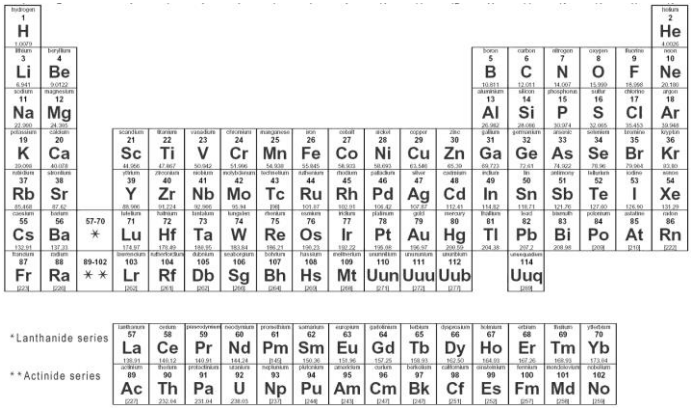
CHALMERS
UNIVERSITY OF TECHNOLOGY

New battery technologies demand new electrolyte concepts?!







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SEVENTH FRAMEWORK PROGRAMME
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R. Palacín


R. Dominko

Layout & Learning Outcomes

Next Generation Batteries (NGBs) – a crash-course

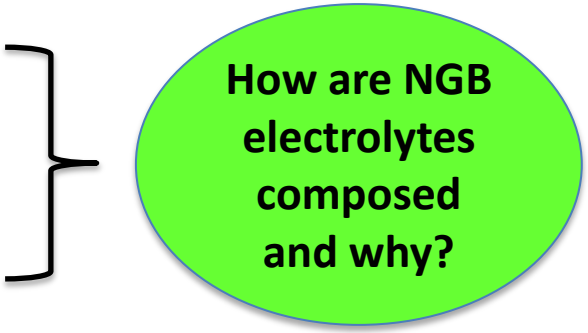
- Why? Who cares?
- 3 Perspectives
- Examples



=> Motivation, basics, examples, critical properties,...

NGB Electrolytes – from fundamentals to application

- General functionalities
- Special NGB demands & limits
- Common measures
- Examples

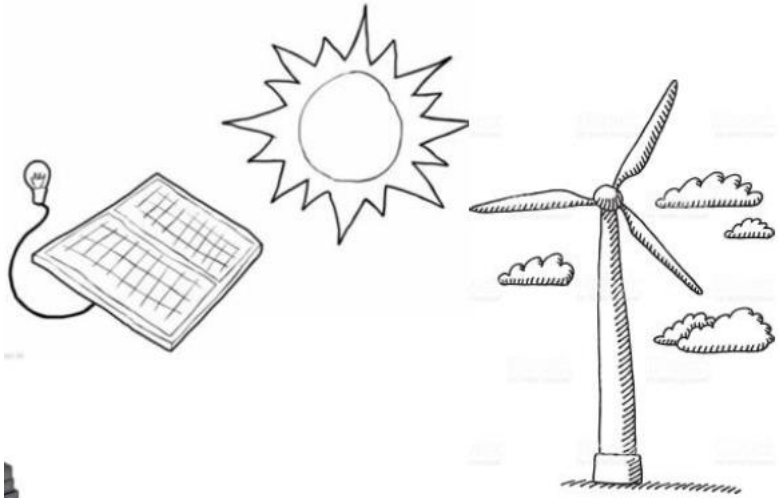


=> Material choices and motivations, differences, problems,...

Who cares about Next Generation Batteries?

WORLD ECONOMIC FORUM Agenda Initiatives Reports Events About







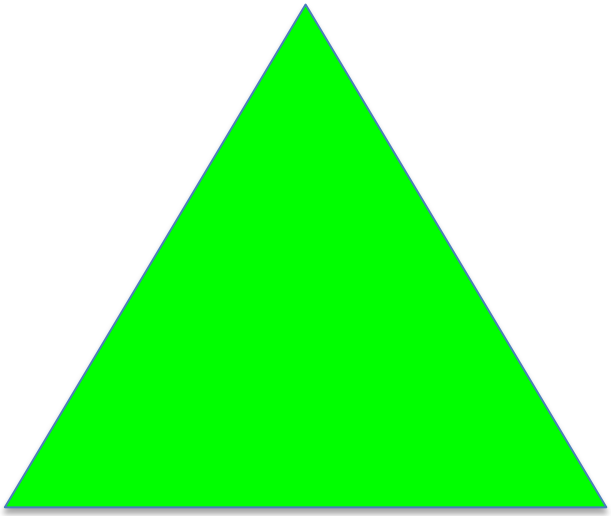
1. Nanosensors and the Internet of Nanothings – With the Internet of Things expected to comprise 30 billion connected devices by 2020, one of the most exciting areas of focus today is now on nanosensors capable of circulating in the human body or being embedded in construction materials. Once connected, this Internet of Nanothings could have a huge impact on the future of medicine, architecture, agriculture and drug manufacture.

2. Next Generation Batteries – One of the greatest obstacles holding renewable energy back is matching supply with demand, but recent advances in energy storage using sodium, aluminium and zinc based batteries makes mini-grids feasible that can provide clean, reliable, round the clock energy sources to entire villages.



3 perspectives on NGBs: 1 - Performance





Performance

- Energy
- Power
- Life-length
- Safety
- Cost
- ...
- Driving range
- Charging time

Increasing size



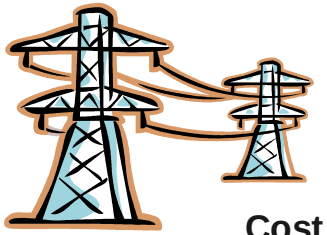
Energy density

Wh



Safety

kWh



Cost

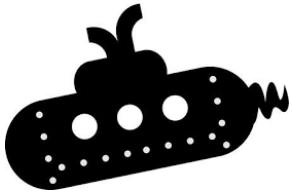
MWh

”New” Applications
=>
New demands









3 perspectives on NGBs: 2 - Sustainability



Sustainability

Resources

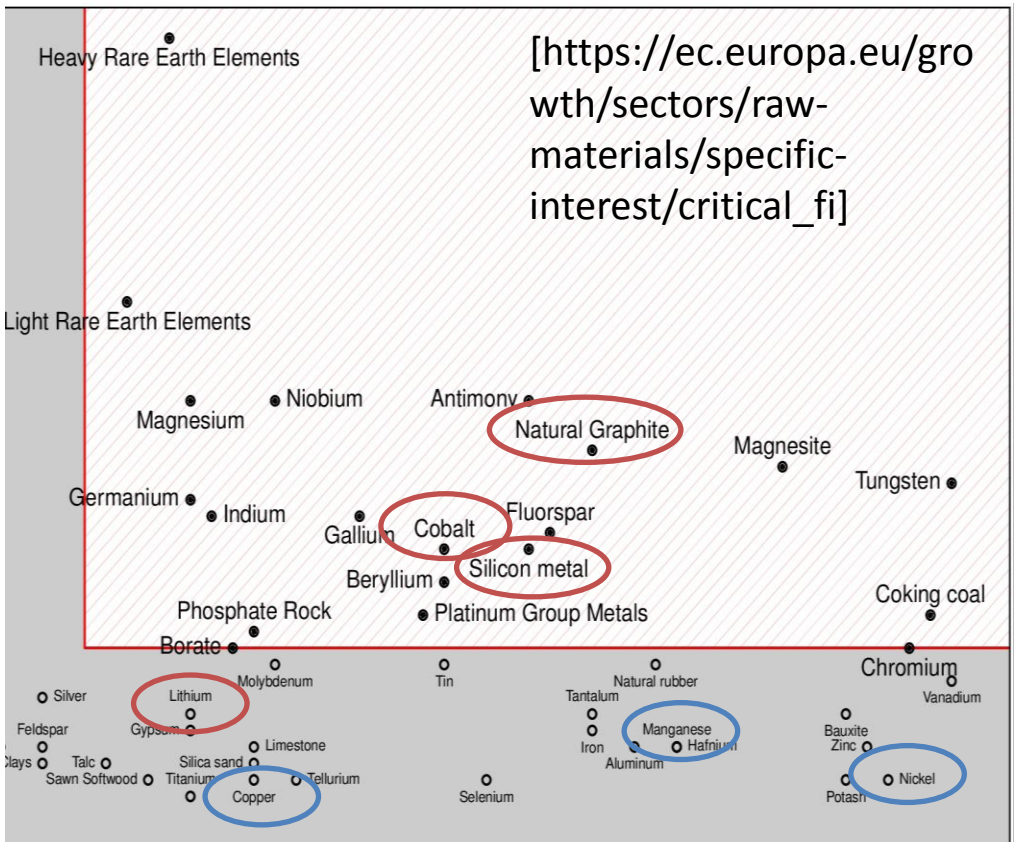
Production

Efficiency

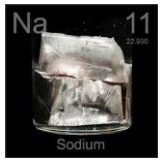
2nd use

Recycling

…







Abundance in Earth's crust:

20 ppm

22700 ppm

3 perspectives on NGBs: 3 – Curiosity



Curiosity

”Technology is always limited by the materials available”

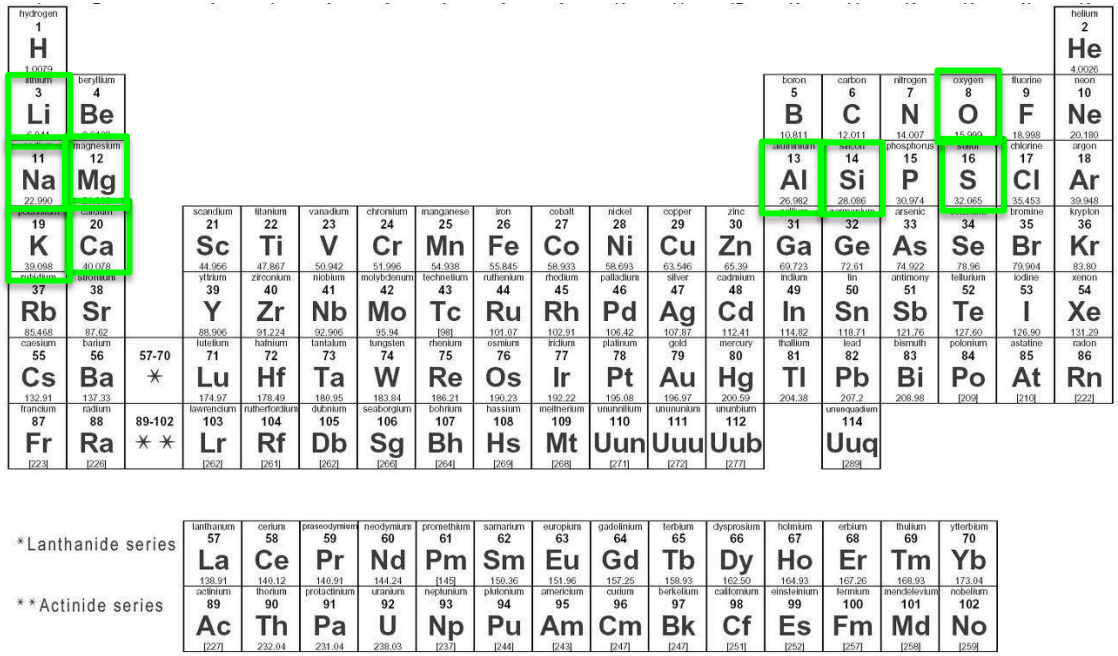
- DARPA 1960’s

What if…?

How can…?

Can we…?

…



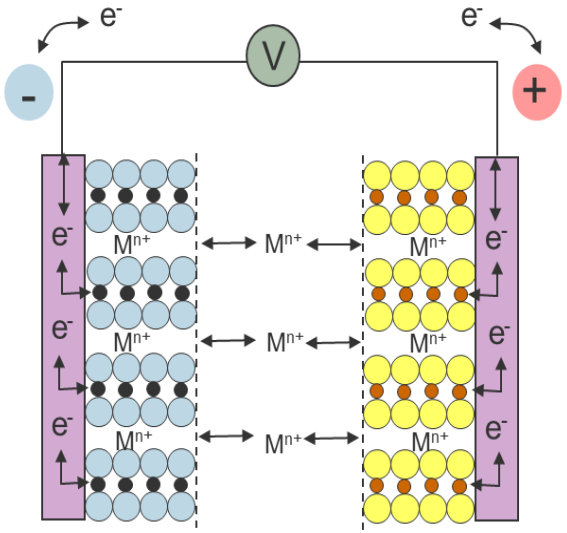
NGB examples



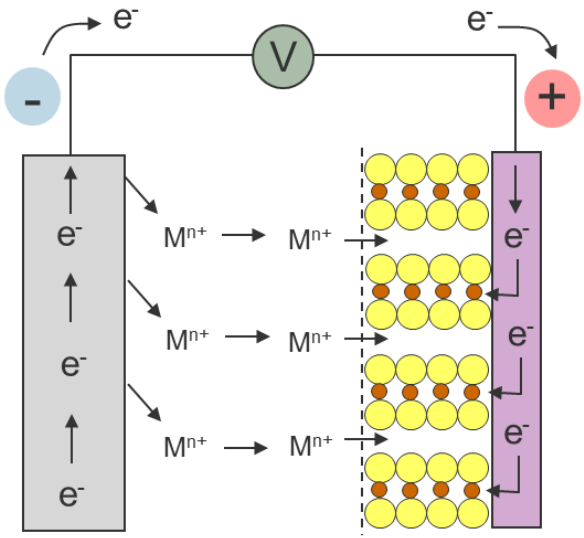
Metal batteries:

- **Li, Li-S, Li-O_2**
- **Na (Na-S)**
- **Mg, Ca, Al**

Metal-ion batteries: Na-ion (SIB/NIB)



Intercalation of M^+ into electrodes
No pure metal inside the battery (= LIBs)
Capacity not intrinsically = f(metal)

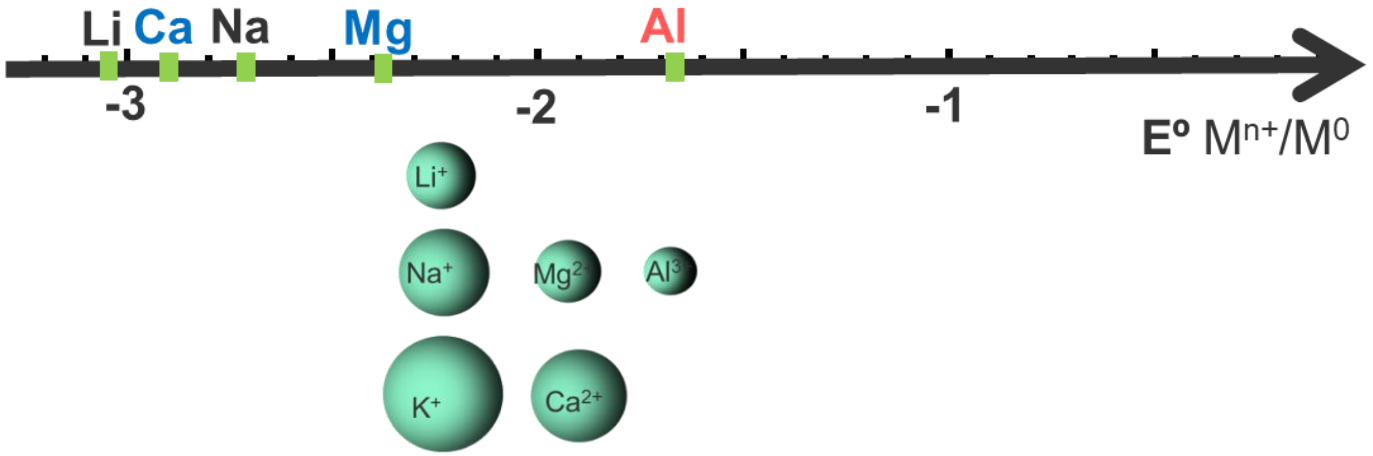


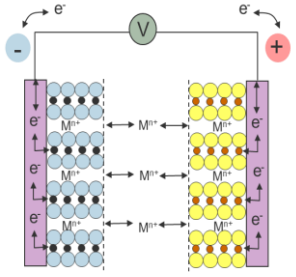
Stripping/plating of metal
Pure metal inside battery
Capacity intrinsically = f(metal)

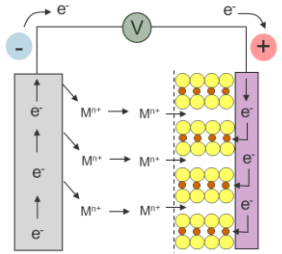
NGB examples

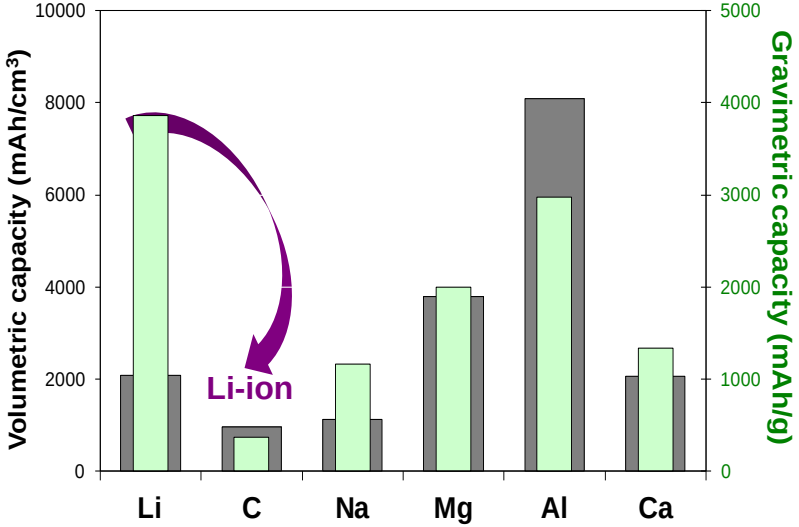


Energy ≈ Potential x Capacity









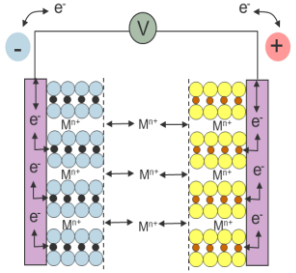
M	Problems/Issues
Li	Unsafe? TMO_x, S or O_2 cathodes?
Na	Low melting/unsafe?! Na-S $T_{op} \approx 200°$
Mg	Stable electrolytes, migration
Ca	Reversible plating/stripping, migration(?)
Al	Reversible plating/stripping, migration

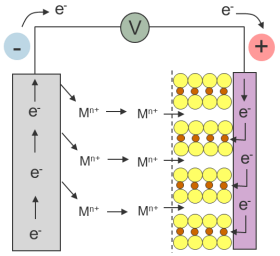
SIBs? Na in C host – as for LIB (~~graphite~~ => HC)

NGB electrolytes: General functionalities



=> Electrolyte = Salt(s) + Solvent(s) + Additive(s) <=

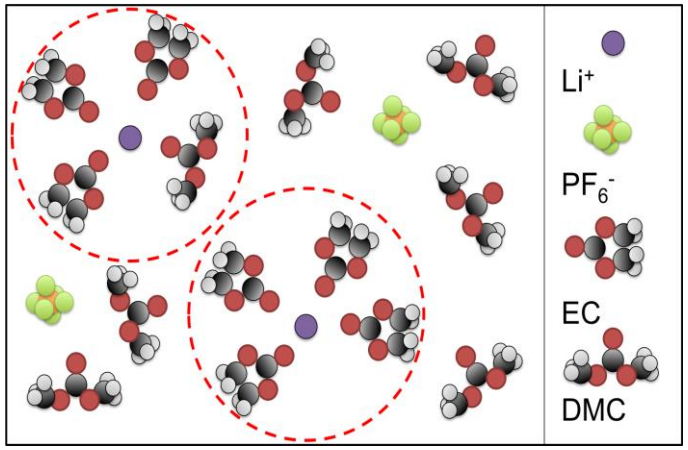




- **Mechanically stable – separate electrodes**
- **No e^- transport**
- **Rapid M^+ transport – ion conductivity**
- **Low viscosity – ion conductivity & cell-making**
- **Electrochemically (meta-)stable - ESW**
- **Acceptable T working range**

- **Sustainable**
- **Non-toxic**
- **Safe**
- **Low-cost**
- **…**

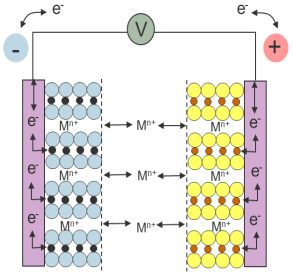
Conventional LIB Electrolytes

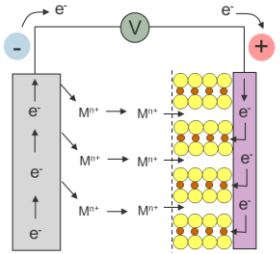


"Standard": 1 M $LiPF_6$ in EC:DMC

Mini-exercise





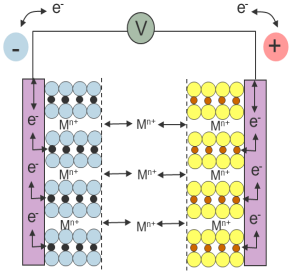


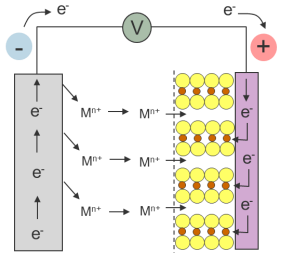
Discuss in groups of 3 persons for ca. 5 minutes

1. **What do you know about electrolytes in general?**
2. **Do you think 1 M $LiPF_6$ in EC:DMC sounds OK?**
3. **What alternatives can you think of?**

NGB electrolytes: Special demands and limits

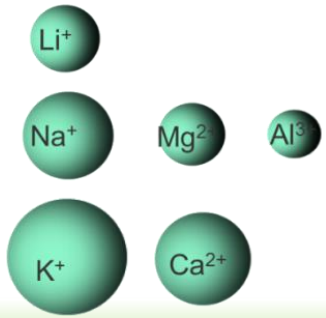






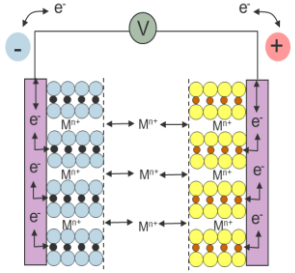
NGB	ESW	Solubility	Other
Li	≈LIB	≈LIB	Stable vs. Li (SEI)
Li-S	*ca.* 2 V	Not S, PS	Stable vs. Li (SEI)
Li-O_2	*ca.* 3 V	Yes O_2	Stable vs. Li_2O_2, Li (SEI)
Na-ion	≈LIB-0.3 V	≈LIB	
Na	≈LIB-0.3 V	≈LIB	Stable vs. Na, high T_{op}?
Mg	*ca.* 3-4 V	salt 0.5 M	Stable vs. Mg
Ca	≈LIB(?)	salt 0.5 M	
Al	reduced, shifted	salt 0.5 M	$[AlCl_4]^-$ transport?

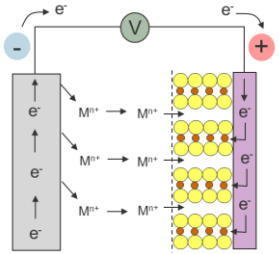




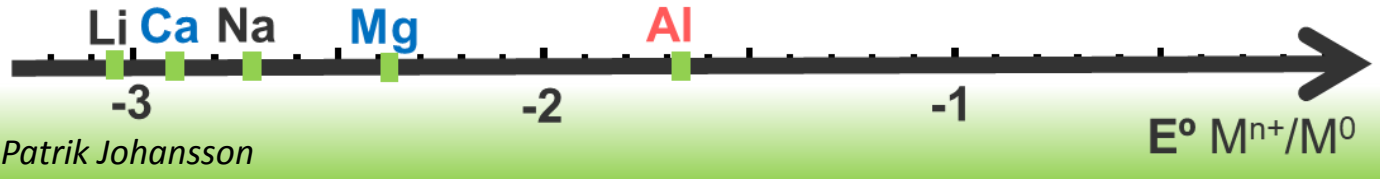
NGB electrolytes: Common measures

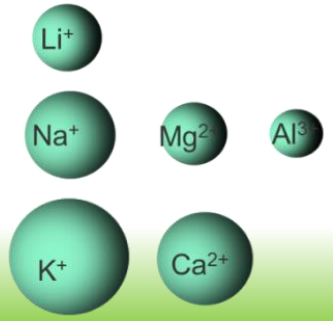






Ion conductivity	**"1 mS/cm"** AC imp., dielectric spectroscopy
Thermal stability	**"-30 - +50 °C mS/cm"** TGA (iso-thermal), DSC
ESW	LSV, CV
Solubility	UV-VIS/cycling for S & PS, microelectrodes & DEMS for O_2
Density, Viscosity	limitations in Wh/kg, transport
NMR, IR, Raman	ion transference/mobility, speciation
Cell cycling	…

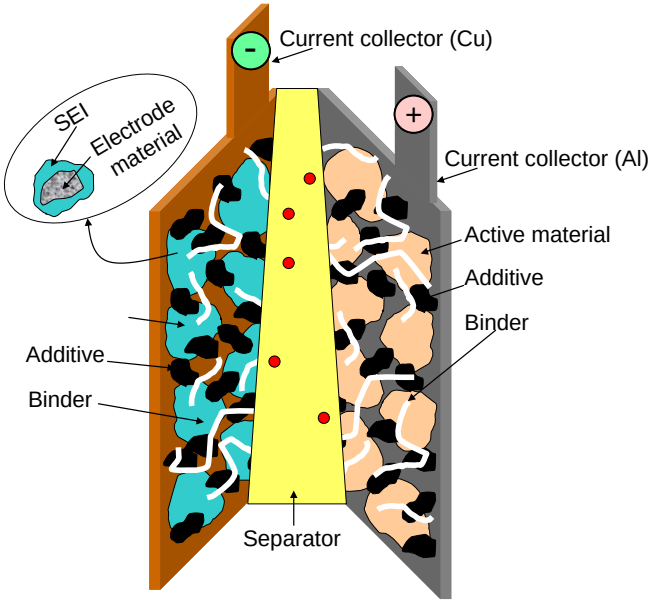




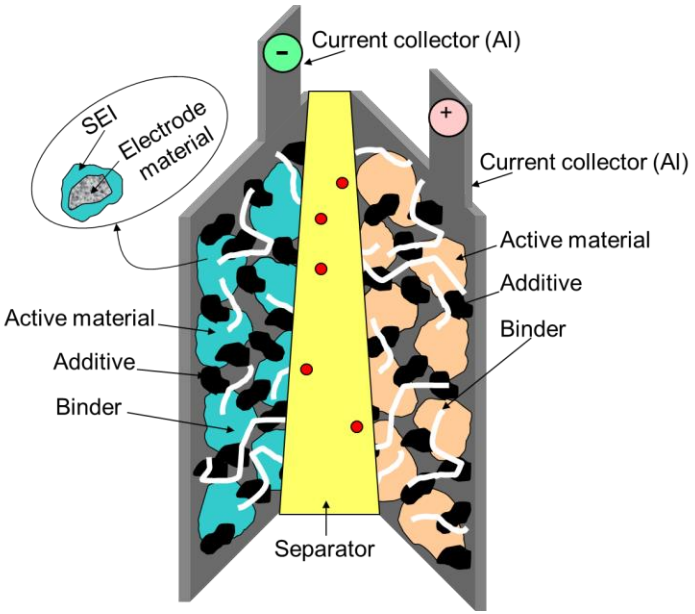
NGB electrolytes: Example of SIB

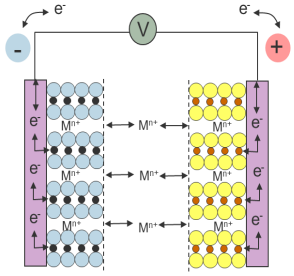


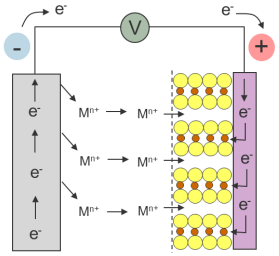
LIB



SIB







Cu-graphite

Same

1 M $LiPF_6$ in EC:DMC

Different

PC exfoliates graphite

Al-HC

1 M $NaPF_6$ in EC:DMC

PC can be (and is) used

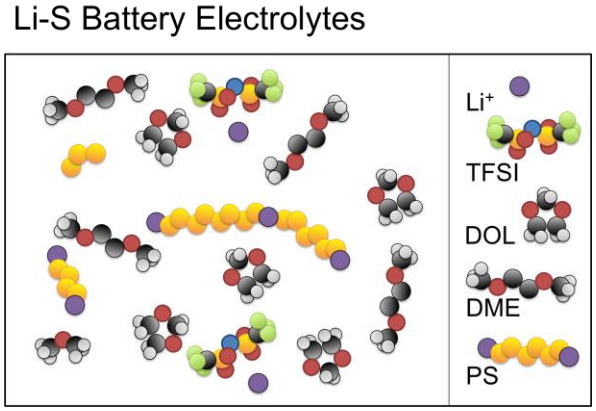
NGB electrolytes: Example of Li-S battery

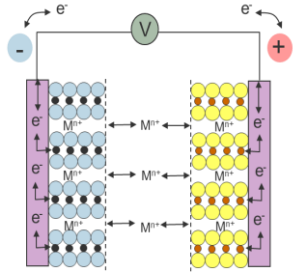


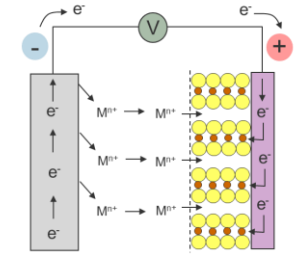
Solubility of S and PS = f(SOC) & cell composition

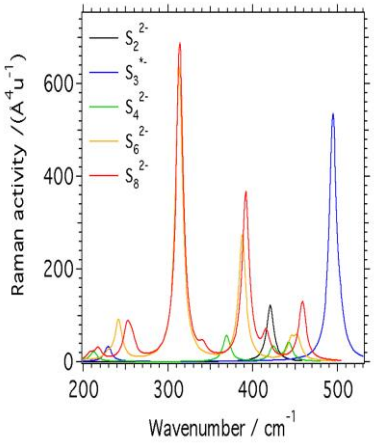
Cell: Li | 1 M LiTFSI in DOL:DME | C/S composite

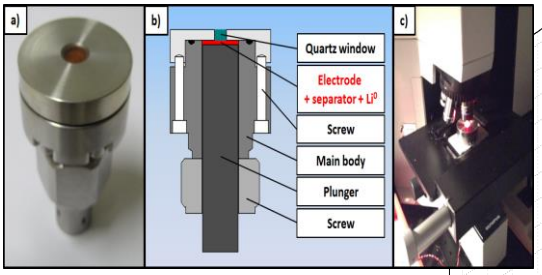
Here: *Operando* confocal Raman + DFT comp.

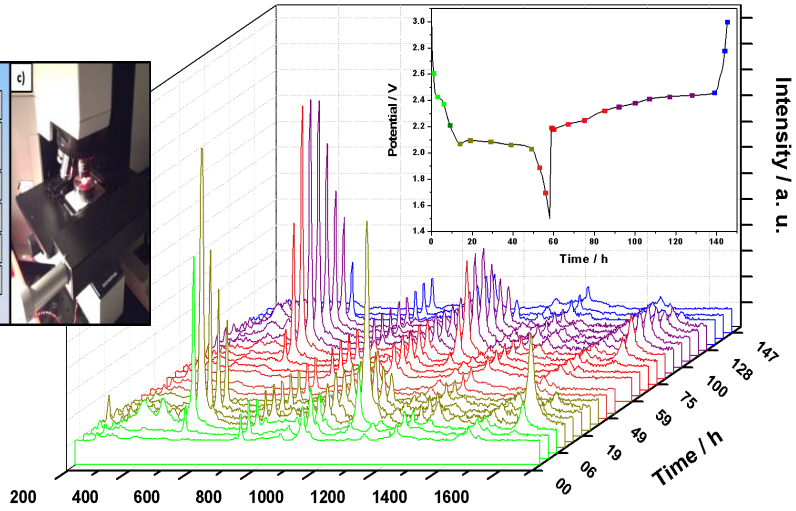


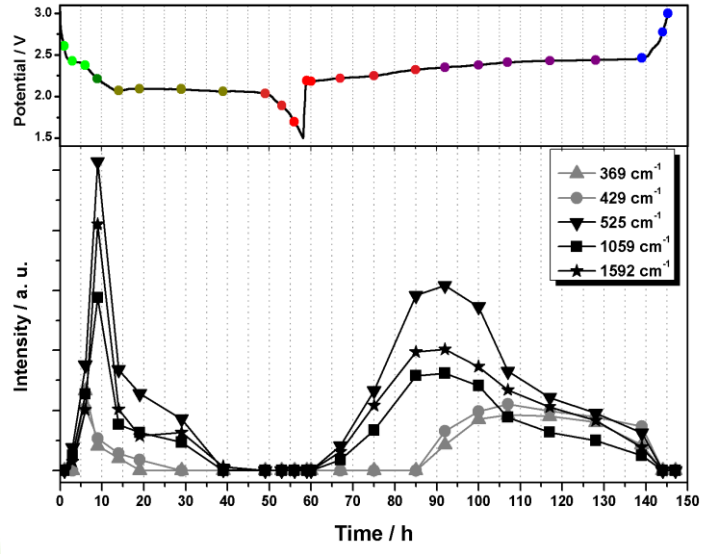










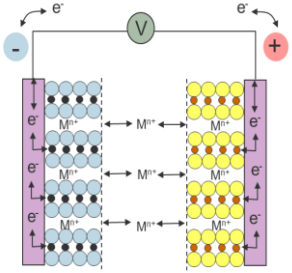


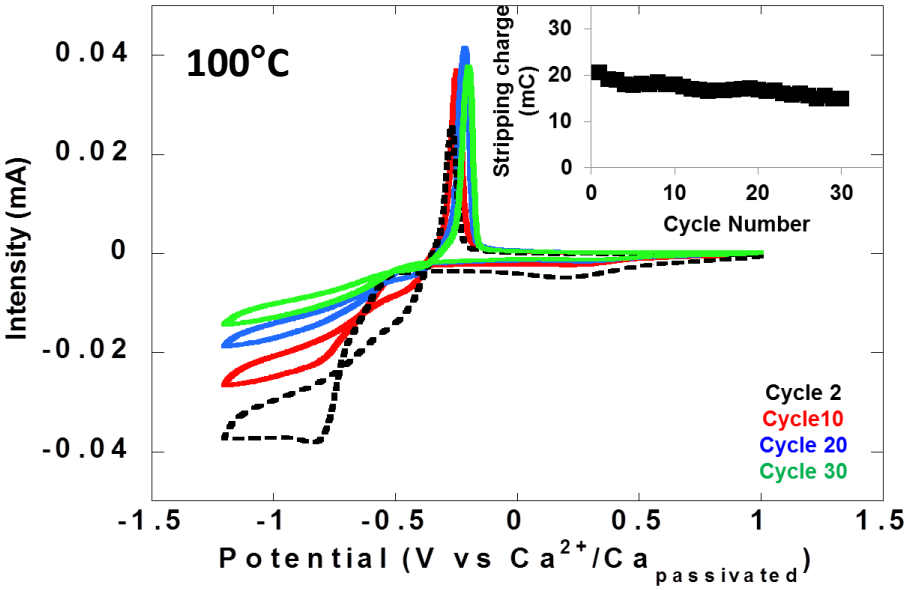
NGB electrolytes: Example of Ca-battery



Stripping/plating of Ca difficult

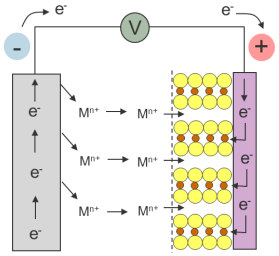
Half-cell: Ca | 0.45 M $Ca(BF_4)_2$ in EC:PC, T_{op} = 100°C



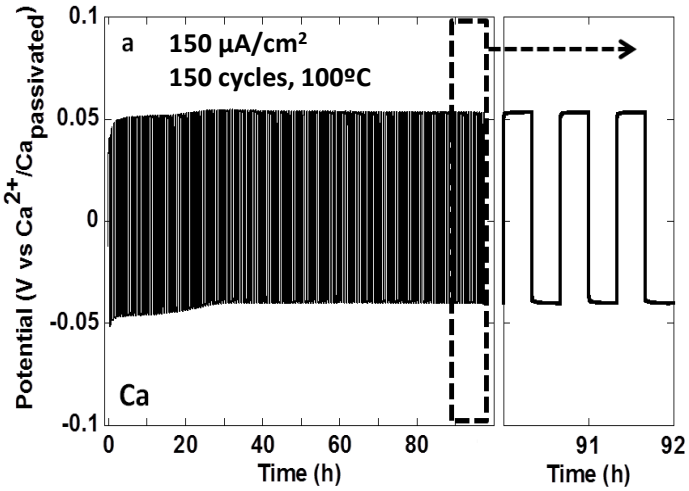


☺ Capacity stable

☹ Large polarisation



☹ Electrolyte decomposes



A. Ponrouch, C. Frontera, F. Barde, M.R. Palacin *Nature Materials* 15, 2016, 169

Summary & Conclusions



NGB electrolytes:

- are often rather similar – also to LIB electrolytes

- have a few or more unique demands, esp. Li-O_2, Li-S

- stability is “always” an issue – esp. vs. metal electrode

- solubility is tricky to handle/measure *realistically*

- progress is in need for many tools and techniques

Concepts/Things I have not (yet) talked about:

- Ionic liquid based electrolytes
- Aqueous electrolytes
- Solid-state electrolytes (ceramics, glasses, polymers)
- ...

Thanks!
What questions do you have now?



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