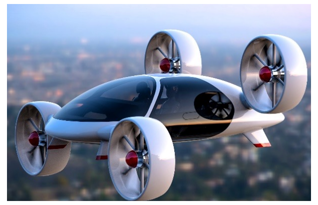
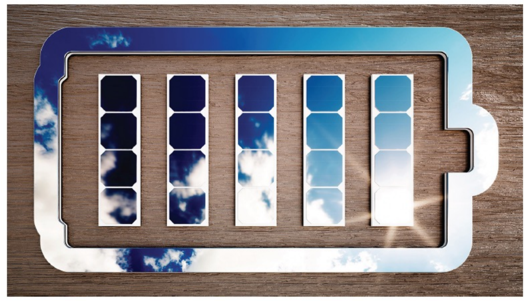
LESC
Laboratory for
Energy Storage and Conversion




All Solid-State Batteries Based on Sodium Electrochemistry

Y. Shirley Meng

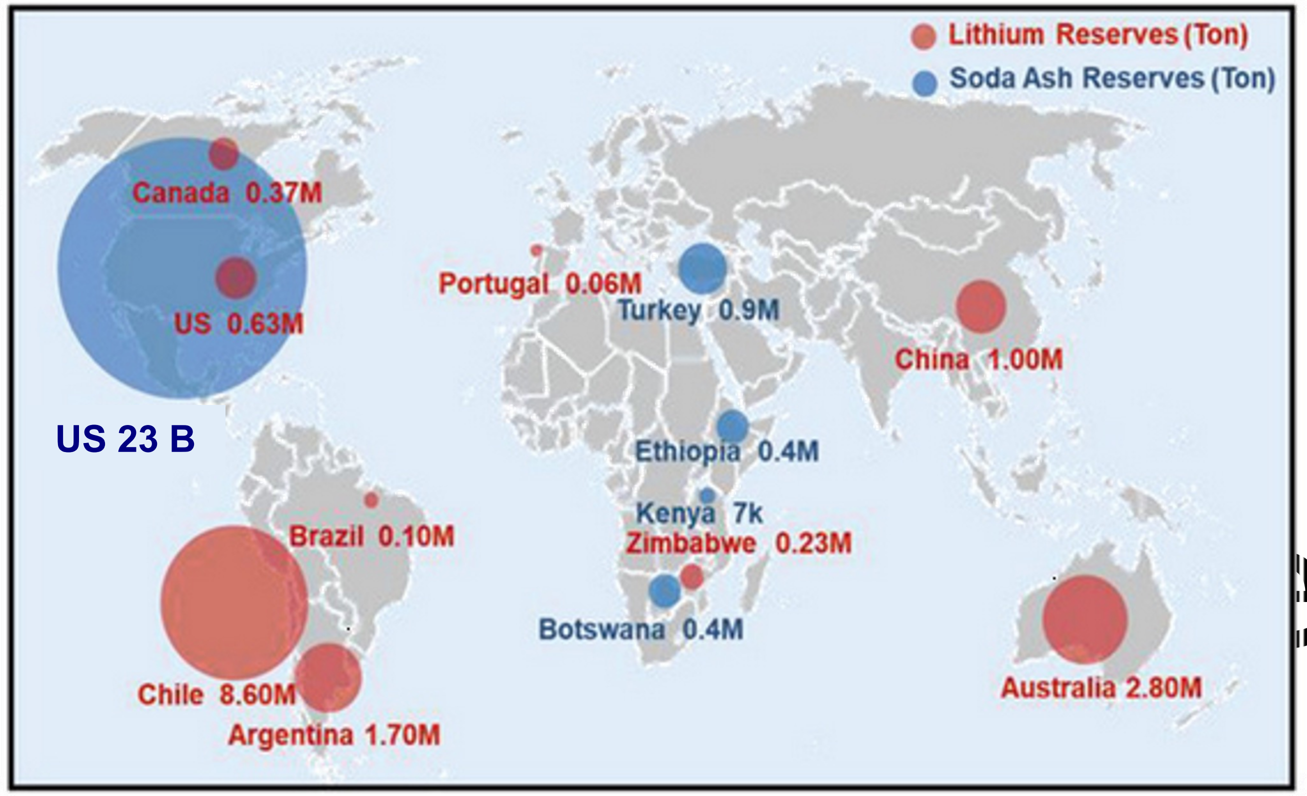
Laboratory for Energy Storage & Conversion (LECS)

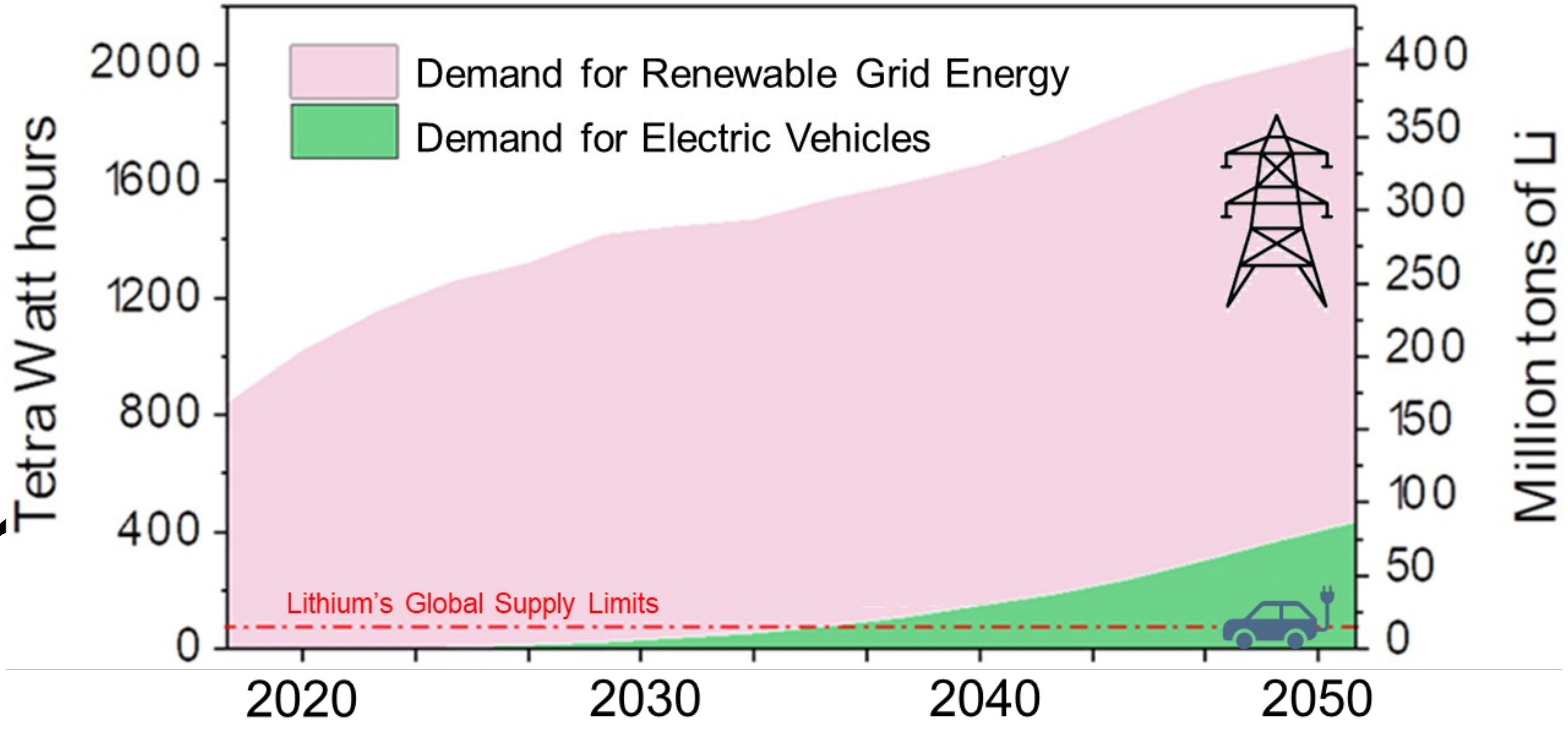
The University of Chicago/UC San Diego

Argonne Collaborative Center for Energy Storage Sciences (ACCESS)

Disclosure – I am a co-founder of UNIGRID a sodium battery startup

Na vs Li Materials Sustainability





US Energy Storage : Scale

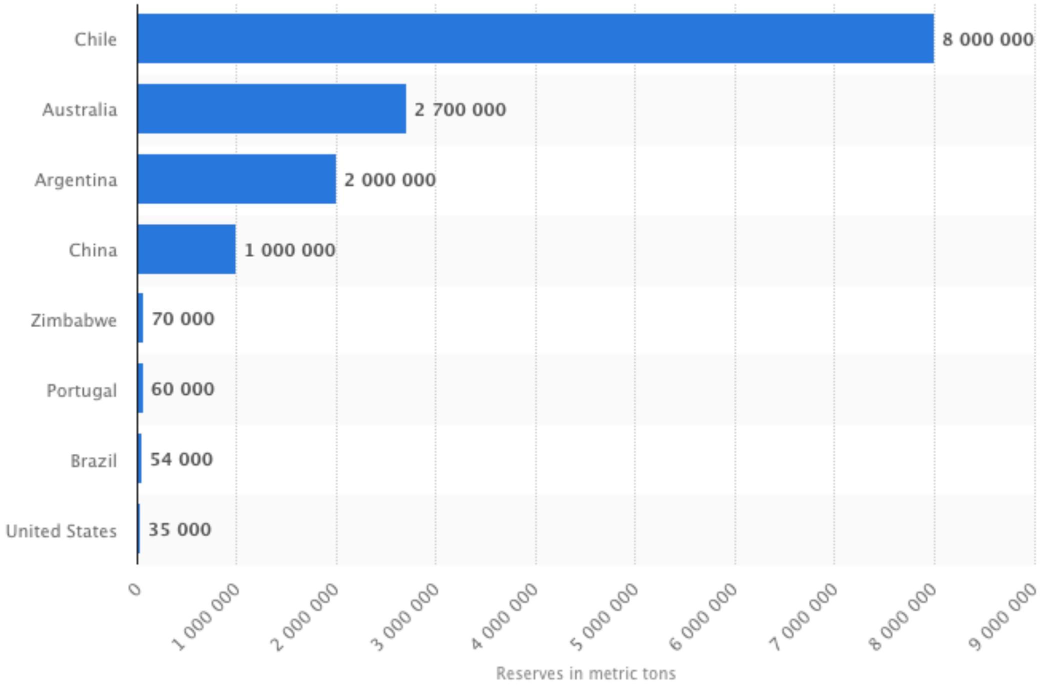
Abundant Sodium in the U.S. is needed to accelerate energy transition

1) Electrical Grid

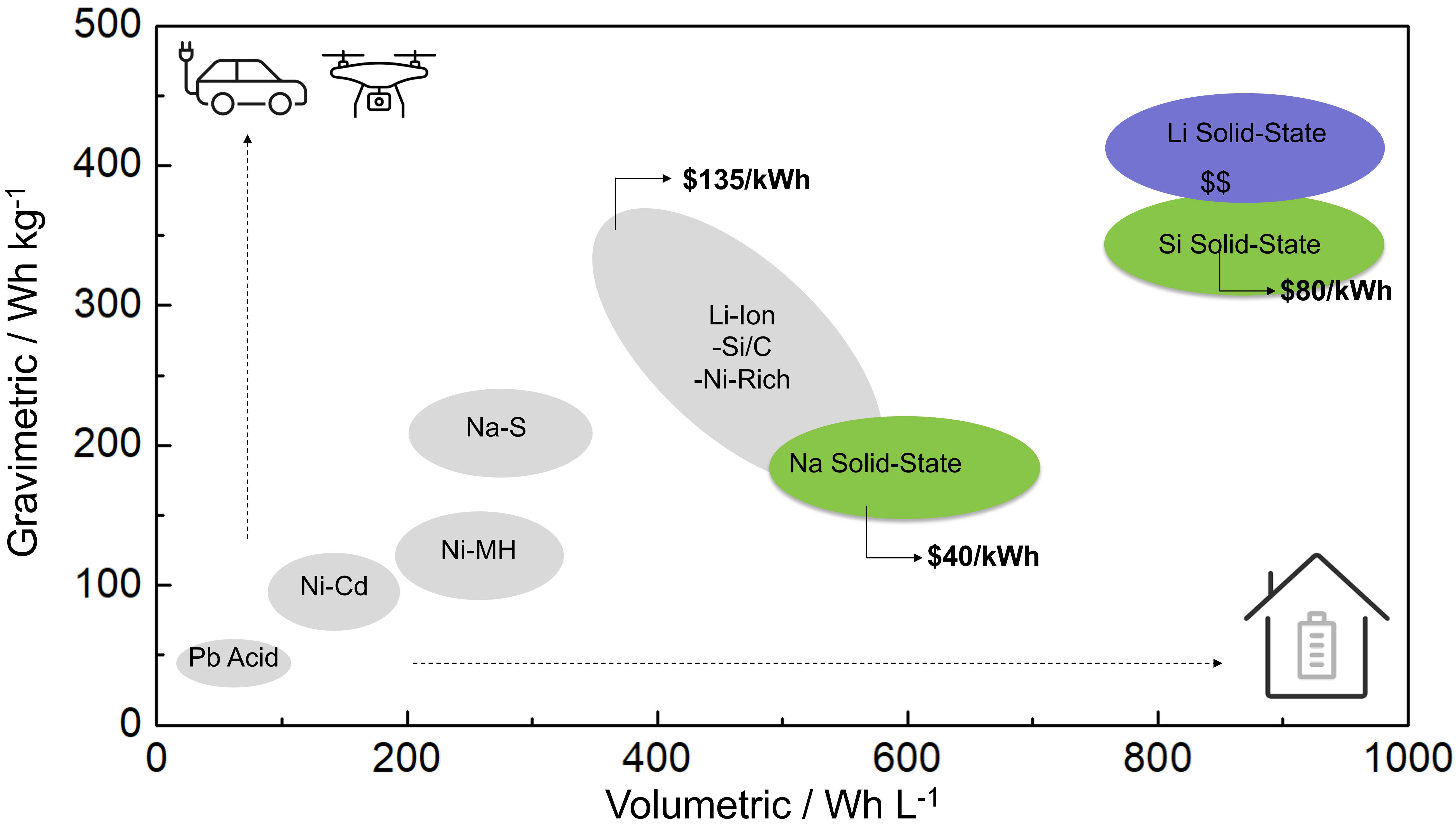
- Per capita - 12000 kWh / year
- 400 tera-watt hours if just 10% storage
  → <u>60 million tons of Li Needed</u>

2) Vehicles

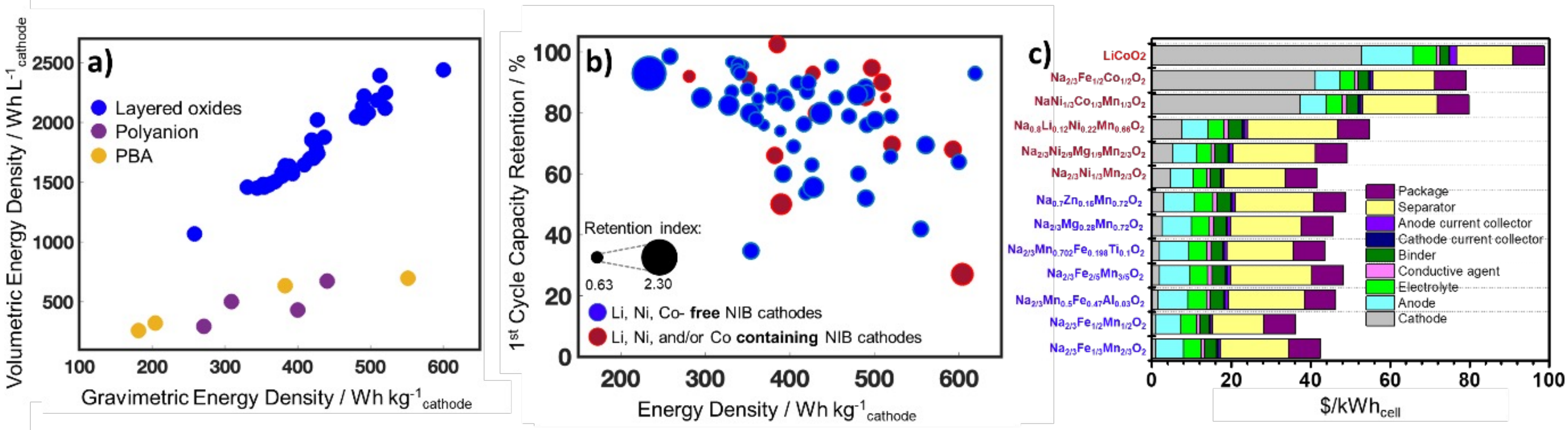
- 17 million / year, if all EVs
- 0.85 tera-watt hours
  → <u>0.13 million tons of Li Needed</u>



Energy Density Road Map



Avenues to Increase the Energy Density and Lifetime of NIBs



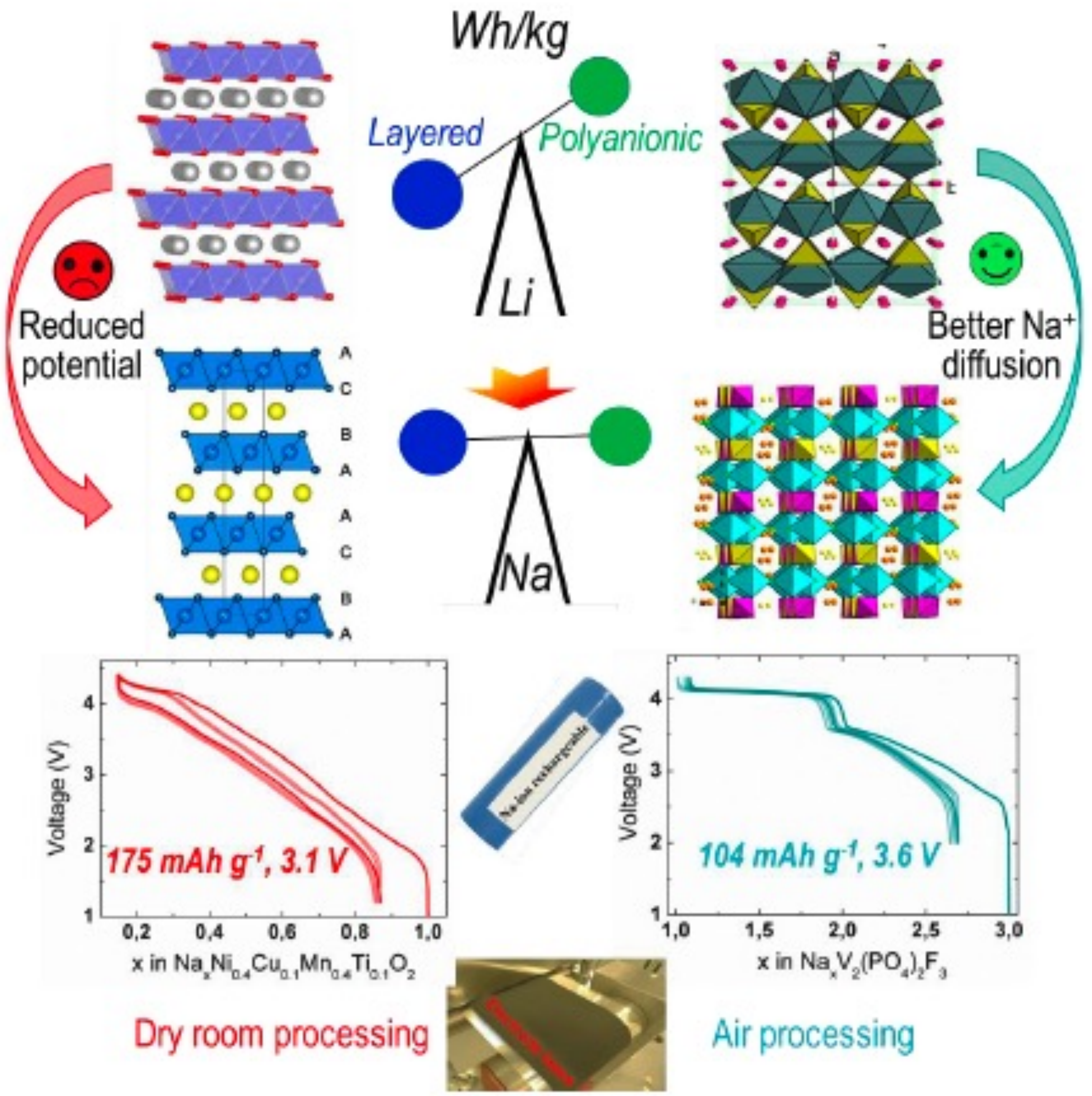
Cathodes:

- Ni, Co-free
- understand the reaction mechanisms
- Interface interactions

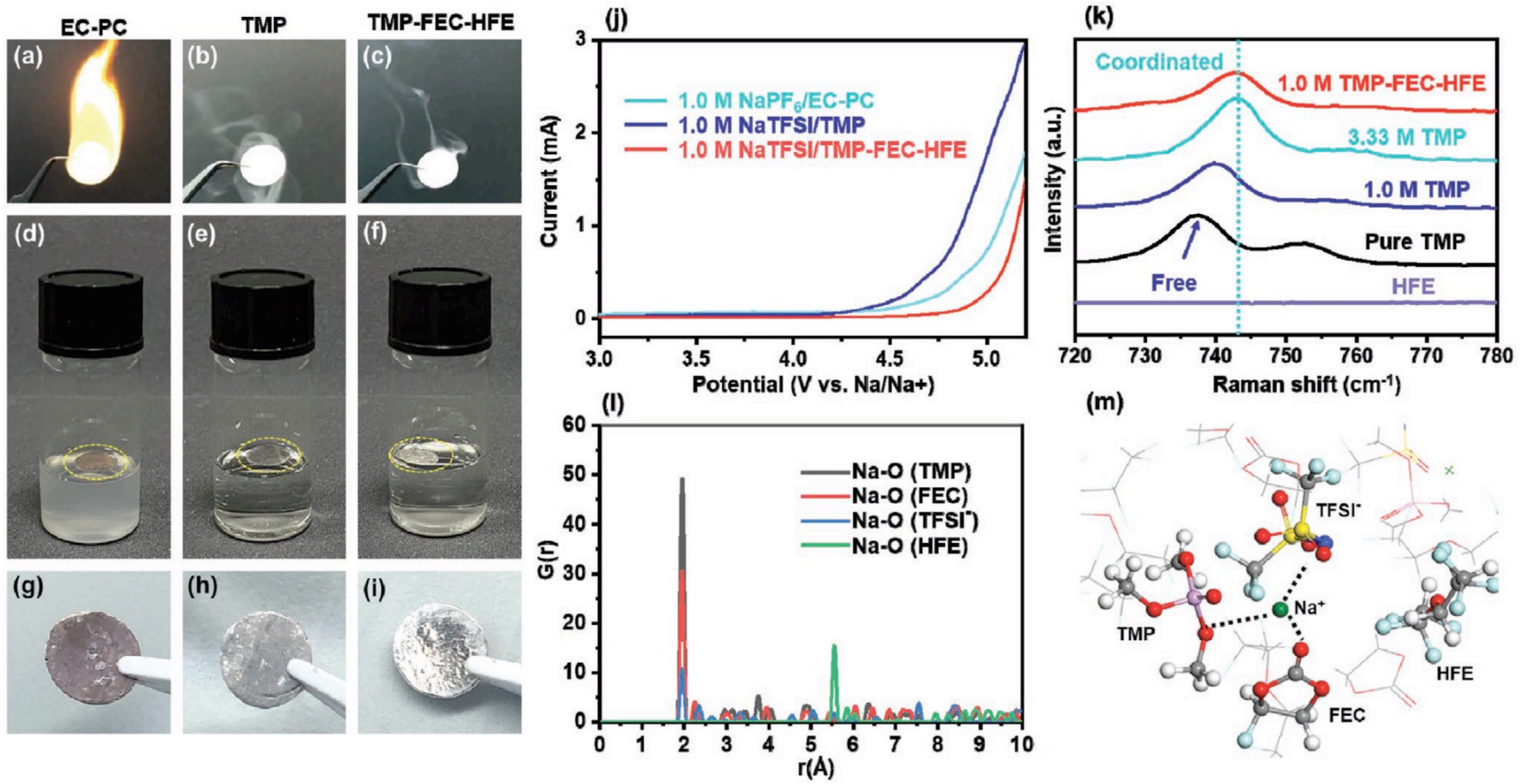
Anodes:

- Electrolyte optimization
- Interface interactions
- Carbon-based materials

H. S. Hirsh et al., Adv. Energy Mater., 10, 1–8 (2020).



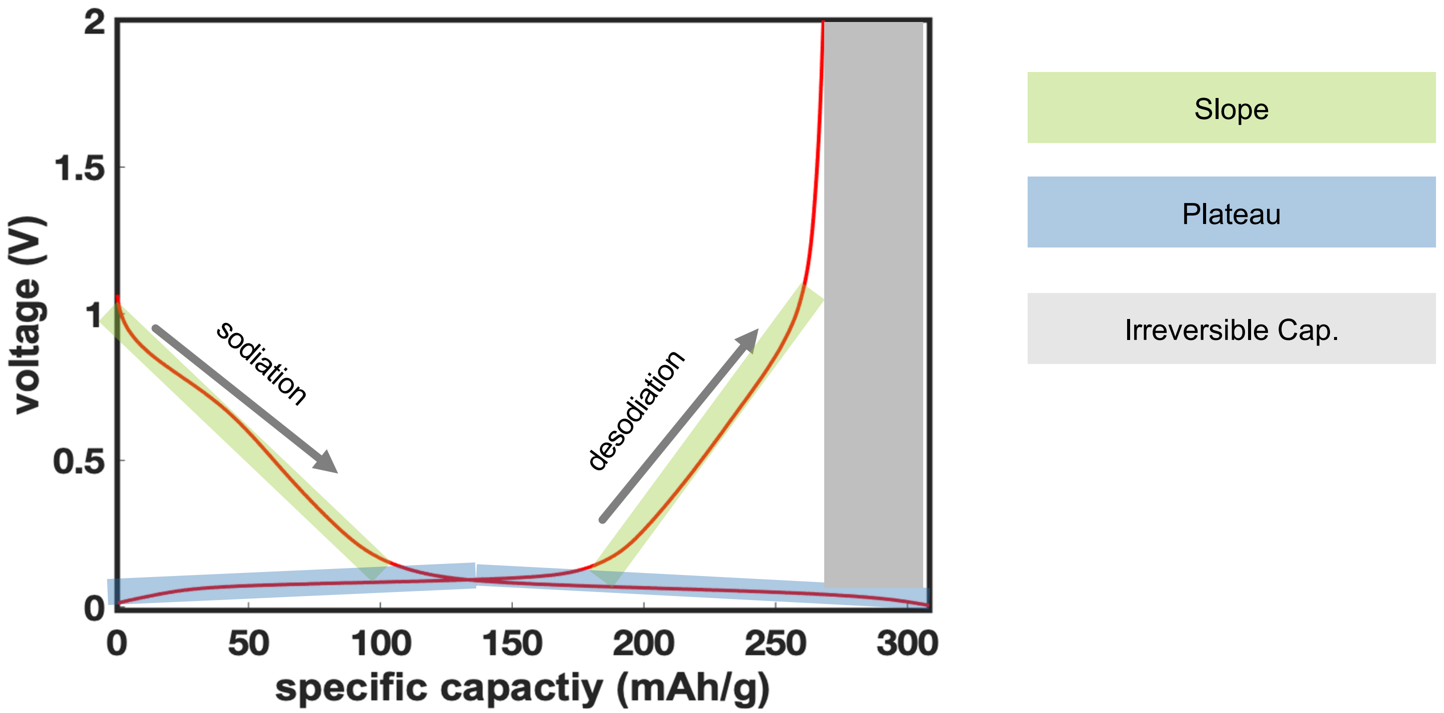
JMT, Joule 2020



Fluoride-Rich Solid-Electrolyte-Interface Enabling Stable Sodium Metal Batteries in High-Safe Electrolytes
https://doi.org/10.1002/adfm.202103522, Advanced Functional Materials Volume31, Issue30 (2021)

Hard Carbon (HC)-Anode Material for NIBs

	Na Metal	HC	Graphite	TiO_2	Sn
Low V	√	√	ok	ok	ok
High cap.	√	√	x	ok	√
High ret.	x	√	√	x	ok
High CE	x	(√)	√	ok	ok



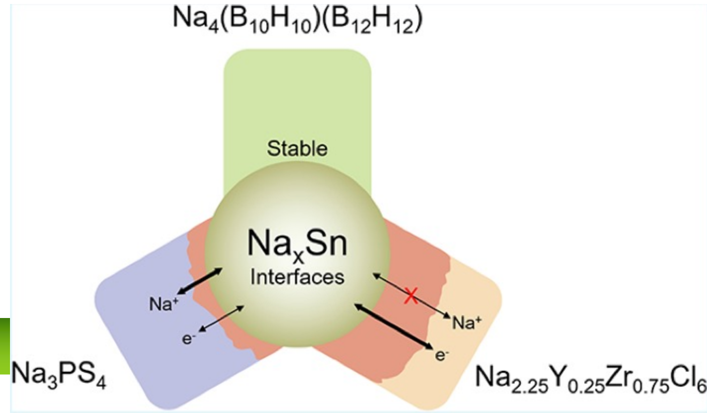
HC is the most promising anode material for liquid NIB full cells

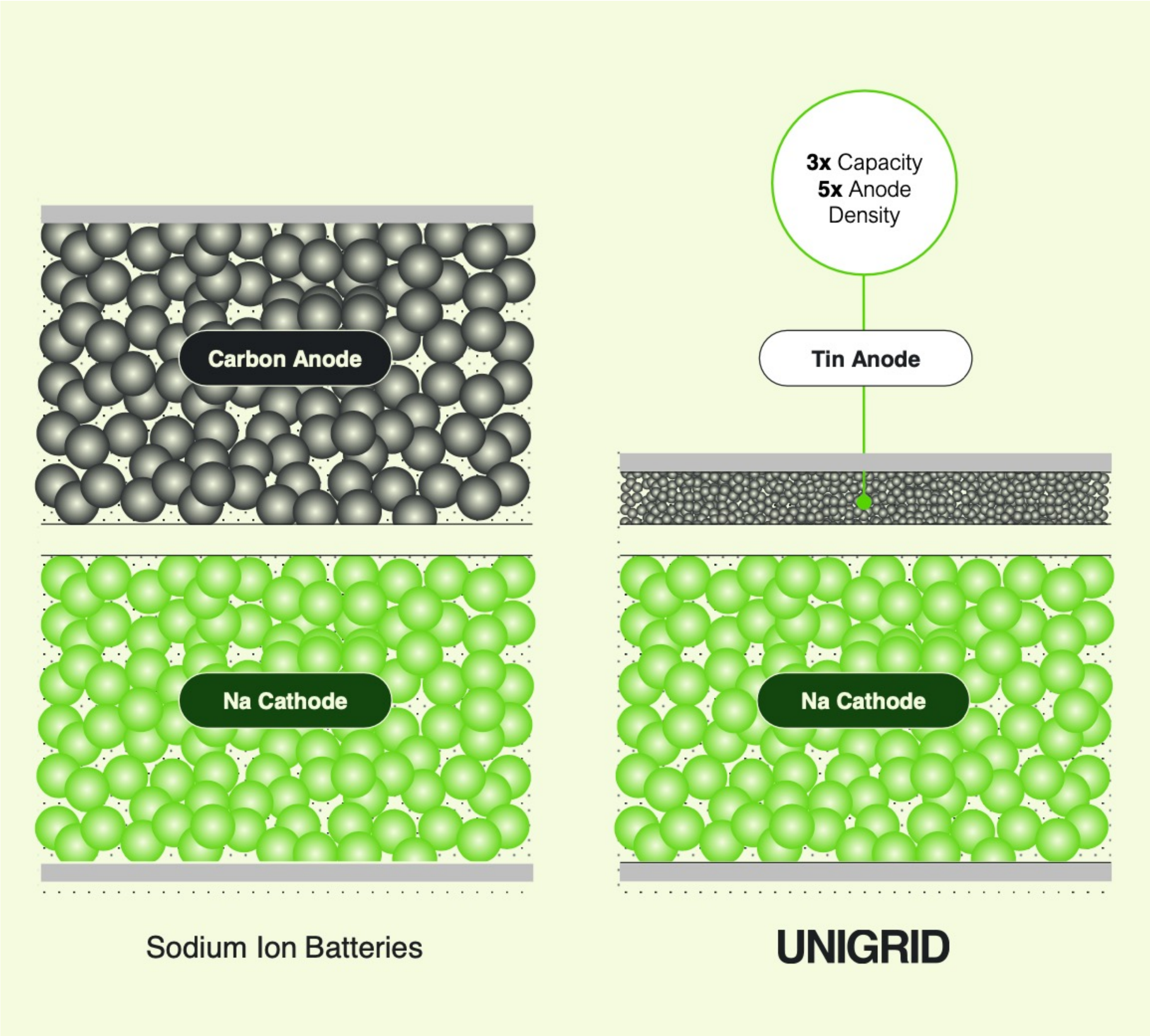
- low voltage → near zero
- high capacity → ~300 mAh/g
- good retention

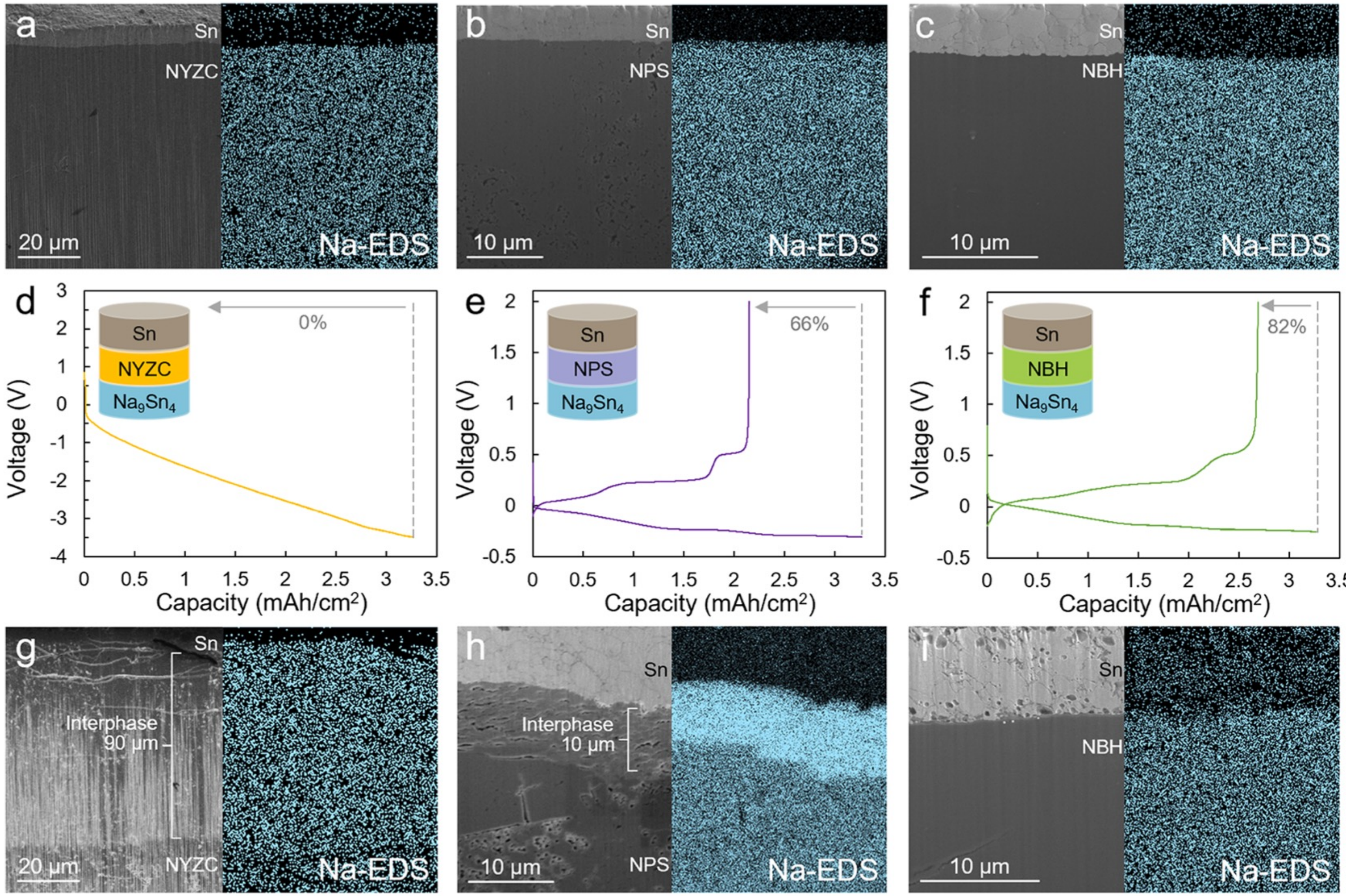
Problems with HC

- low first CE
  - Na trapped in bulk
  - Na used in SEI formation
- poor rate capability
  - slow plateau (de)sodiation processes
  - resistance from SEI

Sn Based Anode Material for NIBs





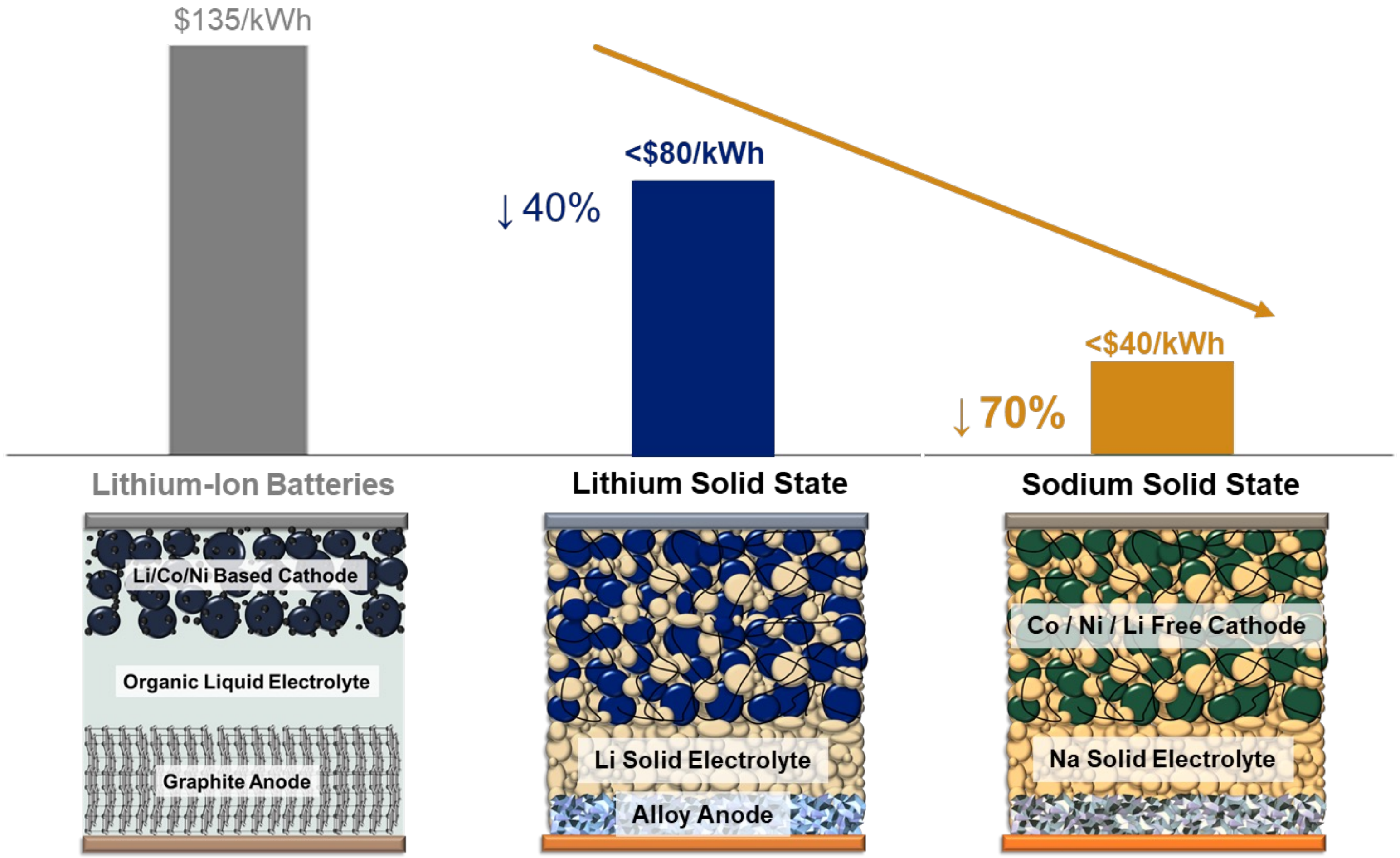


G. Deysher … and Y.S. Meng, ACS Appl. Mater. Interfaces 2022, 14, 47706–47715

Data from ANL BatPac

*Prevailing Li_2S based SSE projections

LIB	Unit Price / kg	Material Cost $/kWh	**Li-ASSB**	Unit Price / kg	Material Cost $/kWh	**Na-ASSB**	Unit Price / kg	Material Cost $/kWh
Graphite	12.50	10.23	Li-Si Alloy	2.10	0.19	Na-Sn Alloy	16.10	11.50
Electrolyte	12.50	10.13	SSE-Sep	*50.00	12.06	SSE-Sep	0.28	0.09
Separator	160.00	24.00	SSE-Cat	*50.00	14.71	SSE-Cat	1.73	0.49
Aluminum	7.41	2.09	Aluminum	7.41	0.98	Aluminum	7.41	2.38
Copper	13.45	12.55	Copper	13.45	5.90	Copper	Not Required	
Cathode	20.00	30.03	Cathode	17.00	25.01	Cathode	1.51	4.89
Manufacturing	35% of Overall Costs		Manufacturing	25% of Overall Costs		Manufacturing	50% of Overall Costs	
Total	**$135/kWh**		Total	**<$80/kWh**		Total	**<$40/kWh (Target)**	



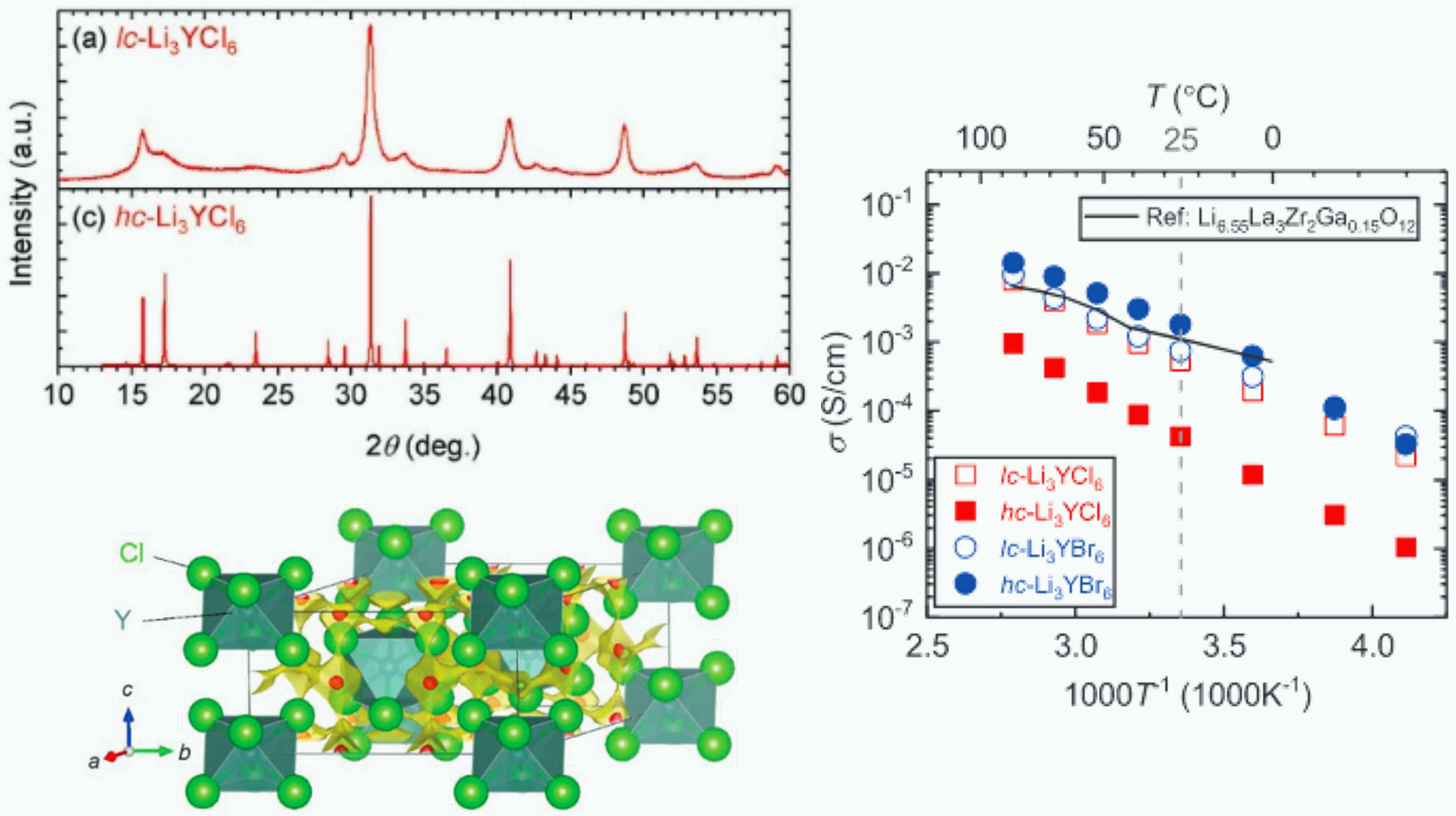
BATTERIES

CATL Reveals Sodium-Ion Battery With 160 Wh/kg Energy Density

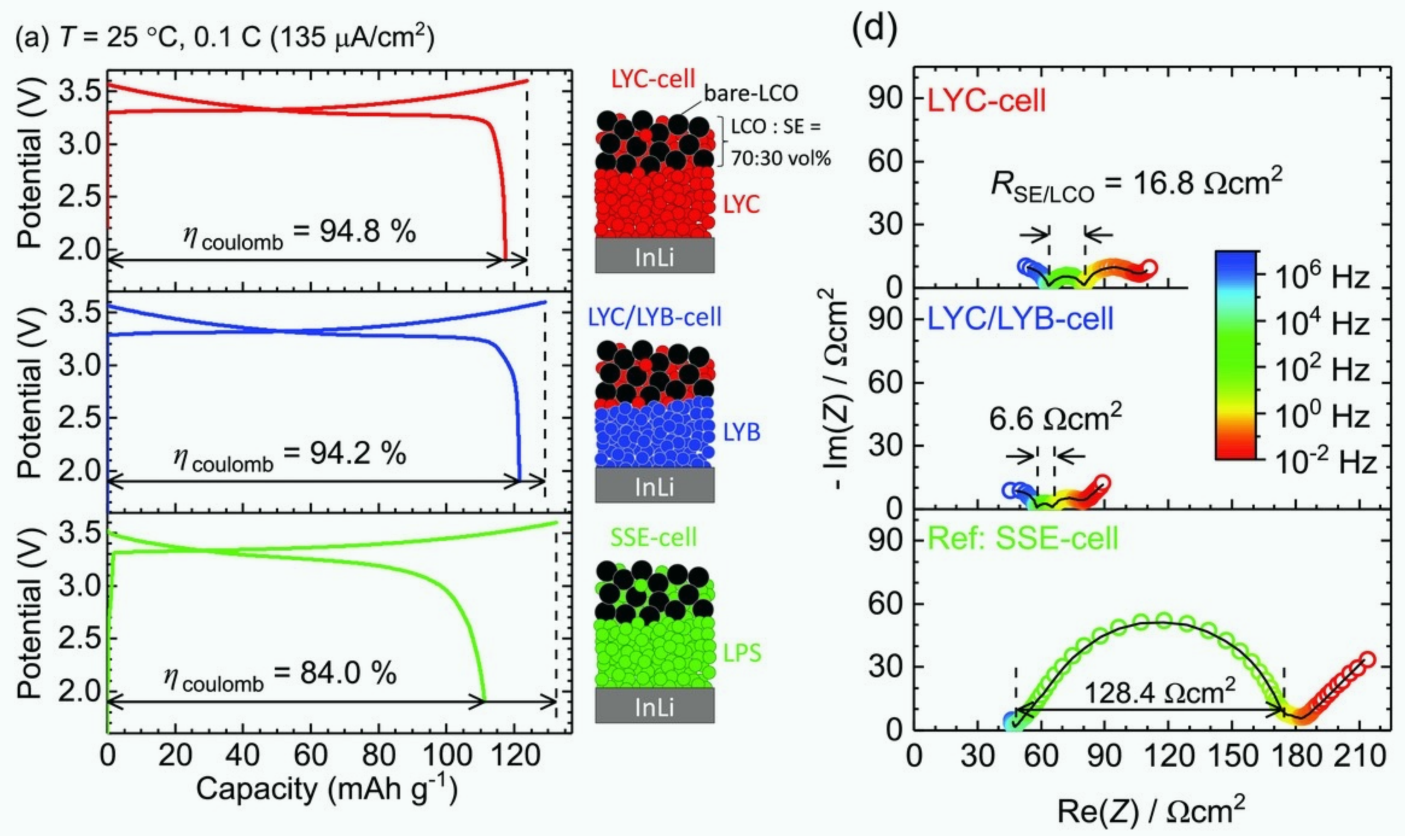
According to Chinese media sources, we can expect the first-generation cells to cost $77 per kWh. With volume production, that figure could drop to below $40 per kWh.

First Demonstration of Li_3YCl_6 in 2018

Crystallinity & Conductivity



Electrochemical Performance

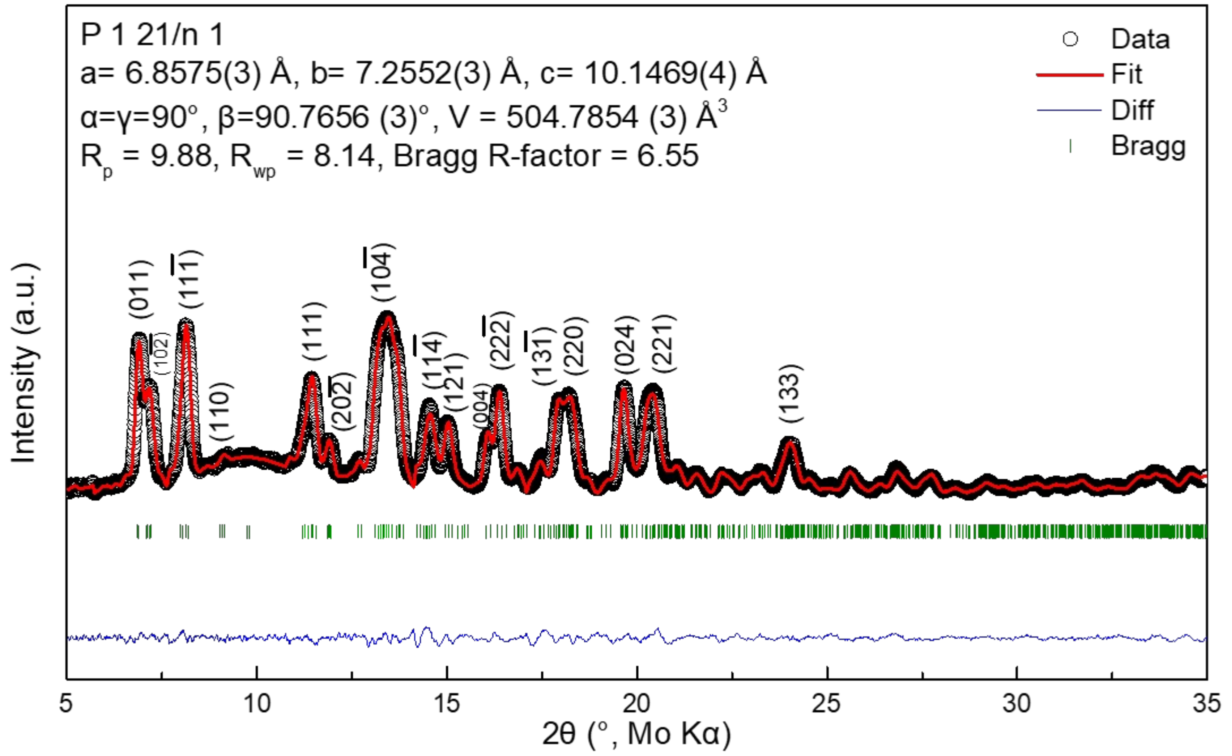


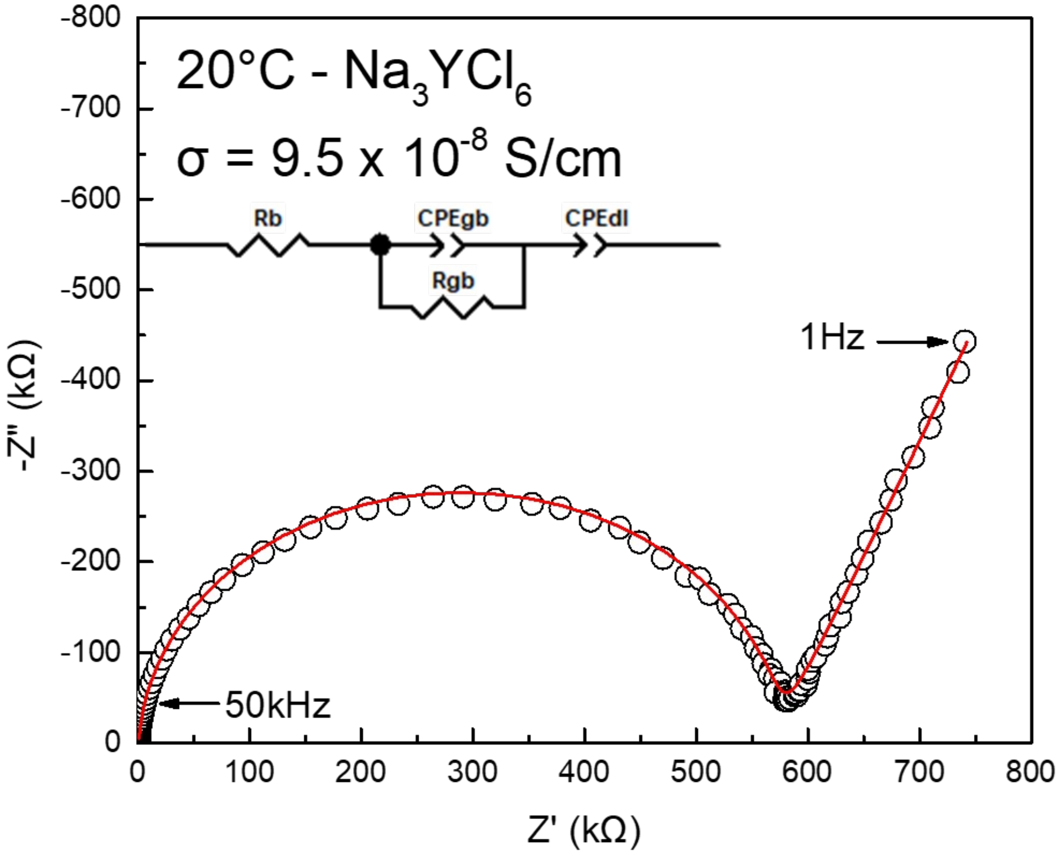
- Reduced crystallinity after ball milling → More isotropic Li^+ diffusion
- Highly conductive LYC → improved ICE with bare-LCO → low interfacial impedance

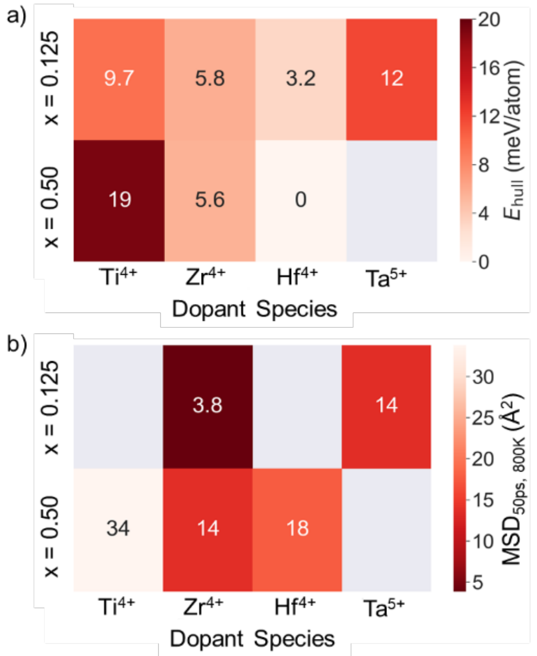
1. Asano, T. et al. Solid Halide Electrolytes with High Lithium-Ion Conductivity for Application in 4 V Class Bulk-Type All-Solid-State Batteries. Advanced Materials (2018).

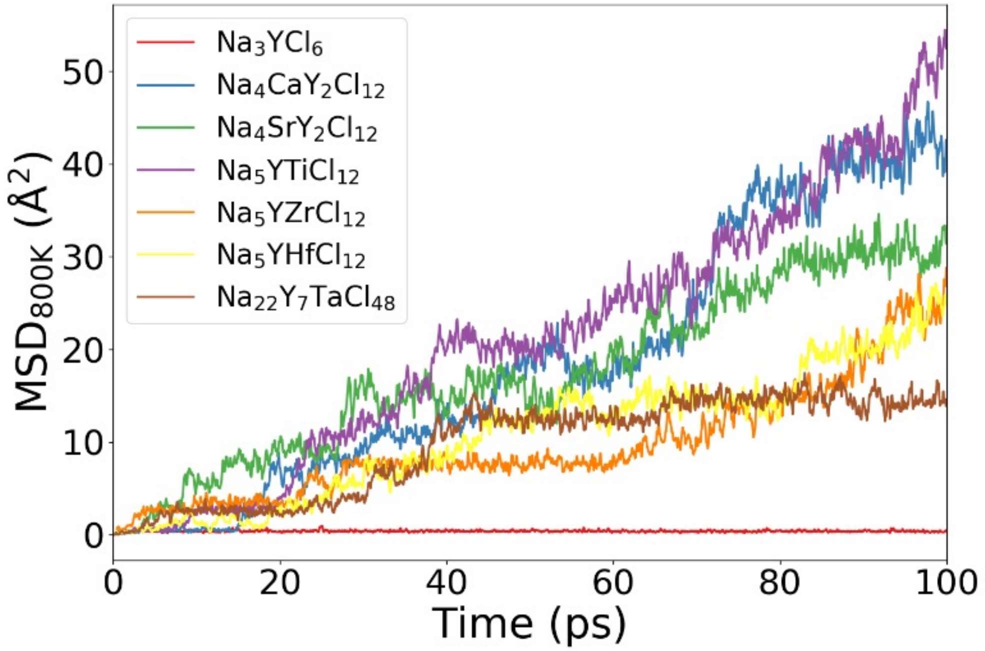
Na-ion Conducting Halides: Na_3YCl_6

Dr. Erik Wu
UNIGRID CTO









- Aliovalent dopant → MSD increases
- Zr^{4+} selected (phase stability)
  → $Na_{3-x}Y_{1-x}\mathbf{Zr}_xCl_6$ (NYZCx)

Wu, E. et al., Nat Commun. 12, 1256 (2021).

Aliovalent Doping of NYC: $Na_{3-x}Y_{1-x}Zr_xCl_6$

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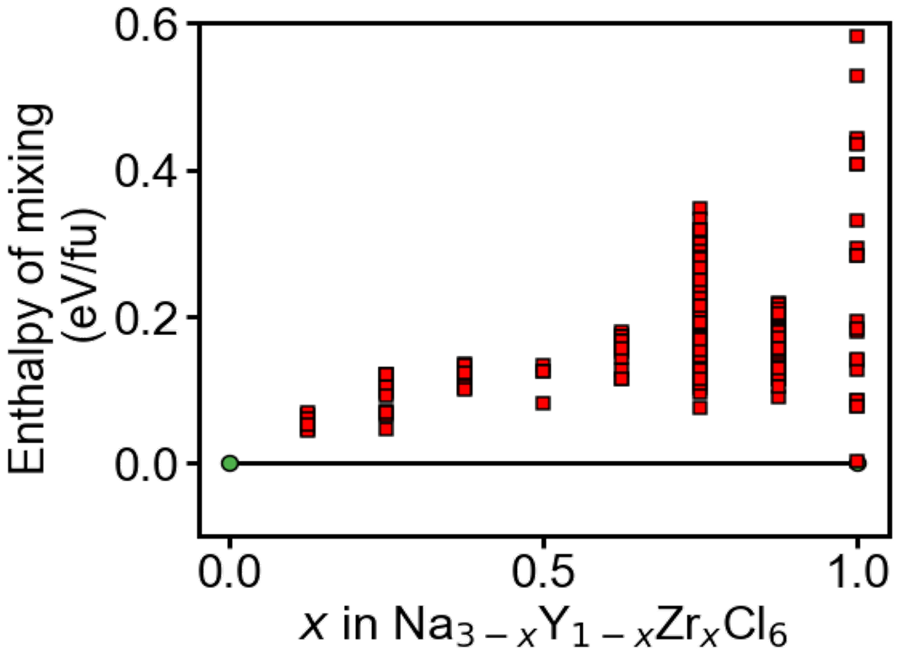
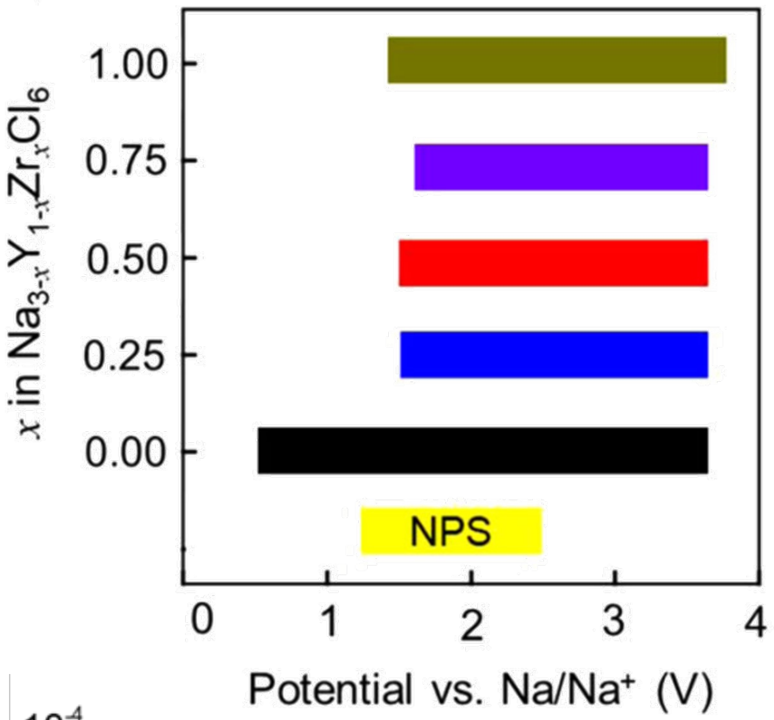
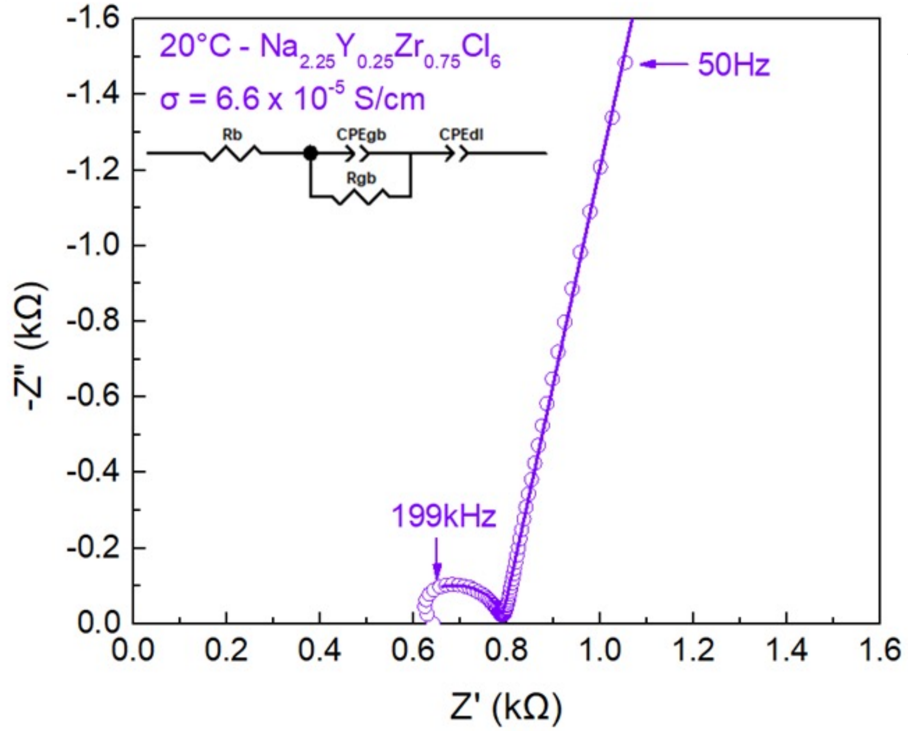
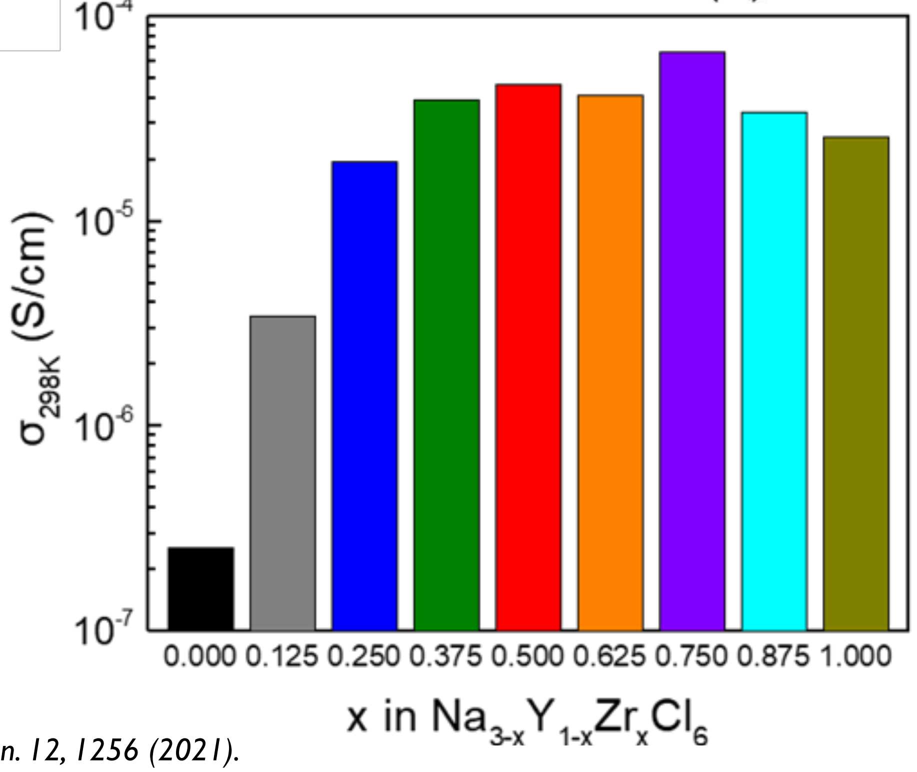
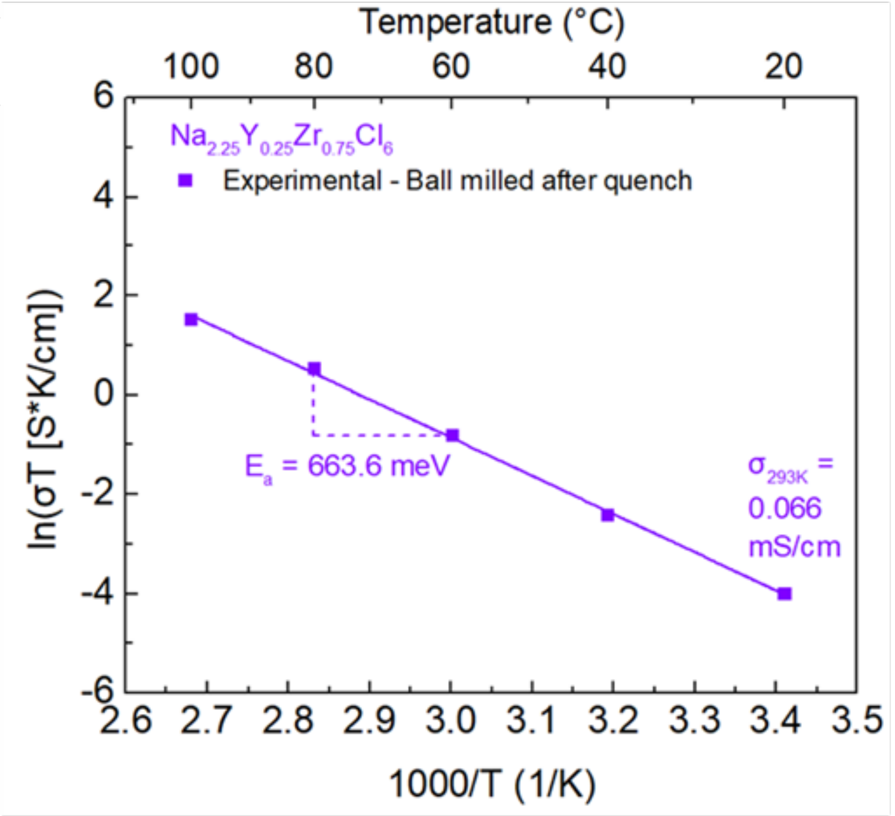




- Zr^{4+} shows **promising phase stability**
- Substitution: **drastic conductivity increase**
- $\sigma_{NYZC0.75}$ = 0.066 mS/cm at RT,
- E_a = 0.66 eV

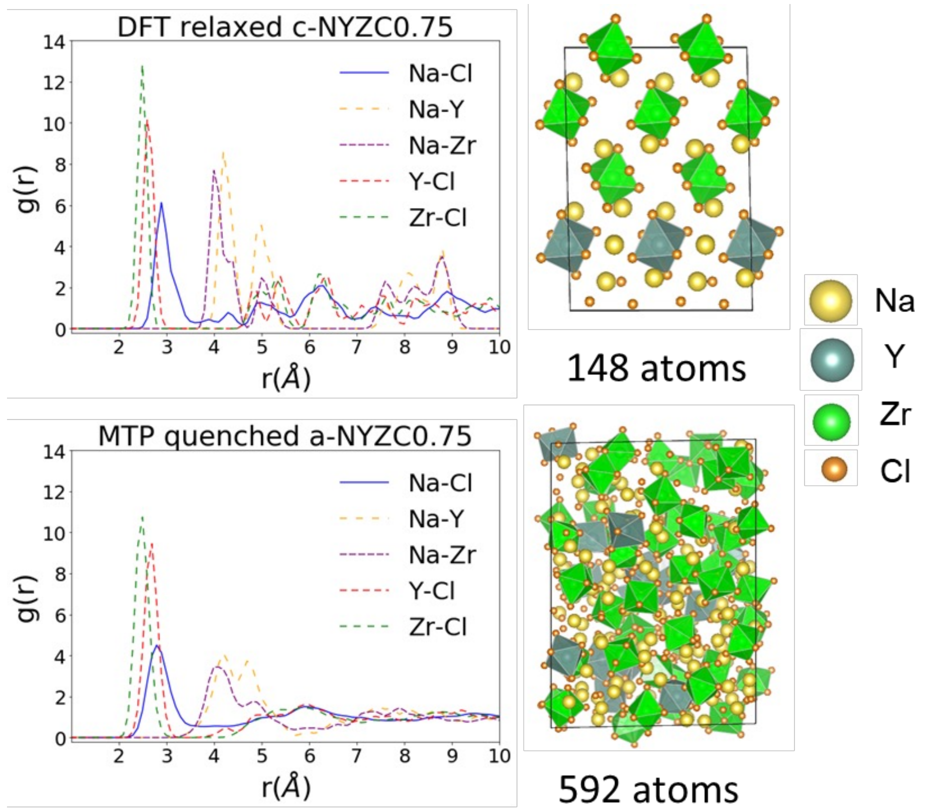


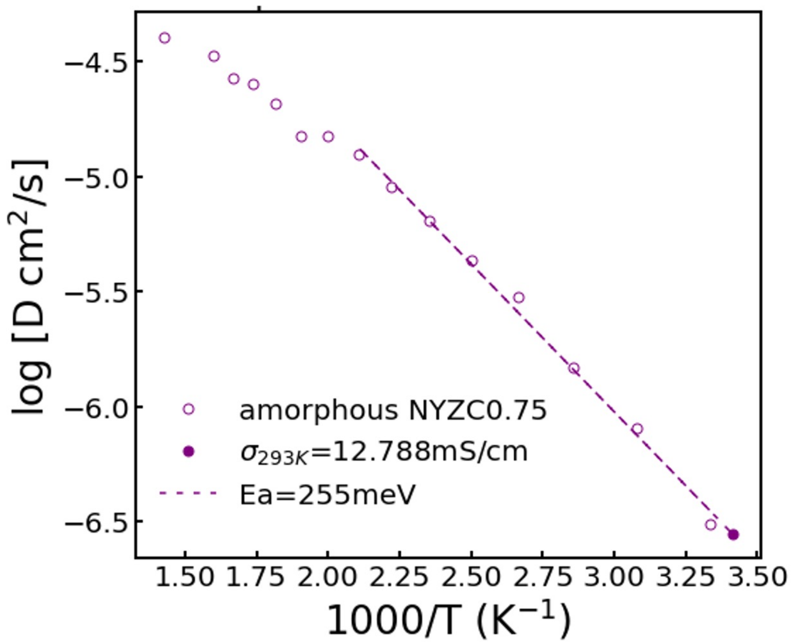


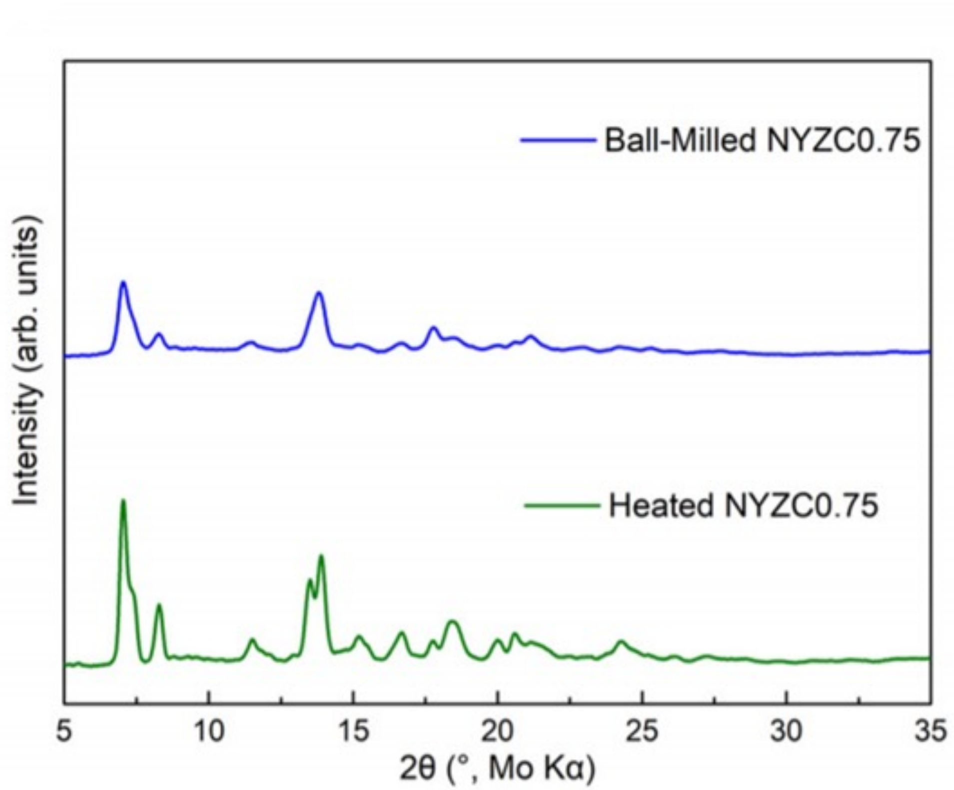


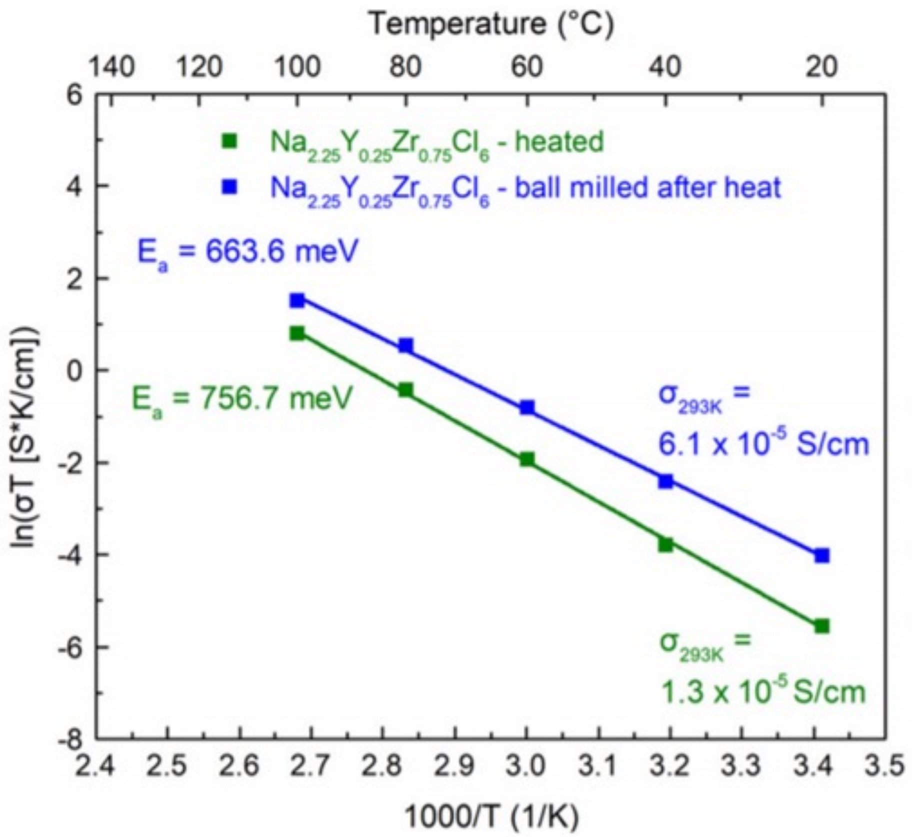
Wu, E. et al., *Nat Commun.* 12, 1256 (2021).

NYZC0.75: Influence of Crystallinity









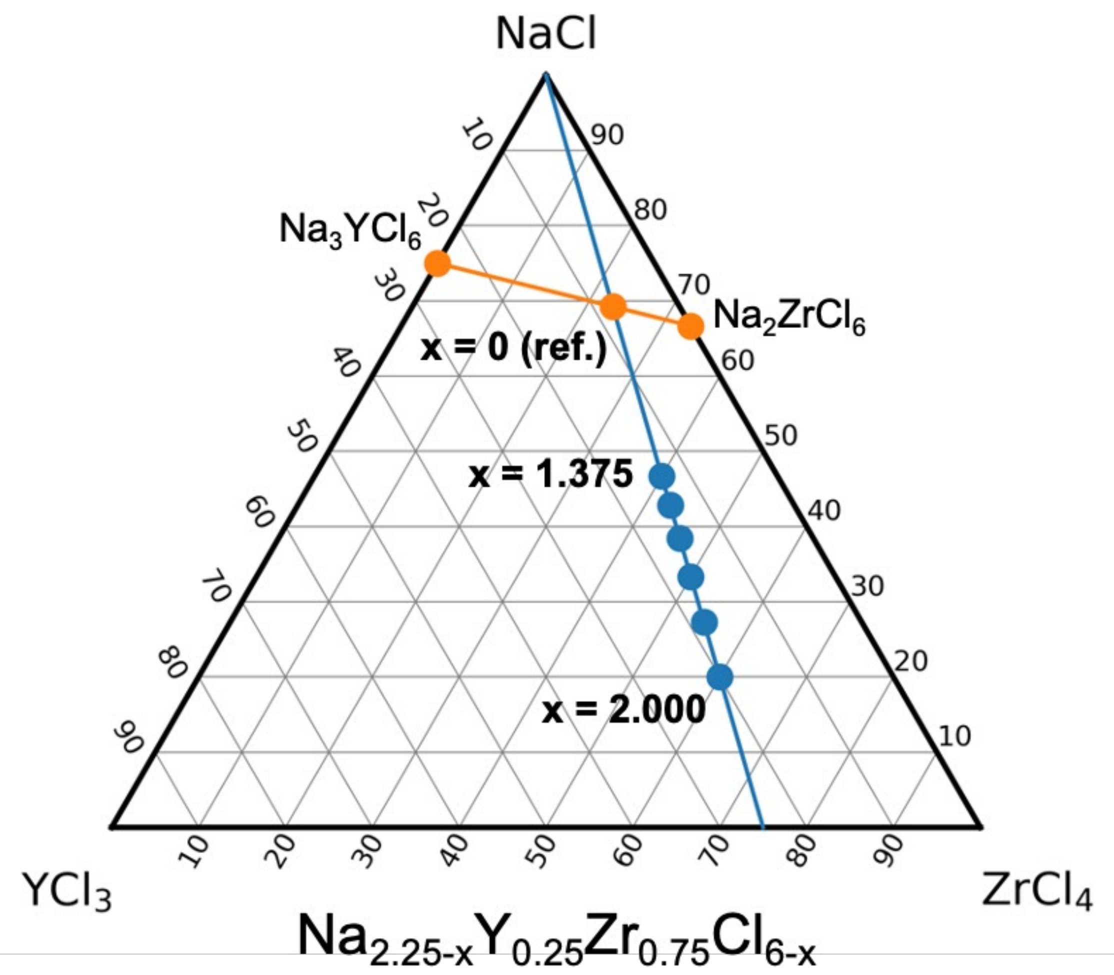
- Computation suggests amorphous NYZC has higher ionic conductivity
- Ball milling efficient at reducing the crystallinity of NYZC0.75
- Ball-milling: $\boldsymbol{\sigma_i}$ x5 at RT

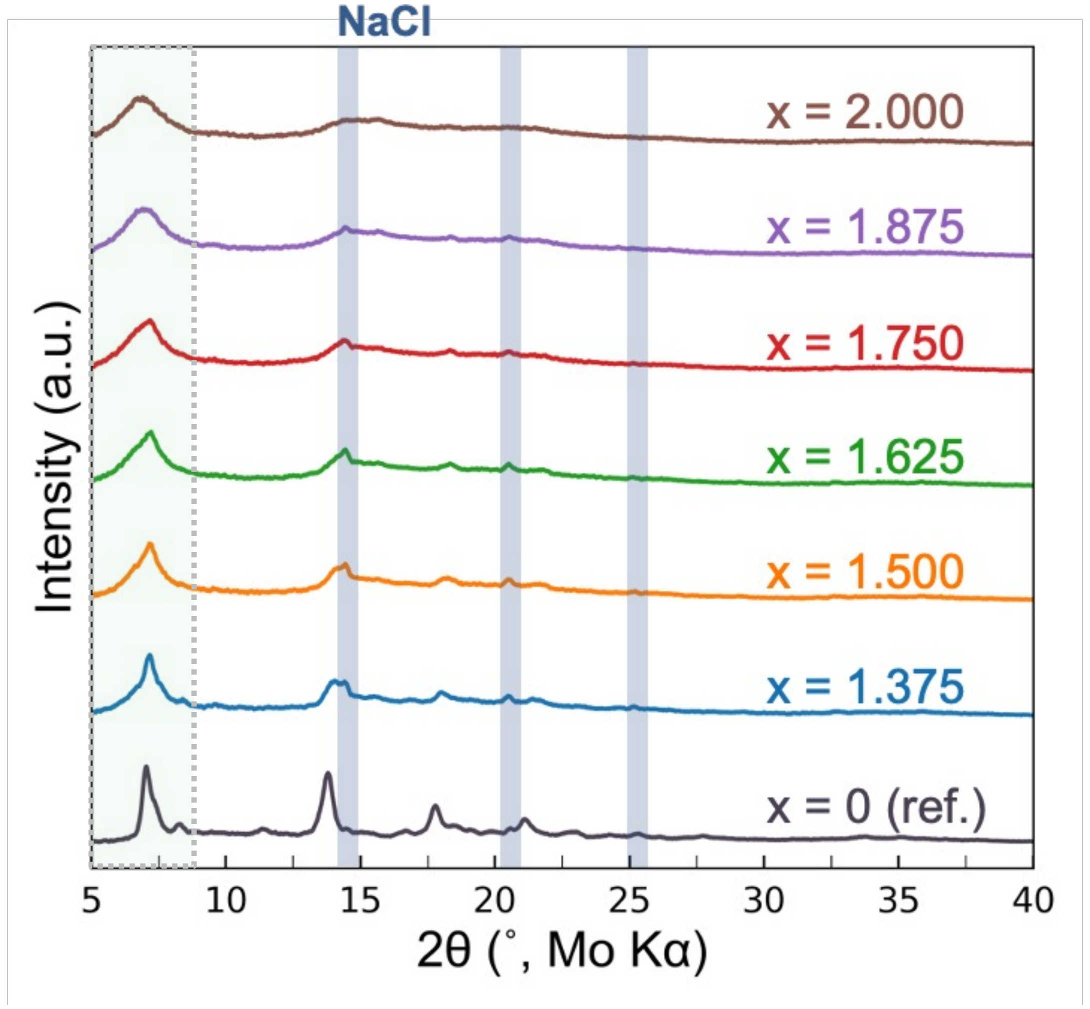
Wu, E. et al., Nat Commun. 12, 1256 (2021).

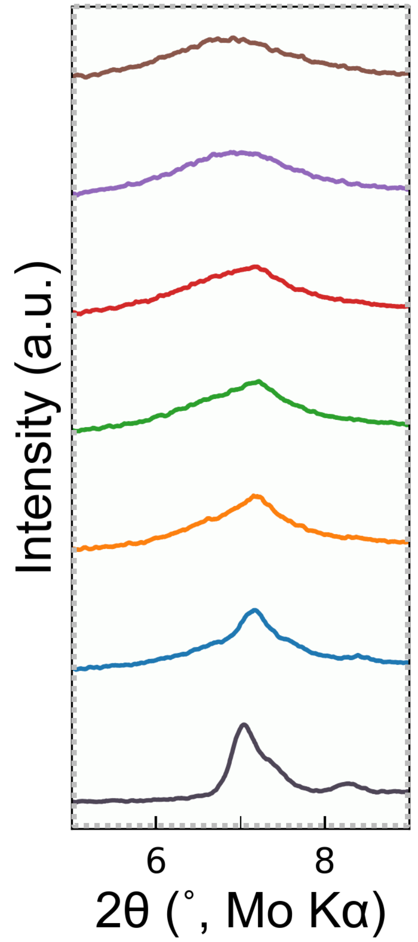
Composition and Crystallinity

Phil Ridley

NaCl-YCl_3-$ZrCl_4$ Compositions





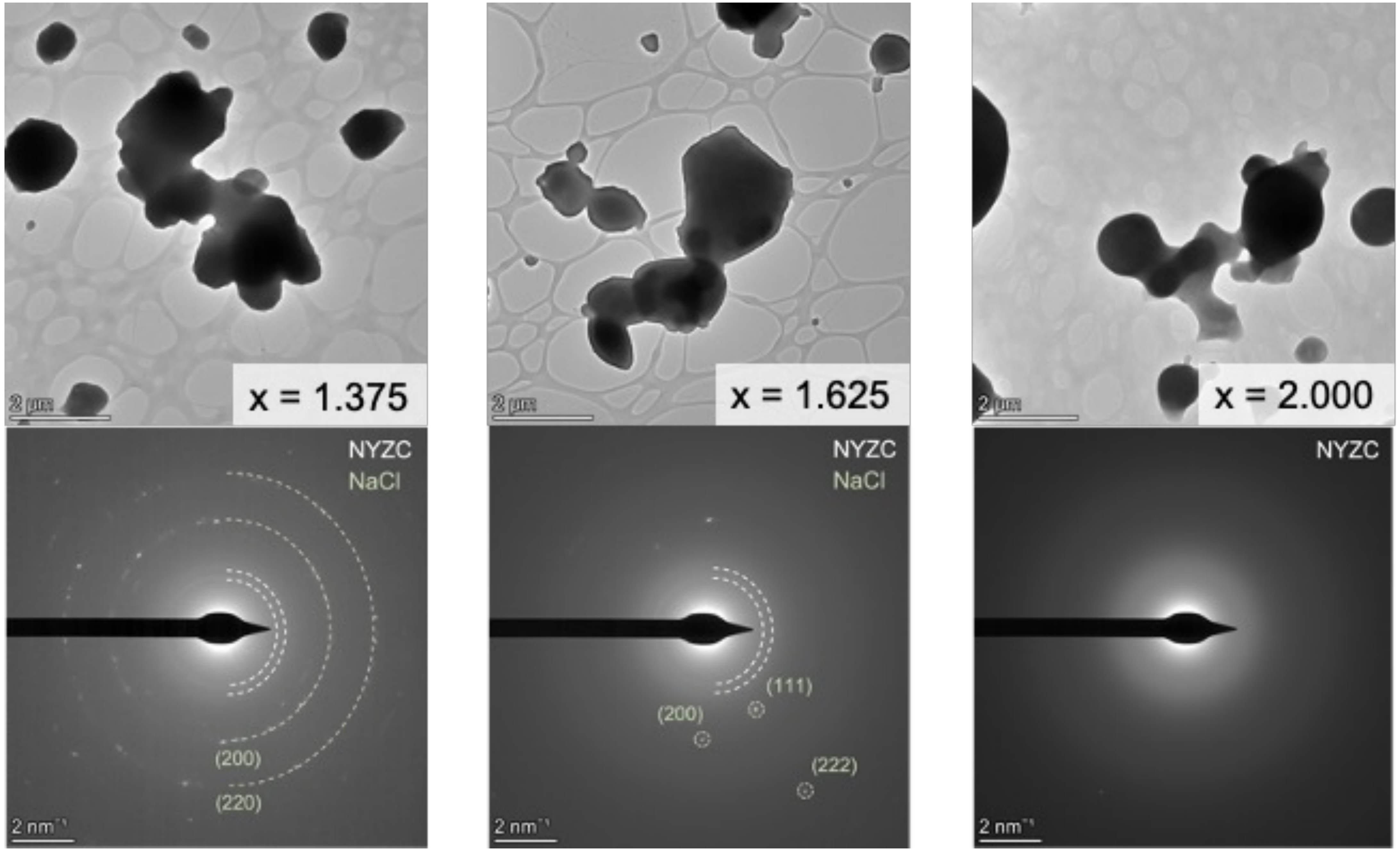


- Low NaCl molar contents → small domains and X-ray amorphous products

Scherrer Equation:

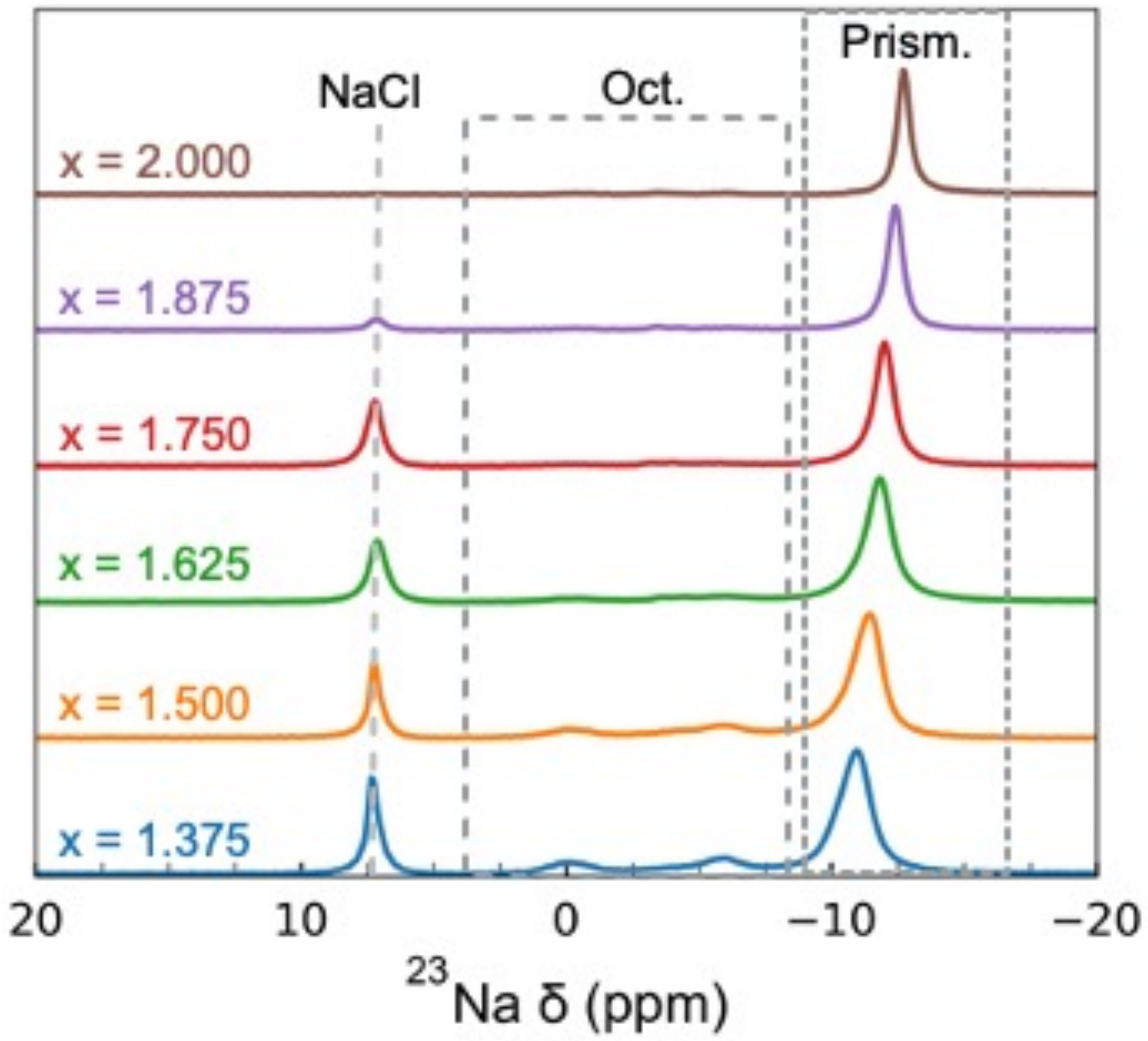
$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

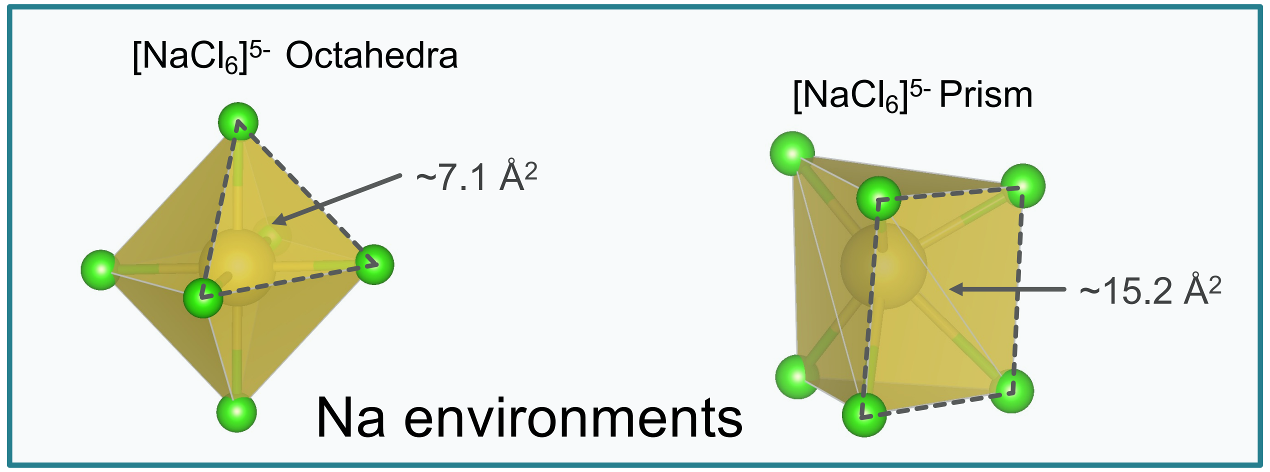
Na-Y-Zr-Cl Solid Electrolyte Microstructure

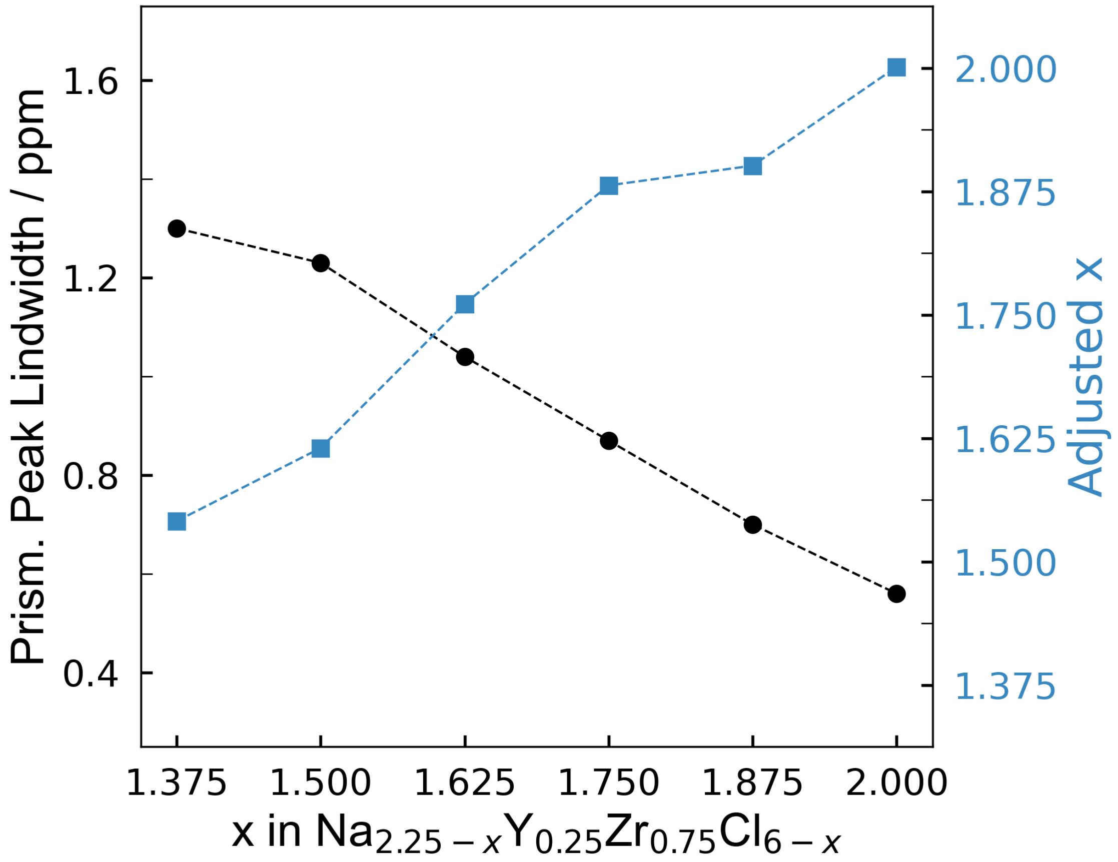


- Particle sizes range from ~ 1 – 3 μm, some < 1 μm
- Samples possess very fine, or nanocrystalline, domains (< 100 nm)

Local Na Environment revealed by SS-NMR



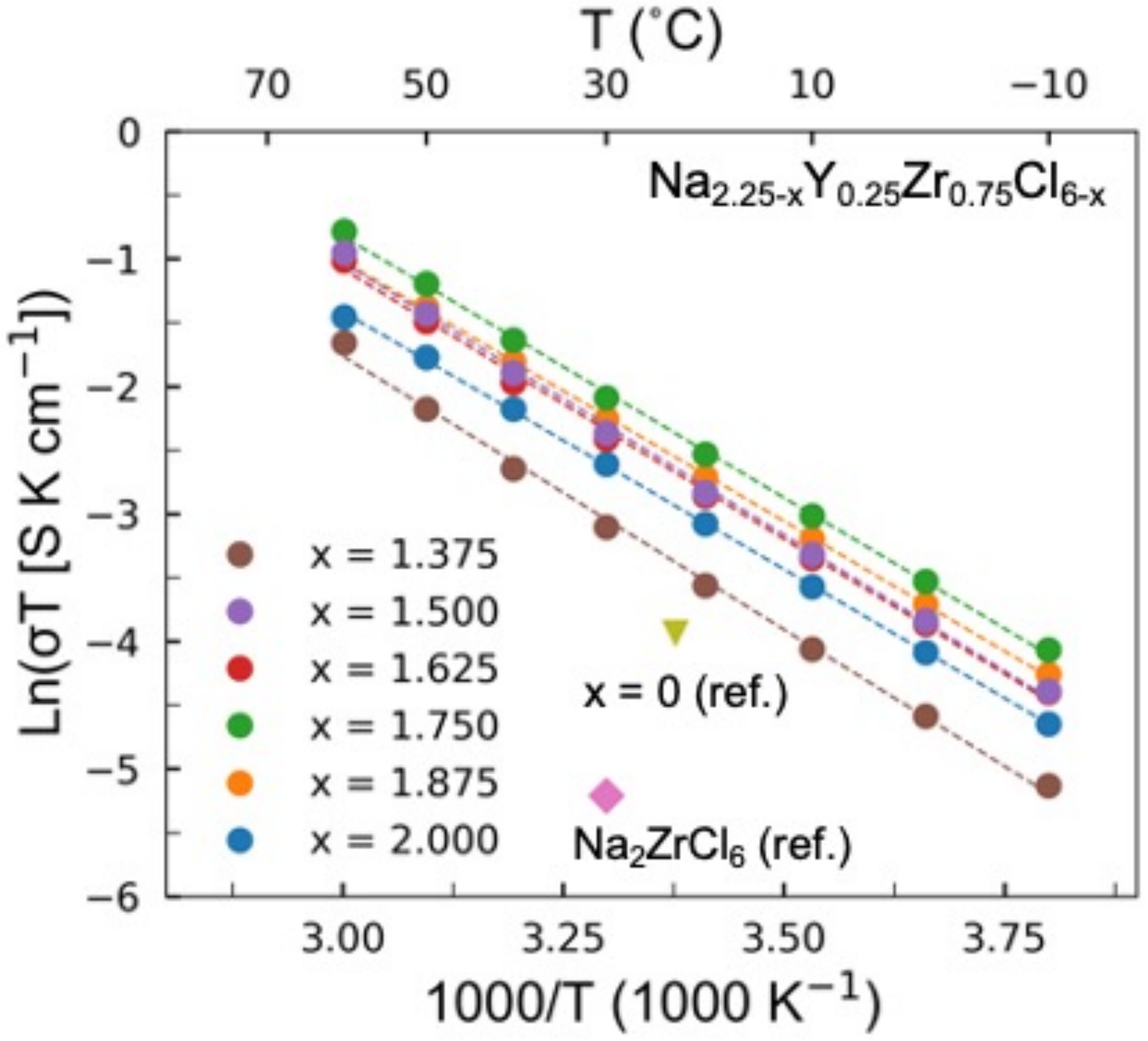


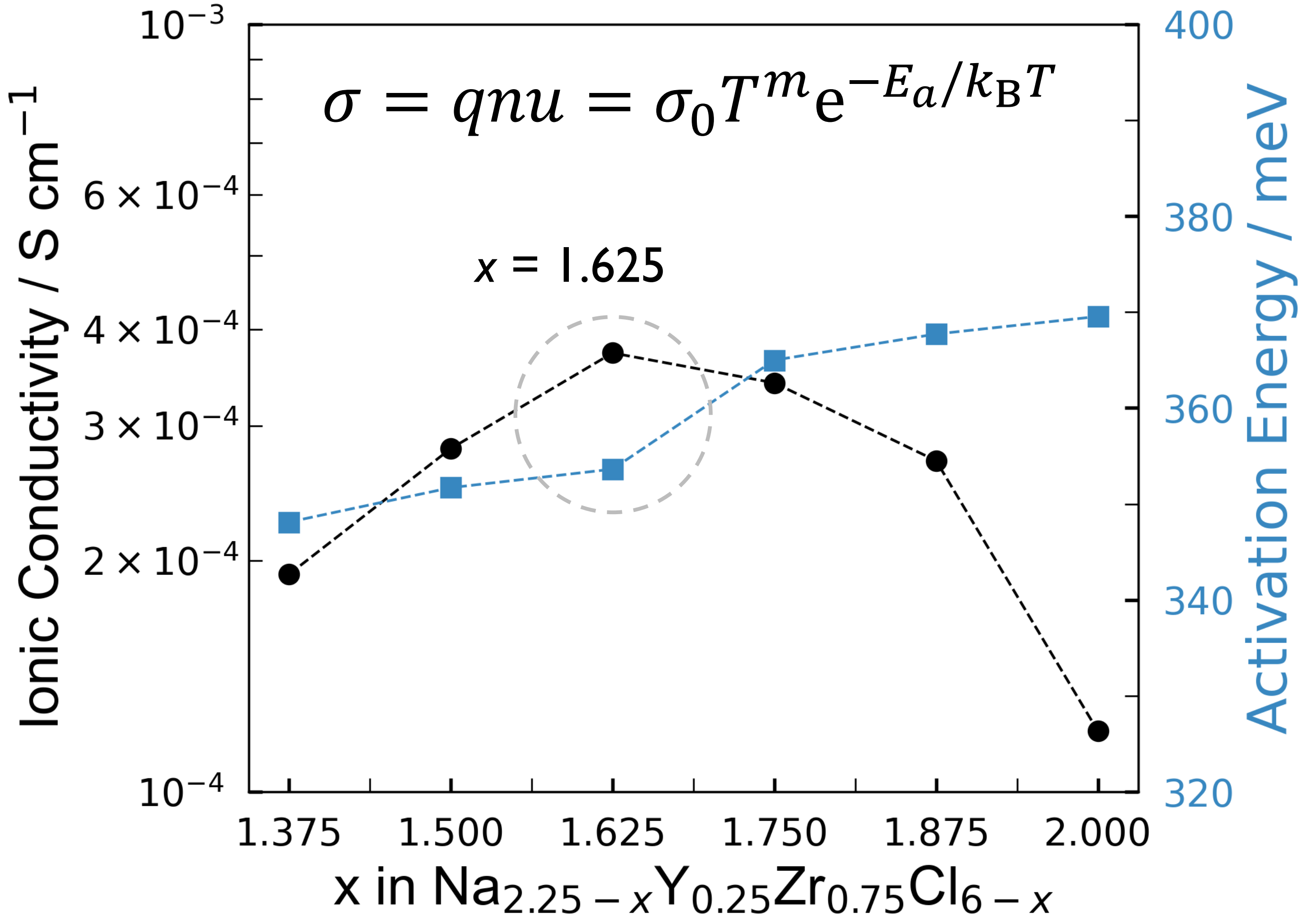


- ➢ Prism. Na environments filled first then oct.
- ➢ fast exchange between prism. environments observed

Sebti, E. *et al. Journal of Materials Chemistry A* **10**, 21565–21578 (2022).

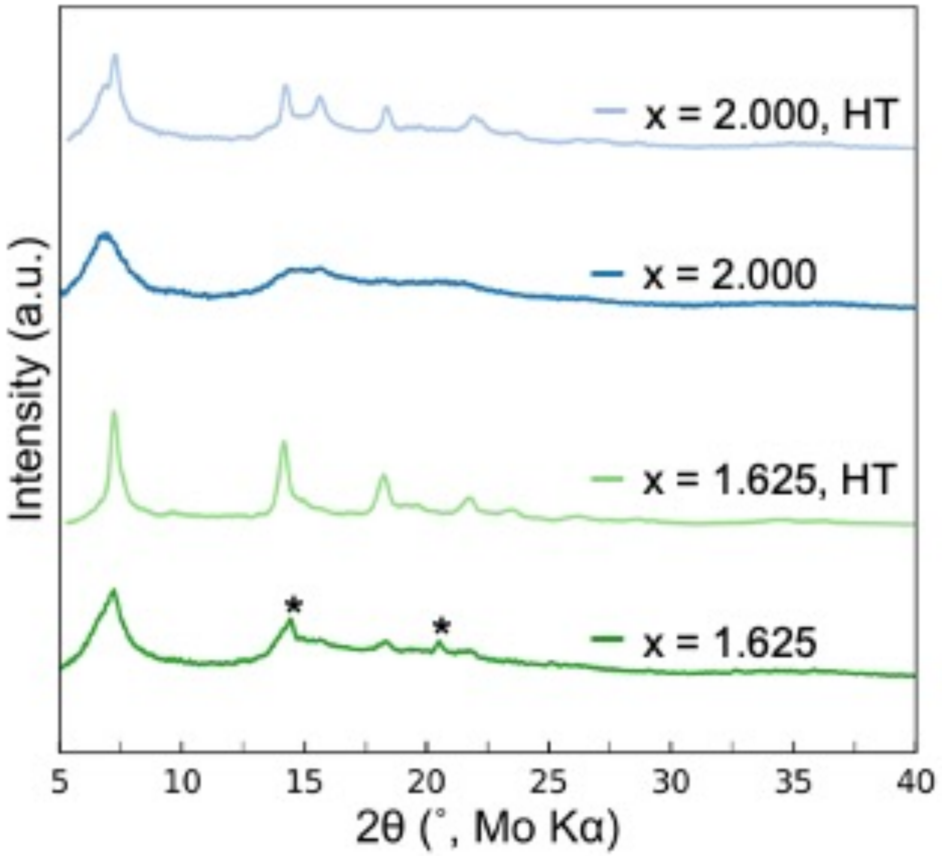
Ionic Conductivity and Activation Energy

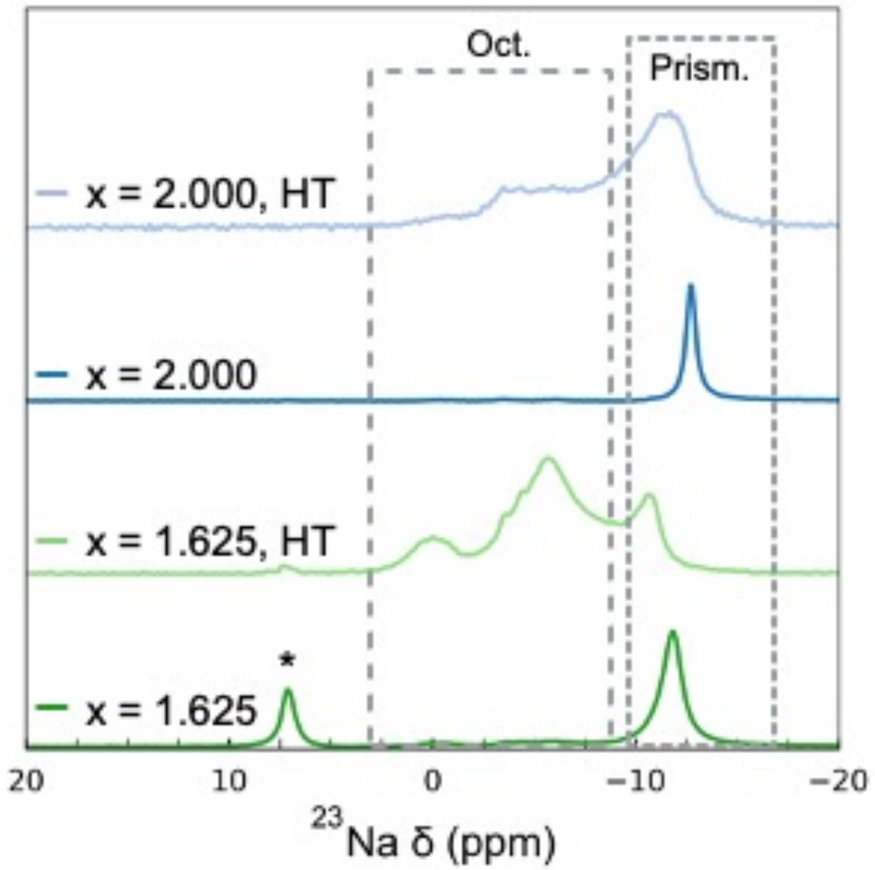


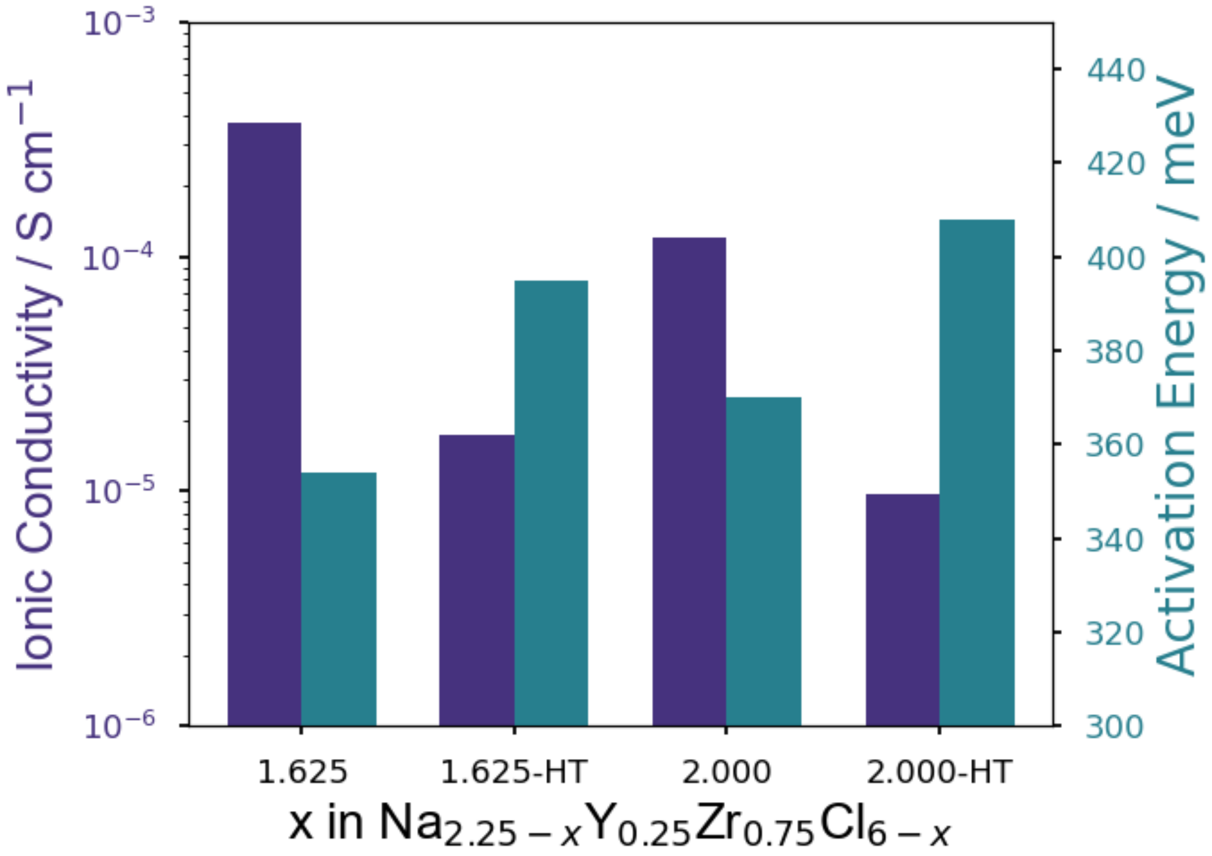


- Low activation energies (340 – 370 meV) observed in all samples
- *x* = 1.625 composition shows optimal balancing between Na^+ per unit volume and their mobility

Crystallinity and Ionic Conductivity



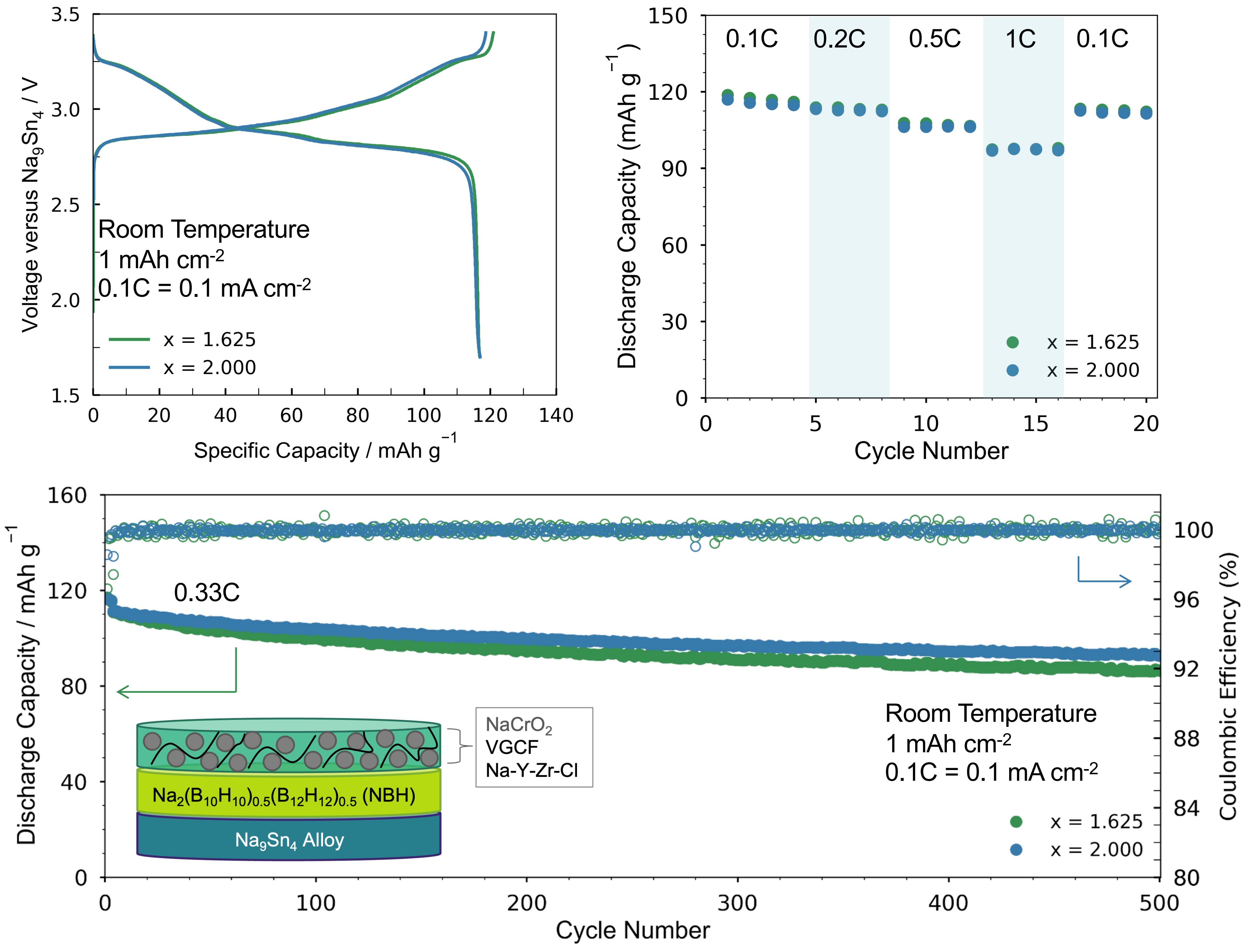




**asterisk corresponds to NaCl*

- ➢ Heat-treatment induced crystallization of both compositions and redistribution of local Na environments
- ➢ Consequently, lower ionic conductivity and increased activation energy

Room Temperature Battery Performance

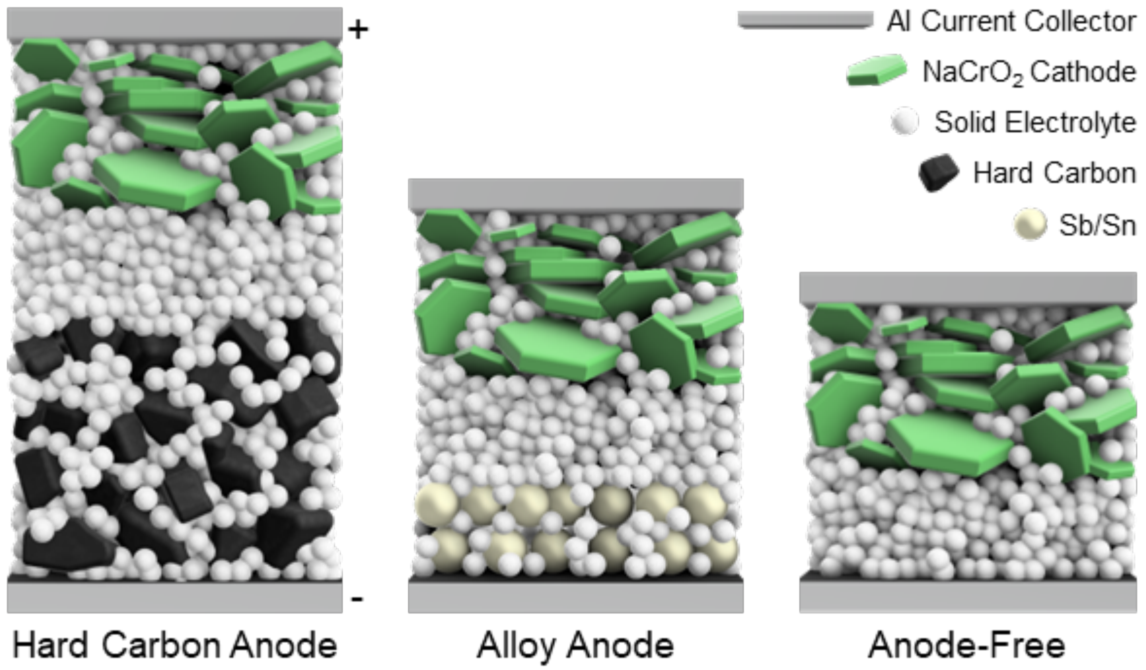


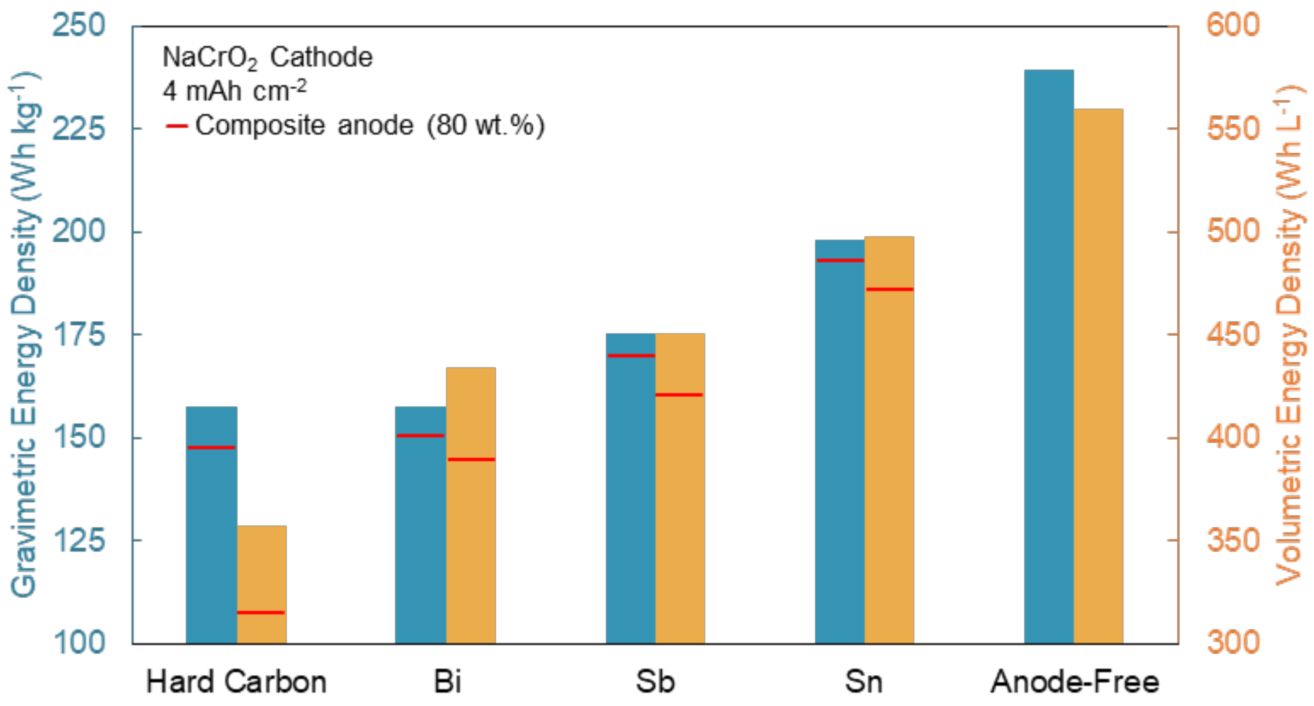
Submitted, under review (archived): 10.26434/chemrxiv-2022-x7llq)

- *Higher conductivity →* **improved capacity utilization** at room temperature
- Owed to *reduced crystallinity and occupancy of*

Anode Selection → Anode-Free Game Changing for Na ASSB

- "Anode-Free": Na/Li metal is directly deposited onto the current collector surface





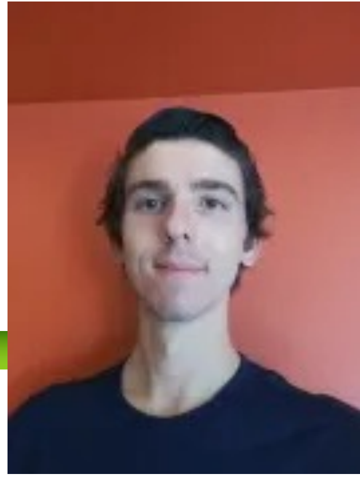
Anode-Free can achieve significantly higher energy density

Zero weight and volume

Lowest reduction potential → highest cell voltage

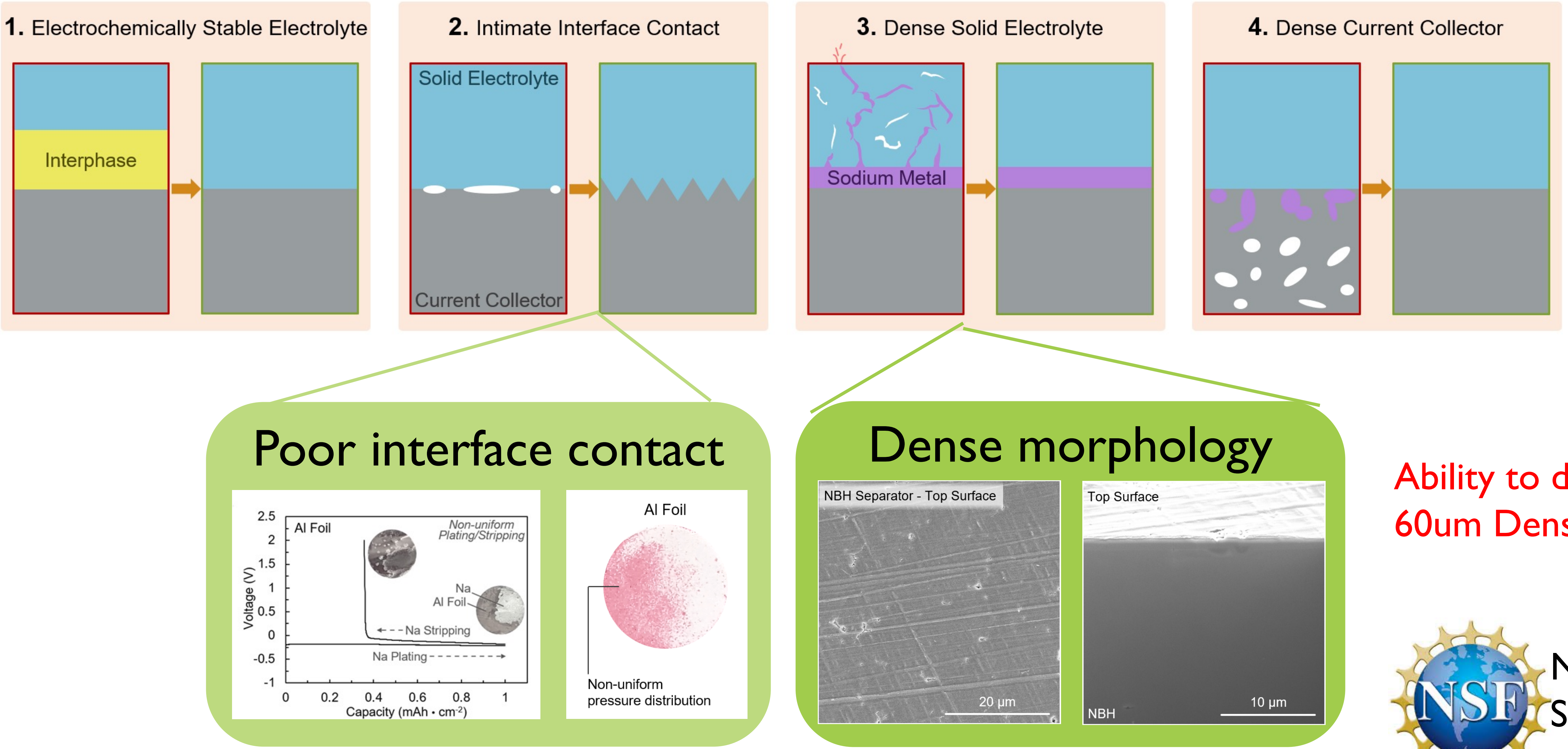
Patent Pending

Anode-Free Solid-State Sodium S^3Batteries



Cell architecture criteria to realize an anode-free ASSB

Grayson Deysher



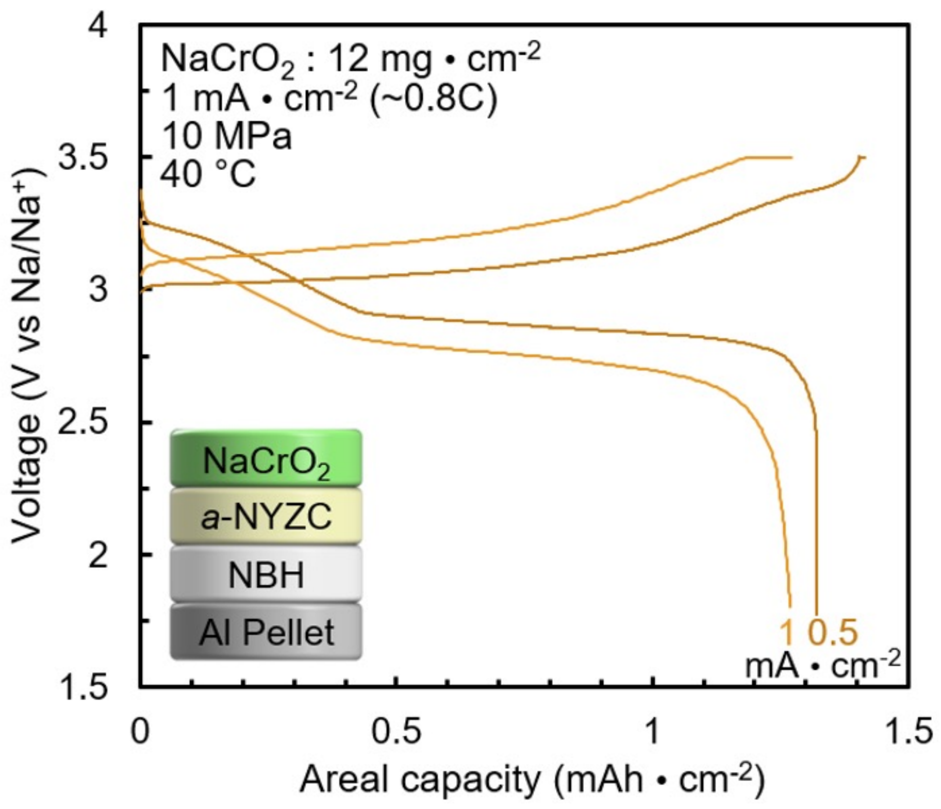
Ability to deposit
60um Dense Sodium !!!

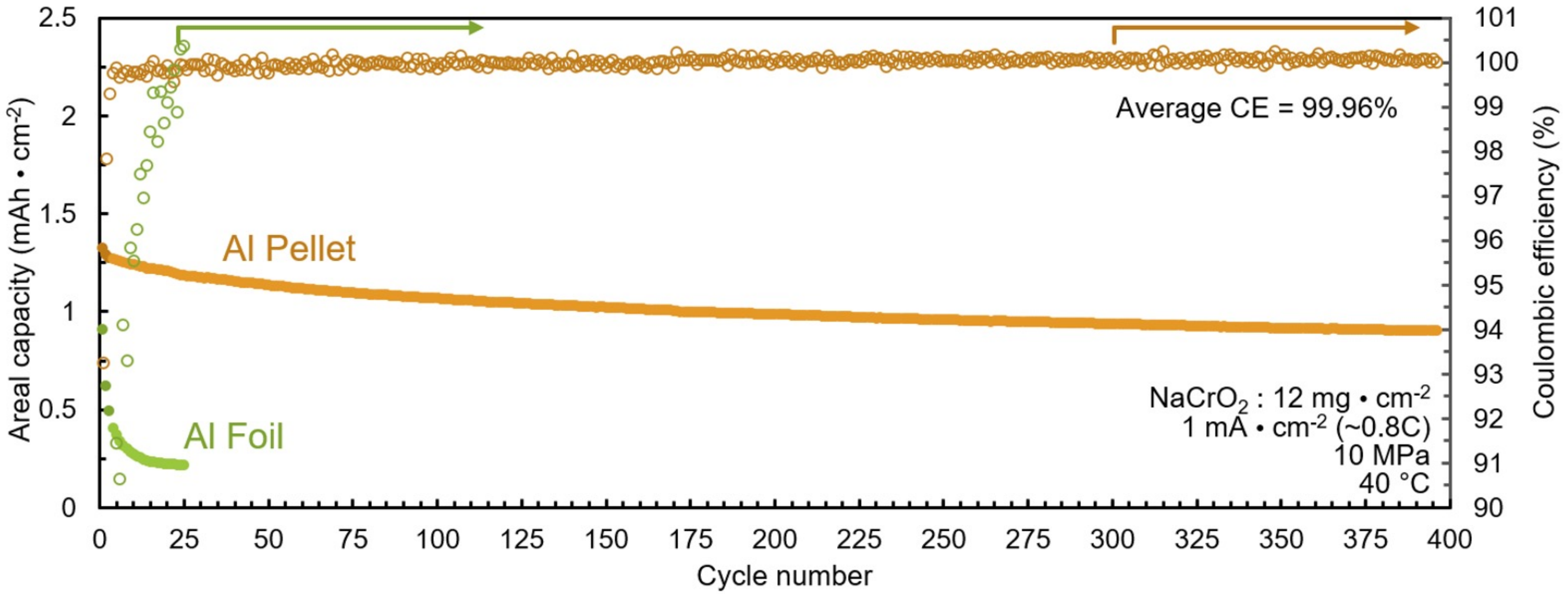
NSF 2010-now
Sodium Battery

Ongoing publication: Deysher, G., Jang, J., Meng, Y.S., 2023. An Anode-Free Sodium All-Solid-State Battery. (submitted) Archived : doi.org/10.26434/chemrxiv-2023-tkcd9

Sodium Anode-Free Solid-State Full Cell

Need to enable full-cell cycling ($NaCrO_2$ cathode)





- High Coulombic efficiency and stable cycling
- Significantly improved compared to traditional foil current collector

Ongoing publication:

Deysher, G., Jang, J., Meng, Y.S., 2023. An Anode-Free Sodium All-Solid-State Battery. (submitted)
Archived : doi.org/10.26434/chemrxiv-2023-tkcd9

Future Outlook-Solid State Battery Recycling

Key Considerations:

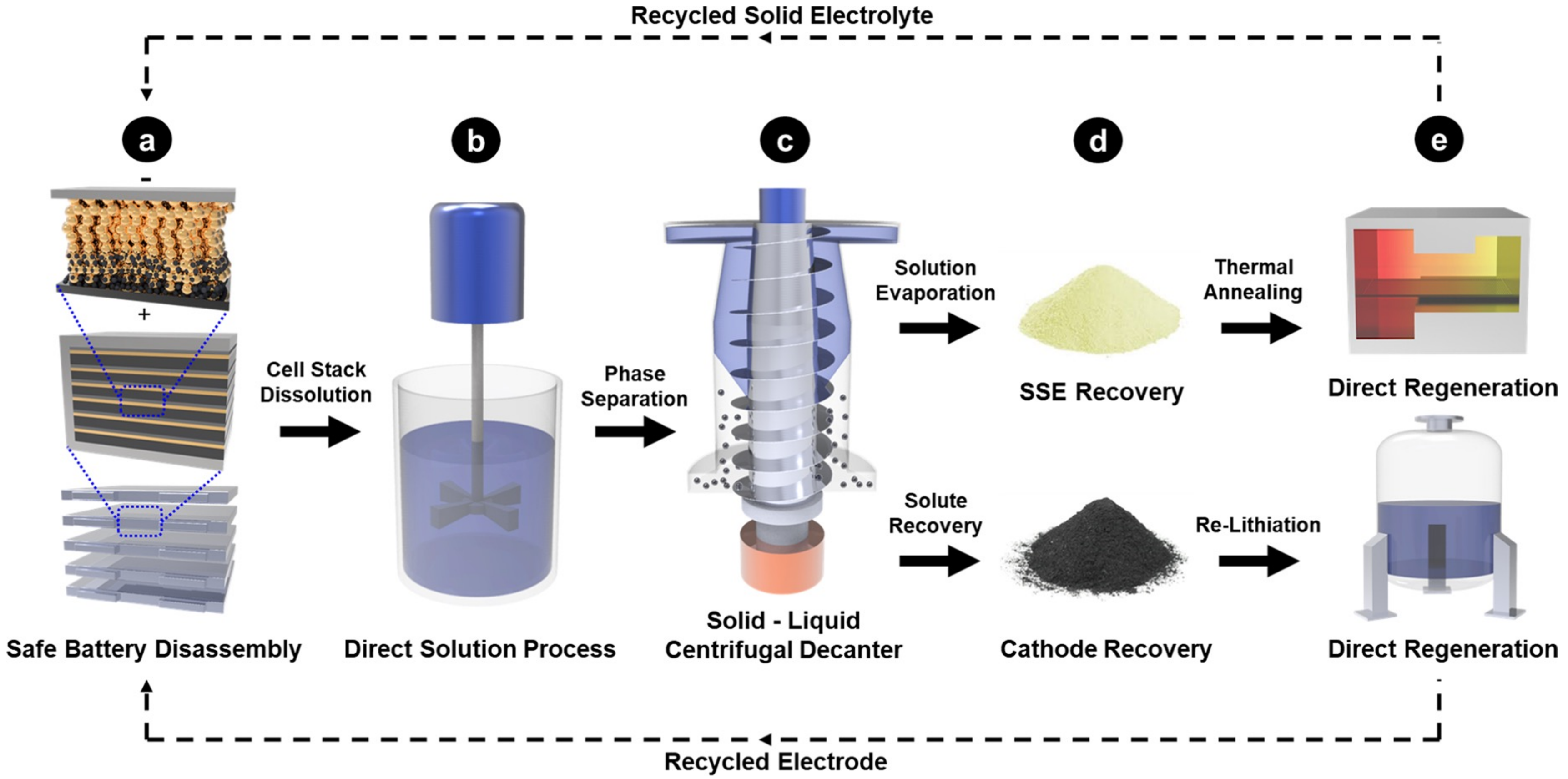
✓ Reduced safety risks

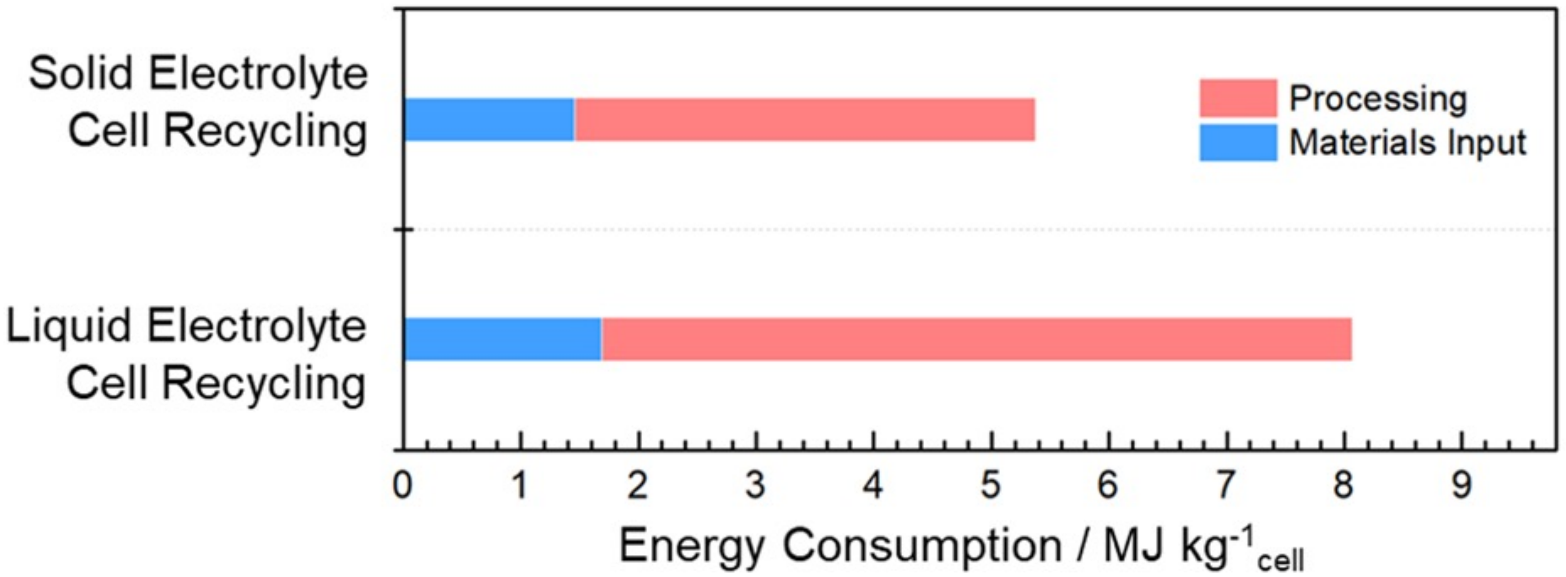
✓ Potential to recover >99% materials of a battery

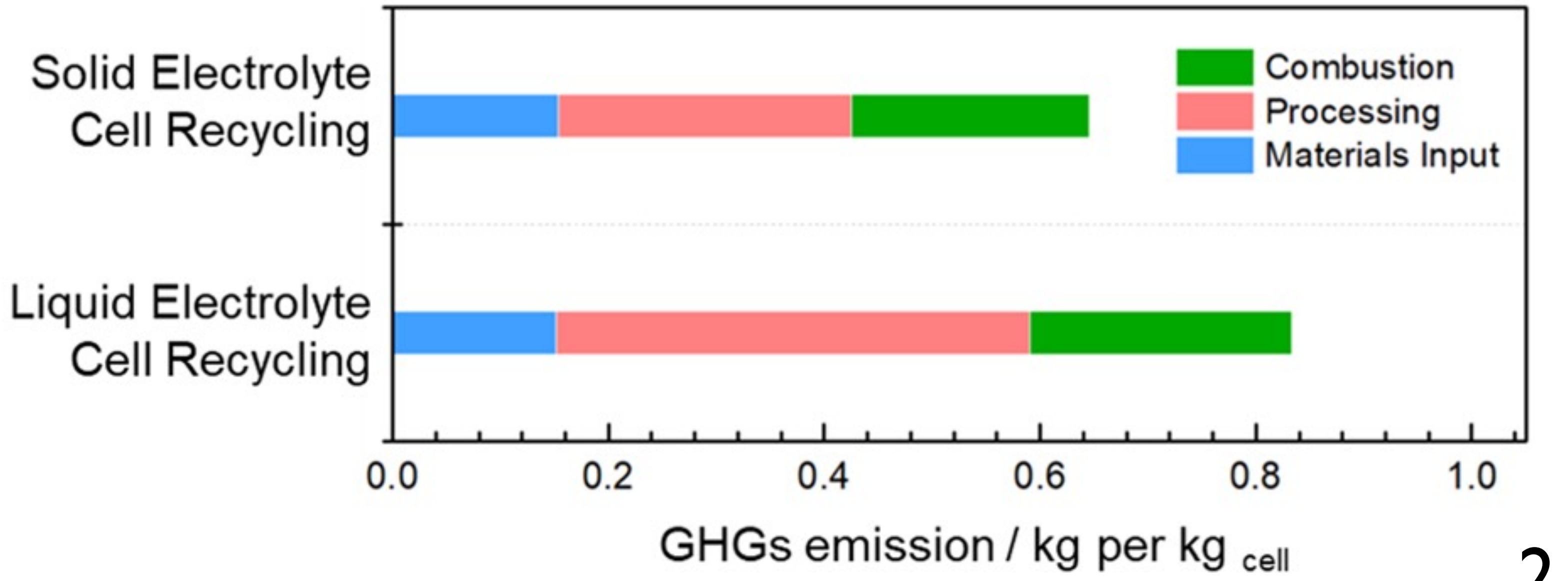
✓ No toxic chemicals used

✓ Low energy processes

✓ Regenerated materials used directly in new batteries







Na Battery will be the next TW-hr scalable technology!

param	Li	Na
relative atomic mass	6.94	23.00
Shannon's ionic radii (Å)	0.76	1.02
$E°$ (vs SHE) (V)	−3.04	−2.71
melting point (°C)	180.5	97.7
cost (for carbonate) ($/ton)	5000	150
Mohs' scale of hardness	0.6	0.4
density (g/cm^3)	0.534	0.97
thermal conductivity (W/(m·K))	84.8	142
ionic volume (Å^3)	1.84	4.44
theoretical capacity (mAh/g)	3829	1165
crystal content (%)	0.0065	2.74
distribution	70% in South America	everywhere

Collaborators and Funding

Laboratory for Energy Storage and Conversion

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Dr. Erik Wu, Dr. Abhik Banerjee,
Dr. Darren Tan, Dr. Hayley S. Hirsh

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PFI (2020- now)

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