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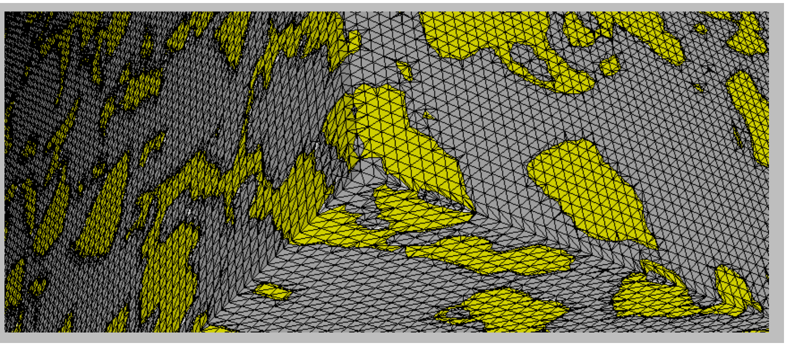
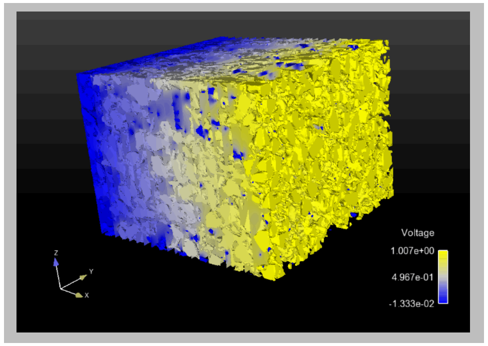
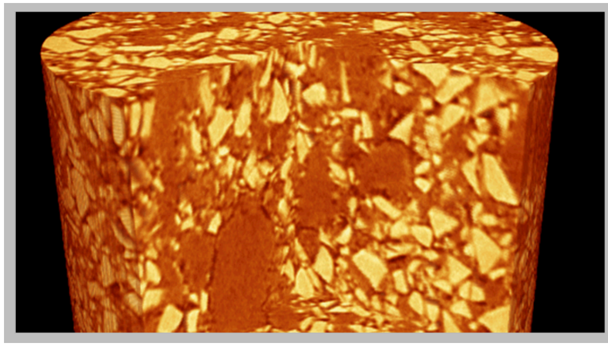






Mesoscale Modeling and Simulation of Composition, Manufacturing, and Microstructure Effects on Electrical Conduction in Thermal Battery Cathodes

Emilee Reinholz

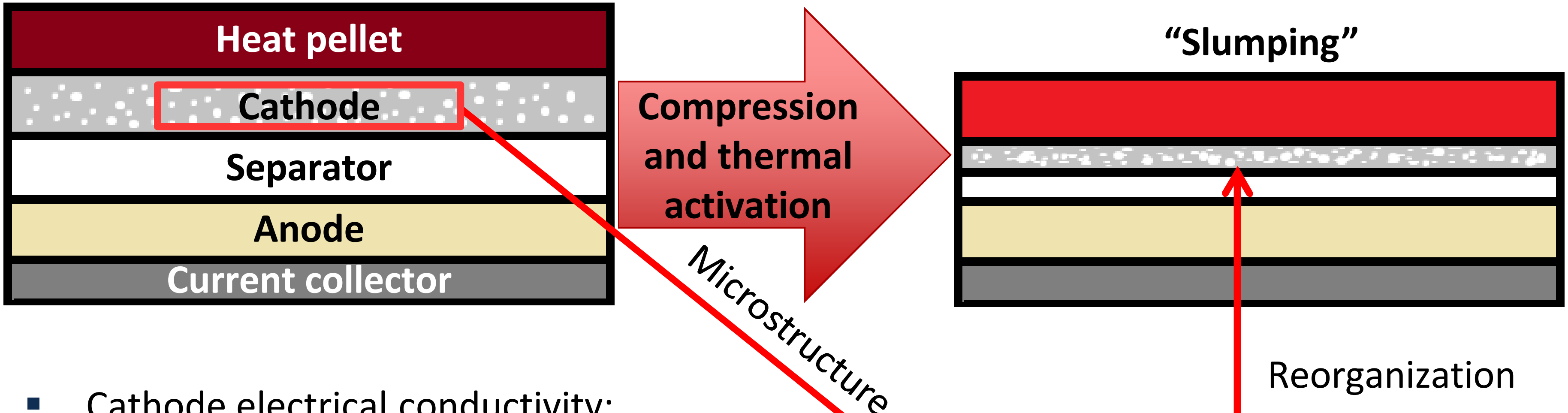
10/13/15

UNM SCHOOL *of* ENGINEERING

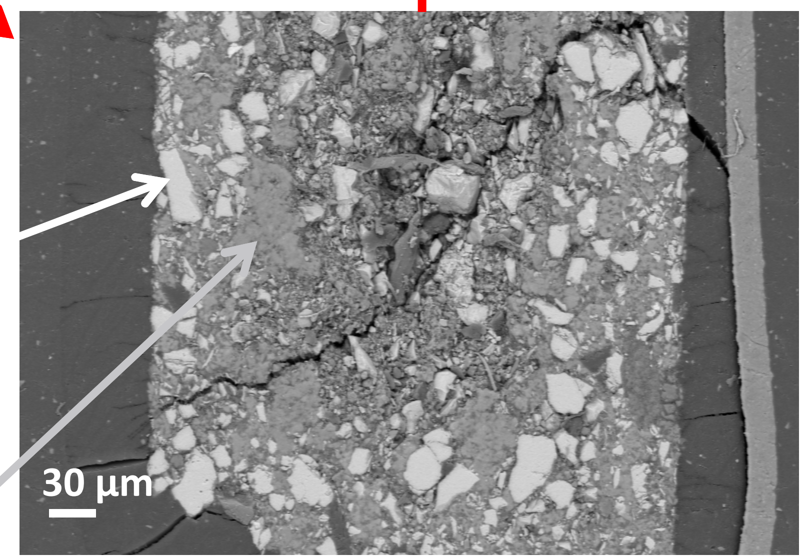
U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

Introduction to Li/FeS_2 Thermal Battery Cathodes



- Cathode electrical conductivity: selected for ease of measurement and impact upon performance [1]
- **Slumping induces a microstructural reorganization, which affects material properties**

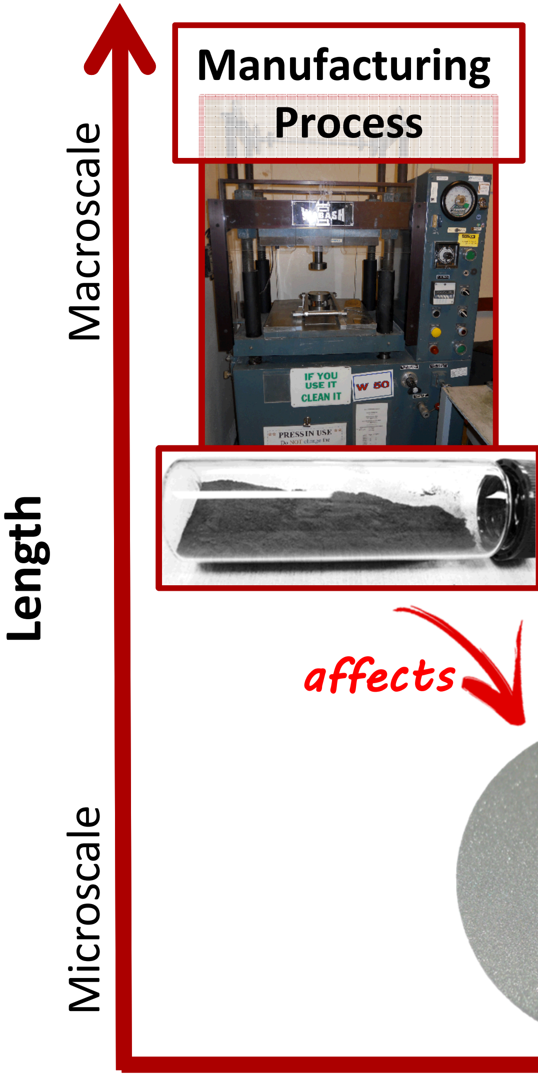


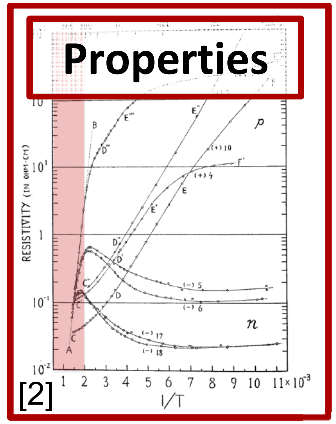
FeS_2

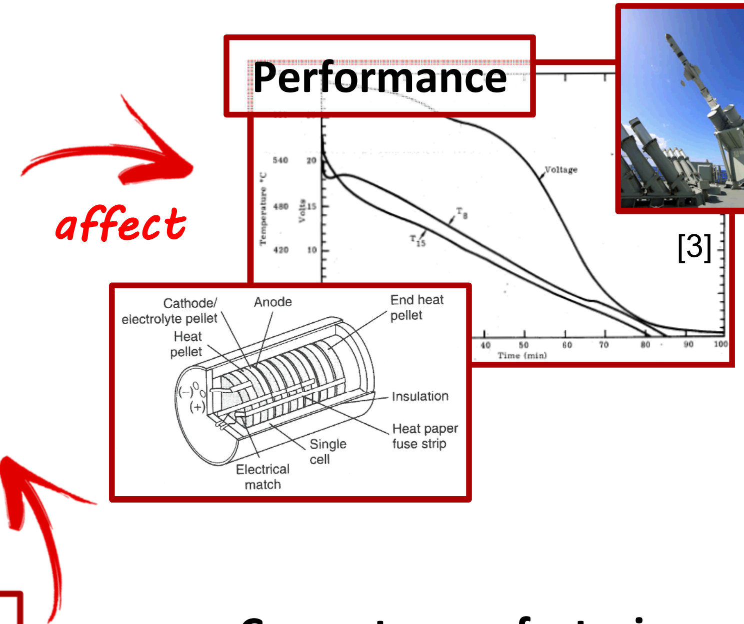
Electrolyte, binder, lithiating agent, and voids

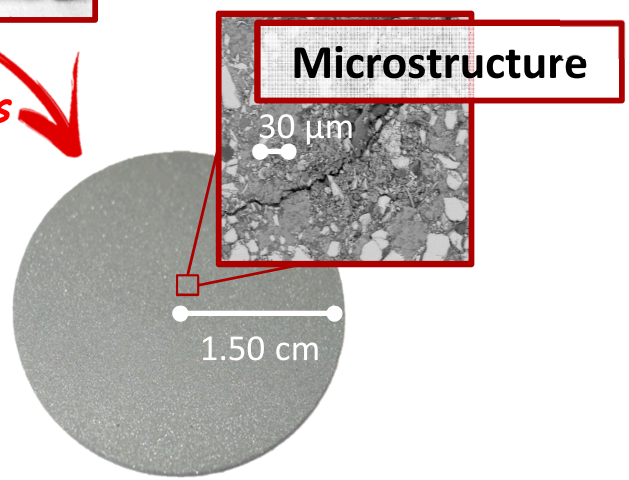
[1] Masset, P. J.; Guidotti, R. J. Power Sources. **2008**, *177,* 595-609.

A Critical Relationship







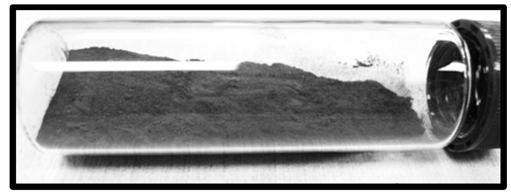


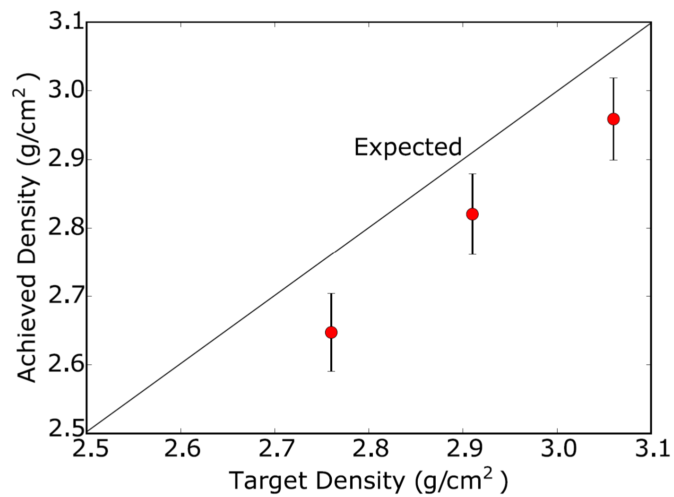
Current manufacturing practices are based on empirical data, but changes to the cathode affect the microstructure, properties, and battery performance

[2] Sasaki, A. *Mineral. J.* **1955**, *1*, 290-302.
[3] Searcy, J. Q. and Armijo, J. R. Technical Report, Sandia National Labs, Albuquerque, NM, June 1982.

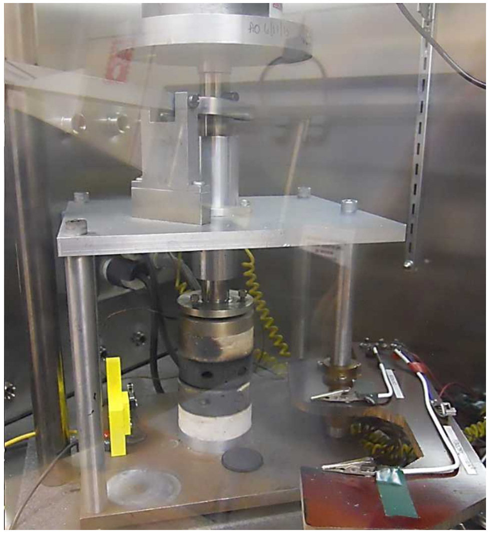
Powder and Pellet Preparation

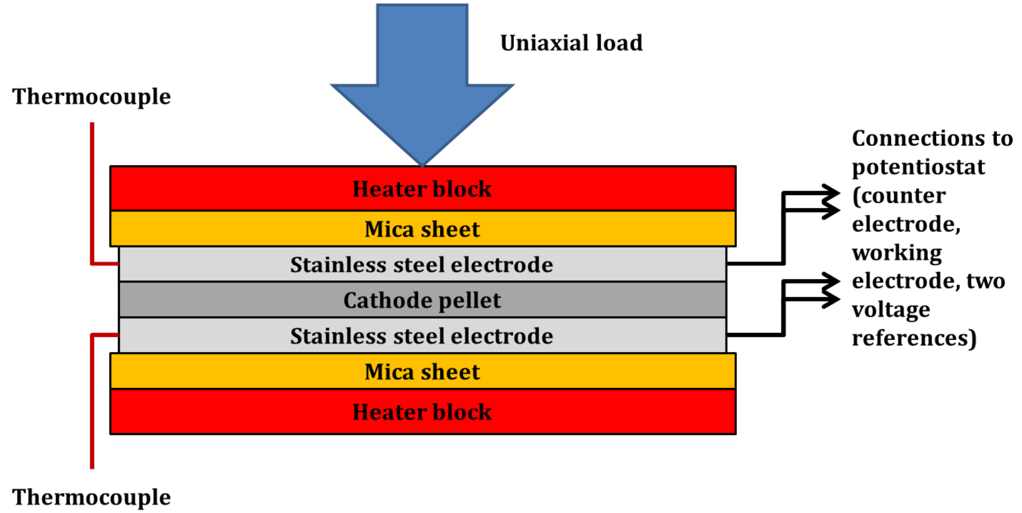
- DOE: Nine pellet types with three variables
    1. Pellet density
    2. Relative FeS_2 content
    3. FeS_2 particle size distribution
- Powder preparation
    - Particle size reduction
    - Sieving to isolate size distributions (32-38, 38-45, 45-53 µm)
    - Fusing
- Pellet preparation: uniaxial cold-press
- **Challenges: limited material, trial-and-error process**
- **Compensation: measured densities**





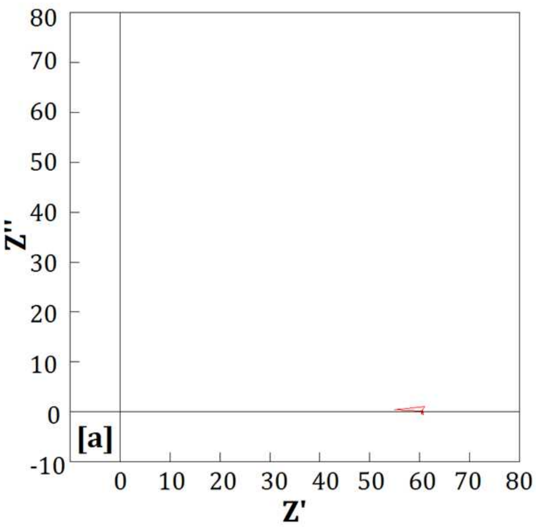
Impedance Spectroscopy

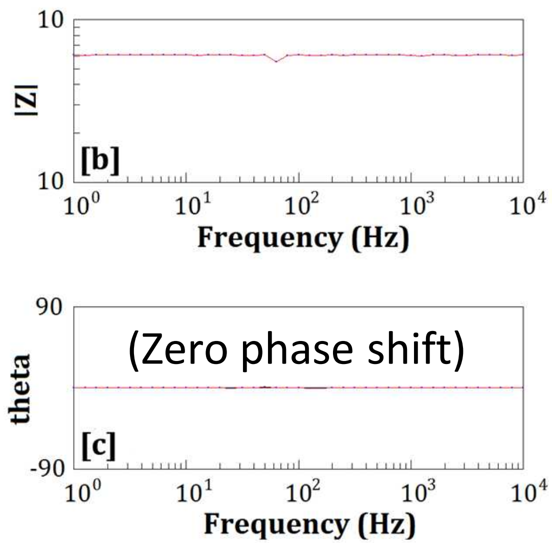




- Minimized interference, inductance, and water contamination
- **Impedance results were fit to a single resistor to calculate conductivity**

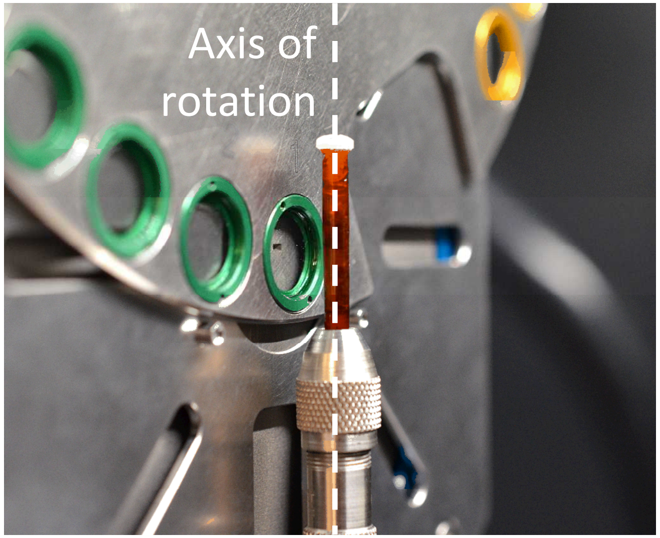
$$\sigma = \frac{l}{R_{fit} A}$$

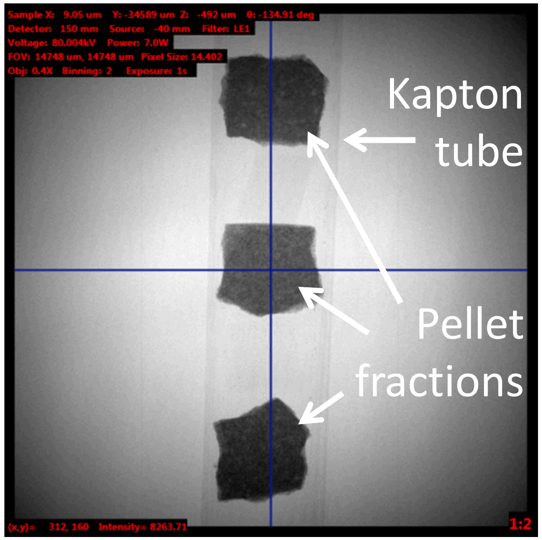


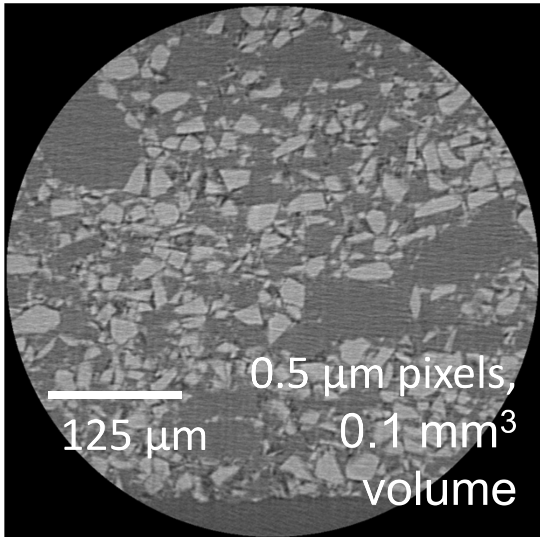


Representative Geometry Construction

- Microcomputed tomography (MicroCT)



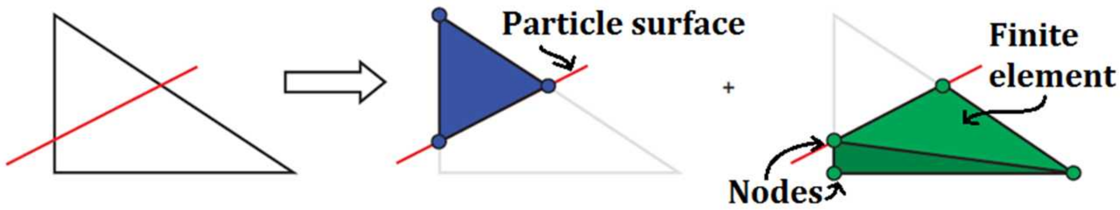


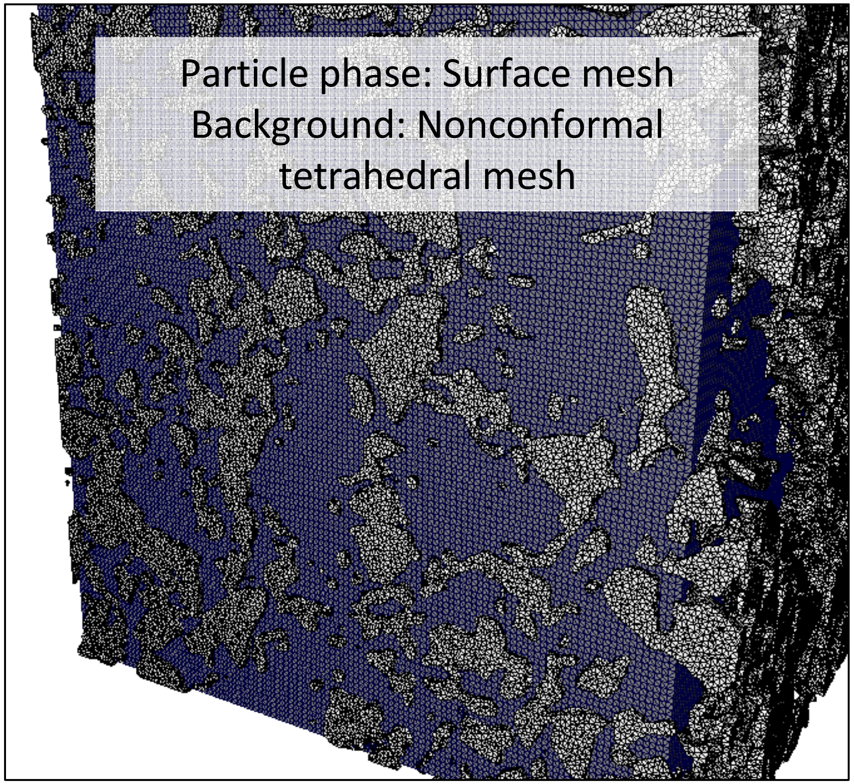


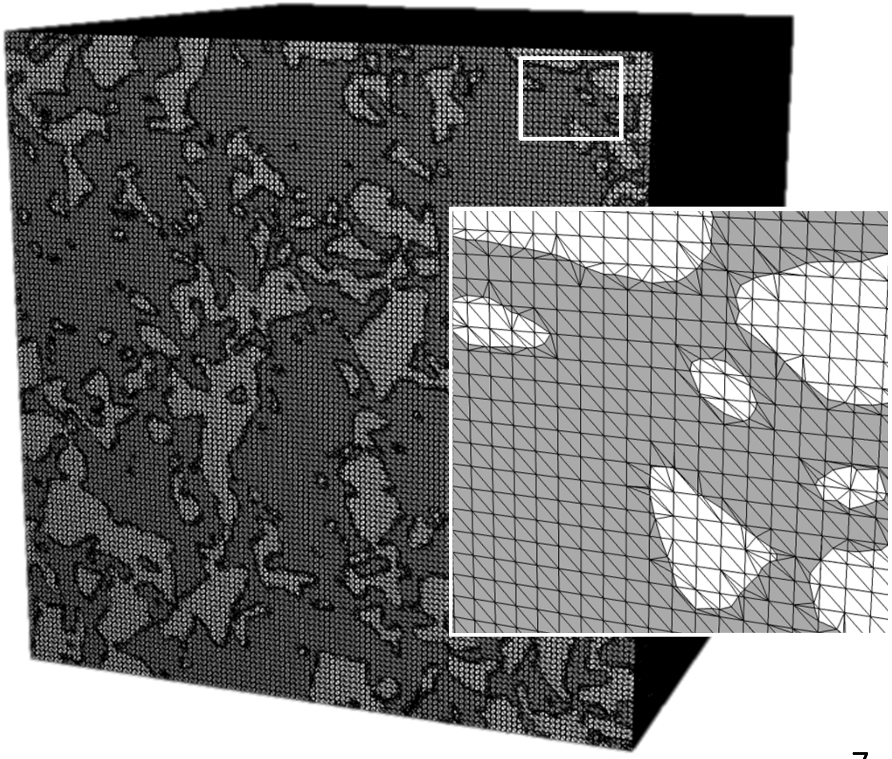
- Reconstruction workflow

Conformal Decomposition Finite Element Method

- Application via Aria, a coupled multiphysics program within Sierra Mechanics







[6] Noble, D.; Newren, E.; Lechman, J. *Int. J. Numer. Methods Fluids*, **2010**, *63*, 725-742.

Governing Equations and Boundary Conditions

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- Ohm's law

$$\mathrm{J} = \sigma \mathrm{E} = -\sigma \nabla V$$

- Steady-state continuity equation for current density

$$\nabla \cdot \mathrm{J} = 0$$

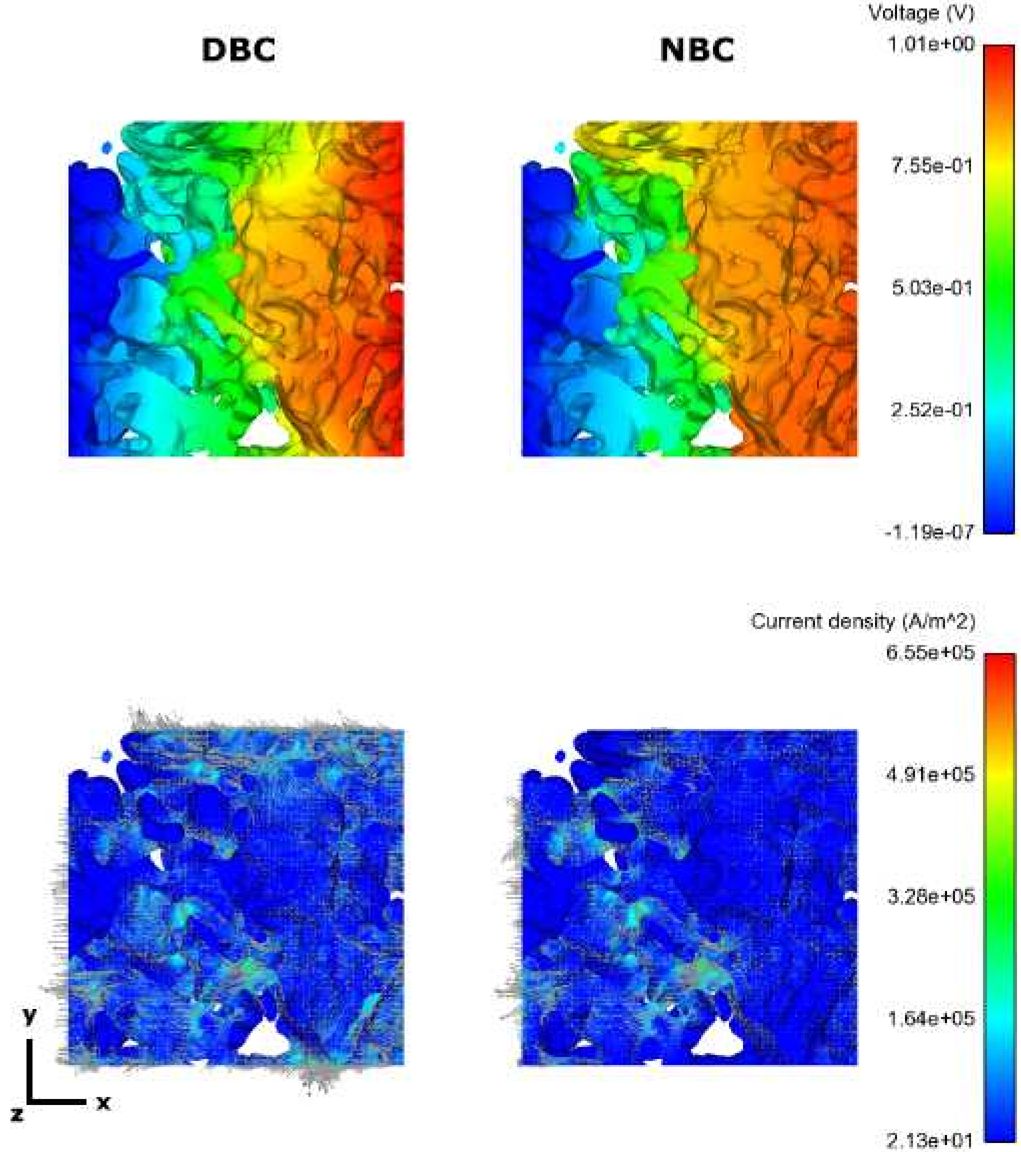
- **Boundary conditions**: Two ways to measure conductivity; apply current or voltage, measure the opposite
  - Upper bound = Dirichlet boundary conditions (DBC) [7]
  - Lower bound = Neumann boundary conditions (NBC) [7]
- Variables

$\mathbf{J}$ Electrical current density vector

$\mathbf{E}$ Electric field vector

V Potential

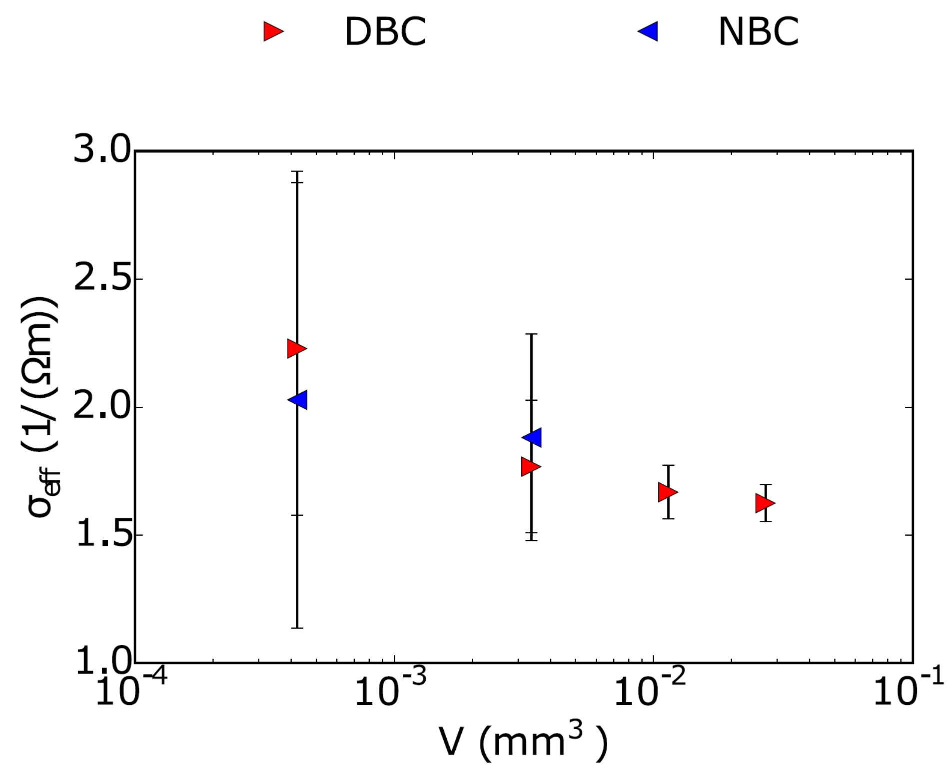
σ Electrical conductivity

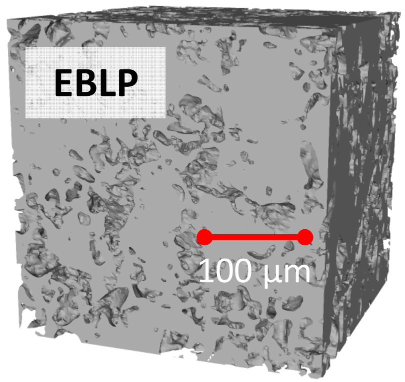


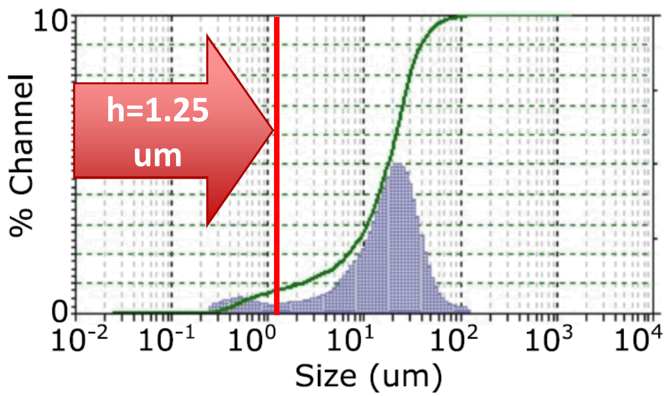
[7] Ostoja-Starzewski, M.; Schulte, J. *Phys. Rev. B*, **1996**, *54*, 278-285.

Verification

- Mesh size
  - Need greater mesh refinement on small particles and between small gaps
- Volume [8]
  - **More error results from the domain volume than the applied boundary conditions**
  - **RVE = 0.310 mm^3, n_{proj} = 91 for 1% RE Anisotropy**

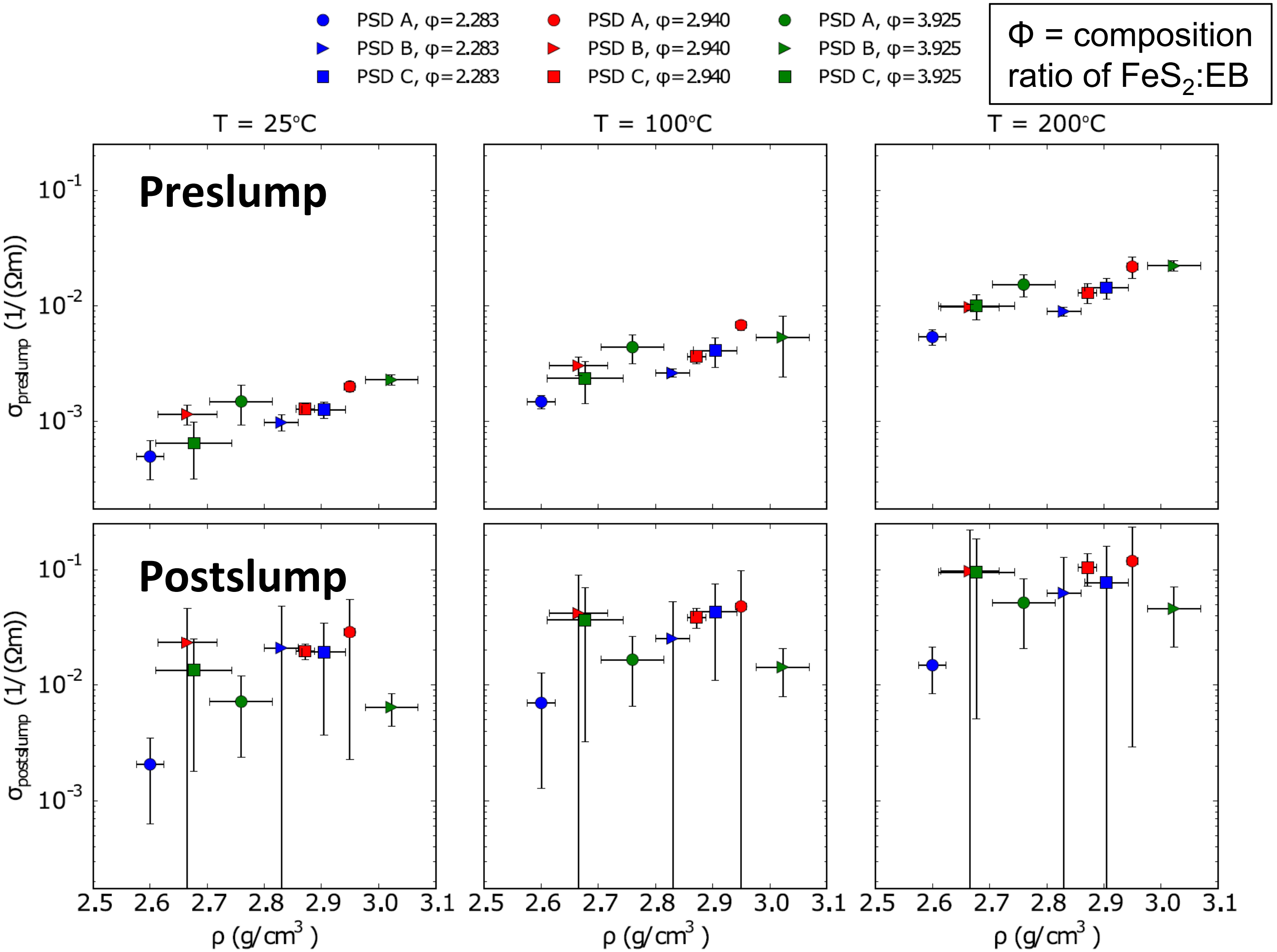






[8] Kanit, T.; Forest, S.; Galliet, I.; Mounoury, V.; Jeulin, D. *Int. J. Solids Struct.*, **2003**, *40*, 3647-3679.

Experimental Results

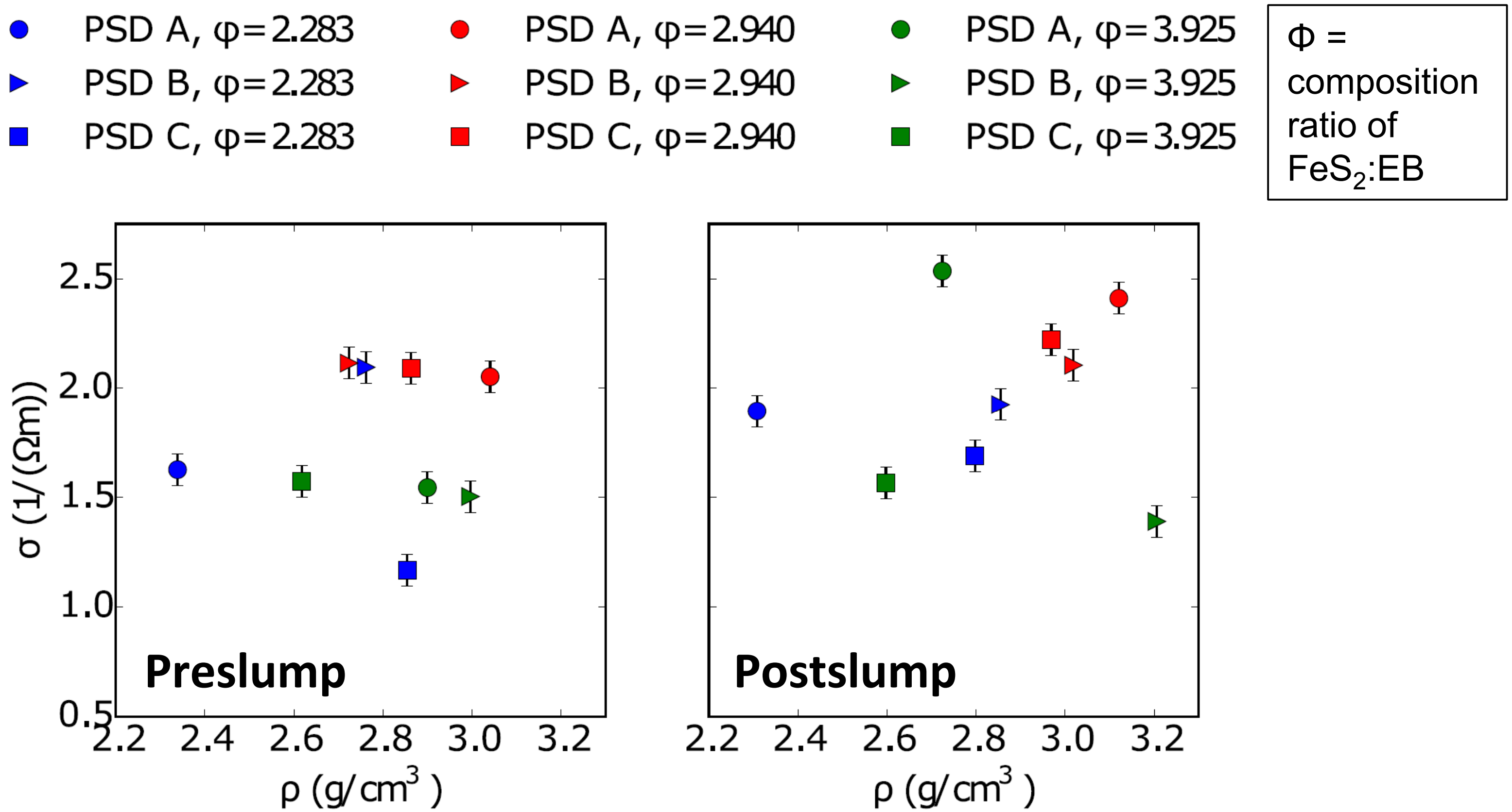


- σ increases with temperature, density, and composition
- Possible causes of scatter: effects of minor or trace elements [9], oxidation [10]

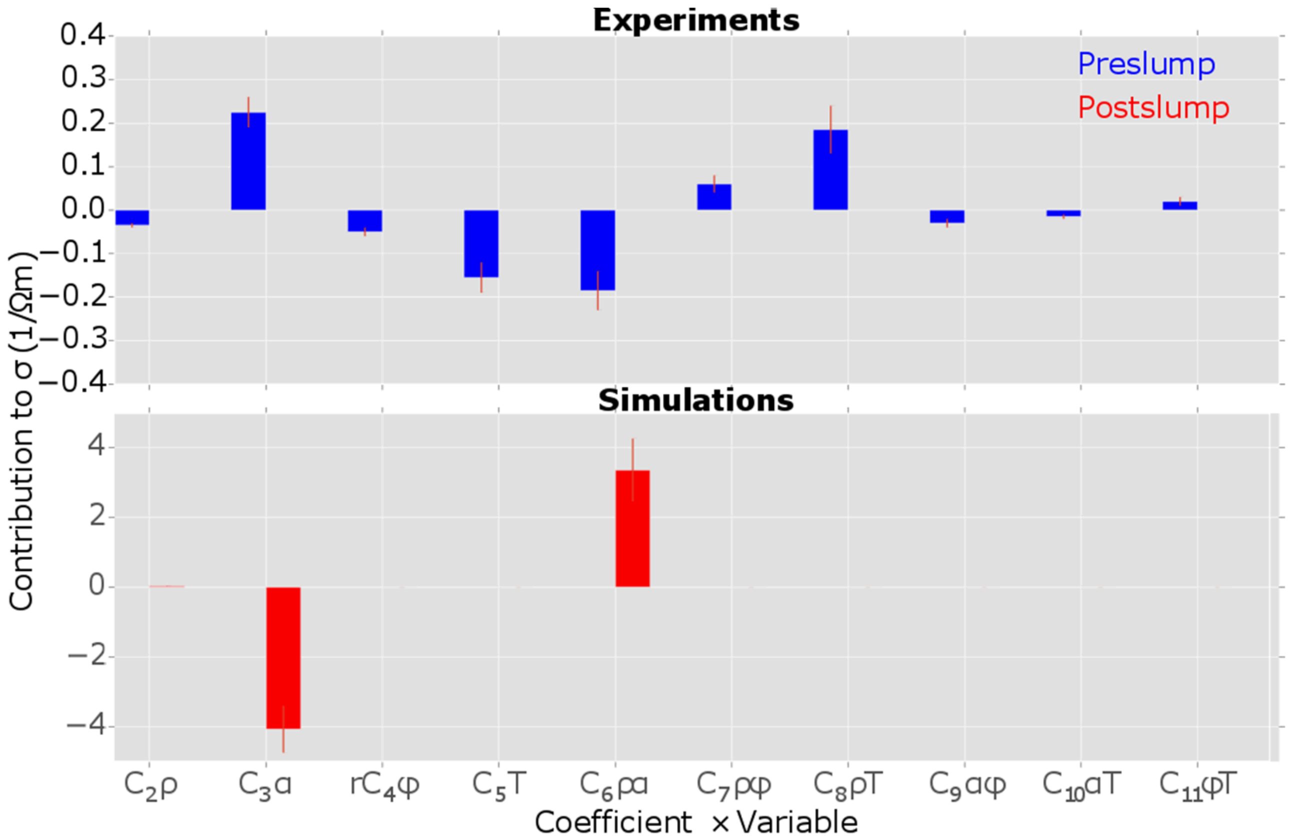
[9] Abraitis, P. K.; Patrick, R. A. D.; Vaughan, D. J. *Int. J. Miner. Process.*, **2004**, *74*, 41-59.
[10] Chandra, A. P.; Gerson, A. R. *Surf. Sci. Rep.*, **2010**, *65*, 293-315.

Simulation Results

- No preslump trend; postslump results show trend with density
- Consider impact of simulation physics, mesh resolution, and domain volume



Regression Analysis



Density and particle size distribution are the most significant processing parameters

ρ = pellet density (g/cm^3)
α = mean target particle diameter (μm)
Φ = composition ratio of FeS_2:EB

Fit	R^2	R^2_{pred}
Experiment, Preslump	88.42	84.48
Experiment, Postslump	33.03	10.96
Simulation, Preslump	92.6	0
Simulation, Postslump	97.74	93.96

Conclusions

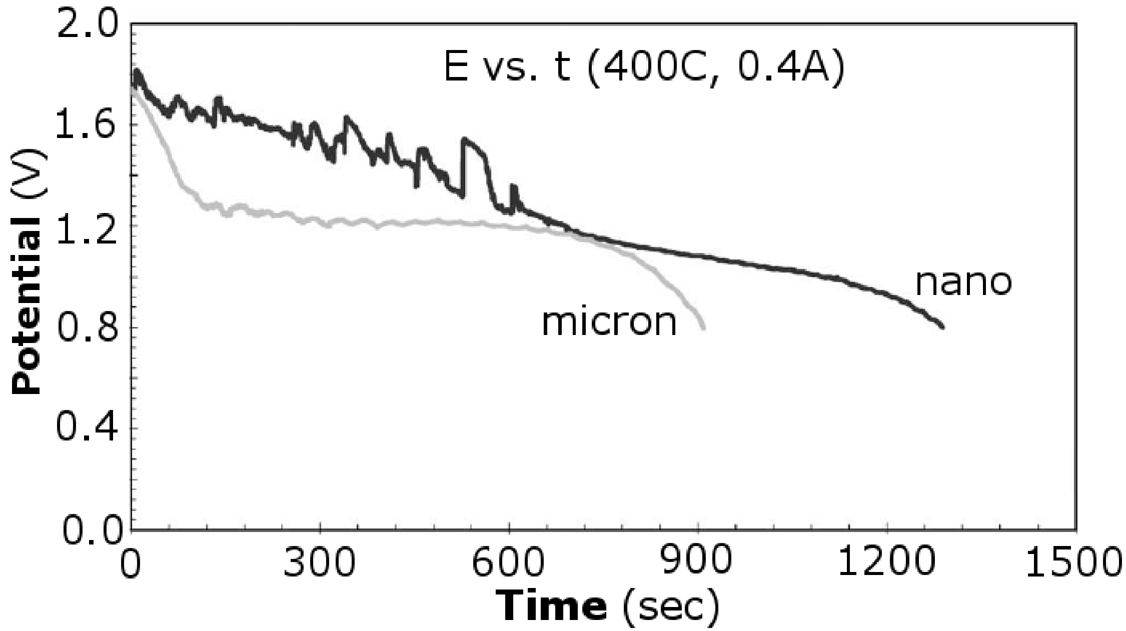
- **Preslump experimental results showed a link between density, composition, particle size, and electrical conductivity**
  - After slumping, this **link appears to be erased**, possibly due to impurities or oxidation
- **Simulation results did not replicate the experimental results**
  - No trend in preslump simulation results
  - **Postslump simulations demonstrated a relationship between particle size distribution, density, and electrical conductivity**, not seen among experimental noise
- The simulations are not representative of the experimental observations, so the **model lacks fidelity**
- However, this work is a **step toward a more fundamental understanding** between processing parameters, microstructure, material properties, and performance
- Additionally, these results suggest that **thermal battery performance will be affected** by (1) variability among FeS_2 material properties and (2) slumping, which should increase electrical conductivity
- **Improvements** include chemical purification and analysis of FeS_2, better microstructure characterization, mesh size, and domain volume
- **Future work**: Simulations to test effects of surface oxidation and contact resistance, effective conductivity with less conductive outer layer

Q&A

Extra Slides

Prior Research

- Prior research studied the effect of **FeS_2 particle size distributions** on performance, effects of **powder composition and forming pressure** on mechanical strength, and **electrical properties** of FeS_2, but not the **relationship** between FeS_2 particle size distributions, powder composition, pellet density, and electrical properties

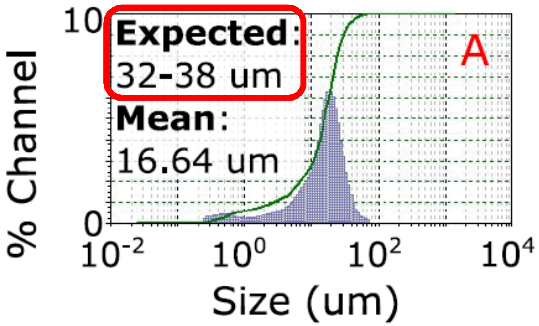


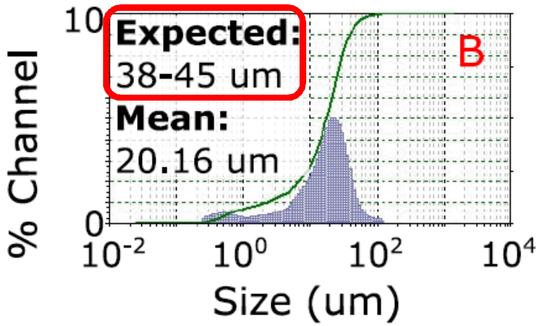
	Max. Voltage (V)	Run Time to 1.46V Cutoff (s)	Capacity to 1.46V Cutoff (mAhr)
Micron Single Cell	1.897	843	82
Avg. Nano Single Cell	2.016	1249	121.4
Average Improvement	6.30%	48.20%	48.00%

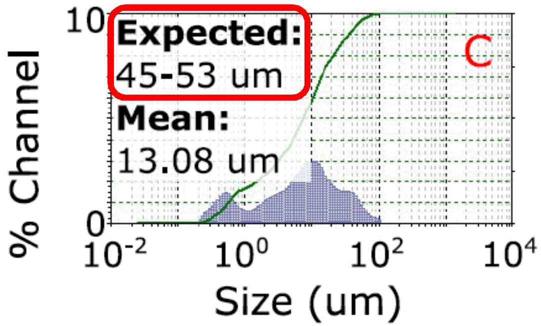
[4] Di Benedetto, G. L.; Carpenter, R. R.; Swanson, D. B.; Wightman, B. D. 46th Power Sources Conference: Orlando, FL, 2014.
[5] M. Au. *J. Power Sources*, **2003**, *115*, 360-366.

Particle Size Analysis

- Performed in water with 1 minute of sonication
- Agglomeration observed
- Applied the expected values due to the manufacturing process

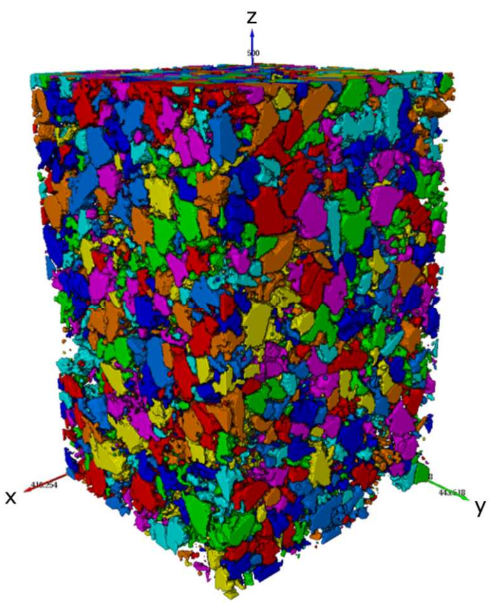


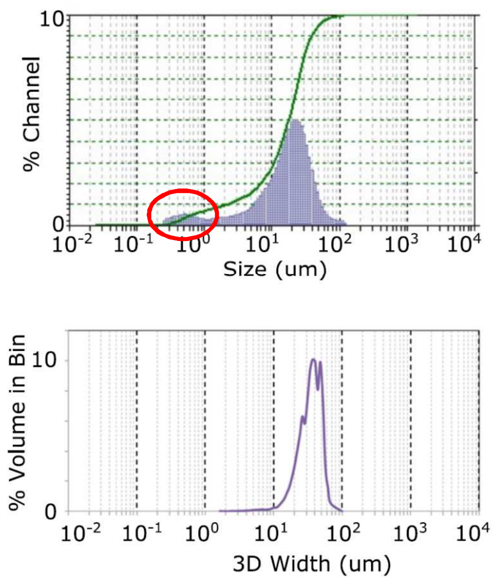


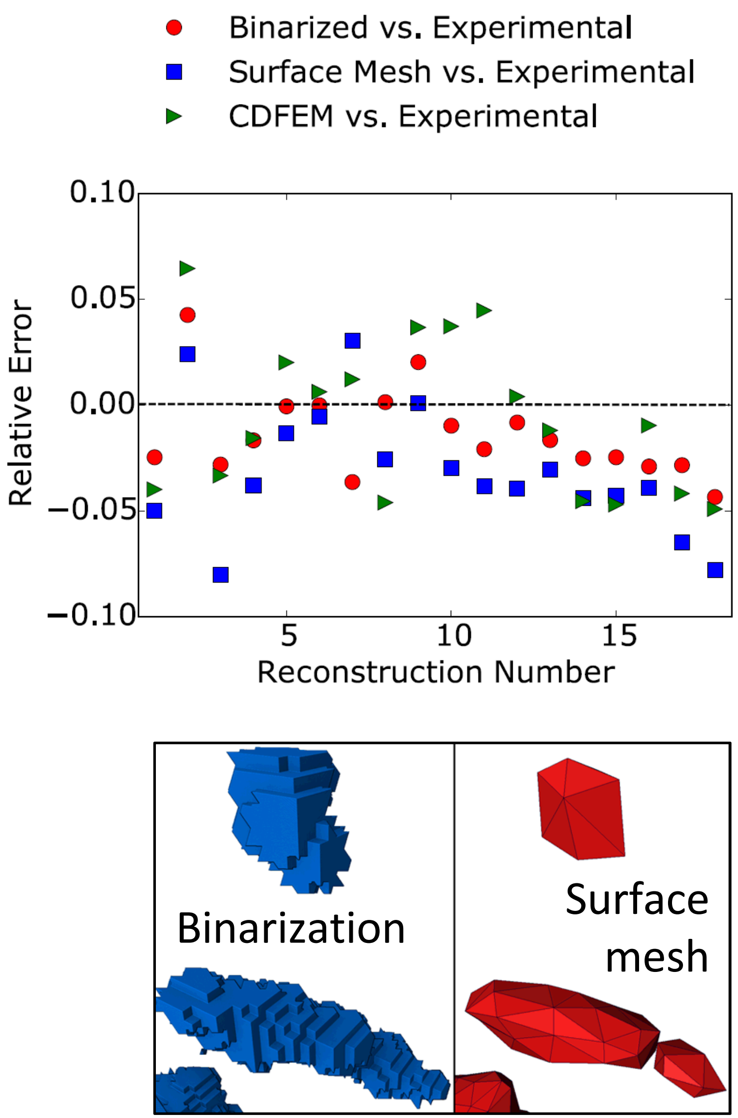


Validation of Reconstruction Method

- Volume fraction changes due to
  - MicroCT resolution
  - Binarization (Watershed)
  - Smoothing for surface mesh
  - CDFEM mesh resolution







Conformal Decomposition Finite Element Method

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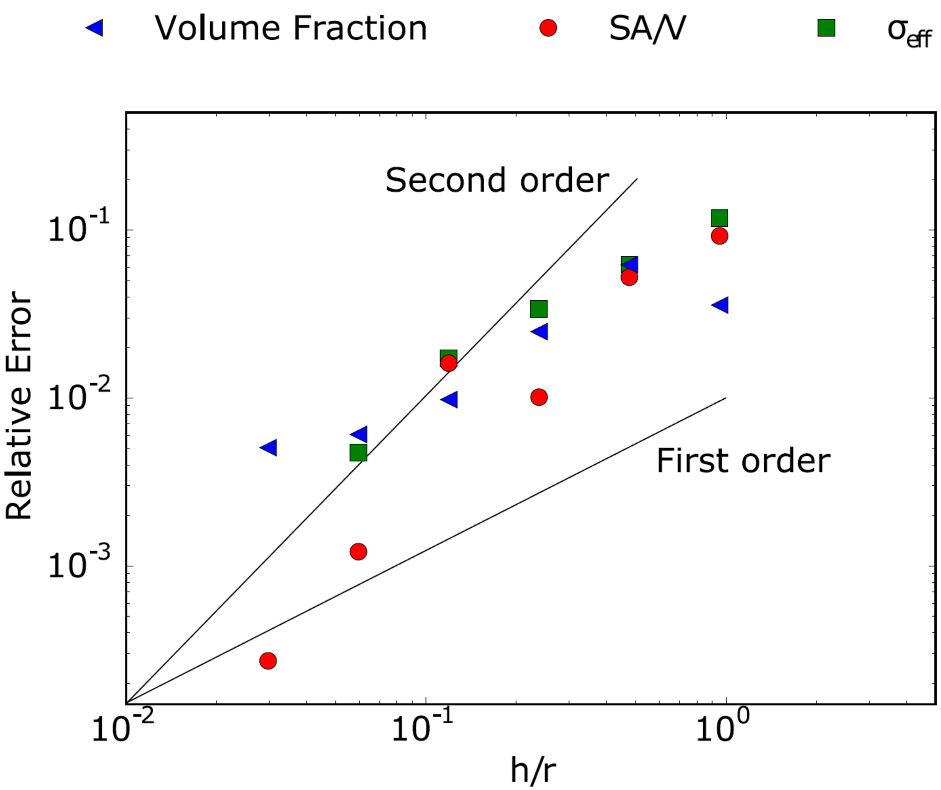
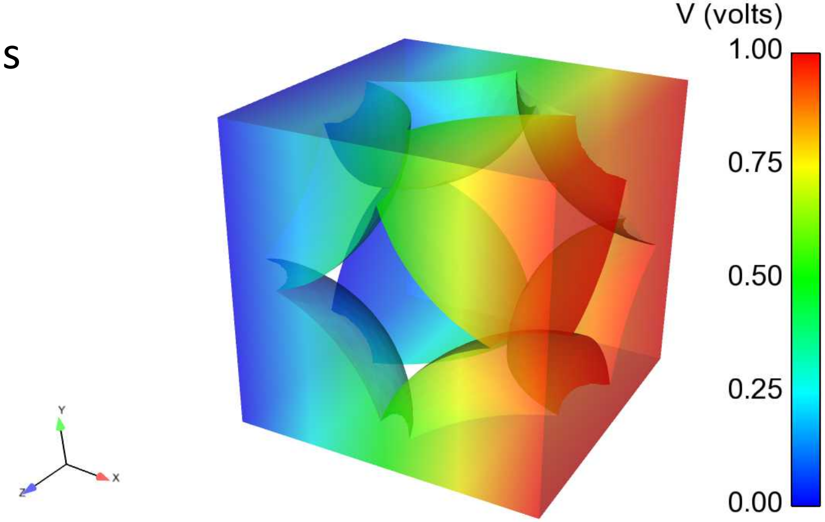
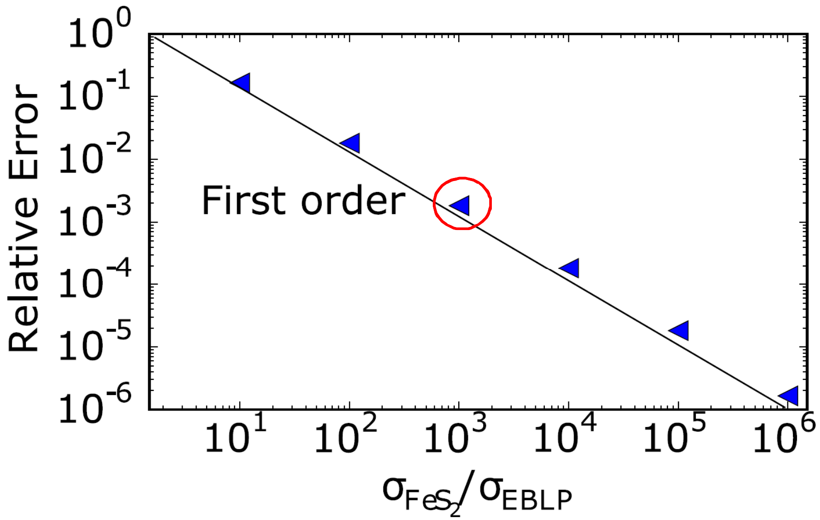
- **Verification**
- Background mesh resolution (h) vs. radius (r) affects the representative geometry
- Sigma ratio = 1000 is sufficient







[6] Noble, D.; Newren, E.; Lechman, J. *Int. J. Numer. Methods Fluids*, **2010**, *63*, 725-742.