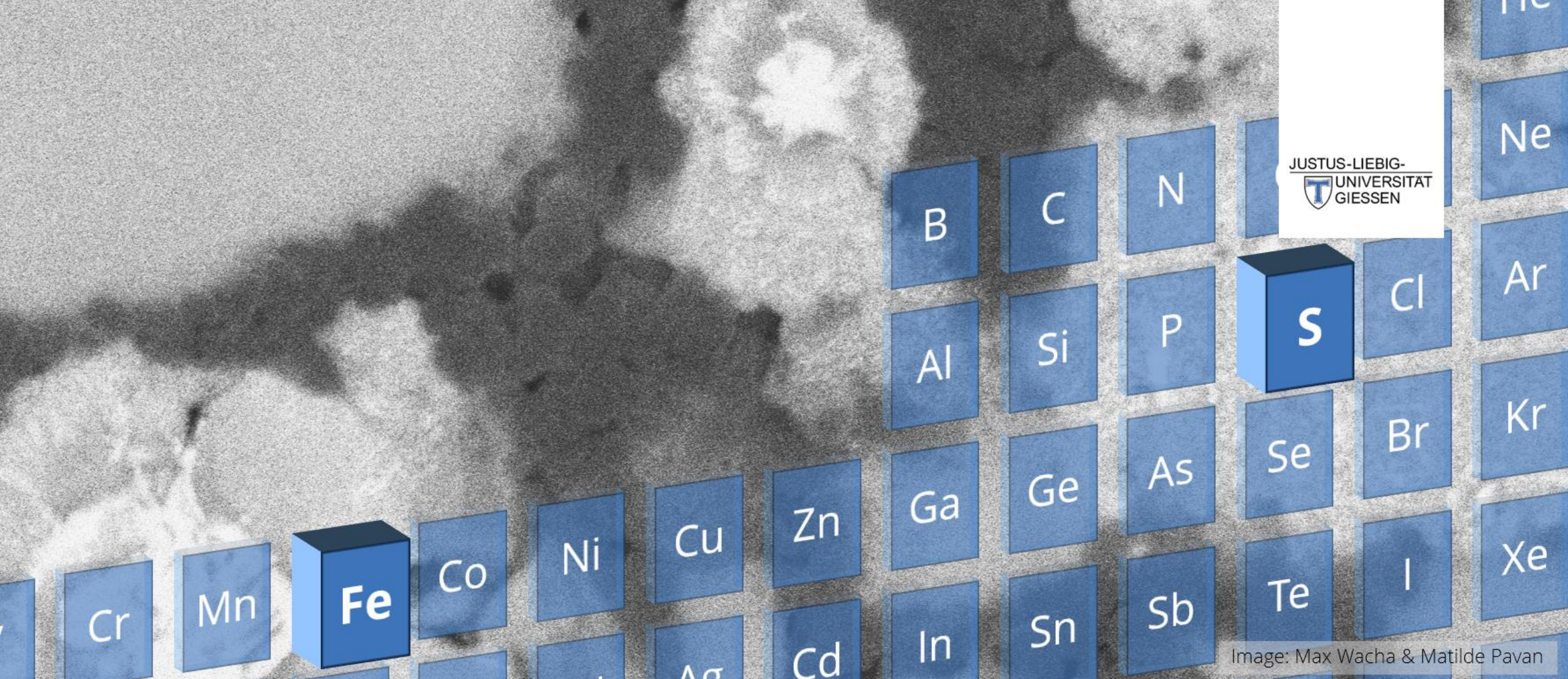




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Image: Max Wacha & Matilde Pavan

Role and Evolution of FeS_2 Cathode Microstructure in Argyrodite-based All-solid-state Lithium-Sulfur Batteries

18.11.2025 12th Workshop Li-S batteries - Dresden

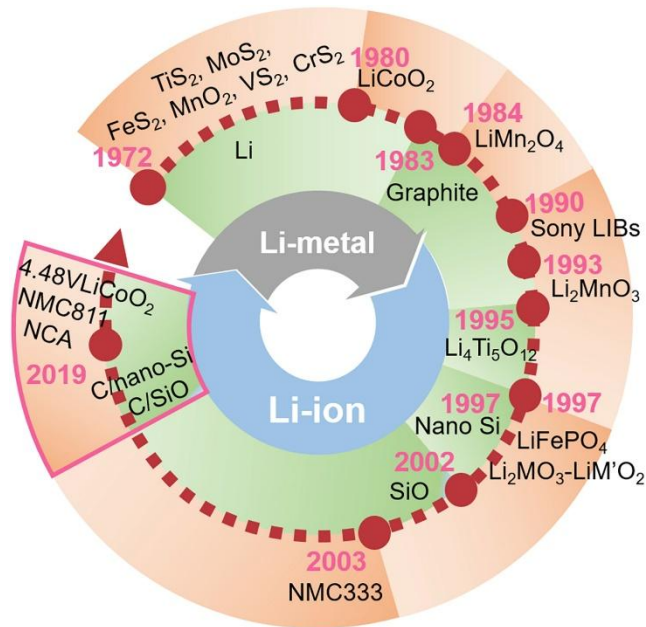
Matilde Pavan, Konrad Münch, Sebastian L. Benz, Tim Bernges, Anja Henss, Wolfgang G. Zeier, Jürgen Janek



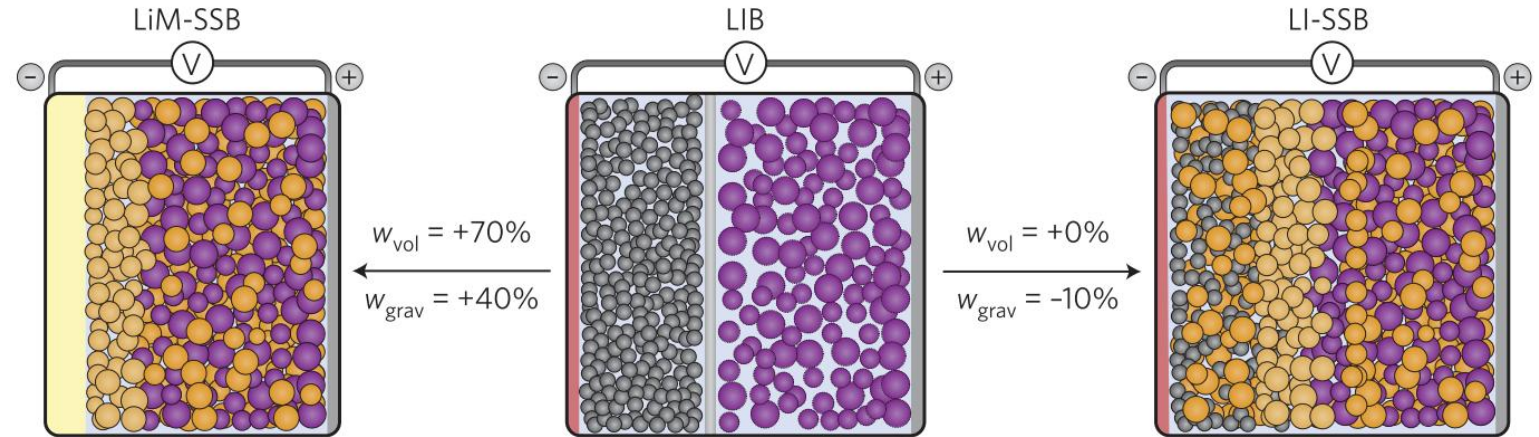
Transitioning to all solid-state batteries

1

Liquid electrolyte



Solid state electrolyte



Potential advantages of ASSBs

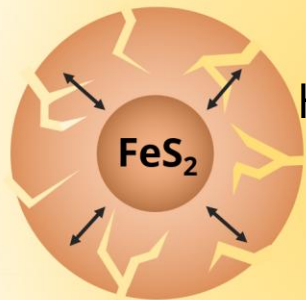
- ✓ Lighter and smaller
- ✓ Faster charging
- ✓ Safer

Li-S batteries

„beyond Li-ion “ technology

- ✓ Lighter
- ✓ Cheaper

Iron disulfide



SOLID ELECTROLYTE

Advantages

High theor. capacity ($894 \text{ mAh}\cdot\text{g}^{-1}$)

Non-toxic

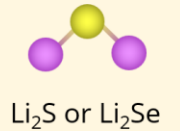
Earth-abundant & cheap

Lithiation is a conversion reaction

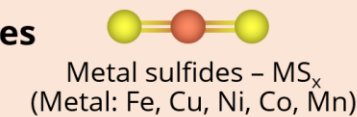
Chalcogens



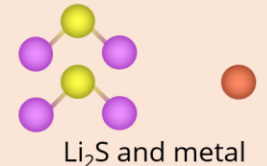
Lithiation



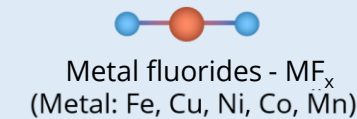
Chalcogenides



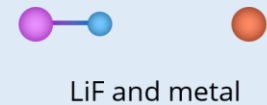
Lithiation

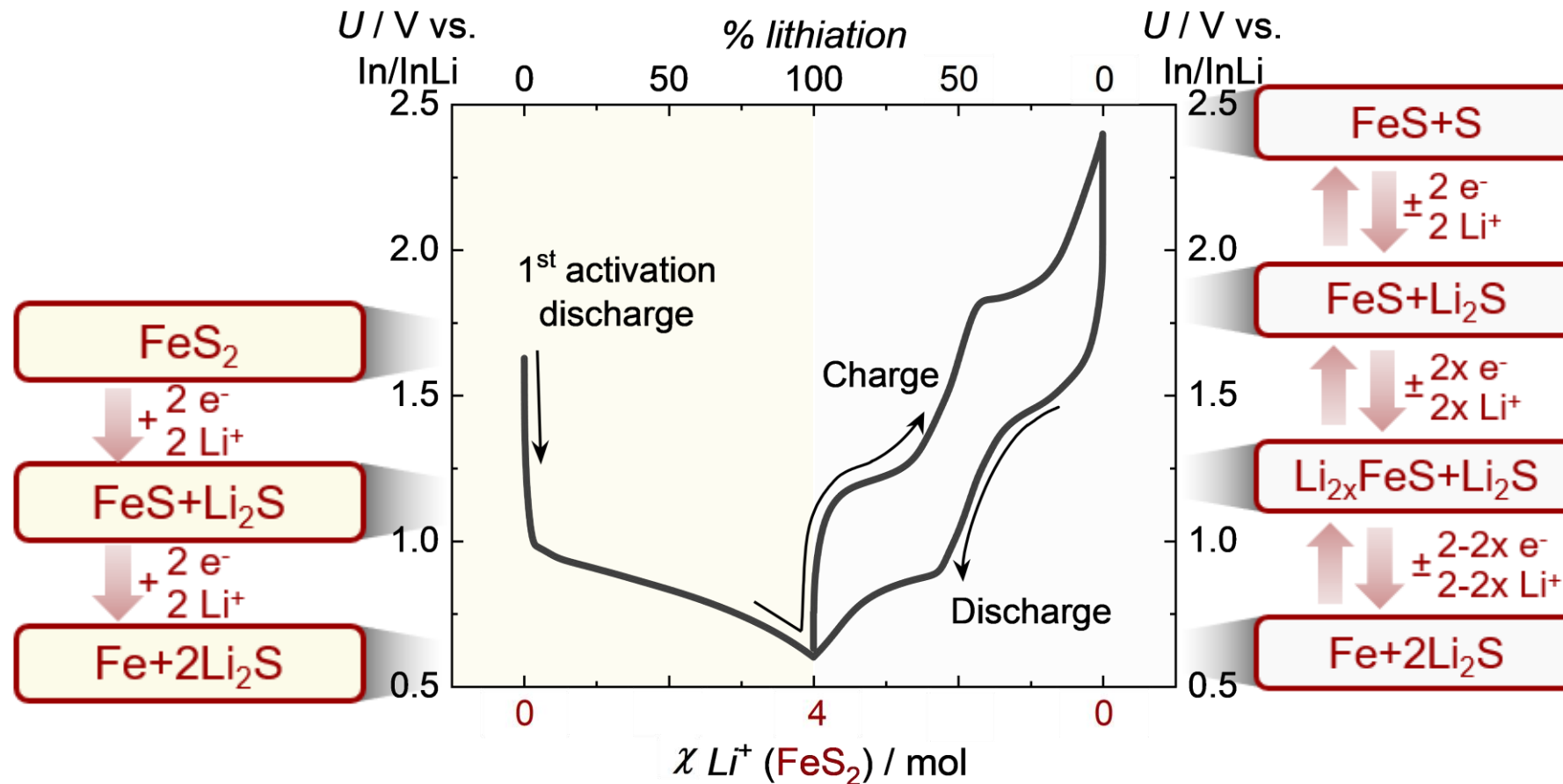


Halides



Lithiation



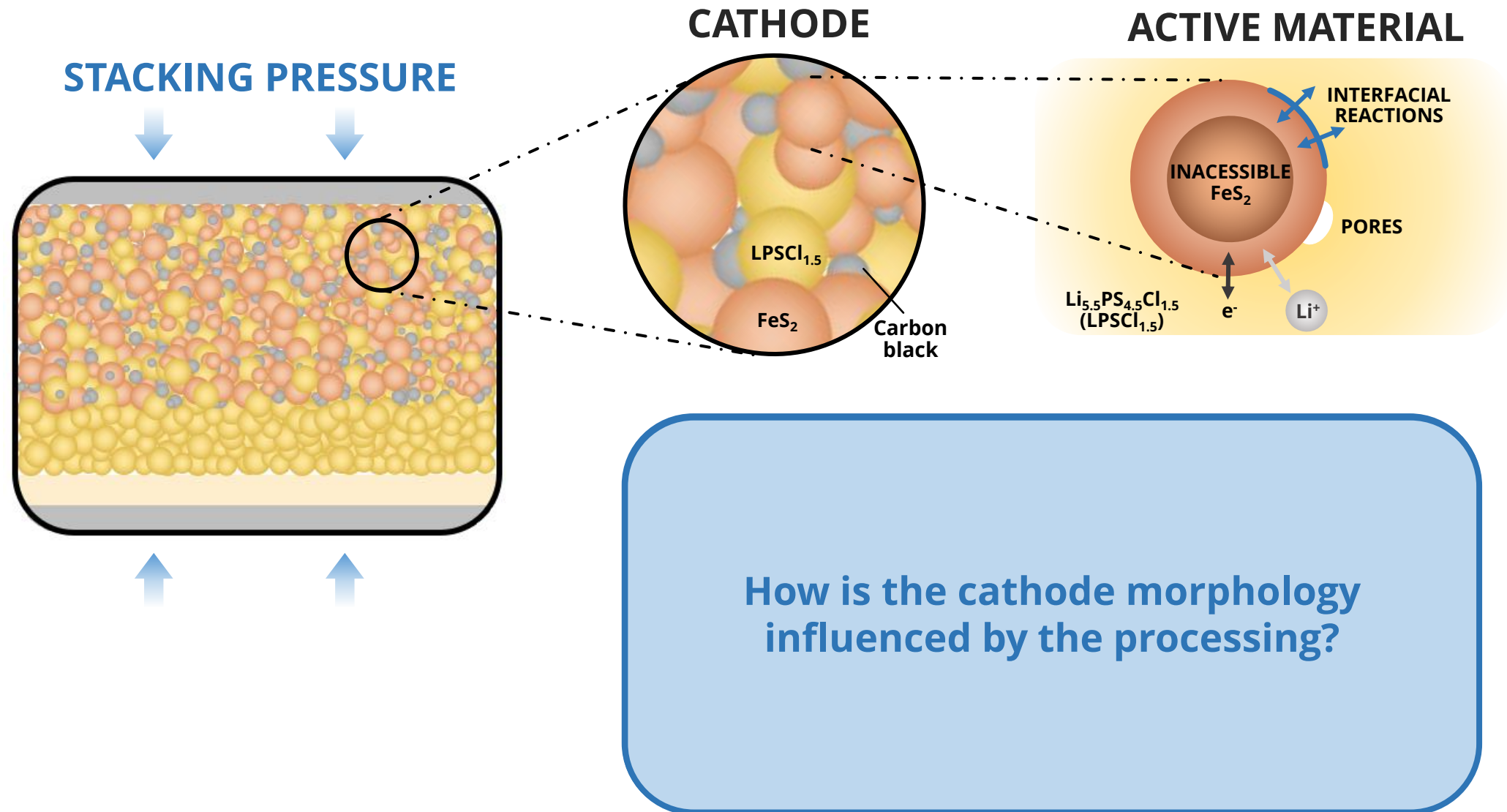


Cell degradation: once Fe⁰ is formed it is kinetically inaccessible (loss of capacity)



The microstructure is crucial for EC performance

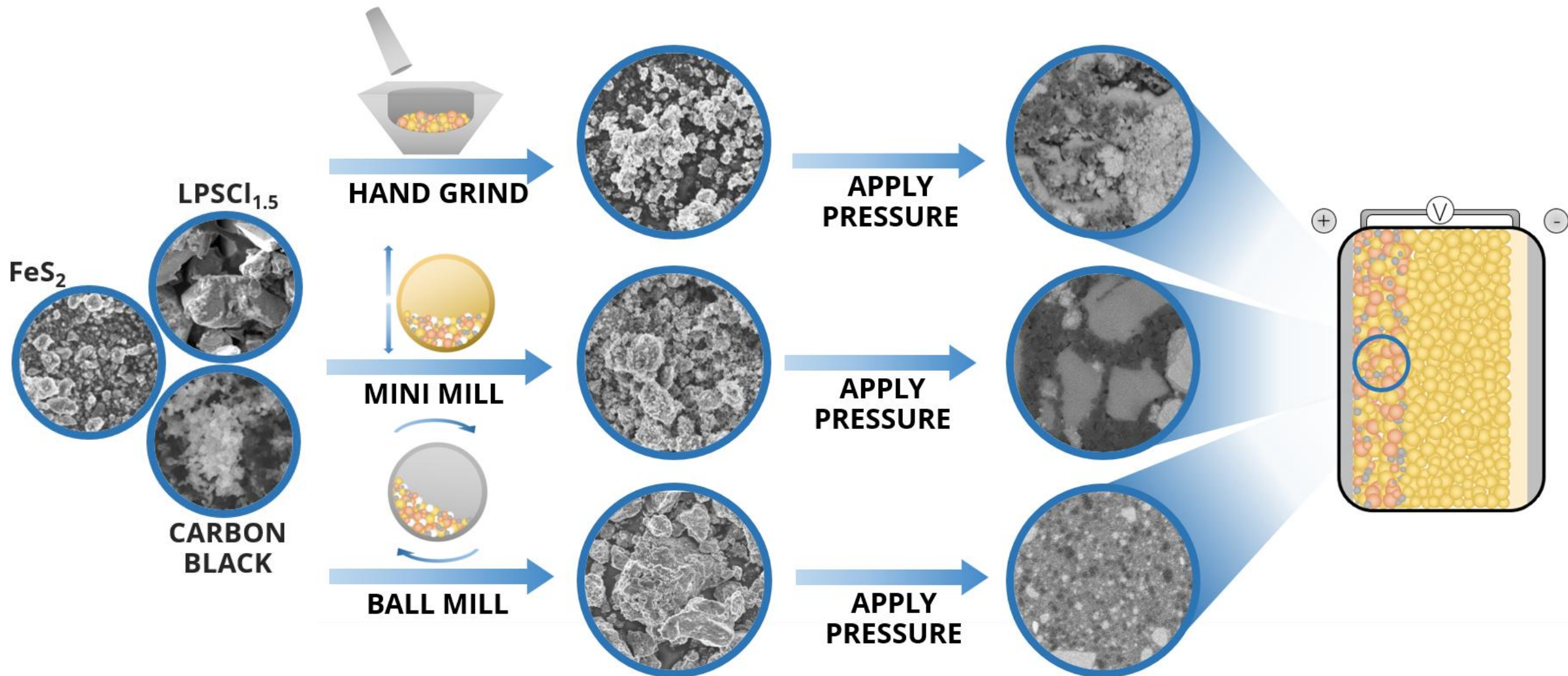
4



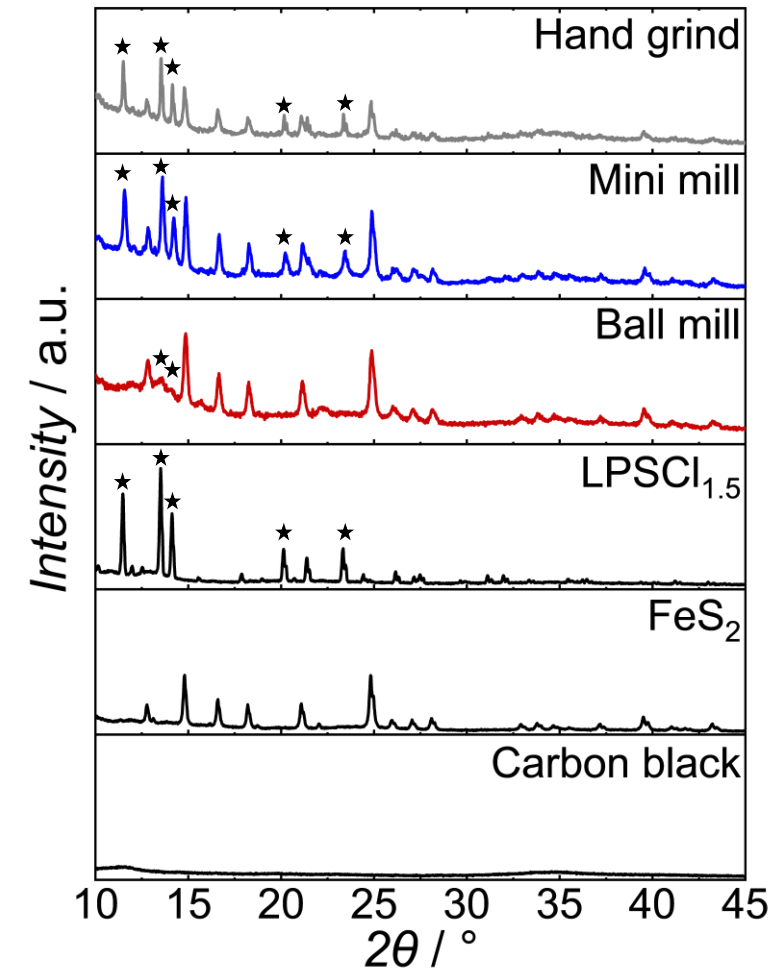
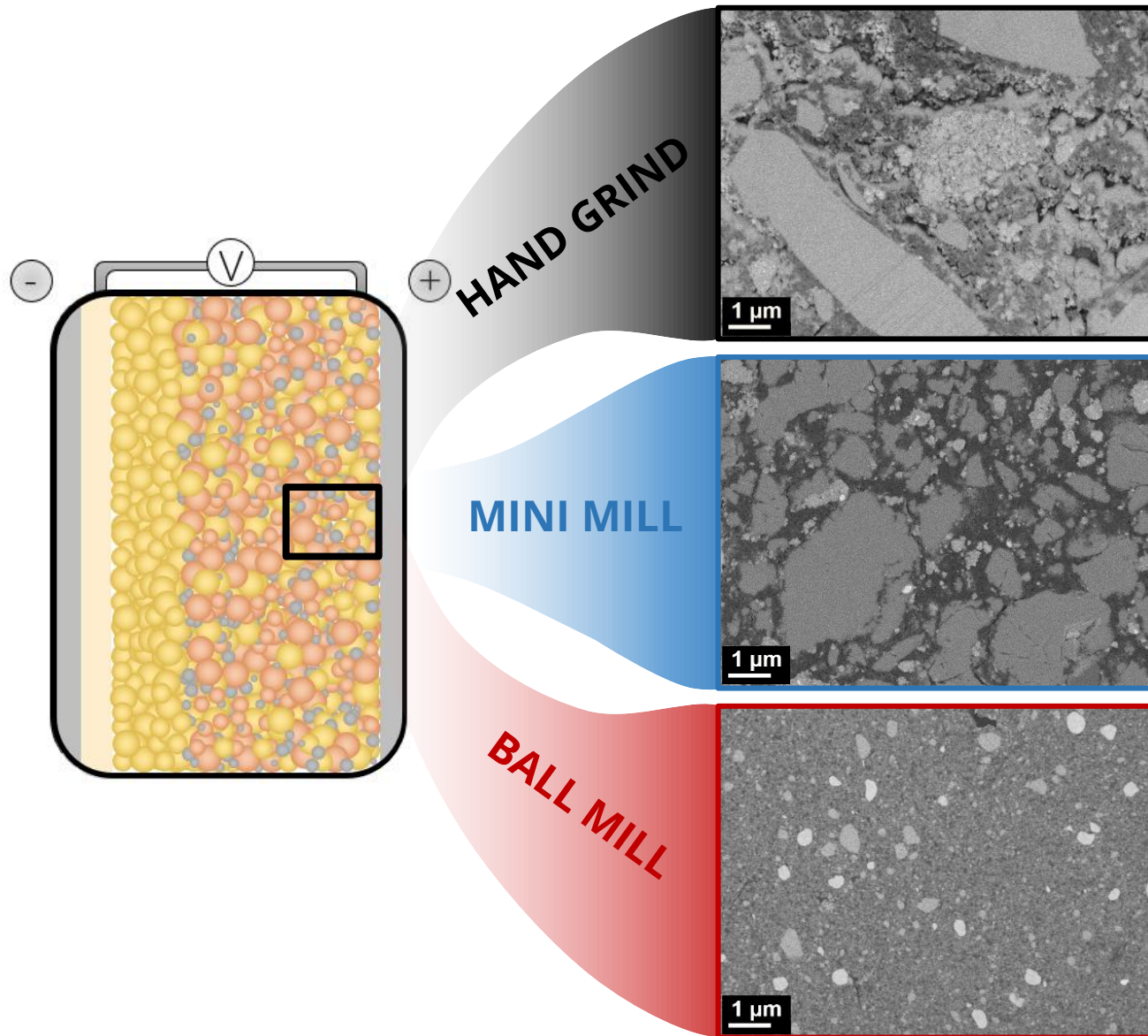
[6] Dewald, G. Influence of Iron Sulfide Nanoparticle Sizes in Solid-State Batteries. Angew.Chem. Int.Ed 60, 33 (2021)

We can control the cathode microstructure

5



The processing influences the microstructure

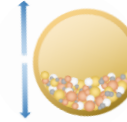


The accessible capacity depends on the morphology 7

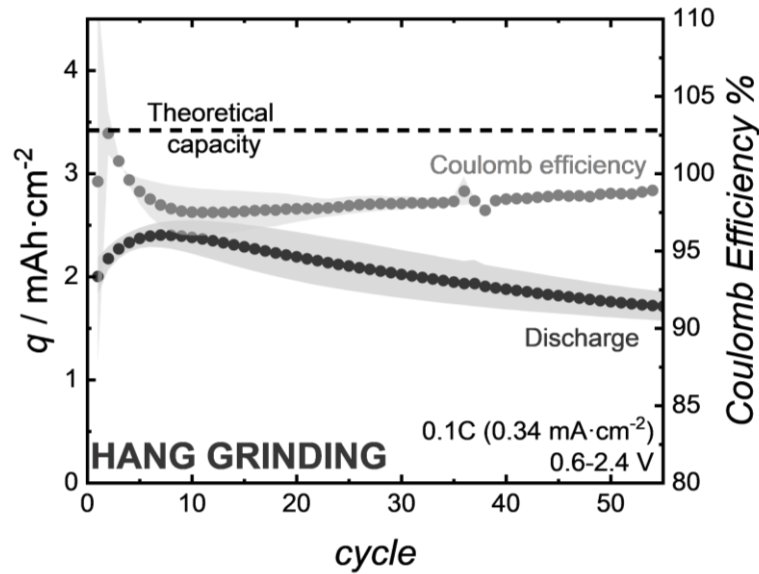
HAND GRIND



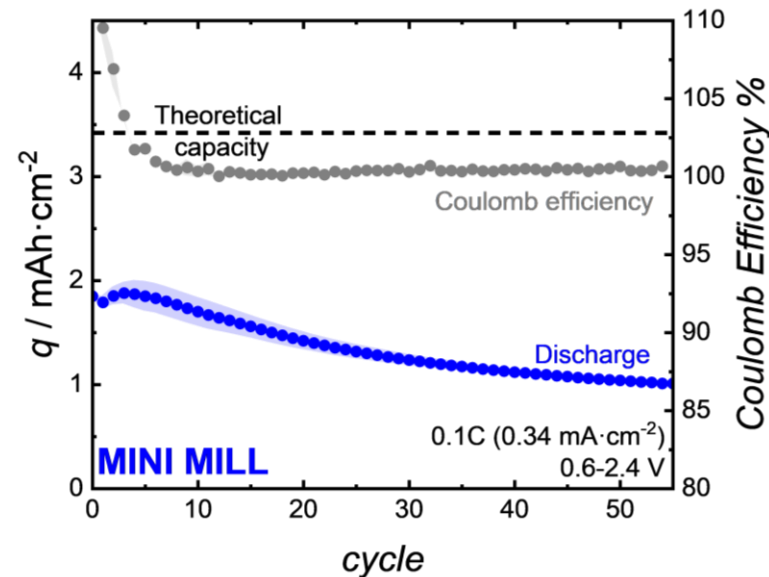
MINI MILL



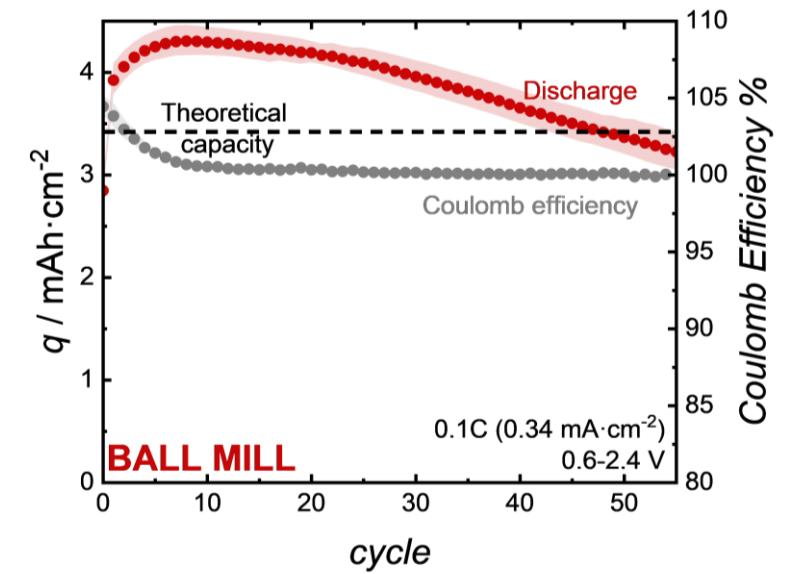
BALL MILL



Capacity retention 82%



Capacity retention 57%



Capacity retention 87%

Smaller FeS₂ particles ↔ higher surface area ↔ prone to react (i.e. lithiation)

FeS₂ / LPSCl_{1.5} / carbon black | LPSCl_{1.5} | In/InLi

FeS₂/LPSCl_{1.5}/CB | LPSCl_{1.5} | In/InLi
Loadings: FeS₂ 3.8 mg cm⁻² and LPSCl_{1.5} 6.4 mg cm⁻²
Q_{th} 3.4 mAh cm⁻² or 894 mAh g⁻¹

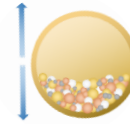
Differential capacity curves show an extra process

8

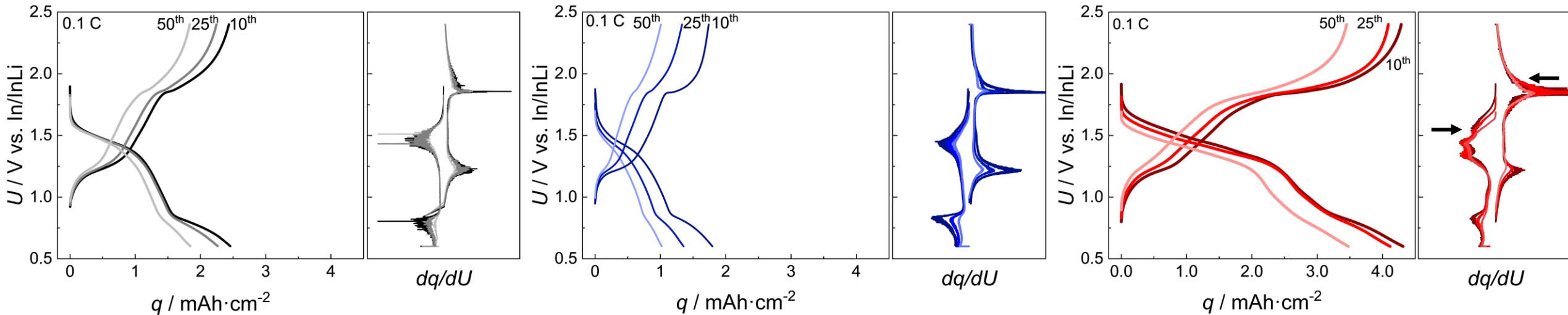
HAND GRIND



MINI MILL



BALL MILL



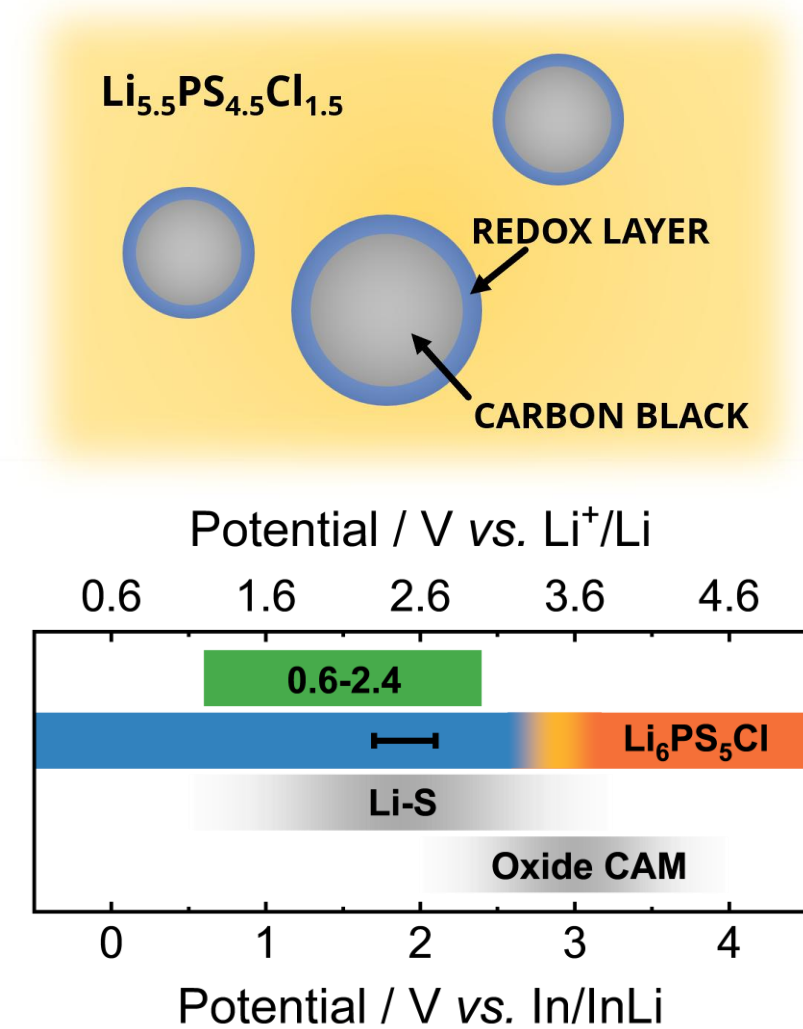
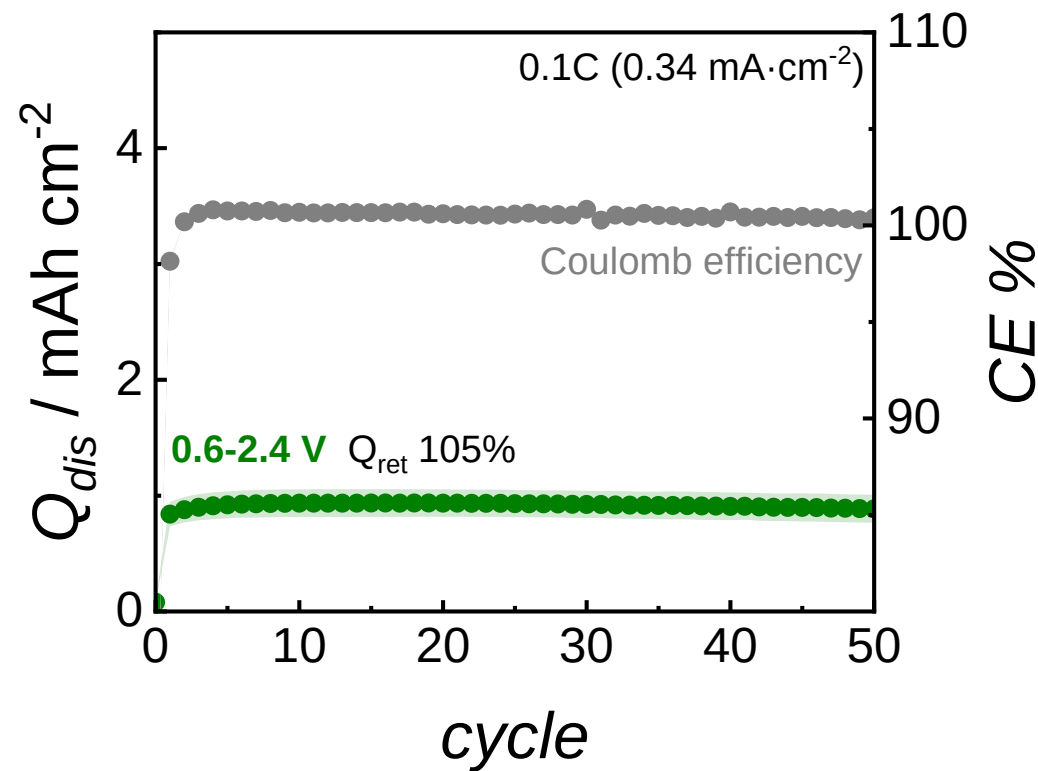
Differential capacity curves of ball milled composite shows a significant secondary process

FeS₂ / LPSCl_{1.5} / carbon black | LPSCl_{1.5} | In/InLi

FeS₂/LPSCl_{1.5}/CB | LPSCl_{1.5} | In/InLi
Loadings: FeS₂ 3.8 mg cm⁻² and LPSCl_{1.5} 6.4 mg cm⁻²
Q_{th} 3.4 mAh cm⁻² or 894 mAh g⁻¹

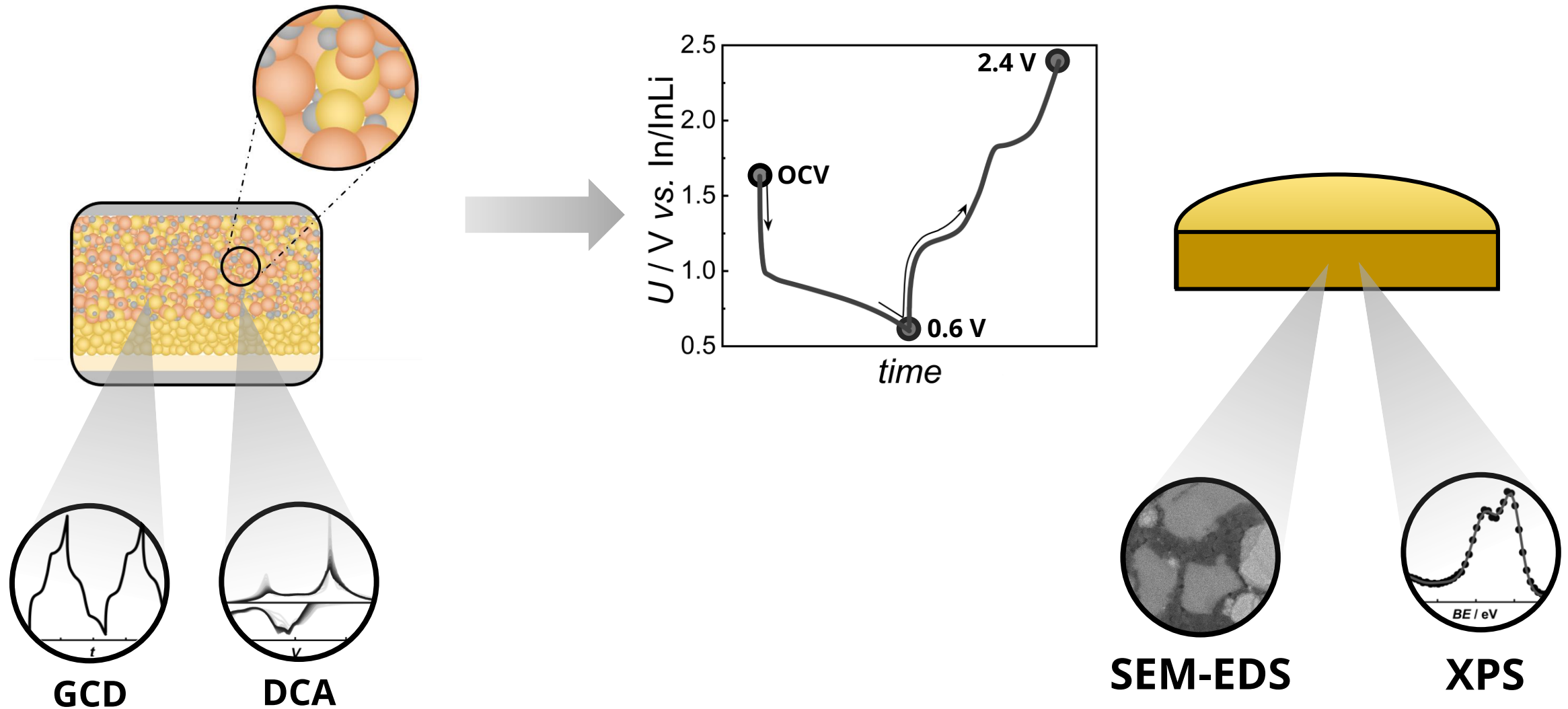
The argyrodite becomes *in situ* active material

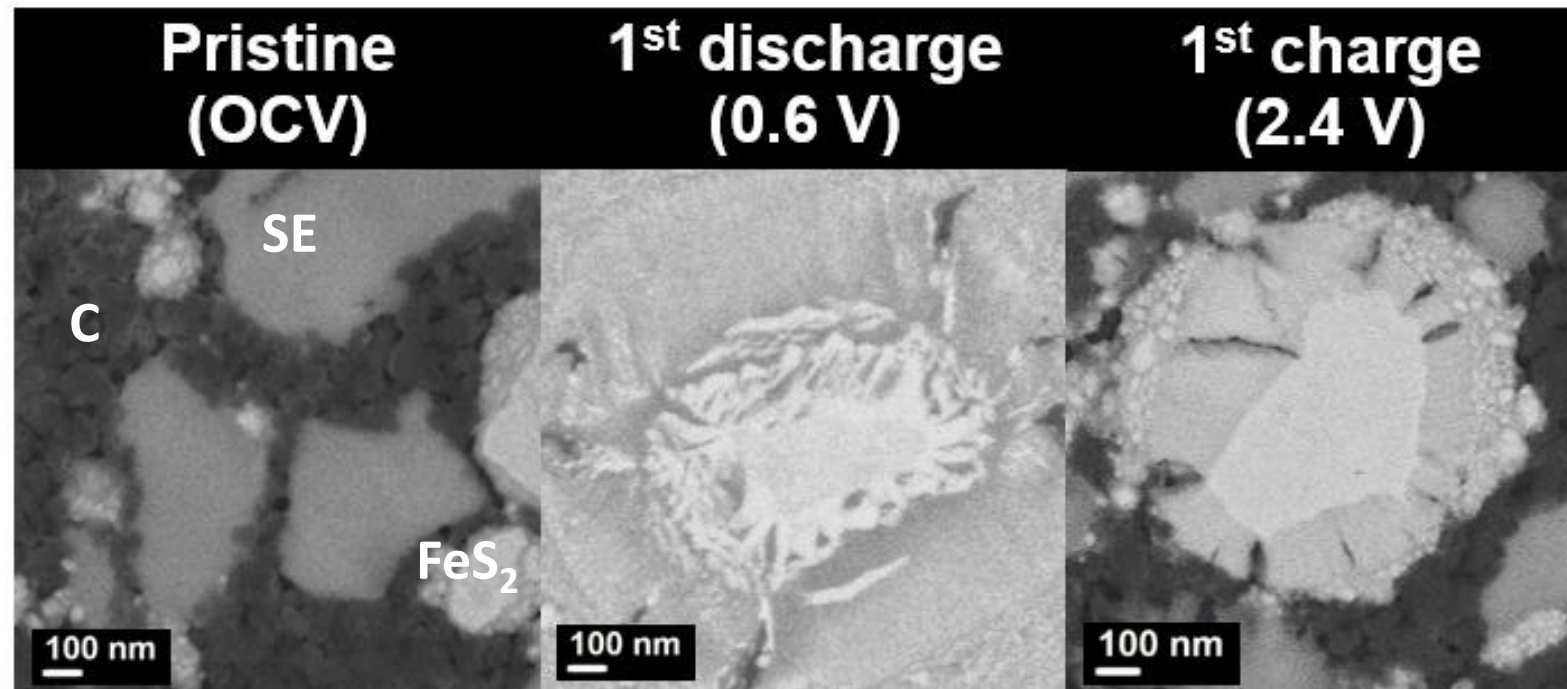
LPSCl_{1.5} / carbon black | LPSCl_{1.5} | In/InLi



Ex situ analyses after cycling

10





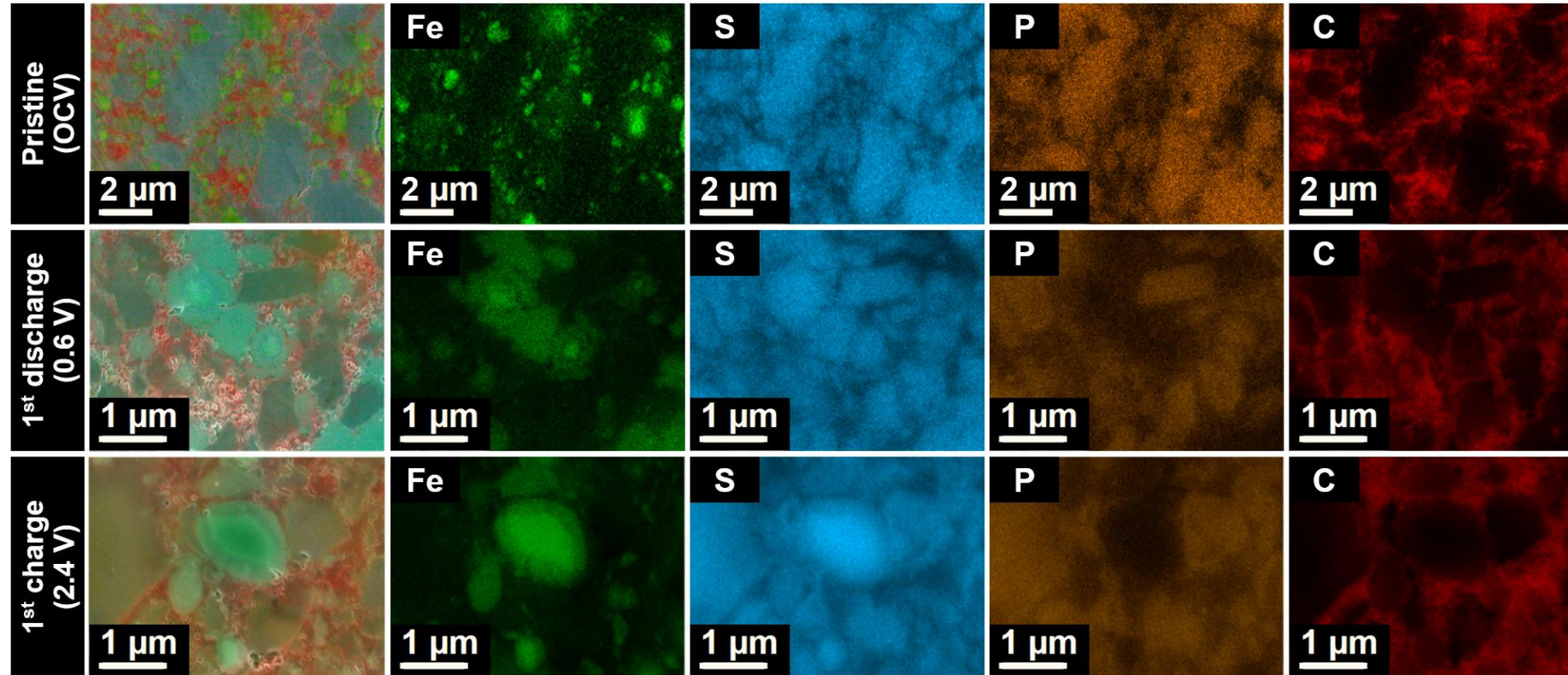
Pristine state

- ✓ Distinguish pristine components

Discharged and charged state

- ✓ Core-shell structures (for medium sized particles) with external cracks
 - ✓ No preferential direction of (de-)lithiation

The active material changes its morphology



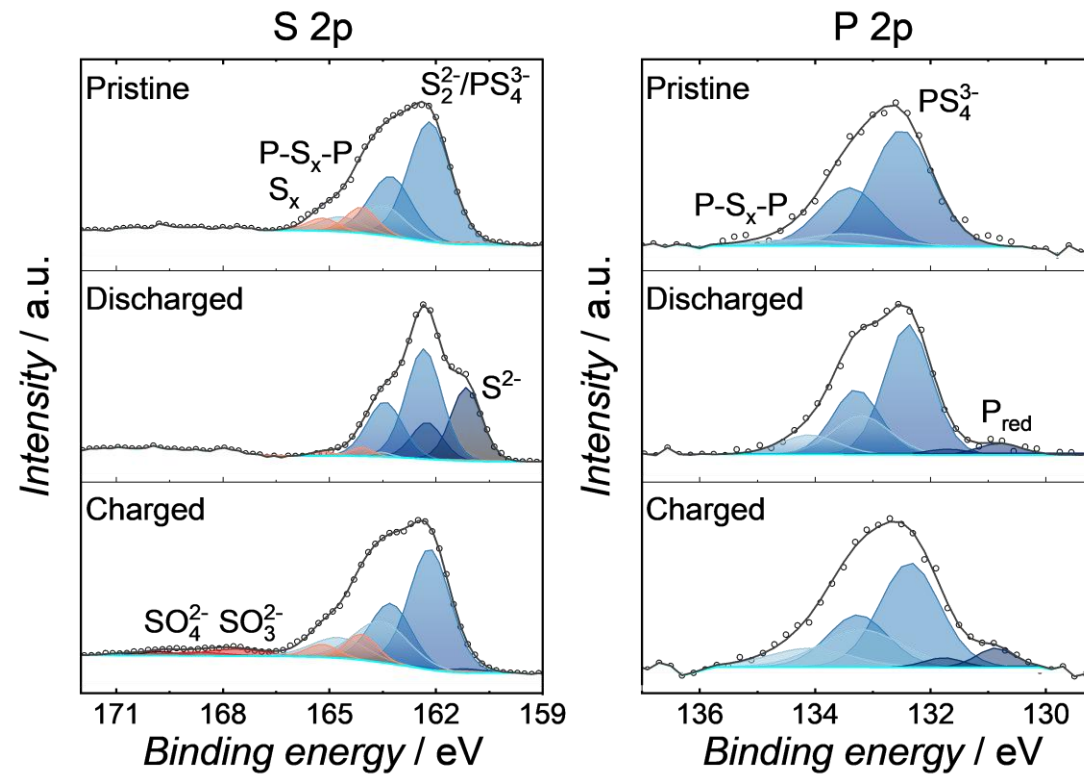
Pristine state: distinguish pristine components

Discharged state: homogenous particles (<100 nm): Fe and S

Core-shell particles: core rich in Fe and S and surrounded by a ring Fe-depleted. The external shell has Fe and S

Charged state: homogenous small particles: both Fe and S

Core-shell particles: core rich in Fe and S and shell has also Fe and S



Pristine state: $LPSCl_{1.5}$ and FeS_2 (PS_4^{3-} and S_2^{2-})

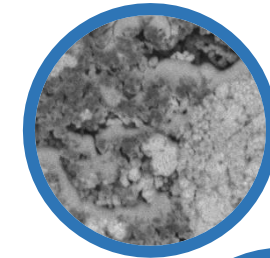
Discharged state: formation of Li_2S (S^{2-}) and reduced P species (P_{red})

Charged state: reduced species are oxidized, formation of polysulfides ($P-S_x-P$ and S_x)

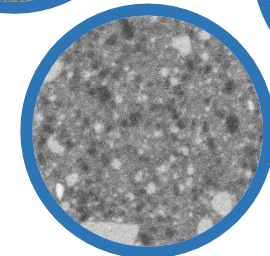
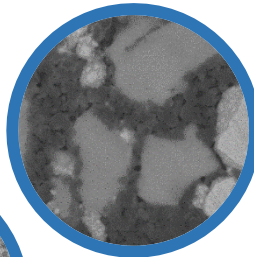
Cathode processing

- ✓ Morphology
Particle size of various components and porosity can be tuned
- ✓ Nanostructured composite via ball mill
Improved capacities – up to $4.3 \text{ mAh}\cdot\text{cm}^{-2}$
Solid electrolyte encapsulates other components

Hand grind

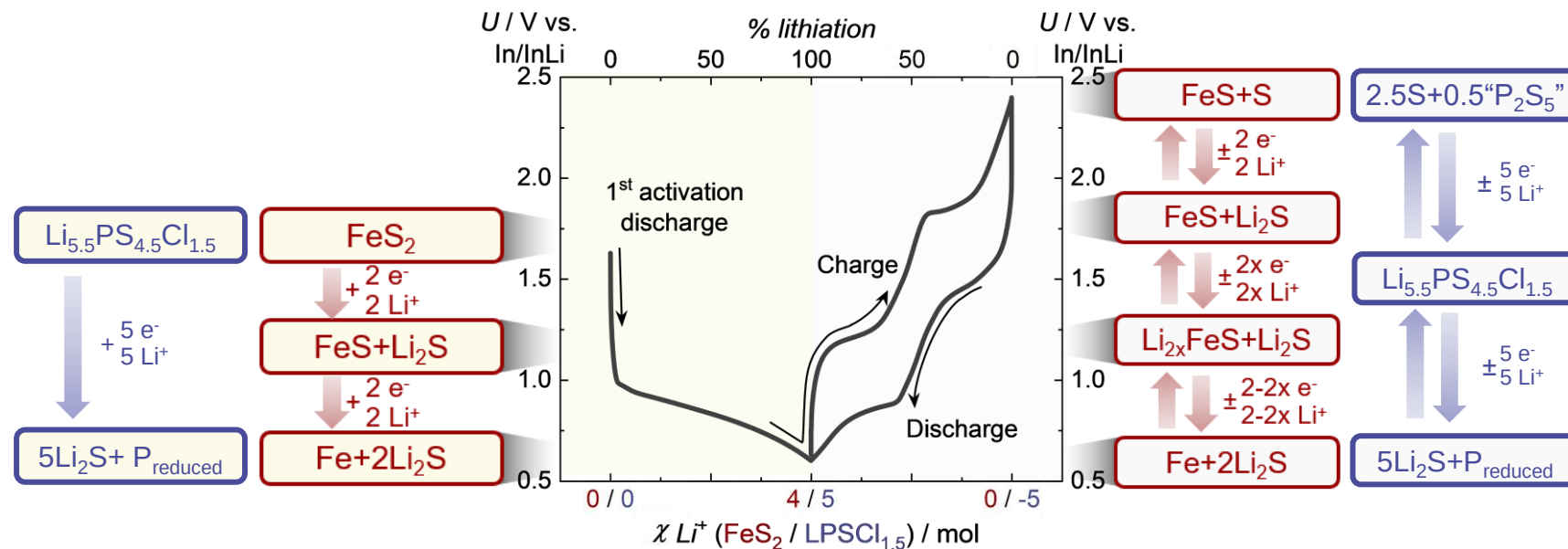


Mini mill



Ball mill

Solid electrolyte contributes to the capacity





Thank you for your attention

Questions?



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und Forschung

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