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Multi-Modal & Multi-Dimensional and *Operando* Synchrotron Investigation of Energy-Storage Materials

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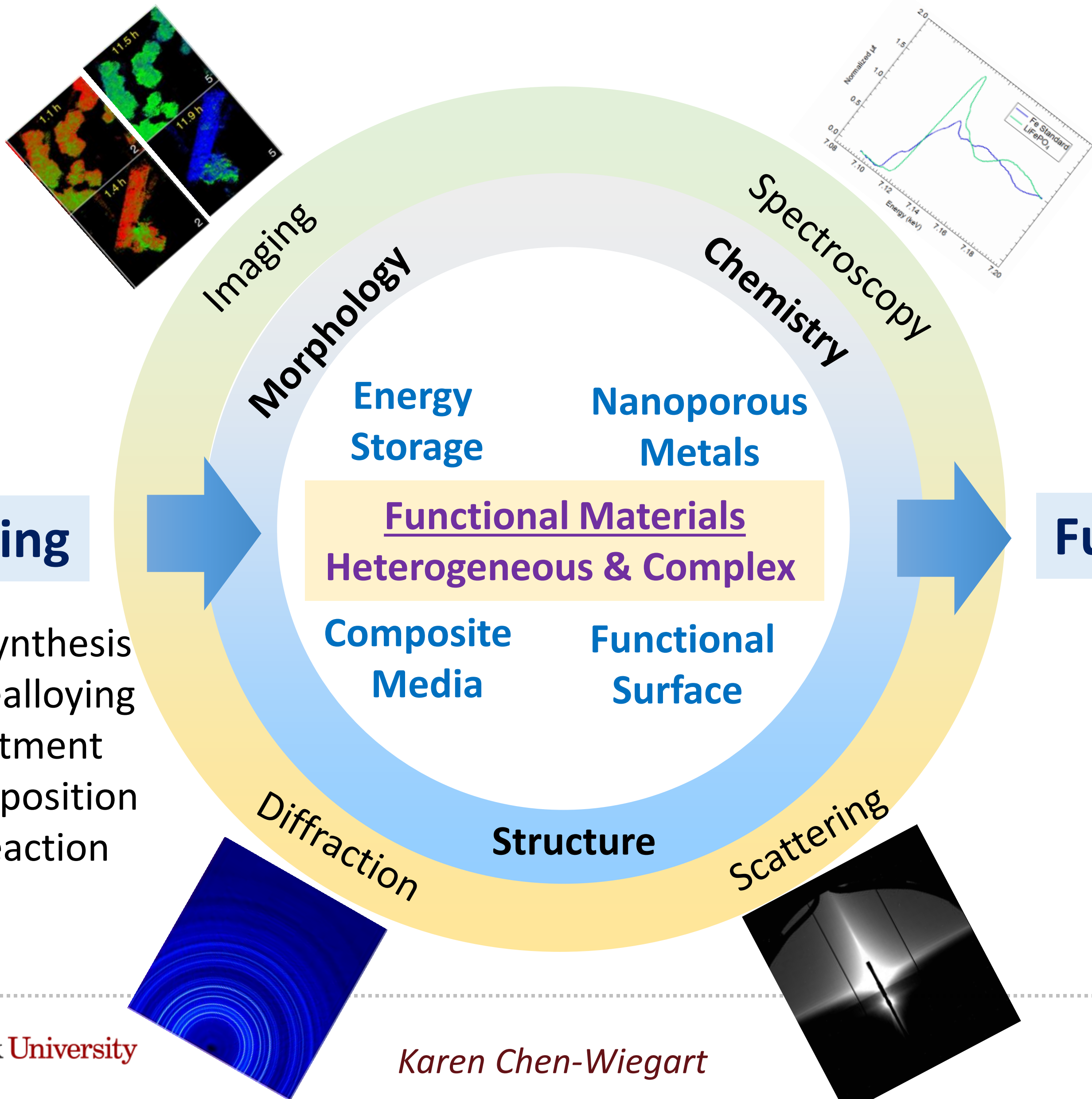
National Synchrotron Light Source – II, Brookhaven National Laboratory

FAR BEYOND

Multi-Modal Synchrotron Approach

Processing

Chemical synthesis
Alloying/dealloying
Heat treatment
This film deposition
Surface reaction



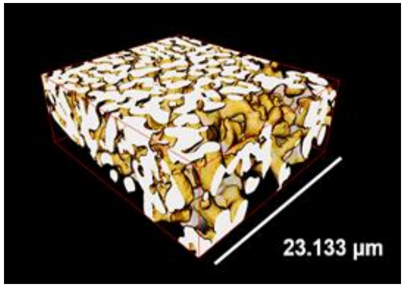
Functionalities

Capacity
Power density
Catalytic activity
Durability
Anti-corrosion

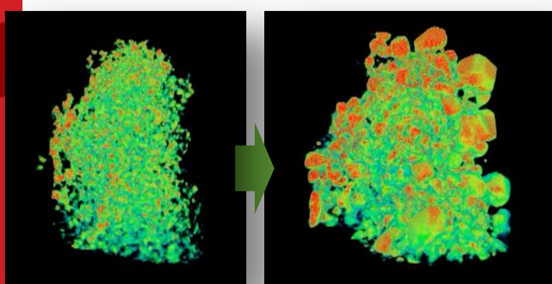
Multi-Dimensional X-ray Imaging

Need 1

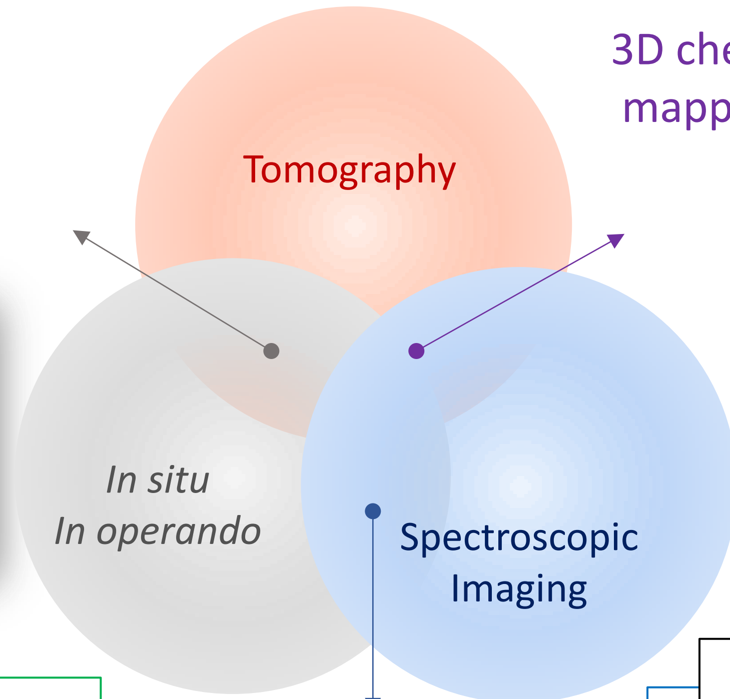
3 Dimensional (Spatial) Characterization



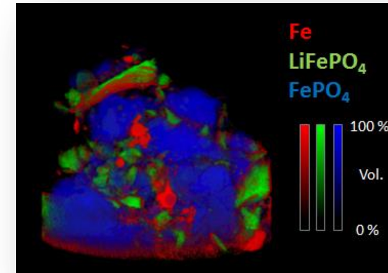
In situ 3D morphology evolution



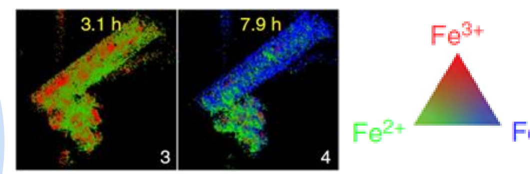
Solid oxide fuel cells



3D chemical mapping



Li-ion Battery



Li-ion Battery

Need 2

Time resolved with real Environment

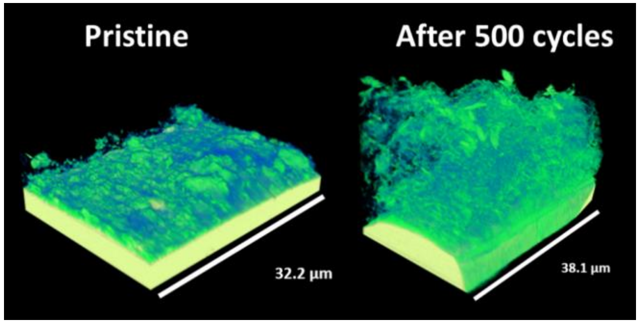
In situ chemical evolution

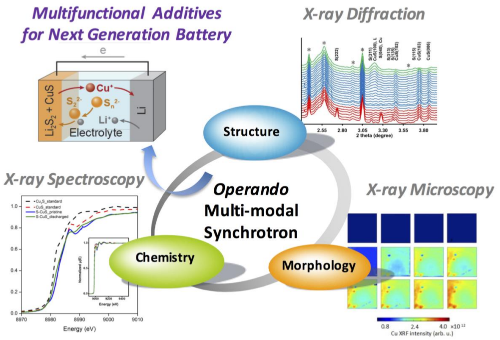
Need 3

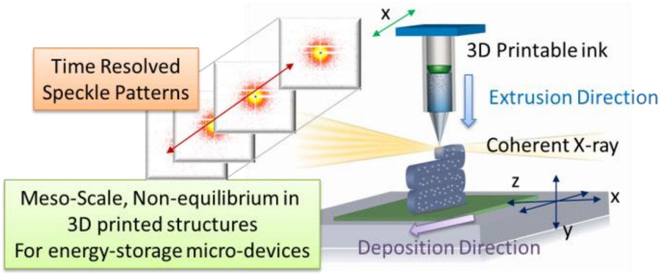
Elemental & Chemical sensitivity

Outline

- Nanoporous-Si Anode
  3D morphological Evolution
  - X-ray Nano-tomography
- CuS Additives in Li-S batteries
  - Multi-modal: XRF, XAS and XRD
- *In situ* study of 3D Printing
  for future energy storage
  - Coherent X-ray Scattering: XPCS







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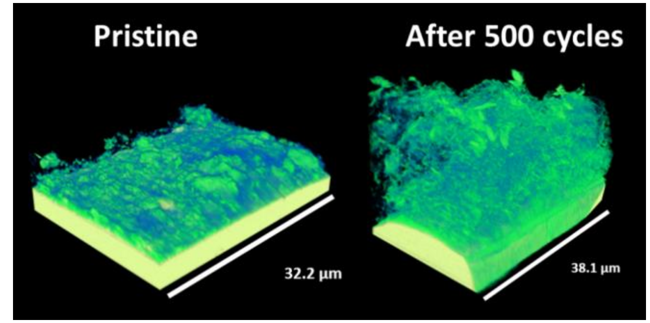

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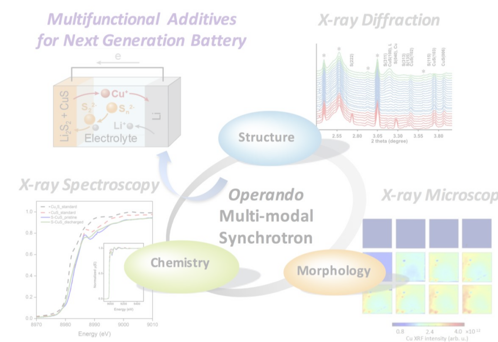

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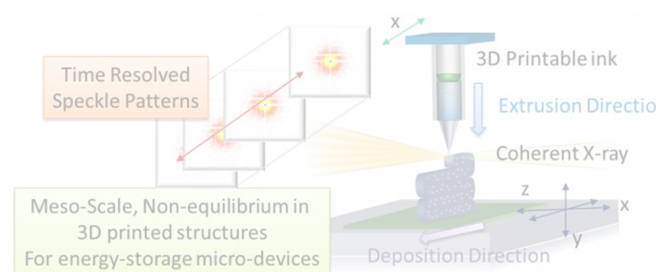
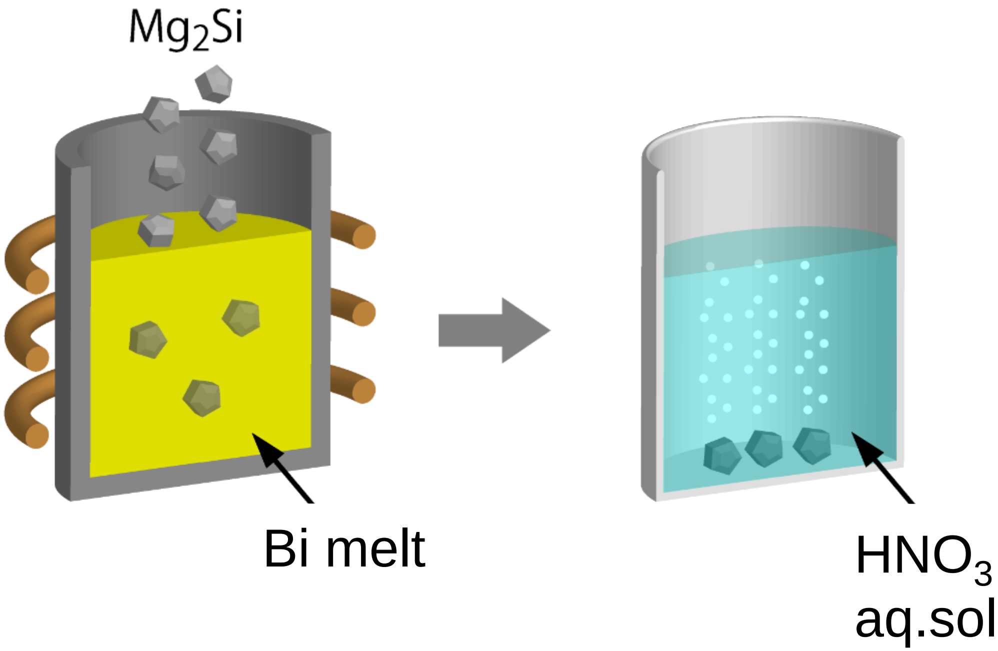
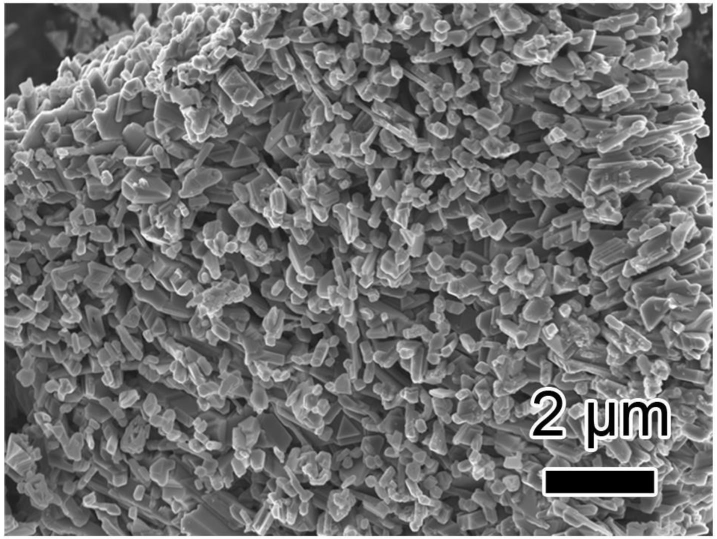
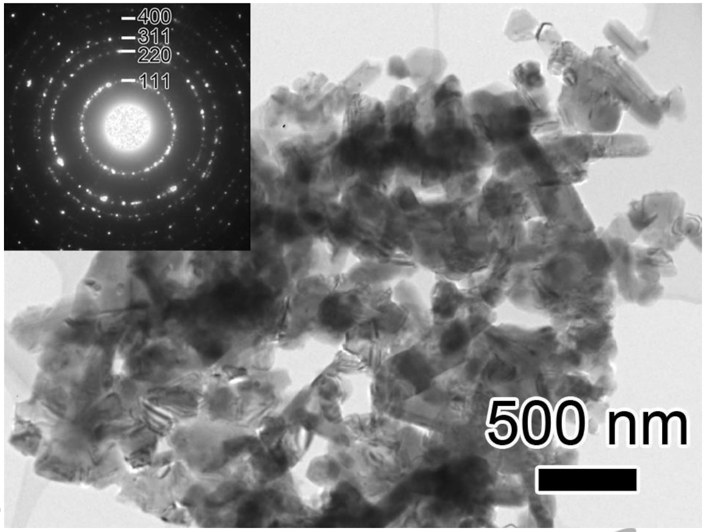


Nanoporous Si for Li-ion Battery Anode



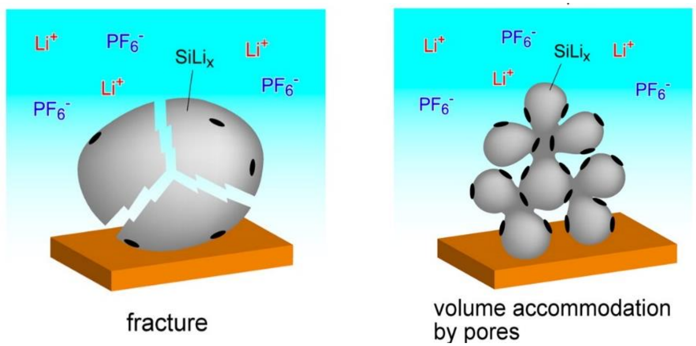




- Immersing Mg_2Si in Bi melt
- Collecting the floating powders(ρ_{Bi} >> ρ_{Si})
- Etching Bi from the collected powders
- Filtering & drying

Figures courtesy of Prof. Hidemi Kato (Tohoku University)

Challenges in nanoporous Si anode



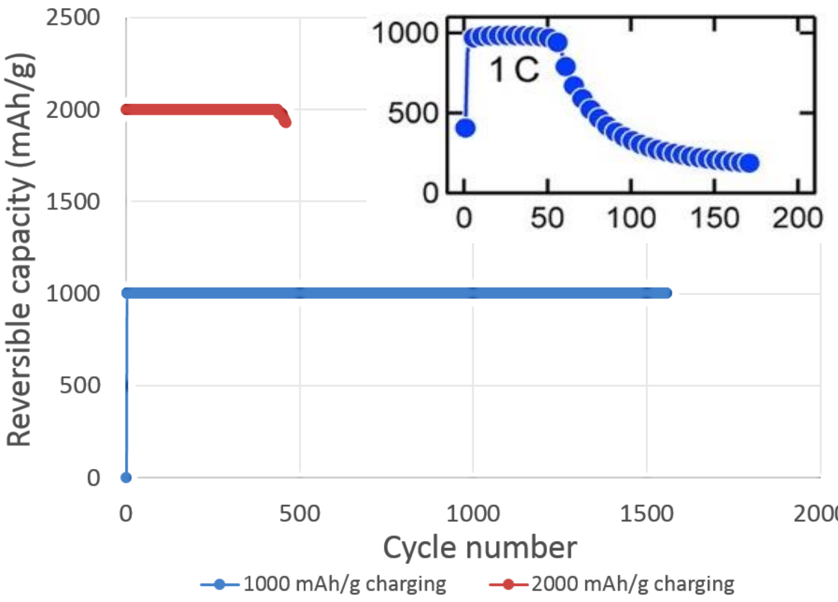
nanoparticle

Bulk 3DNP-Si

- Porosity: 60.4%
- Ideal volume accommodation limit: 253%
- Correspond lithiation capacity:
  – 2000 mAh/g

- Capacity-dependent behavior
  - 1000 mA/h-g: over 1500 cycles
  - 2000 mA/h-g: < 500 cycles

3D morphological change
v.s. different charging capacity?



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Wada, Takeshi, et al. "Bulk-nanoporous-silicon negative electrode with extremely high cyclability for lithium-ion batteries prepared using a top-down process." *Nano letters* 14.8 (2014): 4505-4510.

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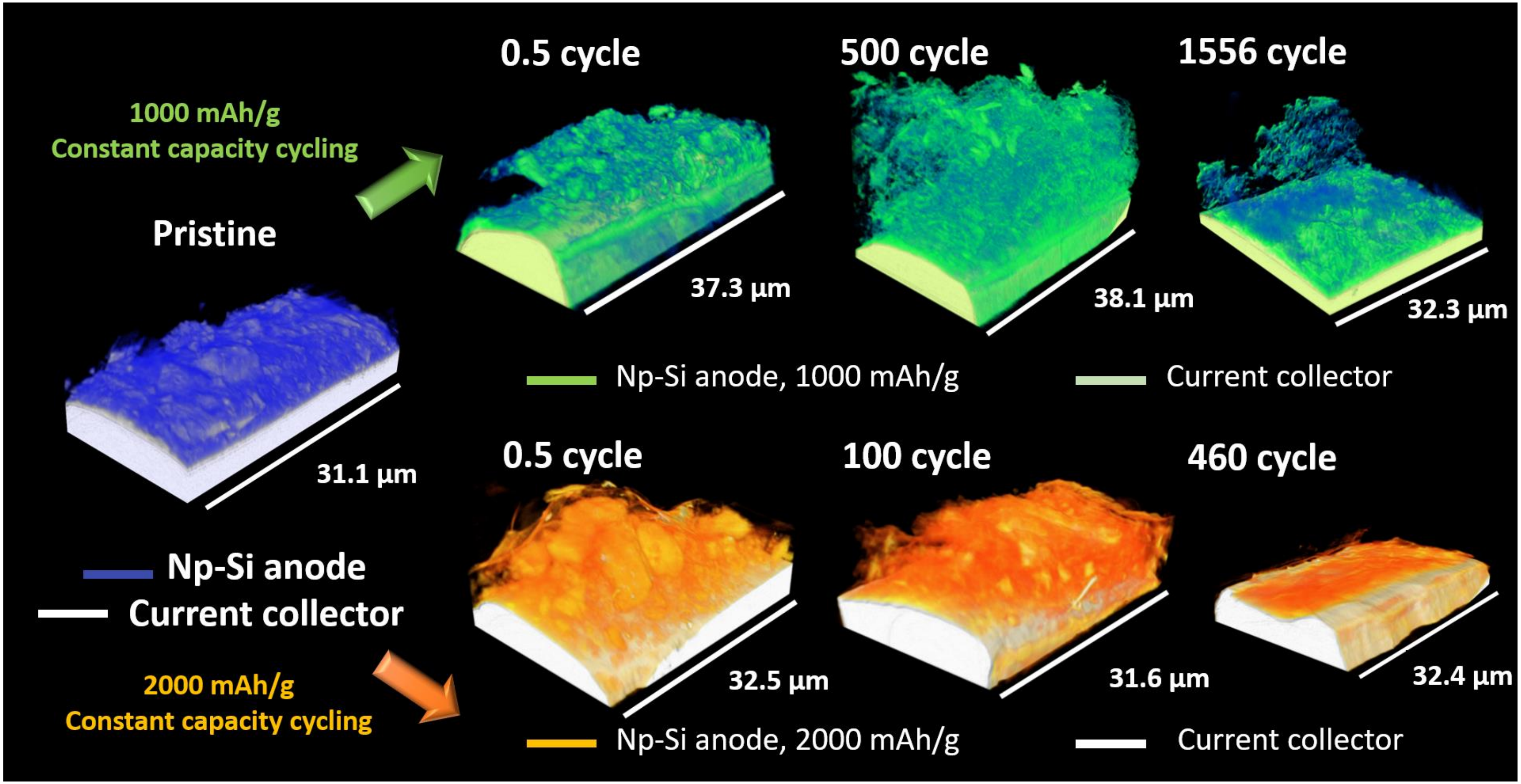
Capacity Dependent 3D Morphological Evolution of Nanoporous Si Anode



Chong Zhao, et al., to be submitted

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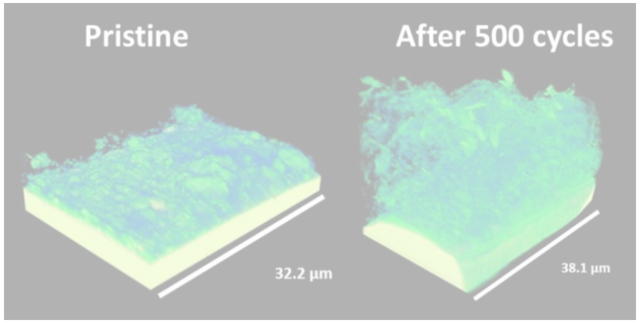
  - X-ray Nano-tomography



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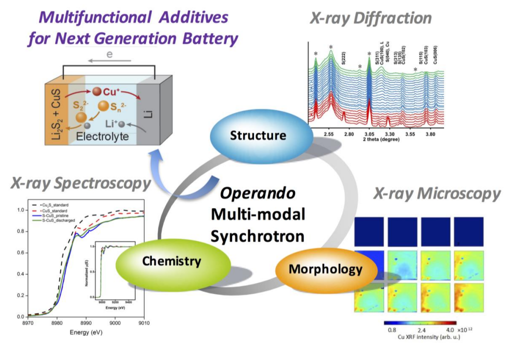

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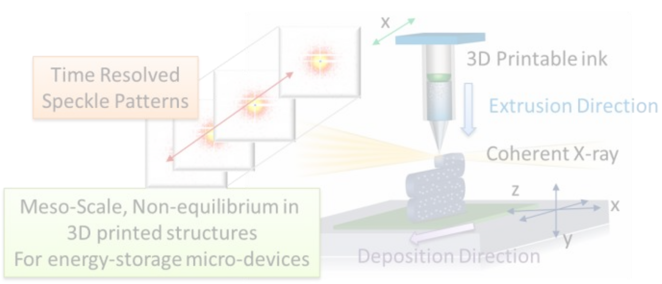
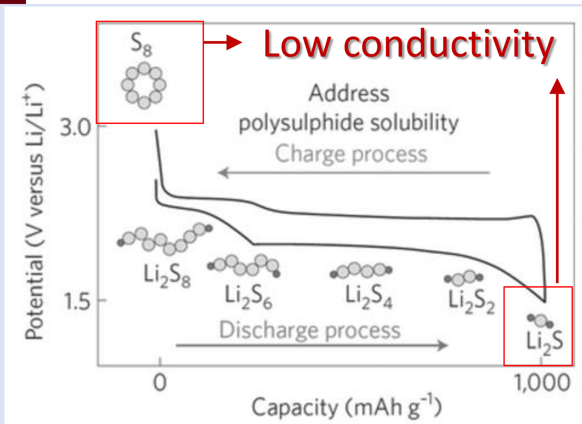


Mechanistic Understanding of Li-S Batteries with Hybrid Electrodes: Multi-functional Additive

- **Li-S battery:** much higher energy density (6x by weight) & lower cost
- Hybrid electrodes utilizing metal sulfide additives: conductivity ↑ & capacity +



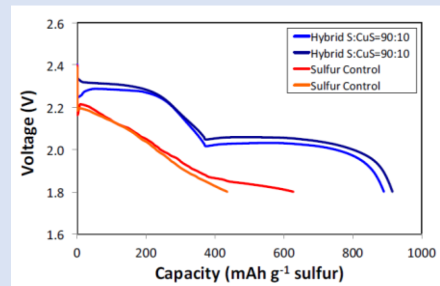
Capacity-Contributing **Conductive** Additives

Metal Sulfide - Sulfur Hybrid Electrode

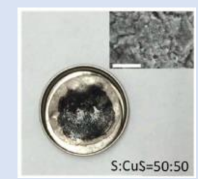
CuS-S, FeS_2-S, TiS_2-S, etc

Higher power capability

Capacity↑ @ high rate discharge



Poorly understood Interactions & Side-reactions

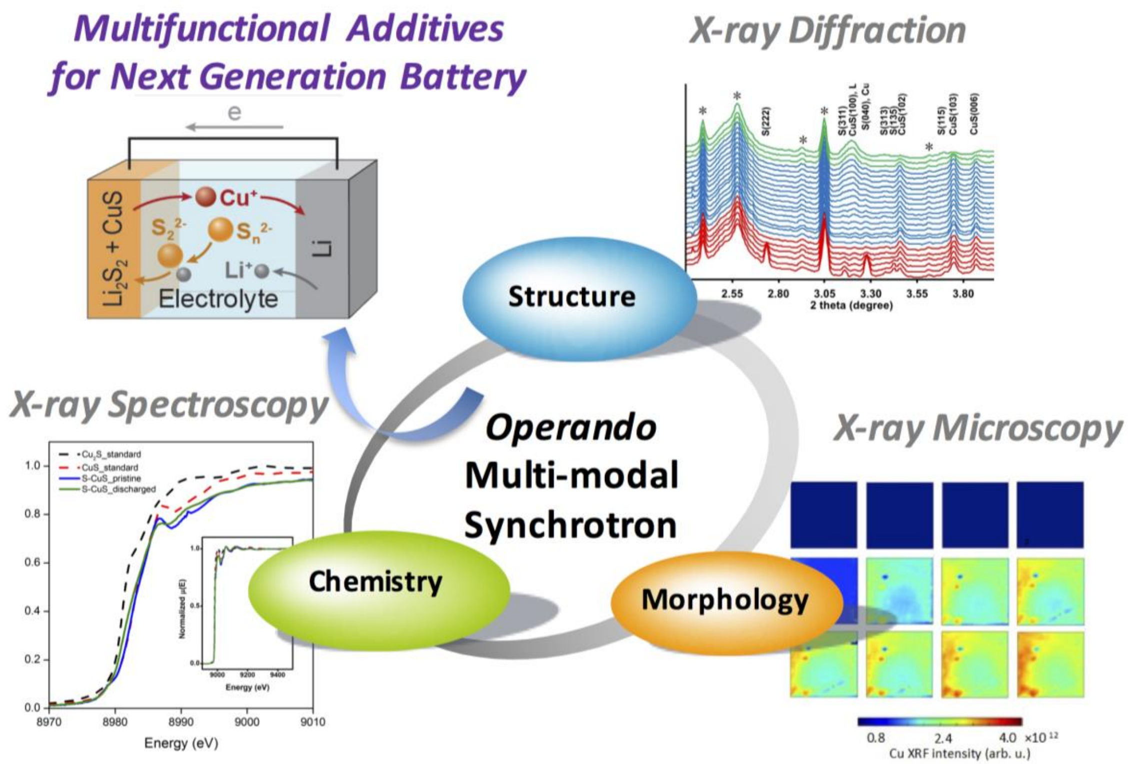


Dissolution/Re-deposition

- **Interaction between components (sulfur cathode, additives, Li anode, & electrolyte) at the system level & side-reactions :**
  complex, specific to each type of additive with vastly different behavior, poorly understood
- **Understanding mechanisms** → guide designing better additives → Li-S performance ↑

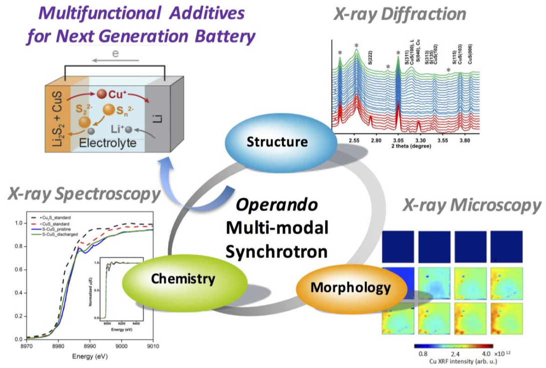
Conventional closed-cell electrochemical characterization
→ average of different processes → no longer sufficient

Operando Multi-modal Synchrotron Investigation for Structural and Chemical Evolution of CuS Additive in Li-S battery



Ke Sun, Chonghang Zhao, Cheng-Hung Lin, Eli Stavitski, Garth Williams, Jaiming Bai, Eric Dooryhee, Klaus Attenkofer, Juergen Thieme, Yu-chen Karen Chen-Wiegart, Hong Gan, Scientific Reports (2017)

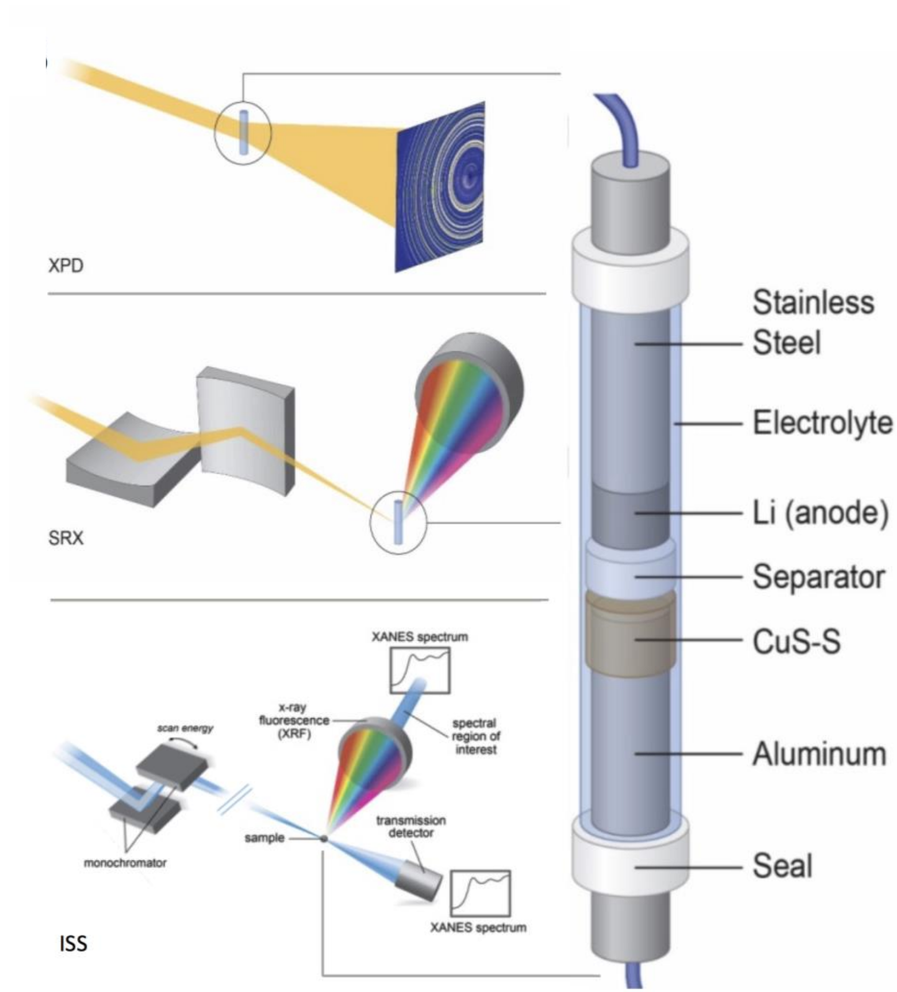
Operando Multi-modal Synchrotron Investigation for Structural and Chemical Evolution of CuS Additive in Li-S battery



X-ray powder diffraction (XPD) 28-ID-2, NSLSII
- Wavelength: 0.1838 & 0.2362 Å
- Beam size: 0.5 mm^2
- Technique: X-ray Powder Diffraction

Inner-Shell Spectroscopy (ISS) 8-ID, NSLSII
- Beam energy: Cu K-edge (8979 eV)
- Spot size: 0.8 mm × 0.3 mm (h × v)
- Technique: X-ray Absorption Spectroscopy

Sub-micron Resolution X-ray Spectroscopy (SRX), 5-ID, NSLSII
- Beam energy: 10 keV
- Spot size: ~ 1 μm
- Technique: X-ray Fluorescence Microscopy



Ke Sun et al., Scientific Reports (2017)

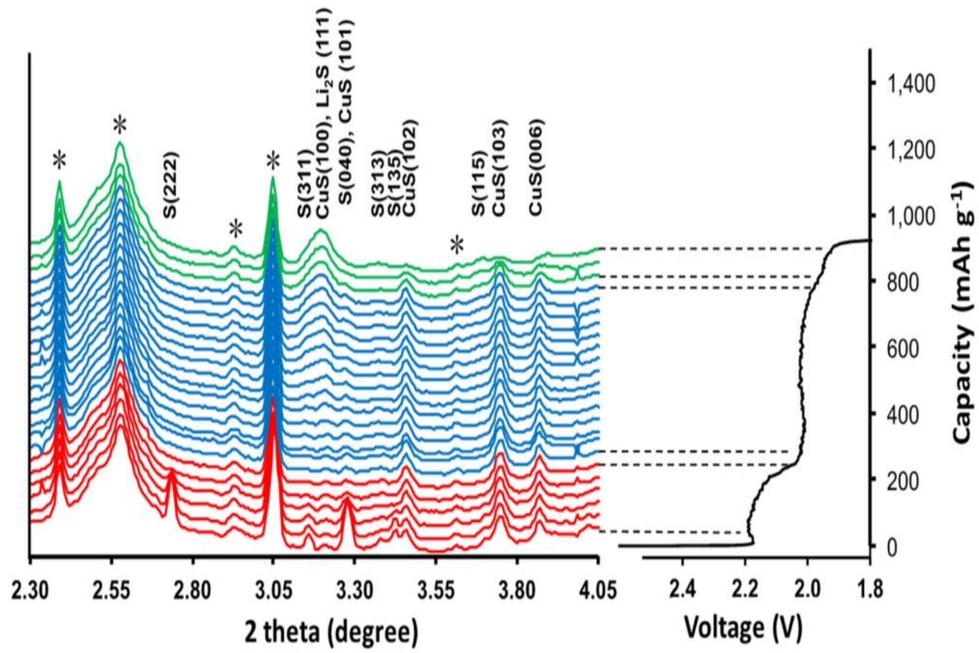
Operando X-ray Diffraction at XPD, NSLS-II

- Reactions during discharge:
  - 2Li + 2CuS ⇒ Cu_2S + Li_2S (~2.14 V with slow rate)
  - $2Li_2S_n$ -> Li_2S_2 (~2 V, liquid-solid reduction)

- The only new peak emerging is Li_2S(111)

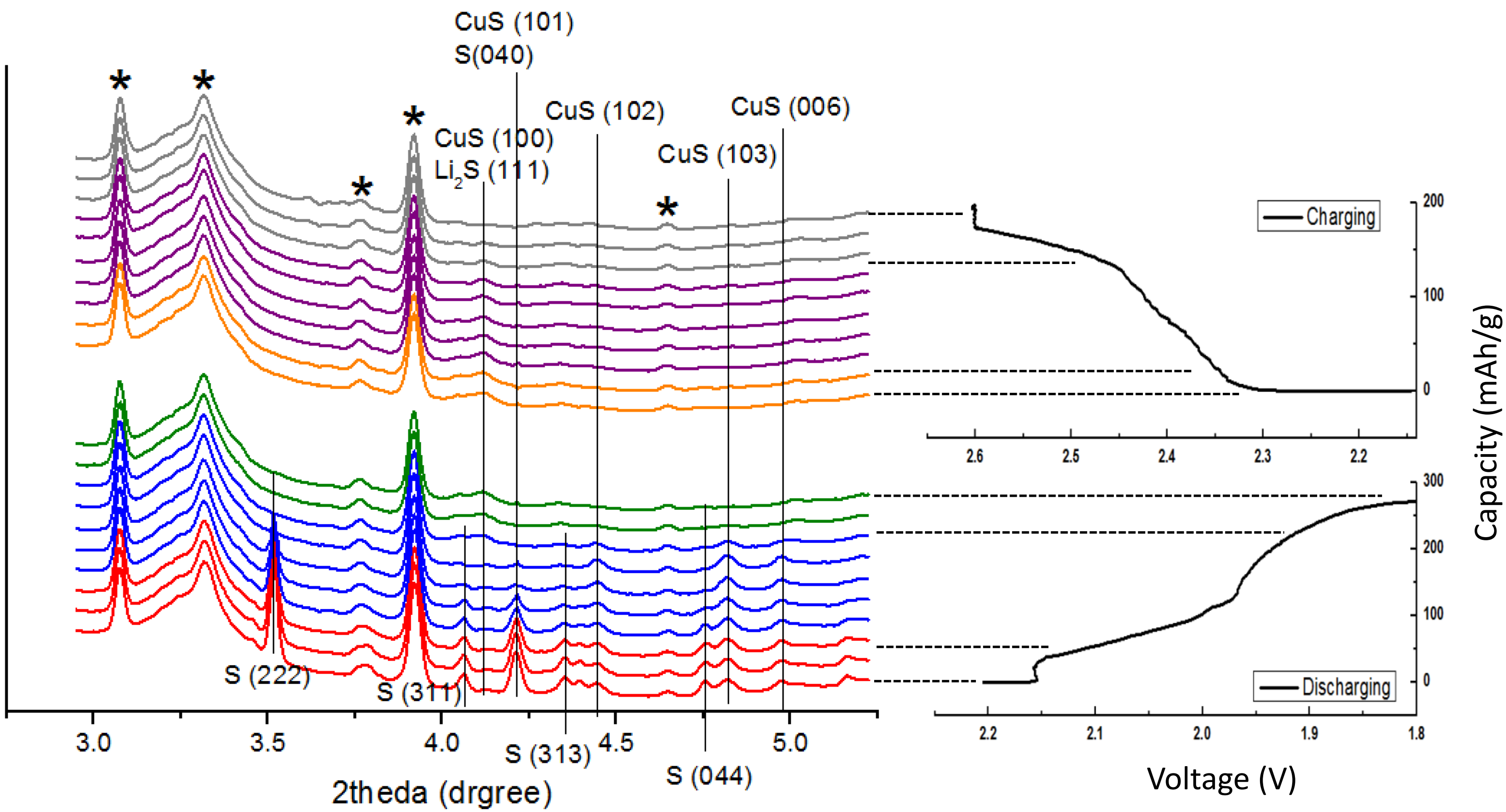
- No Cu_2S detected during the discharge in diffraction patter may be due to amorphous phases

- Metal Cu is also not observed due to the cut-off voltage at 1.8 V.



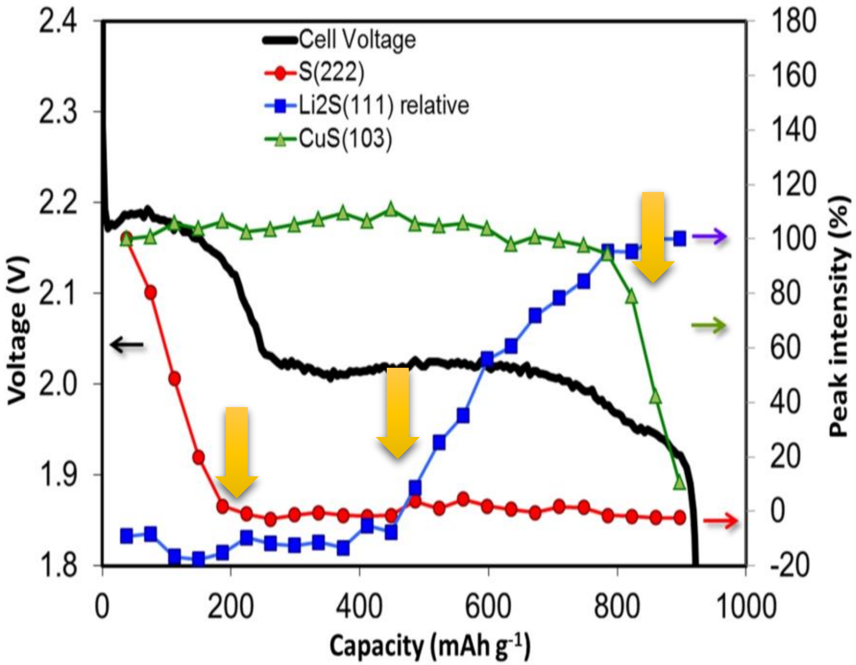
Ke Sun et al., Scientific Reports (2017)

Operando X-ray Diffraction at XPD, NSLS-II Lithiation and De-lithiation



Phase Evolution during Discharge by Operando X-ray Diffraction

The area of three strong peaks were integrated at each depth of discharge.



Ke Sun et al., Scientific Reports (2017)

1) S (222) decreases right after lithiation

→ crystalline sulfur convers in to polysulfides → dissolve into the electrolyte

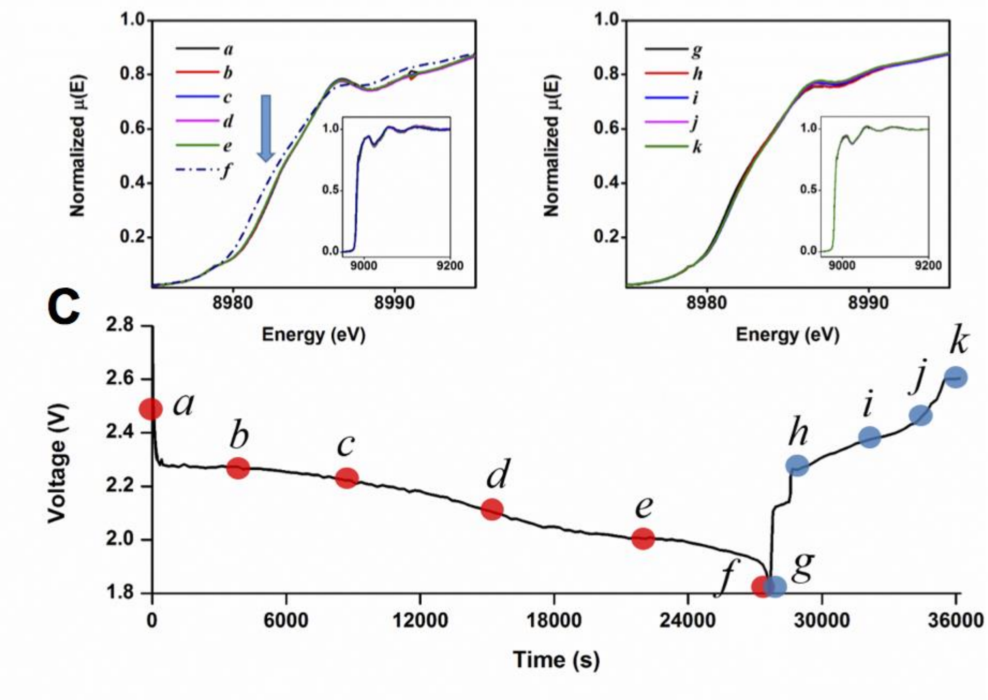
2) Li_2S (111) only appears at ~43% capacity

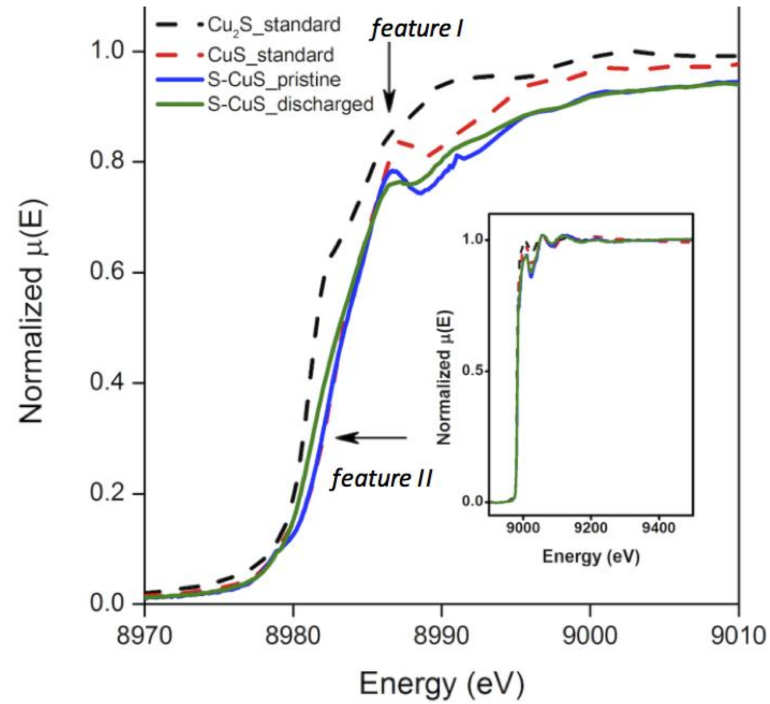
→ nucleation after the solid sulfur is fully converted into polysulfides and Li_2S_2 remains amorphous

3) CuS (103) intensity only decreases until the end of discharge

→ conversion of Li_2S_2 to Li_2S occurs ahead of CuS reduction

Operando X-ray Absorption Spectroscopy (XANES)





- Series of *operando* Cu K-edge XANES spectra during cycling:

→No XANES spectral evolution until end of discharge (point *f*)

→ Consistent with Operando XRD

- At the end of discharge (point f): two changes in the XANES spectum
  - *feature I*, which is characteristic for CuS, in Fig. D becomes less prominent
  - *feature II*, the edge jump shifts to lower energies

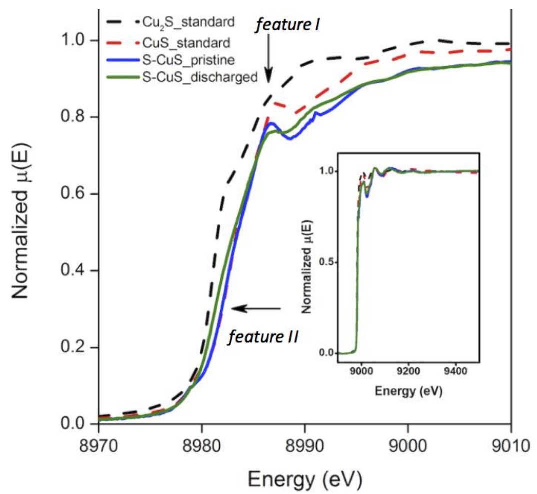
Ke Sun et al., Scientific Reports (2017)

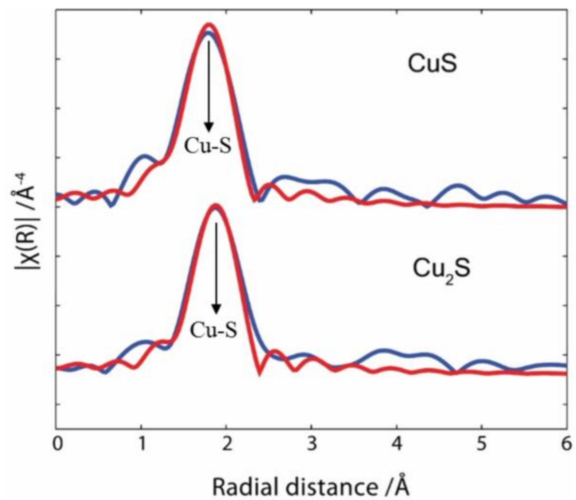
Operando X-ray Absorption Spectroscopy (EXAFS): Structural analysis after full discharge,

- the Cu-S coordination number is reduced from 2.5 to 2.1

→ An elongation of the average bond length from 2.27Å to 2.29Å.

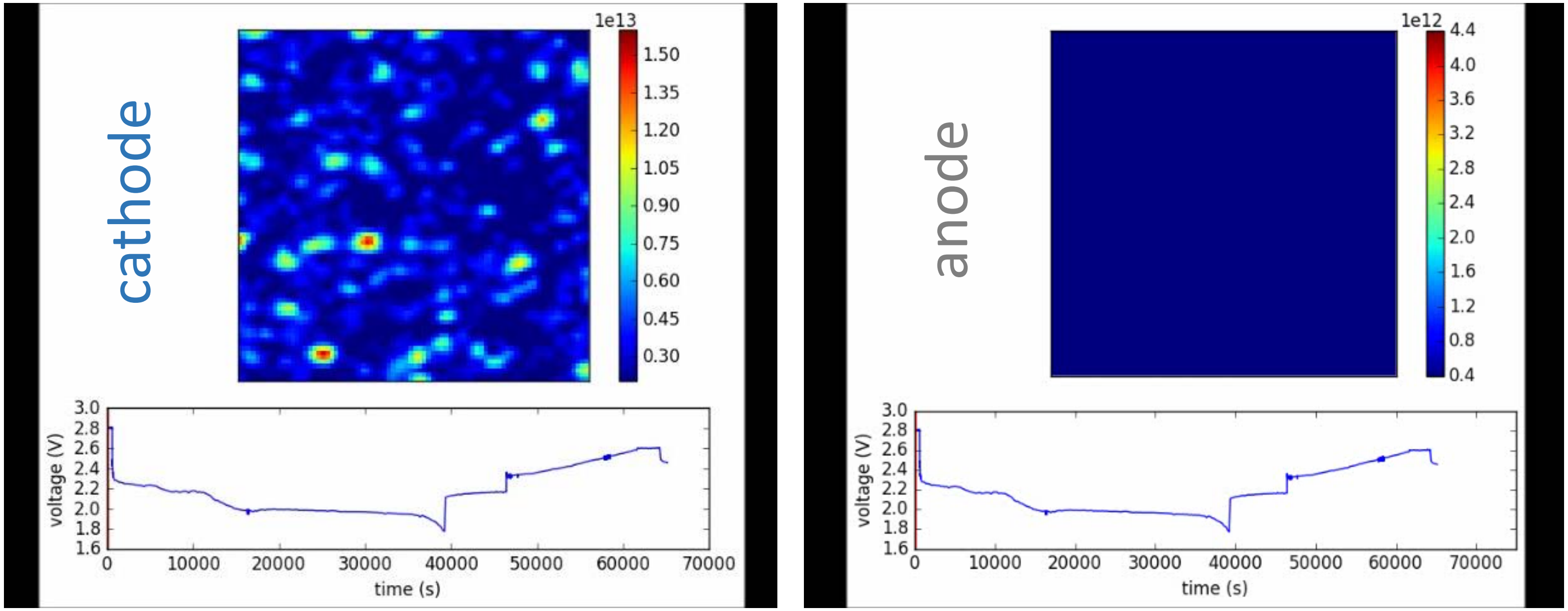
- The average composition of the discharged material ~ $Cu_{1.3}S$.





Sample	Cu-S coordination number	Cu-S distance, Å	Debye-Waller factor
CuS (standard)	2.5 ± 0.2	2.272 ± 0.002	0.01± 0.001
Cu_2S (standard)	1.5 ± 0.3	2.315 ± 0.02	0.02± 0.003
Discharged (point *f*)	2.1 ± 0.2	2.289 ± 0.02	0.01± 0.003

Operando XRF studies on Cu dissolution/re-deposition in Li-S battery with CuS additives



X-ray Spectroscopic Imaging: morphology & chemistry

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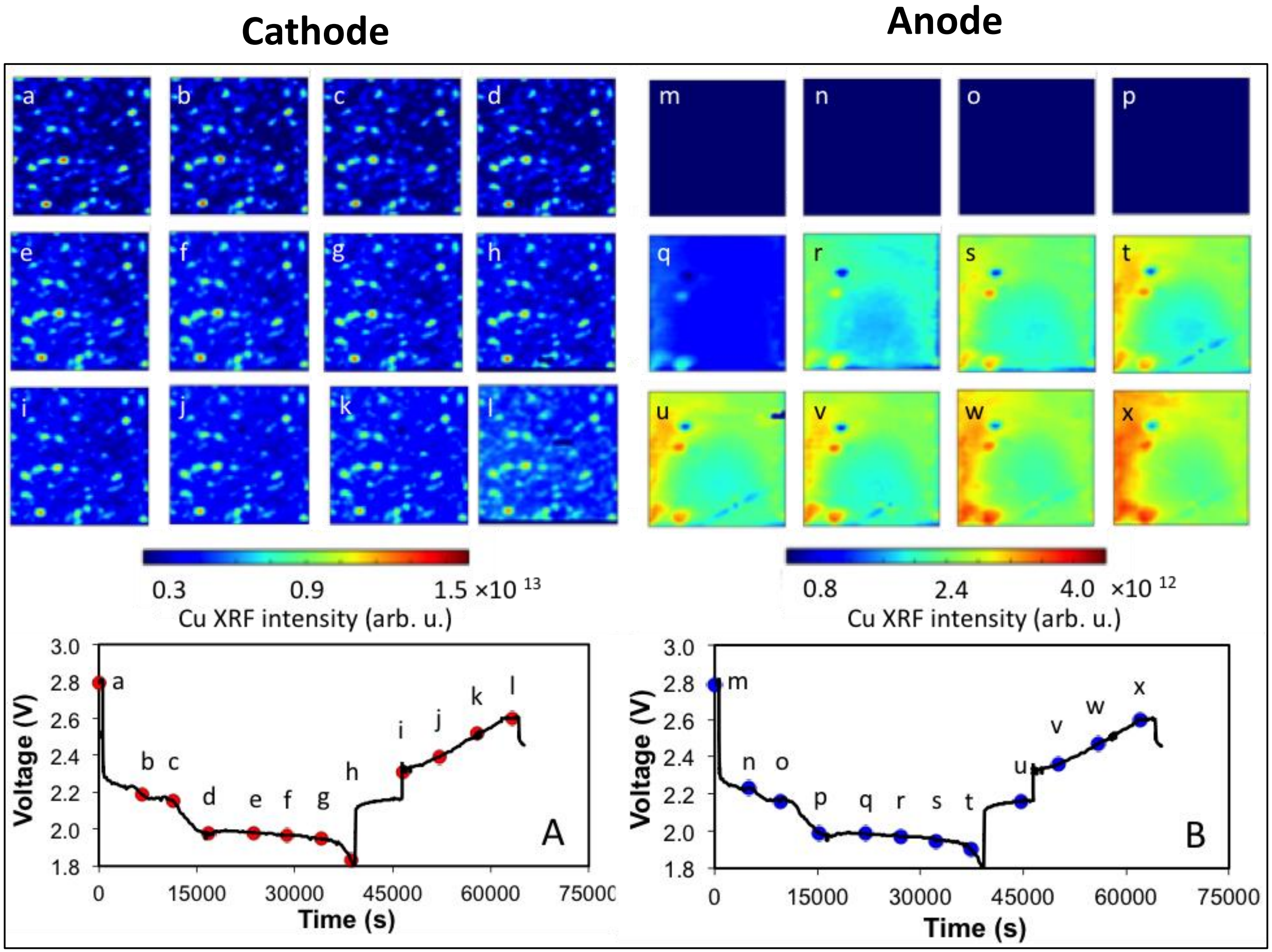
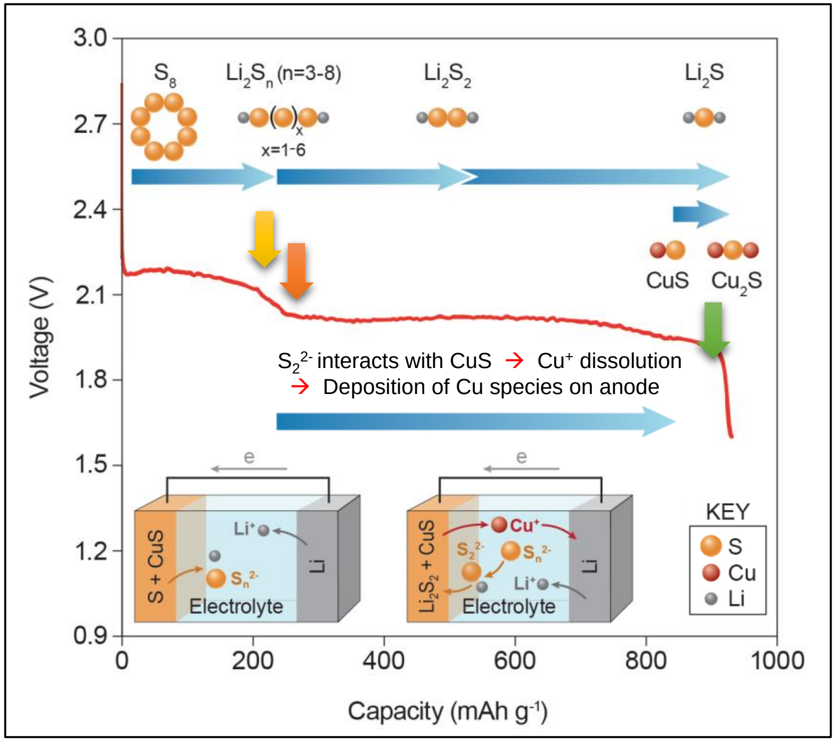


Ke Sun et al., *Scientific Reports (2017)*

Mechanistic Understanding on CuS Additives Interaction in Li-S battery

The crystalline sulfur cathode is completely consumed during the initial 21% of cell discharge, converted to high order polysulfide (Li_2S_n, n = 4 to 8).



The lithiation of CuS starts at the very end of discharge to form amorphous Cu_2S at ~1.95V. During this process, CuS interacts strongly with soluble low order polysulfide species, either super saturated S_2^{2-} or S^{2-} . The dissolved Cu-ions then migrate from the cathode side to the anode side through the electrolyte, changing SEI layer and leading to capacity fade.

Starting from ~25% to ~43% cell discharge (beginning of the plateau discharge region), the conversion of polysulfide to amorphous phase Li_2S_2 happened, followed by conversion of Li_2S_2 into Li_2S by additional lithiation up to ~85% cell discharge.

Ke Sun et al., Scientific Reports (2017)

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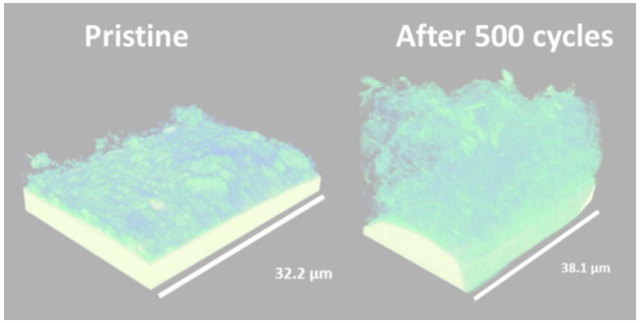

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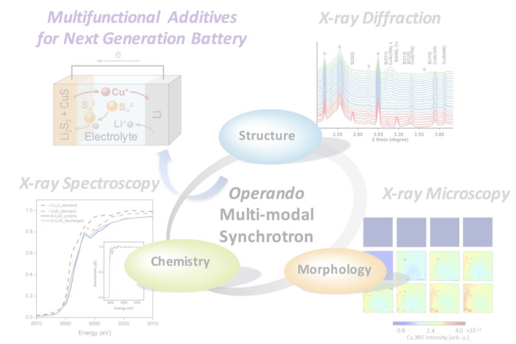

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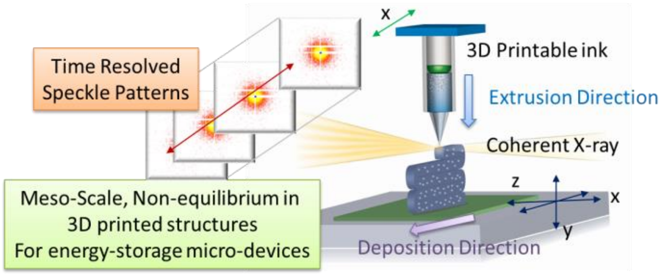
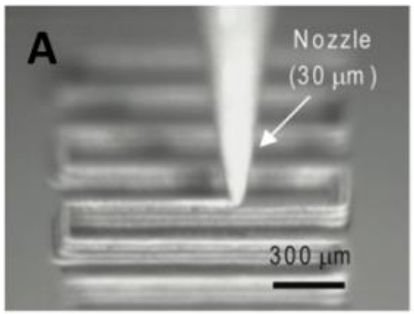
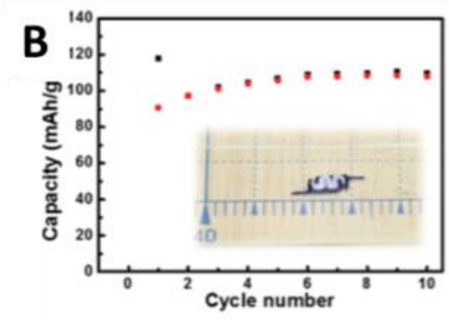


Meso-Scale Dynamics of 3D-Printing by *In Situ* Multi-modal Synchrotron Approach

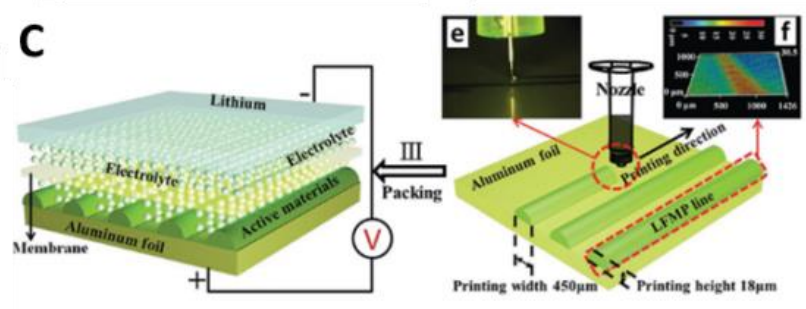
3D printing energy-storage micro-devices, or micro-batteries



Sun et al., Adv. Materials ***2013***

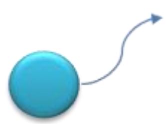


Fu et al., Adv. Materials ***2016***



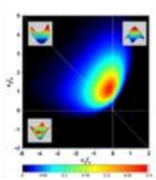
Hu et al., Adv. Energy Mat. ***2016***

Meso-structures determine critical properties in a 3D printed structure

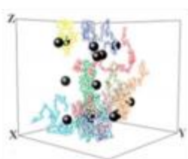


Particle motions

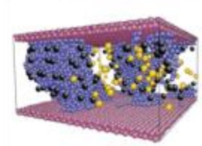
Particle-particle interactions



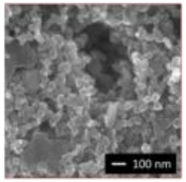
Interfacial phenomena



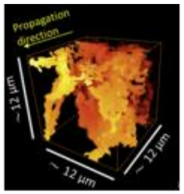
Percolation



Phase distribution/ separation



Porosity/ Pore size distribution



Tortuosity distribution

nm ***Tens of nm*** ***Hundreds of nm*** ***µm***

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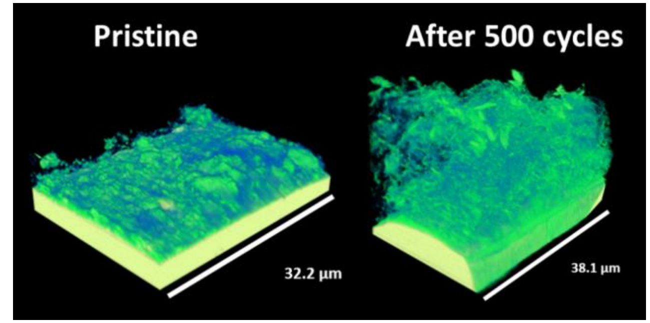

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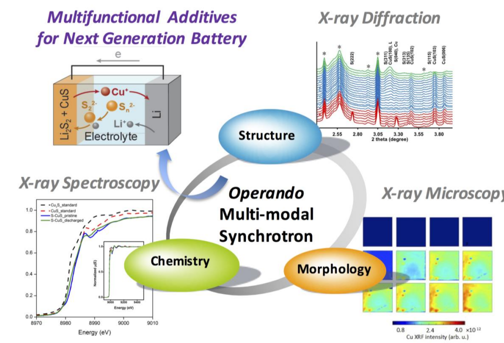

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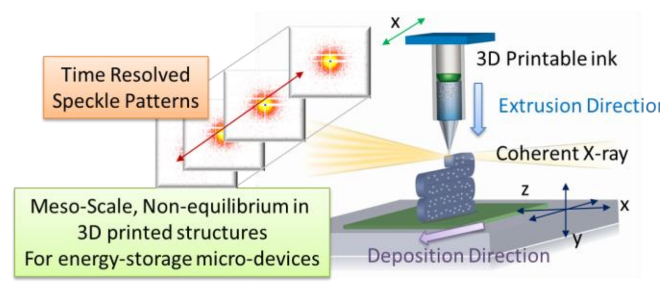


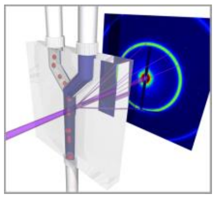
Suite of beamlines with complementary techniques – Enabling time-resolved, *operando*, multi-modal and multi-dimensional studies

Scattering | **Diffraction** | **Spectroscopy** | **Imaging**

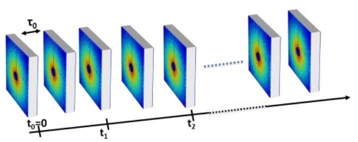
Structure

Chemistry

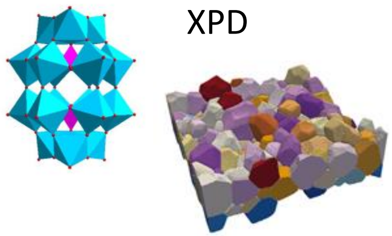
Morphology



CMS

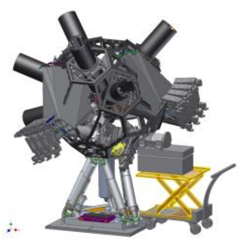


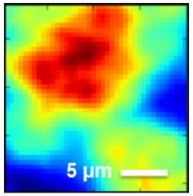
CHX



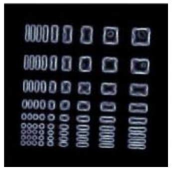
XPD

ISS



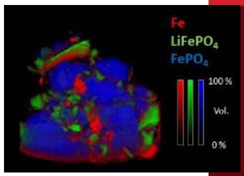


SRX



HXN

FXI



(XPD): X-ray Powder Diffraction

(ISS): Inner Shell Spectroscopy

(SRX): Sub-micron Resolution X-ray Spectroscopy

(CMS): Complex Materials Scattering

(HXN): Hard X-ray Nanoprobe

(CHX): Coherent Hard X-ray

(FXI): Full-Field X-ray Imaging

The Multi-Modal Issues Task Force @ NSLS-II

to identify the issues involved in **utilizing techniques across multiple beamlines** at NSLS-II, and in combining synchrotron techniques with **other techniques, such as the electron-based imaging methods at CFN**.

Potential research schemes and impact

Supporting facilities & functions

User access

Multi-modal Approach

Beamline hardware

Software

Goal

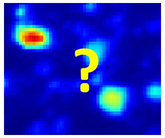
Logistics

Techniques

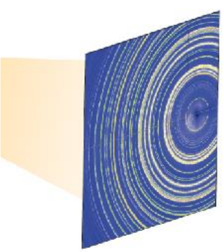
Morphology → imaging

Complex

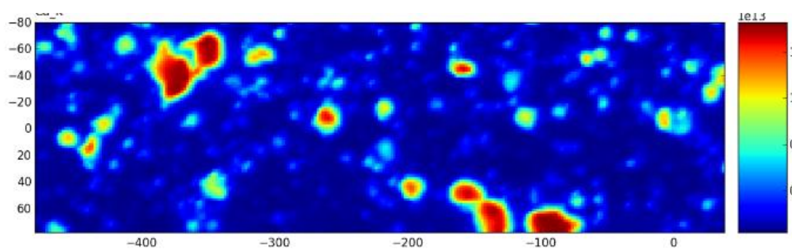
Heterogeneous



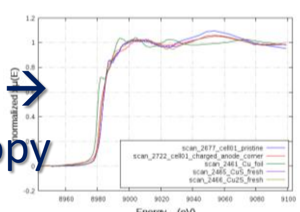
Particles (material)



Structure → diffraction & scattering

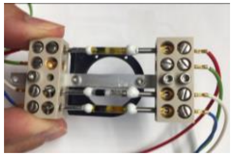


Clusters (Electrodes)



Chemistry → spectroscopy

Li-S battery with CuS addtives



Interfaces & Devices (System)

Acknowledgements

Materials Science and Chemical Engineering
Stony Brook University
https://you.stonybrook.edu/chenwiegart/

NSLS-II, BNL

Juergen Thieme, Garth Williams (SRX)
Jianming Bai, Eric Dooryhee (XPD)
Eli Stavitski, Klaus Attenkofer (ISS)
James Biancarosa & Michael Maklary
DAMA: Li Li, Tom Caswell, Dan Allan

Sustainable Energy, BNL: Hong Gan, Ke Sun
Center for Functional Nanomaterials, BNL
Eric Stach, Fernando Camino, Kim Kisslinger, Gwen Wright, Dmytro Nykypanchuk

APS-TXM

Beamline: Vincent De Andrade
Technical support: Alex Deriy
HPCAT (Glove box): Jessie Smith, Curtis Benson
TXM Optics: Michael Wojcik

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By Laura Mgrdichian

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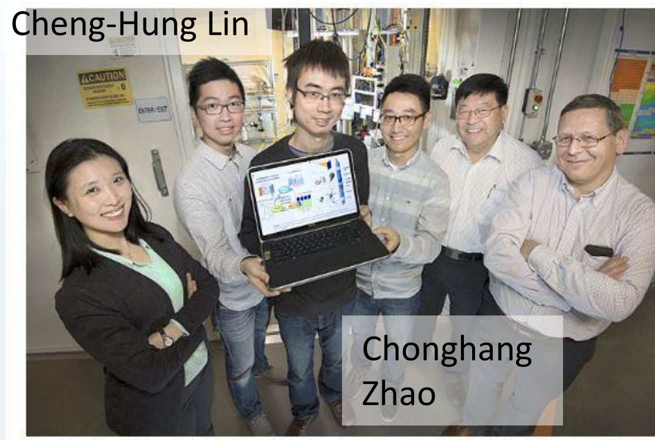
Multi-Modal *Operando* X-Ray Study Yields New Insights on Lithium-Sulfur Batteries

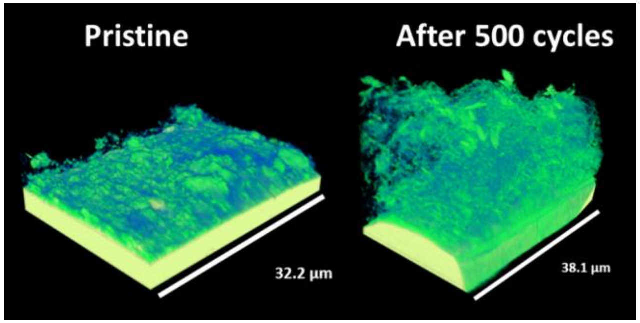
May 2, 2018



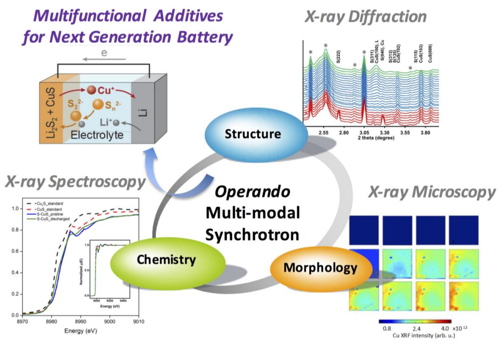
Karen Chen-Wiegart, Cheng-Hung Lin, Ke Sun, Chonghang Zhao, Hong Gan, Klaus Attenkofer (left to right) used the Inner Shell Spectroscopy (ISS) beamline to study the charge and discharge process of a lithium-sulfur battery. + ENLARGE

Thank You!

- Nanoporous-Si Anode 3D morphological Evolution
  - X-ray Nano-tomography



- CuS Additives in Li-S batteries
  - Multi-modal: XRF, XAS and XRD



- *In situ* study of 3D Printing for future energy storage
  - Coherent X-ray Scattering: XPCS