Battronics Engineering

Innovations in Solid-State Batteries & Cathodes for EVs

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β-knowledge

[2]

Challenges for Battery Implementations for OEMs:

- **Literature** on LIB's **is enormous**
- Literature is **often false** or has significant errors
- Specific battery **knowledge of team members varies**
- **Time & Money** should not be invested for searching

Service of β-knowledge:

- **Lectures** on specific topics
- Direct mentioning of **errors in literature**
- Your team gets **very broad knowledge**
- **Avoid implementation errors** of battery systems
- **Avoid communication problems** in your team from f

Don't waste your time & money on the actual meaning of "re-search" - most things are already known on batteries - so be informed !!!

Examples for Li-ion Batteries:

1. Liquid electrolytes:

- T_{min} & T_{max}
- transport properties
- additives

2. Active materials:

- Graphite
- $LiNiMnCoO_2$
- Si
- $LiCoO_2$
- Li-metal
- $LiFePO_4$

3. Periphery:

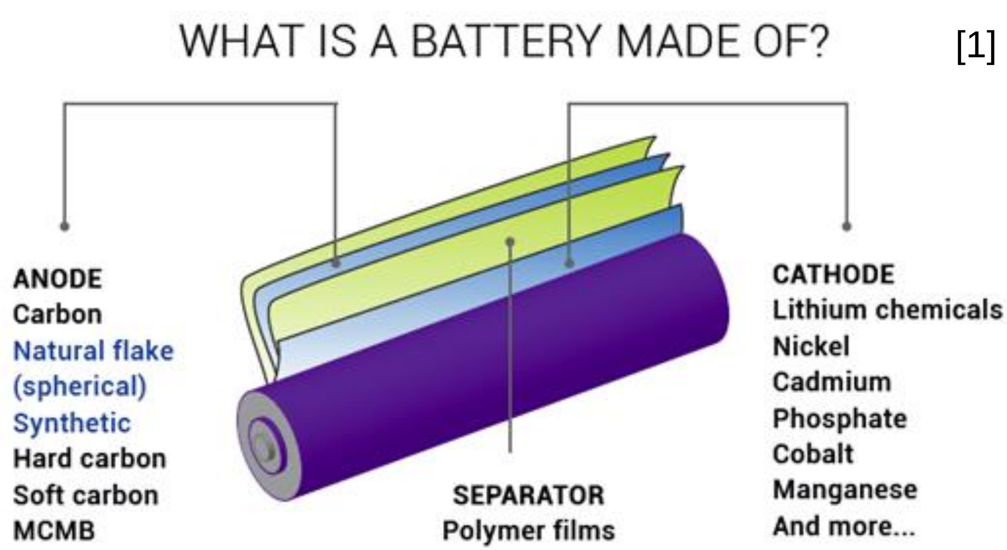
- Separator
- BMS
- Binder
- Temperature control
- SOC/SOH

4. Economics:

- graLiCo supply
- Market trends

Outline

1. Introduction
2. Why liquid electrolytes today?
3. Gains of solid-state batteries
4. Summary



[1]

[1] Moores S, *"The megafactories are coming"*, *Benchmark Minerals Intelligence* (03/2015)

Intro: Are LIB’s a disruptive technology?

Well only history can tell:

• For portable electronics:	yes!
• For bikes:	yes!
• For cars, buses, trucks	not yet
• For energy storage	not yet

But maybe also in transport sector soon …

But by political power !!!

TOP FOUR DISRUPTOR QUOTES [2]

‘If I had asked customers what they wanted, they would have said a faster horse’
HENRY FORD, FORD MOTOR CORP, C. 1919

‘You can’t just ask customers what they want and then try to give that to them. By the time you get it built, they’ll want something new’
STEVE JOBS, APPLE INC, 1989

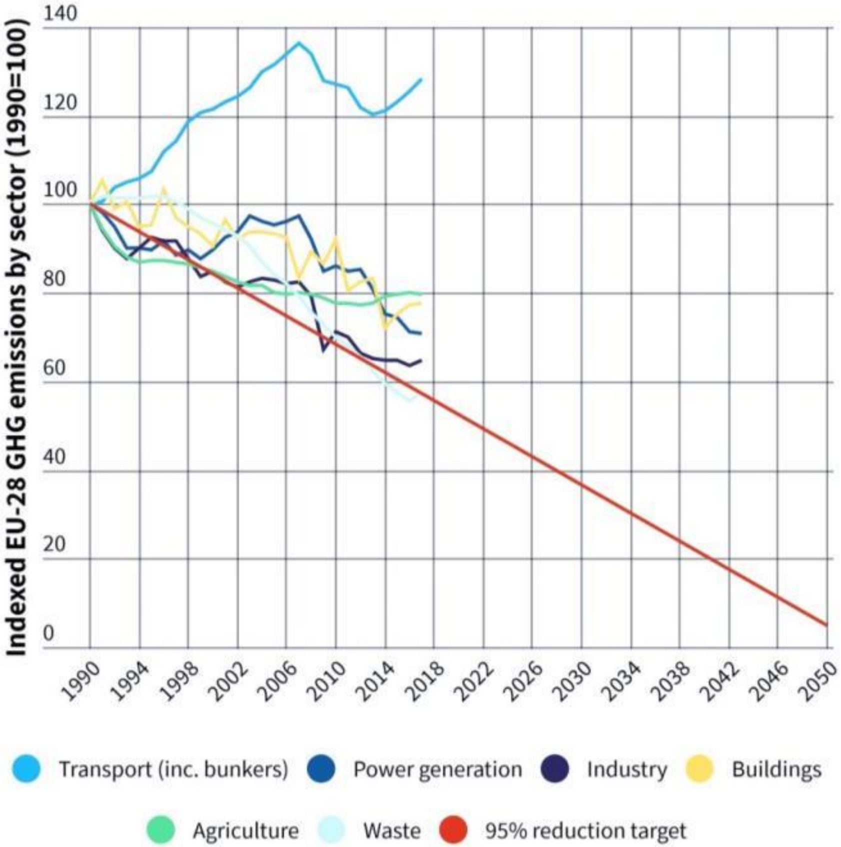
‘It’s what we induce others to do that will have a greater impact than the cars we make ourselves’
ELON MUSK, TESLA MOTORS INC, 2014, ON PRODUCING ITS FIRST EV, THE ROADSTER

‘The great thing about fact-based decisions is that they overrule the hierarchy’
JEFF BEZOS, FOUNDER AND CEO OF AMAZON

[2] Moores S, *“The megafactories are coming”*, *Benchmark Minerals Intelligence* (03/2015).

Adoption rates

EU transport emissions have taken a wrong turn to reach
EU2050 Climate Target of decarbonization



[3]

[3] Transport & Environment via twitter on 27.11.2018

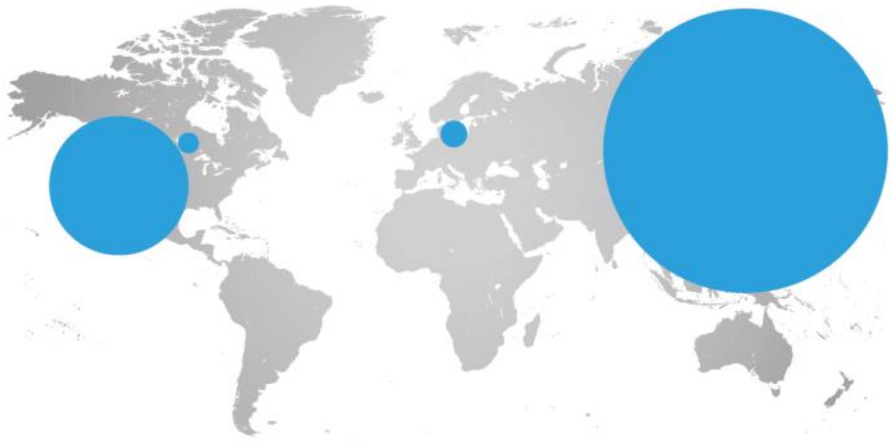
2.1 LIB Supply by continent

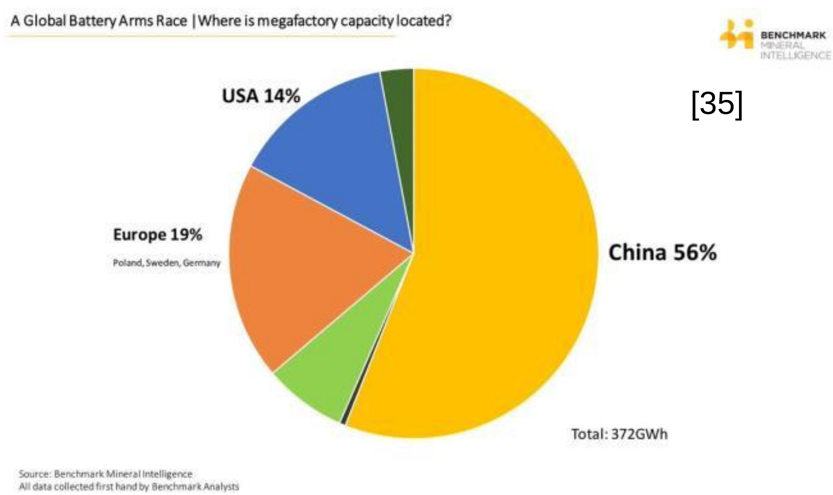
LIB production growth [33]:

- LIB plants: **180GWh of new cap until 2020**
- **70% of new supply from China**
- lower costs in raw materials is less of impact but **decrease of costs mainly due to scale**
- energy storage is connecting industries that are usually separated

Worldwide installations:

[33]





[35]

[33] Moores S., *"Future City 2030"*, *Benchmark Minerals Intelligence* (09/2016)
[35] Moores S., on twitter, Benchmark Mineral Intelligence Q4/2017

2.1 EU commission evaluation

EU evaluation:

- EU is good on research
- but fails to implement economic scheme.
- (similar to digital cameras and LCD-TV where some of the first patents came from Europe but all economy was in Japan)

[21] EU Commission judgement 01/2018
[35] Moores S., on twitter, Benchmark Mineral Intelligence Q4/2017

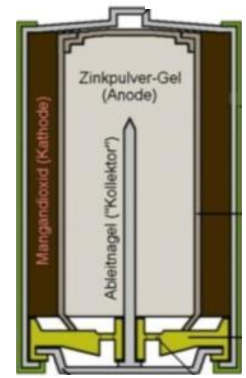
2. Why liquid electrolyte today?

2.1 Electrolytes in Batteries

1. Batteries in general

Alkaline batteries:

- 20 % KOH in H_2O = Ph14 = **6M KOH in water**
- $Zn_{(s)} + 2MnO_{2(s)} \rightarrow ZnO_{(s)} + Mn_2O_{3(s)}$
- $E_0 = 1.43$ V



alkaline

NiMH batteries:

- 20 % KOH in H_2O = Ph14 = **6M KOH in water**
- Neg: $H_2O + M + e^- \rightarrow OH^- + MH$
- Pos: $Ni(OH)_2 + OH^- \rightarrow NiO(OH) + H_2O + e^-$
- $E_0 = 1.32$ V

Lead-acid battery:

- H_2SO_4 solution 1.24-1.3 g/cm^3 = **5.4–6.7M H_2SO_4 in water**
- Neg: $Pb + HSO_4^- \rightarrow PbSO_4 + H^+ + 2e^-$
- Pos: $PbO_2 + HSO_4^- + 3H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$
- $E_0 = 1.8\text{-}2.1$ V (dis-ch)

NiMH

Li-ion battery

- $LiPF_6$ in organic carbonates = **1.2-1.5M $LiPF_6$ in EC:DMC**
- Graphite/LTO vs. LCO/LFP/NMC/NCA/LMO
- $E_0 = 3.8\text{-}4.1$ V (dis-ch)

[1] en.wikipedia.org/wiki/Alkaline_battery & Nickel-Metallhydrid-Akkumulator & Lithium-ion_battery

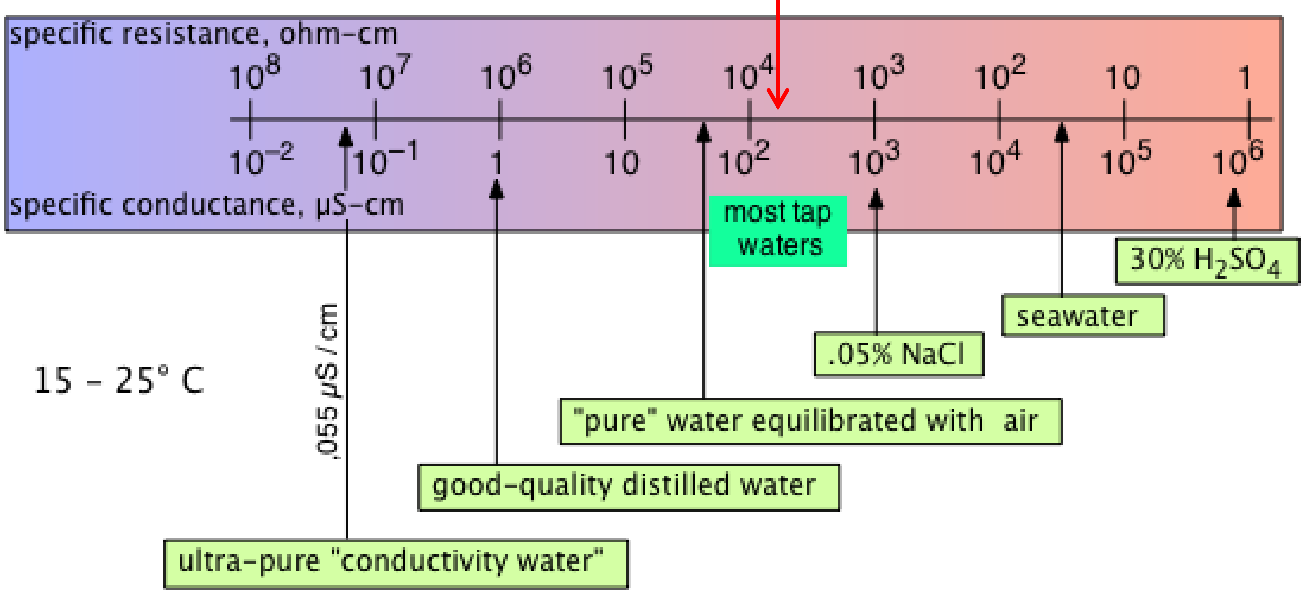
1. Solvation and Stokes radius

Solvation: Hydration numbers [3]

ion	**Li^+**	**Na^+**	**K^+**	Cs^+	Mg^{2+}	Ca^{2+}	Ba^{2+}	Zn^{2+}
radius, pm	**76**	**102**	**152**	167	72	100	149	88
hydra. no.	**3-22**	**3-13**	**1-7**	1-4	5-14	4-12	3-9	6-13

Conductance [4]:

1M $LiPF_6$ EC:DMC (best)



[3] en.wikipedia.org/wiki/Metal_ions_in_aqueous_solution CC-BY-SA 3.0
[4] chem.libretexts.org/…/The_nature_of_ions_in_aqueous_solution CC-BY-SA 3.0

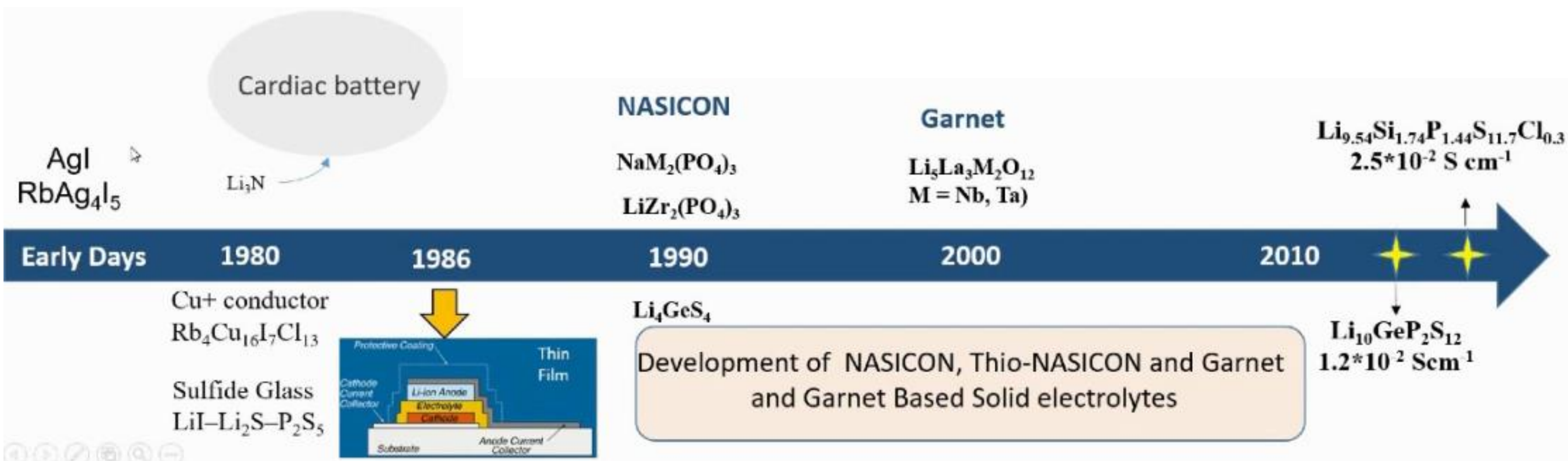
3. Gains of solid-state electrolytes

Risks vs Gains

History of solid-state electrolytes

Solid-state electrolytes long known:
- Oldest commercial one: Na-S since 1966 by Ford Motors
- But Na-S at 300-350°C to get liquid active materials

Often forgotten these days:
- Breakthrough of Li-ion in 1989 by finding stable liquid electrolytes by Sony Corp. leading to commercialization in 1991
- Polymer electrolytes as intermediates of liq. & solid elytes often used in 1990's

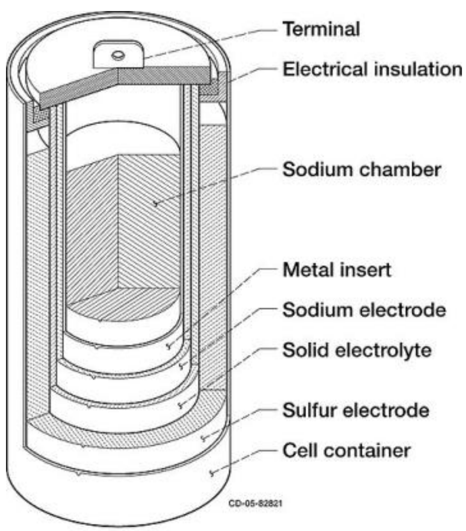


[18] Shirley Meng, Presentation MRS webinar: Solid-State Electrolytes, Nov 2018

Liquid vs solid electrolyte concepts

Na-S battery with β-Al_2O_3 SSE:

- $2Na + 4S \rightarrow Na_2S_4$ or
- $2Na + 3S \rightarrow Na_2S_3$ or
- $2Na + (SSCH_2CH_2)_n \rightarrow Na_2SSCH_2CH_2$ for 90-100°C melting temp., poly(ethylenedisulfide)

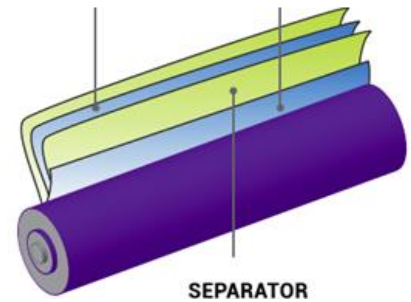


Sodium sulfur battery schematic

[17]

Todays Li-ion batteries with liq. Elytes:

- Solid cathode + anode
- Liquid electrolyte to get perfect wetting

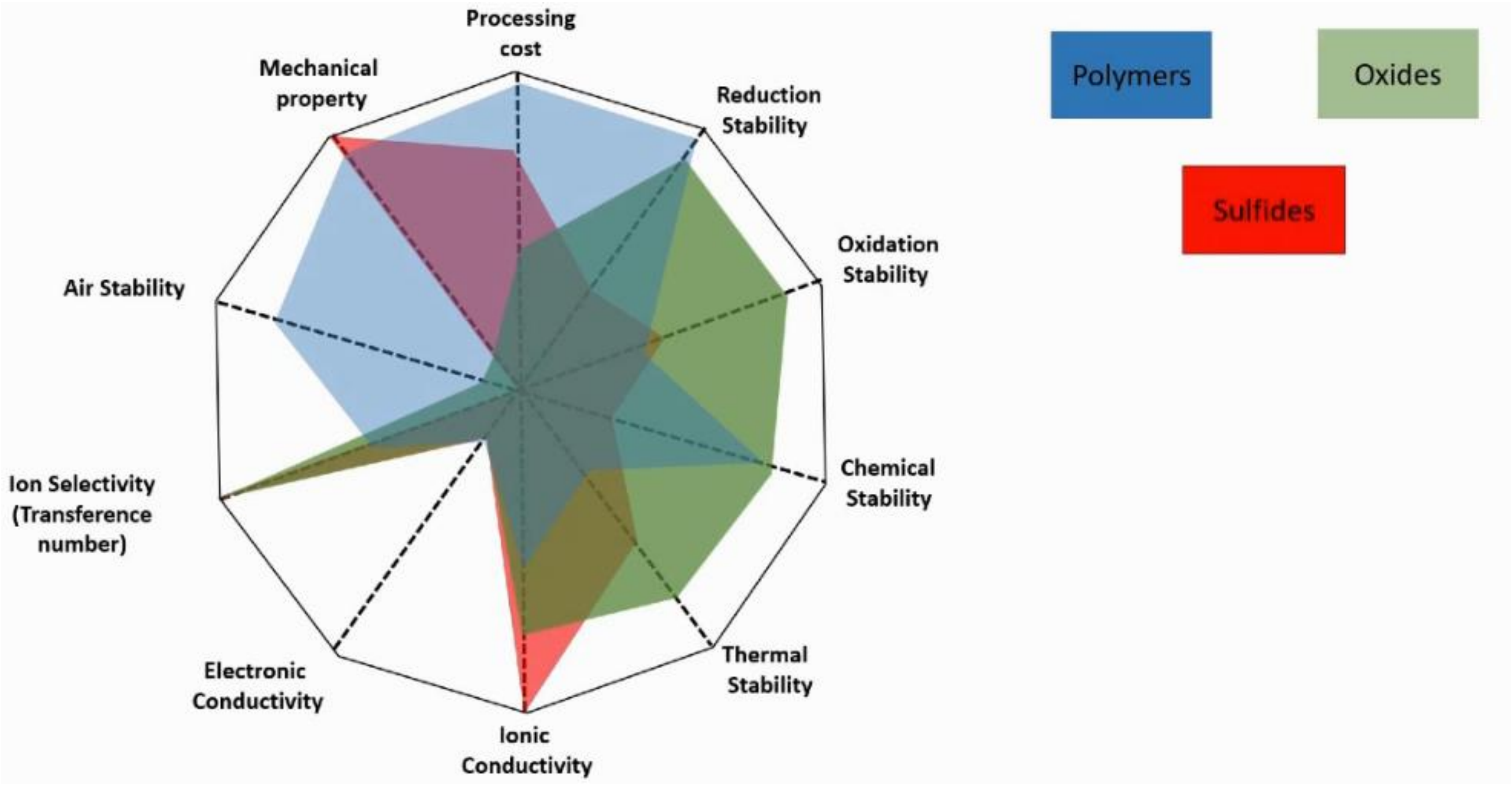


General concept: mixing liquid and solid phases to guarantee coherent interface btw the two during volume changes

[17] Image courtesy of NASA Glenn Research Center

Properties of different solid-electrolytes

[18]



[18] Shirley Meng, Presentation MRS webinar: Solid-State Electrolytes, Nov 2018

Interface engineering for contact solid vs. solid

Engineering Solid-Solid Interfaces:

- Either dropping a bit liquid electrolyte for ionic contact
- Engineering soft interphases that guarantee ionic contact
- Reduce active material volume expansion by using e.g. $LiMn_2O_4$ or LNMO spinel
- Prepare thin-film electrodes + pressure contact
- Many other concepts …

[18,20]

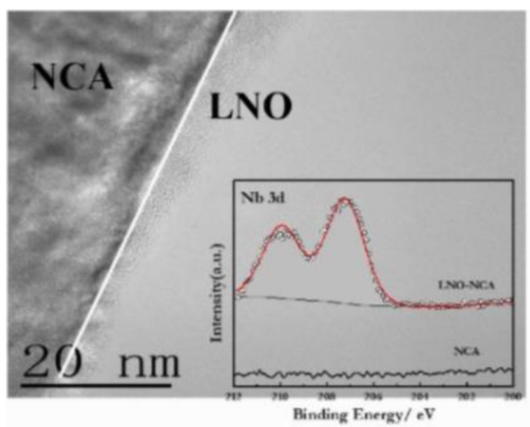


Fig: ca. 5 nm amorphous $LiNbO_3$ coating on NCA cathode particle

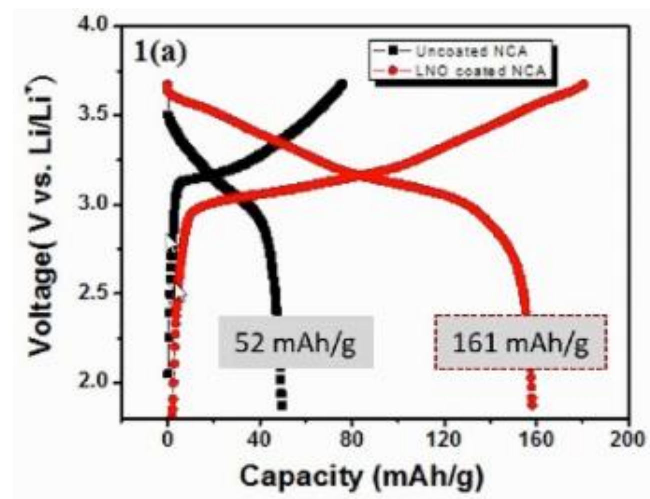


Fig: Comparison cycling with and without $LiNbO_3$ coating

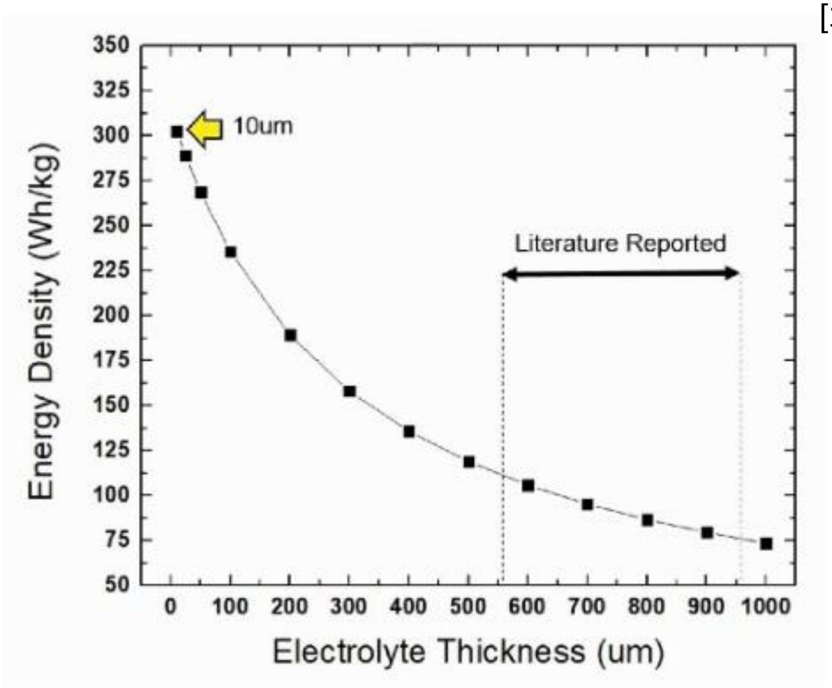
[18] Shirley Meng, Presentation MRS webinar: Solid-State Electrolytes, Nov 2018
[20] Abhik Banerjee et al., in submission 2018

Energy density: liquid vs solid LIB

What is gain of All-Solid-State Batteries:

- Safety to some extend (liq. LIBs can self-combust without external air, ASSB have metallic Li so metal fire of T_m=180.5°C)
- Energy density better only if SSE produced thinner than 50µm
- If they ever become cheaper than liq. LIB is questionable as processing more difficult with Li-metal and SSE sputtering/CVD/sintering/etc
- But lifetime could be improved significantly as SEI formation could be avoided in theory

[18]



[18] Shirley Meng, Presentation MRS webinar: Solid-State Electrolytes, Nov 2018

Contact

Interested in

- **β-knowledge**
- **β-consulting**
- **β-research**

Don’t hesitate

Contact us!

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For a battery future

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