X-Ray Absorption Spectroscopy: Application on Battery Research

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Outline

- General introduction to X-ray Absorption Spectroscopy (XAS)

- Case study

  Capabilities of beamline 9-BM at the APS

  Case 1 Mn species on anode: Capacity fading of LMO/C system

  Argonne (Amine group) and Tsinghua Univ. (Qiu Group)

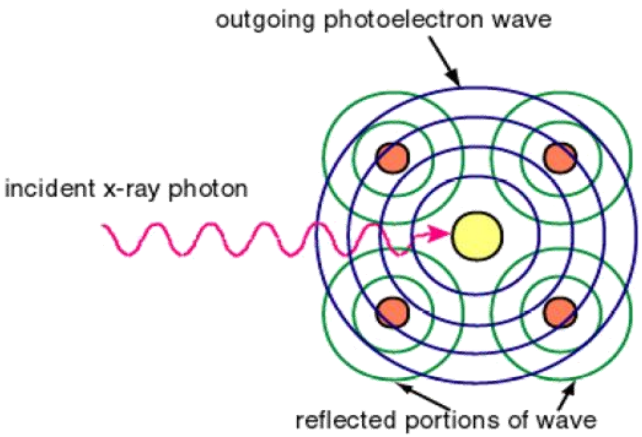
  Case 2 *In situ* Li_2S_9 electrolyte measurement: initial study at 9-BM

  Argonne (Amine group) and APS 9-BM

  Case 3 *In situ* probes of sulfur redox processes for Li-S battery

  Nazar group (general user at 9-BM)

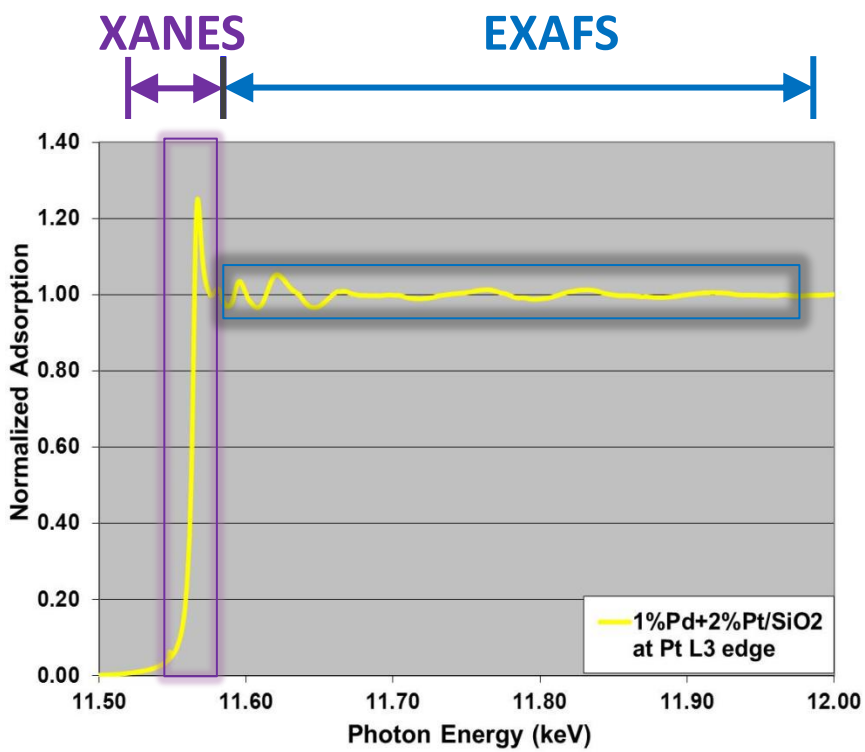
General Introduction to X-Ray Absorption Spectroscopy (XAS)



XAS

XANES = X-ray Absorption Near Edge Structure

EXAFS = Extended X-ray Absorption Fine Structure



- **Element of interest**
- **Orbitals probed:**

  Density of unoccupied (available) states

  K edge: *s*→*p* closer to atom core

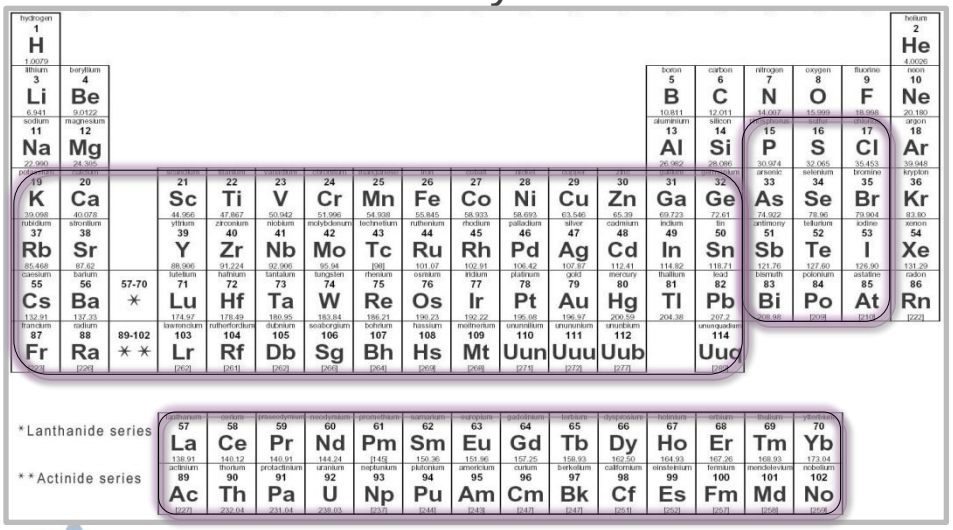
  L edge: *p*→*d* closer to atom surface

- **Element specific**
- **Oxidation State**
- **Coordination environment (sometime)**

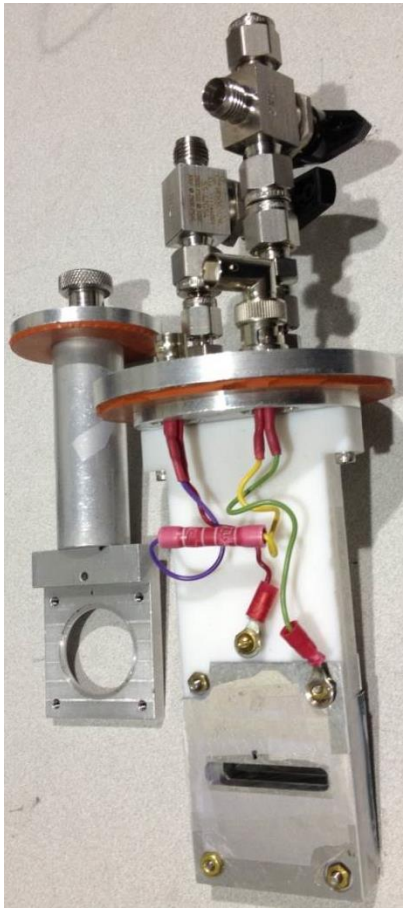
- **Electronic structure**
- **Interaction, bonding, local structure**
- **Coordination environment**

Capability of 9-BM

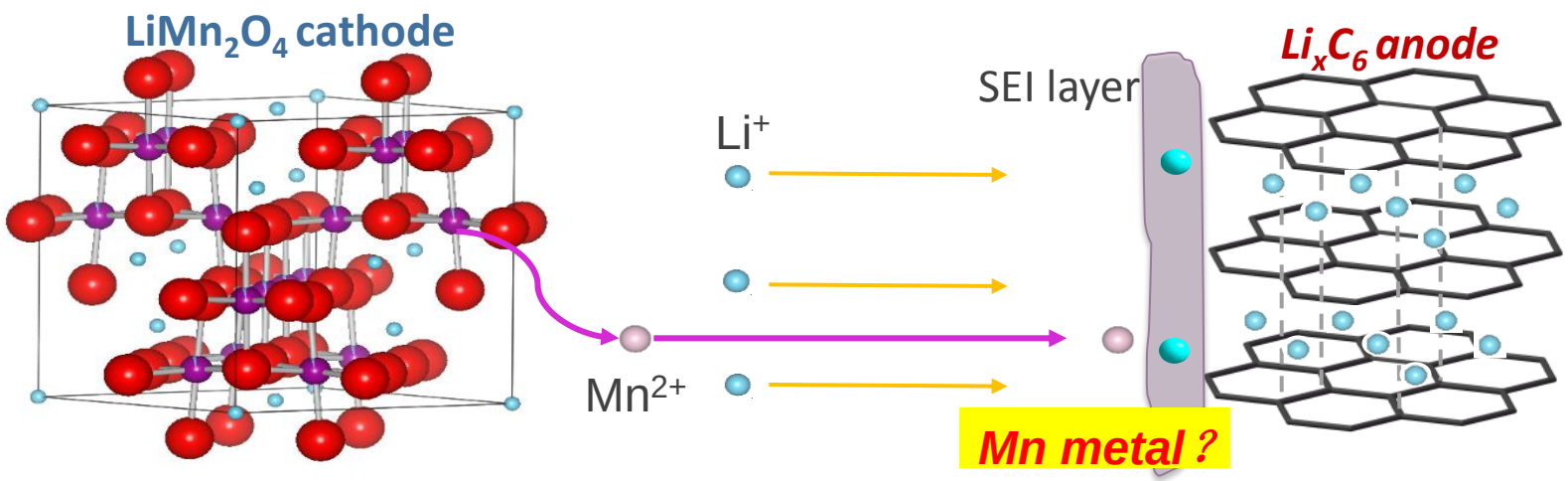
- Source: 1×10^{11} Photons/sec
- Si(111): 2.1 keV to 24.4 keV
- Users:
  - Geology, Earth Science
  - Material Science
  - Catalysis
  - Battery
    - 3d metals
    - Precious metals as catalysts
    - S: Li-S battery
    - K: K battery



- Ex-situ measurement: basic and Total Electron Yield (TEY)
- In-situ measurement for battery



Case study 1: Capacity fading of LMO/C system

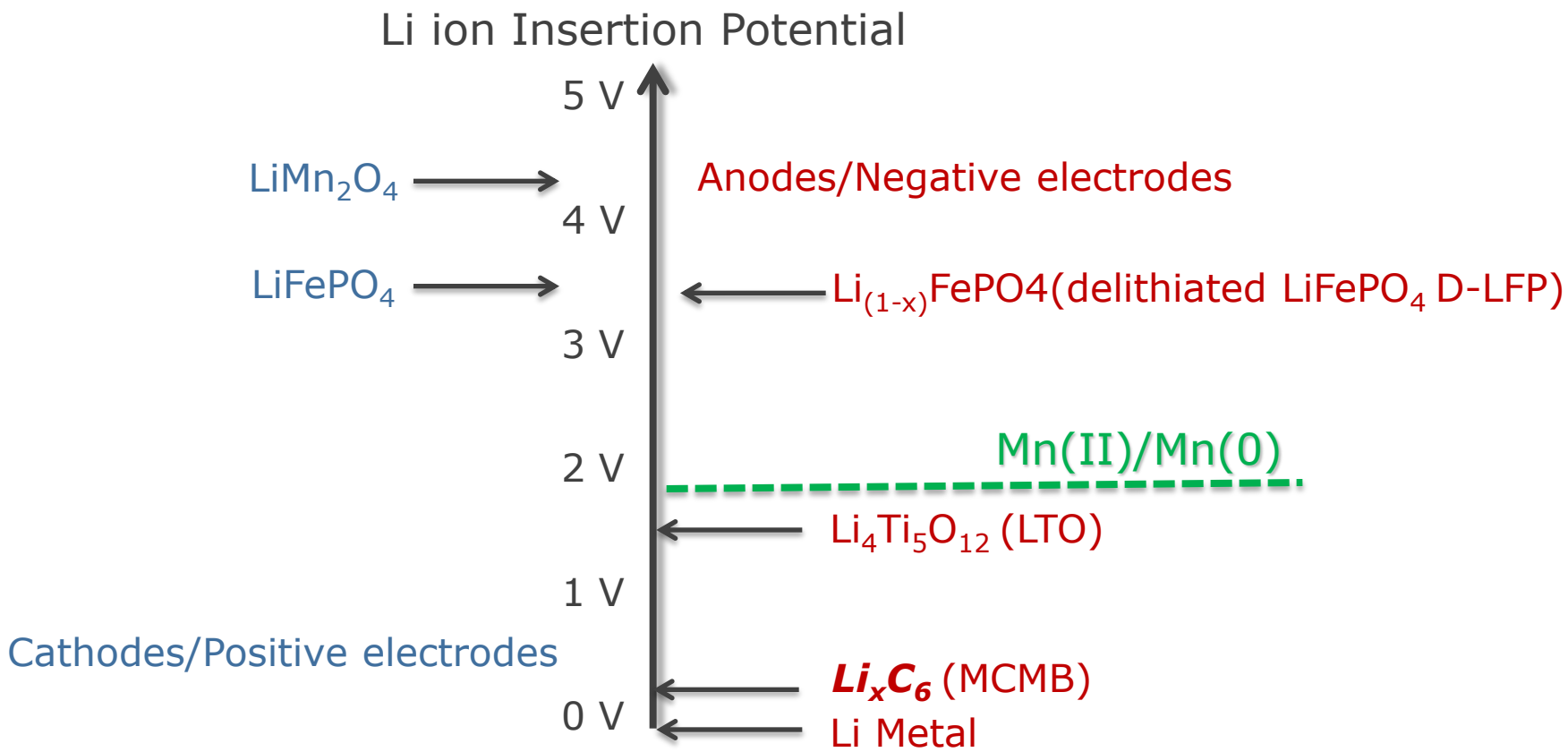


Dissolution-deposition of Mn from $LiMn_2O_4$ cathode to anode

- Disproportionation at interface: $LiMn_2O_4 \rightarrow MnO_2 + Mn^{2+}$
- Mn^{2+} dissolve and diffuse to anode
- Reduction at SEI to form Mn metal
- Inhibits Li^+ diffusion / catalyzes electrolyte decomposition
- Loss of active $LiMn_2O_4$
- Impedance rising due to inactive products

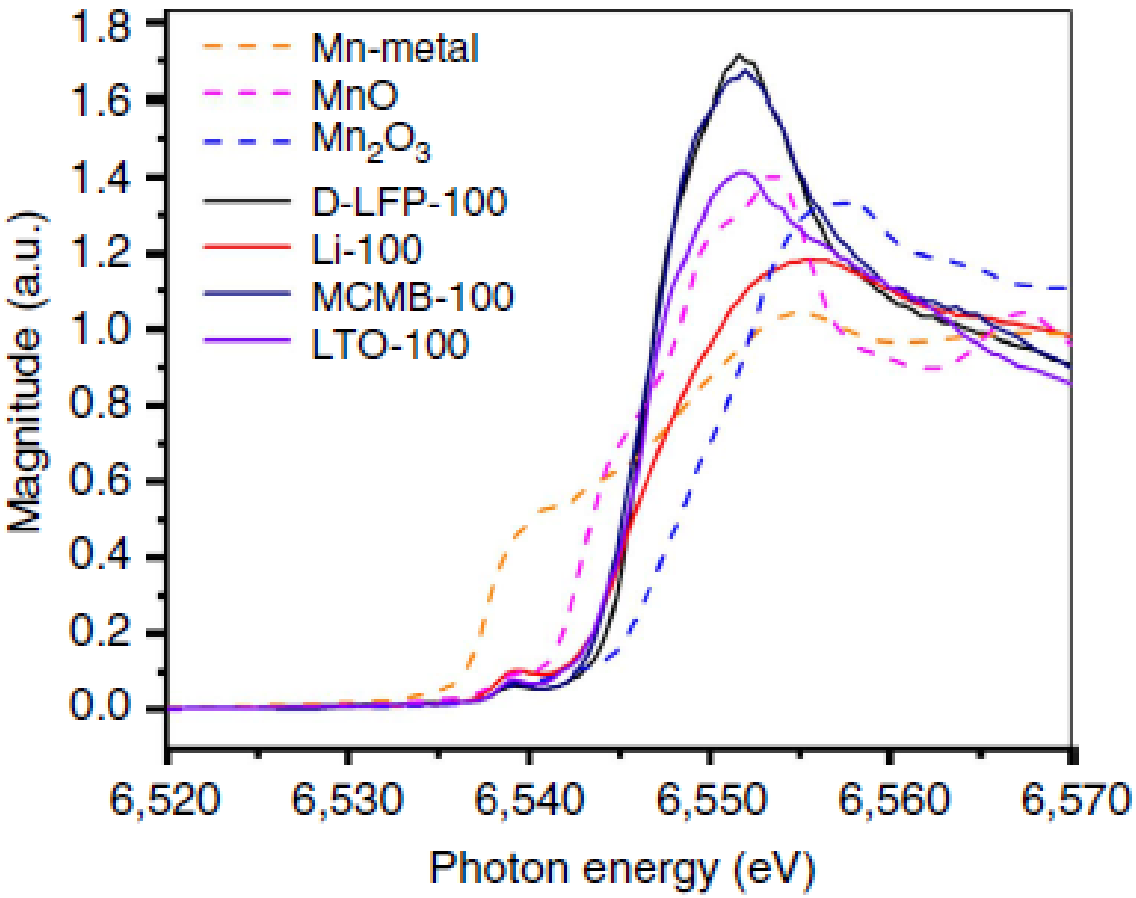
Vetter, J. *et.al* . *Journal of Power Sources* **2005**, *147*, 269.
Whittingham, M. S. *Chem. Rev.* **2004,** 104, 4271-4301

Electrochemistry on the Mn deposition



- Reduction of $Mn^{2+} \rightarrow Mn$
- Speculation in literatures:
  The lithiated anode has low chemical potential and high chemical activity
- Hard to detect the extremely low concentration of Mn species

Mn-K XANES of standards and anode samples

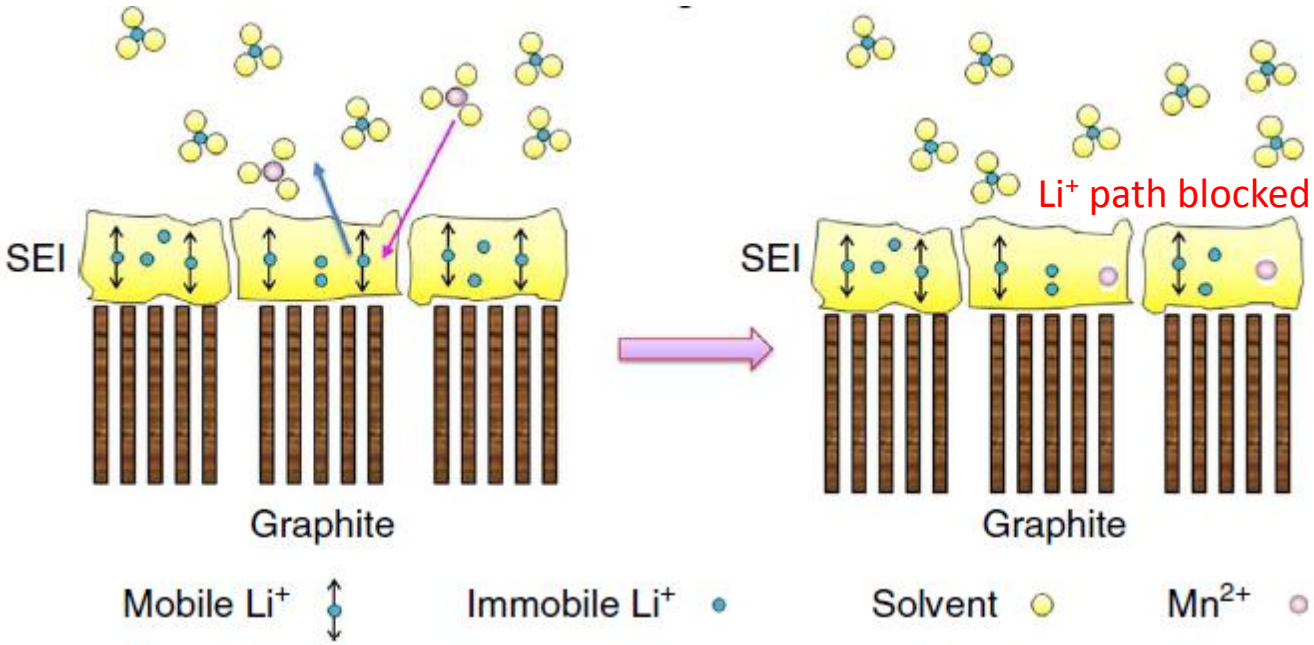


Mn species deposited on anode: Mn^{2+} instead of Mn metal
Independence on cycling AND anode

Nat. Comm. 4, 2437, **2013**

Mn(II) deposition & Capacity fading

Proposed model: Ion exchange instead of reduction

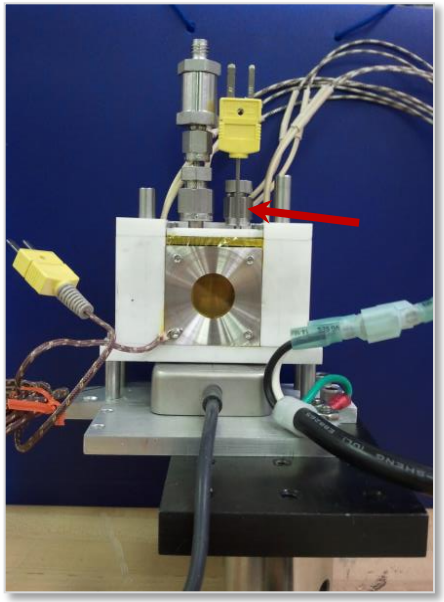


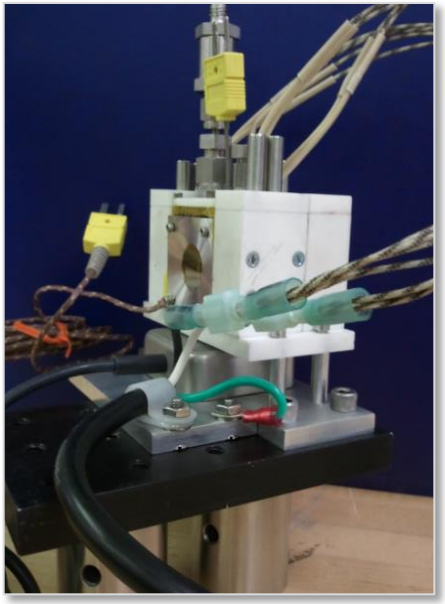
- **Mn^{2+} replaces active Li^{+} in SEI layer**
- **Impedance rises at anode**
- **Capacity fades in battery**

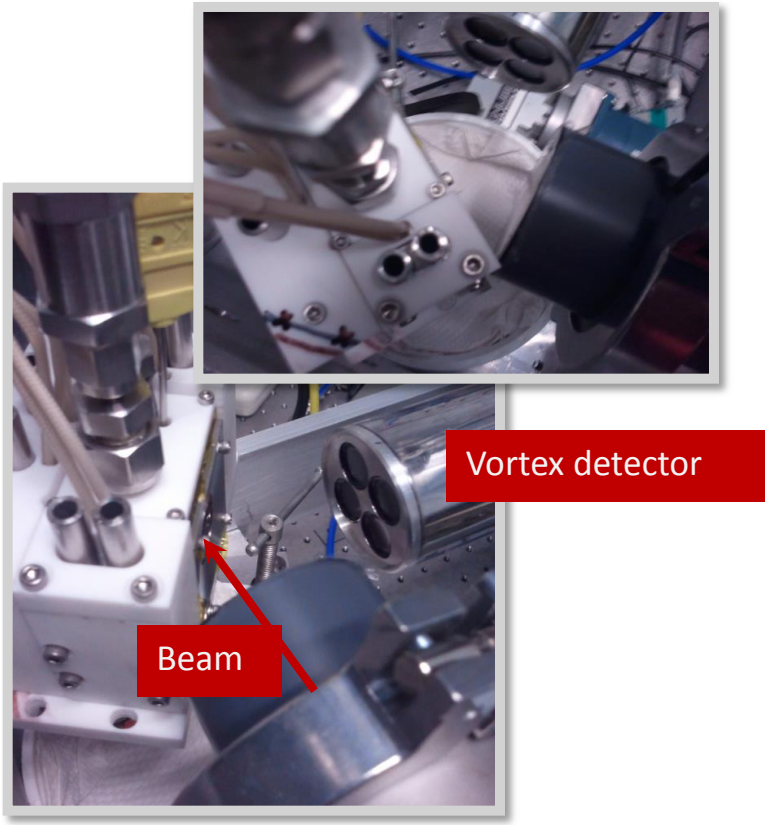
In-situ liquid cell for intermediate energy (~3 keV)

- Material: stainless steel
- Capacity: ~8 mL
- Gas in and out
- Relief valve
- Liquid injection port
- Heat (miniature cartridge) and cool (fluid)
- Macor bar insulator
- Mini stirring system
- Thermocouple: control and over-T (window)
- Kalrez O-ring (-15°C–327 °C)

Trick: window---THIN, SEAL, FLAT

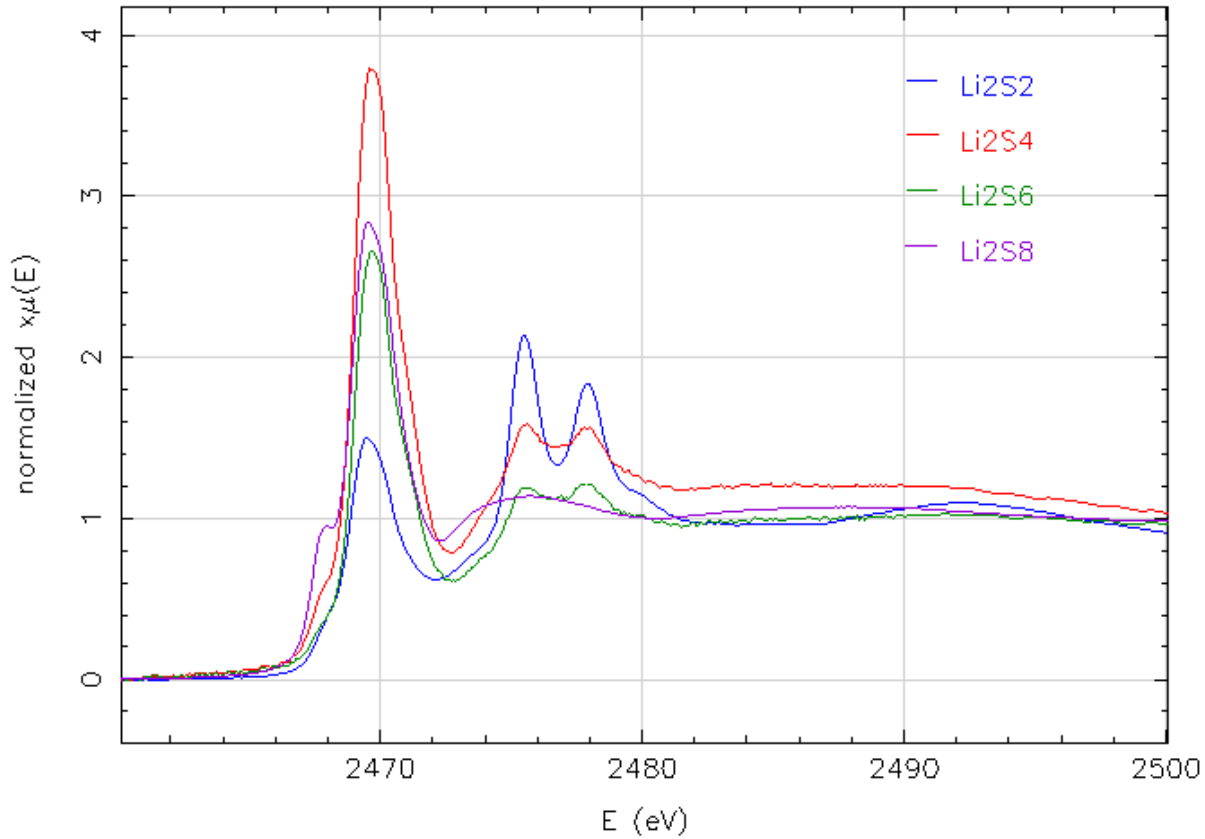






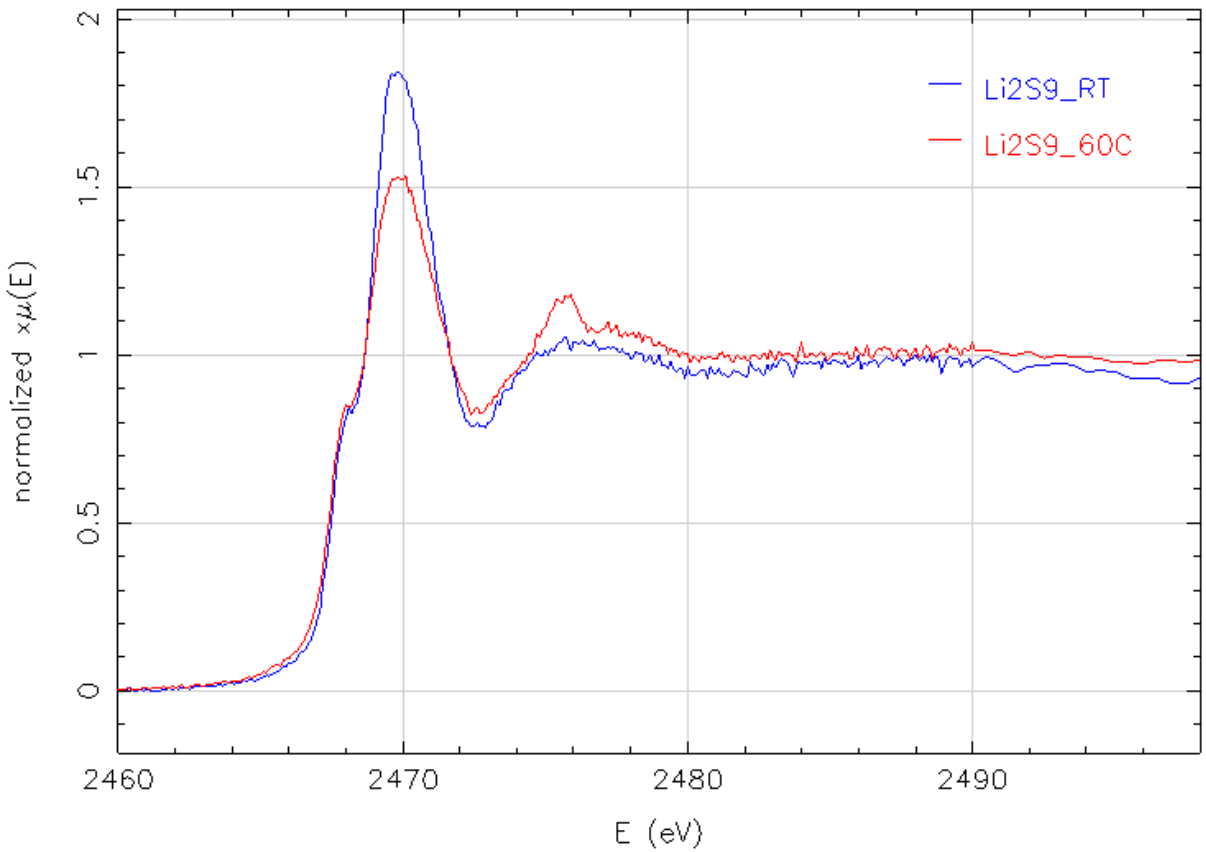
Case study 2: Temperature effect *on* Li_2S_9 electrolyte

S-K edge XANES: Li_2S_x standards in solution (RT)



- Strong absorption ~2469.5 eV (white line) & a higher-energy feature ~ 2476.8 eV: 1s → 3p transition of elementary sulfur
- Features ~2467.7 eV: characteristic of linear polysulfide
- Very sensitive to the compounds

S-K XANES of Li_2S_9 electrolyte: RT vs. 60°C

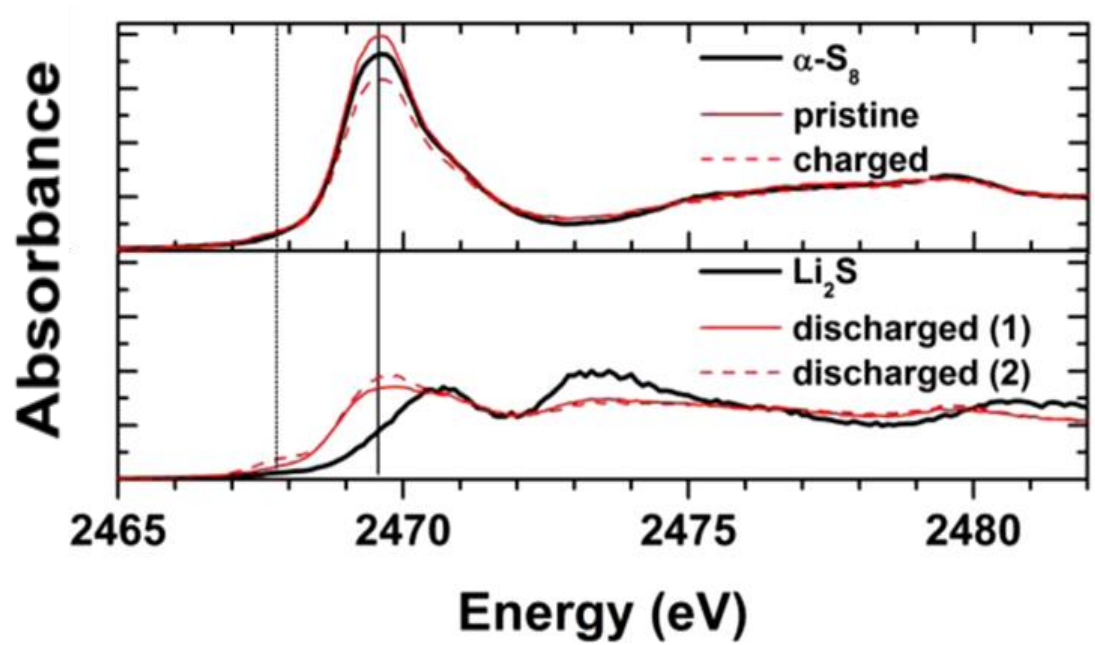


Significant change in white line intensity: sign of S-S cleavage

More work is on the way!

Case study 3: Operando XAS
Mechanisms of Sulfur Redox on cycling of Li−S Batteries

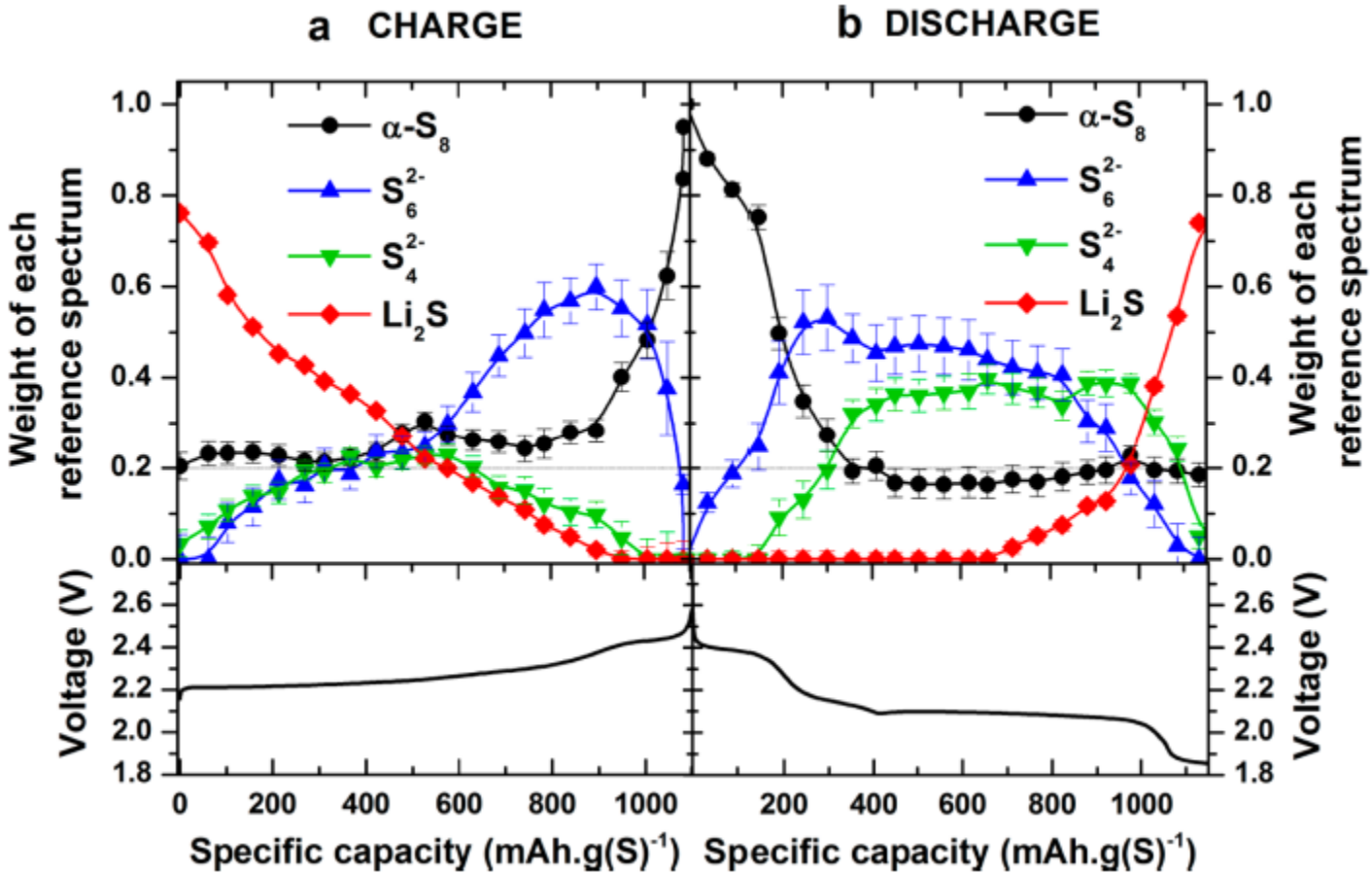
- Cathodes: sulfur impregnated in uniform porous carbon nanospheres (PCNSs)
- α-S_8 and synthesized polysulfides Li_2S_x (x=1.2.4.6.8)as references
- Charge: pure elemental sulfur at the end
- Discharge: Li_2S + α-S_8 remaining at the end, +(linear polysulfide)



J. Phys. Chem. Lett. 4, 3227, **2013**

Evolution of S-K XANES

linear combination of 4 reference compounds: α-S_8, S_6^{2-}, S_4^{2-}, and Li_2S



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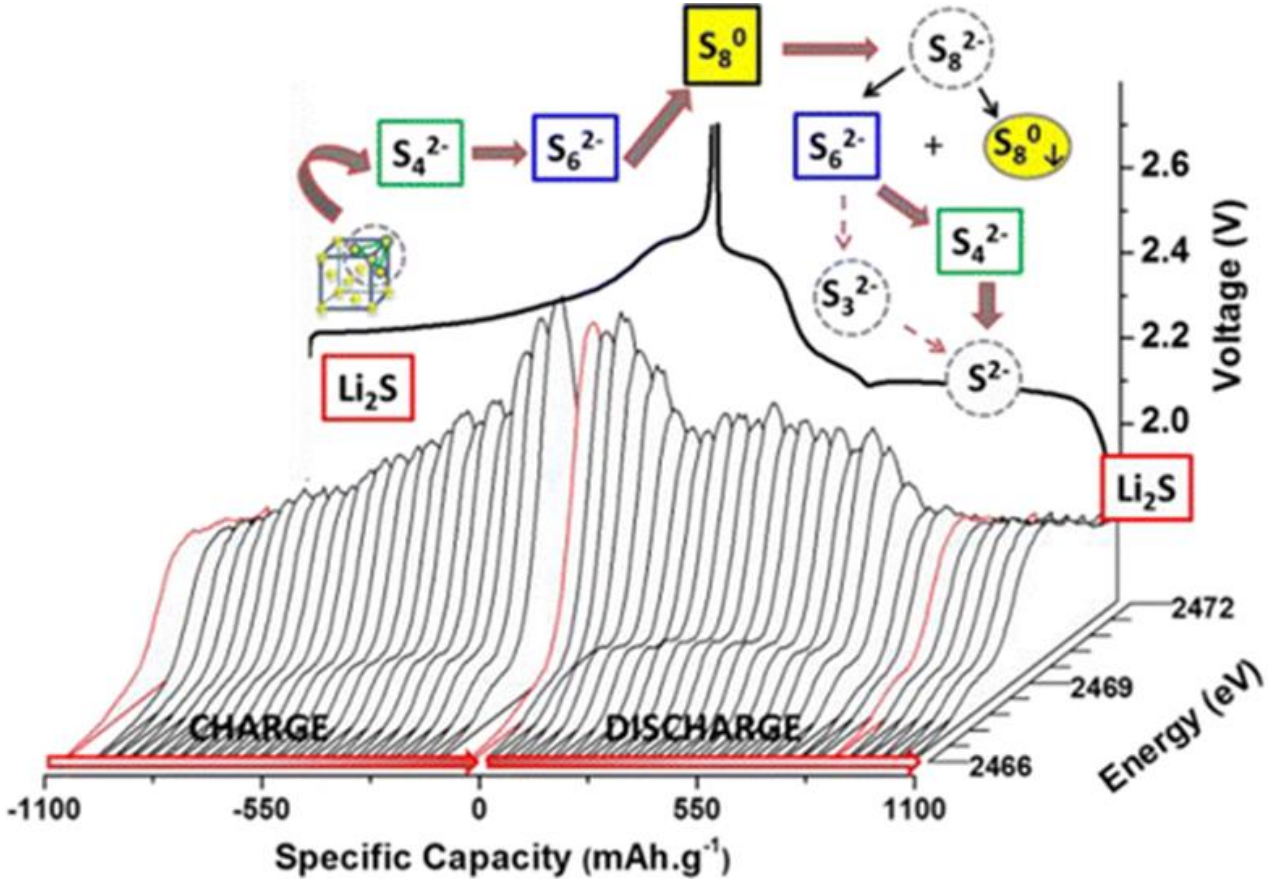


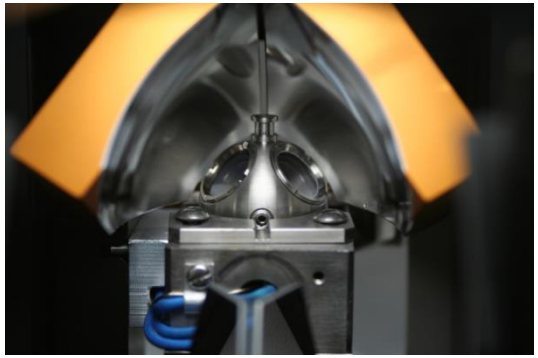
- **Operando XANES identified sulfur species in the cell during cycling**
- **Consistency between XANES evolution and electrochemical profiles →Mechanism**

J. Phys. Chem. Lett. 4, 3227, **2013**

Other capabilities: Concurrent XAS & FTIR setup

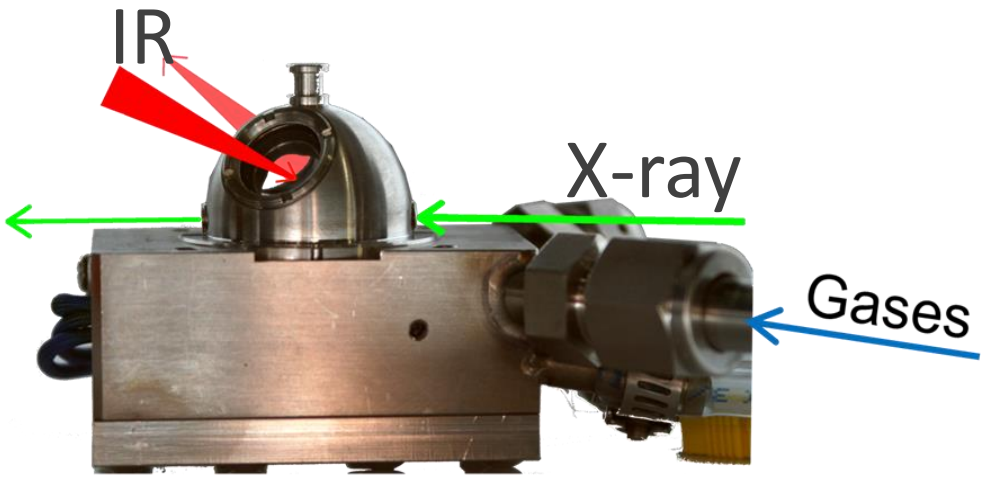
Bruker Tensor 37

- External sample compartment: modified to allow x-ray transmission
- MCT detector



Harrick praying mantis cell

- Special DRIFTS cell dome for x-ray transmission
- Sample holders with various path lengths for XAS

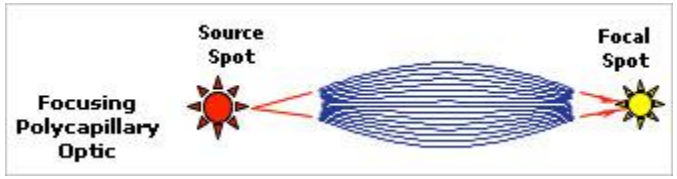


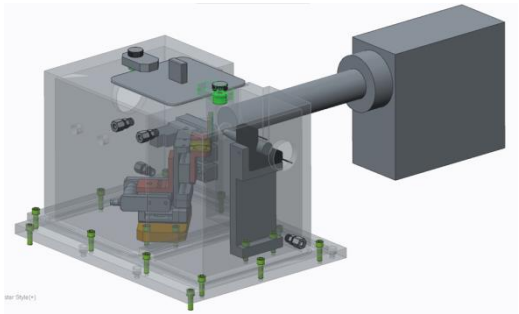
Other capabilities (continued)

- Mass Flow Control System, remote controlled by Labview program
- Glovebox handling air/moisture sensitive samples
- Wetlab for offline sample treatment
- Pfeiffer PrismaPlus Compact Mass Spectrometer System
- Handling hazardous gases

Polycapillary focusing optics

- Small focused beam at the sample surface with diameters around tens of micrometers
- Insensitive to beam motion
- Increased intensity, enhanced spatial resolution





Acknowledgements

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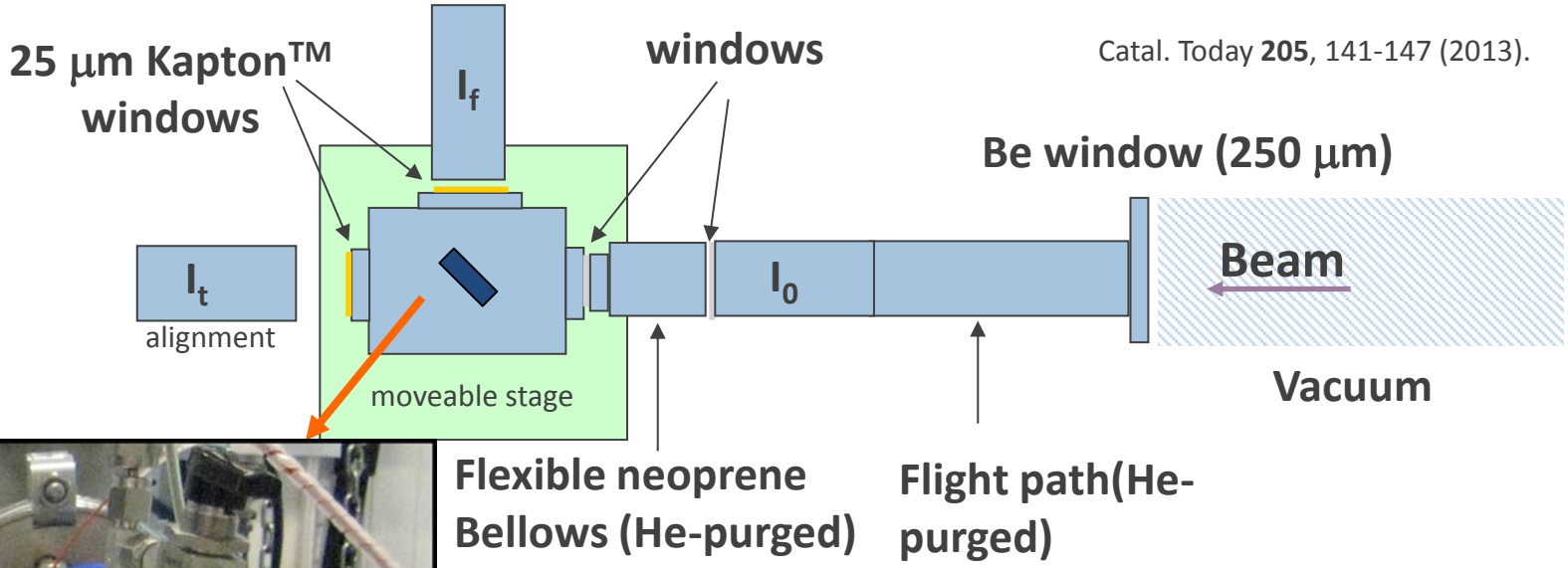
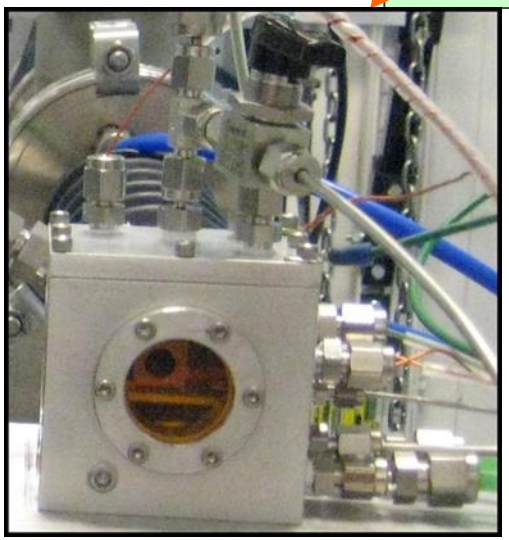
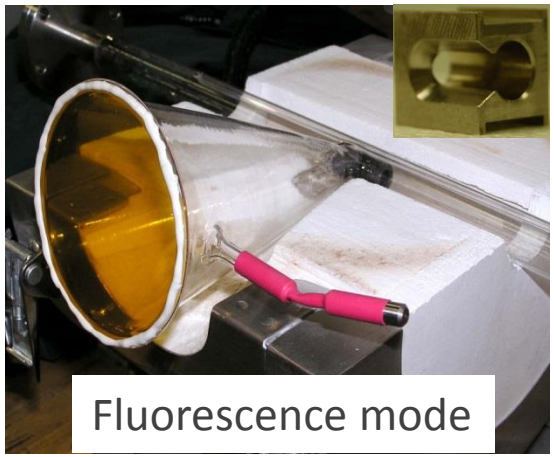
U.S. DEPARTMENT OF ENERGY | Office of Science

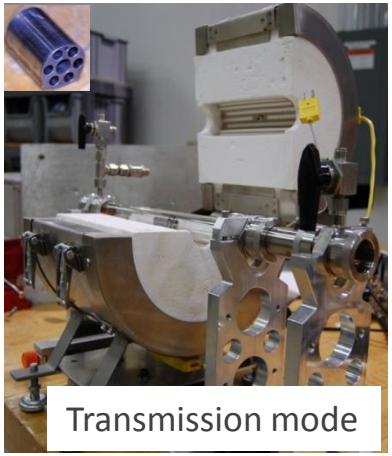
SII Vortex 4-element Si-drift detector

Catal. Today **205**, 141-147 (2013).

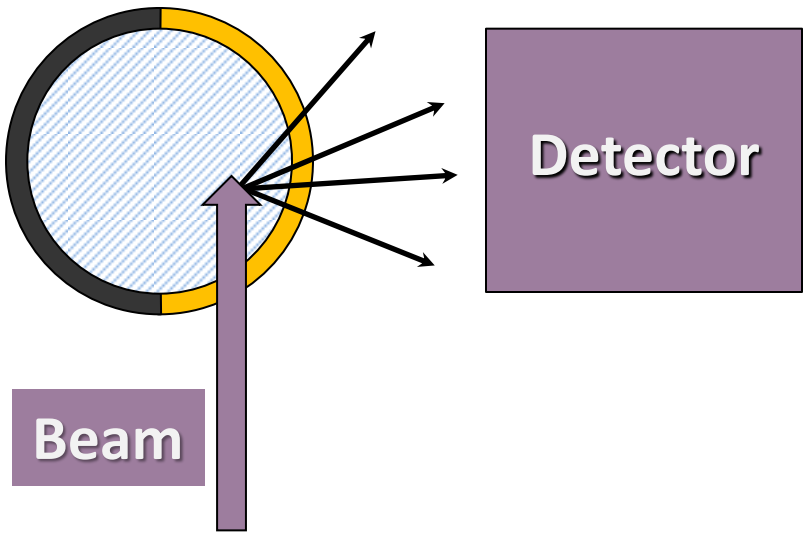


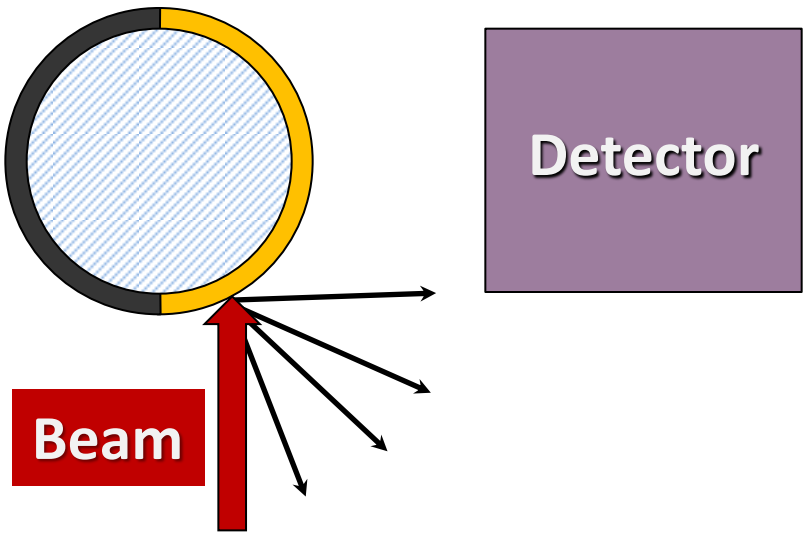






Why is the window flat?



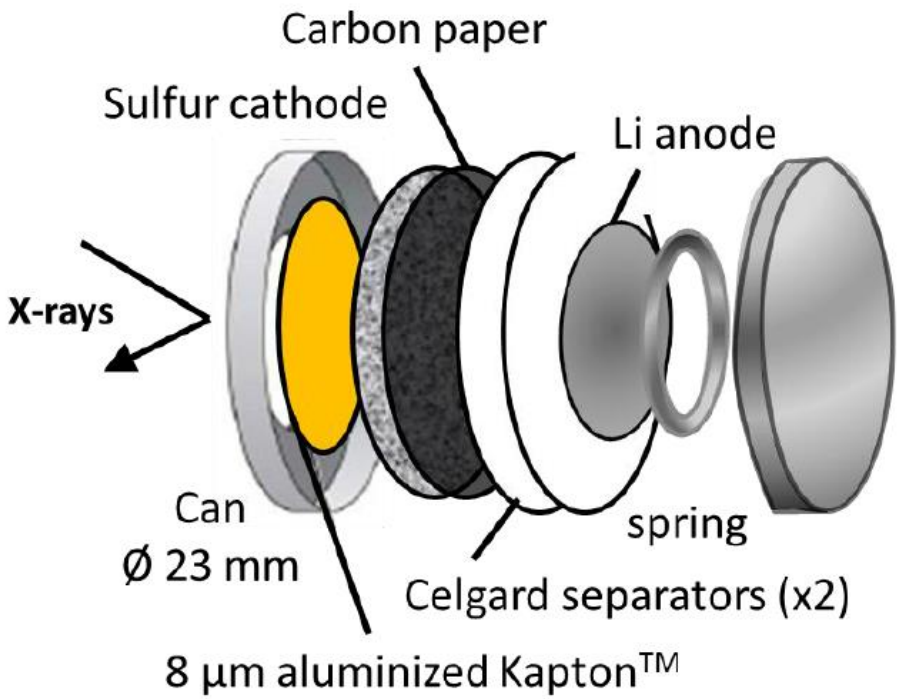


High energy: ~ 11 keV

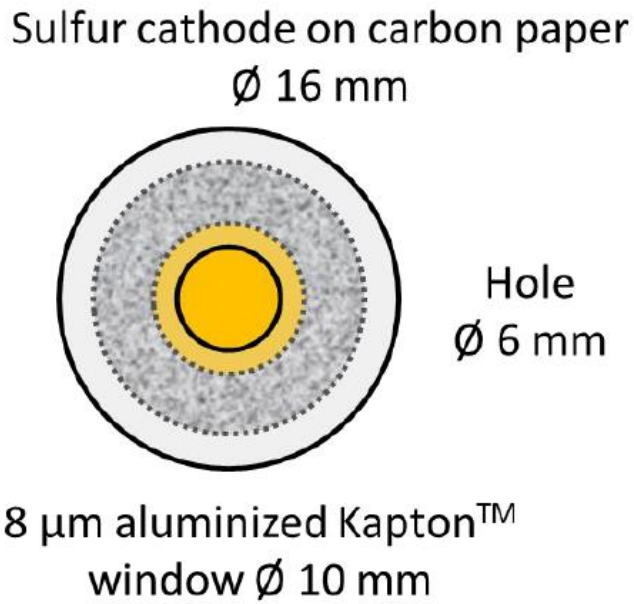
Intermediate energy: ~ 3 keV

Beam penetrates into the sample and fluorescence gets to the detector

Liquids are generally very absorbing
If the beam can get *to* the sample, the fluorescence is deflected backwards



CROSS SECTION



TOP VIEW