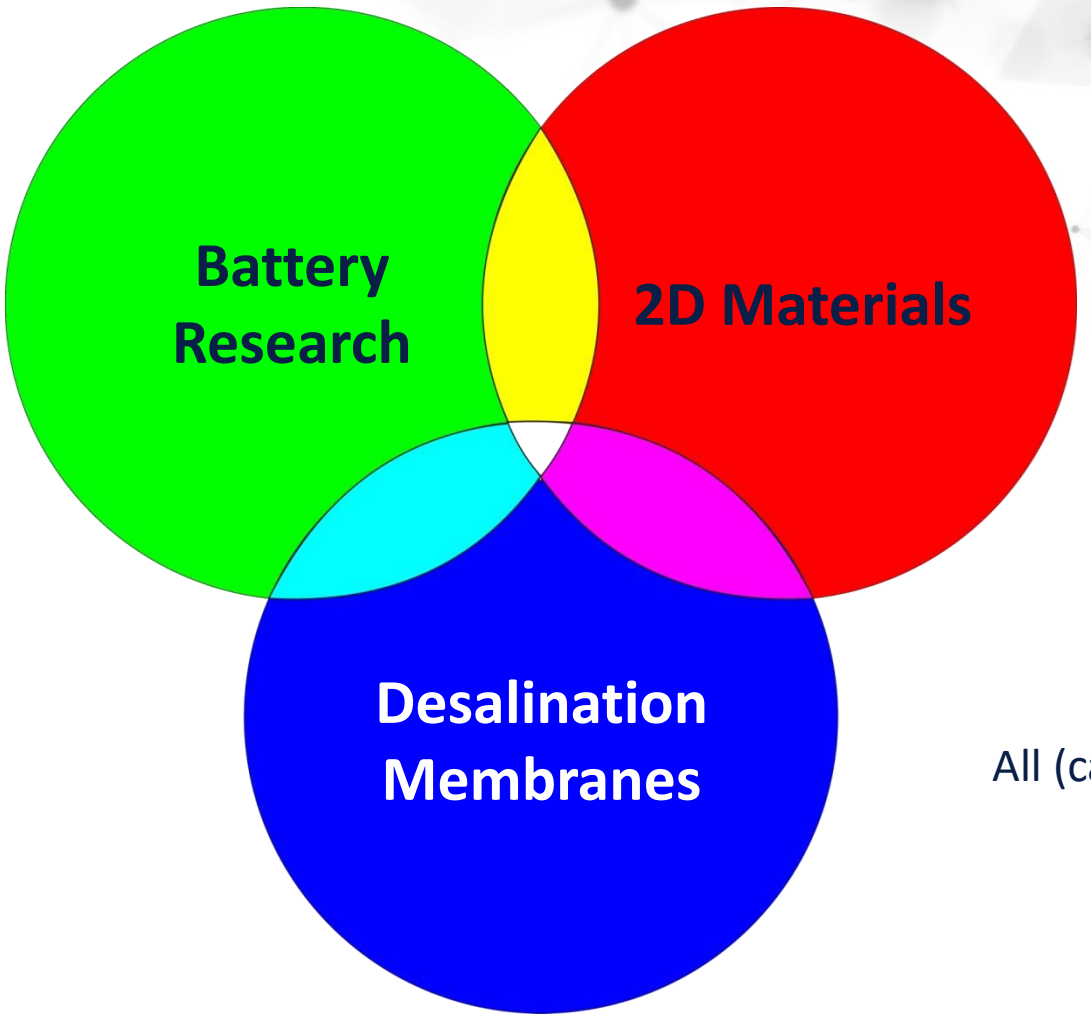
SIBs@LMN

-

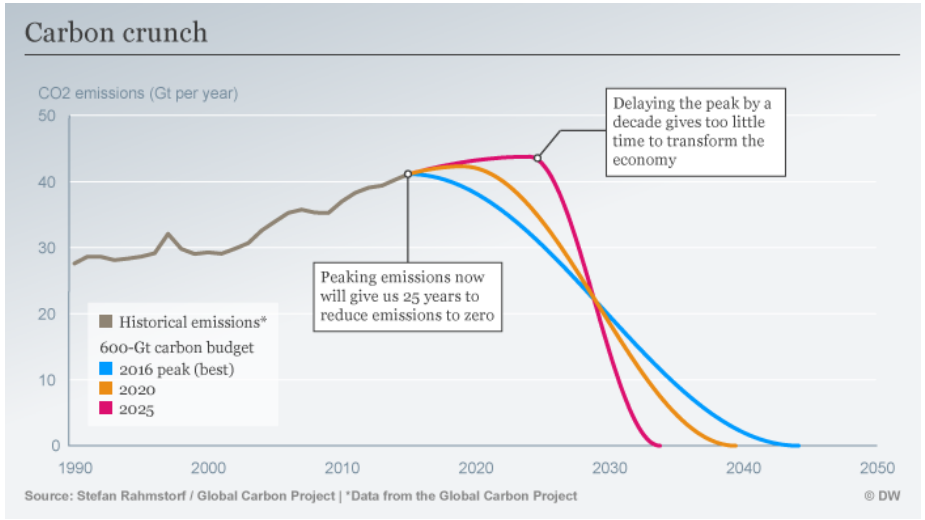
From Research Concept to the First Cell

Research@LMN

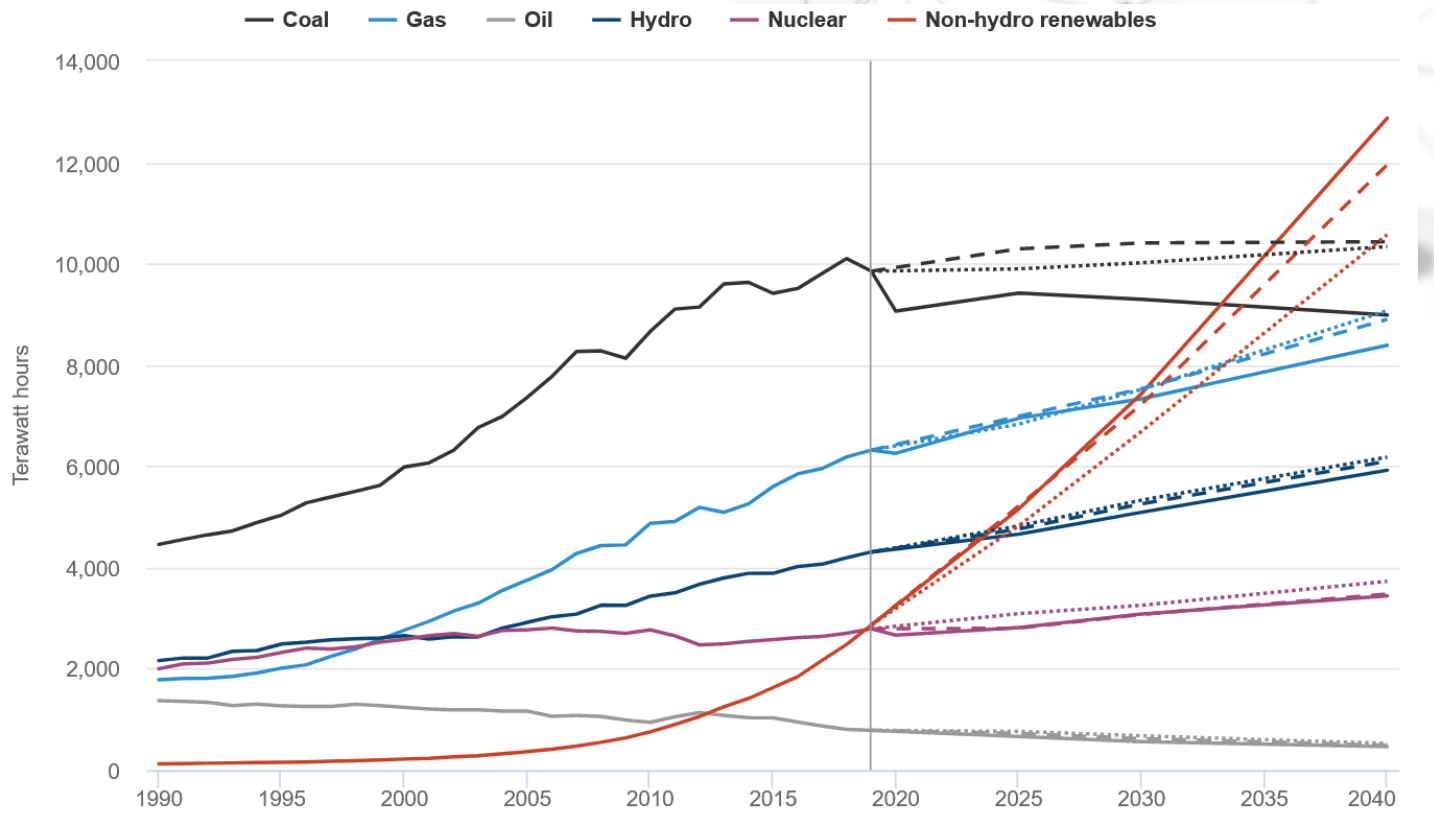


All (can) include 2D materials!

Why Batteries



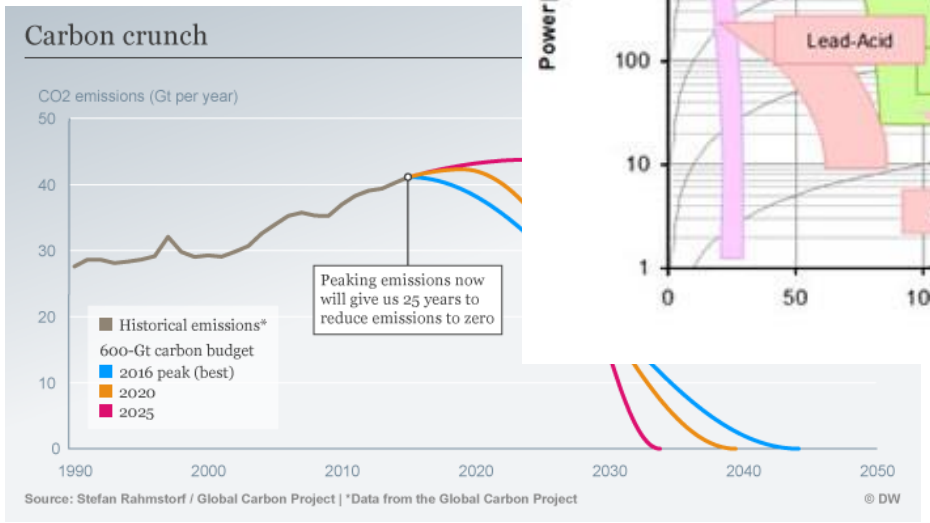
- Supply and demand not constant over day/year
- Both need to be carefully balanced for electricity grid to work

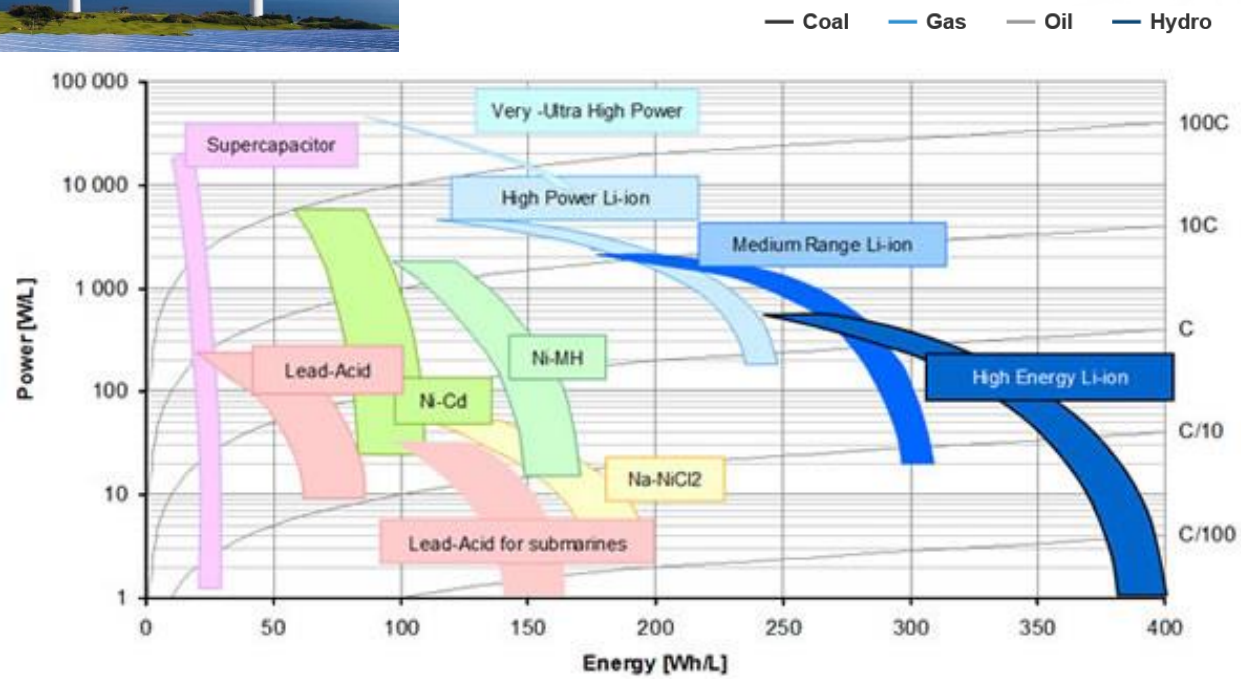


https://www.carbonbrief.org/solar-is-now-cheapest-electricity-in-history-confirms-iea
https://ec.europa.eu/info/news/transforming-power-sector-new-report-about-integrating-renewable-energy-2019-feb-18_en

Why Batteries

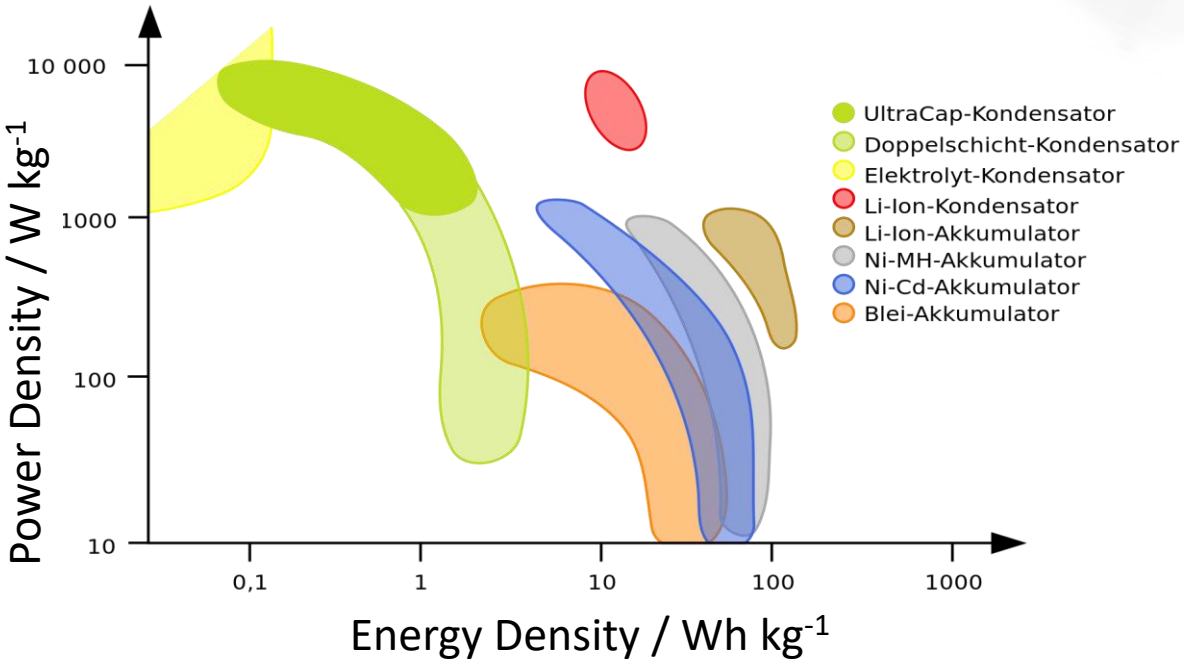
- Supply and demand not constant over day/year
- Both need to be carefully balanced for electricity grid to work
- Only batteries can store considerable amounts of energy

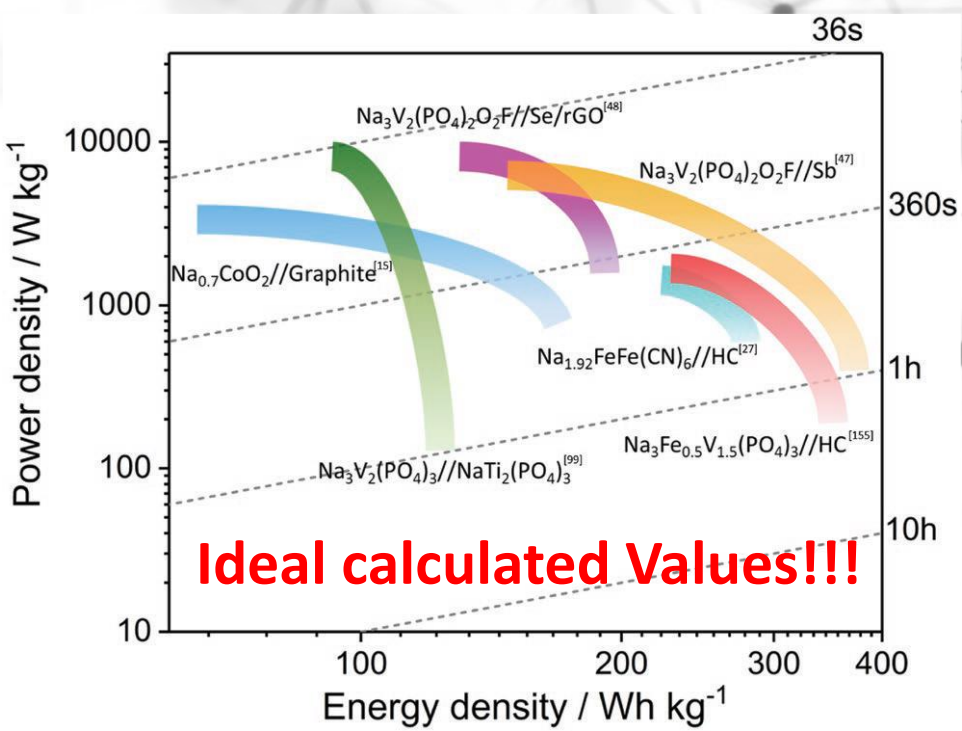




http://www.joules-project.eu/Joules/technologies/storage_distribution_electrical_convertors

Why Na?



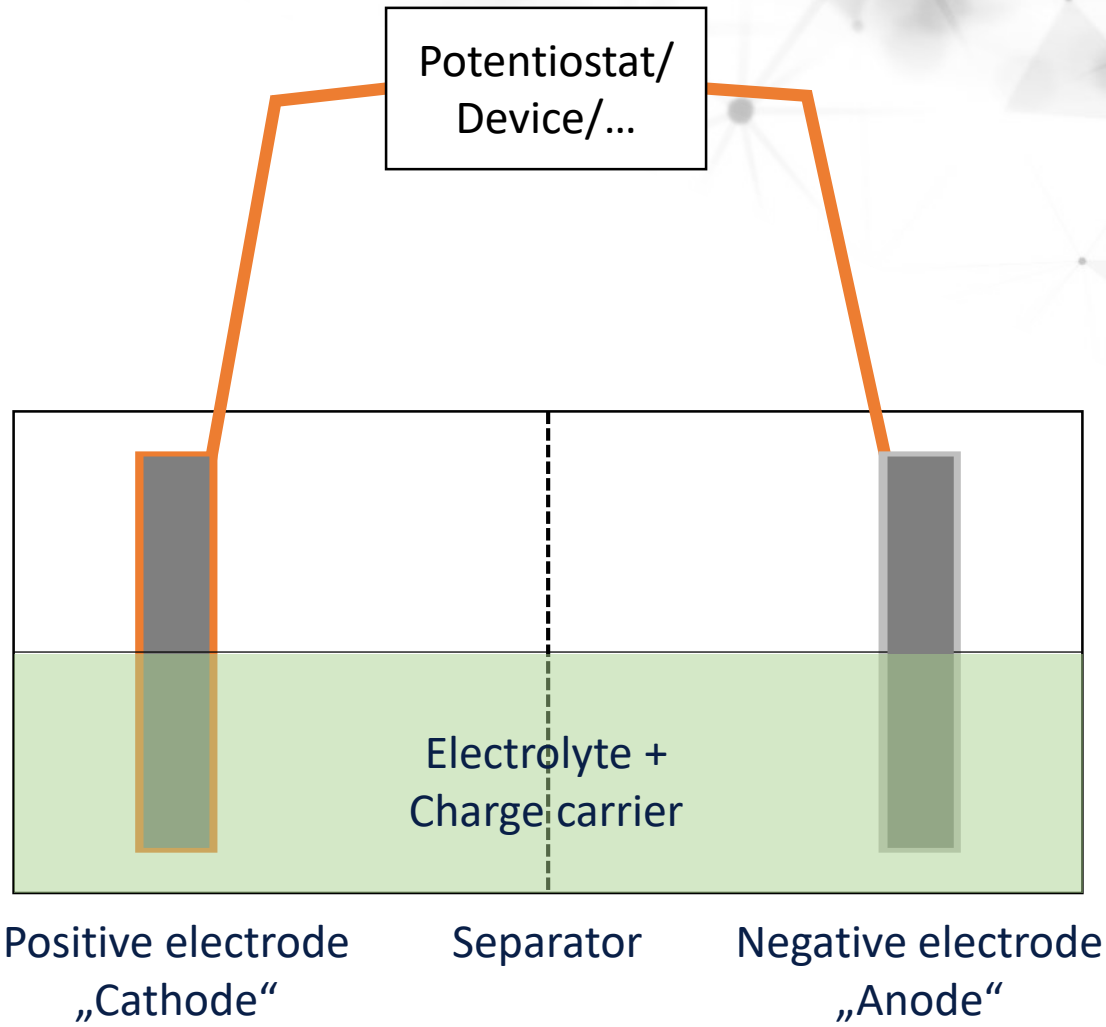


- At least in theory high power and energy density is possible
- So far irreversible changes in cells diminish performance
- Na 1000 more common in earth crust (Na: 2.36%; Li: 0.002%)!

https://de.wikipedia.org/wiki/Ragone-Diagramm
X. Pu et al., *Small* 15 **2019** 1805427.
https://case.edu/its/archives/presidents/ragsummary.htm
ABUNDANCE OF ELEMENTS IN THE EARTH'S CRUST AND IN THE SEA,
CRC Handbook of Chemistry and Physics, 97th edition (2016–2017), p. 14-17

General Setup of a Battery

- Coin cell
- Pouch cell
- Cylindrical cell
- …

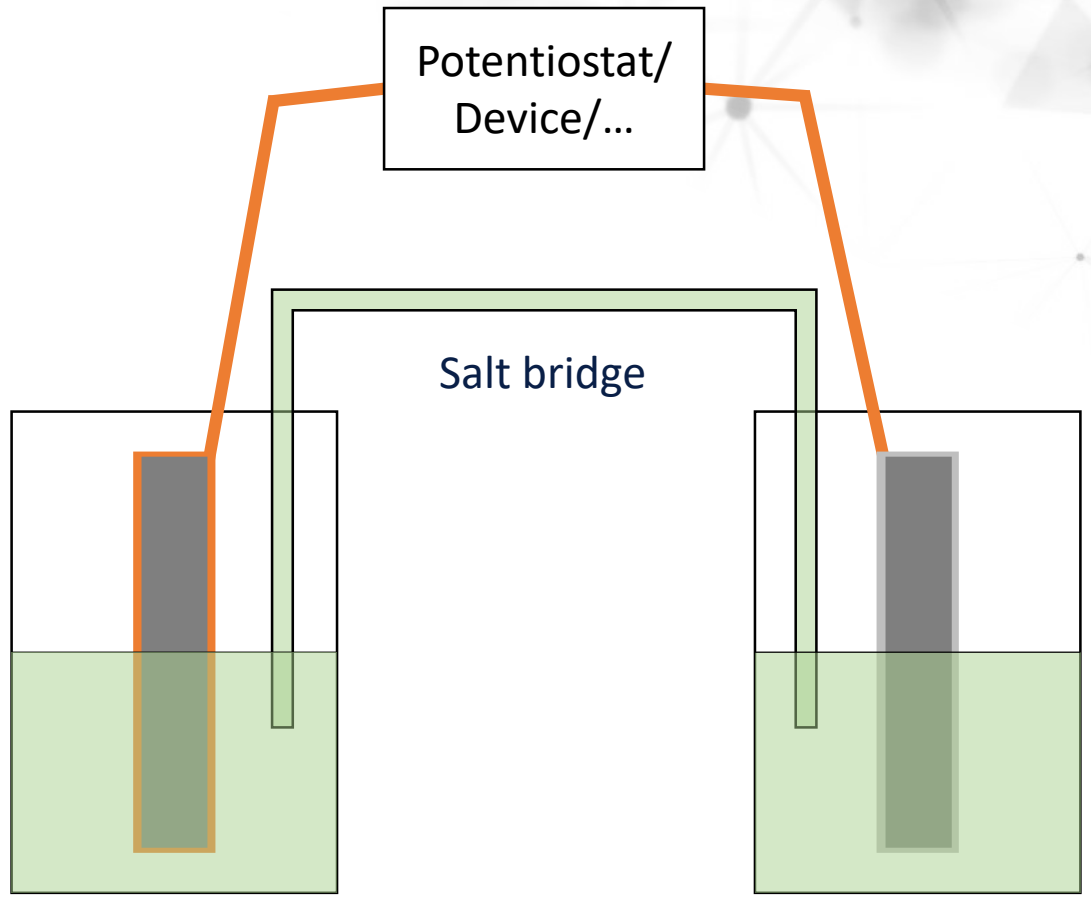


Definition of Electrodes:
Cathode: Undergoing **R**eduction
Anode: Undergoing **O**xidation

Electrocemically correct while performing

General Setup of a Battery

- Lab setup
- Easier to assemble
- TEM preparation of one electrode only

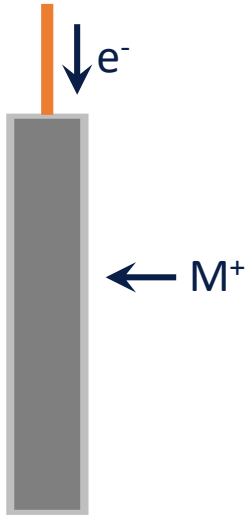


Definition of Electrodes:
Cathode: Undergoing **R**eduction
Anode: Undergoing **O**xidation

Electrocemically correct while performing

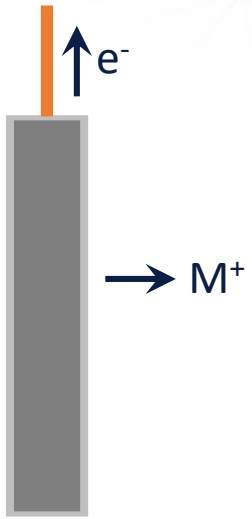
Positive Electrode - „Cathode“ Reaction

Performing



$Pb^{IV}O_2 + 2e^- + 4H^+ \rightarrow Pb^{2+} + 2H_2O$

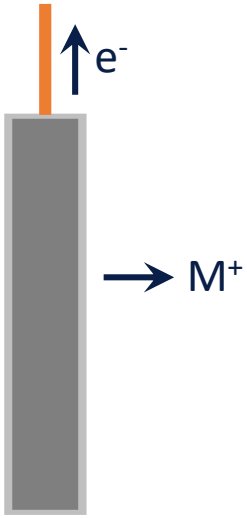
Charging



$Pb^{2+} + 2H_2O \rightarrow Pb^{IV}O_2 + 2e^- + 4H^+$

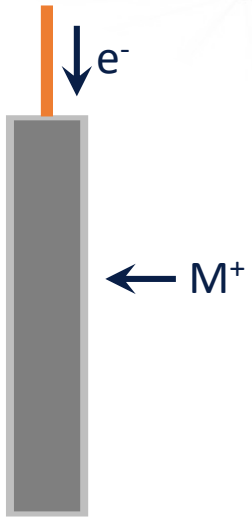
Negative Electrode – “Anode“ Reaction

Performing



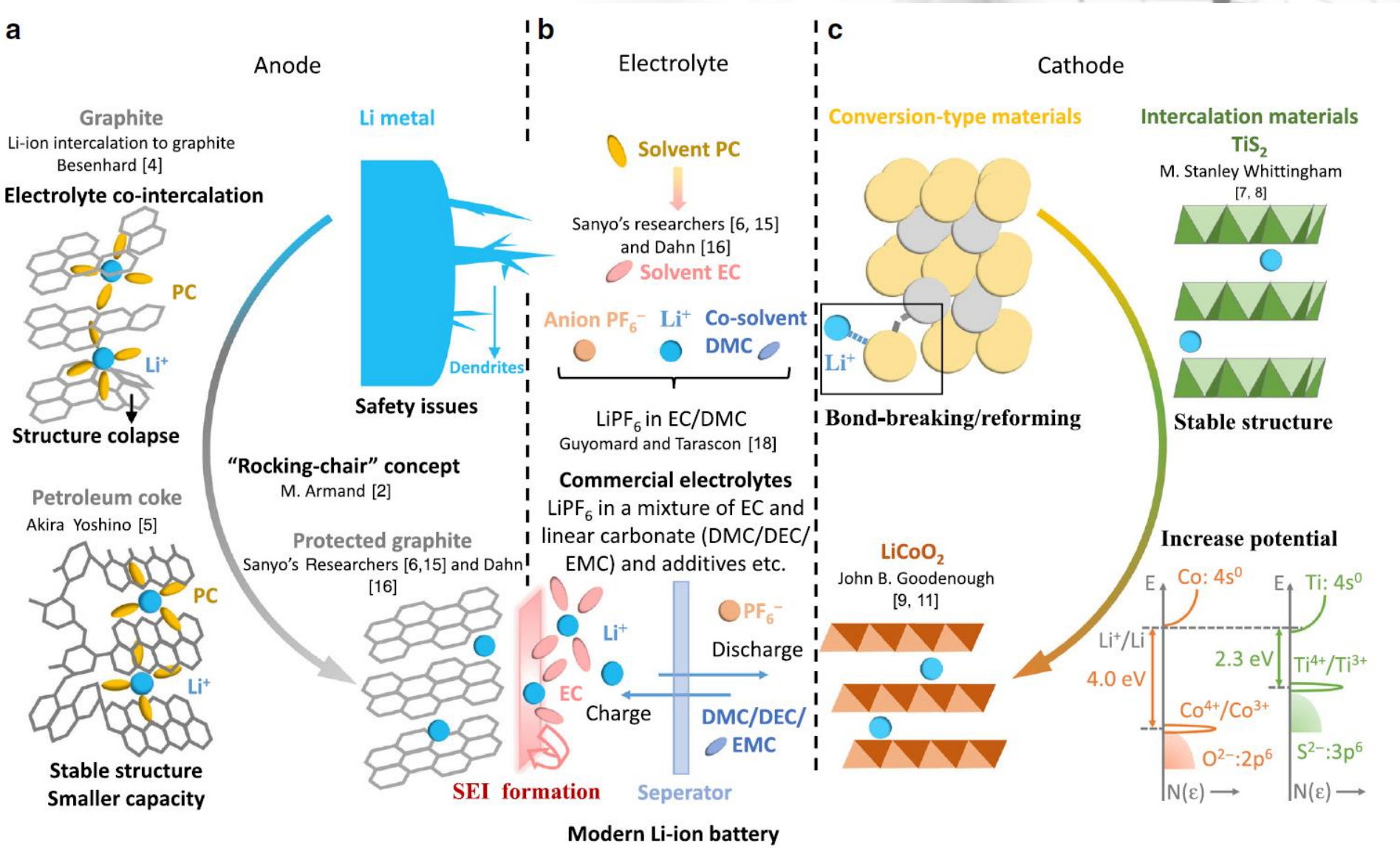
$Pb \rightarrow Pb^{2+} + 2e^-$

Charging



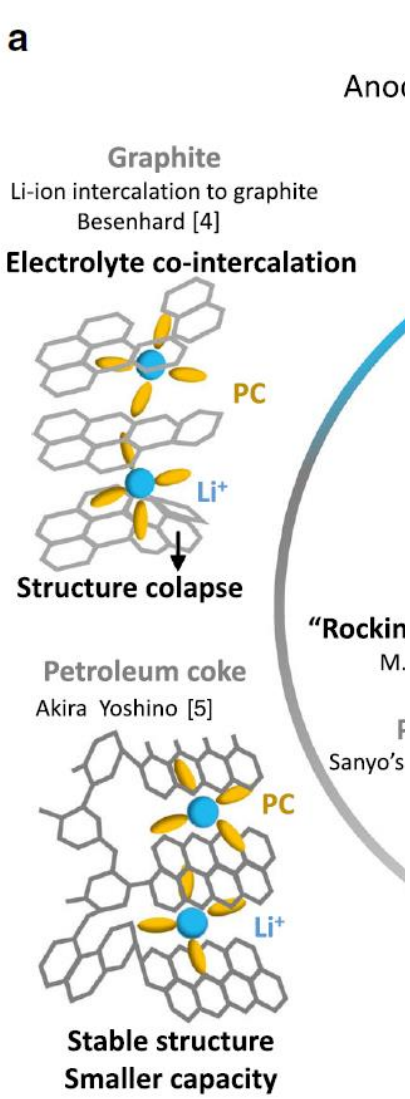
$Pb^{2+} + 2e^- \rightarrow Pb$

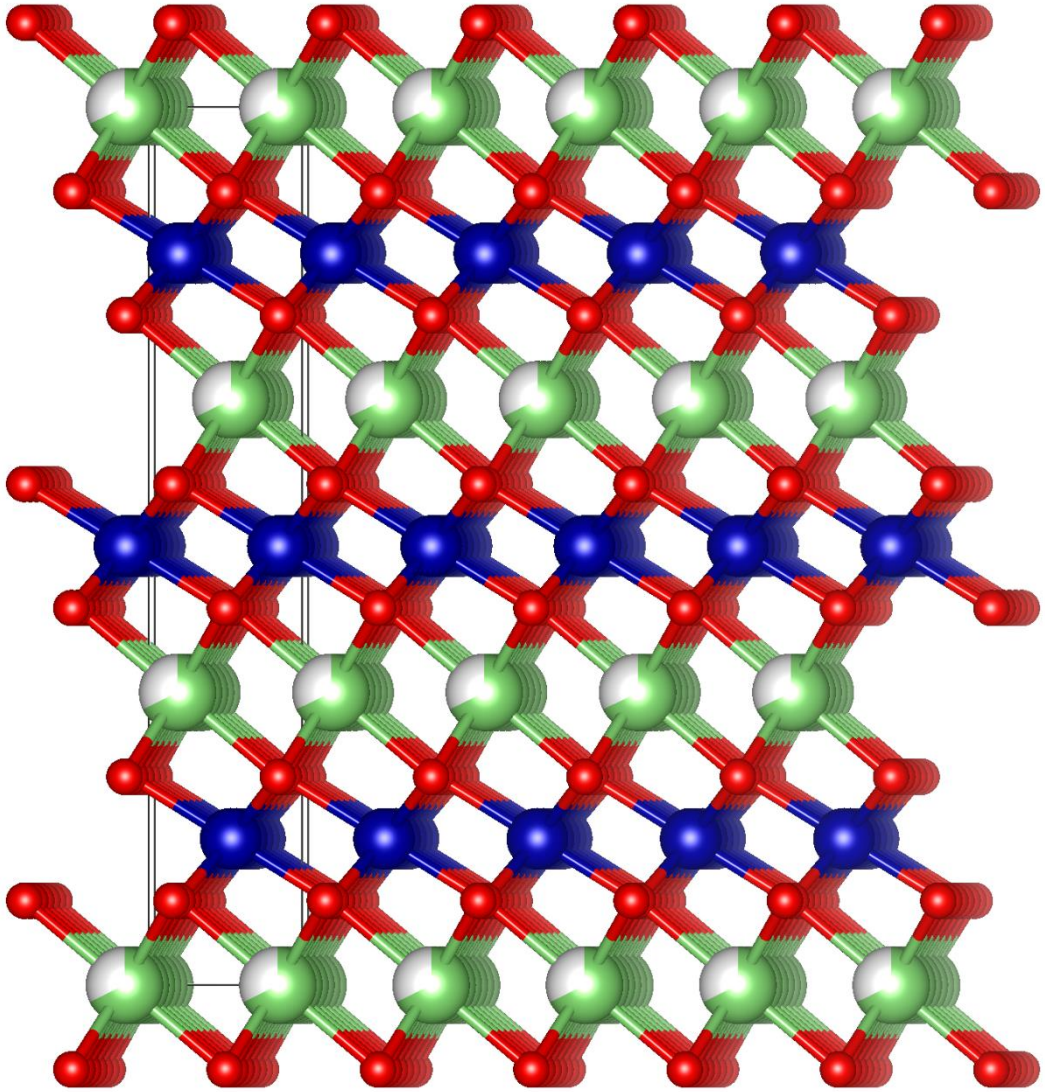
Anodes and Cathodes in Ion Batteries

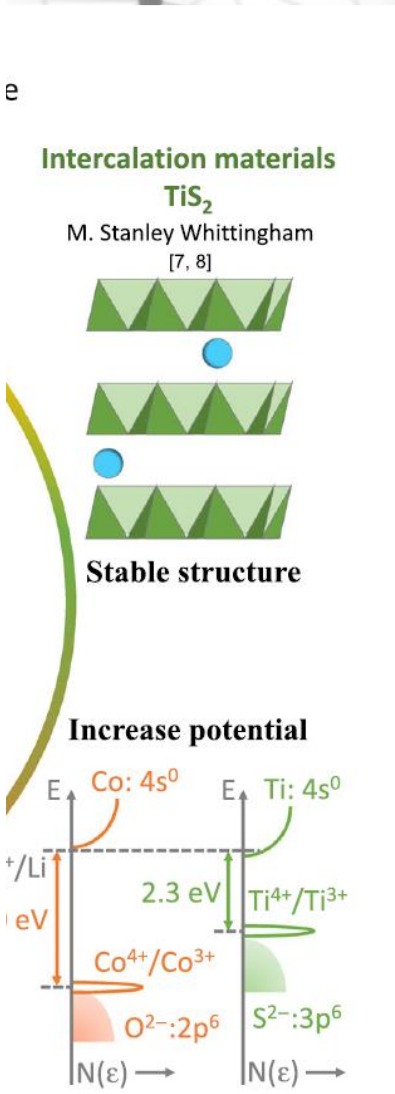


J. Xie et al., *Nature Comm.* 11 **2020** 2499.

Anodes and Cathodes in Ion Batteries



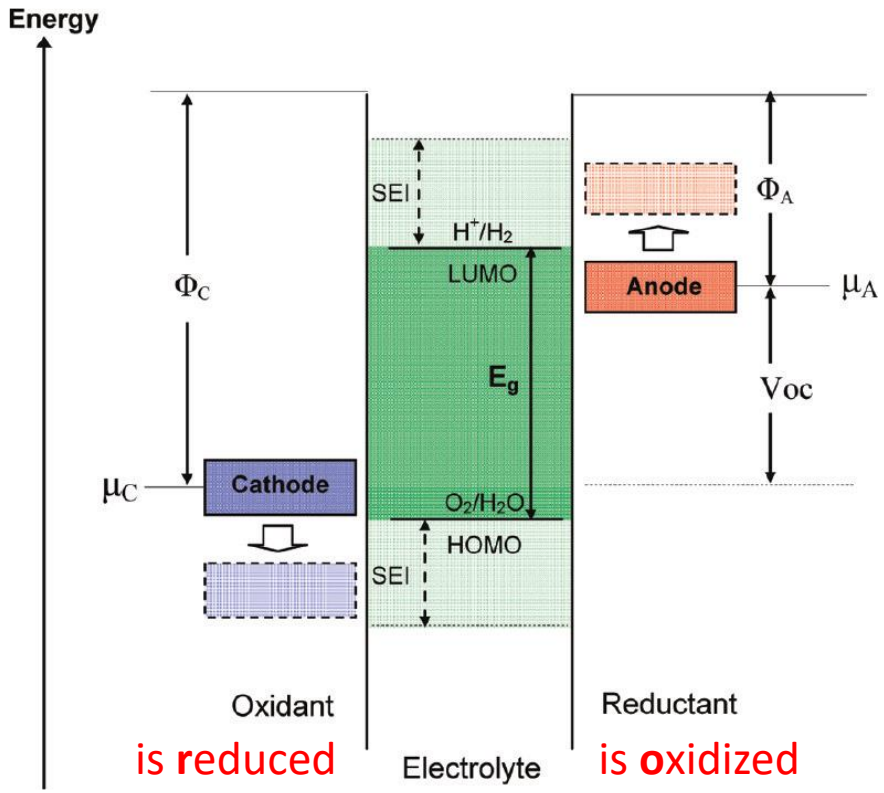




Li Co O

Y. Takahashi et al., *J. Solid State Chem.* 180 **2007** 319-321.
J. Xie et al., *Nature Comm.* 11 **2020** 2499.

Electron Energy Levels of Anodes and Cathodes



Potential vs H^+/H_2

$Li^+ + e^- \rightarrow Li$ -3,04 V

$Na^+ + e^- \rightarrow Na$ -2,71 V

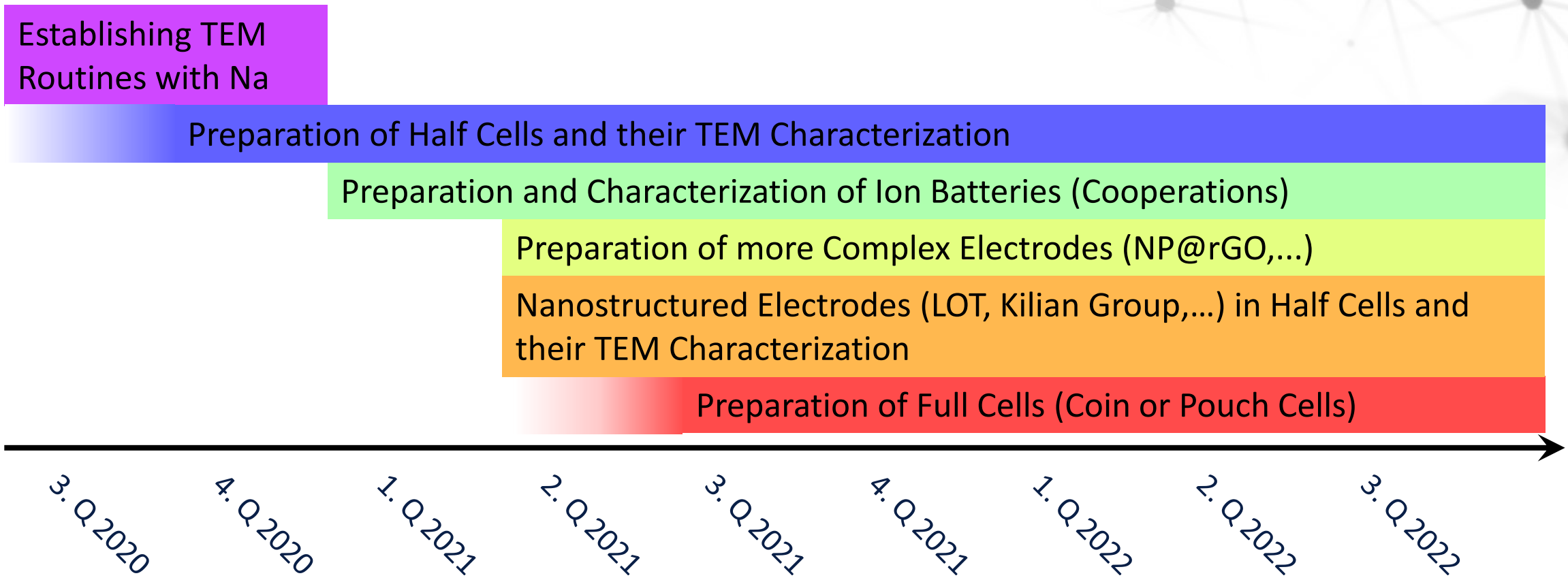
- Plating vs ion intercalation/adsorption depends on voltage and cell composition!
- Usually transition metals and C species undergo redox reaction e.g. $Li_xCo^{III/IV}O_2 \rightarrow LiCo^{III}O_2$ during performance/discharge

SEI: - AF, AOR, A_2CO_3, A(OH)… → SEI consumes A^+
- needs to be A^+ conductive

J.B. Goodenough et al., *Chem. Mater.* 22, 3 **2010** 587-603.
https://de.wikipedia.org/wiki/Elektrochemische_Spannungsreihe

The Plan

- First steps are proof of principle for TEM preparation/characterization
- Beyond these steps we are free to develop our own materials

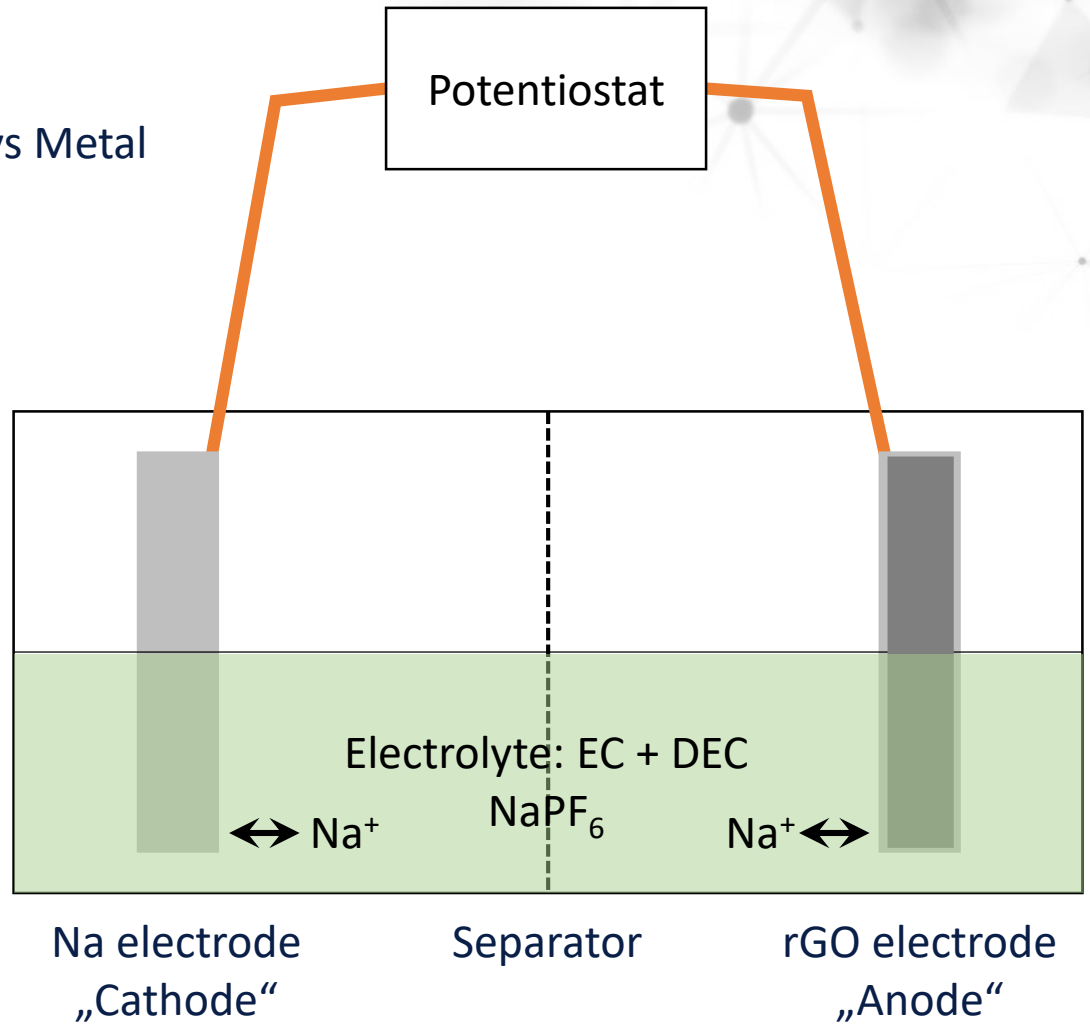


Where to start? What is there to learn?

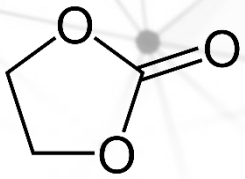
- (Half) Cell Setup: Electrode vs Metal
- SEIs?
- Na^+ or Na?
- Where in/on rGO?

- Why Counter Electrode?

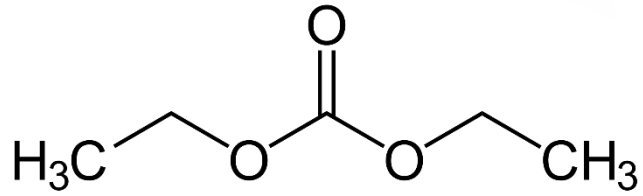
→ Charge Compensation!



EC, Ethylencarbonate



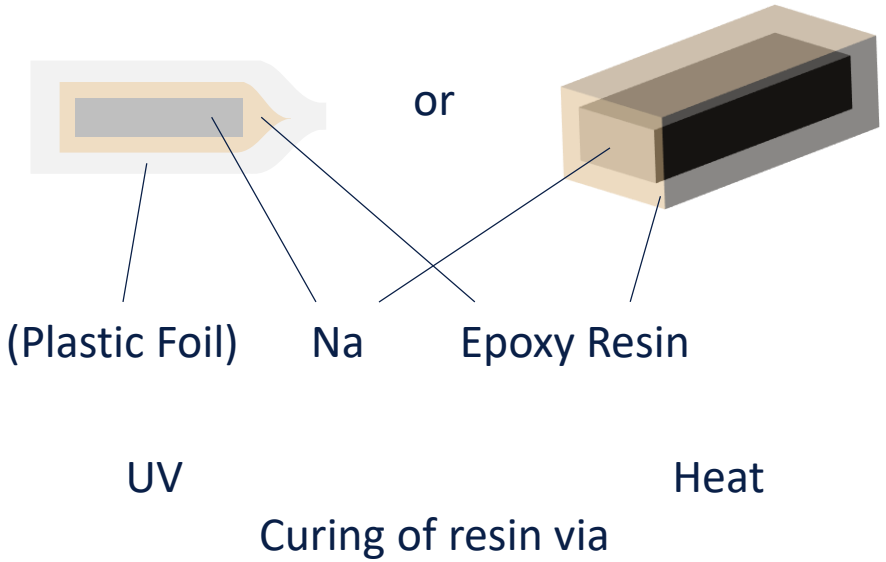
DEC, Diethylcarbonate

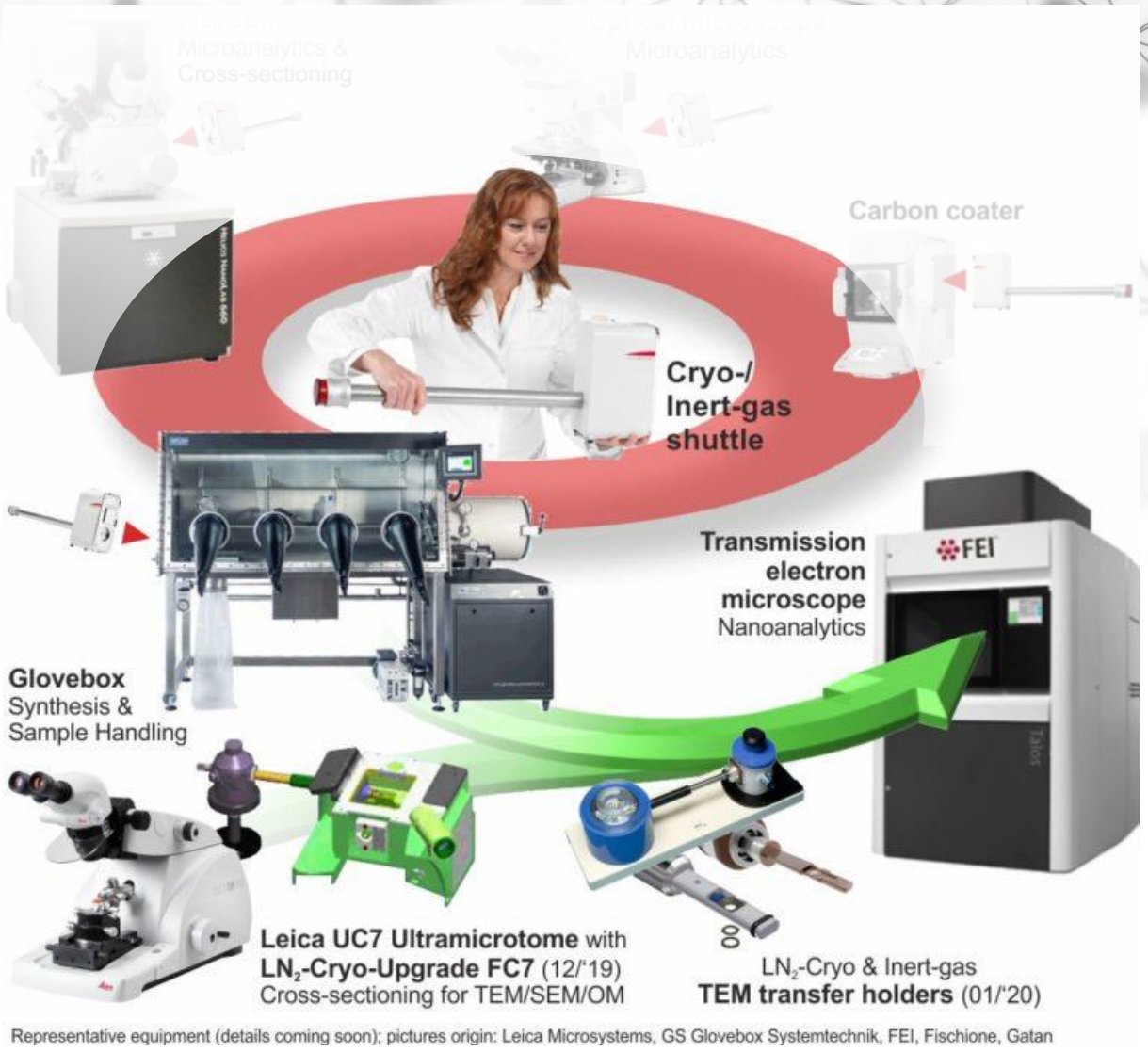


TEM Preparation of Electrodes: Na Proof of Principle

- Na highly reactive
- Handling in inert gas or encapsulated
- Cutting with ultramicrotome
- Transfer to TEM in cryo transfer holder

- STEM-EELS/EDX to check for O





Representative equipment (details coming soon); pictures origin: Leica Microsystems, GS Glovebox Systemtechnik, FEI, Fischione, Gatan

TEM Preparation of Electrodes: Na Proof of Principle

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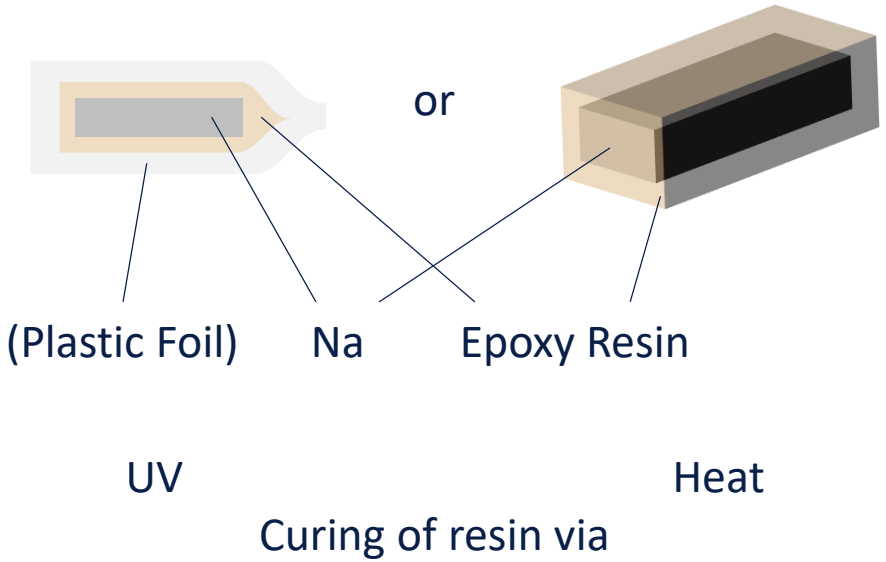
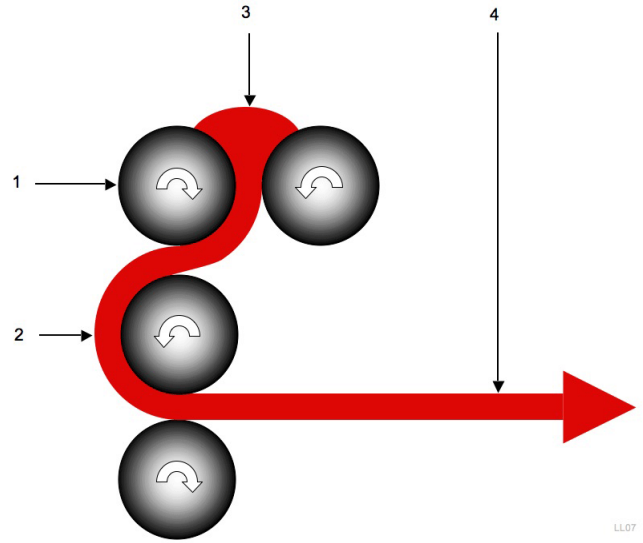


Actual electrodes should be calendered



- Guarantees uniform thickness
- Smoothens surface (increased SEI stability)

https://de.wikipedia.org/wiki/Kalander
J. Conder, *Chem. Commun.* 55 **2019** 1275.

Where to start?

- (Half) Cell Setup: Electrode vs Metal
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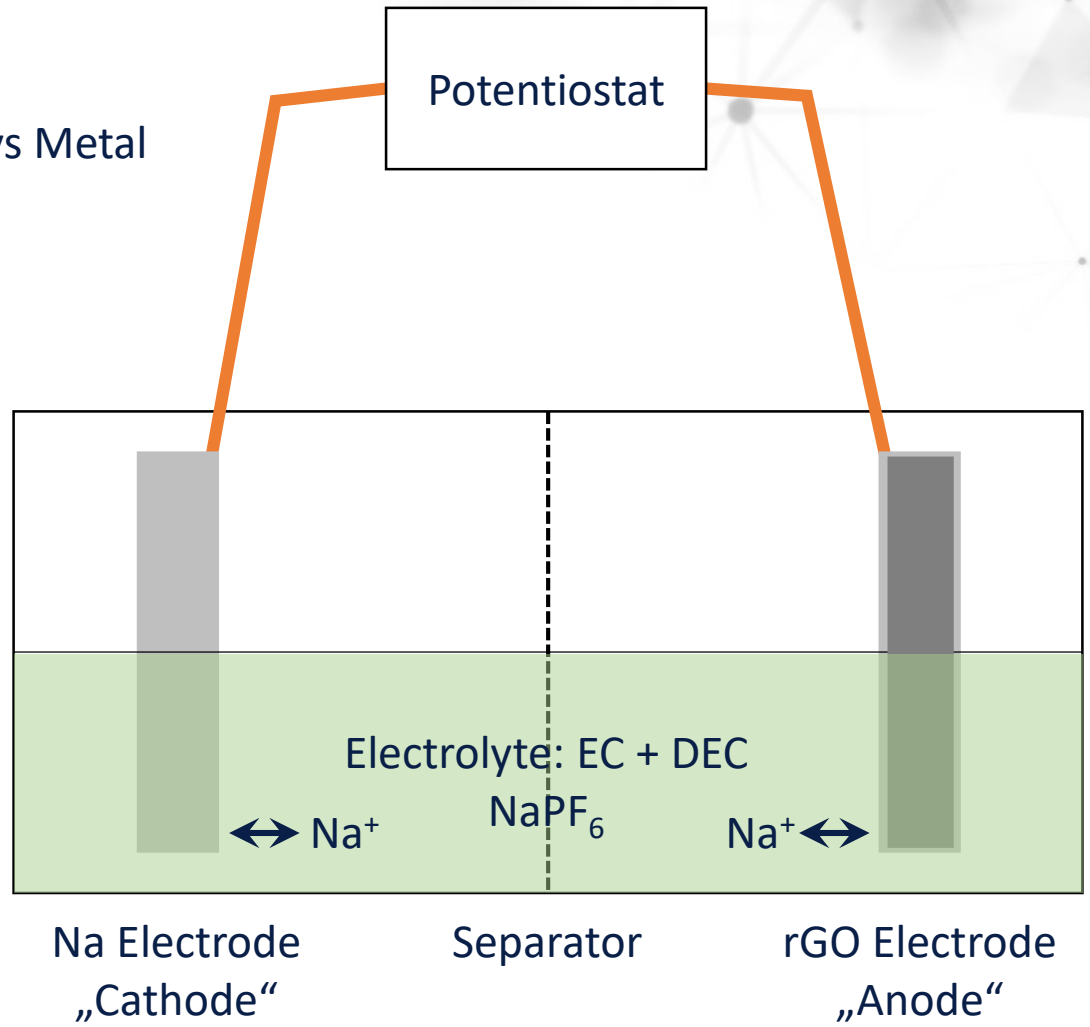

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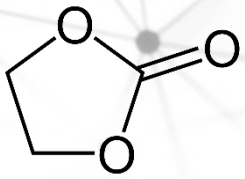

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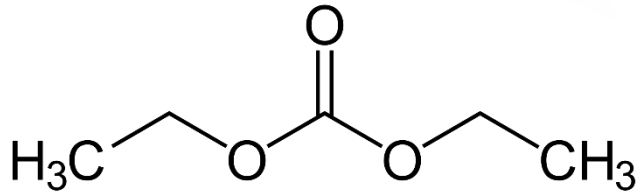
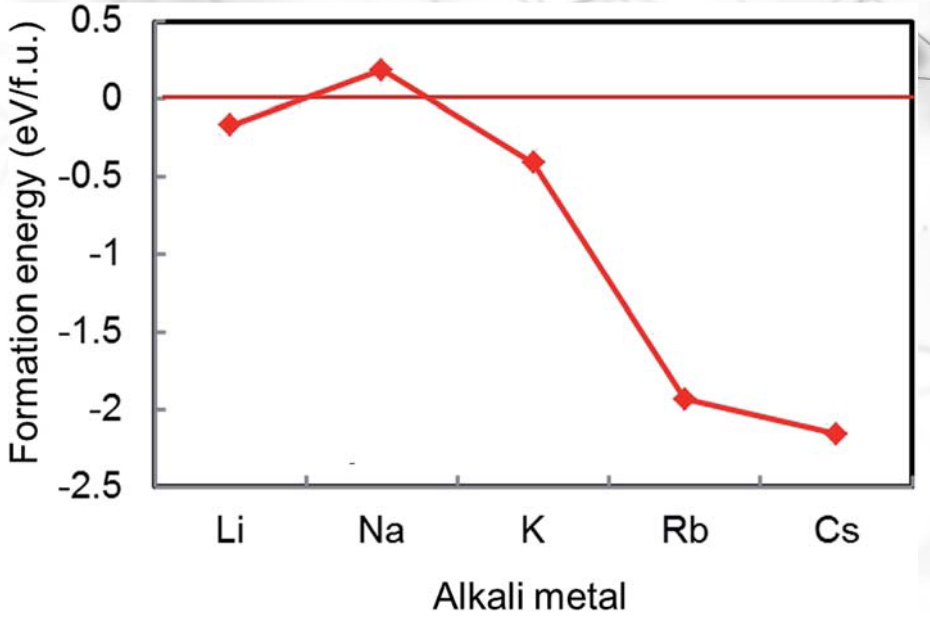


The First (Half) Cell – Why rGO, not Graphite?

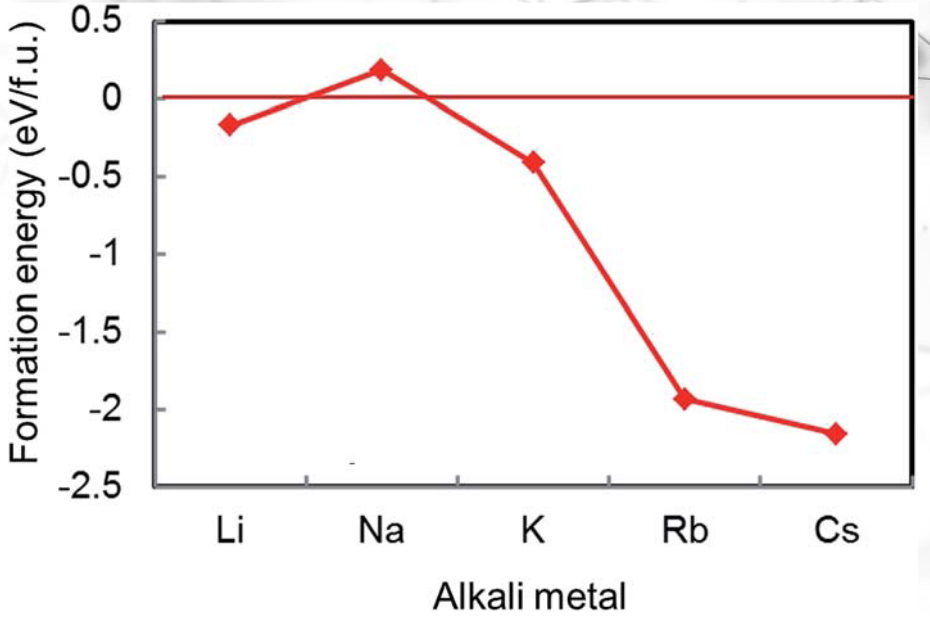
- Simulations hint at change of covalent (Li/C) and vdW (from K/C on) character of ion/graphite bond



H. Moriwake et al., *RSC Adv.* 7 **2017** 36550–36554.

The First (Half) Cell – Why rGO?

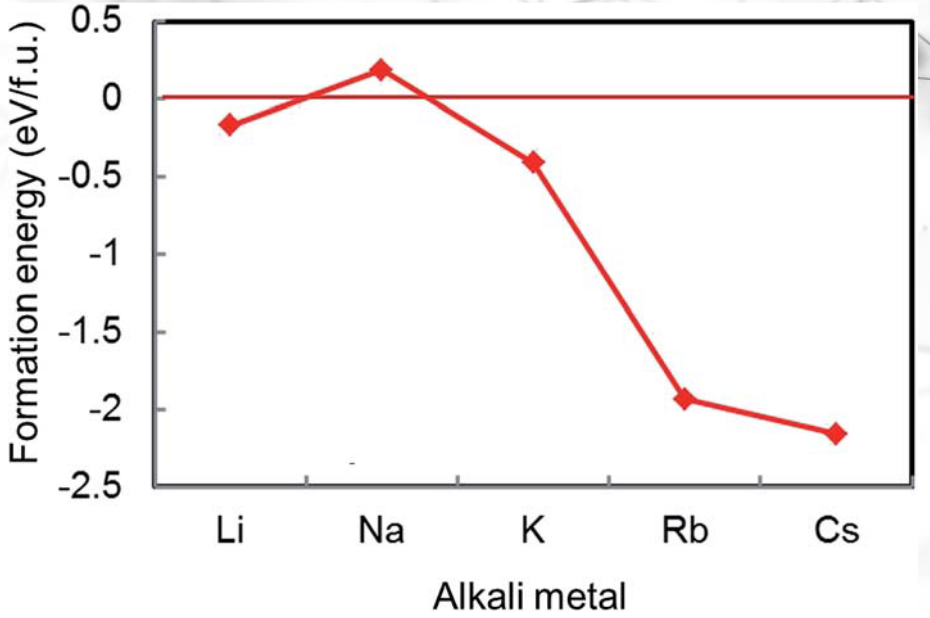
- Simulations hint at change of covalent (Li/C) and vdW (from K/C on) character of ion/graphite bond
- GO in highly oxidized state is an insulator
- Is otherwise reduced during first charging cycle of electrode



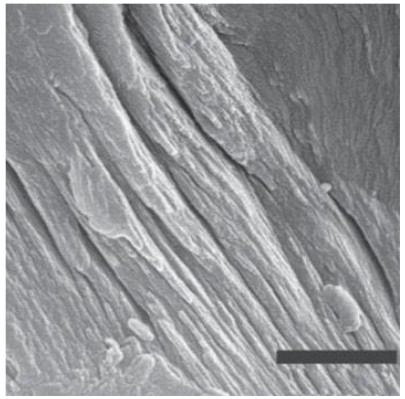
T. Szabó et al., *Carbon* 43 **2005** 87–94.

The First (Half) Cell – Why rGO?

- Simulations hint at change of covalent (Li/C) and vdW (from K/C on) character of ion/graphite bond
- GO in highly oxidized state is an insulator
- Is otherwise reduced during first charging cycle of electrode
- Large accessible surface
- Defects change adsorption behaviour of Na^+

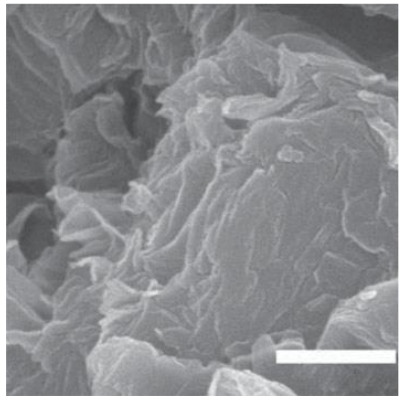


Graphite

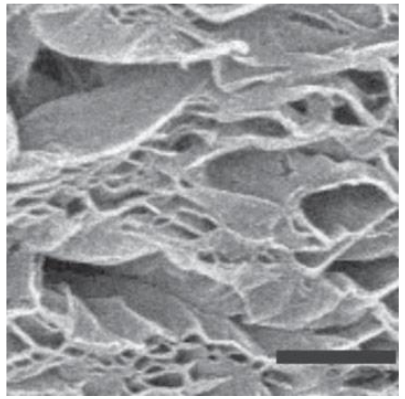


SB: 500 nm

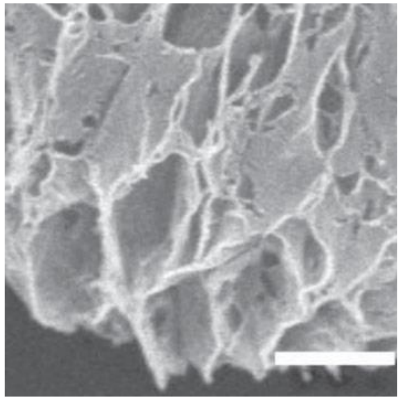
rGO dried at



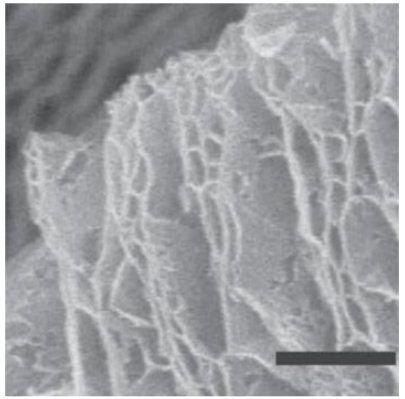
120 °C



200 °C



250 °C

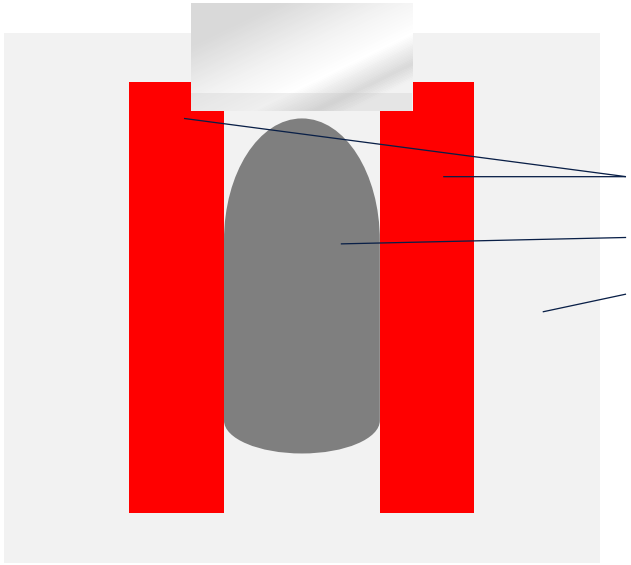


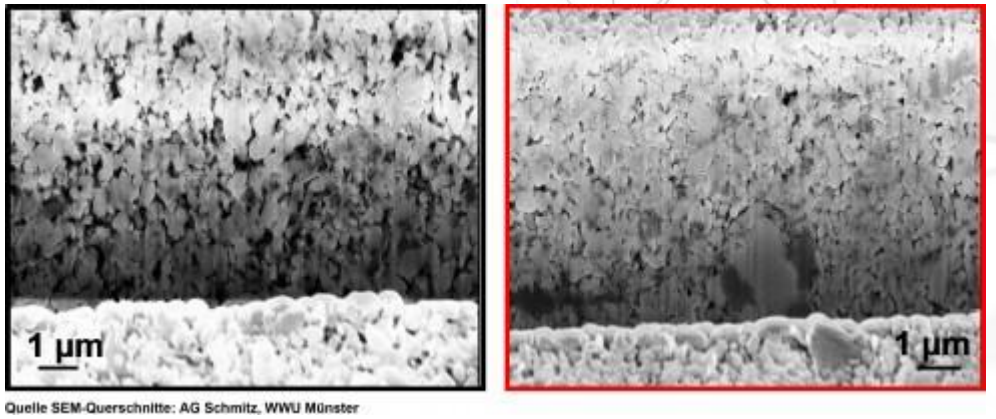
300 °C

Jo J et al. *R. Soc. open sci.* 6 **2019** 181978; D. Datt et al., *ACS Appl. Mater.* Interfaces 6 **2014** 1788−1795.

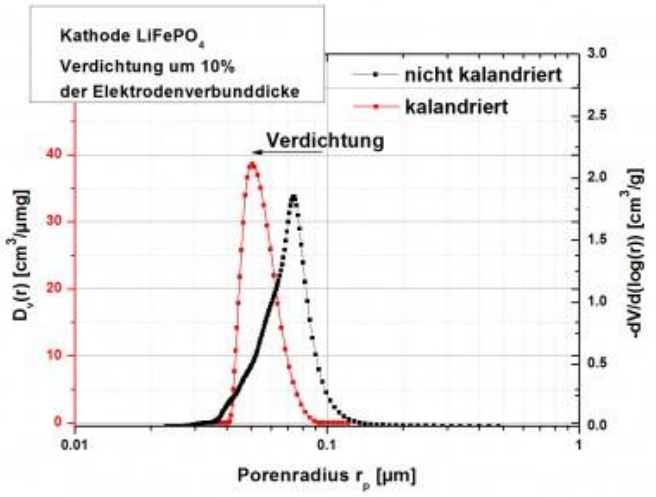
Preparation of Anode

- Dispersion of electrolyte and rGO added to Al foil via doctor blading





Quelle SEM-Querschnitte: AG Schmitz, WWU Münster



- Drying
- Calendaring

https://youtu.be/pm1yzlwaWAU; https://www.ipat.tu-bs.de/de/forschung/elektrochemische-speichertechnik/kalandrierencalendering

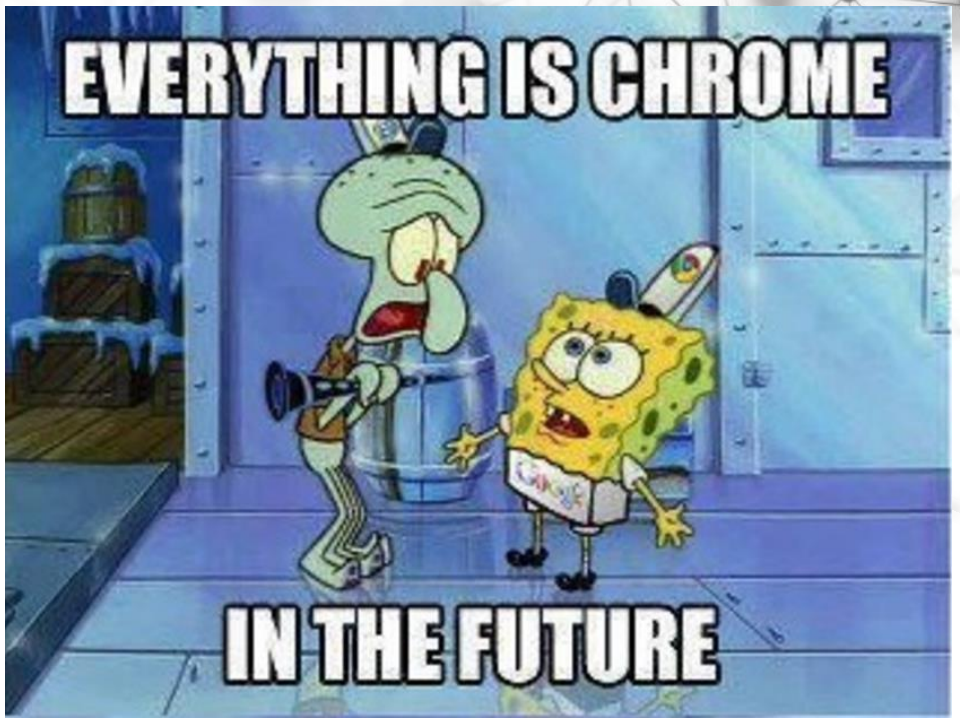
Further into the Future

Changes to rGO
- Defect density
- Dominant type of defects
- Decoration with NP

Preparation of batteries
- Coin vs Pouch Cells
- TEM Preparation of Cathode/Electrolyte/Anode
- Electrochemical cycling of batteries

SEI design
- SEI prepared on electrode
- Assembly of battery
- TEM characterization

Solid electrolytes
Mixed 2D material anodes
Clever anode/cathode design for increased SEI stability
…



But which battery materials will we study?

Thank you for your attention!
Questions?