SIMBA materials development

Final event

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This project has received funding from the European Commission under grant agreement No 963542

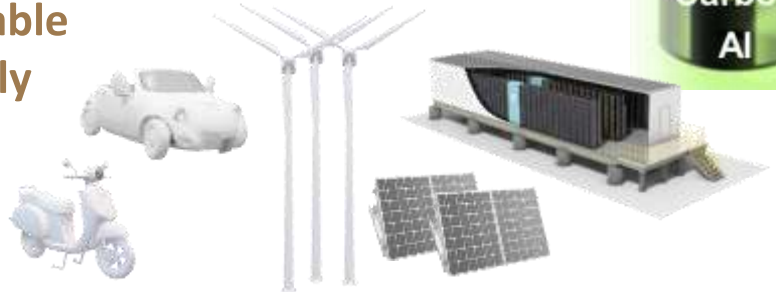
Why sodium-based technology

- Lithium-ion batteries
  - Dependency on critical materials

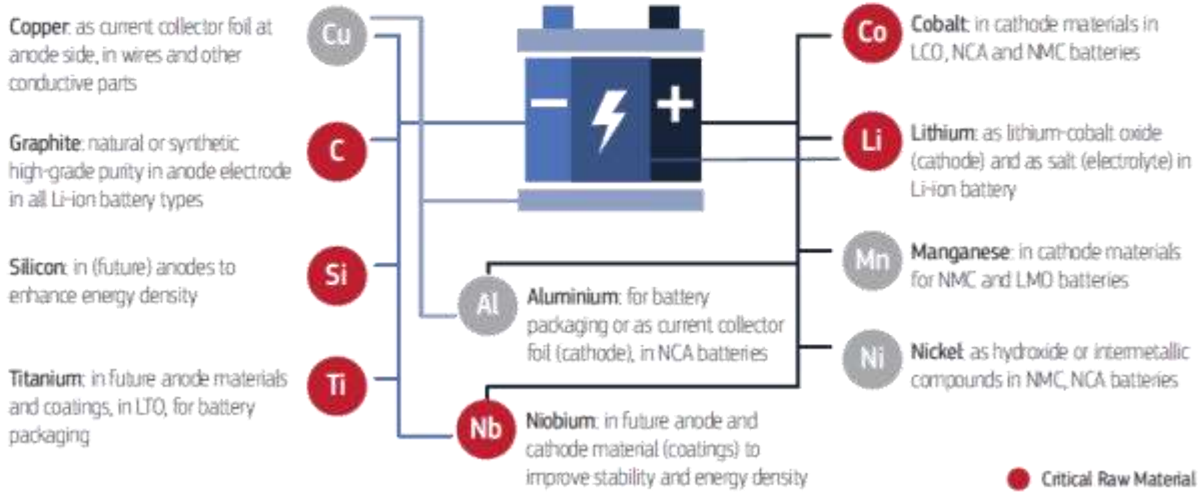
    - Geopolitical supply risks
    - Substitutability supply restrictions
    - Environmental implications

- Sodium-ion batteries
  - No dependency on critical materials

Alternative low-cost, sustainable and environmentally friendly EES



EU critical materials

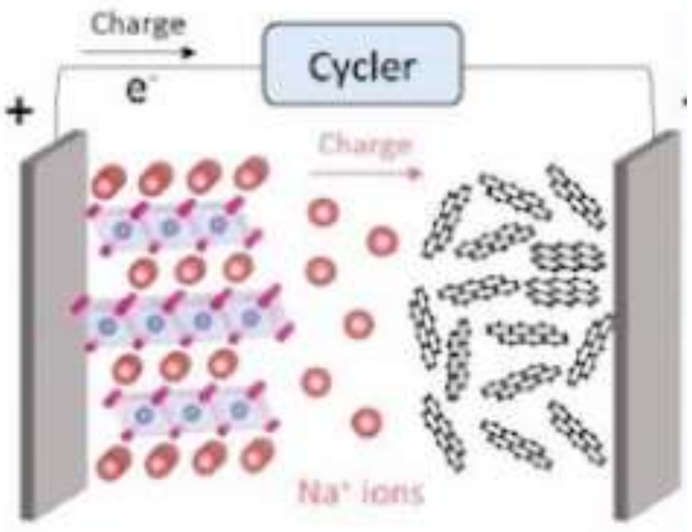


https://single-market-economy.ec.europa.eu/sectors/raw-materials/areas-specific-interest/critical-raw-materials_en

Chemistry of sodium-ion batteries

*LE = Liquid electrolyte

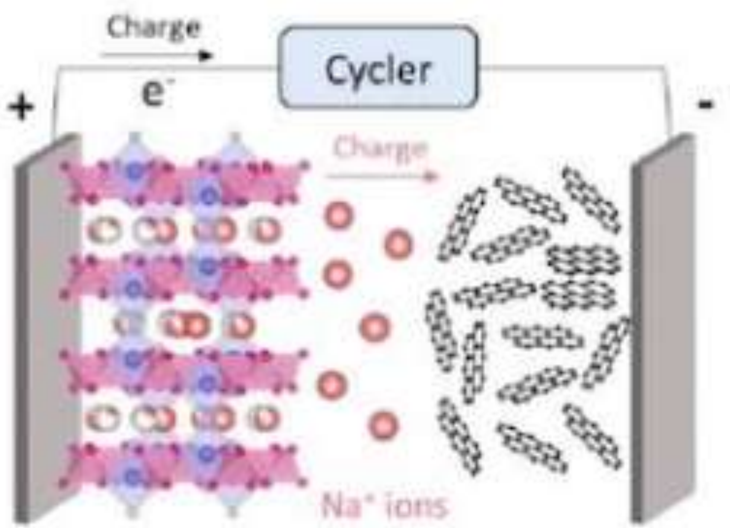
Layered oxide | LE* | Hard carbon



faradion HiNa BATTERY CATL TIAMAT

- High energy density
- Poorer cycling stability
  - Multiple phase transitions of the cathode

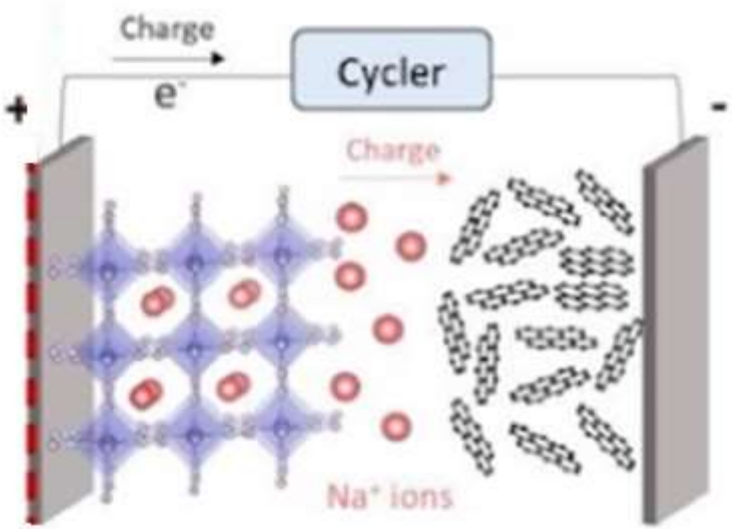
NVPOF | LE* | Hard carbon



TIAMAT

- High power density
- Large lifetime
- Poor energy density
- A complex NVPOF synthesis

Prussian white | LE* | Hard carbon



Altris northvolt CATL

- Low-cost synthesis process
- Moderate energy density
- Poorer cycling stability

https://evreporter.com/sodium-ion-batteries-current-status-of-the-technology-and-supply-chain/

SIMBA project: **Concept**

SIMBA
SODIUM-ION AND SODIUM METAL BATTERIES

Main goal

Development of a **highly cost-effective**, **safe**, **all-solid-state battery** with **sodium** as a mobile ionic charge carrier for **stationary storage applications**

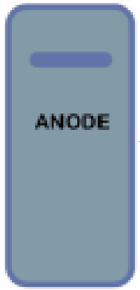
Option 1

Hard carbon (TRL5)

- Sustainable sources
- High capacity (280 mAh g^{-1})

Porous ceramic structure

- Support for Na plating
- High specific capacity (> 500 mAh g^{-1})

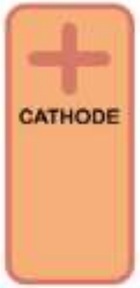


Na+

Solid state electrolyte (SSE) (TRL3-5)

- Single-ion conductive polymers
- Optimized safe Na-ion transport
- Stability window up to 4.4 V
- Ionic conductivities of 10^{-3} S cm^{-1} at RT

Na+



Iron-based Prussian White (TRL5)

- Ultra low-cost (< 4 € kg^{-1})
- Good capacity (165 mAh g^{-1})
- Acceptable working voltage (3 V)
- Scalable

2nd Gen: layered oxide (TRL5)

- High energy material (> 200 mAh g^{-1} and > 3 V)

SIMBA cathode material: **Prussian White**

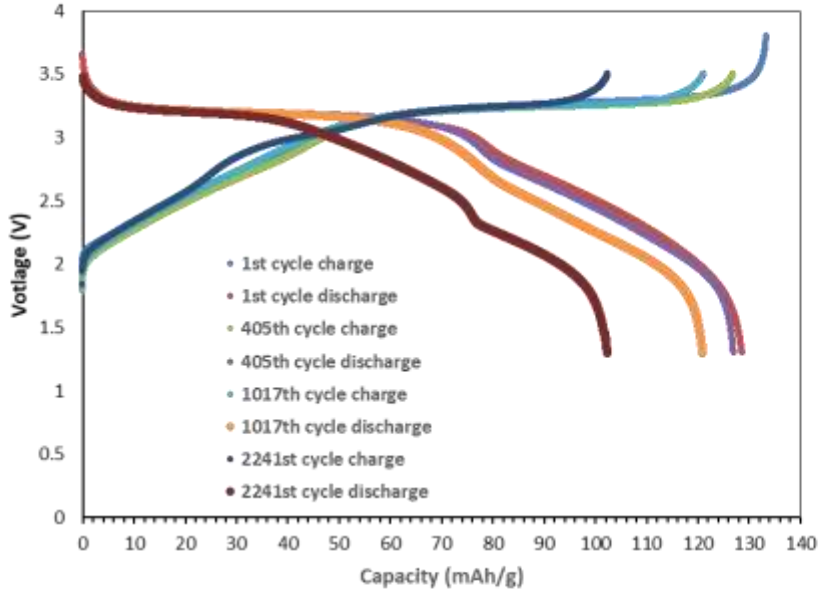
- **Aim: Optimizing synthesis parameters**

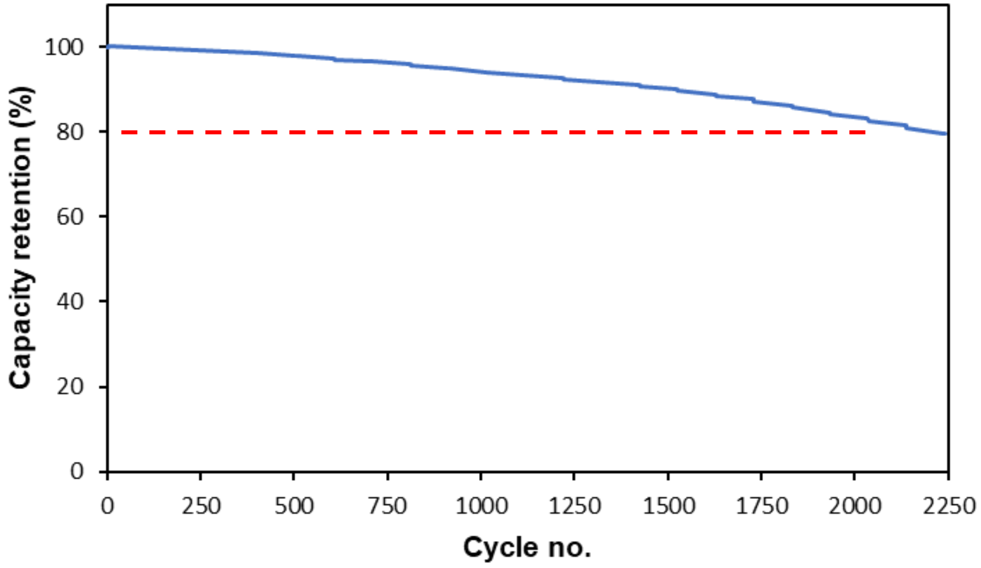
- Within the SIMBA project, **Altris** has optimized the standard PW production process
  - Shortened reaction time by 75% while maintaining yield and material performance
  - Double the yield per liter with equivalent material performance
- -> Can be combined = higher yield in shorter time

- In parallel: Overall increase in first discharge capacity of ~20 mAh/g since the project started

SIMBA cathode material: **Prussian White**

- **Project Objective: > 2000 cycles at 80% discharge retention – reached in Aug 2022**



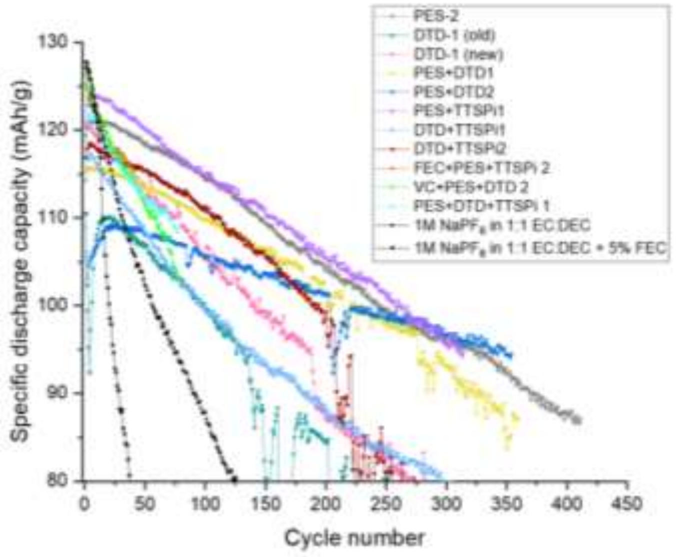


- Full-cell cycle tests show promising results with **80% capacity retention after 2241 cycles**
  - Cell step up: Altris std PSD PW/ non-flammable electrolyte/ hard carbon
  - C-rate was altered between 0.7C and 0.06C.

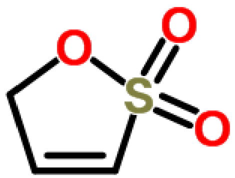
Fulfills the project target to achieve at least 2000 cycles at 80% discharge retention

SIMBA cathode material: Prussian White

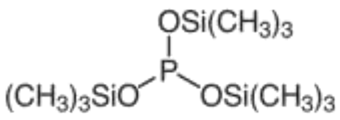
- Electrolyte compatibility
  - **Additive improves the performance of PW/HC full cells**
  - *NaBOB in TEP* -***not flammable electrolyte***-→ poor compatibility with HC
  - Some additives improve the PW/HC electrochemical performance
    - **PES+TTSPi1** or **PES-2** best candidates



PES

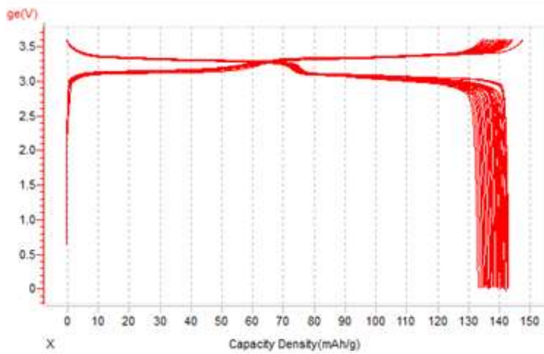


TTSPi1

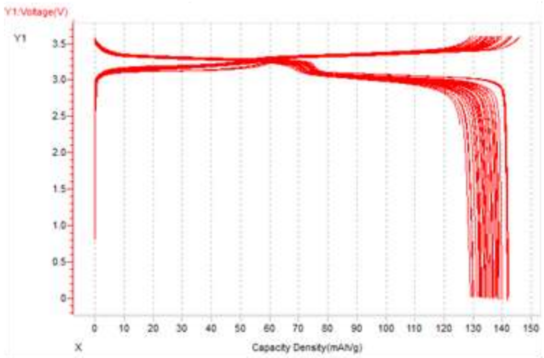


- Electrolyte compatibility
  - **Glyme electrolytes are good candidates in PW anode-less configuration**
  - Aluminum coated by carbon black layer
  - Electrolyte: *$NaBF_4$* in *diglyme* or *tetraglyme*

$NaBF_4$ in diglyme



$NaBF_4$ in tetraglyme



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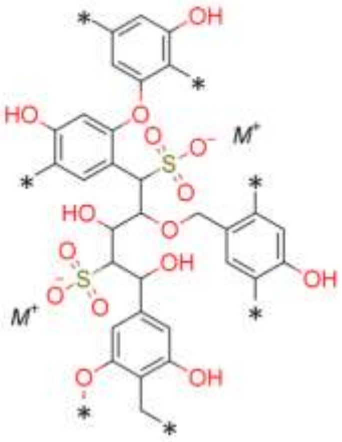
J. Welch, et al. J. Electrochem. Soc. 20222, 169, 120523.

SIMBA anode material: **bio-mass based Hard carbon**

- Three bio-masses under investigation:

Microalgae



Lignosulfonate

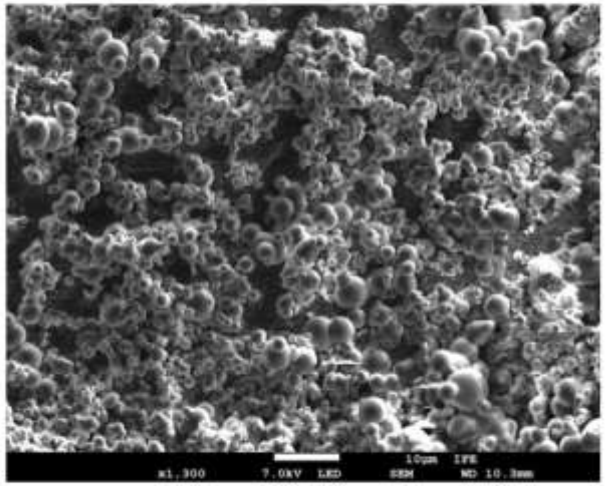
Sawdust
(fully European supply chain)

- <u>Synthesis optimization</u>

Drying 100 °C → Torrefaction 275 °C → Milling & Washing → Biochar formation 600 °C → Pyrolysis 1300 °C

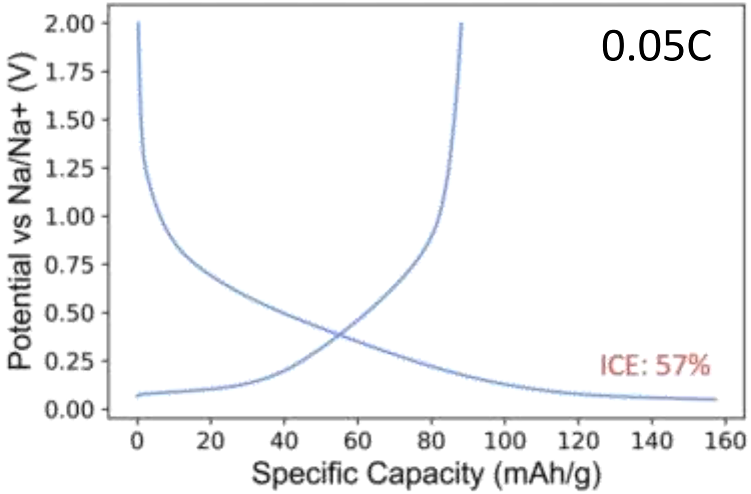
SIMBA anode materials: **bio-mass based Hard carbon**

- Synthesis: **Microalgae**
- Morphological characterization:
  - Synthesis yield: 14%
  - **High** SSA: 847 $m^2 g^{-1}$
  - **Homogeneous** morphology
  - **Small** particle size



- Electrochemical characterization:
  - **Low** ICE: 57%
  - **Low** reversible capacity: < 100 mAh g^{-1}

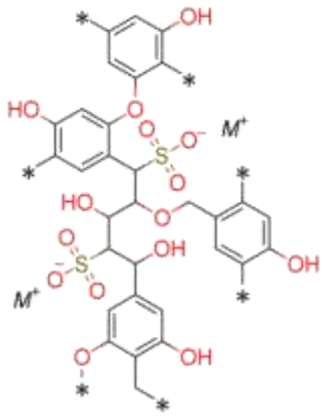
HC | 1M $NaPF_6$ in EC:DEC | Na

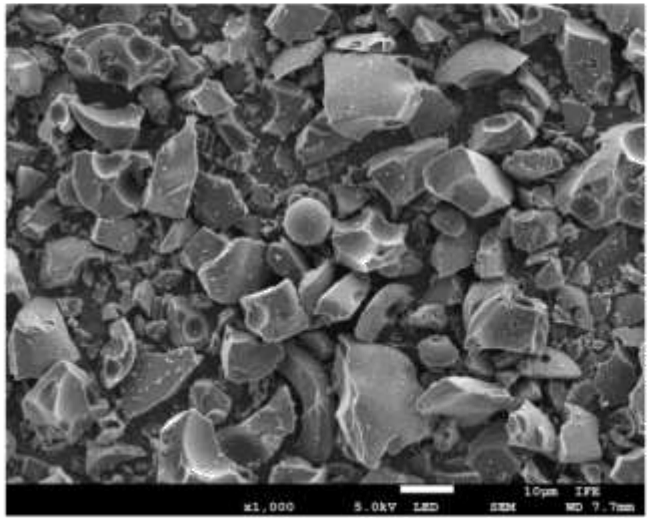


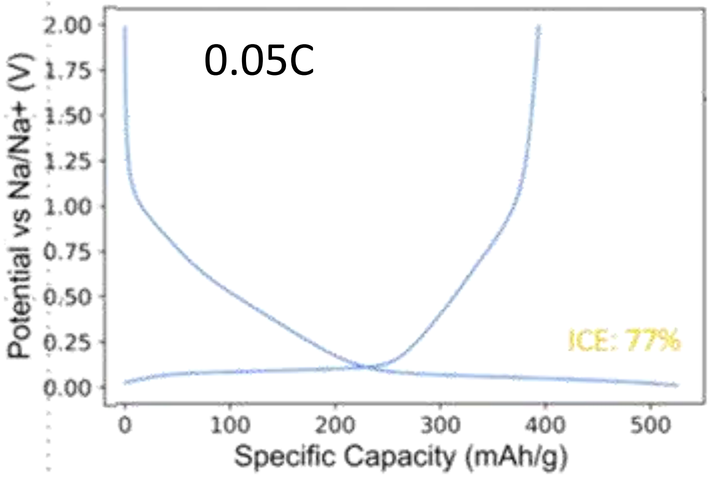
SIMBA anode materials: bio-mass based Hard carbon

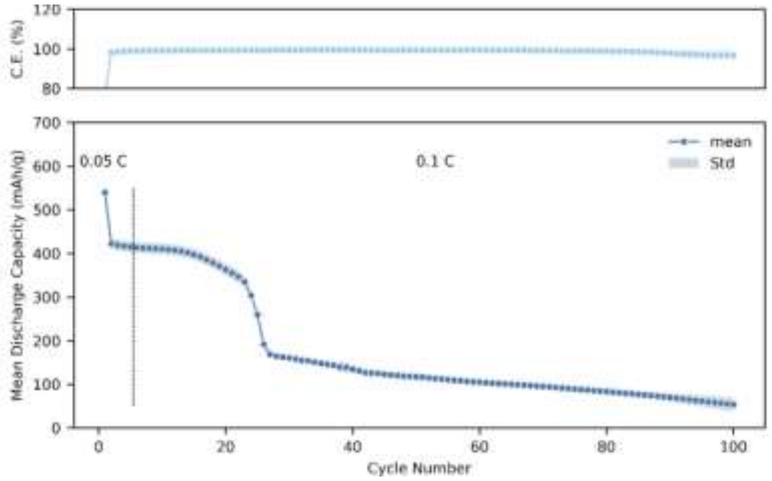
- Synthesis: Lignosulfonate
- Morphological characterization:
  - Synthesis yield: 33%
  - Medium/Low SSA: 27.8 $m^2\ g^{-1}$
  - Inhomogeneous morphology
  - Larger particle size
  - Pore size: 4.8 nm
- Electrochemical characterization:
  - Medium ICE: 77%
  - High reversible capacity: 400 mAh g^{-1}
  - Medium CE: 98.3%
  - Poor capacity retention

HC | 1M $NaPF_6$ in EC:DEC | Na





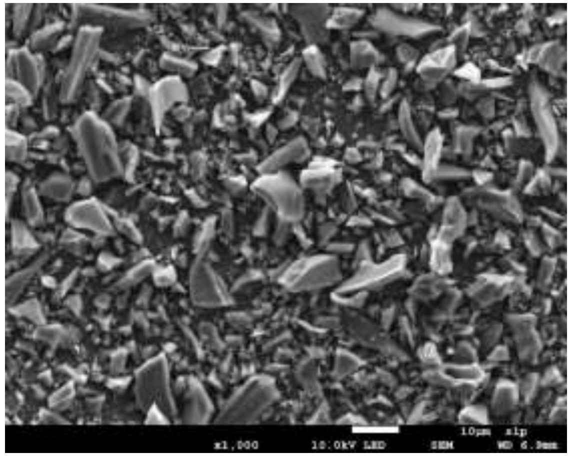


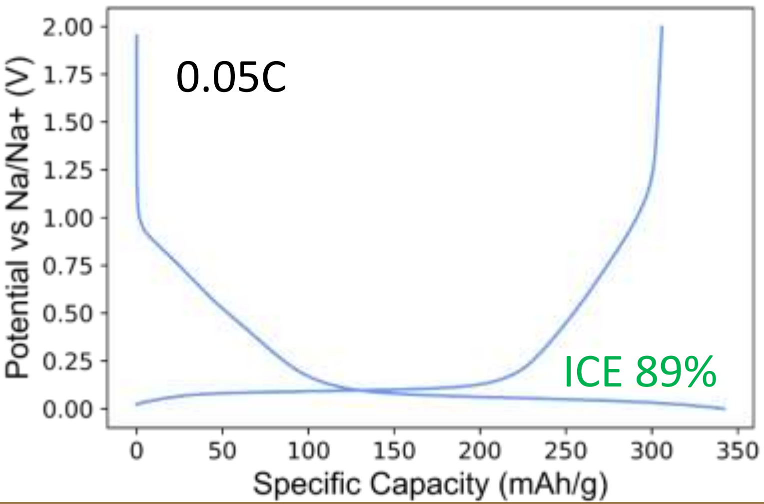


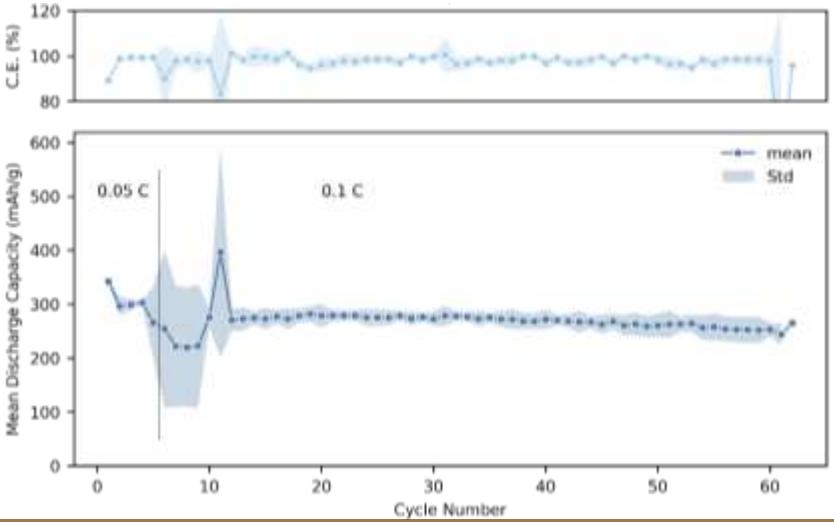
SIMBA anode materials: **bio-mass based Hard carbon**

- Synthesis: **Sawdust**
- Morphological characterization:
  - Synthesis yield: 28%
  - **Low** SSA: 7.4 $m^2\ g^{-1}$
  - **" More" homogeneous** morphology
  - **Small** particle size
  - Pore size: 9.0 nm
- Electrochemical characterization:
  - **High** ICE: 89%
  - **High** reversible capacity: 265 $mAh\ g^{-1}$
  - **Medium** CE: 98.3%
  - **High** capacity retention

HC | 1M $NaPF_6$ in EC:DEC | Na

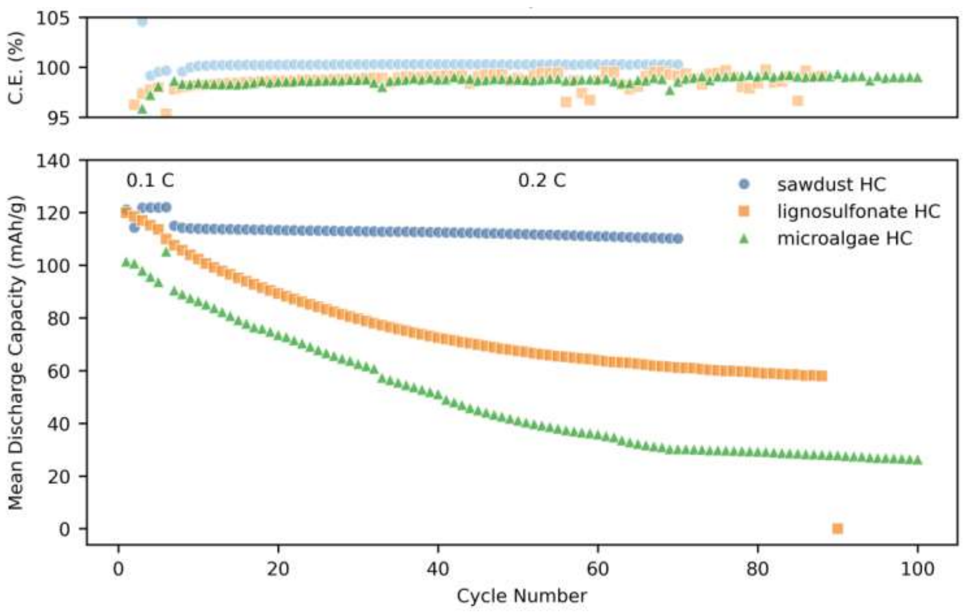




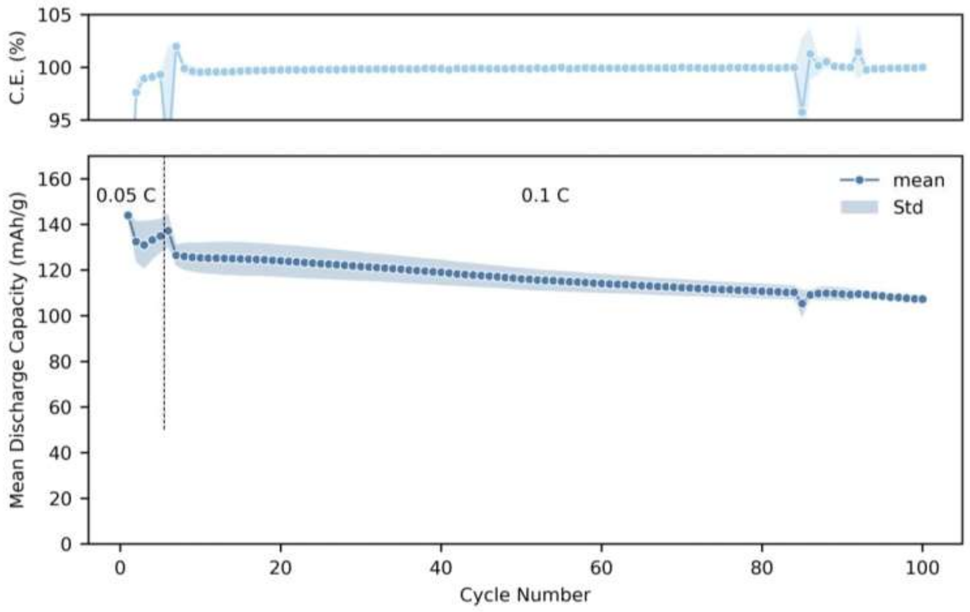


SIMBA anode materials: **bio-mass based Hard carbon**

PW (**Altris**) | 1M $NaPF_6$ in EC:DEC | HC



PW (**Altris**) | 1M $NaPF_6$ in EC:DEC | **HC (sawdust)**



- SIMBA cell: PW | HC **sawdust** full cell delivers specific capacity of 120 mAh g^{-1} at 0.1C and 118 mAh g^{-1} at 0.2C and a capacity retention of 99% (at 0.2C)

SIMBA SODIUM-ION AND SODIUM METAL BATTERIES

SIMBA anode materials: porous ceramic compounds

SiCN

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- Influence of the annealing on the physicochemical and electrochemical properties
- Electrochemical characterization (control plating time/capacity)
- Understand the (de)sodiation mechanism
- Investigate the interfacial properties

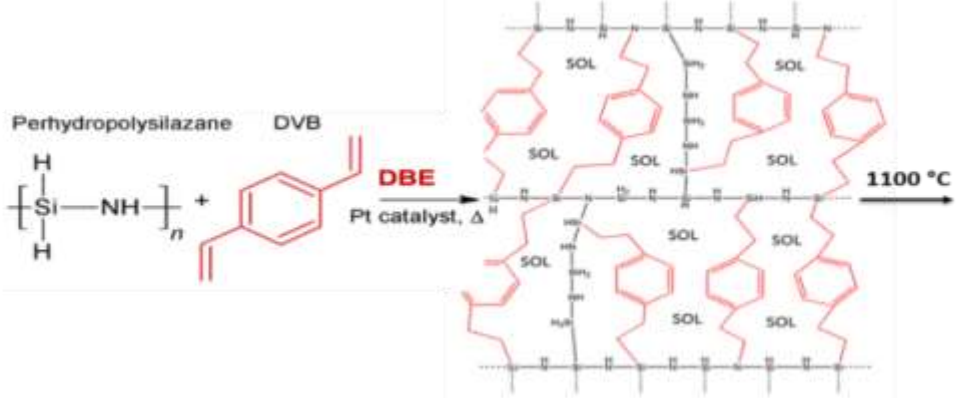
SiOC

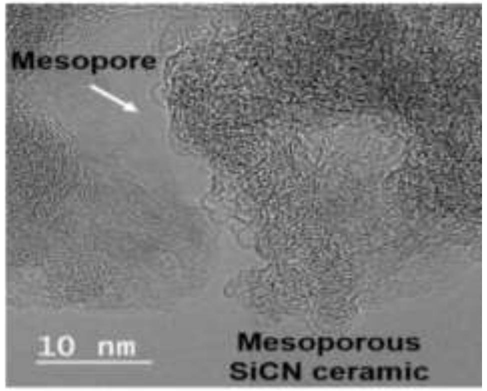
ISICSAS

- Optimization of the synthesis
- N_2 doping
- Electrochemical characterization: influence of the electrolyte
- ZnO interface by ALD to tune the interfacial properties
- Investigate the interfacial properties

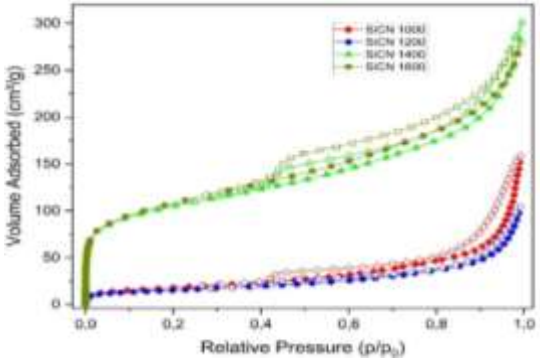
SIMBA anode material: **porous ceramic SiCN**

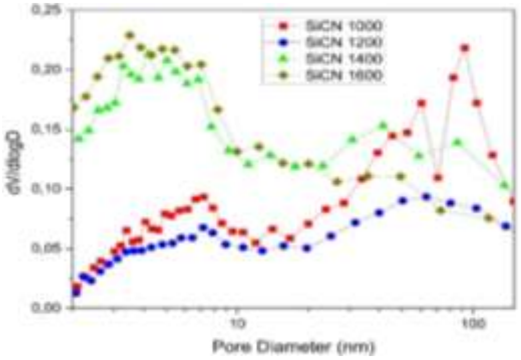
- <u>Synthesis:</u>
  - **One-pot synthesis** at four different temperatures: 1000 °C, 1200 °C, 1400 °C and 1600 °C
  - **SiCN** as Na plating matrix with **tailored porosity** by controlling pyrolysis temperature





- <u>Microstructural characterization:</u>
  - **meso- and macro-porosity nature**
  - Tuneable porosity and pore size
    - At higher temperatures, higher microporosity and smaller pore size





SIMBA anode material: porous ceramic SiCN

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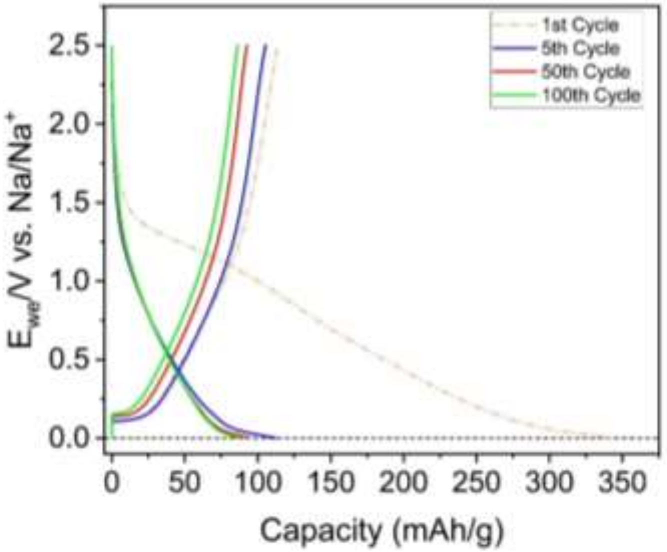
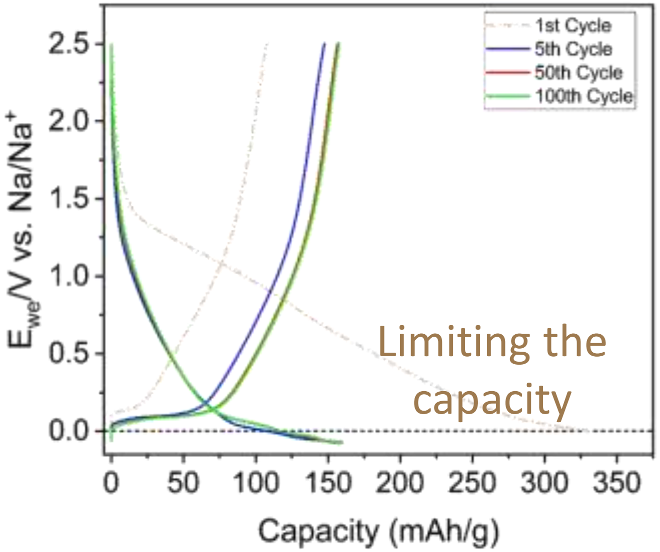
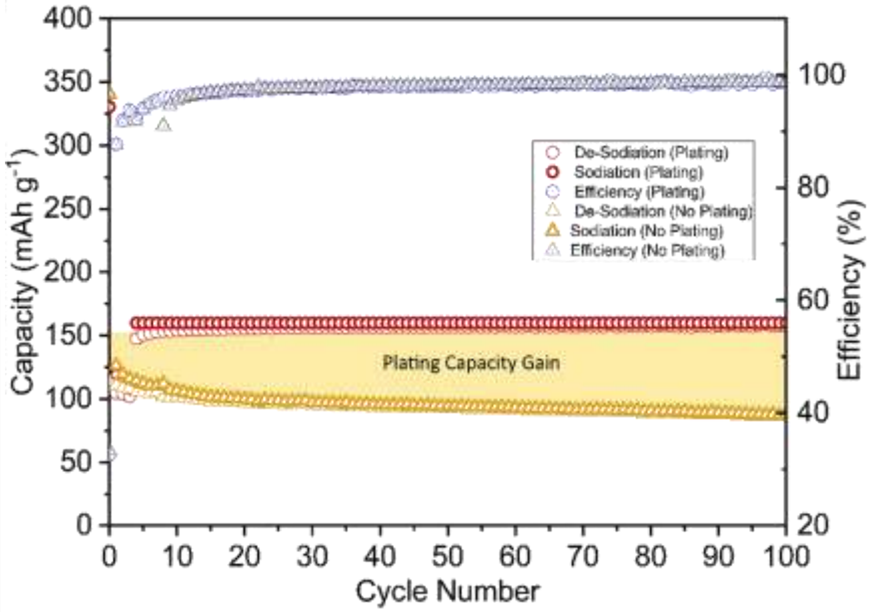
- Electrochemical characterization:
  - **Reversible Na plating** in liquid electrolyte (1M $NaPF_6$ in EC:DEC 3:7 vol%)
  - Limiting the capacity at 160 mAh g^{-1}
    - Capacity gain by the formation of plated species
    - **60% increase on the delivered capacity**
    - CE of 98.8% over 100 cycles
    - Better cycling stability

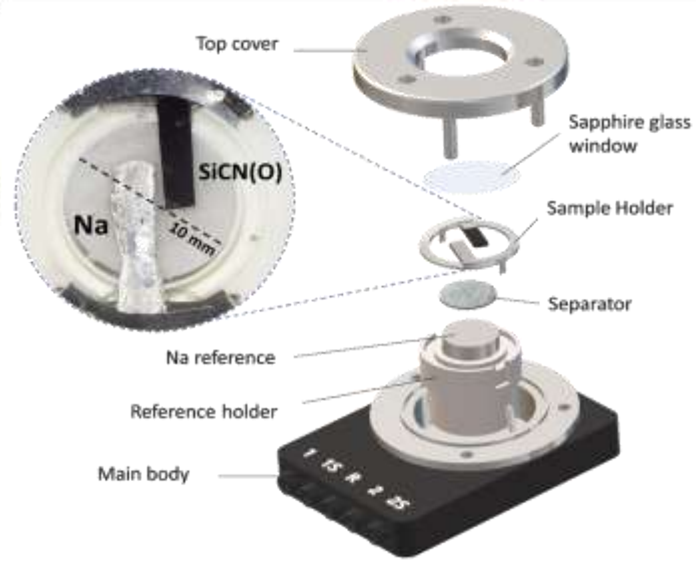


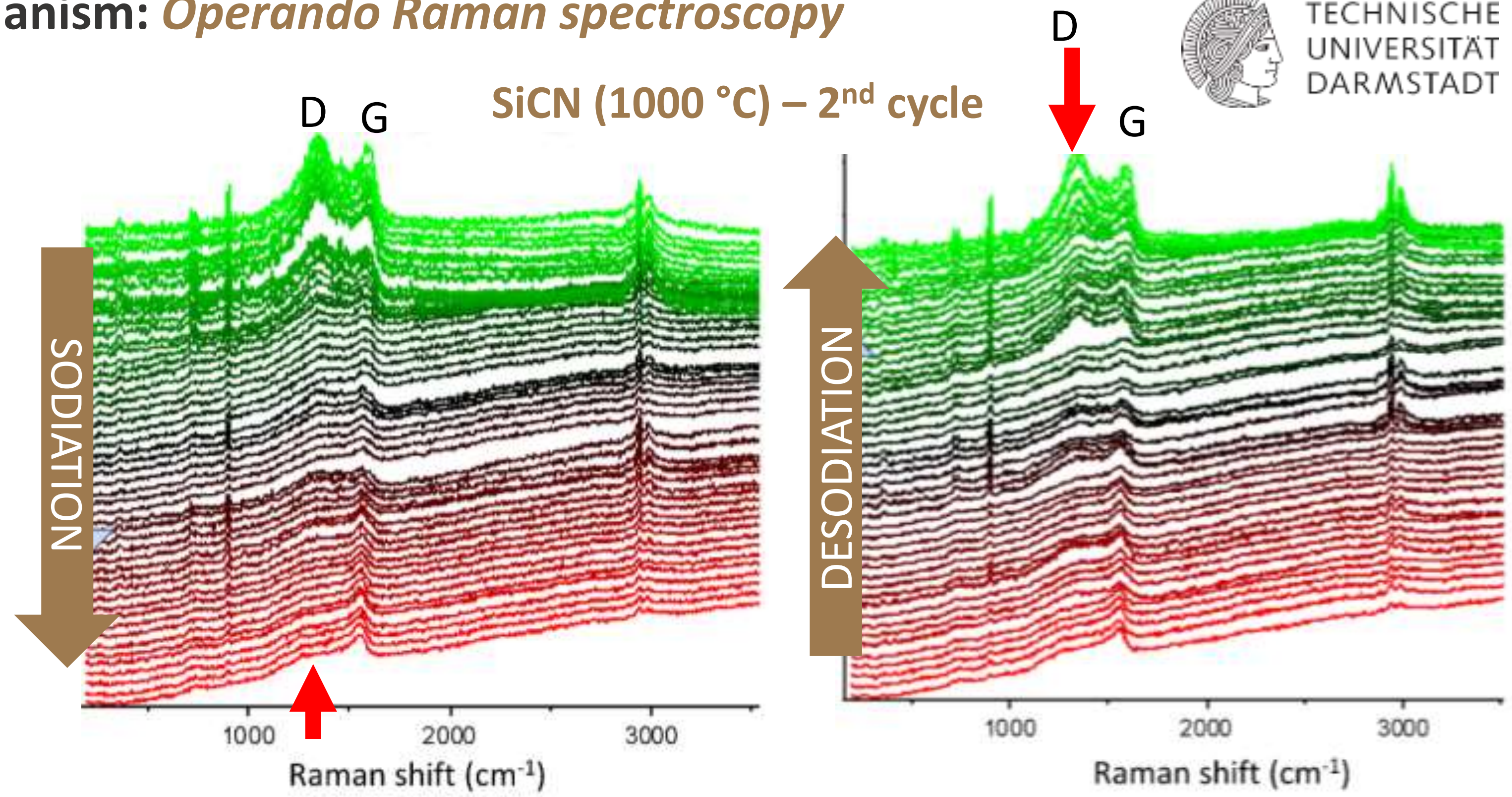




SIMBA anode material: porous ceramic SiCN

- **Understanding the Na storage mechanism:** ***Operando Raman spectroscopy***



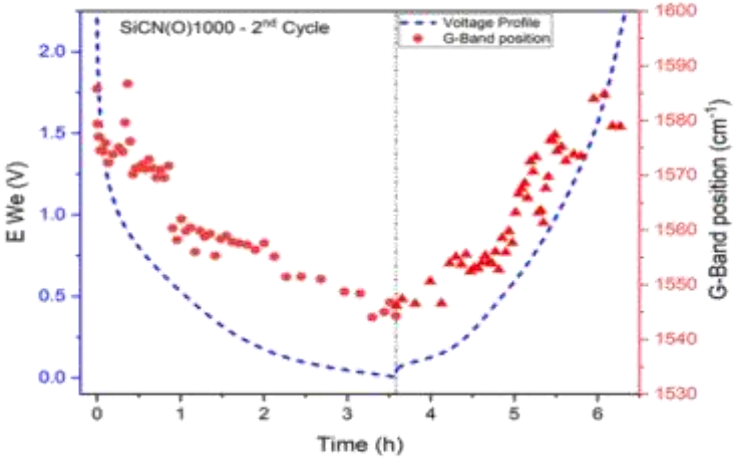


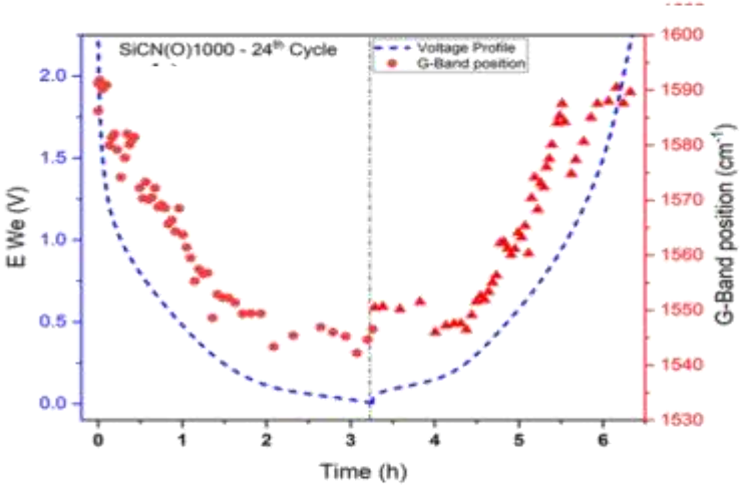
- Experimental details:
  - 2nd and 24th cycle measured
- Difficulties in observing the processes in the 1st cycle
  - SEI formation

- Reversible behavior: *disappearance/appearance of the D-band*
  - Hindering e⁻-hole pair formation and filling the defects

SIMBA anode material: **porous ceramic SiCN**

- **Understanding the Na storage mechanism:** ***Operando Raman spectroscopy***





SiCN (1000 °C) – 2nd cycle

- The *G-band shifting* in presence of Na ions
  - Changes in vibrational properties
- SODIATION:
  - Higher interaction with the lattice
- DESODIATION:
  - Reversible process (good overlapping)

SIMBA anode material: porous ceramic SiCN

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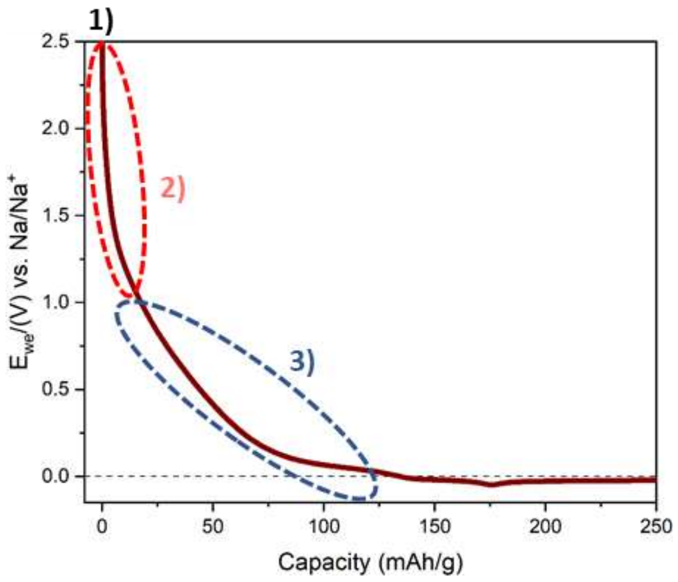
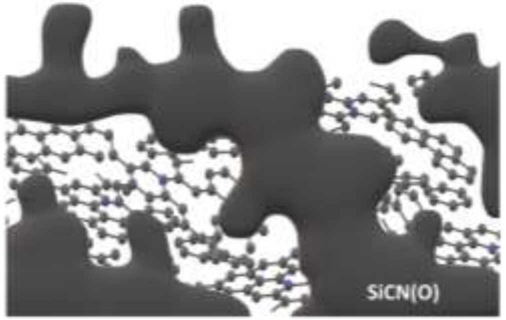
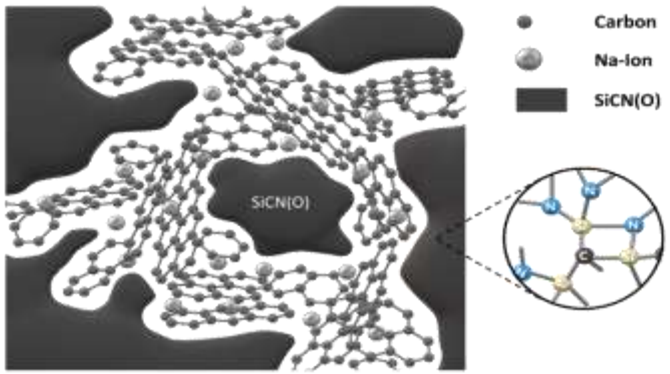
- Na storage mechanism:

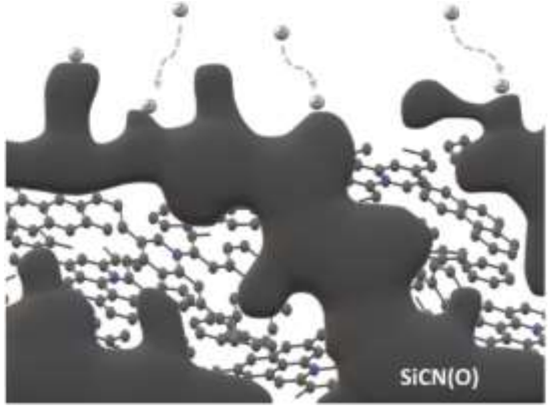


1) Pristine SiCN

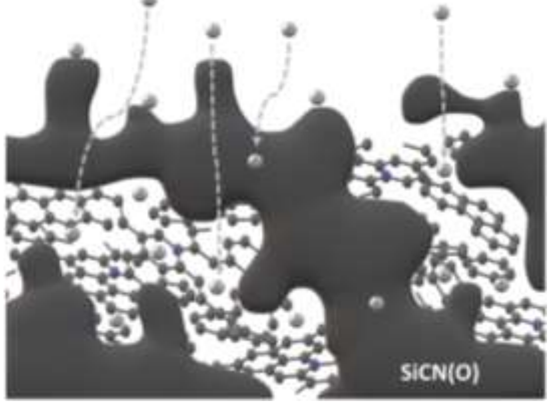




2) **Surface adsorption**



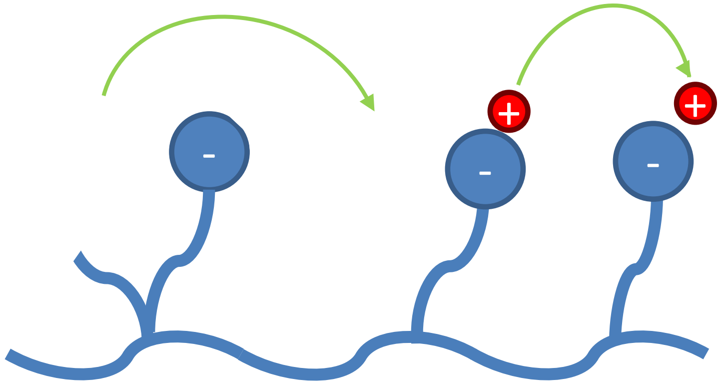
3) Na-ion insertion in the matrix and free carbon

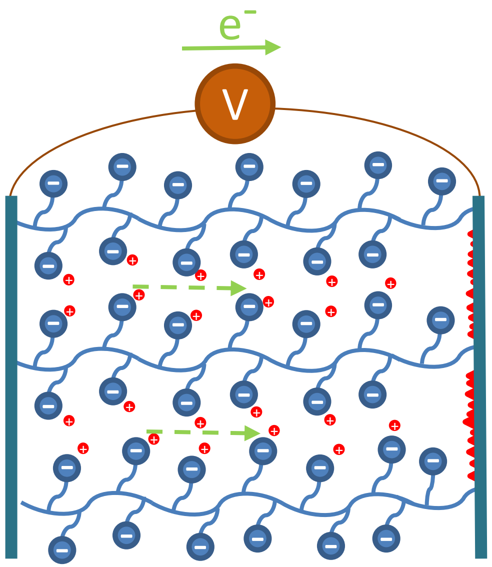


- SiCN(O) mixed-bonds structure provides additional insertion sites

SIMBA electrolytes: **single-ion conductor polymers**

SIPE



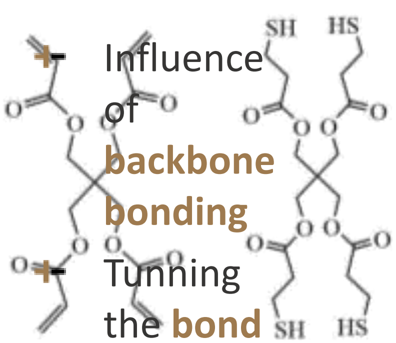


- Anions are chemically bonded to the polymer chain
  - No concentration gradient
  - Enhanced transference number
  - Suppress Na dendrite formation

SIMBA electrolytes: **single-ion conductor polymers**

Key components

Backbone

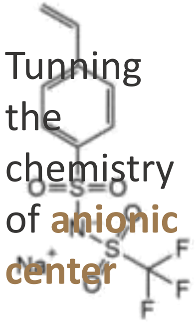


- Influence of **backbone bonding**
- Tunning the bond **chemistry**

PET4A

PETMP

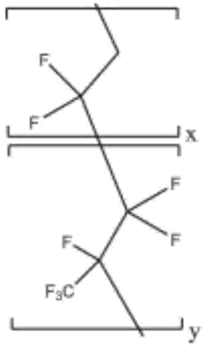
Charge carrier

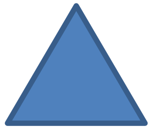


- Tunning the chemistry of **anionic center**
- Tunning the chemistry of **side chain**

NaSTFSI

Support



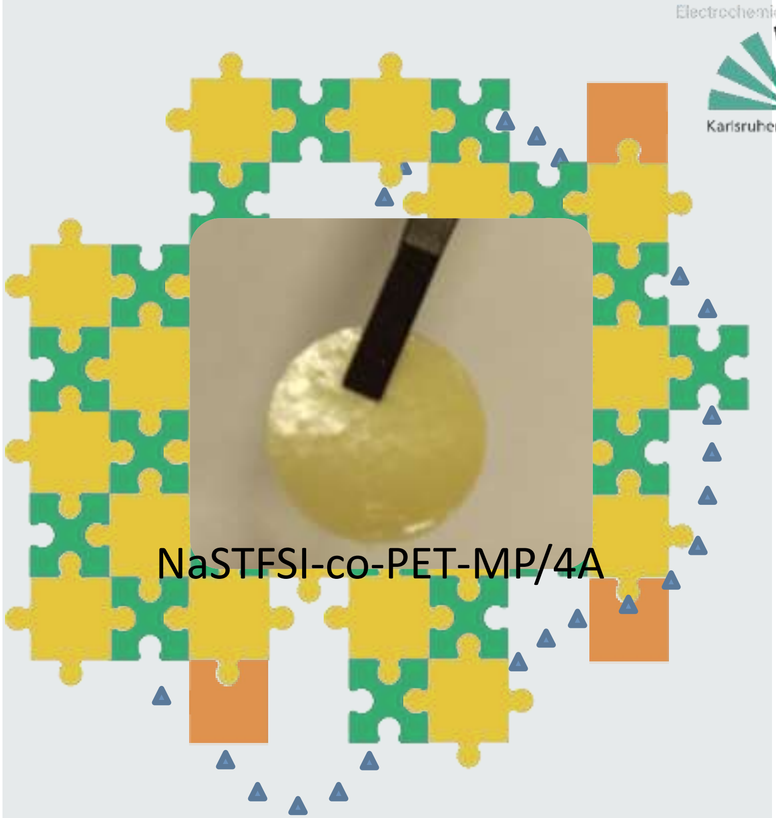


PVDF-HFP

- Optimization of the SIPE component molar ratio

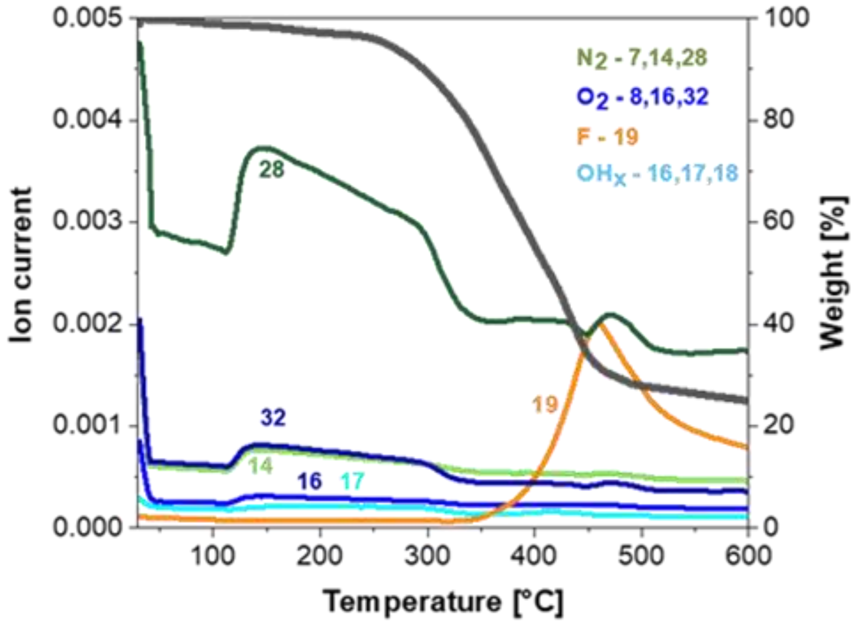
Thermal polymerization

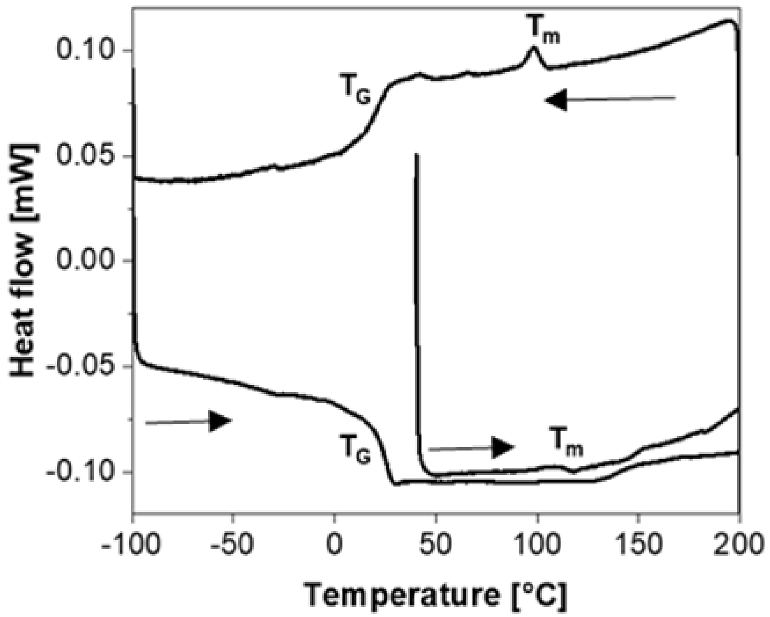
3D polymer electrolyte



Molecular transporter: EC:DMC:FEC (49 wt%)

SIMBA electrolytes: ***NaSTFSI-co-PET-MP/4A*** SIPE



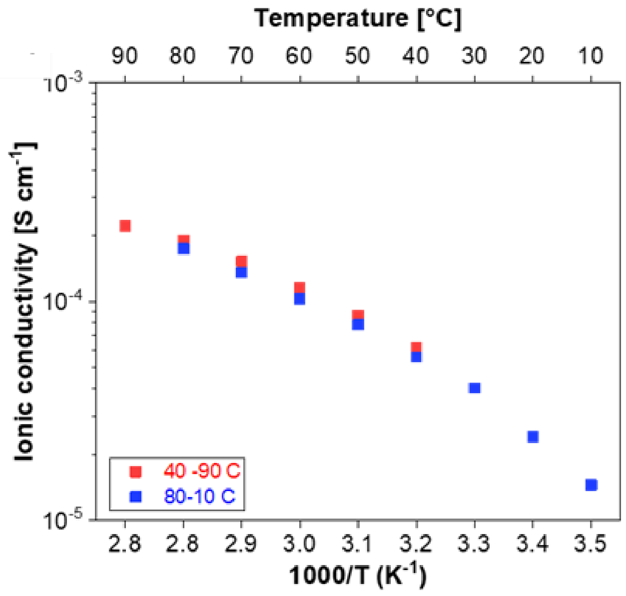


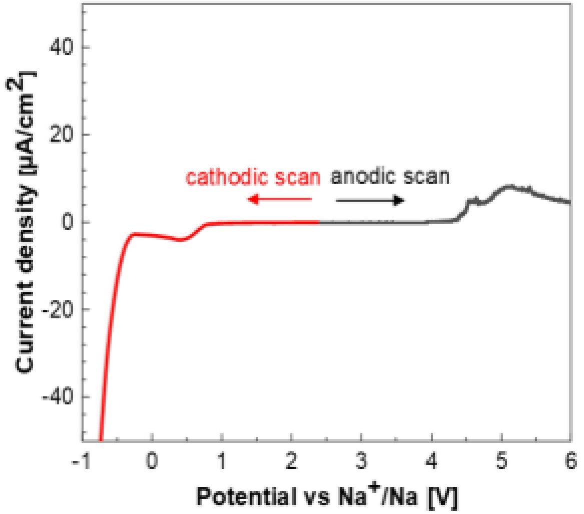
- Some air trapped inside
  - N_2 (m/z = 28), O_2 (m/z = 32), O (m/z = 16), and N (m/z = 14)
- Thermically stable up to 280 °C
- Fluorine is released at > 280 °C

- High thermal stability
- Glass temperature (T_G): 20 °C
- Crystallization and melting (T_M) at 110 °C

C. Wunder el al. (Under revision)

SIMBA electrolytes: ***NaSTFSI-co-PET-MP/4A* SIPE**





- Vogel-Tamman-Fulcher behavior
  - Na^+ ion transport supported by the motion of the anionic side chain and molecular transporters
- Ionic conductivity: $2.0 \cdot 10^{-5}$ S cm^{-1} at RT
  - $2.2 \cdot 10^{-4}$ S cm^{-1} at 90 °C

- Electrochemical stability window
  - Up to 4.5 V vs. Na^+/Na

PW (**Altris**) | *NaSTFSI-co-PET-MP/4A* (**HIU/KIT**) | Na
40 °C

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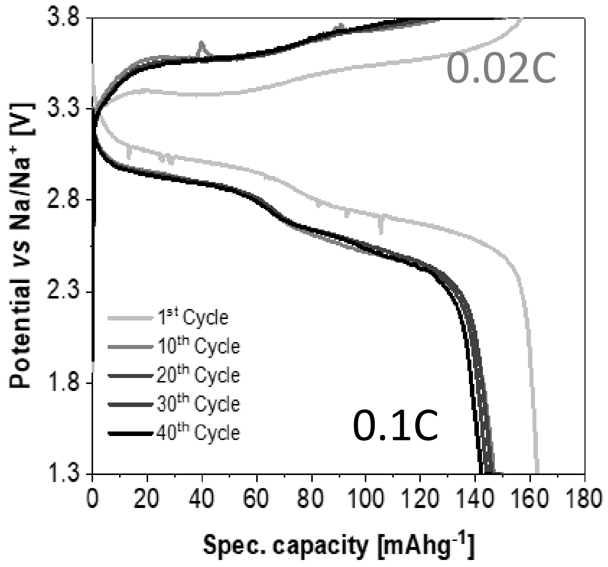
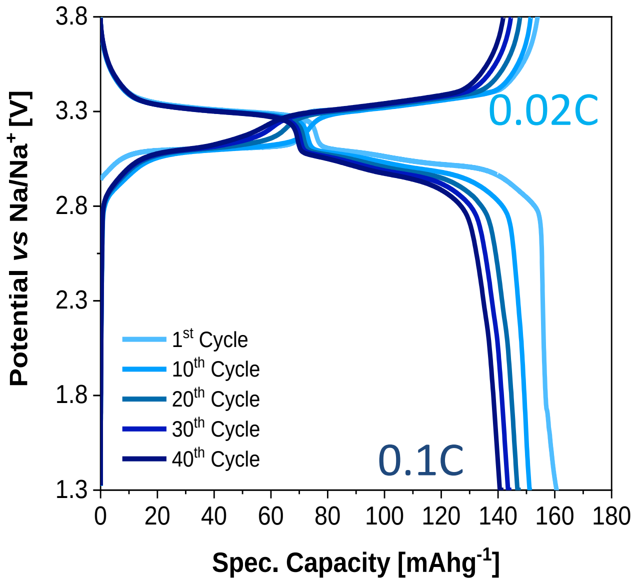


PW (**Altris**) | *1M NaPF6 in ED:DEC*| Na (20 °C)



- PW exhibits two plateaus (3.0 and 3.3 V vs. Na^+/Na)
- High polarization (0.4 V)
- Not influence on the delivered capacity (~160 mAh g^{-1})

Electrode: PW:C45:CMC:SBR (80:10:5:5)
Mass loading ~2.5 mg cm^{-2}
Cell config. 2 electrodes coin cell (PW||Na)
Potential range: 3.8 – 1.3 V (vs. Na^+/Na)
Current density: 1st cycle 0.02C → 0.05C →0.1C
(1C = 150 mAh g^{-1})

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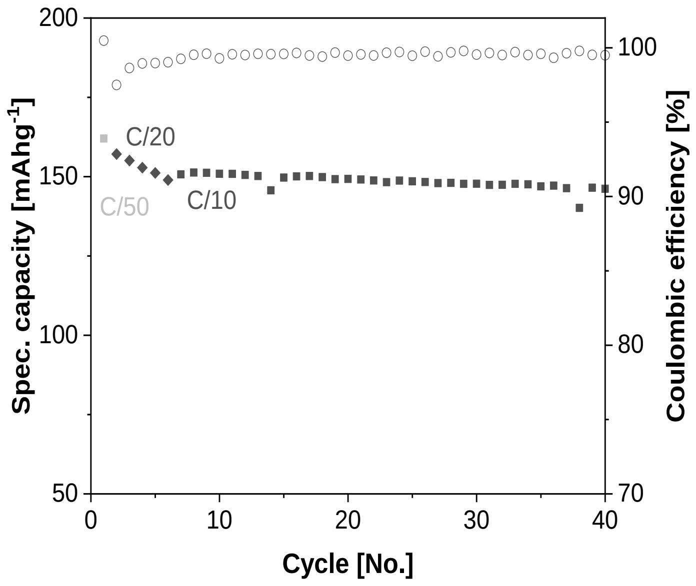
SIMBA electrolytes: *NaSTFSI-co-PET-MP/4A* SIPE

PW (Altris) | *NaSTFSI-co-PET-MP/4A* (HIU/KIT) | Na (40 °C)



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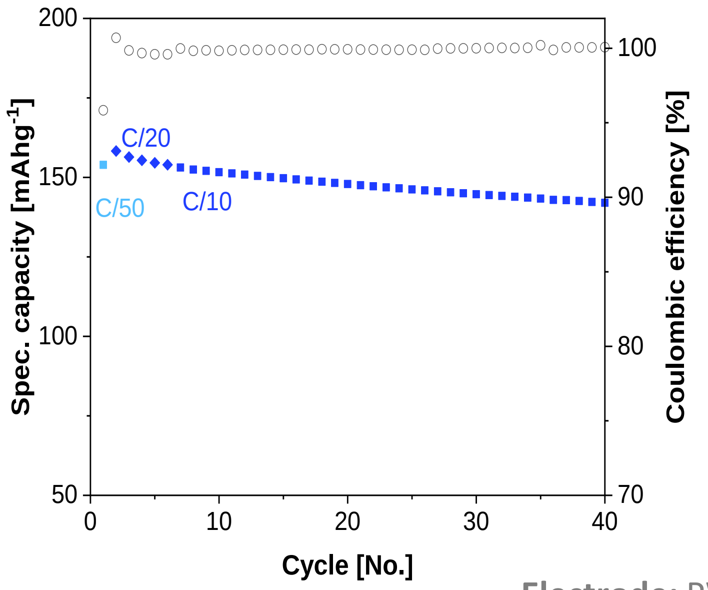

- PW delivers comparable capacities in SIPE and liquid electrolyte
- CE is slightly lower in SIPE (99.0 vs. 99.9%)
- Better capacity retention in SIPE

Electrode: PW:C45:CMC:SBR (80:10:5:5)
Mass loading ~2.5 mg cm^{-2}
Cell config. 2 electrodes coin cell (PW||Na)
Potential range: 3.8 – 1.3 V (vs. Na^+/Na)
Current density: 1st cycle 0.02C → 0.05C →0.1C
(1C = 150 mAh g^{-1})

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Conclusions

Optimize PW cathode materials with an enhanced cycle life of >2000 cycles at 80% depth of discharge

- Optimized Prussian White (**Altris**) achieved the objective

Design and prepare hard carbon anode materials from bio-source

- Hard carbon anodes (**IFE**) were prepared based on three bio-masses
- **Sawdust hard carbon** with low SSA delivers **excellent initial reversibility** and **specific capacity** in PW | LE | HC full cell.

Prepare a highly porous conductive ceramic as anode support

- SiCN (**TUD**)and SiOC (**SAS**/**TUD**) were synthesized as Na support, establishing the Na storage mechanism and investigating the interfacial properties.

Develop a class of single-ion conductor polymer electrolytes with enhanced electrochemical stability up to 4.4 V vs Na^+/Na and ionic conductivity of 10^{-3} S cm^{-1} at RT

- Several SIPEs were developed (**HIU/KIT**) tuning the backbone chemistry, the anionic center of the sodium salt monomer chain.
- The best SIPE delivers 0.58 mS/cm at 20 °C and exhibits a stability window of around 5.0 V vs. Na^+/Na

SIMBA SODIUM-ION AND SODIUM METAL BATTERIES

Thank you!

TECHNISCHE UNIVERSITÄT DARMSTADT

HIU HELMHOLTZ INSTITUTE ULM Electrochemical Energy Storage

KIT Karlsruher Institut für Technologie

JM Johnson Matthey Inspiring science, enhancing life

cea

UPPSALA UNIVERSITET

ICSAS

IFE

Elkem

ALTRIS