Neutrons and X-rays in Sustainable Energy Materials Research

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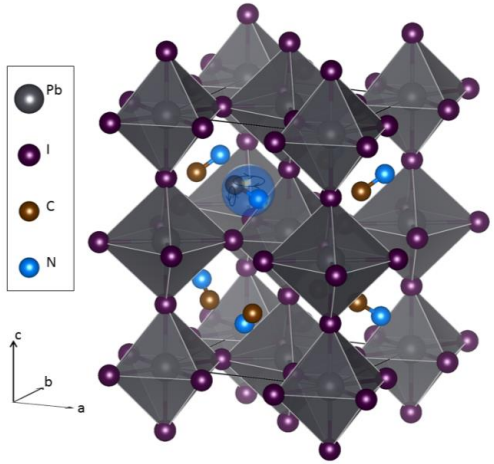
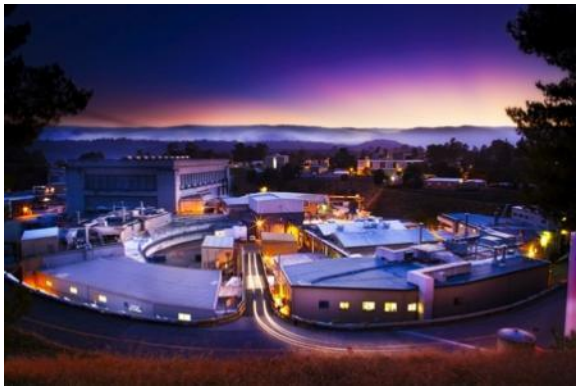
U.S. DEPARTMENT OF ENERGY
Office of Science

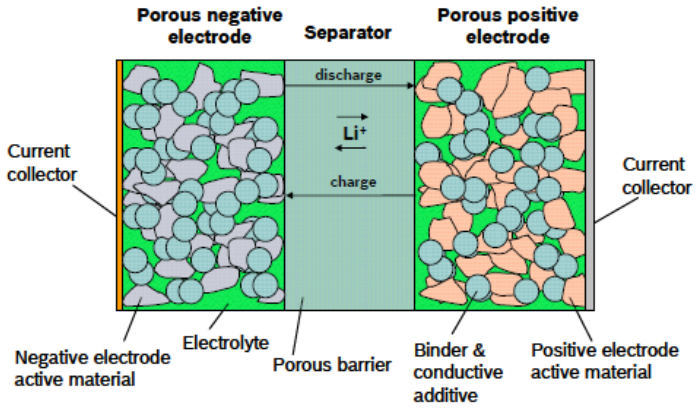
SLAC NATIONAL ACCELERATOR LABORATORY

Outline

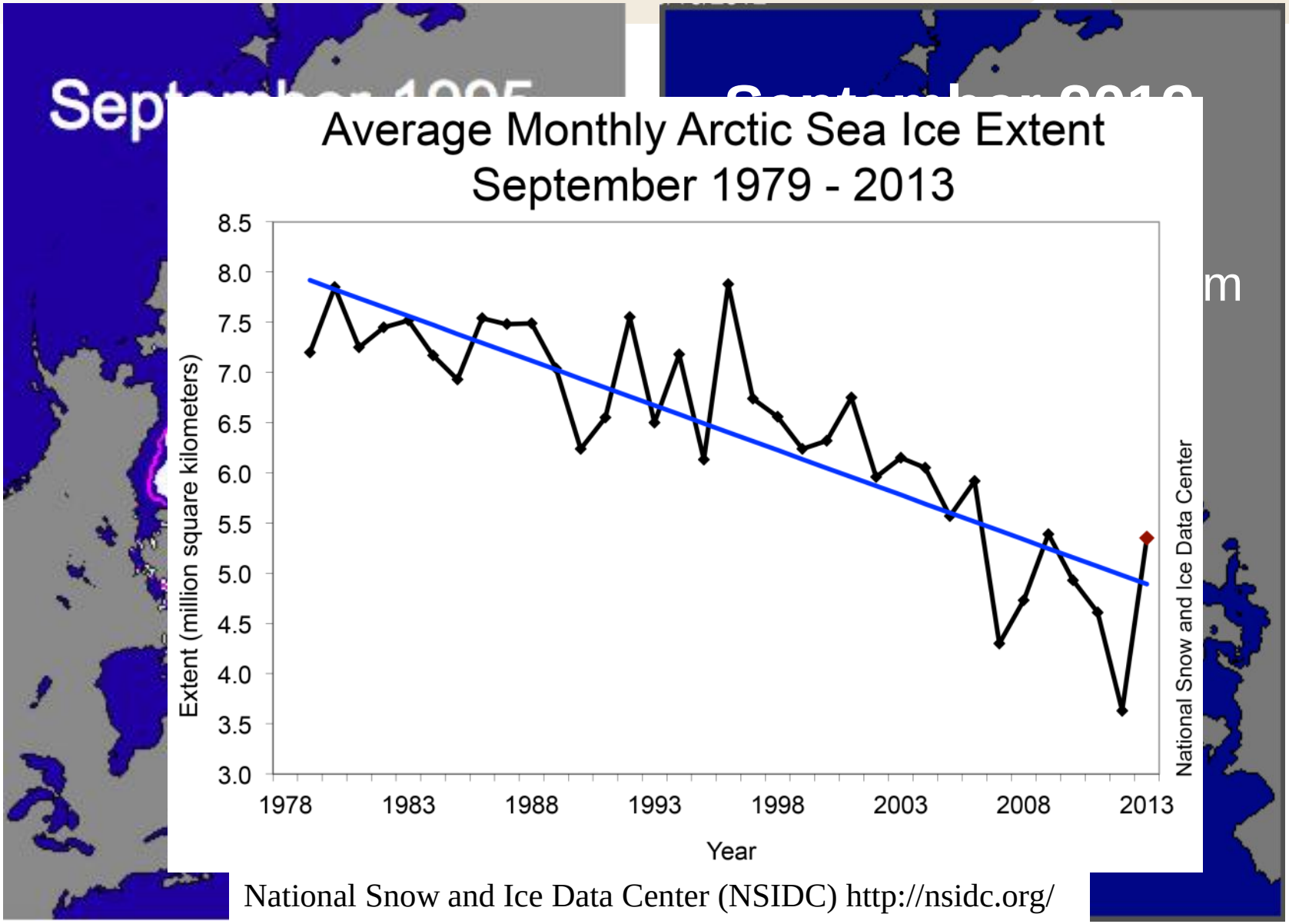
- ★ Why & how sustainable energy materials research
  - ➢ **structure-function, in-situ & operando,**
  - ➢ **multi-modal**
- ★ Energy Storage
  - ➢ **Ge anodes and $LiCoO_2$ cathodes**
- ★ Photovoltaics
  - ➢ **Organics and perovskites**
- ★ Catalysis
- ★ Summary







Climate Change – One (Striking) Example



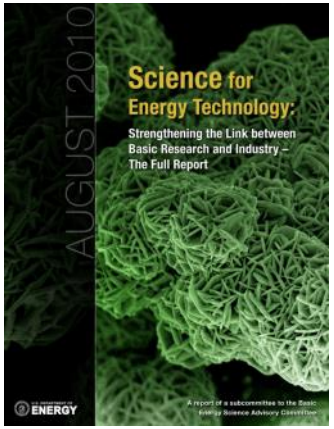
National Snow and Ice Data Center (NSIDC) http://nsidc.org/

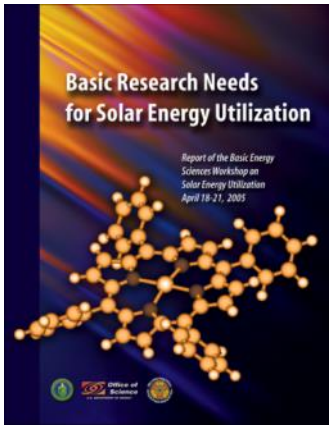
Needs: New Functional Materials

Energy with sustainable levels of CO_2 emission requires: New Functional Materials to decrease cost and increase performance

Basic Research Needs:

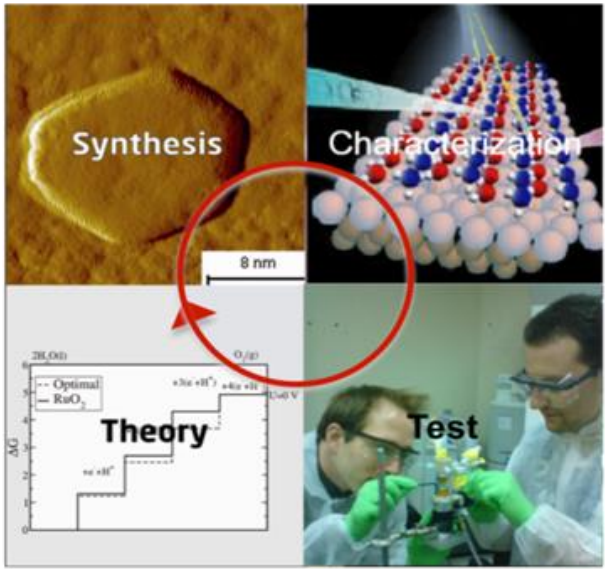
- For solar conversion, "…the range of materials currently available for use in photovoltaics is highly limited compared to the enormous number of semiconductor materials that can in principle be synthesized."
- Science for Energy Technology: "The challenge of creating new materials by design, with specific properties or functionalities, is ubiquitous."





New materials

- Inexpensive & Earth abundant
- High performance: cost = cost/performance ($/Watt or $/kW-hr)
- Materials Sciences (design) in:
  - PV, storage, catalysis, efficiency, transport, nuclear, …



New Functional Materials - Characterization

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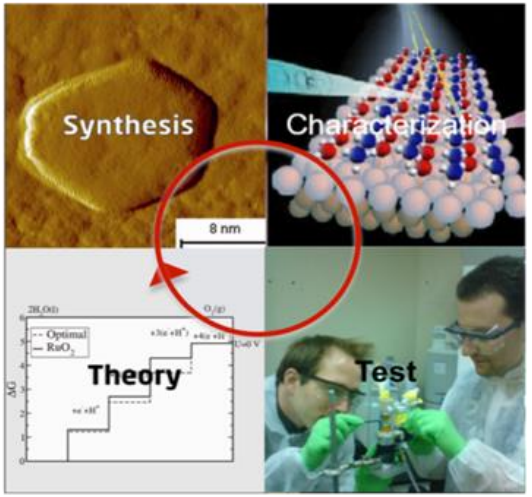
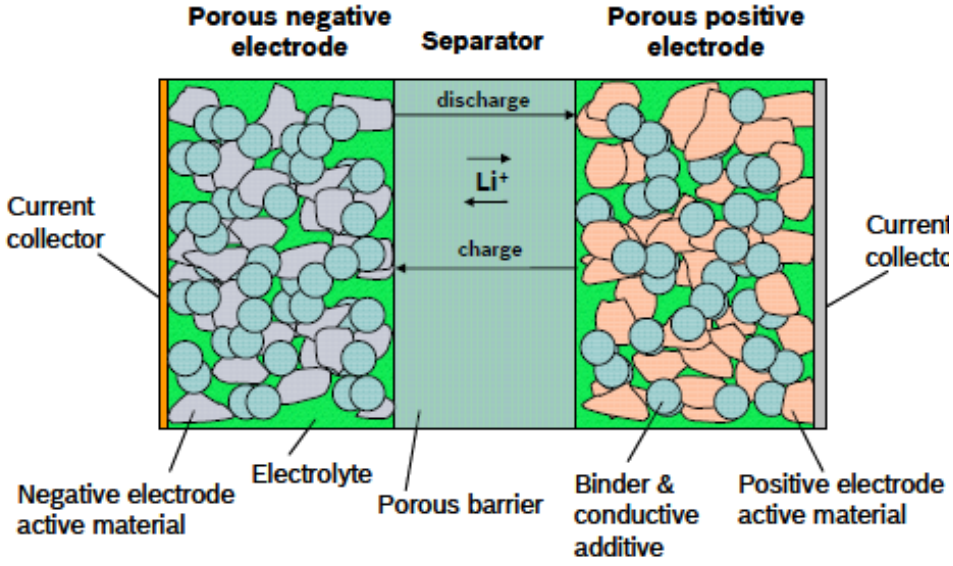
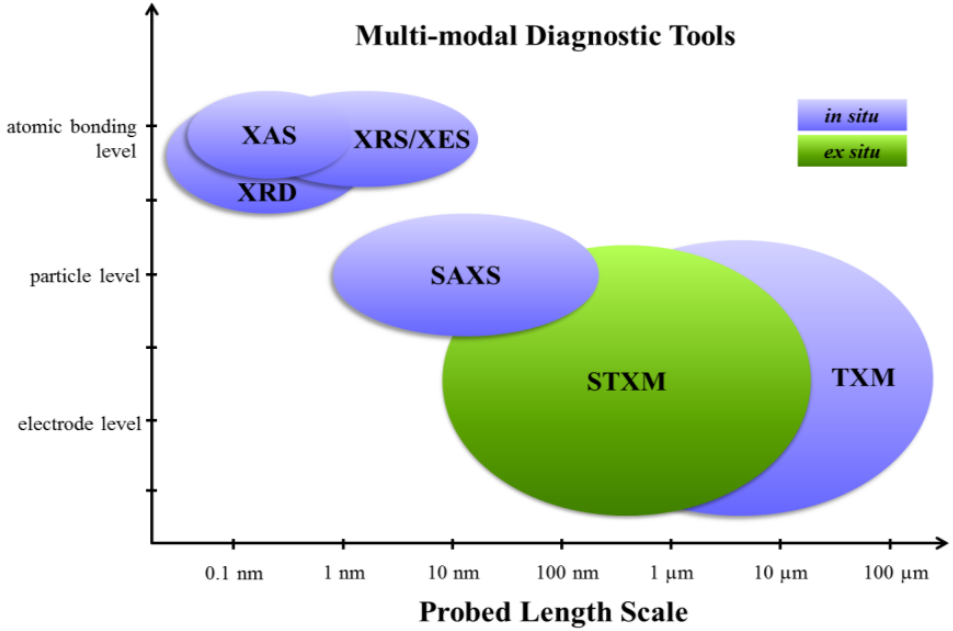
Sustainable energy: generation (solar, PV), storage (batteries), transformation (catalysis)

- **Structure-function** relationships (nms -> microns)
- **Operation**: Where are ions and electrons? And how do they move?
- **Processing**: How are they made?
- **Multi-modal** (many length scales)



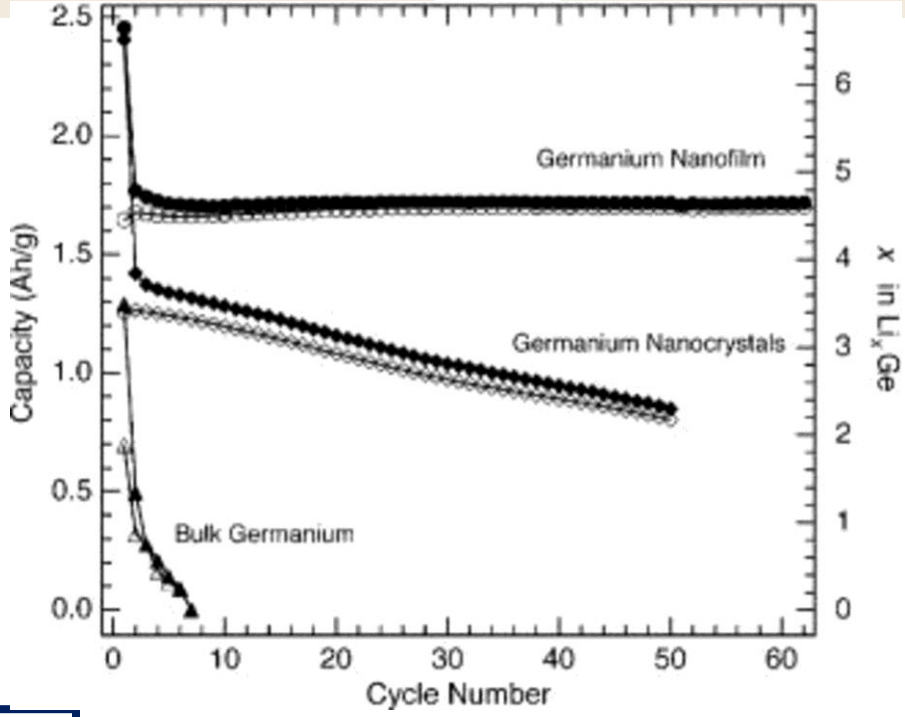




Ge particle anodes

Ge or Si anodes:

- **alloying**: Ge -> $Li_{\approx 4}Ge$
- > 4x more capacity than graphite
- Ge: Li diffusivity ~ 400X Si
- **~370% volume** changes induce cracks and pulverization
- leads to low cycle life



Graetz et al. J, Ekectrochem. Soc. 151, A698 (2004).

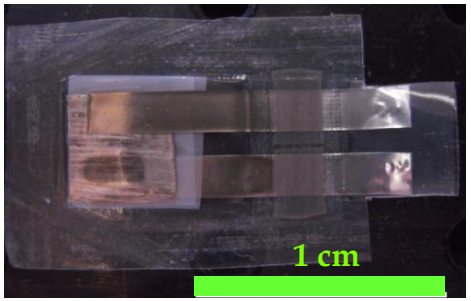
Goals:

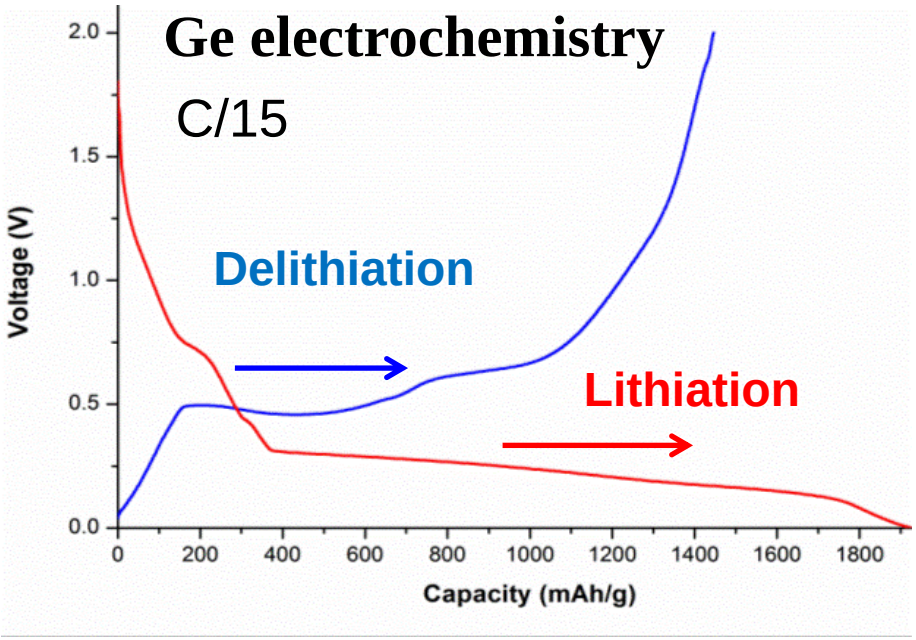
- understand operation and failure: chemistry and morphology
- multi-length scale => multi modal
- during operation

Ge particle anodes

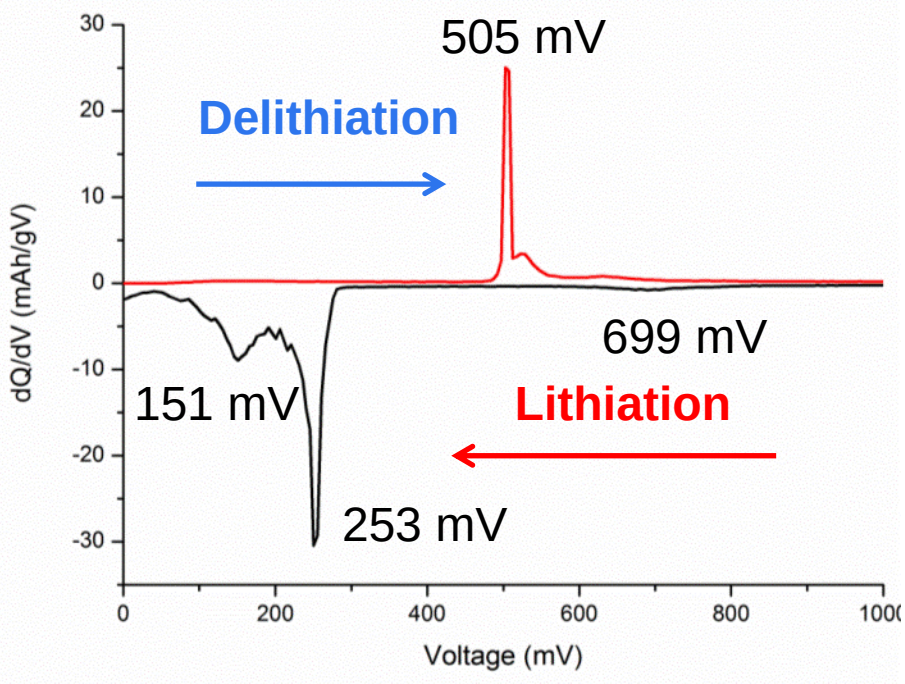
Approach – in-operando, Ge micron particles:

- **XRD** -> ordered structure (phase)
- **XAS** -> local structure (phase) & chemistry
- **TXM** -> morphology



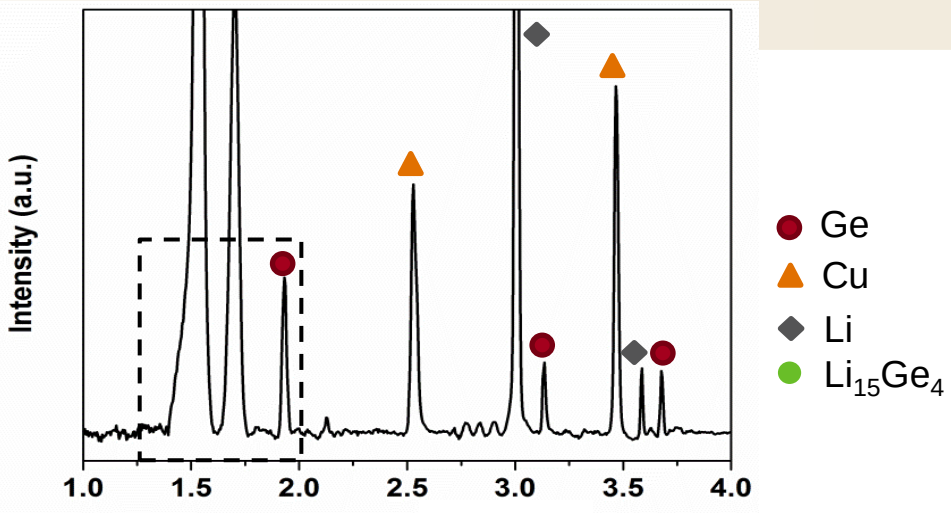


Lim et al., Chem. Mater. **26**, 3739 (2014)



Weker et al., Energy Environ Sci**. 7**, 2771 (2014)

In situ XRD of Ge anodes – first cycle

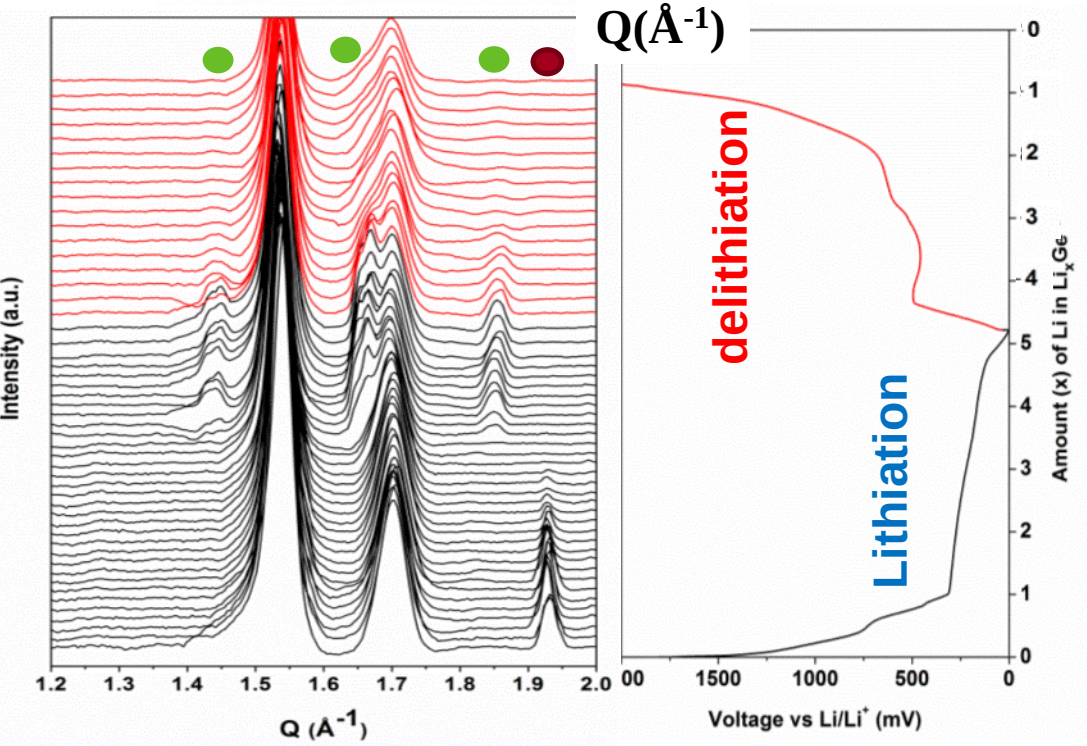


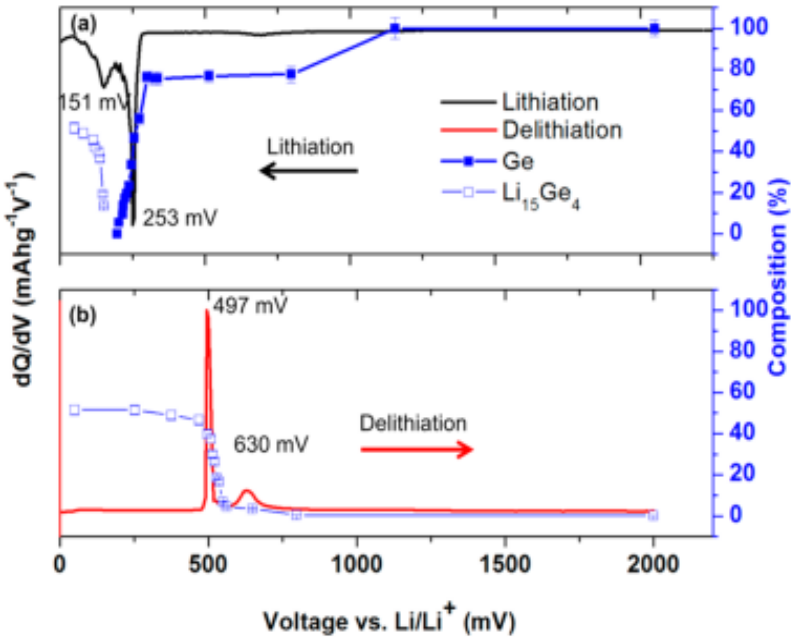
Lithiation:

- >250 mV - crystalline Ge
- 250 mV; c-Ge + amorphous?
- <120 mV: c- Ge_4Li_{15} +?

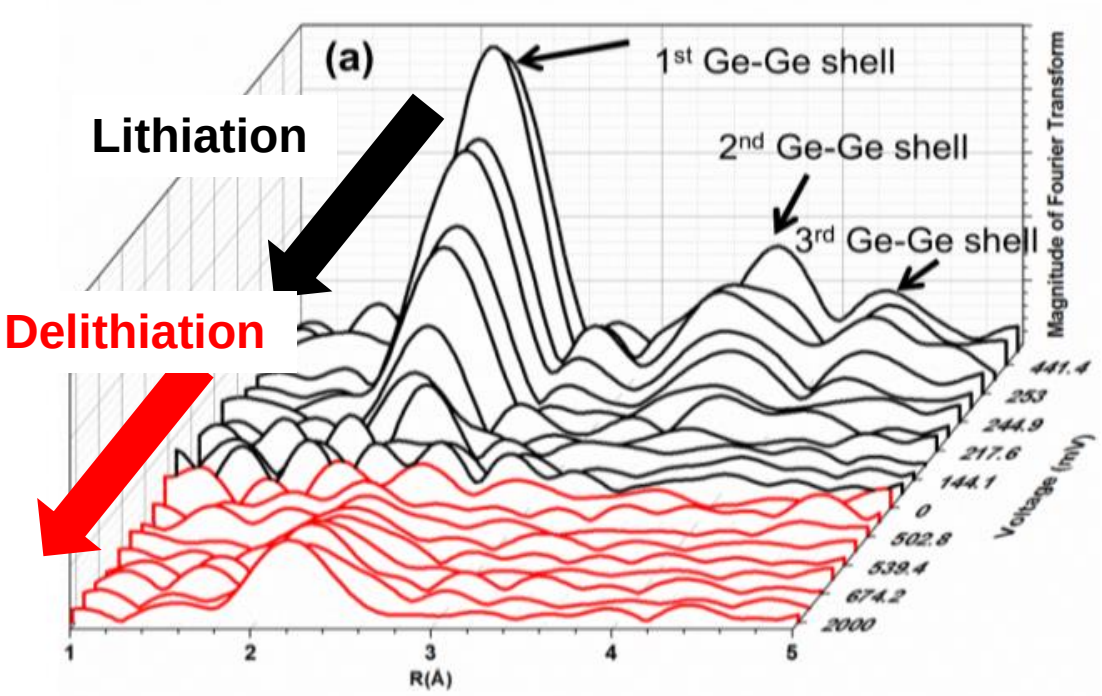
Delithiation:

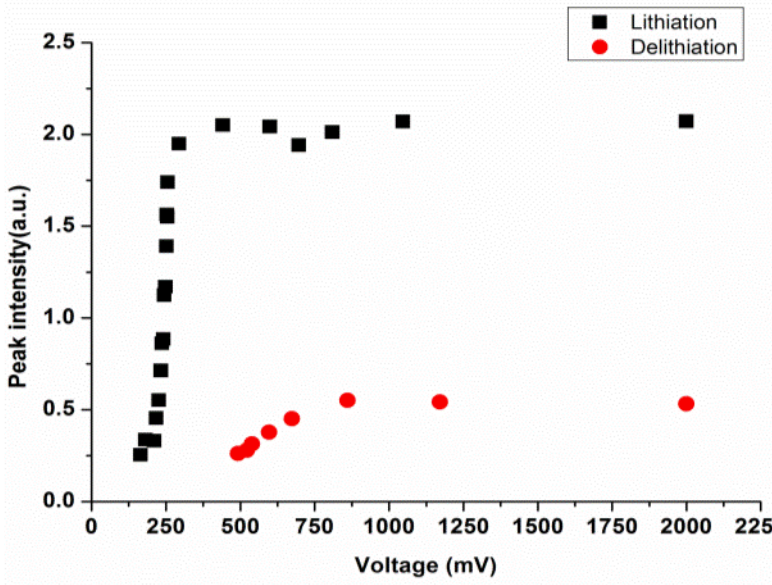
- <500 mv: c- Ge_4Li_{15}
- >600 mV: amorphous ?





In situ XAS of Ge anodes – first cycle – EXAFS





Lithiation

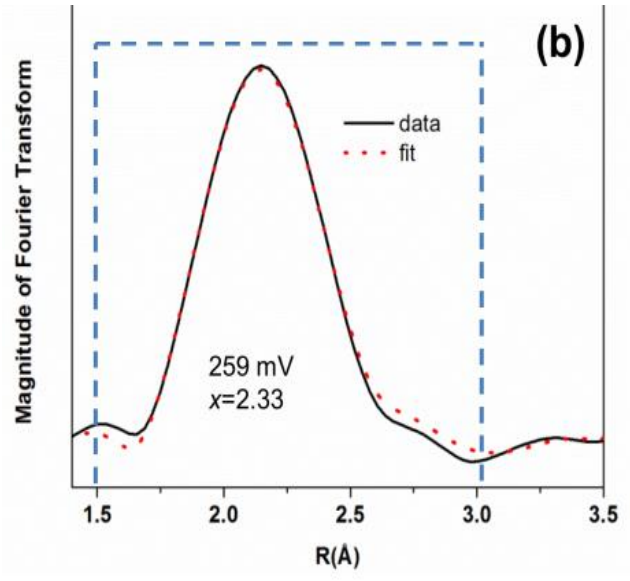
- ≈250 mV. drop in amplitude: Ge -> a-$GeLi_x$
- **modeling** at ≈250 mV: **a-Ge_4Li_9**
- ≈100 mV (end)- dramatic change, **heterogeneous** $GeLi_x$

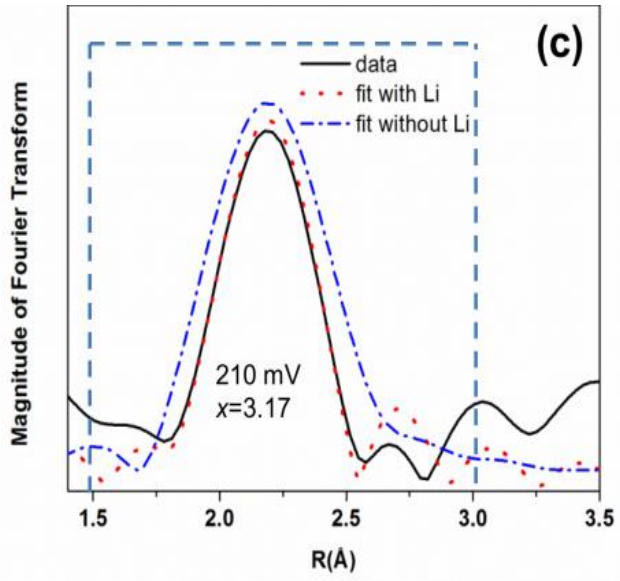
Delithiation

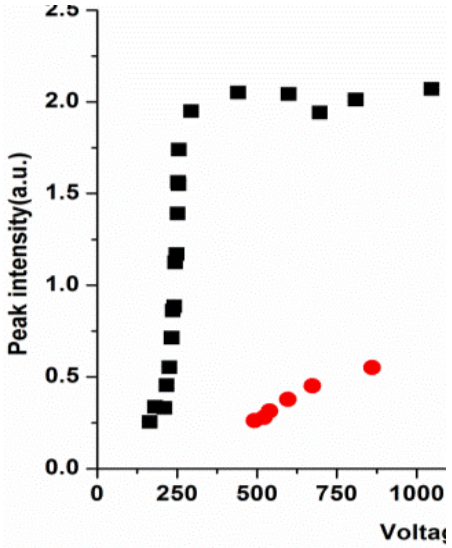
- gradual increase 450-800 mV: c-Ge_4Li_{15} -> a-Ge_4Li_9
- Slow formation to (largely) a-Ge + LiGe

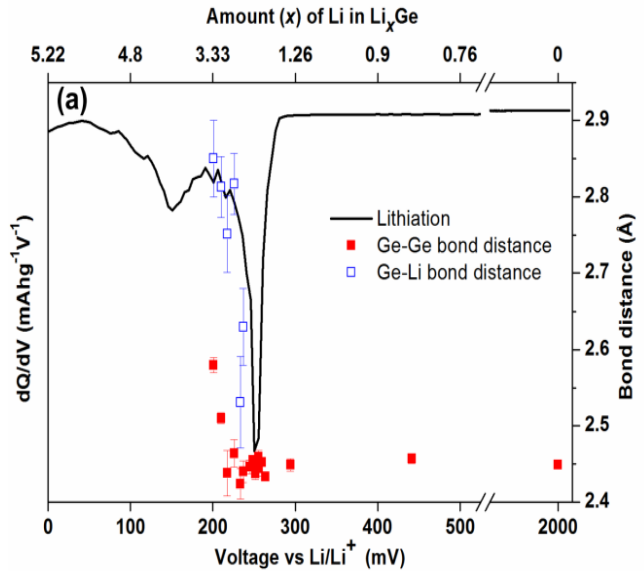
In situ XAS of Ge anodes – first cycle – EXAFS

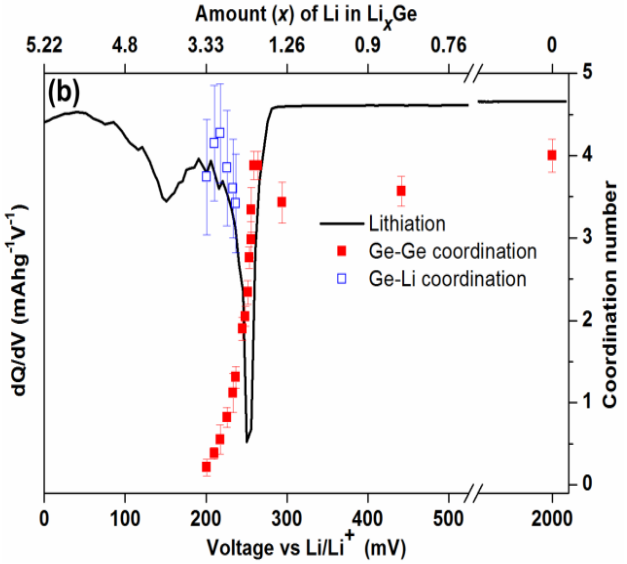
Lithiation: at <≈250 mV: a-Ge_4Li_9 + then a-$GeLi_x$ (Ge_2Li_7)











a-Ge_4Li_9:

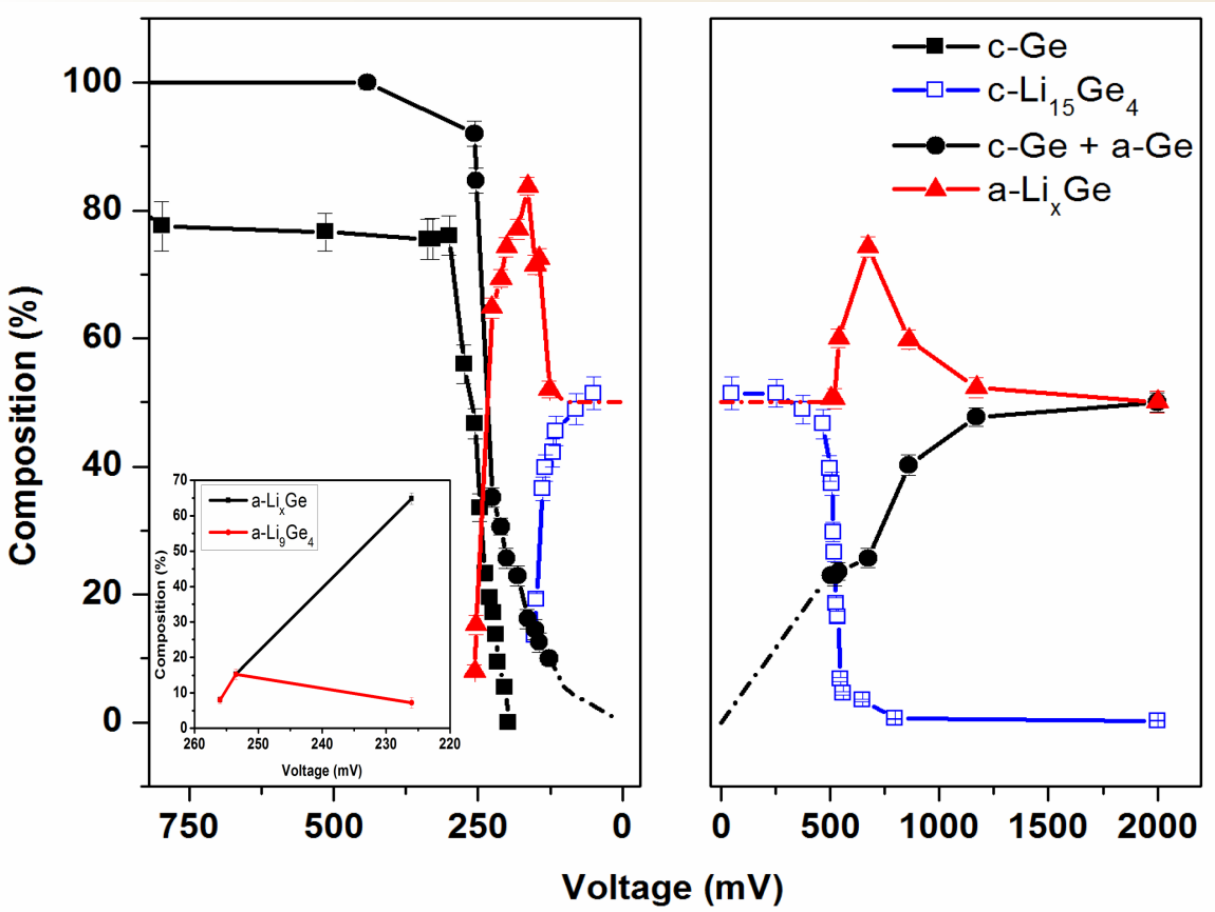
- Ge-Ge: 2.44 Å
- Ge-Li: 2.6, 2.83 Å

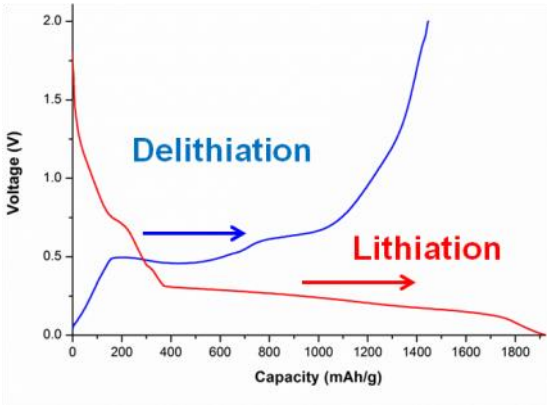
a-Ge_2Li_7:

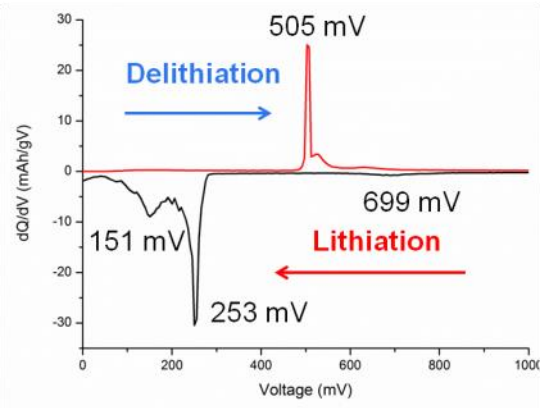
- Ge-Ge: 2.6 Å
- Ge-Li: 2.55, 2.65, 2.7, 2.9 Å

xPDF (total scattering)

In situ XAS of Ge anodes







Lithiation:

- initial: loss of c-Ge & c-Ge -> a-Li_9Ge_4
- intermediate: a-Ge + a-Li_xGe (~a-Li_7Ge_2)
- end: a-Li_xGe + c-Ge_4Li_{15}

Delithiation:

- intermediate: c-Ge_4Li_{15} -> a-Li_xGe +a-Ge
- end: a-Li_xGe + a-Ge

Lim et al., Chem. Mater. **26**, 3739 (2014)

Li-ion Batteries - neutrons

Where's the Lithium – anodes, cathodes, electrolyte (solvation)?

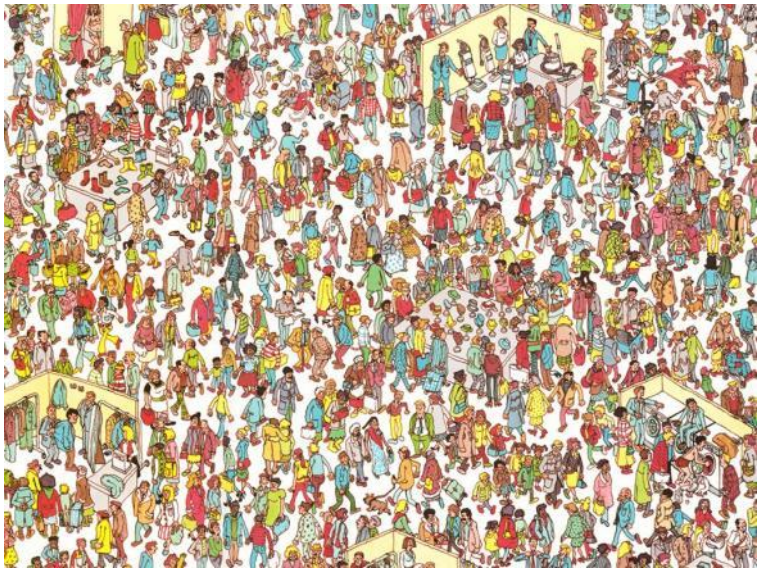
- ordered and disordered materials
- order: neutron powder diffraction
- disordered: neutron total scattering (nPDF)

Where's the Lithium – dynamics

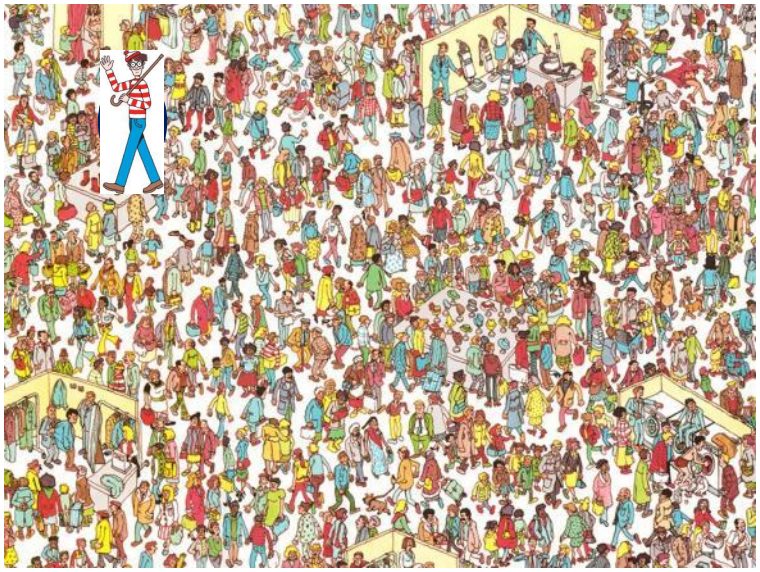
- diffusion - atomic

In-operando

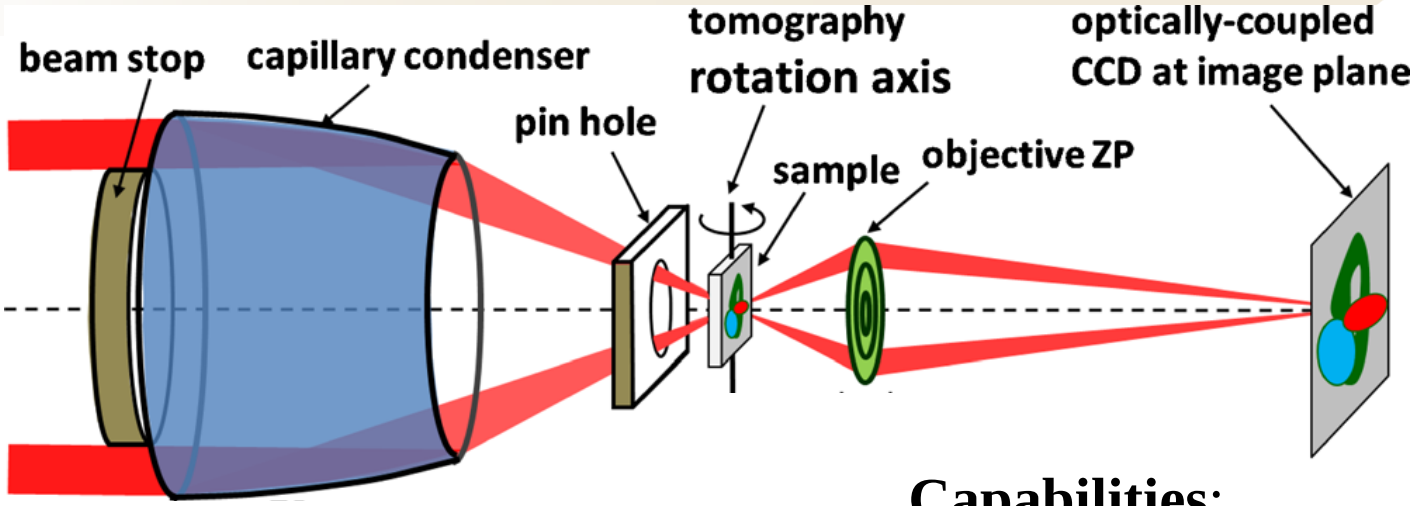
X-ray - Where's Waldo?

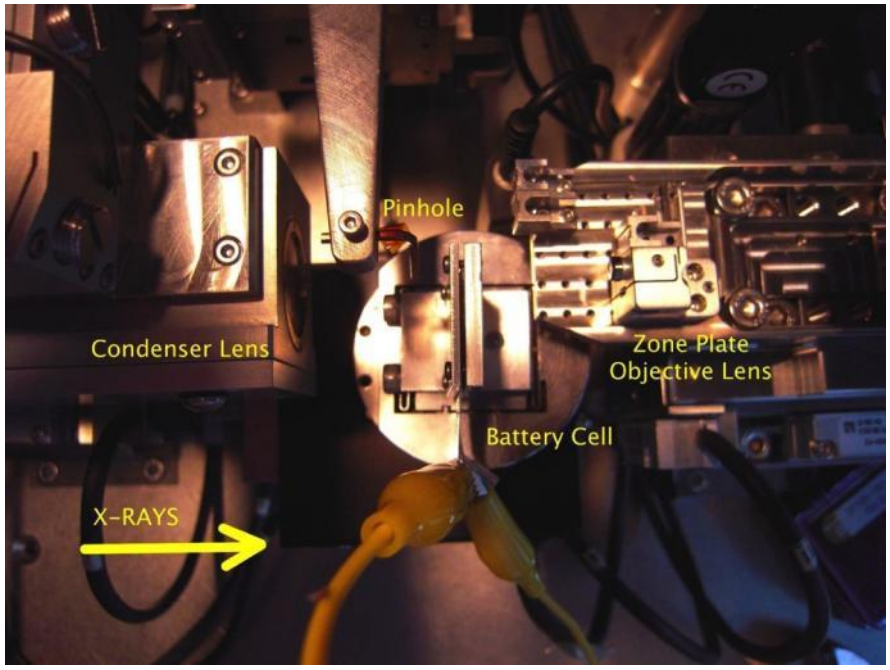


neutron - Where's Waldo?



Transmission X-ray Microscopy





Capabilities:

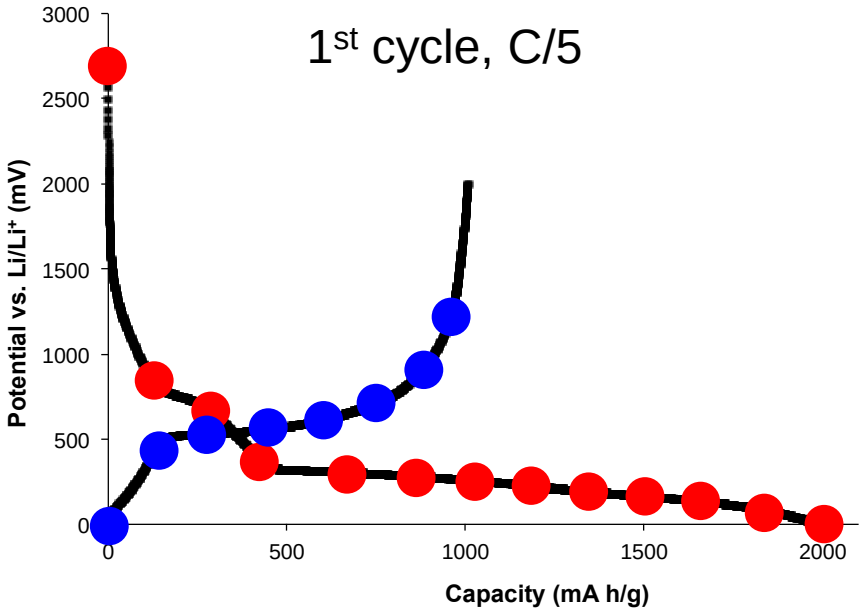
- Morphology – 30 nm resolution. 30 μm field of view
- **2D & 3D imaging** (density)
- **Elemental/chemical** maps

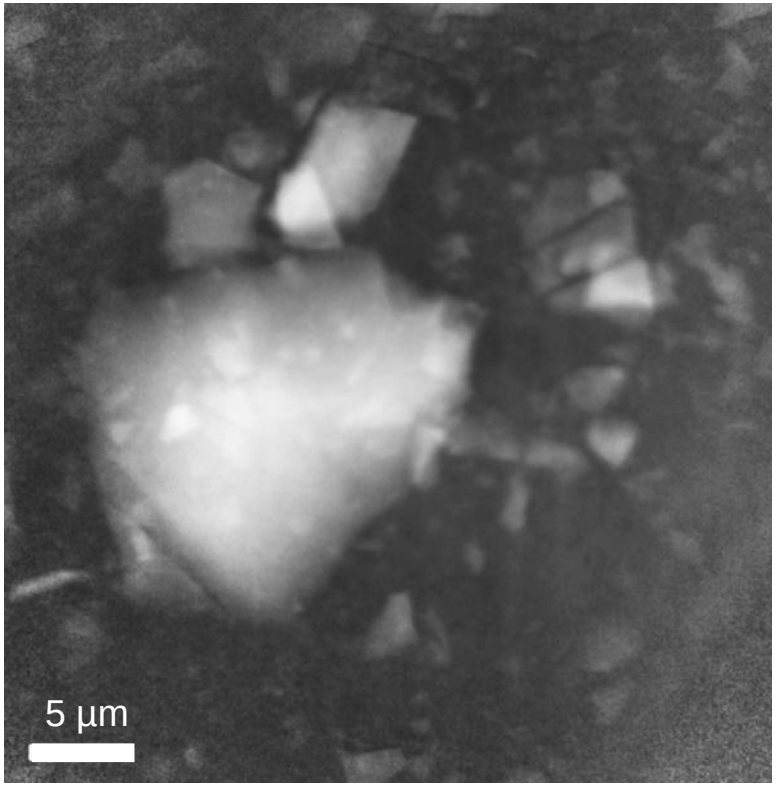
Goals – micron Ge particles:

- Quantify volume changes
- Visualize crack formation
- Quantify porosity changes

Morphology changes during (de)lithiation

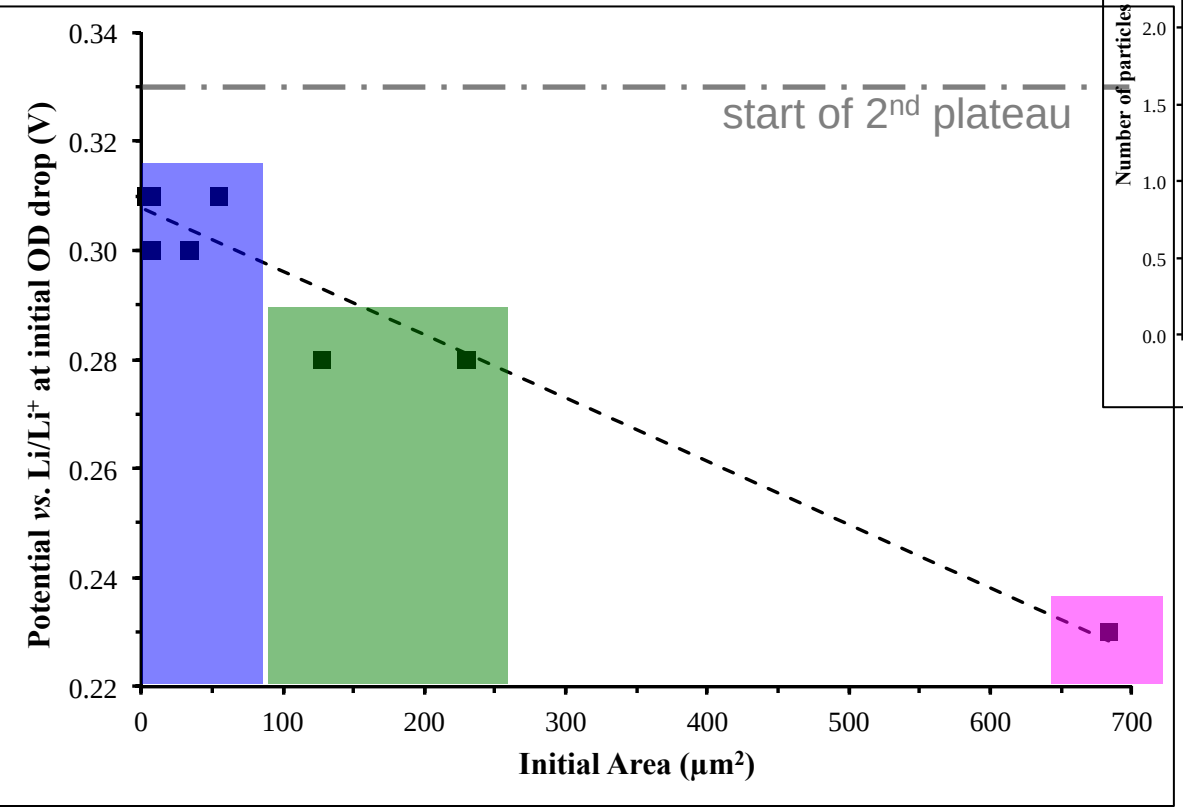
1. Cracks form in larger particles (> 7.6 μm^2 projected area or >3 μm diameter)
2. Cracks fill as lithiation continues
3. Cracks reappear during delithiation
4. After delithiation larger particles are porous

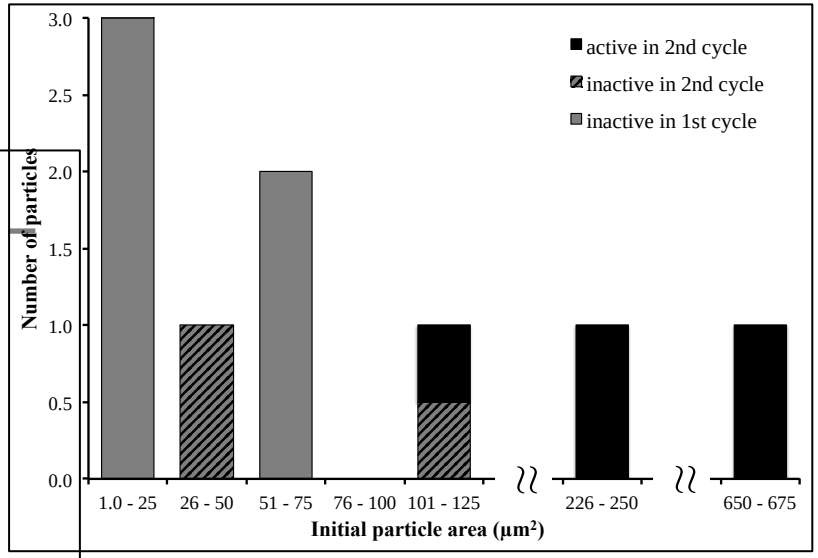


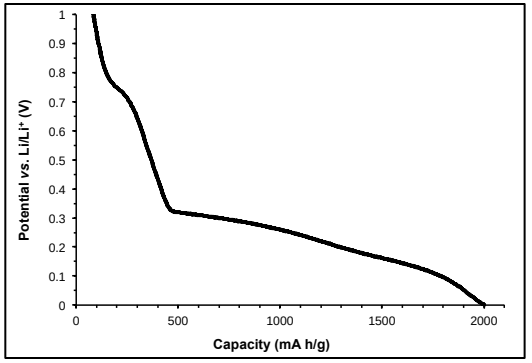


Potential at which expansion starts is size dependent

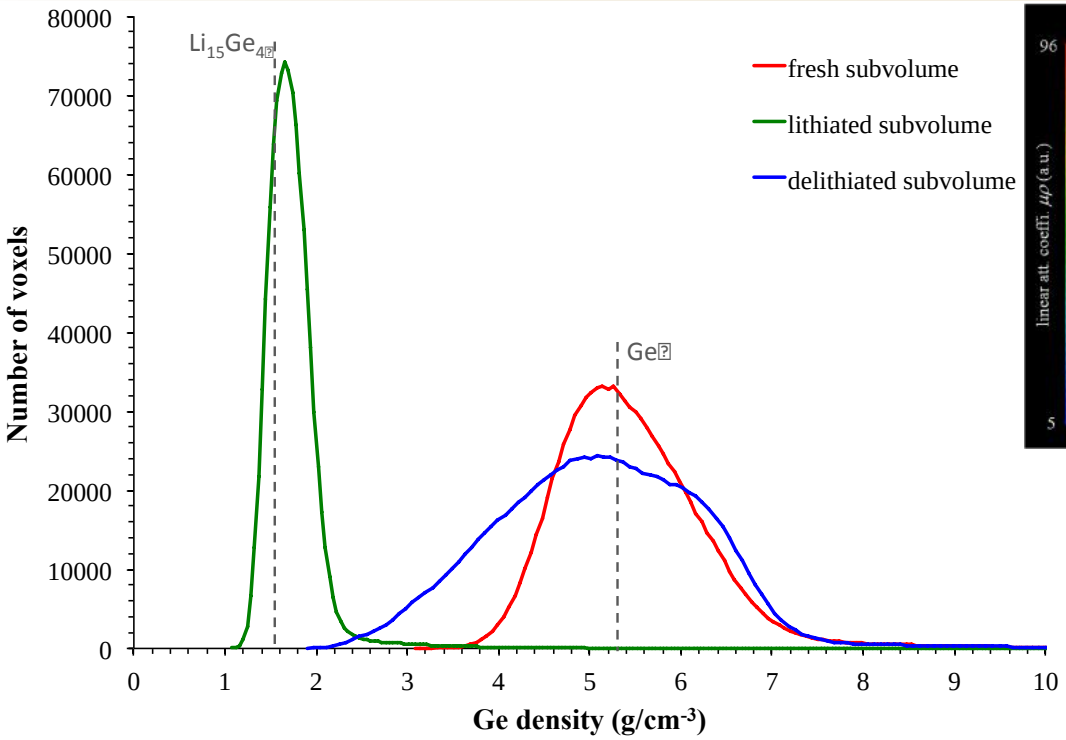
- Tracked drop in optical density (OD) for 9 particles in 5 regions
- Drop in OD → drop in particle density & volume expansion
- **Smaller particles start expanding/fracturing earlier**
- **2nd cycle: only the largest particles expand**

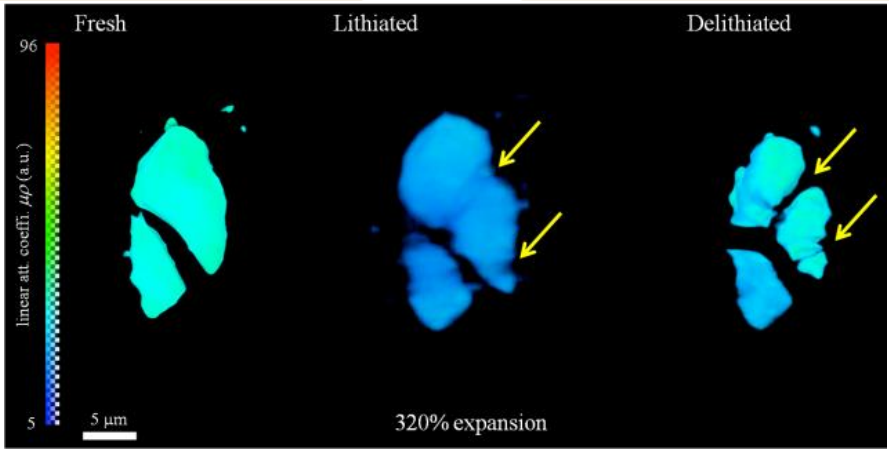


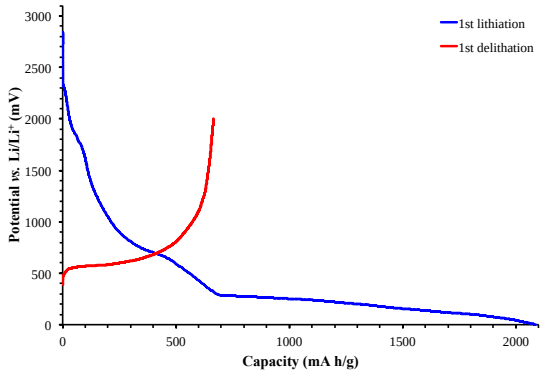




3D imaging: density



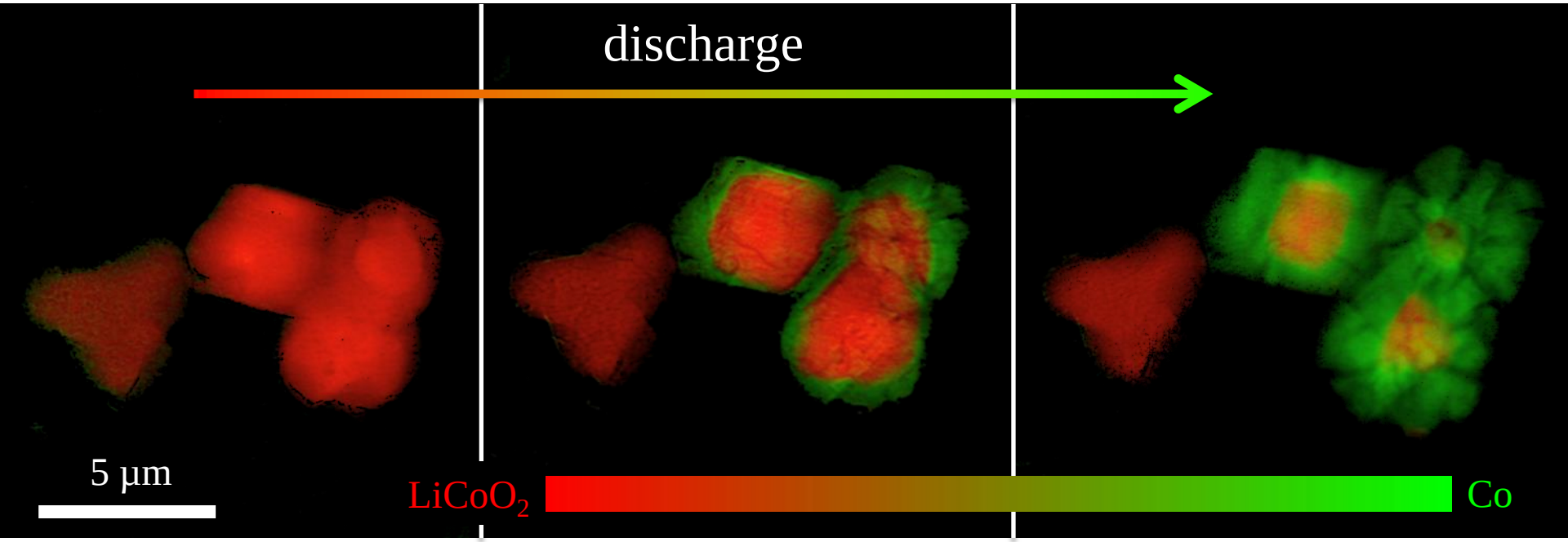


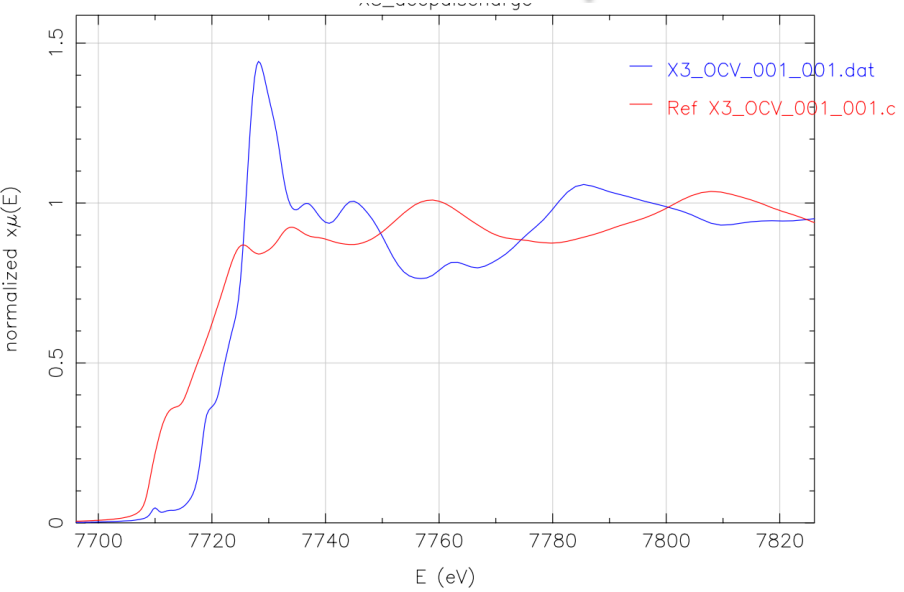


- Lithiated: some ≈$Li_{15}Ge_4$ with other states containing less Li
- Delithiated: broader & shifted to lower density → not completely reversible
- Average expansion on lithiation: 315% of fresh

Weker et al., Energy Environ Sci. **7**, 2771 (2014)

Deep discharge of $LiCoO_2$





- Imaged at 35 energies
- Single-pixel spectra fit with linear combination of two standards
- Co metal; Co II+

Wise, Weker, MFT, unpublished

Li-ion Batteries

Where's the Lithium – anodes, cathodes, electrolyte?

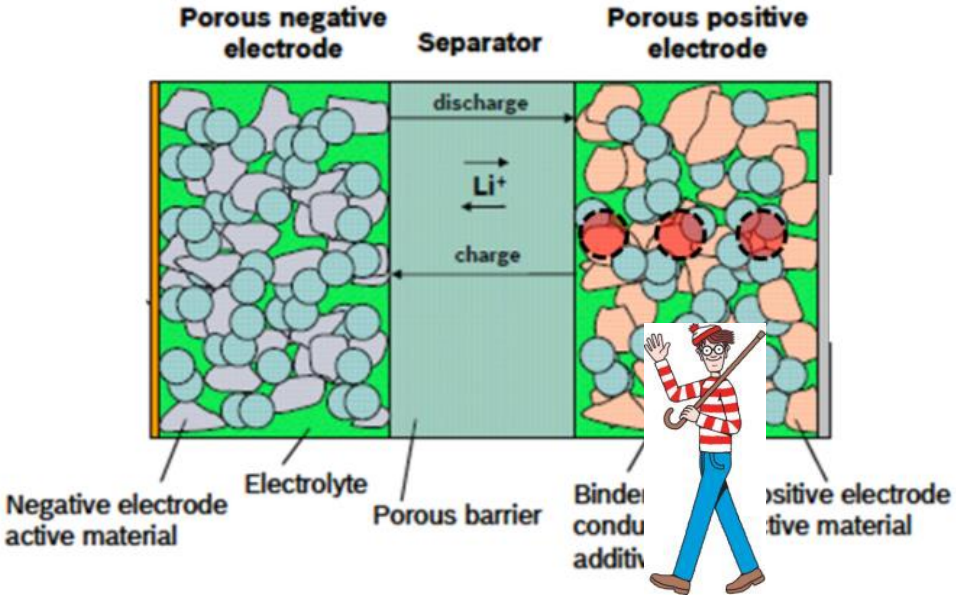
- ordered and disordered materials
- order: neutron powder diffraction
- disordered: neutron total scattering (nPDF)

Where's the Lithium – dynamics

- diffusion - atomic

Where's the Lithium – particle & electrode level?

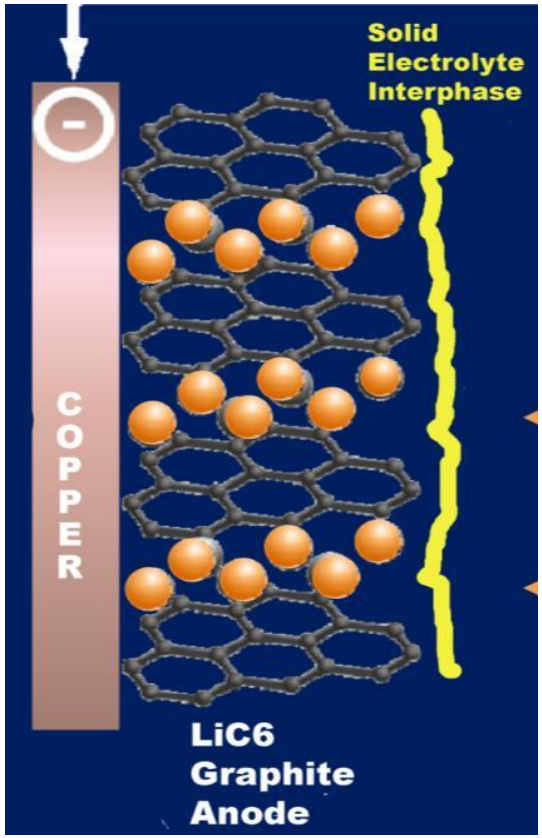
- particle chemistry: core-shell?
- electrode (cell): state-of-charge
- imaging?



Li-ion Batteries - SEI

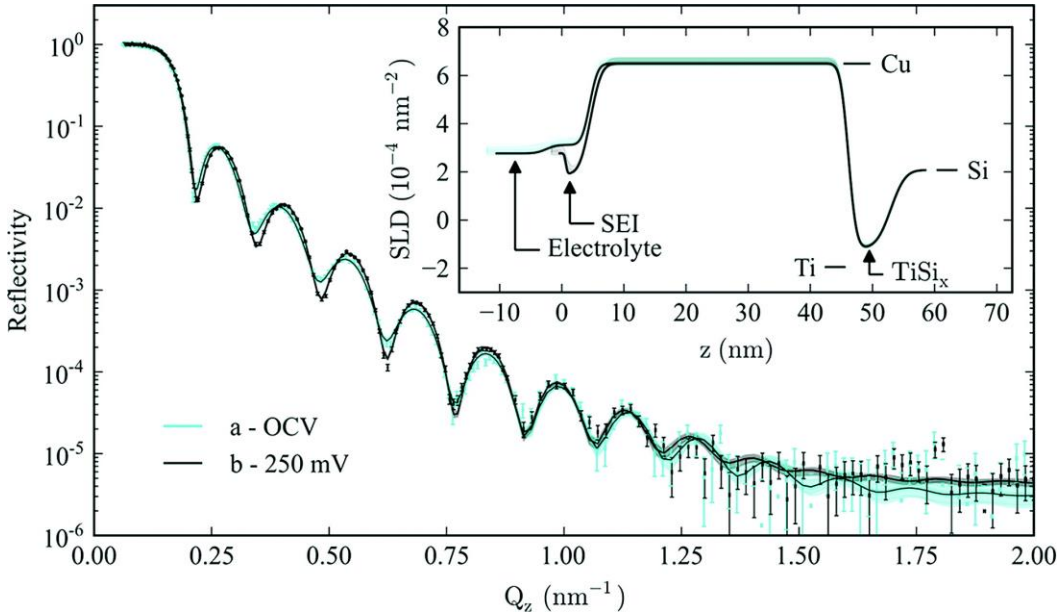
Solid electrolyte interface

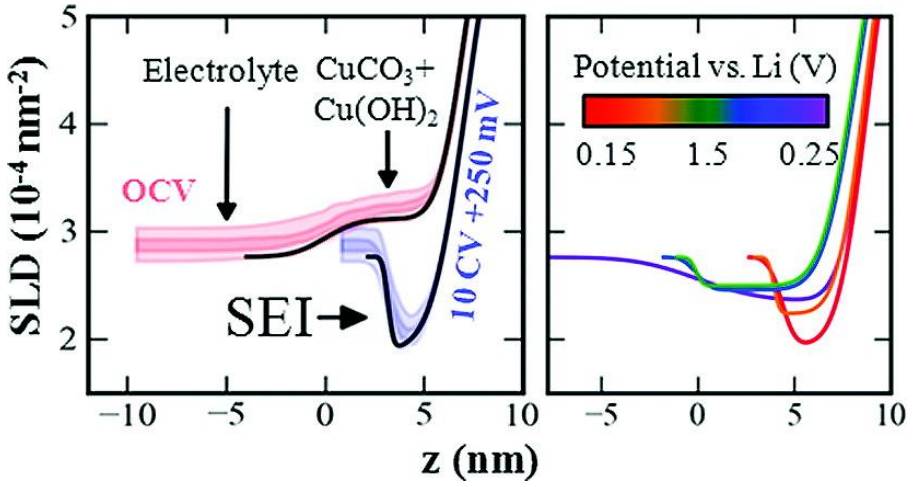
- reflectivity



- spatial resolution
- size

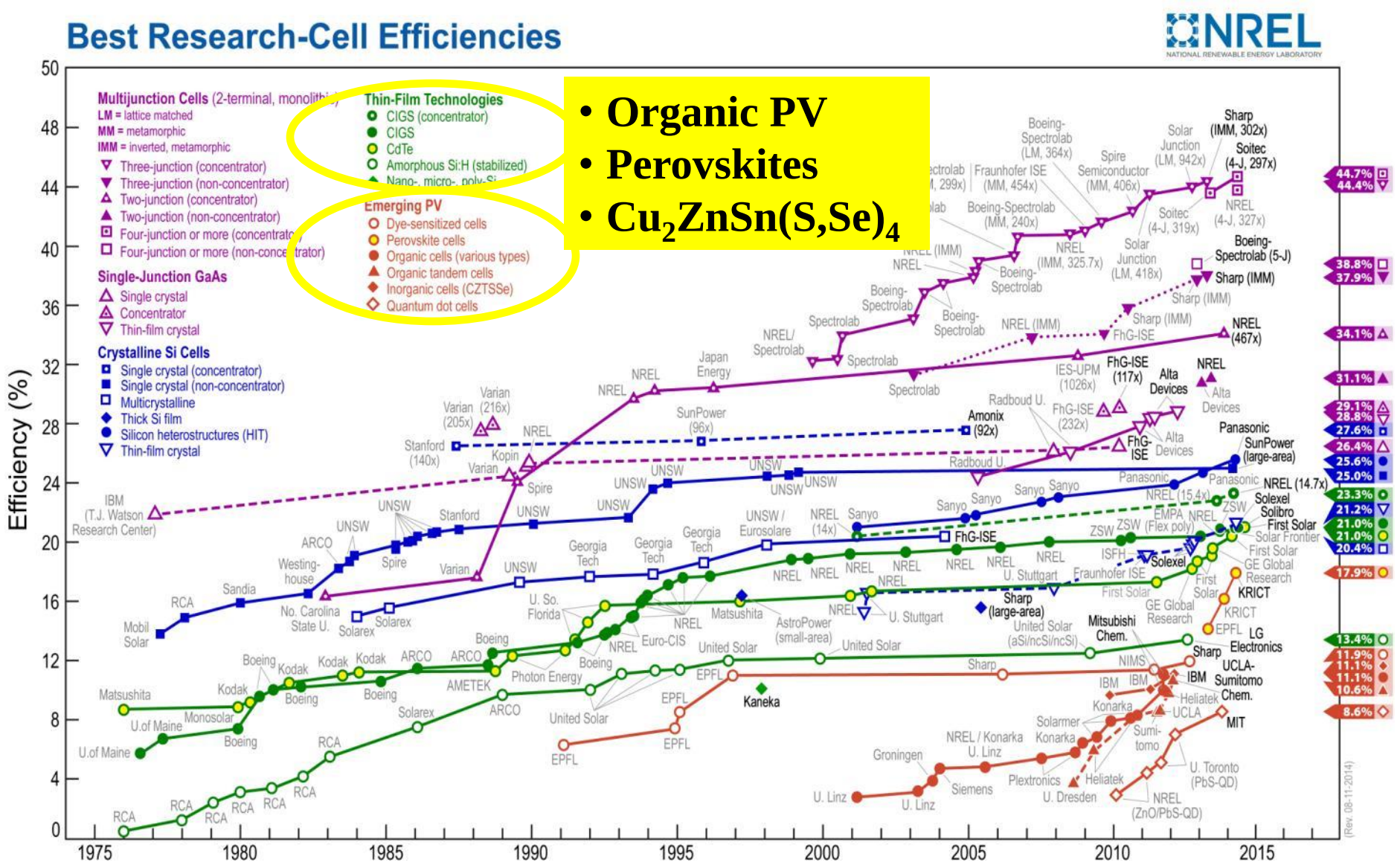
Owejan, …, Dura, *Chem. Mater.* **2012,** 24, 2133





Photovoltaics

SLAC

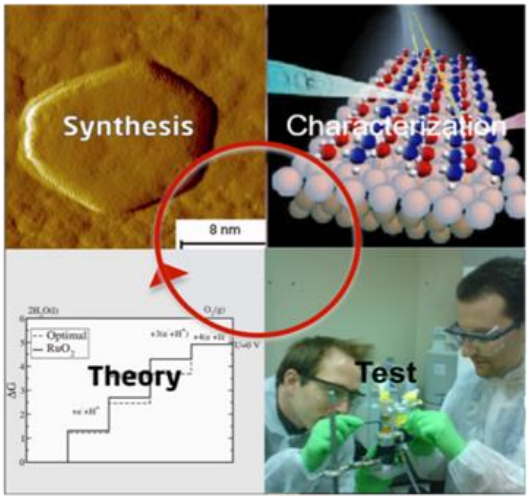


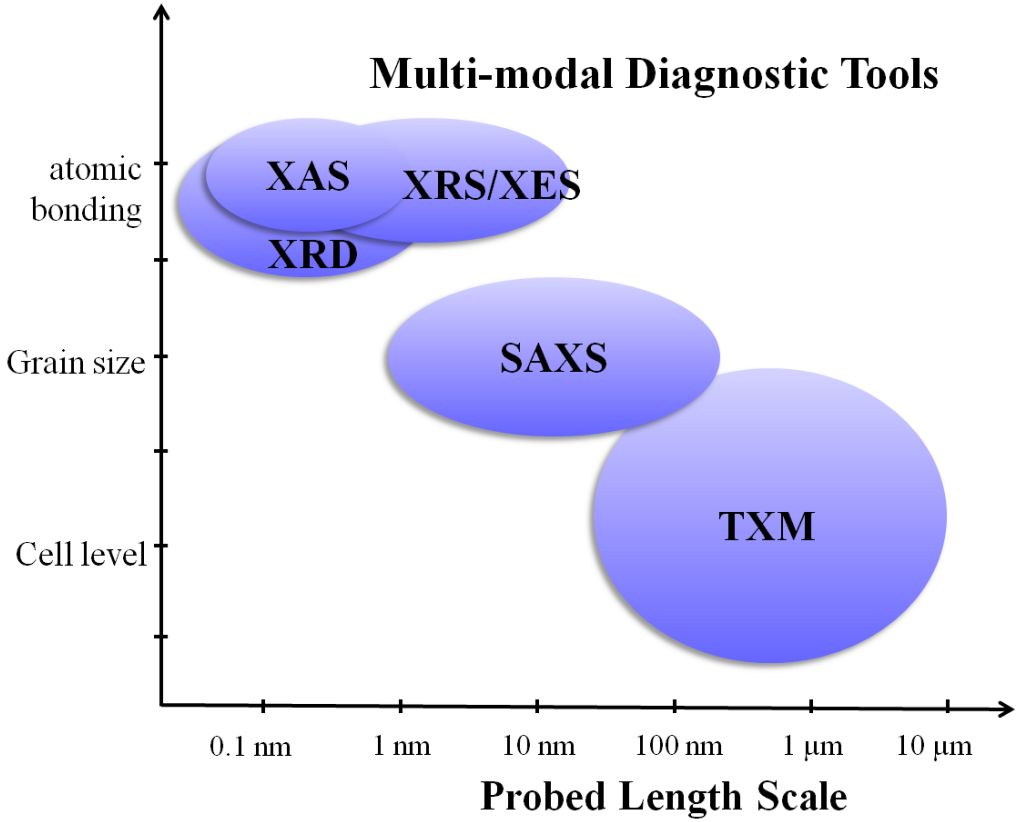
New Functional (PV) Materials - Characterization

SLAC

Sustainable energy: generation (solar, PV)

- **Structure-function** relationships (nms -> microns)
- Operation: Where are ions and electrons? And how do they move?
- **Processing**: How are they made?



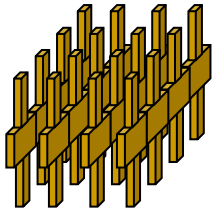


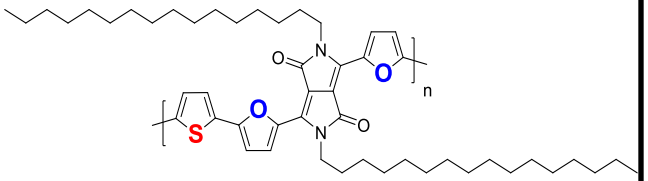
Organic Solar Cells

Organic Solar Cells:

- flexible, solution processable
- inexpensive & mass production
- printing

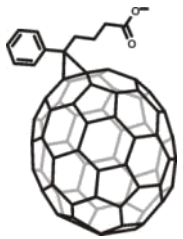
donor: semi-crystalline polymer
P3HT = poly(3-hexylthiophene)





PDPP2FT-C16

acceptor: fullerene phenyl-C61-butyric ester (PC61BM) & PC71BM

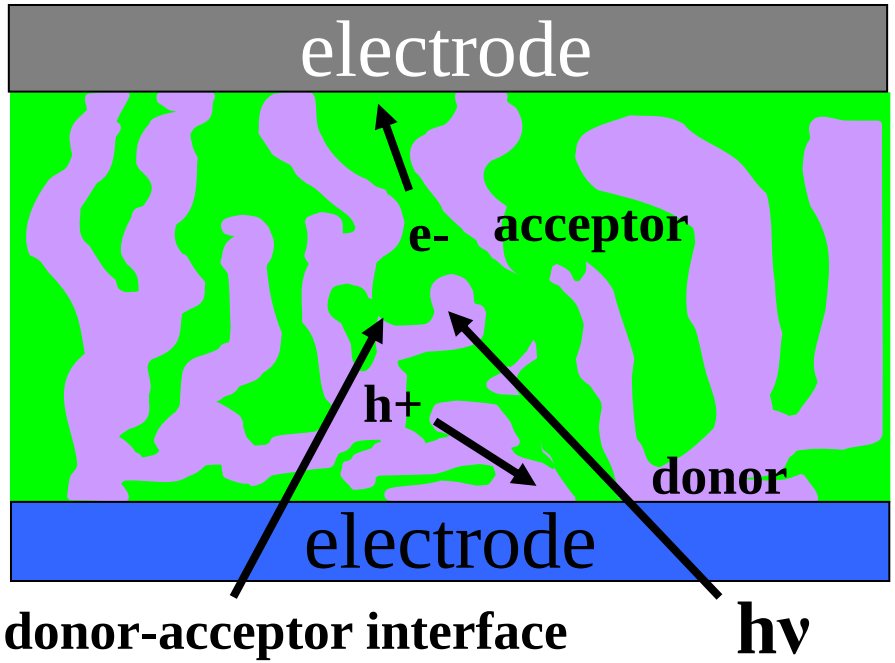


BHJs: 100s nm thick

Organic photovoltaic:

- Bulk heterojunction (BHJ)
- Light creates exciton (e- h+ pair)
- Exciton diffuses to donor/acceptor interface & dissociates
- e- & h+ transport to electrodes

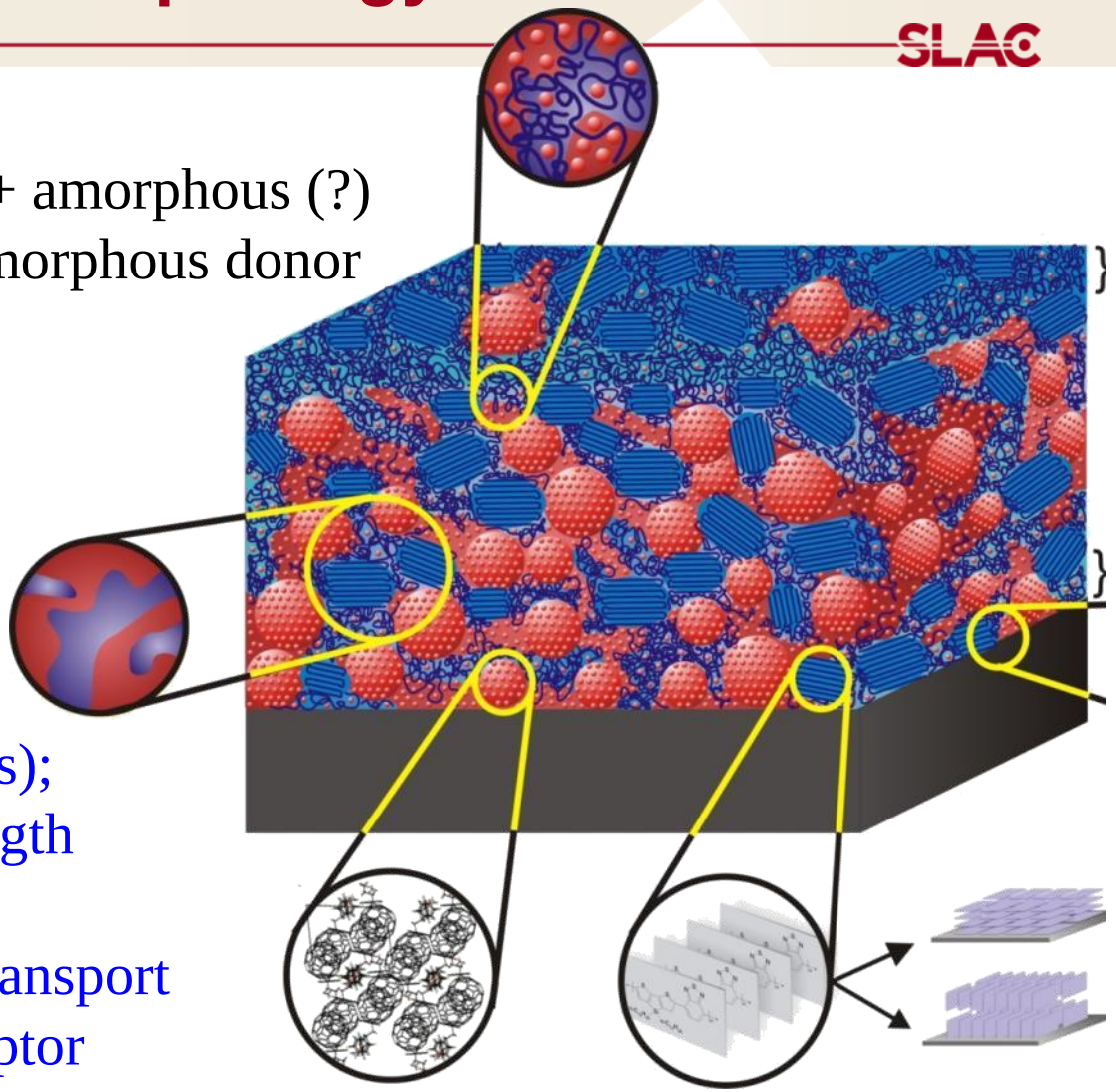
=> Power with PCE ≈ 10-12%



Organic Solar Cells: Morphology

Three separate regions:

- pure donor – semicrystalline + amorphous (?)
- some (ca 20%) fullerene in amorphous donor
- pure fullerene – amorphous

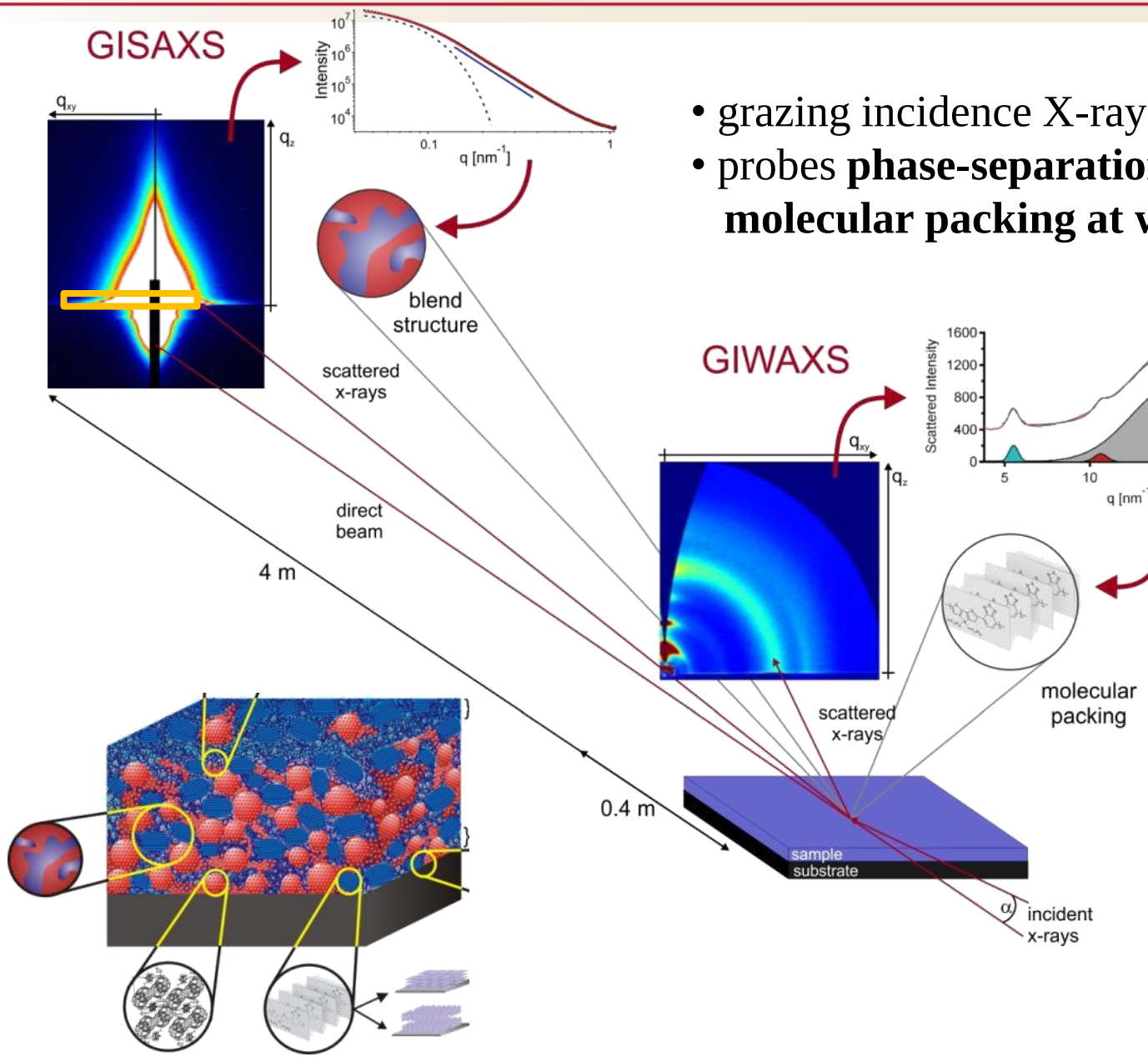


Some issues (X-rays):

- BHJ morphology (nm lengths); close to exciton diffusion length
- Molecular packing in donor polymer: carrier & exciton transport
- Intermixing of donor & acceptor
- Interface structure

Gomez, et al. Chem Comm, **47**, 436 (2011)
Treat, et al., Adv. Energy Mater. **1**, 82 (2011).
Chen et al., NanoLetts. (2011).

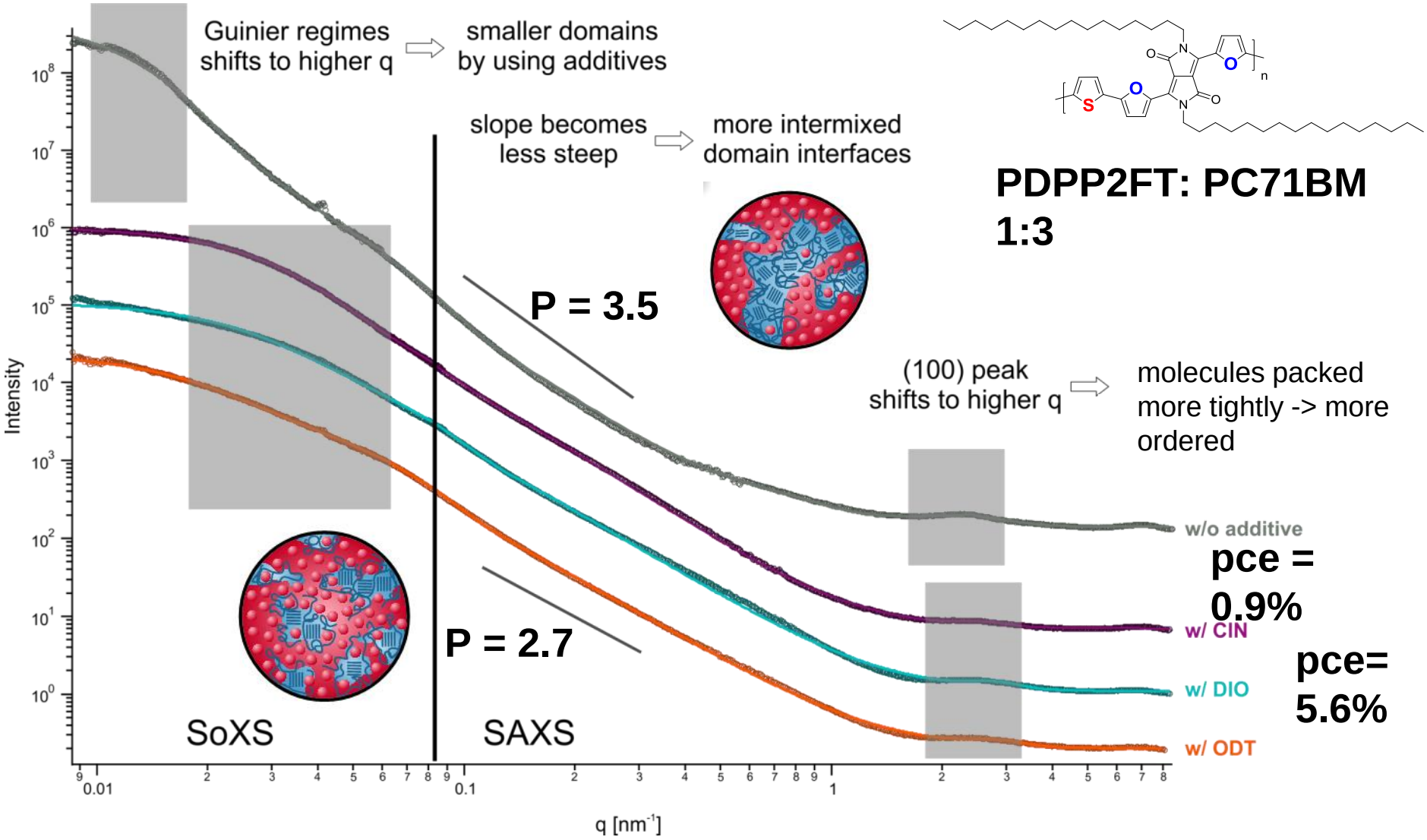
Probe Morphology with Scattering



- grazing incidence X-ray scattering on thin films
- probes **phase-separation at small angles** & **molecular packing at wide angles**

Rivnay et al., Chem. Rev., 2012, 112 (10), 5488

BHJ Structure of C_{16}-PDPP2FT - SAXS



Schmidt et al., Adv. Mat. **26**, 300 (2014)

BHJs: 100s nm thick

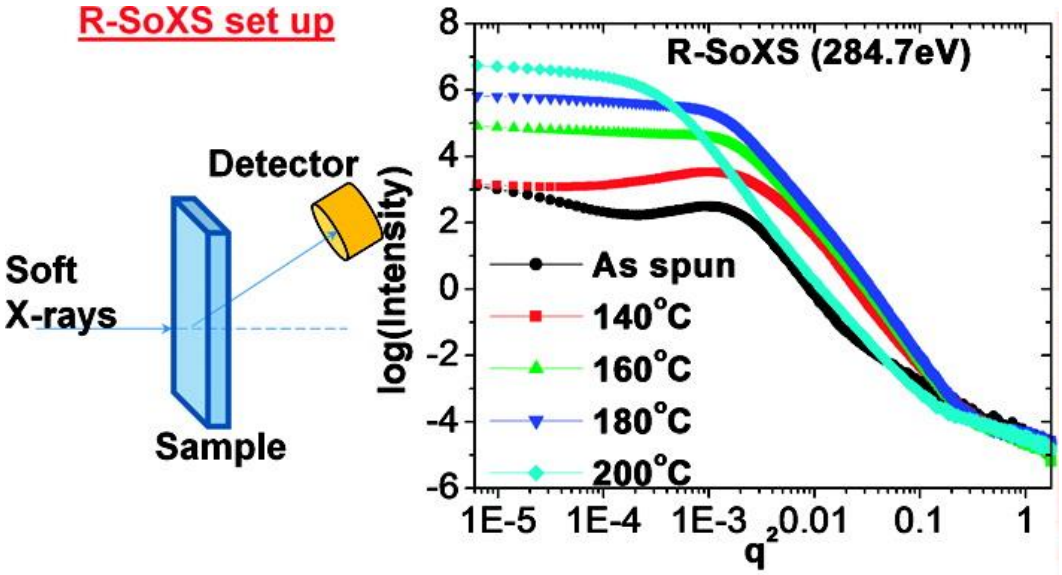
OPV – Soft X-ray Scattering

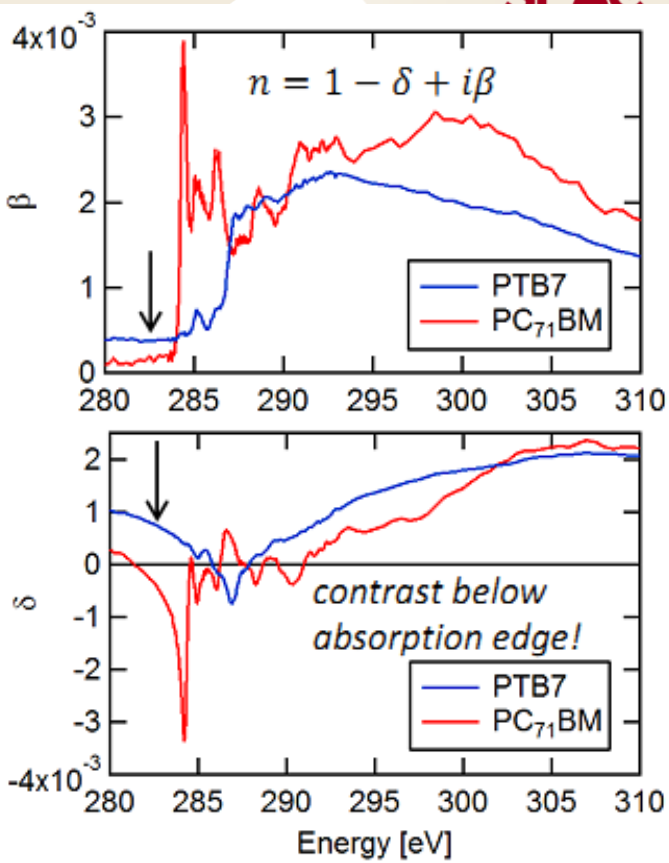
Resonant soft-x-ray scattering (r-SoXS)

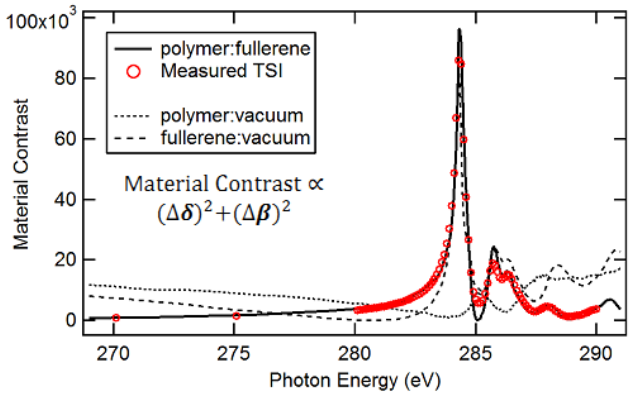
- enhanced contrast between similar components near (C) absorption edge

Polarized soft-x-ray scattering (p-SoXS)

- polarization as a contrast mechanism
- relative alignment of polymer domains







Swaraj, …, Ade; Nano Lett. **10**, 2863 (2010)
Ade & McNeil, J. Mater. Chem. C, 1, 187 (2013)

OPV - neutrons

Some issues in BHJ morphology:

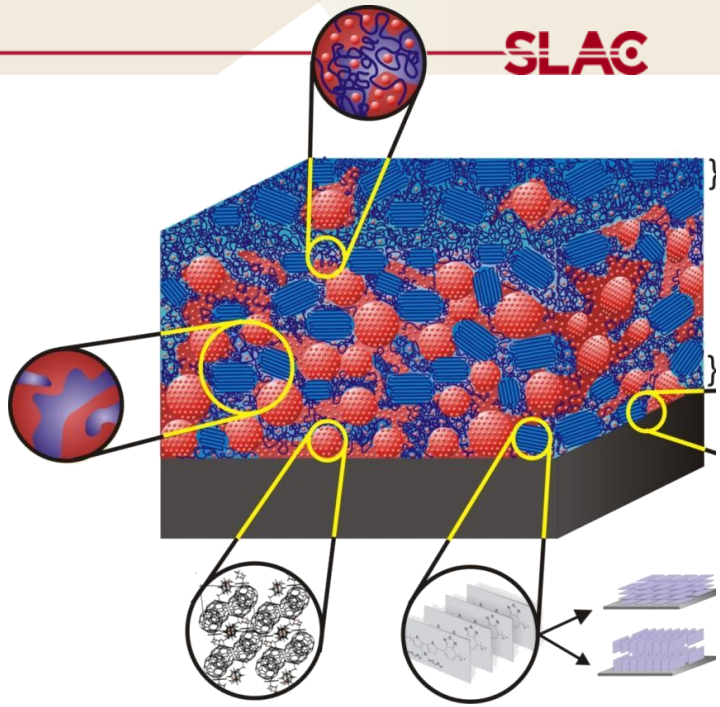
- nm scale phase separation: all 3(4) phases
- mixed (amorphous) polymer + fullerene
- Interface structure
- vertical phase segregation
- molecular packing in polymer, acceptor

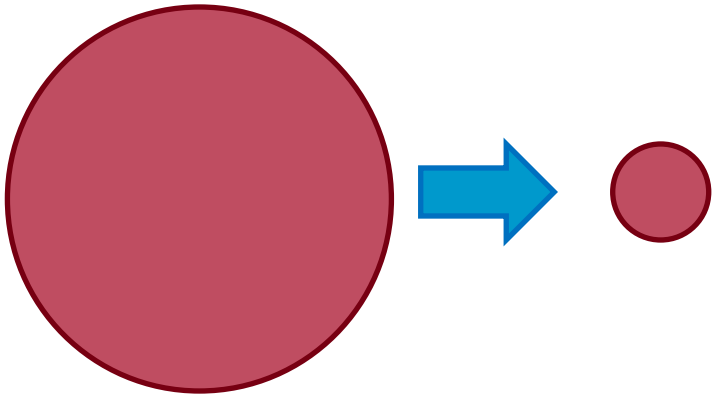
Neutrons:

- SANS, giSANS (?),
- reflectivity - vertical phase separation
- in-situ (processing?)

SANS:

- Mackay, Dadmun. stack



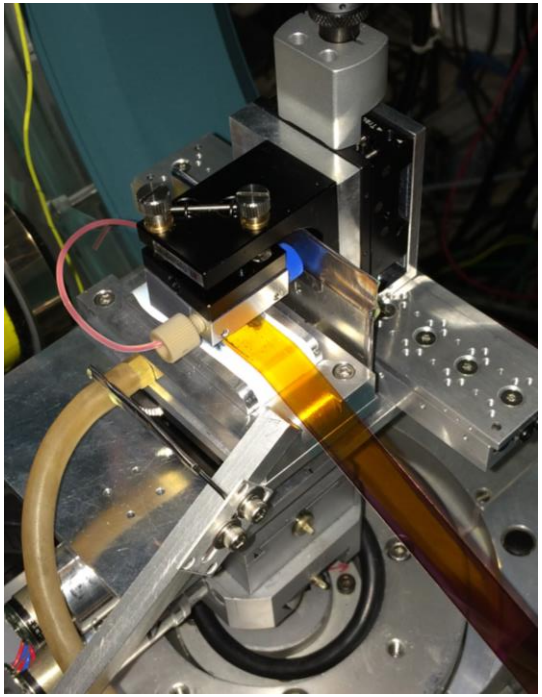


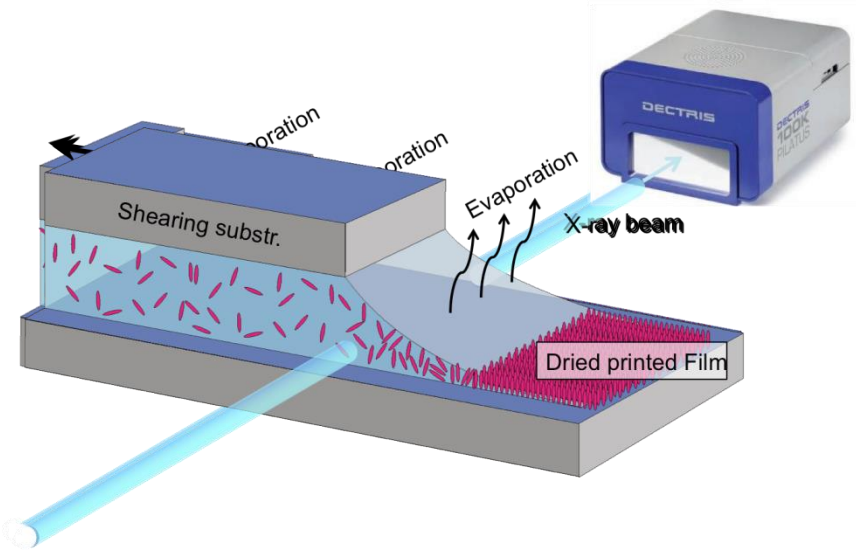
ACS Nano 2011, 5, 4768.

In-situ OPV - processing

OPV processing: in-situ

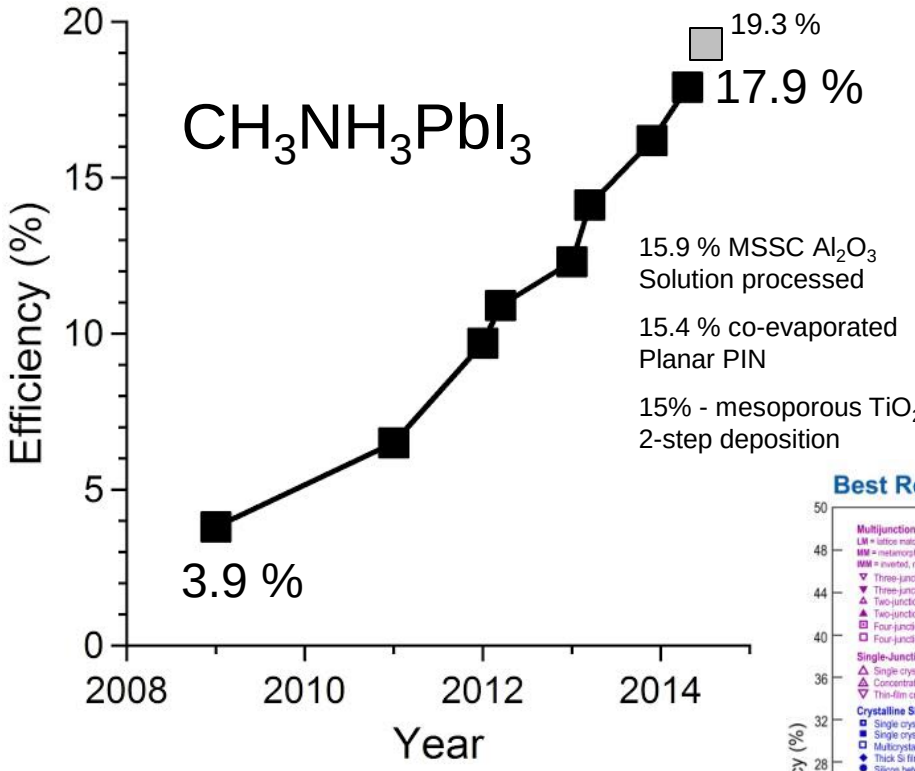
- printing (shearing, roll-to-roll, slot-die)
- thermal annealing
- solvent annealing
- spin coating



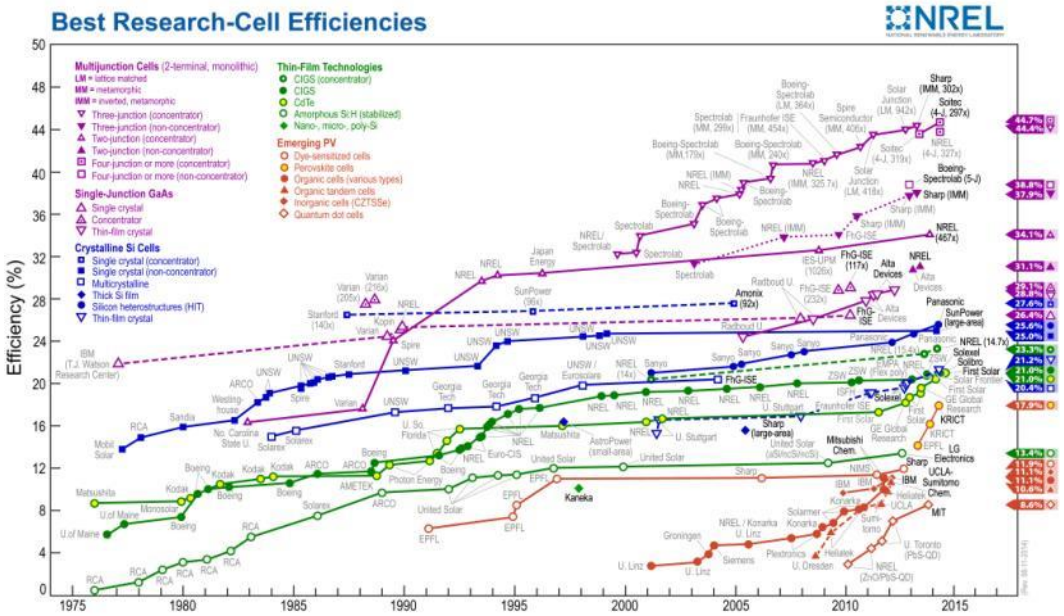


Diao, et al., unpublished

Perovskite solar materials



- Solution processing
- Earth abundant, inexpensive

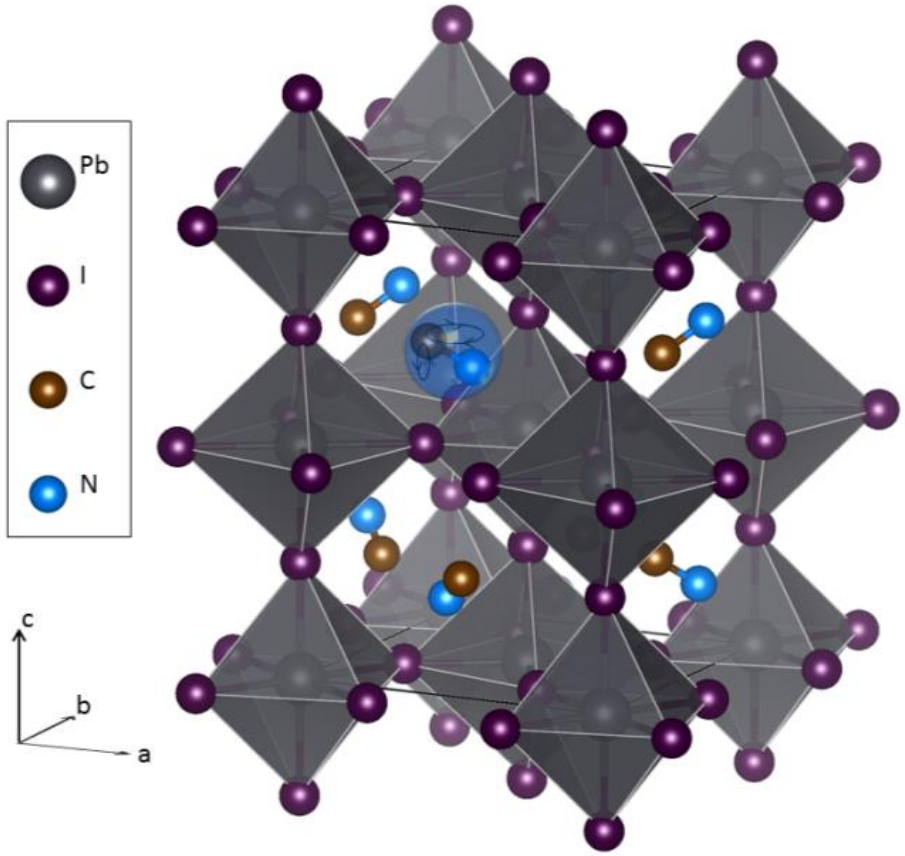


Snaith, J Phys Chem Lett 4, 3623 (2014)

Perovskite PV

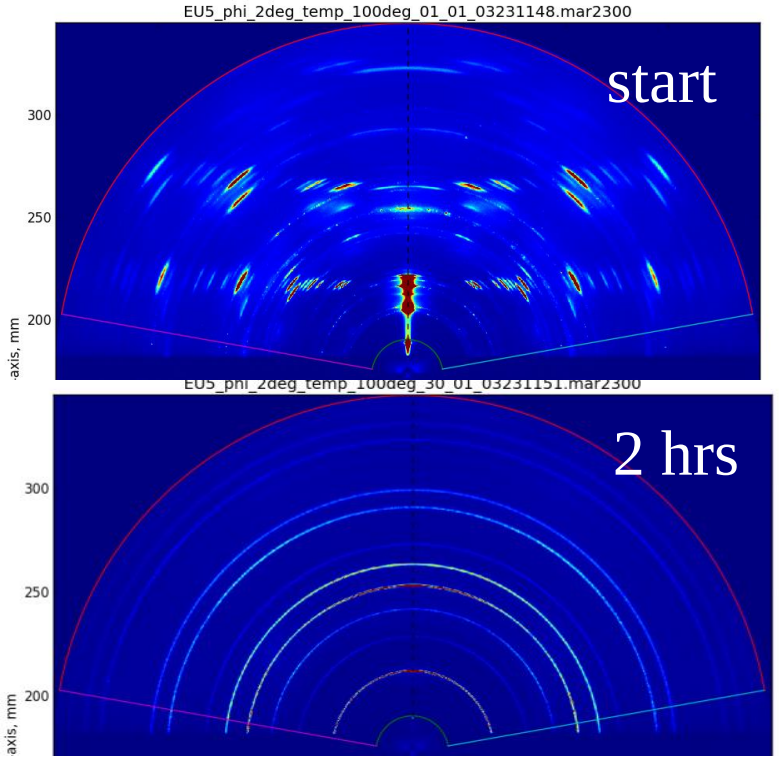
$CH_3NH_3PbI_3$: where's the (organic) atoms + dynamics?

- orientation of $CH_3NH_3^+$ (MA)
- dynamics of MA, I?



$CH_3NH_3PbI_3$

XRD



- films – 100s nm

Summary

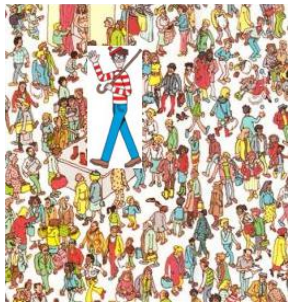
SLAC

Sustainable energy: generation (solar, PV), storage (batteries), transformation (catalysis)

- **Structure-function** relationships (nms -> microns)
- **Operation**: Where are ions and electrons? And how do they move?
- **Processing**: How are they made?

Energy Storage: Where's the Lithium?

- structural- anodes, cathodes, electrolyte, ordered and disordered
- dynamics: diffusion
- particle and cell: morphology & state-of-charge



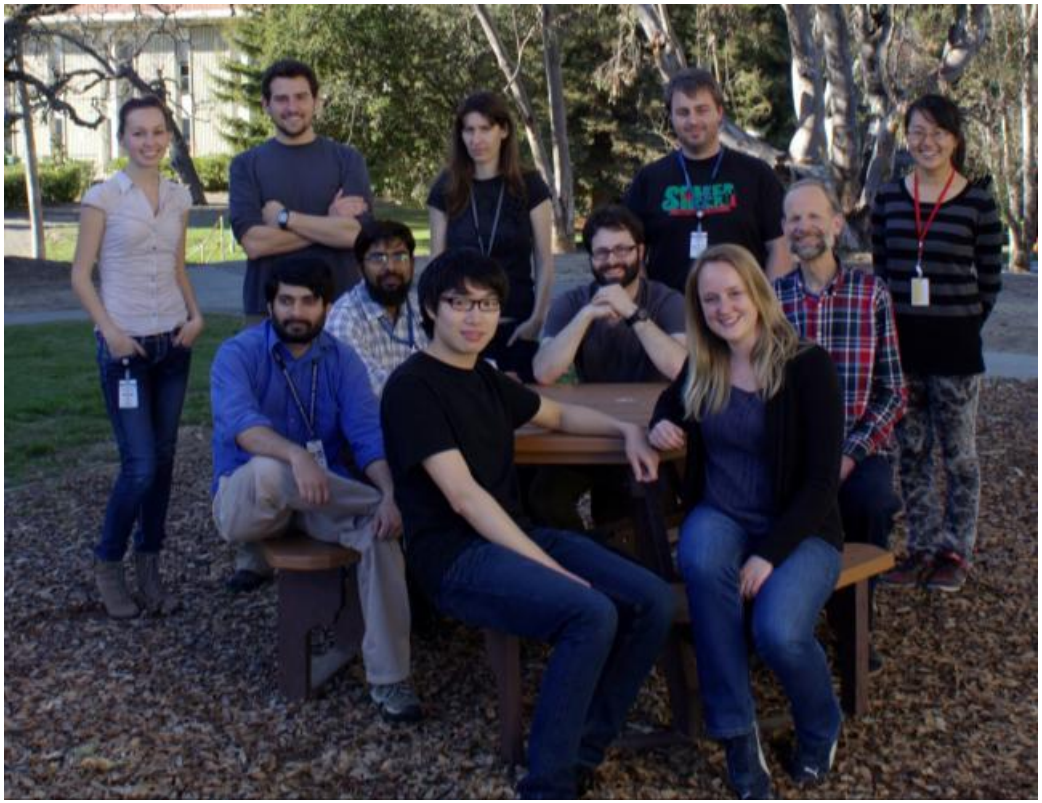
Solar: structure & dynamics

- OPV: nm scale morphology (vertical phase)
- perovskites: MA structure and dynamics
- CZTS: similar Z (Cu, Zn)

See what X-rays can't

Thanks

- SSRL Materials Sciences & Technical Staff
  - Johanna Nelson Weker, Chris Tassone
- Research Group (present and past)
  - Linda Lim, Kristin Schmidt
- Cui & McGehee groups at Stanford

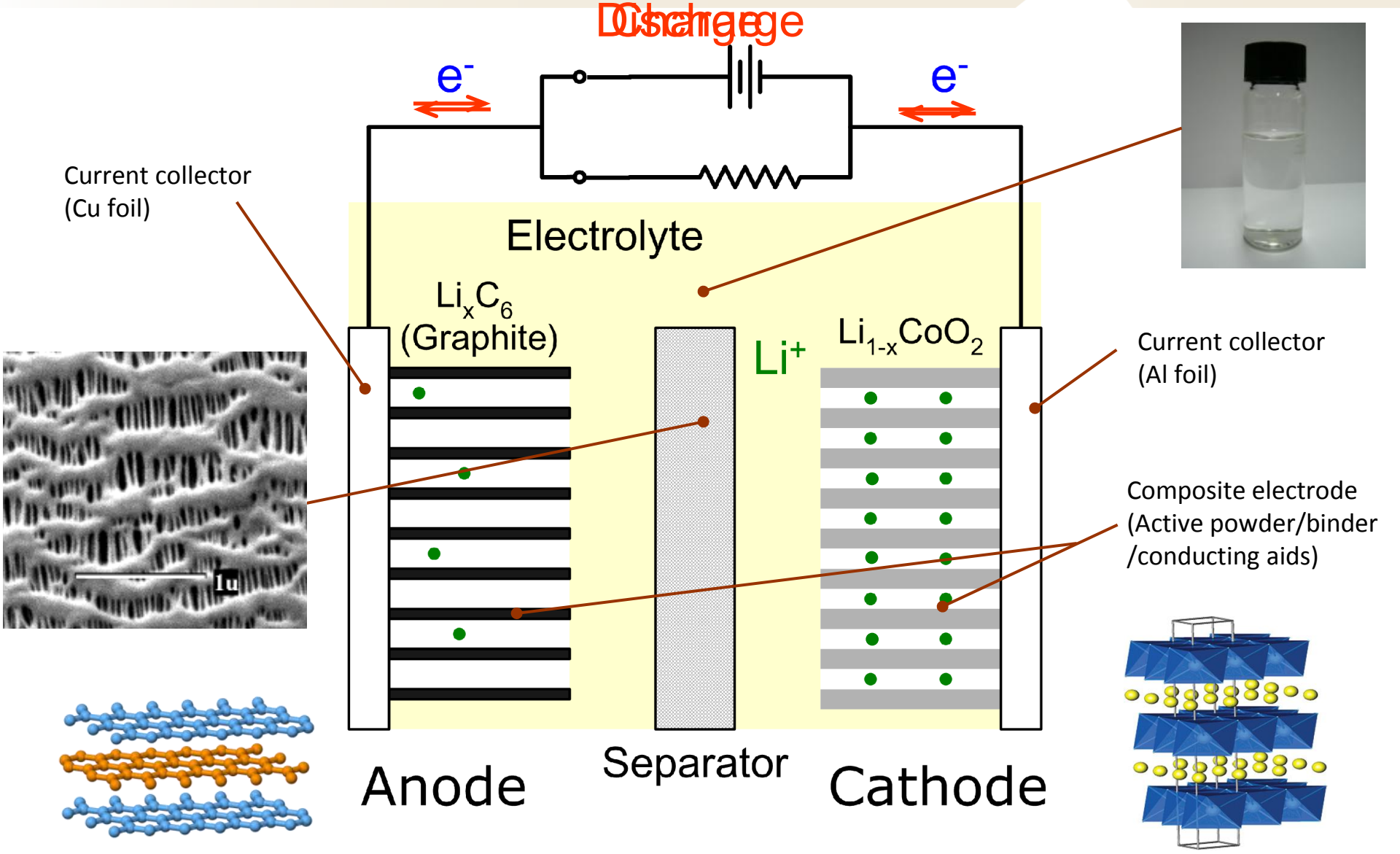


LDRD Laboratory Directed Research & Development

SunShot U.S. Department of Energy

King Abdullah University of Science and Technology KAUST

Battery Operation

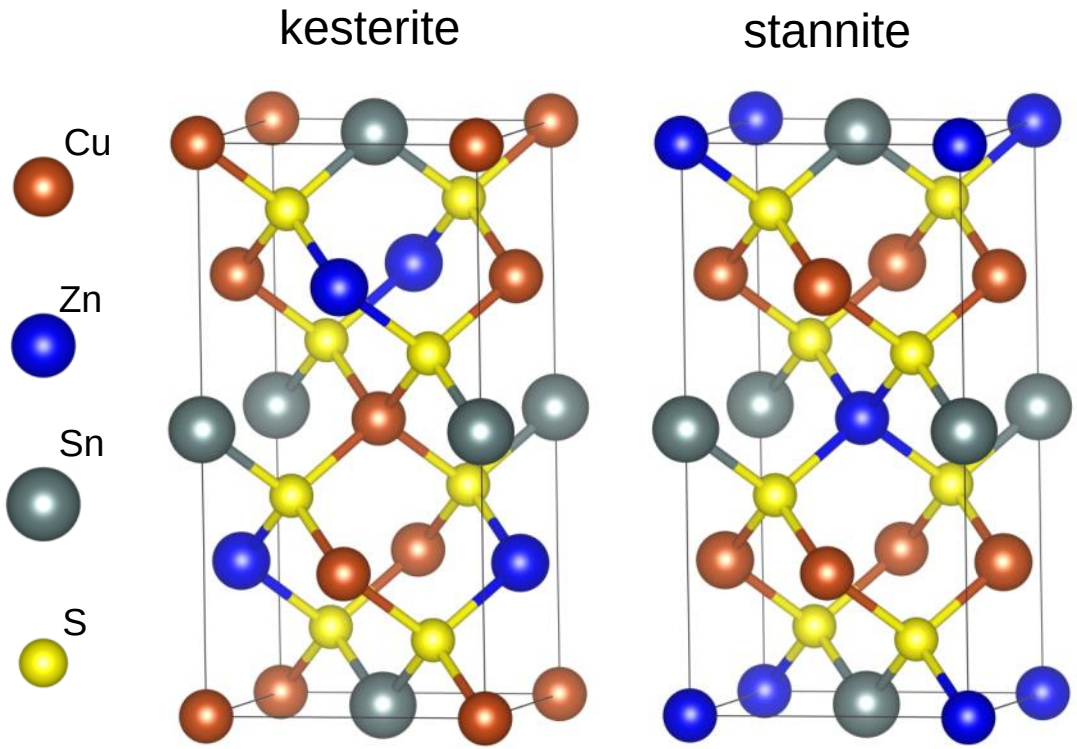


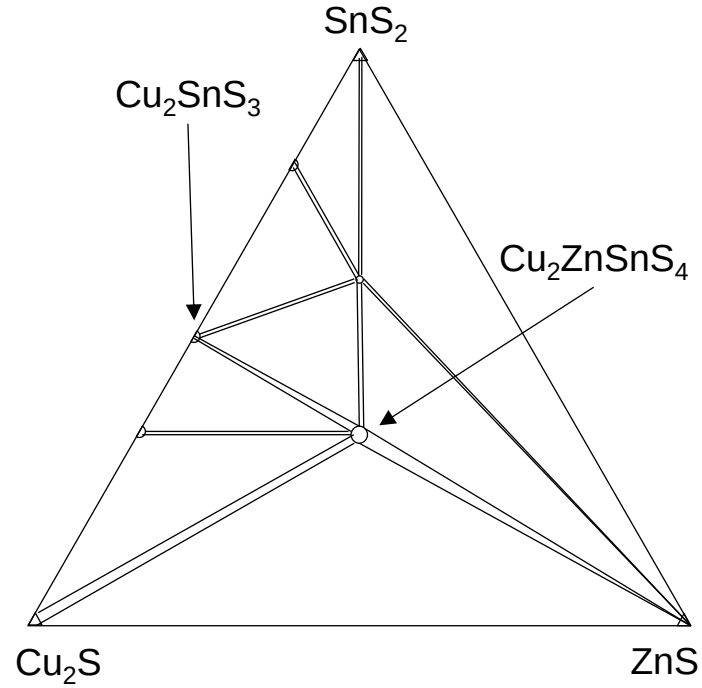
$Cu_2ZnSn(S,Se)_4$ Background: Complexity

SLAC

Potential Complications Inherent to CZTS

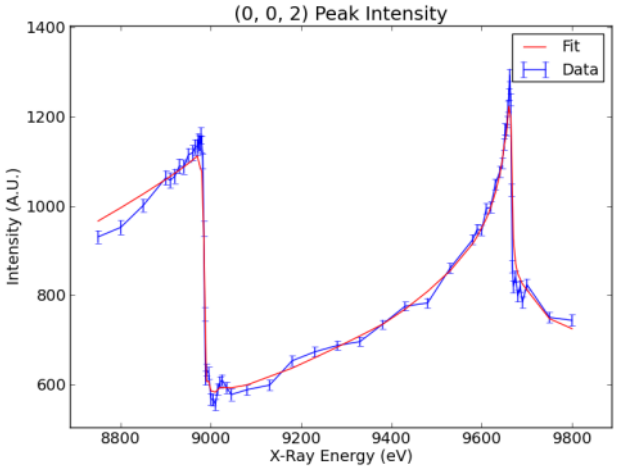
- Multiple crystallographic phases (kesterite vs.stannite)
- Many possible secondary phases (ZnS, CuS, Cu_2S, SnS_2, Cu_2SnS_3)
- Alloying S and Se
- Strong affect on PV

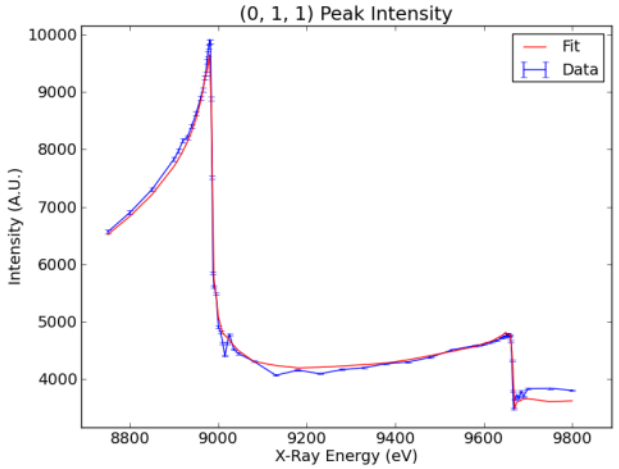


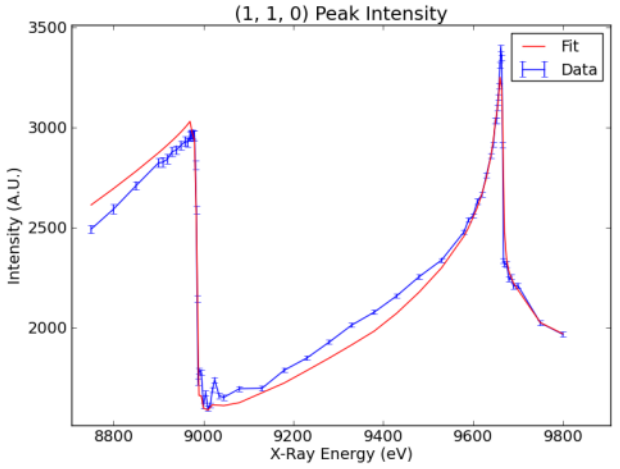


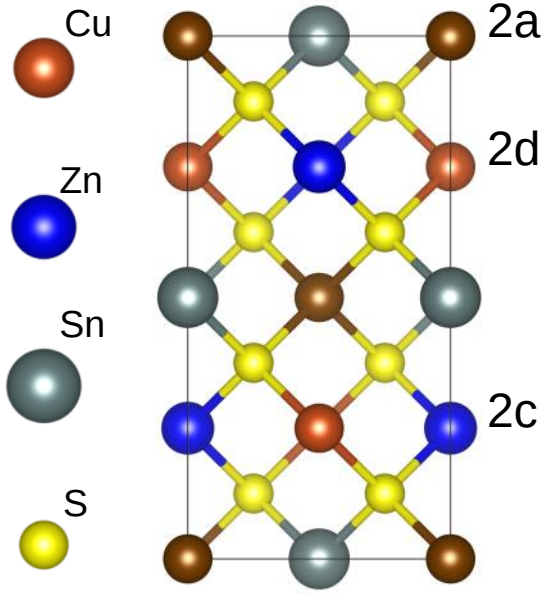
Phase diagram after Olekseyuk et al., J. Alloys and Comp. **368** (2004) 135-143.

Resonant X-Ray Diffraction Model







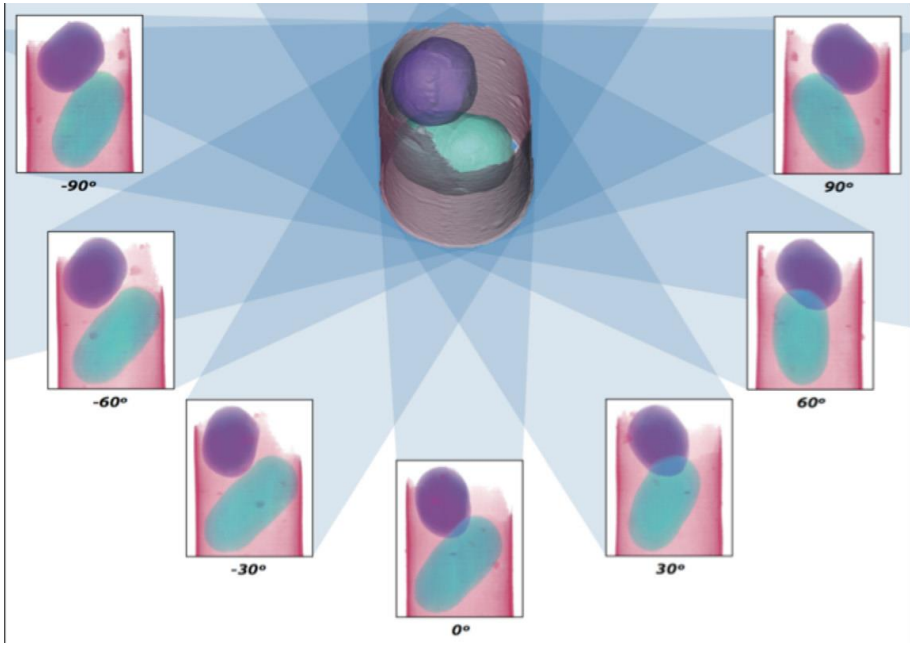


Position	Cu Occupancy	Zn Occupancy	Vacancy
2a $(0,0,0)$	0.90	0.10	0.00
2d $(0,{}^{1}/_{2},{}^{1}/_{4})$	0.50	0.45	0.05
2c $(0,{}^{1}/_{2},{}^{3}/_{4})$	0.45	0.48	0.07

In operando Tomography -> 3D

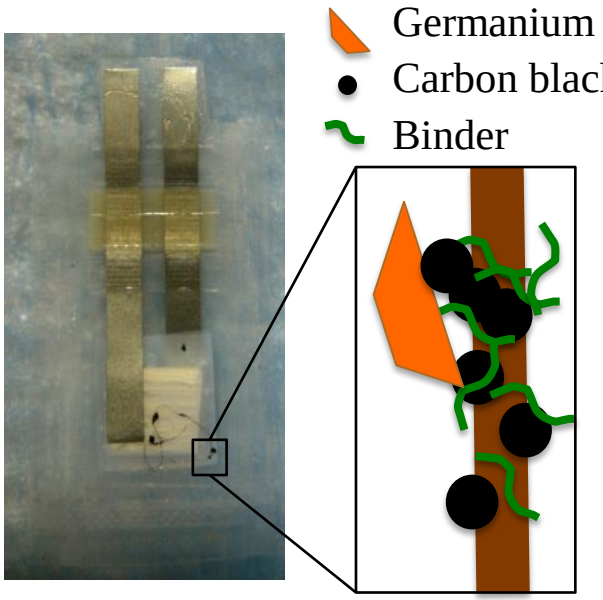
Computed (axial) tomography:

- 2D images at many angles used to form 3D rendering
- "CAT scan"



***In situ* tomography cell:**

- Image over a large range of angles



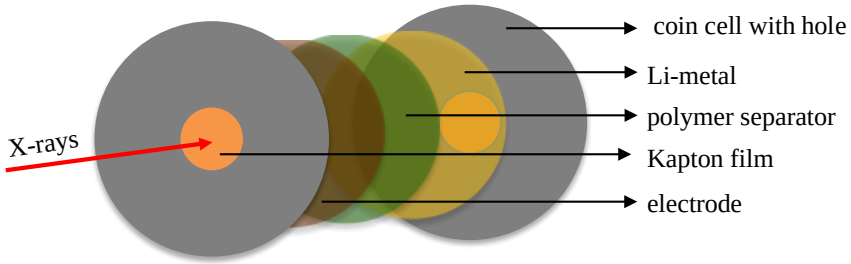
3D Goals: Quantify volume changes

In-situ Methodology

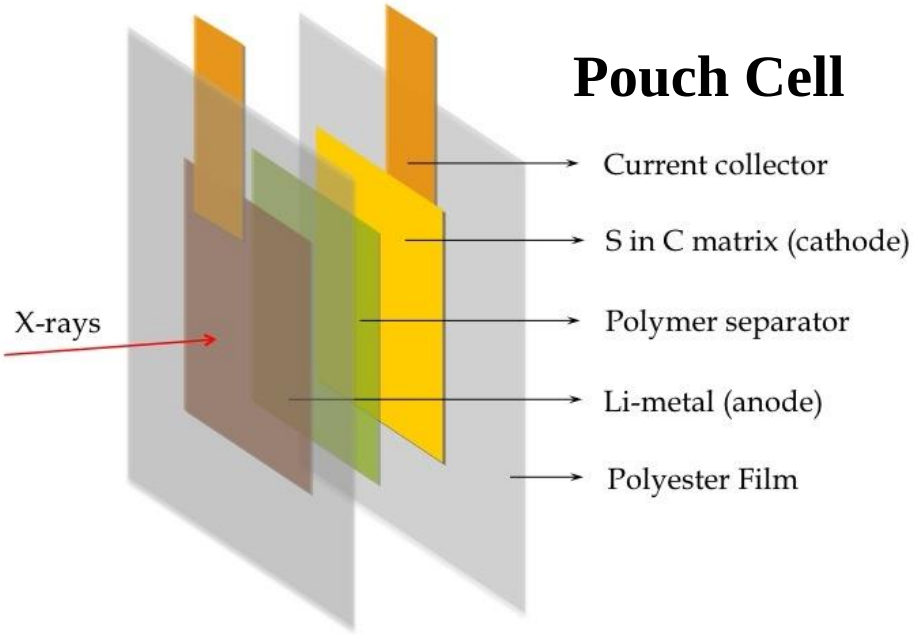
In-situ battery Cell – follow structural & morphological changes:

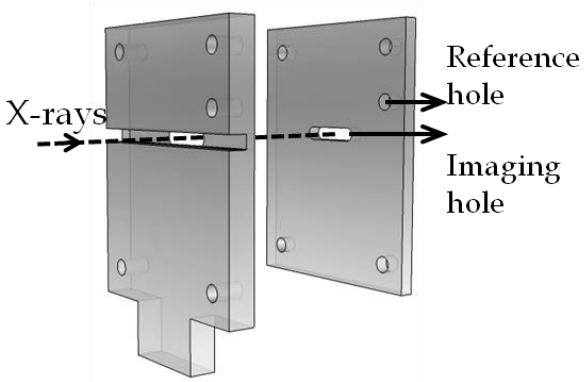
- *In-situ*, in real time (slow – hours)
- X-ray "transparent" cell

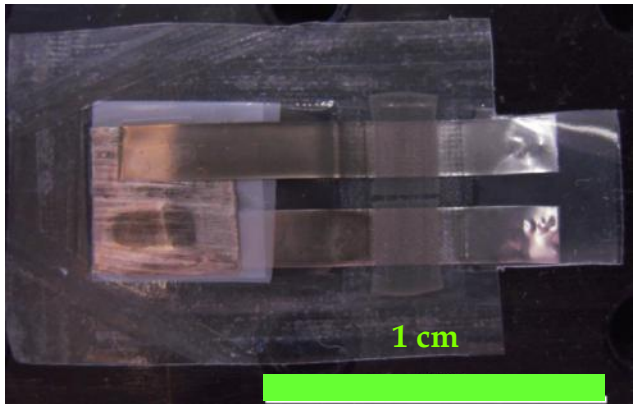
Coin Cell



Pouch Cell







Misra, Liu, Nelson, Hong, Cui, Toney, *ACS Nano.*, (2012).