

Magdalena Fiedler

Influence of carbon porosity on
the sulfur utilization in all-solid-
state Lithium-Sulfur batteries

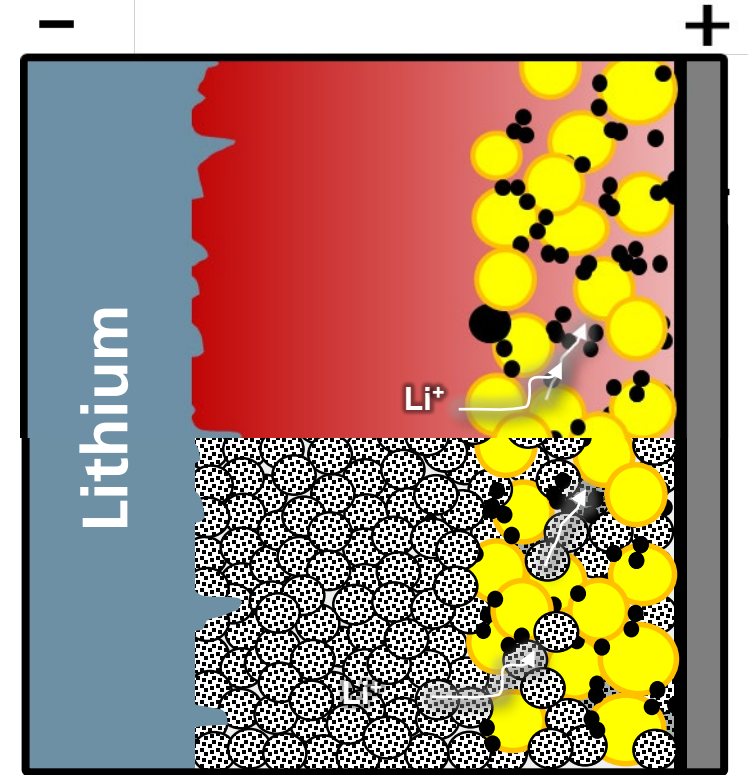
1. Motivation

Liquid LiS-battery:

- + Higher energy density compared to LIB
- + Sulfur = cheap raw material
- Polysulfide (PS)-shuttle

Solid state LiS-battery:

- + Ion selective → No PS-shuttle
- + High (volumetric) energy densities
- + Non flammable
- External pressure necessary



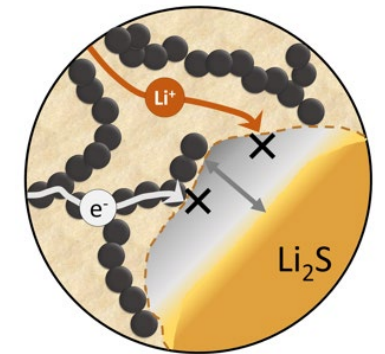
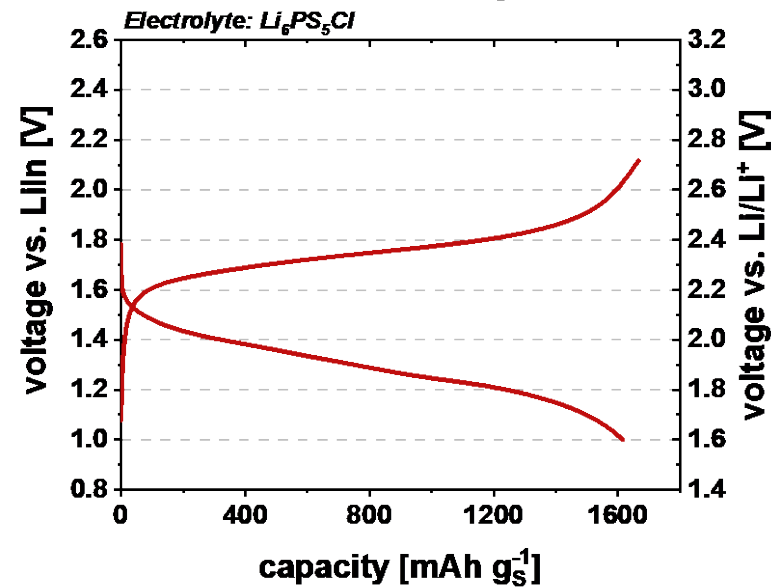
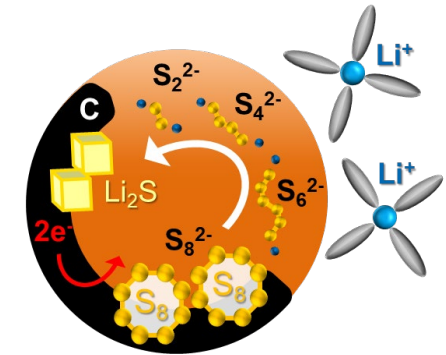
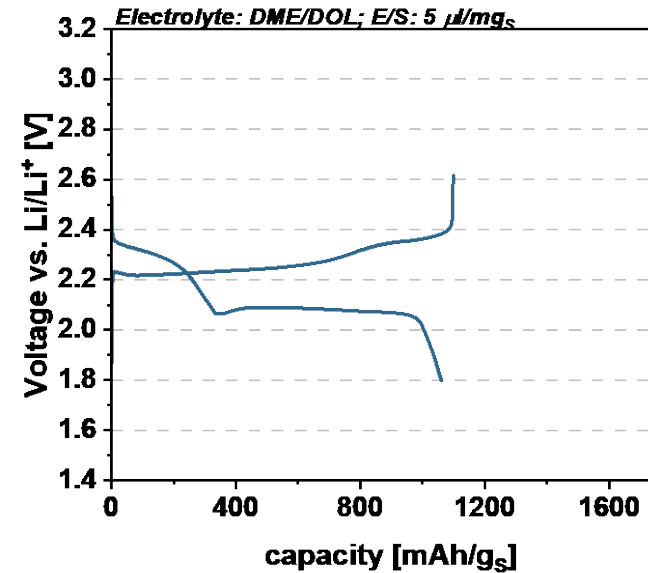
1. Motivation

Liquid:

- Two plateaus during (dis-)charging
- Opening of the sulfur-S₈-ring, formation of soluble polysulfides
- Reduction to short chain polysulfides, disproportionation
- Polysulfide shuttle → capacity loss

Solid state:

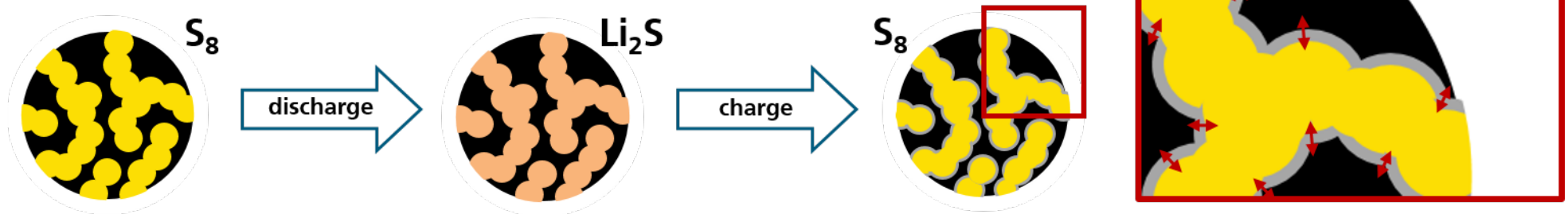
- one plateau during (dis-)charging
- Higher overpotential
- Mechanism not clear yet, assumption: stepwise reaction from S₈ to Li₂S
- **Theoretical capacity of sulfur (1672 mAh/g_S) reached**



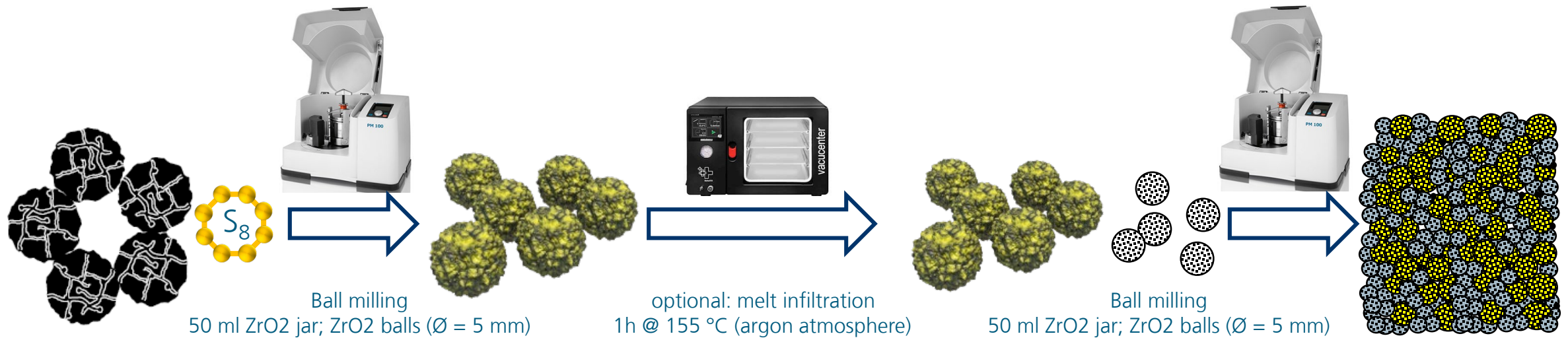
M. Wild, L. O'Neill, T. Zhang, R. Purkayastha, G. Minton, M. Marinescu, G. J. Offer, *Energy Environ. Sci.* **2015**, 8, 3477.
S. Ohno, W. G. Zeier, *Acc. Mater. Res.* **2021**, 2, 869.

2. Challenges

- Balance between ionic & electronic pathways
- Volume change during cycling at anode & cathode → stack pressure crucial in ASSB
- Volume change leads to contact loss → sulfur not addressed
- Pore structures could compensate the volume change of sulfur → investigation of different carbons + carbon structures



3. Cathode preparation

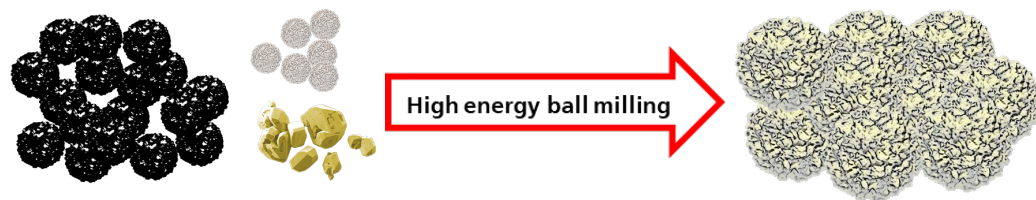


3. Cathode preparation

Influence of ball milling

Routine A – high energy ball milling

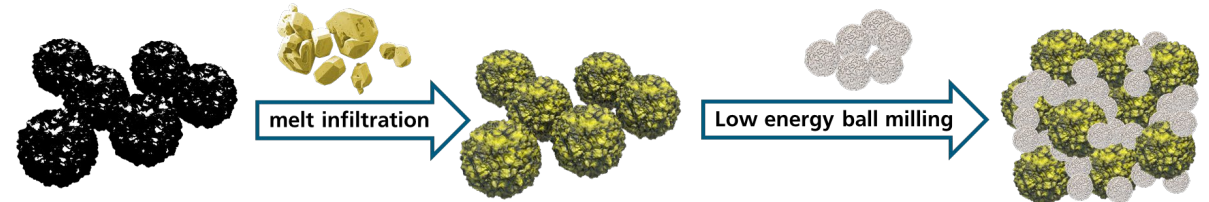
- Carbon structure is destroyed due to ball milling
- Formation of homogenous cathode
- No sulfur infiltration



- No defined particles after ball milling
- Ionic and electronic pathways provided by triple phase boundaries

Routine B – low energy ball milling

- Pore structure maintained → volume change could be compensated
- Sulfur infiltration step
- Particle shape maintained → close packing

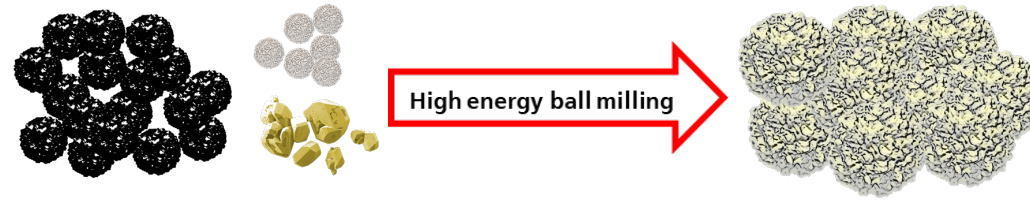


- Lower mechanical stress at cathode side
- Compensation of volume change within the composite

T. ANDO, Y. Sato, T. MATSUYAMA, A. Sakuda, M. Tatsumisago, A. Hayashi, *J. Ceram. Soc. Japan* **2020**, 128, 233.

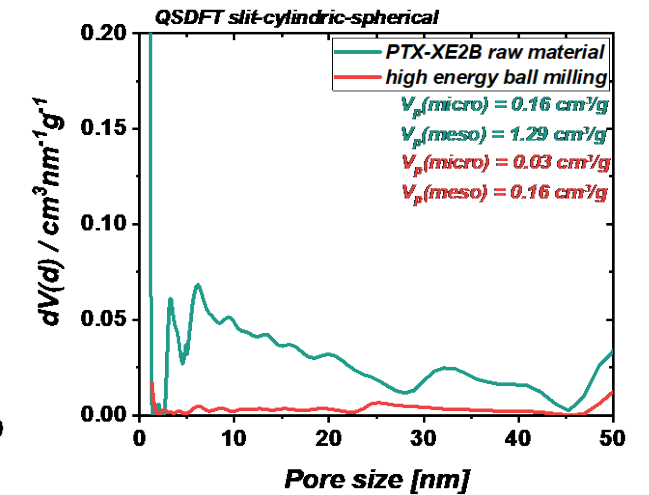
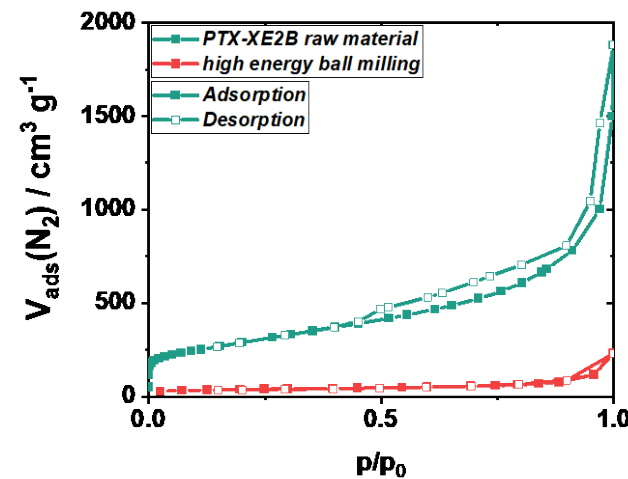
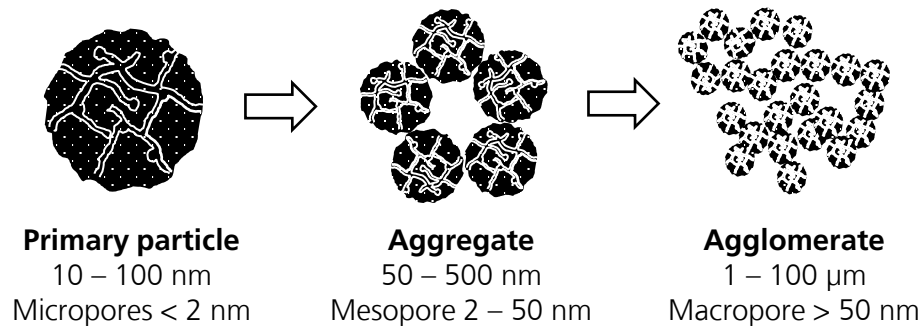
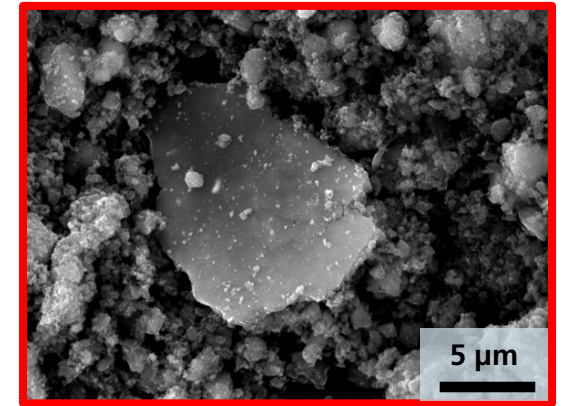
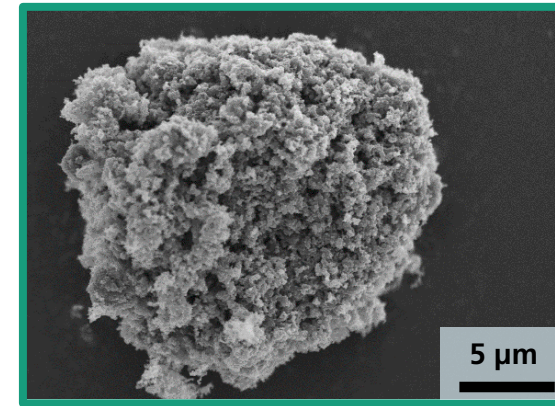
4. Results

4.1. high energy ball milling



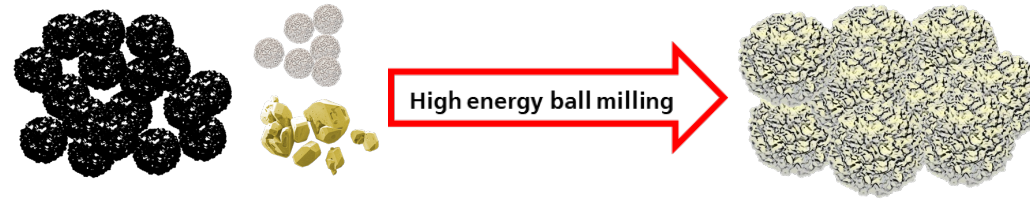
Printex XE2B

- Hierarchical carbon black
- Influence of ball milling: Porosity decreased
- very low pore volume and surface area after ball milling



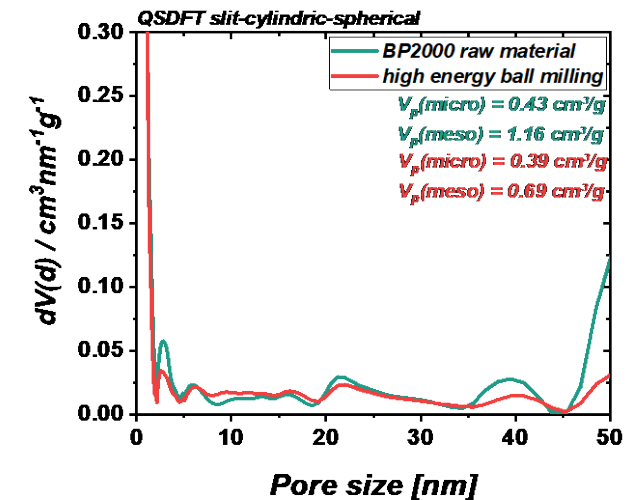
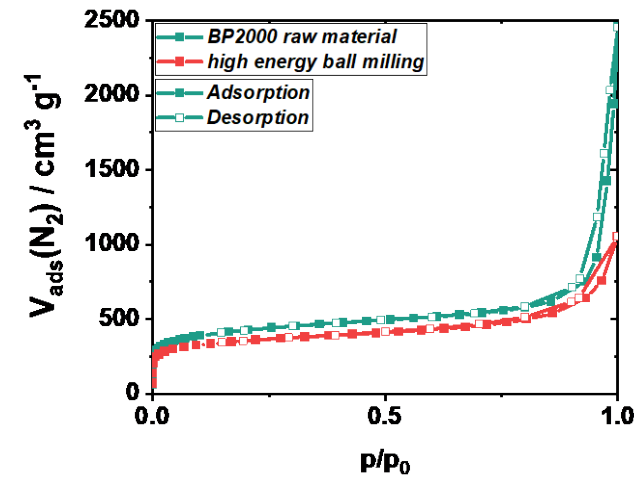
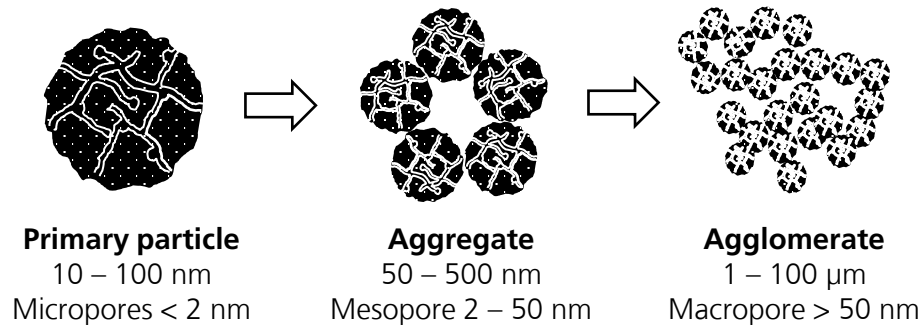
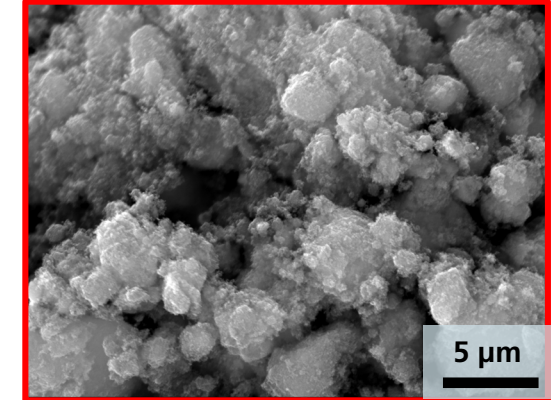
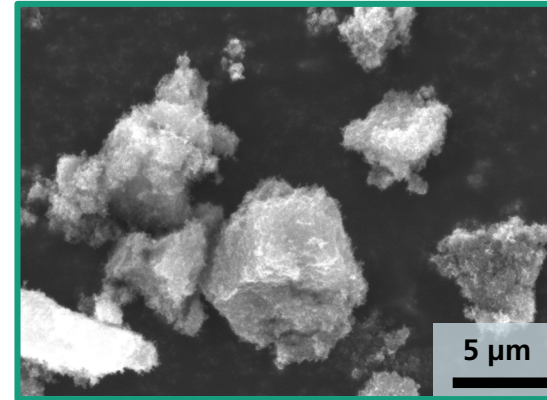
4. Results

4.1. high energy ball milling



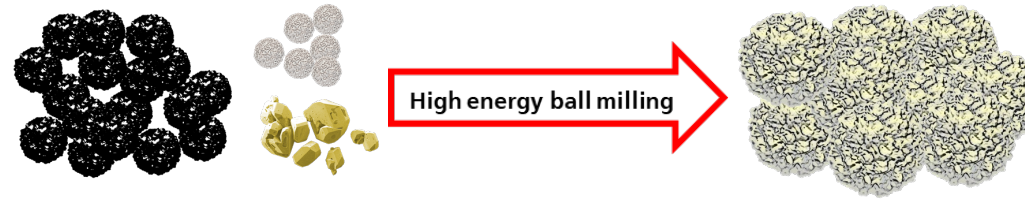
BlackPearls 2000

- Hierarchical carbon black
- Higher surface area than Printex
- Porosity less destroyed during ball milling



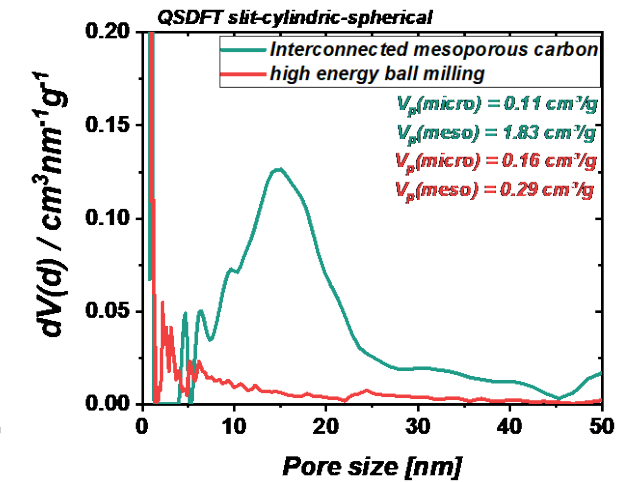
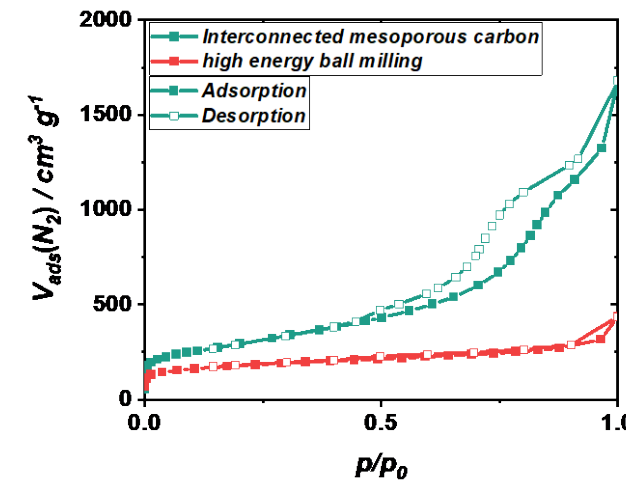
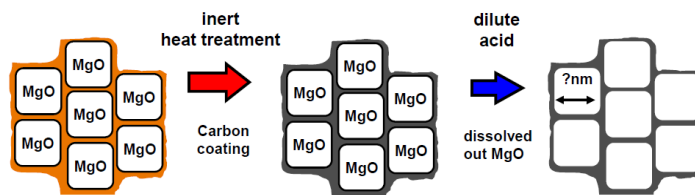
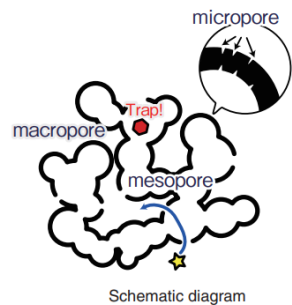
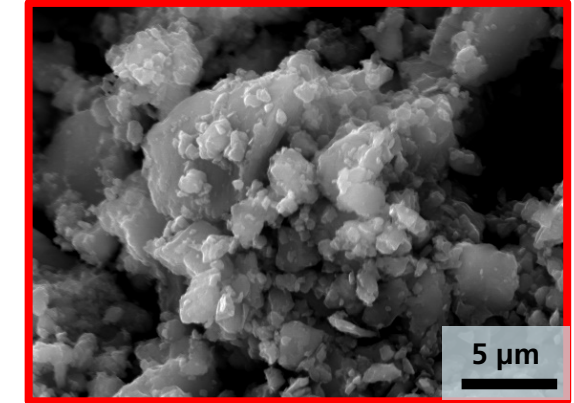
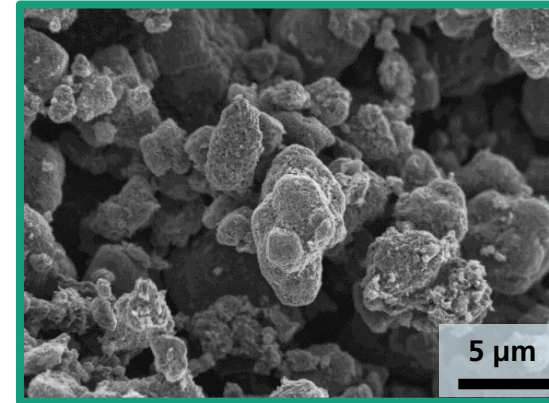
4. Results

4.1. high energy ball milling



Interconnected mesoporous carbon

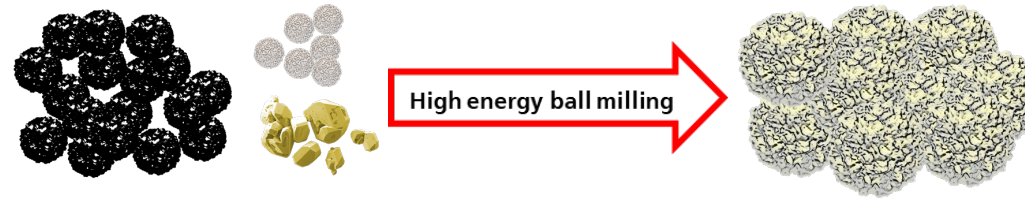
- Template based mesoporous carbon
- Influence of ball milling: meso pore volume decreased
- Powder conductivity is lowered



<https://www.toyotanso.com/Products/cnovel/>

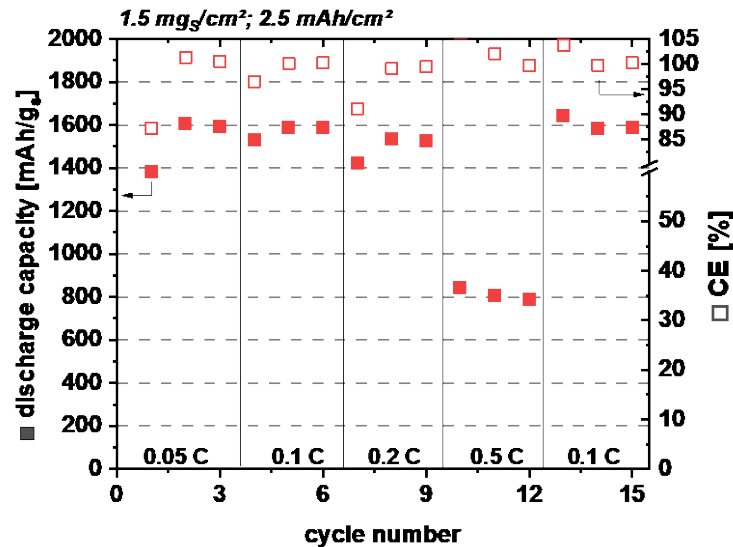
4. Results

4.1. high energy ball milling



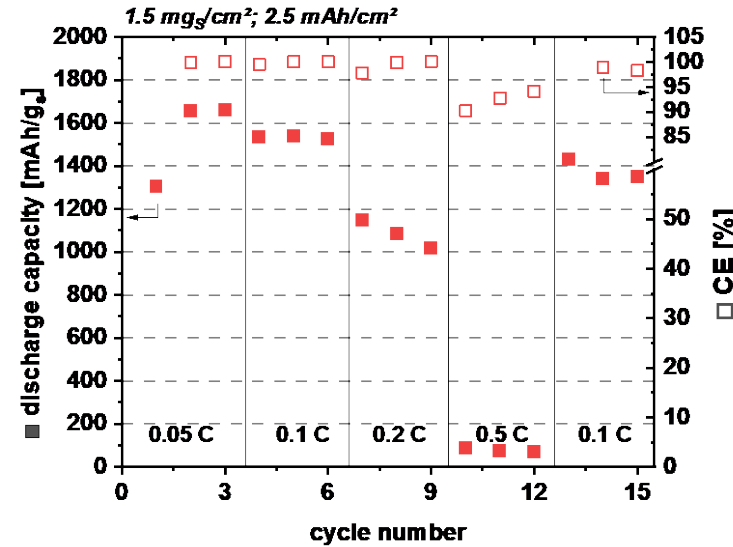
T / °C	25
P / MPa	25 (stack pressure)
Φ_{CAM} / wt. %	30
q_{A} / mAh cm ⁻²	2.5
$j_{\text{chg}}/j_{\text{dschg}}$ / mA cm ⁻²	0.1 C ch / rate test
E / V vs. InLi	1.0 – 2.4

PTX XE2B



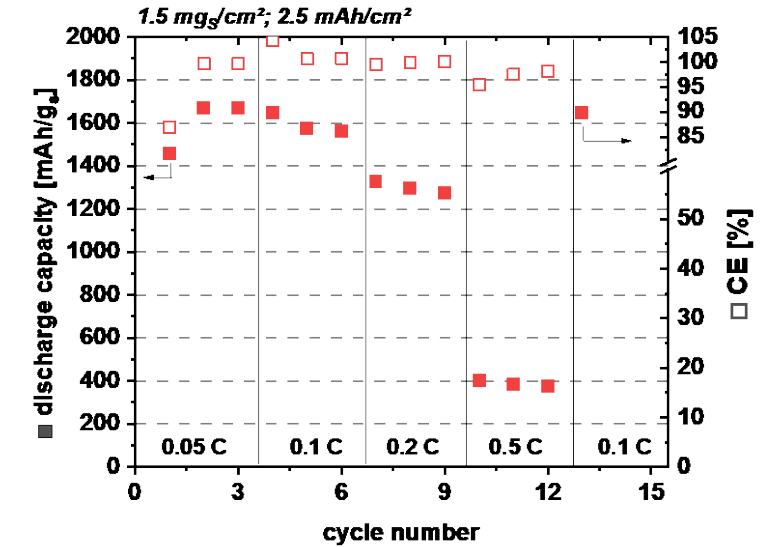
- High sulfur utilization above 1600 mAh/g_s
- More than 800 mAh/g_s at 0.5C

BP 2000



- High sulfur utilization above 1600 mAh/g_s
- Capacity loss at higher C-rates

Interconnected mesoporous carbon

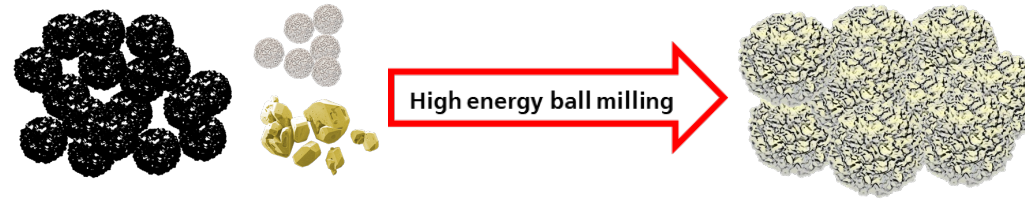


- Different porous structure (mesoporous)
- High sulfur utilization

→ increasing capacities (at higher C-rates) with decreasing pore volume

4. Results

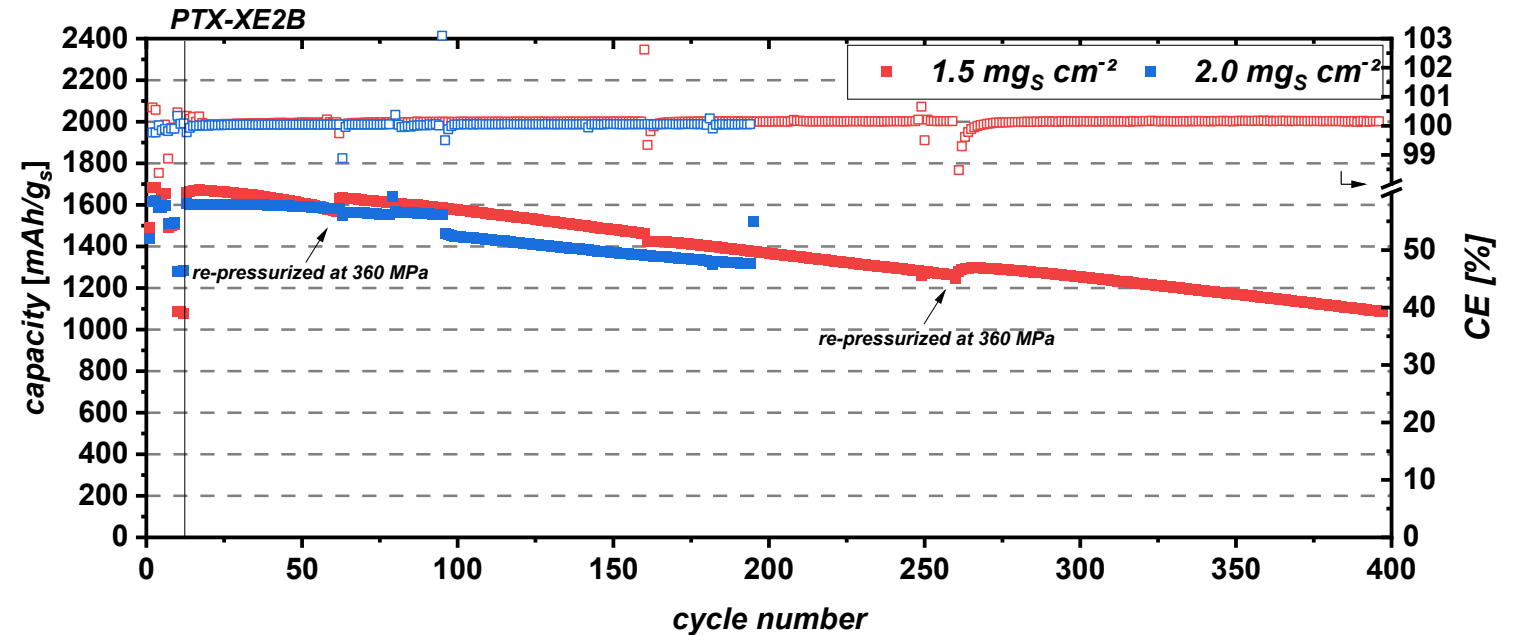
4.1. high energy ball milling



T / °C	25
P / MPa	25 (stack pressure)
Φ_{CAM} / wt. %	30
q_{A} / mAh cm ⁻²	2.5 - 3.2
$j_{\text{chg}}/j_{\text{dschg}}$ / mA cm ⁻²	0.1 C ch / rate test
E / V vs. InLi	1.0 – 2.1

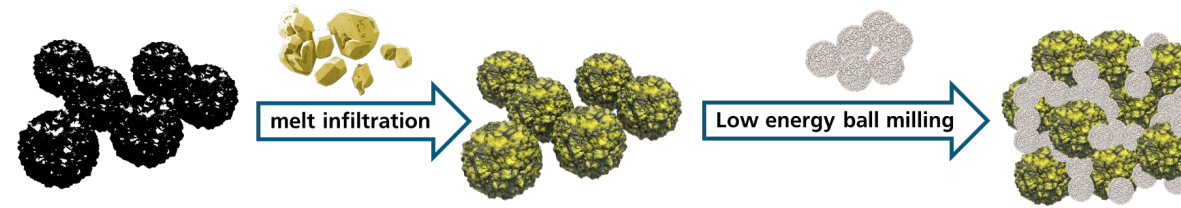
Long term performance

- Adaption of cut-off voltage to 2.1 V
- Improved long term performance
- About 400 deep cycles
- High capacity retention



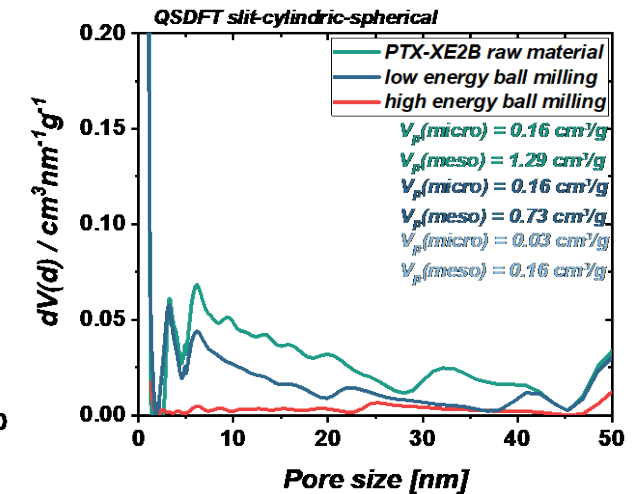
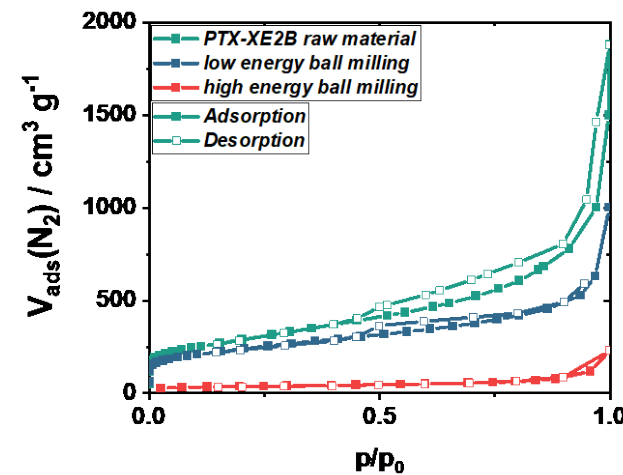
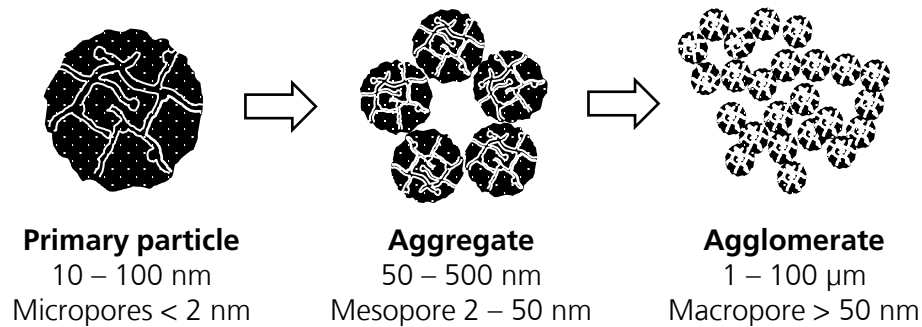
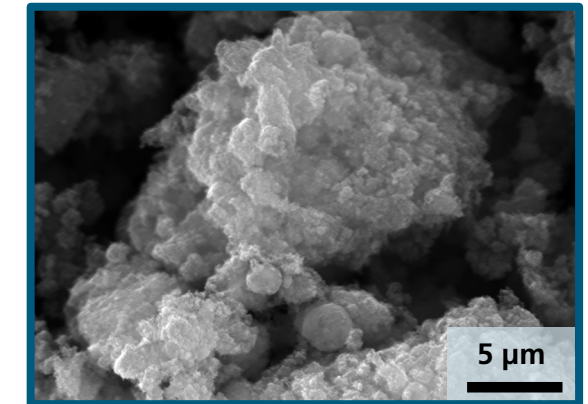
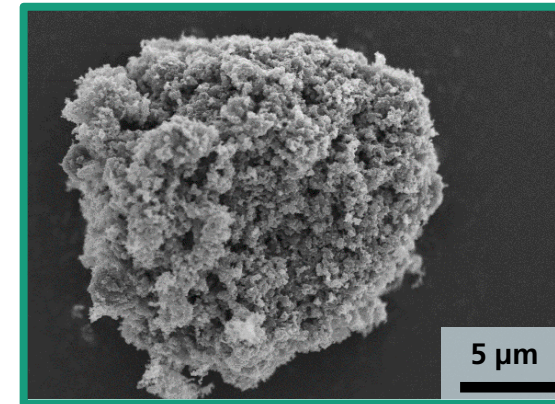
4. Results

4.2. low energy ball milling



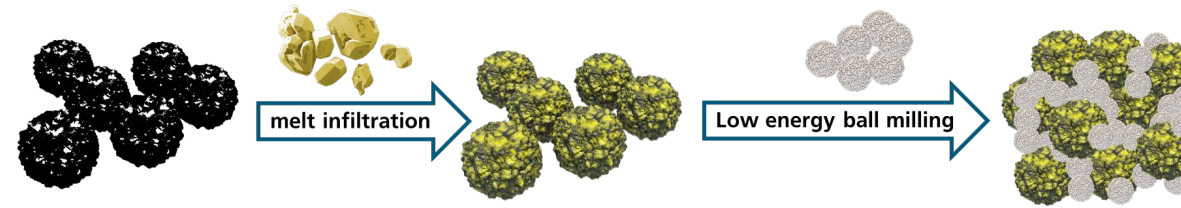
Printex XE2B

- Commercial carbon black
- Porous structure less destroyed
- Higher meso pore volume



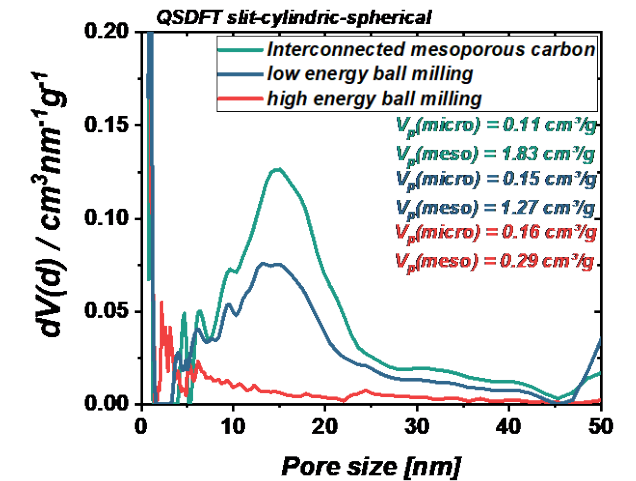
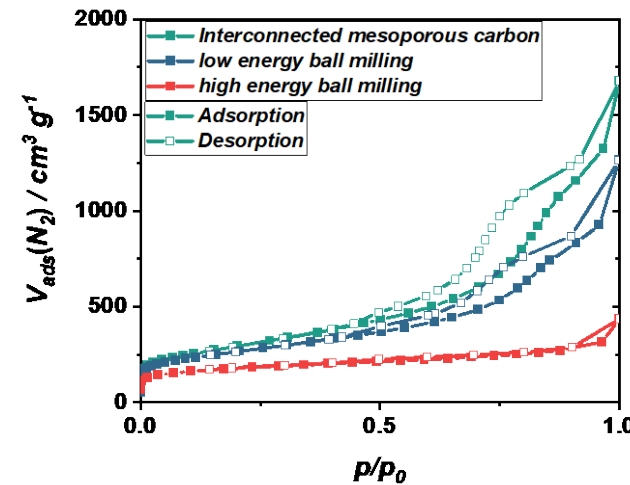
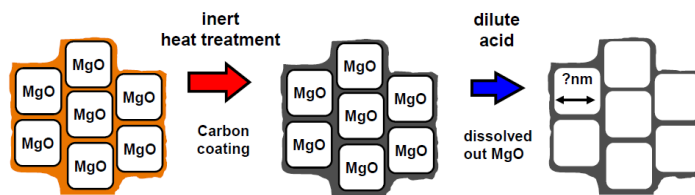
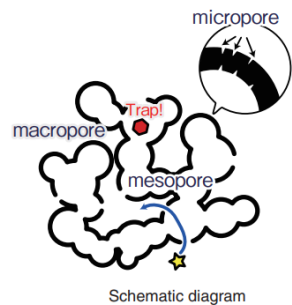
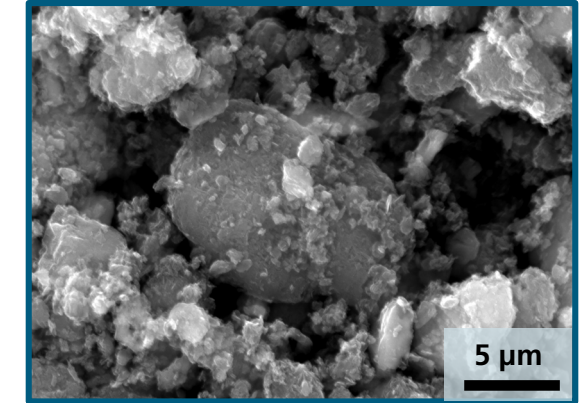
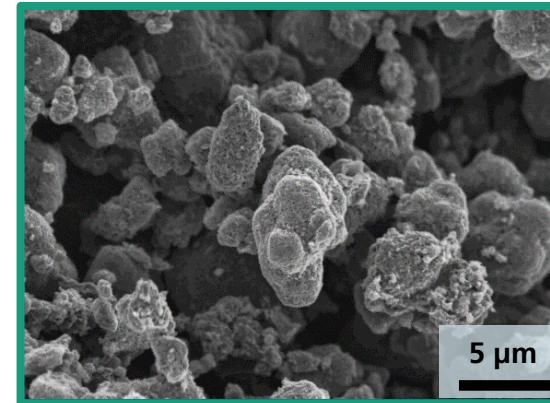
4. Results

4.2. low energy ball milling



Interconnected mesoporous carbon

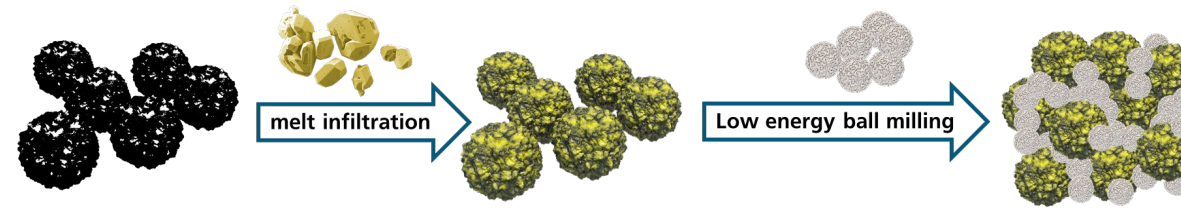
- Influence of ball milling: Porosity decreased
- Carbon structure less destroyed
- High meso pore volume maintained



<https://www.toyotanso.com/Products/cnovel/>

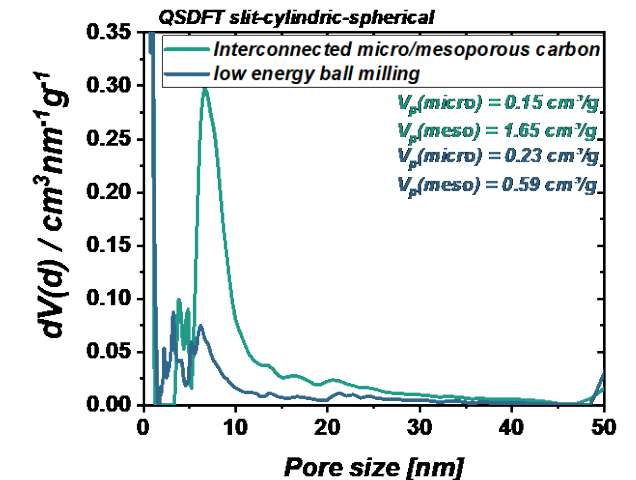
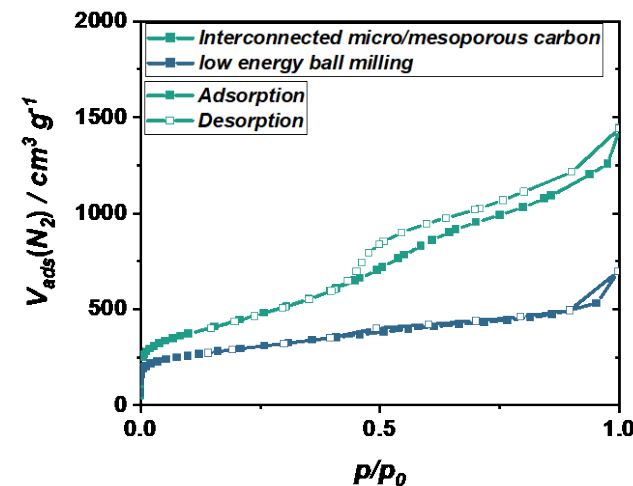
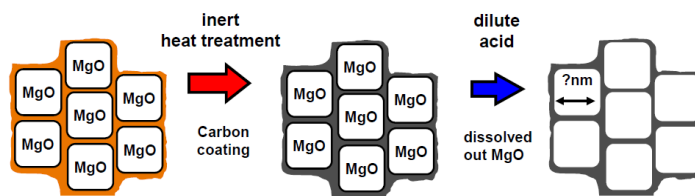
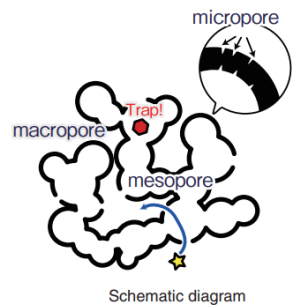
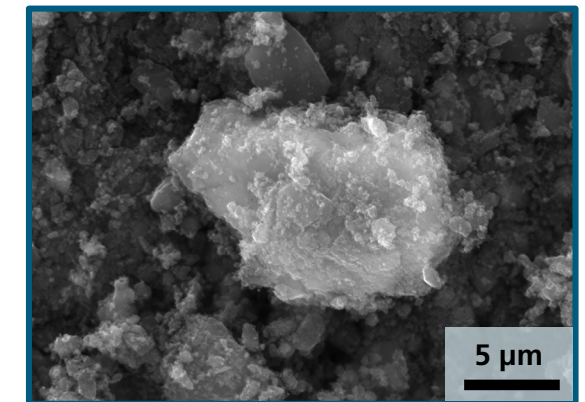
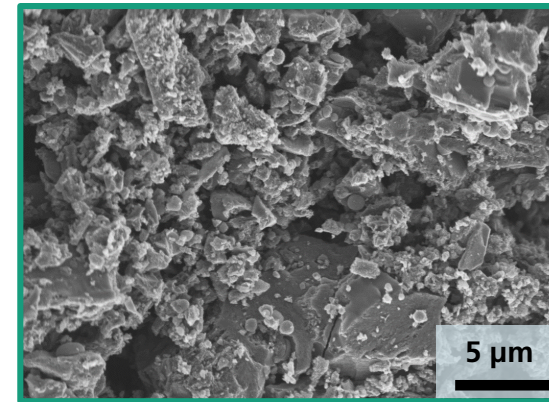
4. Results

4.2. low energy ball milling



Interconnected micro/mesoporous carbon

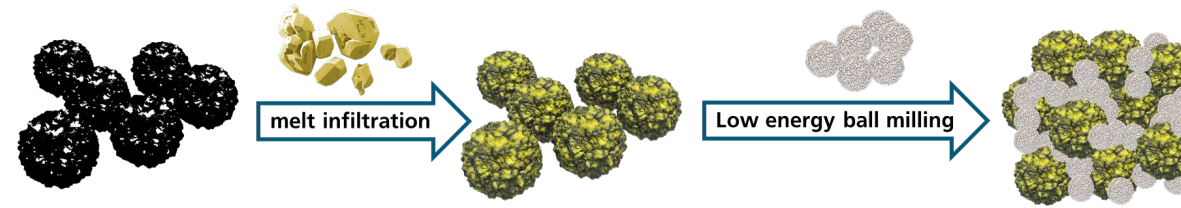
- Smaller pores compared to mesoporous carbon
- After ball milling: pore size below 10 nm



<https://www.toyotanso.com/Products/cnovel/>

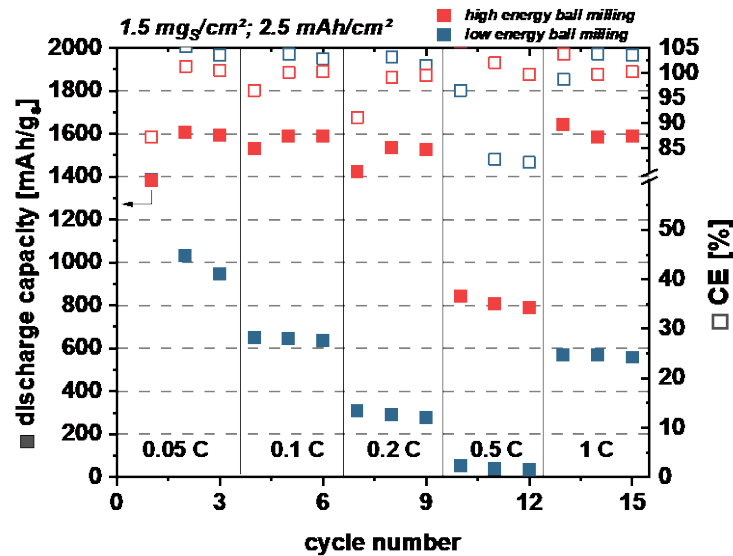
4. Results

4.2. low energy ball milling

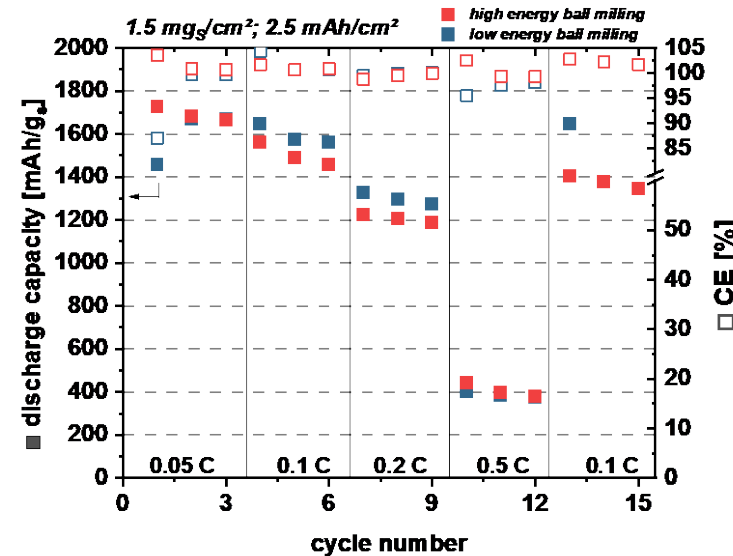


T / °C	25
P / MPa	25 (stack pressure)
Φ_{CAM} / wt. %	30
q_A / mAh cm ⁻²	2.5 - 3.2
$j_{\text{chg}}/j_{\text{dschg}}$ / mA cm ⁻²	0.1 C ch / rate test
E / V vs. InLi	1.0 - 2.4

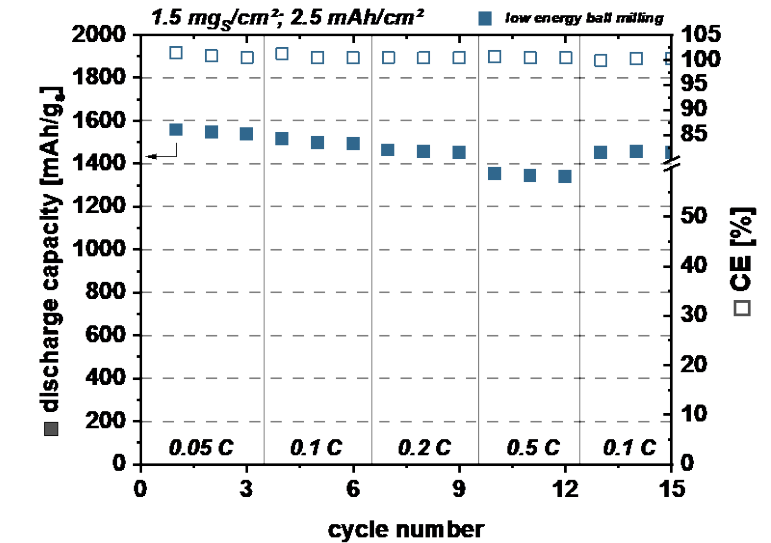
PTX XE2B



Interconnected mesoporous carbon



Interconnected micro/mesoporous carbon



- Lowered sulfur utilization
- Poor performance compared to high energy ball milling

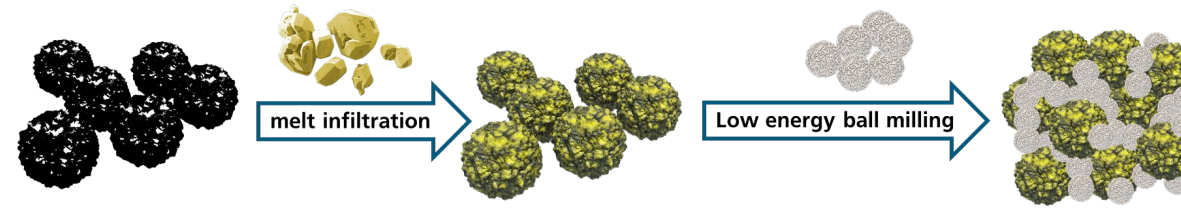
- similar sulfur utilization compared to high energy ball milling

- High sulfur utilization
- More than 1300 mAh/g_s at 0.5 C

→ increasing capacities with increasing micro pore volume and decreasing particle size

4. Results

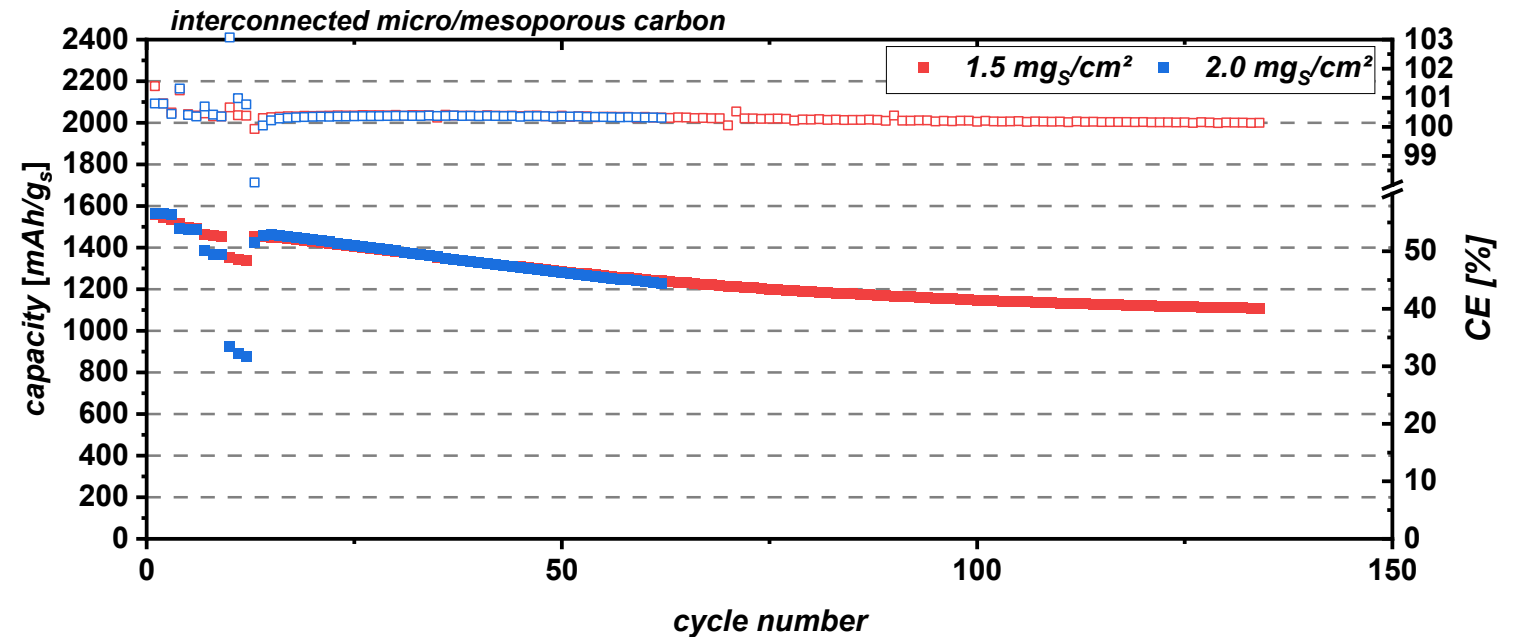
4.2. low energy ball milling



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P /MPa	25 (stack pressure)
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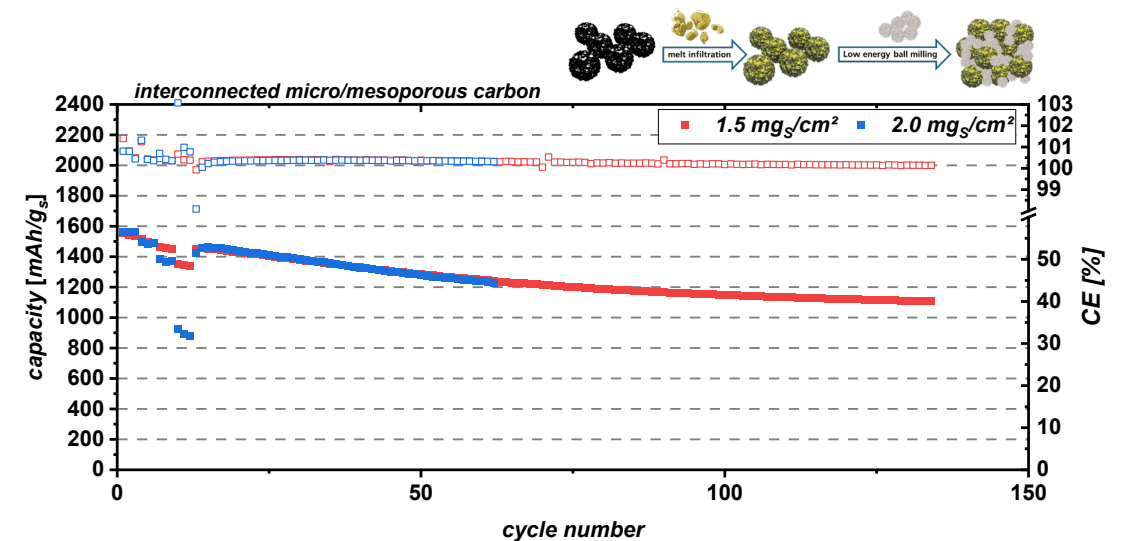
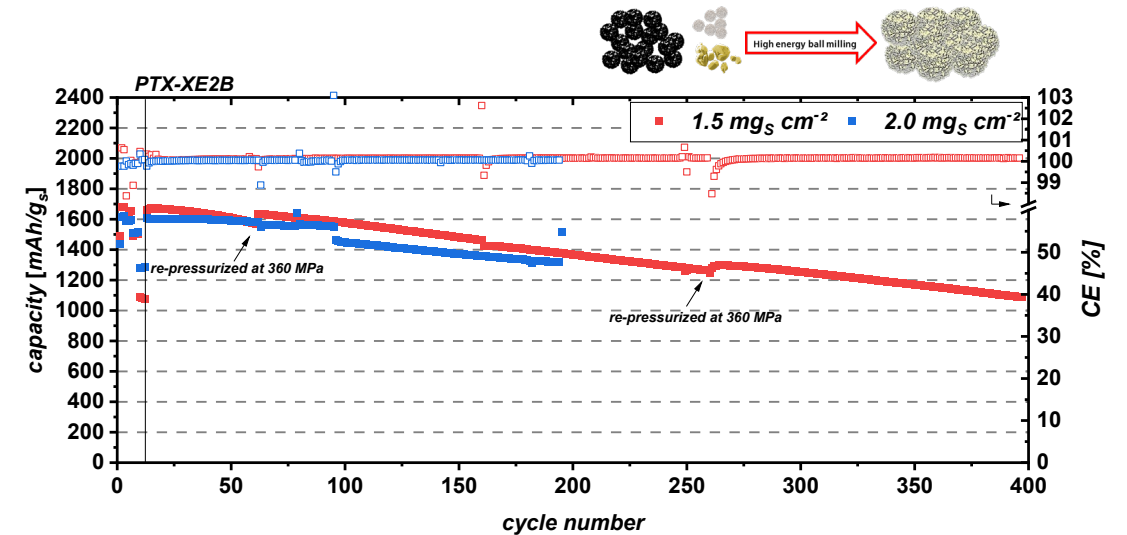
Long term performance

- Adaption of cut-off voltage to 2.1 V
- Improved long term performance
- More than 100 deep cycles
- High capacity retention



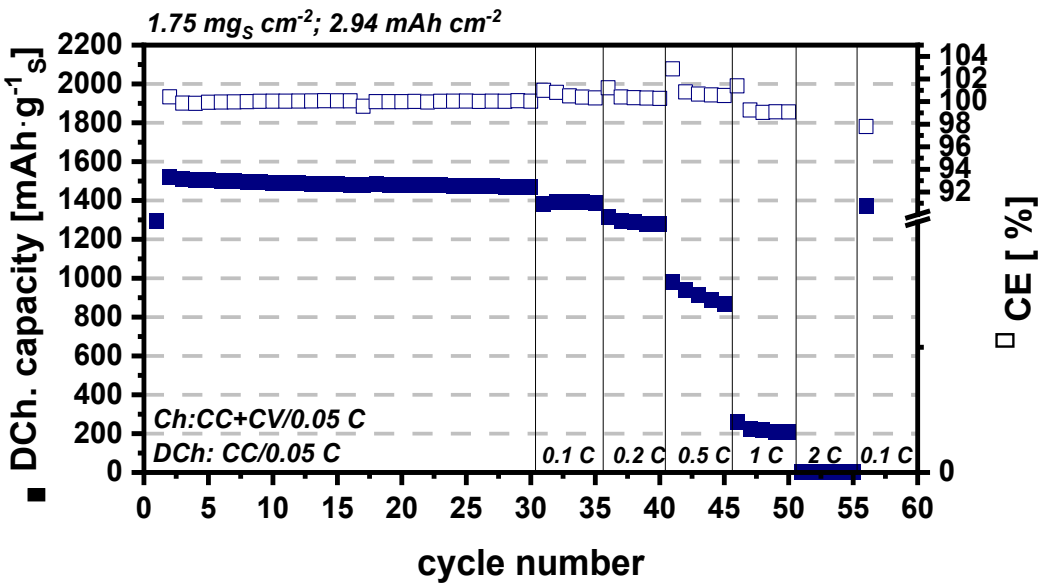
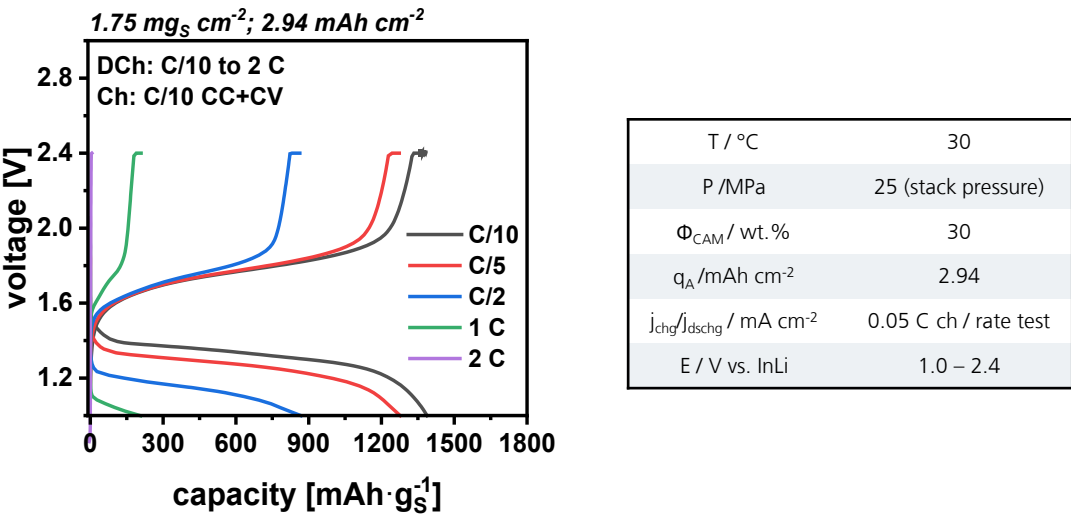
5. Summary

- High sulfur utilization > 1600 mAh/g_s in LiS-SSBs
- High energy ball milling: hierarchical carbon shows best performance
- Low energy ball milling: sulfur utilization increases with decreasing pore size
- cathode preparation needs to be adapted related to the used carbon



6. Outlook

- Further investigation of cathode volume change
- Investigation of microporous carbons
- Investigation of encapsulated sulfur
- Influence of the particle sizes
- Pouch cell assembly



Advanced Battery Technology Center (ABTC)

Contact

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