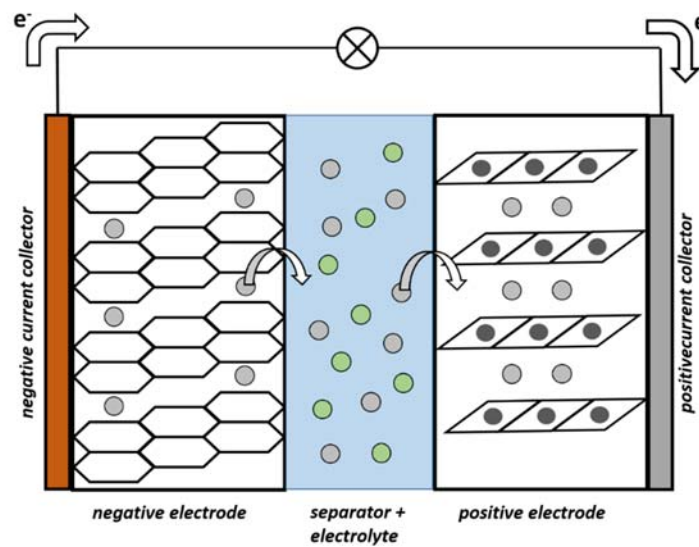**Topic:** Electrochemical energy storage

Battery

Assembly and characterization of a Li-ion cell

Learning targets:

1. Understanding the workwise of an electrochemical Li-ion cell

2. Getting practical experience in electrode preparation and cell assembly

3. Learning to work with gloveboxes properly

4. Analyzing galvanostatic cell-cycling data correctly

Parameters, constants & abbreviations – a selection

$\Delta_r G$	Gibbs free enthalpy in kJ mol^{-1}
z	Number of charges per reaction equivalent
F	Faraday constant: 96485 A s mol^{-1}
E	Cell voltage in V
$\tilde{\mu}$	Electrochemical potential in kJ mol^{-1}
R	Gas constant: 8.3145 J mol^{-1} K^{-1}
T	Temperature in K
a	Activity in mol L^{-1}
q_{th}	theoretical capacity in mA h g^{-1}
m	Mass of active material in mg
M	Molar mass of active material in g mol^{-1}
η_c	Coulombic efficiency
q_{dis}	Discharge capacity in mA h g^{-1}
q_{ch}	Charge capacity in mA h g^{-1}
η_E	Energy efficiency
E_{dis}	Discharge cell voltage in V
E_{ch}	Charge cell voltage in V

SEI	Solid electrolyte interphase
VC	Vinylenecarbonate
FEC	Fluoroethylenecarbonate
CE	Counter electrode
RE	Reference electrode
WE	Working electrode
CB	Carbon black
PVDF	Polyvinylidenefluorid
NMP	N-methyl-pyrrolidone
GCPL	Galvanostatic cycling with potential limits

1. Introduction [1]-[5]   (not necessary for experiment and colloquia)

The subject electrochemistry is often associated with the conversion of chemical energy into electricity and the other way around. Storing and releasing energy on demand, in fact, this is what modern batteries are supposed to do for powering our electro vehicles and consumer electronics. But, it was a long way from first observations and usage of chemical electricity to Li-ion batteries we know today. Historically documented is the 2000 years old "Bagdad battery". This was a salt water filled clay jar with copper and iron metal electrodes inside. Although, the identity as electrochemical device is proven, discussions about its purpose remain. Possible applications were kind of electro therapy or early galvanic processes with noble metal deposition. Another example is the "lemon battery", a famous school experiment, which follows similar workwise. By putting two different metals inside the lemon an electrical voltage of around 1 V appears. Both approaches are easy to realize but, of course, they fail in terms of being a reliable power device, let alone the missing rechargeability. In the end of 18th century ALESSANDRO VOLTA developed the Volta Pile – a stack of alternating zinc and copper plates. The plates were separated from each other by wet towels and were electrically connected by wires. For the first time a sustainable direct current source was available and fast research progress with this revolutionary tool took over: As an example, electrochemical water splitting was discovered and analyzed by the British scientists NICHOLSON and CHARLISLE in 1800 – the same year VOLTA presented his invention in London. 30 years later MICHAEL FARADAY introduced a couple of still valid definitions: anode, cathode, anion, cation, electrolyte and electrolysis. Without doubt, the Volta Pile can be denoted as first commercially available battery in history, but it was heavy, expensive and still not rechargeable. However, myriads of electrochemical explorations were obtained by using this electricity source.

First rechargeable device was invented in 1857 by PLANTE – the lead acid battery. This system exhibits a high reversibility, good temperature tolerance and an output voltage of 2 V per cell unit. Pb-acid batteries were and are of high relevance especially for automotive applications. Hence, Pb-acid systems are still the second biggest participant on world battery market today. One decade later LECLANCHE developed a system based on the irreversible reaction of zinc and MnO_2. The so called Leclanché element was an early version of 1.5 V alkaline batteries we know today. These portable alkaline dry cells were invented independently by YAI, WILHELM and HELLESEN around 1889. Zinc air batteries, we know as tiny coin cells for hearing devices, were developed in 1930s but the designation as fuel cell would be more appropriate due to zinc

combustion by air-oxygen. Taking together lead and zinc were the most important elements towards serving as electrochemical energy source for quite a long time.

Ni/Cd-systems were already investigated by JUNGNER in 1890 but the technology had its breakthrough only in 1947, when it was designed as portable, rechargeable and closed device. Because of its materials toxicity Ni/Cd accumulators are prohibited in European Union since 2004.

High temperature batteries ($\approx$300°C) are usually considered for stationary energy storage and were promoted in late 1970s by the invention of Na-β''- aluminate – a high performance Na-ion conductor. Representatives are the Na/NiCl$_2$- (ZEBRA) and the Na/S-battery so one may say that Na-devices are much older than Li-based ones.

In late 1980s Nickel-metal hydride (Ni-MH) batteries were the rechargeable answer on one way zinc alkaline batteries. They had the same format, similar properties and were able to power the first portable computers without exchange of power supply. Ni-MH batteries are still widely in use, for example in hybrid cars.

In 1991 SONY finally introduced the first mass product Li-ion battery on the market. The revolutionary invention outperformed former technologies in several categories (energy, power, life time) and conquered the market of consumer electronics rapidly. Former Ni/Cd and Ni/MH batteries were quickly superseded. The first Li-ion battery contained graphite and LiCoO$_2$ as electrodes. Although there was a lot of progress in battery optimization in last decades, the general workwise of Li-ion batteries did not change yet. Nowadays, the main challenge of batteries is the promoting subject electro mobility. TESLA, SAMSUNG, SONY, PANASONIC and CATL, to mention a few of world biggest battery producers, are preparing to face this challenge and battery production is expected to rise by 2000% until 2030. An example for these ambitions is the construction of TESLAs and PANASONICs Gigafactory in Nevada. Recently, CATL has announced the construction of a production plant not far away from here, in Erfurt.

A Li-ion-battery currently provides an energy density of 160 Wh kg^{-1} and a specific capacity of around 40 Ah kg^{-1}. These values are already close to the theoretical maximum and further improvement might lead to serious safety drawbacks. In other words: Li-ion technology is facing its technical limits. One may remember the SAMSUNG *Note 7* problem in 2016, when several devices caught accidentally fire. Therefore, by projecting better performance conceptual change is necessary. Candidates for so called post-Li-ion batteries are all solid state approaches, which promise better safety and volumetric energy density or Na-ion batteries containing more abundant materials. The utilization of oxygen or sulfur as electrode material would outperform

Li-ion batteries capacity by factor 10 in theory, but realization is quite challenging. However, we can expect new types of batteries entering the market in upcoming years, but total replacement of Li-ion batteries is unlikely.
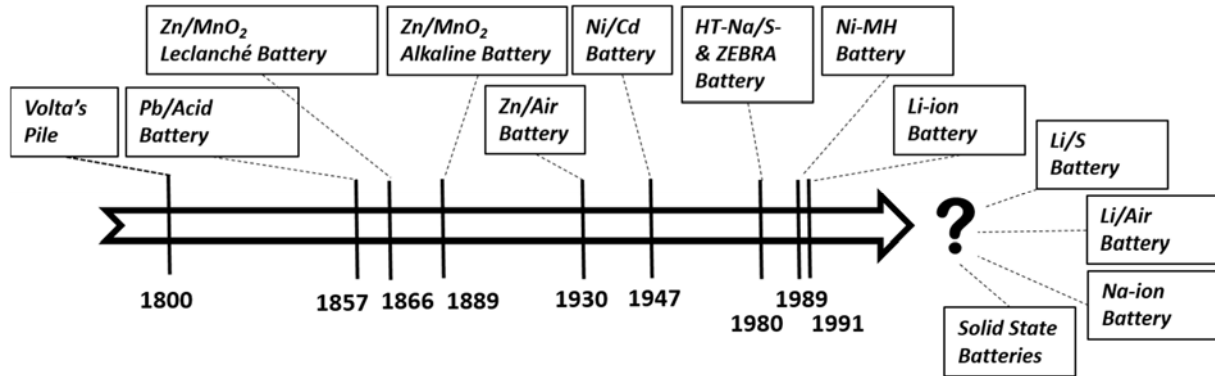

Figure 1:   Time line of battery inventions since 1800 and proposed post-Li-ion technology. Given years rely on start of application.

2. Theoretical Background (Basics) [2]

The word battery actually implies the interconnection of several separate electrochemical cell units, however, nowadays single cells as well as cell stacks are denoted as battery. Here we want to distinguish between both terms. An electrochemical cell usually consists out of two electrodes – a negative and a positive one – and an electrolyte in between. Oxidation reactions are performed at the anode, whereas reduction reactions are taking place at cathode side. By changing the direction of current the designation of anode and cathode exchanges while negative and positive electrode remain the same (Figure 2).
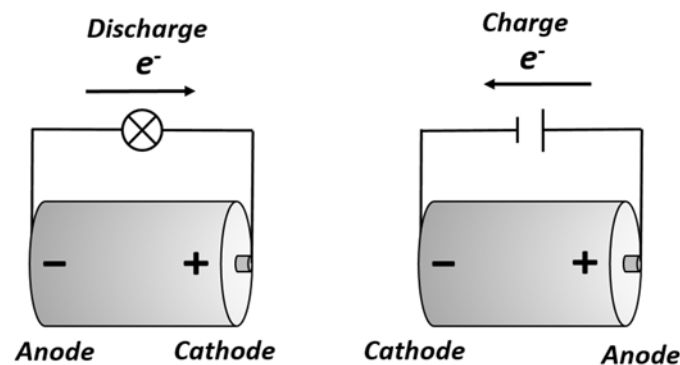

Figure 2:   Definitions of anode, cathode, negative electrode and positive electrode dependent on current direction.

The main difference to chemical redox-reactions is the separation of oxidation and reduction in two half-cell reactions. On this way electrons have to travel from anode to cathode by external conductors and can power a consumer load. Simultaneously, ions are moving between the electrodes for equivalence of charge inside the cell. At least two half-cell reactions can be wrote down for electrochemical processes inside a battery. Examples are given for lead-acid and zinc-alkaline system (Table 1 + Table 2).

Table 1:   Total discharge reaction and half-cell reactions of a Pb/acid-cell. $E \approx 2.0$ V

Total reaction	$Pb + PbO_2 + 2SO_4{}^{2-} + 4H^+ \rightarrow 2PbSO_4 + 2H_2O$
–	$Pb + SO_4{}^{2-} \rightarrow PbSO_4 + 2e^-$
+	$PbO_2 + SO_4{}^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$

Table 2:   Total discharge reaction and half-cell reactions of a Zn/MnO₂ alkaline cell. $E \approx 1.5$ V

Total reaction	$Zn + 2MnO_2 + 2OH^- + 2H_2O \rightarrow Zn(OH)_4{}^{2-} + 2MnO(OH)$
–	$Zn + 4OH^- \rightarrow Zn(OH)_4{}^{2-} + 2e^-$
+	$2MnO_2 + 2H_2O + 2e^- \rightarrow 2MnO(OH) + 2OH^-$

Rechargeable devices like Pb/acid accumulators are denoted as secondary batteries. Primary batteries like the Zn/MnO₂ alkaline system on the other hand are either not rechargeable or recharge is too inefficient for application.

The driving force of an electrochemical reaction is the potential gap between both electrode reactions and measured in Volts. If the number of charge transfers per reaction equivalent is known, open cell voltage can be directly converted into a Gibbs energy value (eq.1).

$$\Delta_r G = -z \cdot F \cdot E \quad (eq.\,1)$$

Considering the relation between activity and (electro)-chemical potential (eq.2) ends up in famous Nernst-equation (eq.3). Anode and cathode potentials are a function of concentration of ions participating the reaction, more precisely, ion activity. Therefore, for some cell chemistries the cell voltage might change depending on progress of reaction.

$$\tilde{\mu}_i = \tilde{\mu}_{i,0} + R \cdot T \cdot \ln a_i \quad (eq.\,2)$$

$$E = \varphi_{0,cath} - \varphi_{0,an} + \frac{R \cdot T}{z \cdot F} \cdot \ln \frac{a_{i,ox}}{a_{i,red}} \quad (eq.\,3)$$

Besides thermodynamic view different kinetic phenomena are taking place while cycling a cell and overpotentials are often associated with this electrochemical kinetics. Different overpotentials caused by charge transfer, ohm-resistance or diffusion are known and all of them result in efficiency losses. Consequence is that the required voltage for charging is always higher than given voltage during discharge.

3. Li-ion Batteries: Structure and Materials [2], [3]

During charge and discharge of a Li-ion battery Li^+ is released by one electrode and simultaneously stored by the other one. Other ions are not participating the reactions as it is the case for many aqueous systems, so the reaction equations are easier, at least on paper (Table 3).

Negative electrodes exhibit a low potential vs. Li/Li^+ and commonly consist out of graphite as proven active material. Stoichiometrically, six carbon atoms are able to store 1 Li^+-ion at potentials close to 0 V vs. Li/Li^+ ending up in a specific capacity of 372 mAh g^{-1}. Besides graphite, several more options are discussed (Table 4). Especially silicon and Li-metal are very attractive due to their outperforming theoretical capacity but they face some issues in terms of stability. Negative electrodes are hold together by a polymeric binder and are usually carried by a copper current collector. Less noble metals would react with electrodes active material.

As the cell voltage is made out of the potential gap between both electrodes, positive electrodes exhibit very high potentials of around ~4 V vs. Li/Li^+ (Table 4). Material class of choice in commercial batteries are layered transition metal oxides and most known representative is $LiCoO_2$, which was discovered by Mizushima and Goodenough in 1980 and promoted the fast development of Li-ion batteries. Inside these layered oxides Li^+ is stored either in prismatic or octahedral coordination. Towards better lifetime, these materials are lithiated and delithiated incompletely; taking the example of LCO, only 0.5 Li^+-ions can be reversibly stored for each reaction equivalent. Modern positive electrodes are trying to replace more and more cobalt by abundant metals like manganese, nickel and aluminum. Examples for non-layered oxide elec-

trodes are LiFePO$_4$ or Li$_2$S, which follow other storage mechanisms. Like negative ones positive electrodes are hold together by polymeric binder on top of a current collector; here aluminum is used. Often the active materials of positive electrodes have poor electronic conductivity, so carbon needs to be added as conductive support.

Table 3:   Total discharge reaction and half-cell reactions of Li-ion battery using Graphite and LiCoO$_2$. E ≈ 4.0 V

Total reaction	$LiC_6 + 2Li_{0.5}CoO_2 \rightarrow 6C + 2LiCoO_2$
−	$LiC_6 \rightarrow Li^+ + 6C + e^-$
+	$2Li_{0.5}CoO_2 + Li^+ + e^- \rightarrow 2LiCoO_2$

Liquid electrolytes based on organic solvents and conduction salts enable the Li$^+$-ion transport between the electrodes. Nearly all Li-ion batteries make use of carbonate electrolytes and the most suitable composition is a 1:1 mixture of ethylenecarbonate (EC) and dimethylcarbonate (DMC). Conduction salt of choice is often LiPF$_6$ in concentrations > 1M; ionic conductivity values are in range of a few mS cm^{-1}. For preventing electrodes from getting contact with each other a mechanical separation foil is implemented between them. The foil is less than 25 μm thick, whereas the electrodes score several 100 μm.

Table 4:   Various electrode and electrolyte materials for Li-ion batteries

Electrode materials		Electrolyte materials	
Negative	**Positive**	**Solvents**	**Salts**
- Graphite	- LiCoO$_2$ (LCO)	- Ethylenecarbonate (EC)	- LiPF$_6$
- Hard carbon (HC)	- LiFePO$_4$ (LFP)		- LiBF$_4$
	- LiMn$_2$O$_4$ (LMO)	- Dimethyl-carbonate (DMC)	- Li-Triflate (Li-OTf)
- Li-metal	- LiNi$_{1-x-y}$Co$_x$Al$_y$O$_2$ (NCA)	- Propylenecarbonate (PC)	- Li-trifluoro-sulfonimide (LiTFSI)
- Silicon	- LiNi$_{1-x-y}$Co$_x$Mn$_y$O$_2$ (NMC)		
- Li$_4$Ti$_5$O$_{12}$ (LTO)		- Diethylcarbonate (DEC)	

There is no known organic solvent, which has thermodynamic stability against the potentials occurring in a Li-ion battery. So actually the cell is supposed to degrade at electrode/electrolyte interfaces. Nevertheless, electrodes are operating reversibly. How is this possible? The answer is the formation of a suitable solid electrolyte interphase (SEI) during the first cycles. Indeed, electrolyte will be decomposed but in a controlled manner resulting in a thin film of about 10-100 nm, which is passivating the electrode against further reaction with electrolyte. Simultaneously, Li-ions are still able to pass this film.

Hence, the SEI film consists out of decomposition products induced by side reactions of electrolyte at electrodes surface. Because of 3-dimensional character SEI has to be understood as interphase rather than interface. Of course, not every electrolyte provides beneficial SEI formation. In this regard carbonate type solvents were identified as best choice, so far. However, modern electrolytes contain a cocktail of additives like vinylenecarbonate (VC) and fluoroethylenecarbonate (FEC) aiming in better SEI formation control.

In total, an electrochemical Li-ion cell can be understood as thin sandwich like structure between two current collector foils exchanging electrons with the electrodes, while Li^+-ions are transported between and stored by these electrodes (Figure 3).
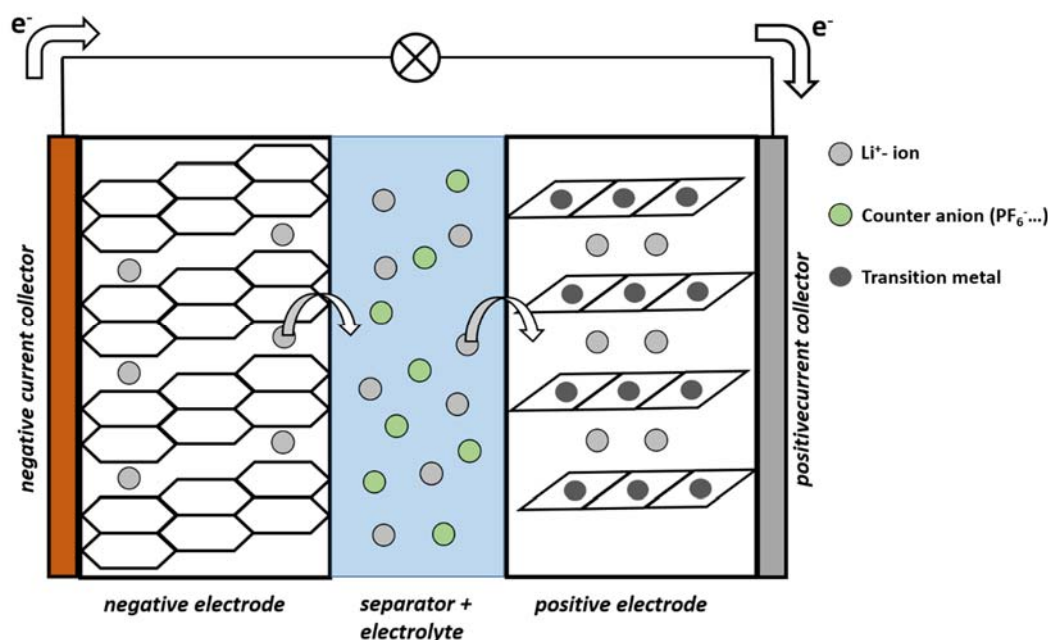

Figure 3:　　　*Scheme of a Li-ion cell: Two electrodes are able to store Li-ions at different potentials and are separated by a Li^+-conducting electrolyte in between. Shown is the discharge process.*

4. Li-ion batteries: Electrochemical Characterization

Towards characterization of single electrode materials it is useful to arrange a 3-electrode cell design: counter electrode (CE), reference electrode (RE), and working electrode (WE) whereas the WE contains the material of interest and limits the charge which can be stored inside the cell. CE and RE are usually made out of Li-metal. A various number of electrochemical methods is available for detailed characterization of an electrochemical cell. Because some methods are investigated separately during lab course and due to limited time we want to focus on evaluation of galvanostatic cycling (GCPL) in this experiment. A simple cycling curve, obtained by applying a defined current rate, reveals already a lot of information about cell chemistry and cell performance. An important property of an electrode material is the theoretical capacity: Which amount of charge per gram can be stored? If the exact reaction formula is known, the theoretical capacity can be calculated by equation 4 and is usually wrote down in Ah kg^{-1}. Comparing this value with experimental discharge data reveals the capacity yield of an electrode material.

$$q_{th} = \frac{m \cdot z \cdot \mathrm{F}}{\mathrm{M}} \quad (eq.\,4)$$

Efficiency values are of high relevance to evaluate further the conversion of energy and charge storage inside an electrochemical cell. Two efficiencies can be distinguished from each other: Coulombic efficiency η_c and energy efficiency η_E. η_c is nothing else than the comparison of discharge capacity with former charge capacity (eq. 5). Deviations from 100% can indicate side reactions like SEI formation or irreversible loss of active material, for example.

$$\eta_C = \frac{q_{dis}}{q_{ch}} \quad (eq.\,5)$$

While η_c considers charge amounts only, η_E takes additionally voltage into account (eq. 6). The integration of voltage over capacity directly results in an energy value. Of course, charging requires always more electrical energy than the system can release in following discharge step. This relation is given by η_E, which is mainly influenced by overpotential effects.

$$\eta_E = \frac{\int E_{dis}\,\mathrm{d}q_{dis}}{\int E_{ch}\,\mathrm{d}q_{ch}} \quad (eq.\,6)$$

The voltage profile itself provides already information about reaction mechanisms taking place at working electrode. As mentioned in 3. electrode materials can either perform insertion reactions or conversion reactions. Because $\tilde{\mu}$ does not change in terms of part by part conversion of a material, the voltage profile is expected to have plateau like character. Insertion materials on the other hand exhibit solid solution behavior. $\tilde{\mu}$ changes with ongoing lithiation and voltage profile ends up with sloping shape.

5. Experimental Section

This experiment includes the preparation of two electrode films and testing of these electrodes in 3-electrode, half-cell configuration. The cells will be assembled under inert conditions inside an argon filled glovebox. Electrochemical properties will be measured by using galvanostatic cycling protocol.

5.1 Part 1: Electrode Preparation

Three battery active materials are available: $LiFePO_4$, $LiCoO_2$ and Graphite. Two of them need to be chosen. Besides the active material, conductive carbon black (CB) and binder solution is required. The binder solution is poly-vinyldifluoride (PVDF) dissolved in N-methyl-pyrrolidone (NMP) - (50 mg mL^{-1}). Electrode preparation starts with mixing defined amounts of active material, CB and PVDF inside a 5 mL glass vial with magnetic stirrer. Choose the following mass compositions:

- 170 mg $LiFePO_4$, $LiCoO_2$ or Graphite
- 20 mg CB
- 10 mg PVDF

Add pure NMP drop by drop via syringe until the suspension gets a semifluid consistency. Subsequently, the suspension needs to stir for 1 hour. Next step is casting of the electrode suspension as a thin film on top of a current collector foil. The foil is made of either aluminum or copper. Fixate a rectangular piece of foil on top of the filmapplicator table by vacuum support and some tape (Figure 4). The foil should have enough space for both films. The electrode film needs to be casted by doctor blade technique. Adjust the slit size of doctor blade to 200 μm and put the device onto the current collector foil. Turn vacuum off, spread your electrode suspension in front of the blade and start the film applicator. Take care that the mobile fume hood is turned on. Clean the doctor blade with acetone and repeat the procedure for the second suspension. The electrode film needs to dry for 24 h. Electrode cutting will be done by assistant.

Attention: N-methyl-pyrrolidone is toxic! Lab coat, safety goggles and gloves are mandatory! Handle NMP with fume hood, only!
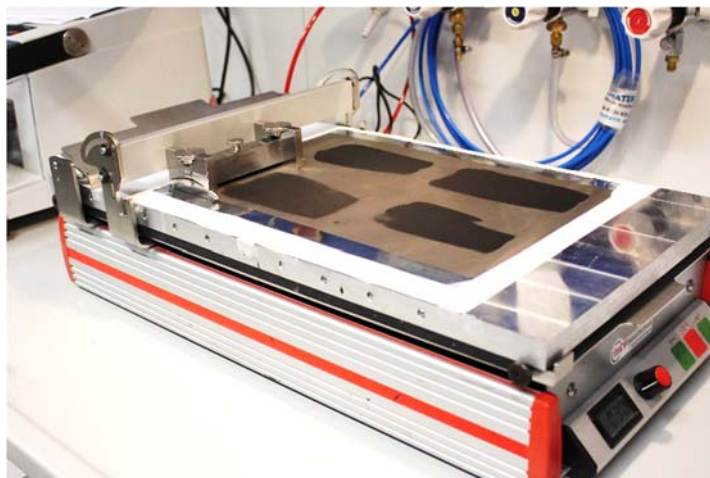

Figure 4:   Filmapplicator table with doctor blade

5.2 Part 2: Cell Assembly and Characterization

The cell assembly will take place inside a glovebox. Electrodes will be ready as small discs with 12 mm diameter. 3-electrode Swagelok-cell design will be used for assembly. One cell set consists out of 21 single parts (Figure 5, Table 5).
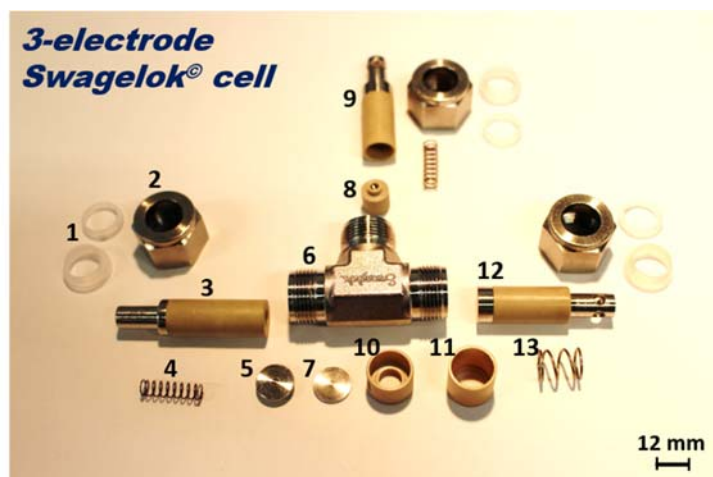

Figure 5:   3-electrode Swagelok cell set

Table 5:   *List of single cell compartments*

1	Small + big sealing ring (x3)	8	Reference electrode holder
2	Screw nut (x3)	9	Reference electrode punch
3	Negative electrode punch	10	Peek electrode shell
4	Small spring (x2)	11	Peek spring shell
5	Steel plate with contact part	12	Positive electrode punch
6	Housing	13	Big spring
7	Steel plate		

Besides two cell-sets, ensure that the following list of materials is complete before starting cell assembly. All equipment can be found inside the glovebox (Table 6).

Table 6:   *List of equipment for cell assembly*

-	Li pieces for CE and RE (x2)	-	12 mm separator discs (x2)
-	Electrolyte: EC/DMC 1M LiPF$_6$	-	Separator stripes (x2)
-	Pipette + tip: 10 – 100 µL	-	12 mm hole punch
-	Tweezers (x2)	-	Hand brush
-	Cling film	-	Wipes

Start with punching out 12 mm Li-metal CE discs and clean the Li-surface carefully with the hand brush. You can use a layer of cling film as background. Put part **5** into part **10** and place the Li-disc on top. Now lead the separator stripe through the small hole of part **10**. Subsequently, place a 12 mm separator disc on top. Take the pipette with tip and add 40- 50 µL electrolyte solution. Next step is the implementation of your electrode by putting it upside down on top. Finalize the cell sandwich by adding the steel plate (part **7**). Now put part **10** into the housing (part **6**) in a way you can see the separator stripe from RE-side. Add part **11** as well as part **13** and close WE-side by using the positive electrode punch, 2 sealing rings and a screw nut (parts **1, 2** and **12**). After this, close CE-side on the same way by connecting part **4** and part **3** before. Last sequence is the preparation of reference electrode. For this, place a small piece of Li on the tip of part **8** and place it upside down inside the remaining hole in a way that the Li has contact to the wet separator stripe. In case the separator stripe is not wet or damaged you

have to add a further piece of separator and wet it with 10 µL of electrolyte before implementation of part **8**. Finally, close the RE side like you closed the CE side. Cell assembly is completed!

Galvanostatic cycling will take place at a MPG-2 battery cycler (*Biologic*) at a current rate of C/5 e.g. 5 h for each discharge and charge step. For this, connect the WE with red cables, the CE with blue cables and the RE with the white cable. Potential limits depend on the active materials inside the working electrode and will be discussed before starting the cell. 5 discharge and charge cycles are projected.
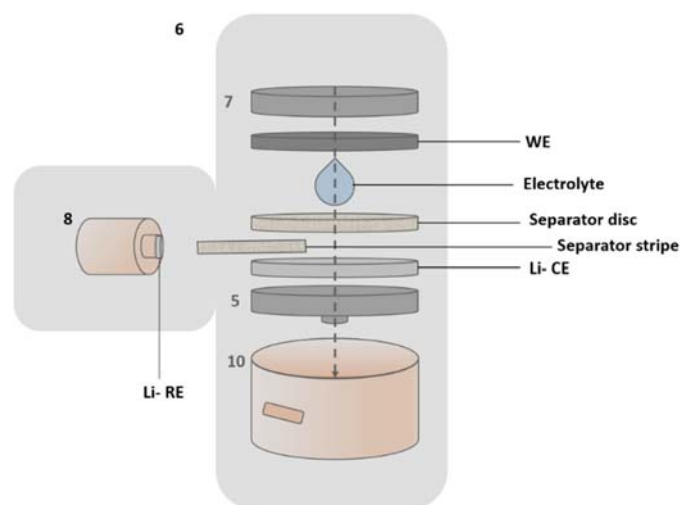

Figure 6:   *Central part of Swagelok cell assembly. Numbers correspond to Table 5.*

5.3 Working with Gloveboxes

A glovebox is a tool which allows easy handling of air and water sensitive materials like alkali metals. The box is completely filled with pure argon; water and oxygen is kept below 1 ppm, respectively. Materials can be transferred from outside to inside and other way around via vacuum-antechambers. Towards keeping moisture out, materials must be dried before transfer inside. Once dried materials are inside the antechamber, it needs to be evacuated and subsequently refilled with argon at least three times. Keep the antechamber under vacuum if it is not in use. Due to hygienic reasons it is necessary to take on one way gloves before entering the big gloves of the box. Although the gloves are resistant against a lot of chemicals it is not allowed to touch alkali metals. Use tweezers instead. Clean the gloves with disinfectant after finishing work inside the box.

Glovebox works require attention and patience, particularly for beginners. Mistakes might lead to severe disturbance of other experiments. In interest of all users: Do not start working without supervision of respective lab course assistant!

Figure 7:   Glovebox (MBraun)

6. Report and Data Analysis

Several days after experiment you will receive the cycling results of your battery as ".xls". Please pay attention in your report for the following tasks:

-   Calculate the theoretical capacity of your active material and compare with your achieved capacities. Try to give reasons for differences.
-   Plot 1st, 2nd and last cycle, respectively (E vs. q). Explain the shape of your cycling curves.
-   Plot discharge- and charge capacity vs. cycle number. Calculate the coulombic efficiency η_C for each cycle. Why is η_C so different in first cycle?
-   Calculate the energy efficiency for last cycle, respectively. Give reasons for your values.

7. References

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