Characterization of LiS batteries using lab-based sulfur XES

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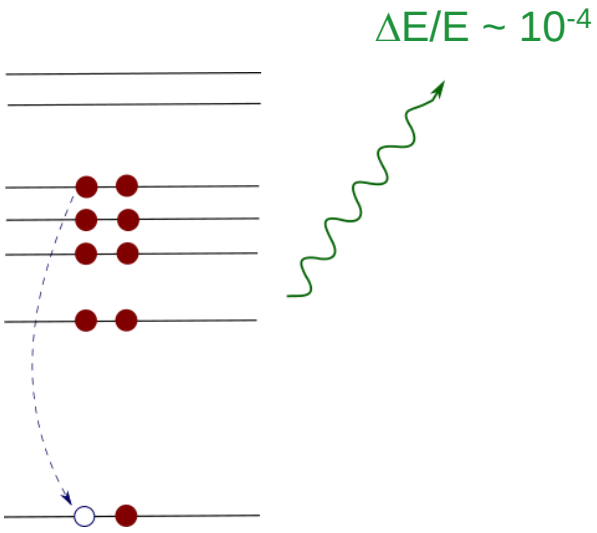
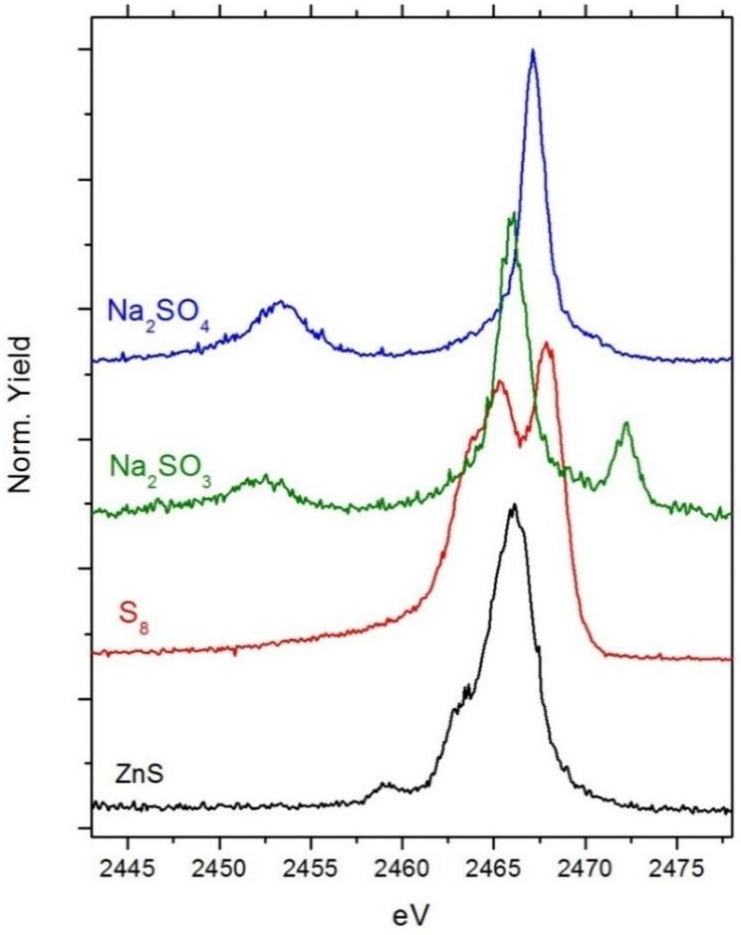
X-ray Emission Spectroscopy (XES)

- Element/Site Specific
- Probes local occupied electronic structure
- Sensitivity to
  - Oxidation State/Valency
  - Symmetry
  - Spin





Tender XES:

Table 1-1. *Electron binding energies, in electron volts,*

Element	K 1s
16 S	2472

X-Ray Data Booklet Table 1-2. *Photon energies, in electron volts,*

Element	Kα_1	Kα_2	Kβ_1
16 S	2,307.84	2,306.64	2,464.04

Attn length 1/μ (2.5 keV) = 2.30 μm

In-air transmission (Kα line, 10 cm of air) = 1.52 %

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Products

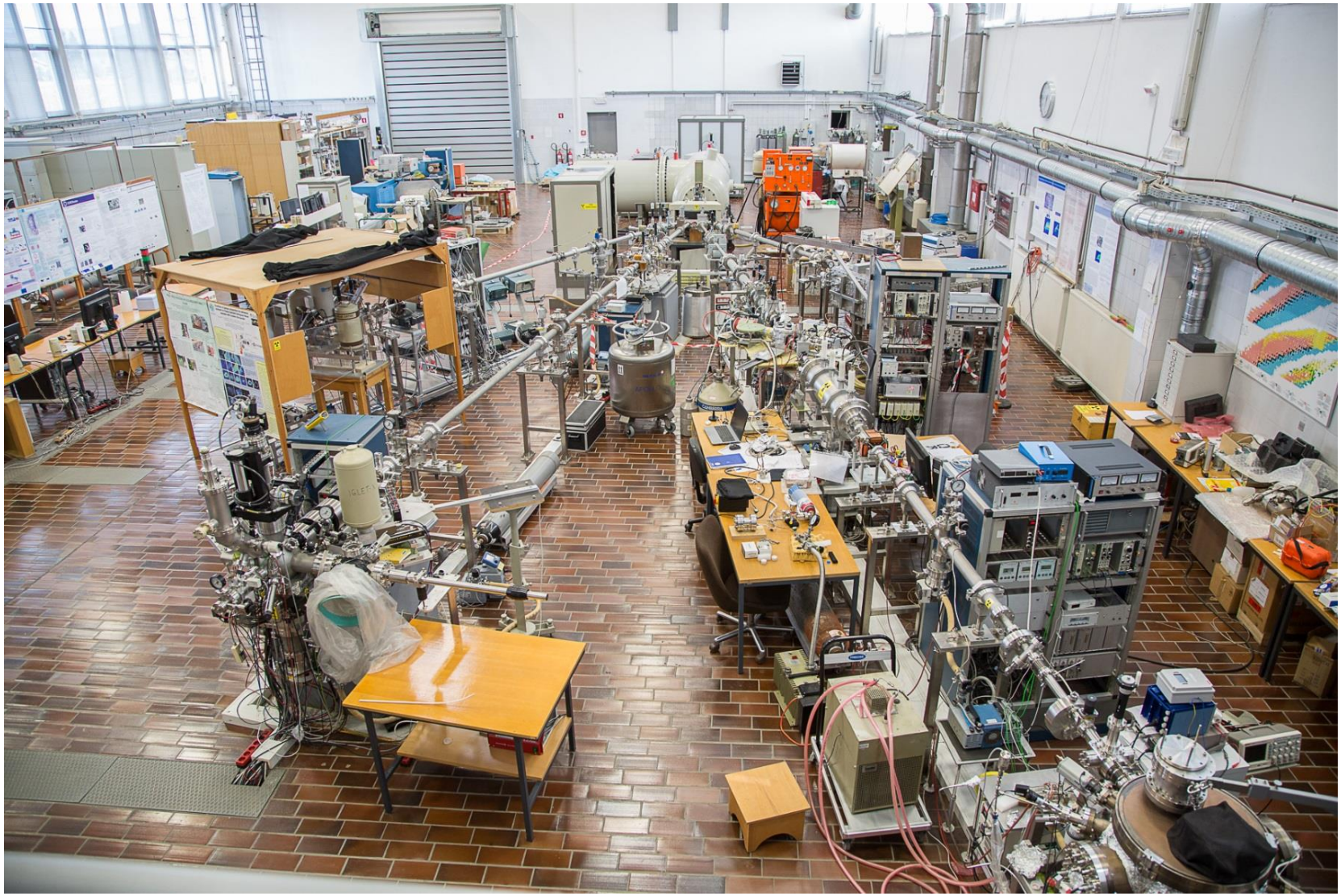
Tender x-ray Products

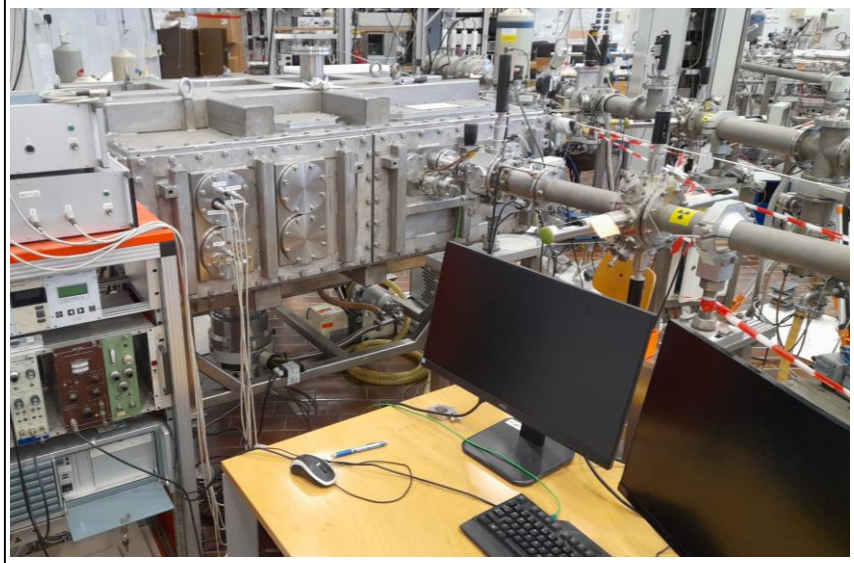
Hard x-ray spectrometers

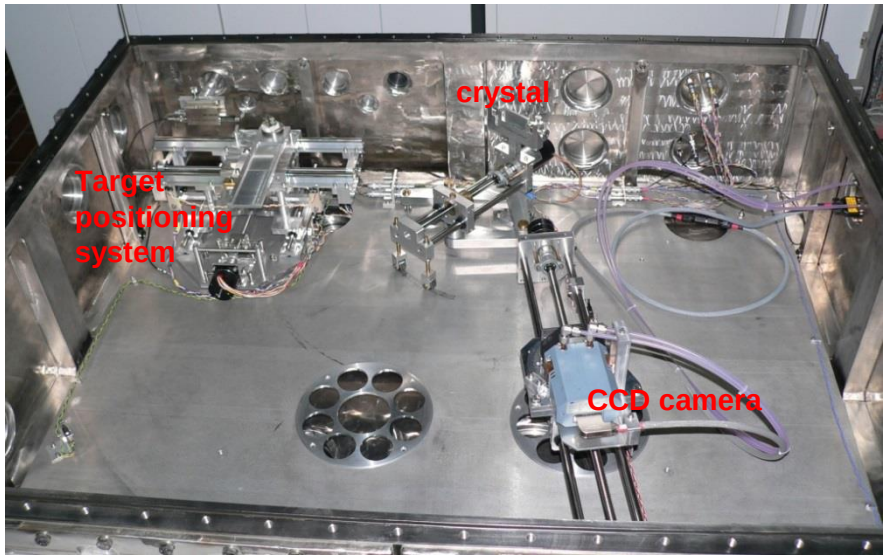
Instrument Data

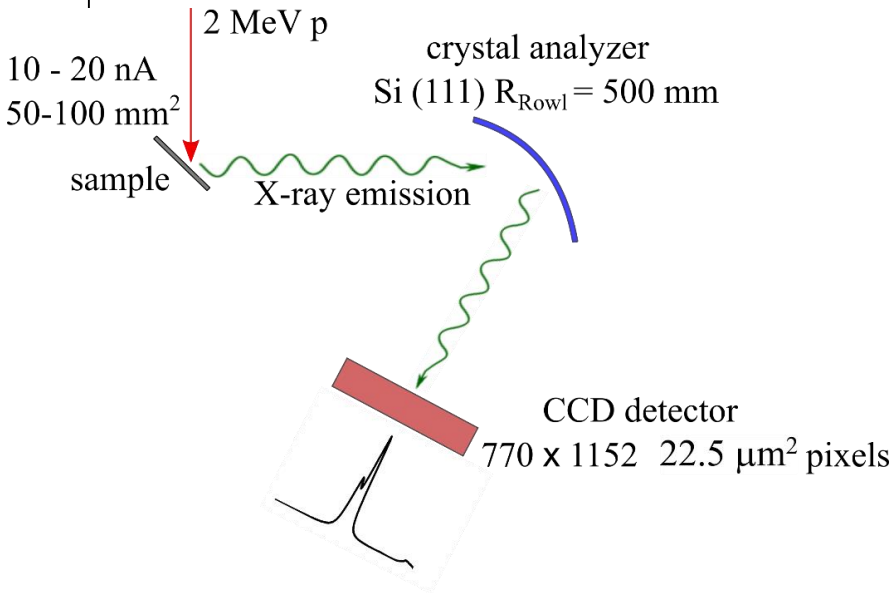
Specifications

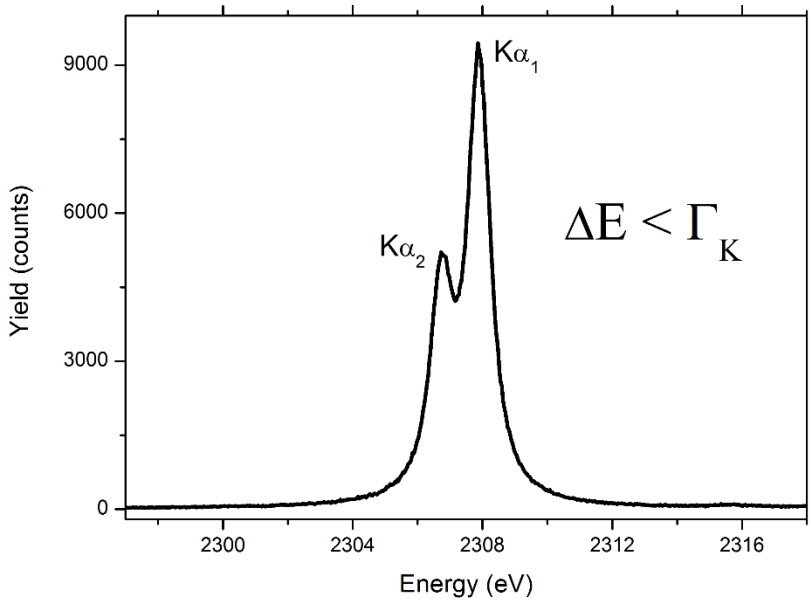
Rowland Circle Size	10 centimeters
Measurement Mode	XES only
X-ray Source (XES)	100-W air-cooled X-ray Tube
Energy Range*	Recommended: 2-5 keV






crystal
Target positioning system
CCD camera

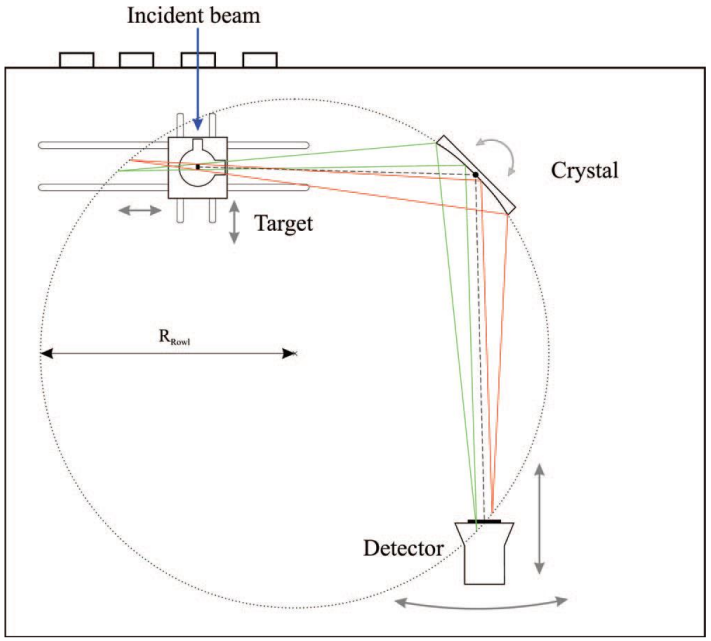

2 MeV p
10 - 20 nA
50-100 mm²
crystal analyzer
Si (111) R_Rowl = 500 mm
sample
X-ray emission
CCD detector
770 x 1152 22.5 μm² pixels

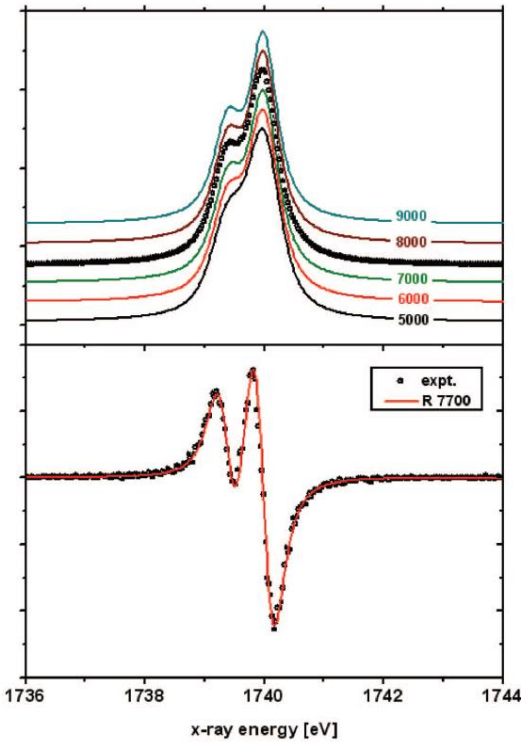

Kα1
Kα2
ΔE < Γ_K
Yield (counts)
Energy (eV)
0
3000
6000
9000
2300
2304
2308
2312
2316

Tender XES setup @ JSI:

- Johansson geometry, R_{Rowl} = 500 mm
- complete in-vacuum installation
- off-Rowland circle target position
- dispersive mode of operation

	2d [Å]	E range [keV]
Quartz ($10\bar{1}0$)	8.510	1.6–2.9
Si(111)	6.271	2.2–4.0
Si(220)	3.840	3.6–6.5





REVIEW OF SCIENTIFIC INSTRUMENTS 83, 033113 (2012)

Design and performance of a versatile curved-crystal spectrometer for high-resolution spectroscopy in the tender x-ray range

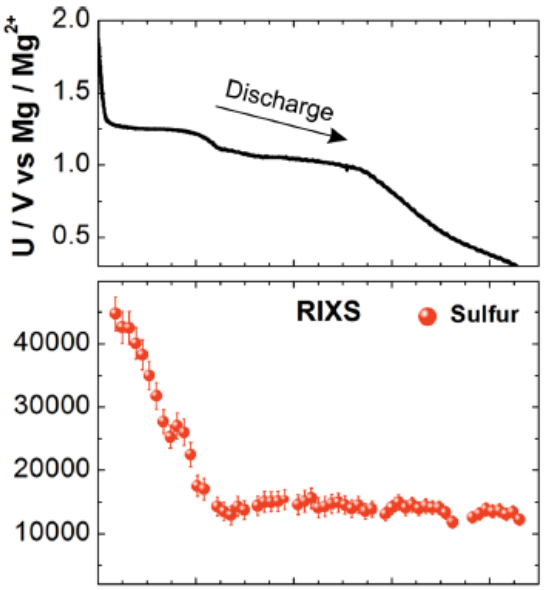
M. Kavčič,[a] M. Budnar, A. Mühleisen, F. Gasser, M. Žitnik, K. Bučar, and R. Bohinc
J. Stefan Institute, Jamova 39, SI-1001, Ljubljana, Slovenia

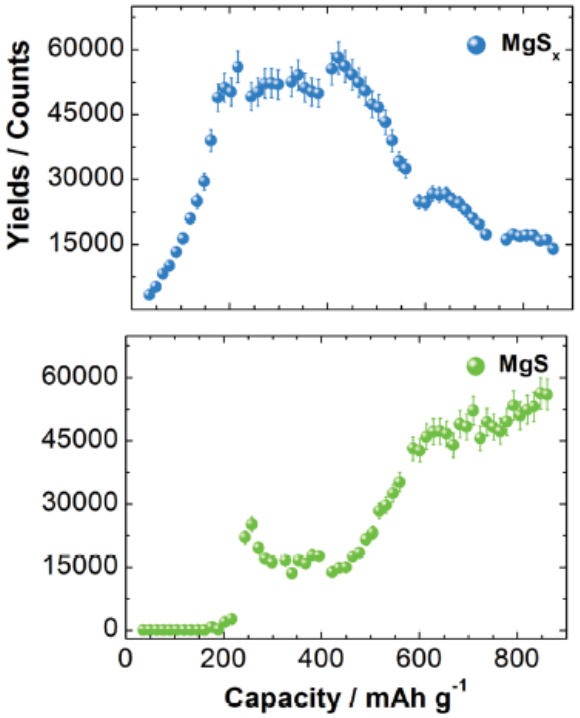
ID26 beamline @ ESRF

- M. Kavčič et al., Phys. Rev. Lett. 102, 143001 (2009).
- R. Alonso Mori et al., Anal. Chem 81, 6516 (2009).
- M. Kavčič et al., Phys. Rev. Lett. 105, 113004 (2010).
- R. Alonso Mori et al., Inorg. Chem. 49, 6468-6473 (2010).
- T. Marchenko et al., Phys. Rev. X 5, 031021 (2015).
- J. Niskanen et al., Sci. Rep. 6, 21012 (2016).
- A. Robba et al., Chem. Mater. 29, 9555−9564 (2017).
- S.M. Butorin et al., ACS Appl. Energy Mater. 1, 4032−4039 (2018).
- A. Robba et al., J. Phys. Chem. Lett. 11, 5446−5450 (2020).

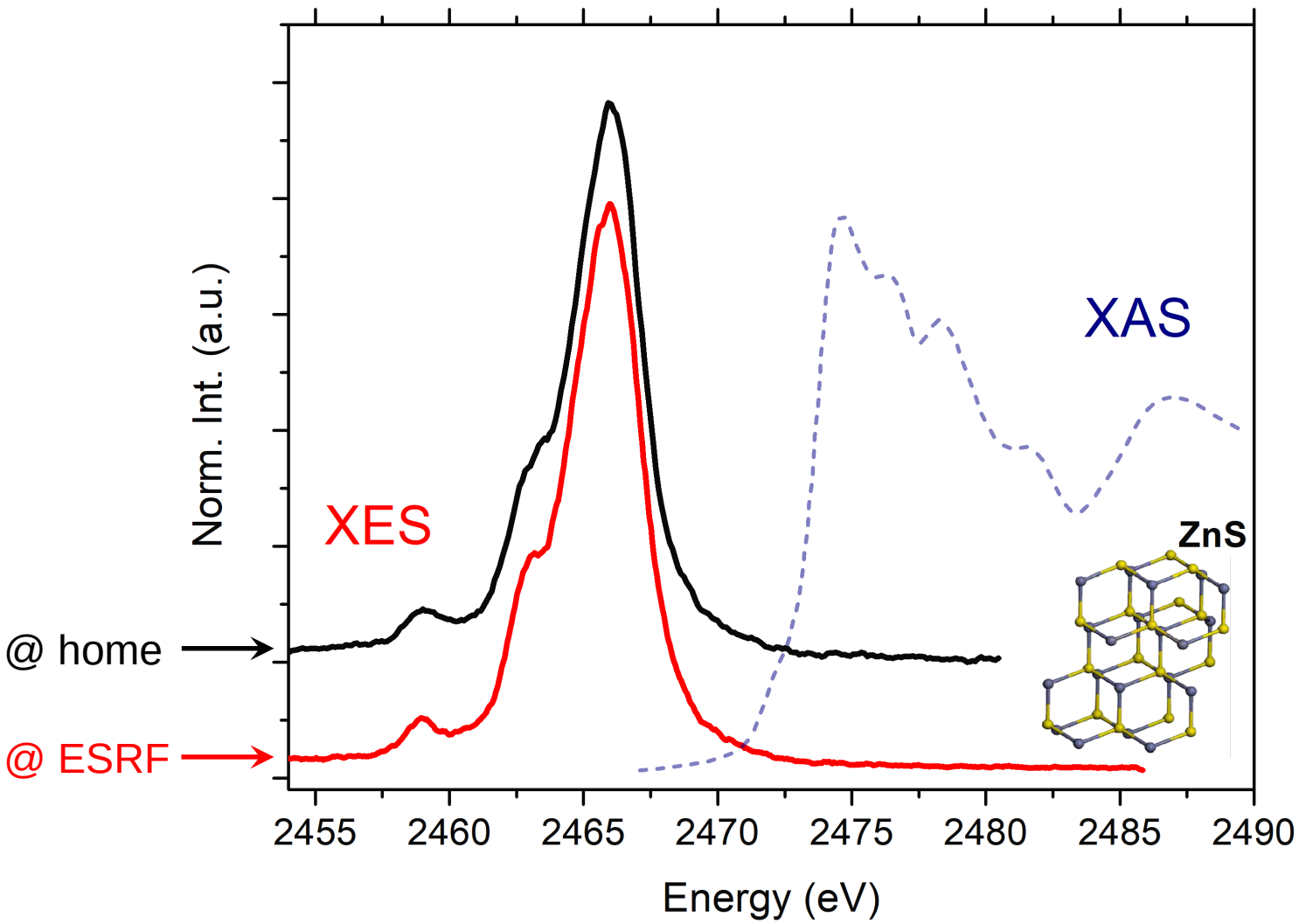
MAGNESIUM–SULFUR BATTERY MECHANISM STUDIED BY RIXS/XAS SPECTROSCOPY AT THE SULFUR K EDGE

The magnesium-sulfur battery is an attractive alternative for future energy storage solutions. A combination of *operando* RIXS and XAS spectroscopy at the sulfur K edge has been used to follow the electrochemical sulfur conversion in the cathode during discharge and to determine the working mechanism of Mg-S batteries.





A. Robba, A. Vizintin, J. Bitenc, G. Mali, I. Arčon, M. Kavčič, M. Žitnik, K. Bučar, G. Aquilanti, C. Martineau-Corcos, A. Randon-Vitanova and R. Dominko, Chem. Mater. 2017, 29, 9555−9564.


Norm. Int. (a.u.)
XES
XAS
ZnS
@ home
@ ESRF
2455
2460
2465
2470
2475
2480
2485
2490
Energy (eV)

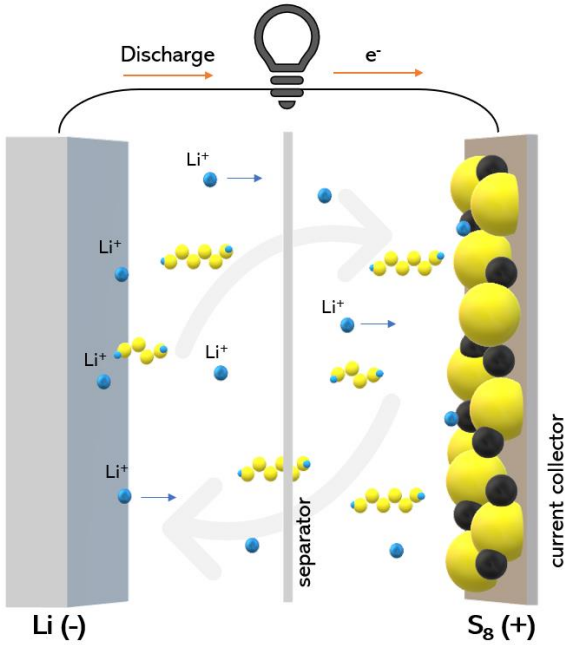
Group for Modern Battery Systems @ NATIONAL INSTITUTE OF CHEMISTRY

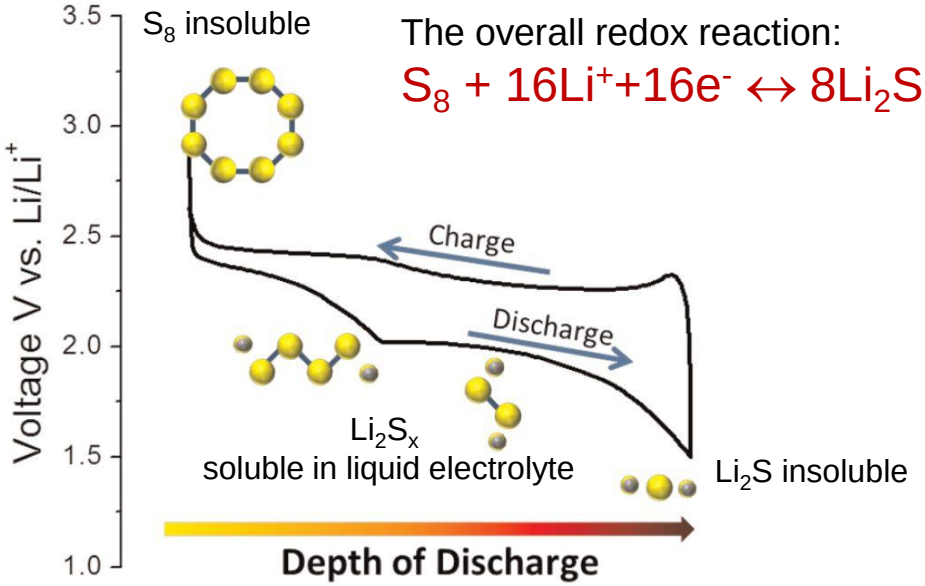
Lithium-Sulfur (Li-S) batteries:

Li-ion:
cathode capacity ~ 250 mAh/g
energy density ~ 800 Wh/kg

Li-S:
theoretical cathode capacity ~ 1675 mAh/g
theoretical energy density ~ 2600 Wh/kg

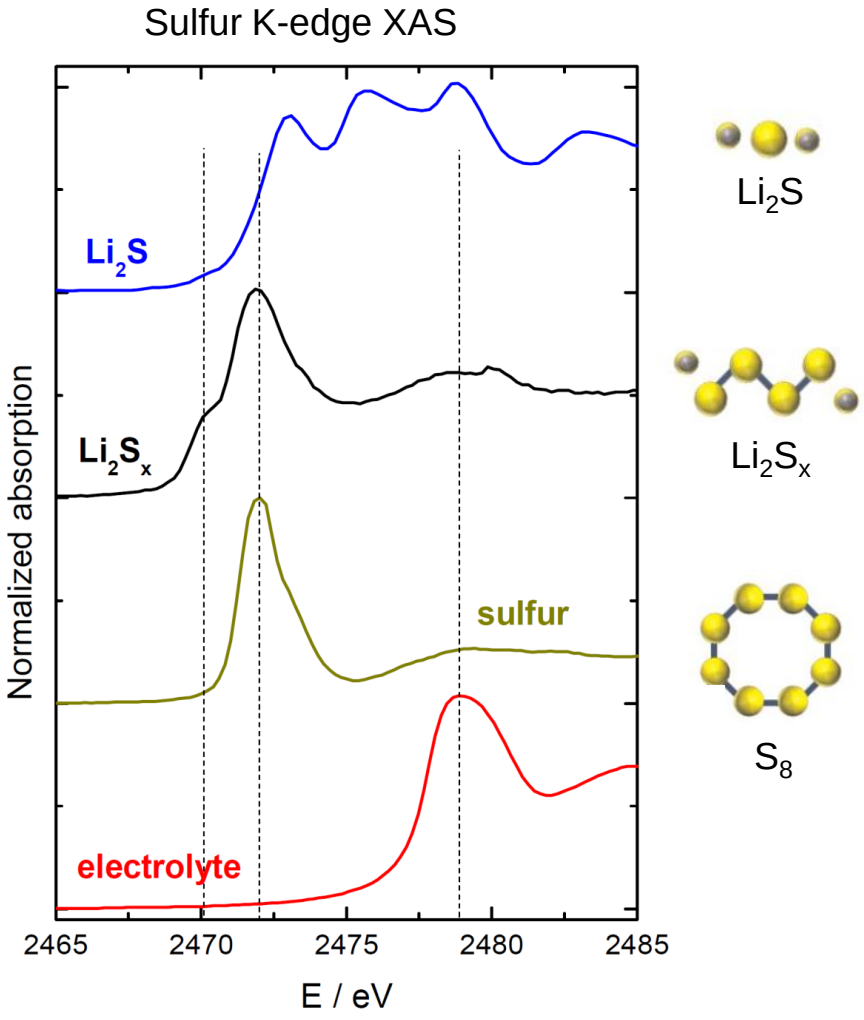
(S. Evers, L. F. Nazar, Acc. Chem. Res. 2013 (46), 1135-1143)

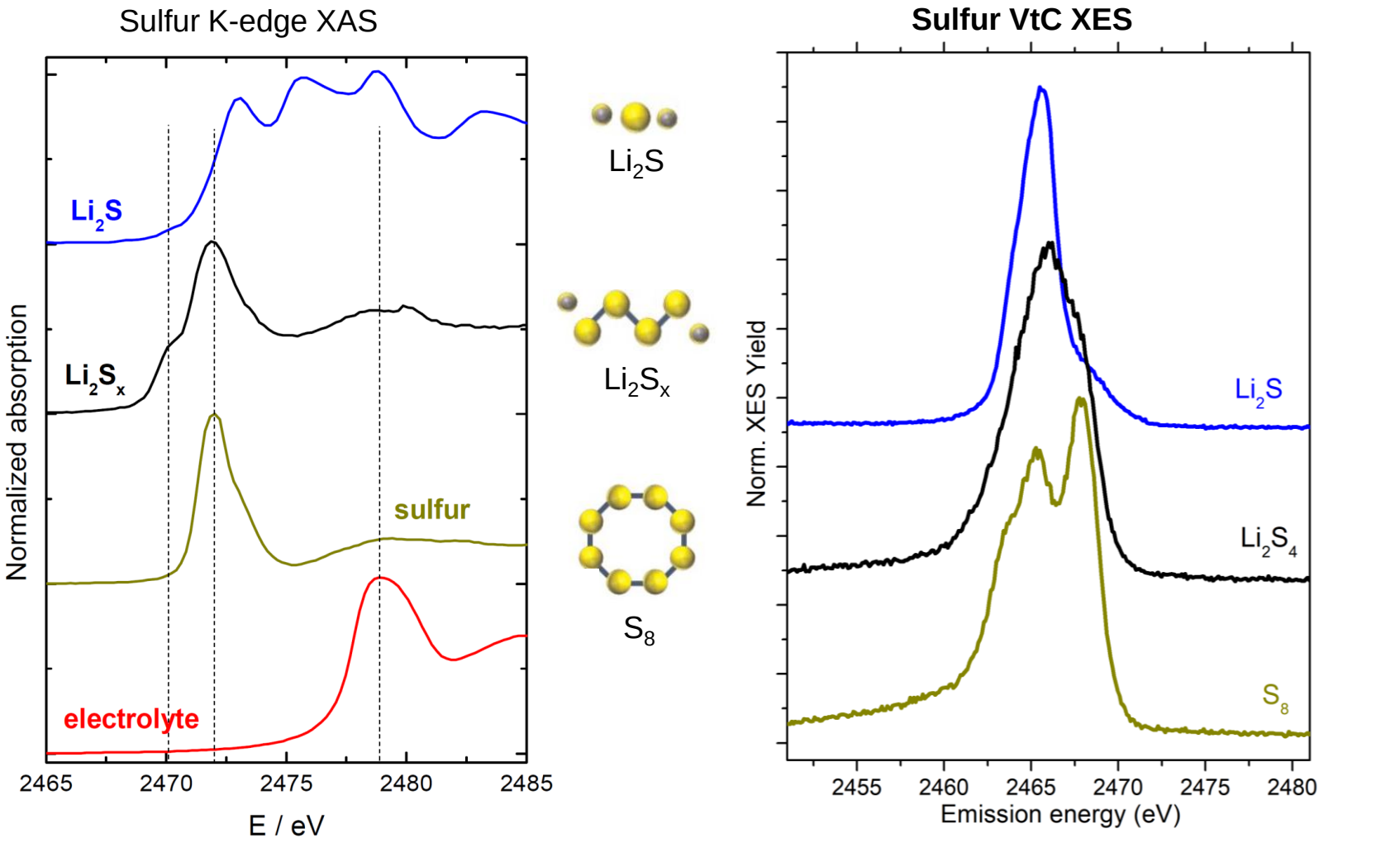




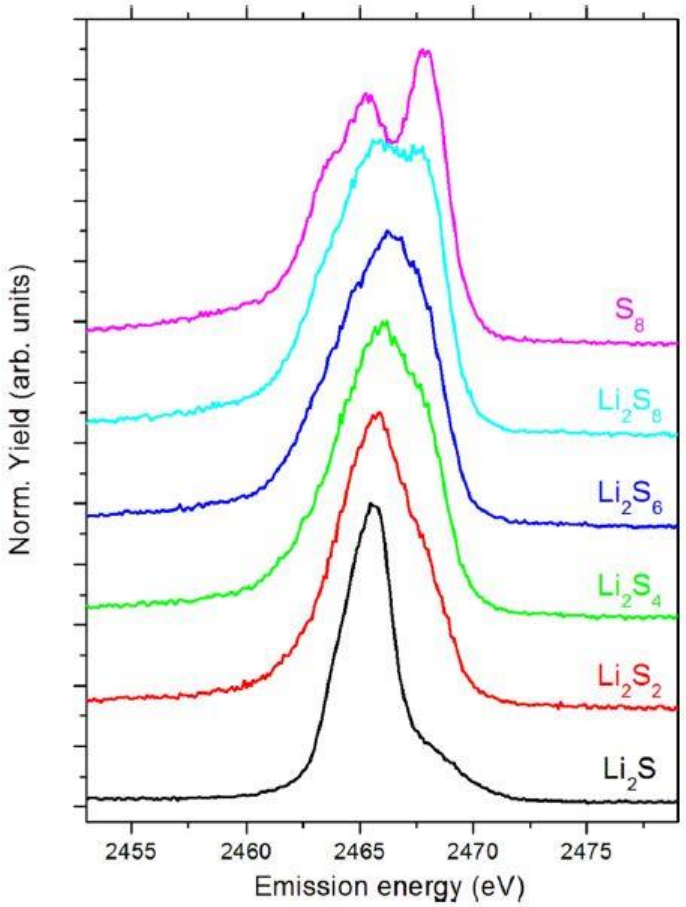
The overall redox reaction:

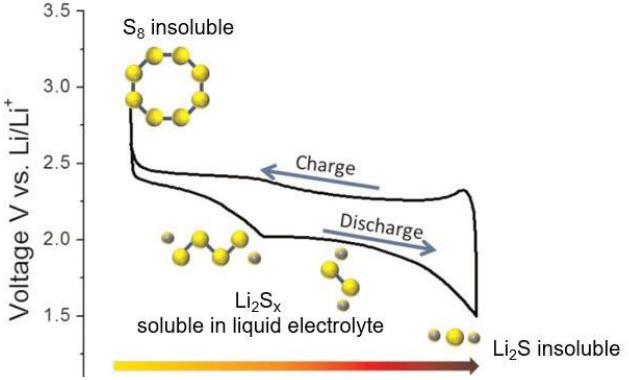
$S_8 + 16Li^+ + 16e^- \leftrightarrow 8Li_2S$


Sulfur K-edge XAS
Li2S
Li2Sx
sulfur
electrolyte
Normalized absorption
2465
2470
2475
2480
2485
E / eV
Li2S
Li2Sx
S8

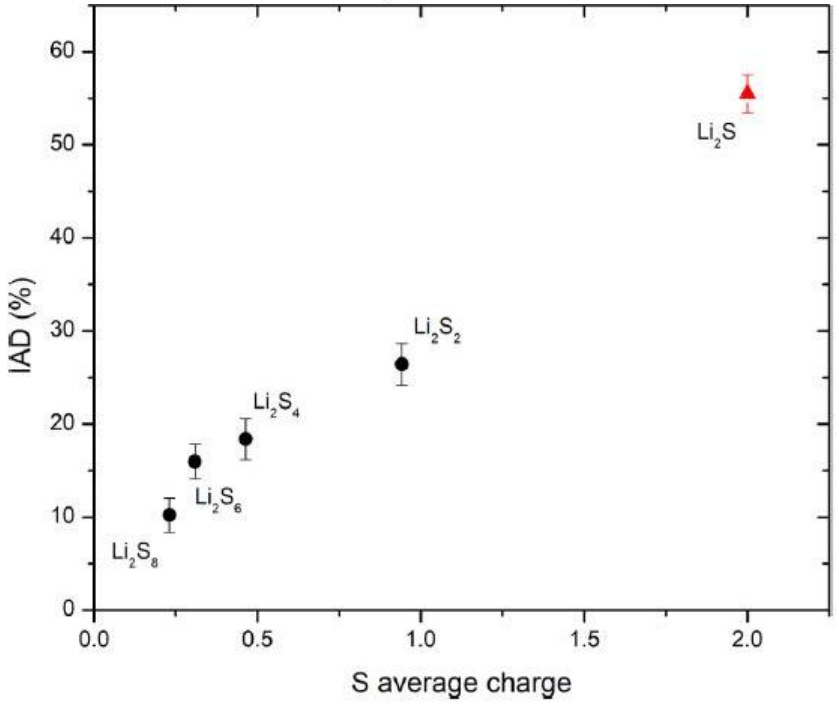

Sulfur K-edge XAS
Li2S
Li2Sx
sulfur
electrolyte
Normalized absorption
2465
2470
2475
2480
2485
E / eV
Li2S
Li2Sx
S8
Sulfur VtC XES
Li2S
Li2S4
S8
Norm. XES Yield
2455
2460
2465
2470
2475
2480
Emission energy (eV)

Lab XES on Lithium-Sulfur (Li-S) batteries:

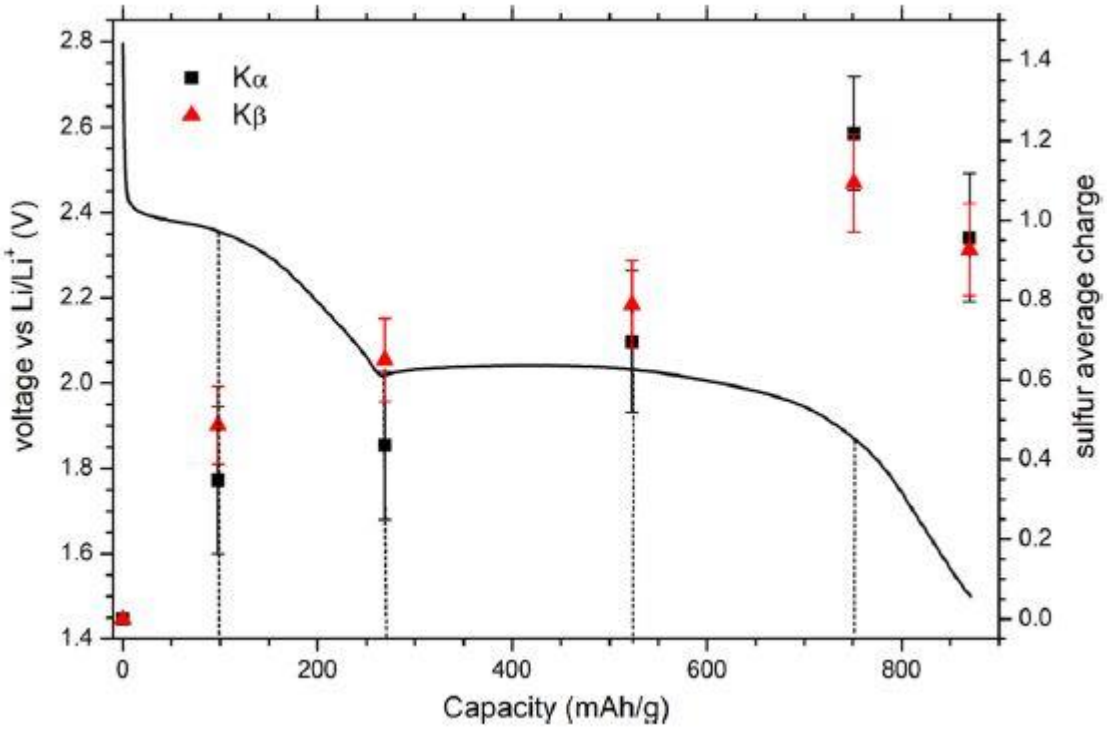


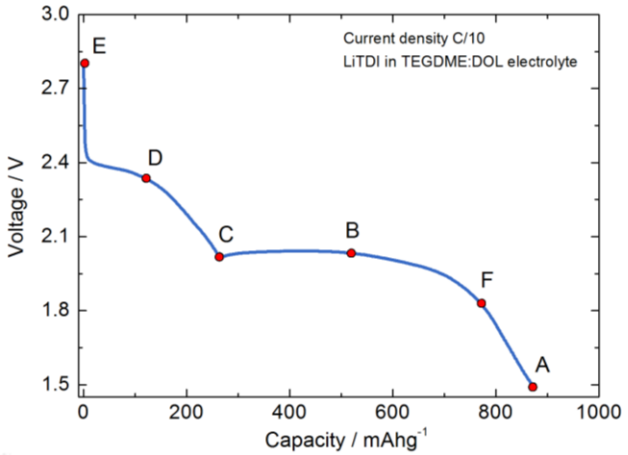


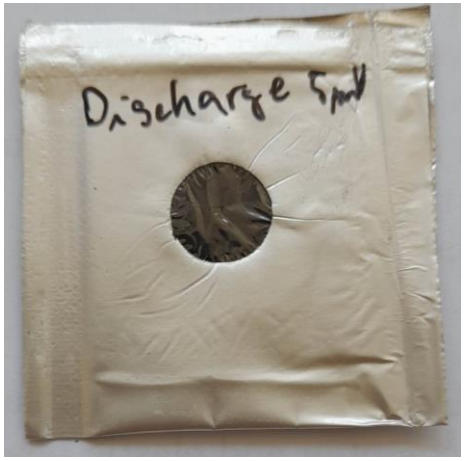
$$IAD_{Li_2S_X} = \int |Y_{Li_2S_X}(E) - Y_{S_8}(E)| dE = \sum_i |Y_{Li_2S_X}(E_i) - Y_{S_8}(E_i)|$$



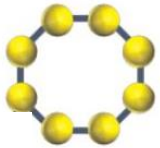
Ex Situ XES on Precycled Battery Cathodes.

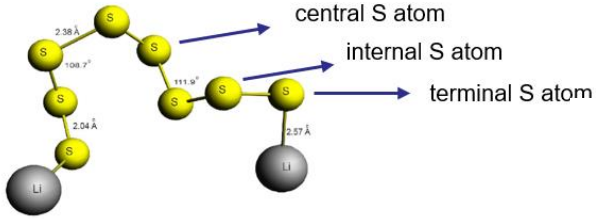


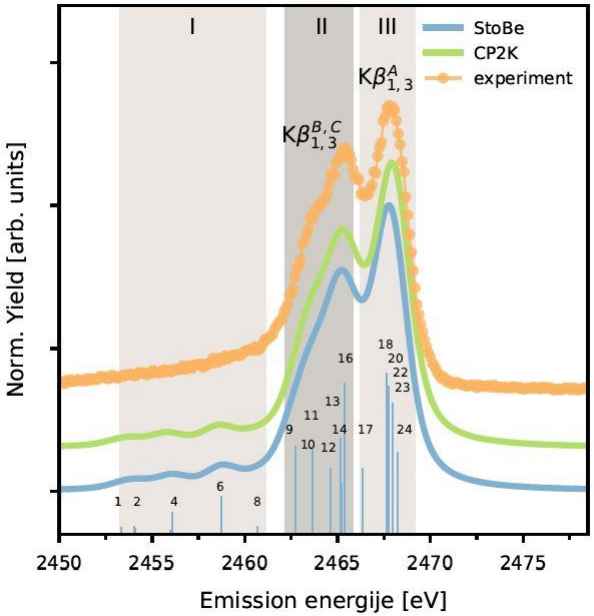


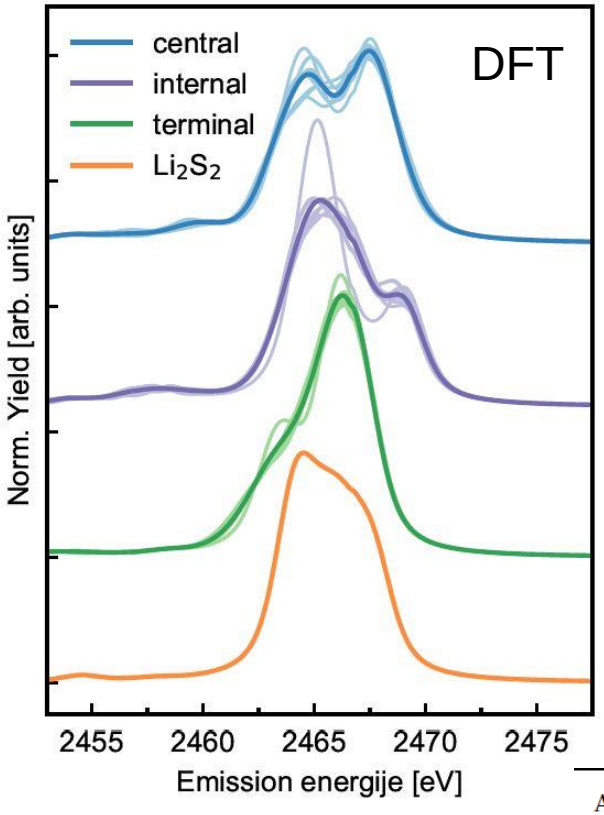


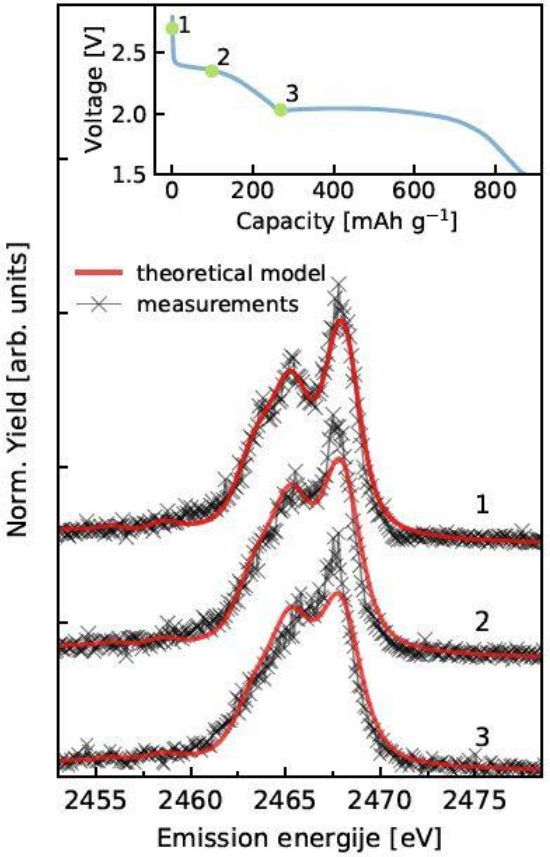
M. Kavčič, M. Petric, A. Rajh, K. Isaković, A. Vižintin, S. Drvarič Talian, R. Dominko, ACS Appl. Energy Mater. 2021, 4, 2357−2364.









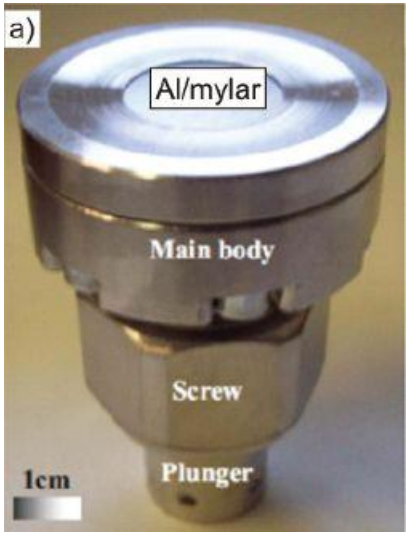


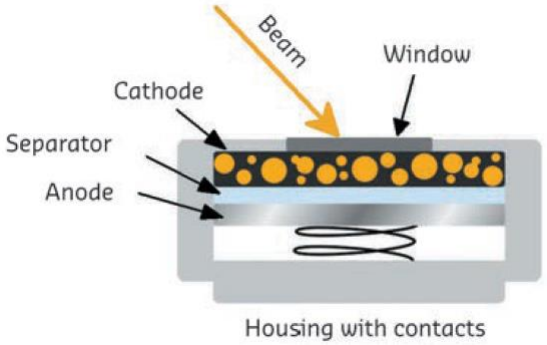
Amplitudes of	Sample 2	Sample 3
Elemental S	0.64(3)	0.48(3)
Central atoms	0.13(6)	0.27(7)
Internal atoms	0.11(3)	0.12(4)
Terminal atoms	0.11(3)	0.12(4)

M. Petric, A. Rajh, A. Vizintin, S. Drvarič Talian, R. Dominko and M.Kavčič, Chem. Comm., 2021, 57, 7573.

Operando lab XES on Lithium-Sulfur (Li-S) batteries:

In situ Swagelok cell:

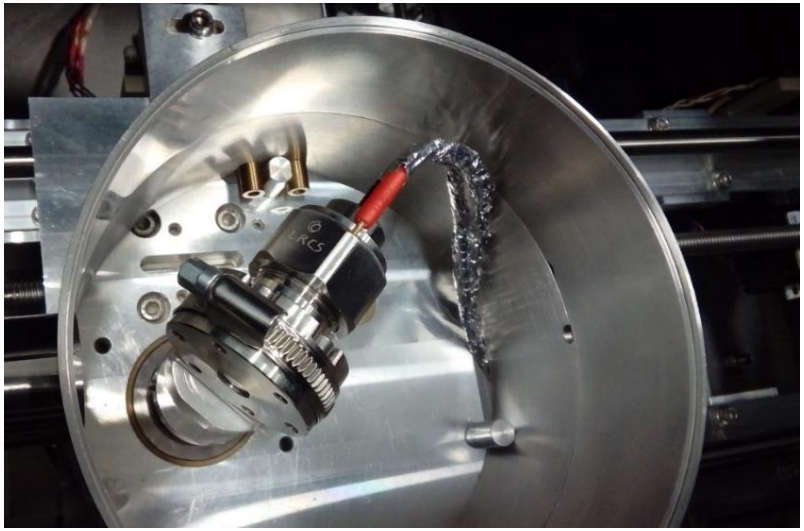


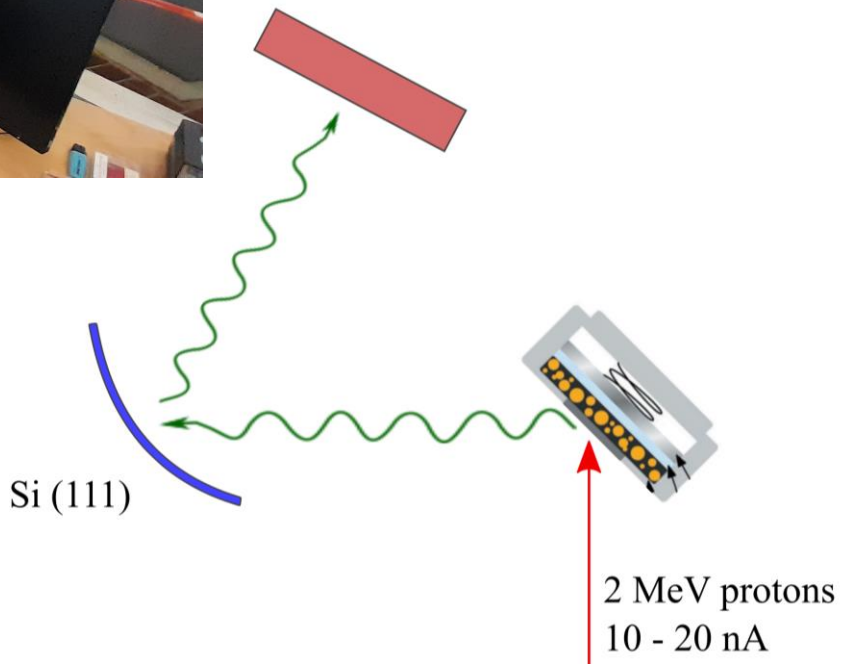


- back of the battery cathode facing the cell window
- 6-μm-thick mylar foil plated with aluminum (500 Å) on the side facing the cathode

J. B. Leriche et al., J. Electrochem. Soc. 157, A606 (2010).

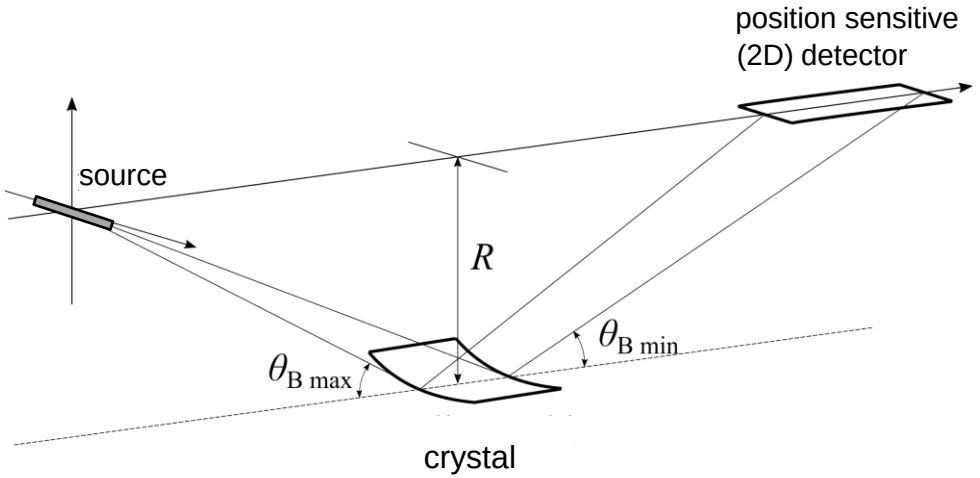
Operando lab XES on Lithium-Sulfur (Li-S) batteries:



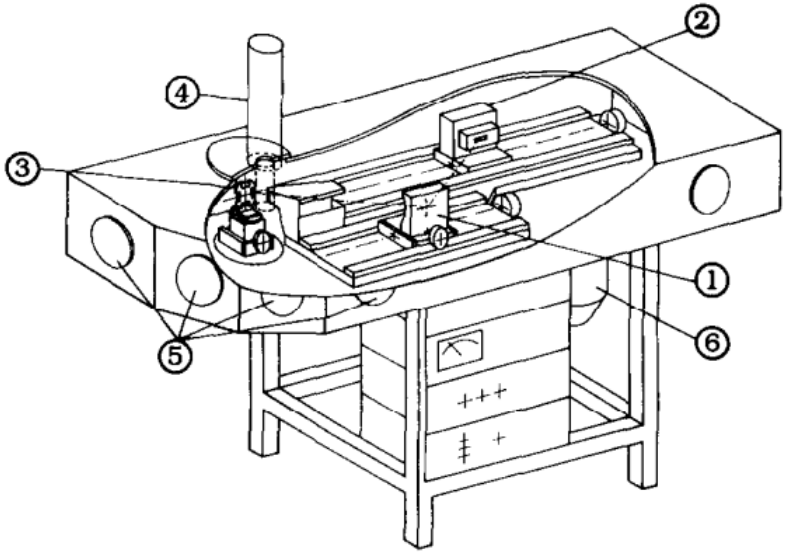


UNIVERSITÉ DE FRIBOURG
UNIVERSITÄT FREIBURG

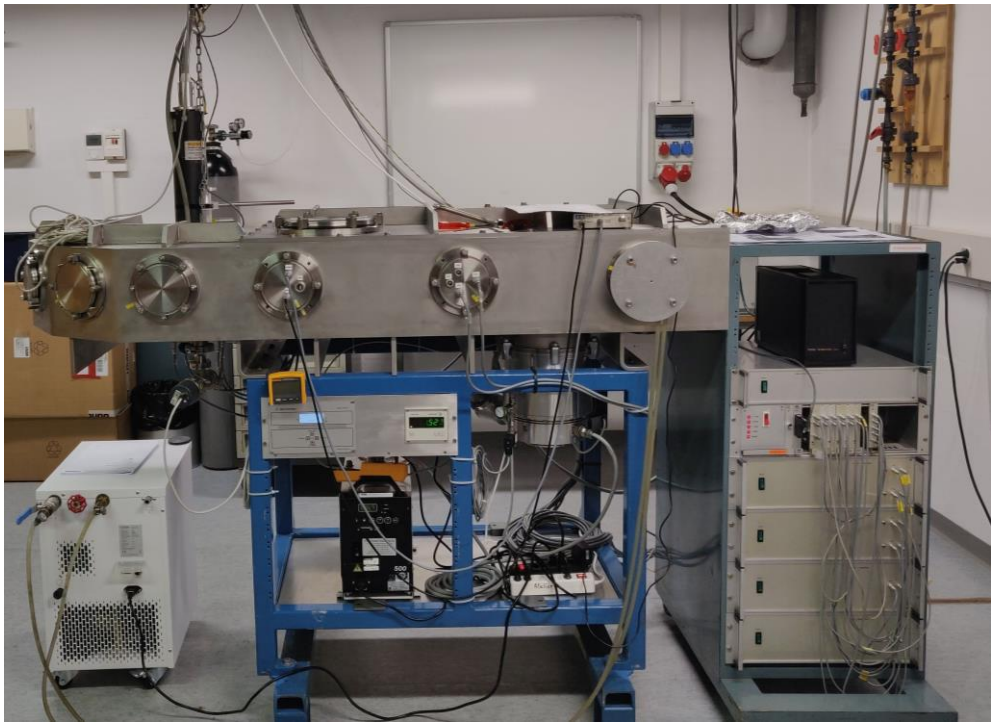
Von Hamos spectrometer @ UNI Fribourg:

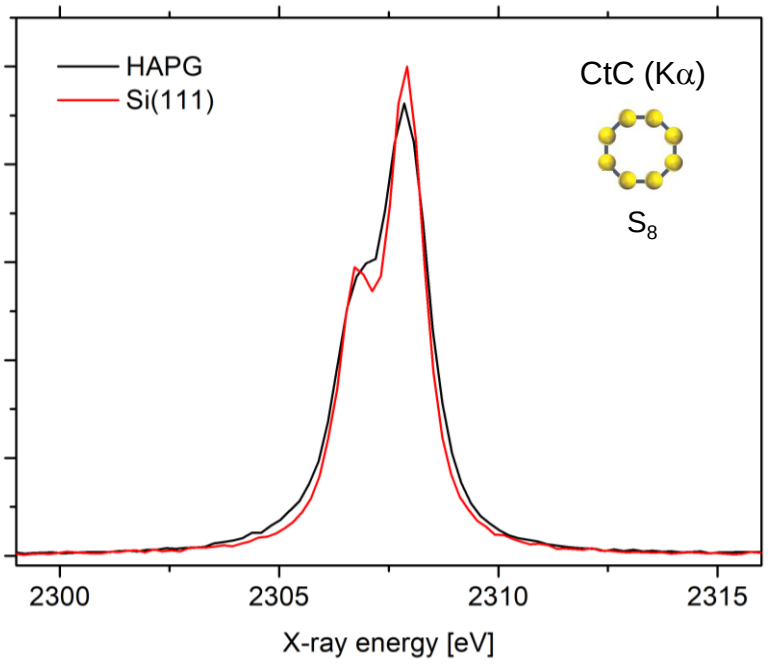


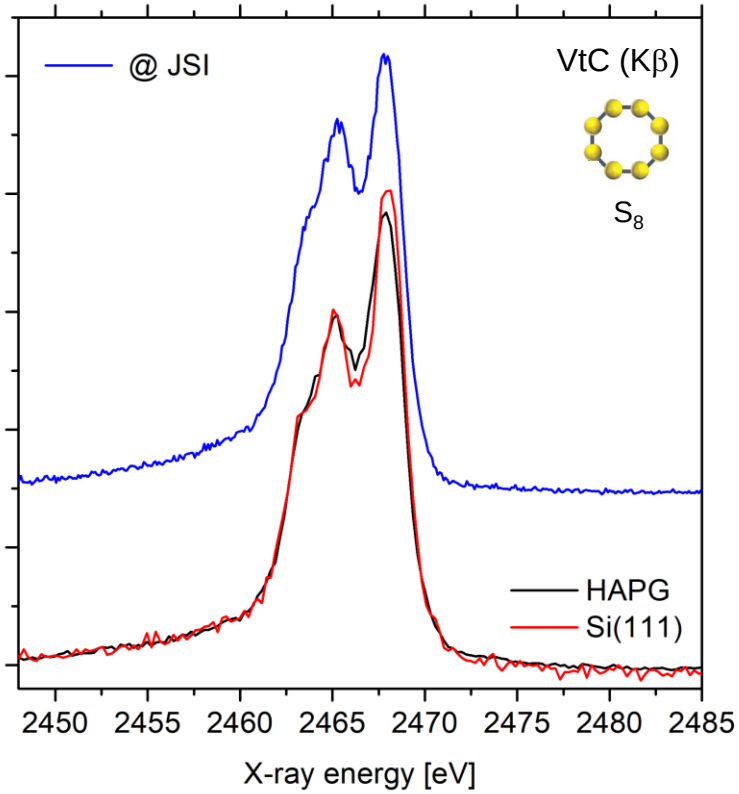
- Sc X-ray tube operating at 40 kV and 35 mA
- HAPG (2d = 6.708 Å) crystal, R = 25 cm

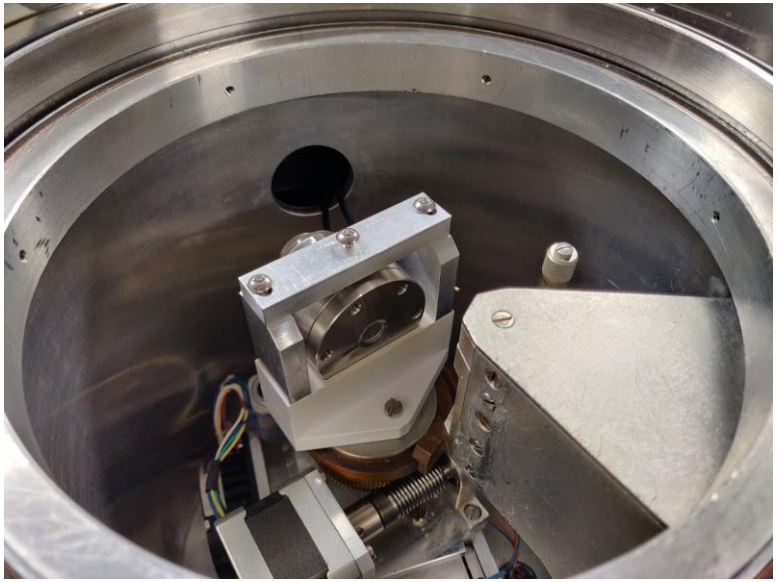


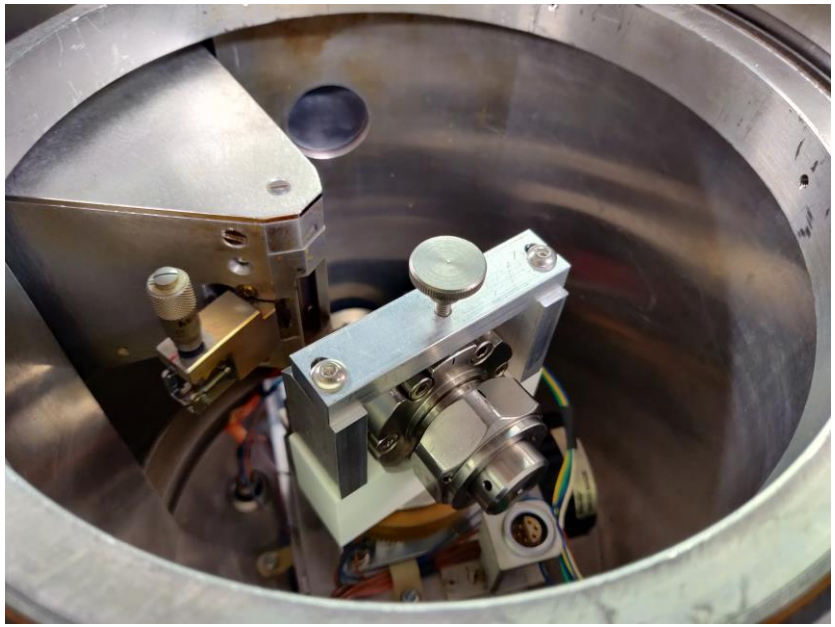
J. Hoszowska et al.,
Nucl. Instr. Meth. Phys. Res. A 376 (1996) 129–138.



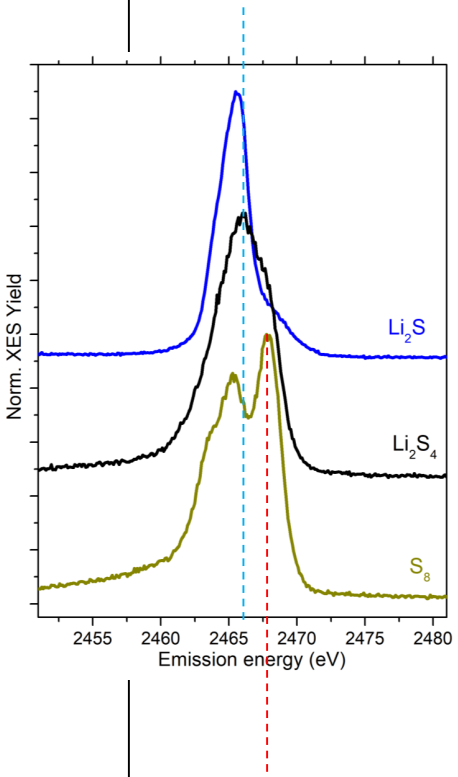

HAPG
Si(111)
CtC (Kα)
S8
2300
2305
2310
2315
X-ray energy [eV]

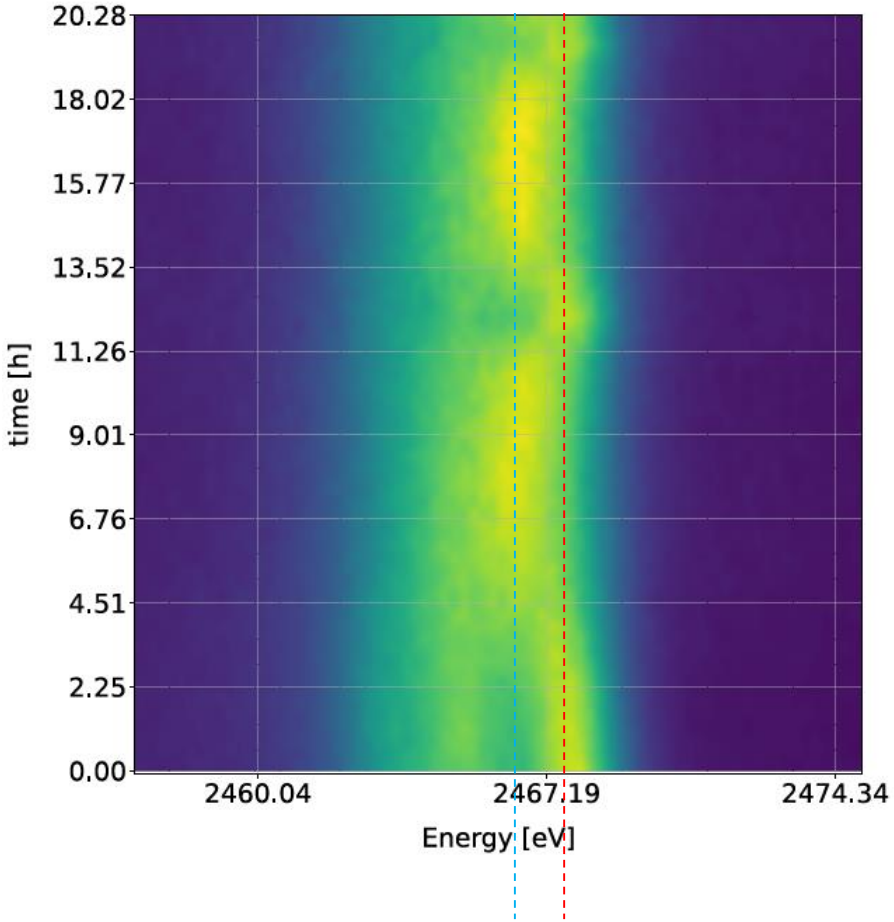

@ JSI
VtC (Kβ)
S8
HAPG
Si(111)
2450
2455
2460
2465
2470
2475
2480
2485
X-ray energy [eV]

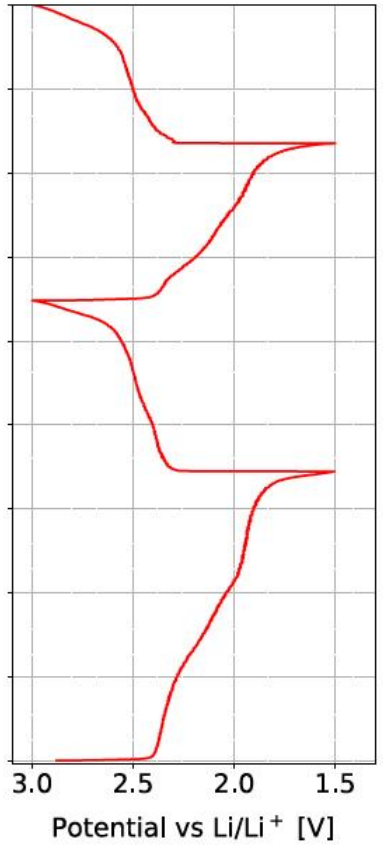




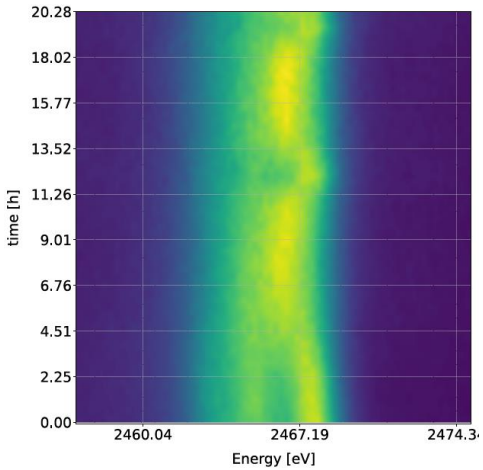
- two full battery cycles (20 hours)
- a series (over 100) of Kβ S spectra (each correponds to 10 min acquisition)

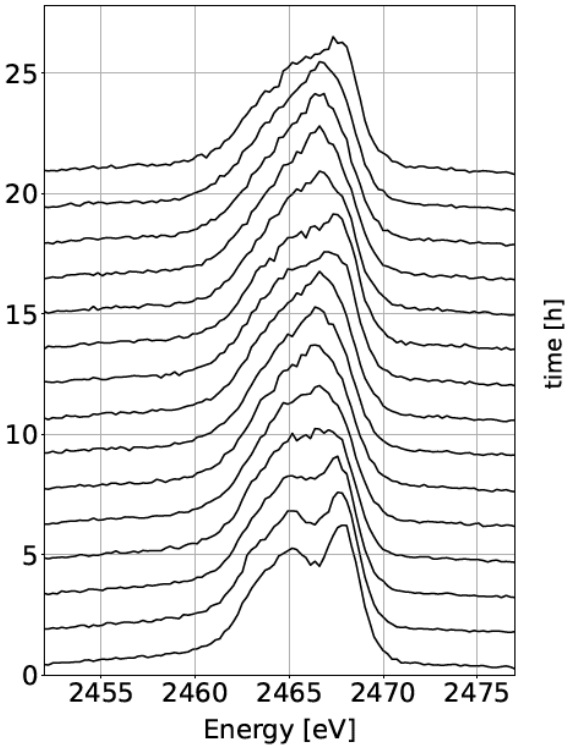


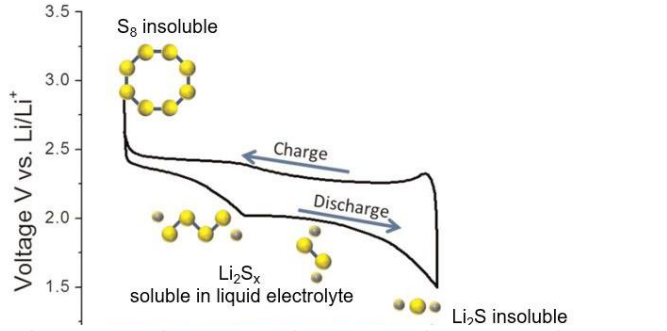


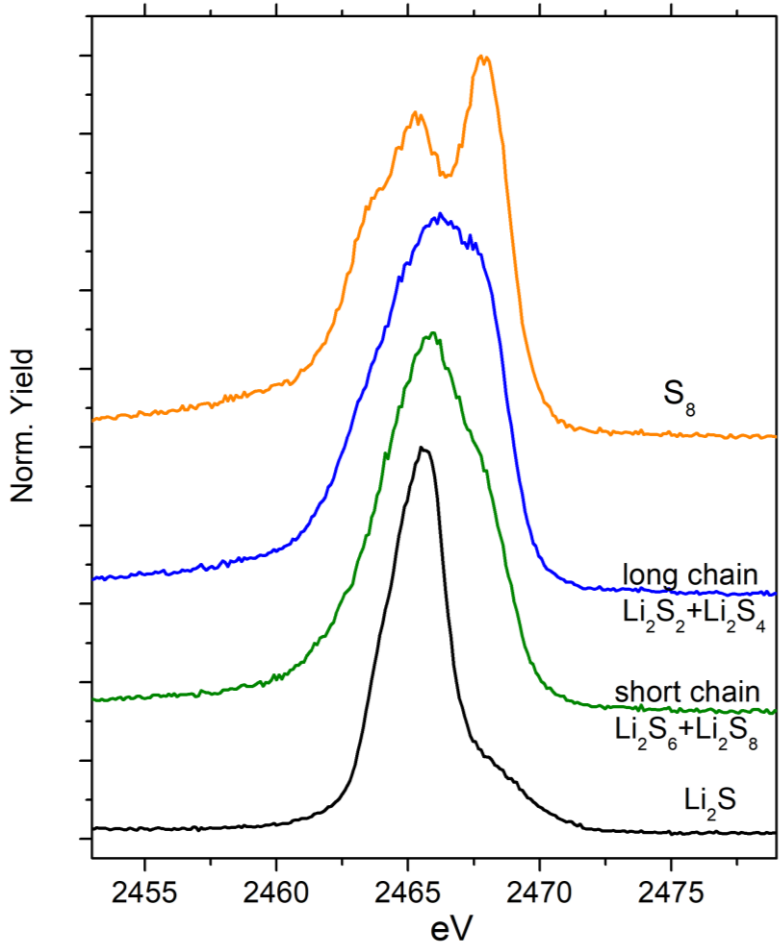


LCF analysis of operando XES spectra:

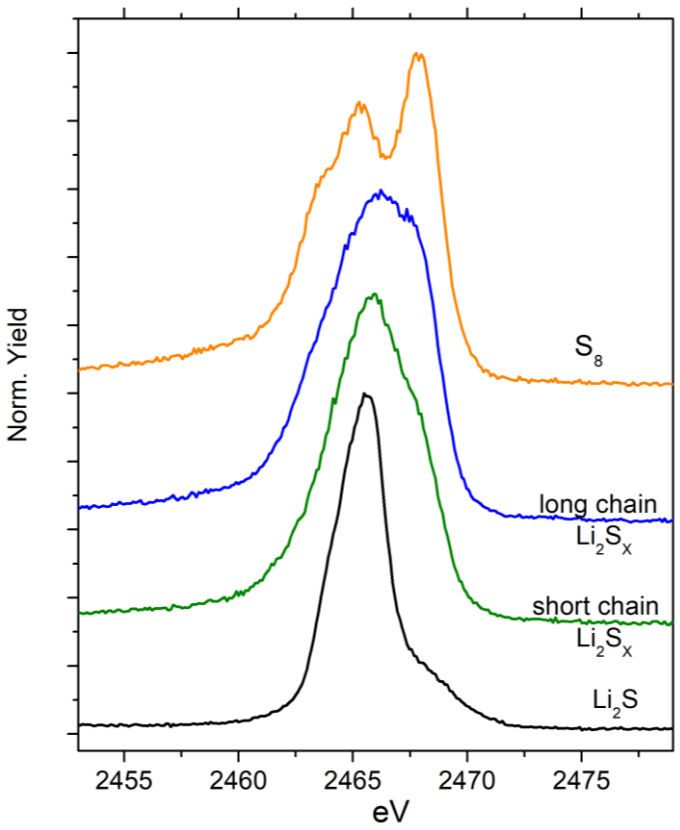


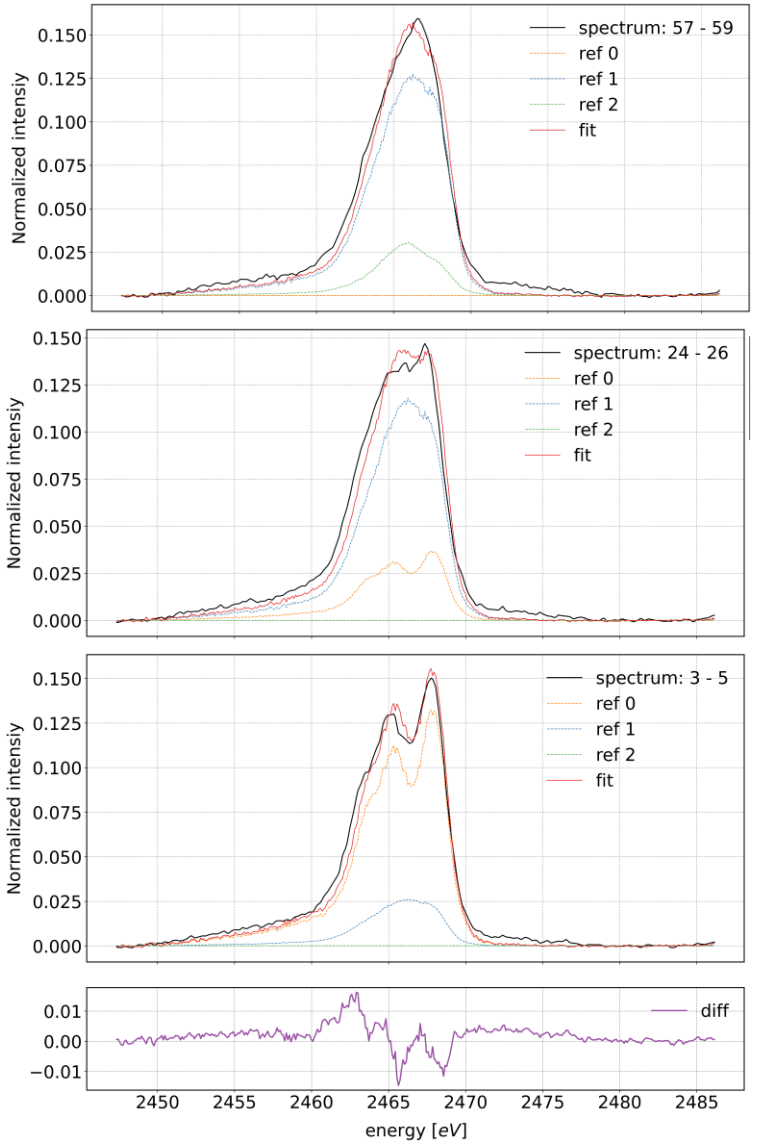




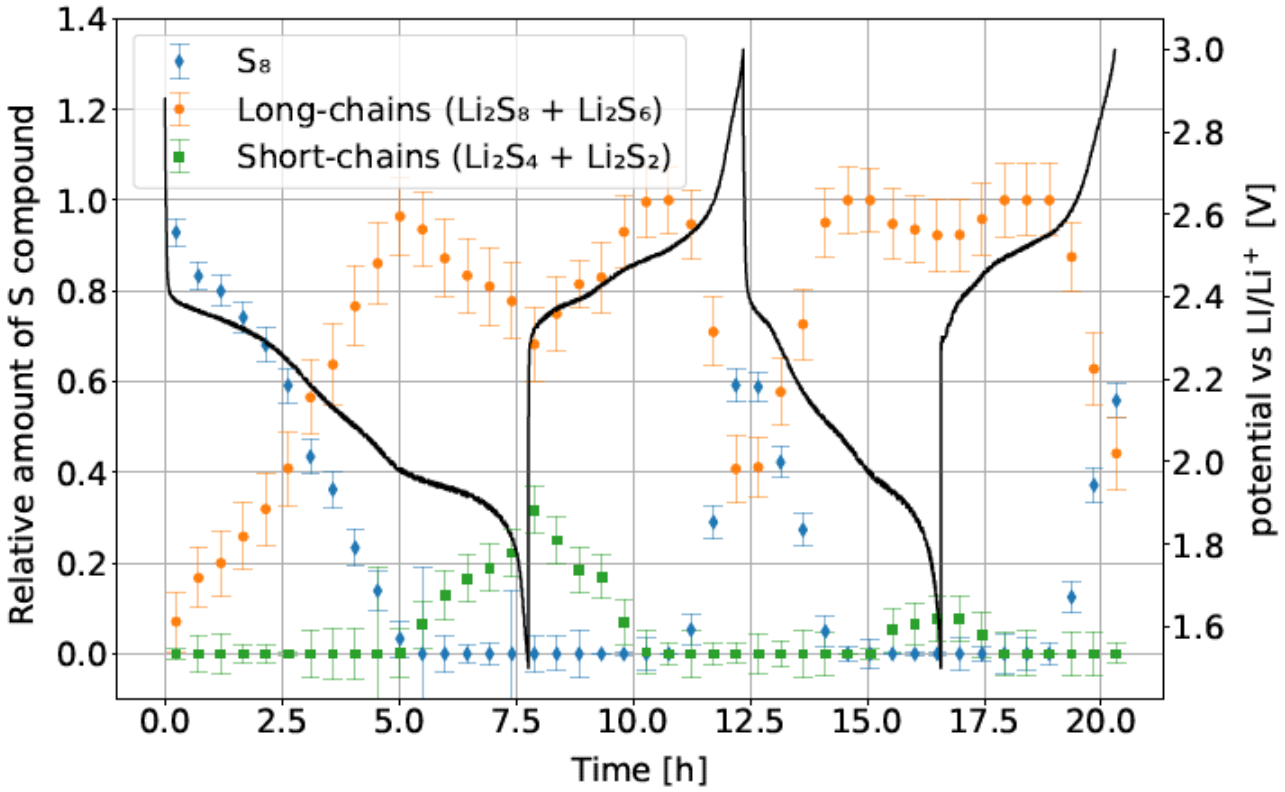


LCF analysis of operando XES spectra:





Relative intensities of different S species within the battery during two consecutive discharge/charge cycles:



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Summary:

- Laboratory XES is shown to be an effective and accurate S speciation method for operando measurements on Li-S batteries. The measurements are performed on concentrated samples without any dilution, they provide reasonable time resolution and the results are comparable to XAS analysis performed at synchrotron facilities.

- This study demonstrates the capability of laboratory-based XES spectroscopy for sulfur speciation in Li-S and other metal-S batteries, opening the door for more routine operando analysis on numerous battery samples over large number of cycles.

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