

Lithium Polymer Battery Technology

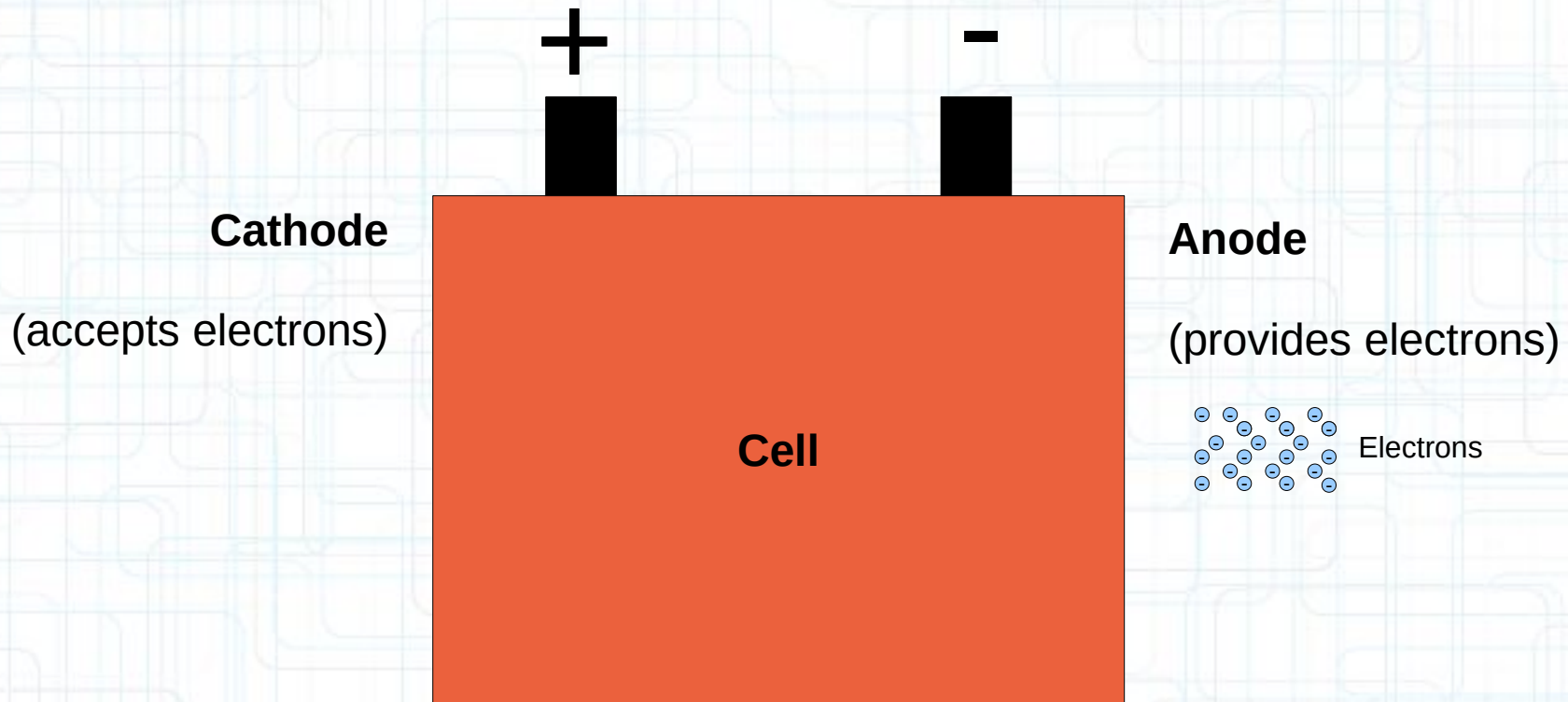
An introduction

with special consideration of RC model lithium batteries

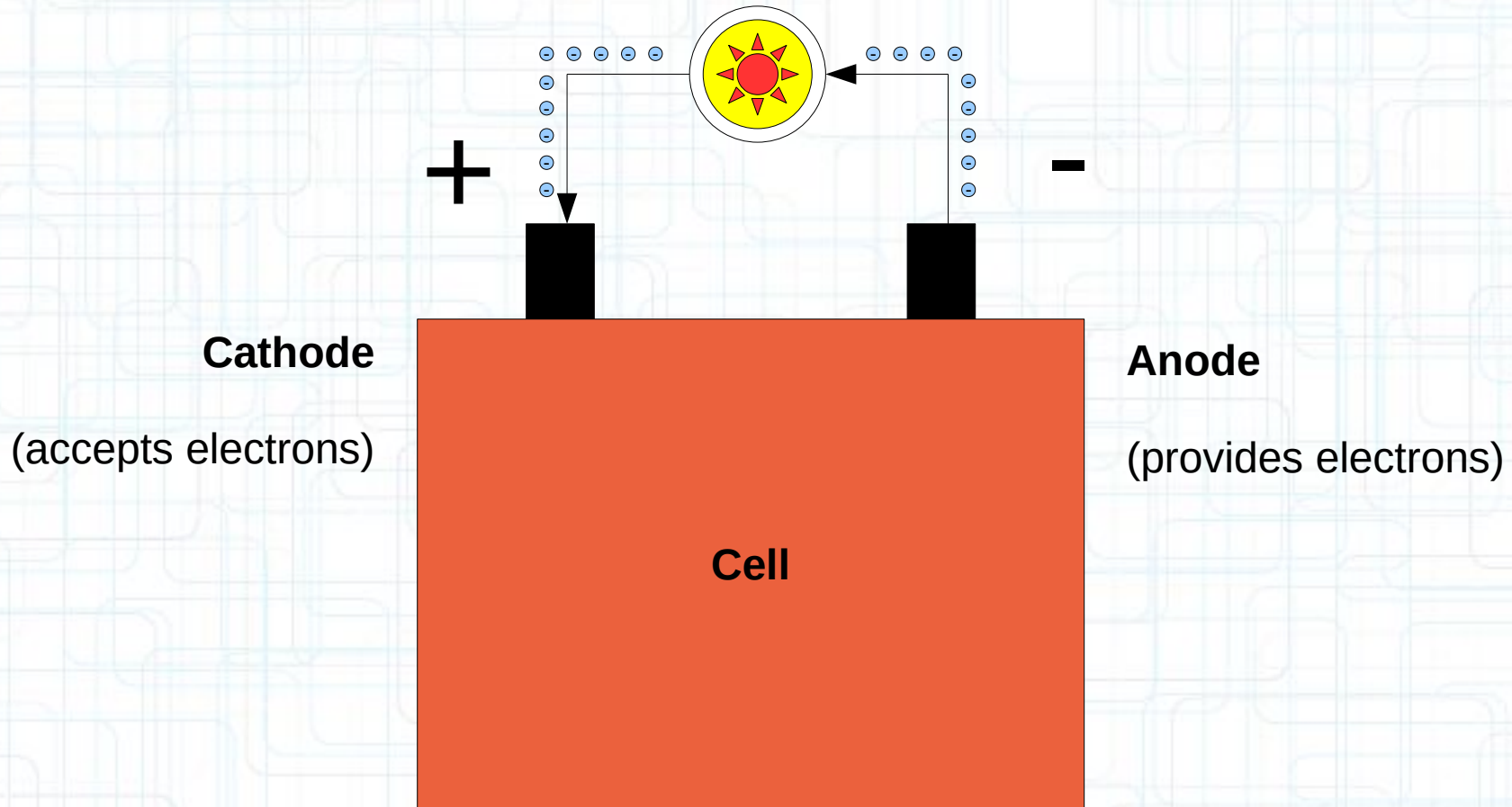
Dipl.-Ing. Frank Siegert

tl;dr: Summary on page 78

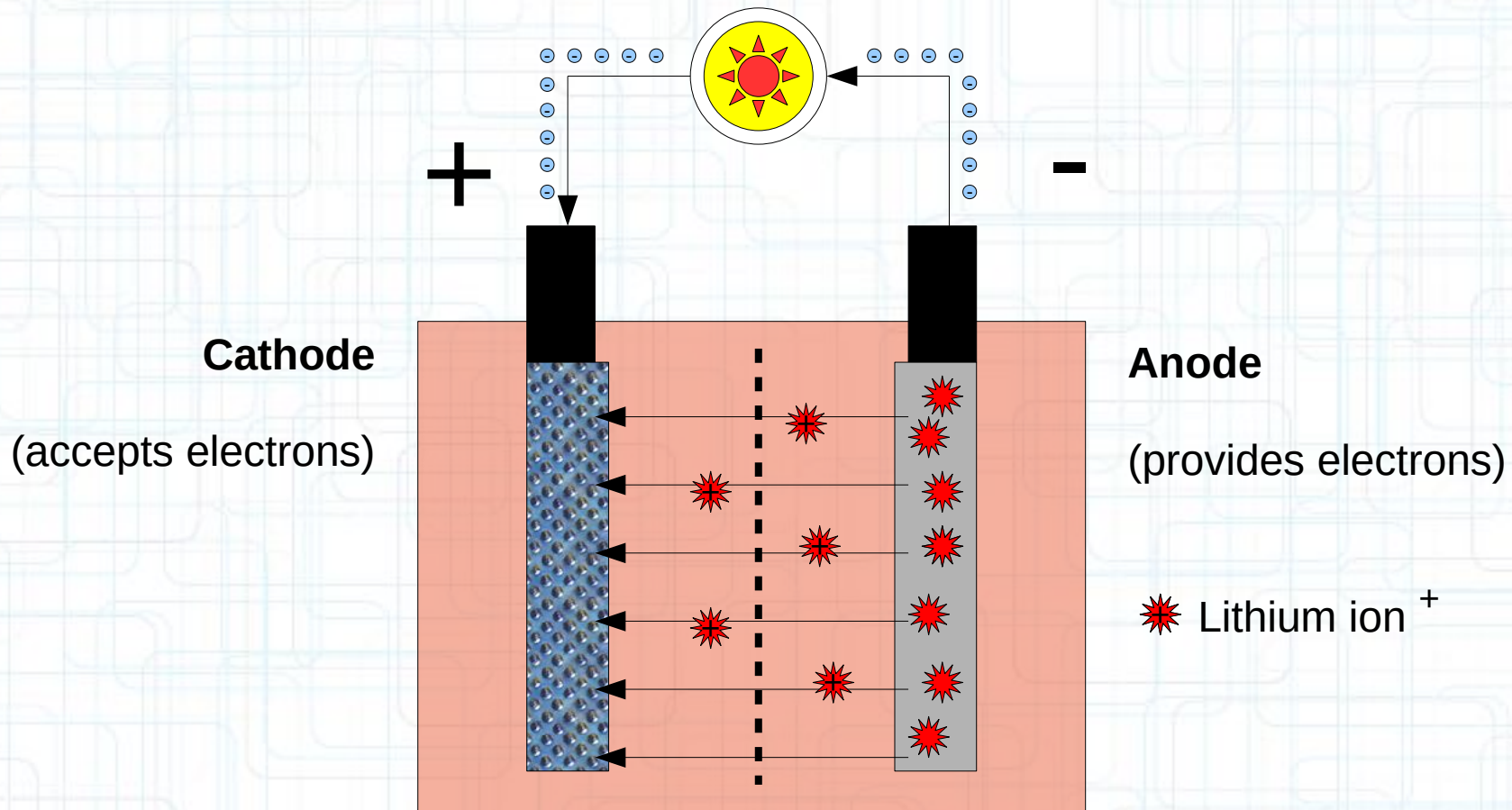
An outside look



Discharge – from the outside



Discharge – the inside



Electrons flow on the outside
 Li^+ -Ions flow in the cell

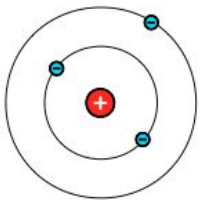
For electrons the cell is non-conducting

Lithium

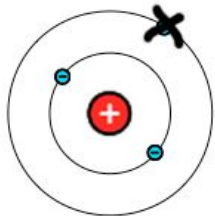
Periodensystem der Elemente

Hauptgruppe(1-2)		Beschreibung: Aggregatzustände: Stoffgruppen: Stoffreihen:										Hauptgruppe(3-8)																									
I.	II.	III.		IV.	V.	VI.	VII.	VIII.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.																					
1 H	2 He	Ordnungszahl		Elektronen negativität		Li : Fest		Nichtmetalle		Alkalimetalle		III.		IV.		V.		VI.		VII.		VIII.															
3 Li	4 Be	Ordnungszahl		Elektronen negativität		He : Gasförmig		Metalle		Erdalkalimetalle		5 B		6 C		7 N		8 O		9 F		10 Ne															
11 Na	12 Mg	Ordnungszahl		Elektronen negativität		Br : Flüssig		Übergangsmetalle		Erdmetalle		13 Al		14 Si		15 P		16 S		17 Cl		18 Ar															
Nebengruppe																																					
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe		
55 Cs	56 Ba	Lanthanoide (57-71)		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	87 Fr	88 Ra	Actinoide (89-103)		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
Lanthanoide (57-71)		57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu																					
Actinoide (89-103)		89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr																					

Quelle: Wikipedia: PSE, Julien Kluge, Hochwertiges Periodensystem der Elemente.

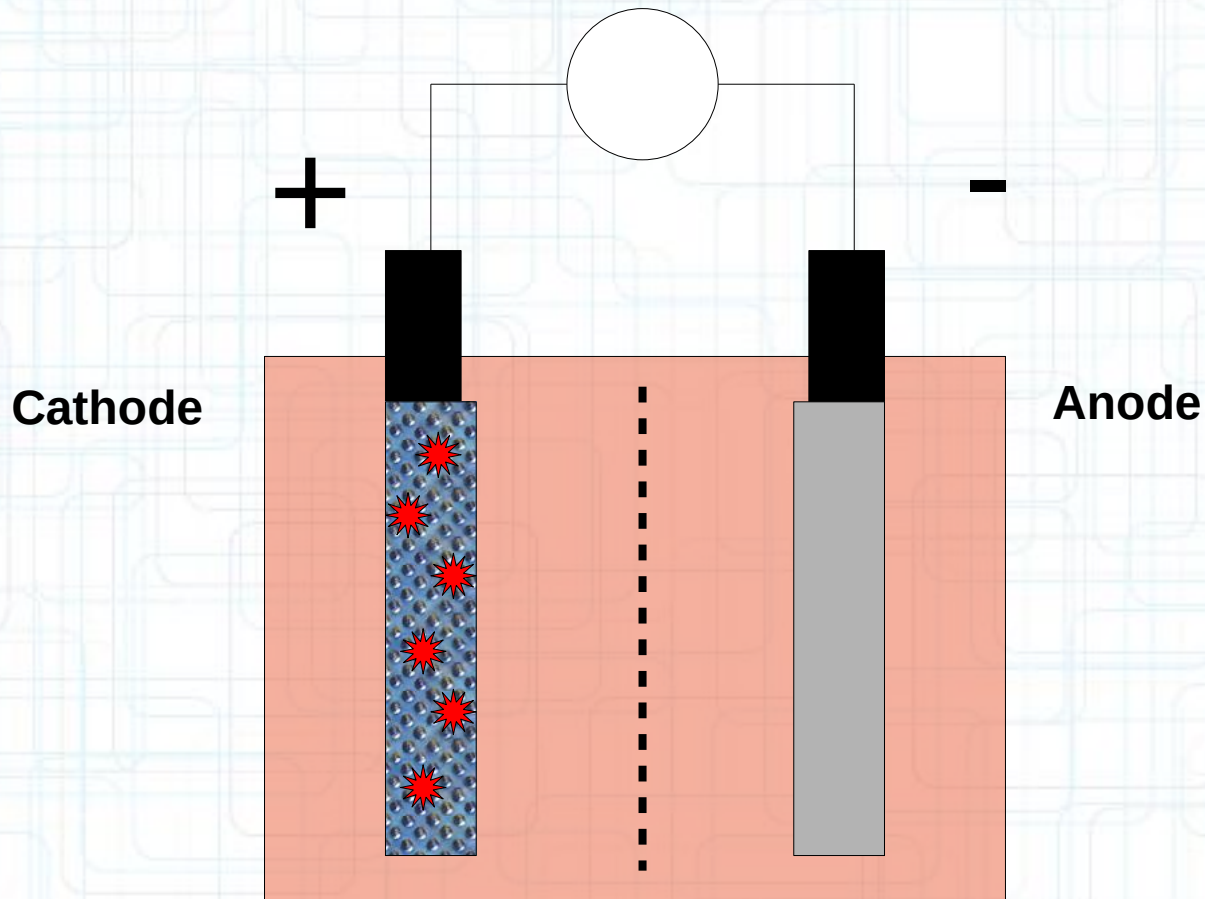


Lithium, 3 protons, 3 electrons



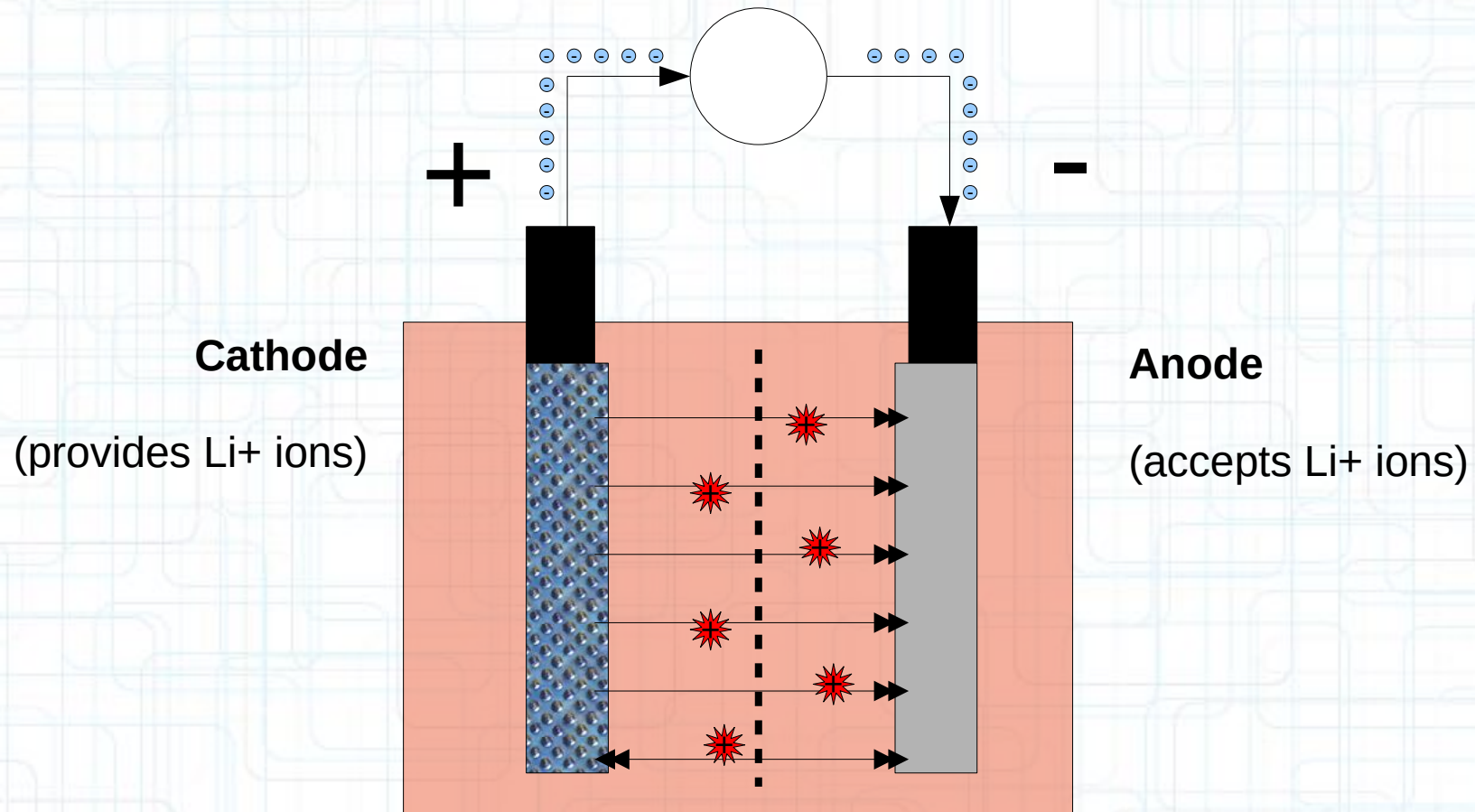
Lithium ion, 3 protons, 2 electrons, appears therefore positively charged

Newly formed Cell



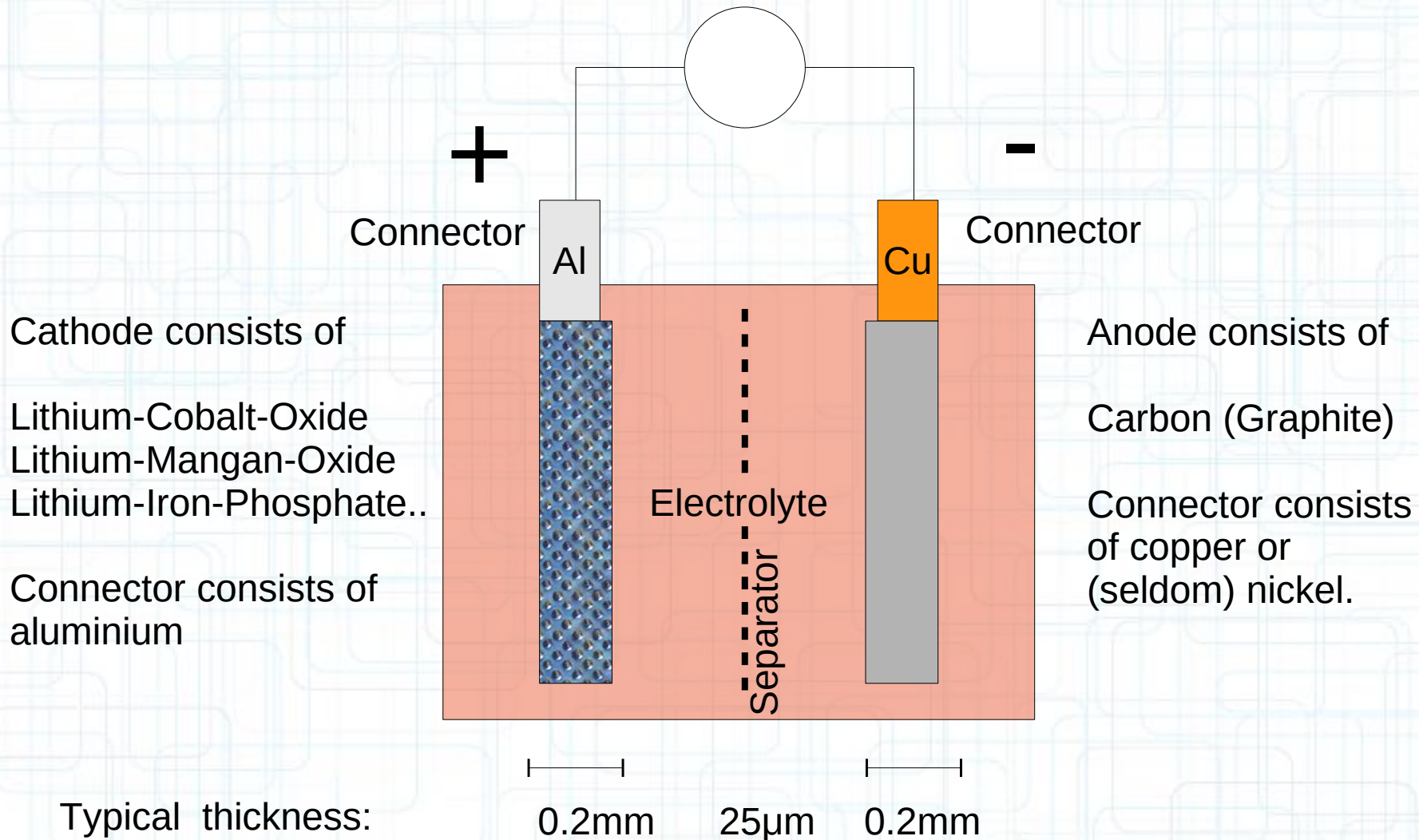
The cell tries to reach the lowest energy state. This point is reached when the cathode is fully filled with Lithium. It defines the fully discharged state.

Charging



Li⁺ ions are pushed into the anode.

Cell construction



Cell construction

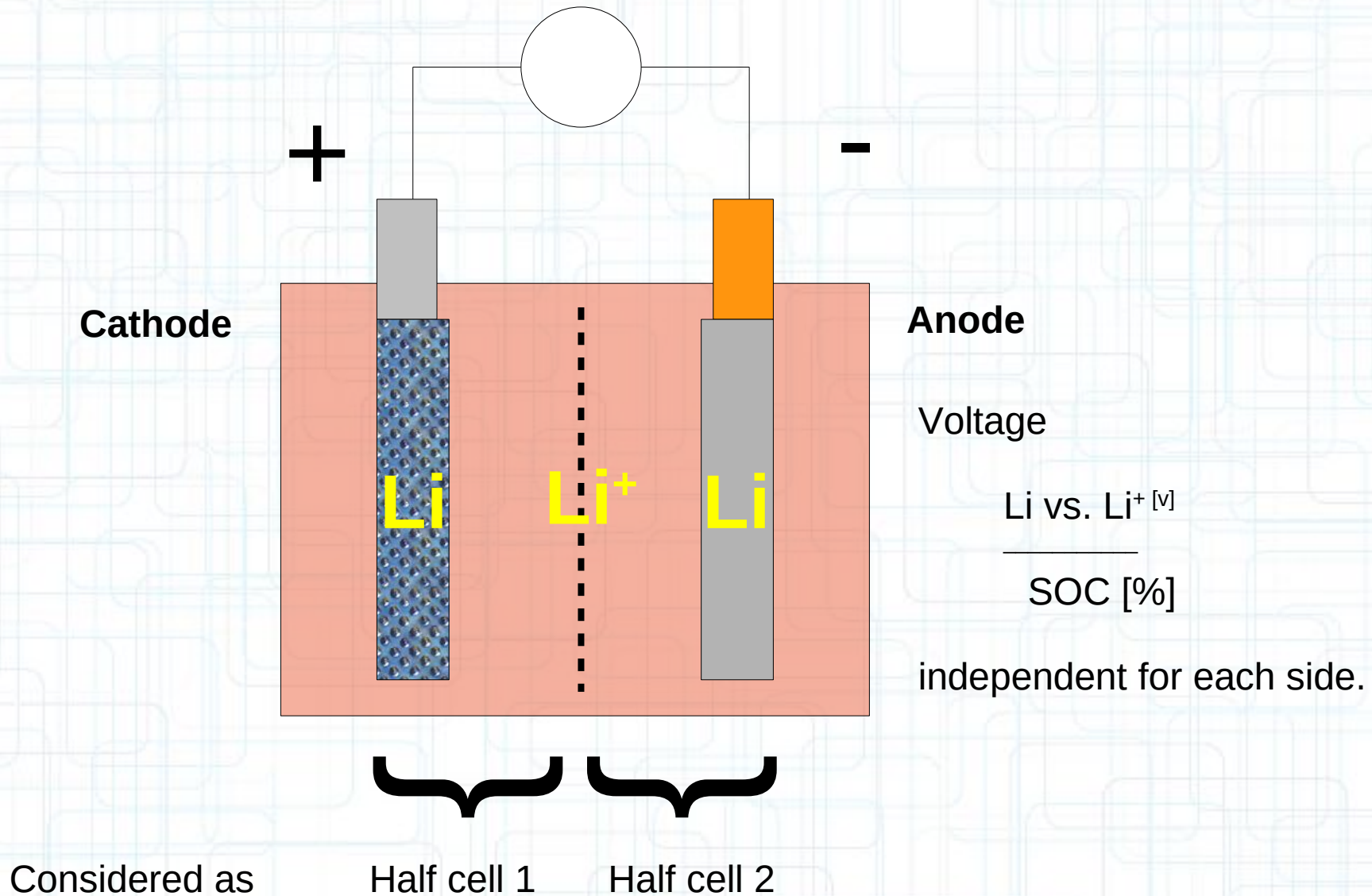
Fun fact: At 1A current each second

$$6.2 * 10^{18}$$

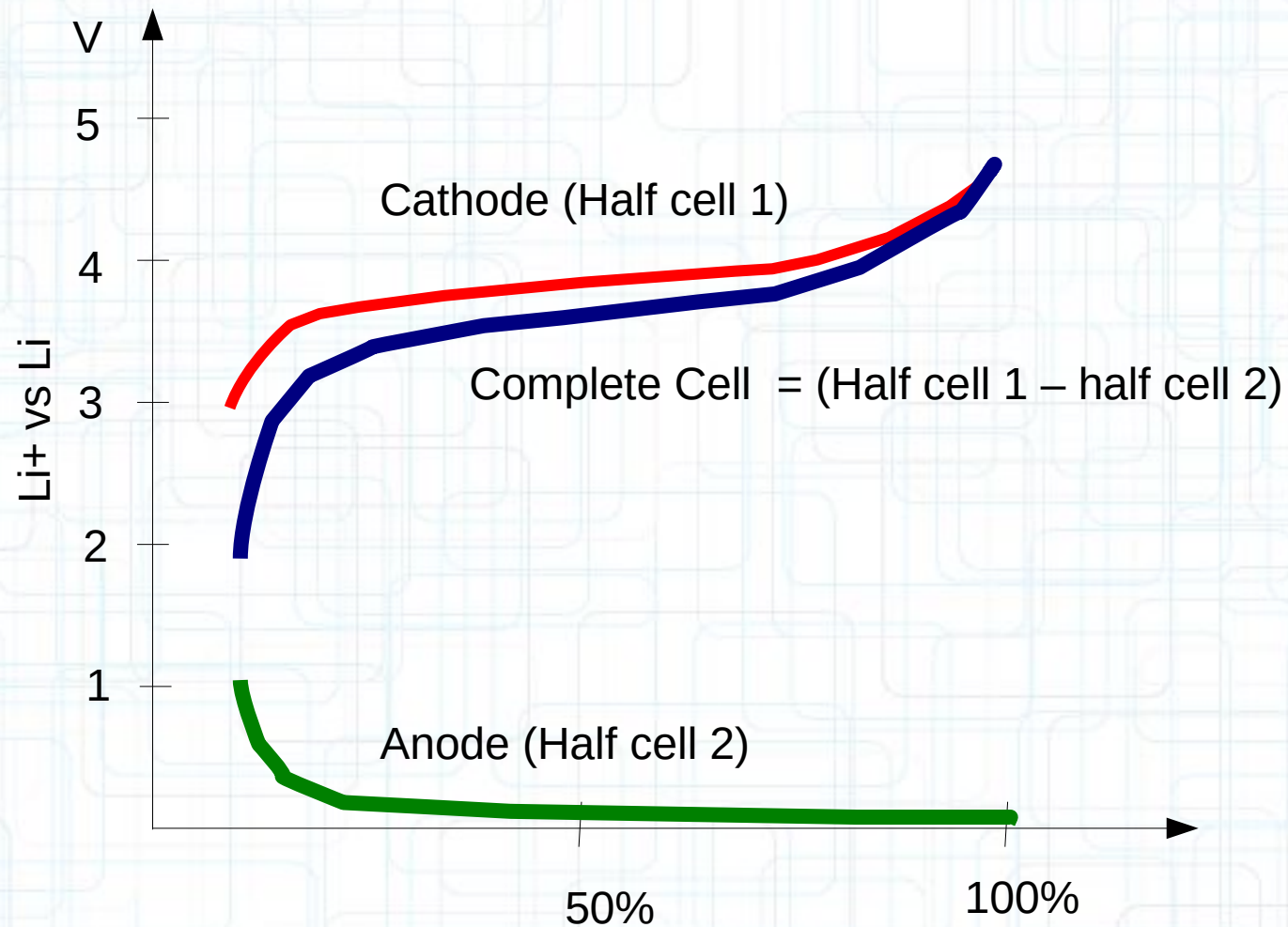
Li⁺ ions flow through the cell.

(Yes, there is actually stuff moving!)

Cell voltage source

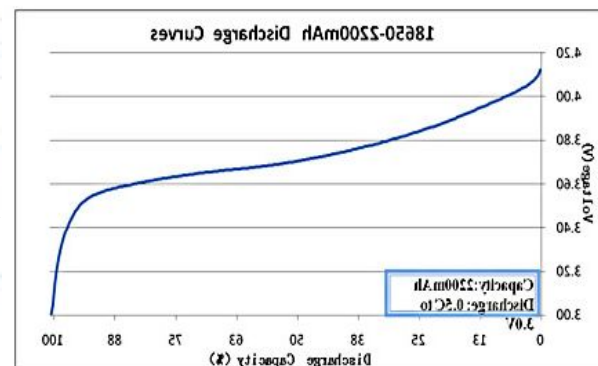
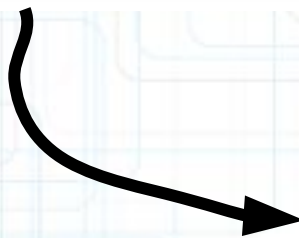
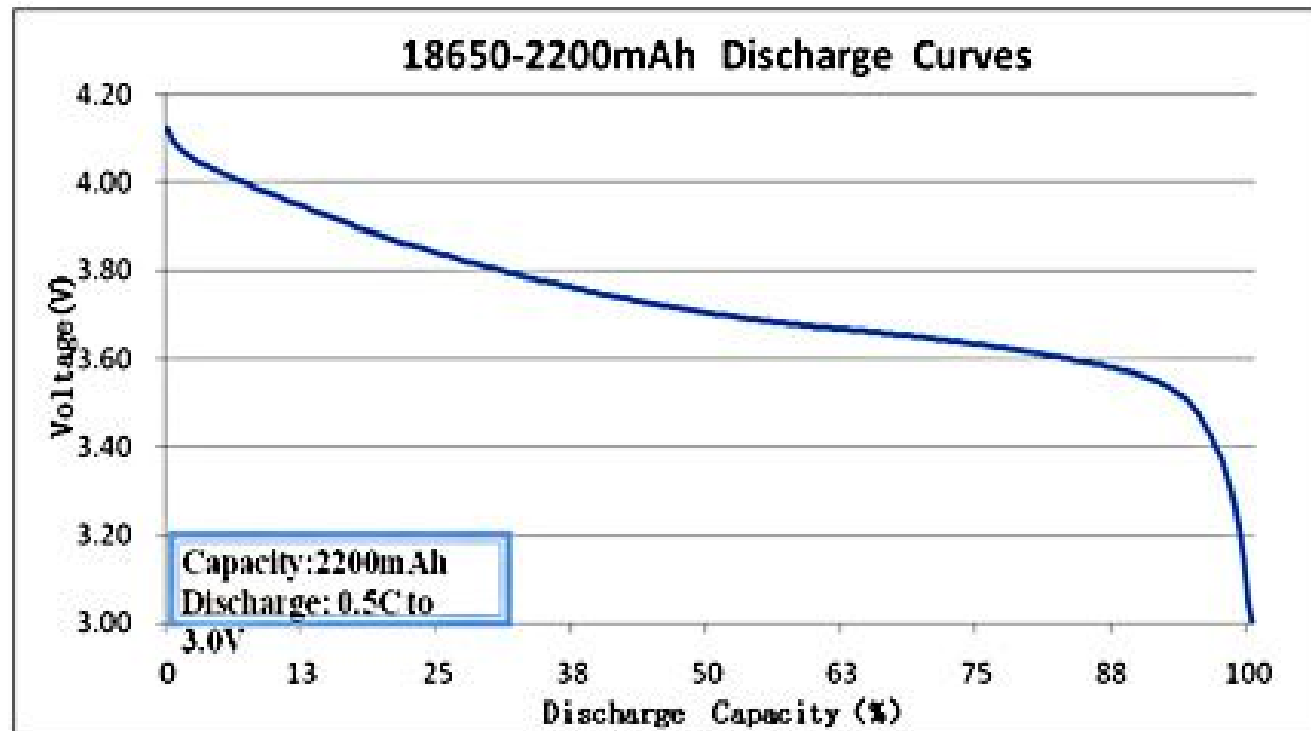


Cell voltage source



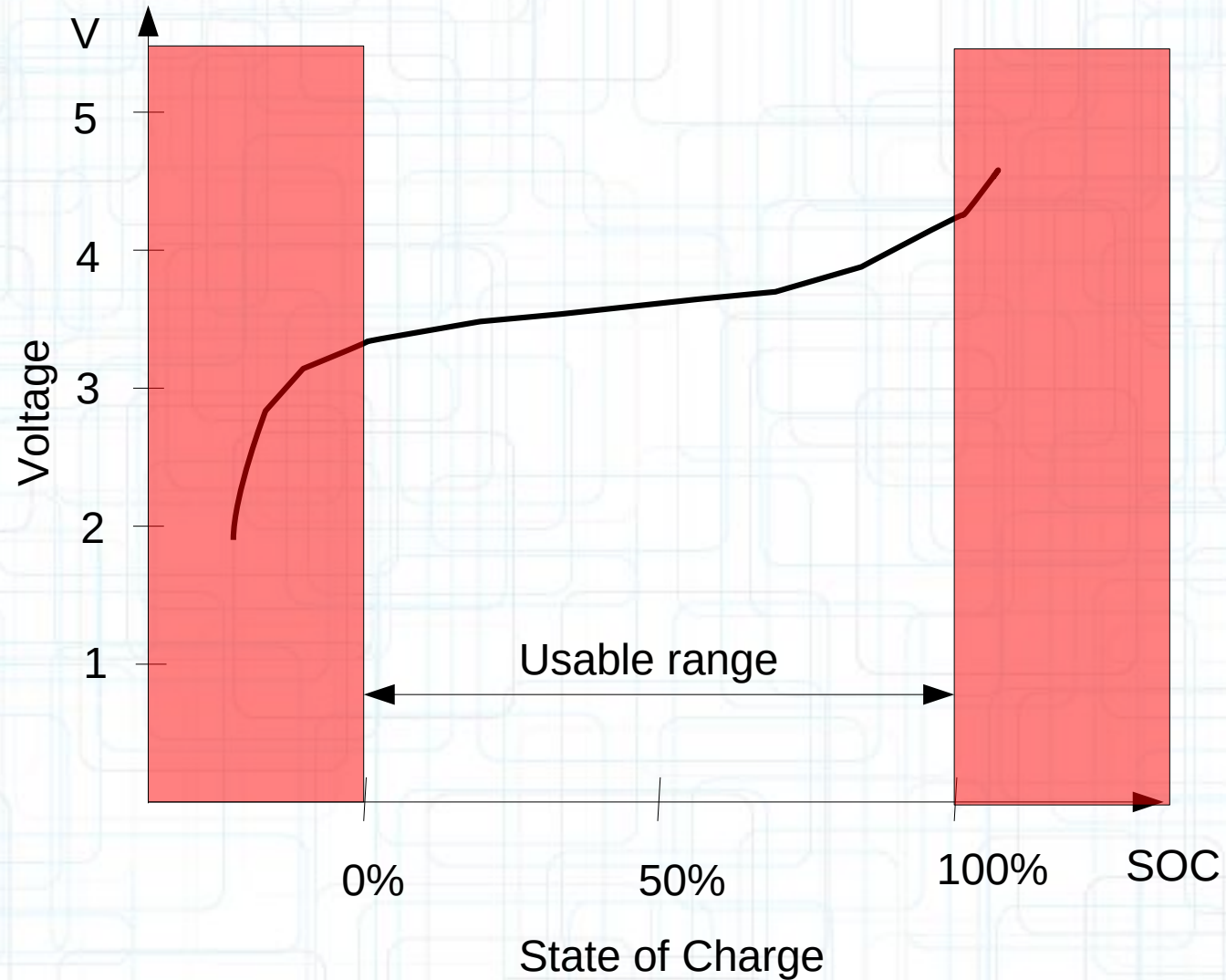
Cell voltage - Measured

Voltage in unloaded condition gives direct measure of the state of charge (SOC)

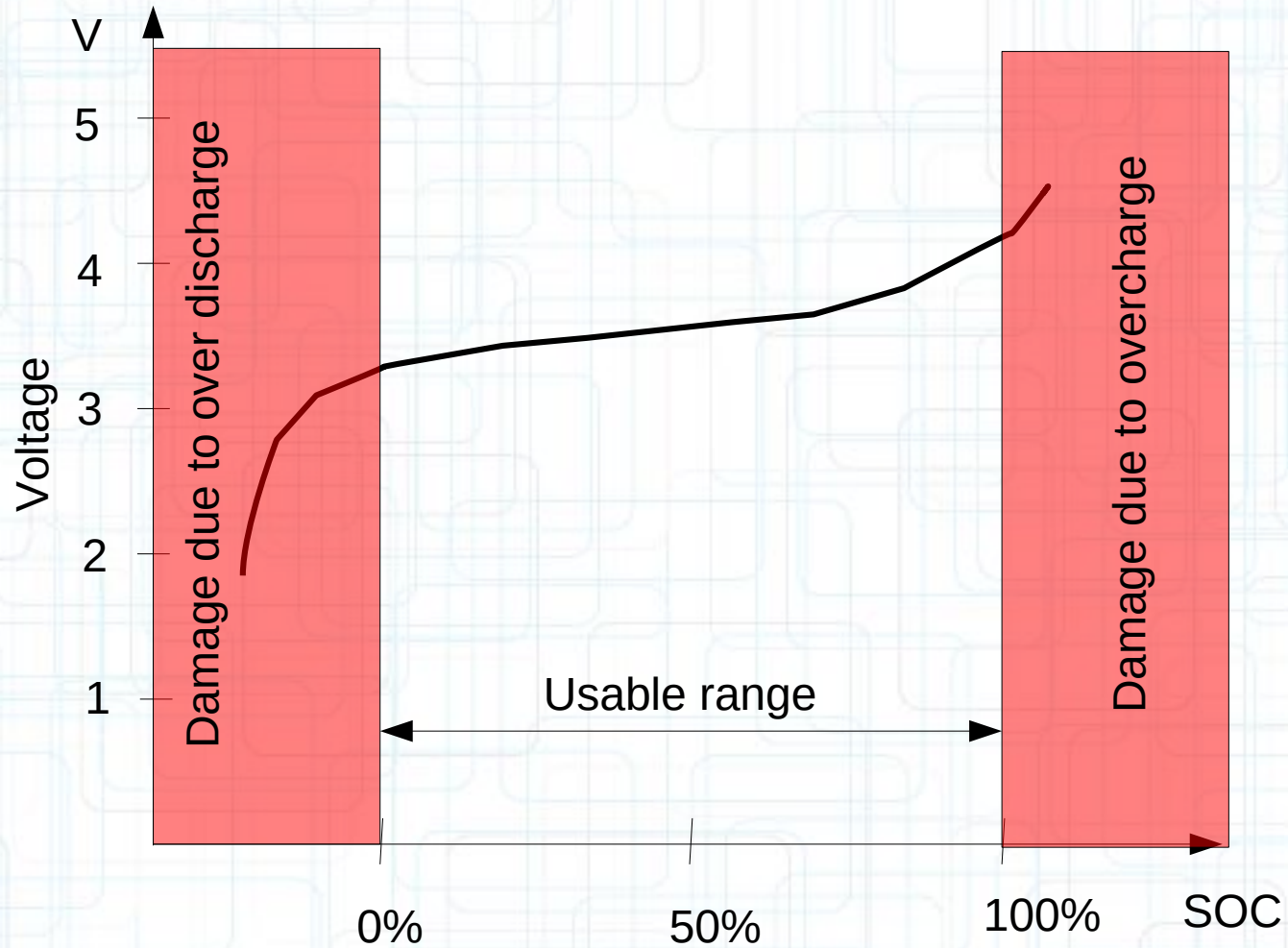


Curve remapped to SOC.
Matches theory (see
Previous page)

Voltage vs. SOC

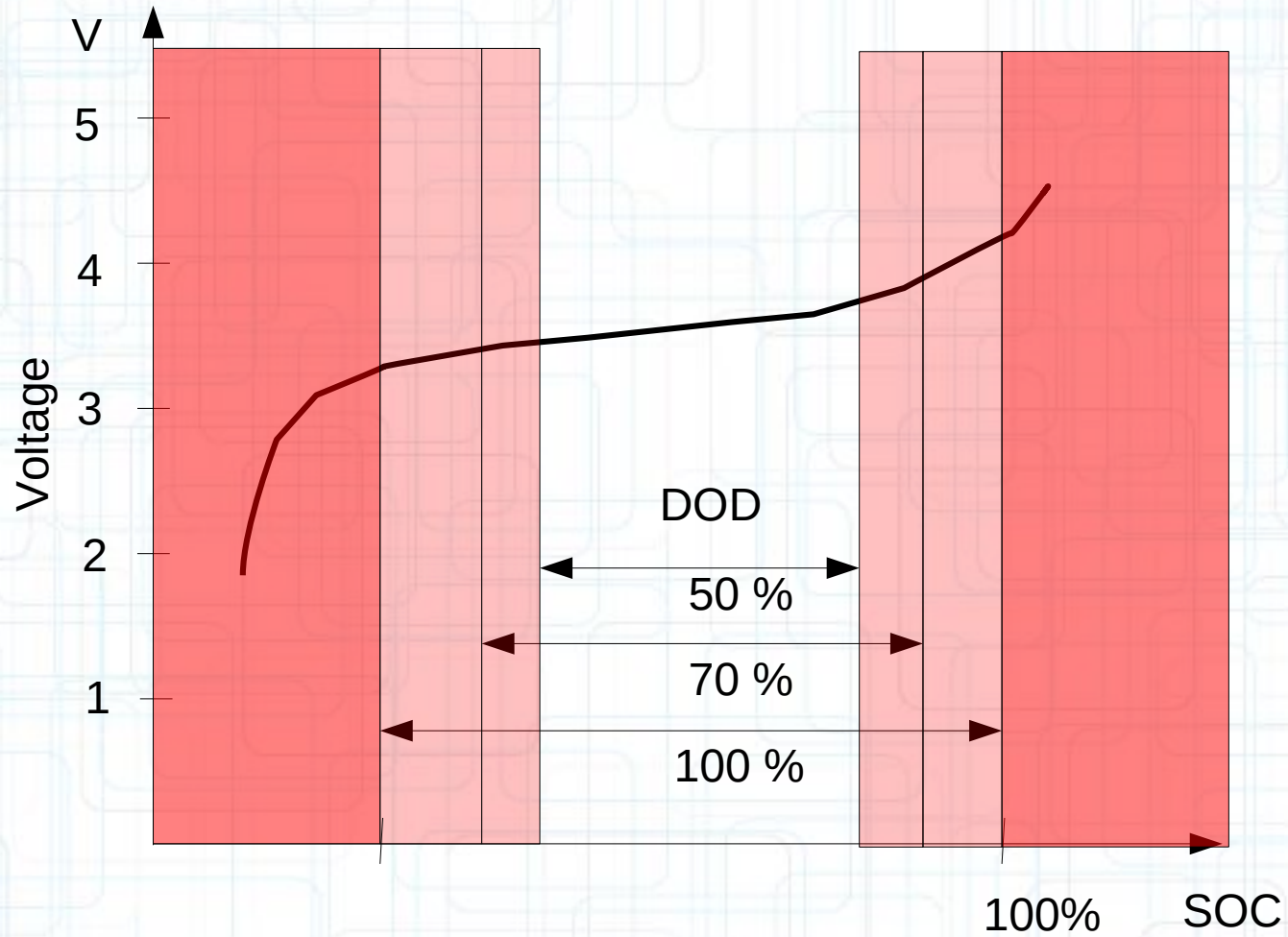


Voltage vs. SOC



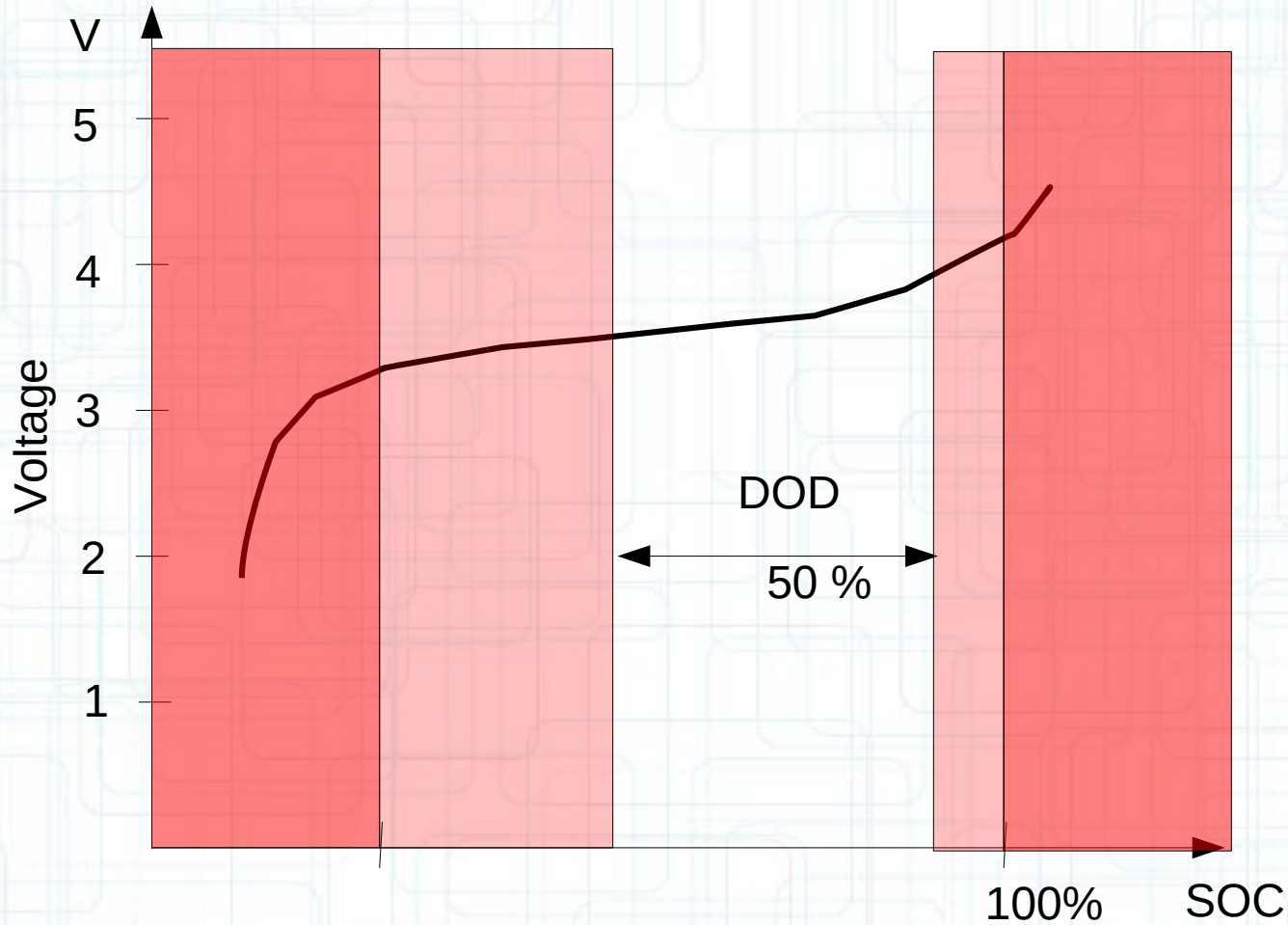
SOC = State of Charge

Voltage vs. DOD



DOD = Depth of Discharge
("How much of the available capacity is used")

Voltage vs. DOD



DOD = independent of the initial SOC, however other aging factors become noticeable at higher SOC or very low SOC, so for max. cell life is recommended not to charge fully (SOC < 100%) and not to use the full available capacity and not to drain the cell completely, see next slide.

Ageing - Cycles

Depth of discharge	Discharge cycles	Table 2: Cycle life as a function of depth of discharge A partial discharge reduces stress and prolongs battery life. Elevated temperature and high currents also affect cycle life.
100% DoD	300 – 500	
50% DoD	1,200 – 1,500	
25% DoD	2,000 – 2,500	
10% DoD	3,750 – 4,700	

Source: Batteryuniversity.com

Maximum use of capacity → Minimal Lifetime

Above numbers are defined for low current (~ 1C) discharge.
Higher discharge currents means less cycle life, especially at low temp.

Maximal Current → Minimal life time

Ageing – Storage

Temperature	40% charge	100% charge	Table 3: Estimated recoverable capacity when storing Li-ion for one year at various temperatures Elevated temperature hastens permanent capacity loss. Not all Li-ion systems behave the same.
0°C	98%	94%	
25°C	96%	80%	
40°C	85%	65%	
60°C	75%	60% (after 3 months)	

Source: Batteryuniversity.com

Storage ageing is dependent on

- Storage voltage (higher, the greater the ageing)
- Storage temperature (higher, the greater the ageing)

Ageing

The full ageing process is a combination of

Cycle ageing:

Damage due to charge/discharge cycles

Storage ageing:

Damage due to storage

$$\text{Ageing} = \text{Ageing}^{\text{Cycle}} + \text{Ageing}^{\text{Storage}}$$

Ageing

Effects of ageing

- **Capacity (lower)**
- **Resistance (higher)**
- **Discharge current ability (lower)**
- **Charge current ability (lowers)**

Ageing does not happen linearly, but accelerates later in cell life (See cell chemistry section for details).

Temperature effects

Cell performance is highly affected by temperature.

Performance numbers of a cell are valid only for temperatures at or higher than 30 °C. C-Rates drop dramatically below 20 °C both for discharge and especially charge rates.

At 0 °C the maximum allowed charge rate typically drops to 0.1C, discharge rates to 5C even for high performance cells rated at 30C+ nominally.

- **Maximum C-Rates drops with temperature. Heat the cell to >30 °C before use.**
- **Exceeding max. discharge and charge rates at low temperatures causes permanent damage**

Temperature effects

At high temperatures $> 55\text{ }^{\circ}\text{C}$ degeneration effects set in and cycle ageing is accelerated.

- **Always keep a cell below $55\text{ }^{\circ}\text{C}$ during use.**
- **Exceeding max. discharge and charge rates at high temperatures causes permanent damage and shortens cell life.**
- **Do not store a battery at high ambient ($> 25\text{ }^{\circ}\text{C}$) temperatures for long periods, as storage aging is accelerated too. The higher the storage charge, the more pronounced is this effect.**

Physical construction

- “Pouch cell”
- Layered or wound
- In plastic bag
- Filled with electrolyte (gel/liquid)



Source: Wikipedia

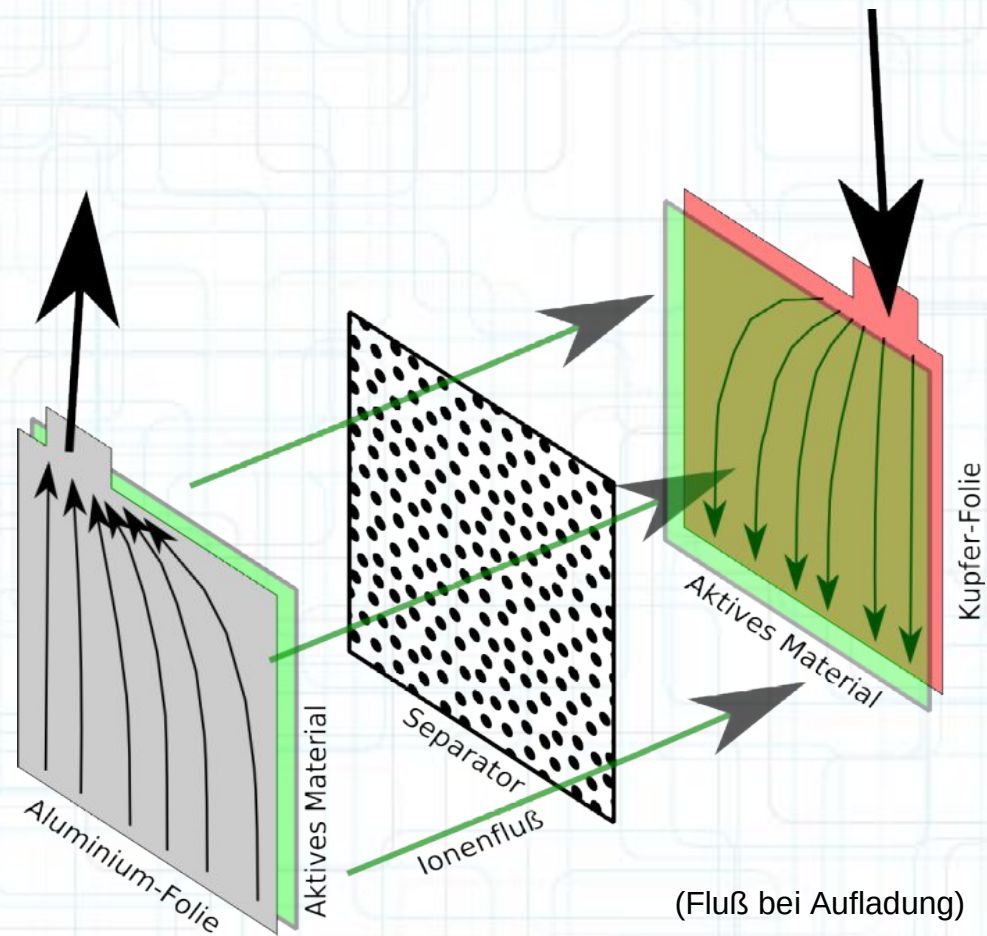
Construction

Thin layers, wrapped and stacked for maximum surface area



Source: Wikipedia

Current / Ion flow



- The flow of current in the cell is not evenly distributed but concentrated at the connectors.

Heat generation

Heat generation in the cell during charge / discharge comes from two sources:

- Irreversible heat generation

Through normal resistive resistance (Ohms law) and irreversible chemical changes in the cell (damage).

- Reversible heat generation

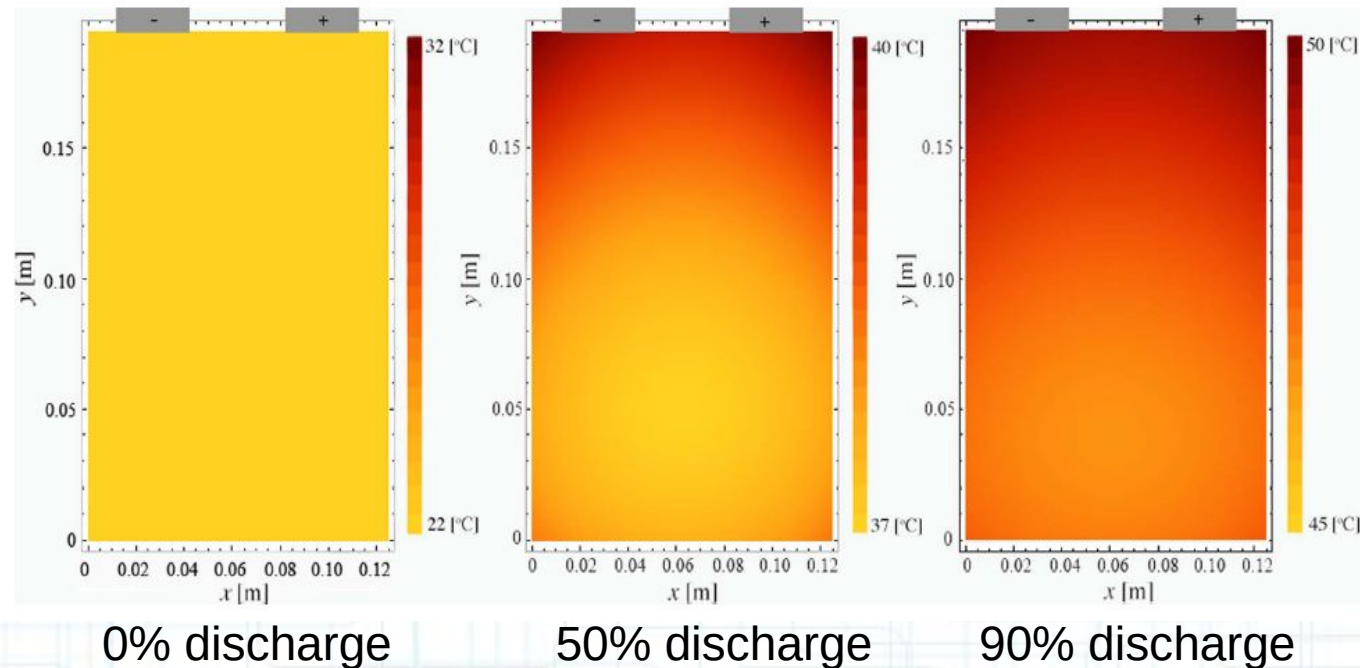
Electrochemical changes in the charge / discharge cycle.

For high current application the irreversible heat generation dominates.

For a long cell cycle life it is important to use the cell within the design specifications. Cycling at too low temperature damages as much as cycling at too high temperature, however the type of damage is different.

Heat generation

The irreversible heat generation is not evenly distributed but more pronounced near the connectors.

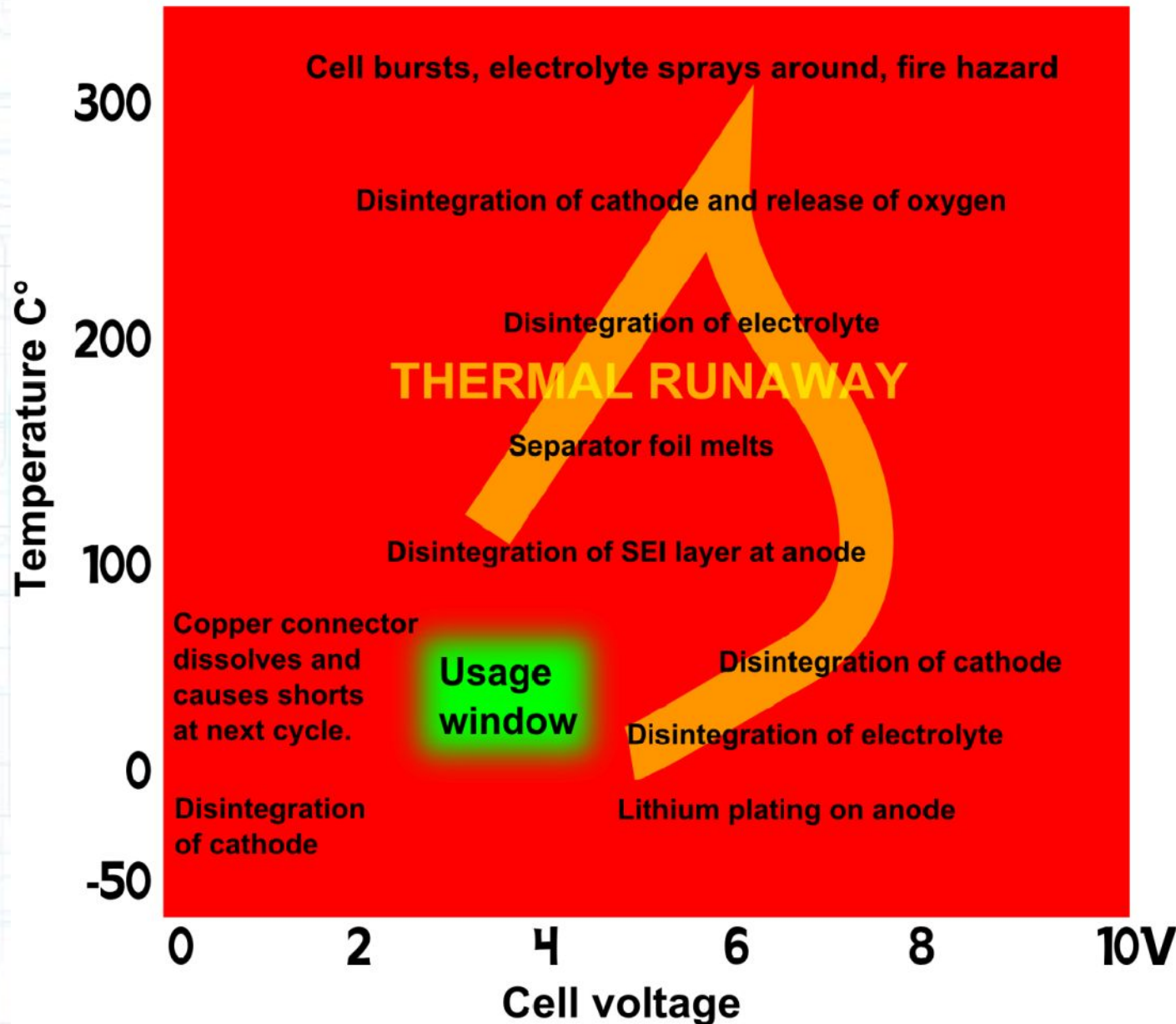


→ Cells do not age uniformly, there are areas that are more effected by high current flow.

→ Packs of cells (batteries) do not age uniformly, as the inner cells get hotter during high current cycling.

Window of safe use

“Better stay in the green... dragons outside!”



Cell chemistry

Positive electrode (Cathode): Lithiated form of a transition metal (e.g. Lithium-cobalt(III) oxide LiCoO_2 , lithium-nickel oxide LiNiO_2 or Lithium-manganese oxide LiMn_2O_4) as active material.

Negative electrode (Anode): Carbon (C) as graphite (C_6)

Electrolyte: Lithium salts (LiPF_6 , LiBF_4 , LiClO_4) and organic solvents (ethylene carbonate, dimethyl carbonate, ...)

Cell chemistry

- Reaction (Charge)

- Cathode



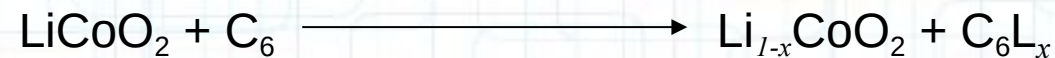
Inner transport: Ions

Outer transport: electric current

- Anode



- Main



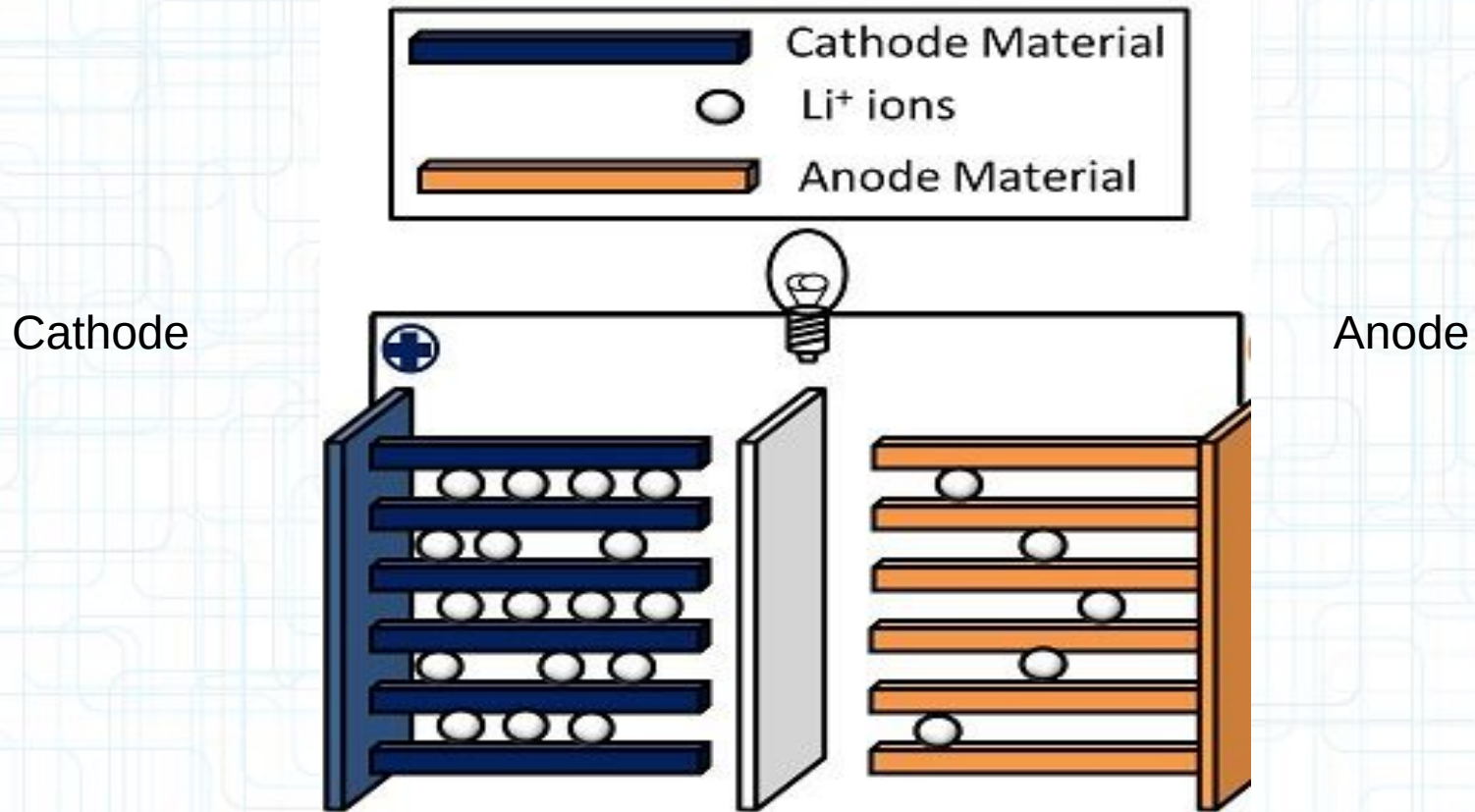
Cathode is losing lithium during charge, Anode is filled with lithium.

Cell chemistry

Intercalation

By intercalation (from Latin intercalare = insertion) in the chemical sense is meant the incorporation of molecules, ions (rarely also atoms) in chemical compounds, which do not change their structure during the storage process significantly.

Cell chemistry



Source: Wikipedia

Cell Chemistry

The ability of the cell to provide high current/capacity depends on:

For high currents: Ion transport capacity
“How many ions can flow through the cell in a given time?”

→ High current cell (higher weight / mAh)

Limited by:

- Surface area**
- Interfaces (transitions between layers)**
- Connectors**
- Temperature**

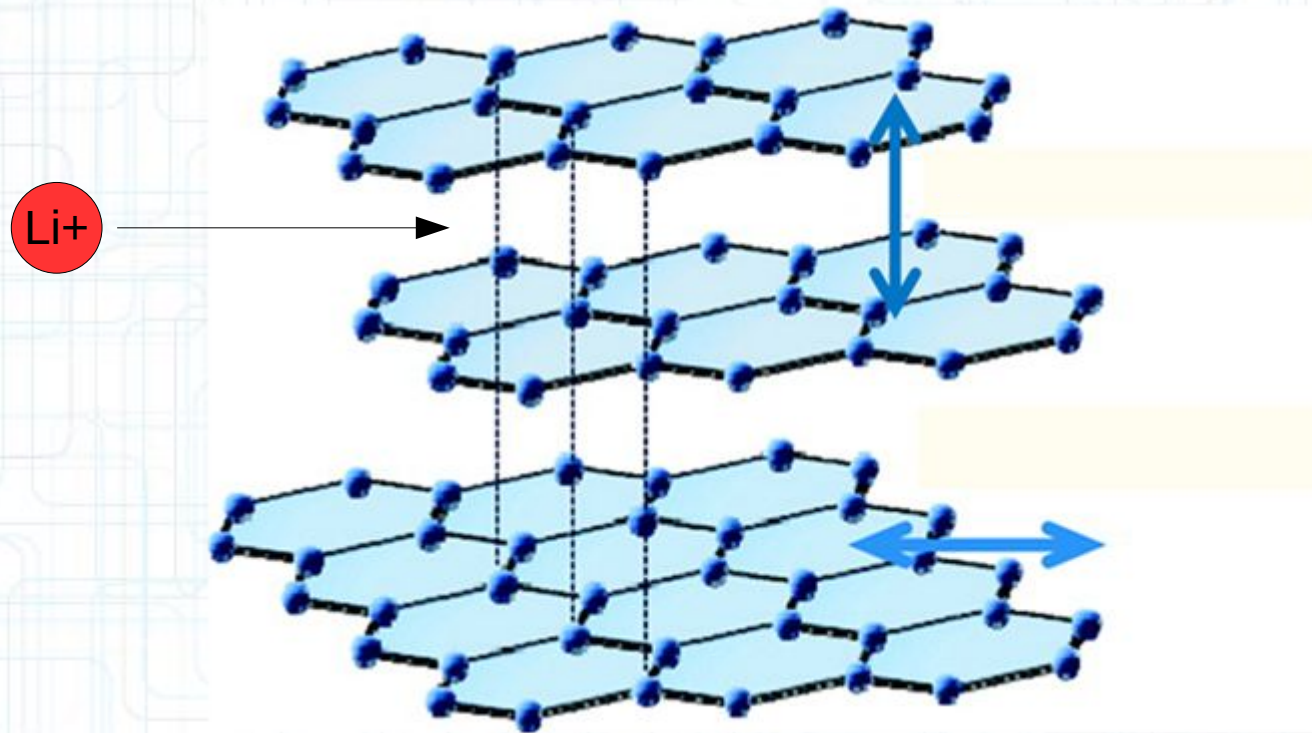
For high capacity: Ion supply and acceptance limits
“How many ions can be moved through the cell during a charge / discharge cycle?”

→ High capacity cell (lower weight / mAh)

Requirements are not compatible. Cells tuned for high capacity (e.g. EV cells) cannot provide high currents and vice versa. Cells used for RC models are usually tuned for high currents.

Cell chemistry - Anode

The graphite of the anode consists of layers:



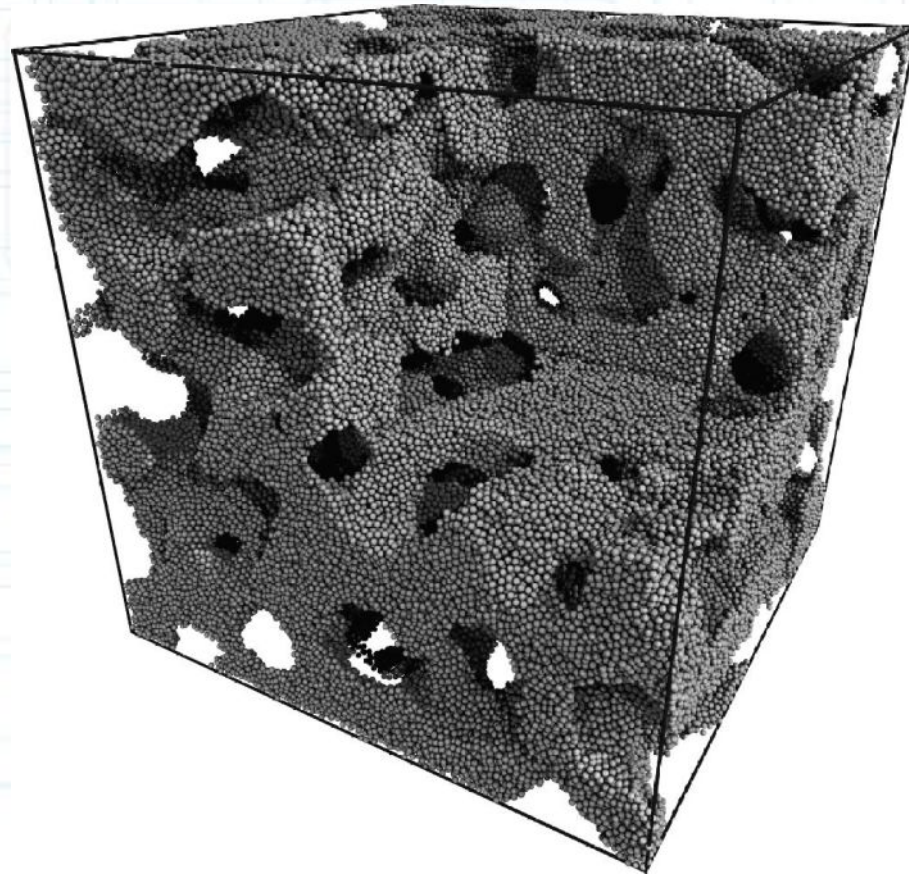
Lithium ions can only enter “from the side”.

→ Charge current is always smaller than Discharge current (“it is easier to pull a key than to insert it into the same lock”)

Cell chemistry - Anode

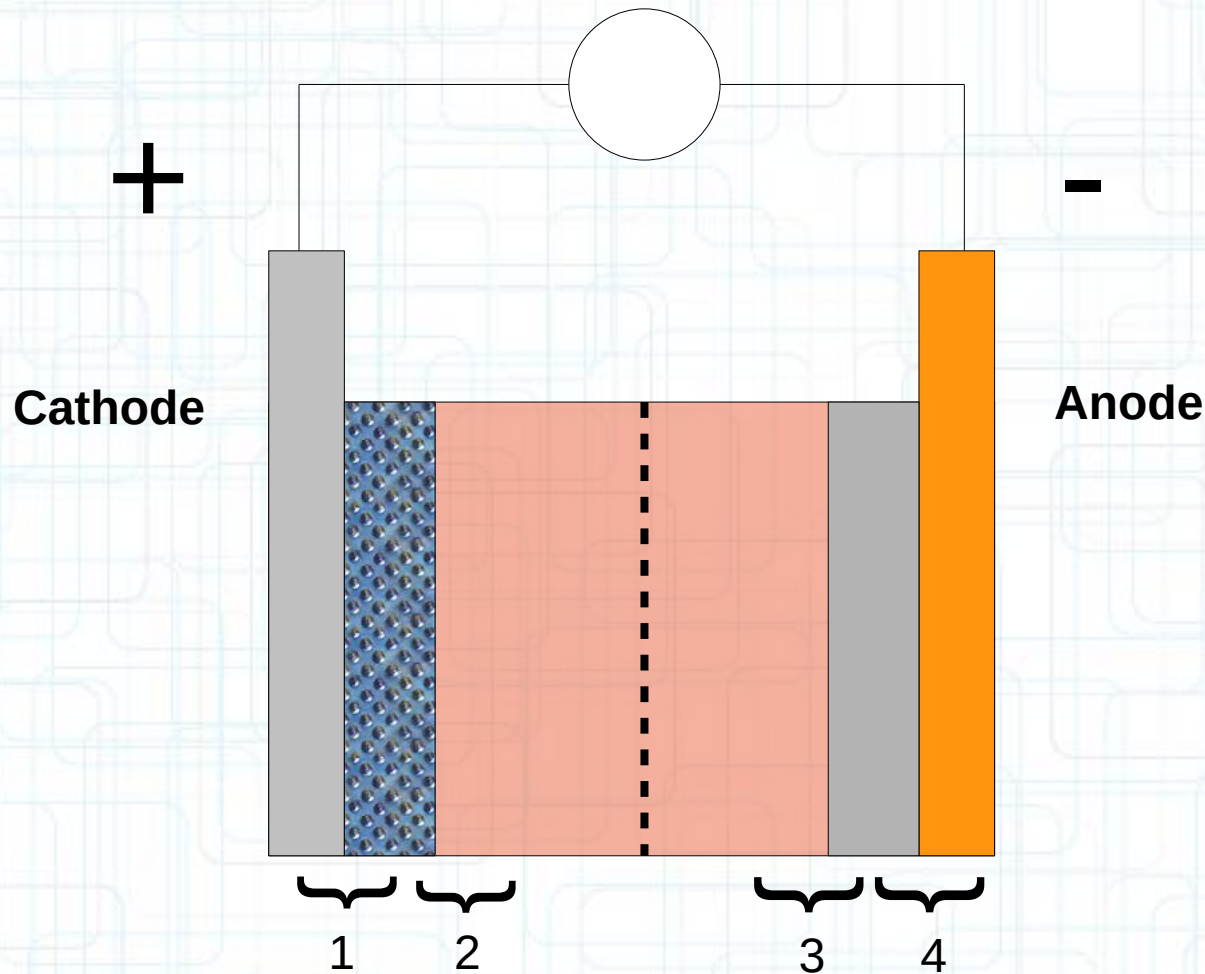
“Nanotechnology”:

Graphite layer with micro structure (“nanoporous”)
→ larger active Surface.



'Nanoporous Carbon', Source: ncsu.edu

Transition areas (interfaces)

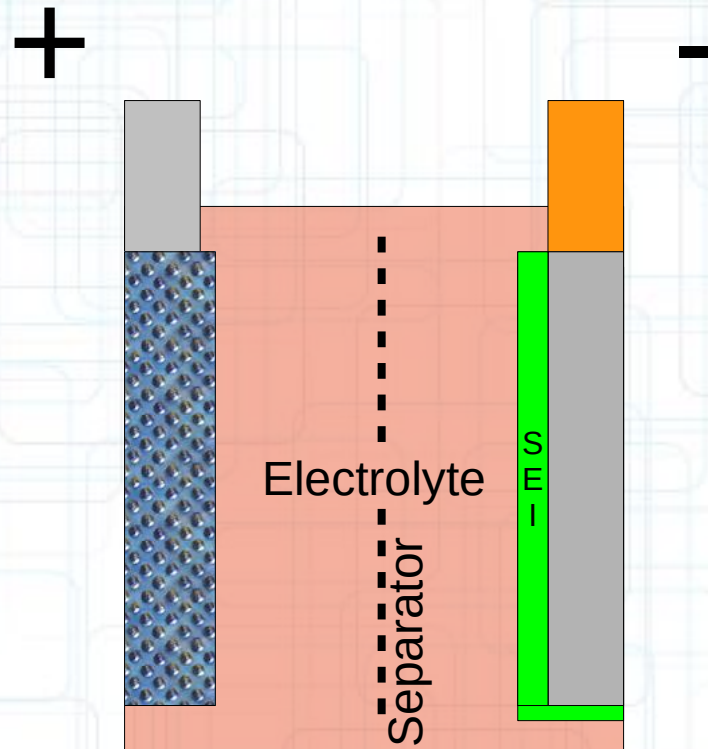


Relevant are zone 2: "Cathode – Electrolyte" and 3: "Electrolyte – Anode", Especially the later is very important for proper cell function.

Cell chemistry - Anode

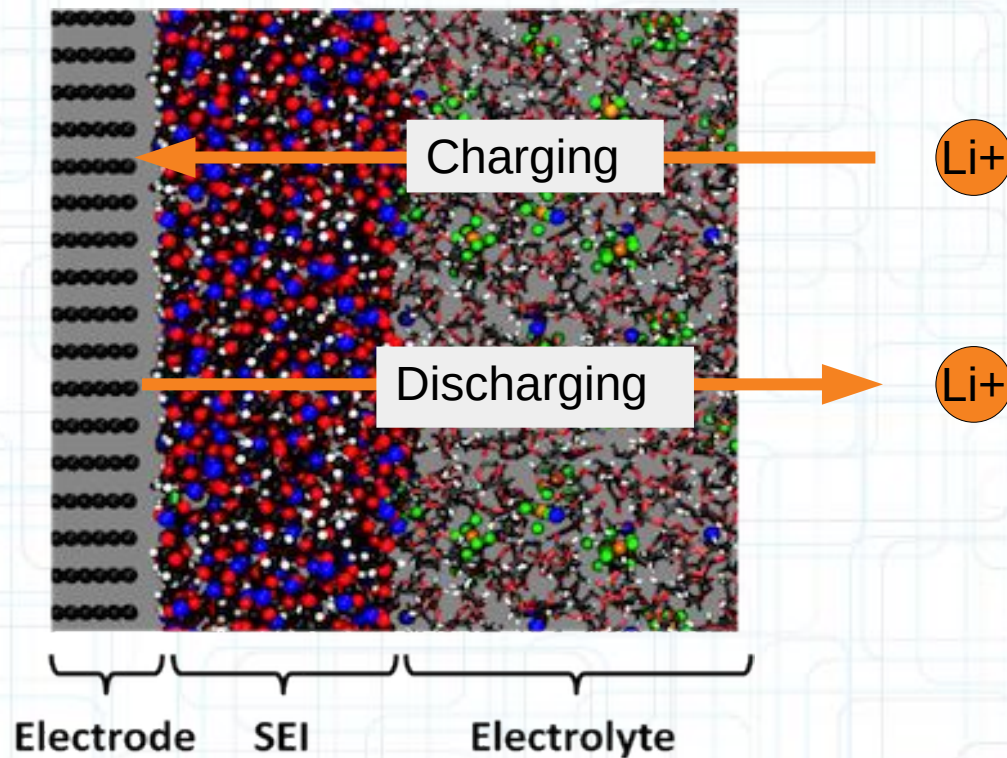
The anode would be destroyed quite fast by reactions with the electrolyte. The electrolyte is designed therefore to create reaction products that coats the areas where it is in contact with the anode. This zone is called

Solid Electrolyte Interphase (SEI)



Cell chemistry - Anode

The SEI layer is created during manufacturing during the very first cell cycle. Lithium ions have to travel through it during charge and discharge.



Source: 'A snapshot of the interfaces between the graphitic anode, a representative SEI, and the electrolyte.' The University of Chicago, Searle Chemistry Laboratory, 2012, Martin McCullagh, Ruibin Liang, <https://vothgroup.uchicago.edu/research/renewable-energy-materials> (Arrows and text fields added)

Cell chemistry - Anode

SEI layer:

- **Protection of the anode and electrolyte**

Without SEI the cell would die after a few cycles

But also

- **Increases resistance**

The thicker the SEI layer the higher the resistance.

- **Loss of free lithium**

The thicker the SEI layer the less capacity the cell retains.

- **Limiting Lithium transport ability**

The thicker the SEI layer the more the cell is effected by plating during charge.

Cell chemistry - Anode

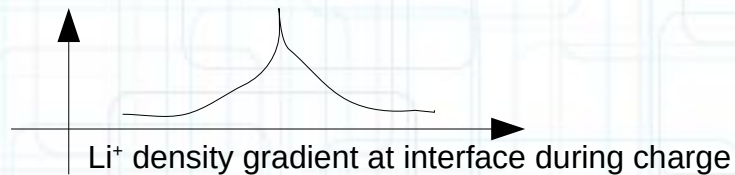
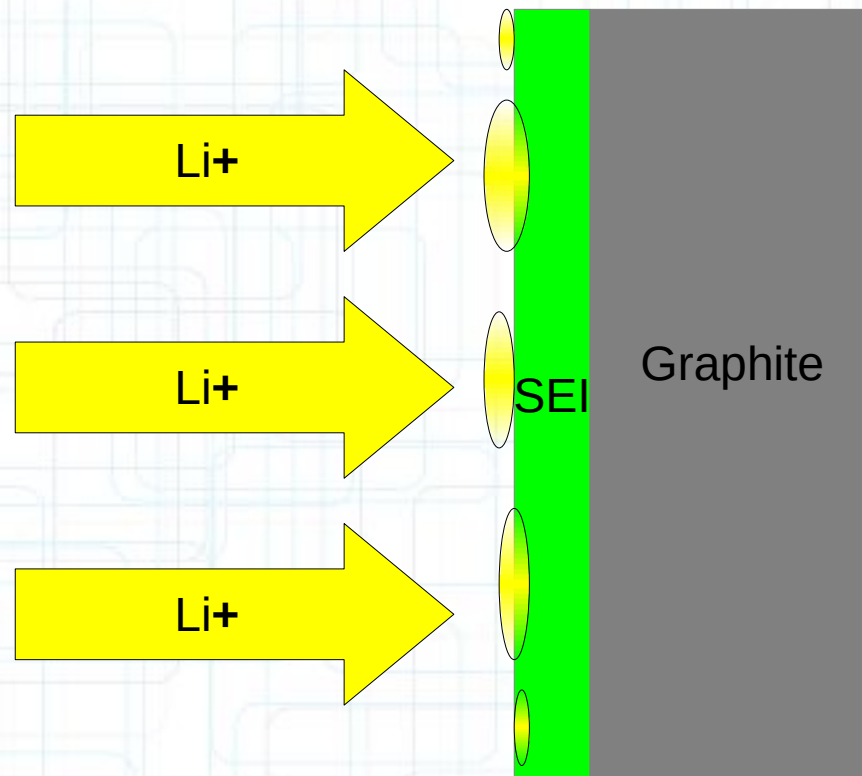
The SEI layer is created during manufacturing.

Every cell on the market has at least gone through one charge/discharge cycle. This cycle is crucial to build the SEI layer initially.

The SEI layer thickness increases during the lifetime of the cell. High current load and too high temperatures accelerates the process.

Cell chemistry - Anode

Plating: Deposition of metallic lithium at the interface



Cell chemistry - Anode

Plating occurs when 'more Li^+ ions are pressed into the anode' than transport and holding capacity is available.

→ During charge, not discharge

Holding capacity reached:

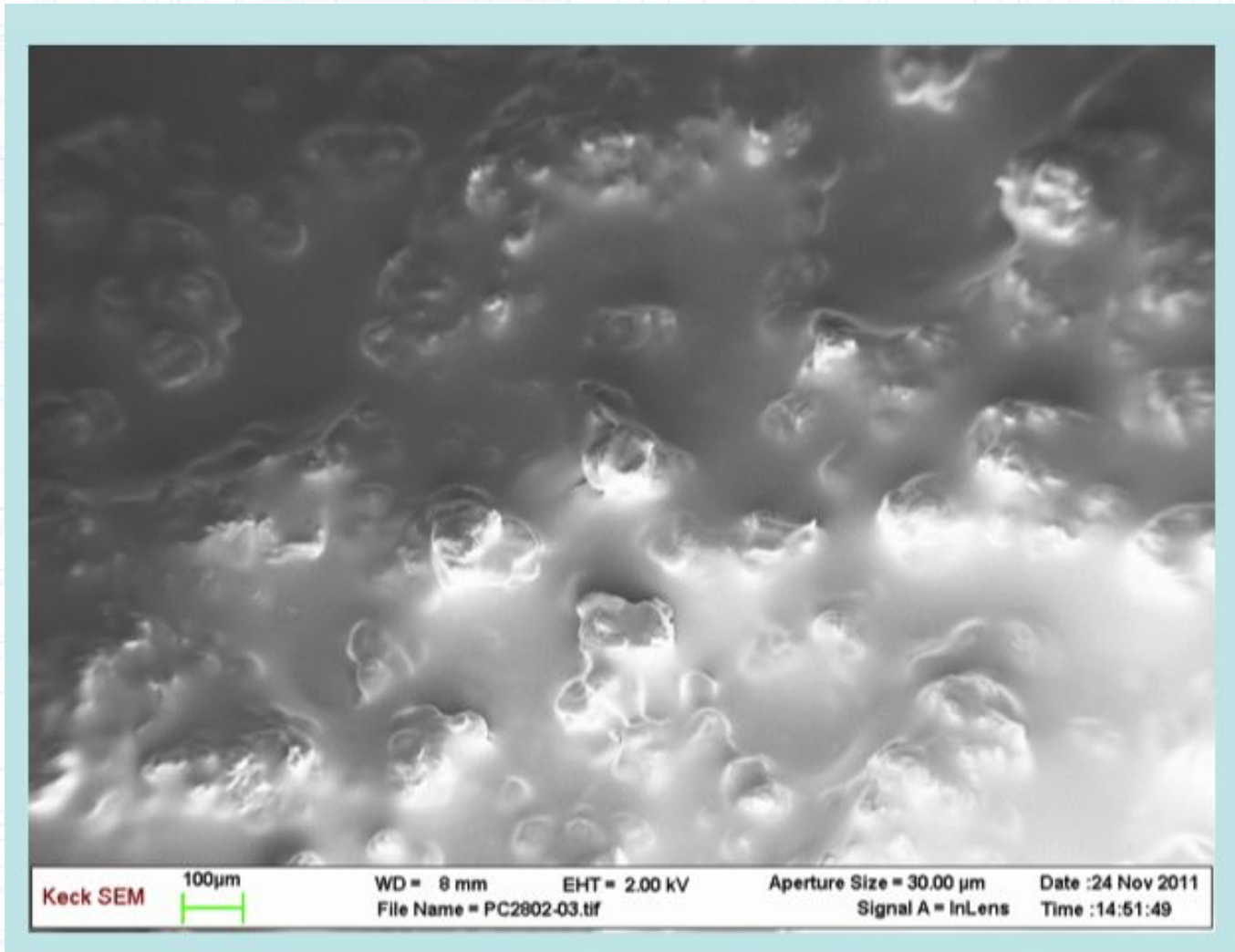
- Overcharge condition, anode material fully filled up (> 4.2V for normal cells, >4.3/4.4V for HV)

Transport capacity reached:

- Too high charging current
- Depends on temperature (lower temp, higher plating)
- Depends on cell age and SEI layer thickness, older cells are more prone to plating.

Cell chemistry - Anode

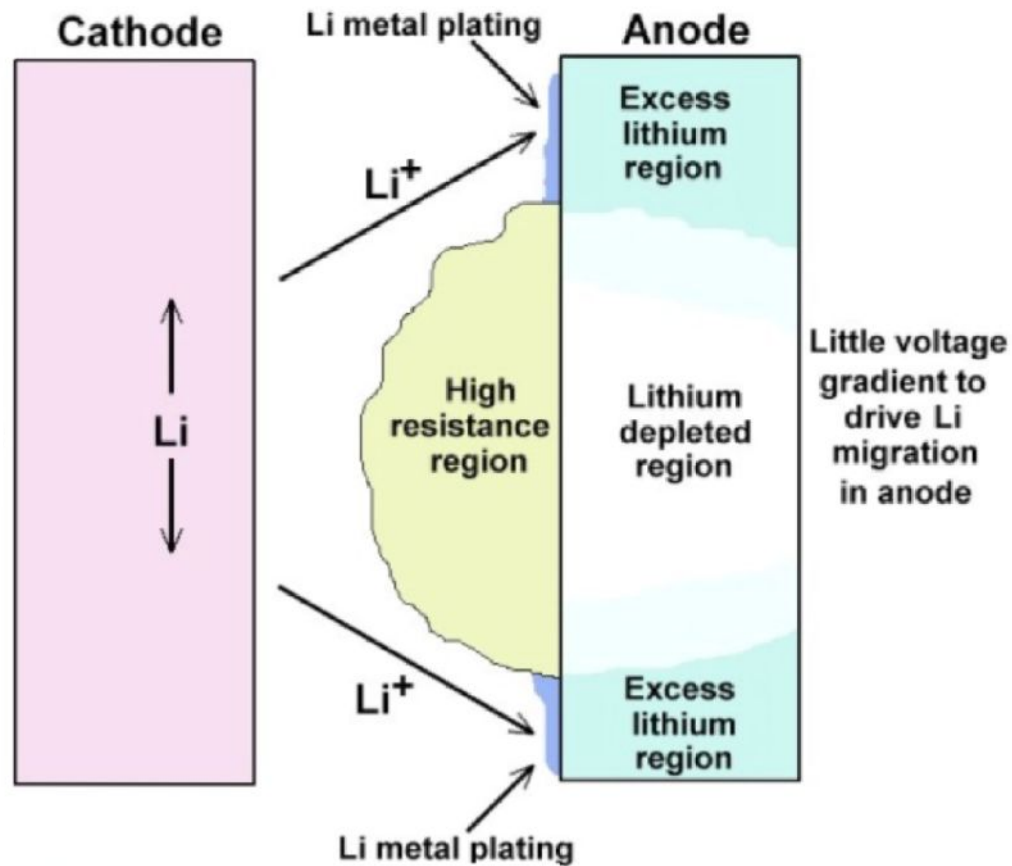
Li plating builds up not simple layers but 3d structures (Dendrites):



Source: Archer Group - Cornell University, 2011

Cell chemistry - Anode

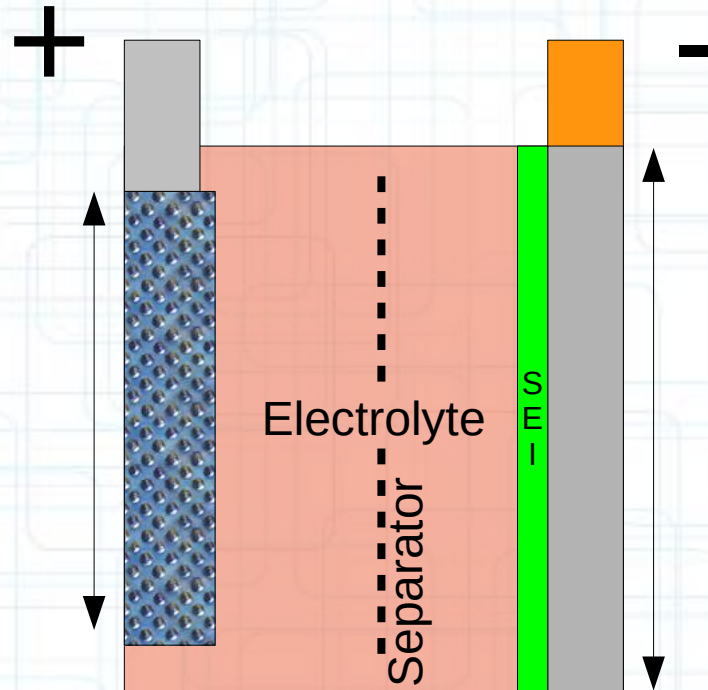
Plating is also caused by imperfections in the cell



Source: Lithium Plating in Lithium-Ion Cells, Albert H. Zimmerman and Michael V. Quinzio
The Aerospace Corporation, Presented at the NASA Battery Workshop 16-18 November 2010, pg. 9

Cell chemistry - Anode

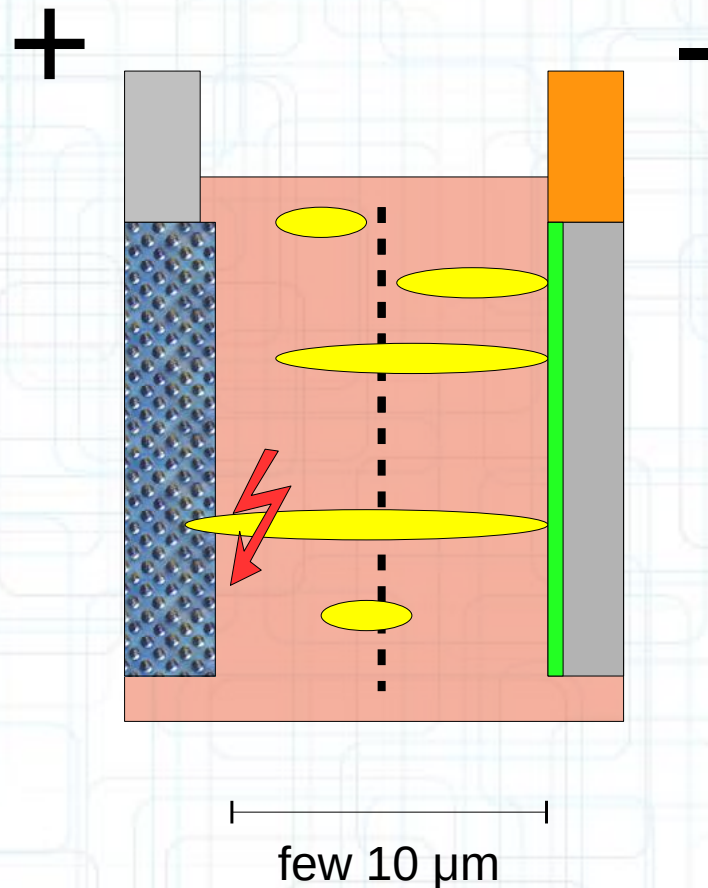
Fun fact: During manufacturing the anode is made a bit larger than the cathode to prevent plating.



This excess is also called "Overhang".

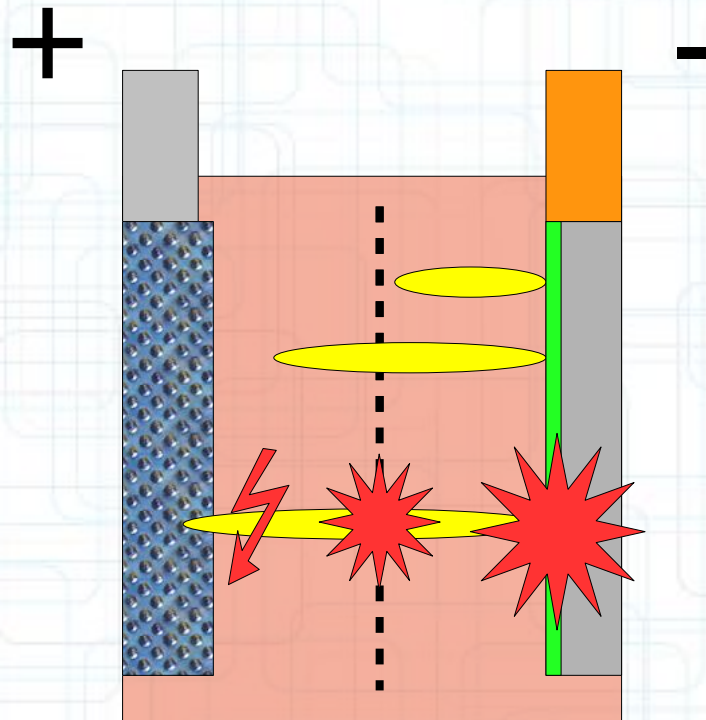
Cell chemistry - Anode

Plating causes: Loss of Lithium / Build up of Dendrites
When the separator is bridged a "Micro Short" appears.



Cell chemistry - Anode

“Micro Shorts” can grow into “Macro Shorts”:



Extreme local temperature increase:

- Separator is damaged
- Local breakdown of SEI layers: generates extra heat!
- These new imperfections in the cell cause more plating

Cell chemistry - Runaway

When “self heating rate” reaches +10 °C / Minute
then at around 150 C° → Thermal Runaway

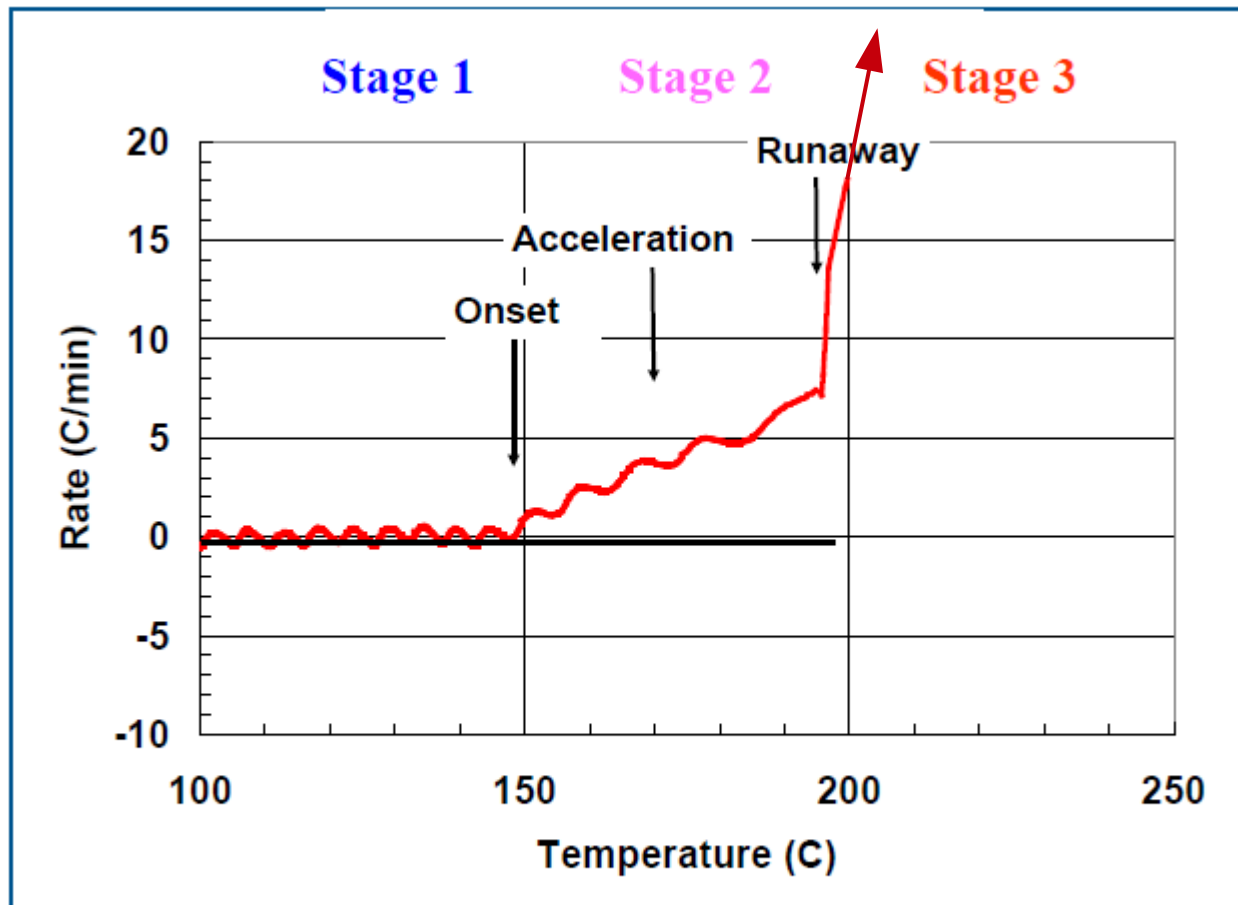


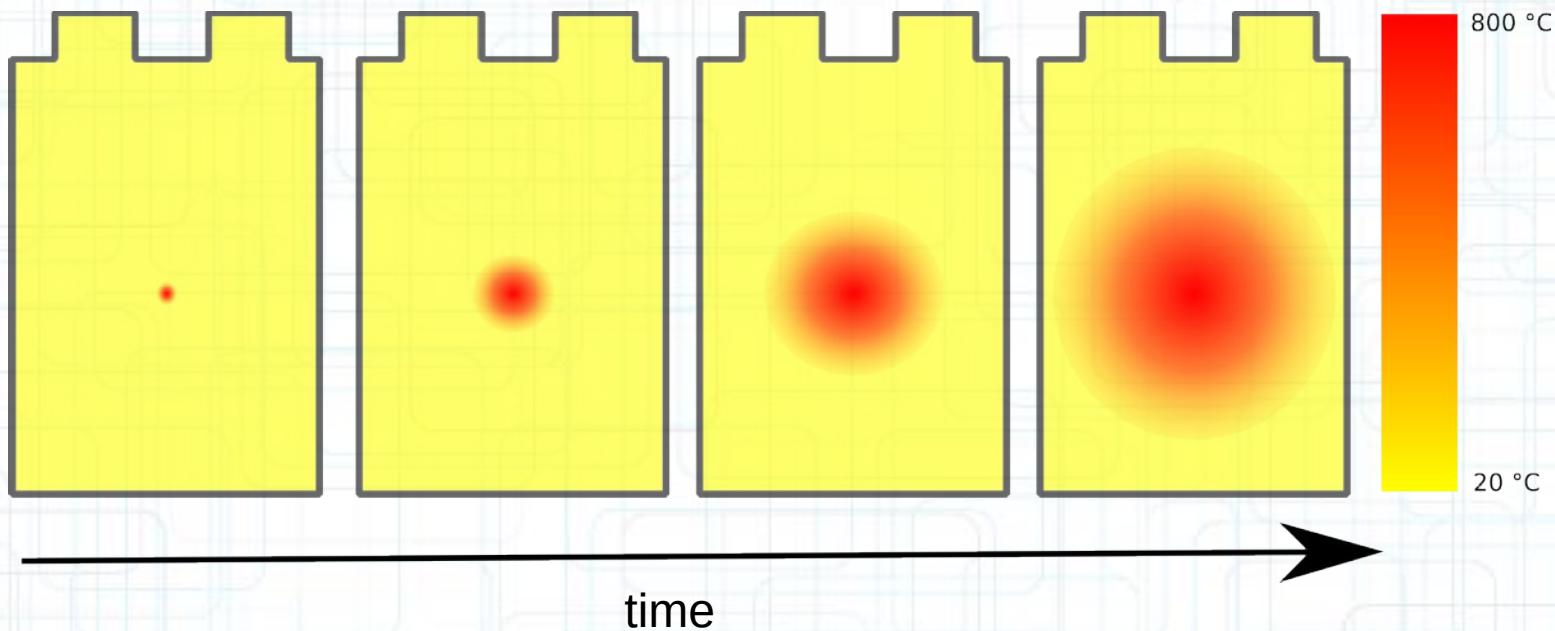
FIG. 3. Cell self-heating rate during forced thermal ramp test of Li-ion Gen 2 chemistry: anode = MCMB | electrolyte = 1.2 M LiPF₆ in EC:PC:DMC | cathode = LiNi_{0.8}Co_{0.05}Al_{0.05}O₂ | separator = Celgard 2325 trilayer. (From Ref. 10)

Source: A general discussion of Lilon Battery safety, Dan Doughty, E. Peter Roth, The electrochemical society Interface 2012. pg 39 (Red Arrow inserted)

Cell chemistry - Runaway

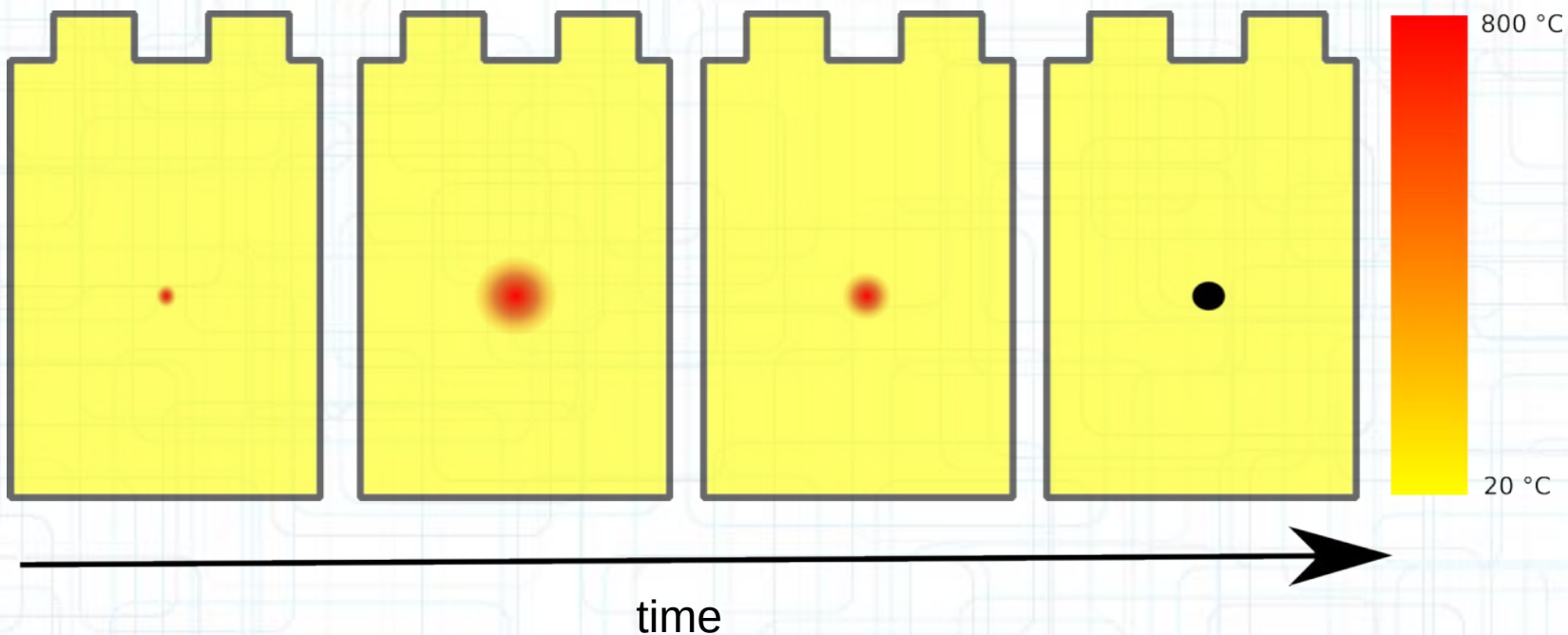
Runaway starts at temperatures exceeding 150 °C. The heat generation until 'Onset' is driven by resistance heating due to the current through the "Short", at temperatures higher than 250 °C significant exothermal decay processes begins.

If the runaway temperature is reached locally and the effected area is large enough, it spreads fast throughout the cell.



Cell chemistry - Runaway

If the heat generation is not sufficient, only a new imperfection occurs. This self limiting happens due to the separator expanding at higher temperatures and thus limiting the process. As long as the separator holds and does not melt the short is limited this way. This new imperfection can however cause more plating later.



Cell chemistry - Runaway

The temperature rise until 'onset' can also be slow (minutes to hours). As soon as it is reached, the heat generation is rapidly accelerating.

Heating up to onset draws its energy from the charge of the cell. In a cool storage environment a higher heat development is necessary to reach onset. This also increases the necessary size of the triggering 'shorts'. Bigger 'shorts' are more rare and at a certain size only caused by mechanical damage.

From the outside, these processes in the cell are not easy to recognize.

A slightly larger self discharge rate can indicate such imperfections in the cell, but with larger cell capacity this signal is getting harder to detect. In such cells only elaborate test runs by repeated low current cycling well into the low cell voltage range ($<3.3\text{V}$) and measuring current "noise" can be used to detect them.

→ Micro-shorts can not be ruled out easily, so safe usage patterns must be implemented to minimize the chance of triggering runaways.

Cell chemistry - Anode

- To reach runaway onset the cell must be charged above a certain level. The stored charge must be sufficient to heat the cell locally to onset temperature.
- High ambient temperature favours runaway.
 - **Store cool (< 20°C) and “empty” (discharged at 3.7-3.75V/cell)!**

Cell chemistry - Anode

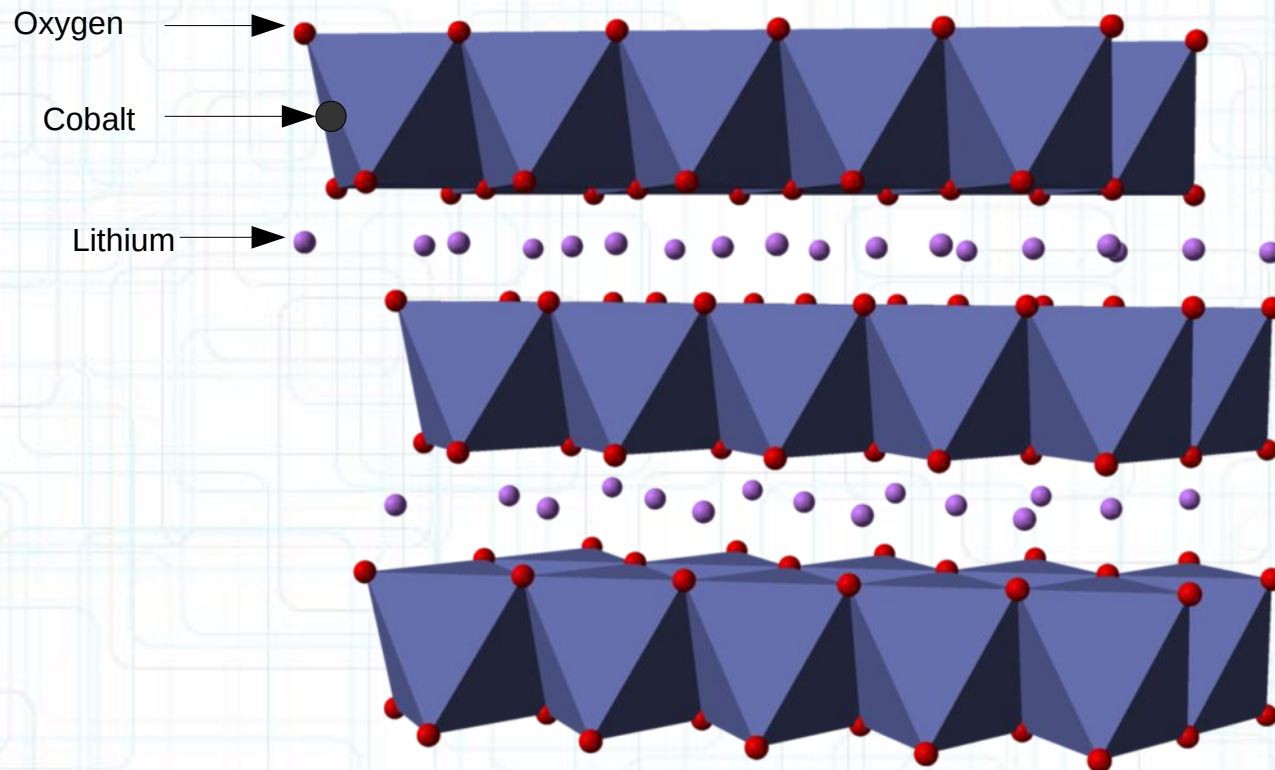
Factors that favours plating:

- High charge current
- Low temperatures (during charge)
- Old/Mistreated Cells (thick SEI layer)
- Initial imperfections (manufacturing faults)
- Excess discharge current (explanation see Cathode discussion)

→ Never charge cold cells at high C-rates!

Cell chemistry - Cathode

Cathode usually consists of Lithium metal oxides, e.g. LiCoO_2



Quelle: Wikimedia.org

Cell chemistry - cathode

- During charge the cathode provides Li^+ ions
- During discharge the cathode accepts Li^+ ions
- As with the anode there exists an interface to the electrolyte.
- But at this interface no SEI layer is growing, instead reaction products migrate into the electrolyte.

Cell chemistry - cathode

Cathode is under mechanical stress during discharge. The higher the current, the higher the stress.

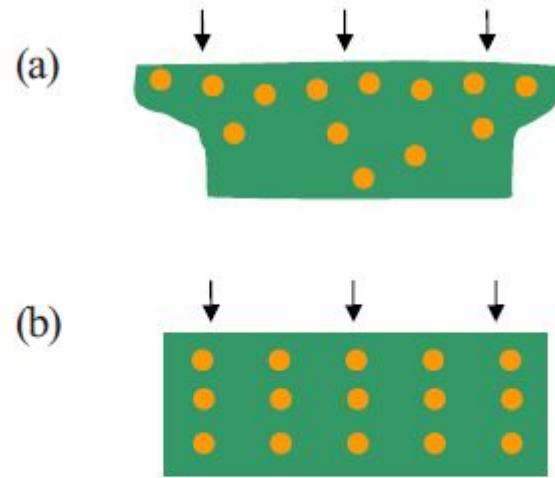
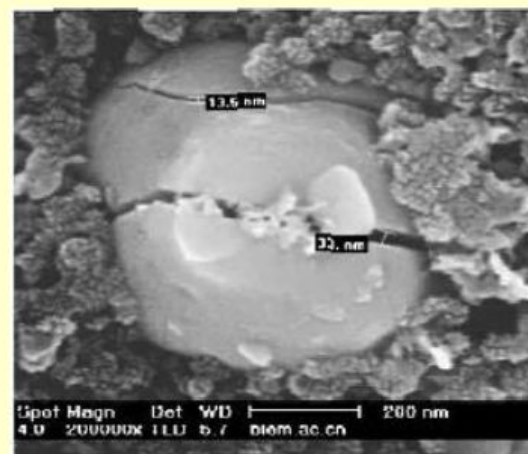
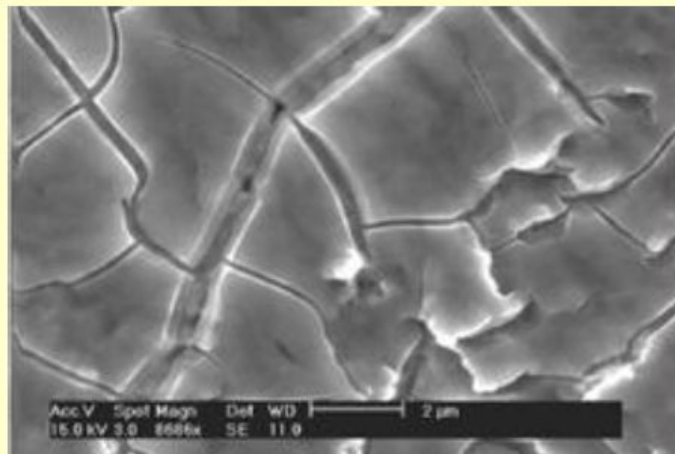


FIG. 2. (Color online) (a) When the rate of discharging is high, the distribution of lithium in the active particle is inhomogeneous, which causes a field of stress in the particle. (b) When the rate of discharging is low, the distribution of lithium in the particle is negligible. The arrows indicate the direction of lithium insertion.

Cell chemistry - cathode

Too high discharge rates, especially at low temperatures causes cracks and breaks in the cathode material.



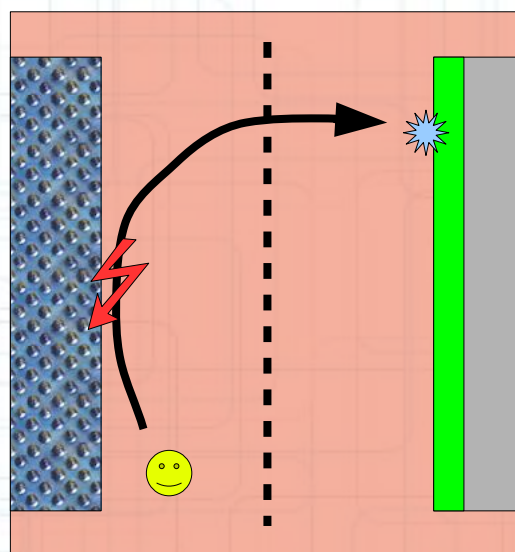
Source: Stress and Deformation Caused by Insertion in Li-ion Batteries,
Department of Physics, Harvard University, Cambridge, MA 02138, USA

→ Never draw high current from cold cells !

Cell chemistry - cathode

Too high temperatures - even locally – and/or cell voltage above ($>4.1\text{V}$) can cause disintegration (mainly through oxidation) of the electrolyte at the cathode.

Cathode

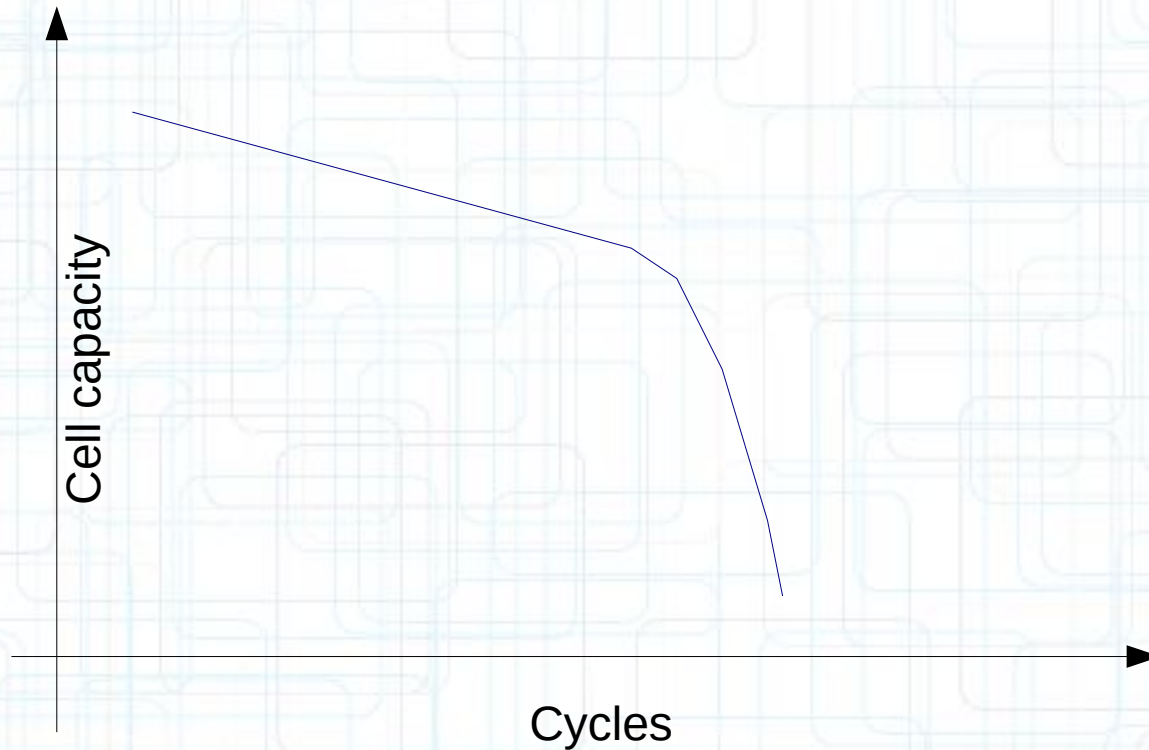


Anode

The reaction products migrate through the cell to the SEI layer and increase its thickness → causing higher resistance + loss of lithium (and therefore loss of capacity).

These reactions also generate gases (mostly CO_2), the main reason for irreversible “puffing” through overload / storage fully charged (especially at high ambient temperatures).

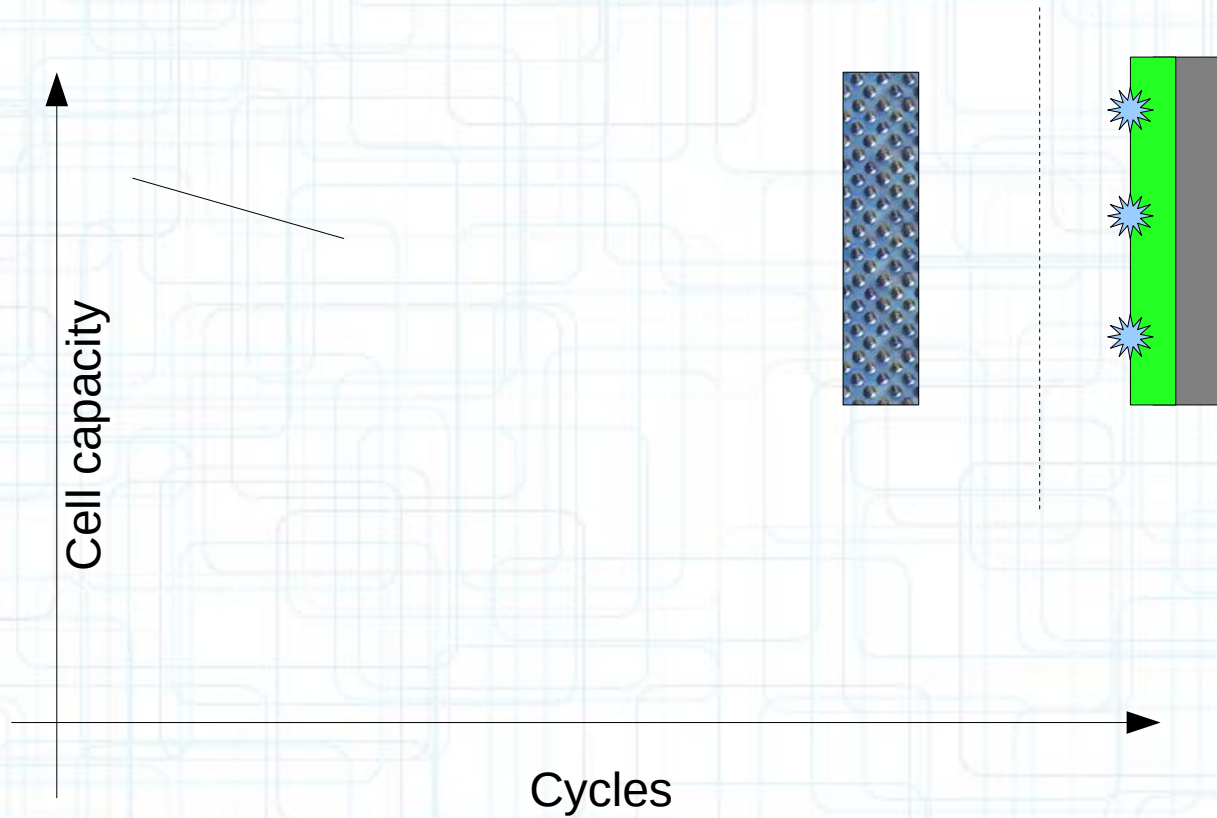
Cell chemistry - Cathode



The migration of debris/oxidation products to the SEI layer is also the main reason for the non-linear ageing of cells.

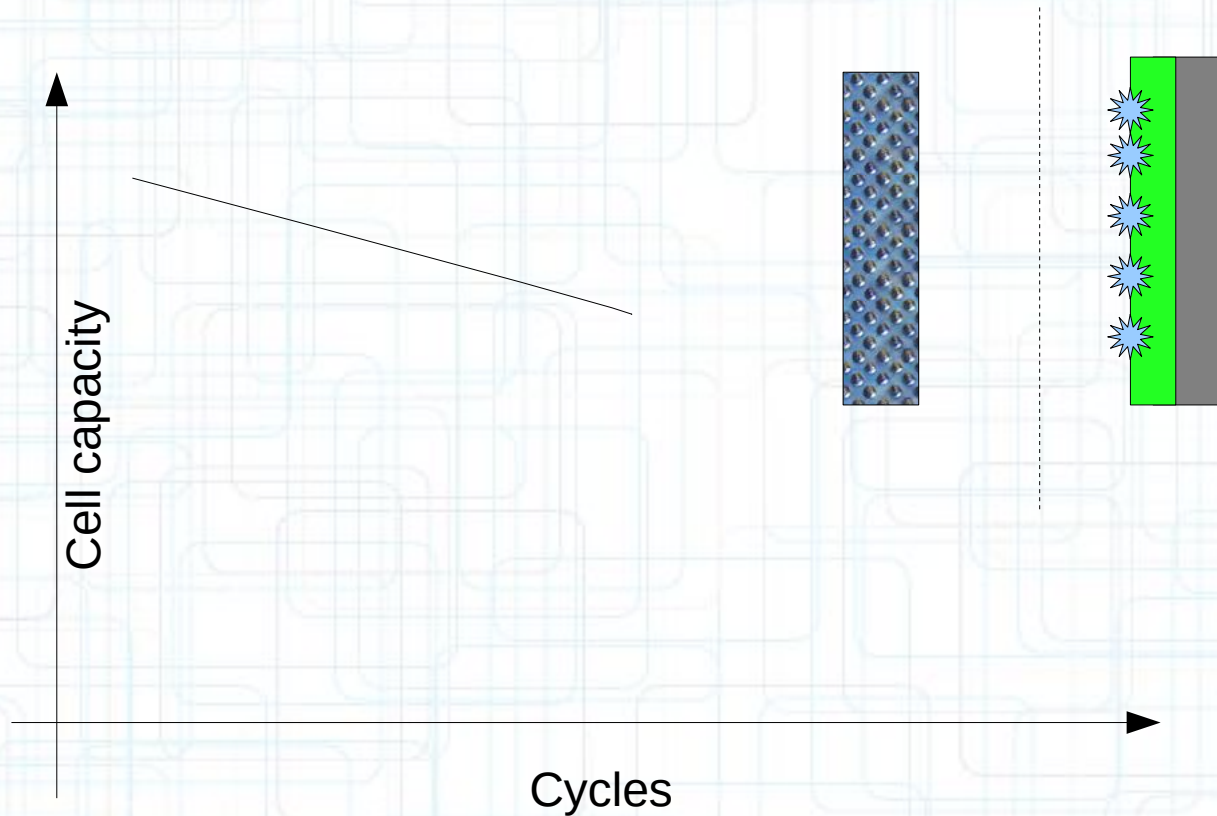
(Capacity loss and increase of resistance are connected)

Cell chemistry - Cathode



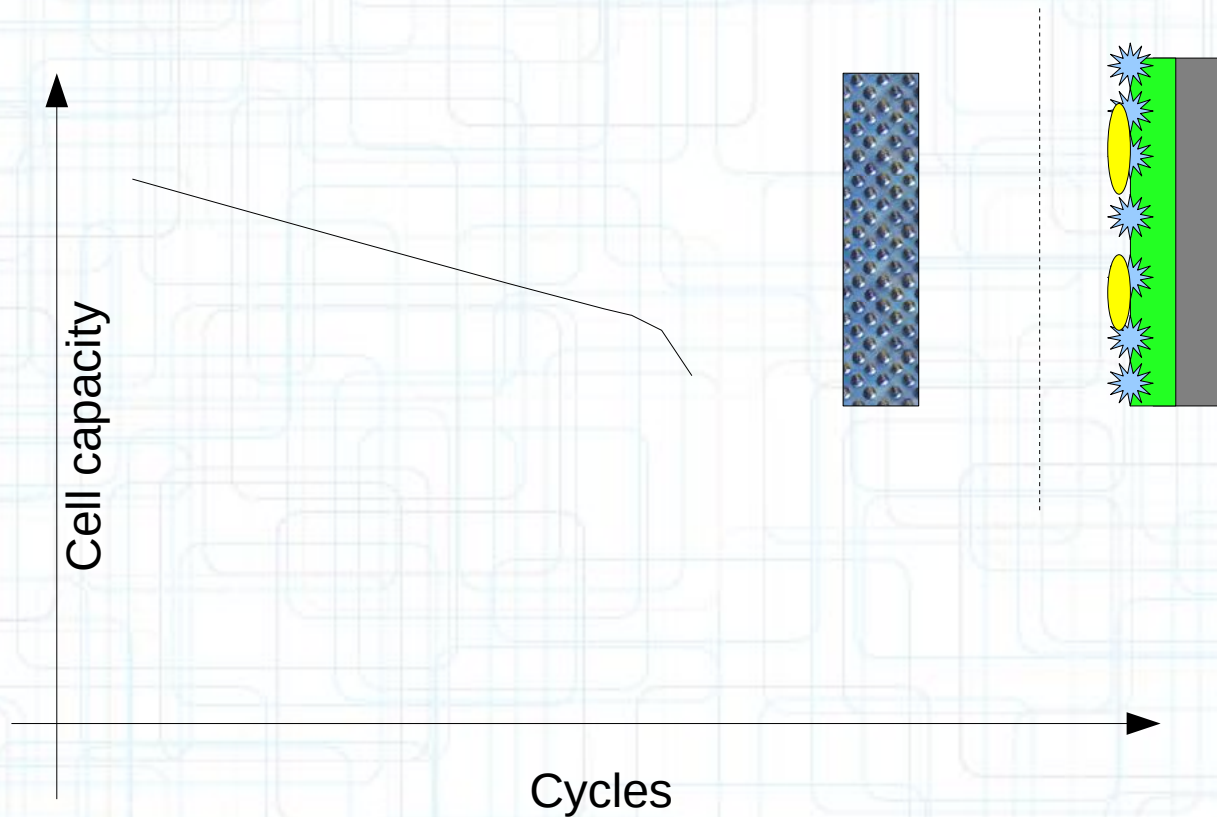
For young cells the effect is minimal, SEI surface more than enough

Cell chemistry - Cathode



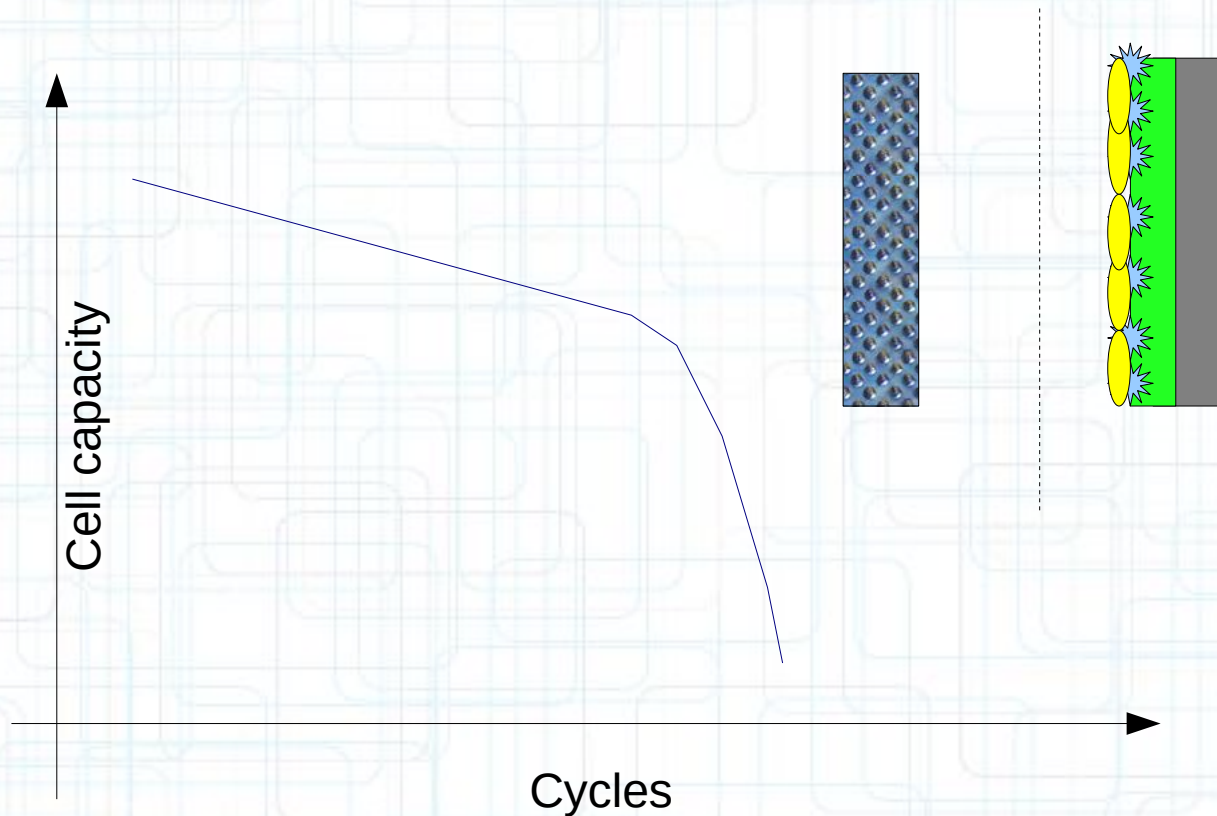
More cell cycles, the effect starts to become noticeable.
But cell capacity is still sufficient.

Cell chemistry - Cathode



Even more cycles, the beginning of accelerated cycle ageing
Resistance increased noticeable, the cells current delivery
ability degenerates. Capacity loss gets quite noticeable.

Cell chemistry - Cathode



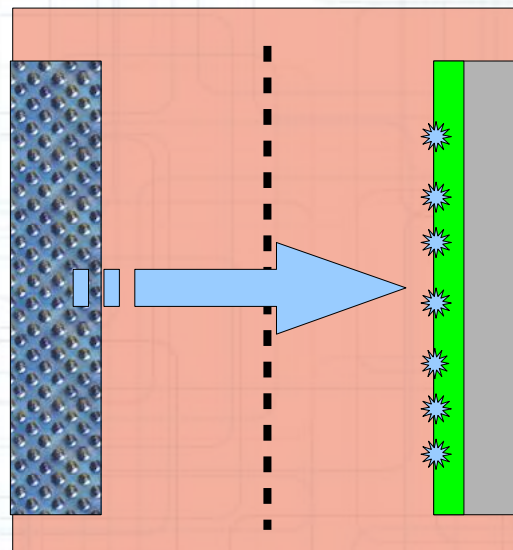
Plating gets problematic during charge, Lithium loss gets high, Cell loses lots of capacity. Puffing noticeable. High resistance.

- Never overload / overcharge cells, especially older (high cycle, long storage) cells. Decrease charge current for older cells below 1C.

Cell chemistry - Cathode

Too high temperatures also cause release of metals at the cathode.

Cathode



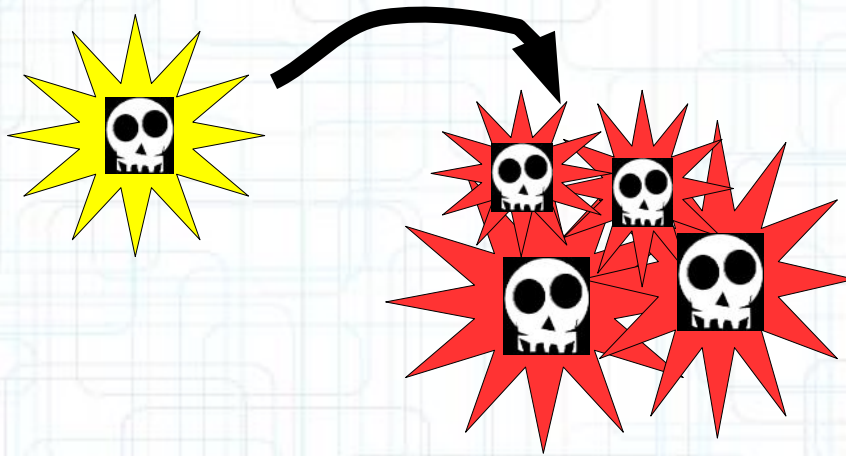
Anode

→ Also cause SEI layers degeneration (“poisoning”)

Problem is especially prevalent with LiFePO_4 cells → Release of iron at temperatures $> 45\text{ }^\circ\text{C}$.

→ **Do not store cells at high ambient temperatures!**

“Damage memory”



Damage in the cell due to misuse accumulates over time!

A cell does not forget mistreatment!

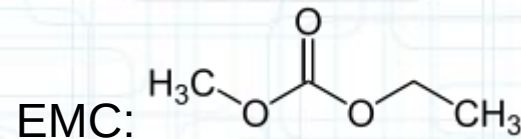
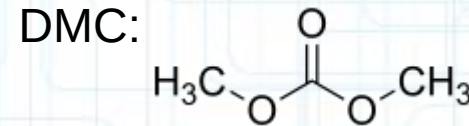
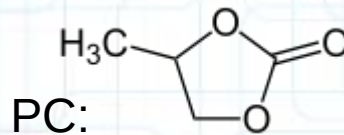
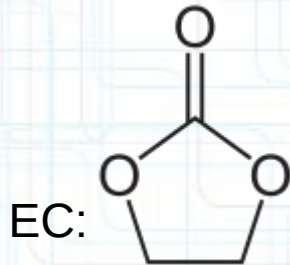
Cell chemistry - Electrolyte

- Liquid or gel
- Three main constituents:

- "active salt" (LiPo): LiPF_6



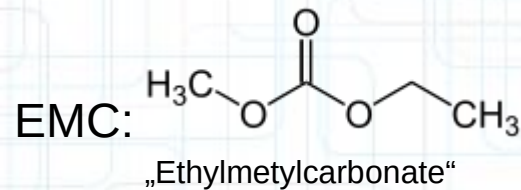
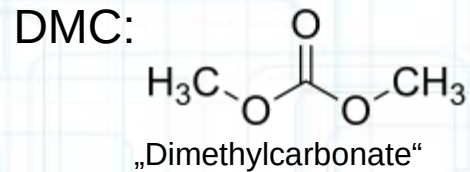
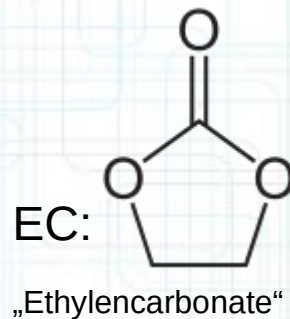
- organic solvents, e.g..



- additive, e.g. Vinylene carbonate

Cell chemistry - Electrolyte

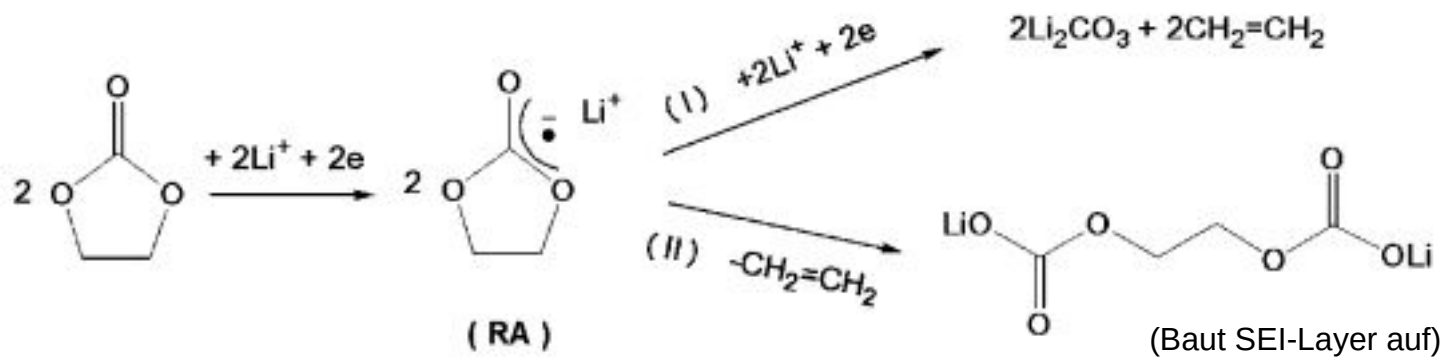
The mixing ratio of the organic solvents defines the viscosity of the electrolyte.



Simplified: The higher the EC ratio, the higher the viscosity.

Cell chemistry - Electrolyte

Ethylencarbonat (EC) is always part of the mixture as it is needed to build up the SEI layer during initial charge.



Source: A review on electrolyte additives for lithium-ion batteries, Journal of Power Sources 162 (2006) 1379–1394

EC $\xrightarrow{\text{first cycle, formation}}$ Building SEI layer

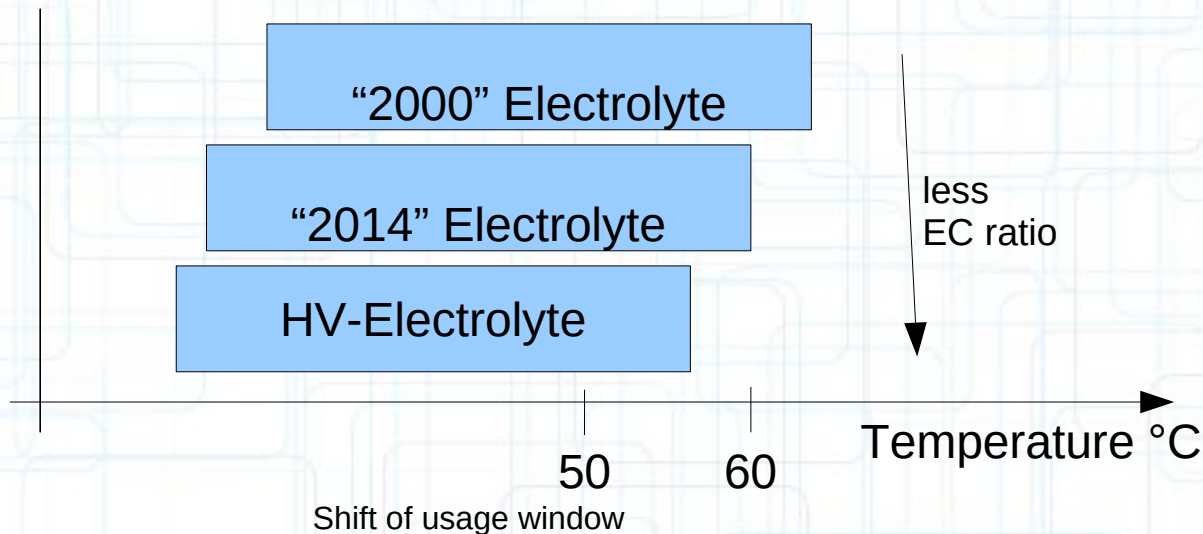
Cell chemistry - Electrolyte

Mixing ratio defines temperature- and also voltage stability.

EC/DMC 1:1 electrolyte gets unstable at around 4.25V.

In comparison: EC/DMC/Diethylcarbonate (DEC) in ratio of 3:3:4 is stable until 4.5V.

The EC proportion has decreased over the years (~ 50% → ~ 25%).
HV cells also contain a smaller ratio of EC in the electrolyte
and therefore are a bit more negatively effected at higher temps.



Cell chemistry - Electrolyte

Depending on the constituents of the electrolyte and their mixing ratio, the formation of the SEI layer may not have fully concluded After one cycle. It could be beneficial to start using a “new” cell at Lower charge and discharge rates to maximize capacity and minimize resistance.

Electrolyte-Type	Rev. Cap mAh/g (1st Cycle)	Irr. Cap mAh/g (1st Cycle)	Rev. Cap mAh/g (5th Cycle)	Irr. Cap mAh/g (5th Cycle)
EC+DEC+DMC (1:1:1)	306.5	51.8	310.8	85.9
EC+DEC+DMC+MA (1:1:1:1)	201.5	36.9	236.5	56.9
EC+DEC+DMC+EA (1:1:1:1)	210.4	49.9	214.2	68.5
EC+DEC+DMC+EP (1:1:1:1)	233.4	49.06	340.75	88.30
EC+DEC+DMC+EB (1:1:1:1)	272.0	55.6	309.46	90.86

Reversible and irreversible capacities of graphite electrodes (Li-C cell) in contact with various electrolytes.

Source: The Role of Electrolyte Upon the SEI Formation Characteristics and Low Temperature Performance of Lithium-Ion Cells with Graphite Anodes, M. C. Smart, B. V. Ratnakumar, S. Greenbaum and S. Surampudi, Jet Propulsion Laboratory;
MA = methyl acetat, EA = ethyl acetat, EP = ethyl propionate, EB = ethyl butyrate, PC = propylen carbonate

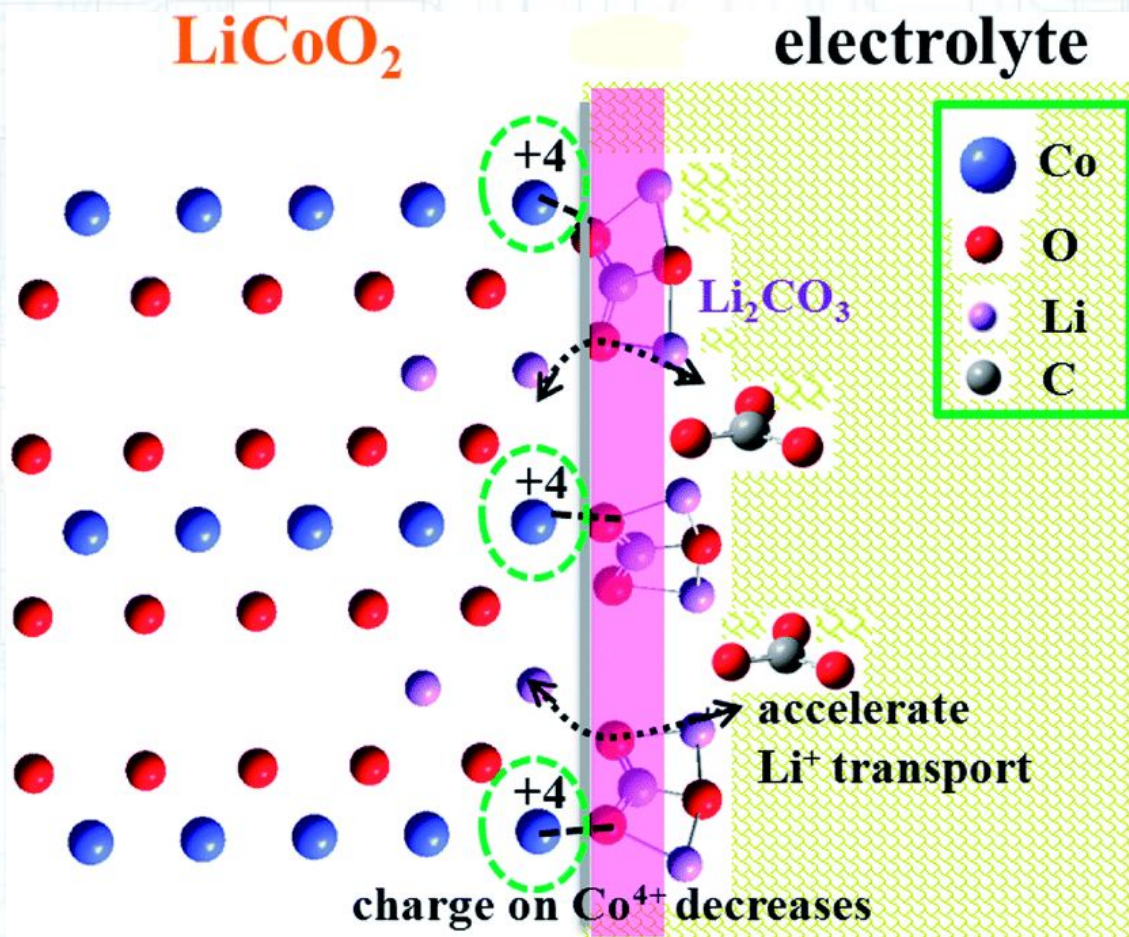
Cell chemistry - Additives

- Improve initial formation of SEI layer
- Protects cathode/electrolyte (limits oxidation / Li retention)
- LiPF_6 temperature stabilisation
- Overcharge protection (“Redox shuttle”)
- Fire retardant
- 'Wetting agent' (Manufacture, Wetting of electrodes)
- Corrosion protection
- ...

Several additives can be found in most any cell

Cell chemistry - Additives

E.g.: Improved cathode stability through additive Li_2CO_3 for HV cells



Source: Effect of lithium carbonate precipitates on the electrochemical cycling stability of LiCoO₂ cathodes at a high voltage, RSC Advances, Issue 20, 2014

Cell failure modes

Depending on cell voltage:

Too high (> 4.25V):

Cathode:

Mechanical stress,
Too little Lithium,
Fracturing

Anode:

Lithium plating

Electrolyte:

Degradation

Too low (< 2V):

Cathode:

Mechanical stress
(too much Lithium)
Release of oxygen

Anode:

copper connector
dissolves
→ Cu dendrites (causing shorts)

Electrolyte:

Cell failure modes

Temperature effects:

Too high (> 60 °C, > 55 °C for newer cell types):

Cathode:

Anode:

Electrolyte:

Release of oxygen

SEI disintegration

Disintegration

Increased danger of Thermal Runaway!

Too low (< 15-20 °C, high C-Rate):

Cathode:

Anode:

Electrolyte:

Stress through
too high Li⁺ flow,
Fracturing/Cracks
(at discharge)

Lithium plating
(at charging)

Cell failure modes

Current effects:

Too high (Discharge):

Cathode:

Oxidation of electrolyte
(esp. at high Temp.)

Stress through too high
Li⁺ flow, Fractures / cracks
(esp. at low Temp.)

Anode:

Accumulation of
disintegration
products

Electrolyte:

Disintegration

Too high (Charge, esp. at low temperatures):

Cathode:

Anode:

Electrolyte:

Plating

Cell failure modes

“Puffed” cells are caused by two different mechanisms:

“Reversible” puffing:

- happens at high current / temp., vanishes after cooling
 - Reason: Solvents in the electrolyte evaporate
 - Indicator for over load, but cell can still be used normally.

“Irreversible” puffing:

- does not vanish after cooling.
 - Reason: Disintegration of electrolyte releases CO_2 and other gasses.
 - Indicator of a defect in the cell. Capacity loss and higher resistance to be expected.
 - If it happens during over-discharge immediately dispose of the battery, high chance of shorts in the battery due to copper dendrites and likely problems (fire risk) at next charge.

Cell failure modes

Ruptured cells smells 'sweet' / 'fruity' if electrolyte is released.

Such cells should be disposed of as soon as possible. Use protective gloves (nitrile type, rubber gloves do not work for organic solvents), Electrolyte constituents are toxic, acidic, some are carcinogenic and could do permanent and persistent health damage even through skin. Never inhale electrolyte mist or smoke for fires. Severe lung damage could occur. See a doctor as soon as possible.

Conducting salt ("LiPo") LiPF_6 :

R34: Causes burns.

R24: Toxic in contact with the skin.

R22: Harmful if swallowed.

Conducting salt ("LiFePo4") LiBF_4 :

R20 / 21/22: Harmful by inhalation, in contact with and if swallowed and at contact with the skin.

R31: In contact with acid, develops toxic gas.

R34: Causes burns.

R36 / 37/38: Irritating to eyes, respiratory system and skin.

R23 / 24/25: Toxic by inhalation, in contact with skin and if swallowed with the skin.

R11: Highly flammable.

Long cell life tips

- Store cool, dry and “empty” (3.7 – 3.75V / cell) ($< 20\text{ }^{\circ}\text{C}$)
- Before charge and discharge heat the cell up to $> 25\text{ }^{\circ}\text{C}$
- Never over-charge ($> 4.2\text{V}/\text{cell}$, $>4.25\text{-}4.35\text{V}/\text{cell}$ for HV)
- Never over-discharge ($< 3.0\text{V}/\text{cell}$, If it happens, immediately charge to $> 3.7\text{V}!$)
- Working temperature $> 25\text{ }^{\circ}\text{C}$, optimal 30 - 40 $^{\circ}\text{C}$, remember “C” ratings are only valid in this temperature range. “Heating up” a cell at lower temp. by high current flow will cause damage to the cell and shortens lifetime.
- Only keep at working temperature during use, as short a time as possible
- Do not use at too high temperatures (keep $< 55\text{ }^{\circ}\text{C}$, never exceed $60\text{ }^{\circ}\text{C}$)

Even longer life:

- Do not charge until 4.2V (cycle lifetime doubles at 4.1V top voltage)
- Never use full capacity, shallow cycles (cycle lifetime doubles at $<70\%$ DOD)
- Keep current load lower than nominal C rating, never charge at rates higher than 1 C (esp. at low temperatures).

Temperature °C to F

This presentation uses °C (Celsius) for temperatures. In Fahrenheit the relevant values are:

0 °C	32 F
20 °C	68 F
25 °C	77 F
30 °C	86 F
55 °C	131 F
60 °C	140 F
150 °C	302 F

Credits

Created by

Dipl.-Ing. Frank Siegert
eMail frank@wizards.de

Learned something new? Like my work? You can support me and my work on Paypal. Thank you.

Original: June 2015,
revised and translated 2019 with the help of John Julian
(johnjulian@me.com).



*This work is licenced under a Creative Commons license
<https://creativecommons.org/licenses/by-nc/3.0/>
Attribution-NonCommercial 3.0 Unported (CC BY-NC 3.0,)
Citations covered by their own copyright.*

Disclaimer

To the best of my knowledge the information presented within this presentation is correct at the time of release.

However the material and information contained in this presentation is for general information purposes only. You should not rely upon the material or information presented as a basis for making any business, legal or any other decisions.

Whilst I endeavour to keep the information up to date and correct, I make no representations or warranties of any kind, express or implied about the completeness, accuracy, reliability, suitability or availability with respect to this presentation or the information, products, services or related graphics contained within for any purpose. Any reliance you place on such material is therefore strictly at your own risk.

References :

Page 6: Illustration: Wikipedia, Source: <https://commons.wikimedia.org/wiki/File:PSE.png>

Page 18 and 19: Tabellen: Battery University, Source:

http://batteryuniversity.com/learn/article/how_to_prolong_lithium_based_batteries

Page 24 and 25: Bilder Lithium Pouch Cell, Source:

https://commons.wikimedia.org/wiki/File:3.7V_1000mAh_Li-Polymer_Battery.jpg

<https://de.wikipedia.org/wiki/Datei:Lipolyo4rp.jpg>

Page 29: A Distributed Analytical Electro-Thermal Model for Pouch-Type Lithium-Ion Batteries

Maryam Yazdanpour, Peyman Taheri, Abraham Mansouri, and Majid Bahramia,

Laboratory for Alternative Energy Conversion (LAEC), School of Mechatronic

Systems Engineering, Simon Fraser University, Surrey, BC V3T 0A3, Canada, Department of

Mechanical Engineering, American University in Dubai, Dubai 28282, UAE, Journal of The Electrochemical

Society, 161 (14) A1953-A1963 (2014), Page 1962

Page 30: Own work, inspired by: <https://www.quora.com/Is-a-lithium-battery-that-dangerous-If-yes-what-should-I-prevent-it-from>

Page 33: File:Schematic of a Li-ion battery.jpg, Public Domain,

https://commons.wikimedia.org/wiki/File:Schematic_of_a_Li-ion_battery.jpg

Page 36: Nanoporous Carbon, Development of Improved Molecular Models of Amorphous Nano-porous Materials,

Gubbins Group, <http://chumba.che.ncsu.edu/research.html>

References (cont.) :

Page 39: 'A snapshot of the interfaces between the graphitic anode, a representative SEI, and the electrolyte.'

The University of Chicago, Searle Chemistry Laboratory, 2012, Martin McCullagh, Ruibin Liang,

<https://vothgroup.uchicago.edu/research/renewable-energy-materials>

Page 44: Archer Group, Electrochemical Energy Storage, Dendrite propagation, 348 Olin Hall

Cornell University, Ithaca, NY 14853, https://archergroup.cbe.cornell.edu/dend_grw.html

Page 45: Lithium Plating in Lithium-Ion Cells, Albert H. Zimmerman and Michael V. Quinzio

The Aerospace Corporation, Presented at the NASA Battery Workshop 16-18 November 2010, pg. 9

Page 49: A general discussion of Lilon Battery safety, Dan Doughty, E. Peter Roth, The electrochemical society

Interface 2012. pg 39 (Modified: Red arrow inserted, Verändert: Roter Pfeil eingefügt)

Page 55: File:Lithium-cobalt-oxide-3D-polyhedra.png, Public Domain,

<https://en.wikipedia.org/wiki/File:Lithium-cobalt-oxide-3D-polyhedra.png>

Page 57: Effect of Ion flow on cathode. Journal of applied Physics 108, 073517 2010, Kejie Zhao, Matt Pharr,

Joost J. Vlassak, and Zhigang Suo, School of Engineering and Applied Sciences and Kavli Institute,

Harvard University, Cambridge, Massachusetts 02138, USA, pg 2

Page 58: Stress and Deformation Caused by Insertion in Li-ion Batteries, Department of Physics,

Harvard University, Cambridge, MA 02138, USA

Page 68: A review on electrolyte additives for lithium-ion batteries, Journal of Power Sources 162 (2006) pg. 1379

References (cont.) :

Page 71: The Role of Electrolyte Upon the SEI Formation Characteristics and Low Temperature Performance of

Lithium-Ion Cells with Graphite Anodes, M. C. Smart, B. V. Ratnakumar, S. Greenbaum and S. Surampudi,

Jet Propulsion Laboratory;

Page 73: Effect of lithium carbonate precipitates on the electrochemical cycling stability of LiCoO₂ cathodes at a high

voltage, RSC Advances, Issue 20, 2014

Special thanks to:

I thank Gerd Giese for his helpful tips, John Julian for help with the English translation and proofreading and Ludwig Retzbach for his helpful hints. Also, my thanks go to RC-Network.de and RCGroups.com for providing a platform for discussion about RC model related Lithium battery technology.