



Sulfur crystallization behavior in different electrolytes

Crystal growth visualized by X-ray radiographic methods

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ABSTRACT:

Fascinating crystals of elemental sulfur are formed during charging of lithium–sulfur batteries. The behavior of the phase, morphology, and spatial distribution of crystallization is strongly influenced by the electrolyte environment. Using X-ray imaging, we directly visualize sulfur nucleation and growth in various electrolytes, revealing the distinct crystallization pattern and kinetics. But does the shape influence the performance?

Motivation

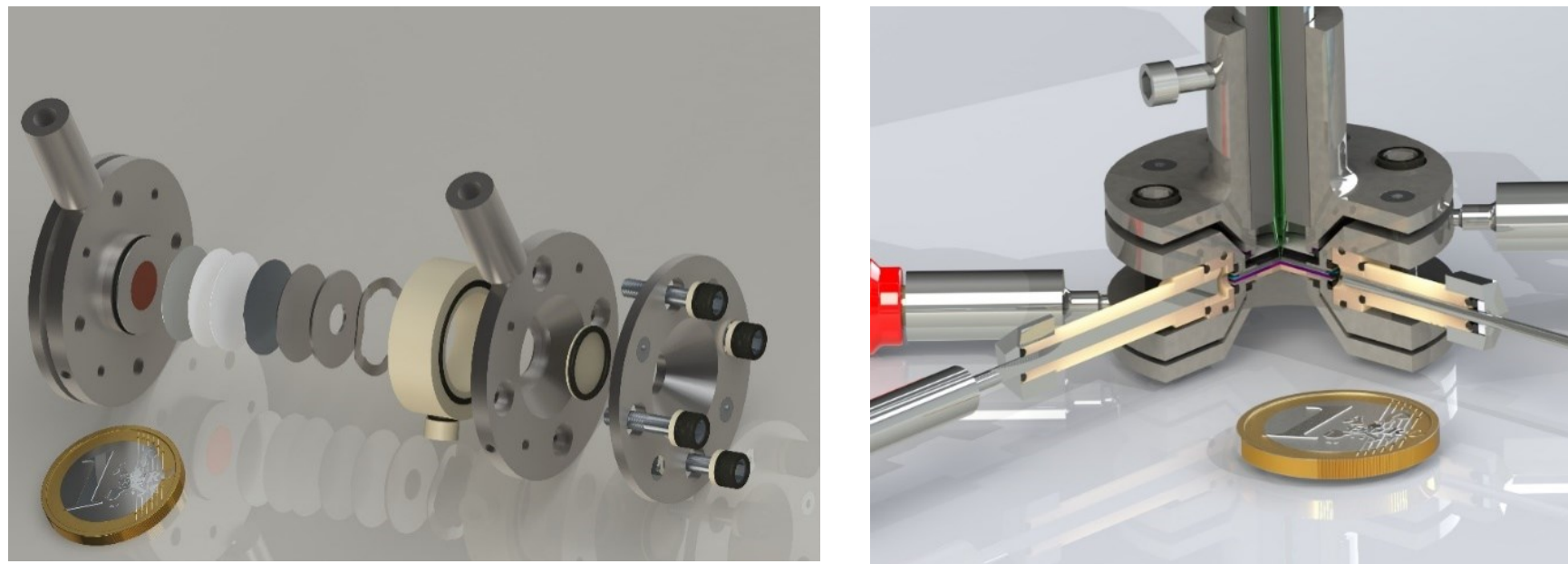
The phase and state transformation processes in lithium–sulfur (Li–S) battery technology are subject to ongoing refinement. Kinetics & thermodynamics are determined by:

- ❖ Electrolyte formulation, solvation properties, and distribution
- ❖ Electrode pore sizes and nucleation sites

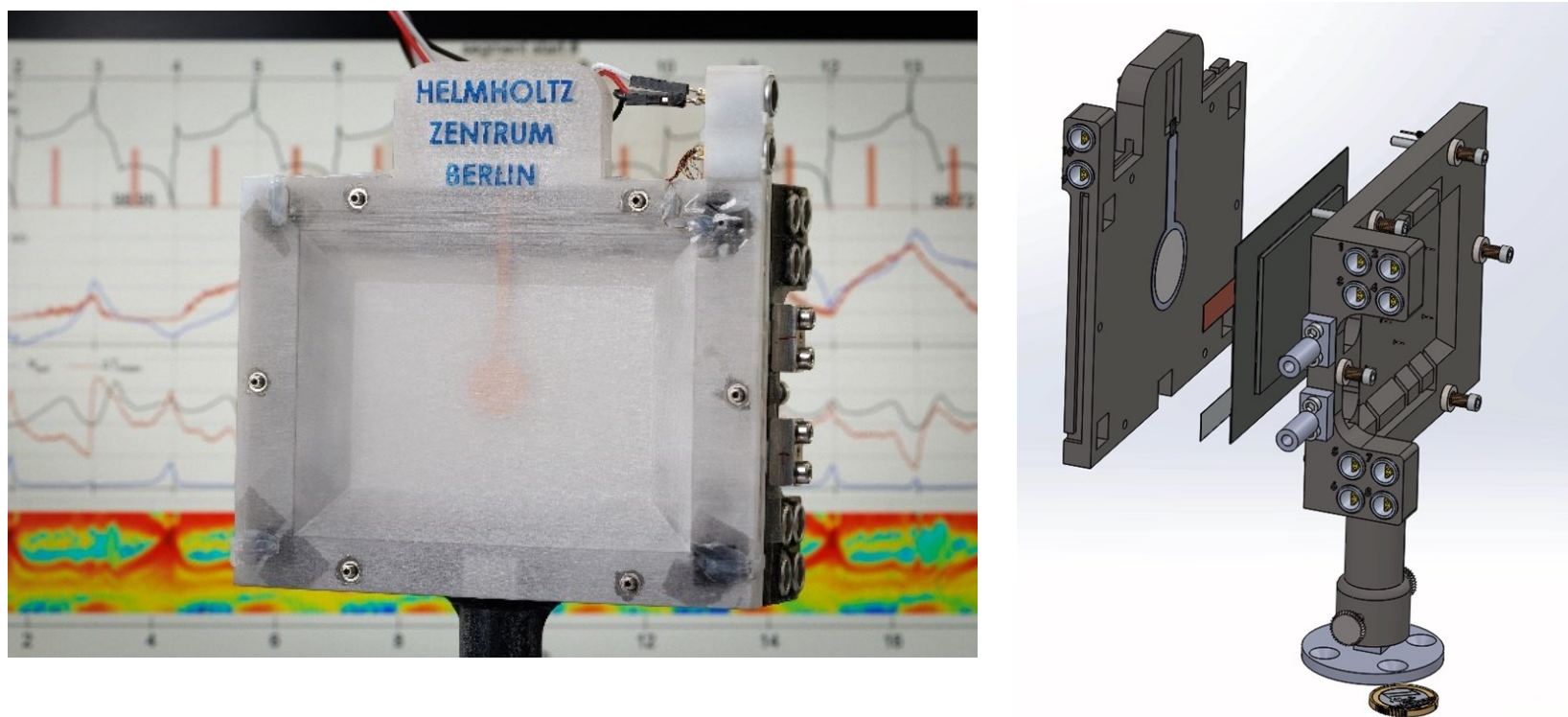
Research targets:

- Multimodal operando investigation (X-ray, EIS, T, p)
- Understanding of complex kinetic and mechanistic behavior
- Identification of allotropes, crystal phase, and physical state

Setup



The multimodal coin and pouch cell holder

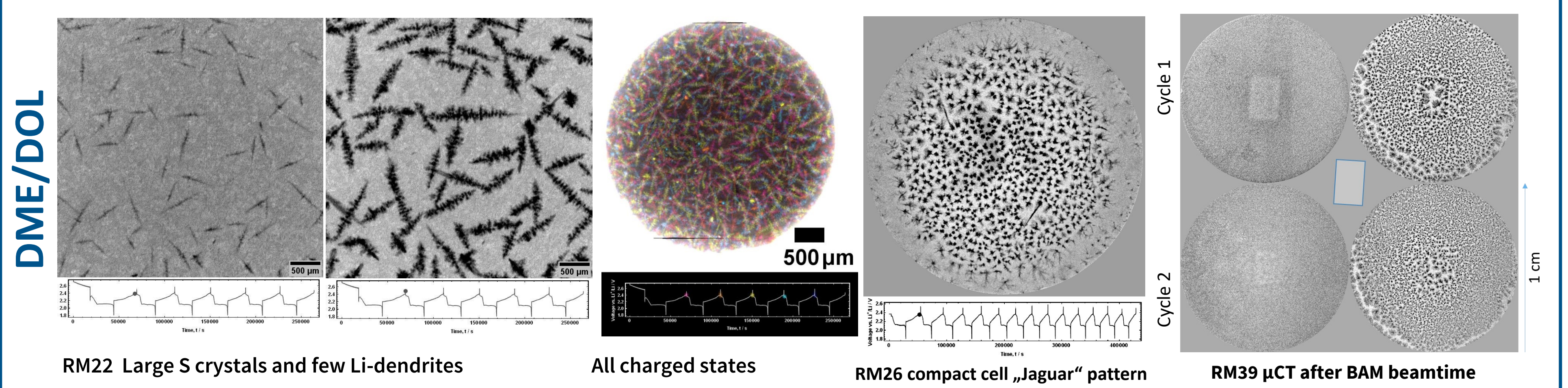


Cell parameter

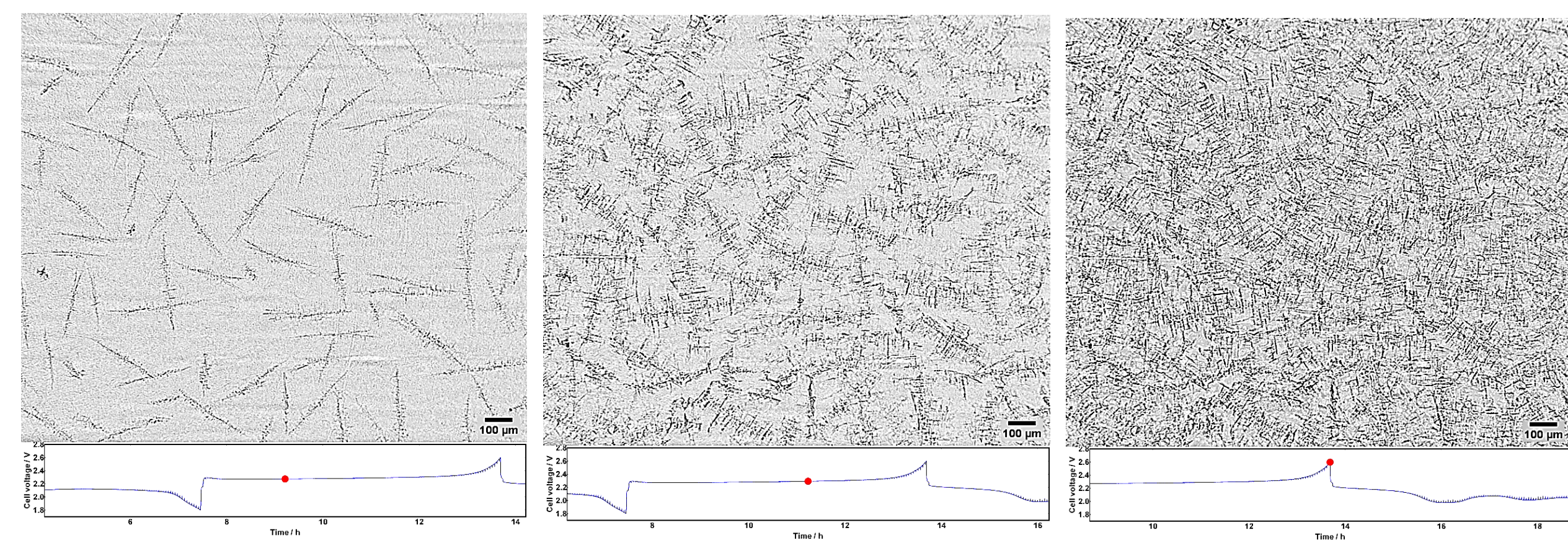
Cell	Type	Electrolyte	Method	E/S mL/mg
RM 22	Coin	DD	Micro CT	20
RM 26	Coin	DD	Micro CT	34.8
RM 39	Coin	DD	BAM/Micro CT	14.6
RM 46	Coin	HD	BAM	31.7
RM 47	Coin	HD	BAM	37.2
RM 36	Coin	TT	BAM	15.8
IWS71	Pouch	TT	Micro CT	35.8

Typical conditions:
Cathode: CNT-BP/S
30–50% sulfur loading
C-rate 0.1 C–0.3 C

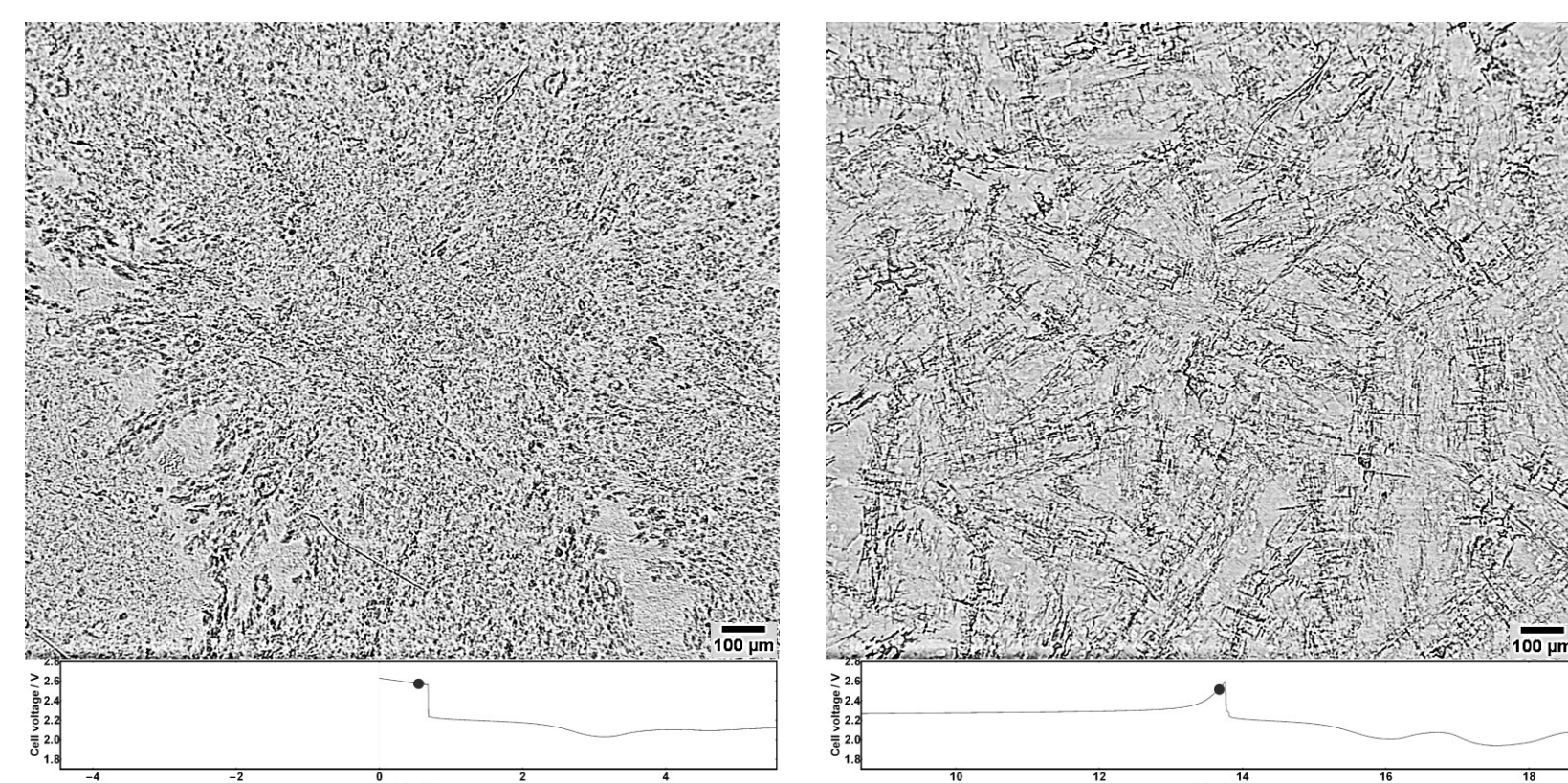
X-ray images zoom and full cells



DME/HME



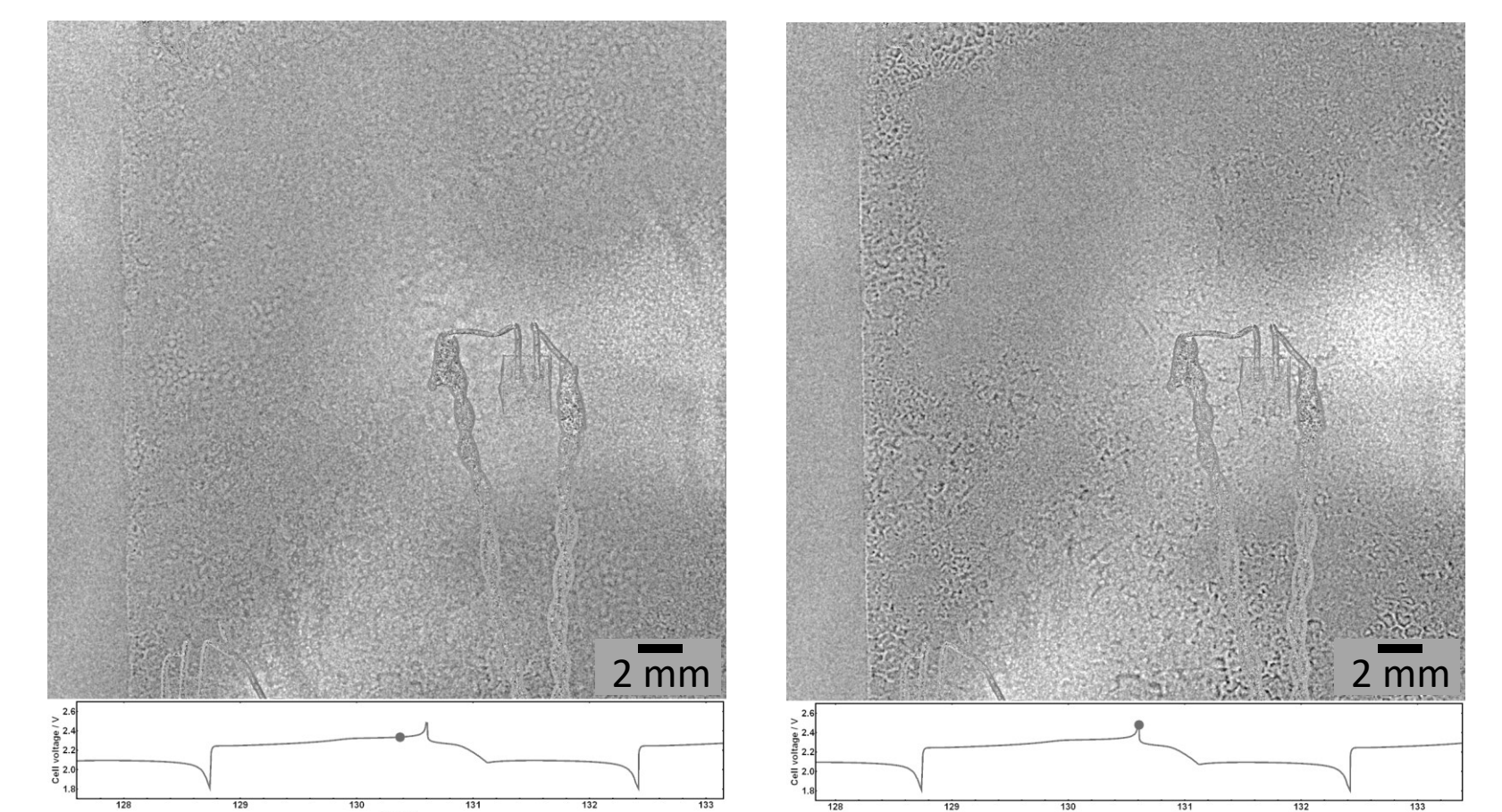
Synchrotron BAMline phase contrast RM47



Pristine RM46

First charged state

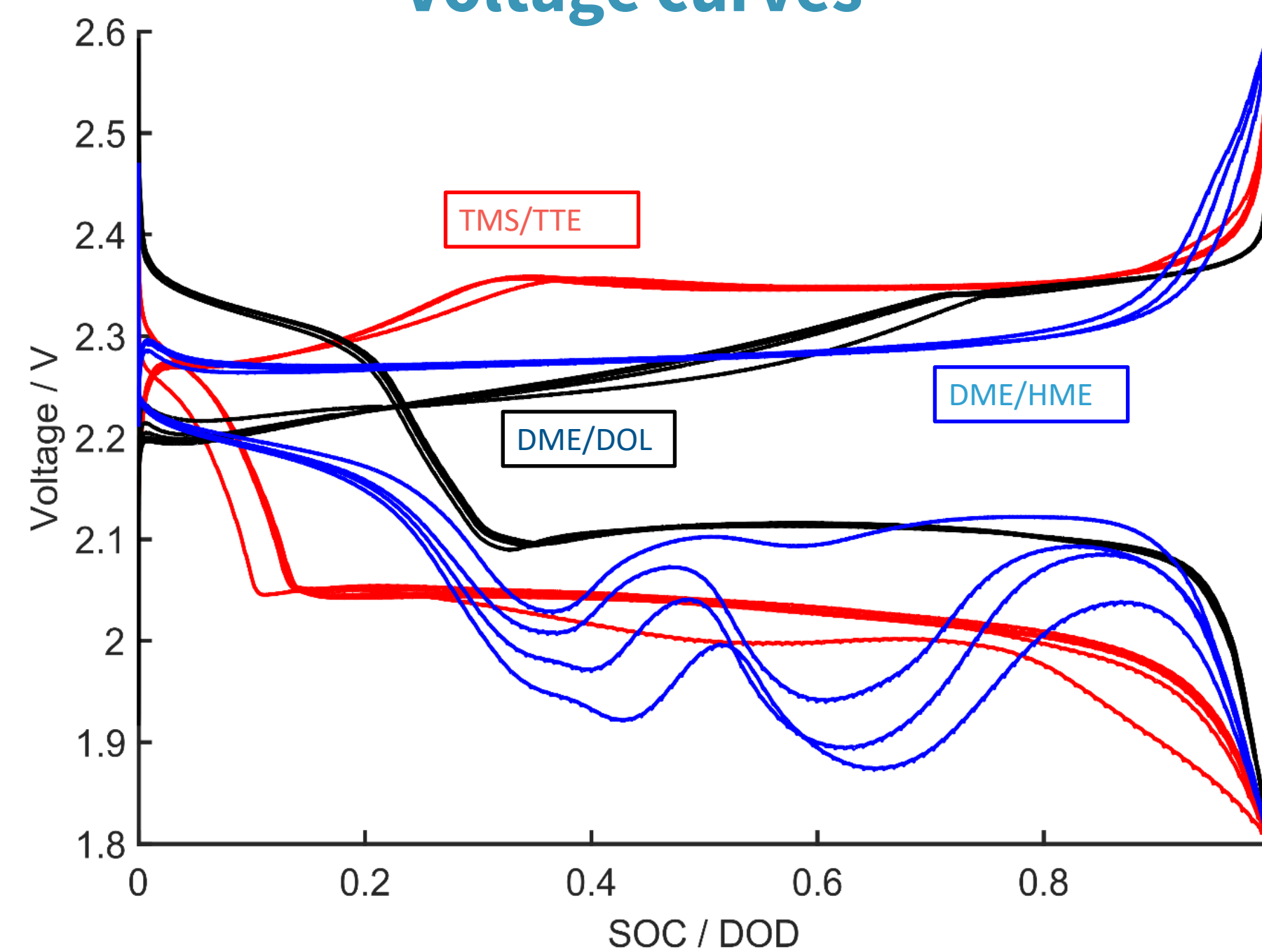
TMS/TTE



Pouch cell μCT: no visible crystals, just void filling

BAMline coin cell: Only few slightly visible spots → Video

Voltage curves



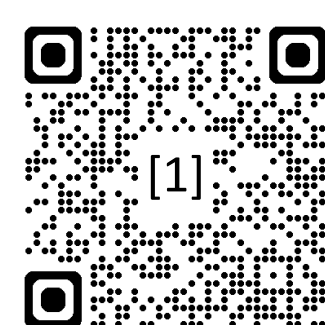
Conclusions

- TMS/TTE no macroscopic crystallization
- DME/DOL largest crystal formation, strongly local electrolyte volume dependent
- DME/HME early needle crystallization and continuous growth
- Indirect implications for performance
- ! Beware beam influence !

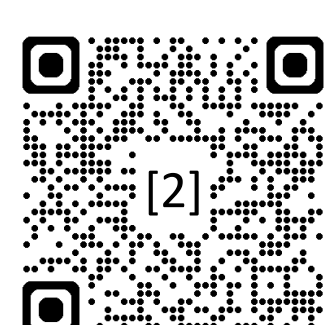
* Outlook: Another DME/TTE electrolyte shows a unique, quickly reversible intermediate phase deposition
→ paper submitted → contact author

REFERENCES

[1] R. Müller, I. Manke, A. Hilger, N. Kardjilov, T. Boenke, F. Reuter, S. Dörfler, T. Abendroth, P. Härtel, H. Althues, S. Kaskel, S. Risse: “Operando Radiography and Multimodal Analysis of Lithium–Sulfur Pouch Cells—Electrolyte Dependent Morphology Evolution at the Cathode”, *Adv. Energy Mater.* **2022**, 12, 2103432

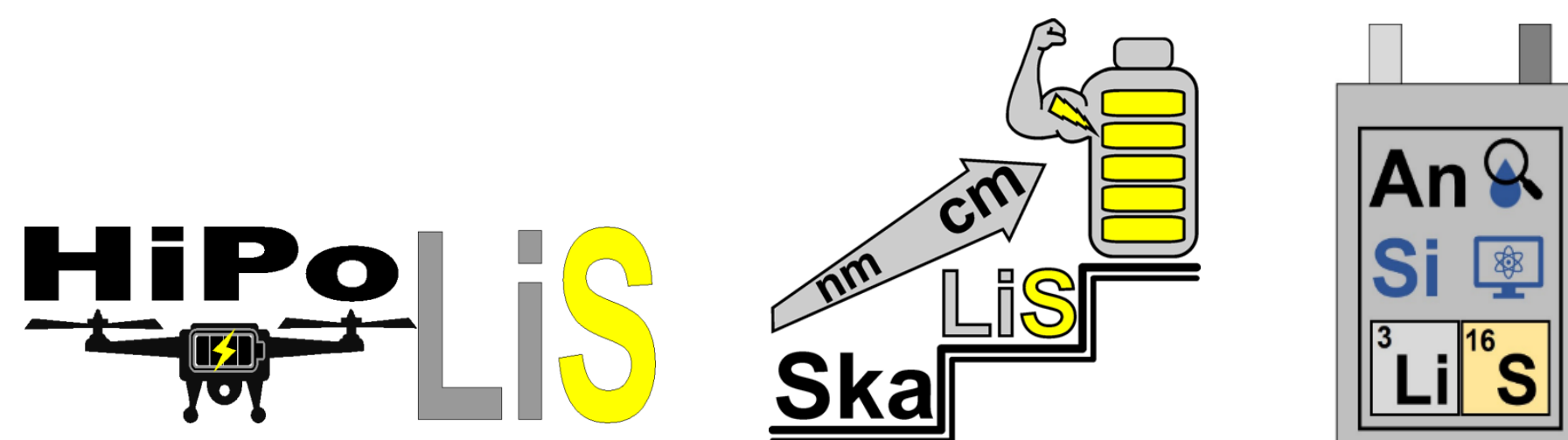


[2] R. Müller, T. Boenke, S. Dörfler, T. Abendroth, P. Härtel, H. Althues, S. Kaskel, N. Kardjilov, H. Markötter, M. Sintschuk, A. Hilger, I. Manke, S. Risse, “Multimodal Operando Analysis of Lithium Sulfur Multilayer Pouch Cells: An In-Depth Investigation on Cell Component Design and Performance”, *Adv. Energy Mater.* **2025**, 15, 2404256.



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MORE INFORMATION

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