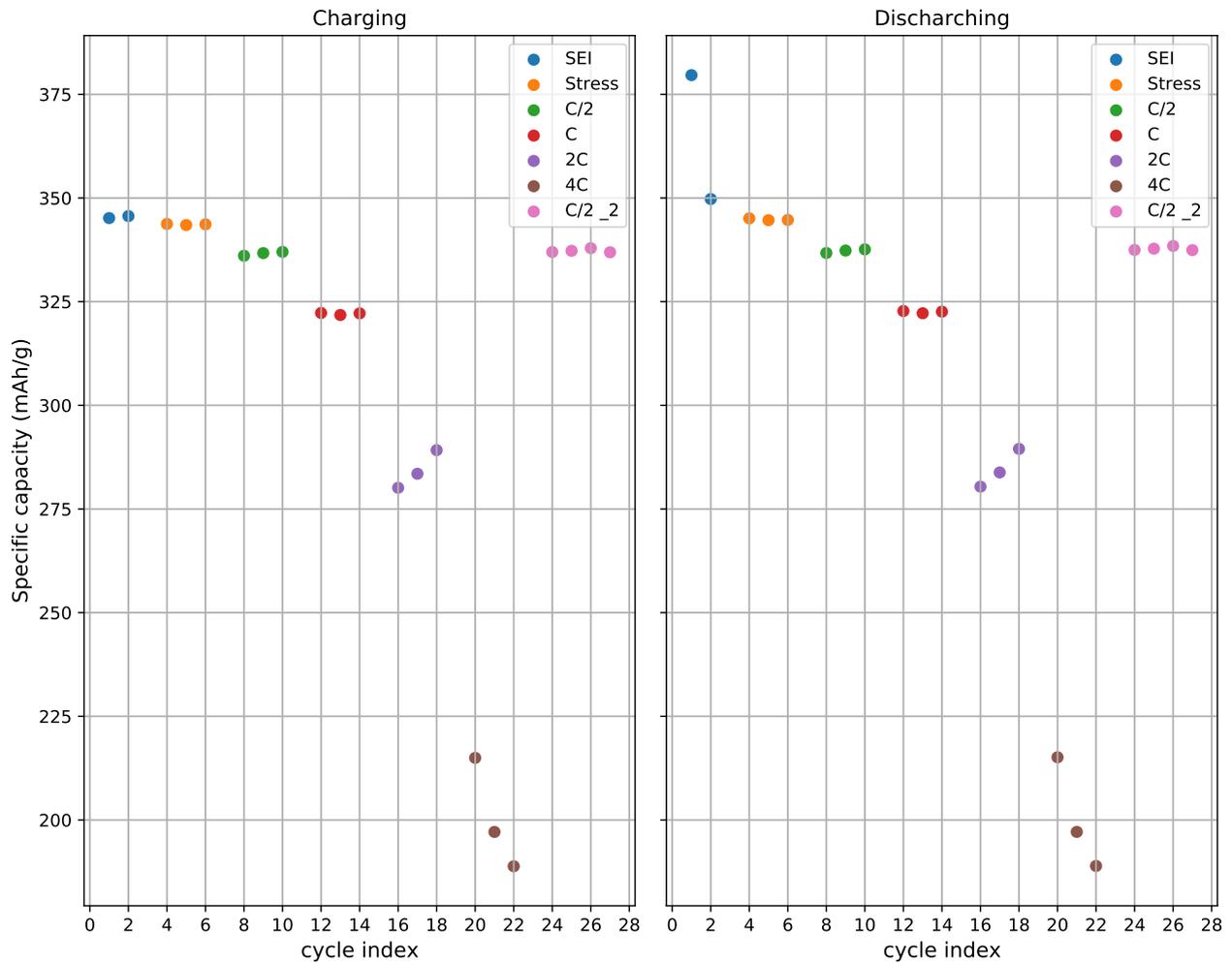

Figure 7: Specific capacity vs C-rate for the calendered cell

4.2.3 Differential capacity (dQ/dE)

The differential capacity for the calendered cell is shown in figure (8) plotted against the potential.
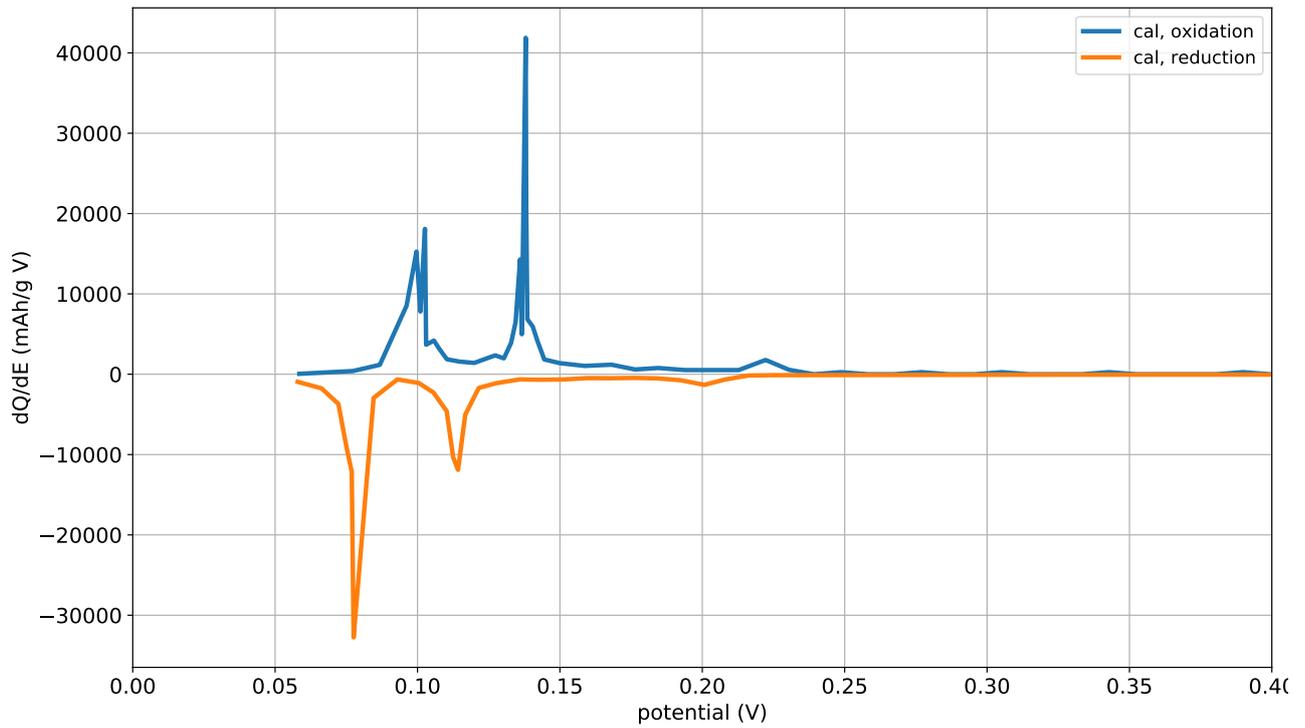
Figure 8: differential capacity (dQ/dE) vs potential for the calendered cell

Similar to the uncalendered cell we see irregularities in both processes.

4.3 Comparison of the two coin-cells

4.3.1 Charge-discharge curves

When one compares both half-cells one notes significant differences between them. Whereas the measured potential of the cells reach roughly the same values the values for the specific capacity differ strongly. The calendered one is far superior than the uncalendered half-cell throughout all cycles, in concern of specific capacity.

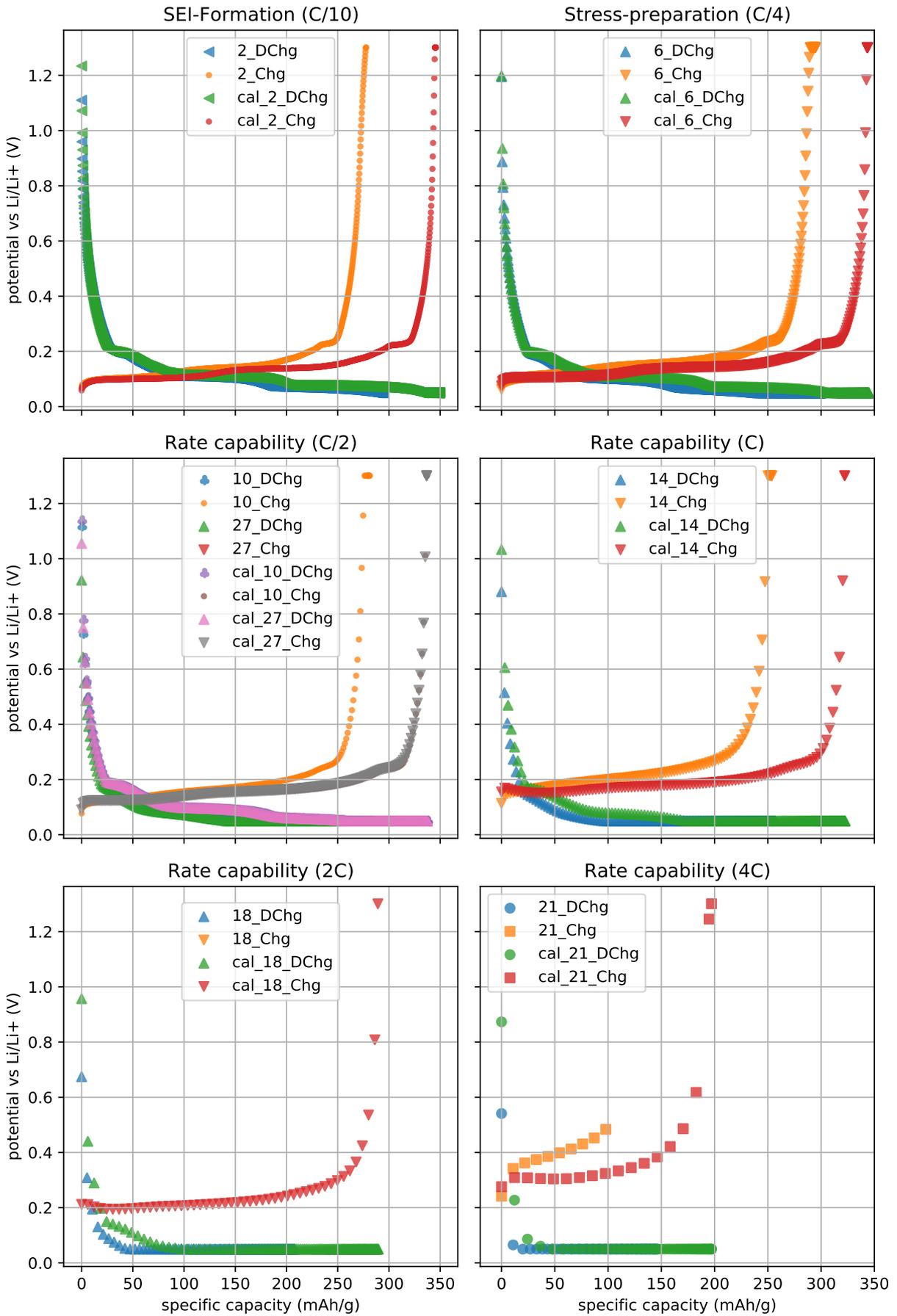Figure 9: Comparison of the cells: Charge-discharge curves (potential vs specific capacity) for each setting

4.3.2 Rate capability

When one overlays the scatter plots for the uncalendered and calendered half cells one can clearly obtain that the calendered one has from start to end a much higher specific capacity throughout all cycles and even the difference of both C/2 rates is for the calendered one even smaller. The most striking difference is that in the 2C rate the specific capacity of the calendered half cell increased significantly throughout this rate, whereas the uncalendered one constantly decreased its value of its specific capacity.
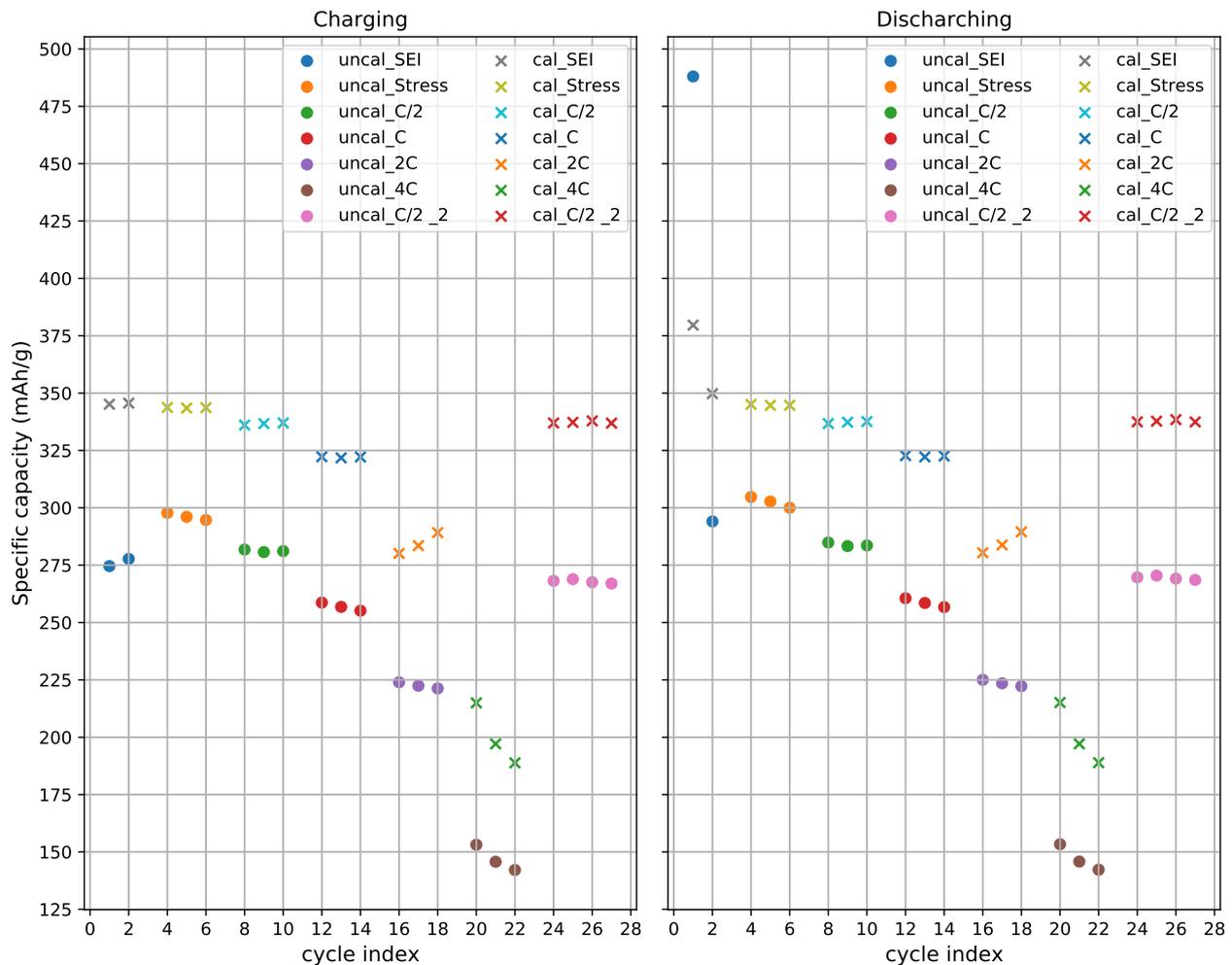

Figure 10: Comparison of the cells: specific capacity vs C-rate

4.3.3 Differential capacity (dQ/dE)

In figure (11) the differential capacity for both cells was plotted against the potential in order to compare the two.
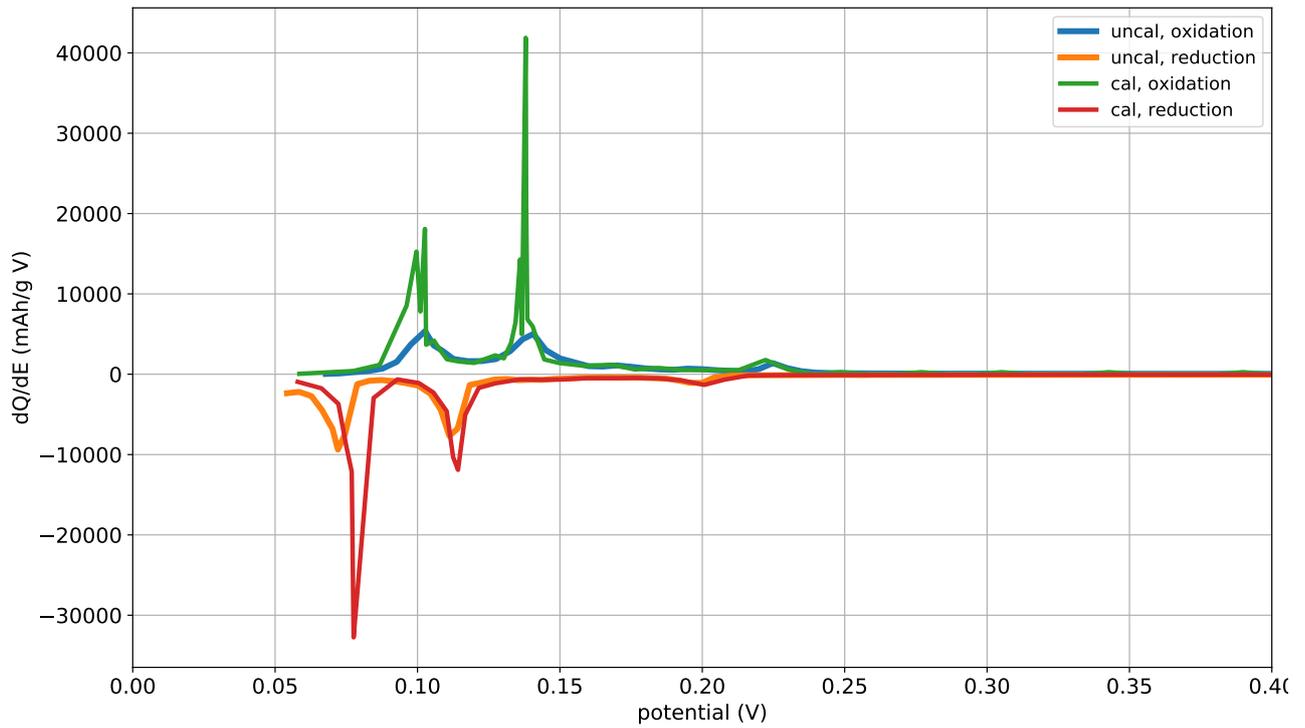
Figure 11: Comparison of the cells: differential capacity (dQ/dE) vs potential

The comparison graph shows that both cells have irregularities in their respective differential capacity and also the area in which they show these irregularities are roughly the same. This direct comparison also shows that the calendered cell has stronger irregularities than the uncalendered one. The reason for that could be the lower porisity of the calendered cell. The (de-)intercalation processes then cannot proceed as steady as in the uncalendered one, because the lithium ions are more restricted in their movement.

4.4 Conclusion

In summary, the specific capacitance of the half-cell depends strongly on the C-rate at which it is charged or discharged. Furthermore, it makes a big difference in terms of specific capacitance and longevity whether the graphite layer has been calendered or not. In both categories, the calendered one has better values over a longer period.

5 Questions

1. **What is a half-cell and why is this configuration used in the coin cell? Compare the setup to a three-electrode configuration.**
   In a half cell the potential of the working electrode is measured against a reference electrode whose potential should remain constant throughout the measurement in order to correlate the acquired voltage profile to the electrochemical potential of the working electrode alone. The reason for this is that the voltage response of a full-cell represents on the combined behaviour of both electrodes, which makes it impossible to investigate the performance of only the cathode or the anode.
   Keeping the potential of the reference electrode (RE) constant can be achieved by either installing a separate counter electrode (CE) or using an electrode with a very narrow potential window for its electrochemical reactions as both RE and CE.
   The Coin Cell uses a two electrode setup with Lithium metal as both RE and CE because of the smaller form factor that is necessary to fit everything in a small coin cell.

2. **What are the differences between the two coin-cells?**
   One of the coin-cells has been calendered, which means it has been pressed to a certain the porosity. It has more C-atoms per volume than the other cell.

3. **Why do we need to prepare the cell in the glovebox? How might battery companies do that at large scale?**
   The metallic lithium, which is used is used as counter and reference electrode, must be kept away from water and oxygen because of the rigorous interaction with water and oxidisation.
   Battery companies can do this at large by having their assembly machines inside a sealed space, which is evacuated or filled with noble gas.

4. **What is the respective active mass of our samples? How is the specific capacity obtained?**
   The active mass of the cell is only the mass of the graphite portion. Therefore, we have to have to subtract the weight of the copper current collector and account that only 95% of the remaining mass is graphite: $m_{\text{active}} = (m_{\text{total}} - m_{\text{Cu}}) \cdot 0.95$. For the calendered cell we obtained $m_{\text{active,cal}} = 4{,}104 \, \text{mg}$ for the calendered cell and $m_{\text{active,uncal}} = 2{,}679 \, \text{mg}$ for the uncalendered cell.
   With the active mass, we can obtain the specific capacity by dividing the measured capacity through the active mass: $C_{\text{spec}} = \frac{C_{\text{measured}}}{m_{\text{active}}}$.

5. **What are the electrochemical oxidation and reduction equations of the graphite half-cells (including the lithium counter electrode)? Which direction refers to charging and discharging?**
   The redox equation at the graphite electrode is:

   $$\text{C}_6 + \text{x Li}^+ + \text{x e}^- \rightleftharpoons \text{Li}_x\,\text{C}_6, \tag{2}$$
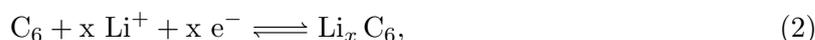
   where ($\longrightarrow$) applies to the charging (reduction) and ($\longleftarrow$) to the discharging (oxidation) process.
   At the lithium counter electrode, the equation is:

   $$\text{x Li} \rightleftharpoons \text{x Li}^+ + \text{x e}^-, \tag{3}$$

   where ($\longrightarrow$) applies to the charging (oxidation) and ($\longleftarrow$) to the discharging (reduction) process.

6. **Calculate the theoretically expected specific capacity of the described reaction and compare with your results.**
   The theoretical specific capacity is given by

   $$C_{\text{m,theo}} = \frac{F \cdot n_{Li}}{M_{\text{active}}}, \tag{4}$$

where $F = 26\,801\,\mathrm{mAh/mol}$ is the Faraday constant, n_{Li} is the number of transferred electrons and M is the molecular mass of the active electrode material. Here we have $M(\mathrm{C_6}) = 72{,}07\,\mathrm{g/mol}$ and $n_{\mathrm{Li}} = 1$, so using formula (4) we obtain $C_{\mathrm{m,theo}} = 371{,}9\,\mathrm{mAh/g}$.

The measured specific capacity for the uncalendered cell varies from $300\,\mathrm{mAh/g}$ for low C-rates down to around $140\,\mathrm{mAh/g}$ while for the calendered cell it varies from $350\,\mathrm{mAh/g}$ for low C-rates down to around $180\,\mathrm{mAh/g}$. That means that the theoretical value could not be reached for both cells, but the calendered comes very close.

7. **Why are the cells not cycled to a battery voltage of 0V (complete discharge)?**
   The anode potential increases abnormally during overdischarge; thus, the Cu current collector of the cell is oxidized to Cu2+. Simultaneously, over-deintercalation of lithium at the anode during overdischarge causes decomposition of the solid electrolyte interface (SEI) and the decomposition of SEI generates gases, including carbon dioxide. New SEI films form on the anode when the cell is recharged. The growth of the SEI films can lead to degradation of the electrochemical charge transfer processes in the electrodes, as indicated by the impedance increment at low frequency. Moreover, the morphology of the cathode materials also changes during overdischarge. The side reactions that occur during extreme overdischarge result in the solid-state amorphization of the transition metal compounds. The changes in the morphology of the components within the lithium ion battery lead to capacity degradation. The dissolution of the Cu collector also affects the lifespan of the battery [1].

8. **What is the Solid-Electrolyte-Interphase (SEI) and why is it both detrimental and protective to the battery?**
   The Solid-Electrolyte-Interphase is a layer between the anode and the electrolyte that forms when the first come in contact with each other. The SEI limits the rate at which lithium ions can travel from the electrolyte to the anode, thereby increasing the lifetime of the battery and protecting it from overheating. If the SEI grows too thick, it can prevent lithium ions from passing through, making the battery non-functional.

9. **What is the role and use of the electrolyte? How does it contribute to the SEI formation?**
   The electrolyte must be an electric insulator and a ionic conductor, so that the electrodes exchange charge within the battery only through the lithium ions, but not through electrons.
   In general, SEI growth results from irreversible electrochemical decomposition of the electrolyte, which competes with the desired faradaic half-cell reaction at the electrode surface. In the case of Li-ion batteries, SEI is formed at the negative electrode because typical electrolytes are not stable at the operating potential of this electrode during charging. The product of this decomposition forms a solid layer (LiF, Li2O, LiCl, Li2CO3 compounds) on the surface of the active material [2].

10. **Discuss the SEI formation based on your graphs and calculate the initial coulombic efficiency**
    In the graphs (3) and (6) it is visible that after the SEI formation the capacity decreased quit a lot as described before. The coulombic efficiency was calculated using formula (5).

$$\text{coulombic efficiency} = \frac{C_{\mathrm{discharged}}}{C_{\mathrm{charged}}} \cdot 100 \tag{5}$$

For the uncalendered cell we obtained a value of 105,9 and for the calendered one a value of 101,2.

11. **Why is an organic electrolyte used? Could an aqueous electrolyte be used in this configuration as well (e.g. 1M NaCl in water)?**
    With an aqueous electrolyte, one can only obtain a cell voltage 1-2 V, whereas an organic electrolyte can achieve a cell voltage of 3-4 V. An organic electrolyte is also advantageous because it allows the use of graphite as anode material, which is very cost effective.

12. **Why can a battery not be cycled at super high rates? What might limit the rate capability? How is it reflected in our two different coin cells?**
Possible rate limiting processes at the electrode level are electron transport in the solid phases, including contact resistances in the composite and at the current collector interface, ion transport in the solid and liquid phases, such as solid-state diffusion limitations or SEI resistance, and the charge transfer reaction at the solid/electrolyte interface. Under load, any hinderance of these transport processes contributes to the overvoltage necessary to drive the cell reaction. The overvoltage increases with increasing current, narrowing the voltage window, and reducing the attainable capacity. Thus, the more incisive the specific kinetic and transport limitations, the higher the rate performance restrictions [3].
The decrease in capacity at higher currents is clearly visible in the specific capacity vs C-rate plots (figures 4, 7 and 10).

13. **Compare the obtained half-cell voltage at the different C-rates to the previously measured open-circuit potential. Why do they deviate?**
The open circuit potential that was measured in the video was 2,8 V whereas the obtained half-cell voltage at the different C-rates dropped to around 1,3 V after the first SEI- formation circle and remained nearly constant at that value for the entire experiment.
So reason for the deviation seems to be the SEI-formation.

14. **How is the energetic efficiency of the cell influence by the C-rate?**
A higher C-rate leads to more heat generated inside the battery, which will accelerate degradation and reduce energy efficiency.

15. **Why can Li metal not be used as anode in commercial organic electrolyte batteries? What is the idea behind the so called "all solid-state-battery"?**
Li metal cannot be used as anode in commercial organic electrolyte batteries, because of the intrinsic properties of lithium metal. Lithium anode has many notorious problems in the process of charging/discharging: The formation of dendrites, the corrosion of lithium, dead lithium, and volume expansion. These problems will lead to severe capacity loss and even explosion of lithium metal batteries after long operation [4].
The idea if an "all solid-state-battery" is to use only solid components, including a solid electrolyte. This would reduce the size and mass of the battery and might also make it safer.

16. **Imagine you build a full-cell battery with graphite as the anode and NMC as the cathode: What would be the expected open-circuit voltage and energy density?**
A battery using NMC as cathode can achieve a open-circuit voltage of around 3,8 V. The energy density varies from 180-280 Wh/kg, depending on which type of NMC is being used [5].

A   Appendix

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