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# Lithium Ion Battery

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# 1 Introduction

In this experiment we produced a lithium-ion battery in a half-cell configuration and analysed how the capacity and the energy are changing between different charge-discharge cycles. The analysis of the Charge-Discharge curves give us an inside on what is the most optimal procedure to build a LIB and how the C-Rate influences the capacity of the battery. We will find out that the calendaring process is crucial to building better LIBs.

## 2 Theory

### 2.1 Fundamentals of a Lithium-ion battery (LIB)

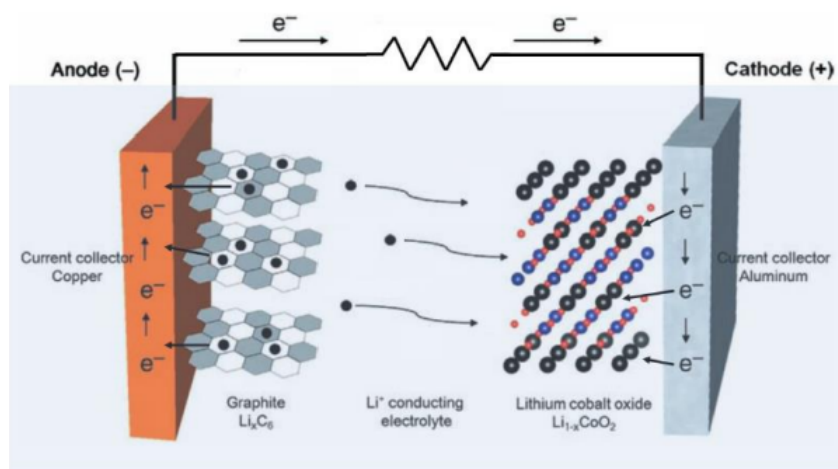


Figure 1: Schematic representation of a LIB in discharge mode with graphite as the anode and  $LiCoO_2$  as the cathode[1].

To understand how a LIB is working one can take a look at figure 1 where a basic construction of a battery is shown. On the side of the cathode we can find metallic Lithiumoxid. To charge the battery we use a power source to pull out the electrons from the anode (OX) and create a current towards the side to the anode (RED). This is a Redoxreaction where one electrode gets oxidized (OX) while the other one gets reduced (RED). Due to the increasing potential the Li-ions start to pass through the electrolyte towards the other side and are stored in the graphite layers. This process is called intercalation of the Li-ions and is going further until the battery is fully charged.

To discharge the battery we have to remove the power source. Now due to the developed electrochemical potential the Li-ions are starting to go back through the electrolyte to get in a state which is stable. Now also the electrons start to go back over the circuit until the battery is fully discharged.

However in this experiment we are only using a Half-Cell setup. With this setup it is possible to analyse just one side of the battery (in our case the anode with the graphite) and see how much of the potential is contributed by it. Here we can use Li as CE and RE because the potential remains mainly constant over the charge-discharge cycle which is a characteristic we need for a representative reference electrode. In figure 2 we can see the internal structure of such a half-coin-cell.

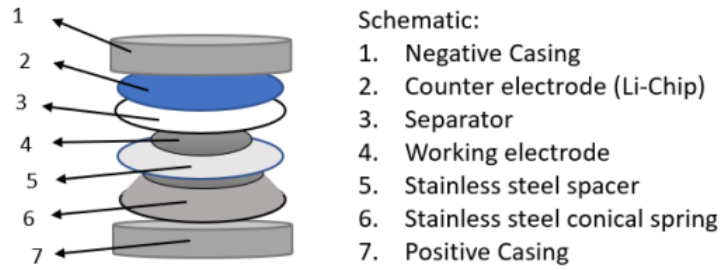


Figure 2: Internal structure of a coin-cell.

### 3 Experimental Procedure

#### 3.1 Electrode preparation and coin cell assembly

First we need to prepare the electrodes of our coin cells. To prepare the graphite anode, we combine

- 95% graphite (solid),
- 5% polyvinylidene fluoride (solid; binding material), and
- n-methyl-2-pyrrolidone (liquid)

with an approximate ratio of 5:4 solid to liquid and mix it with a mortar until we get a "slurry-like" consistency.

This slurry then gets pasted and evenly distributed on a copper-foil, which acts as a current collector.

In a fume hood, we let the copper foils with the slurry dry out for 10 to 20 minutes. This process can be further accelerated by putting the copper foils on a hot plate covered with aluminium.

Lastly, the electrodes will be punched into 12 mm circles so they can fit in the metal case of the battery.

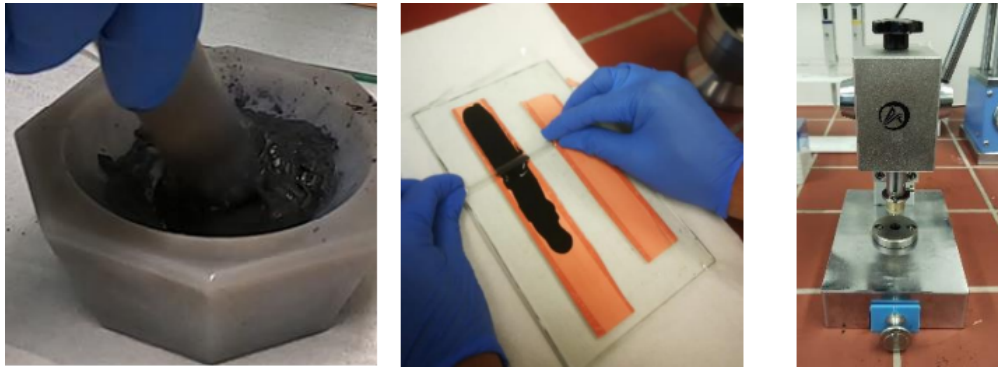


Figure 3: Pictures of the electrode preparation with the slurry preparation (left), slurry coating (middle) and the punching (right)[1]

Next, we assemble our coin cells according to figure 2, for which we have to keep the following points in mind. Since we are handling metal lithium, we have to assemble the coin cell in a oxygen free space and carefully scratch the surface of the metal with a clean surgical blade, the lithium will act as a counter and

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reference electrode in the half cell. Also, the previously prepared electrode has to face towards the separator with its active side. Additionally we have to act fast after adding the electrolyte since it evaporates fast. After checking if the cell potential is around the expected value, the cell is ready for testing.



Figure 4: A Glovebox (left) with an inert atmosphere to allow the safe and non-corrosive handling of metallic lithium, and a battery tester (right)

### 3.2 Testing Setup

The coin-cells are tested by the potentiostat in figure 4. Here we apply constant-current (set in terms of C-Rate [1/h]) techniques and cycle both battery cells in the potential range 0.05 V to 1.4 V vs.  $Li$  for every experimental setup. We collect data for charge-discharge curves in

- SEI formation for two cycles with  $C/10$ ,
- stress preparation for 3 cycles with  $C/4$ , and
- rate capability test for 3 cycles each with  $C/2, 1C, 2C, 4C$  and again  $C/2$  to test stability.

## 4 Analysis & Results

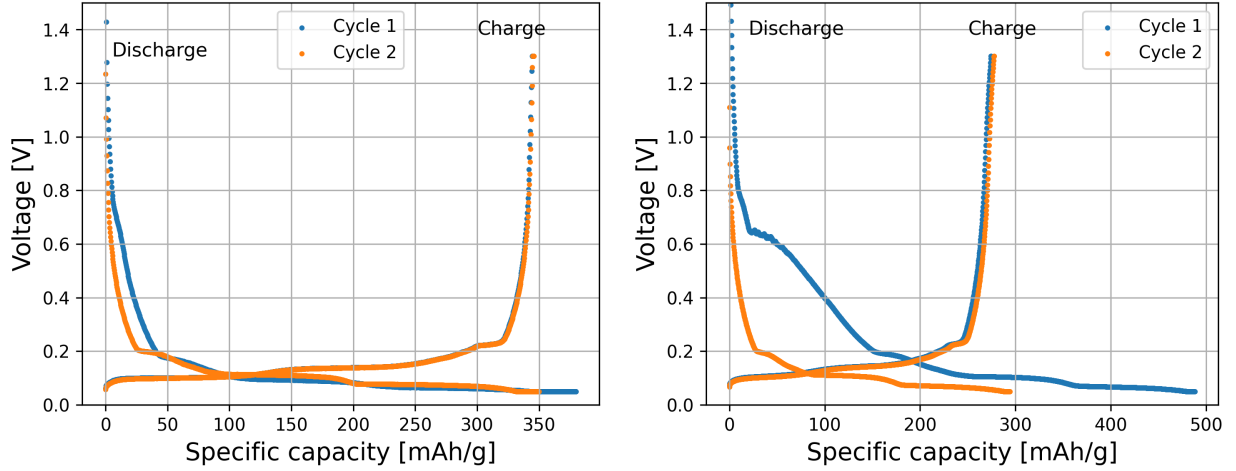


Figure 5: Charge-Discharge curves for a calendared(left) and uncalendered(right) coin cell in the SEI formation with C-Rate  $C/10$

As shown in figure 5, after SEI formation the charge - discharge curves in stress preparation don't differ in both cycles. However the calendaring affects a lot in specific capacity, with the calendared cell showing almost twice as much maximum specific capacity as the uncalendered cell. This phenomenon is less profound in rate capability test.

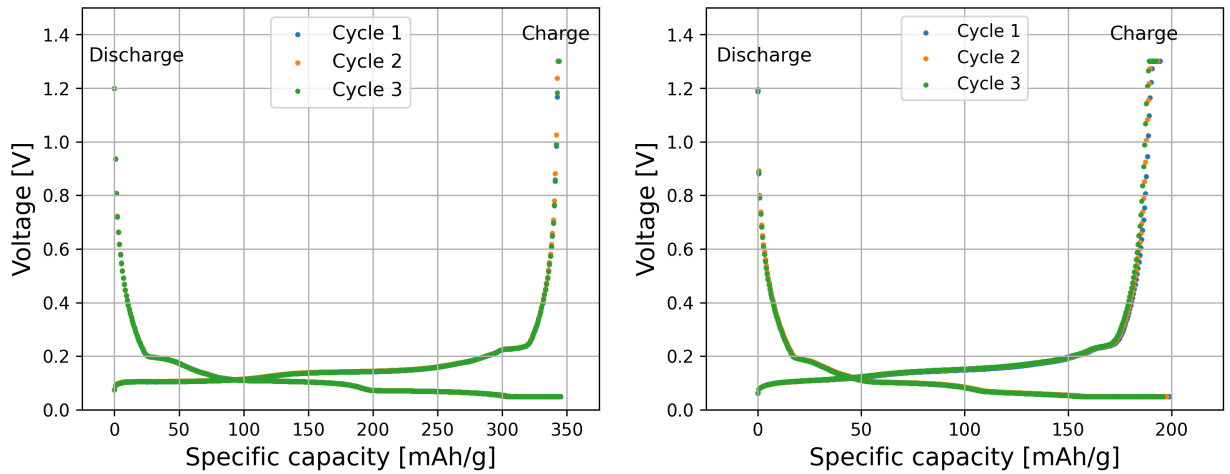


Figure 6: Charge-Discharge curves for a calendared(left) and uncalendered(right) coin cell in the stress preparation with C-Rate  $C/4$

One Interesting observation is that the uncalendered cell showing almost overall higher specific capacity

in rate stability test than in stress preparation process. The discharging process of the first cycle even reaches theoretically impossible levels of specific capacity.

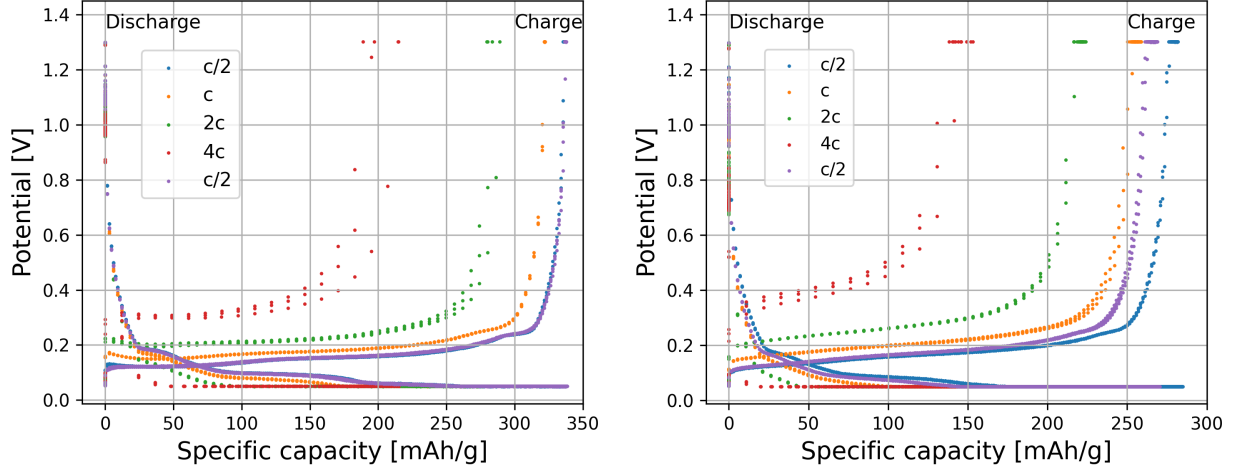


Figure 7: Charge-Discharge curves for a calendered(left) and uncalendered(right) coin cell in the rate capability test

As we can see in figures 7 and 8, with increasing charging rate, the maximum specific capacity decreases, especially rapidly from 2c to 4c, as well as the values differ more from each cycles. While charging with 4c rate the cell reaches its full potential with around half of the maximum capacity. The calendaring certainly help the battery keeping its maximum specific capacity after high rate charging. As shown in figure 8, the maximum capacity of uncalendered cell decreases around 8% after the test. Overall the discharging process is less affected by charging rate, cycles or calendaring.

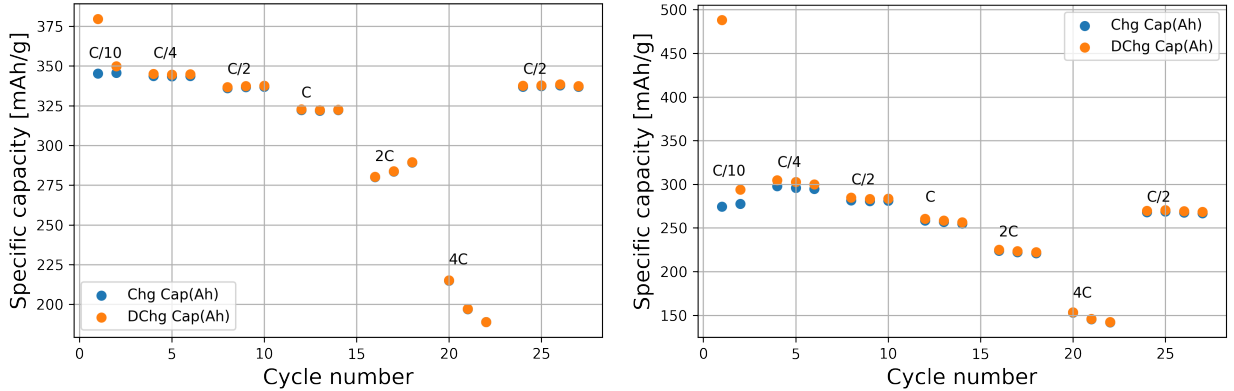


Figure 8: Specific capacity vs. cycle number for a calendered(left) and uncalendered(right) coin-cell in the rate capability test

In figure 9, the differential capacity is plotted against the potential. The oxidation process is plotted extra with negative sign. Just as previous observation, the cycle number doesn't affect the much of the character

of the calendered cell. For the uncalendered cell, in the second reduction, namely charging cycle, there is a clear decrease of the differential capacity within the low potential range. For the discharging process, both stay uninfluenced by cycle number, whereas the uncalendered cell owns a slightly minimum value.

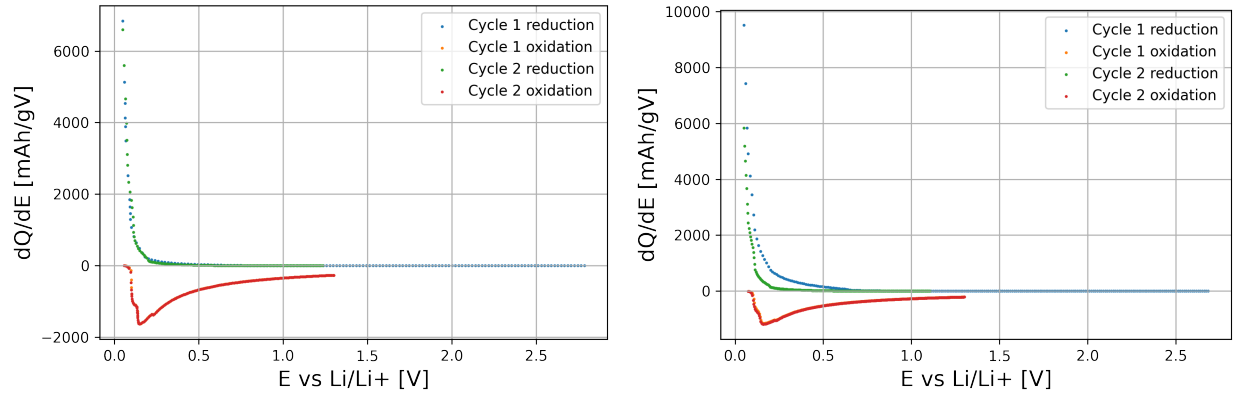


Figure 9: Differential capacity vs. potential for a calendered(left) and uncalendered(right) coin-cell for different cycles

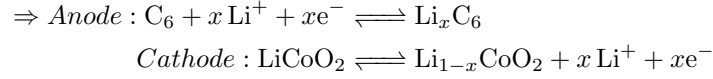
So far, we can conclude that calendering help increasing the overall capacity and longevity in regard to fast charging.

## 5 Short 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.  
 $\Rightarrow$  A half-cell is an open circuit 'two-electrode configuration', consisting a working electrode and a reference electrode, which has constant electrochemical potential at lower current. The three-electrode configuration contains additional counter electrode, which close the circuit and maintains constant interfacial potential regardless of current. In the coin cell it is basically a three-electrode configuration with Lithium metal working both as reference and counter electrode. The half-cell configuration enables the measurement and control of the potential of the working electrode.
2. What are the differences between the two coin-cells?  
 $\Rightarrow$  The graphite slurry of one of the both coin-cells is being calendered to reduce and reach certain porosity.
3. Why do we need to prepare the cell in the glove box? How might battery companies do that at large scale?  
 $\Rightarrow$  Lithium reacts intensely with water, releasing flammable Hydrogen gas and heat. For safety, the glove box in the lab is filled with Argon, which is an inert gas. For large scale production, we consider Nitrogen to be an considerable substitute for better cost efficiency.
4. What is the respective active mass of our samples? How is the specific capacity obtained?  
 $\Rightarrow m_{cal} = 4.104\text{mg}$ ,  $m_{uncal} = 2.679\text{mg}$ . The specific capacity is capacity divided by the active mass.



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5. What are the electrochemical oxidation and reduction equations of the graphite halfcells (including the lithium counter electrode)? Which direction refers to charging and discharging?



From left to right refers to charging and right to left is discharging process.

6. Calculate the theoretically expected specific capacity of the described reaction and compare with your results.  
 $\Rightarrow$  Each  $\text{C}_6$  cyclic compound can store exactly one electron in the intercalation process, which is why the specific capacity of the reaction is,

$$\frac{e}{m(\text{C}_6)} \approx 371.90 \frac{\text{mAh}}{\text{g}}.$$

The SEI formation and growth consumes active  $\text{Li}^+$ -ions and electrolyte material which in return lowers the specific capacity of the LIB [2]. This explains the difference between the measured values and the theoretical value.

7. Why are the cells not cycled to a battery voltage of 0V (complete discharge)?  
 $\Rightarrow$  When discharged below its safe low voltage some of the copper in the anode copper current collector can dissolve into the electrolyte. The copper ions then in turn can stick on to the anode during charging by chemical reduction and cause dendrites. The dendrites might cause a short circuit inside the battery.
8. What is the Solid-Electrolyte-Interphase (SEI) and why is it both detrimental and protective to the battery?  
 $\Rightarrow$  The SEI is a passivation layer formed on the electrode surfaces from decomposition products of electrolytes. It allows  $\text{Li}^+$  transport and blocks electrons in order to prevent further electrolyte decomposition and ensures continued electrochemical reactions [2]. Because of the SEI, LIBs have a higher lifetime and better efficiency.
9. What is the role and use of the electrolyte? How does it contribute to the SEI formation?  
 $\Rightarrow$  The electrolyte is in charge of conducting  $\text{Li}^+$ -ions from one electrode to the other, which is crucial for the electrochemical reactions at the anode and cathode, and preventing unwanted currents flowing between the electrodes.. In non-aqueous electrolytes a layer of solid electrolyte (about 1 nm thickness) forms on the surface of the anode.
10. Discuss the SEI formation based on your graphs and calculate the initial coulombic efficiency.  
 $\Rightarrow$  As figure 5 and the calculation below the growth of the SEI is indicated by the growth of the capacity and the growth of the coulombic efficiency after each cycle.

$$CE_{cal}^{Cycle1} = \frac{\text{Charging capacity}}{\text{Discharging capacity}} \approx 90.9192\%$$

$$CE_{cal}^{Cycle2} \approx 98.8234\%$$

$$CE_{uncal}^{Cycle1} \approx 56.2647\%$$

$$CE_{uncal}^{Cycle2} \approx 94.4490\%$$

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11. Why is an organic electrolyte used? Could an aqueous electrolyte be used in this configuration as well (e.g. 1M NaCl in water)?  
⇒ The SEI doesn't form on the electrodes in aqueous electrolytes, meaning the electrolyte will partake in the electrochemical reaction and decompose. Water will then split into hydrogen and oxygen, which blows up the battery cell.
  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?  
⇒ To cycle at a high rate means that the conductivity has to be really good. However the ion-conductivity is a lot slower than it is from the electrons which limits the rate. Also the speed of the intercalation or REDOX reaction itself is limited like any electrochemical reaction.
  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 is 2.8112V for calendered cell and 2.6950V for uncalendered cell. Undergoing charge-discharging-process, the maximum potential detected is 1.30V for both cells. OCV is the potential for battery under negligible light load, whereas the potential of 1.30V is under the load of potentiostat.
  14. How is the energetic efficiency of the cell influence by the C-rate?  
⇒ In figure 7 we can see that the energetic efficiency which we can imagine as the integral of U integrated over the specific capacity is decreasing the higher the rate is.
  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"?  
⇒ The problem with Li metal as an anode material is that after discharging the battery there won't be a flat surface on the side of the anode because some of the Li-ions are remaining there. This means that when we charge the battery again, the Li-ions are binding more likely to the part of the metal which is nearest. This means, that after a few cycles the side of the anode is growing towards the other side which will generate a connection between cathode and anode at some point which will lead to a short circuit. So the idea behind an "all solid state battery" is that we can use Li metal as an anode material because then we have a physical barrier so that the "growing" of the Li is not such a big problem.
  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?  
⇒ The expected OCV of a fully charged NMC-cell would be 4.2V[3], with an energy density around 250 Wh/kg.

## 6 Literature

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