

Assembly and Characterisation of Batteries in SoSe 2024

Lab Assignment 2: Assembly of Lithium-Ion Batteries

Version: 1.0 (14th May 2024)

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1 Introduction

After an introduction to the structure, electrochemical principles, and industrial production of lithium-ion batteries (LIB), a pouch cell is disassembled, measured, and reassembled in a smaller test cell format in this experiment. The disassembly, measurement, and assembly are carried out in a glovebox filled with argon. It is necessary to know the theoretical capacity of the cell in order to determine a suitable forming and subsequent cycling current. In order to determine this, the thickness of the active material is determined using a laser scanning microscope (LSM) with the aid of the known volumetric loading of the cell components. After assembling the cell components (anode, cathode, separator), the test cells (coin cell; type: 2032) are assembled. Finally, the assembled cells are formed and cycled on a battery tester.

2 Fundamentals

2.1 Structure of the LIB

Figure 1 shows a galvanic cell with two electrodes during the discharge process. The electrodes consist of substrate and coating, a separator, and the electrolyte. In a conventional LIB, the cathode consists of an aluminium carrier foil coated with lithium metal oxide and the anode consists of a copper carrier foil coated with graphite. The two electrodes are electrically separated from each other by a separator. The microporous separator is ionically conductive and consists of a single-layer or a multi-layer polymer and/or a ceramic foil. The electrolyte, usually a liquid, consists of an organic solvent and a conducting salt. It fills the remaining space within the cell to ensure the transport of ions between the electrodes. Electron conduction outside the cell is made possible by cable connections via the current collectors of the electrodes. [8]

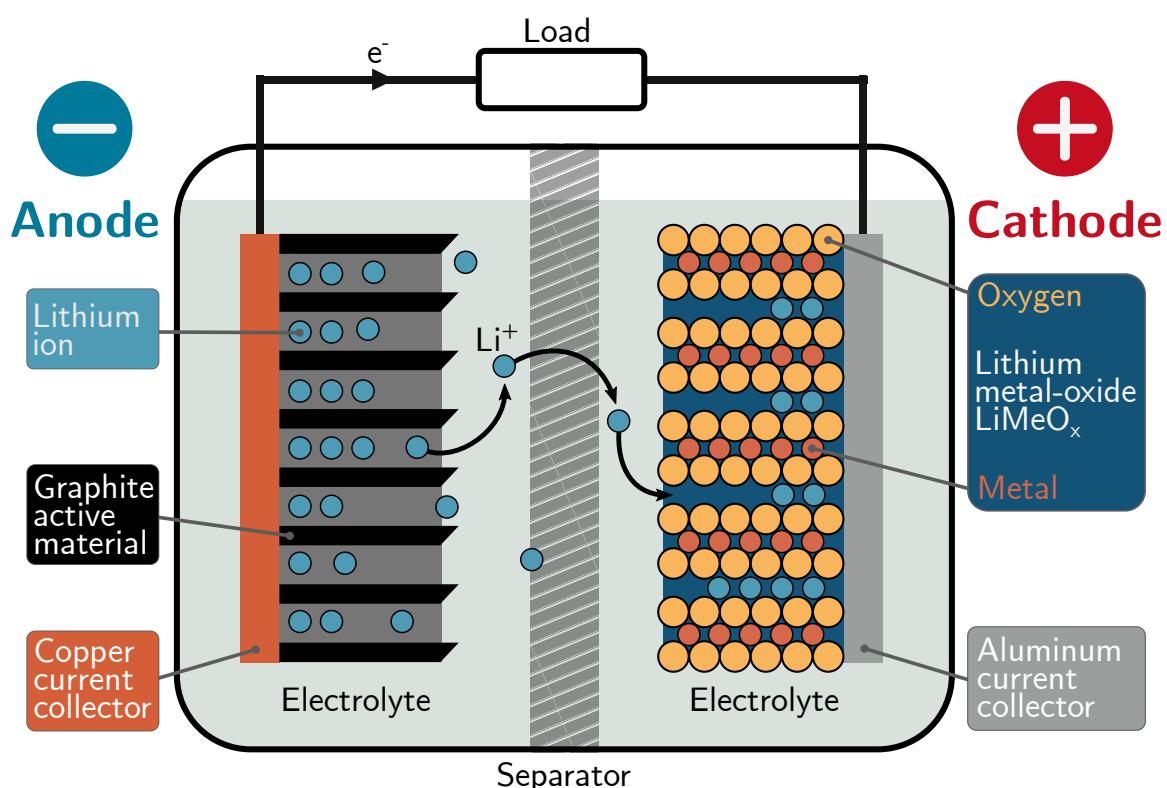
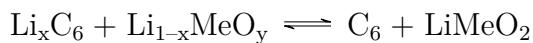


Figure 1: Galvanic cell during the discharge process

2.2 Reaction during Charging and Discharging

In a fully charged LIB, all lithium ions have been intercalated in the anode. This means that the ions occupy free spaces between the graphite grids of the anode without having reacted chemically with the anode material. This intercalation leads to an increase in the volume of the anode of approx. 10 %.

When the cell is discharged, the lithium ions are de-intercalated from the anode and are converted into Li^+ ions. These ions then migrate via the electrolyte to the cathode, where they are deposited in the metal oxide of the cathode and form a lithium metal oxide. For each de-intercalated Li^+ ion in the anode, a single electron is released, which flows through the external circuit. The entire cell reaction can be described using the following equation:



where x describes the ratio of lithium ions still in the anode. The anode can have different lithiation levels, representing different proportions of lithium ions in the graphite lattice. “Me” stands for a group of metals used in LIBs. These include, for example, nickel, cobalt, manganese, or iron. Most modern LIBs use material mix of different metals (often NMC – “nickel-manganese-cobalt”), in order to balance out the favourable and detrimental properties of each material.

This process is reversed during the charge process: the lithium ions move back from the cathode to the anode, where they receive an electron each.

LIBs are very sensitive to overcharging and undercharging, so the cell must be operated within a voltage range adapted to the materials used. For this reason, LIBs are usually charged using the so-called CCCV charging method. CCCV stands for “constant-current constant-voltage”, which means that the battery is first charged with a constant current up to the end-of-charge voltage (normally 4.2 V) and then continuously charged while maintaining the voltage level until the current has fallen below a specific threshold.

Fig. 2 shows the voltage, current, and state-of-charge curves for a CCCV charging process. Here, I_{ch} is the charging current during the CC phase, I_{thres} is the threshold current that ends the charge in the CV phase and V_{max} and V_{min} are the final charge and final discharge voltages of the cell respectively. During the CC phase, the cell is typically charged up to 80 %, with the CV phase adding the remaining charge in a similar or even higher amount of time.

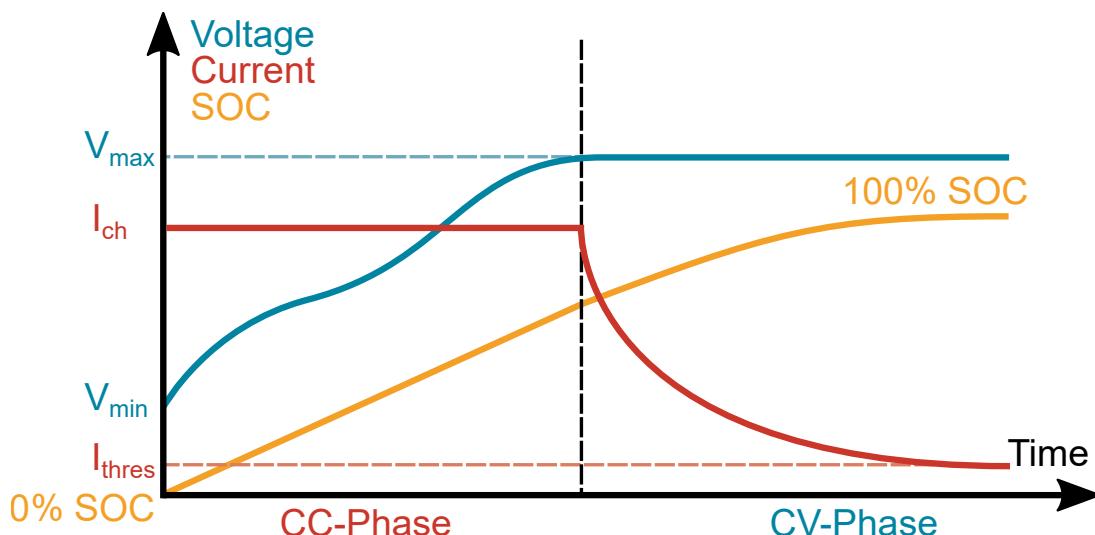


Figure 2: Current, voltage, and SOC during a CCCV charge

2.3 Industrial Production

The production process of a LIB is fundamentally divided into electrode production, cell assembly, formation, and ageing [6]. The individual process steps and their key quality characteristics are described below according to [11].

2.3.1 Electrode Production

Electrode production takes place in six steps:

1. Mixing the coating material
2. Coating of the carrier foils
3. Drying
4. Calendering (compacting)
5. Slitting (cutting to size)
6. Vacuum drying

During mixing, the active material - conductive carbon black - , the solvent, the binder, and the additives are mixed under inert gas for approx. two to six hours to form a so-called slurry. The slurry formulations of the electrode and counter electrode differ mainly in the active materials used (graphite or lithium metal oxide). During the subsequent coating process, the slurry is applied to the substrate material intermittently or continuously using an application tool (e.g., a slotted nozzle).

At coating speeds of $(80 \dots 120) \frac{\text{m}}{\text{min}}$, typical coating thicknesses are between $(200 \dots 250) \mu\text{m}$. Coming directly from the coating process, the electrode strip material is fed through a floatation dryer at $(80 \dots 120) \frac{\text{m}}{\text{min}}$ with the help of several air nozzles. The floating electrode foil moves sinusoidally through various dryer zones at temperatures of $(80 \dots 160)^\circ\text{C}$. After exiting the suspension dryer and subsequent cooling to room temperature, the porosity of the substrate is approx. 50 %.

With $(80 \dots 150) \frac{\text{m}}{\text{min}}$, the dried electrode strip material is compacted over several pairs of rollers at line pressures of approx. $1500 \frac{\text{N}}{\text{mm}}$ to a porosity of $(30 \dots 40) \%$. The strip material is then wound into so-called mother coils. In this process step, the wide electrode strip of the mother coils is separated thermally by laser cutting or mechanically by knife cutting and rewound into several daughter coils. Typical cutting speeds are $(80 \dots 150) \frac{\text{m}}{\text{min}}$.

In the final step of electrode production, the daughter coils are cleaned of moisture and solvent residues at $(60 \dots 130) \frac{\text{m}}{\text{min}}$ for approx. $(24 \dots 48) \text{ h}$ in vacuum furnaces.

2.3.2 Cell Assembly

Cell assembly is basically divided into four steps: separation, stacking or z-folding, packaging, and electrolyte filling.

For the production of pouch cells, the electrodes are thermally separated from the secondary coils by laser cutting or mechanically by shear cutting (punching) and stacked in magazines or processed further directly. Electrodes, separator, and counter electrode are brought together in a repetitive cycle by single-sheet stacking or z-folding. In z-folding, the already separated electrode sheets are inserted into the z-folded separator. Folding and insertion take place simultaneously. While in z-folding the separator is in the form of strip material, separator sheets are used in single-sheet stacking.

After bonding the conductor foils to the cell collector of the pouch cells using ultrasonic or laser welding, the electrode stack is inserted into the packaging and sealed. The cell is continuously or cyclically filled with the electrolyte (e.g., lithium hexafluorophosphate - LiPF_6) via a mandrel insert with a sealing cap or sealing seams while being cyclically evacuated with inert gas and/or vacuum).

2.3.3 Formation and Ageing

The sub-processes of formation, degassing, sealing, folding, ageing, and end-of-line testing (EOL testing) are summarised under formation and ageing [6].

During initial charging and discharging (formation), the solid electrolyte interphase (SEI) forms on the graphite of the anode. The structure of the SEI (thickness, homogeneity, etc.) depends on many parameters and is decisive for the subsequent properties of the LIB. The lithium is present in the metal oxide of the cathode before formation. When the current is applied, lithium ions are released from the cathode. In the process, the lithium ions solvate with molecules of the electrolyte and move through the separator to the graphite. Solvation is an interaction of a solute with the solvent, which leads to stabilization of the solute species in the solution.

Due to the high reactivity of lithium, a reaction with the electrolyte molecules and the formation of the SEI on the graphite surface, which is permeable to lithium ions, mainly occurs during the first charging process. Solvent molecules cannot pass through the SEI, which protects the graphite layer from excessive destructive volumetric changes during charging and discharging. [10]

In the case of flexible pouch cells, gas that may be produced during the formation process is then pressed out of the cell into a gas pocket using an increased external ambient pressure. The cell is then finally sealed between the gas pocket and the main pouch. The gas pocket is separated, and the sealing edges are then folded.

The final step in cell production involves storing the cells for around three weeks with regular performance tests to characterise them. If there are no significant changes during this time, the cells are functional and can be assigned to different quality classes.

In addition to the costs for the materials, the processes of electrolyte wetting and formation are the second-largest cost item in LIB production. The formation process, which is currently widespread in the industry, is very energy-intensive and time-intensive and is often the bottleneck of the entire cell production process. After the complex electrolyte filling process, the cells are first stored under vacuum at elevated temperatures for a period of up to several days in order to ensure that the anode surface is completely wetted with electrolyte. Several cycles are then run at very low C-rates (usually C/20) and sometimes at elevated temperatures to enable the stable formation of the SEI layer [1].

The entire process can take between 1.5 and 3 weeks. The process heat and energy required for cycling accounts for a significant part (18 % to 32 %) of the production process costs. Disregarding the cycling and floor space required, as well as the heating elements,

the energy costs account for up to 6.4 % of the total cell costs [12]. However, these cost-intensive formation conditions are necessary to ensure a competitive service life of the cells. The service life of lithium-ion cells with a graphite anode depends largely on the stability of the SEI layer, which is determined during the formation process.

The aim is to produce a stable SEI for the given cell chemistry with the lowest possible process and time expenditure, which enables a good service life performance of the cells.

The ideal SEI is according to [12]:

- as thin as possible (but thick enough to prevent further reactions with the anode surface),
- electrochemically inactive,
- highly resistive,
- highly ion-conductive, and
- helpful in stripping the solvate sheaths.

The formation of the SEI layer depends on the composition of the electrolyte (solvent, conducting salt, any additives) and the properties of the anode material used (particle size, crystal structure, pore size, surface properties, ratio of plane arrangement) [1]. A precise examination of the materials used is therefore necessary to optimise the formation process. Chemical analyses (Hg porosimetry), optical processes (laser scanning microscope-LSM, spectroscopy, scanning electron microscope-SEM), and electrical measurements (cyclic voltammetry-CV, electrochemical impedance spectroscopy-EIS) are suitable for this. Based on these results, various steps can then be taken to generate the SEI more effectively. Possibilities are [1]:

1. Select electrolyte additives that form the SEI faster or modify its composition.
2. Modify graphite anode chemistry using binders and additives that improve wetting or conductivity.
3. Customise the formation cycles to specific voltage windows in which certain reactions take place.
4. Change the temperatures during certain formation phases.

There are also various approaches in the literature for optimising the formation process and making it less time-consuming and cost-intensive [7, 9]. However, these would have to be tested for the existing cell chemistry and adapted if necessary.

2.4 Production of Coin Cells

In the research and development of battery materials, coin cells are a common means of achieving results quickly and cost-effectively. The structure of coin cells can vary depending on the materials used and the desired quality characteristics. The structure (as used in the field), the individual components and tools, a suitable assembly sequence, and the formation and cyclic ageing of the coin cell are presented below.

2.4.1 Structure

As shown in Fig. 1, a coin cell also consists of an anode, a cathode, a separator, the electrolyte, and a housing with a seal.

Figure 3 shows the schematic structure of a coin cell.

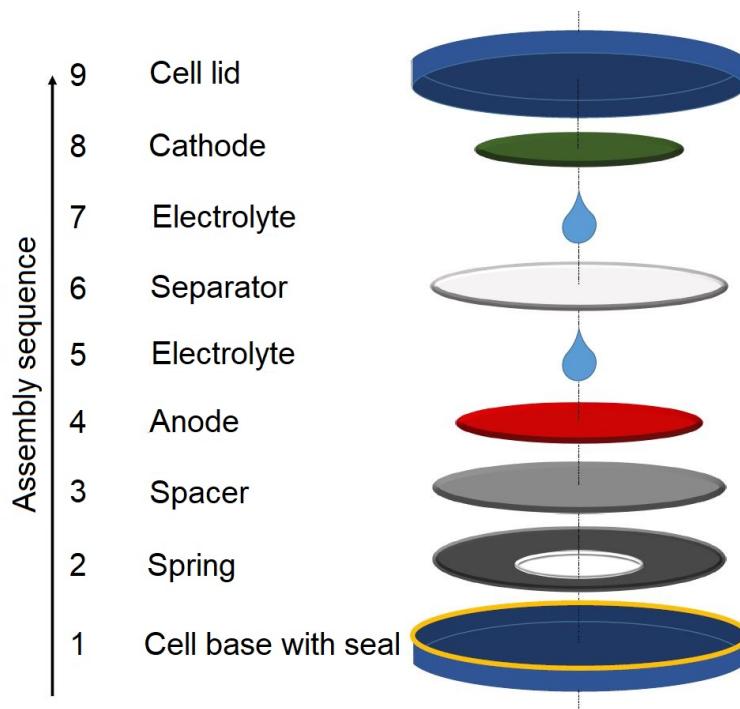


Figure 3: Schematic structure of a coin cell

2.4.2 Cell Components

The housing of coin cells is usually a steel housing of type R2032. The “20” stands for a diameter of 20 mm and the “32” for a height of 3.2 mm.

There is a spring in the housing to minimise the distance between anode and cathode. This can be a disc spring or a wave spring. To ensure that the pressure exerted on the cell assembly (cathode, anode, separator) is homogeneous, there is also a spacer between the spring and anode. Depending on the thickness of the cell composite, this spacer can be thicker or less in multiple cell versions.

The electrodes in a coin cell are coated on one side. The substrate surfaces (anode: copper foil; cathode: aluminium foil) face outwards towards the housing halves. In most cases, the anode is larger than the cathode. By overlapping anode and cathode, the active materials always match each other.

The diameter of the anodes for full cells is usually (12 ... 16) mm and for cathodes (10 ... 14) mm. To avoid contact between node and cathode (short circuit), the diameter of the separator is chosen to be at least as large as that of the anode. The liquid electrolyte used here consists of LiPF₆(1.2 mol_l⁻¹) in EC¹:EMC² (3:7). The amount of electrolyte should be a multiple of the pore volume of the electrodes. Here, 100 µl is used.

2.4.3 Tools

The following tools are required for the production and testing of coin cells:

- glovebox (Fig. 4)
- battery tester (manufacturer: Neware)
- laser scanning microscope (LSM) (Fig. 6)
- electrode punching tool (Fig. 7)
- scissors
- punch and punching pad (punching of separator)

¹EC - ethyl carbonate

²EMC - ethyl methyl carbonate



Figure 4: Glovebox [4]

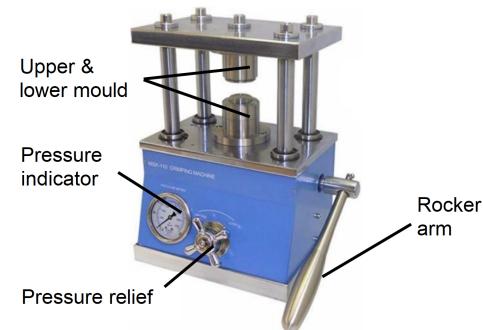


Figure 5: Coin cell press [13]

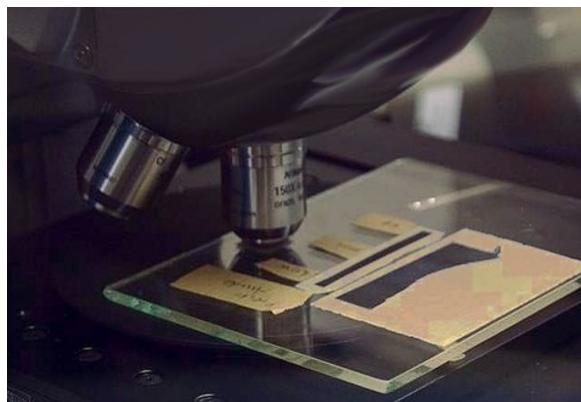


Figure 6: LSM



Figure 7: Punching tool [5]

2.4.4 Coin Cell Assembly

The following instructions (according to [3]) for coin cell assembly strive for the highest possible reproducibility and include the following main points:

- materials
- tools
- working environment
- cell assembly
- measurement

Materials: All materials, especially electrodes, separator, and electrolyte, must be stored in a clean, sealed environment. It is recommended that these materials be stored outside the working environment to prevent contamination. Damage caused by accidents or third-party influences can thus be effectively avoided. The more sensitive the materials are, the more important this is. Checking incoming and outgoing materials and monitoring storage

parameters are standard industrial practices and are of great importance for high-quality results in research and development. In case of doubt, materials whose quality cannot be verified must be rejected. Otherwise, the quality and reproducibility of the manufactured cells cannot be guaranteed.

Tools: All tools, such as tweezers, pipettes, punches or electrode-cutting tools, must be kept clean throughout the production process. This includes cleaning the tools immediately before and after use.

Working environment: The working environment must always be kept clean and tidy, whether inside a glovebox or outside. This includes cleaning the work surfaces before and after cell assembly. Contamination is a disruptive factor that significantly impairs the quality of results. It is recommended to define a system for organising tools and other objects and ensure this is adhered to. Ideally, each tool has an assigned place to which it is returned clean after use. The atmospheric parameters in the glovebox must be monitored regularly and kept constant.

Cell assembly: The coin cell must be assembled starting with the housing base with a seal towards the top. The assembly sequence is shown in Fig. 3.

A plastic plate or a paper towel can be used as a work surface. The assembly takes place in a glovebox. The individual materials are placed using tweezers, with separate tweezers for each cell component to avoid cross-contamination. The electrolyte is applied using a piston pipette.

The cell must be crimped once all materials and components have been assembled, as shown in the Fig. 3, and the housing cover has been fitted. The pressure must be within (950 ... 1000) psi. After assembly, the cells are cleaned with a paper towel and removed from the glovebox.

Measurement: The cells are to be measured uniformly with a formation and cycling protocol. The atmospheric parameters must be kept as constant as possible during the measurement.

2.5 Formation and Ageing

As explained in section 2.3.3, formation is an important step that influences the subsequent performance of a battery cell.

In this practical course, the cells are placed in a twelve-hour rest phase (rest) after production. They are then formed with a current of 0.3 mA until the cells reach a voltage of 4.2 V. This corresponds approximately to a C-rate of C/10. The subsequent CV phase is cancelled at a current of 0.056 mA, and the formation is terminated after this first charging process.

After a rest of ten seconds, the cells are cycled with a current of 1.5 A (approx. C/2) within the limits of (4.2 ... 2.5) V. A total of 30 cycles are performed. Formation and cycling are carried out using the Battery Testing System (BTS) from Neware. The formation and cycling protocol can be set and started via a desktop application. The program enables continuous cell parameter monitoring by visualising the current, voltage, and capacity curves.

Figure 8 shows the typical current and voltage curves for the formation and cycling protocol. A cell is considered functional if current and voltage behave this way over the set number of cycles. Otherwise, it is classified as non-functional.

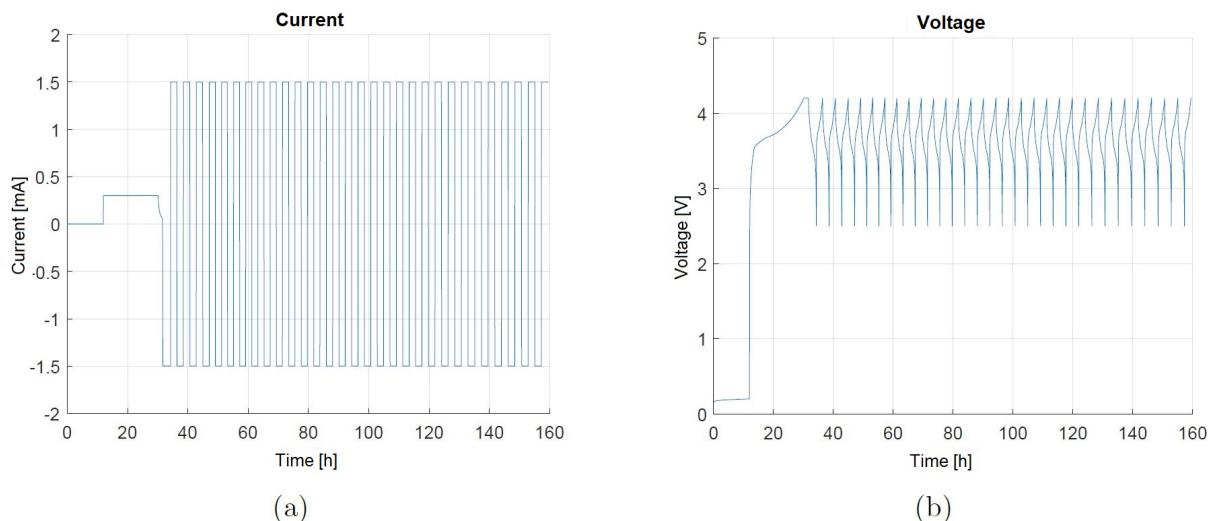


Figure 8: Formation and cycling: (a) current curve, (b) voltage curve [3]

3 Pre-Tasks

18 P Task 1: Fundamentals

- (a) What are the main formats of batteries? Name one advantage, one disadvantage, and one application of each type. 8 P
- (b) Define the term C-rate and illustrate it with an example. What is the advantage of using it, and what is the alternative? 5 P
- (c) How does the internal resistance of a large pouch cell compare to that of a small laboratory cell? 2 P
- (d) Why is the formation process for LIBs prior to cell usage necessary? 3 P

17 P Task 2: Cell Assembly

- (a) What distinguishes a commercial cell from a laboratory cell? 3 P
- (b) Why is it difficult to directly use the cell materials from a commercial cell for test-cells without modifications? 2 P
- (c) What errors can occur during manual test-cell assembly? 4 P
- (d) During test-cell assembly, you can use electrodes coated on both sides and electrodes coated on one side. You can also use one or more layers of separator foil. What differences do you expect between cells with electrodes coated on one or both sides? What differences do you expect when using several layers of separator foil compared to one layer? 4 P
- (e) There are four channels available for the electrical measurements. Think about the type of cells you want to produce with the variations mentioned in the previous task in order to test the behaviour you suspect. Only one cell can be tested on each channel. 4 P

15 P Task 3: Carrying out the Experiment

- (a) Create a list of the materials, tools, and equipment required for the individual experiments. 6 P
- (b) Write down the procedure for all experiments as you would implement it in the lab assignment. Please note that section 4 does not contain all the details of the assembly and that further measures must also be carried out (see section 2.4). 9 P

4 Experimental Procedure

General Safety Instructions

When working in the glovebox, it is advisable to wear a long-sleeved top. Please be sure to observe hazard symbols and safety instructions when handling chemicals. If you have any questions, please don't hesitate to contact the supervisor.

Attention: All cell materials may only be handled with gloves!

Experiment 1: Cell Opening

In this experiment, a commercial 18650 round cell is opened in the glovebox under a protective argon atmosphere.

1. Weigh the cell before opening.
2. Use scissors to open the pouch cells (without electrolyte).
3. Separate and sort anodes, cathodes, and the separator.
4. Determine the dimensions of the electrodes and their coating.
5. Use the micrometre screw to determine the thickness of the electrodes. Also, determine the thicknesses of the collector foils and the separator.
6. Prepare a sample of each anode, cathode, and separator and stick it on double-sided adhesive tape in preparation for microscopy.
7. Determine the thickness of the layers again using the laser scanning microscope (LSM).
8. Also, take a picture of the anode and cathode in which the particles of the active materials can be seen.

Experiment 2: Coin Cell Assembly

Dry, open pouch cells are given for this part of the task. Both the cell material coated on one side and the cell material coated on both sides can be removed from these cells. The removed cell components (anode/cathode/separator) are then assembled as coin cells (type 2032).

1. In the pouch cells provided, there are anodes coated on one and two sides, cathodes coated on both sides, and a ceramic separator. Punch anodes and cathodes so that you can ensure that the anode and cathode overlap. Recommendation: anode diameter: 16 mm, separator diameter: 16.5 mm and cathode diameter: 14 mm. Avoid cross-contamination by using a separate tool for each cell component. After punching the materials, they are temporarily stored in the tubes provided.
2. Position all required cell components and tools to ensure a quick and reproducible cell assembly.
3. Position all housing covers (+) in front of you and assemble one cell at a time. Use figure 3 as a guide.
4. After crimping the cells, they should be wiped with a cloth and then ejected.
5. Connect the cells to the Neware channels and start the provided and modified scripts.

5 Evaluation

[10 P] Form

- general layout
- quality of diagrams, tables, and figures
- clarity and comprehensibility
- correct citation of sources

[5 P] Introduction and Summary

[25 P] Experimental Procedure

- detailed description of the performance of all experiments
- description of relevant observations
- record any deviations from the planned experimental procedure
- if applicable: sketch or photo of the experimental setup

[60 P] Evaluation

- General Requirements

[10 P]

- if applicable: theoretical derivations and explanations
- preparation and presentation of the measurement results
- interpretation and comparison with theory/simulation
- error analysis

• Focus on Experiment 1:

25 P

- Determine the particle sizes for the anode and cathode active material from their LSM images.
- Compare the thicknesses of the cell components between the micrometer screw and the LSM.
- Calculate the loading in $\frac{\text{Ah}}{\text{cm}^3}$ using the capacity of the opened cell and the determined cell parameters.
- Calculate the theoretical energy density using the previously calculated charge and compare it with the real energy density.
- Is the opened cell a high-energy cell or a high-performance cell? Which properties of the cell components would have to be changed in order to obtain the other cell type?

• Focus on Experiment 2:

25 P

- Calculate the theoretical capacity of your coin cell using the previously calculated charge. Assume that all lithium was previously present in the cathode in bound form.
- Compare the calculated theoretical capacity with the actual discharge capacity of the third cycle. Explain the possible deviation between theoretical and actual capacity.
- What potential difference do you expect directly after cell assembly and before forming?
- What voltage can you measure with a multimeter directly after cell assembly? How do you explain the difference between the expected and measured potential difference?
- Name three ways to further reduce the internal ohmic resistance of your coin cell.

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