Understanding and mitigating mechanical degradation in Li-S batteries via nanomechanical experiments and additive manufacturing

Max A. Saccone[1], Julia R. Greer[2]

[1]Division of Chemistry and Chemical Engineering, California Institute of Technology
[2]Division of Engineering and Applied Science, California Institute of Technology

Caltech

Mechanical degradation in Li-S batteries

Discharging reaction: S_8 + 16 Li^+ + 16 e^- → 8 Li_2S

- Lithium-sulfur (Li-S) batteries have **high theoretical energy density/capacity** (2600 Wh kg^{-1},1672 mAh/g) and use low cost, earth abundant materials
- **80% volume expansion during discharge** causes mechanical degradation and capacity fade
- **When and how does Li_2S yield, deform, and fail?**
- Need **expansion-tolerant architectures** to mitigate mechanical degradation

Summary

Nanomechanical experiments

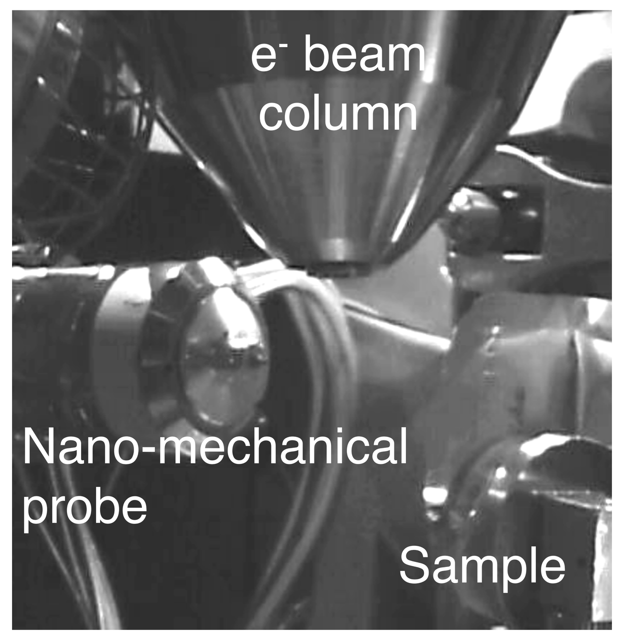
- We perform **in-situ SEM compression testing** of air-sensitive μm-sized Li_2S particles
- Li_2S yields and cracks at **contact pressures of ~500 MPa**, much higher than reported nominal stresses in composite Li-S cathode materials[3]
- Important to consider **spatially resolved stresses** and high stress configurations

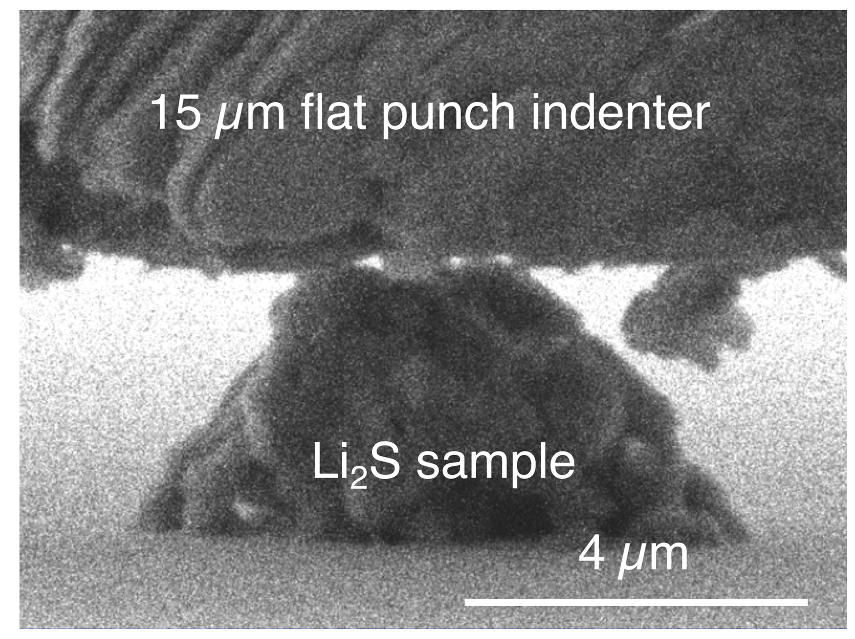
Additive manufacturing of Li_2S cathodes

- We introduce **emulsion stereolithography** and demonstrate fabrication of **Li_2S-C composites** with **50 μm feature sizes** (3x better resolution)
- Li_2S-C composites are tested as **free-standing cathodes for Li-S batteries**
- Promising route towards fabrication of expansion-tolerant cathode architectures

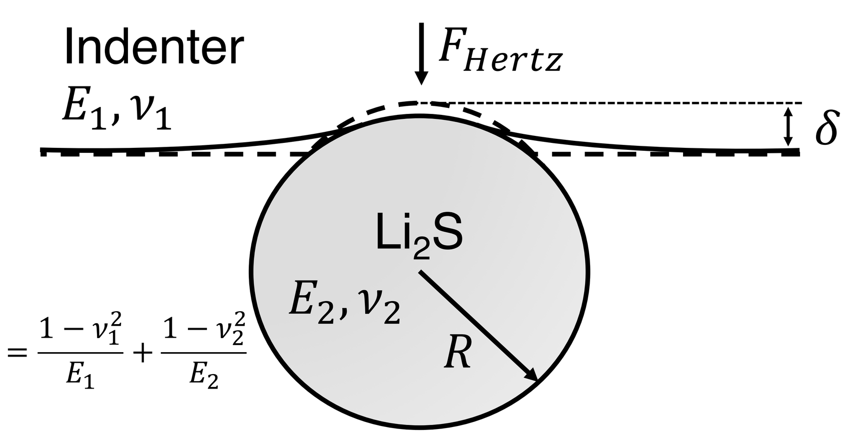
In-situ SEM Li_2S particle compression methodology

- Air-free transfer device allows Li_2S powder to be brought into SEM chamber for compression and imaging
- Probe **displacements are prescribed with nm precision** and resultant loads are measured
- **Hertzian model of elastic contact** between sphere and half-space[1] used to fit elastic portion of loading data
- Young's modulus E_1 and Poisson's ratio ν_1 are known properties of indenter, ν_{Li_2S} is predicted[2]





Hertzian elastic contact model

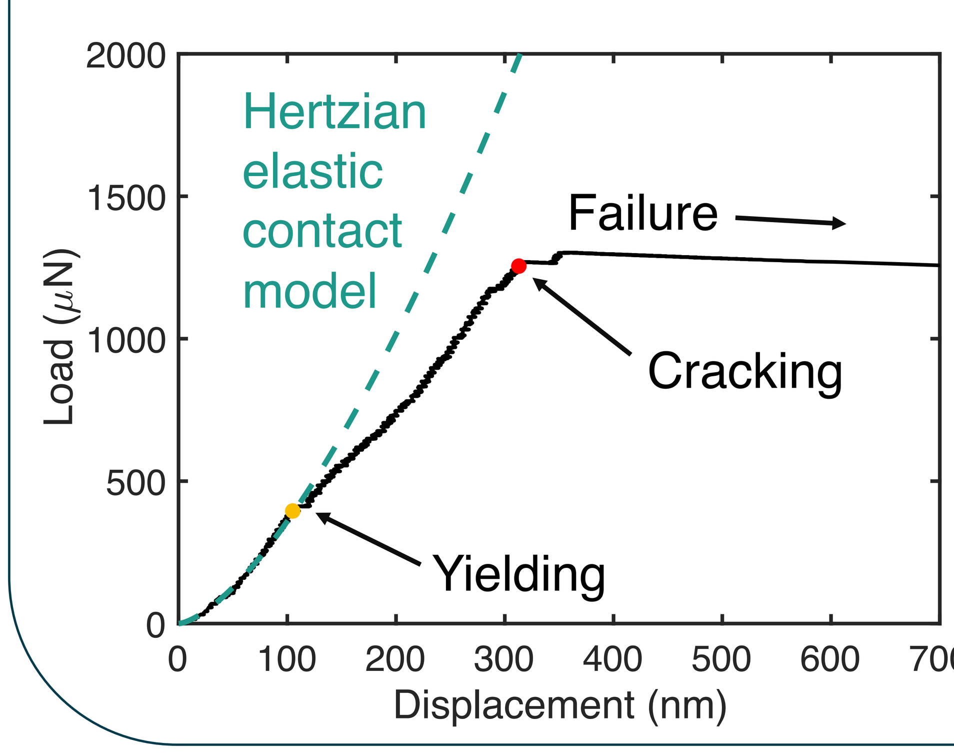


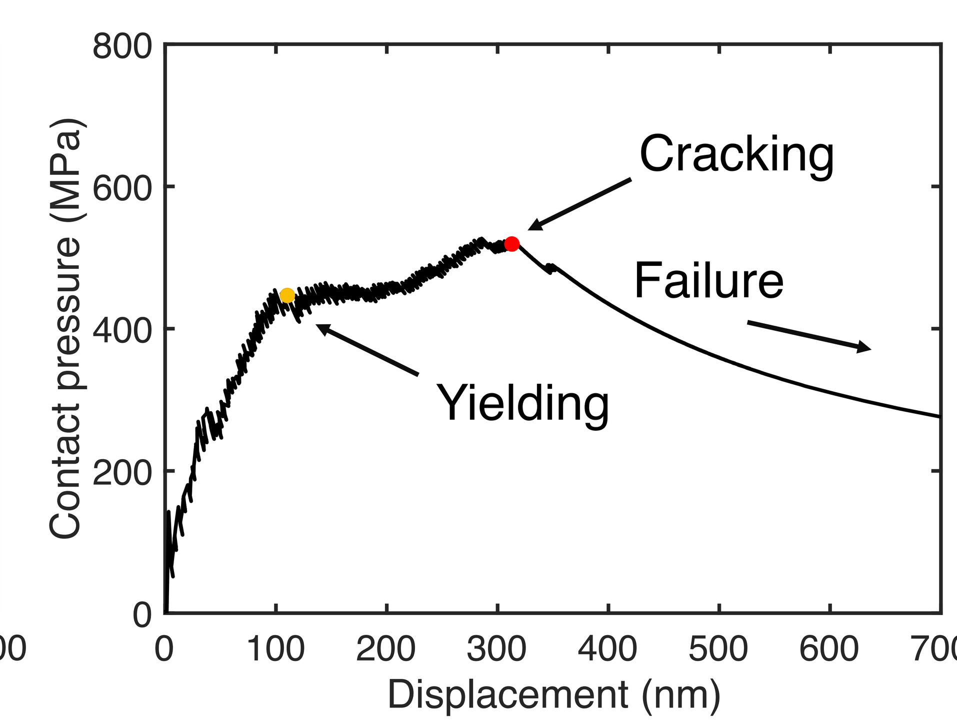
$$\frac{1}{E_R} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2}$$

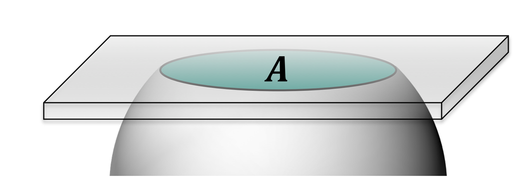
$$F_{Hertz} = \frac{4}{3} E_R R^{1/2} \delta^{3/2}$$

Yielding and mechanical deformation of Li_2S particles

- Hertzian elastic contact model matches experimental data until a **yielding event initiates plasticity**
- Ultimate failure is caused by **crack initiation and propagation**
- E_{Li_2S} is the free parameter in Hertzian elastic contact model, least squares fit gives $E_{Li_2S} = 7$ GPa



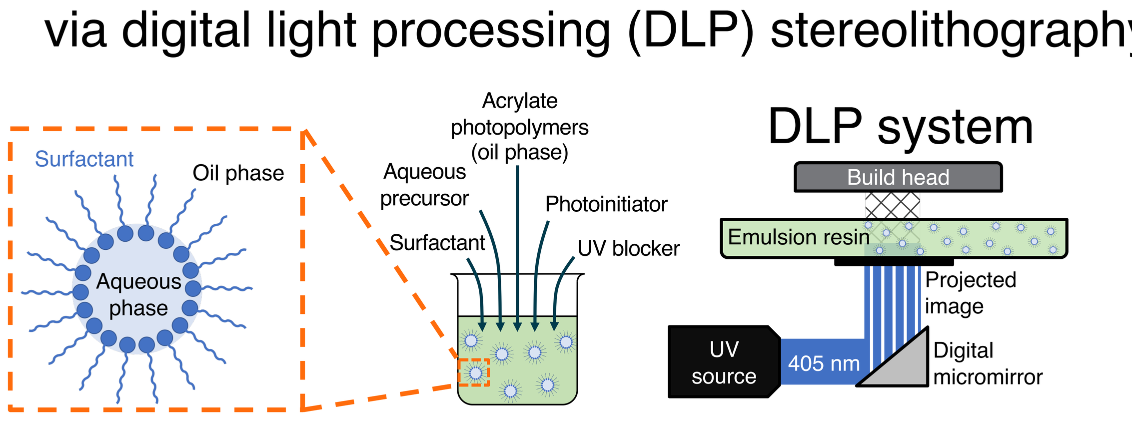


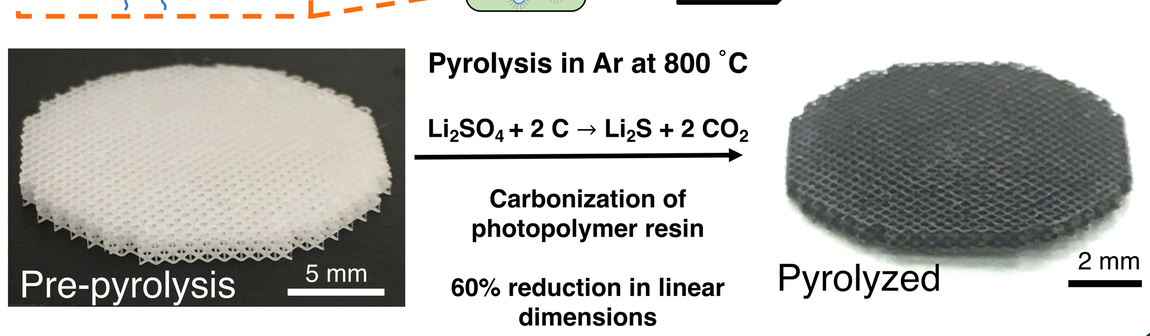


Contact pressure $P = \frac{F}{A}$

Additively manufactured Li_2S cathodes

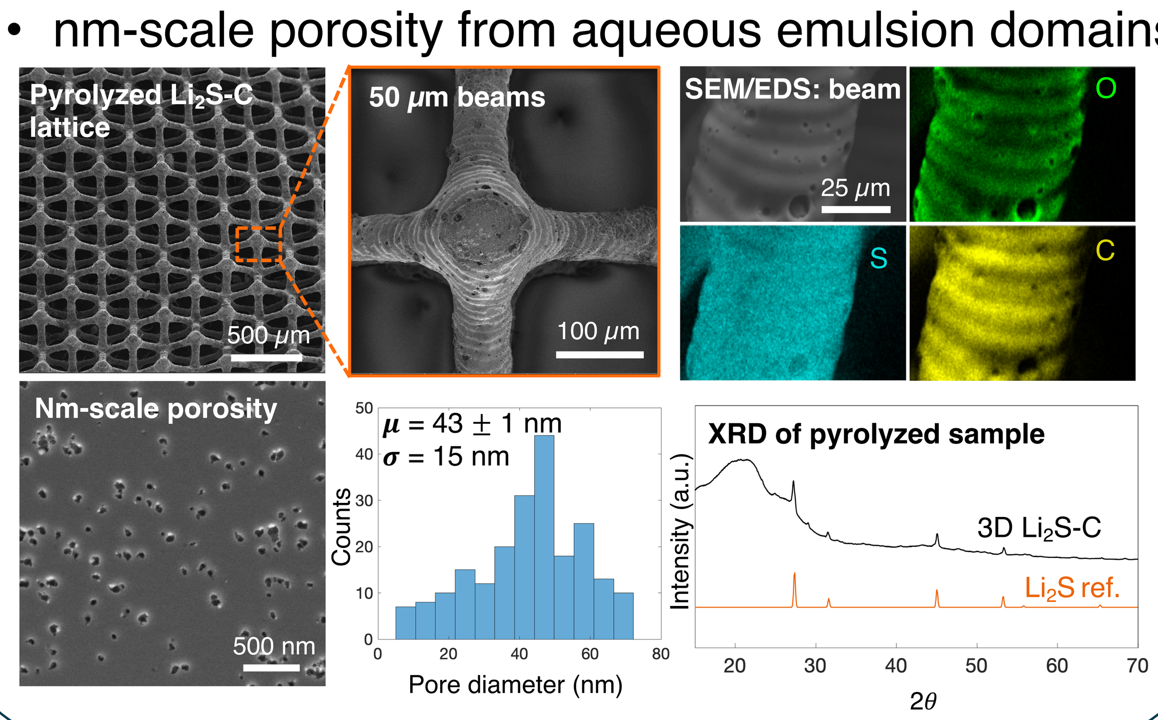
- **Emulsion resins** enable fabrication of composites via digital light processing (DLP) stereolithography



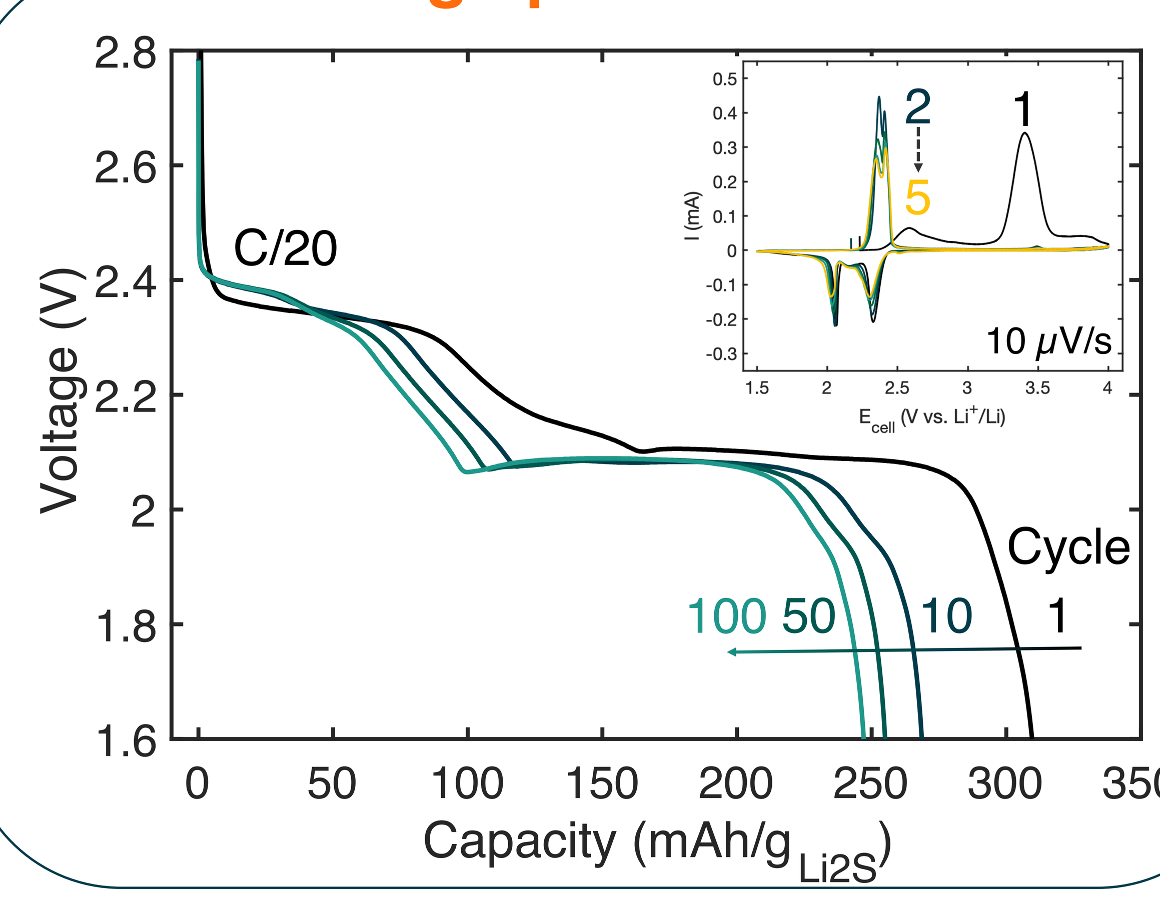


Structural and chemical characterization

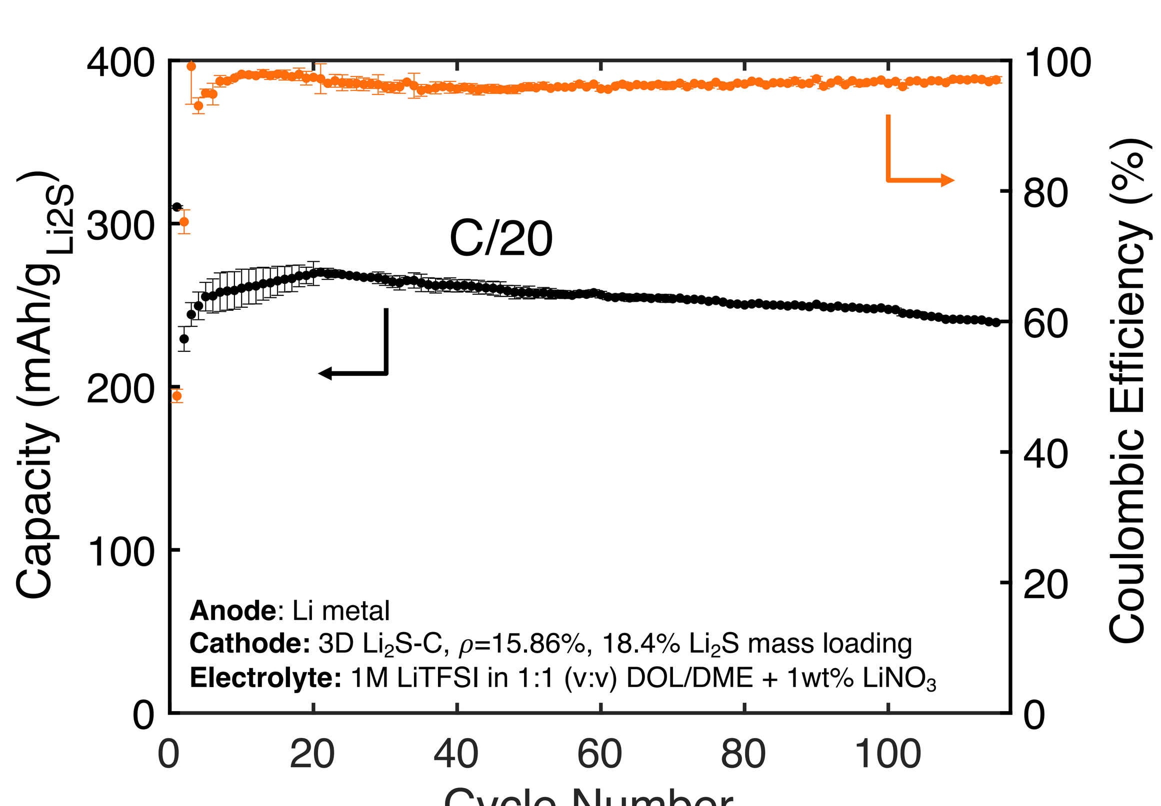
- EDS and XRD confirm crystalline Li_2S in structure
- nm-scale porosity from aqueous emulsion domains



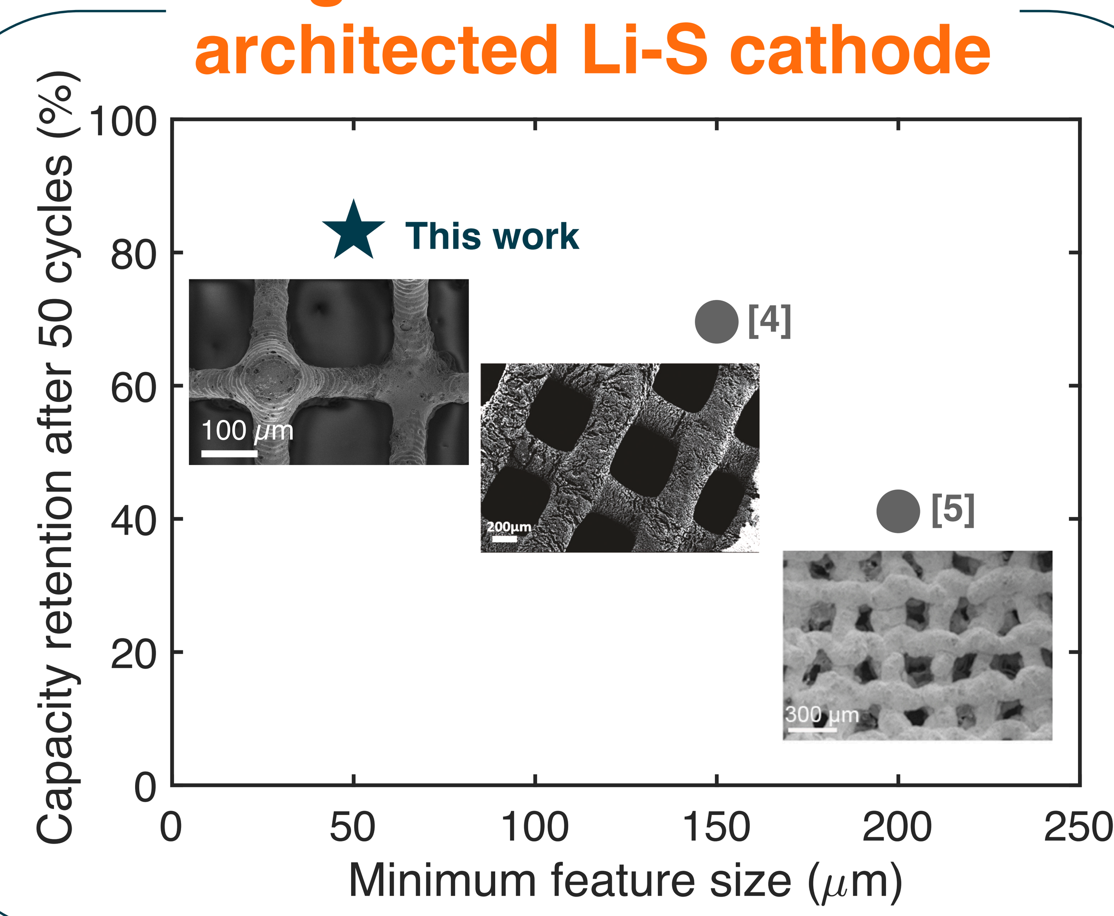
Discharge profiles and CV



Cycling performance



Highest resolution 3D architected Li-S cathode



Acknowledgements

Fellowship support from the **Resnick Sustainability Institute at Caltech** is gratefully acknowledged. Thanks to Professor Kimberly See (Caltech) for facilities and electrochemistry advice, and to Haolu (Jane) Zhang and Bryce Edwards for nanomechanics assistance.

Caltech

RESNICK INSTITUTE
science + energy + sustainability

References

1. H. Hertz, *J. Reine und Angewandte Mathematik* **1882**, 92, 156.
2. M. De Jong, *et al. Sci. Data* **2015**, *2*.
3. Y. Zhang, *et al. Energy Storage Mater.* **2019**, *16*, 491.
4. K. Shen, *et al. Adv. Energy Mater.* **2018**, *8*, 1701527.
5. X. Gao, *et al. Nano Energy* **2018**, *56*, 595.