Selected examples of work on mono- and multivalent batteries from POLiS

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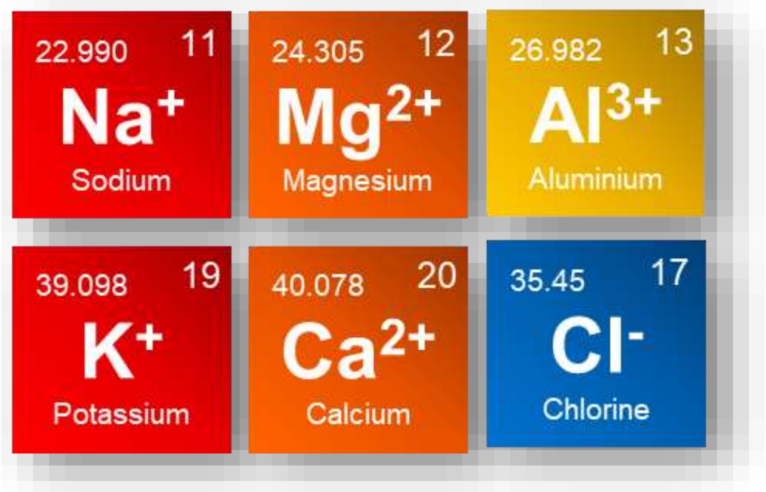
ZSW

The Cluster

DFG Cluster of Excellence
2019 – 2025
47 Mio. €
120+ researchers

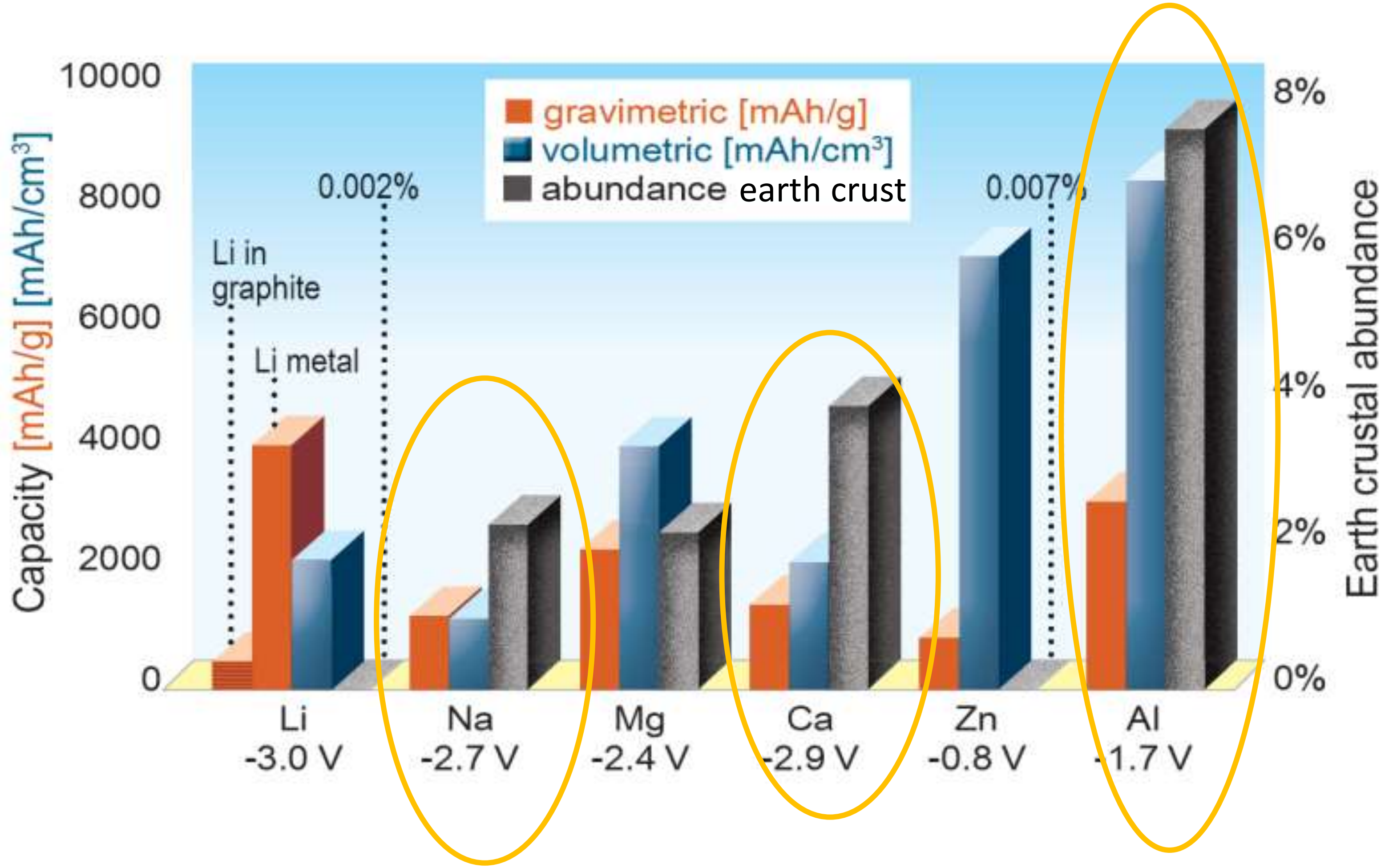
Together with Cluster 3DMM2O corner stone of KIT‘s University of Excellence status

Batteries Beyond Lithium



Post Lithium Storage Cluster of Excellence

www.postlithiumstorage.de



Sodium Ion Batteries

Sodium ion batteries may come without critical raw materials

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Li-Batteries

Al

Li
Ni
Mn
Co

Graphite

Cu

Critical/expensive/toxic raw materials

Na-Batteries

Al

Na
Fe
Mg
Mn

Hard carbon

Al

Sustainable/cheap/abundant raw materials

How the type of battery chemistry/ specific energy enables driving range in EVs

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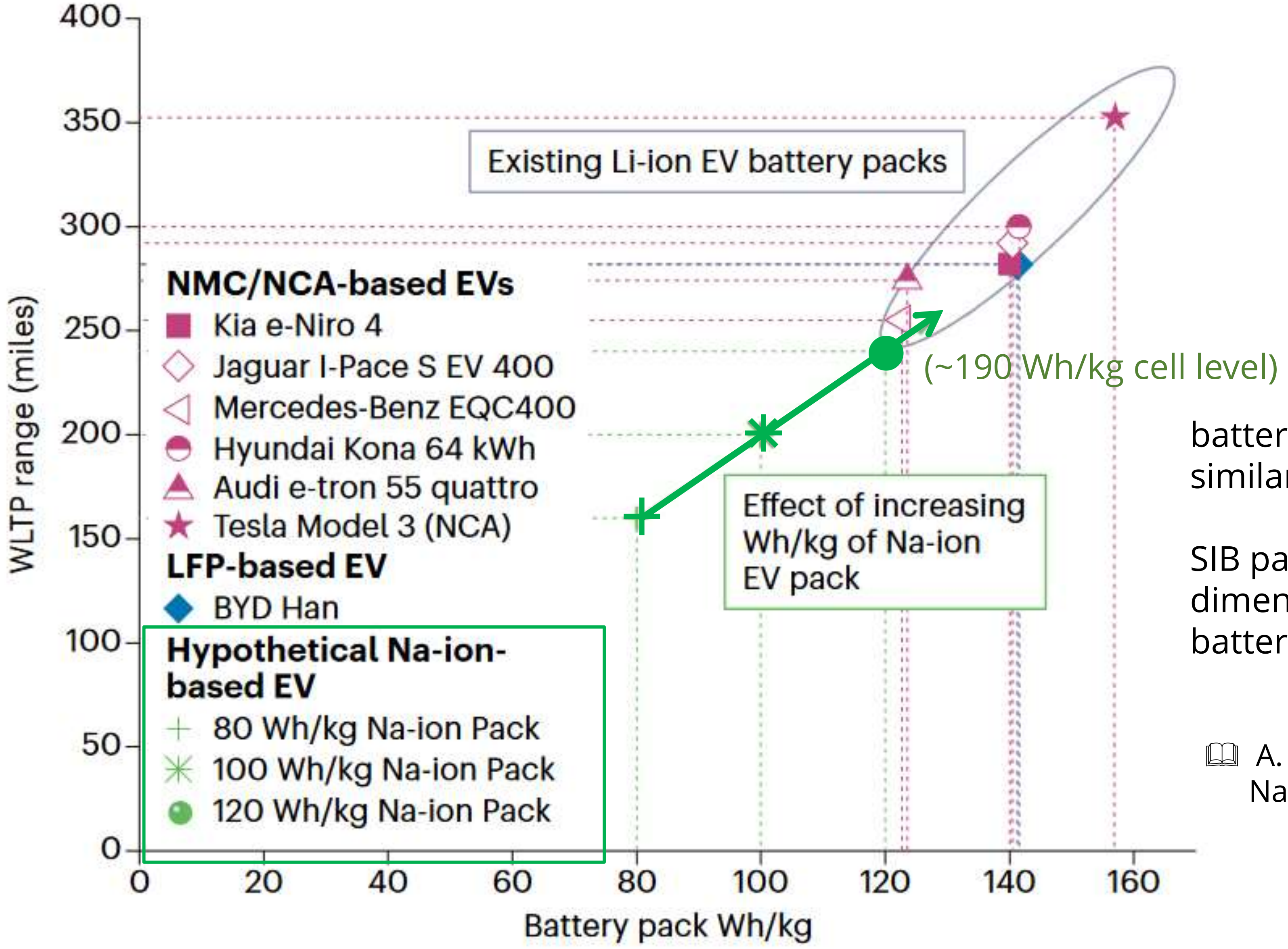
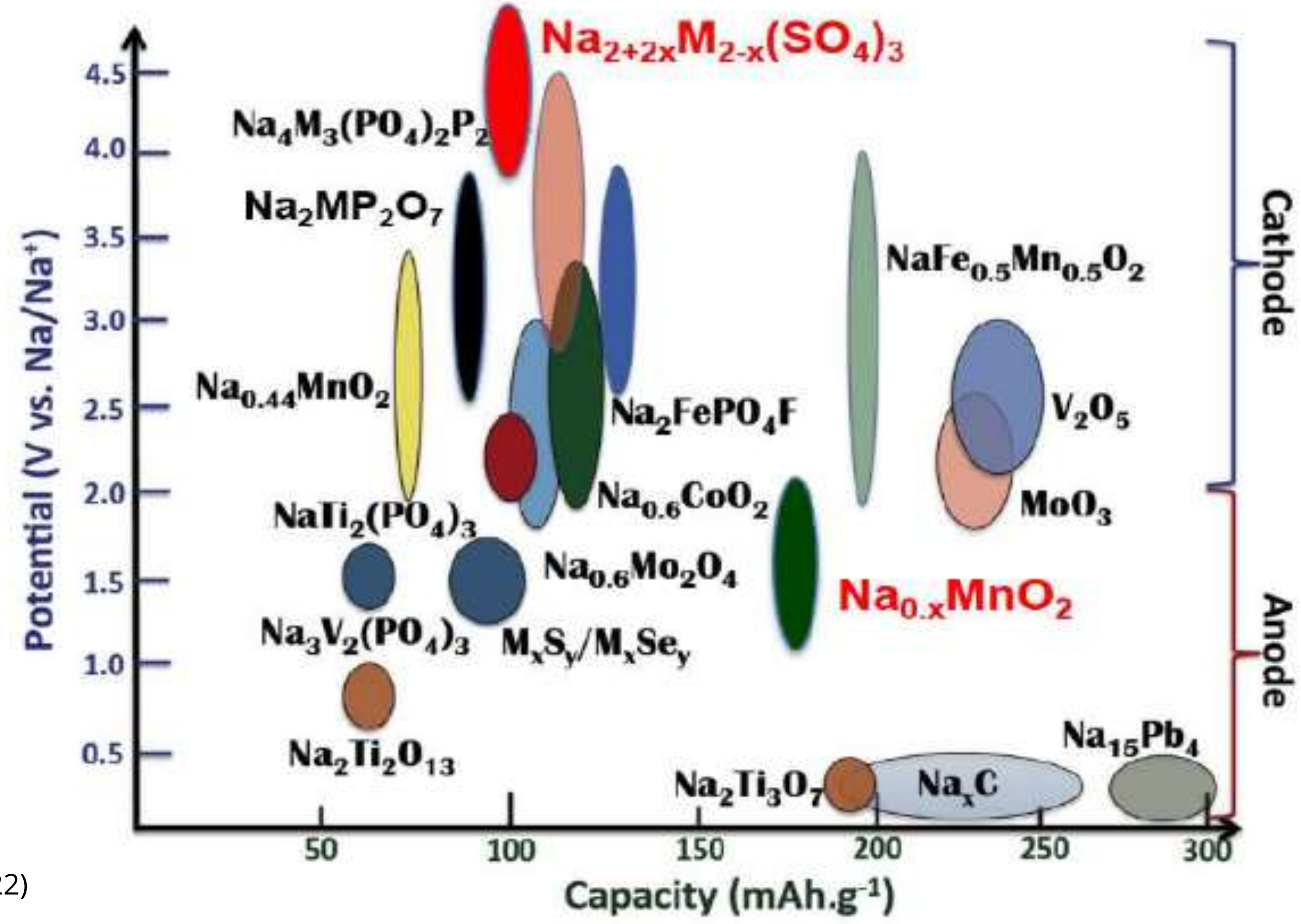


battery packs with similar dimensions

SIB packs based on dimensions of CTP battery from BYD Han

A. Rudola *et al.*, Nature 8 (2023)

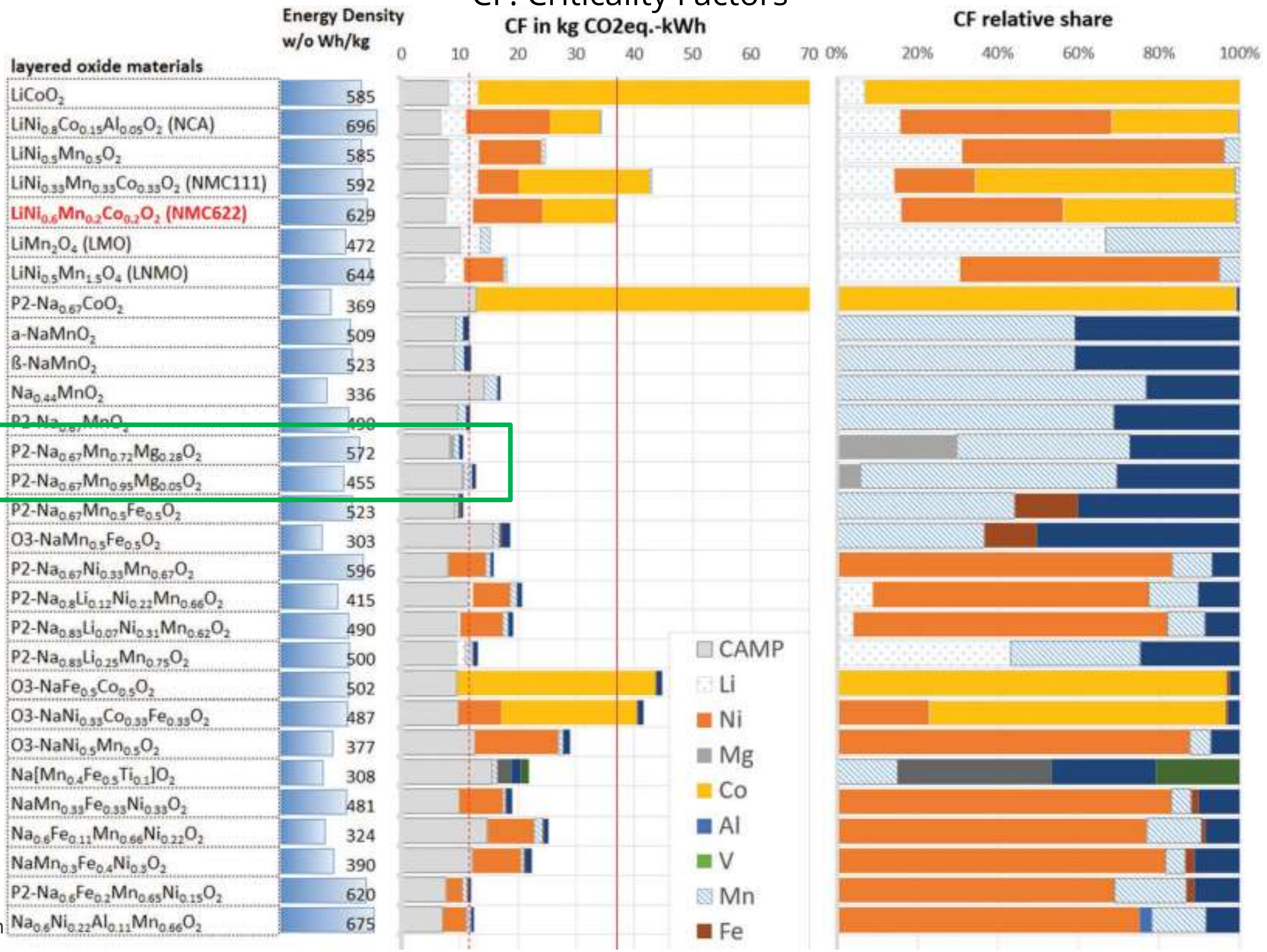
Sodium ion batteries: electrode materials



📖 P. Barpanda, pers. communication (2022)

Electrode materials: elemental content matters

CF: Criticality Factors



📖 M. Baumann, *et int.* M. Weil, *Adv. Energy Mater*. **2022**,

Low criticality factor for P2-NMMO

Stabilizing a layered cathode material

NMMO = $Na_{0.7}Mn_{0.9}Mg_{0.1}O_2$

Polycrystalline vs. single crystalline materials

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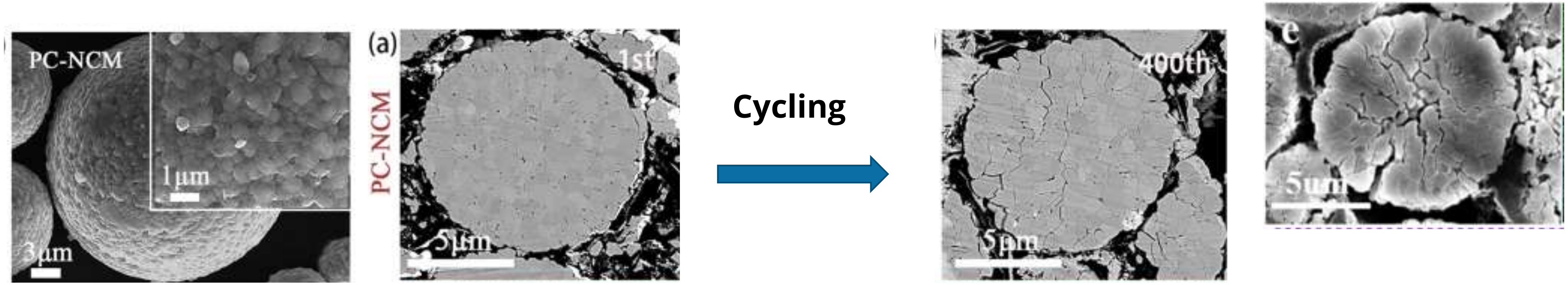
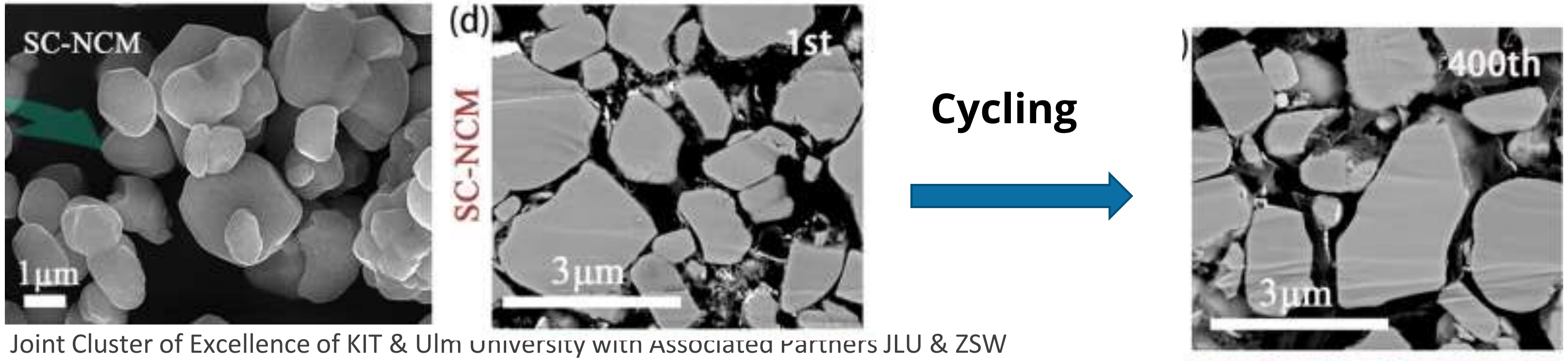
- Conventional electrode materials are *polycrystalline* with primary particles of 200-500 nm size fused together to form secondary particles of **10-15 µm**.



Single crystal → crystal lattice without any grain boundaries.

- *Single crystal electrodes* show a particle size of **~ 3 µm**, with no grain boundaries.



📖 Jing Li *et al.*, J. Electrochem. Soc., 2017
📖 Xinming Fan *et al.*, Nano Energy, 2020
📖 Peipei Pang *et al.*, Electrochim. Acta, 2021
📖 Jin Leng *et al.*, Small, 2021

Cathode materials as large single crystals; Preparation of $Na_{0.7}Mn_{0.9}Mg_{0.1}O_2$

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Precursor

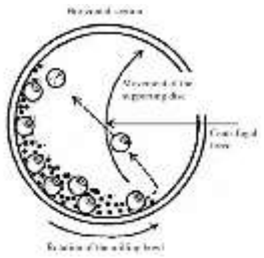
calcining 12h, 900°C, air

polycrystalline NMMO

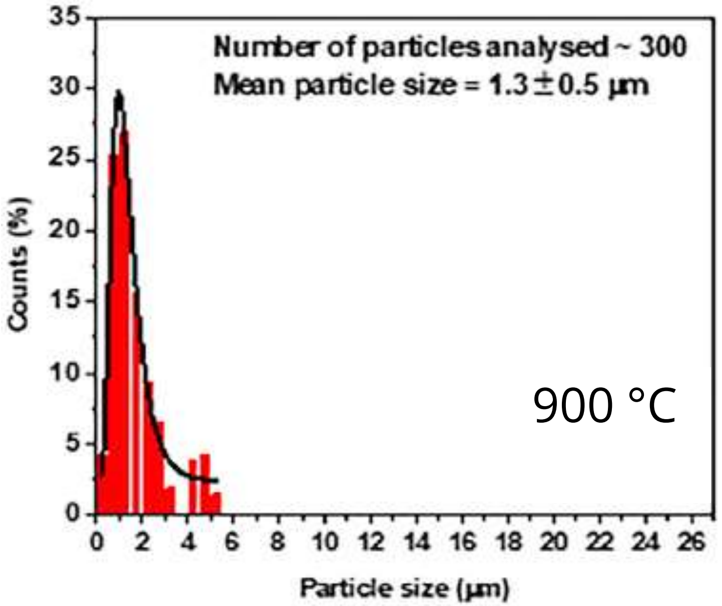
T: 900-1150°C
12h in air

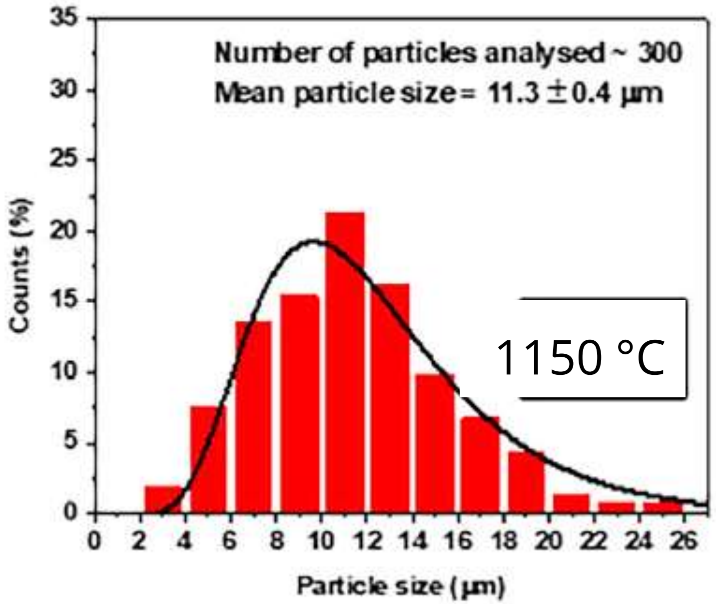
NMMO – 900
NMMO – 1000
NMMO – 1050
NMMO – 1100
NMMO – 1150

2h
500 rpm



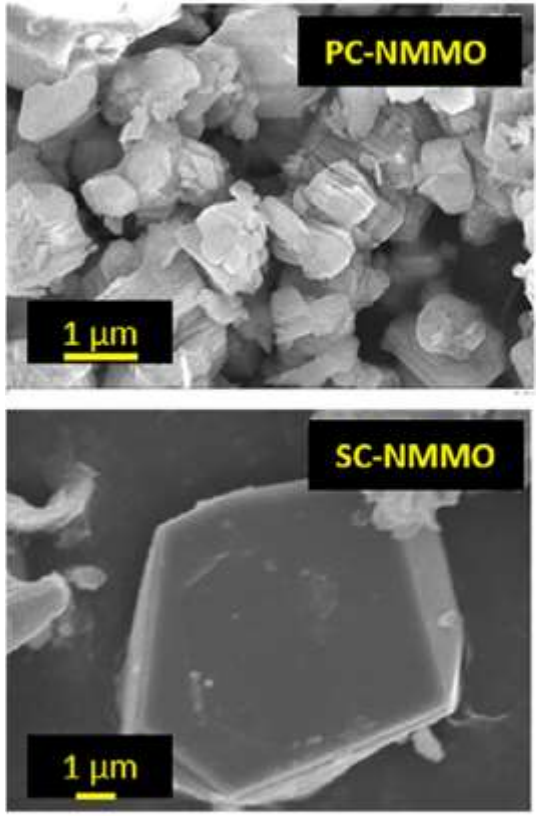
Stoichiometric mixture
Na_2CO_3, MnO_2, and MgO

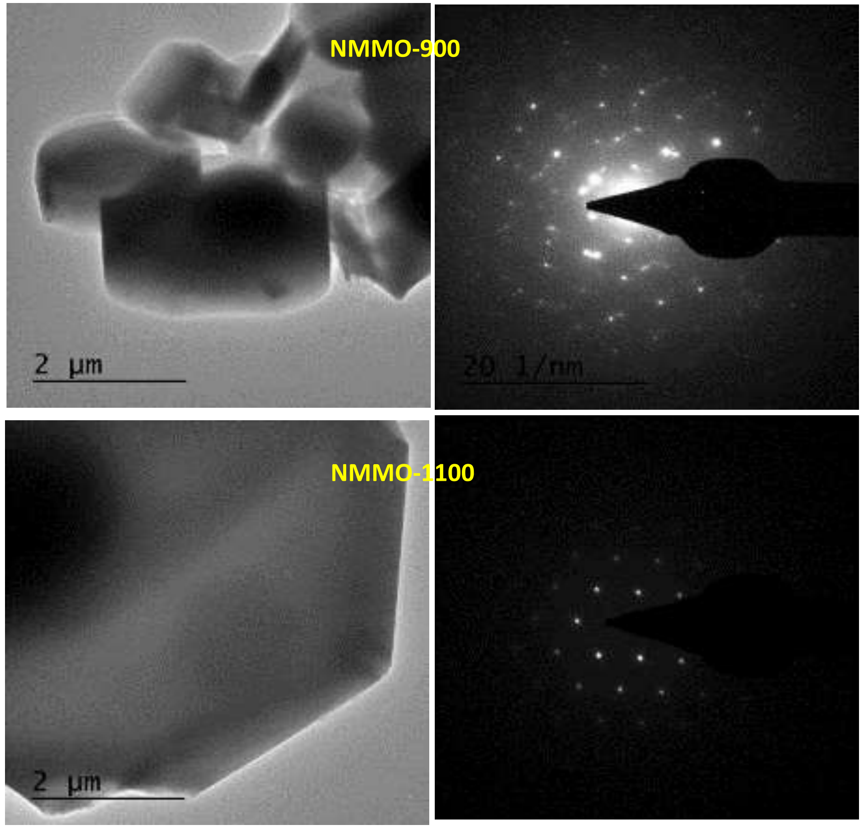




Cathode materials as large single crystals

NMMO = $Na_{0.7}Mn_{0.9}Mg_{0.1}O_2$





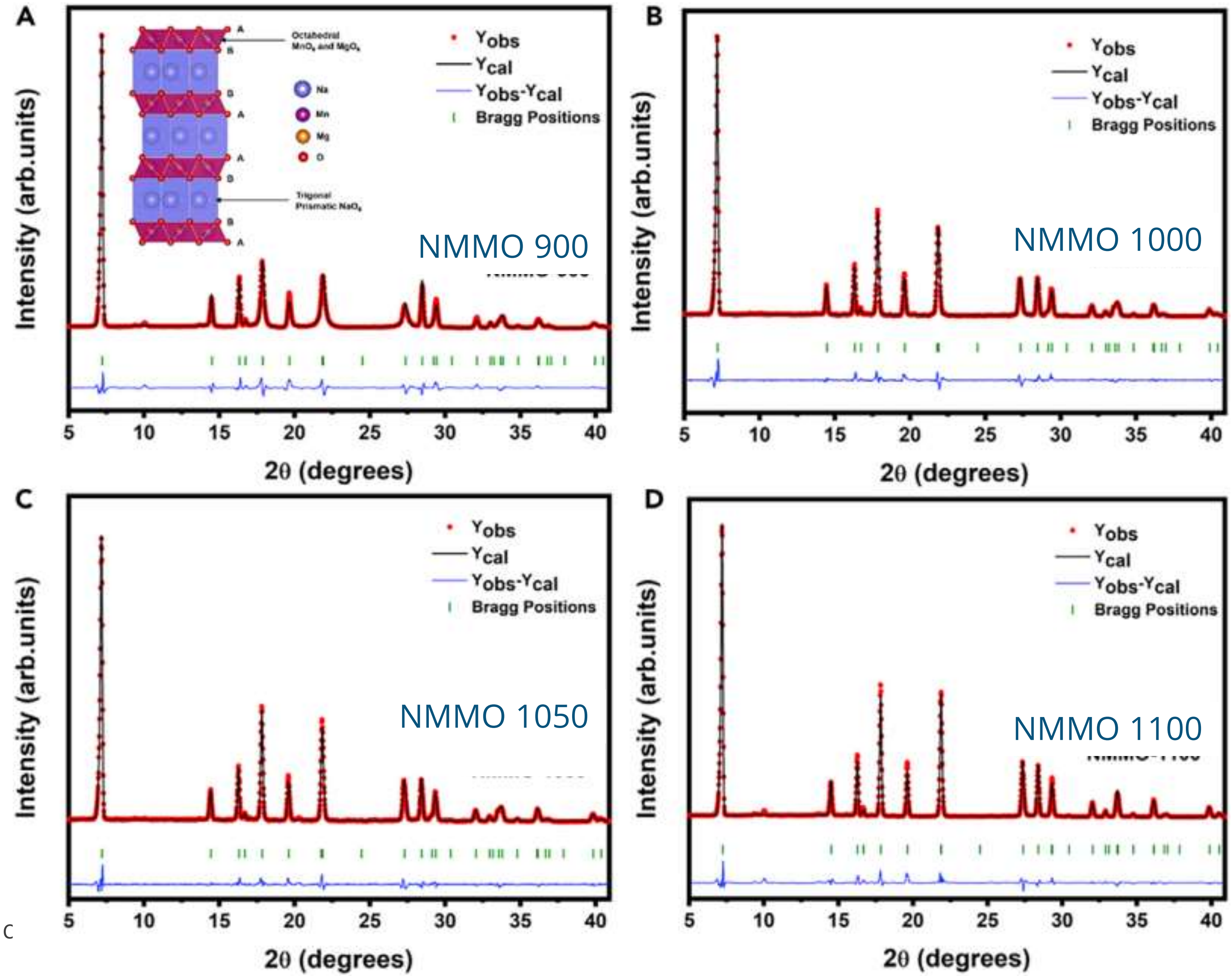
Dotted ring SAED pattern confirms polycrystalline nature

Dotted hexagonal SAED pattern confirms single crystal nature

📖 V. Pamidi, *et al. Micron Sized Single Crystal Cathodes for Sodium Ion Batteries*, iScience 25 (2022).104205

📖 V. Pamidi *et al.* , *Material with Improved Cycling Stability for Sodium Ion Batteries,* ACS Appl. Mater. Interf. (2024) accepted

XRD of products



Rietveld-refinement:
Phase-pure product

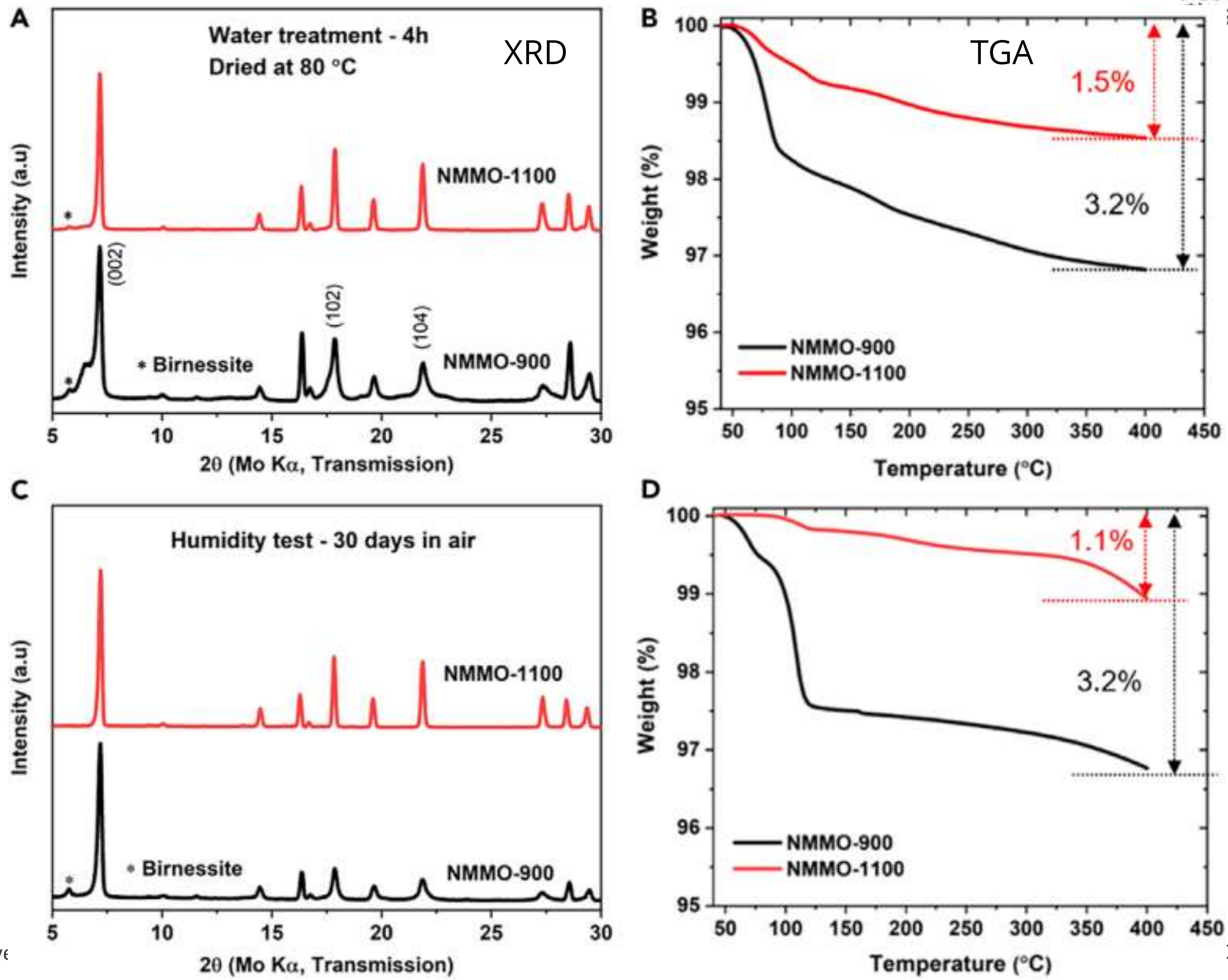
Slight shift to lower angles at elevated T

- → loss of Na^+ in the layers
- → increasing the slab distance due to higher repulsion

PC and SC materials in contact with moisture

Water treatment 4h

30 days in ambient air



Electrochemical properties

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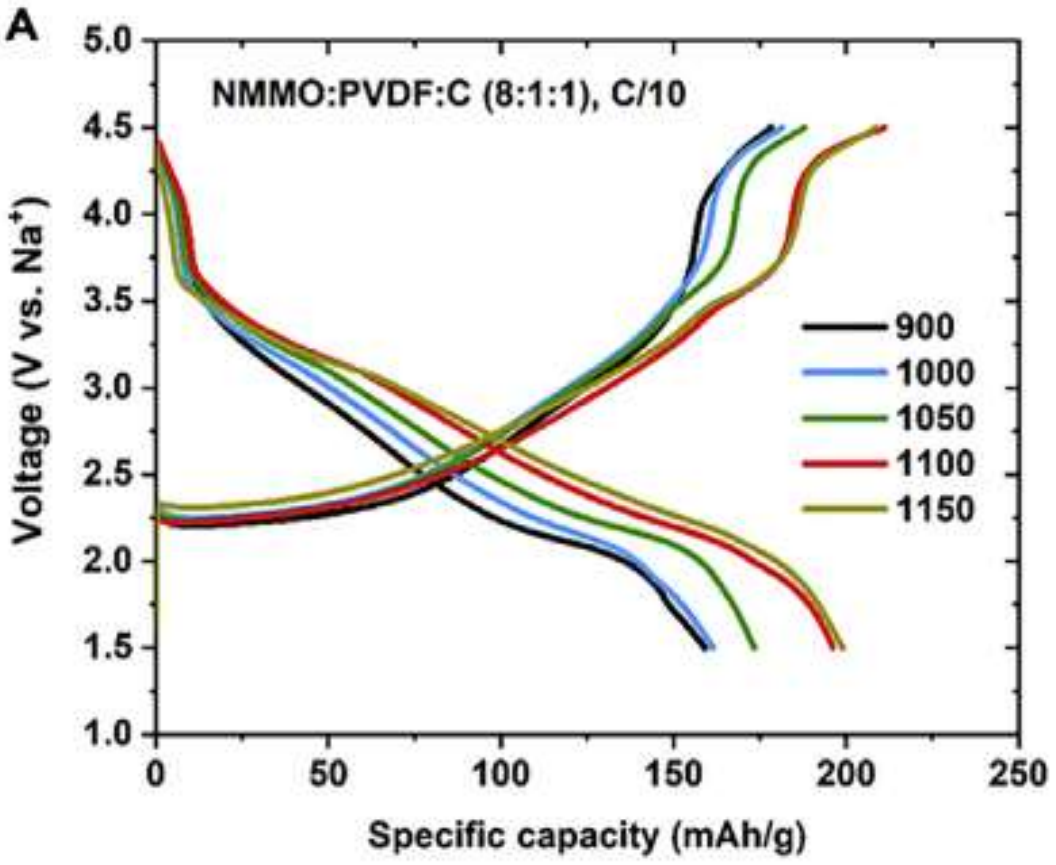
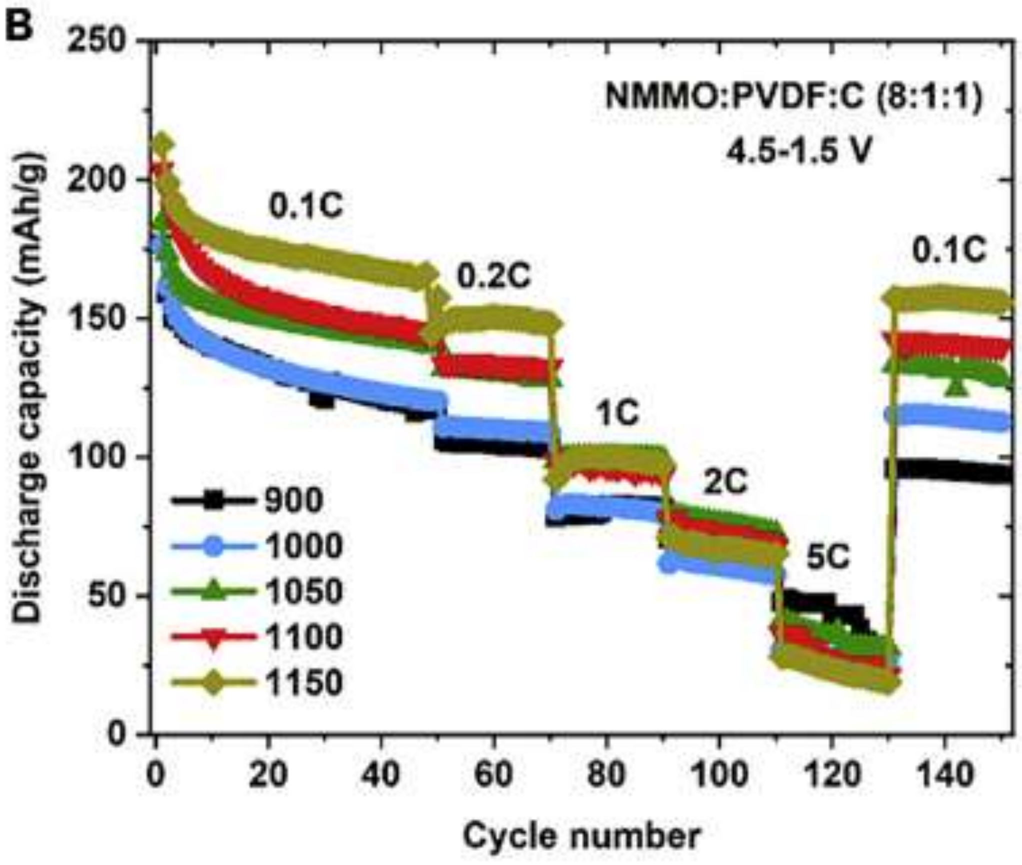
NMMO = $Na_{0.7}Mn_{0.9}Mg_{0.1}O_2$



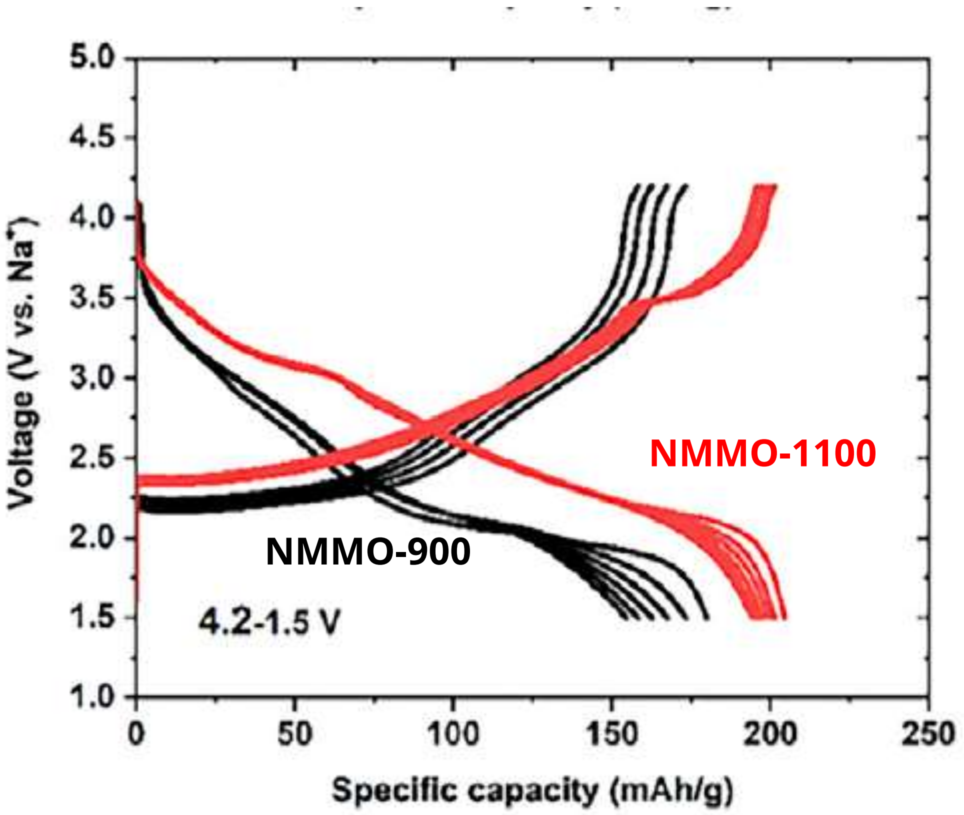


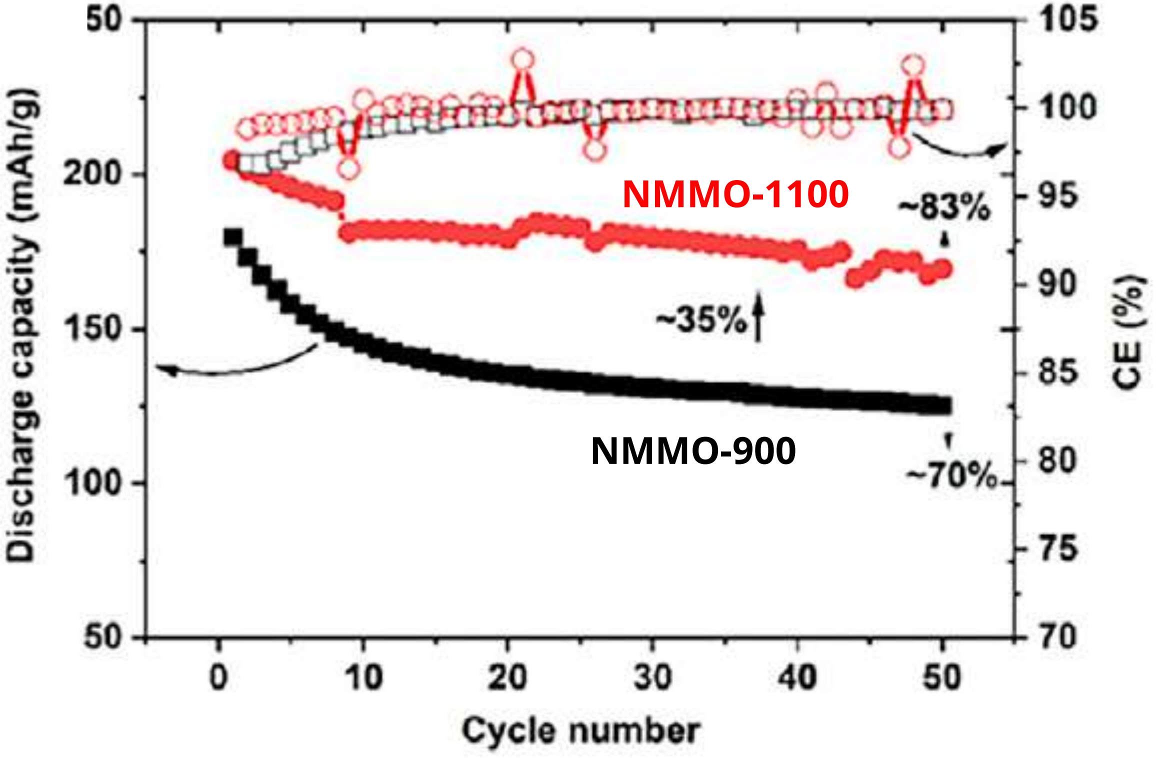
- 4.5–1.5 V at a current rate of C/10.
- second charge/discharge

V. Pamidi, *et al*. *Micron Sized Single Crystal Cathodes for Sodium Ion Batteries*, iScience 25 (2022).104205

V. Pamidi *et al.* , *Material with Improved Cycling Stability for Sodium Ion Batteries,* ACS Appl. Mater. Interf. (2024) accepted

Electrochemical properties of NMMO-900 and NMMO-1100





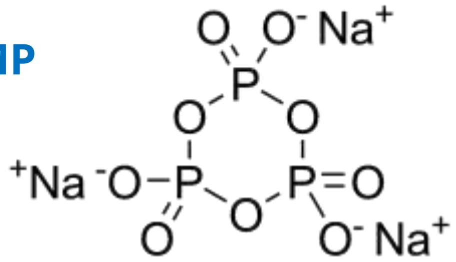
Summary

Property	Polycrystalline	Single crystal
Air stability	☹	☺
Cycling stability	☹	☺
Rate capability	☺	☹
High voltage stability	☹	☺
Thermal Stability	☹	☺
Mechanical Integrity	☹	☺

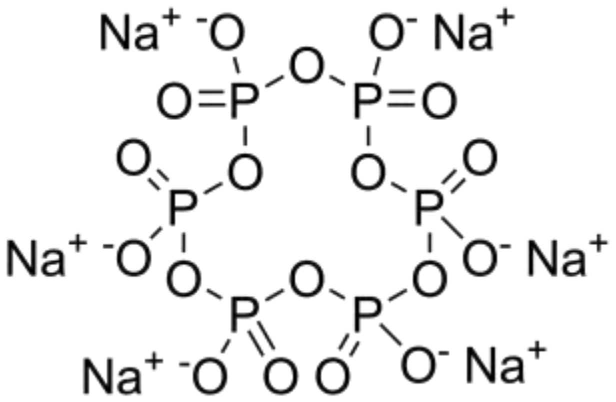
Multifunctional inorganic aqueous binders

Multifunctional aqueous binders for sodium ion batteries

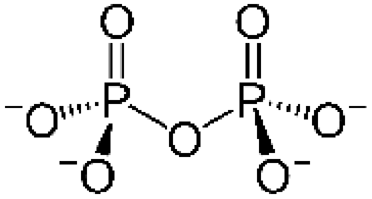
STMP



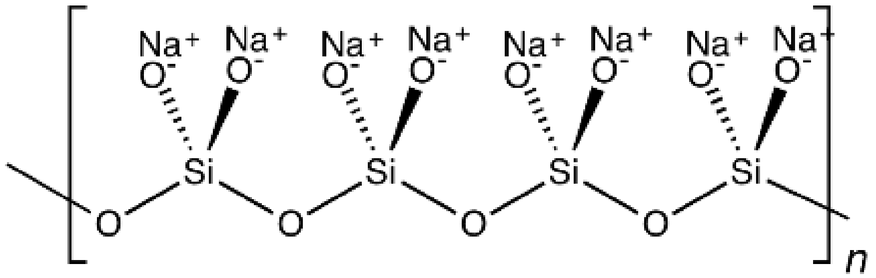
SHMP



SPP



SMS



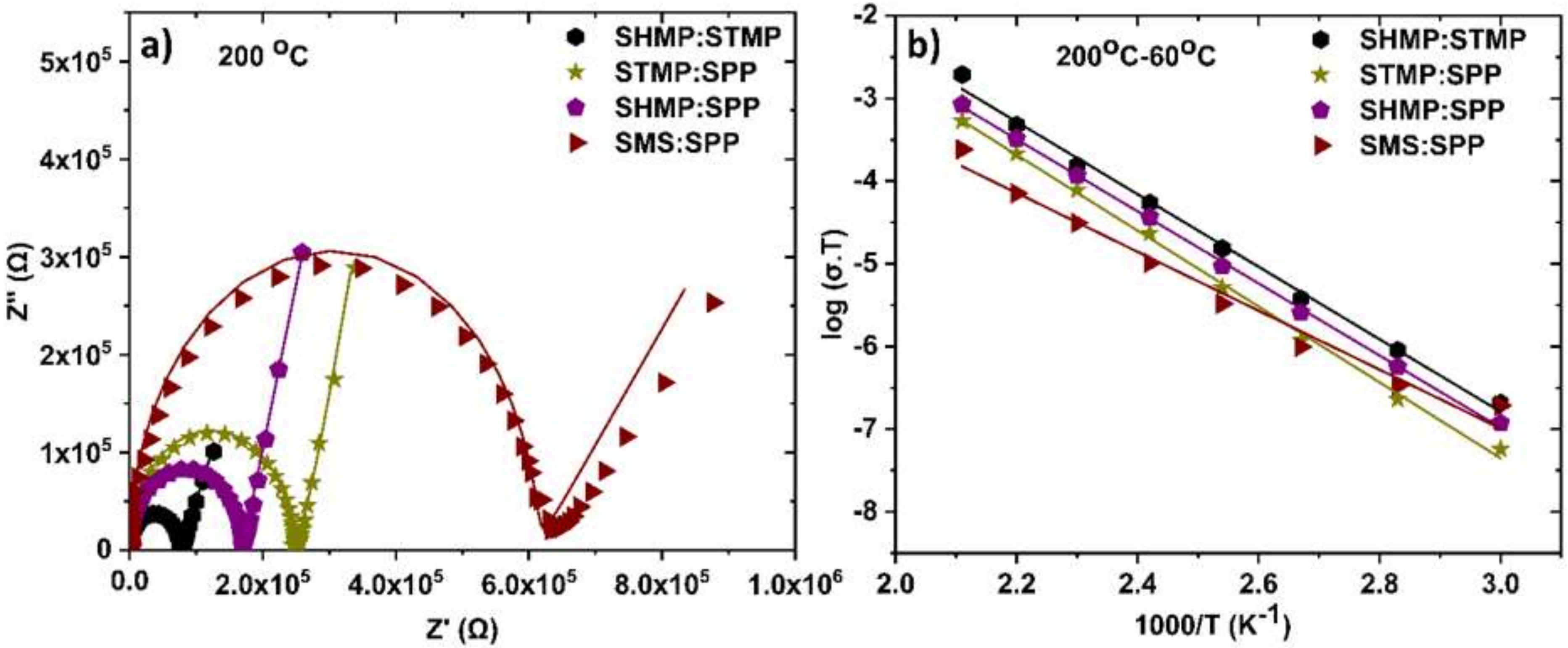
📖 S. Trivedi, V. Pamidi, M. Fichtner, M. Anji Reddy
Green Chemistry 24, **2022,** 5620

📖 R. Xu *et al.*, *Greener, Safer and Better Performing Aqueous Binder for Positive Electrode Manufacturing of Sodium Ion Batteries*, ChemSusChem, **2024**, e202301154

Ionic conductivity of inorganic binders (phosphates/silicates)

Binding ability **plus** ionic conductivity

EIS measurements



Multifunctional aqueous binders / thermal properties

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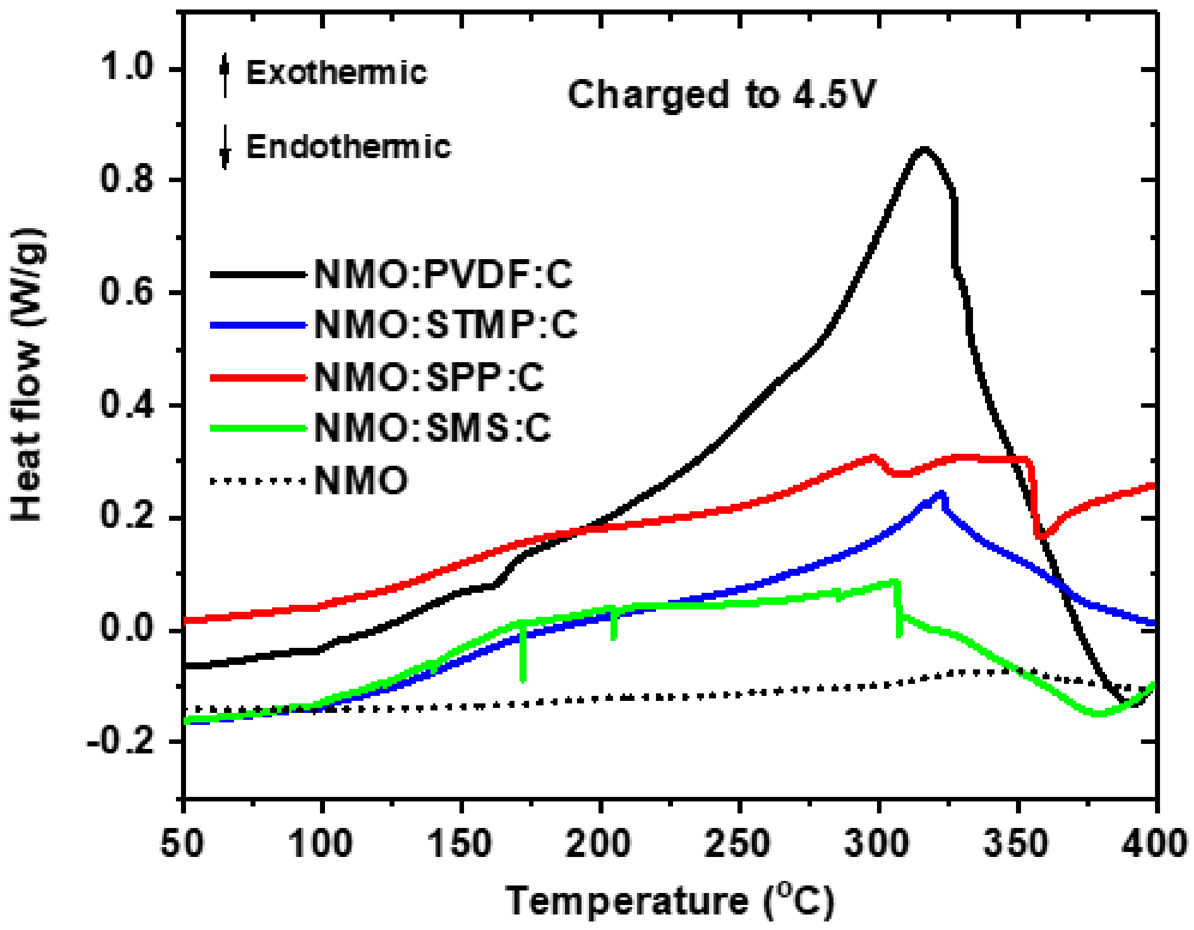
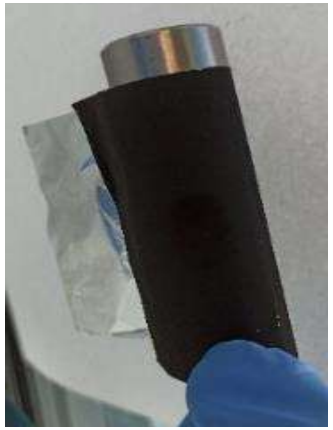
DSC in air



Multifunctional aqueous binders / mechanical properties

NMO:SPP:C (8:1:1)



Flexible

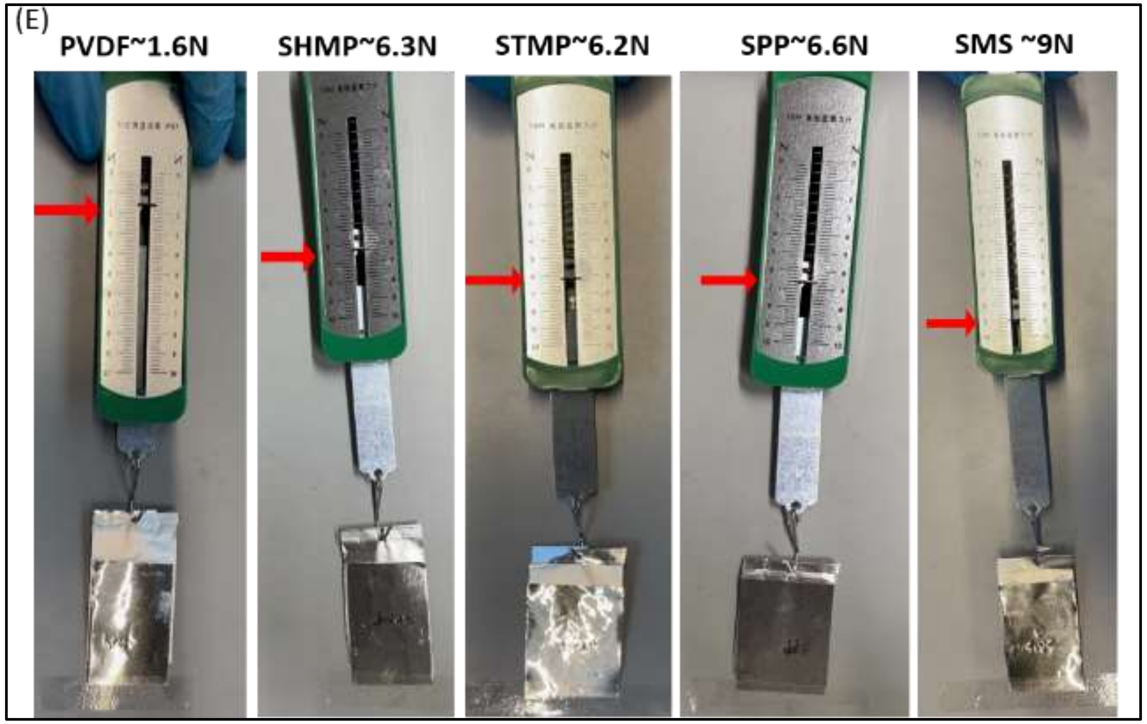
Rollable

Binding at elevated temperatures

NMO:PVDF:C @ 400°C/2h

NMO:STMP:C @ 600°C/2h

Binding strength /peel test experiments



Multifunctional aqueous binders for sodium ion batteries

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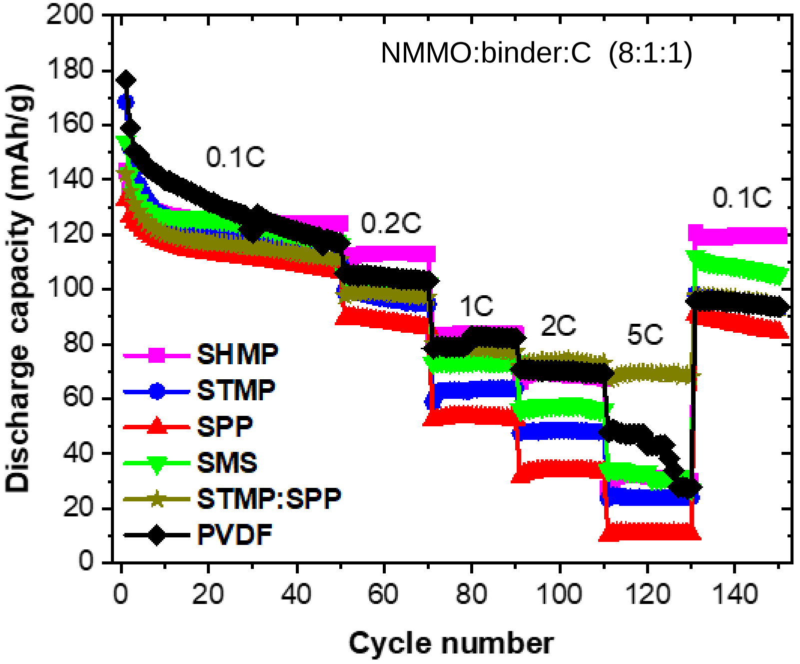
NMMO = $Na_{0.7}Mn_{0.9}Mg_{0.1}O_2$

1C = 180 mAh/g. ΔV = 4.5-1.5 V

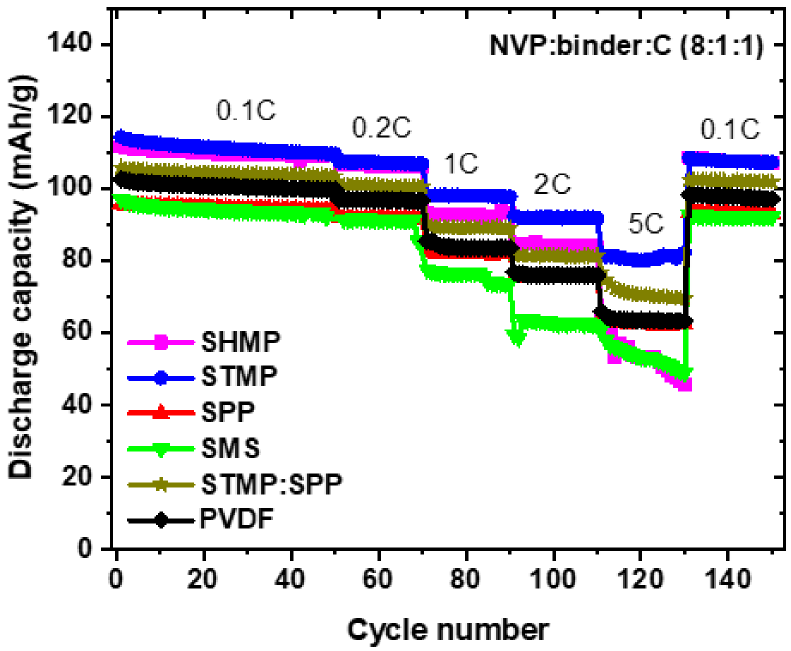


Binder	Cap Retent (%)
STMP:SPP (1:1)	~69
SHMP	~87
STMP	~61
SPP	~66
SMS	~74
PVDF	~59

28% improvement after 150 cycles

NVP = $Na_3V_2(PO_4)_3$

1C = 118 mAh/g ΔV = 3.8-2.5 V

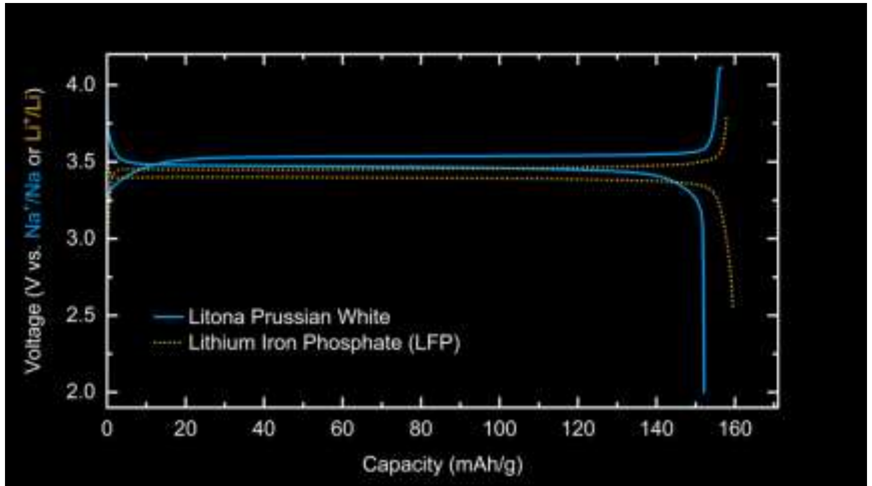


Binder	Cap Retent (%)
SPP	96
STMP	94
SHMP	97
SMS	95
STMP:SPP	96
PVDF	95

Na‖ 1 M $NaClO_4$/(98%)PC/(2%)FEC‖ NMO,NVP; Swagelok cell

Technology Transfer and Spin-Off

Spin-Off Company for SIB materials



Voltage curves of the second C/20 charge and discharge of Litona Prussian White in a sodium half cell compared to commercial Lithium Iron Phosphate (LFP) in a lithium metal half cell. The LFP data was used from Lyle et al.[1]

[1] Erin Lyle et al 2022 J. Electrochem. Soc. 169 060527

"Litona stands for high-quality, environmentally friendly and yet affordable energy storage."

Scale-up of PBA materials and distribution
https://www.litona-batteries.de/

Multivalent Batteries

Aluminum

Calcium

High-capacity aluminum-organic battery

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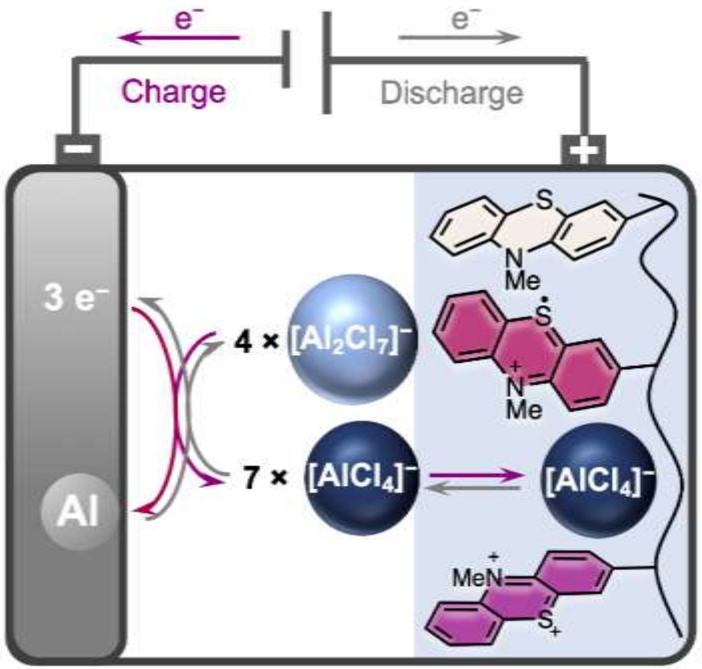
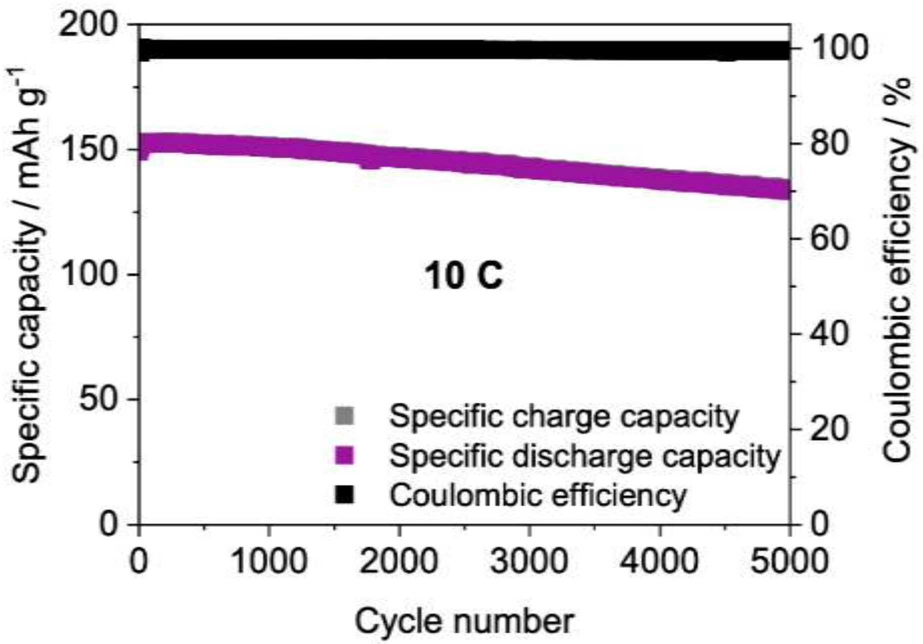
- **X-PVMPT** as positive electrode material in Al-based batteries (Cross-linked poly(3-vinyl-*N*-methylphenothiazine)
- Reversibly inserts $[AlCl_4]^-$ ions at potentials of 0.81 and 1.65 V *vs.* Al|Al^{3+}
- Specific capacities of up to 167 mAh g^{-1} → higher than graphite as positive electrode material
- 5,000 cycles at a 10 C rate: 88% capacity retention



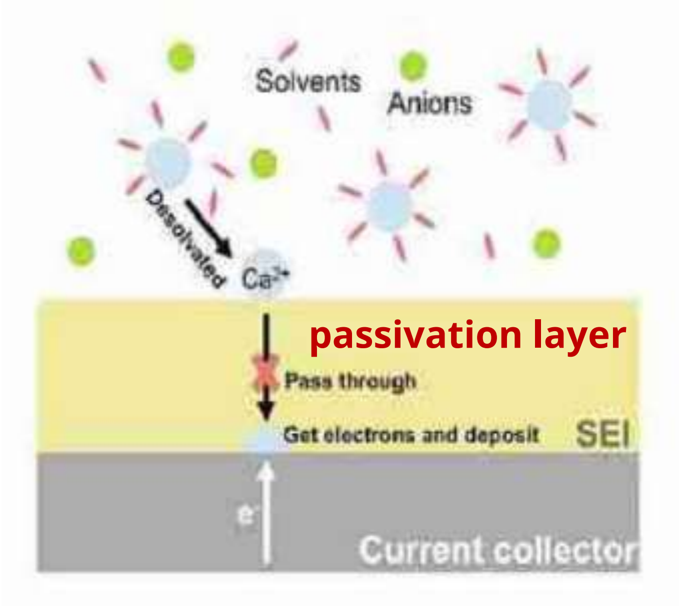


📖 "On a high-capacity aluminium battery with a two-electron phenothiazine redox polymer as positive electrode." G. Studer, A. Schmidt, J. Büttner, A. Fischer, I. Krossing, B. Esser, *Energy Environ. Sci.* **2023**,

Calcium batteries

Development of Ca electrolytes

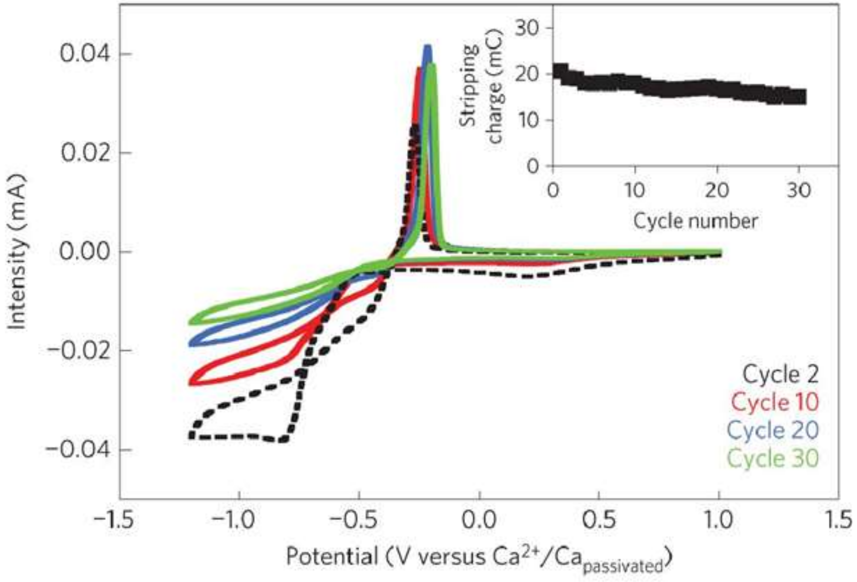
Ca metal is highly reactive



Ca electrolytes

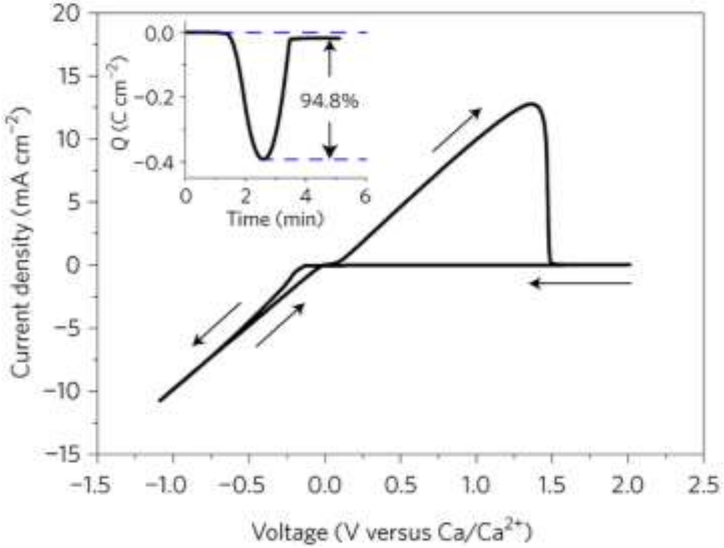
$Ca(BF_4)_2$/EC-PC

- Plating/stripping **at >75 °C**.
- Oxi. stability 4 V
- Low deposition efficiency
- Surface layer CaF_2, $CaCO_3$, etc



A. Ponrouch, R. Palacin et al, *Nat. Mater.* (2016)*15,169*

$Ca(BH_4)_2$/THF



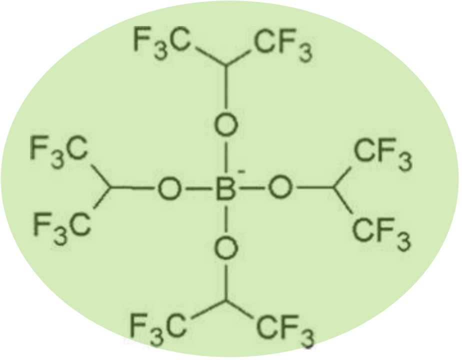
- Plating/stripping **at r.t.**
- Deposition efficiency ~95%
- Oxi. stability <3 V
- Surface layer CaH_2, reactive

Wang, D.; Gao, X.; Bruce, P. G. *et al*, *Nat. Mater.* (2018) *17,16*.

A first room-temperature Ca electrolyte with viable properties

Ca-salt with weakly coordinating anions

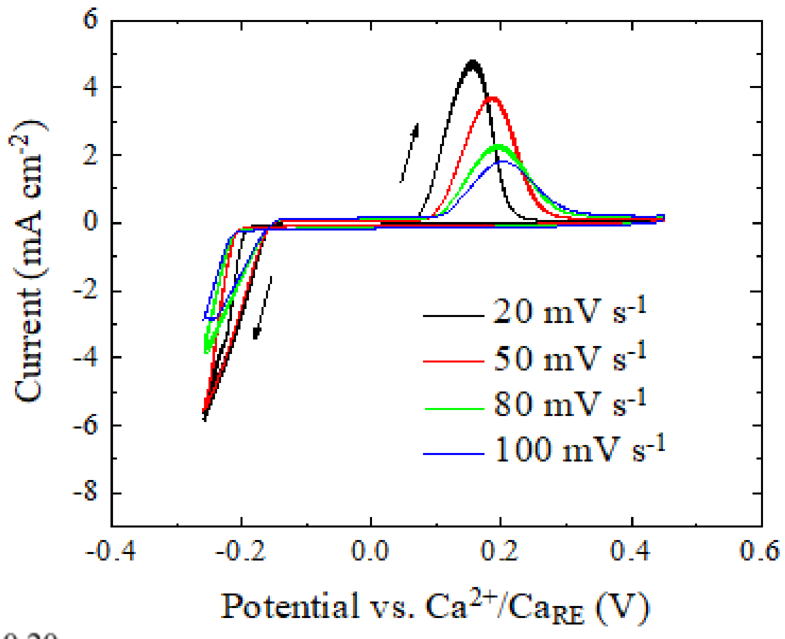
Ca^{2+}



$[B(hfip)_4]^-$

Fluorinated anion:

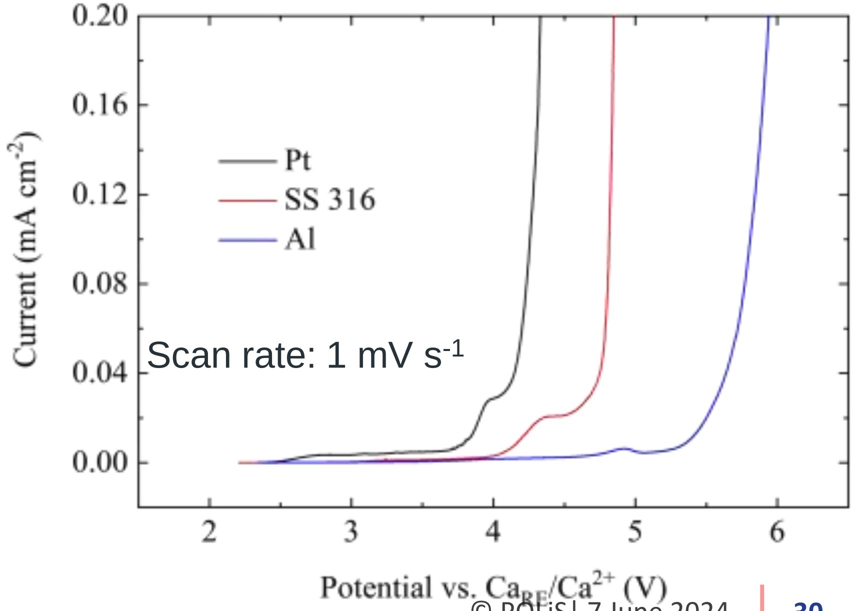
- delocalized charge, weak interaction
  - ➡ high ion mobility
- High stability
  - ➡ wide electrochemical window



$$Ca(BH_4)_2 + 8(CF_3)_2CHOH \rightarrow \mathbf{Ca[B(OCH(CF_3)_2)_4]_2} + 4H_2\uparrow$$

solvent: 1,2-dimethoxyethane (DME)

- ✓ Easy and quantitative synthesis
- ✓ Reversible Ca plating/stripping at RT
- ✓ Electrochemical stability (~4 V)
- ✓ **Ionic conductivity > 8 mS cm^{-1}**
- ✓ Compatible with sulfur cathodes



📖 Z. Li, M. Fichtner, Z. Zhao-Karger, *Energy Environ. Sci.*, **2019**, *12*, 3496.

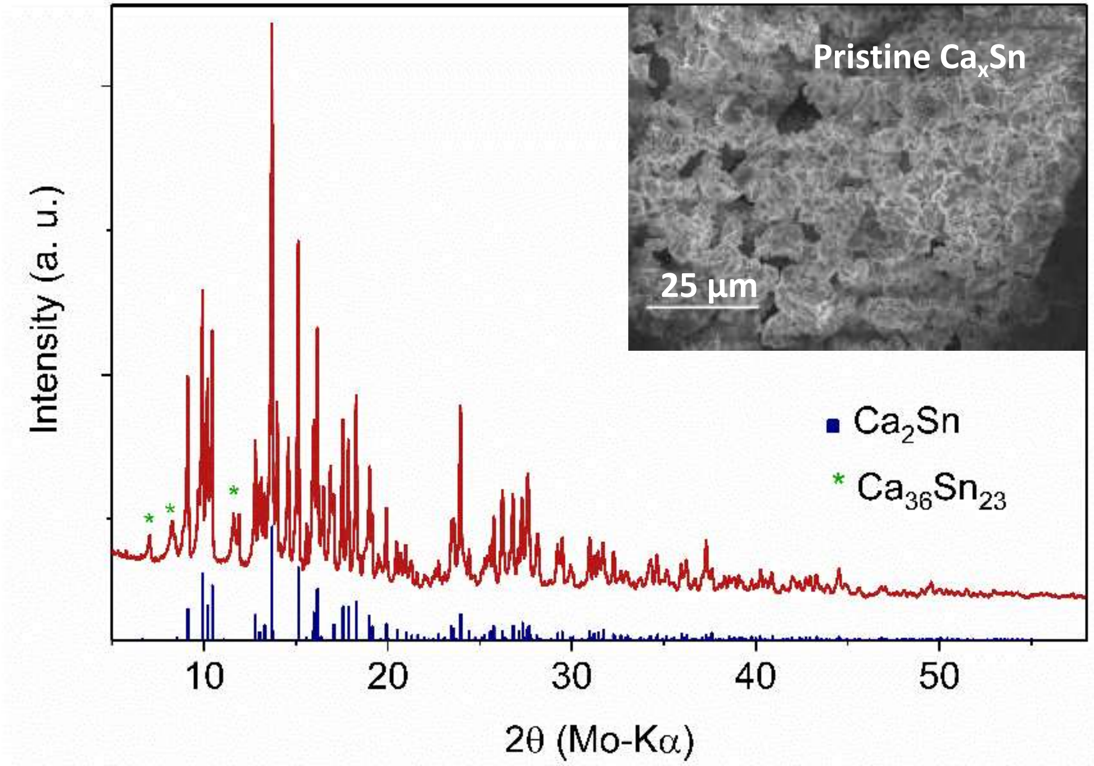
The anode problem

- Ca is reactive and gets easily passivated
- rollover after short cycling period of several 10 cycles only

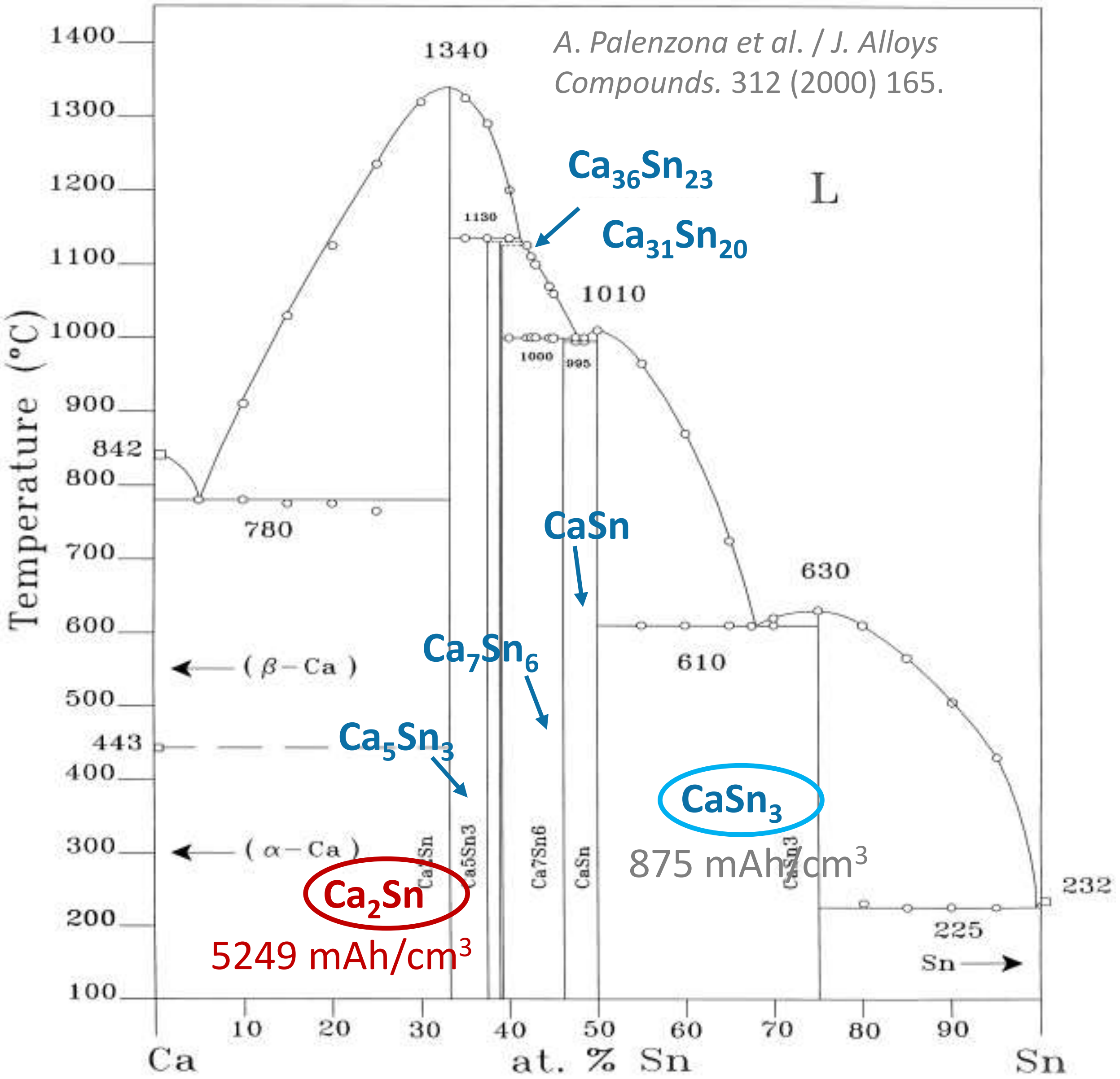
Development of Ca-Sn alloy bulk anodes

Bulk material preparation:

2.2 Ca + Sn —(900 °C/1h, Ar)→ Ca_xSn

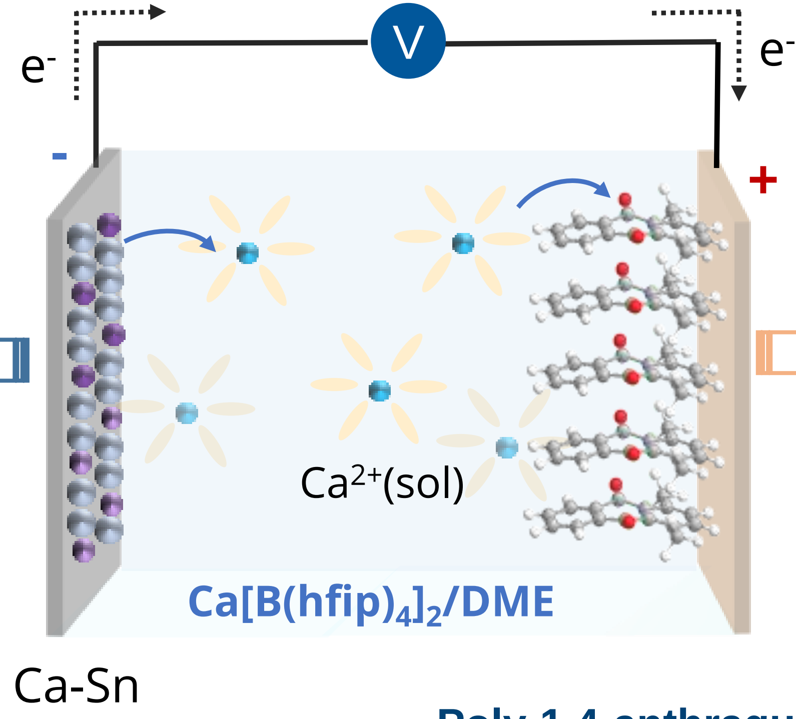


Z. Zhao-Karger, Y. Xiu, Z. Li, A. Reupert, T. Smok, M. Fichtner, *Nat. Commun.* **2022**, *13*, 3849.



Full cells with Ca-Sn alloy anodes

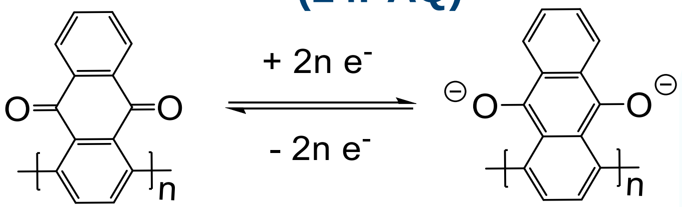
Alloy anodes:
- ✓ Bypass Ca passivation
- ✓ High capacity
- ✓ Low calciation voltage



Organic materials:
- ✓ Flexible structure
- ✓ Fast ion diffusion kinetics
- ✓ Tunable properties
- ✓ Large-scale production
- ❖ Low electronic conductivity
- ❖ Low volumetric energy density

$$Ca_xSn \underset{+\,2x\,e^-}{\overset{-\,2x\,e^-}{\rightleftharpoons}} xCa^{2+} + Sn$$

Poly-1,4-anthraquinone (14PAQ)



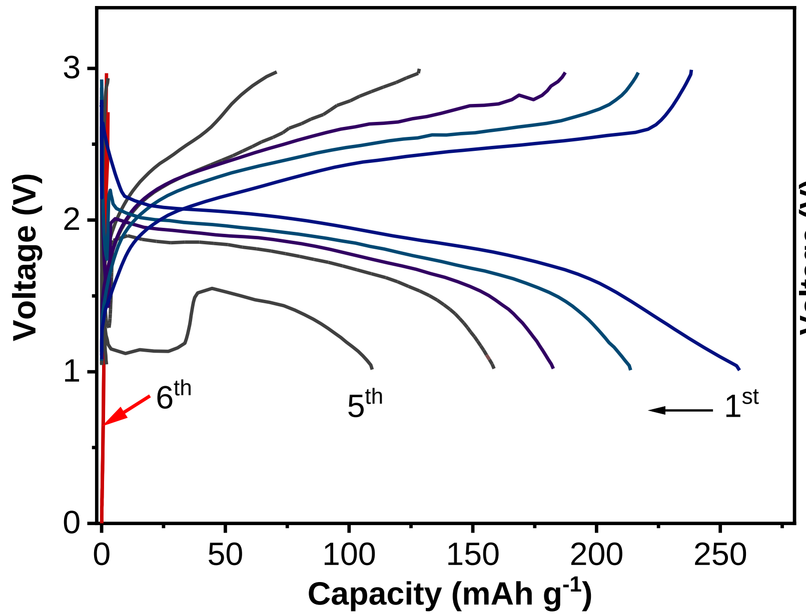
Theor. capacity ~260 mAh g^{-1}

Mg || $Mg[B(hfip)_4]_2$ ||14PAQ
1000 cycles, ~60% capacity retention

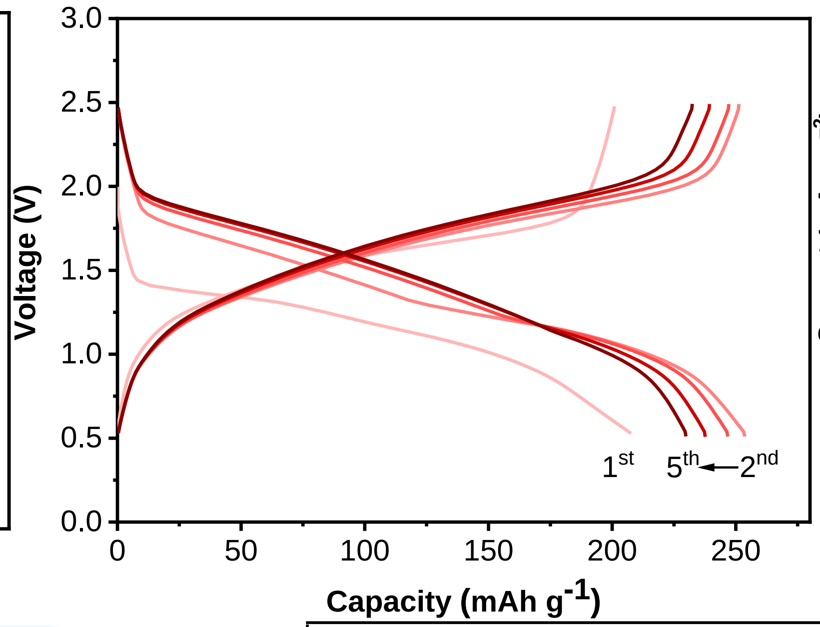
Y.Xiu, M.Fichtner, Z.Zhao-Karger et al. *Batteries & Supercaps.* **2021**, 4, 1850

Full cells with Ca and Ca-Sn alloy anodes

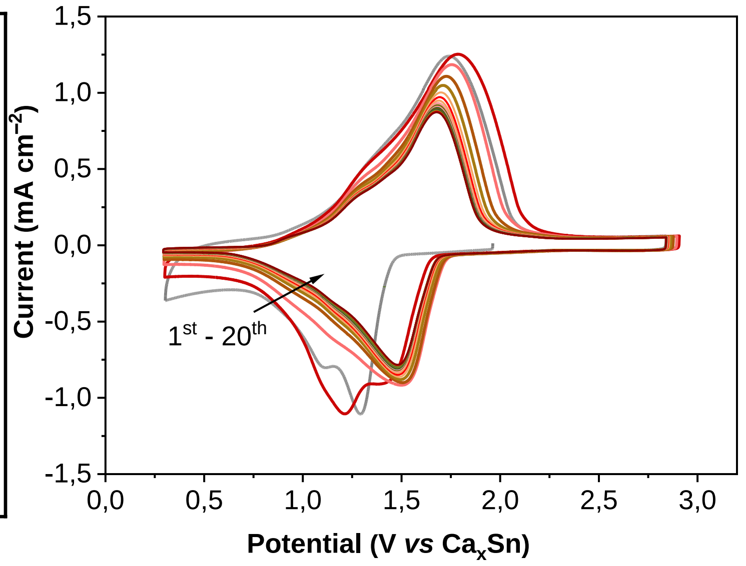
Ca || Ca[B(hfip)$_4$]$_2$ || 14PAQ



Ca$_x$Sn || Ca[B(hfip)$_4$]$_2$ || 14PAQ



low hysteresis

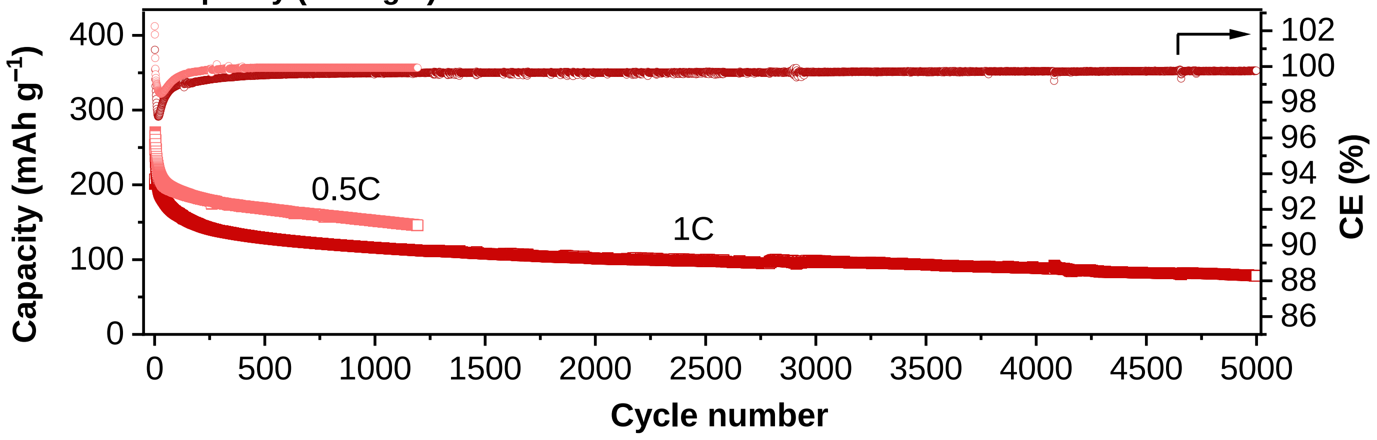


Coin-cells:

Cathode: 14PAQ/Ketjenblack/PTFE (45/45/10)
active mater. ~1.5 mg/cm^2

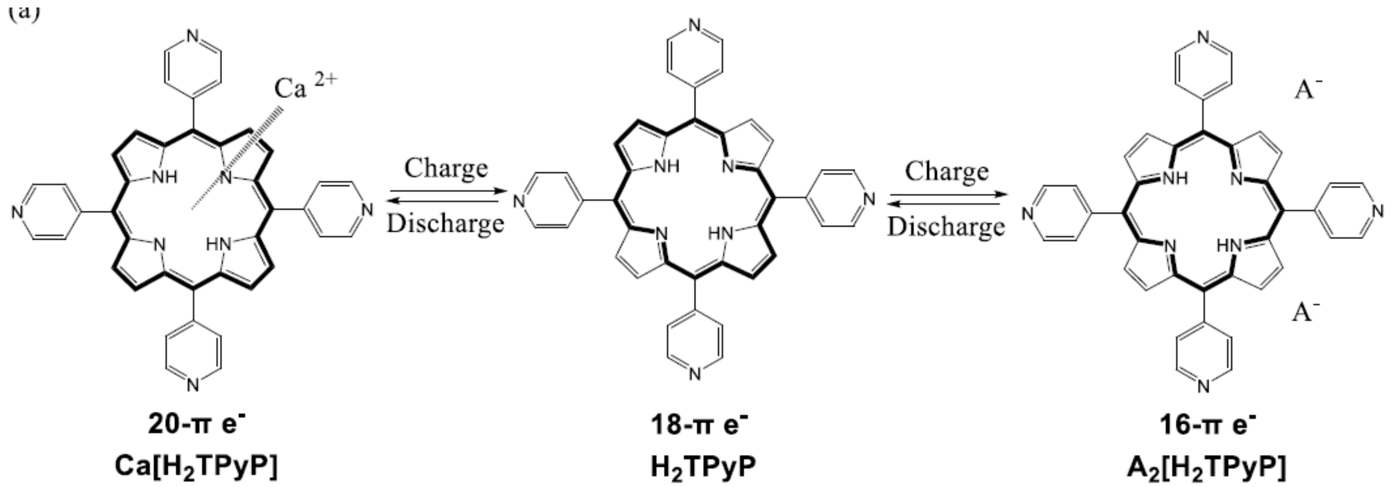
Anode: active mater. ~12 mg/cm^2

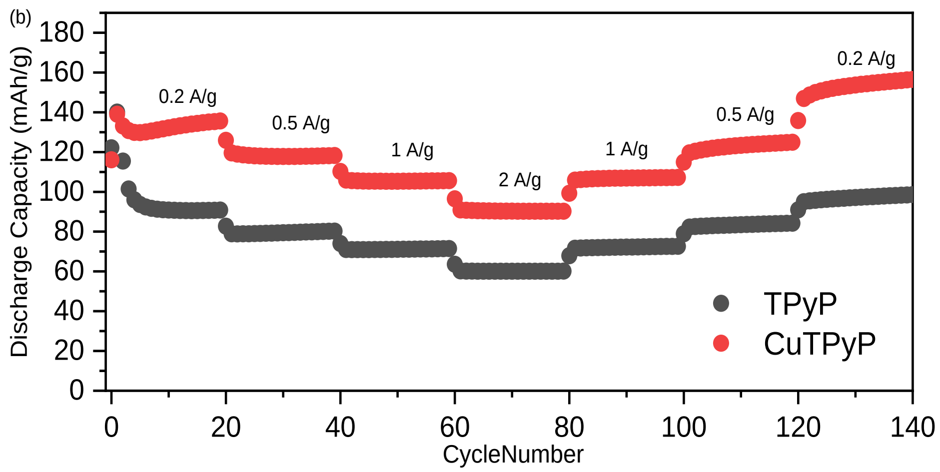
Current density: 260 mA/g (1C)

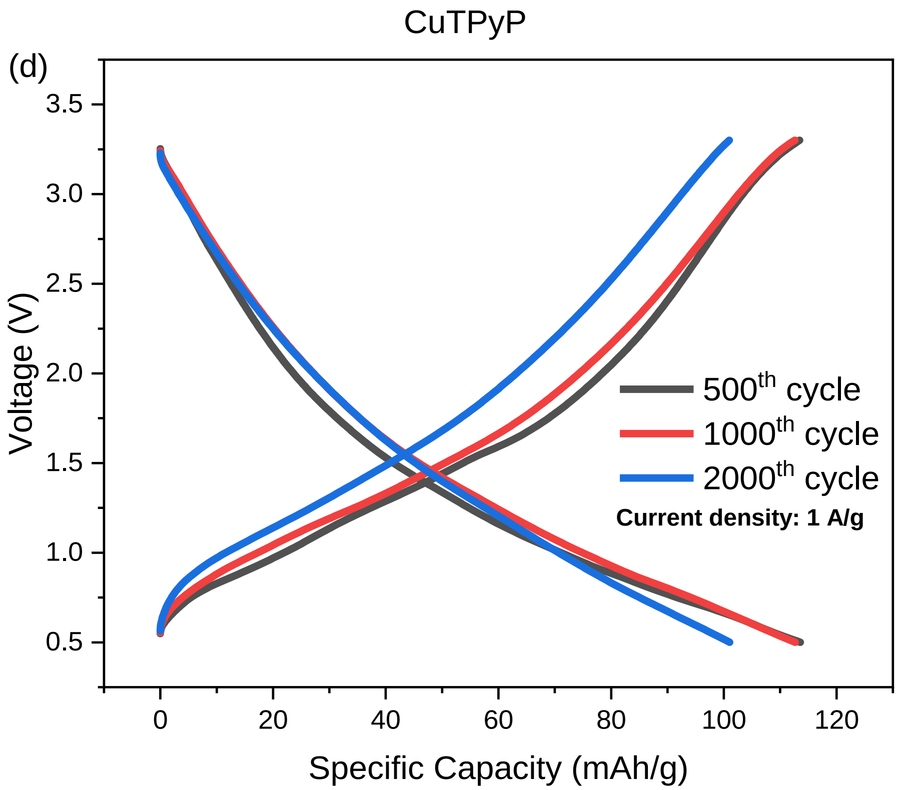


Z. Zhao-Karger, Y. Xiu, Z. Li, A. Reupert, T. Smok, M. Fichtner, *Nat. Commun.* **2022**, *13*, 3849.

A π-conjugated Porphyrin Complex as Cathode Material for Fast and Stable Energy Storage in Calcium Batteries







📖 T. Smok *et al.*
A π-conjugated Porphyrin Complex as Cathode Material Allows Fast and Stable Energy Storage in Calcium Batteries, submitted (2024)

Summary

- ✓ Better stability of layered cathode materials for Na-ion batteries
- ✓ Inorganic Na-conducting binders
- ✓ First TERS studies of SIB-SEI on hard carbon
- ✓ Spin-off for SIB materials
- ✓ Long-lasting Al batteries with organic cathode
- ✓ First RT electrolyte for calcium batteries
- ✓ Ca battery with maximum stability
- ✓ Fastest Mg battery
- ✓ High capacity Mg battery
- ✓ First solid electrolyte for chloride ion batteries
- ✓ Internationally unique Materials Acceleration Platform (MAP) with autonomous, AI-controlled robotics
- ✓ ...

THANK YOU !

(What are highlights and) why do we need them?

- **It is a central goal of the cluster to create impact**
- **Facile Communication; demonstration of scientific/technical progress**
- **Reputation: creation of followers**
- **Justification of a huge coordinated effort vs. funding organization**