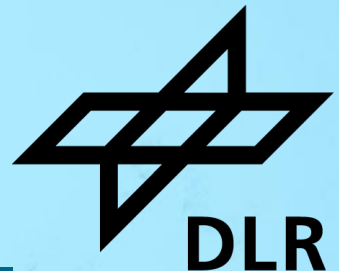


MORPHOLOGIC SIMULATIONS OF LITHIUM-SULFUR CATHODES USING THE LATTICE BOLTZMANN METHOD

Julius Weinmiller, M.P. Lautenschläger, B. Kellers, T. Danner, A. Latz

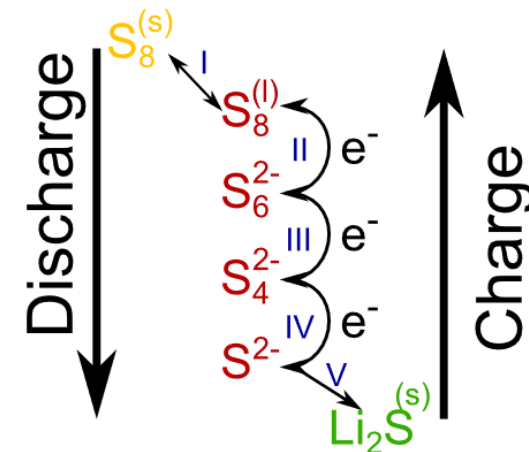
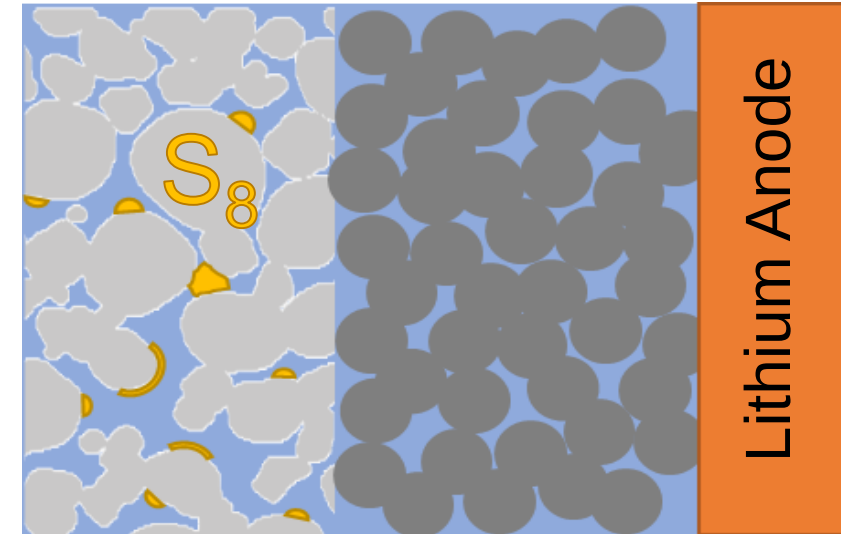
German Aerospace Center (DLR) – Institute of Engineering Thermodynamics
Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU)



Research Motivation

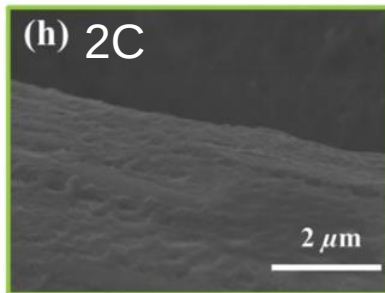
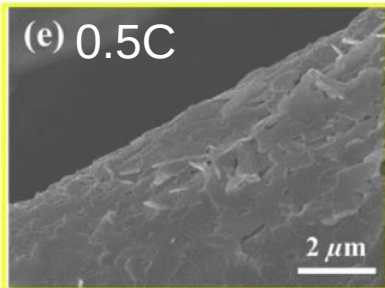
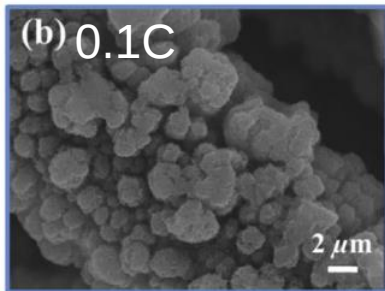
- Lithium-Sulfur batteries
 - High gravimetric specific capacity
 - Varied applicability: e-Flight
- Morphological characteristics
 - Pore clogging
 - Surface passivation
- Morphological impact
 - Battery longevity
 - Performance impact

Lithium–Sulfur cell schematic



Morphological Characteristics: Experiments

Li₂S precipitates



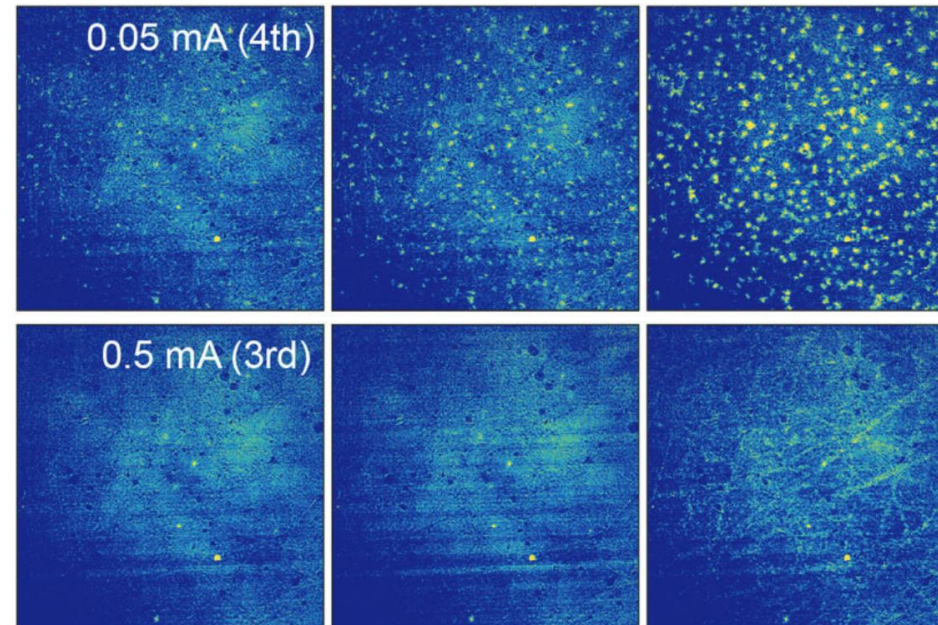
Fractal like

Film growth

Higher
current

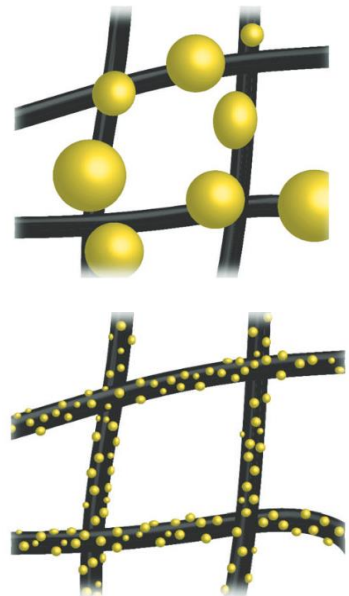
Y.Ren, T.Zhao, et al.
J. Power Sources (2016) **336** 115

S₈ precipitates



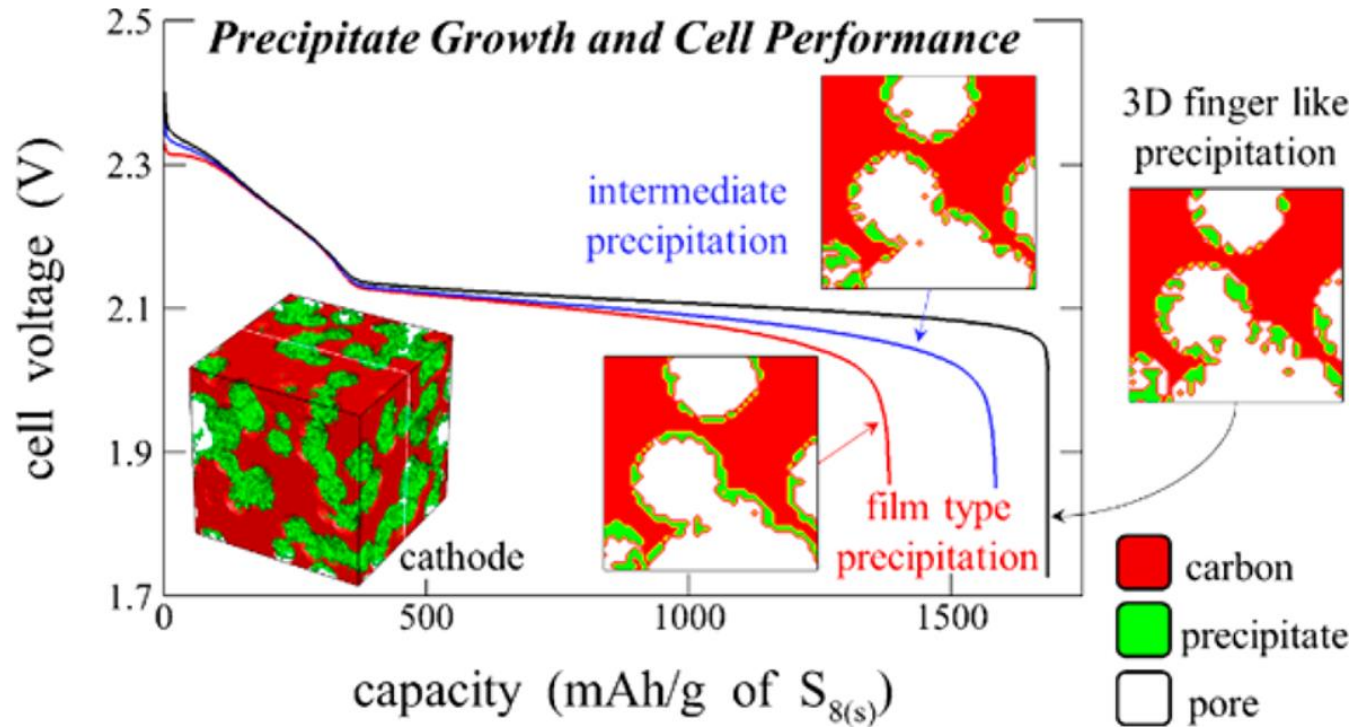
Charging

Sulfur
Carbon



S.Yu, X.Huang, et al.
Energy Environ. Sci. (2018) **11** 202

Modelling Morphological Impact



A.Mistry and P.Mukherjee
J. Phys. Chem. C (2017) **121** 26256

Research questions:

- Precipitates evolution
- Film growth conditions
- Pore clogging
- Electrochemical impact

Microscopic effects with macroscopic impact → difficult to analyze

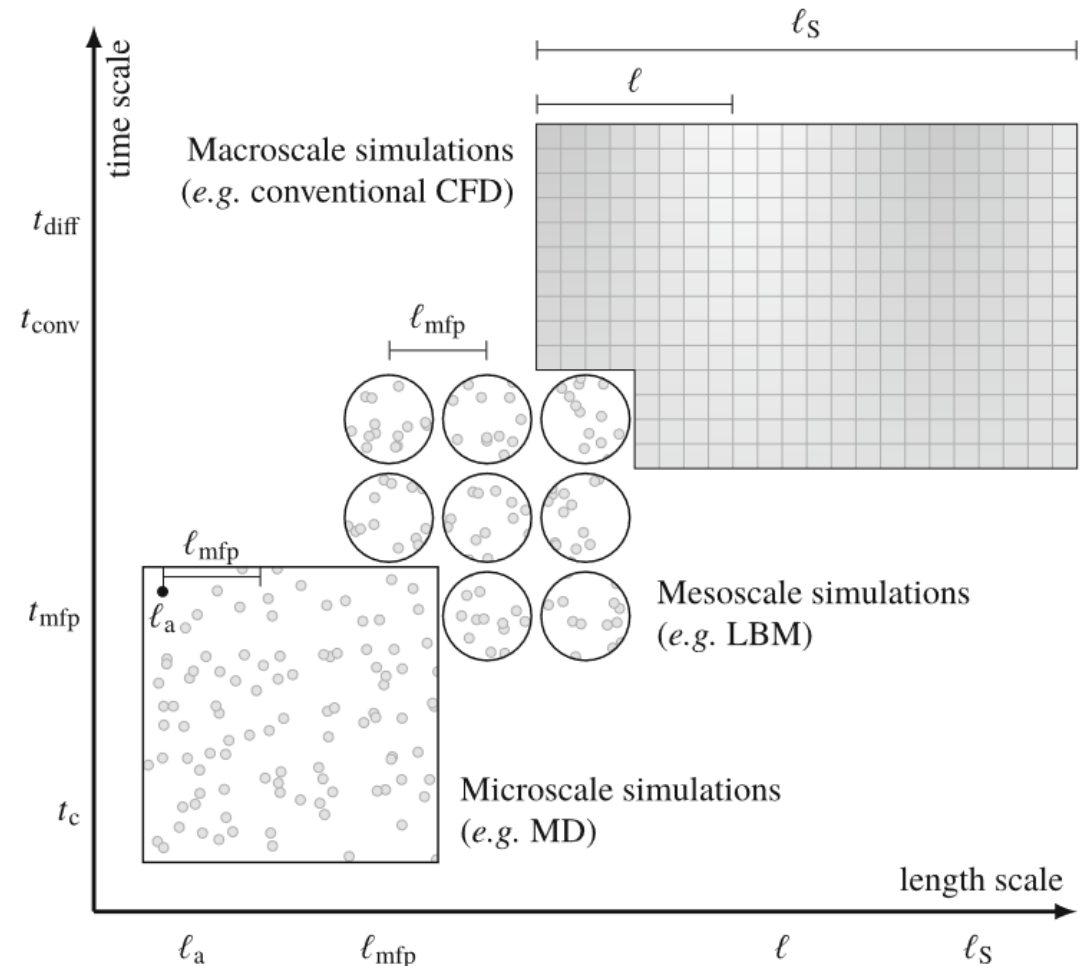
Lattice Boltzmann Method

Kinetic theory of fluids

- Solves Boltzmann equation
- Molecular non-equilibrium dynamics
- Emerging macroscopic phenomena

Advantages

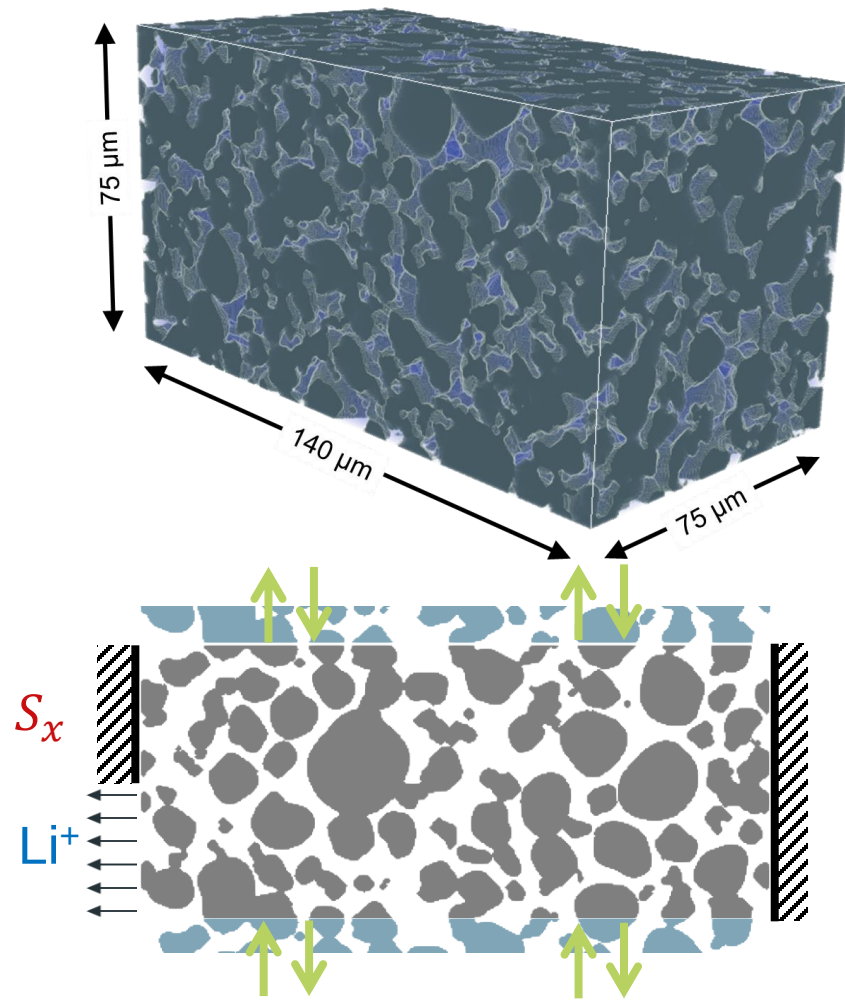
- Highly parallelizable
- Framework: PaLaBoS
- Strong applicability to porous media



T. Krüger, et al. *The Lattice Boltzmann Method: Principles and Practices*
Springer Int. Publishing (2017)

Simulation Setup

Pore scale investigation

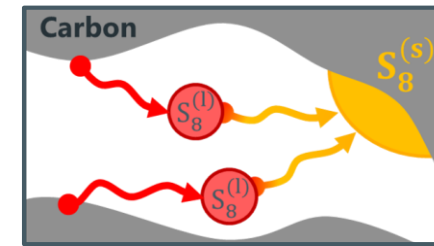


Detailed structures

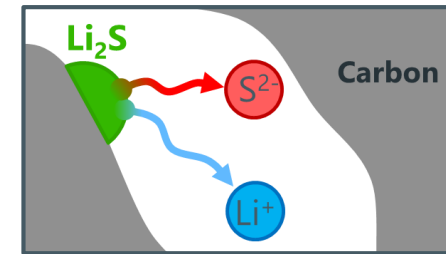
- Generated
- Imaging

Voxels: 350 x 170 x 170

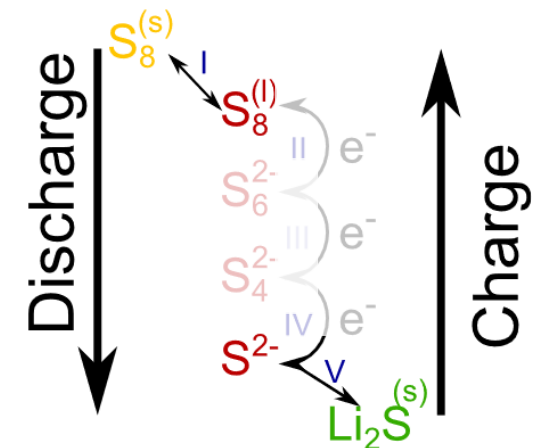
Precipitation



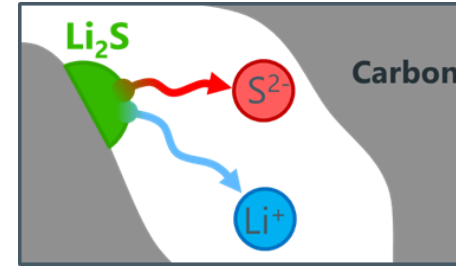
Dissolution



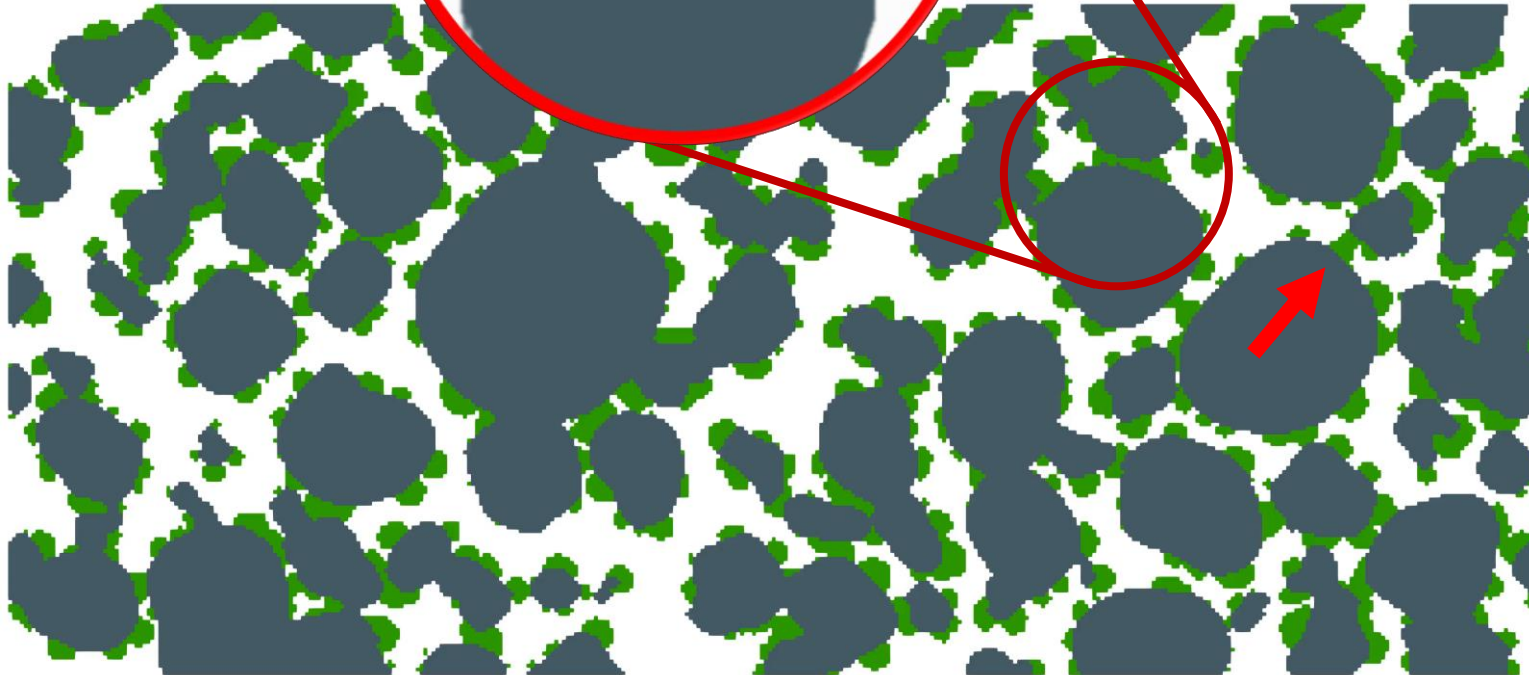
Reaction pathway



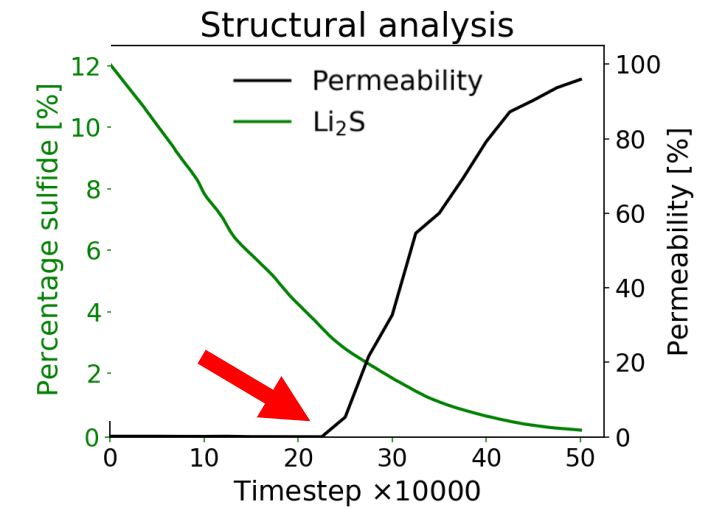
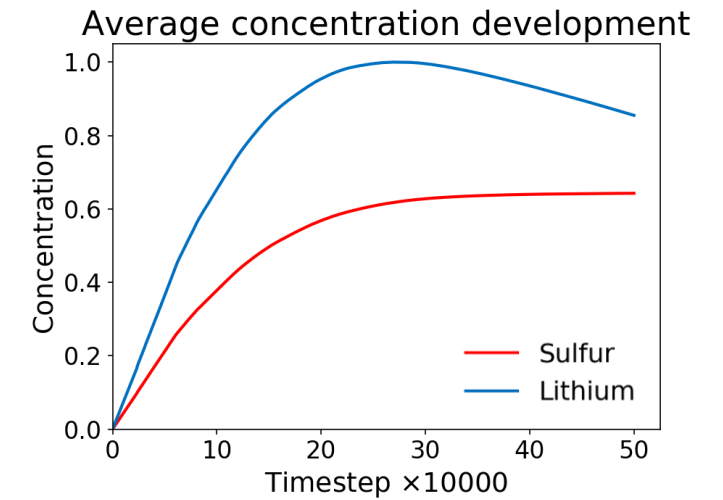
Dissolution



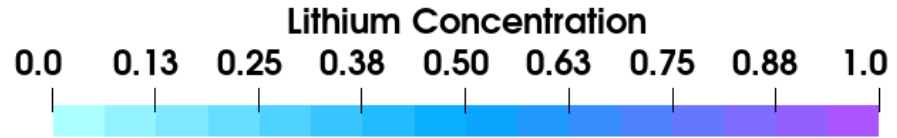
Added Li_2S to pristine carbon structure



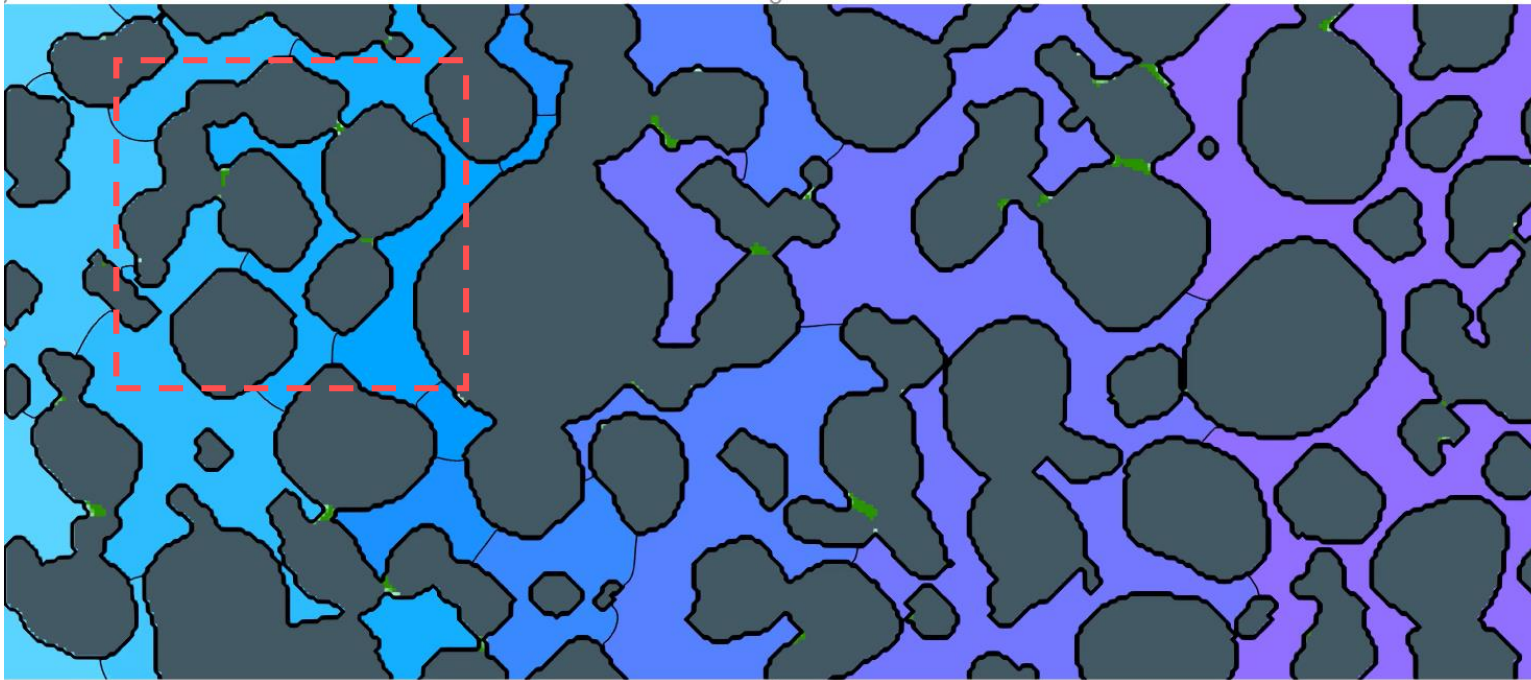
□ Pore space
■ Carbon
■ Li_2S



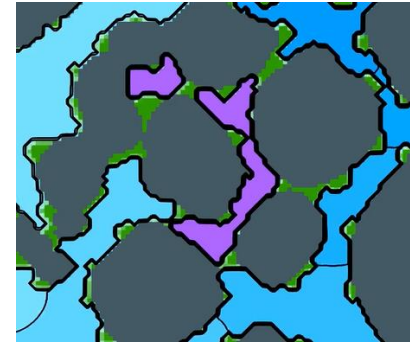
Dissolution



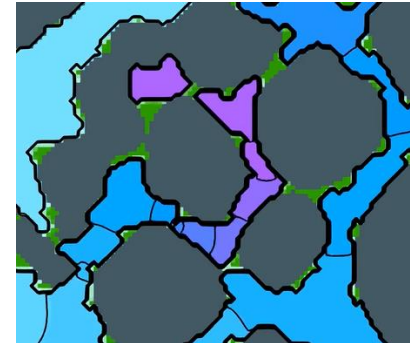
$0.9 \cdot \Delta t_{max}$



$0.4 \cdot \Delta t_{max}$



$0.45 \cdot \Delta t_{max}$

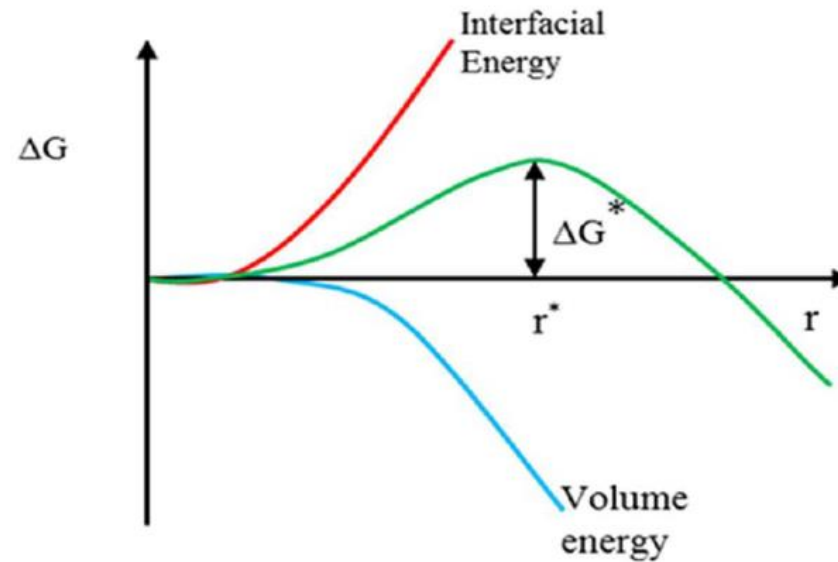
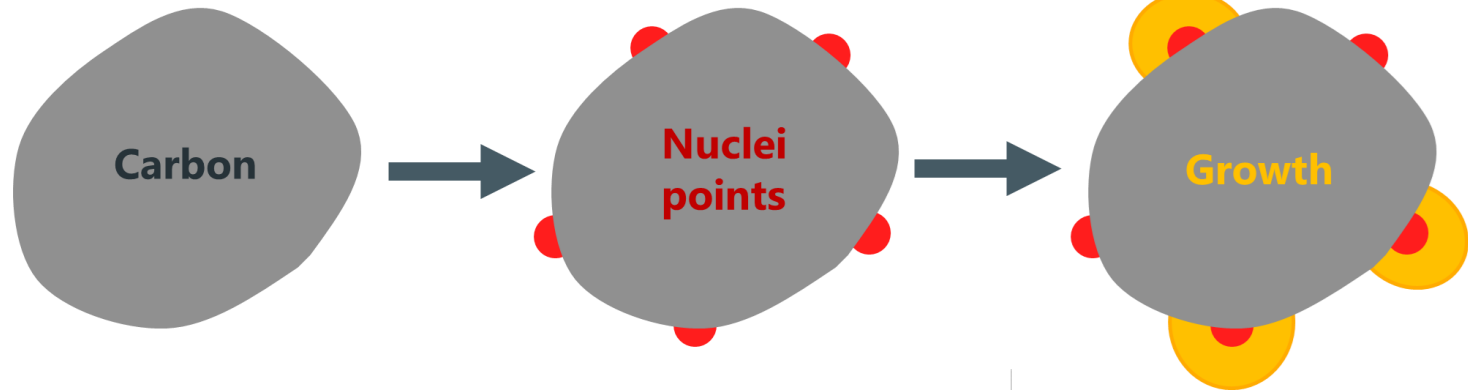
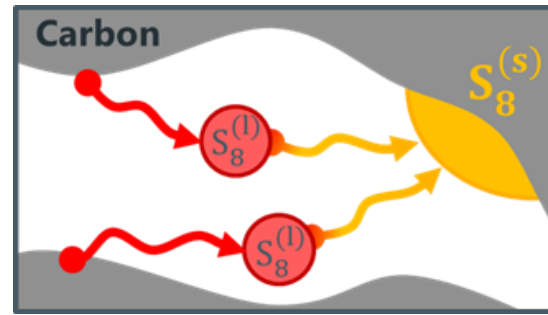


→ Full tracking of species inside complex structures

Precipitation

Nucleation

- Classical nucleation theory
- Physically based random nuclei distribution
- Sub-grid modelling



S.Karthika, et al.
Cryst. Growth Des. (2016) **16** 6663–6681

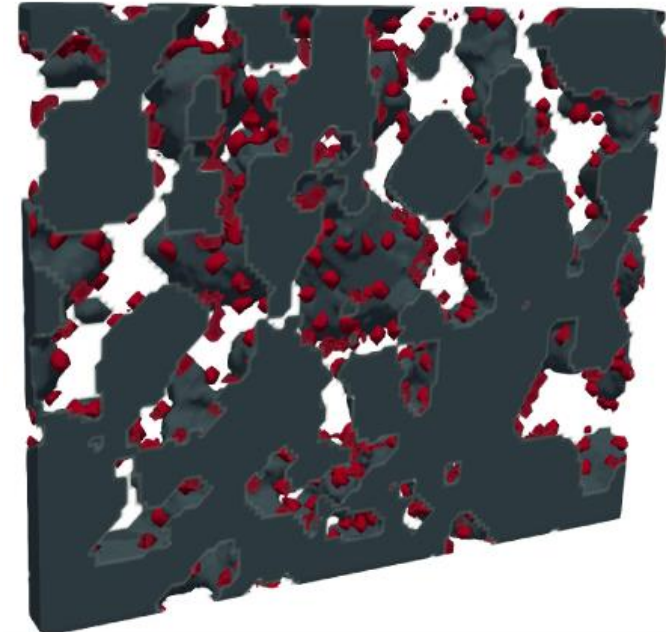
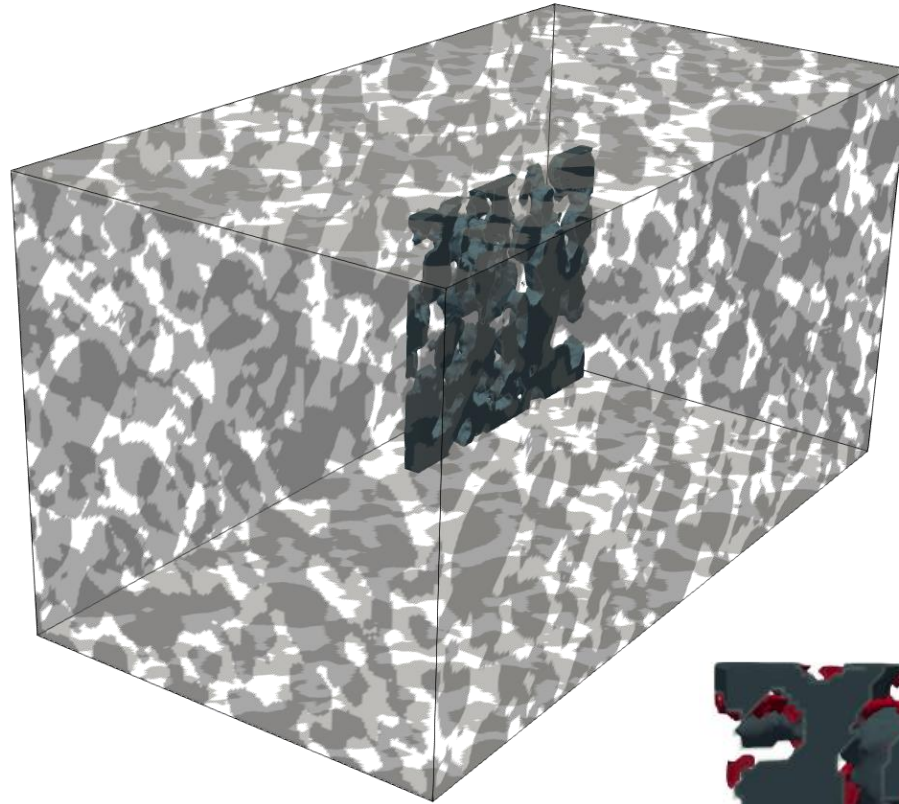
Precipitation

Nucleation

- Classical nucleation theory
- Physically based random nuclei distribution
- Sub-grid modelling

Rate of Charge

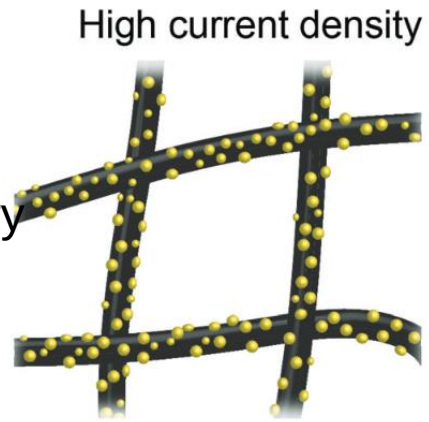
- $2C$
- $1C$
- $C/2$
- $C/5$
- $C/10$



Precipitation

Nucleation

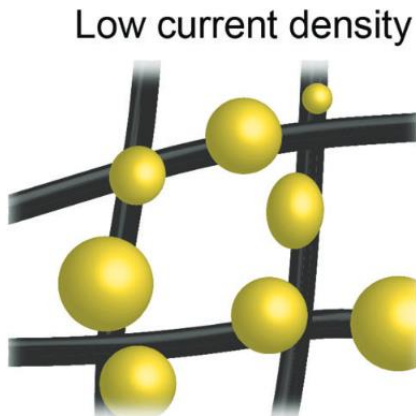
- Classical nucleation theory
- Physically based random nuclei distribution
- Sub-grid modelling



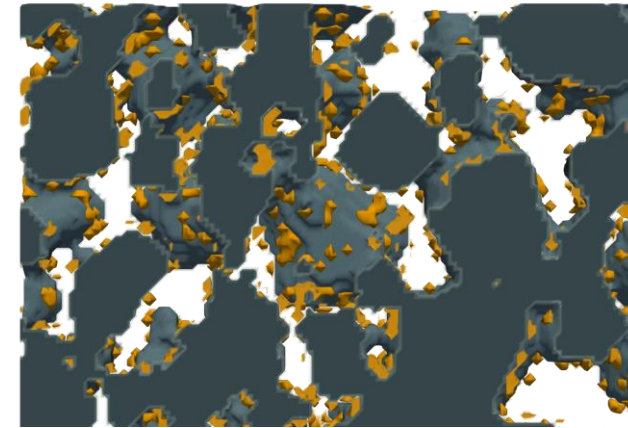
S.Yu, X.Huang, et al.
Energy Environ. Sci. (2018) **11** 202

Rate of Charge

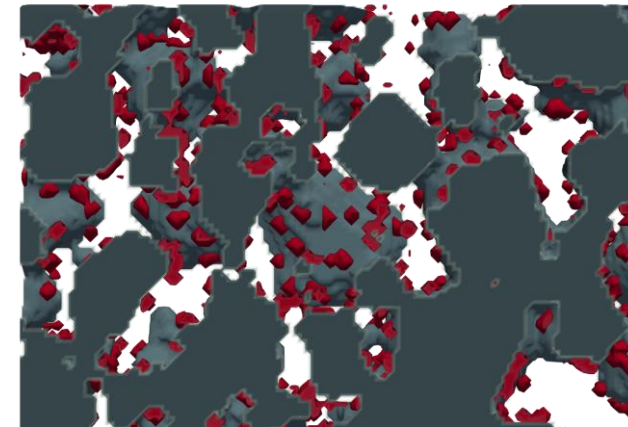
- 2C
- 1C
- C/2
- C/5
- C/10



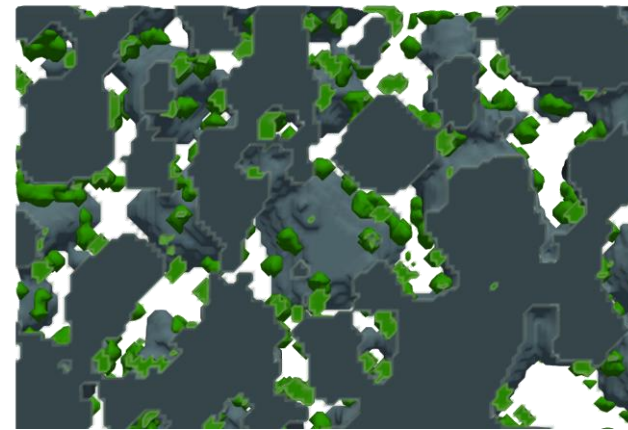
1C



C/2



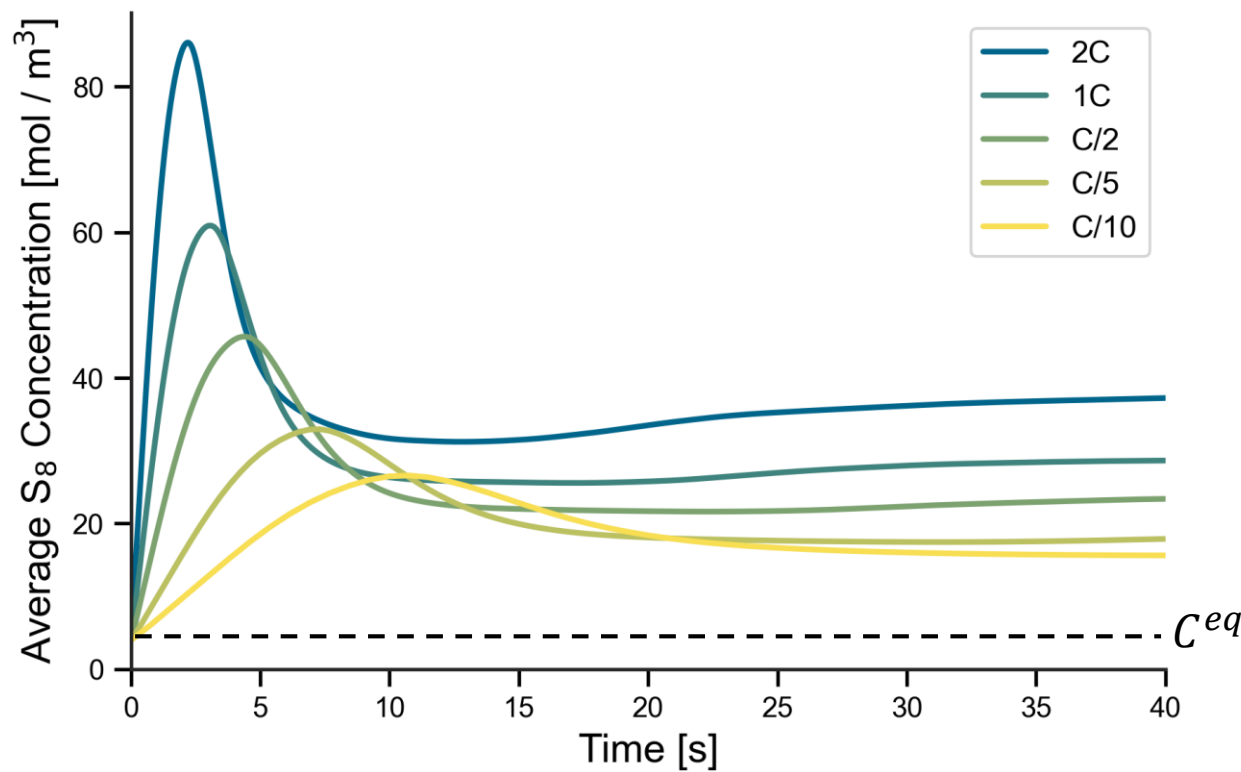
C/5



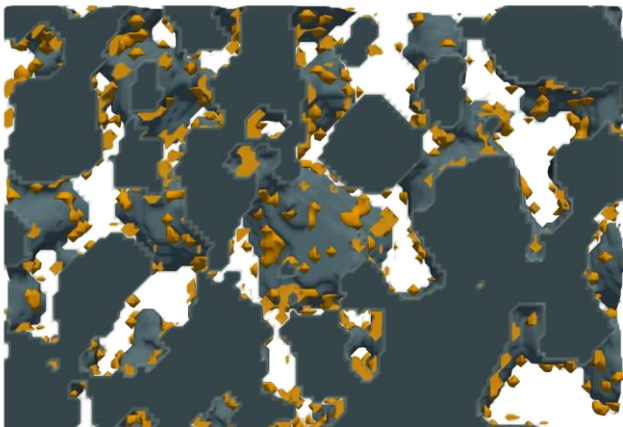
Precipitation Analysis



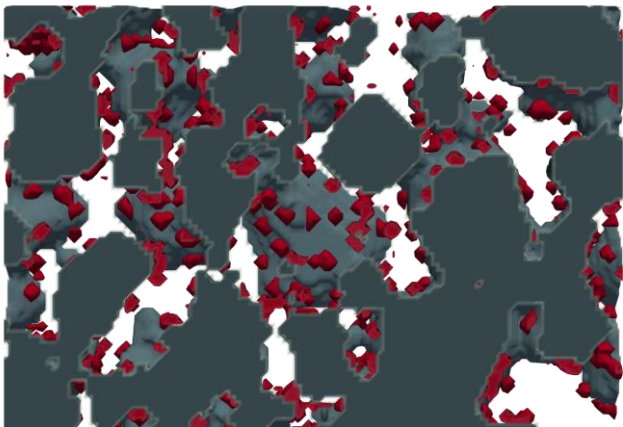
Average Sulfur Concentration



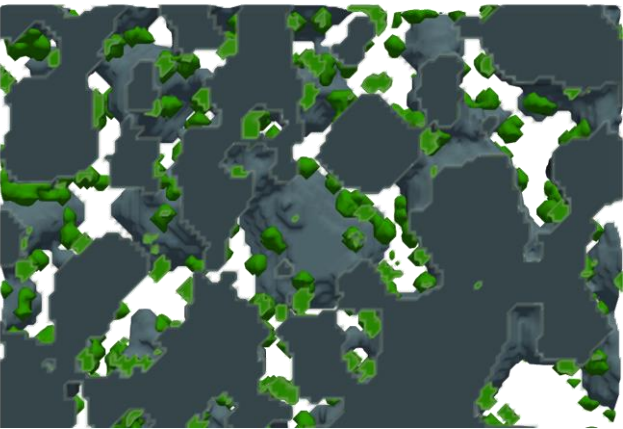
1C



C/2

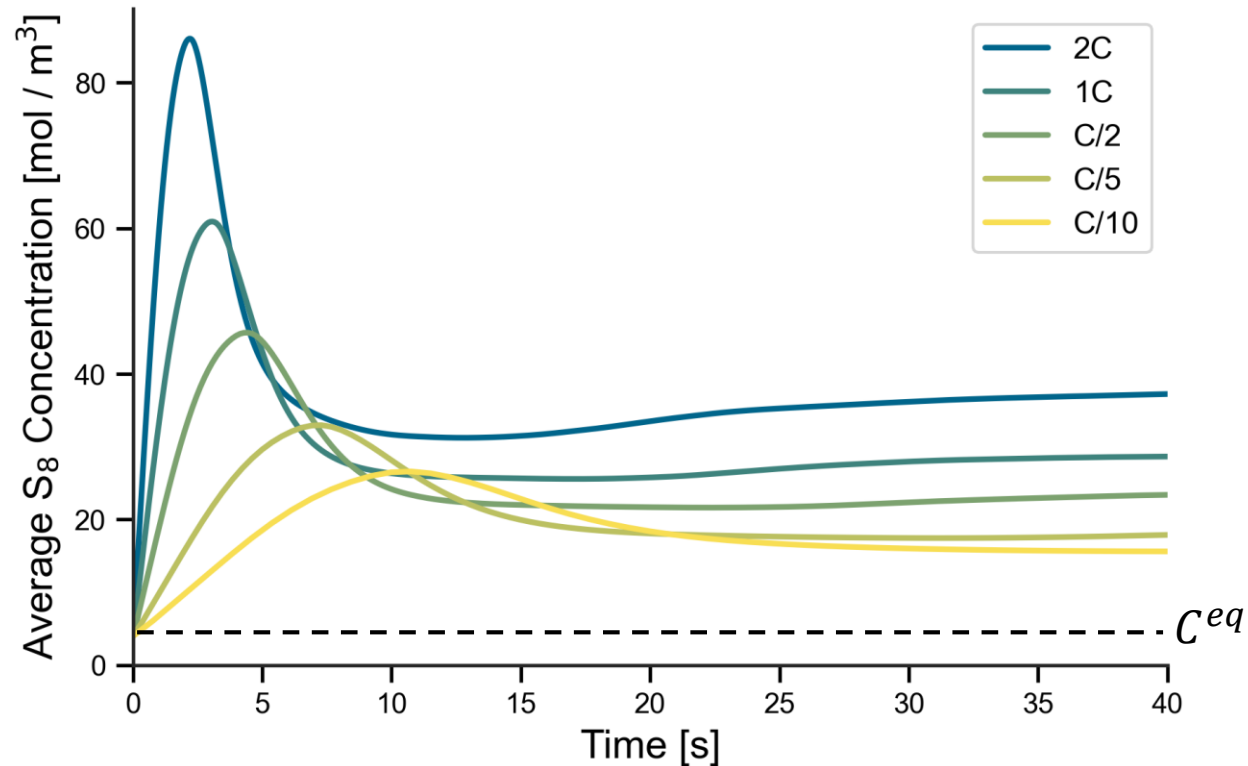


C/5



Precipitation Analysis

Average Sulfur Concentration



Research questions:

- ✓ Precipitates evolution
- Film growth conditions
- Pore clogging
- Electrochemical impact

→ Successful simulation of nucleation and precipitate evolution in dynamic setting

Precipitation Analysis



Film growth



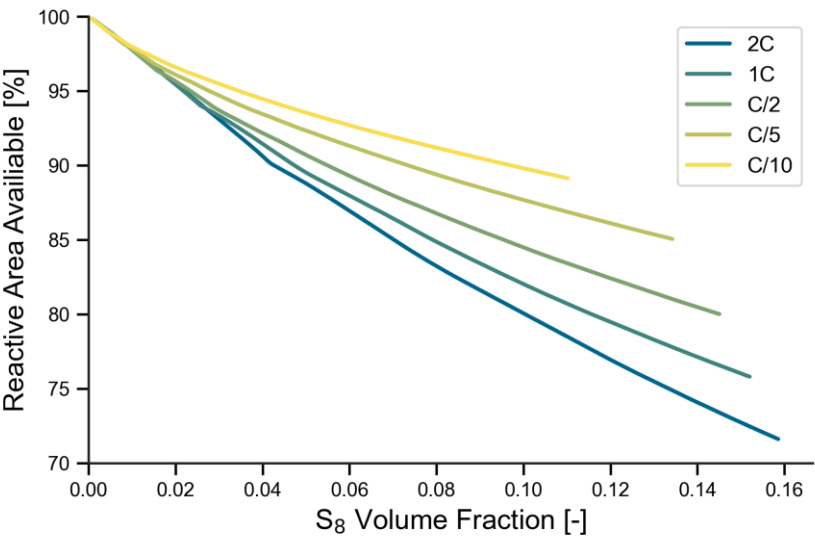
2D example image

Pore clogging

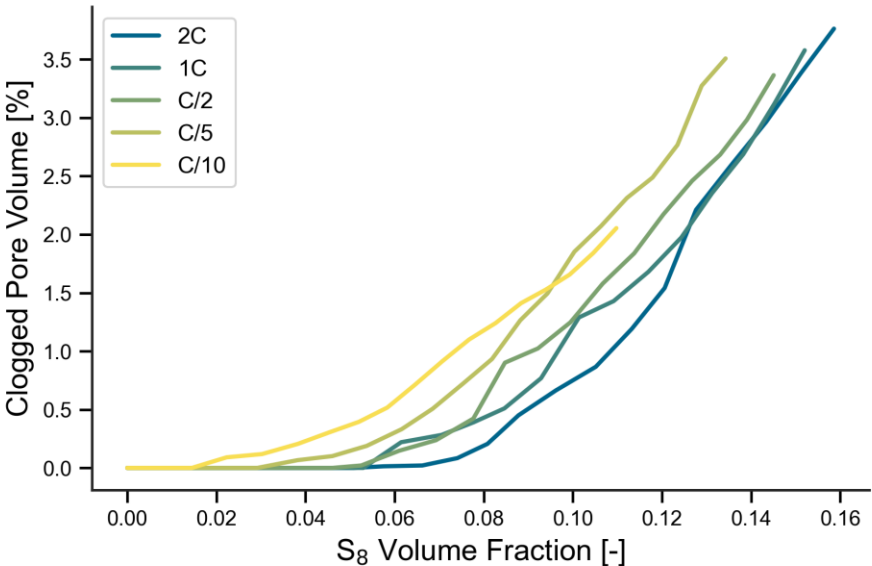


2D example image

Reactive Surface Area



Blocked Pore Volume



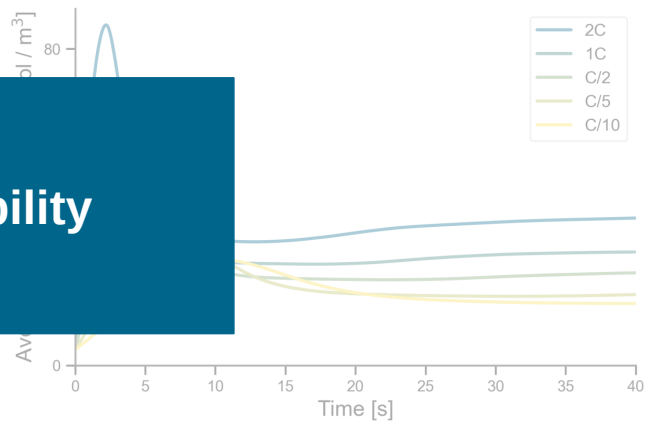
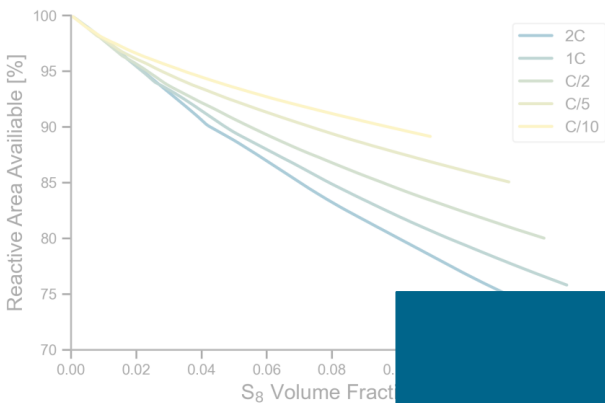
Precipitation Analysis



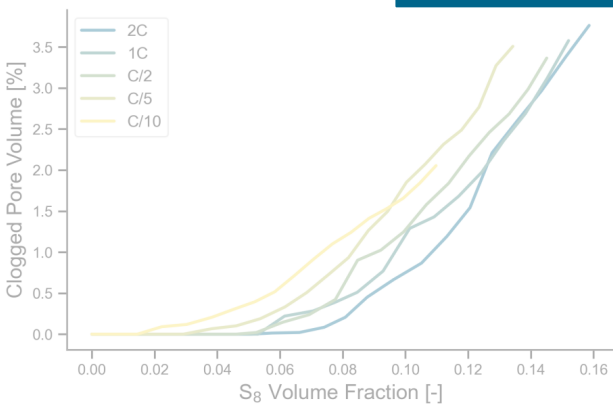
Film growth



Pore clogging

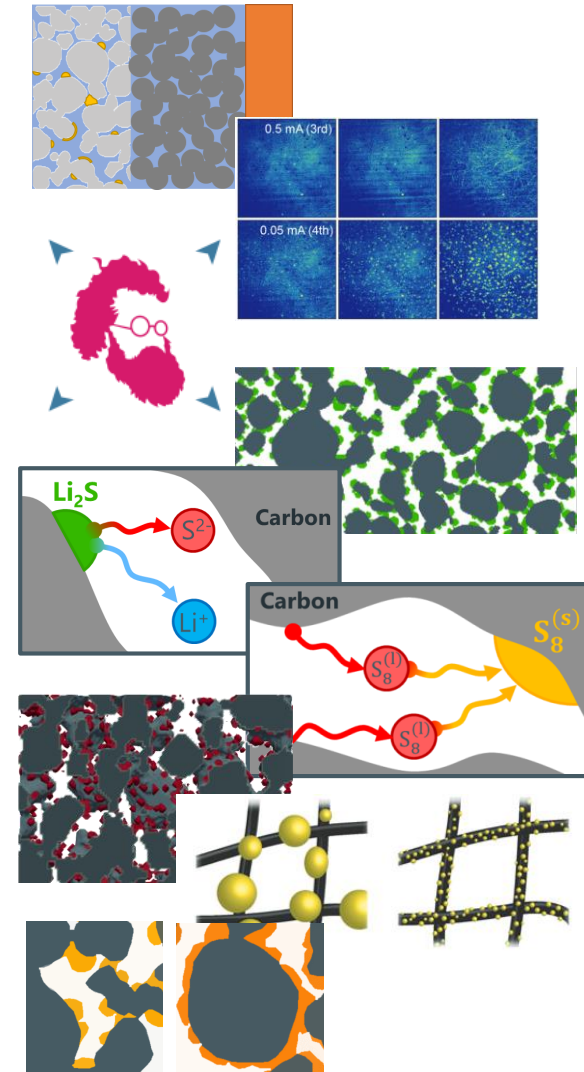


Vast Analysis Capability



Takeaway

- Lattice Boltzmann method shows great potential
 - Applicable for in between conventional and molecular scales
 - Straight forward meshing and parallel computing
 - Fully resolved cathode structure simulations
- Extensive pore-scale analysis is possible
 - Simulates dissolution, nucleation and precipitation
 - Captures pore-clogging and film growth
 - Bridging microscopic phenomena to macroscopic impacts

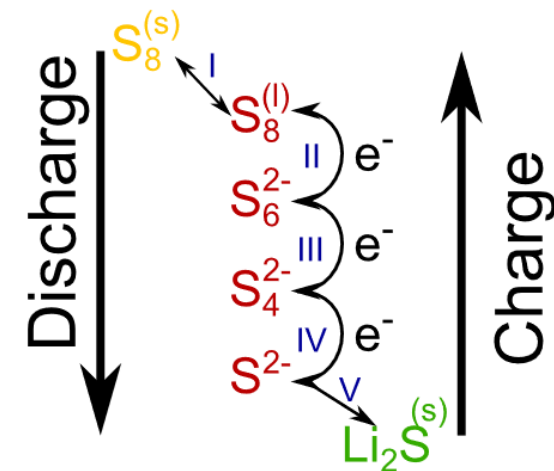


- Multi-species interaction & electron transfer
- Full cathode cycling
- Multi-scale morphology investigation
- Cooperation with other project

→ Main goal: aid in Li-S battery design

Research questions:

- ✓ Precipitates evolution
- ✓ Film growth conditions
- ✓ Pore clogging
- Electrochemical impact





HIU HELMHOLTZ
INSTITUTE
ULM
Electrochemical Energy Storage



H L R I S

High-Performance Computing Center Stuttgart

Project LaBoReSys

GEFÖRDERT VOM



Bundesministerium
für Bildung
und Forschung

03XP0491A

