Batteries

Prof. Dr. Moniek Tromp
Chair of Materials Chemistry
Zernike Institute for Advanced Materials


SUSTAINABLE DEVELOPMENT GOALS
1 NO POVERTY
2 ZERO HUNGER
3 GOOD HEALTH AND WELL-BEING
4 QUALITY EDUCATION
5 GENDER EQUALITY
6 CLEAN WATER AND SANITATION
7 AFFORDABLE AND CLEAN ENERGY
8 DECENT WORK AND ECONOMIC GROWTH
9 INDUSTRY, INNOVATION AND INFRASTRUCTURE
10 REDUCED INEQUALITIES
11 SUSTAINABLE CITIES AND COMMUNITIES
12 RESPONSIBLE CONSUMPTION AND PRODUCTION
13 CLIMATE ACTION
14 LIFE BELOW WATER
15 LIFE ON LAND
16 PEACE, JUSTICE AND STRONG INSTITUTIONS
17 PARTNERSHIPS FOR THE GOALS
SUSTAINABLE DEVELOPMENT GOALS

Energy

- how much potential a physical system has to change. In physics, energy is a property of matter and space, objects and fields.










Conservation of Energy

- Energy can be transferred between objects and can also be converted in form. It cannot, however, be created or destroyed (**conservation of energy**).

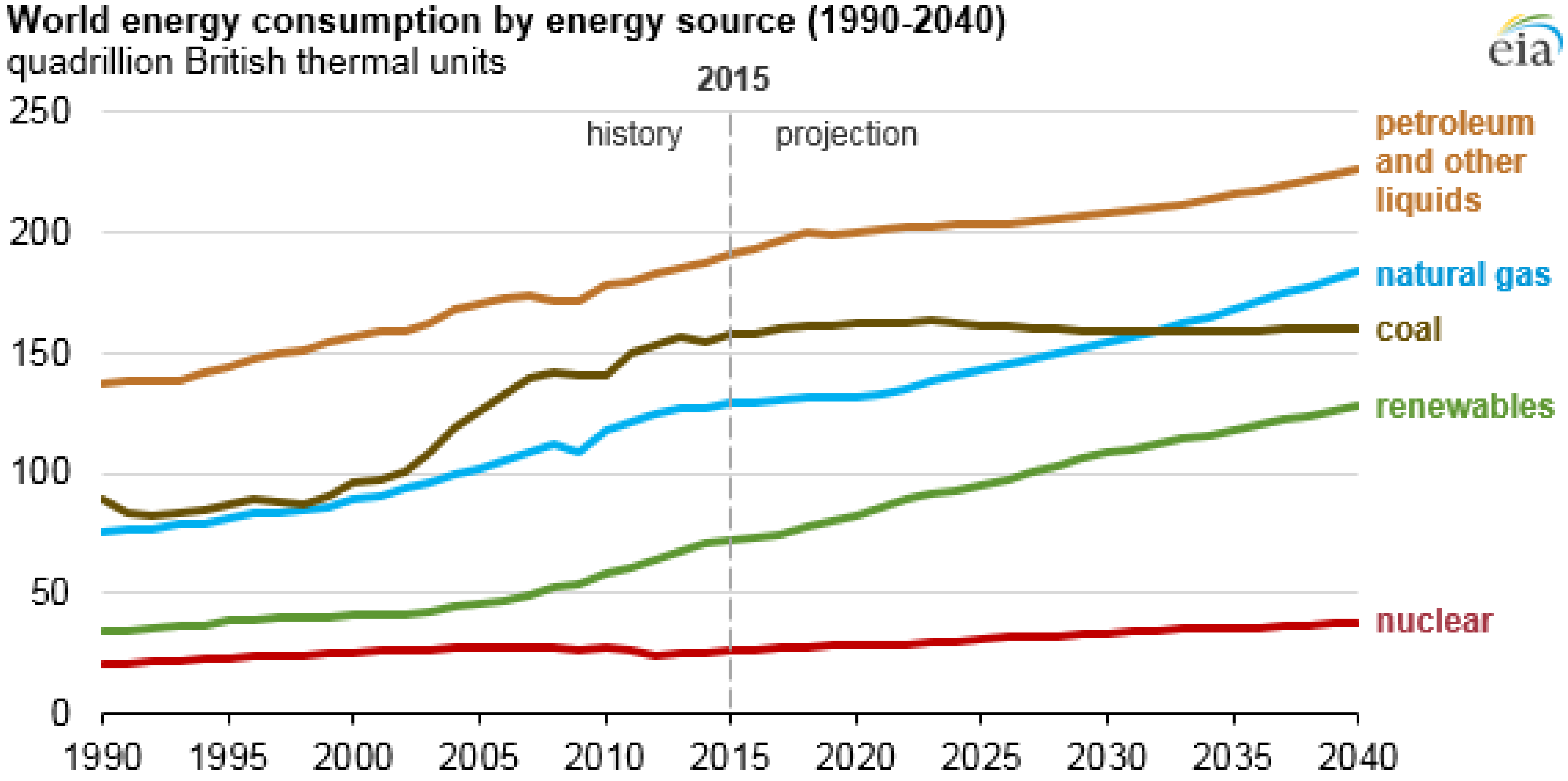
Electricity → light

Fuel → movement

Movement → electricity → light

university of groningen

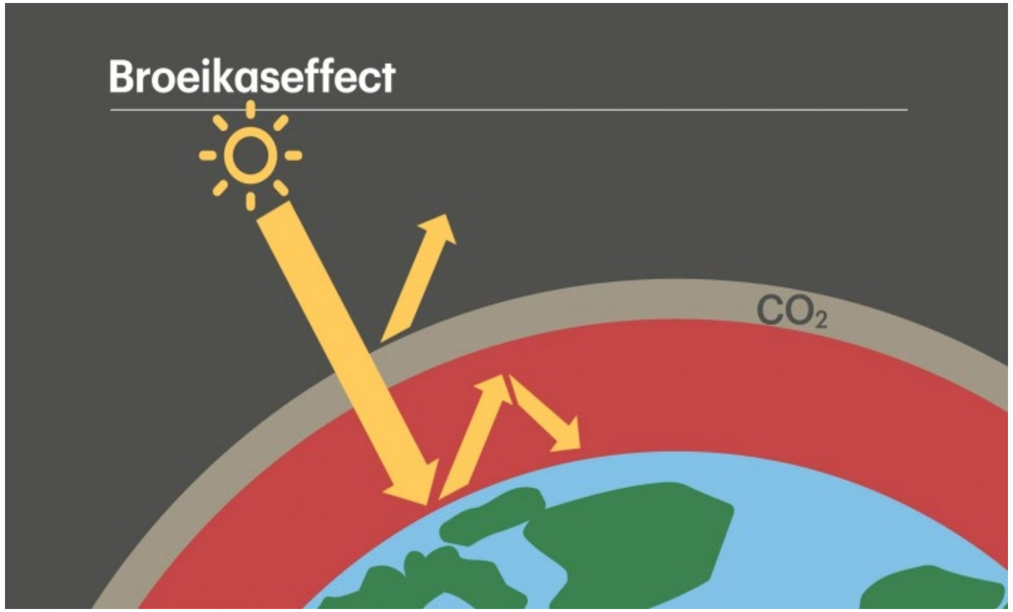
Energy Required

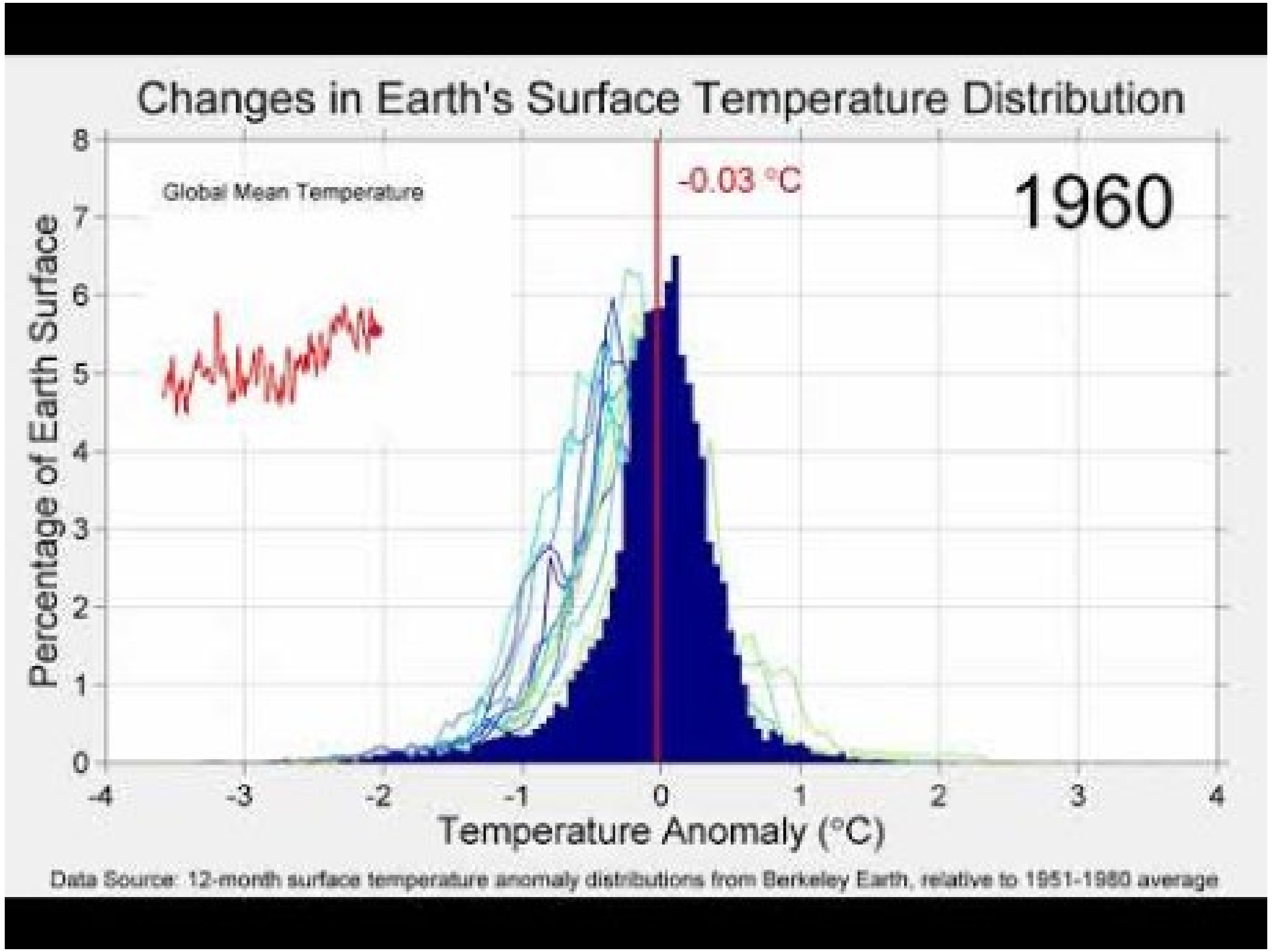


- 28% increase in energy from 2015 to 2040

Sources: US Energy Information Administration. International Energy Outlook.

Climate Change

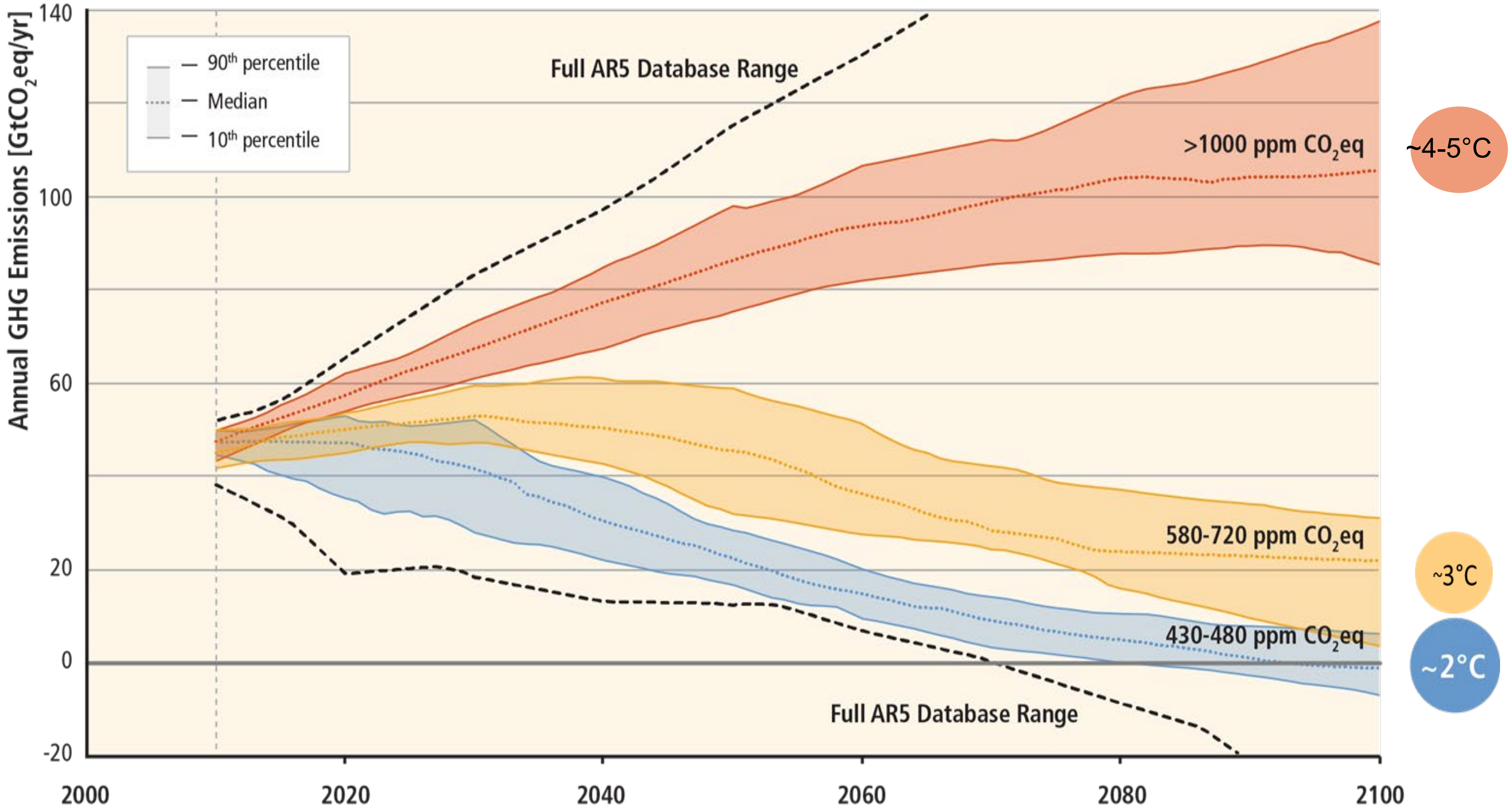




Robert Rhode

https://www.youtube.com/watch?v=xWpTGbZhZfQ

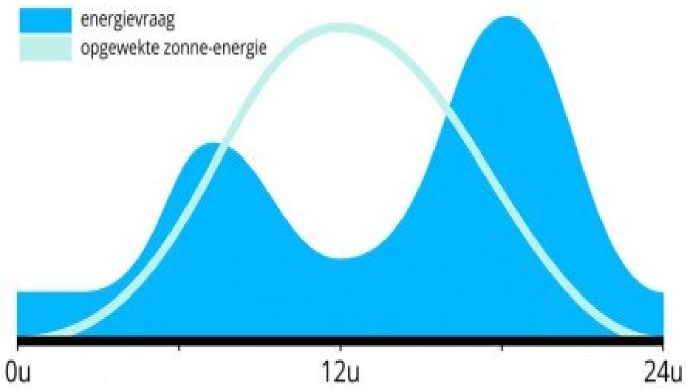
CO_2 Temperature Scenarios

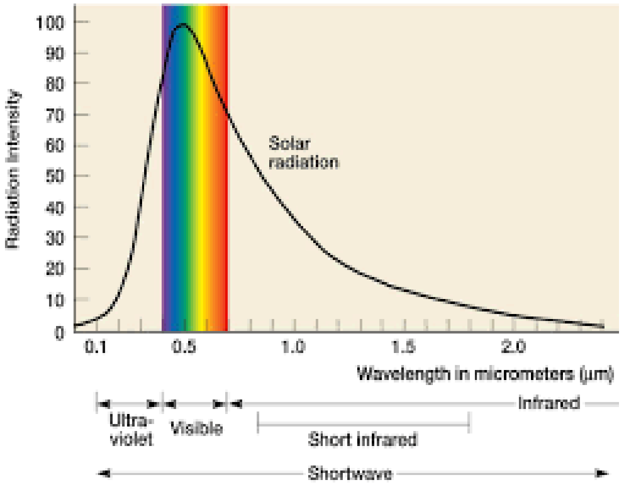


Source: IPCC, AR5, 2014 & Bob van der Zwaan (TNO-ECN/UvA)

Sustainable Energy

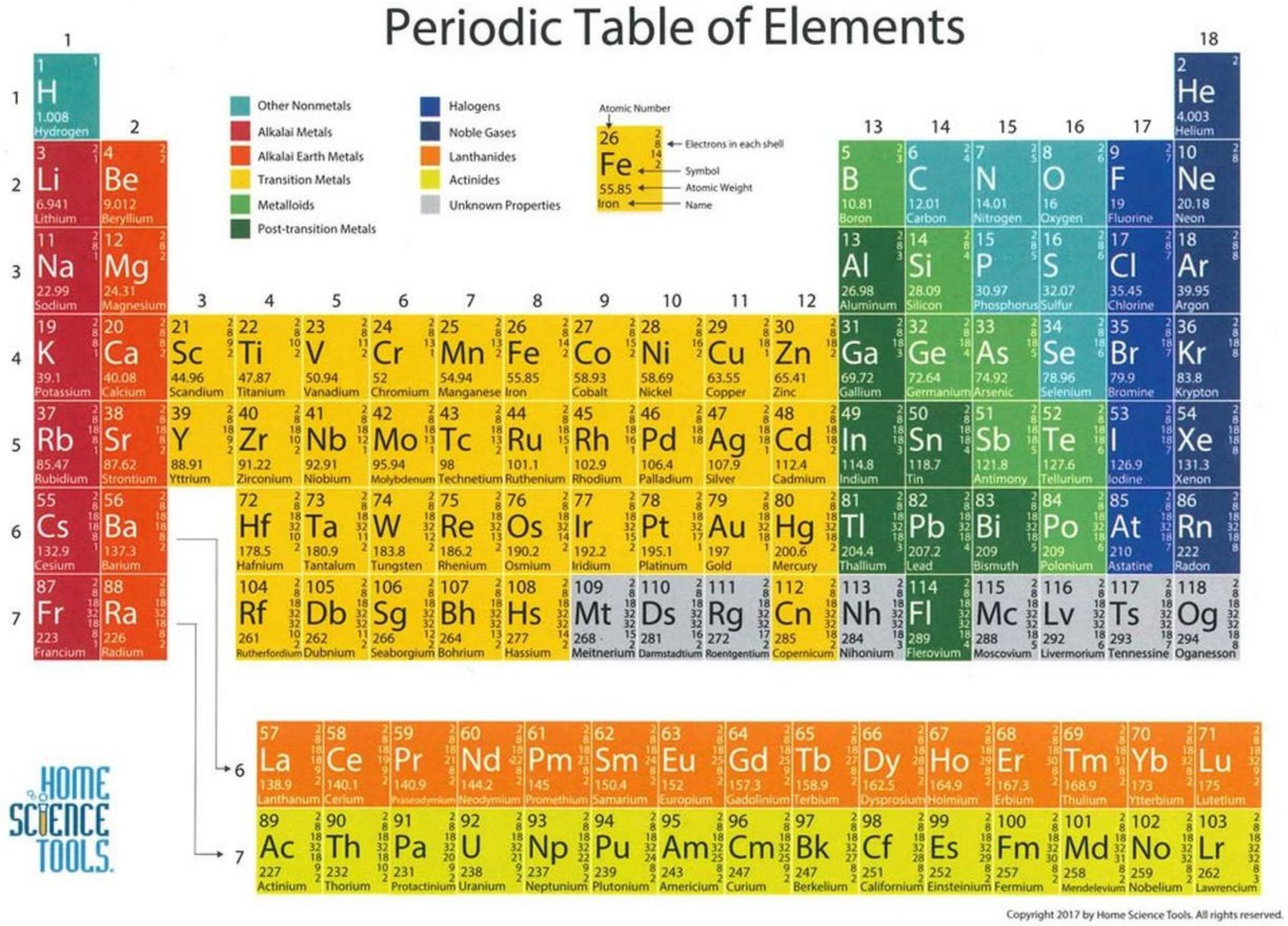
For example Sun:

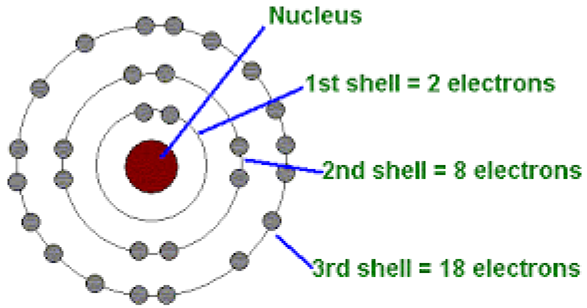


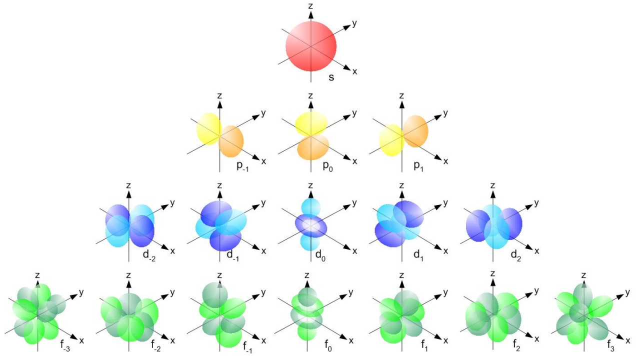


- ➢ Sun: **9000x** the required energy
- ➢ Intermittent availability → **STORE**
- ➢ Not all energy is easy “to catch””

BATTERIES

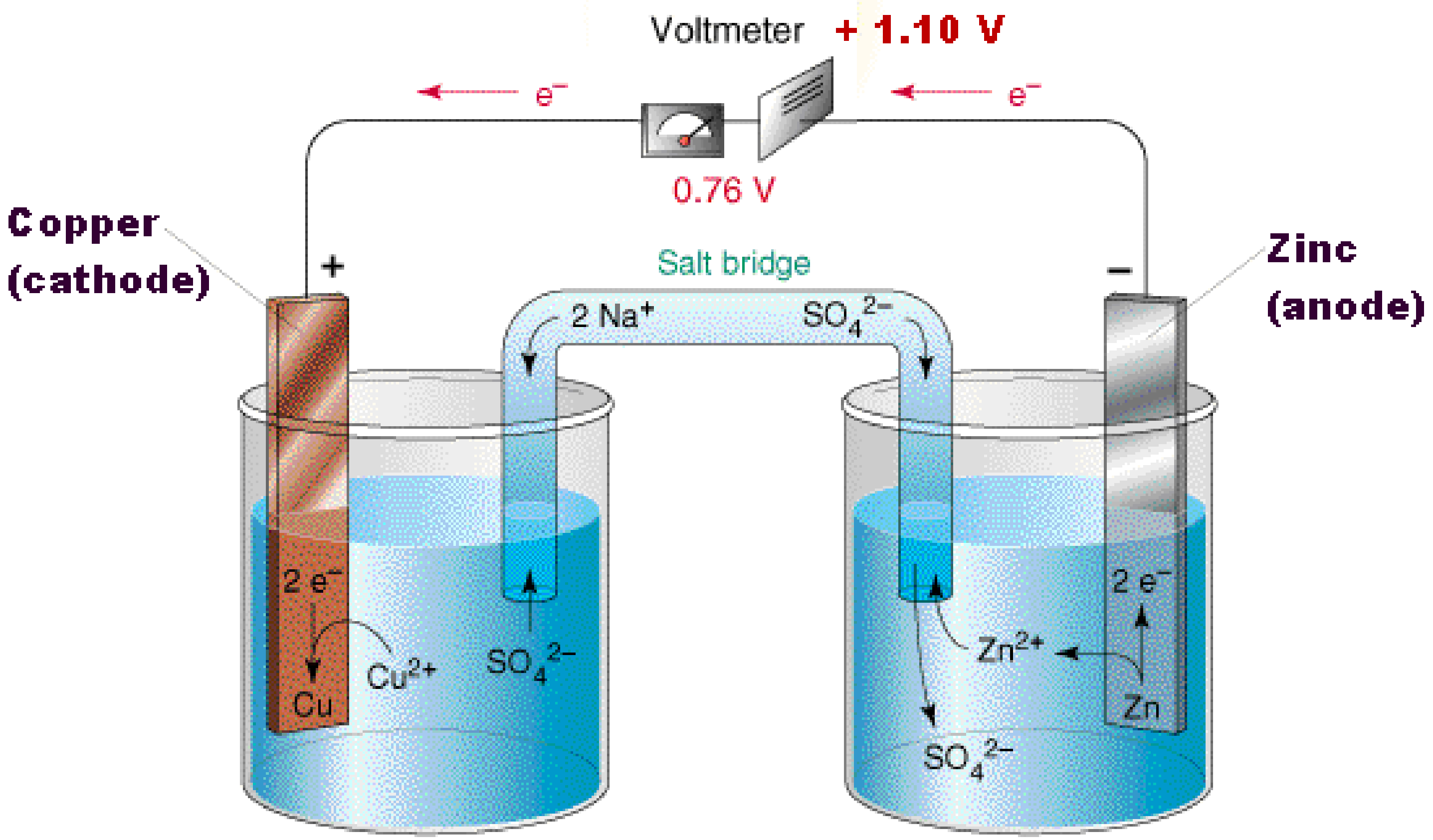






Most stable configuration: filled outer shell

Electrochemical/Galvanic Cell Cu-Zn



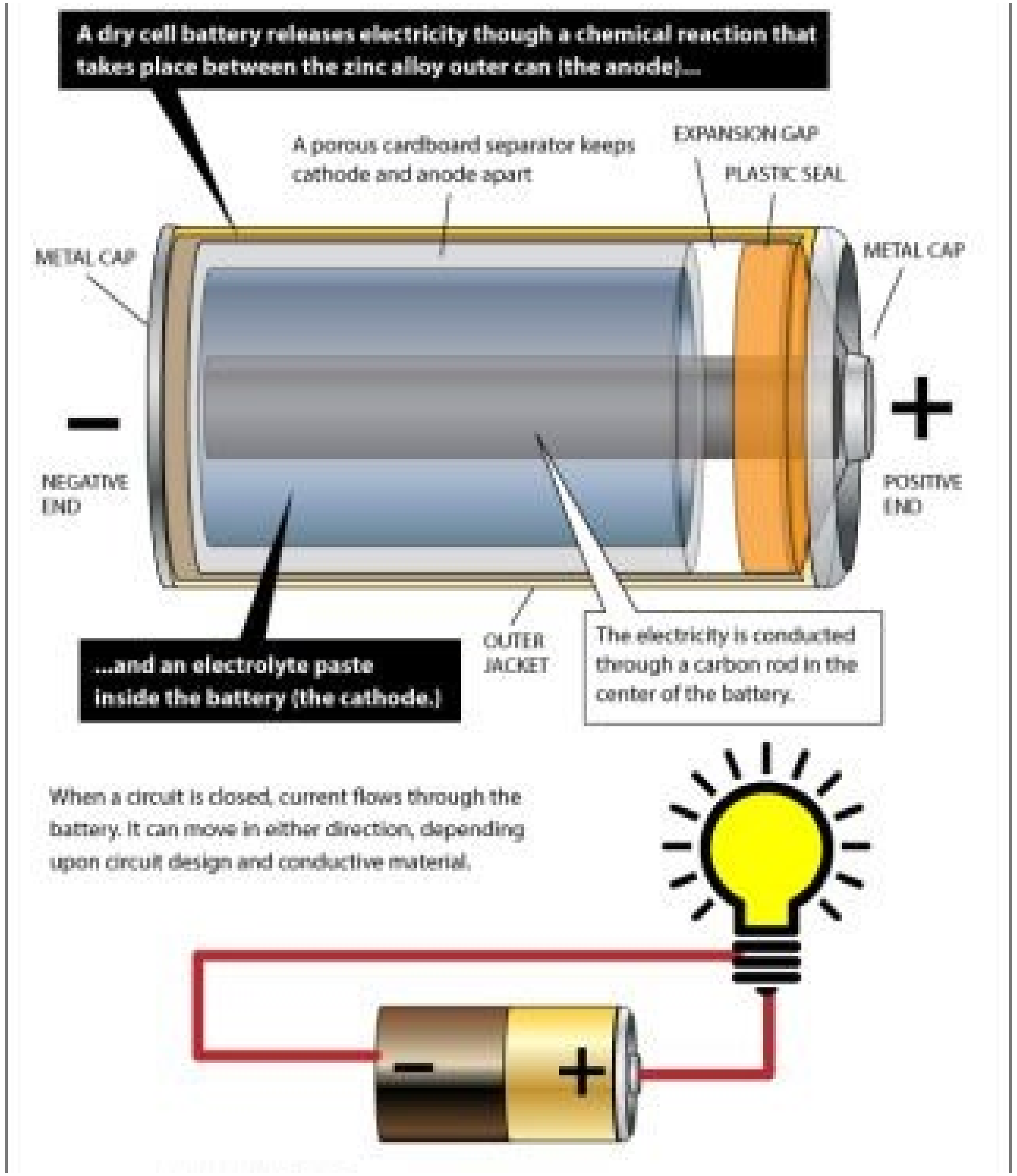
Reduction $Cu^{2+} + 2e^- \rightarrow Cu(s)$ **+0.34 V**

$Zn(s) \rightarrow Zn^{2+} + 2e^-$ **+ 0.76 V** Oxidation

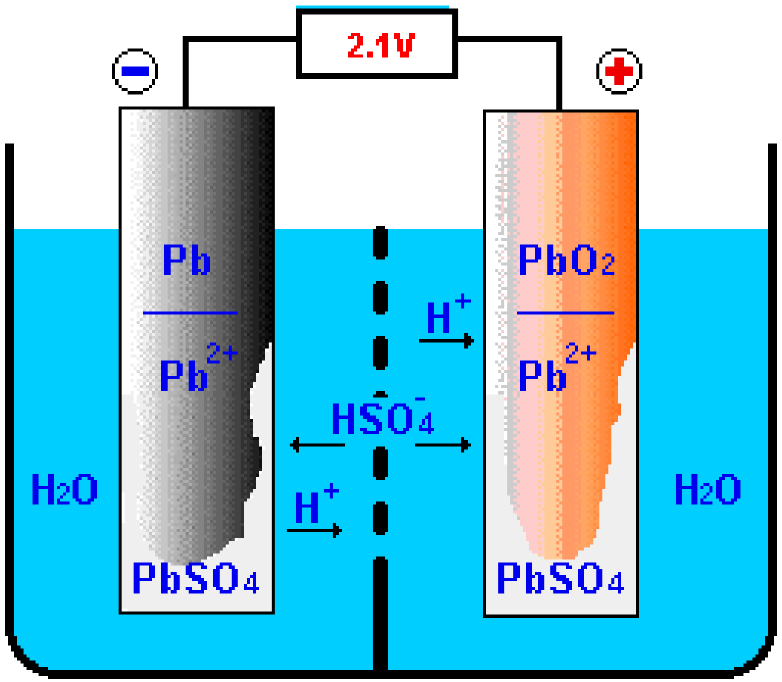
$Cu^{2+} + Zn(s) \rightarrow Zn^{2+} + Cu(s)$

Redox reactions

Battery


A dry cell battery releases electricity though a chemical reaction that takes place between the zinc alloy outer can (the anode)....
A porous cardboard separator keeps cathode and anode apart
EXPANSION GAP
PLASTIC SEAL
METAL CAP
METAL CAP
–
NEGATIVE END
+
POSITIVE END
...and an electrolyte paste inside the battery (the cathode.)
OUTER JACKET
The electricity is conducted through a carbon rod in the center of the battery.
When a circuit is closed, current flows through the battery. It can move in either direction, depending upon circuit design and conductive material.
–
+

Lead Acid Battery



Discharge		Charge	
Positive Electrode Anode (+)	Negative Electrode Cathode (-)	Positive Electrode Anode (+)	Negative Electrode Cathode (-)
$PbO_2 + HSO_4^- + 3H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$	$Pb + HSO_4^- \rightarrow PbSO_4 + H^+ + 2e^-$	$PbSO_4 + 2H_2O \rightarrow PbO_2 + HSO_4^- + 3H^+ + 2e^-$	$PbSO_4 + H^+ + 2e^- \rightarrow Pb + HSO_4^-$
Overall Cell Reaction		**Overall Cell Reaction**	
$Pb + PbO_2 + 2H^+ + 2HSO_4^- \rightarrow 2PbSO_4 + 2H_2O$		$2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H^+ + 2HSO_4^-$	

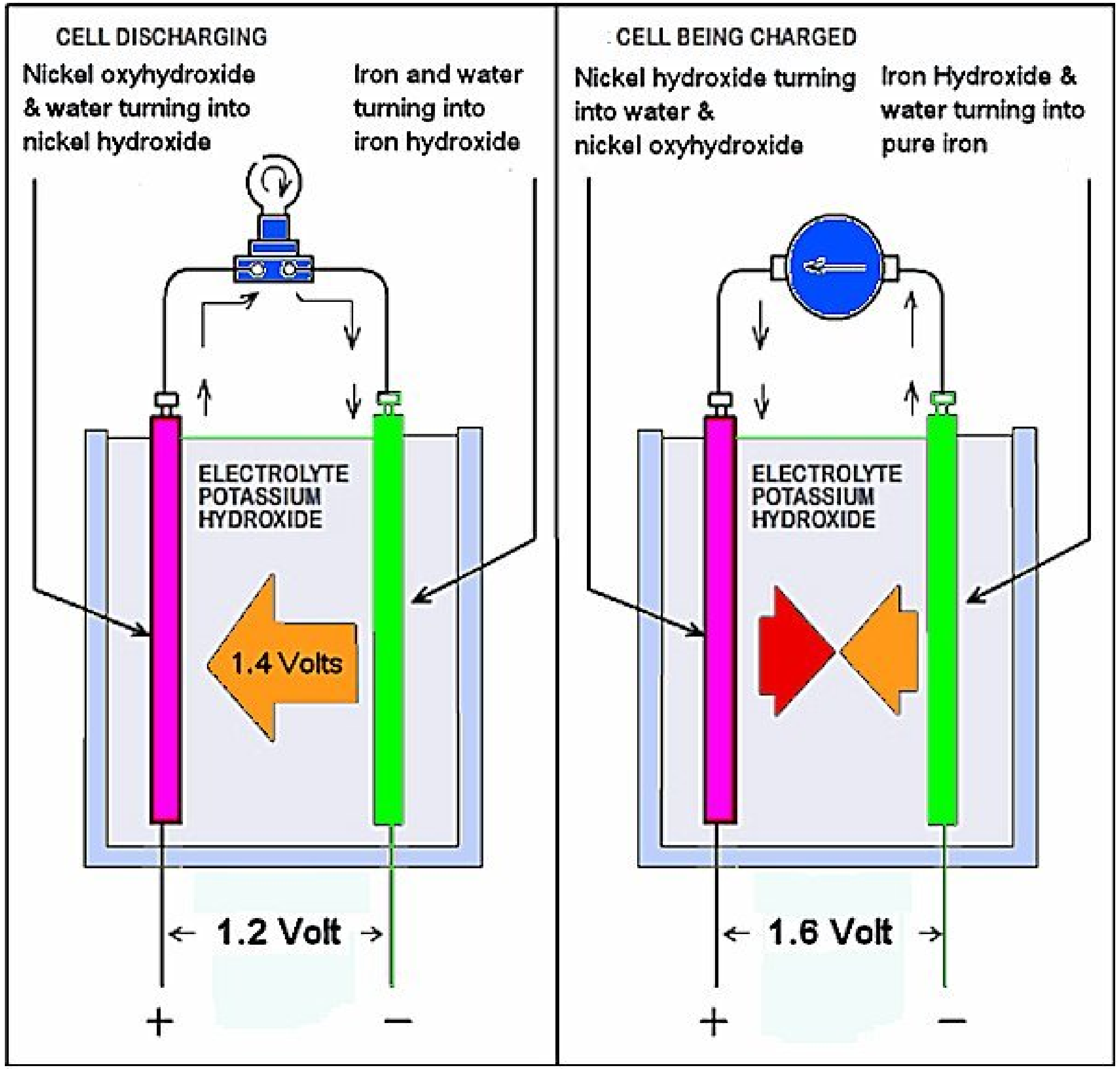
- Low volumetric and gravimetric capacity
- Sulfuric acid, lead….
- But, high surge current and large power-to-weight ratio
- Low cost

→ **Car battery**

Planté, G., Comptes Rendus Acad. Sci. 1860; Planté, G. The Storage of Electrical Energy: And Researches in the Effects Created by Currents Combining Quantity with High Tension; London: Whittaker, 1887.

university of groningen

NiFe Battery (Edison)



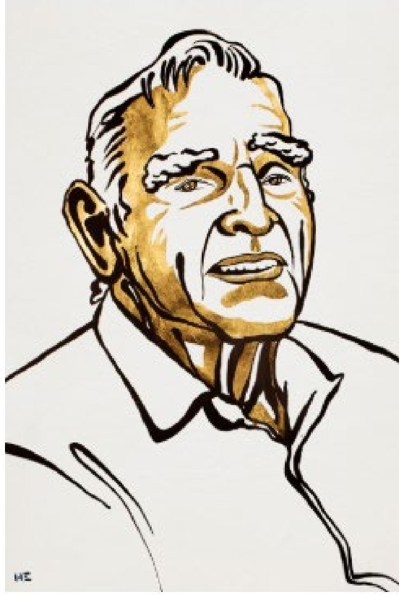
- Cheap
- Low efficiency of charge
- H_2 gas formation in side-reaction

$$2\ NiO(OH) + 2\ H_2O + 2\ e^- \leftrightarrow 2\ Ni(OH)_2 + 2\ OH^-$$

$$Fe + 2\ OH^- \leftrightarrow Fe(OH)_2 + 2\ e^-$$

Jungner, E. W. Sätt. Swedish patent no. 15567, 1901.
Jungner, E. W. Swedish patent no. 10177, 1899.
Edison, T. A. Reversible Galvanic Battery. US patent no. 692,507, 1902.

The Nobel Prize in Chemistry 2019



Ill. Niklas Elmehed. © Nobel Media.

John B. Goodenough

Prize share: 1/3

Ill. Niklas Elmehed. © Nobel Media.

M. Stanley Whittingham

Prize share: 1/3

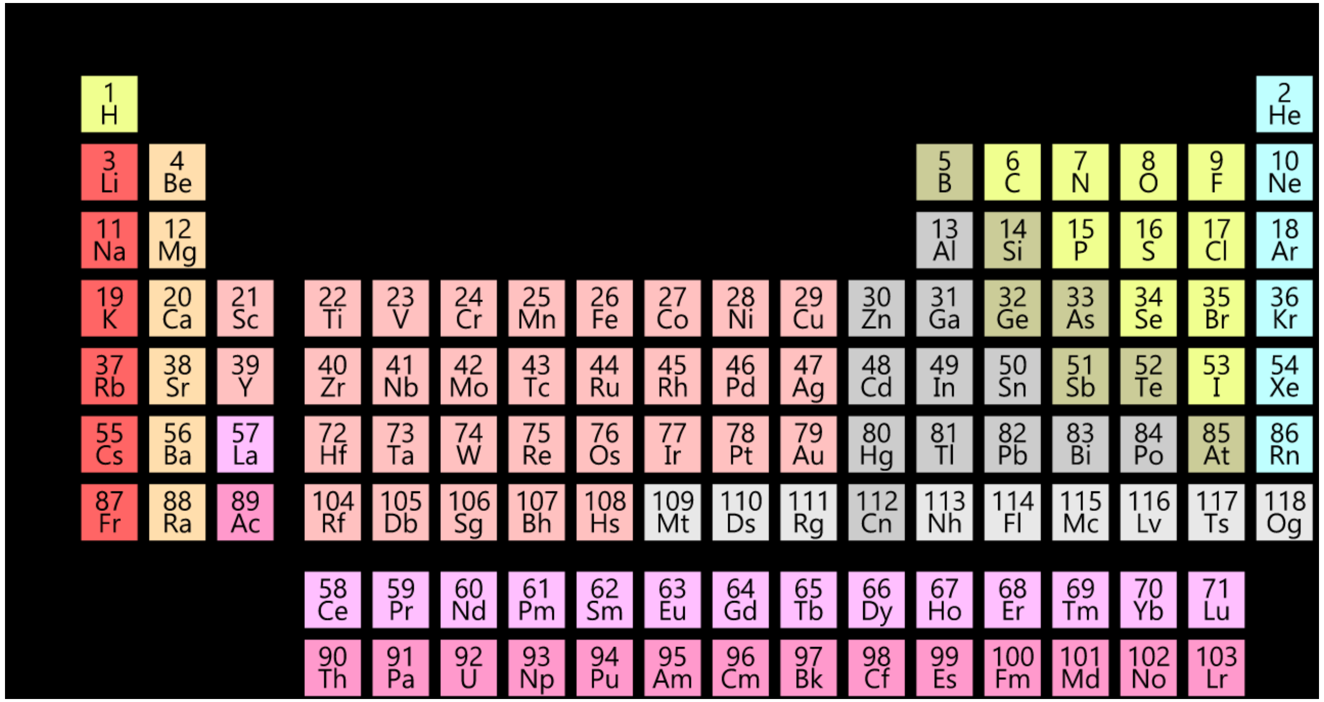
Ill. Niklas Elmehed. © Nobel Media.

Akira Yoshino

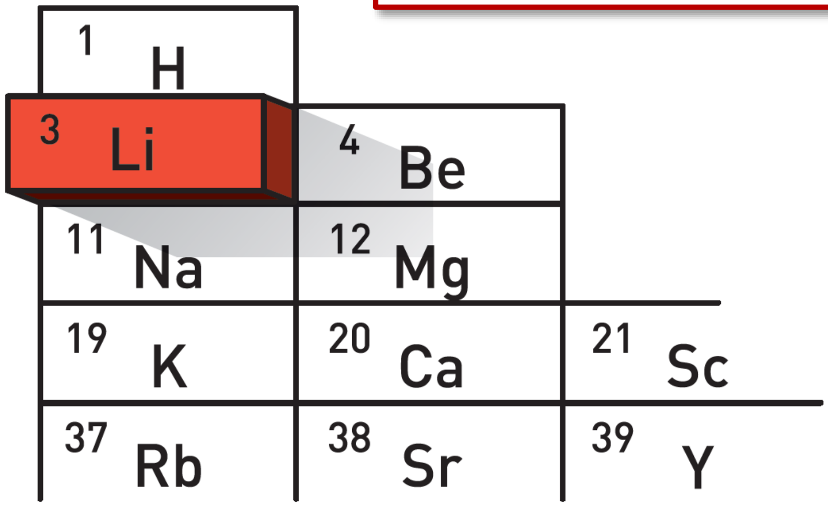
Prize share: 1/3

The Nobel Prize in Chemistry 2019 was awarded jointly to John B. Goodenough, M. Stanley Whittingham and Akira Yoshino "for the development of lithium-ion batteries."

Periodic Table and Lithium



Very reactive with oxygen, air and water!
→ Water and oxygen free system and solvent

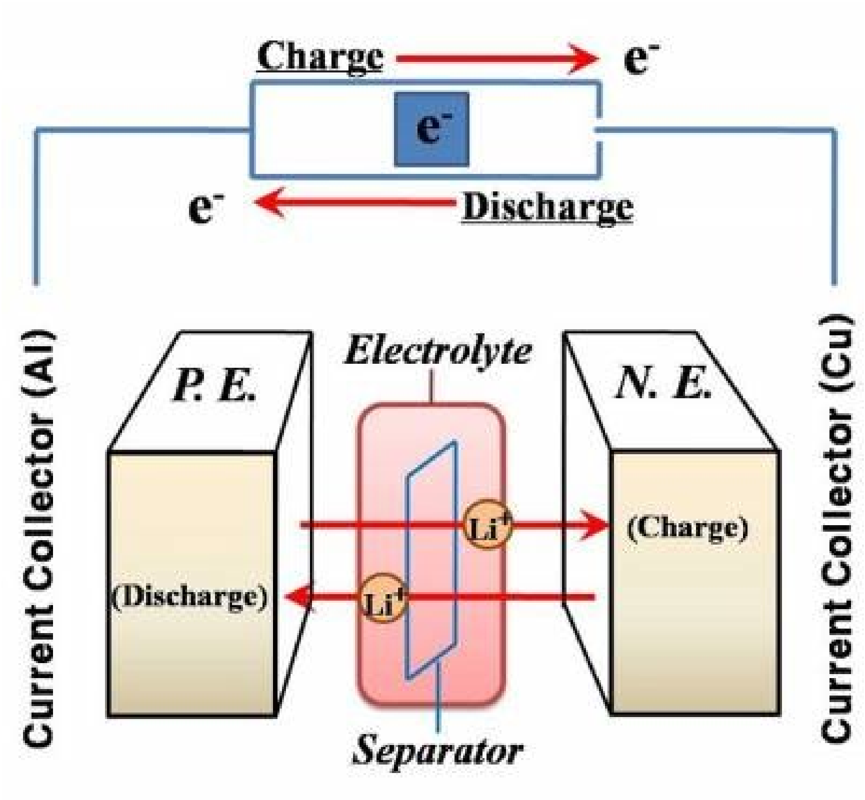


- Lightest metal with density 0.53 g/cm^3
- Low standard reduction potential Li^+/Li = -3.05 V vs SHE

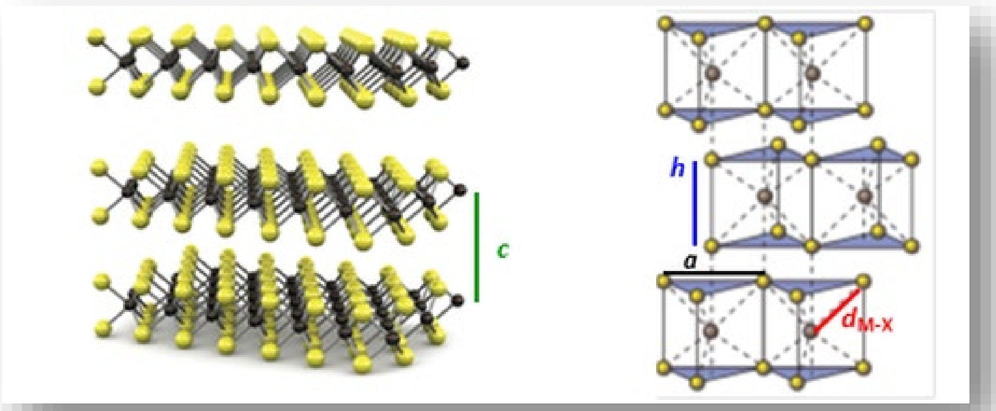
→ High density, high voltage battery

Li ion Battery

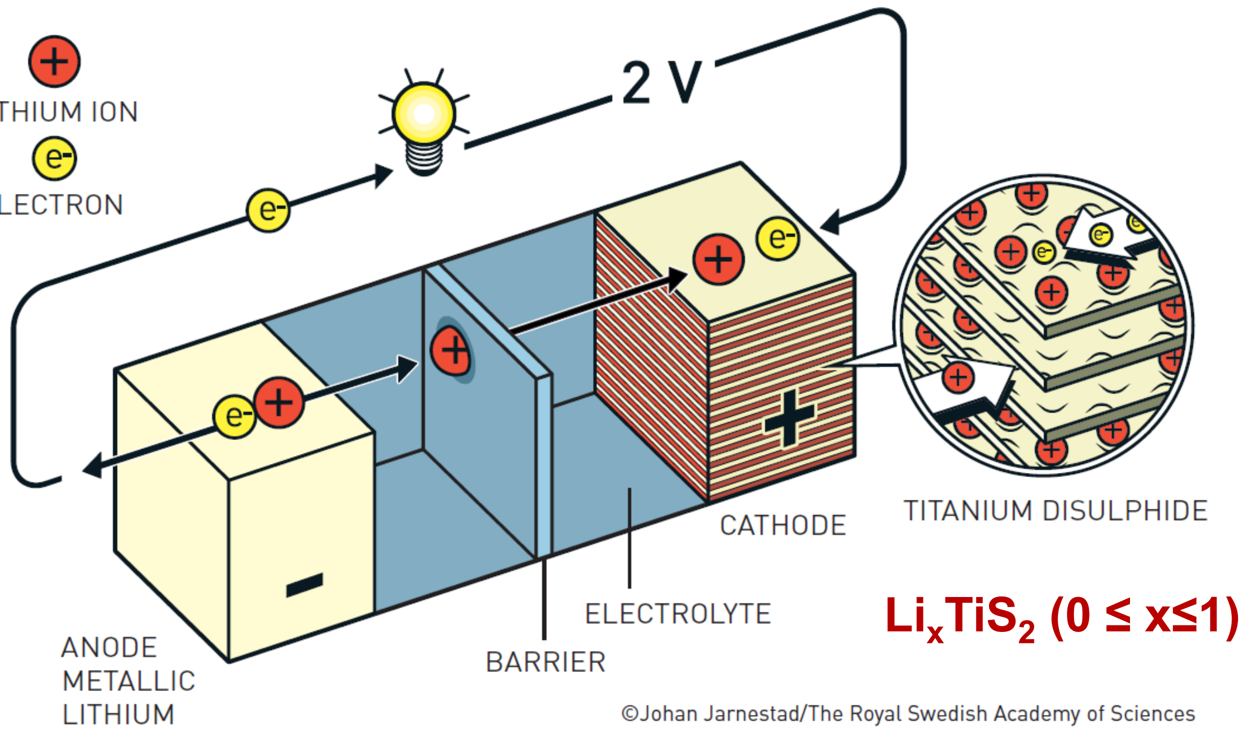
› Lithium anode → cathode should be able to incorporate Li^+ ions



(1) large, constant intercalation free energy change
(2) accommodate the guest ion with minimal structural
(3) high diffusivity of the alkali ion within the structure
(4) allow the intercalation reaction to proceed reversibly
(5) display good electronic conductivity
(6) be insoluble in the electrolyte, no co-intercalation of electrolyte components
(7) operate under close to ambient conditions.

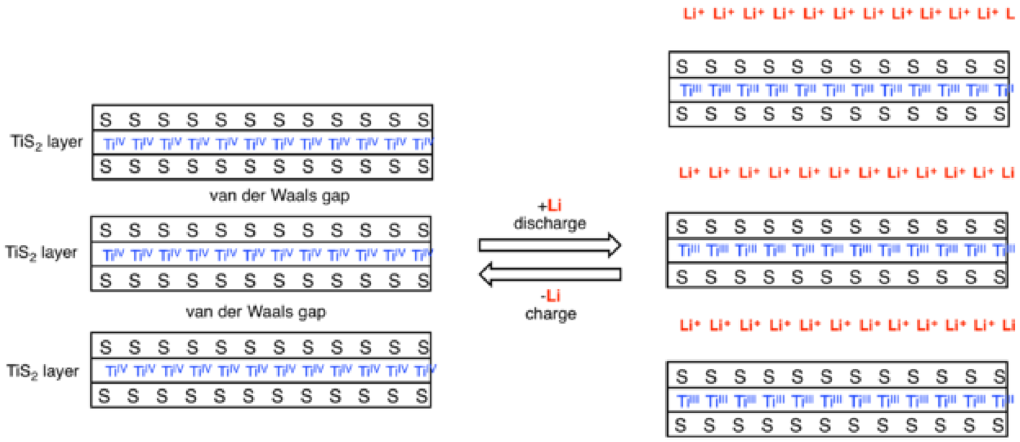


Whittingham (~1976)



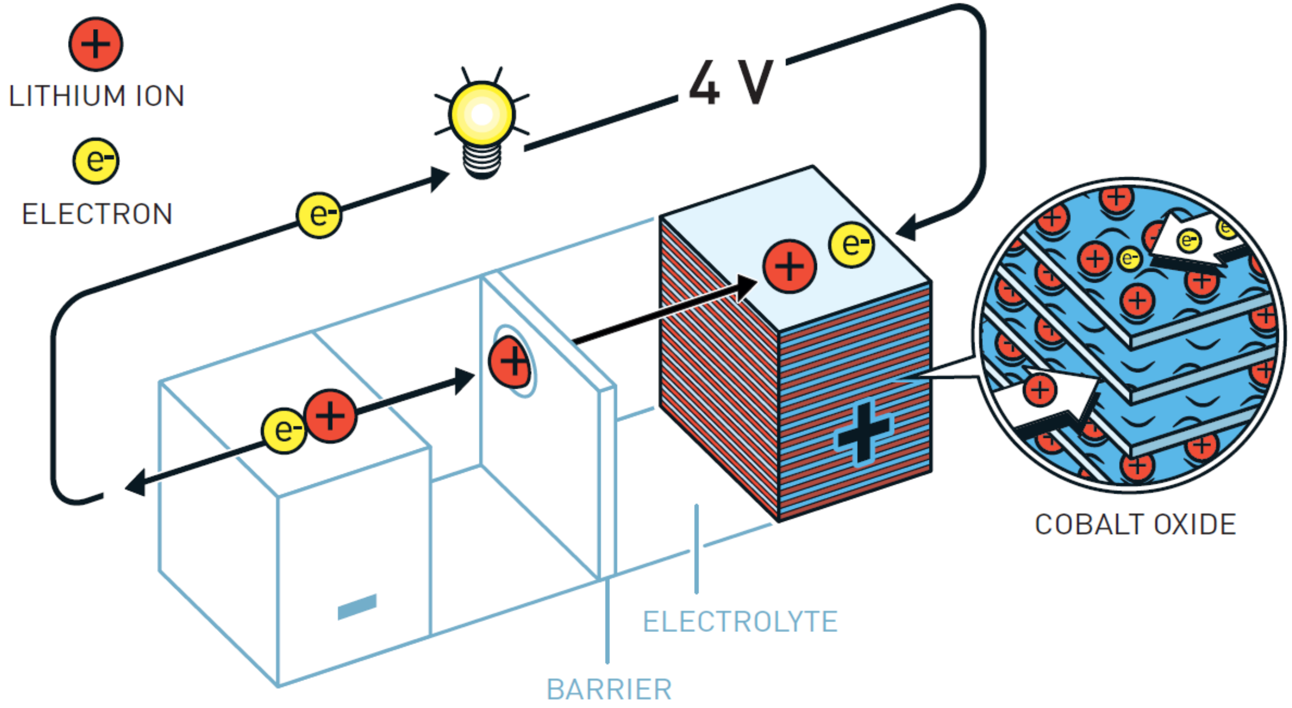
©Johan Jarnestad/The Royal Swedish Academy of Sciences

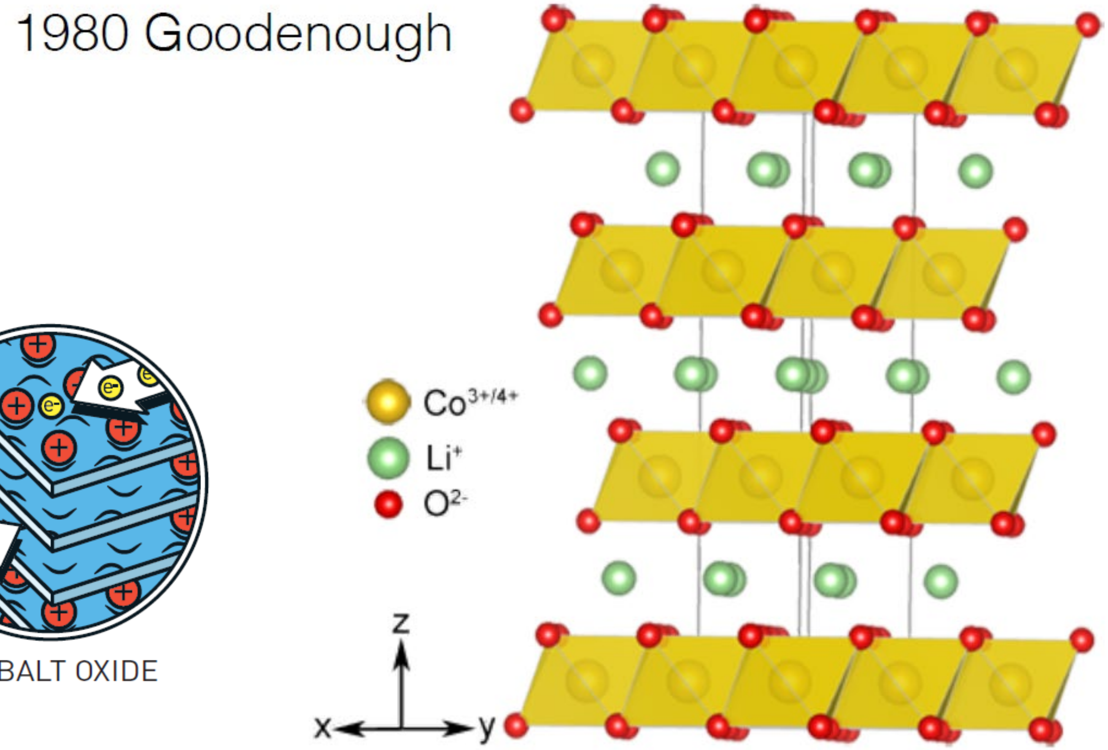
Li_xTiS_2 ($0 \leq x \leq 1$)



Whittingham, M. S. J. Chem. Soc., Chem. Commun. 1974, 328–329; Whittingham, M. S. Belgian patent no. 819672, 1975; Whittingham, M. S. Science 1976, 192 (4244), 1126–1127.

Goodenough (~1980)



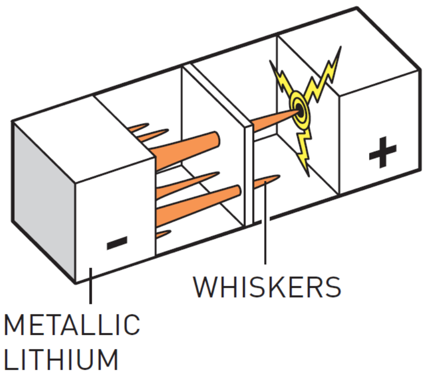


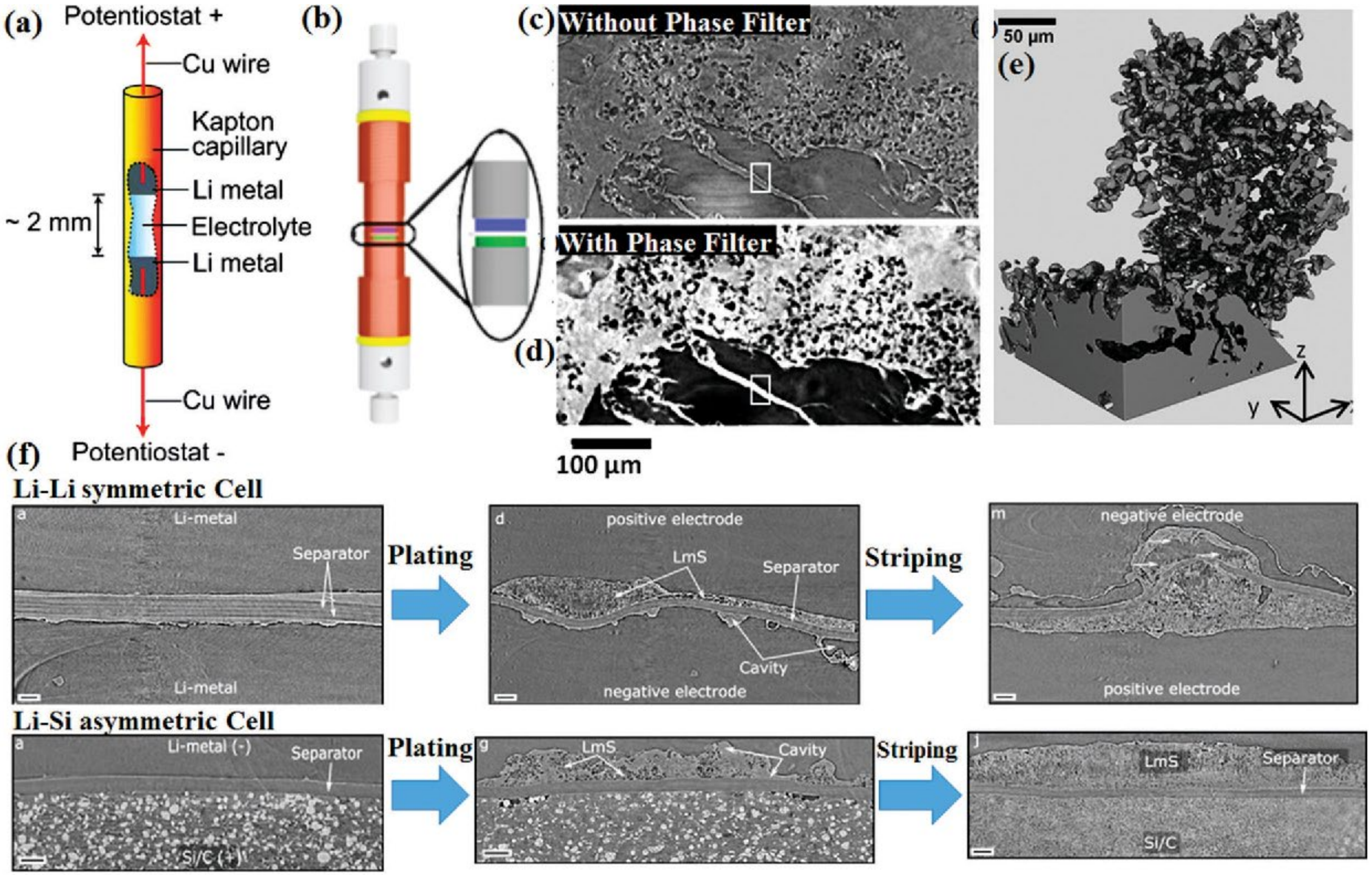
Oxygen small electronegative element: cation uptake large negative free energy change and high cell voltage: 4-5 V

Lithium Anode

- Whiskers and/or dendrites
→short-circuit

- ‘Dead’ lithium – no longer available for EC

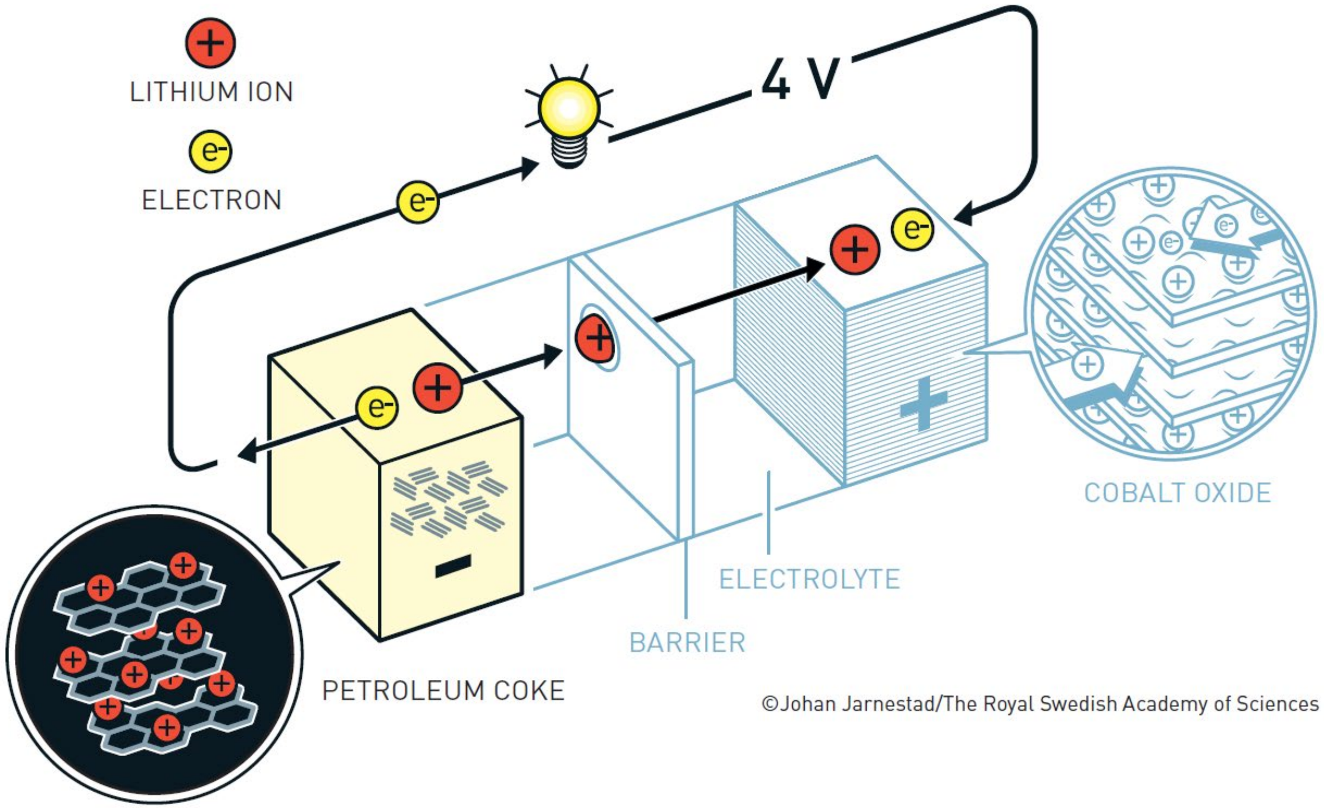


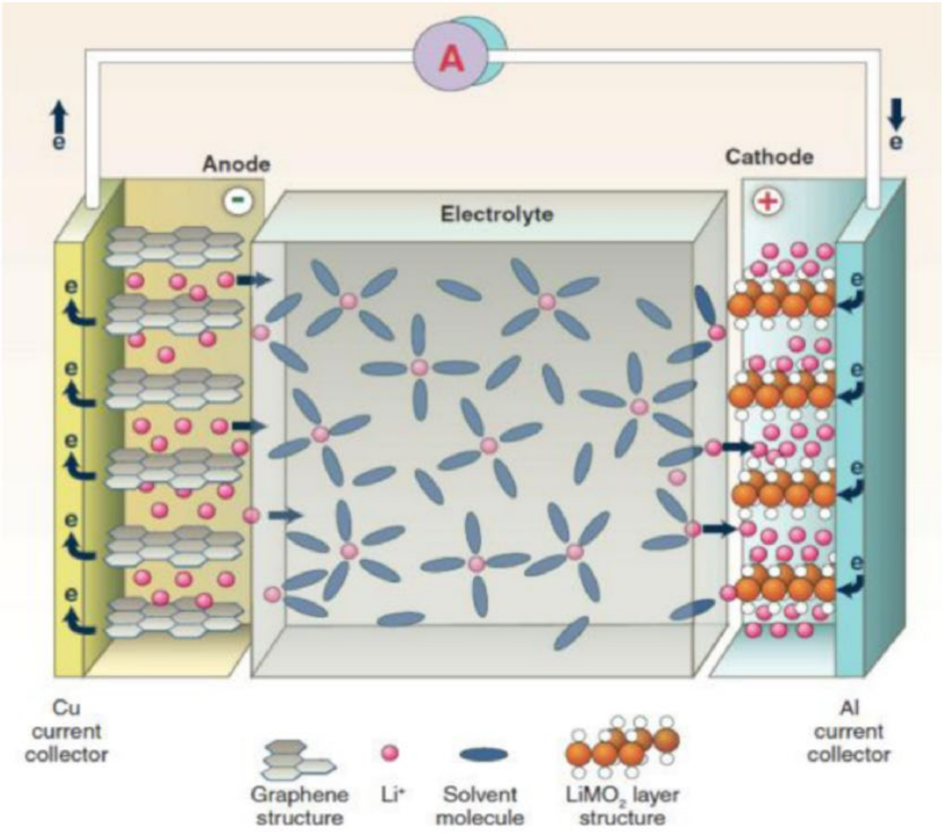


In situ X-ray tomography observation of lithium dendrites: (a) schematics of an *in situ* cell (Eastwood *et al*).[200] Reproduced from ref. 20

Chemical Society reviews 2018, DOI:10.1039/c7cs00180k

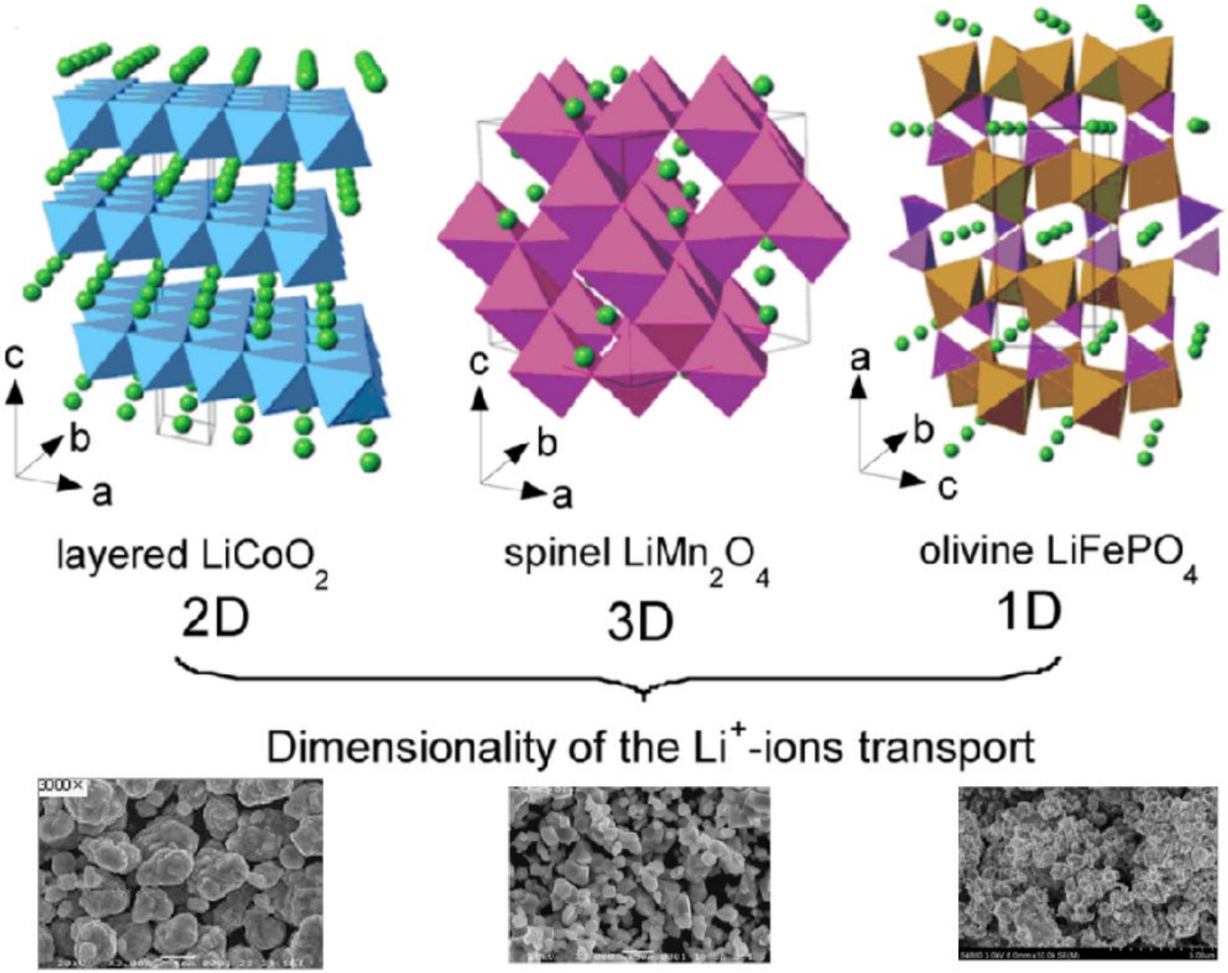
Yoshino (~1985)





Anode material: Intercalation Li not easy, (carboneceous) material not stable → Petroleum coke stable; mixture of crystalline and non-crystalline coke
4.2 V; 400 Wh/l

Cathode Development

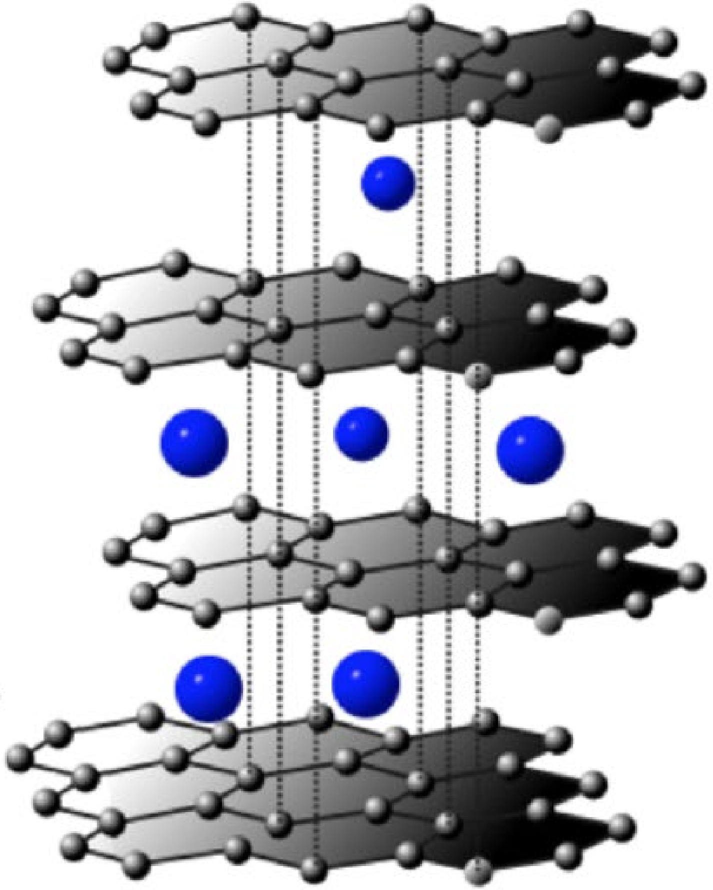


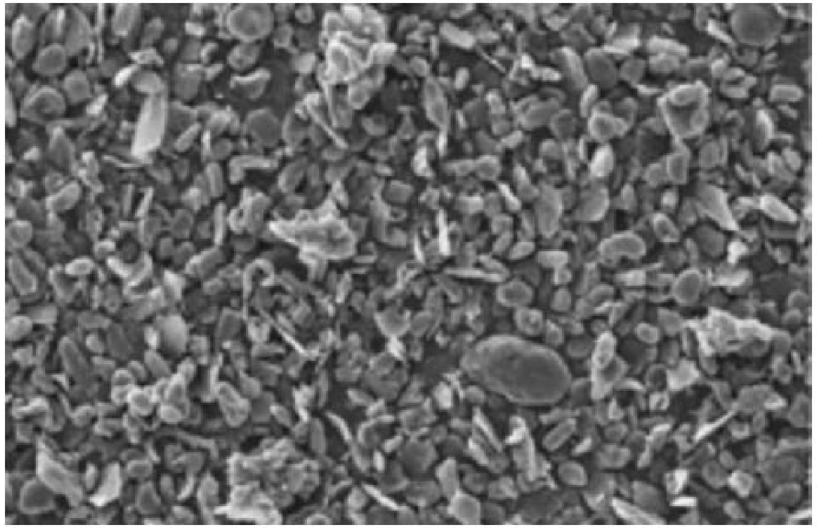
Oxide of choice:

NMC – Ni, Mn, Co oxide

Padhi, A. K.; Nanjundaswami, K. S.; Goodenough, J. B. J. Electrochem. Soc. 1997, 144, 1188–119; Thackeray, M. M.; David, W. I. F.; Bruce, P. G.; Goodenough, J. B. Mater. Res. Bull. 1983, 18, 461–472.

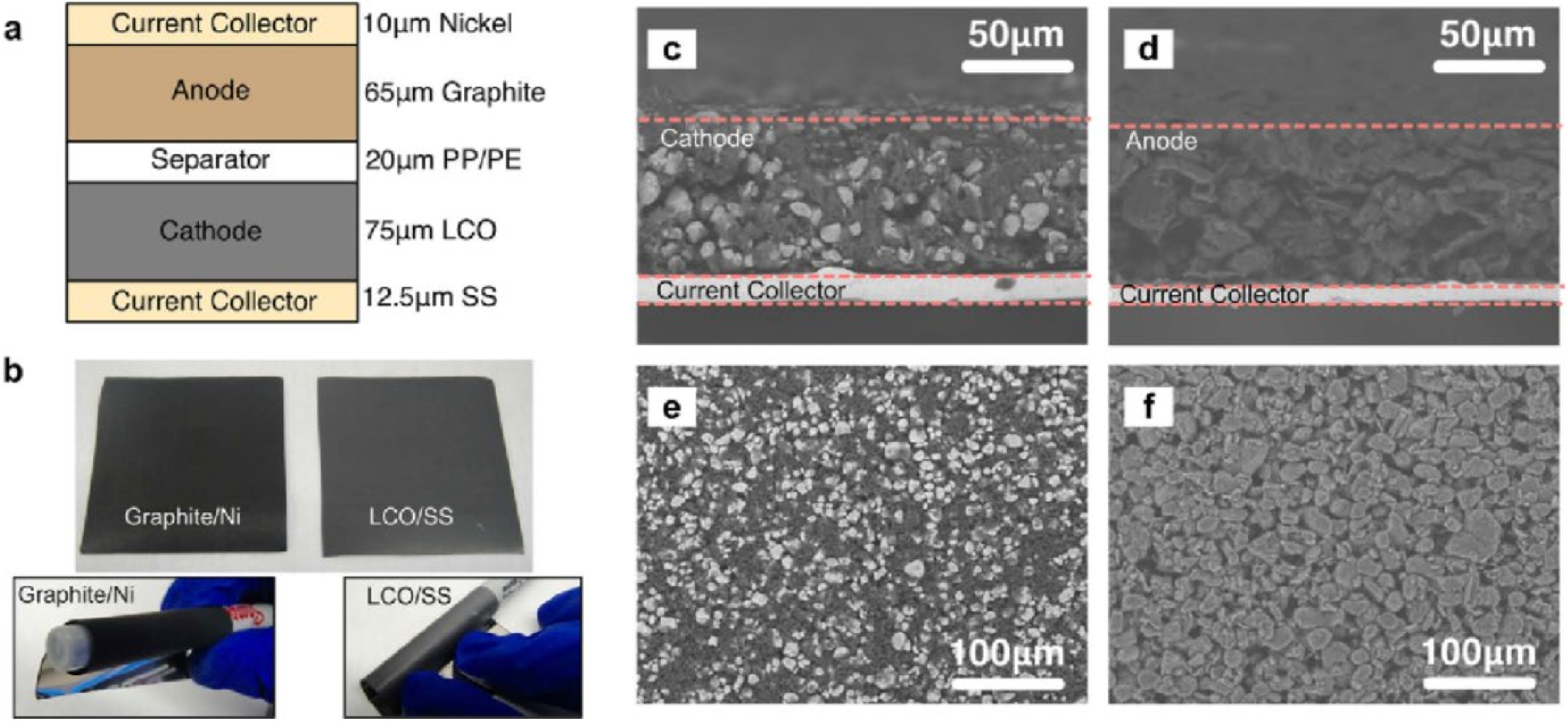
Anode



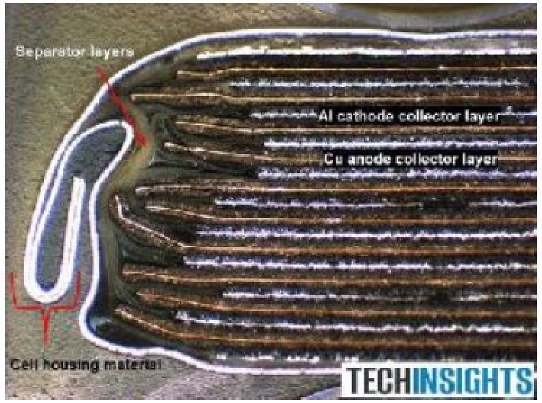


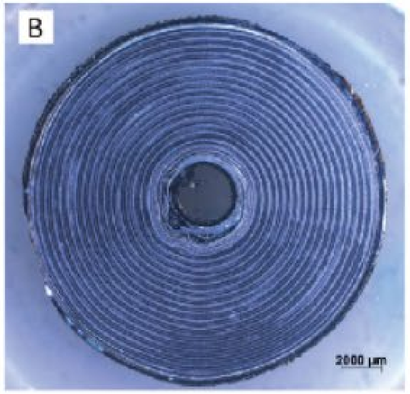
per 1gm Graphite (LiC_6)
$= 26.8/(12*6)$ Ah/g
$=0.370$Ah/g

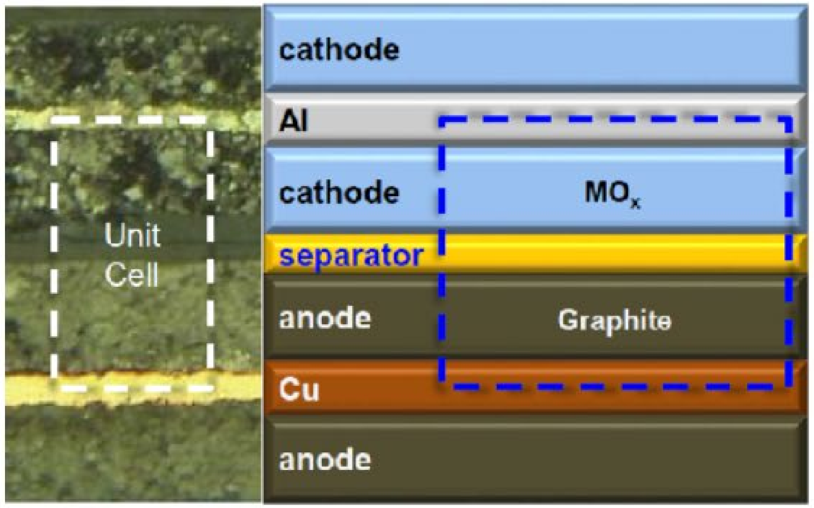
LCO / Graphite Battery



Battery Build-up







Metal Foil - Current Collector

Cathode

Separator

Anode

Metal Foil - Current Collector

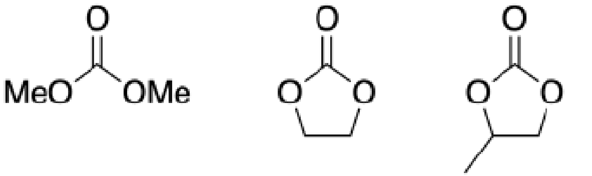
WHAT IS NEXT?

Safety

- Li dendrites/Whiskers
- Electrolyte stability

https://www.youtube.com/watch?v=SMy2_qNO2Y0
start and after 1.50 minutes

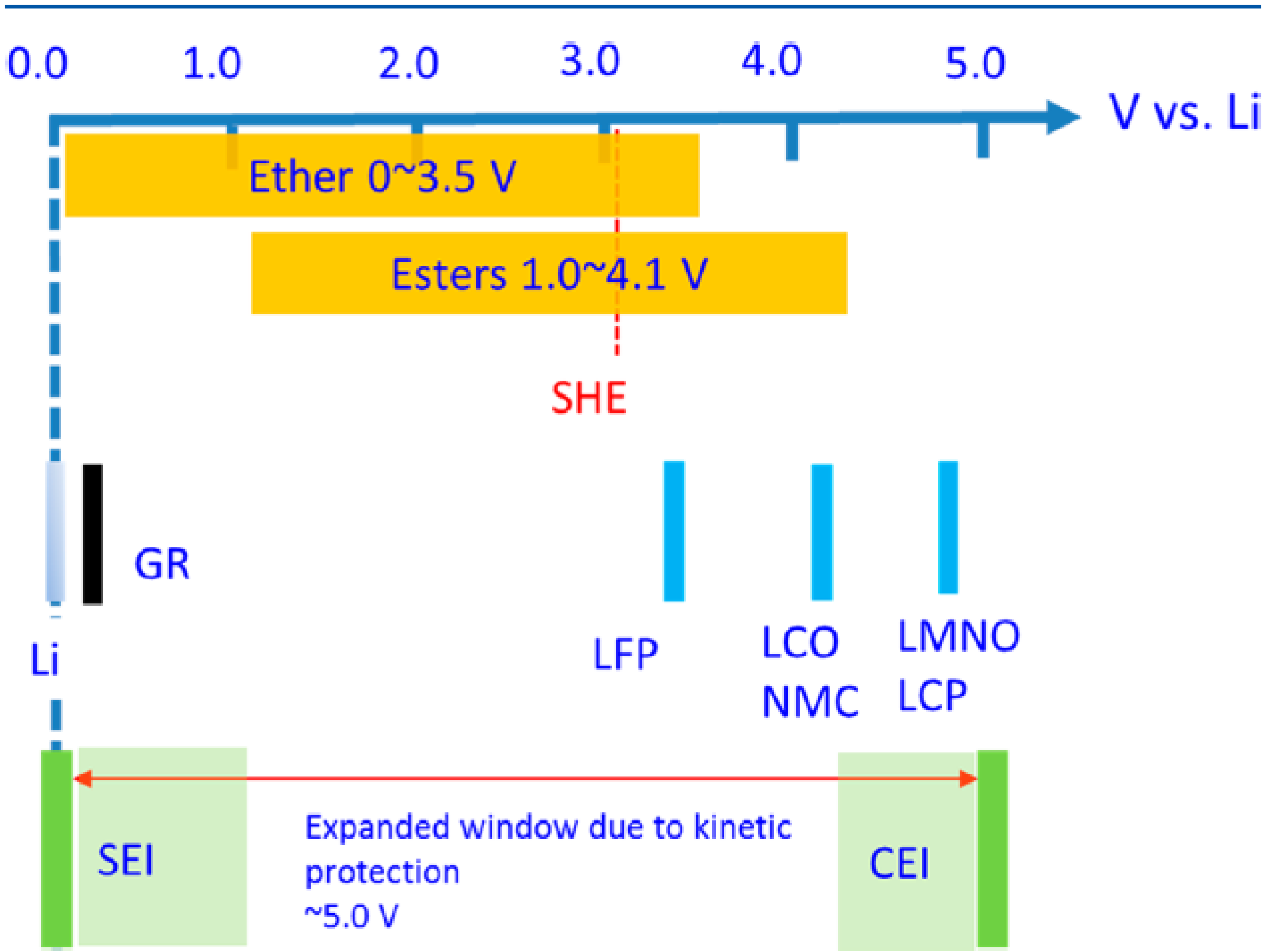
Electrolytes



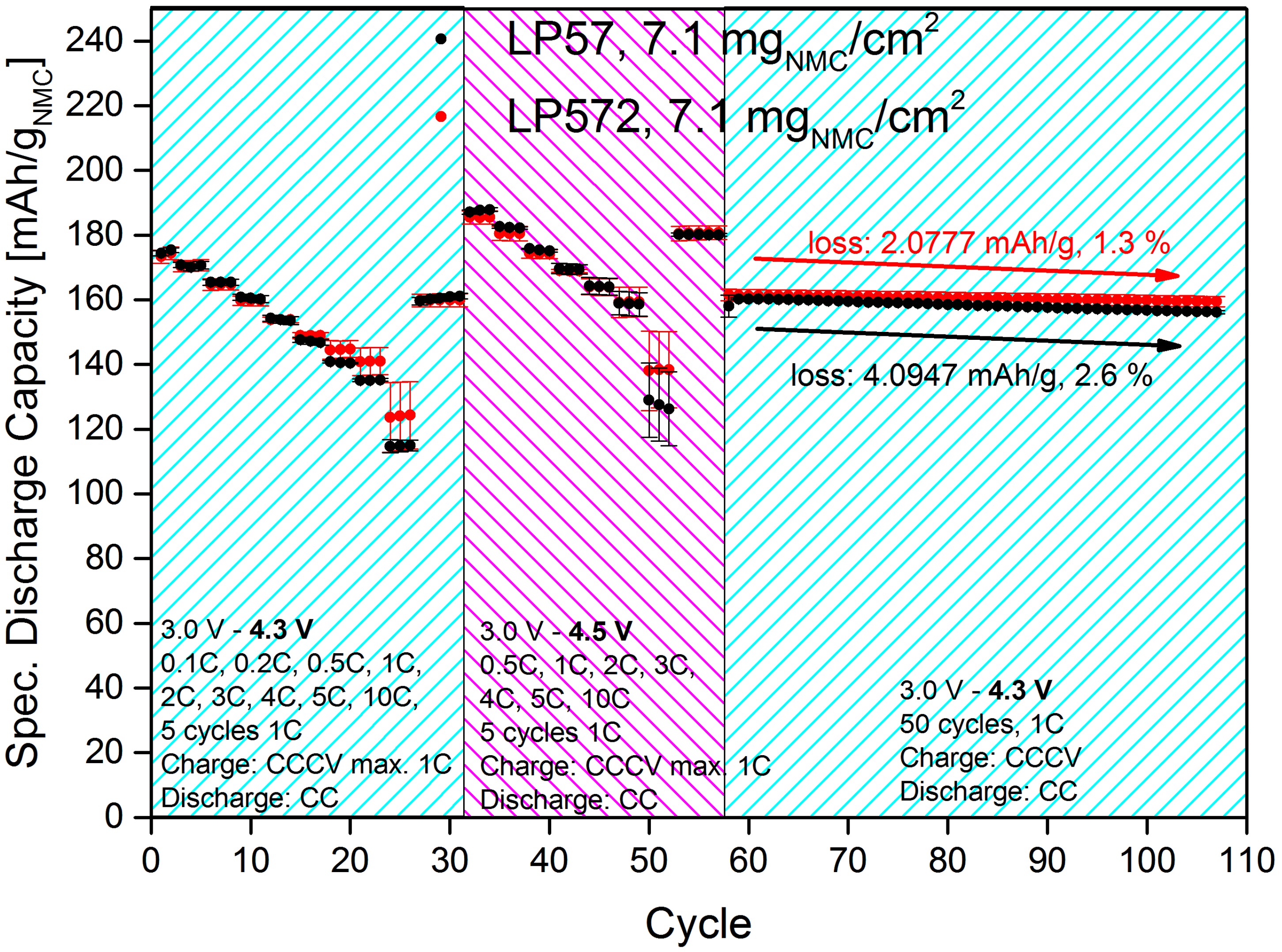
dimethyl carbonate

ethylene carbonate

propylene carbonate



Stability Li Ion Batteries



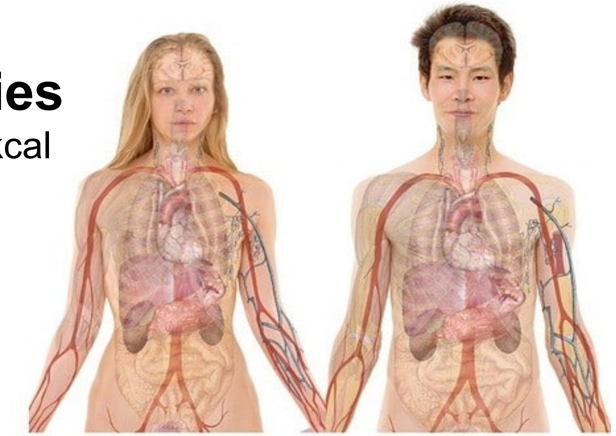
Dissolution metal ions?

BMW
Varta
VW

Penlite (AA)
Energy = 5Wh = 18 kJ

4 batteries
21 Wh = 76 kJ

55 batteries
2000 – 2500 kcal
1000 kJ



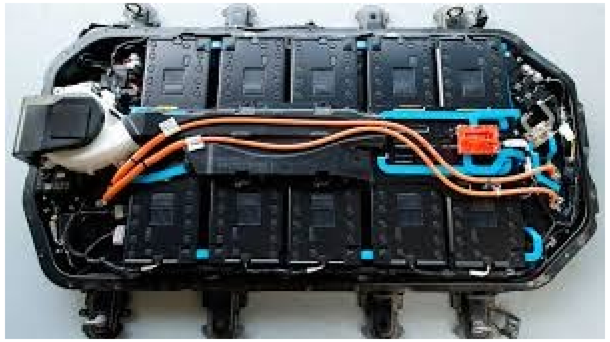
100 km
3200 AA batteries
16 kWh = 57600 kJ
1 l / 56 km!

Huishouden (4 personen)
8 miljoen batteries per day
55 biljoen (10^{12}) Joules per year

60 biljoen (10^{12}) batteries
1075 peta (10^{15}) Joules per year

Volumetric and Gravimetric Capacity

- Store large amounts of energy
- Weight or volume important?



5Wh = 18 kJ

20 kWh = 72*10^6 J

100 kWh = 360*10^6 J

Capacity – Electric Cars

› Projected mectrics for current Lithium Ion Battery and BEV Technology:

- 200 $Wh/kg_{battery}$ [1]
- 95% discharge efficiency
- 80% state-of-charge range
- 250 $€/kWh_{battery}$ (2030 estimate)[2]
- 100 Wh/km (4-passenger car)

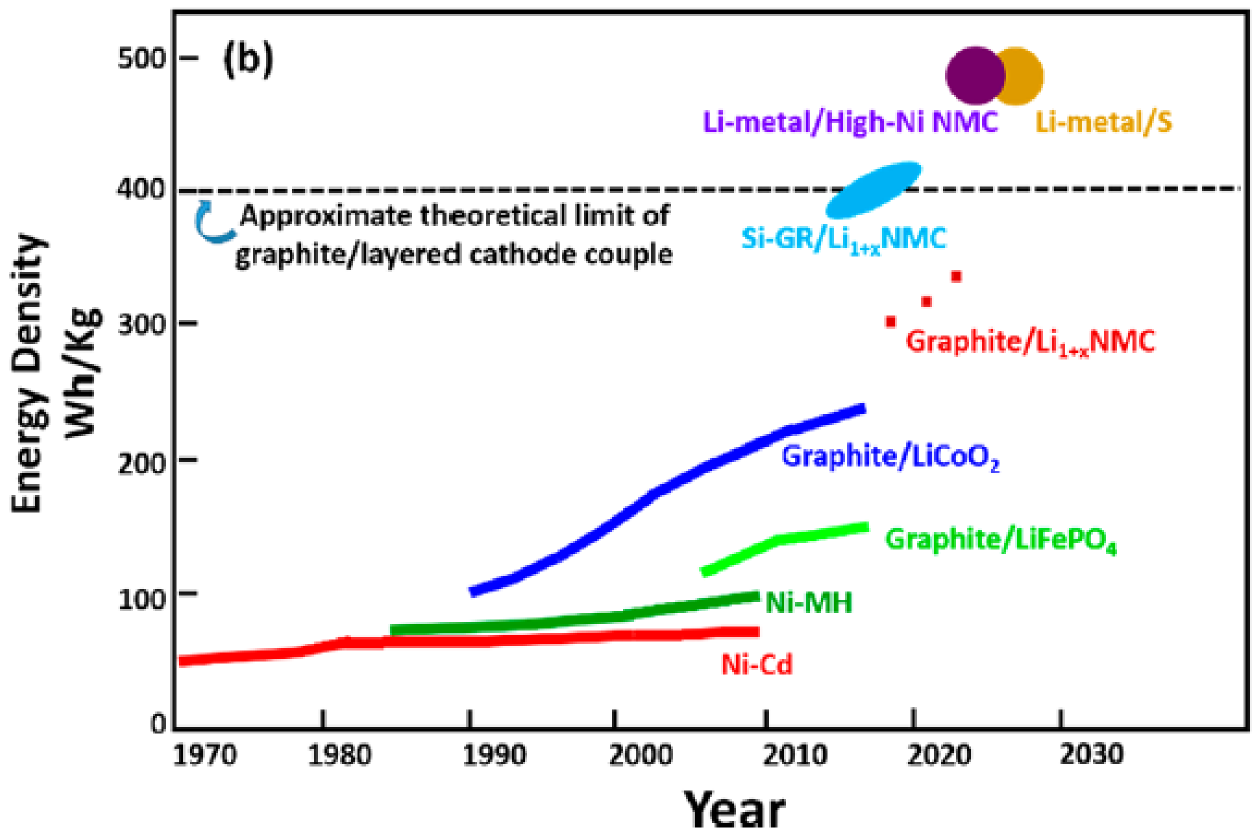
	150 km range	**500 km range**
Required energy	20 $kWh_{battery}$	66$kWh_{battery}$
Battery weight	100 kg	330 kg
Battery cost	5000 €	16500 €

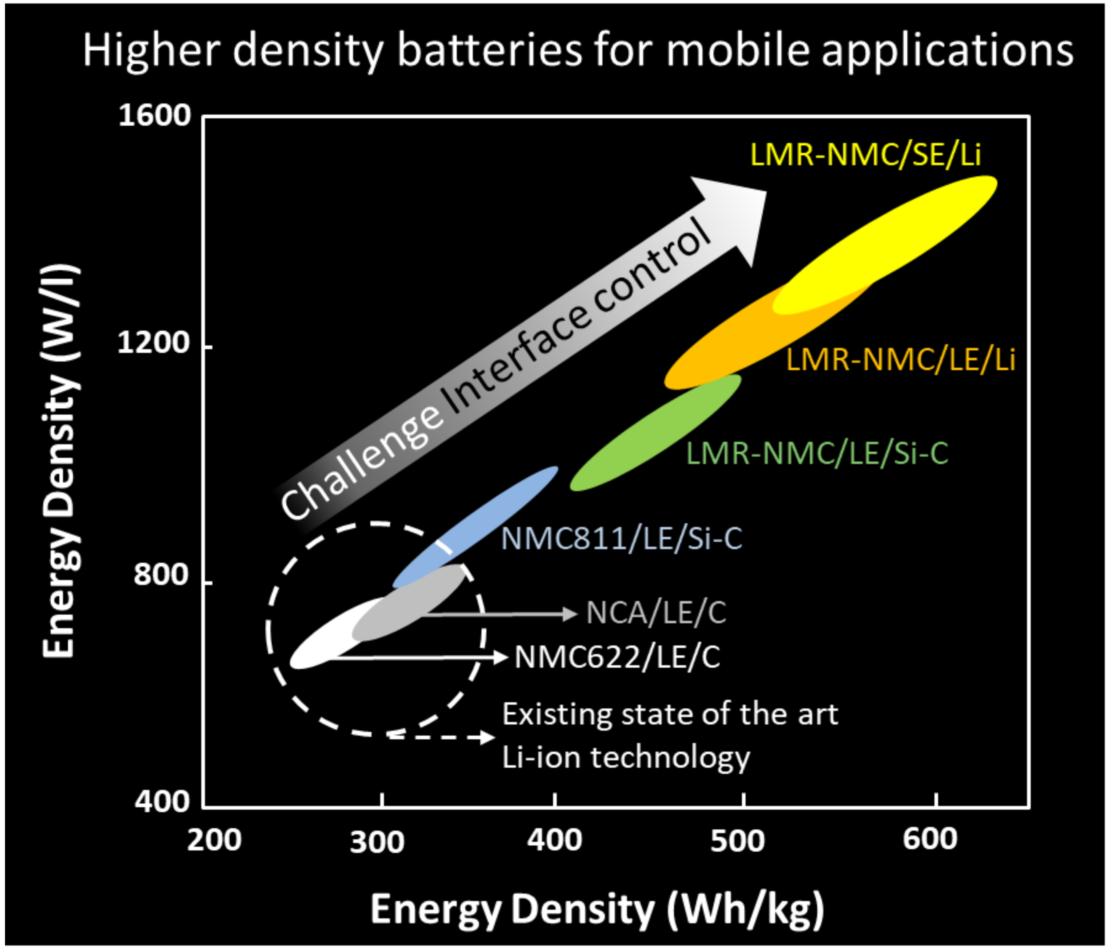
↳ **Current technology only feasible for short-range BEVs**
→ *Range anxiety may limit market-penetration*

➢ **Additional issues like safety, deactivation, etc.**
➢ ***Similar problems stationary storage***

1. F. T. Wagner, B. Laksmanan, M. F. Mathias; J. Phys. Chem. Lett. (2010) 1, 2204
2. Transition to Alternative Transportation Technologies – PHEV, National Research Council (2010)

Capacity Compared

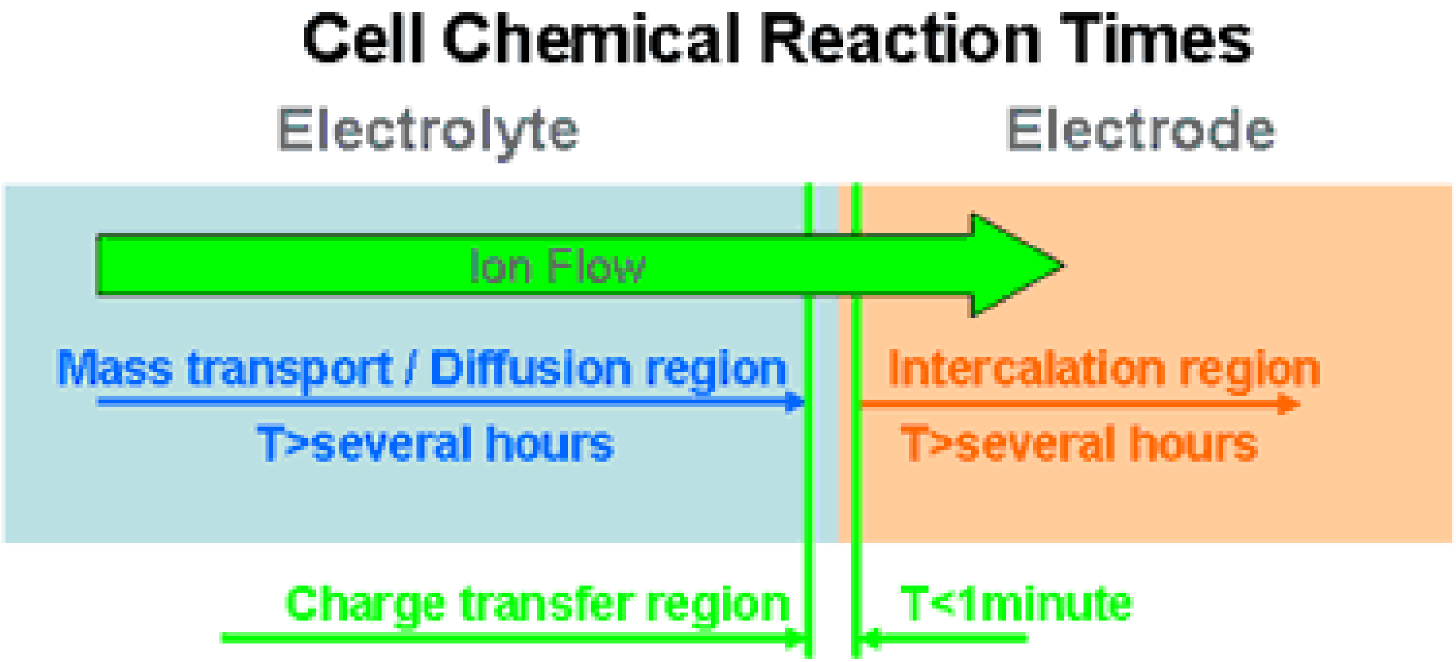




Liquid → solid electrolytes

Lithium ions → Lithium metal

Battery Processes



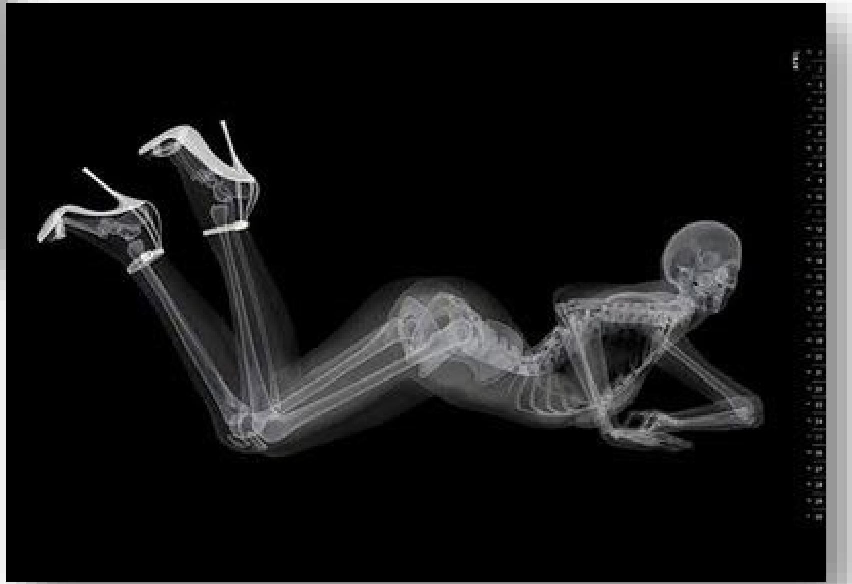
Charge transfer / chemical conversion at the electrode surface (Short time constant)

Mass transfer / diffusion of ions in the electrolyte bulk
(Long time constant. Continues until all materials have been transformed or transferred)

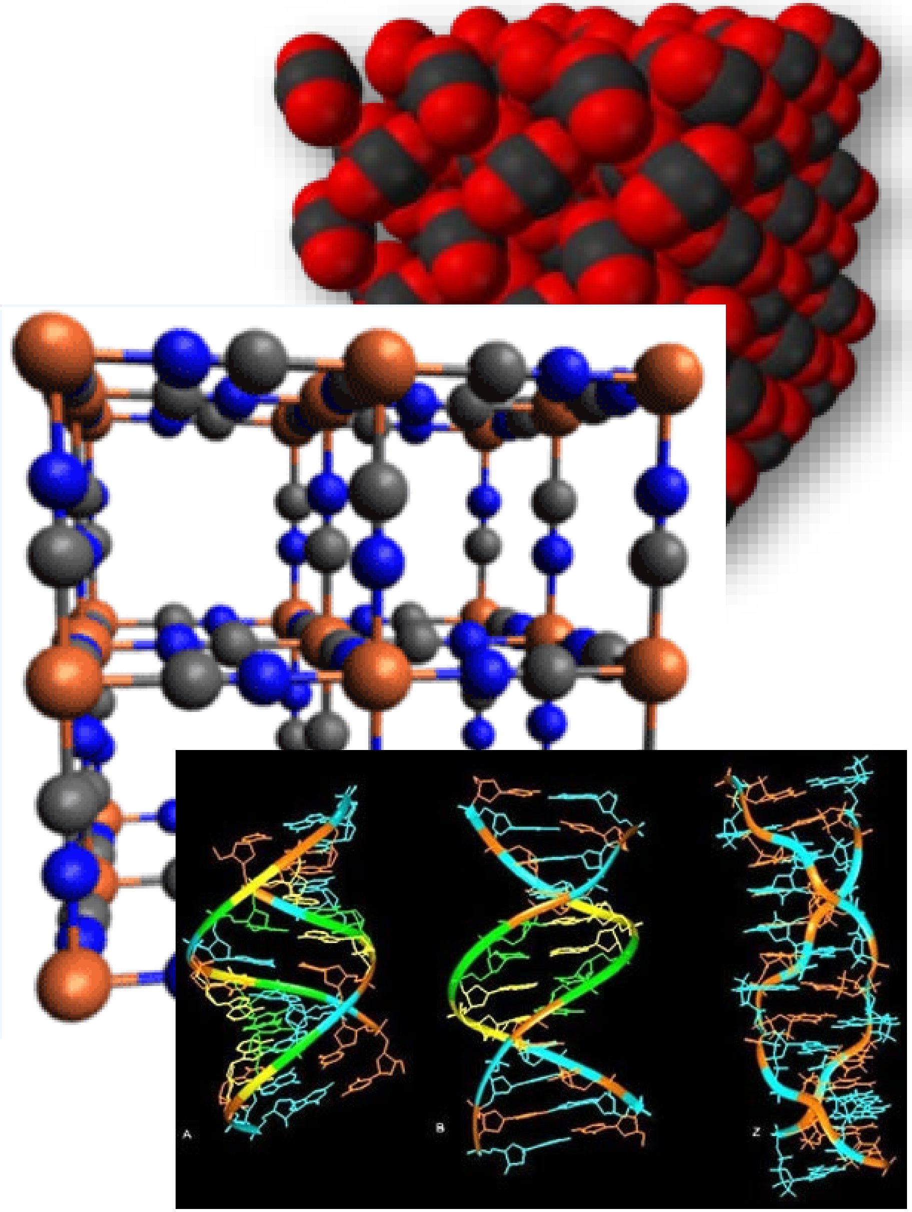
Intercalation of ions in the electrode bulk (Long time constant)

1896

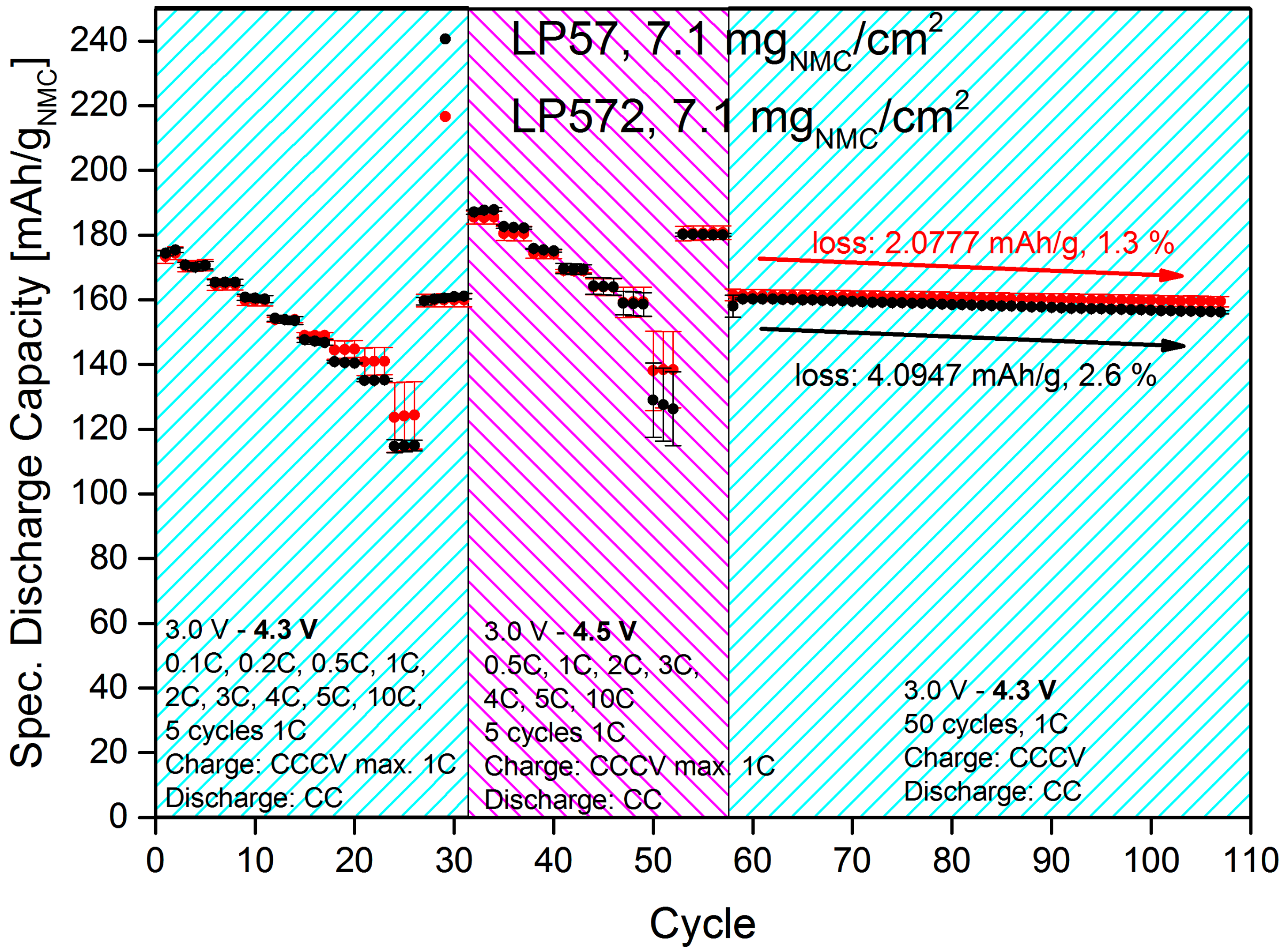
Rontgen Nobel Prize 1901



Museum Boerhave, 2015



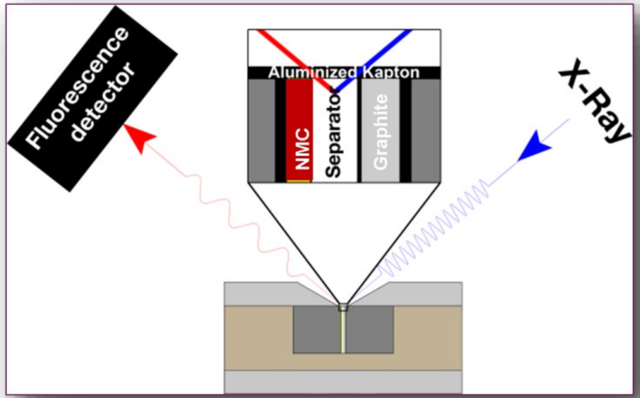
Stability Li Ion Batteries

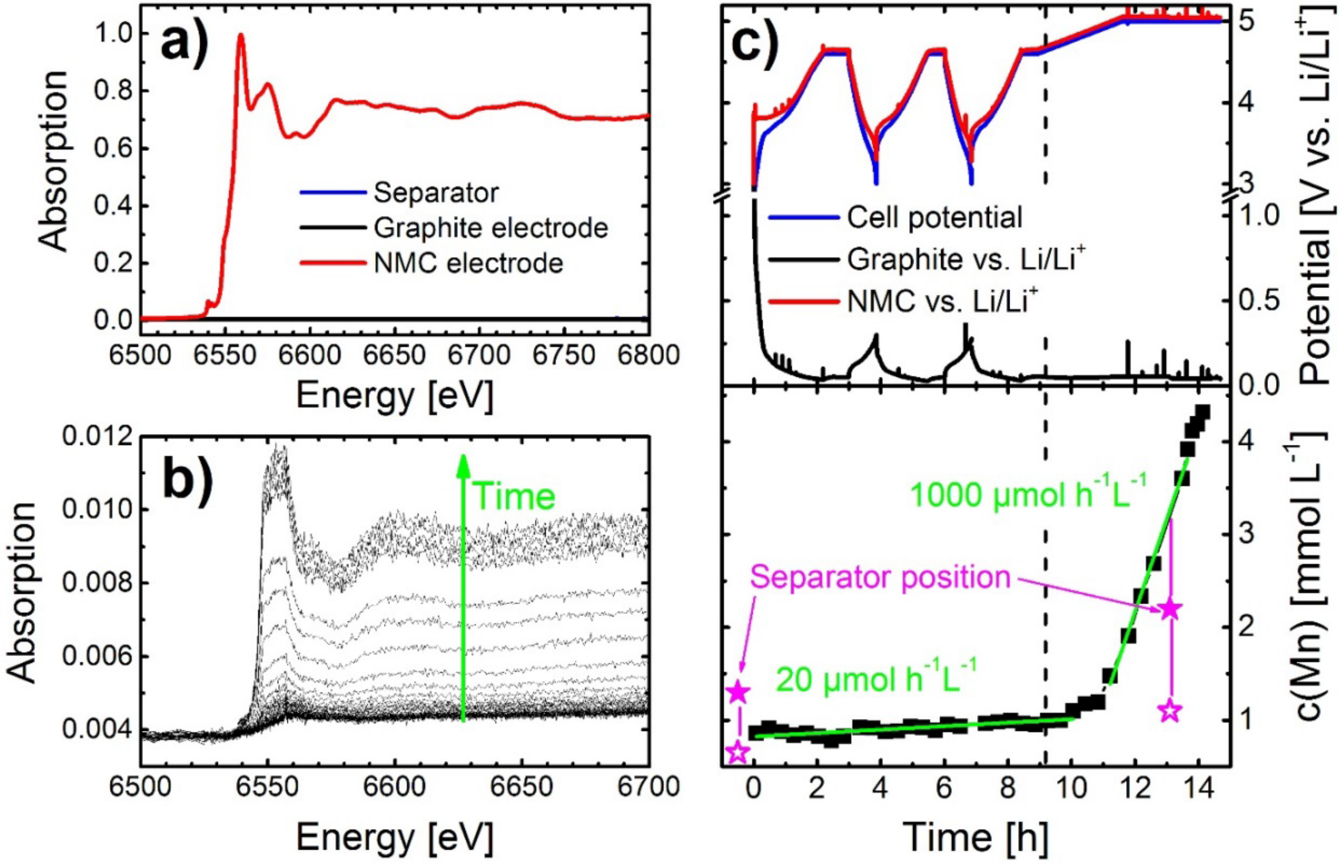


Dissolution metal ions?

BMW
Varta
VW

Li-ion Deactivation: Metal Dissolution





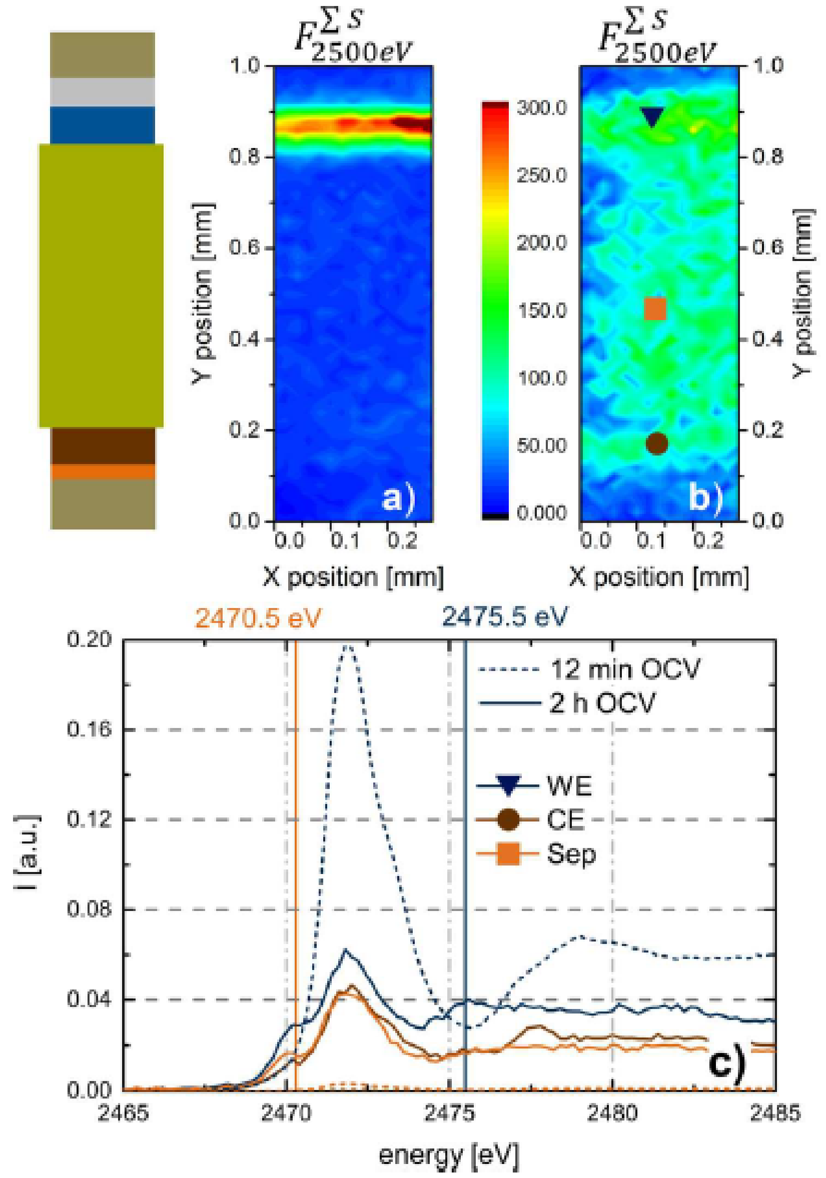
- Dissolution of TM (and accumulation on graphite anode) → no longer available for EC
- Compare ‚dead‘ Li

J. Mater. Chem. A **2016**,4, 18300.

Challenges: Self-Discharge

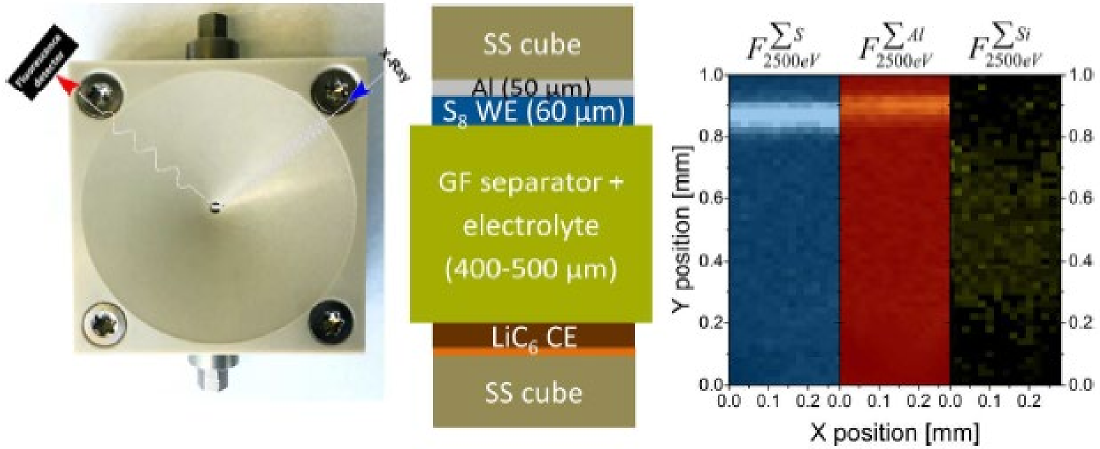
LiS battery

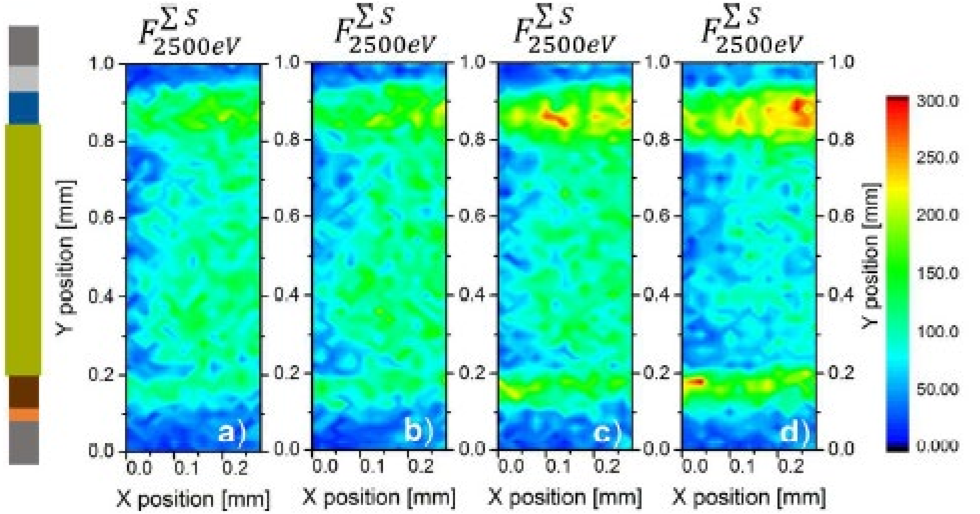
- Dissolution S_8
- Migration of sulfur through cell
- Formation of polysulfides S_x^{2-}

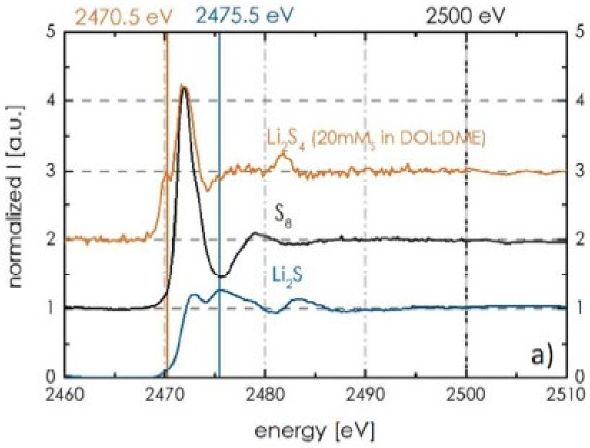


JES **2018** 165(7) A1288; *J. Phys. Chem. C* **2018**. 122 (10), 5303

LiS Battery: Discharge

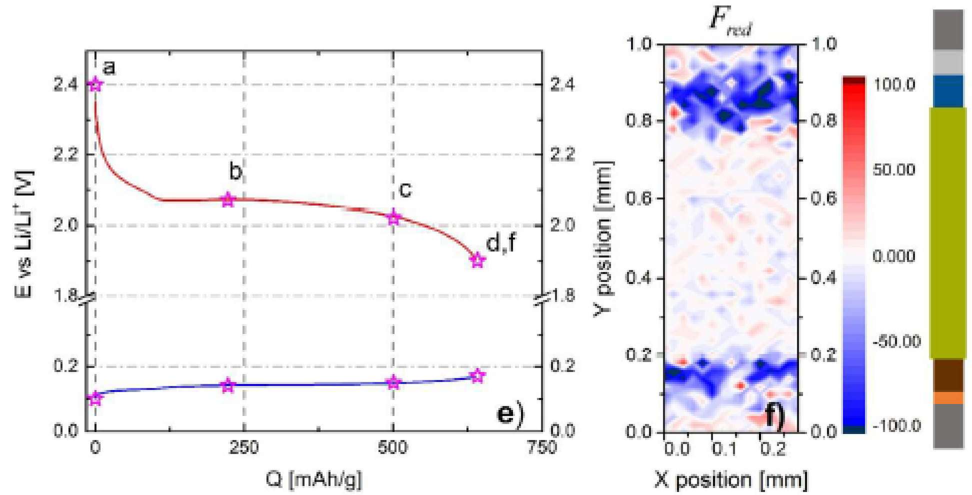






$$F_{red} = F^{\sum S}_{2500\ eV} - F^{Li_2S}_{2475.5\ eV}$$

- $F_{red} << 0$: Li_2S (blue)
- $F_{red} >> 0$: S_8 (red)
- $F_{red} \sim 0$: S_x^{2-} (white)



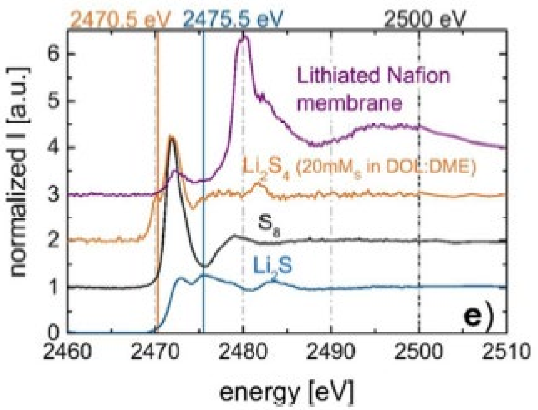
Formation inaccessible Li_2S at counterelectrode

JES **2018** 165(7) A1288; *J. Phys. Chem. C* **2018**. 122 (10), 5303

university of groningen

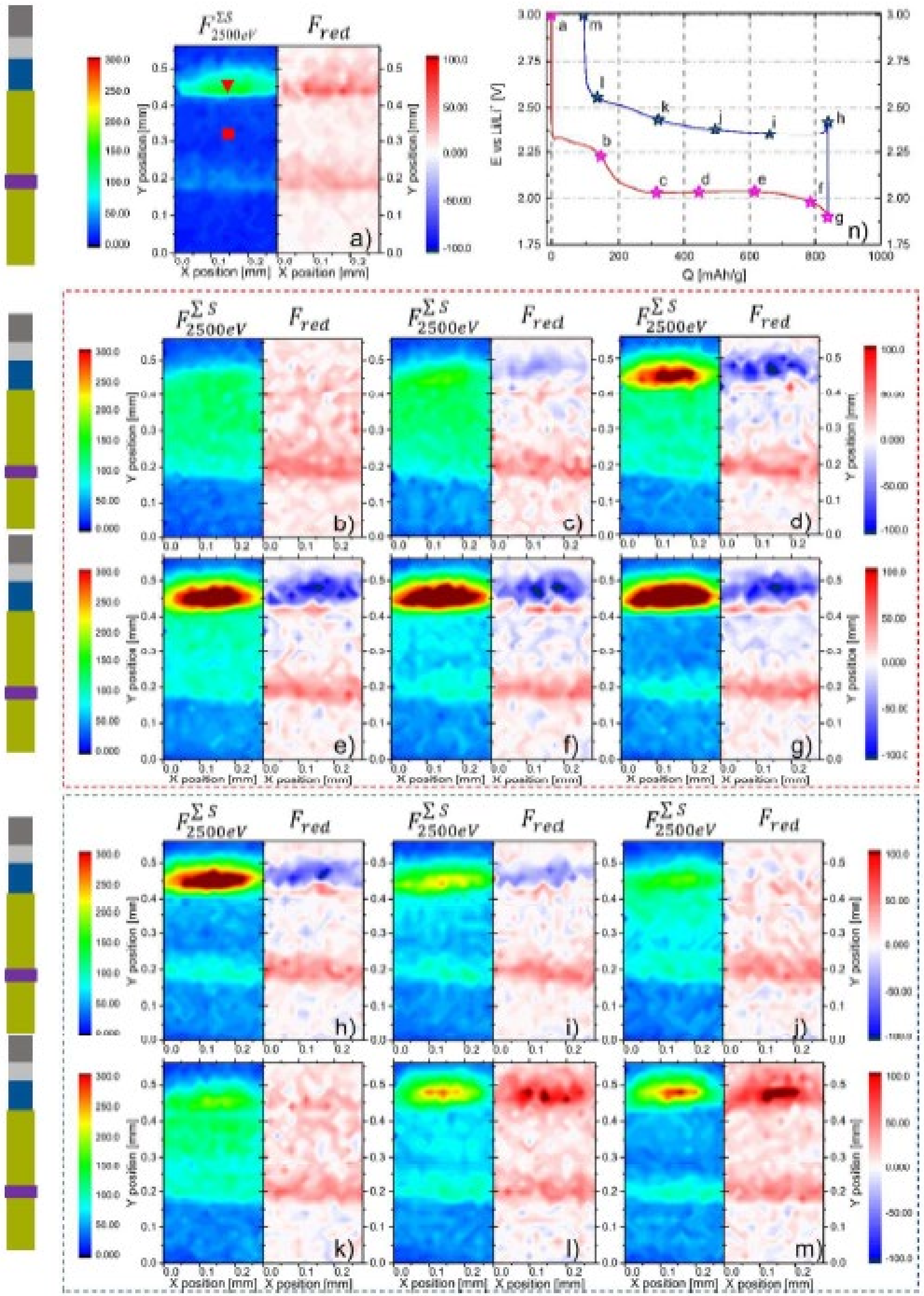
LiS Cycling

- *Lithiated nafion membrane*



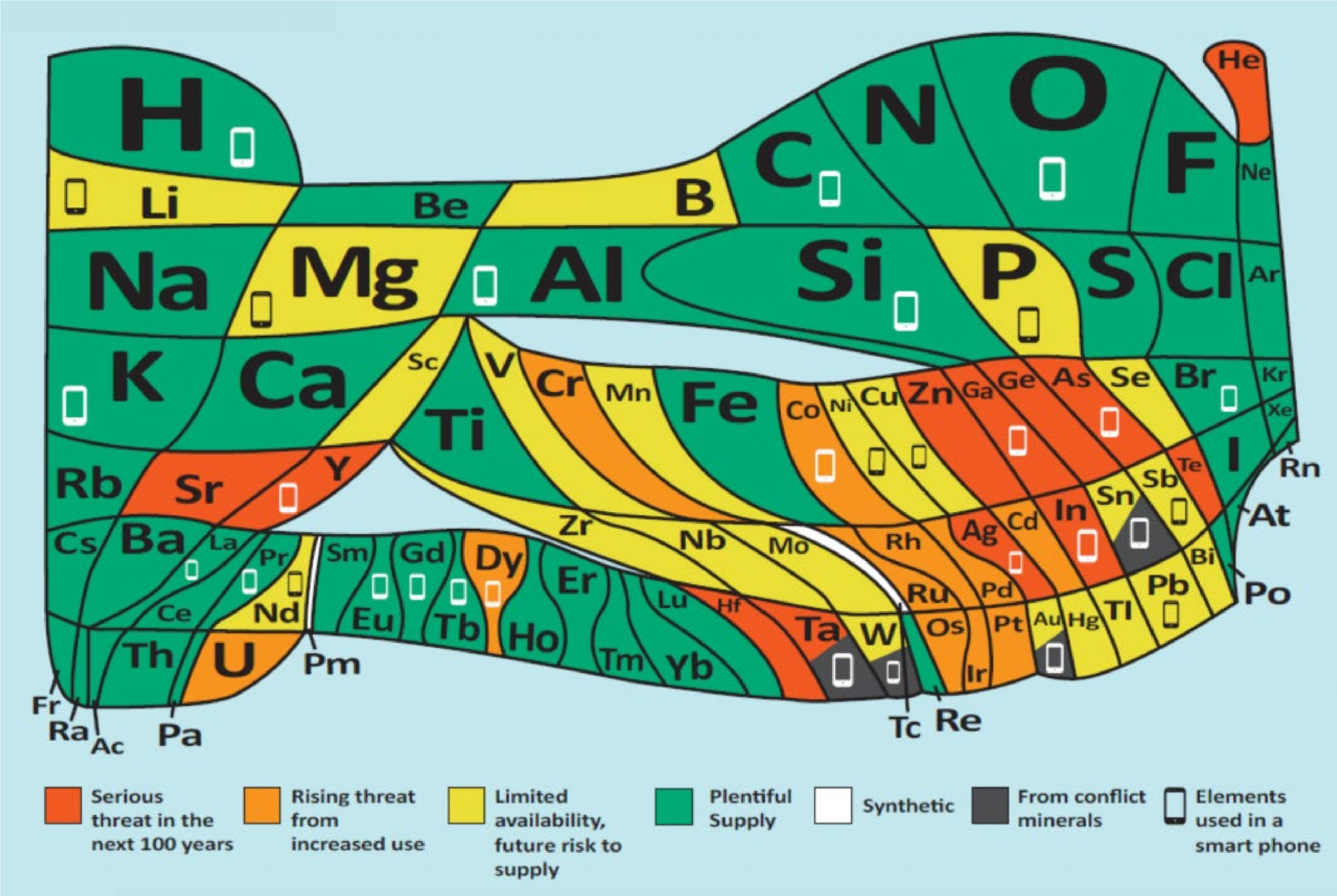
$$F_{red} = F_{2500\ eV}^{\Sigma S} - F_{2475.5\ eV}^{Li_2S}$$

› F_{red}<<0: Li_2S (blue)
› F_{red}>>0: S_8 (red)
› F_{red}~0: S_x^{2-} (white)



JES **2018** 165(7) A1288; *J. Phys. Chem. C* **2018**. 122 (10), 5303

Rare Element Availability



Lithium, Cobalt and graphite

Lithium availability? Lithium extraction from brine and minerals

Cobalt is mined in the Democratic Republic of Congo (slave and child labor) and political situation is unstable

OTHER BATTERY CHEMISTRIES?

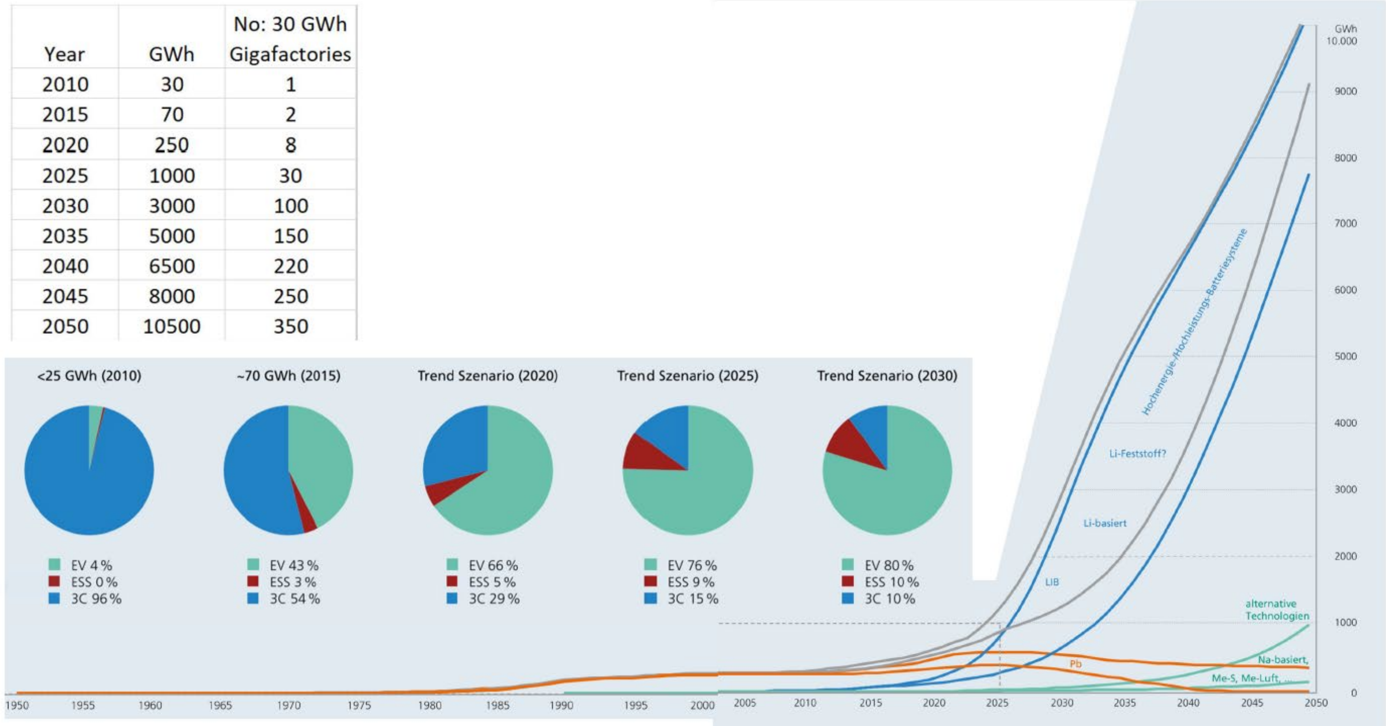
university of groningen

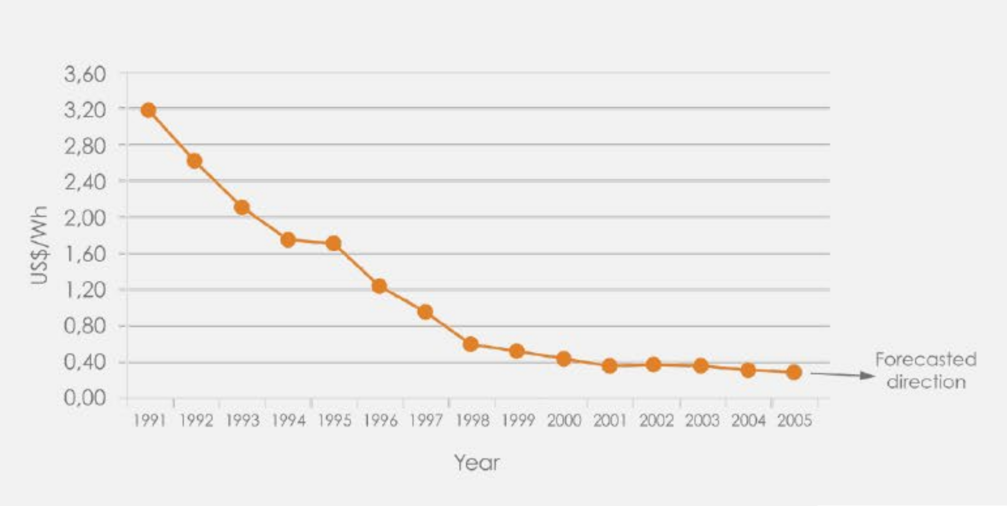
Recycling E-waste

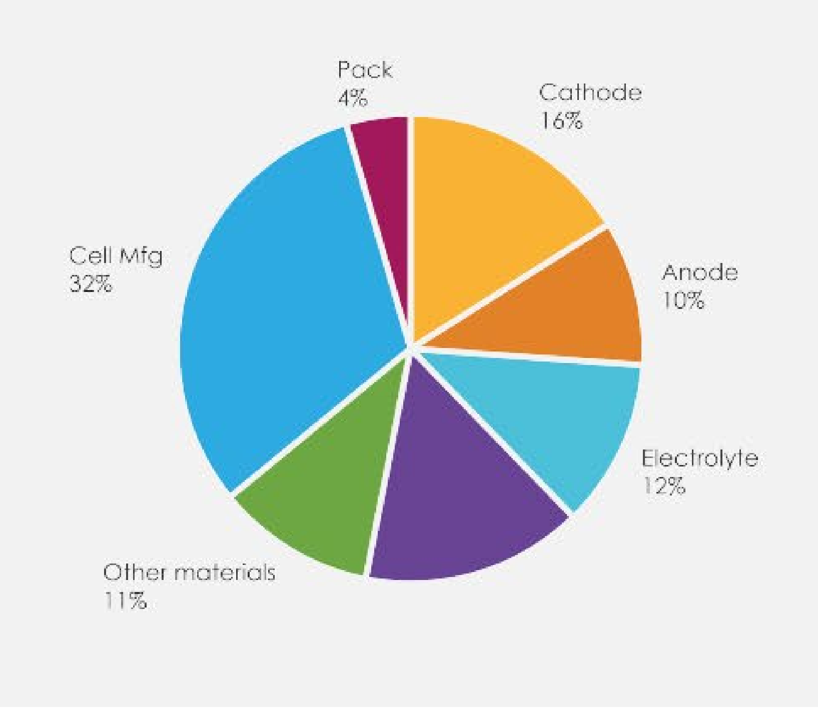
Not easy
Safety aspects
Energy and costs associated
Lots to be done!

Projected Demands and Costs

Year	GWh	No: 30 GWh Gigafactories
2010	30	1
2015	70	2
2020	250	8
2025	1000	30
2030	3000	100
2035	5000	150
2040	6500	220
2045	8000	250
2050	10500	350

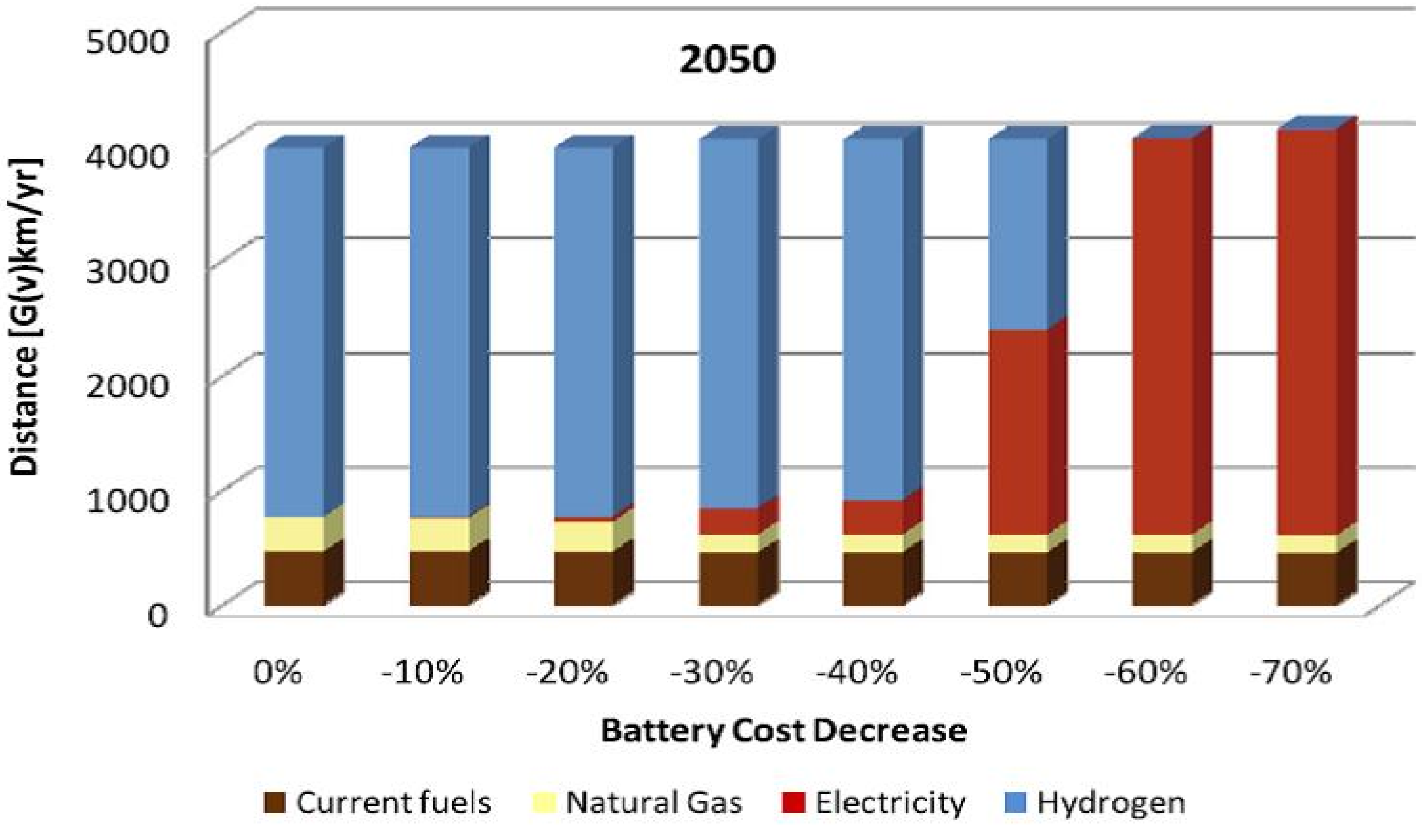






InnoEnergy

Projections Mobility



TIAM-ECN calculation of the distance travelled in 2050 by type of energy carrier for passenger cars in Europe under stringent climate policy and 100$/bl oil prices with varying assumptions for the cost of batteries.

Sust. En. Tech. Ass., **2014**, *5*, 106

university of groningen

Future

NO. 001 — 04 DECEMBER // 2038 — WWW.HOLLANDCHEMISTRY.NL

Holland Chemistry Times

HOLLAND CHEMISTRY TIMES 01

Queen opens electrical cracker

Yesterday, Queen Amalia switched on the third electrical cracker in the renovated chemistry complex in Rotterdam Pernis. The Queen praised the "e-Refiner" launched in 2018. This national initiative for the development and scaling up of electrochemistry was success-

HOLLAND CHEM

Most garages could have these shortly: environmentally friendly, safe and affordable battery packs that store electricity for the entire household

Dutch chemists create breakthrough

A GENUINELY CLEAN AND CHEAP BATTERY

GRONINGEN - Environmentally friendly, safe and affordable battery packs for the storage of electricity at home has been a holy grail for many years. However, Dutch researchers have now turned this into a reality in collaboration with industry.

By Bastienne Wentzel

A group of Dutch chemists have developed batteries that contain just iron and carbon and that make use of air. These are more environmentally friendly, safer and cheaper than standard batteries.
The battery is ready for the market: the first megafactory in Groningen was opened on 1 October 2038.
These batteries are expected to replace the nickel-containing variant and the lithium batteries that many people have at home to store electricity from solar panels. A previous pilot from E-Stone, which in 2018 was involved in the development of the nickel-iron-sulphur battery, has already demonstrated that the new batteries provide just as much energy, have a longer lifespan, are just as efficient and also cheaper.
Professor of sustainable energy storage Moniek Tromp, who has collaborated with E-Stone from the outset, explains: 'At the start of the 2030s, we started a project to make iron-air batteries suitable for use on a large scale. The technology was shown to work in the lab back in 2025, more than five years after we had developed a nickel-sulphur battery, but we then encountered practical problems. For example, it took us a long time to find the right combination of graphene and porous carbon to increase the efficiency of the air electrode. Just like with its predecessor, the stability and cost-efficient reproducibility on a large-scale was also a problem. However, we have solved that now.'

Capital injection

'E-Stone received a large order for nickel-iron-sulphur batteries and that made it possible to further develop the environmentally friendly variant. E-Stone provides all storage capacity for the largest Dutch offshore wind park, "IJmuiden Ver", which has been operational since 2030. That order gave us sufficient capital to develop the nickel-free battery.
Nickel continued to be a thorn in the eye. Although the safety of the battery is guaranteed and it cannot explode like a lithium-ion battery, nickel-sulphur compounds can be detrimental to human health. Furthermore, nickel has to be extracted from mines and this has a considerable environmental impact. Plus the price of nickel has risen considerably.
A battery that just contains iron, carbon and air is genuinely environmentally friendly', states Tromp. 'Iron is widely available, and easy and clean to extract and recycle. Carbon and air do not cause any environmental problems either.'

Cars and mobile phones

For the time being, the iron-air battery is not yet suitable for use in mobile equipment. 'The systems for the air inlet in the iron-air battery are still too complex for use in portable electronics.'
The researchers are also working on a variant of these batteries for use in electric cars and buses. 'The batteries need to be able to charge and discharge very quickly. We are currently working on that', says Tromp. 'We have demonstrated that it is possible. Vehicles can currently only travel 400 kilometres on an iron-air battery. The best lithium batteries have a range of 800 kilometres - we therefore still have a long way to go. The weight of the iron-air battery needs to be halved for the same energy content. That is theoretically possible, but it requires a better understanding of the reactions involved. Recent research into new catalysts has brought this a step closer, as well as the falling price of materials such as graphene. We think that we can now more accurately control the reactions that take place in that cell. However, it will certainly be another ten years before these batteries can be launched on the market.'

Energy Storage