Sodium-ion cells prototypes: a journey in the SIMBA project results

Ivana Hasa, Faduma Maddar (WMG, University of Warwick)
and all our amazing collaborators ☺

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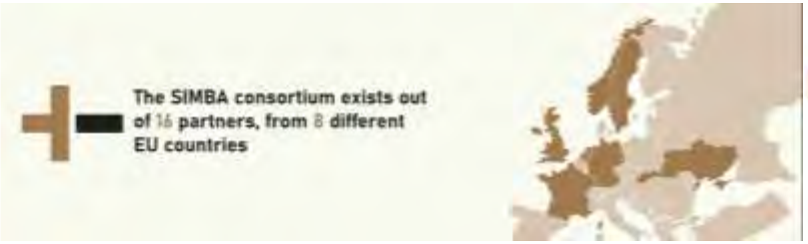
Outline

- The journey towards the SIMBA baseline cell
  - From materials to cell prototypes
  - Cell manufacturing and characterization
- Sensor integration
- Polymer electrolyte incorporation
- Conclusions



+SIMBA

SODIUM-ION AND SODIUM METAL BATTERIES

This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement no. 883753.

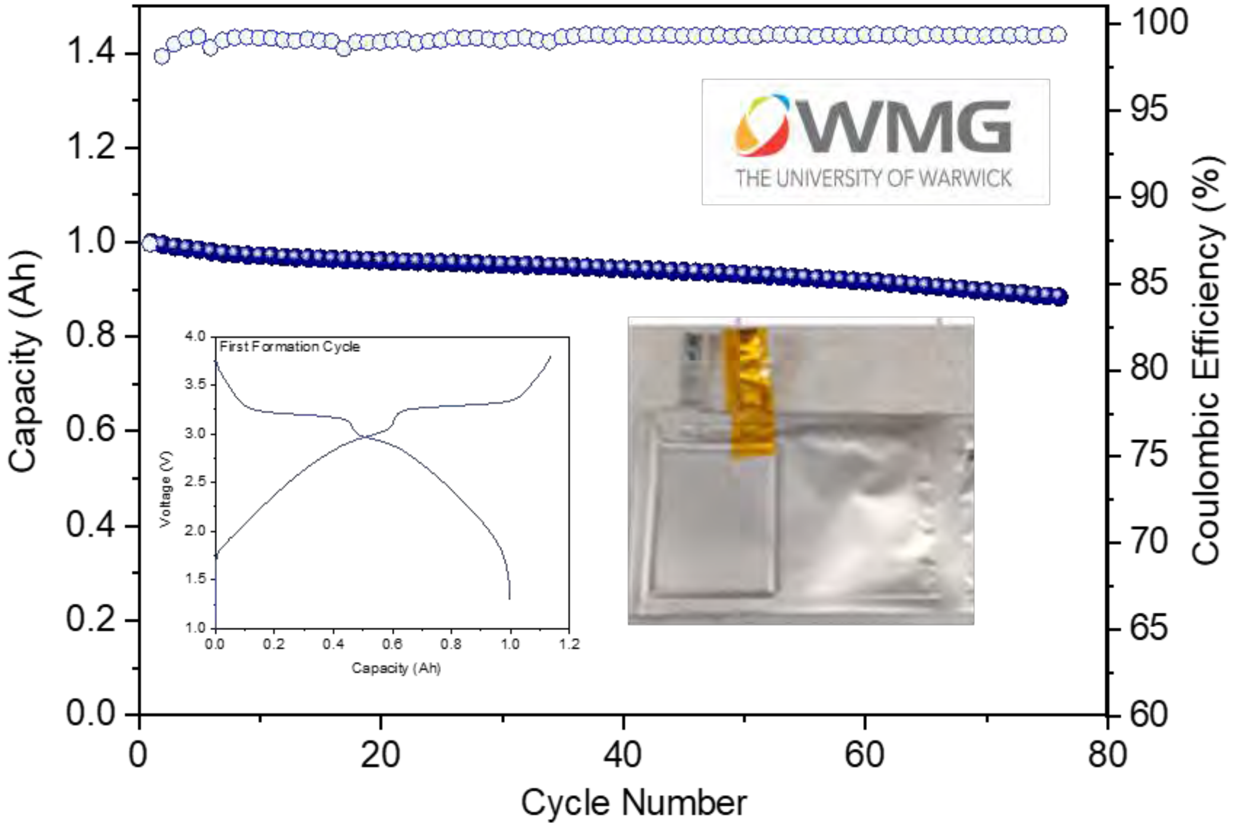
www.simba-h2020.eu

1237 days ago…

Developing sodium-ion battery cells: **The SIMBA baseline cell**

Cathode: Prussian White (https://www.altris.se/technology/) ALTRIS
Anode: Hard Carbon
Electrolyte: Liquid electrolyte.

SIMBA baseline cell



Cathode: $Na_{2-x}Fe[Fe(CN)_6]_y.mH_2O$ Altris technology.
Anode: Commercial Hard.
Electrolyte: $NaPF_6$ based electrolytes.

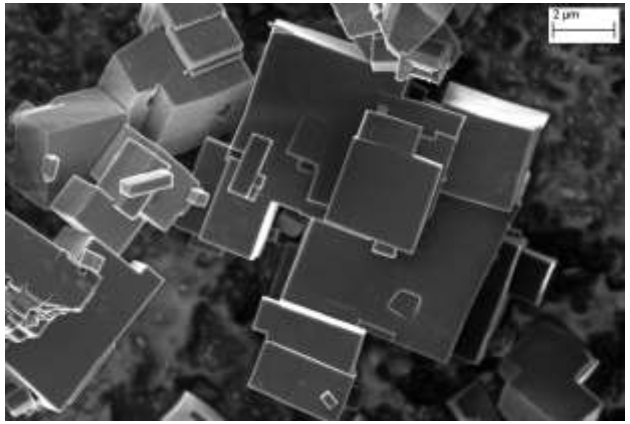
1st objective and milestone of WP4 achieved.
Great collaborative effort!

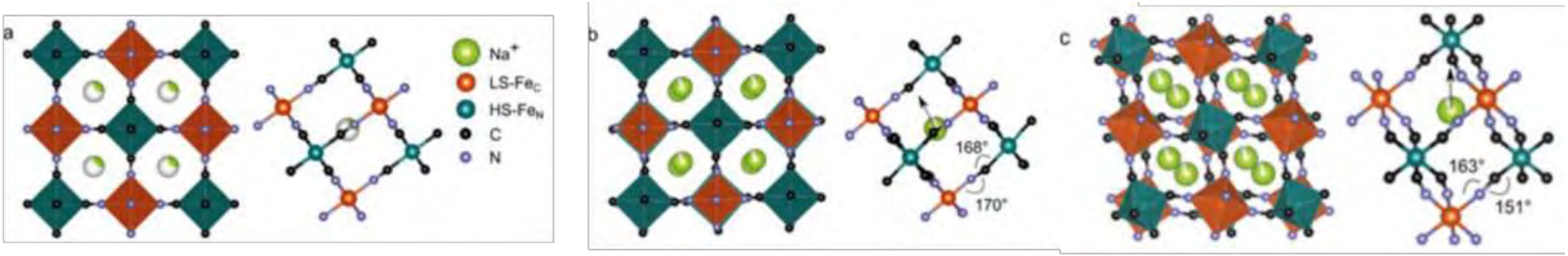
Prussian White Cathode

Prussian White Cathode in SIMBA project

$Na_{1.80(5)}\,Fe\,[Fe\,(CN)_6]\cdot 1.84(3)\,H_2O$

ALTRIS





Low Na content
cubic
*Fm*3̄m structure

hydrated, high sodium content
monoclinic
P21/n structure

Anhydrous, high sodium content
rhombohedral
*R*3̄ structure

https://www.altris.se/
W. R. Brant et al, Chem. Mater. 2019, 31, 18, 7203–7211

Prussian White Cathode

The effect of water on PW presents two main challenges:

1. Controlling water during material synthesis.
2. Controlling water/moisture reactivity after synthesis.

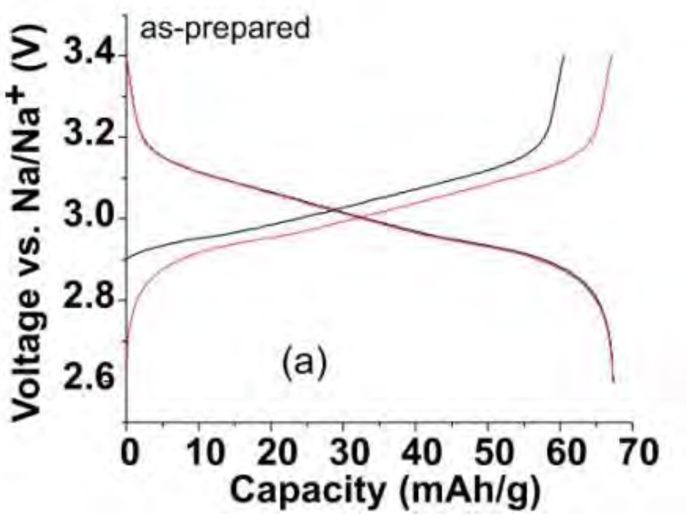
By eliminating water in the structure

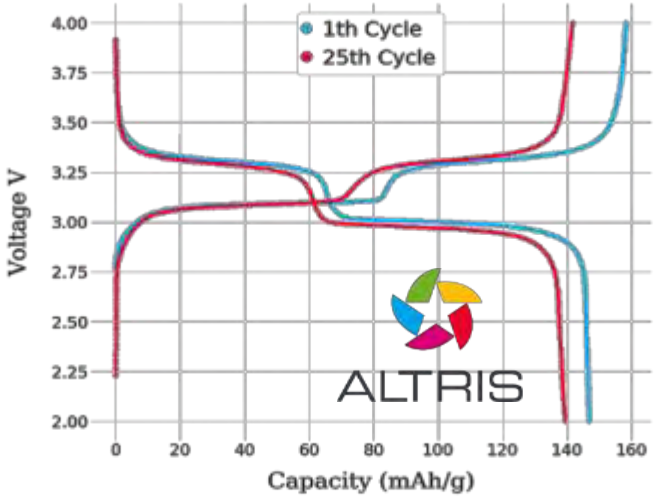
Air/moisture contact

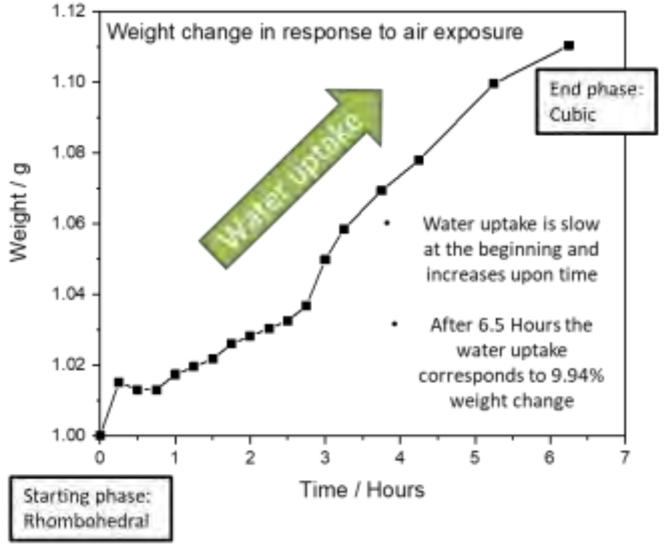
Prussian White is in its **MONOCLINIC PHASE.**

The **RHOMBOHEDRAL PHASE** is VERY sensitive to air/moisture

PW changes to **CUBIC** upon water and oxygen adsorption.





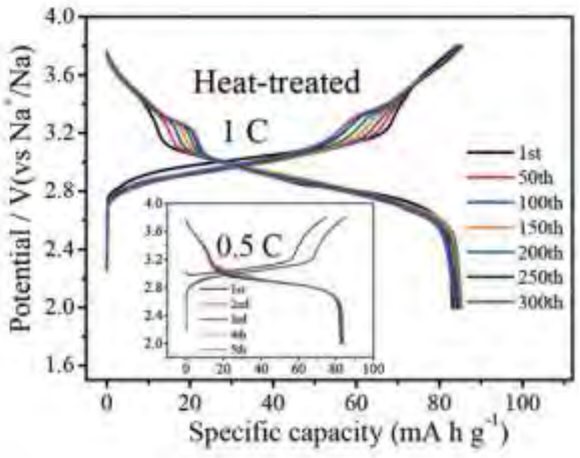


https://www.altris.se/
W. R. Brant et al, Chem. Mater. 2019, 31, 18, 7203–7211
W. R. Brant et al, ACS Appl. Mater. Interfaces 2021, 13, 8, 10054–10063

Prussian White Cathode

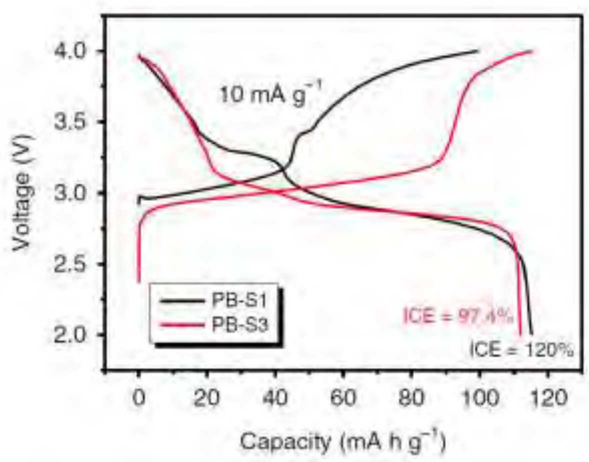
The effect of water on PBAs electrochemistry presents two main challenges:

$Na_{2-x}FeFe(CN)_6$



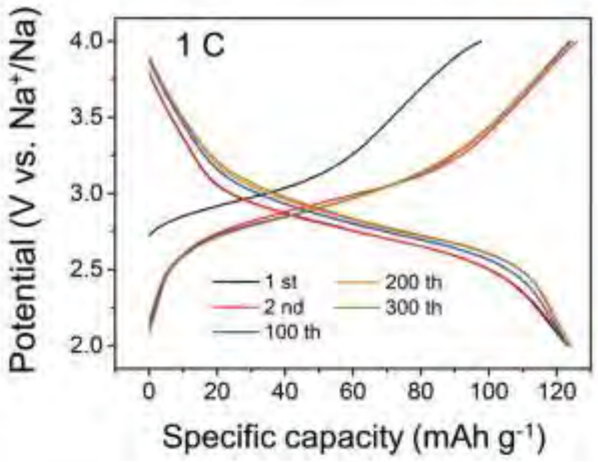
Adv. Funct. Mater. 2022, 2111727

$Na_{1.73}Fe[Fe(CN)_6]\cdot 3.8H_2O$



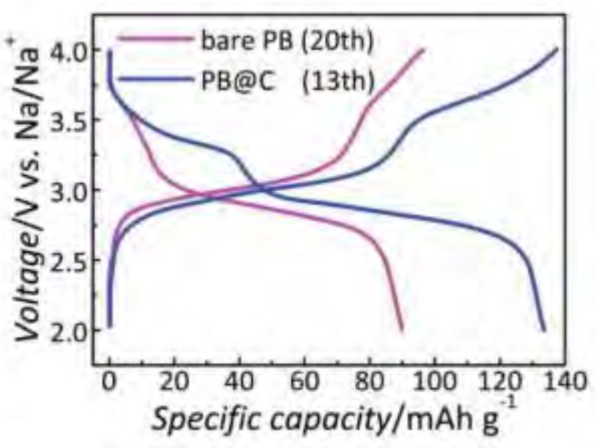
Nat Comm, volume 11, 980 (2020)

$(Na_{3.1}Fe_4[Fe(CN)_6]_3$



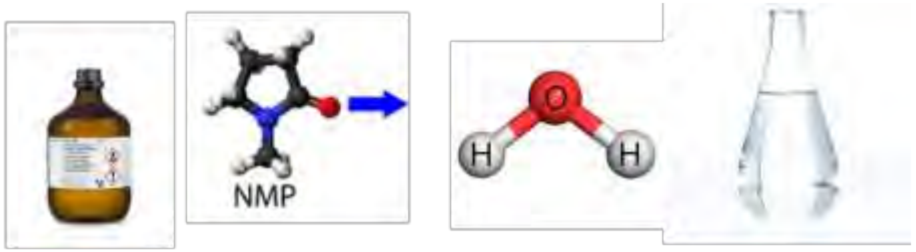
Adv. Funct. Mater. 2019, 29, 1806405

$Na_{0.647}Fe[Fe(CN)_6]_{0.930.07}\cdot 2.6H_2O$



Adv. Funct. Mater.2016, 26, 5315–5321

Can we instead process these materials in water without losing their promising electrochemical properties?

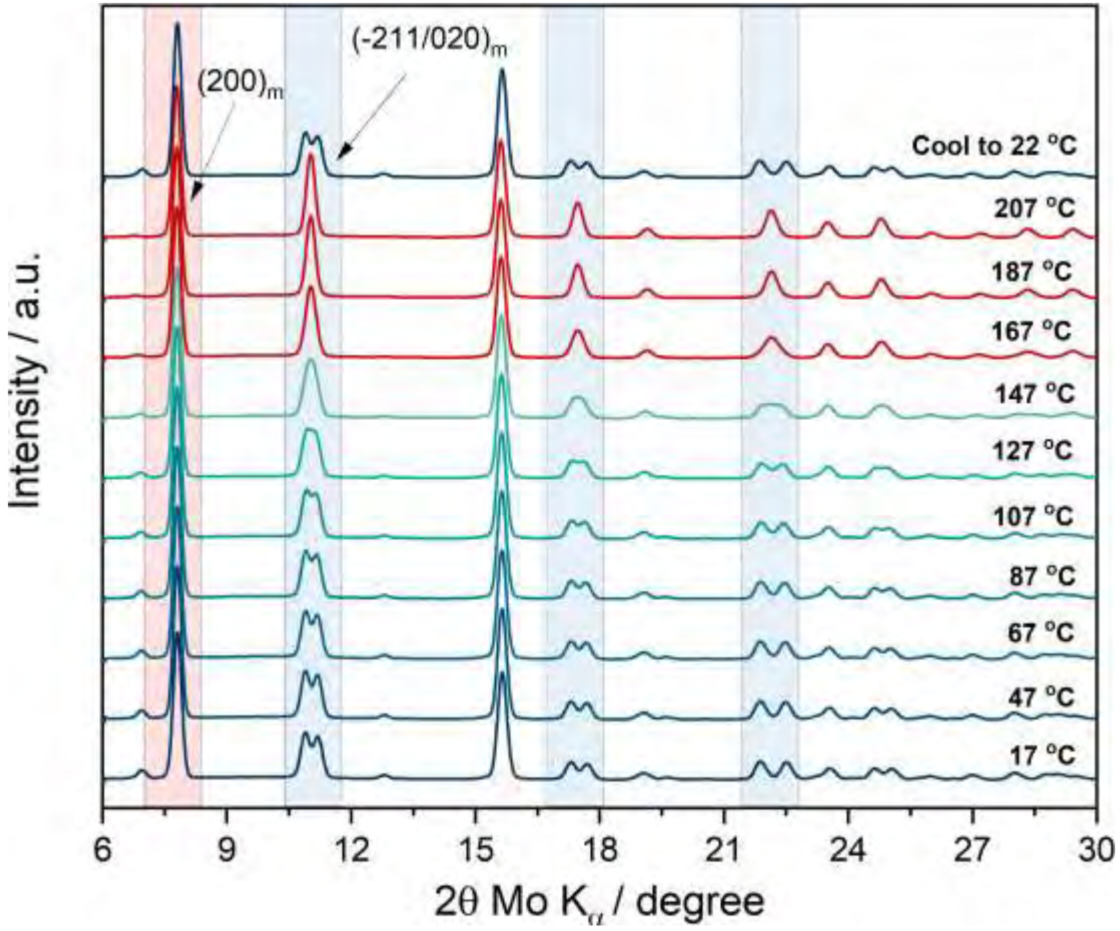


PW material: structural considerations

Temp control env.

Closed capillary:
the closed system enables water re-adsorption once the temperature is decreased

In situ XRD – *closed capillary in an inert atmosphere*



Faduma Maddar

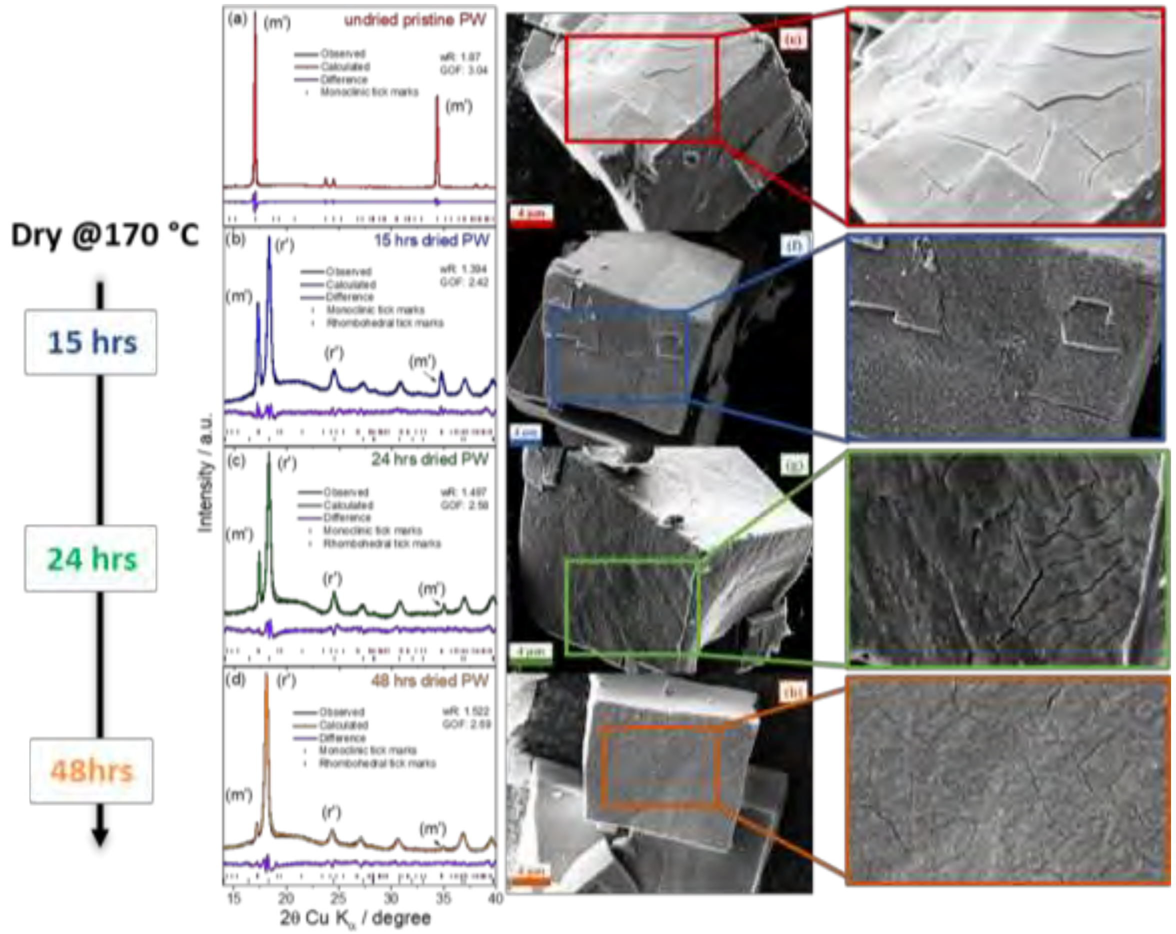
Effect of water removal at the powder level

Drying temperature is key!

170 °C was chosen as temperature for further studies to enable water removal.

PW material: structural considerations

Effect of length of dehydration at 170 °C on PW structure and morphology?



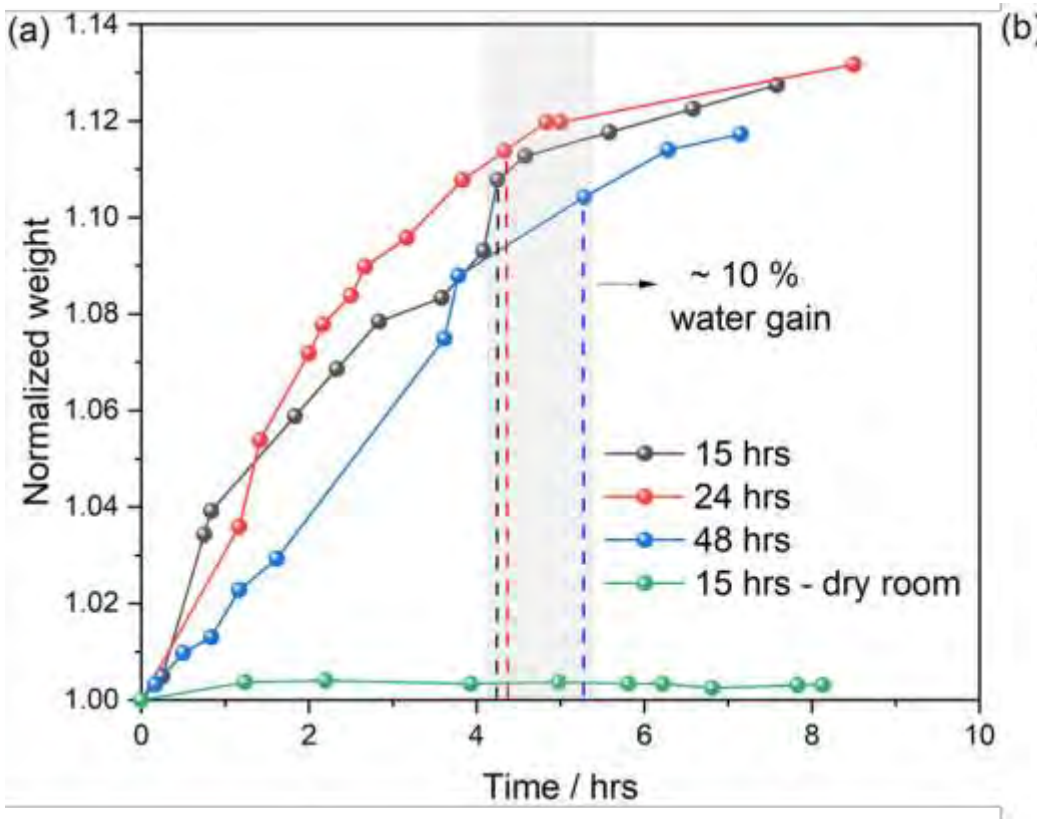
	Monoclinic phase	Rhombohedral phase
Sample	Vol (Å³)	Vol (Å³)
Undried	566.43(1)	-
15hrs dried	552.39(1)	705.67(3)
24hrs dried	538.89(3)	702.86(2)
48hrs dried	536.64(7)	701.0(6)

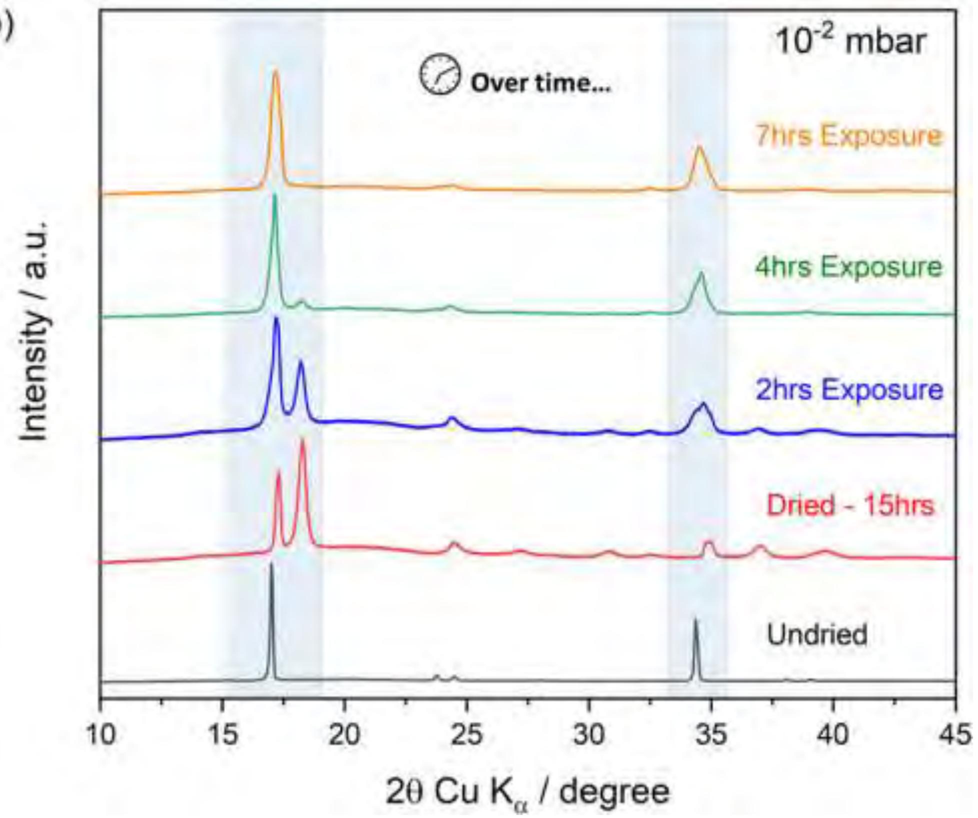
Upon dehydration, the **unit cell volume** of both the monoclinic and rhombohedral phase **decreases**.

Volume contraction reflected in the appearance of cracks loss of crystallinity (increase of the FWHM of the diffraction peaks).

PW material: structural considerations

Moisture reactivity of the dehydrated phase: exposure to air





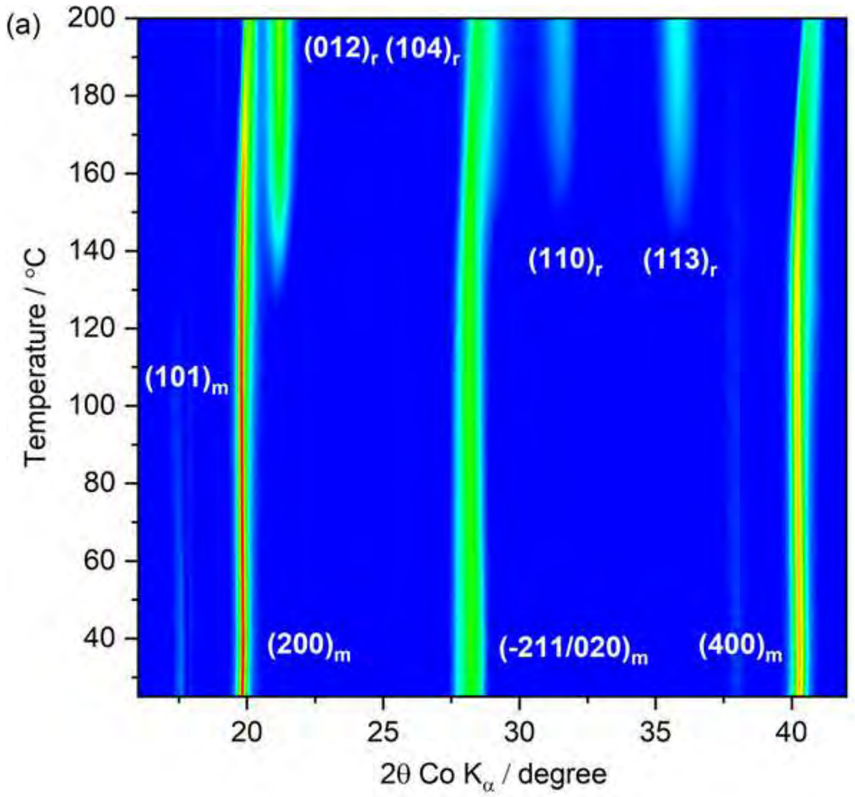
Dried material must be handled thoroughly to avoid any water uptake

F. Maddar et al., J. Mater. Chem. A, 2023,**11**, 15778-15791

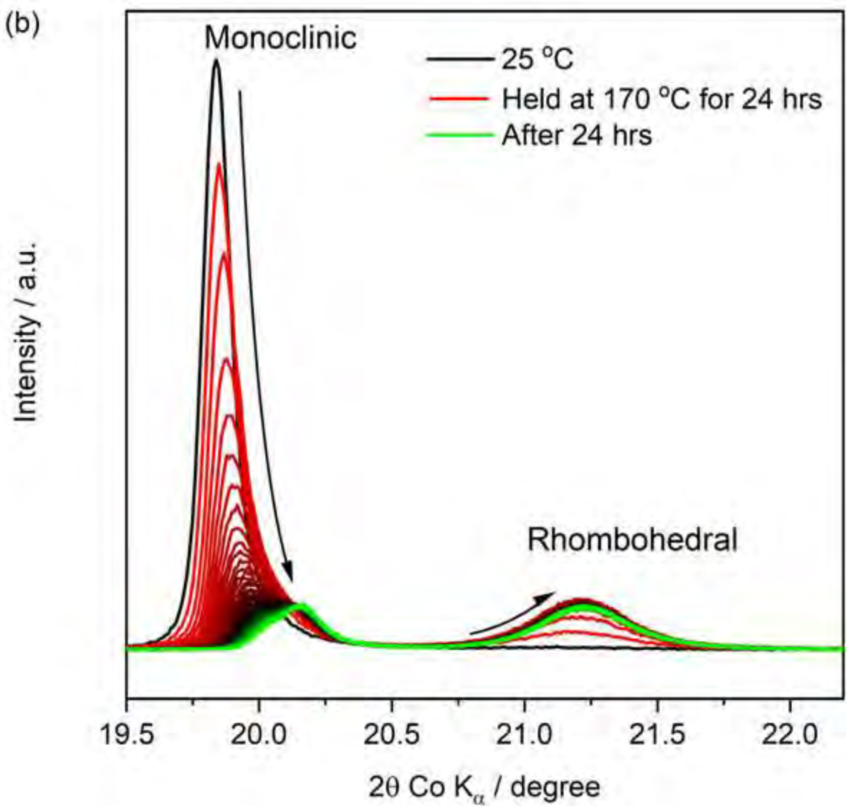
PW electrodes: structural considerations

From powders to electrodes

In situ XRD measurement as a function of temperature on pristine PW-based composite electrodes.



(a) from room temperature (25 °C up to 200 °C, heating rate: 5 °C min^{-1}). Dynamic vacuum (10^{-2} mbar).

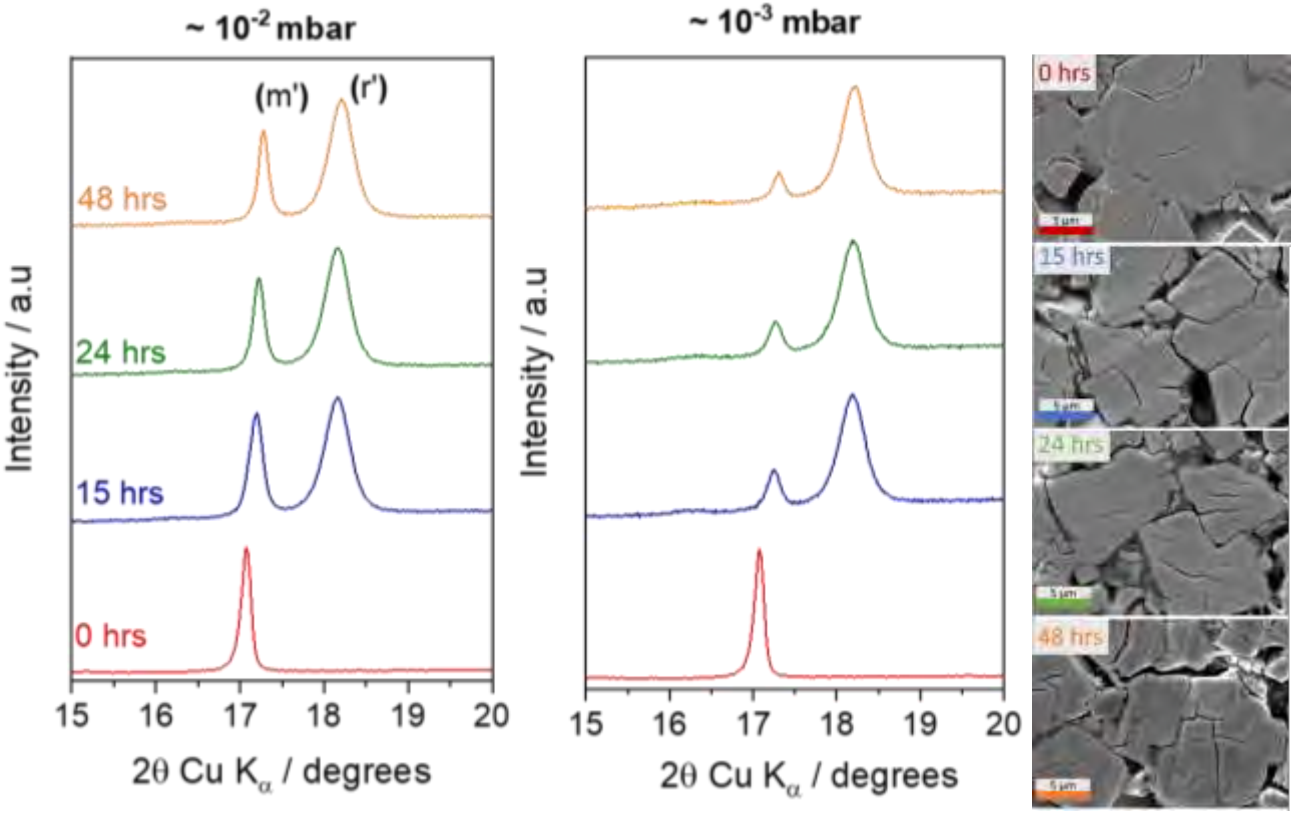


(b) From room temperature up to 170 °C with holding step for 24 hours. Dynamic vacuum (10^{-2} mbar).

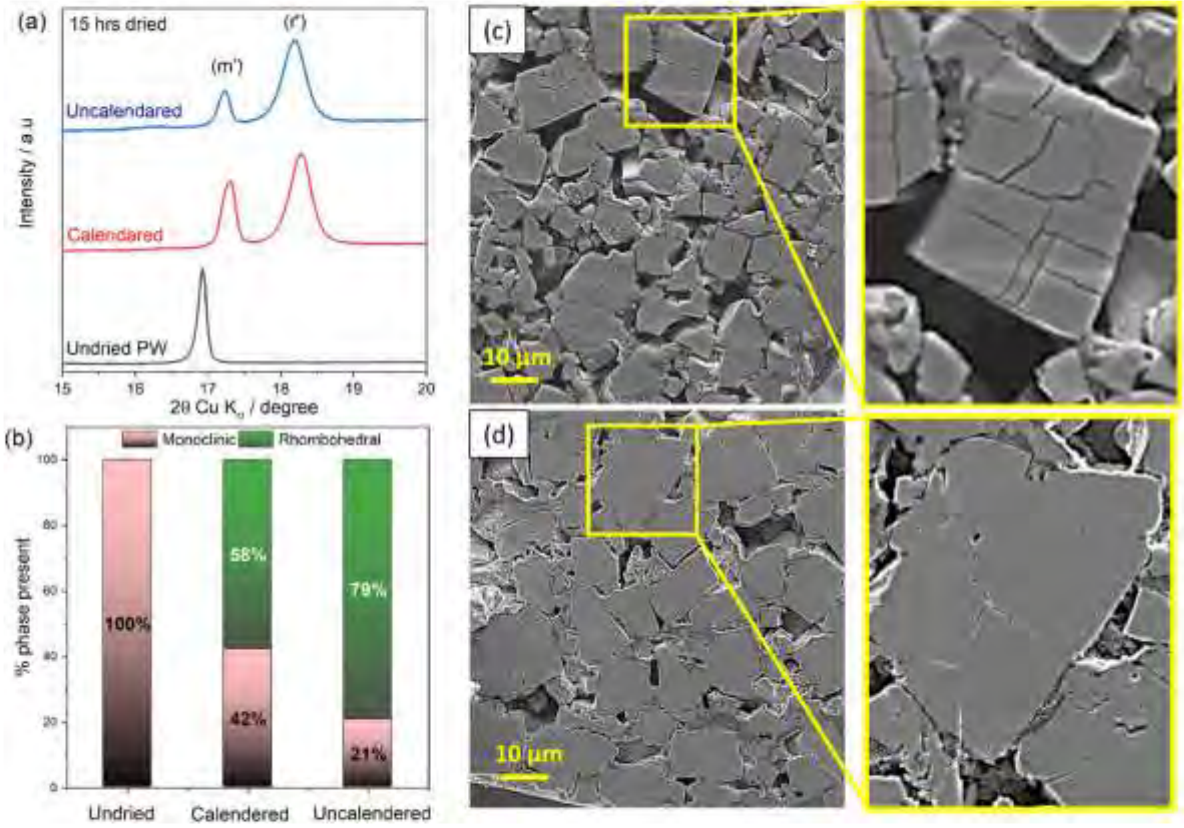
F. Maddar et al., J. Mater. Chem. A, 2023,**11**, 15778-15791

PW electrodes: structural considerations

Drying pressure is key too!



Calendering affects dehydration!

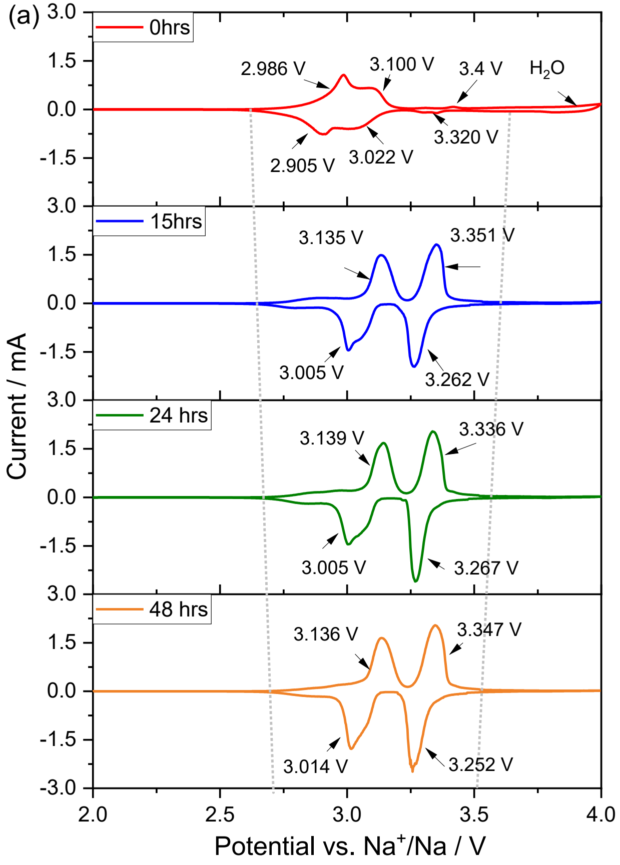


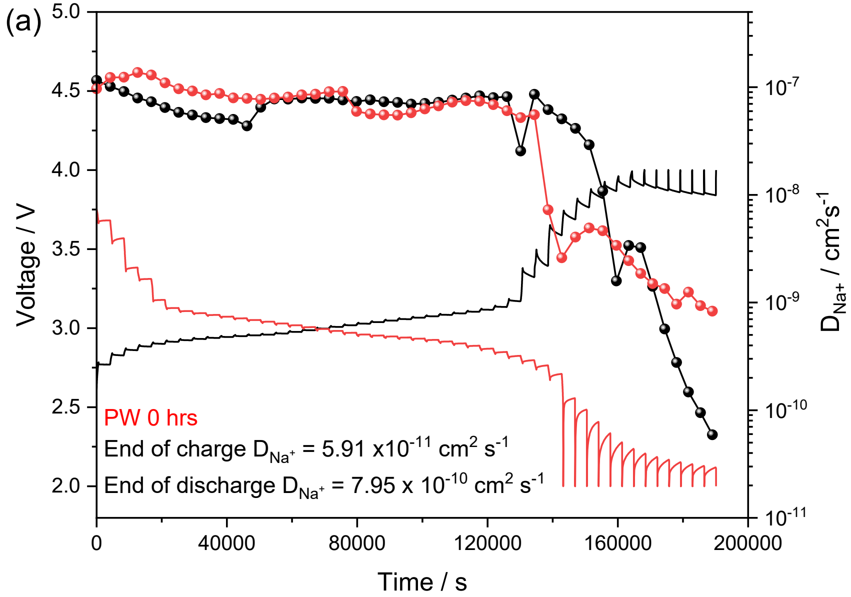
Controlled dehydration required to achieve desired phase with the higher capacity

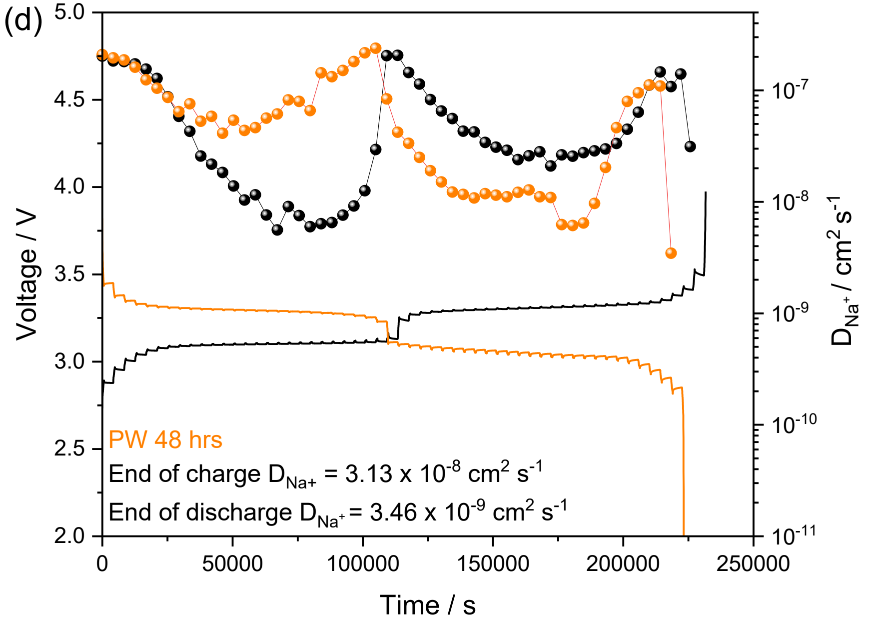
PW electrodes: structural considerations

What happens to the PW while removing water?

Water affects the low spin Fe^{2+} / Fe^{3+}.







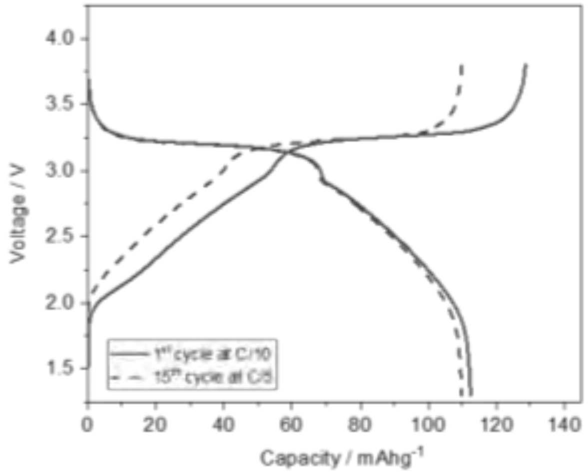
Removal of interstitial water facilitate sodium ion diffusion as demonstrated by GITT analysis.

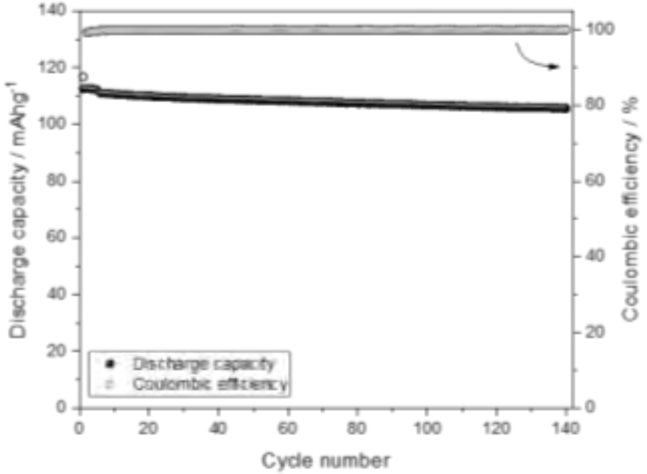
SODIUM-ION AND SODIUM METAL BATTERIES

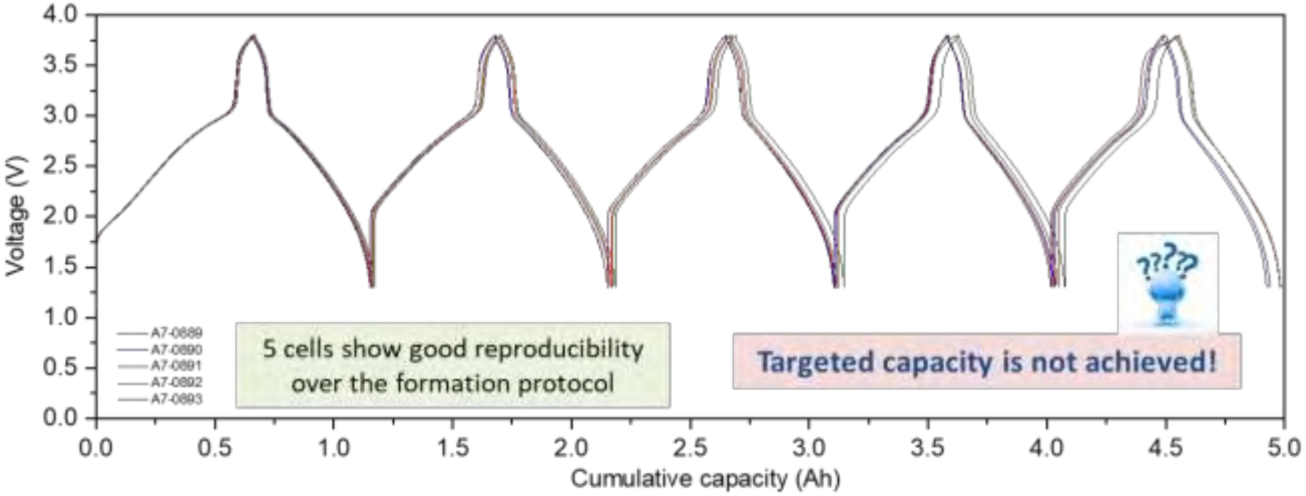
From lab to upscaled cell prototypes

From coin-cells

To Multi-layer pouch cells







- **Upscaling is not a linear process**.
- Lessons learned at lab scale level do not necessarily translate at upscaled levels.
- Structure property correlations and degradation processes are cell format and scale dependent!

SIMBA
SODIUM-ION AND SODIUM METAL BATTERIES

A multifaceted challenge: upscaling

Material

Electrode

Cell

Mixing

Lab scale mixing: mg →g

Upscaled mixing: 1L→10L

- High **solid content**;
- **Rheology** analysis for viscosity;

Coating

Lab scale coating and drying

Roll to roll coater pilot line

- **Homogeneous** distribution;
- **Adhesion** properties;

Manufacturing

Lab scale mixing: electrode

Upscaled mixing: electrode

- **Relevant GSM** (loadings);
- **Electronic conductivity** of electrodes;
- **Porosity** and **density** of final electrode sheets (calendaring);

Environment

Glove Box

Dry Room

- **Operational environment**;
- **Moisture** sensitivity;

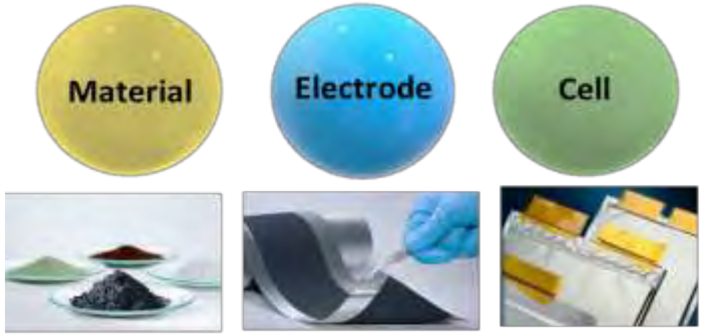
Cell form factor

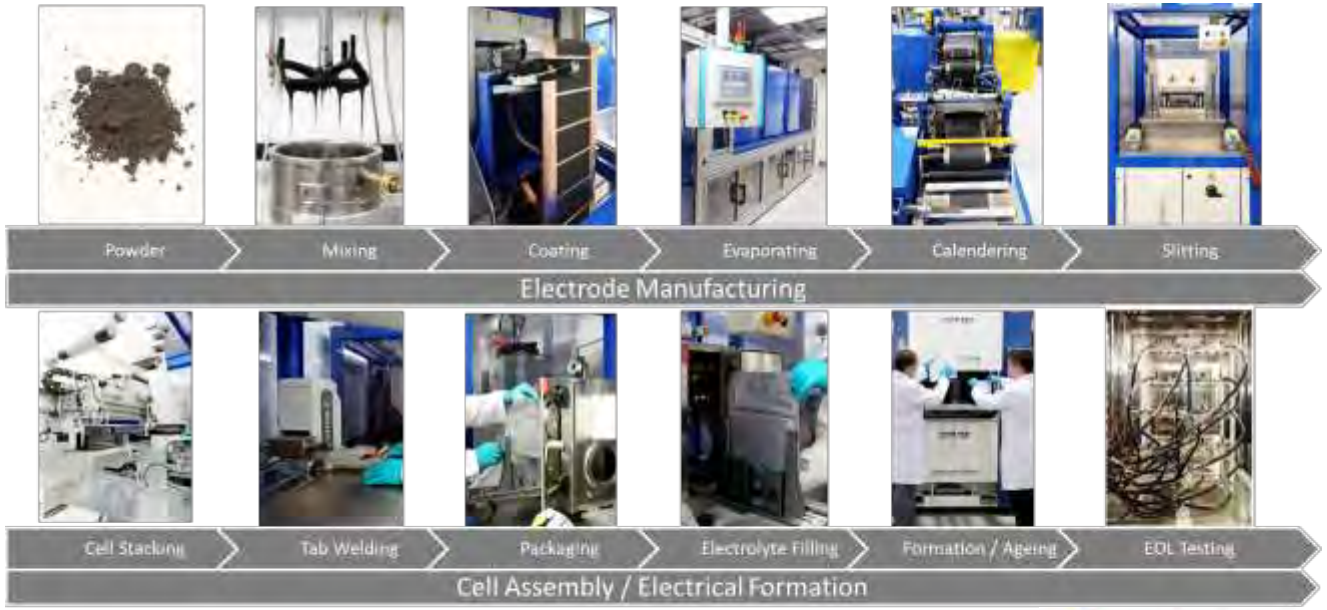
Coin cells and T cells

Multilayer Pouch Cells

- Cell format: **Electrolyte amount**;
- Optimized **N/P ratio** and formation cycling;
- **Gas formation** and degassing protocols;
- **Pressure** applied to the cell;
- Defined **testing protocols**;

A multifaceted challenge: upscaling



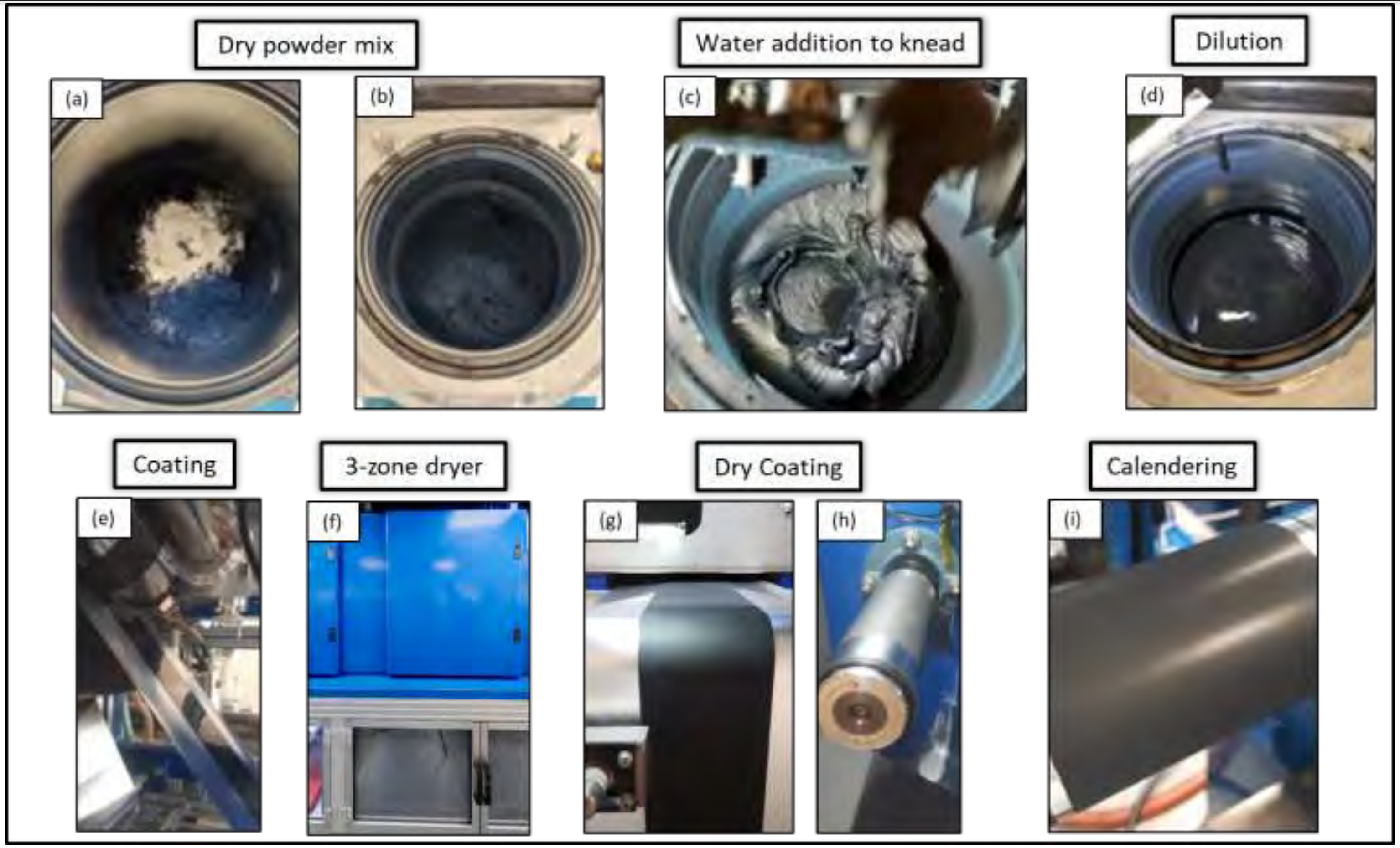


- High solid content;
- Relevant GSM (loadings);
- Rheology analysis for viscosity of slurries;
- Homogeneous distribution of the electrode components;
- Adhesion properties and binder content;
- Electronic conductivity of electrode foils;
- Porosity and density of final electrode sheets (calendaring);

- Electrolyte amount;
- Optimized N/P ratio and formation cycling;
- Gas formation and degassing protocols;
- Pressure applied to the cell;
- Defined protocols test for performance benchmark;

Sodium-ion cell manufacturing steps

Mixing and coating process for aqueous based sodium-ion battery cathode



Battery Scale Up facility at Energy innovation Centre (WMG)

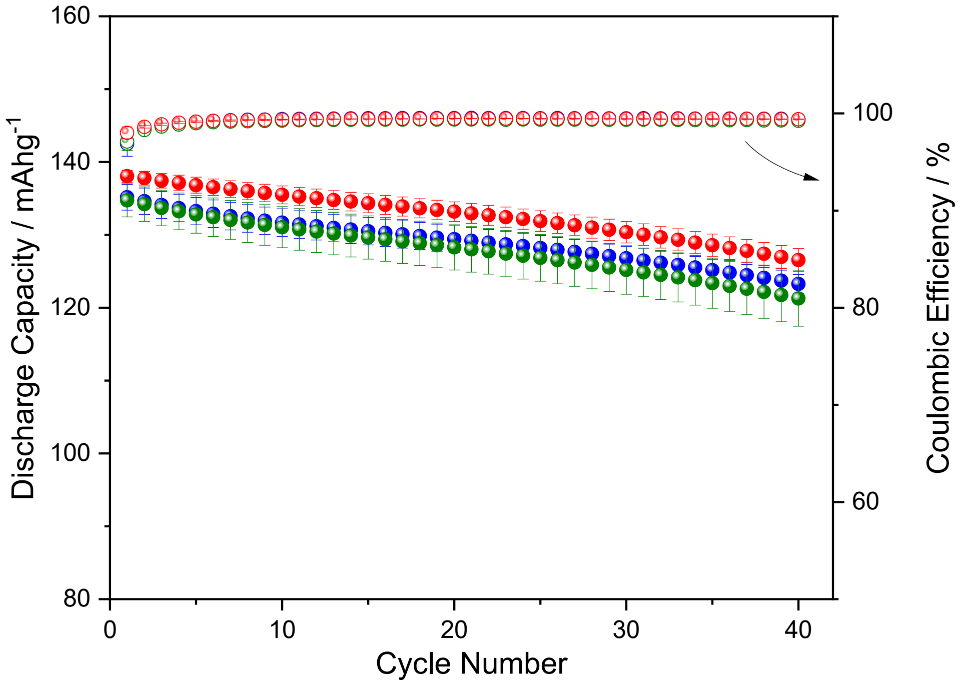
SIBs are a drop in technology! Current manufacturing facilities can be employed!

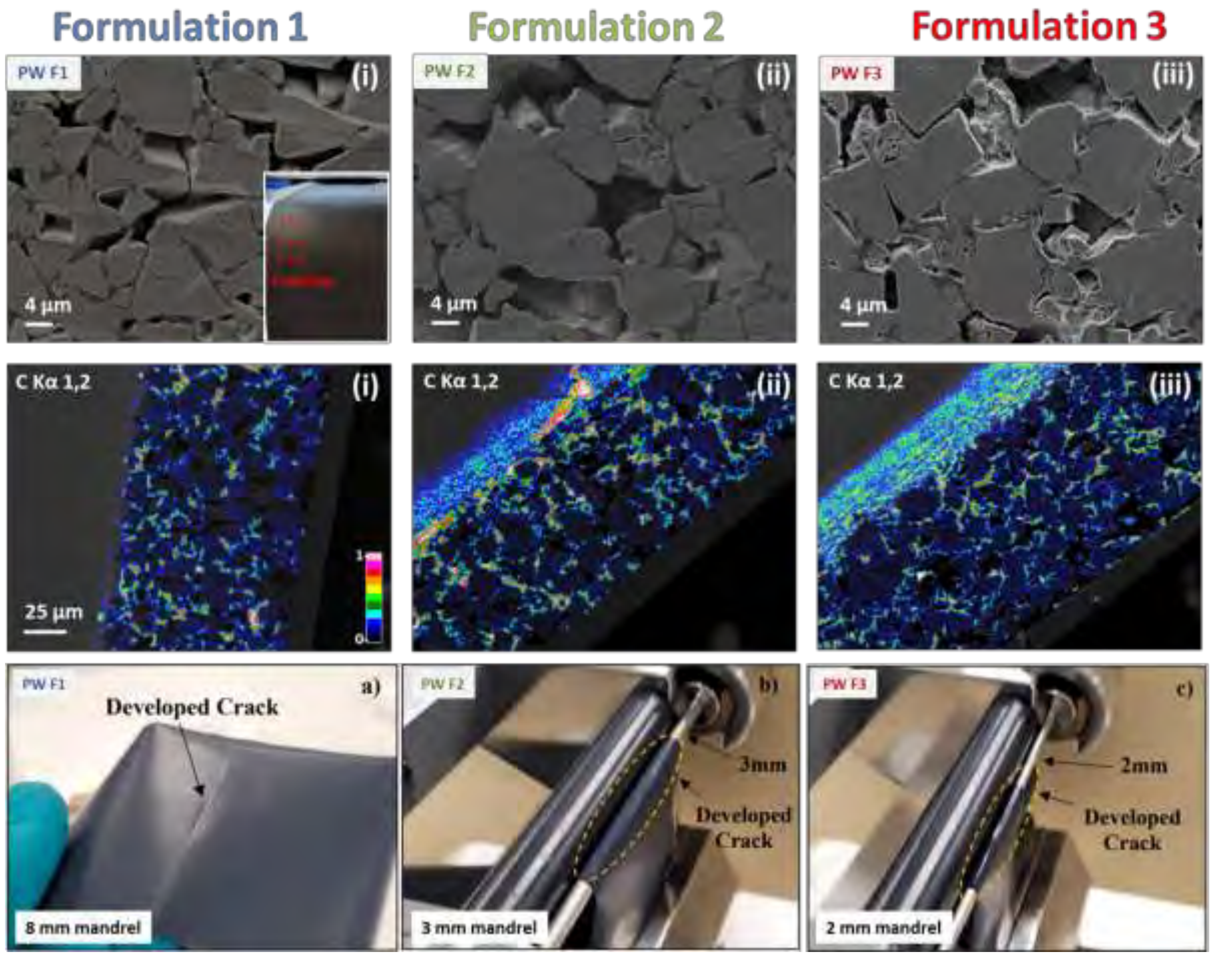
Sustainability:
Aqueous electrode processing for both anode and cathode materials.

Upscaled slurry: formulation optimization

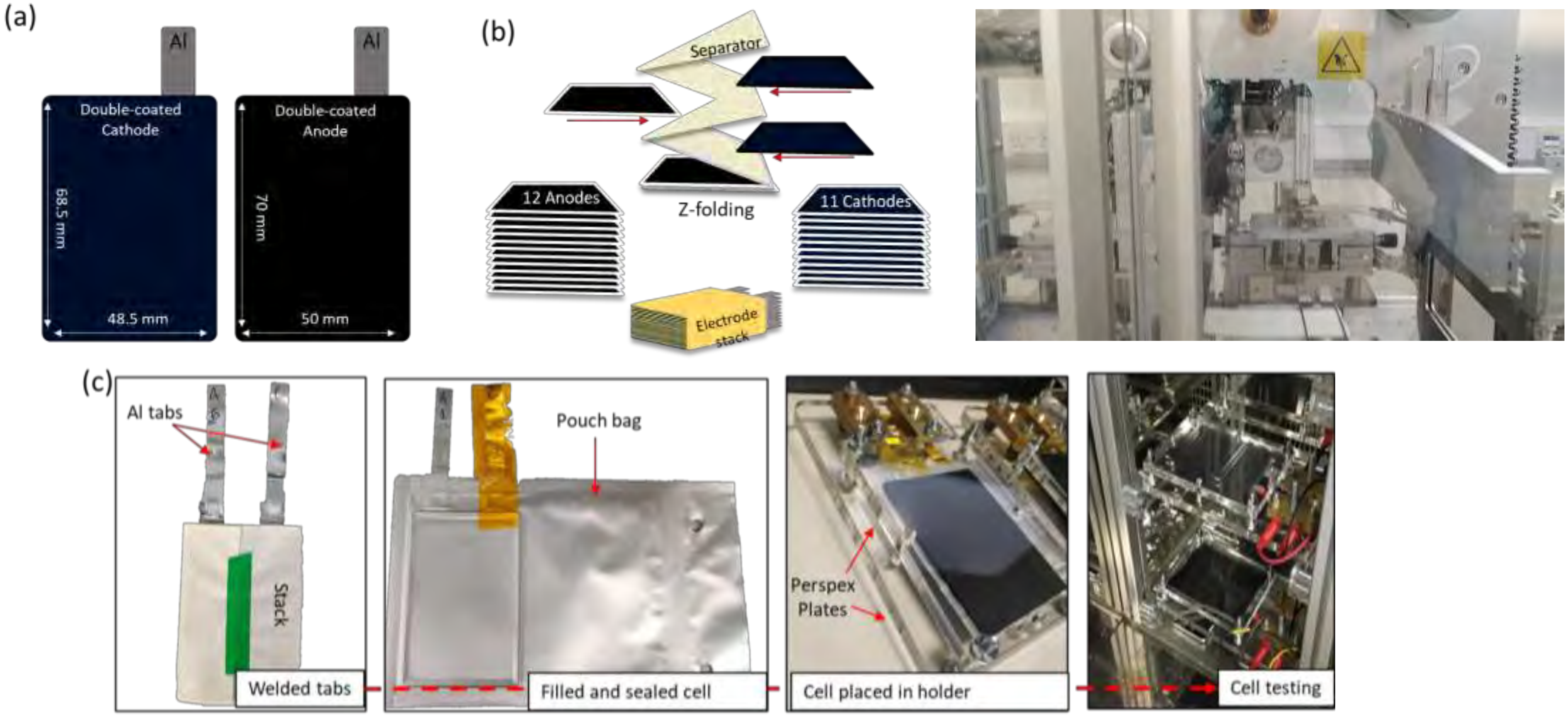
Formulation development targeting:

- Increasing active material content.
- Optimizing carbon additive nature and content.
- Improving adhesion and structural stability by binder optimization.





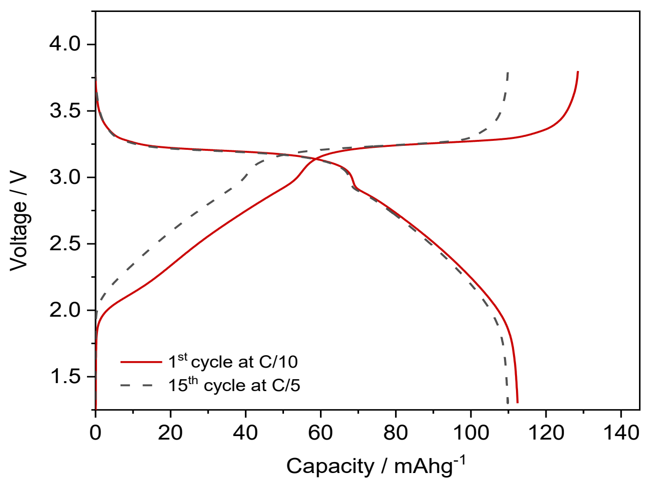
Sodium-ion cell manufacturing steps

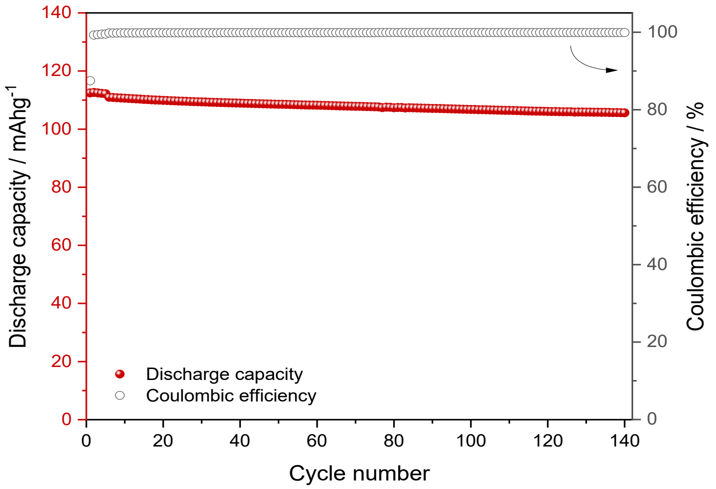


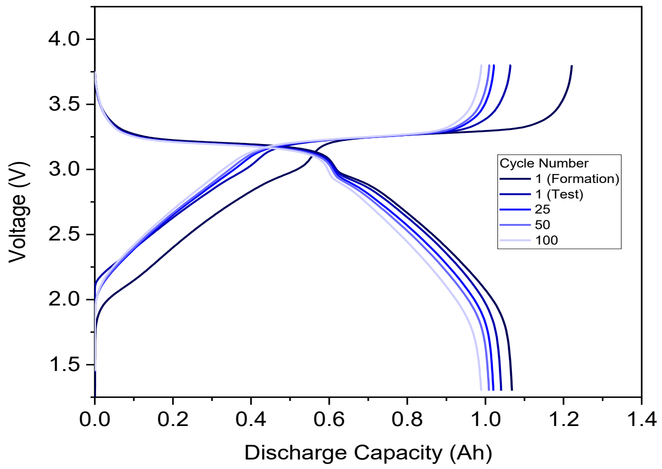
1Ah A7 Multilayer Sodium-ion Pouch Cells

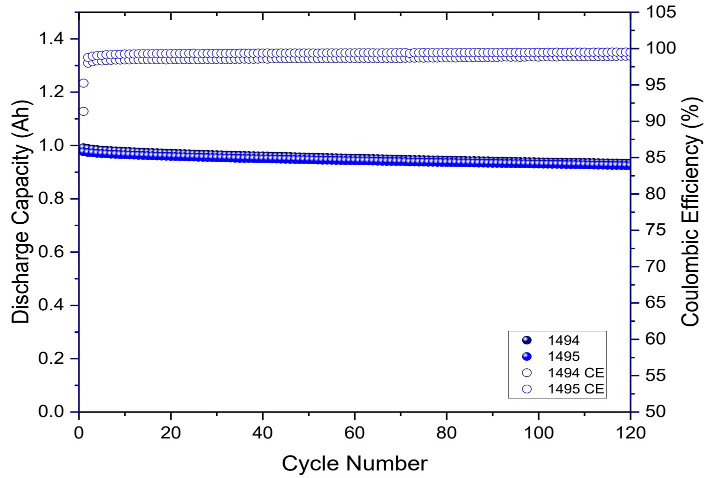
From coin-cells

To Multi-layer pouch cells



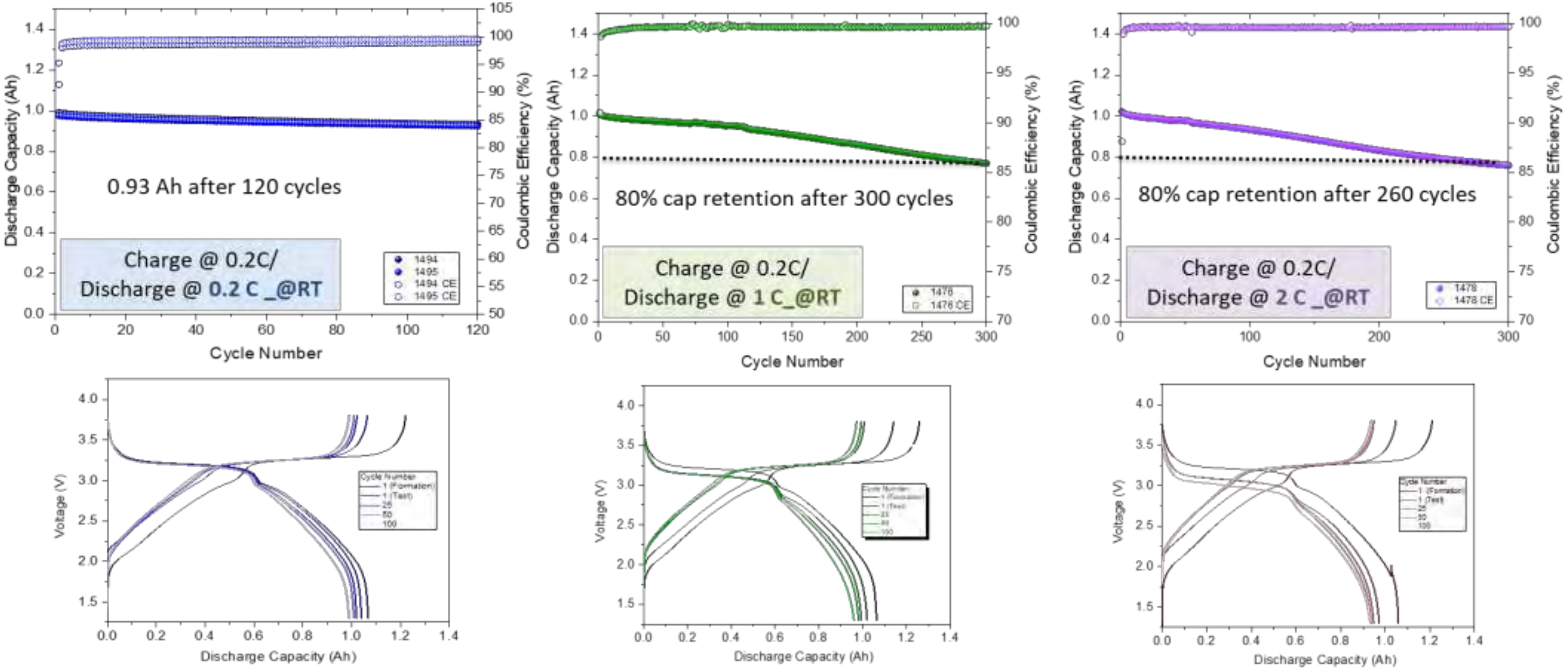






SODIUM-ION AND SODIUM METAL BATTERIES

1Ah A7 Multilayer Sodium-ion Pouch Cells



Getting closer to relevant cell prototypes and a more realistic benchmark of the SIB technology

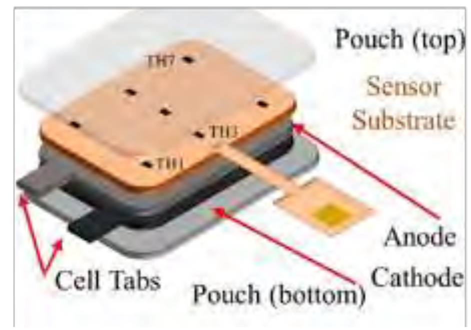
Matching KPIs defined charge and discharge rate in domestic and industrial stationary storage applications.

Batteries & Supercaps, June 24, Manuscript submitted

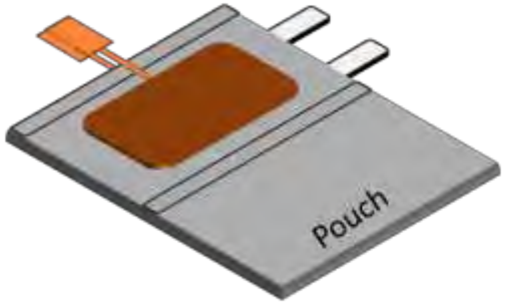
Incorporation of sensors into cells

Temperature monitoring with thermistors during cell operation

Sensor inside the cell



Sensor outside cell

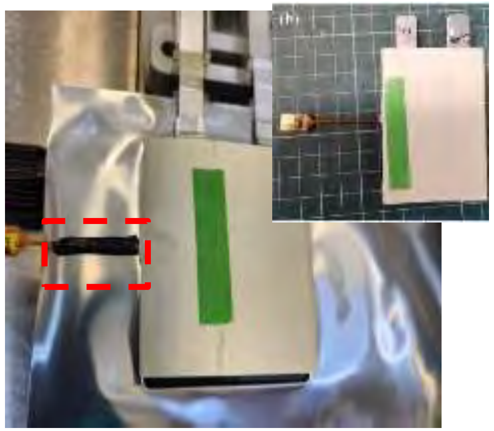


Internal cooperation within SIMBA with Timothy Vincent, Sheng Chao, James Marco

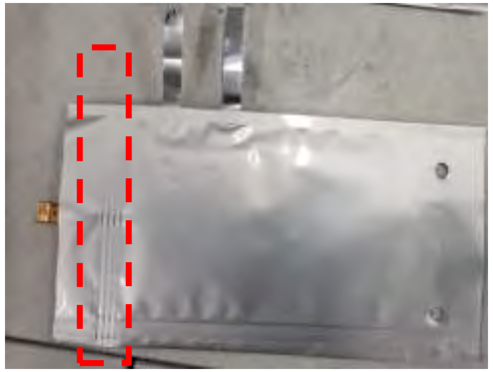


Incorporating sensors into single layer pouch cells

Epoxy coated sensor



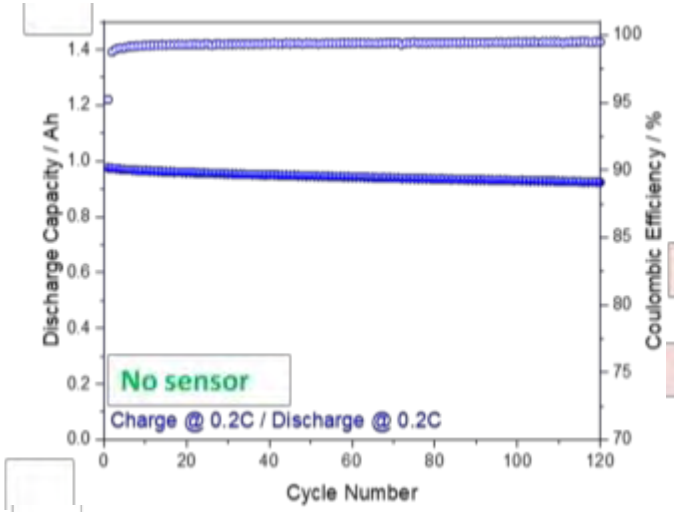
Hot melt tape used to protect sensor during sealing

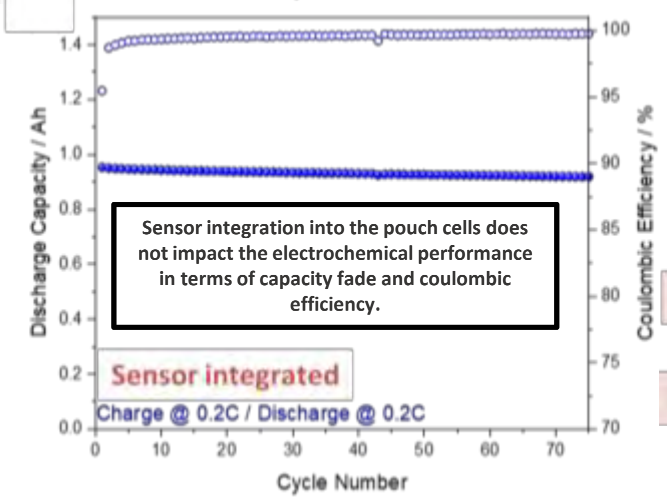


Sealing

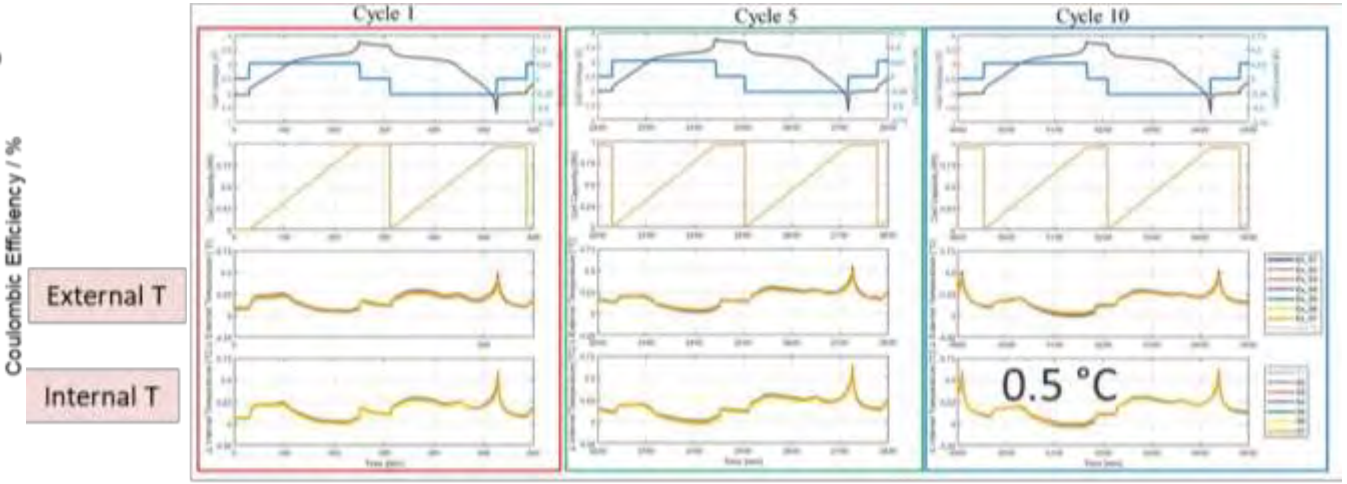
Testing

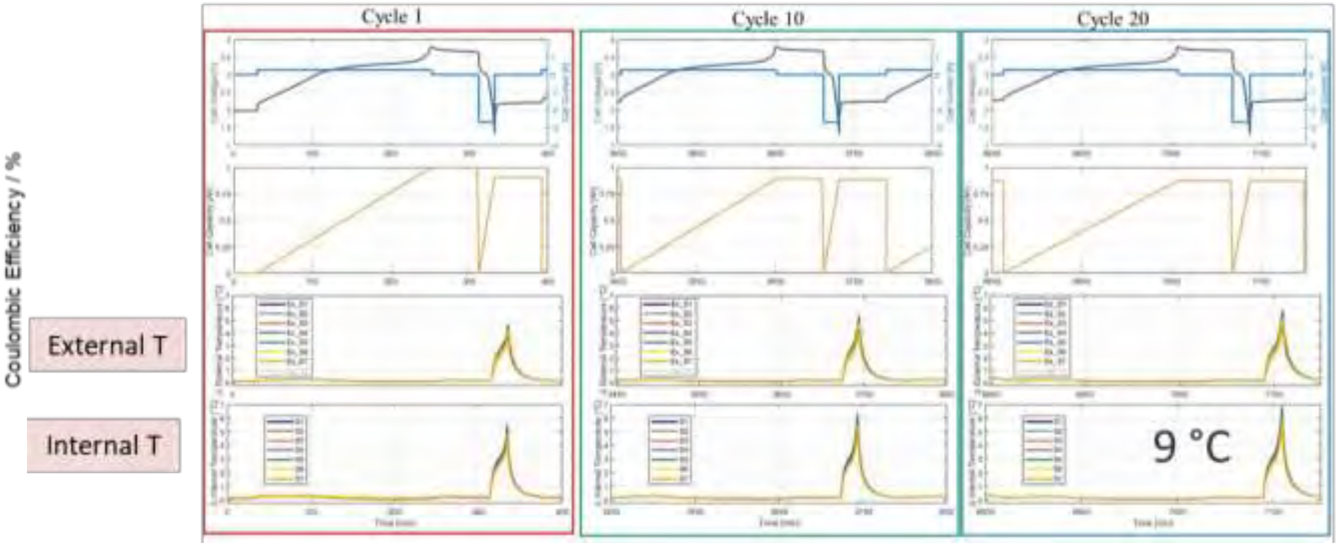
Incorporation of sensors into cells





Sensor integration into the pouch cells does not impact the electrochemical performance in terms of capacity fade and coulombic efficiency.





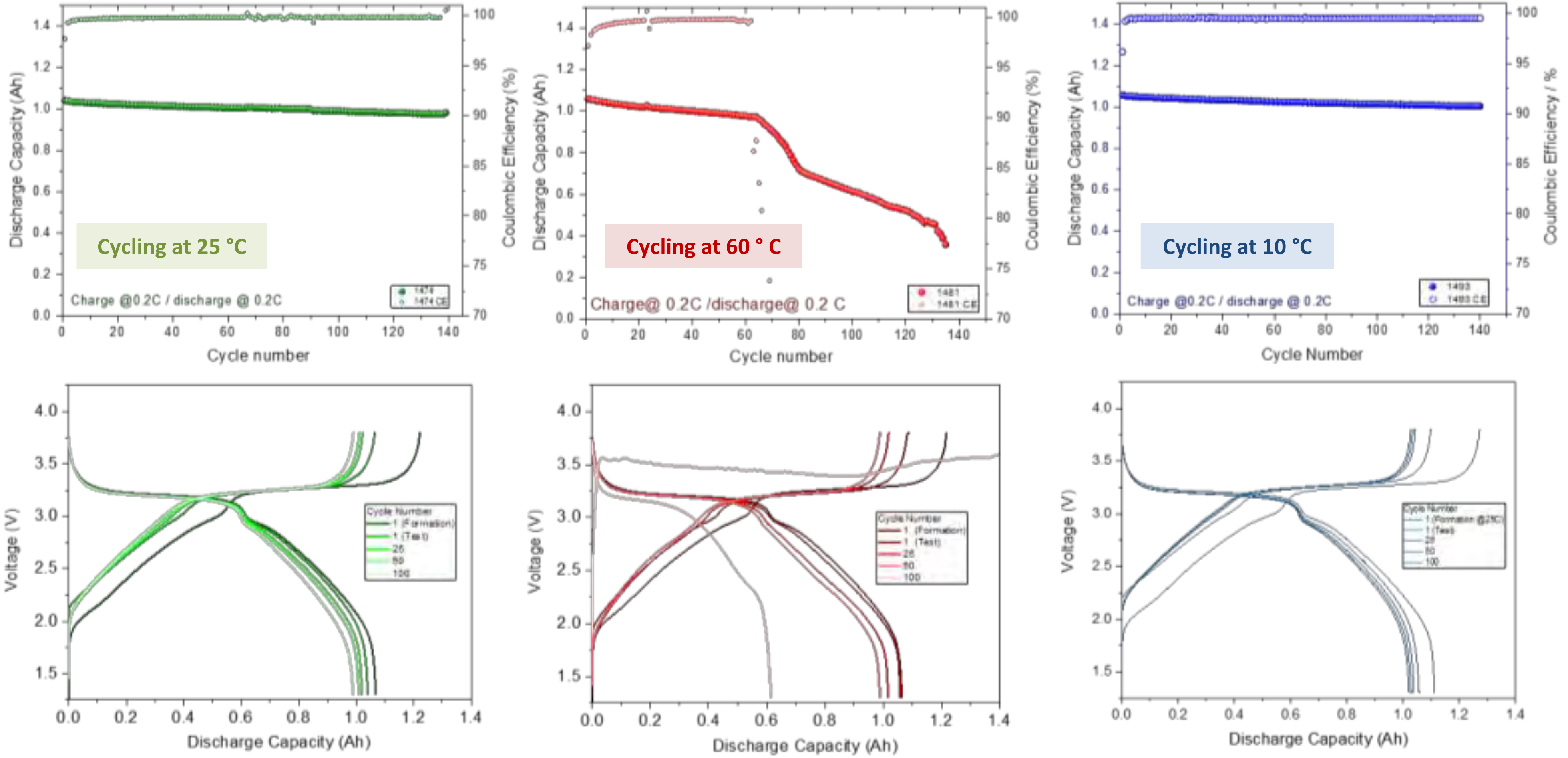
*(Charge @ 0.2C / **Discharge @ 0.2C**)*

0.3 °C difference reported between the internal and external arrays (internal hotter).

*(Charge @ 0.2C / **Discharge @ 2C**)*

After 20 cycles, peak discharge temperature of almost ~9 °C above ambient temperature was seen.

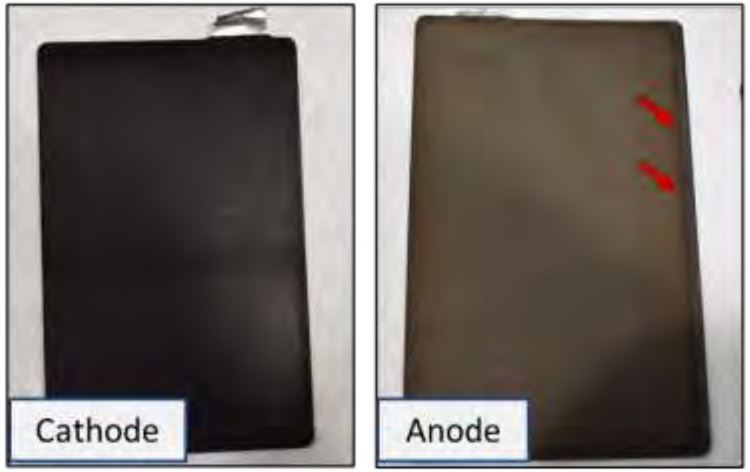
1Ah A7 Multilayer Sodium-ion Pouch Cells



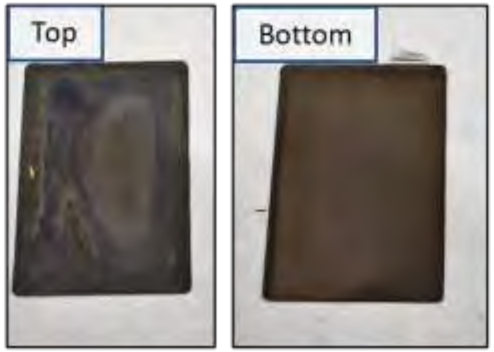
- Cells showed stable cycling performance at 25°C and 10°C, Cells cycled at 60°C failed after ~60 cycles

Forensic analysis of sodium-ion pouch cells

Cell Disassembly – Cell Discharged @ 0.2C @ 25°C



Cell Disassembly – Cell Discharged @ 0.2C @ 60°C

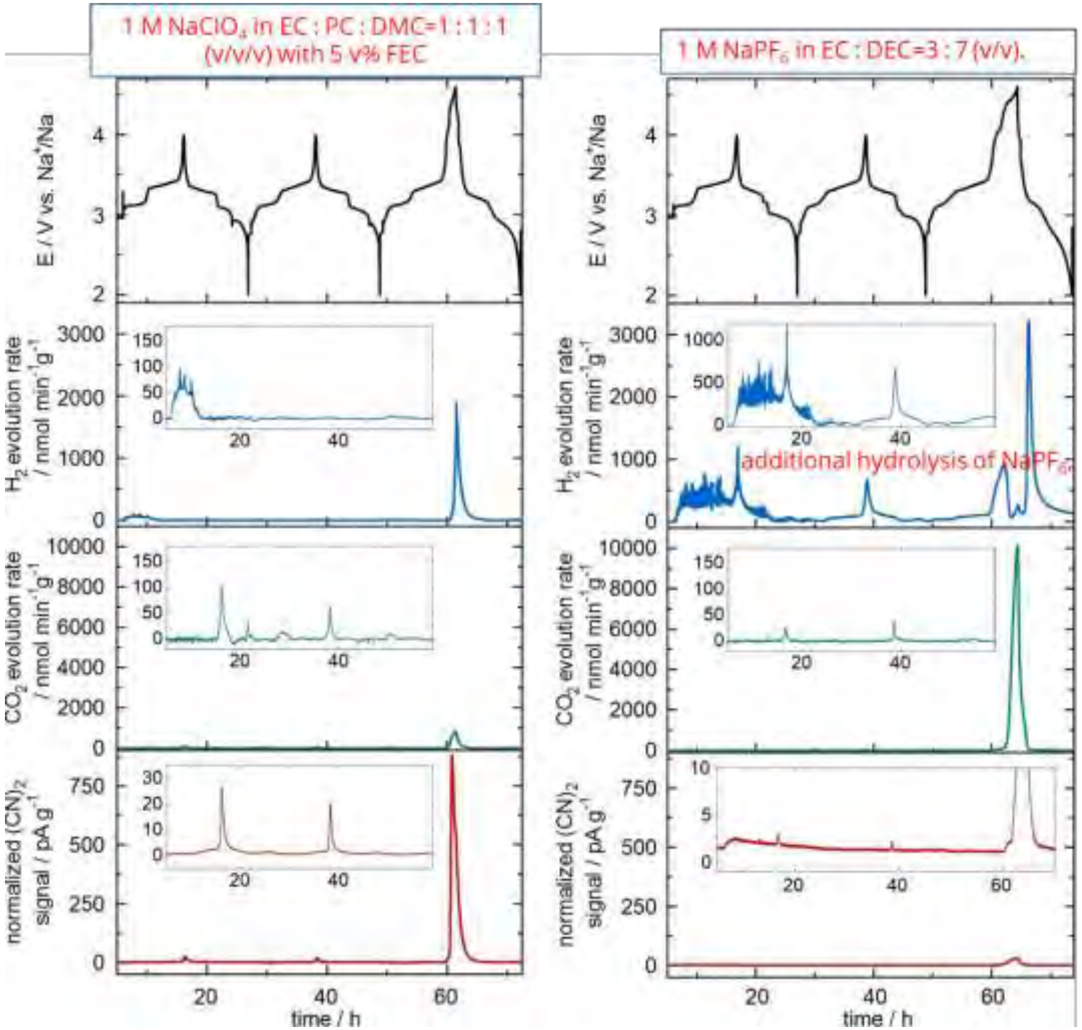


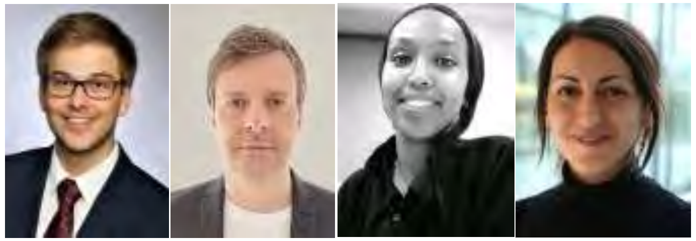
Cathode is relatively featureless and appears stable after cycling. Anode presents main changes with deterioration observed

Visible Na deposition at the anode and delamination. Cathode shows a mottled/non-homogeneous surface

Gas analysis upon cycling

What about potential Hydrogen Cyanide release?





Collaboration BELLA LAB-KIT WMG-Warwick

S. L. Dreyer, F. Maddar, I. Hasa, T. Brezesinski et al, Batteries& Supercaps 2024, e202300595

Gas analysis upon cycling

Hydrogen formation: main gas generated

- H_2 is most likely associated to reduction of residual electrolyte moisture at the anode side.

- Coordinated water in the PW, which cannot be removed during dehydration, leads to potential further water release in the form of $Na(OH_2)^+$ into the electrolyte during de-sodiation, and particularly so at the end of charge, where the coordination becomes weaker.

- Larger amount of H_2 with $NaPF_6$ can be explained considering acidic conditions due to HF formation.

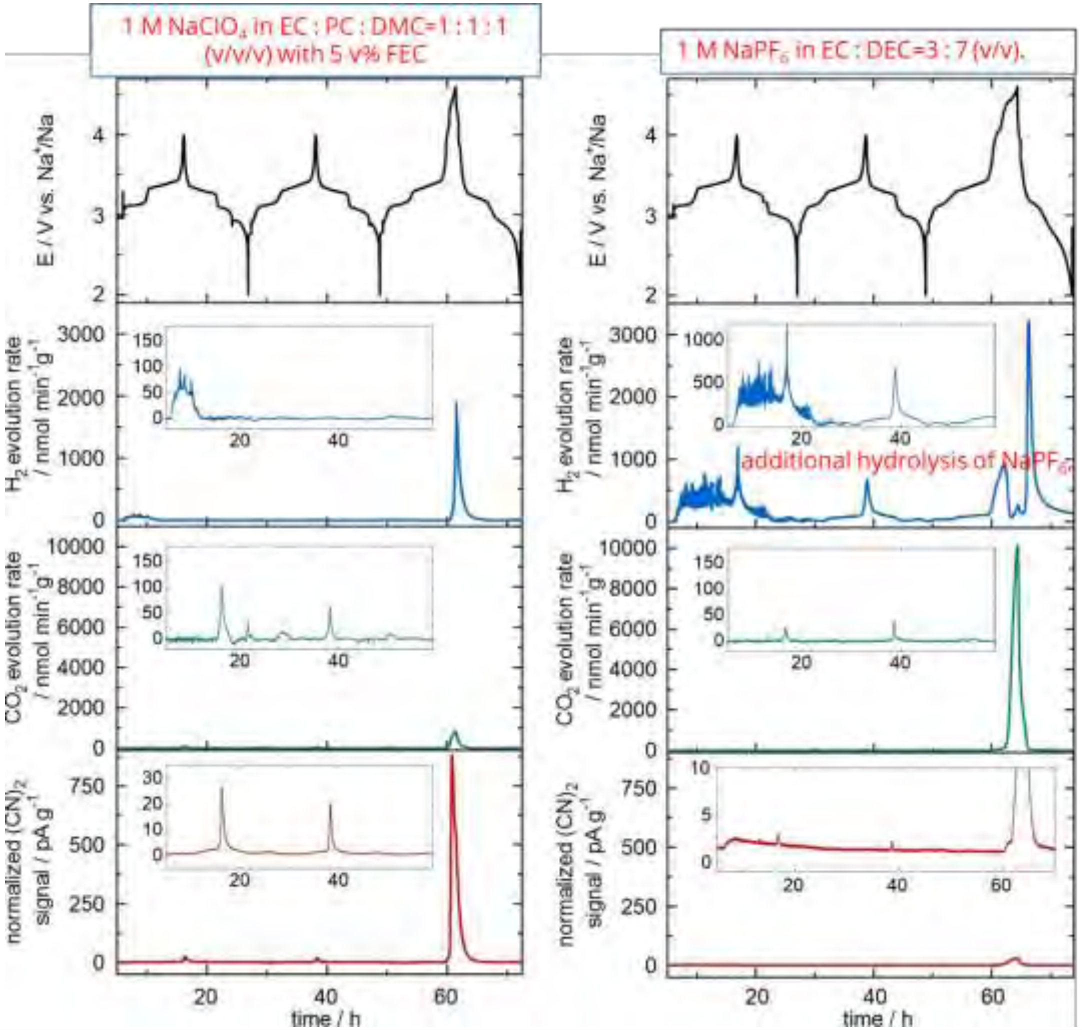
Carbon dioxide formation:

- Basic conditions formed using $NaClO_4$ lead to hydrolysis of EC and formation of CO_2. More CO2 is observed in NaPF6 electrolyte due to the presence of DEC solvent (more oxidation-sensitive).

Cyanogen formation:

- $(CN)_2$ evolution is observed at high SOC and potential near the end of charge, yet the evolution is far stronger for the cell containing $NaClO_4$-electrolyte, and during regular cycling hardly visible against the background for the cell containing $NaPF_6$-electrolyte.

- As oxidation of cyanide anions is required to form $(CN)_2$, the presence of the ClO_4^- anion with its oxidative properties appears to be an explanation for the formation of cyanogen.



Incorporation of polymer electrolyte

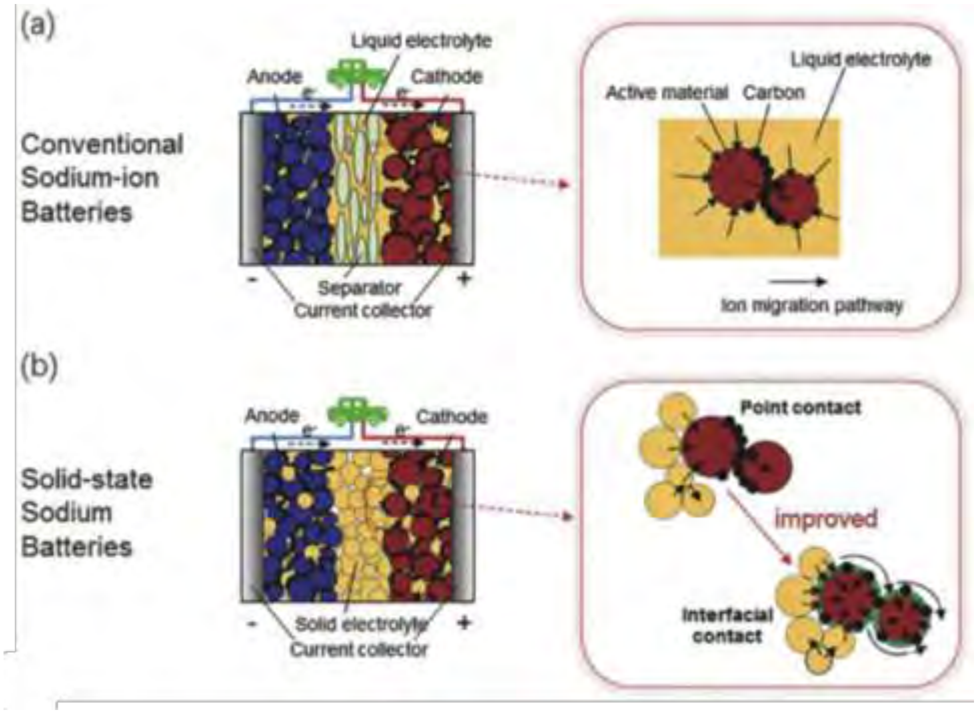
Task 4.6 Incorporation of polymer electrolytes

Partners: **CEA, KIT, WMG**

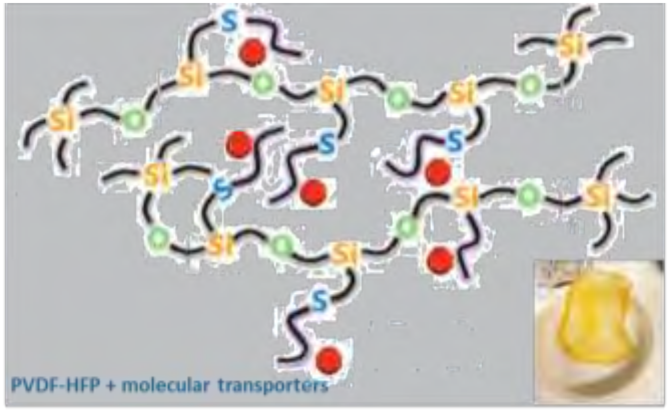
- **KIT** will scale-up the polymeric electrolyte in sufficient quantity and transfer it to WMG and CEA for processing. KIT will also electrochemically test it at coin cell-level. The results will feed attempt of upscaled processes carried out by WMG.
- **WMG** will carry out wet casting routes to incorporate the SIPE into the pouch cells. For performance comparison it will be substituted for the liquid electrolyte in the baseline cell.
- **CEA** will apply solvent-free extrusion to try to develop all-solid composite electrodes and to assemble up to 5 small multilayer prismatic cells of 0.1Ah

CEA: development of a solvent-free extrusion;
KIT: SIPE development, scale-up and electrochemical evaluation at coin cell level, which will feed into larger scale in terms of processing and slurry optimisation;
WMG: Development, processing and evaluation of pouch cells

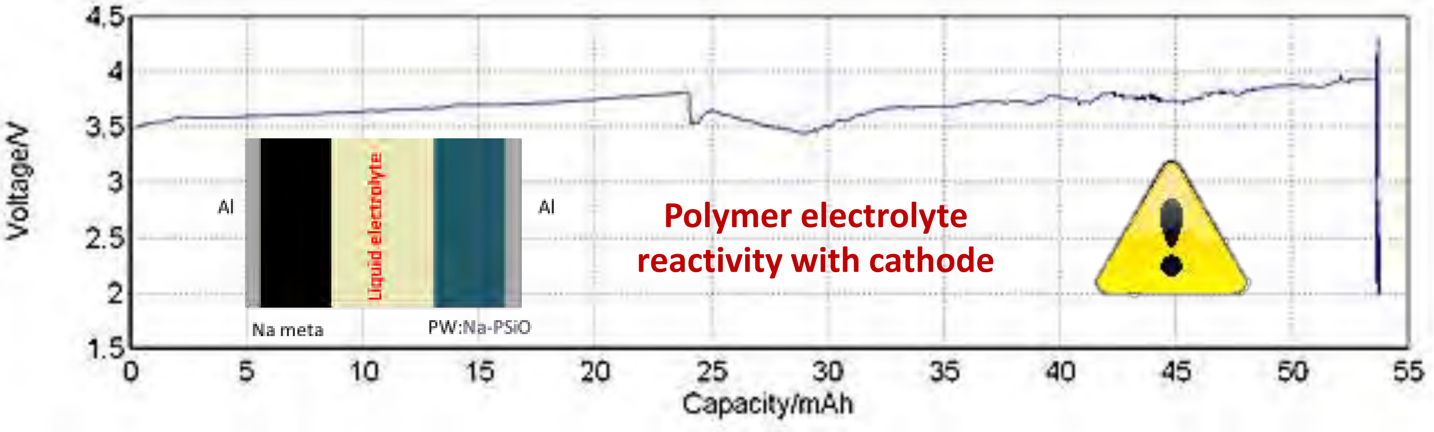
Incorporation of polymer electrolyte



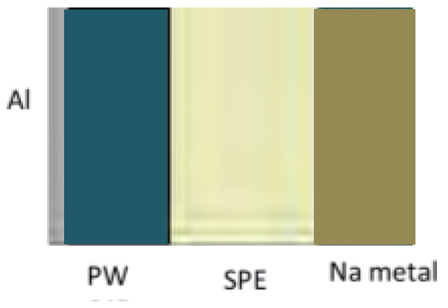
C. Zhao, et al., Adv. Energy Mater.2018, 8, 1703012



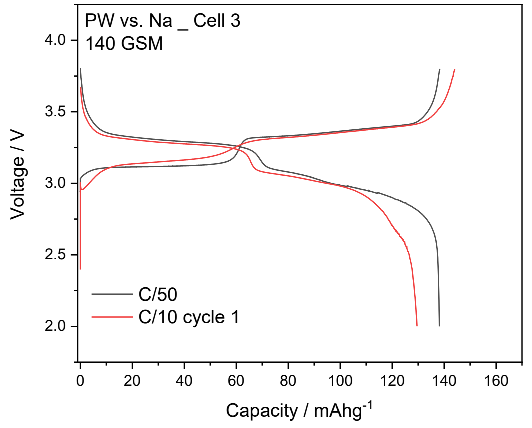
*Modified from: H. Liang et al. Adv. Energy Mater. 2022, 12, 2200013

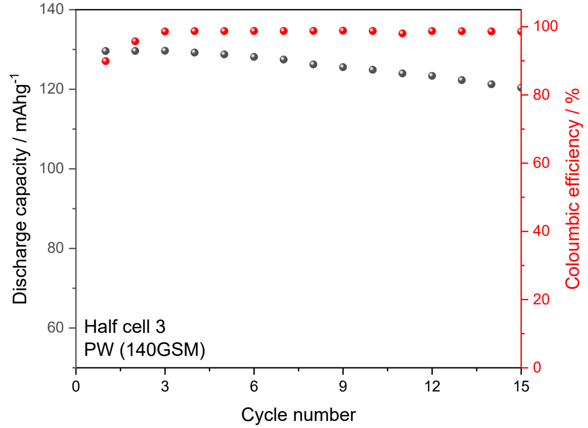


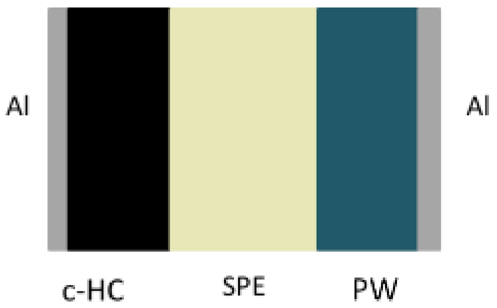
Incorporation of polymer electrolyte



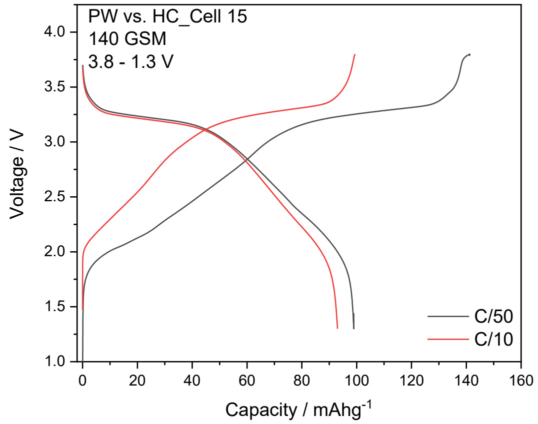
Coin cell
Half cells

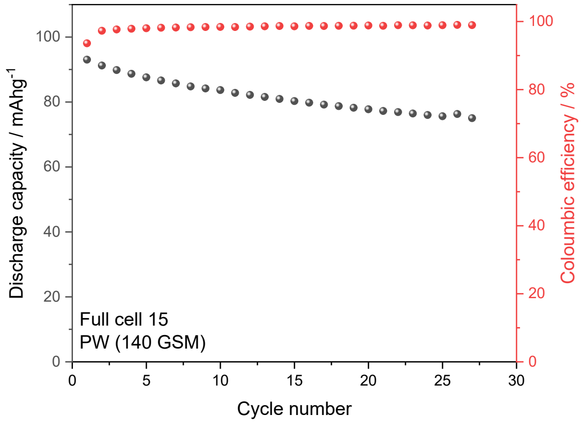






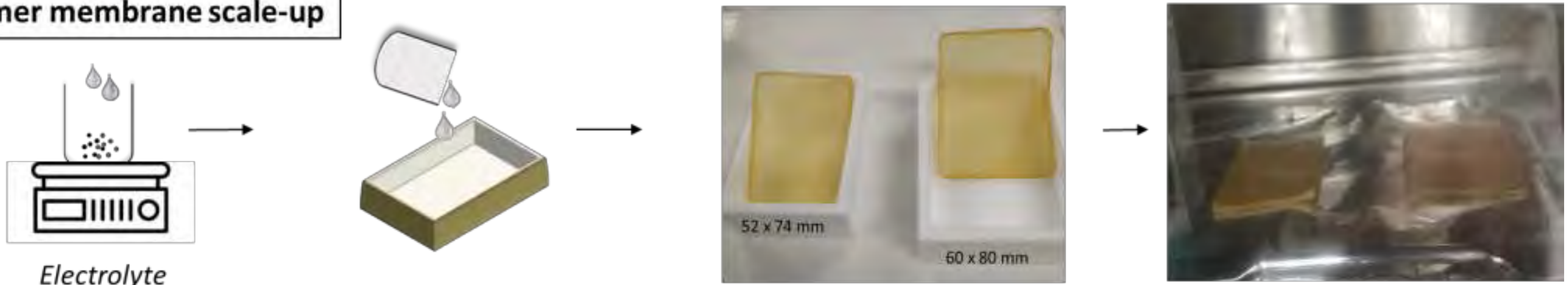
Coin cell
Full cells





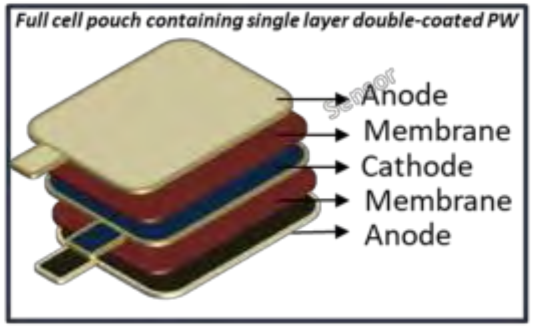
Incorporation of polymer electrolyte

Polymer membrane scale-up



Electrolyte components mix → Solvent evaporation → Dry polymer membrane → Further drying

Pouch cell components

a)


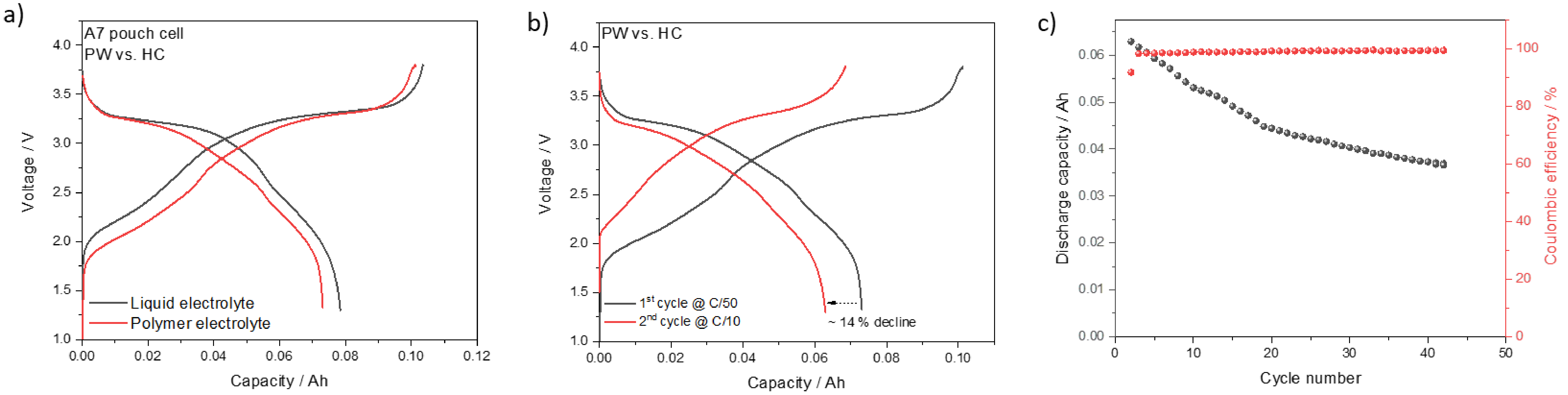
A7 Single layer pouch cells :

b)


c)


Incorporation of polymer electrolyte

- **Task 4.6** Incorporation of polymer electrolytes   Task leader: **CEA** Duration: **M18-M36**



- **Drying electrode and polymer longer resulted in improved capacity though further optimization is required to improve cycling stability over time**

Scaling up challenges

Encouraging results but…

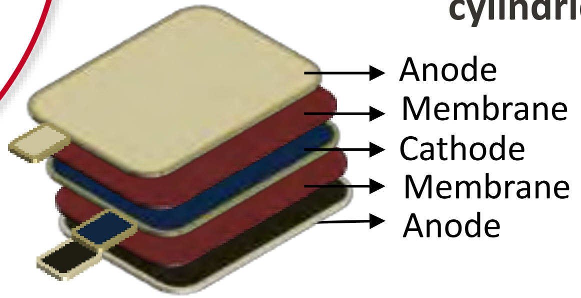
- Optimization of the molecular transporter addition process needs to be addressed to ensure homogenous uptake of the molecular transporters used.

Scalability
+
Processability challenges

Although the polymer powder has been shown to be scaled up, scalability of the polymer membrane requires further work

- Scaling up of membrane preparation process to produce "membrane" rolls to be used as separators.

- Flexibility of membrane should be considered for multilayer pouch cells or cylindrical cells.



Conclusion

- SIBs offer a “drop in” approach, as they do not require a different cell design and, therefore, can be manufactured in similar production lines as those used for LIBs
- Sustainable, low-cost aqueous processing has been applied both at the cathode and anode.
- Upscaling is not only a technical challenge. A rational understanding of the materials properties is crucial to be able to scale up new battery chemistries. A scientific approach to the technical challenge is needed to generates knowledge while benchmarking the progress of the developed battery materials.
- Prussian white cathode represent a valid cathode chemistry exhibiting very promising electrochemical performance matching KPIs for stationary storage applications.
- Encouraging results have been obtained with the polymer electrolyte

A big thank you to all partners

It has truly been an amazing journey...