In-operando XAS analysis of Li-ion and Li-sulphur batteries

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Motivation for in-operando XAS analysis on Li-ion batteries

- Searching for new cathode materials for high energy Li-ion batteries with fully reversible lithium extraction that can deliver high battery capacitiy.
- Some candidates **Li_2VTiO_4, Li_2FeTiO_4** and **$Li_2(Fe_xMn_{x-1})SiO_4$**
- Exploiting the reversable oxidation potential of Fe^{2+}/Fe^{3+}, $Mn^{2+}/Mn^{3+}/ Mn^{4+}$ and $V^{2+}/V^{3+}/V^{4+}$ redox couples without collapse of the structure.

☺ Theoretical specific capacity ~ **166 mAh/g**

(**332 mAh/g** if both Li equivalents are extracted);

☺ Thermal stable cathode materials;

☺ Cheap and environmental acceptable cathode materials;

Aim of in-operando XAS on Li-ion batteries

- The feasibility and reliability of **in situ** XANES and EXAFS analysis as **a tool to monitor gradual changes of oxidation state and local structure** of transition-metal cations during lithium exchange, i.e. during charging and discharging of the Li-ion battery.

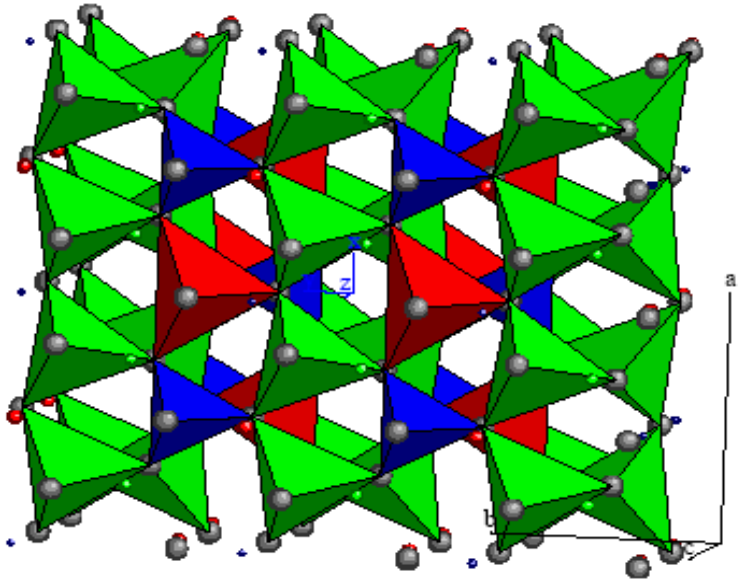
- Provide the information on the dynamics of the battery operation on the atomic level and clarify the role of transition-metal cations (Fe, Mn, V) in the electrochemical activity of the material. Determine the degree of reversibility of the process in one or several cycles.

R. Dominko, I. Arčon, et al., Journal of Power Sources 189 (2009) 51–58

Some basic facts about the $Li_2(Fe_{0.8}Mn_{0.2})SiO_4$ meterial

XRD data :

- Monoclinic crystal structure with *P121/n1* space group. a = 8.245 Å, b = 5.018 Å and c = 8.246 Å
- The structure is composed of MnO_4, FeO_4, SiO_4 and LiO_4 tetrahedra.
- The crystal structure contains empty octahedral interstitial cavities that form empty channels, which enables transport of Li^+ ions.



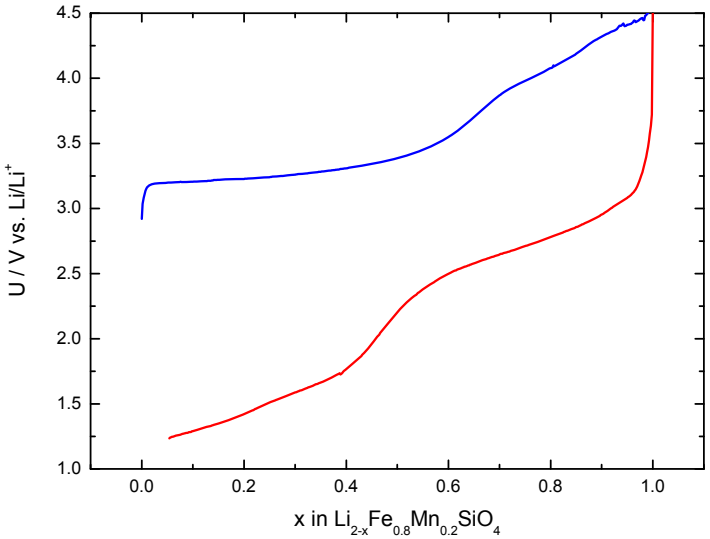
R. Dominko, M. Bele, M. Gaberšček, A. Meden, M. Remškar, and J. Jamnik, *Electrochem. Commun.* **8**, 217 (2006).

Advantages:

- high capacity (200 mAh/g at a C/50 cycling rate)
- good thermal stability

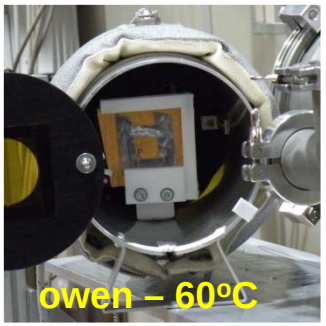
Moesbauer data on Fe valence in as synthesized $Li_2Fe_{0.8}Mn_{0.2}SiO_4$:

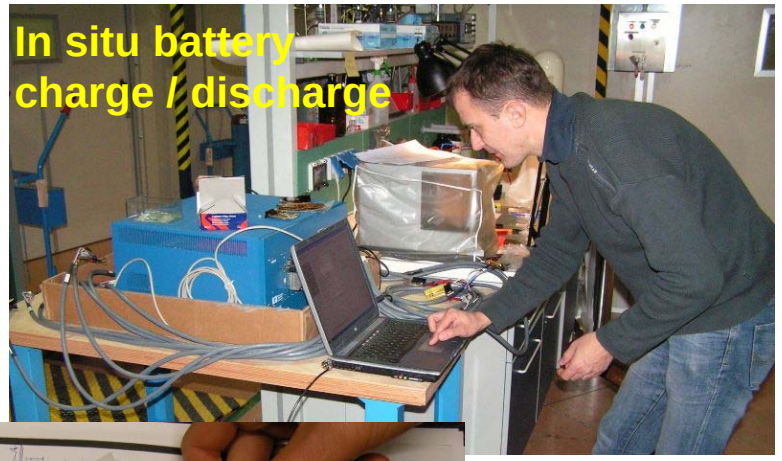
- 80% Fe^{2+} (tetrahedral iron in crystal structure)
- 20% Fe^{3+} (tetrahedral iron in crystal structure)



Charge / discharge curves in the first cycle at C/15 current density at 60 oC. Exchanged of 1 mol Li.

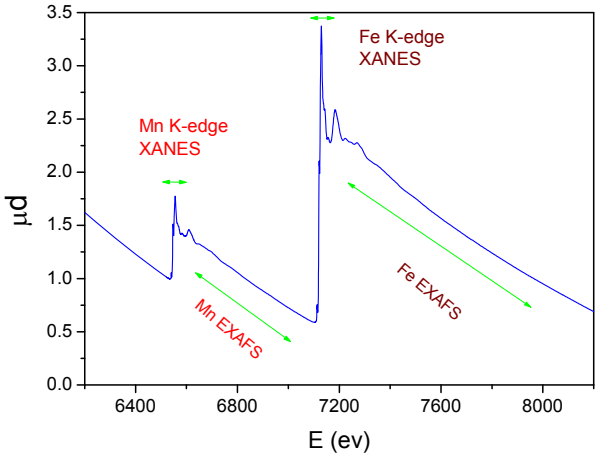
In operando XAS experiment





Half-battery sealed in triplex foil:

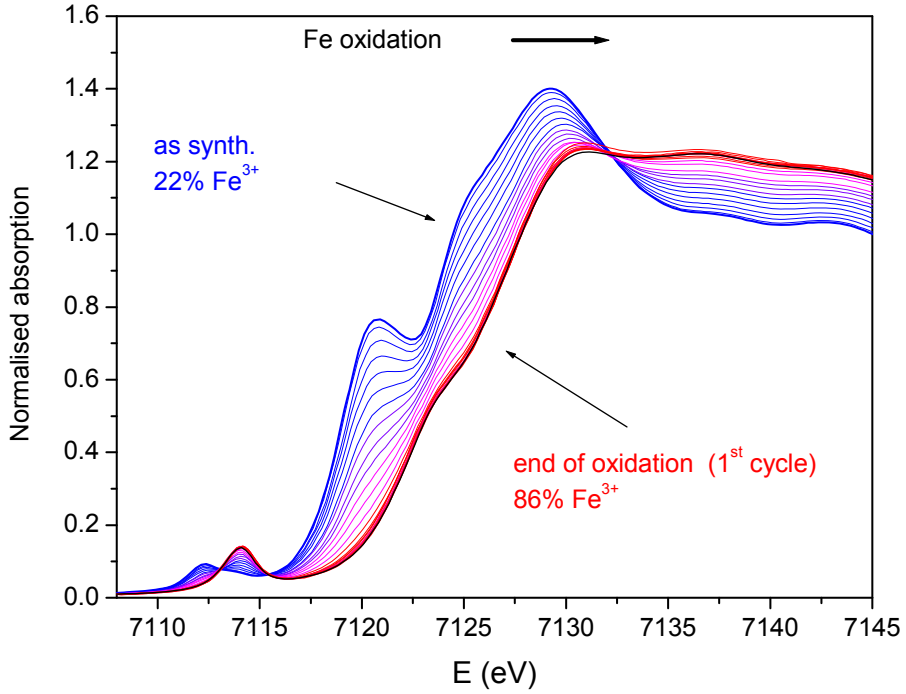
- **Li_2FeTiO_4** charging (411min), discharging (192 min) at RT with C/10 current density in time intervals of 25 min.
- **$Li_2Fe_{0.8}Mn_{0.2}SiO_4$: In situ charging (908 min), discharging (852 min) at 60 °C with C/15 current density** in time intervals of 50 min
- XAFS beamline at ELETTRA and C beamline in HASYLAB at DESY, Hamburg. A Si(111) double crystal monochromator with about 1 eV energy resolution at Fe k-edge (7112 eV) was used. Exact energy calibration with simultaneous absorption measurements on a 5 mm thick V, Fe or Mn metal foil. Absolute energy reproducibility of the measured spectra was ±0.05 eV.



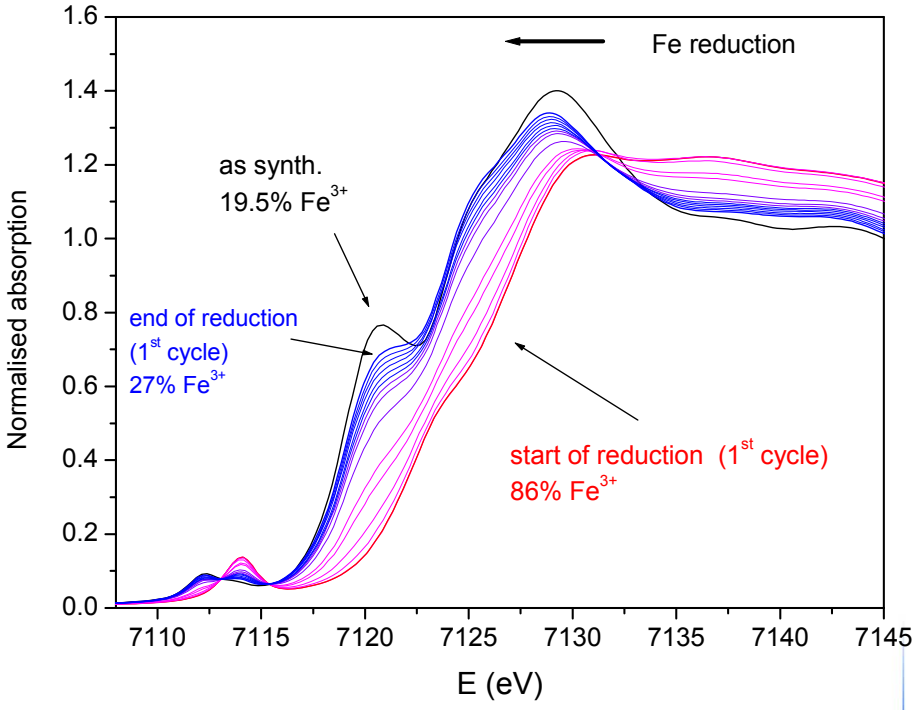
Fe and Mn XANES and EXAFS spectra were measured in time intervals of of 55 min.

$Li_{2-x}Fe_{0.8}Mn_{0.2}SiO_4$

battery charging



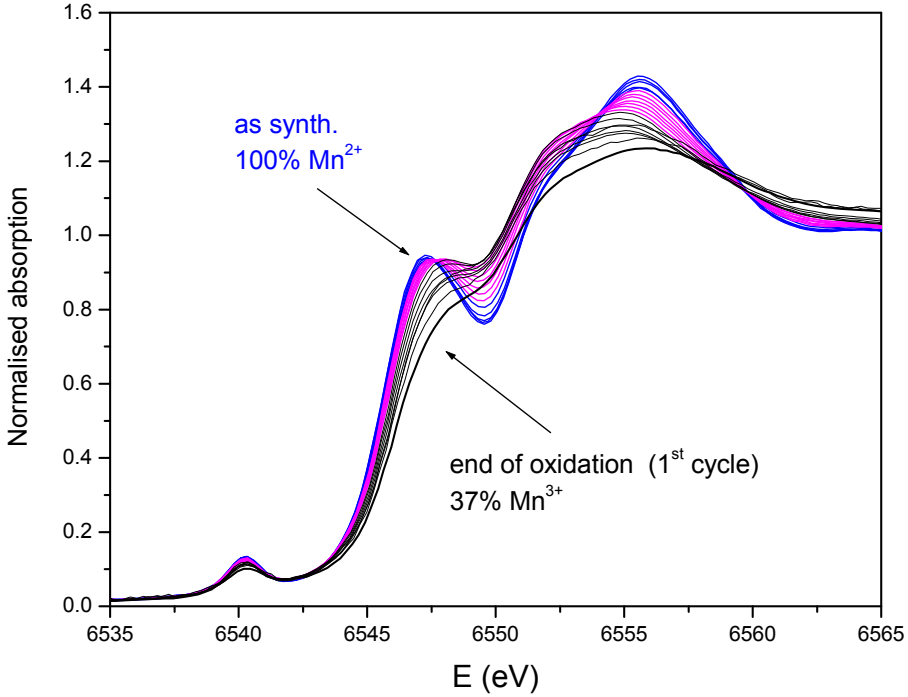
battery discharging



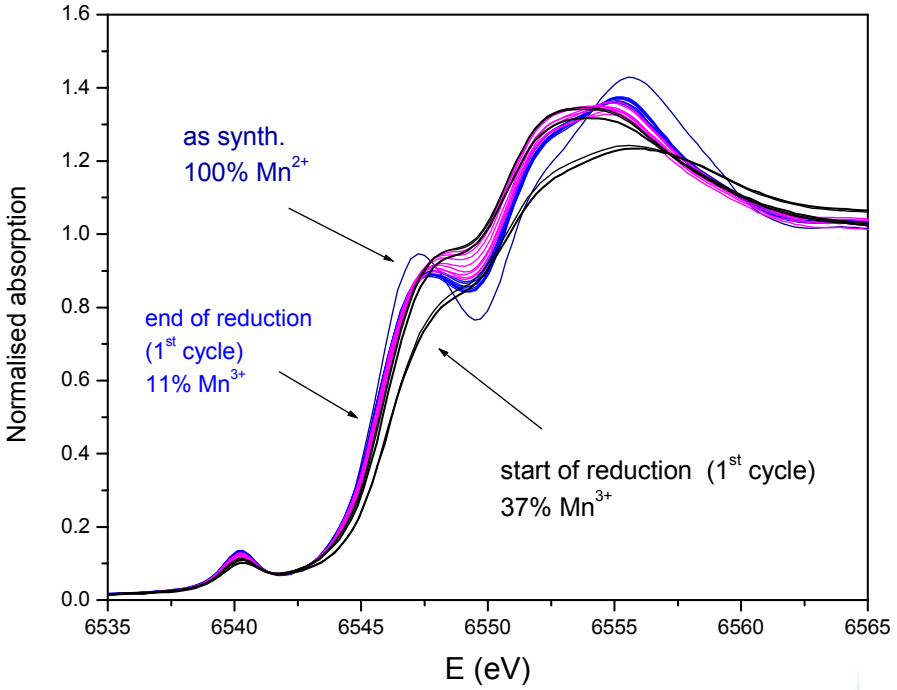
R. Dominko et al., Journal of The Electrochemical Society, **157** 12 A1309-A1316 2010

$Li_{2-x}Fe_{0.8}Mn_{0.2}SiO_4$

battery charging
Mn oxidation



battery discharging
Mn reduction

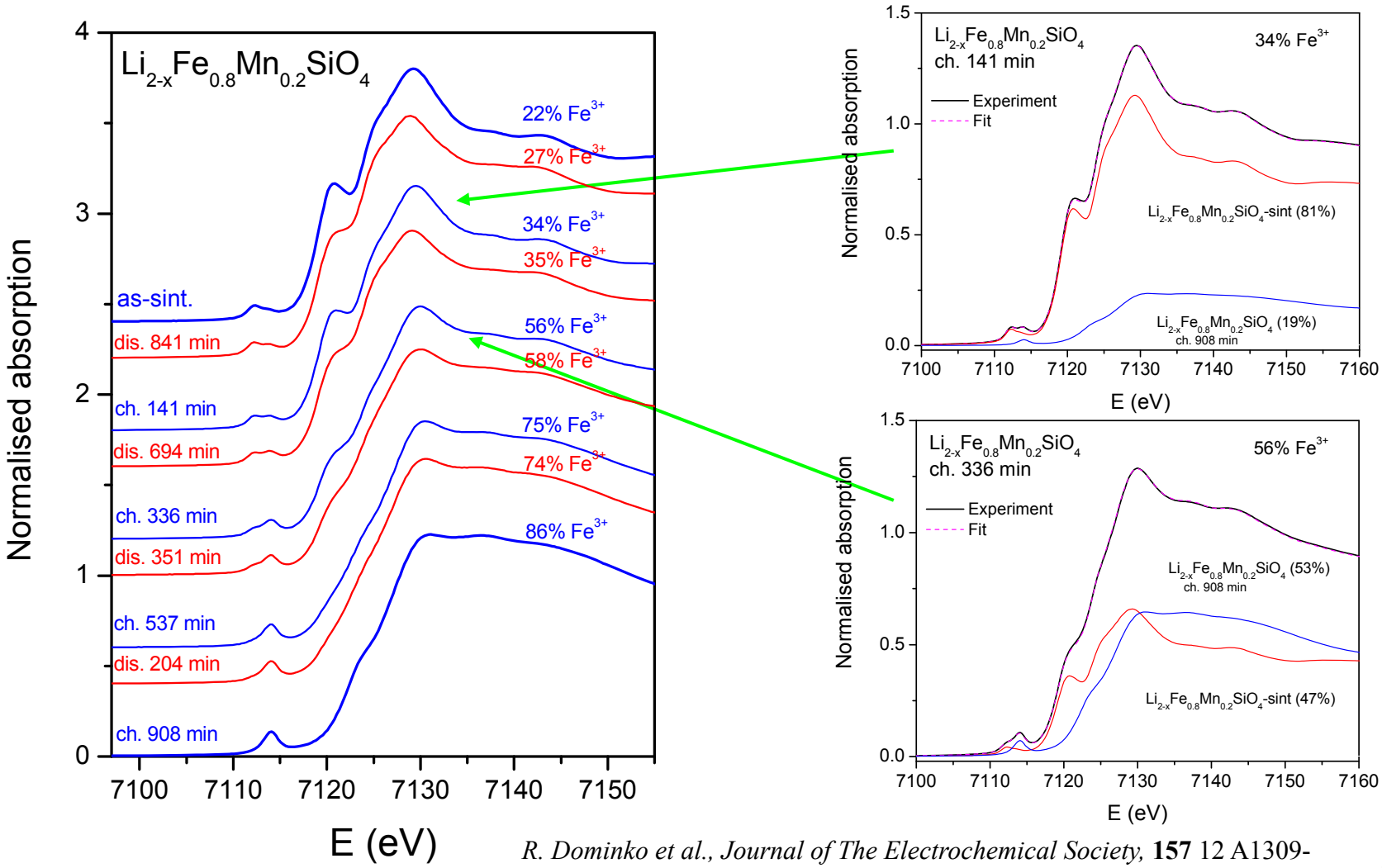


R. Dominko et al., Journal of The Electrochemical Society, **157** 12 A1309-A1316 2010

$Li_{2-x}Fe_{0.8}Mn_{0.2}SiO_4$

Linear combination fit

of XANES spectra of intermediate states with the spectra of the starting and the most charged state.



R. Dominko et al., Journal of The Electrochemical Society, **157** 12 A1309-A1316 2010

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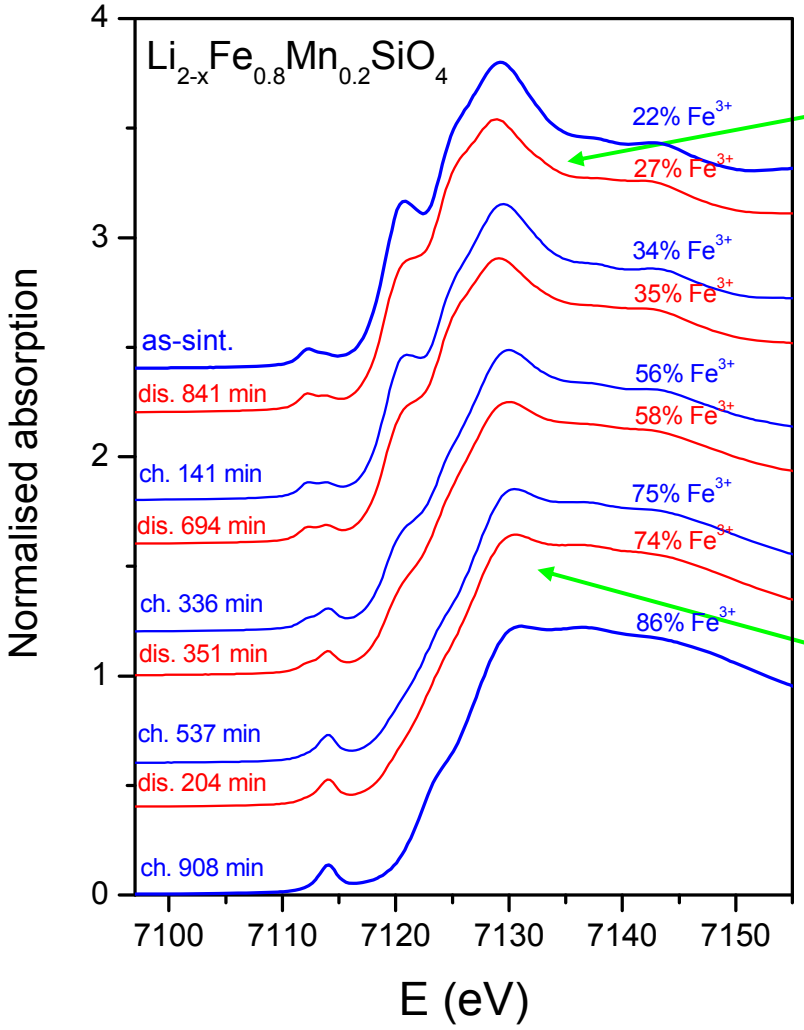
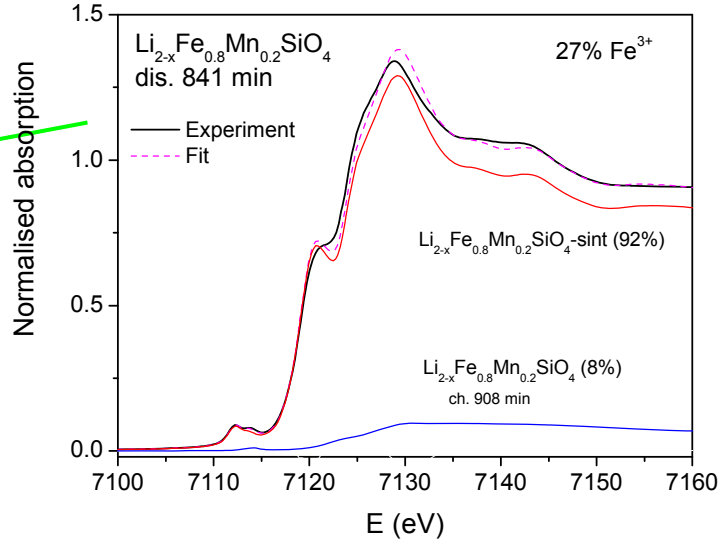
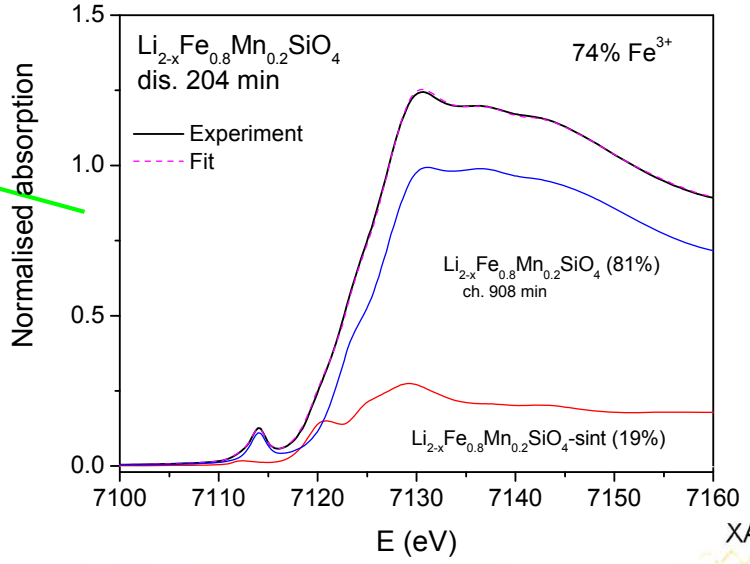
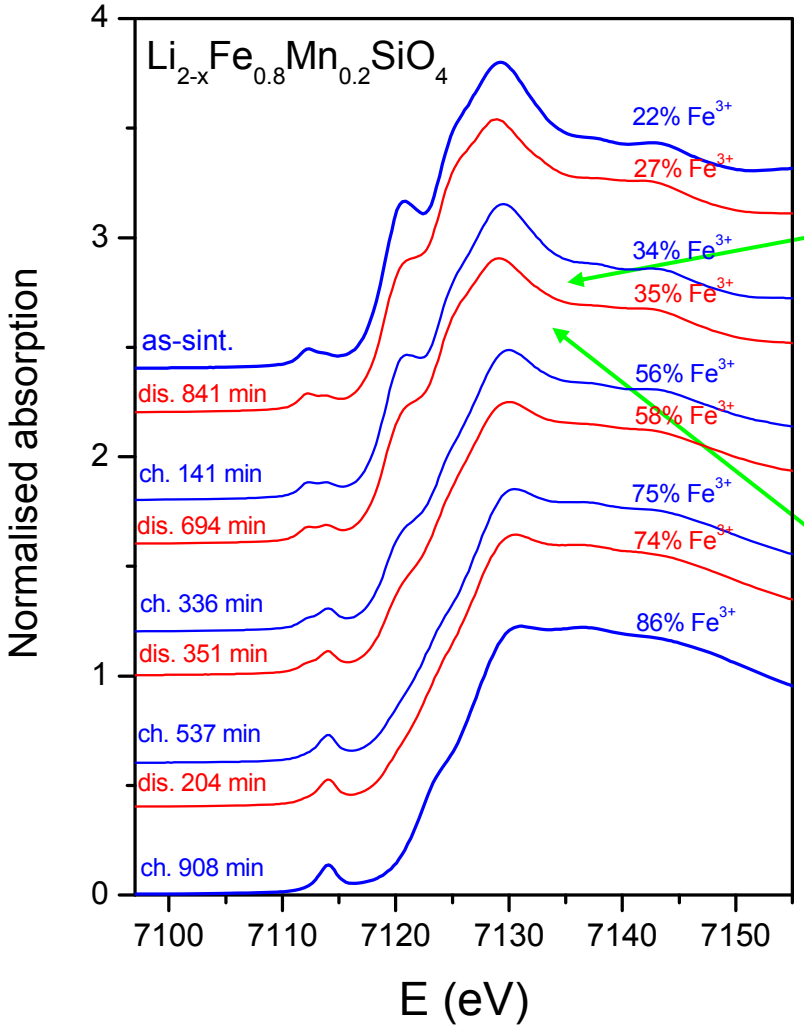




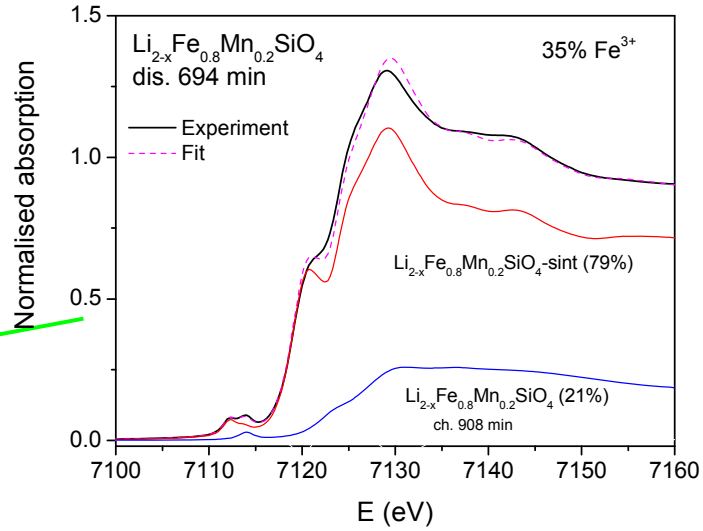


R. Dominko et al., Journal of The Electroch. Society, **157** 12 A1309-A1316 2010

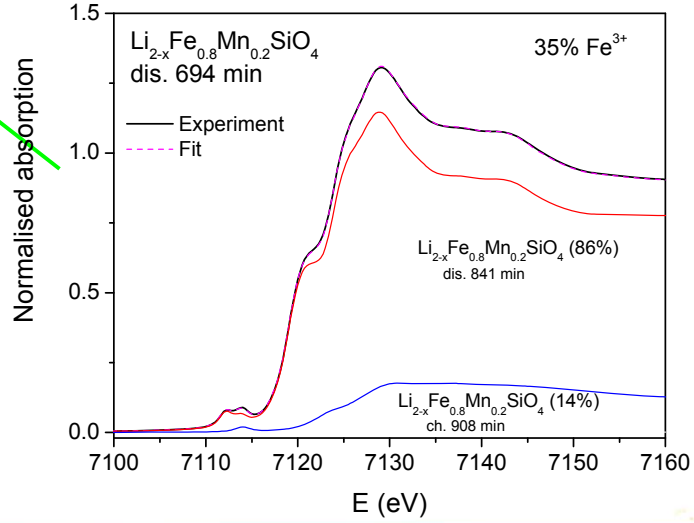
$Li_{2-x}Fe_{0.8}Mn_{0.2}SiO_4$



Linear combination fit with XANES spectra of
"as-sint." and "ch. 908 min"



Linear combination fit with XANES spectra of
"dis. 841 min " and "ch. 908 min"



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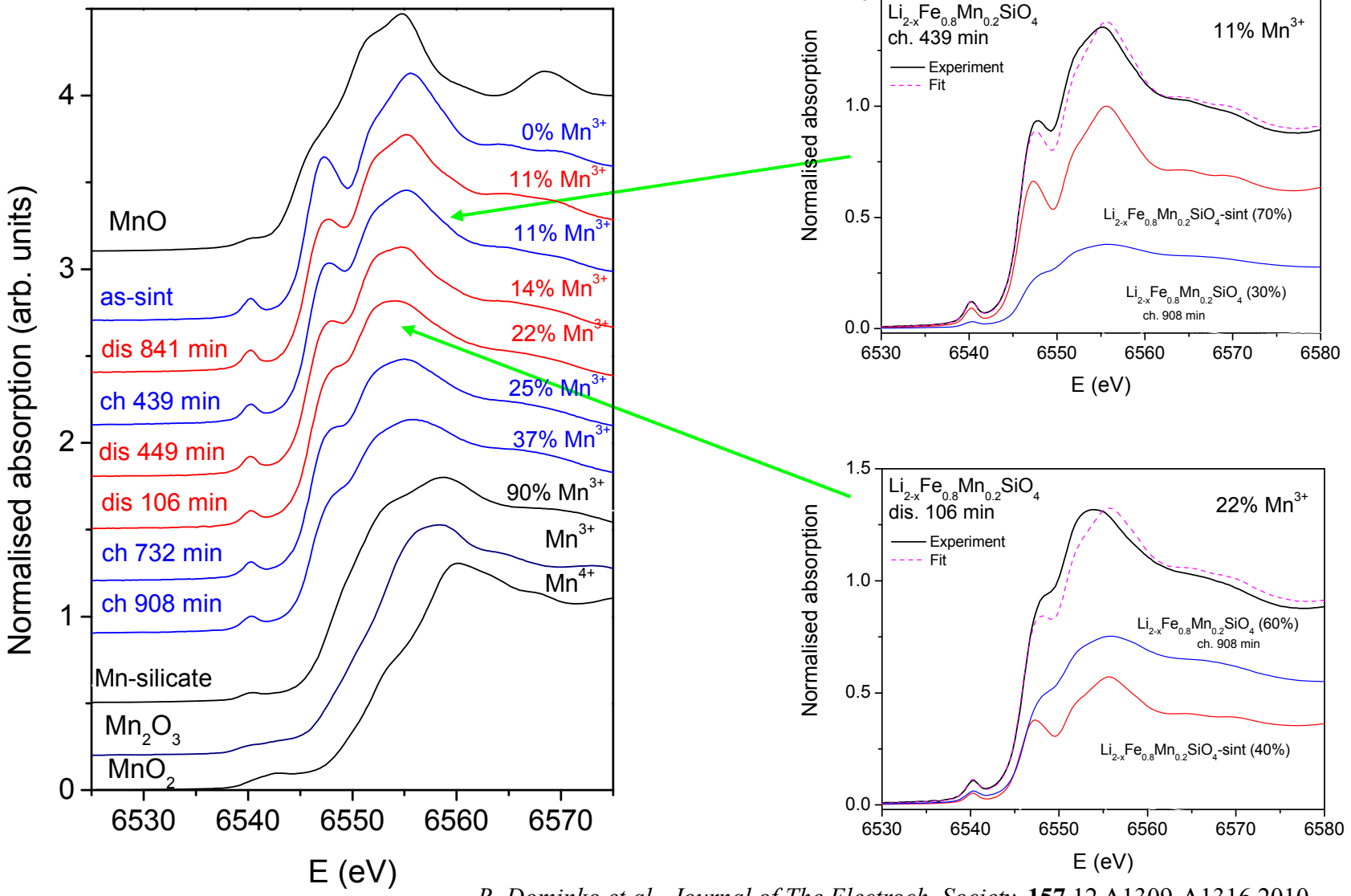
$Li_{2-x}Fe_{0.8}Mn_{0.2}SiO_4$

Linear combination fit with XANES spectra of
"as-sint." and "ch. 908 min"



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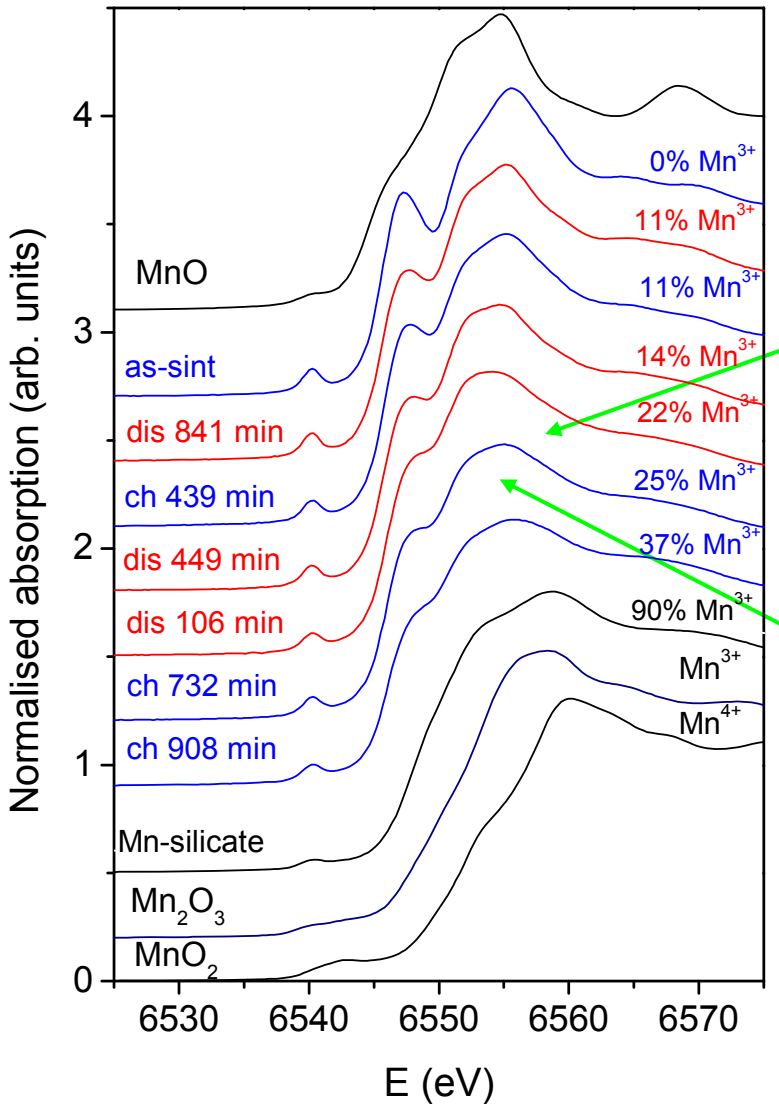
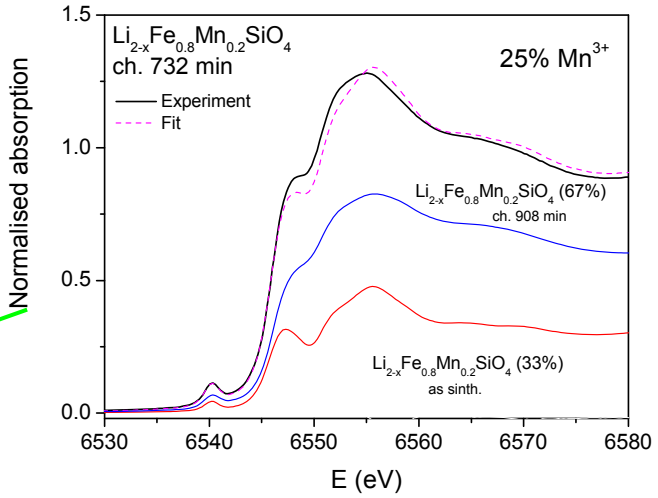
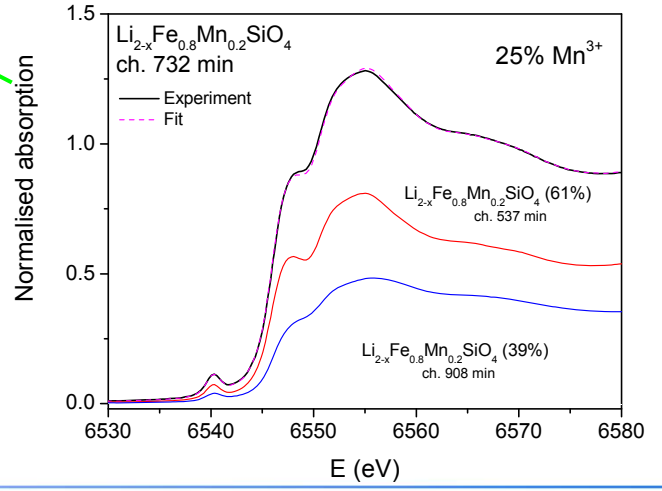
$Li_{2-x}Fe_{0.8}Mn_{0.2}SiO_4$



Linear combination fit with XANES spectra of "as-sint." and "ch. 908 min"

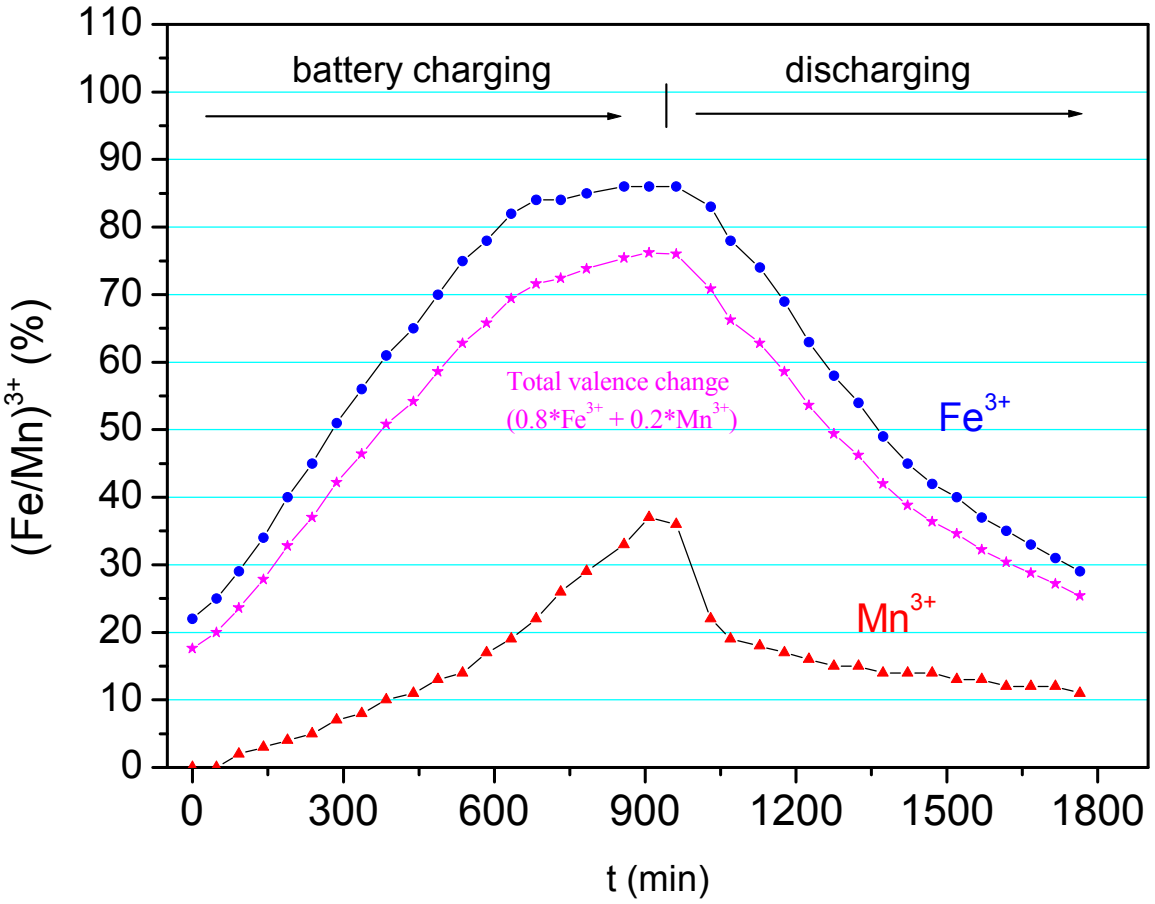


Linear combination fit with XANES spectra of "ch. 537 min " and "ch. 908 min"



Relative amount of Fe^{3+} and Mn^{3+} in $Li_{2-x}(Fe_{0.8}Mn_{0.2})SiO_4$

during the the proces of battery charging and discharging



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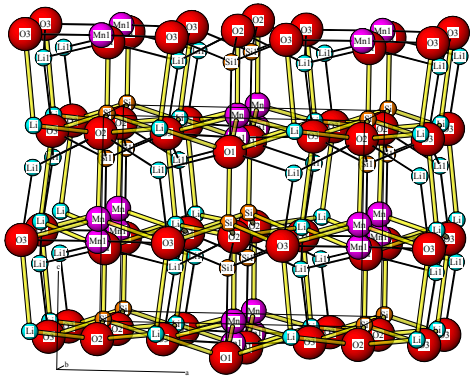
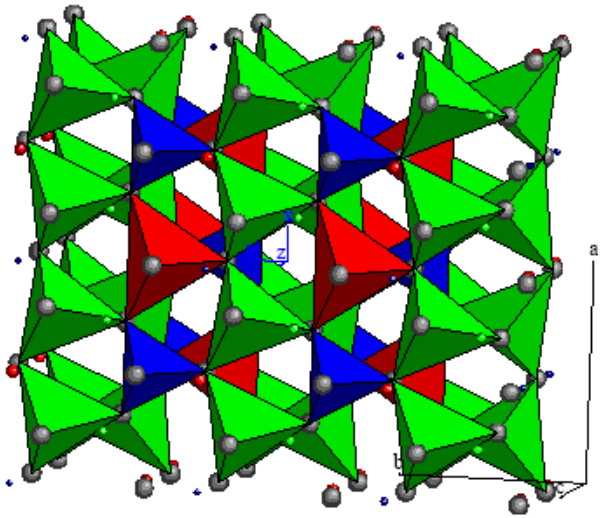
EXAFS analysis: model local structure around Mn and Fe cations in $Li_2(Fe_{0.8}Mn_{0.2})SiO_4$

Fe/Mn neigh.	Coord. No.	Distance R(Å)
O	2	1.99
O	1	2.03
O	1	2.11
Li	1	2.79
O	1	2.92
Li	1	3.04
Si	1	3.05
Li	4	3.10
Si	2	3.13
Li	1	3.16
Si	1	3.18
…	…	…

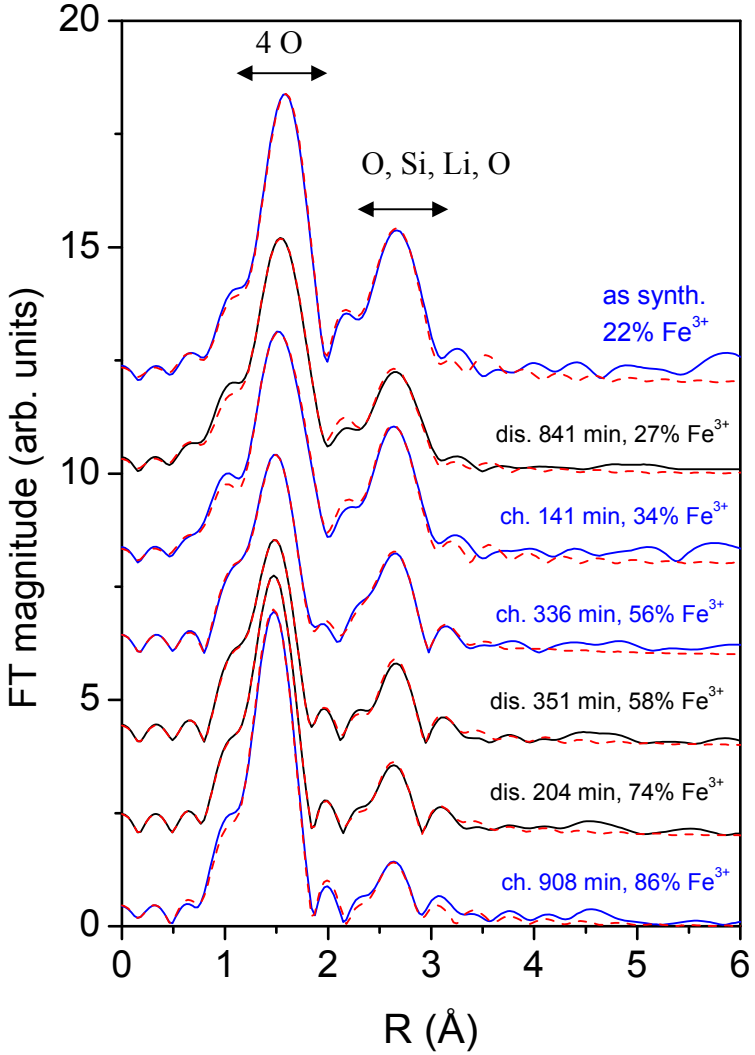




The model is based on monoclinic **$Li_2(Fe_{0.8}Mn_{0.2})SiO_4$** crystal structure with P121/n1 space group. a = 8.245 Å, b = 5.018 Å and c = 8.246 Å obtained by powder XRD.

The structure is composed of MnO_4, FeO_4, SiO_4 and LiO_4 tetrahedra. R. Dominko, M. Bele, M. Gaberšček, A. Meden, M. Remškar, and J. Jamnik, *Electrochem. Commun.* **8**, 217 (2006).

In operando Fe EXAFS spectra of $Li_{2-x}Fe_{0.8}Mn_{0.2}SiO_4$



Changes of Fe local structure during charge/discharge process:

- modifications of FeO_4 tetrahedra
- increase of disorder in the second coordination shell (Si)

R. Dominko et al., Journal of The Electroch. Society, **157** 12 A1309 (2010)

as synthesized
22% Fe^{3+}

1 **O** at 1.94 Å
3 **O** at 2.03 Å
$\sigma^2_{Fe\text{-}Si} = 0.009$ Å^2

reduced
27 % Fe^{3+}

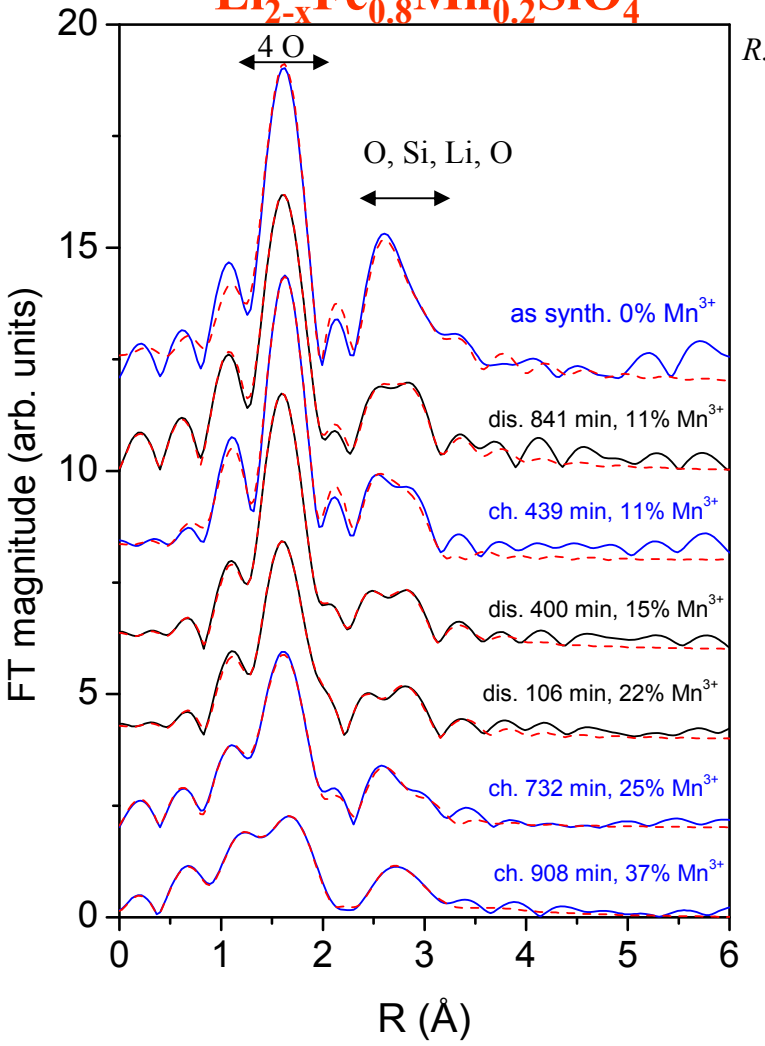
4 O at 1.99 Å
$\sigma^2_{Fe\text{-}Si} = 0.008$ Å^2

Oxidized
86% Fe^{3+}

4 **O** at 1.88 Å
$\sigma^2_{Fe\text{-}Si} = 0.022$ Å^2

Experiment – (solid line); EXAFS model – (red dashed line)

In operando Mn EXAFS spectra of $Li_{2-x}Fe_{0.8}Mn_{0.2}SiO_4$



Changes of Mn local structure during charge/discharge process:

- modifications of MnO_4 tetrahedra
- increase of disorder in the second coordination shell (Si)

R. Dominko et al., Journal of The Electrochemical Society, **157** 12 A1309-A1316 2010

as synthesized
0% Mn^{3+}

3 **O** at 2.04 Å
1 **O** at 2.21 Å
$\sigma^2_{Mn\text{-}Si} = 0.007$ Å^2

reduced
11 % Mn^{3+}

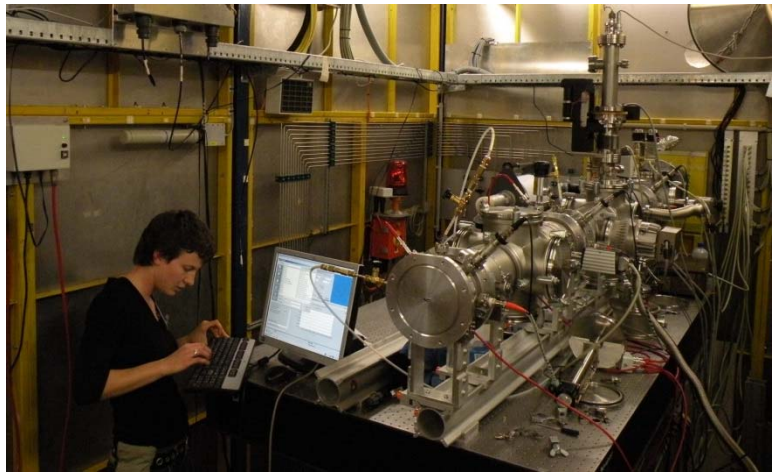
3 **O** at 2.04 Å
1 **O** at 2.17 Å
$\sigma^2_{Mn\text{-}Si} = 0.008$ Å^2

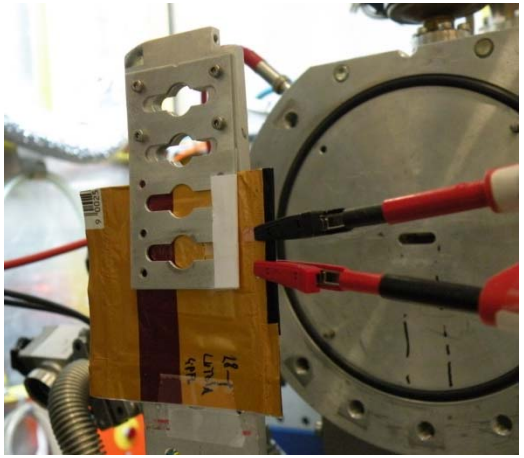
Oxidized
37% Mn^{3+}

1 **O** at 1.85 Å
3 **O** at 2.05 Å
$\sigma^2_{Mn\text{-}Si} = 0.016$ Å^2

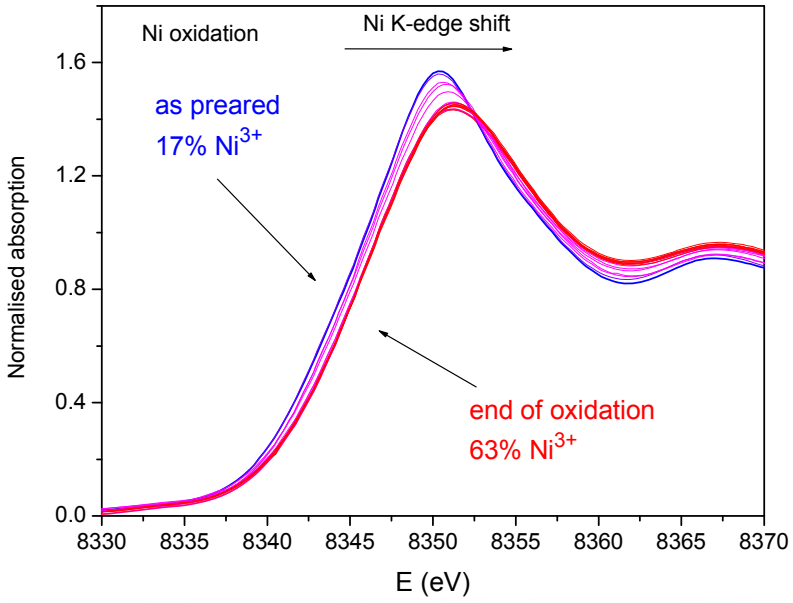
Experiment – (solid line); EXAFS model – (red dashed line)

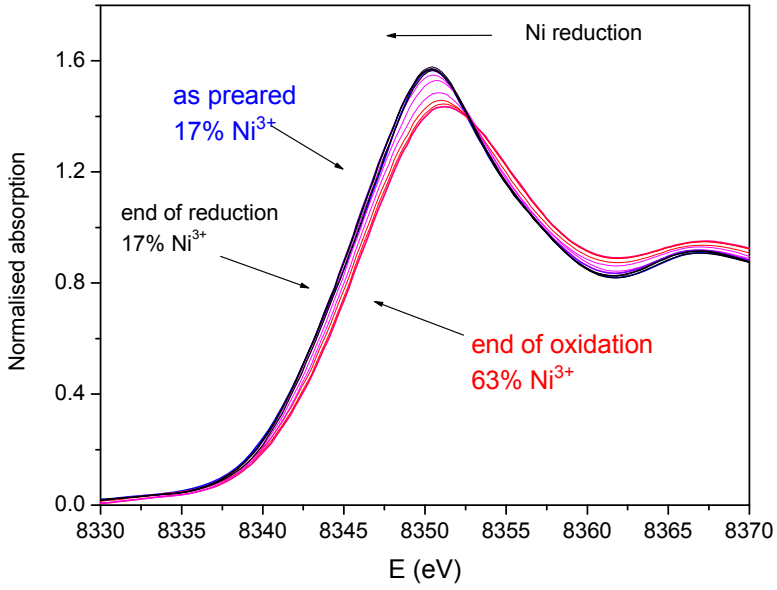
In operando XANES and EXAFS analysis of $Li_{2-x}NiTiO_4$ cathode materials for Li-ion batteries





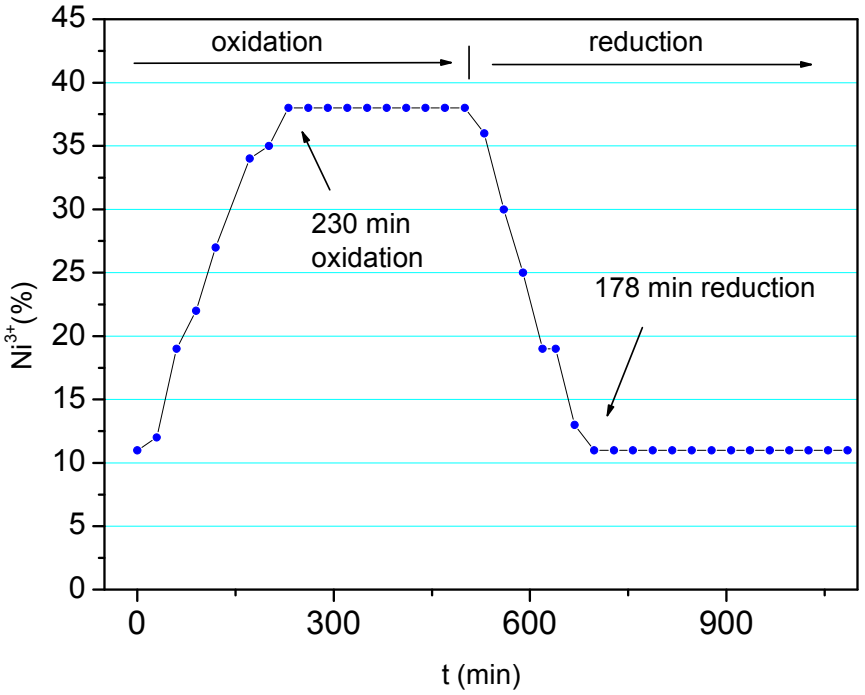
I.Arčon, M.Küzma, R. Dominko, M.Gaberšček, In situ XANES and EXAFS analysis of Li_2NiTiO_4 cathode materials for Li-ion batteries, EXRS2012 confernce presentation, June 18 – 23, 2012

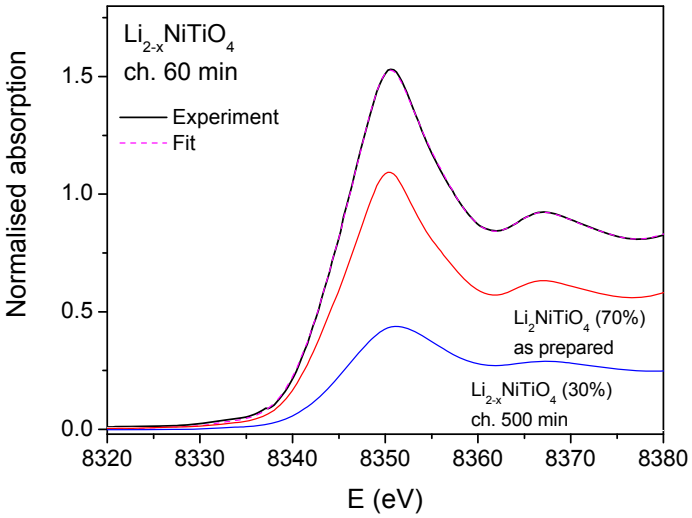


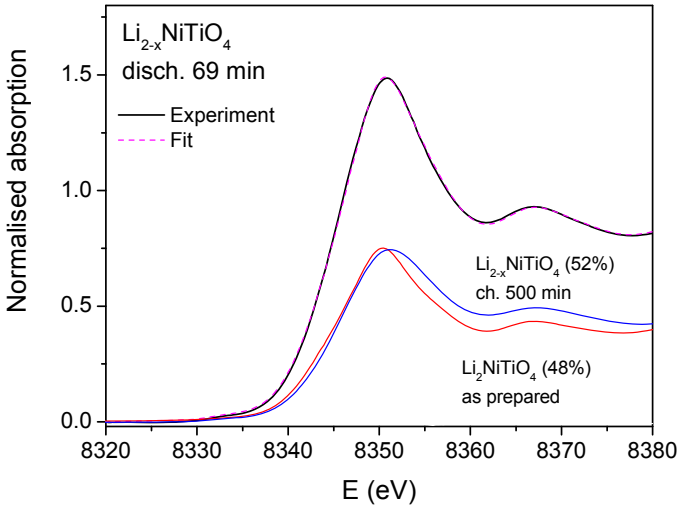


In operando XANES analysis of $Li_{2-x}NiTiO_4$ cathode materials for Li-ion batteries

I.Arčon, M.Küzma, R. Dominko, M.Gaberščček, In situ XANES and EXAFS analysis of Li_2NiTiO_4 cathode materials for Li-ion batteries, EXRS2012 confernce presentation, June 18 – 23, 2012





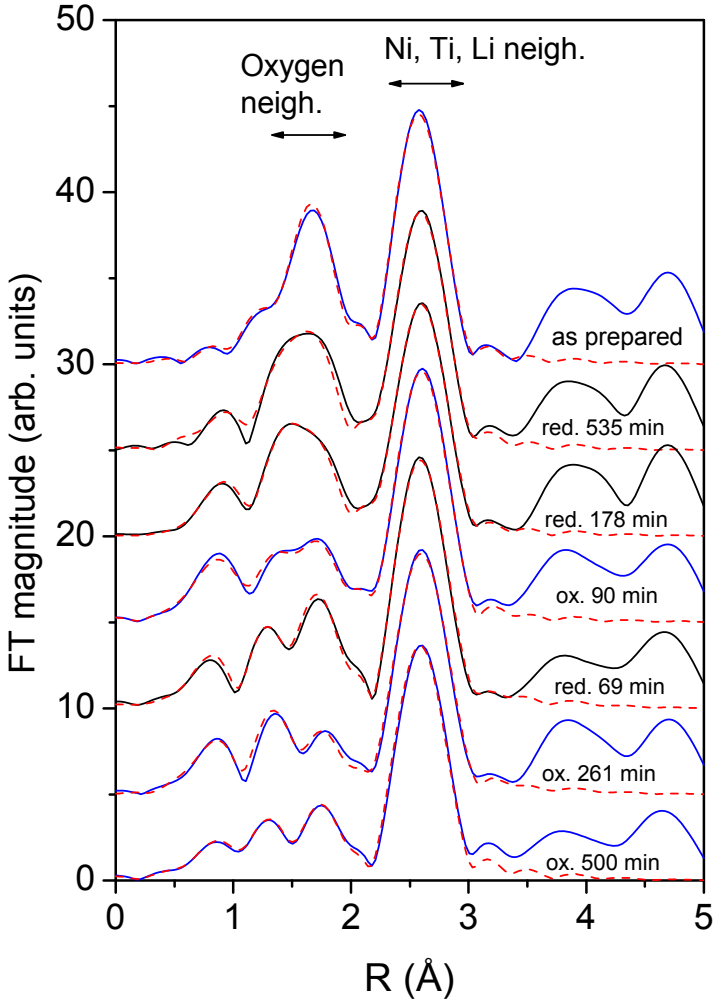


In operando EXAFS analysis of $Li_{2-x}NiTiO_4$ cathode materials for Li-ion batteries

The EXAFS spectra were modeled with an ab initio FEFF model based on the crystallographic data of Li_2NiTiO_4 with rock salt structure.

In this structure Ni atoms are located at the centers of oxygen octahedra with Ni-O distance of 2.074 Å. The second coordination sphere at the distance of 2.933 Å is occupied randomly by six Li, three Ni and three Ti atoms, followed by more distant coordination shell of eight O atoms at 3.59 Å.

The structural changes during oxidation/reduction are limited to the nearest oxygen coordination shell. There are no significant changes of local structure in more distant coordination spheres.



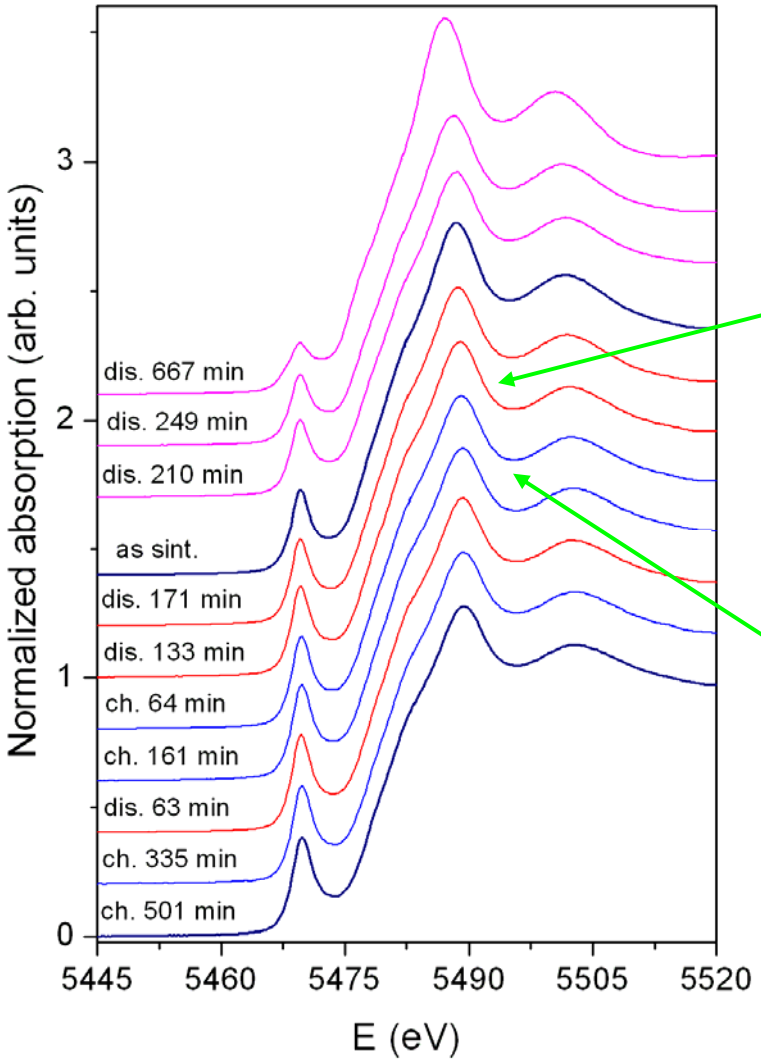
I.Arčon, M.Küzma, R. Dominko, M.Gaberšček, In situ XANES and EXAFS analysis of Li_2NiTiO_4 cathode materials for Li-ion batteries, EXRS2012 confernce presentation, June 18 – 23, 2012

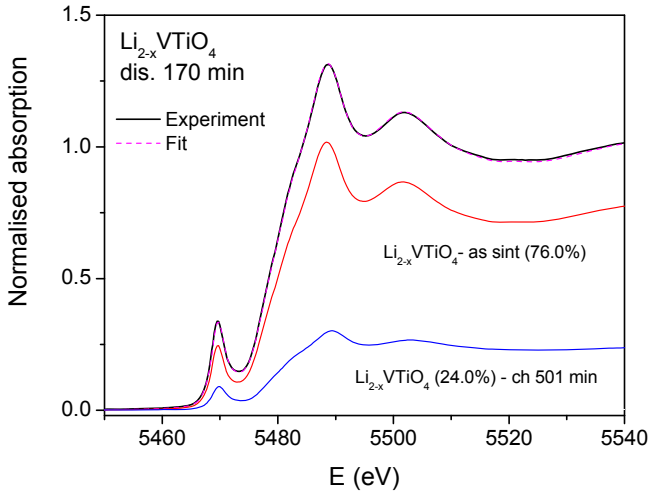
$Li_{2-x}VTiO_4$

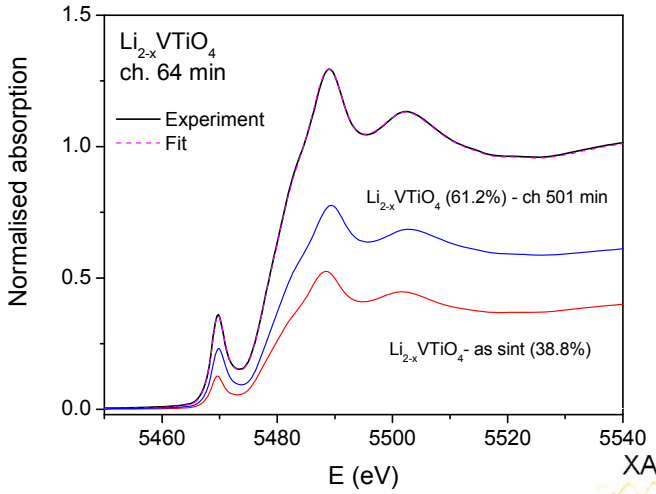
rock-salt crystal structure

Linear combination fit

of V XANES spectra of intermediate states with the spectra of the starting and the most charged state.





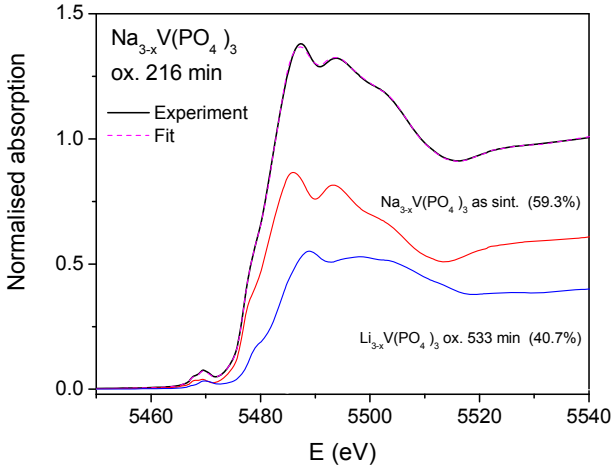


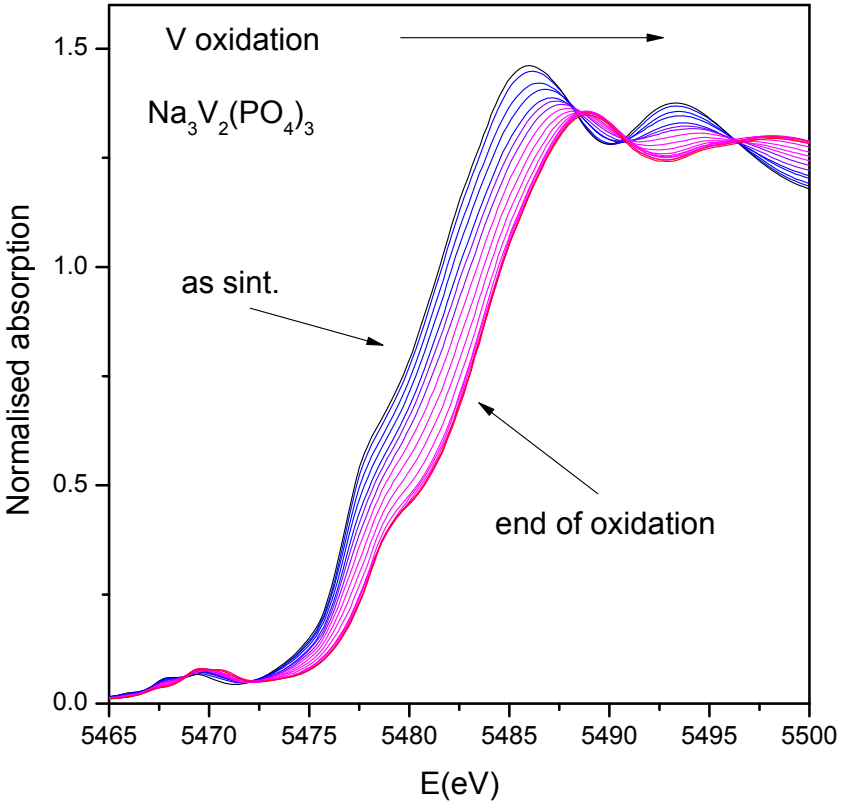
R. Dominko, et al., J. Power Sources (2010), doi:10.1016/j.jpowsour.2010.09.004

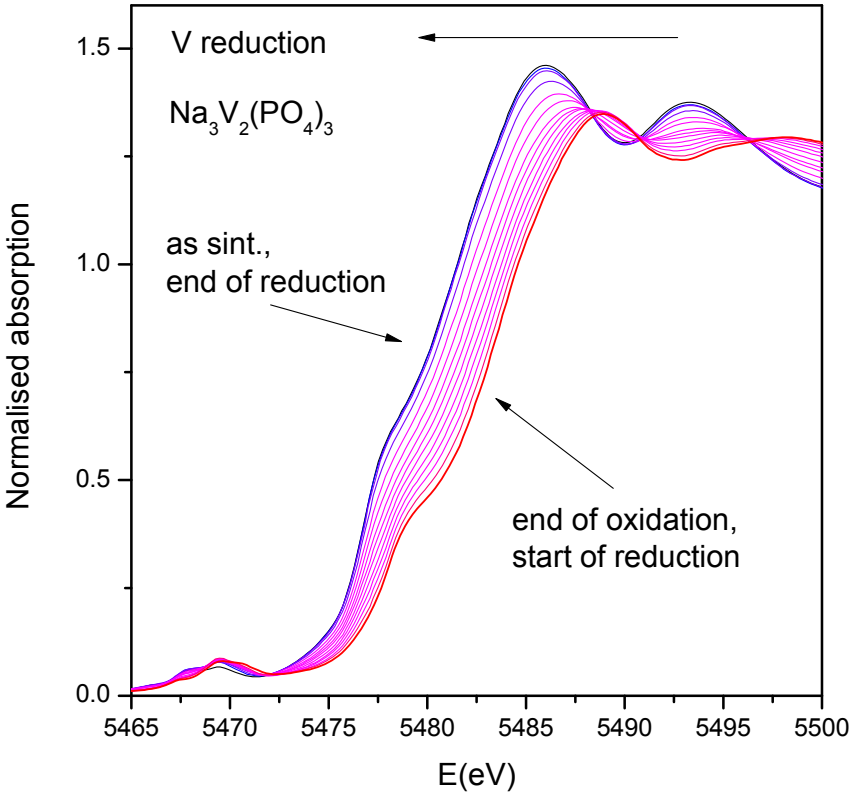
$Na_{3-x}V_2(PO_4)$

Linear combination fit

of V XANES spectra of intermediate states with the spectra of the starting and the most charged state.

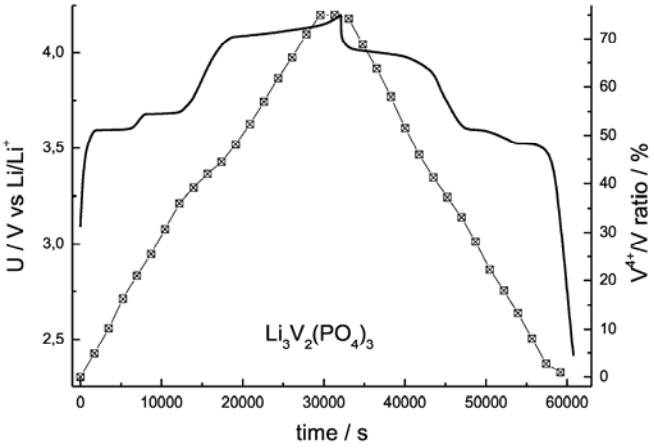


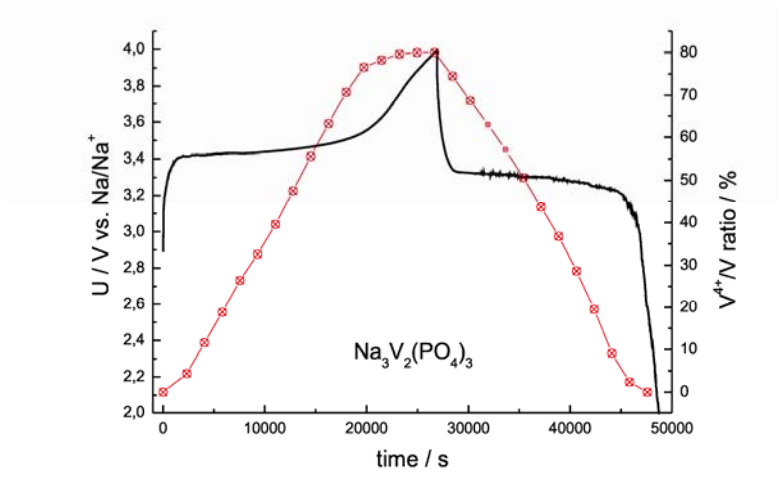




R. Dominko, et al., J. Power Sources (2010), doi:10.1016/j.jpowsour.2010.09.004

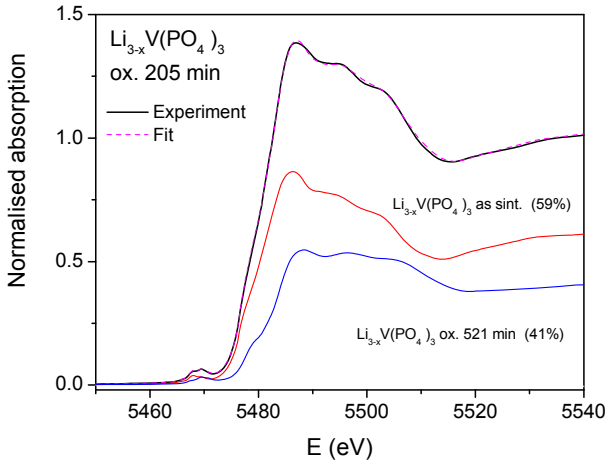
$Na_{3-x}V_2(PO_4)$ and $Li_{3-x}V_2(PO_4)$

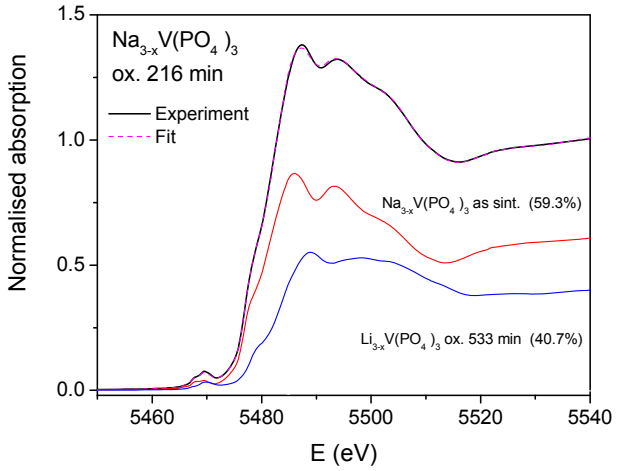




Linear combination fit

of V XANES spectra of intermediate states with the spectra of the starting and the most charged state.





M. Pivko, I. Arčon et al., Journal of Power Sources 216 (2012) 145-151

Li-S batteries are most promising solution for automotive applications

Properties:

- high energy density
- small size, low weight,
- safe and a reliable operation,
- environmental friendly,
- cost effective.

Not yet successfully commercialized:

Li-S cell technology has to be developed and optimized.

Key points:

- Understand the mechanisms of operation, nano-structuration and electrochemical processes in the cathode material and in the electrolyte during battery operation.
- Design new Li-S cathode materials with superior properties.

Advanced European lithium sulphur cells for automotive applications

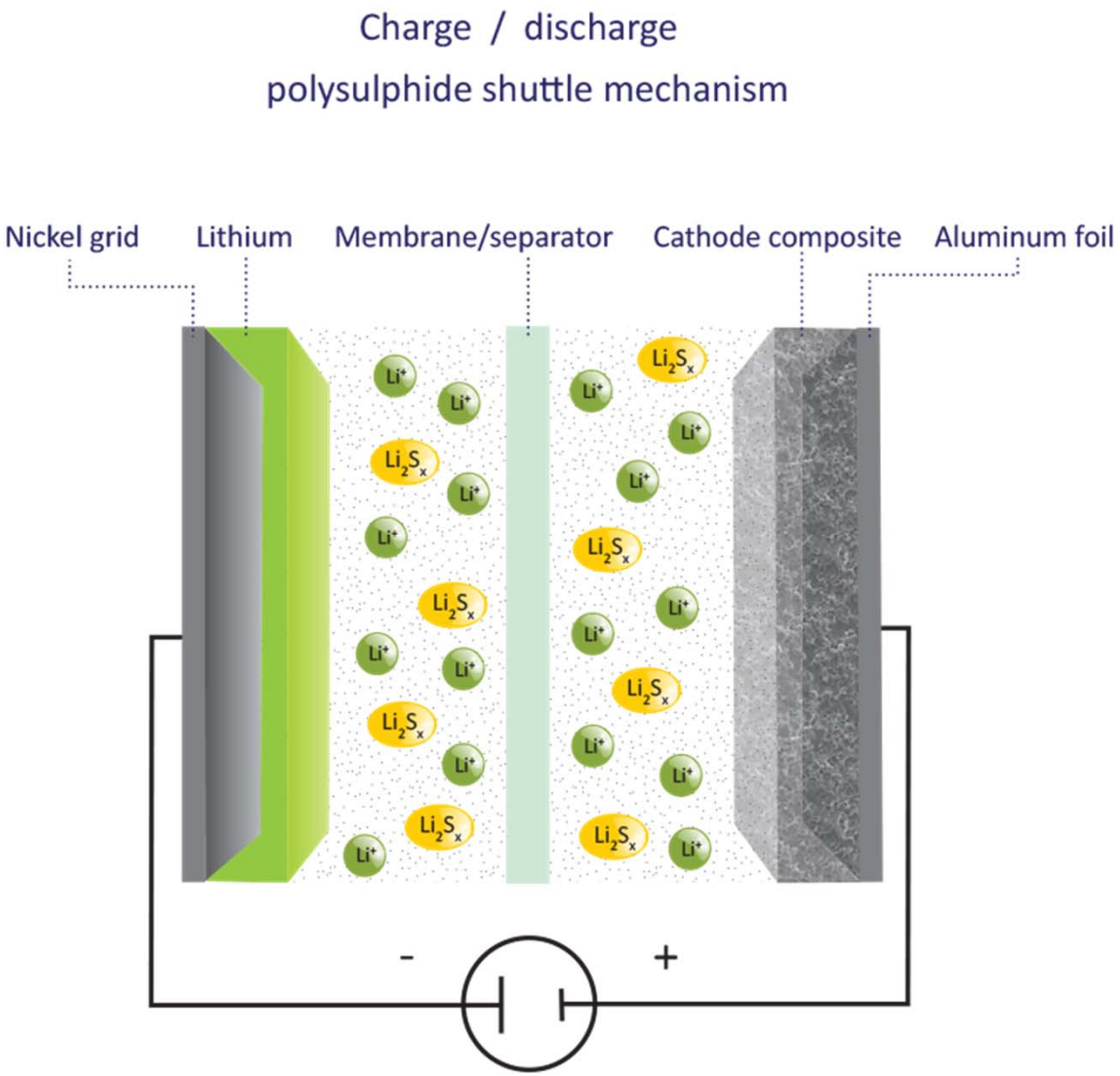
Collaborative project
FP7-2012-GC-MATERIALS
Eleven European partners
Sponsored by the European commission
Started in 2012

Project coordinator: Robert Dominko
National Institute of Chemistry, Slovenia

www.eurolis.eu

European Green Cars Initiative

Lithium sulphur cell



Resarch, development & engineering:

a. Cathode composite

- Host matrix
- Sulphur deposition
- binder

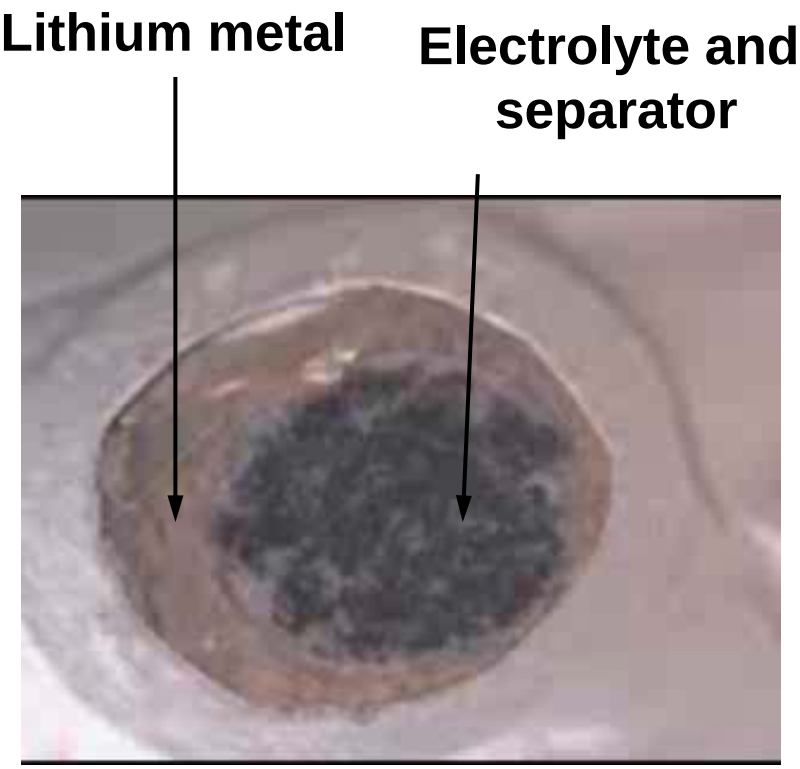
b. Electrolyte

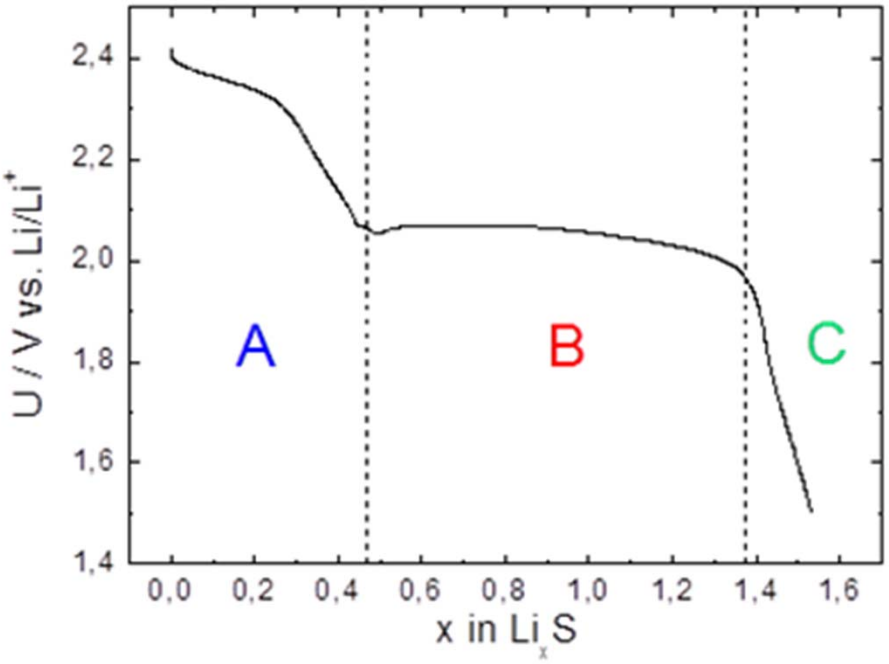
- Solvent(s)
- Salt(s)
- Polymers
- Ionic liquids

c. Separator

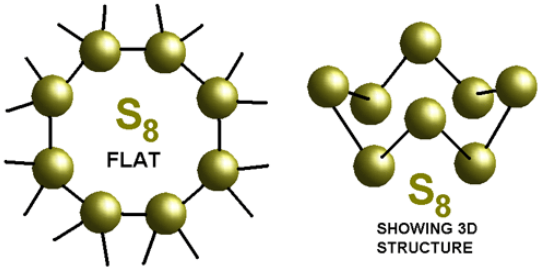
d. Additives

Formation of polysulphides





Cathode (sulphur)



$$S_8 \xrightarrow{+2Li} Li_2S_8 \xrightarrow{+2/3Li} 4/3Li_2S_6$$

$$8/3Li_2S_3 \xleftarrow{+4/3Li} 2Li_2S_4 \xleftarrow{+4/3Li}$$

$$+ 8/3Li \rightarrow 4Li_2S_2 \xrightarrow{+2Li} 8Li_2S$$

Aim of in-operandoXAS study of Li-S battery

The feasibility and reliability of sulphur K-edge XANES and EXAFS analysis of Li-S batteries **in operando** as a tool for:

- characterization of the redox chemistry during charging and discharging of the battery.
- information on changes in the **molecular structure of sulphur** and **sulphur oxidation state** in the cathode material.
- **monitoring polysulfide formation** to understand the interactions of sulfur and polysulfides with a host matrix and electrolyte.

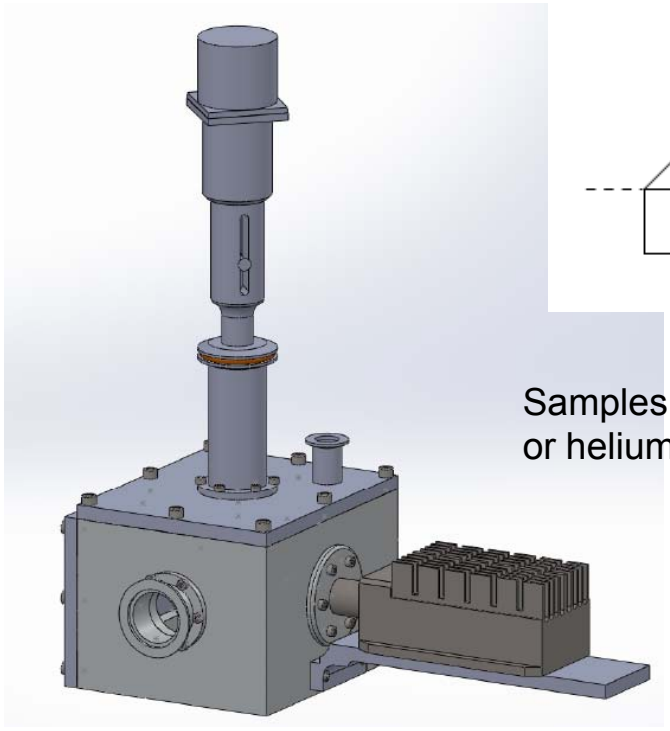
This information is esential for the development of long cycle life of lithium sulfur (Li-S) batteries.

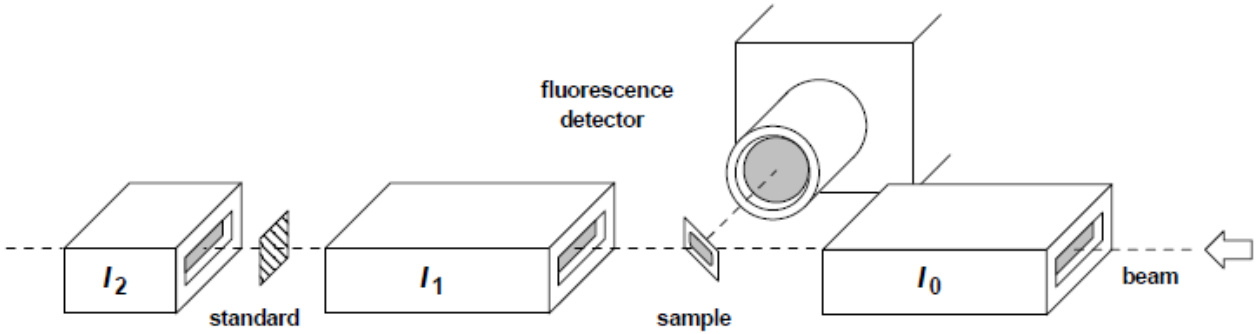
Experimental: setup

XAFS beamline at Elettra

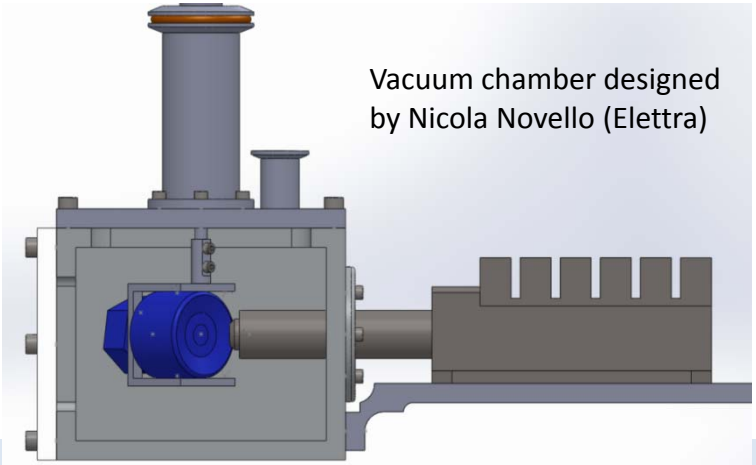
Sulphur K-edge (2472 eV)

Fluorescence detection mode ($\mu(E) \propto I_F/I_0$)





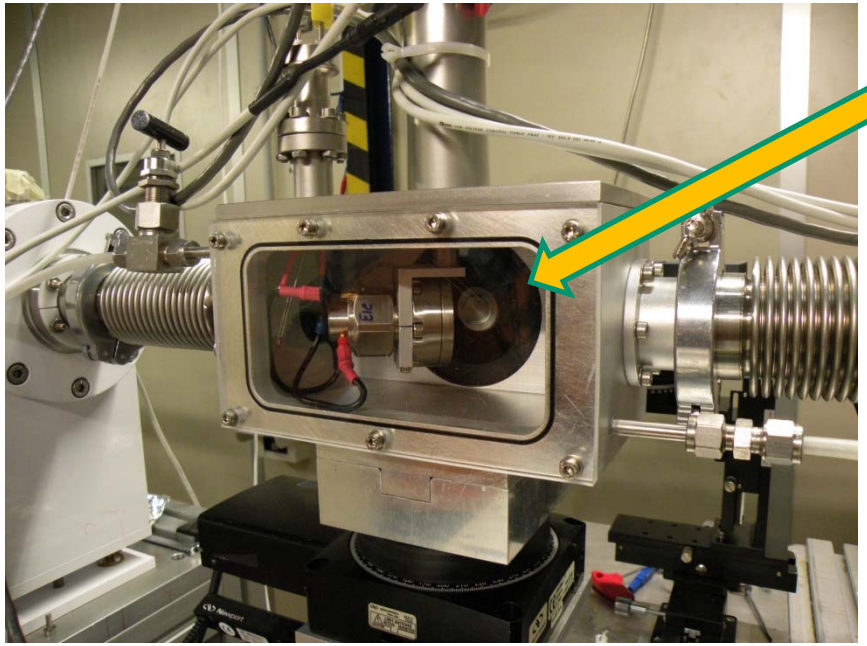
Samples in vacuum
or helium atmosphere

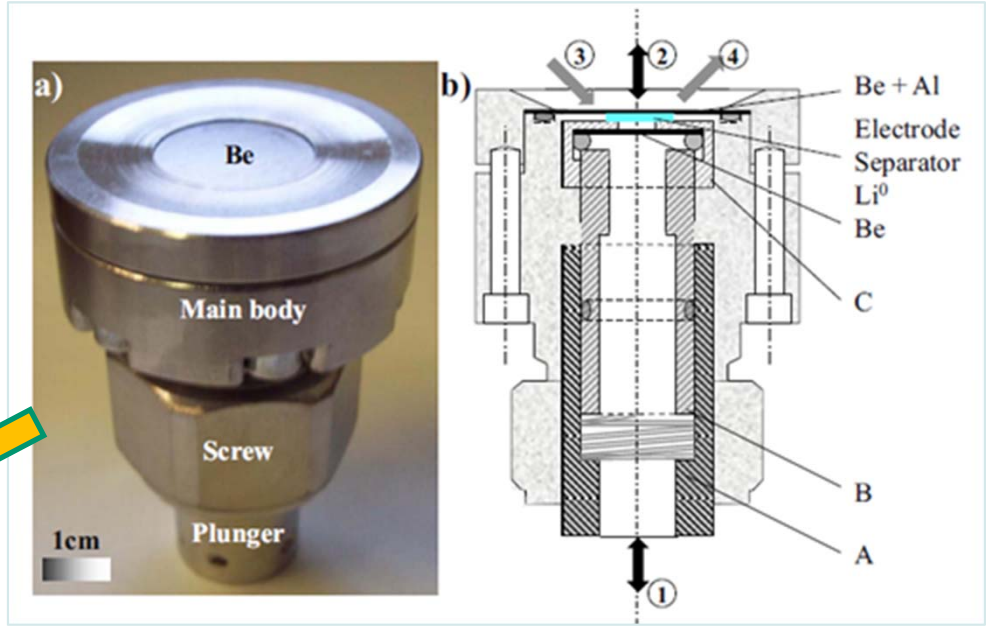


Vacuum chamber designed
by Nicola Novello (Elettra)

In operando XAS measurements

Modified 4-electrode Swagelok cell
for in operando XAS measurenets
with 13 micron Be window

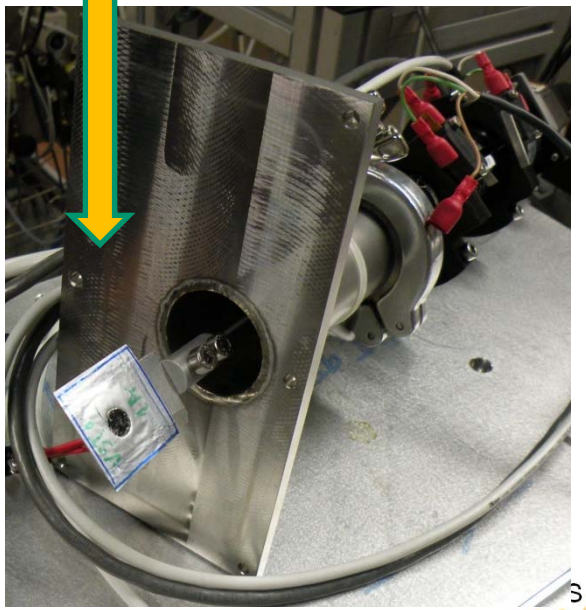




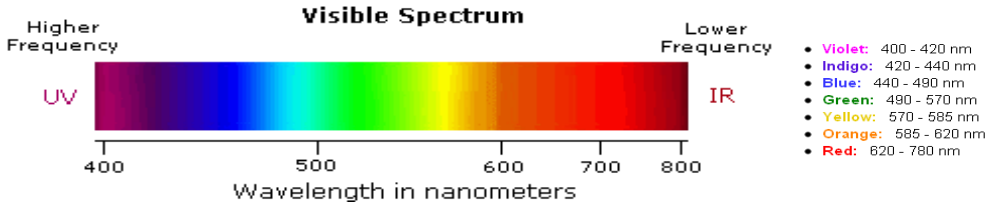
Li-S battery

In operando „coffee bag“ cells for XAS spectroscopy

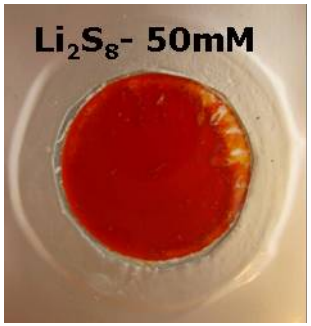
Cell after assembling



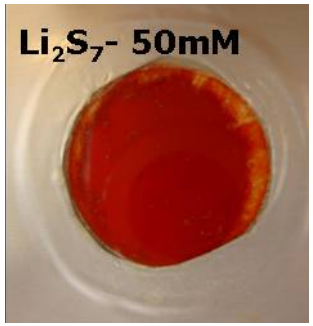
Reference: different polysulfides



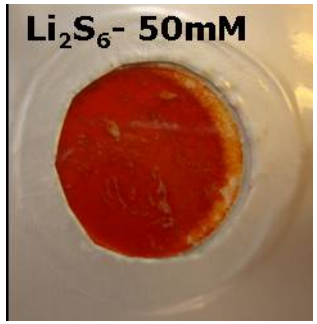
Change in colors depending on the length of polysulfides



572nm

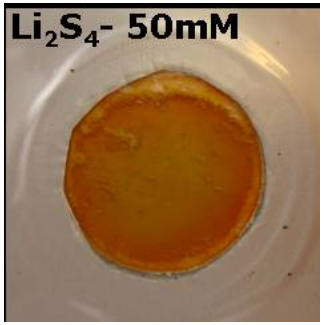


567nm

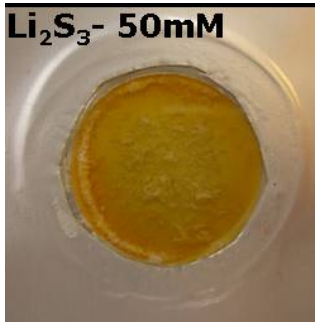


555nm

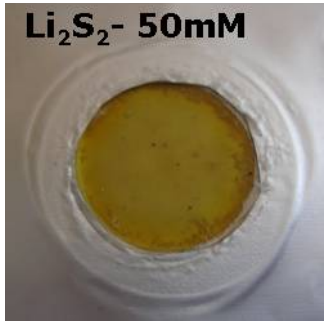
536nm



513nm



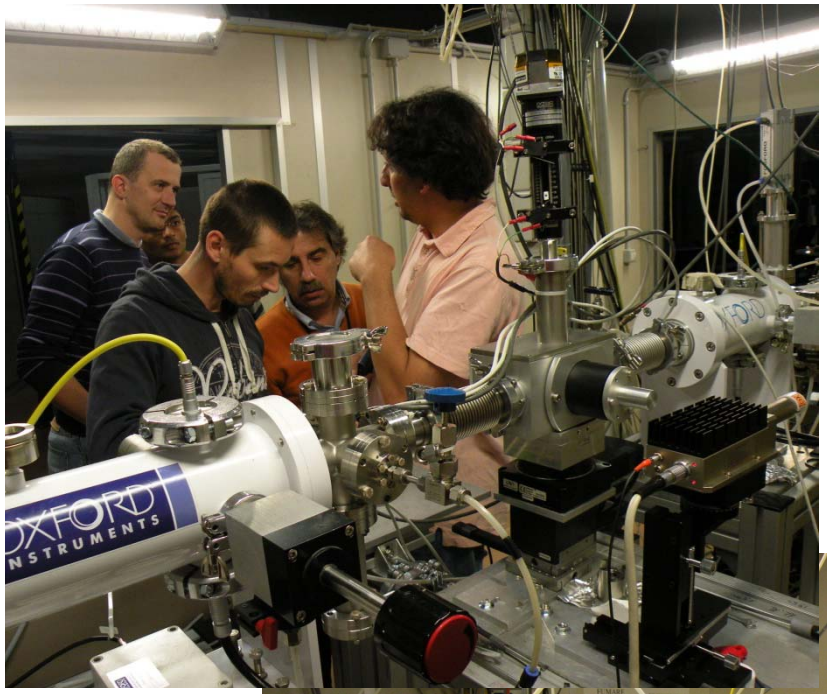
494nm

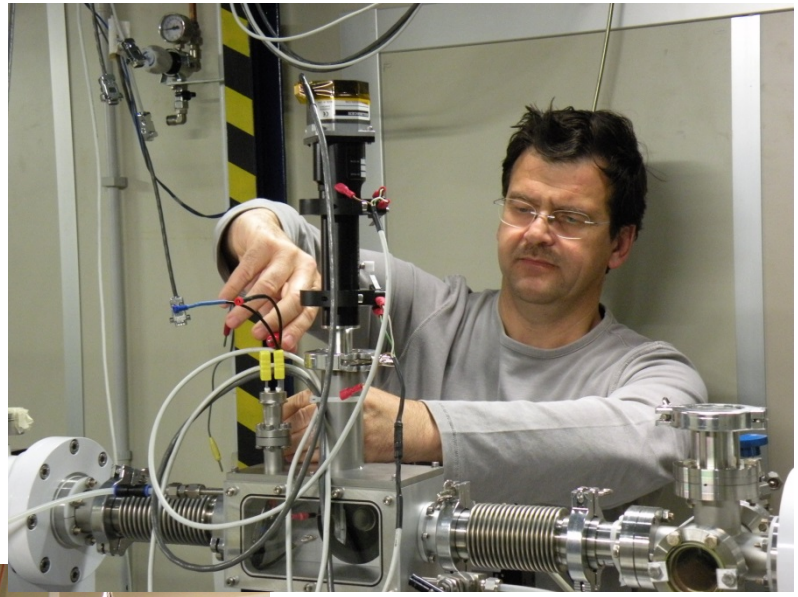


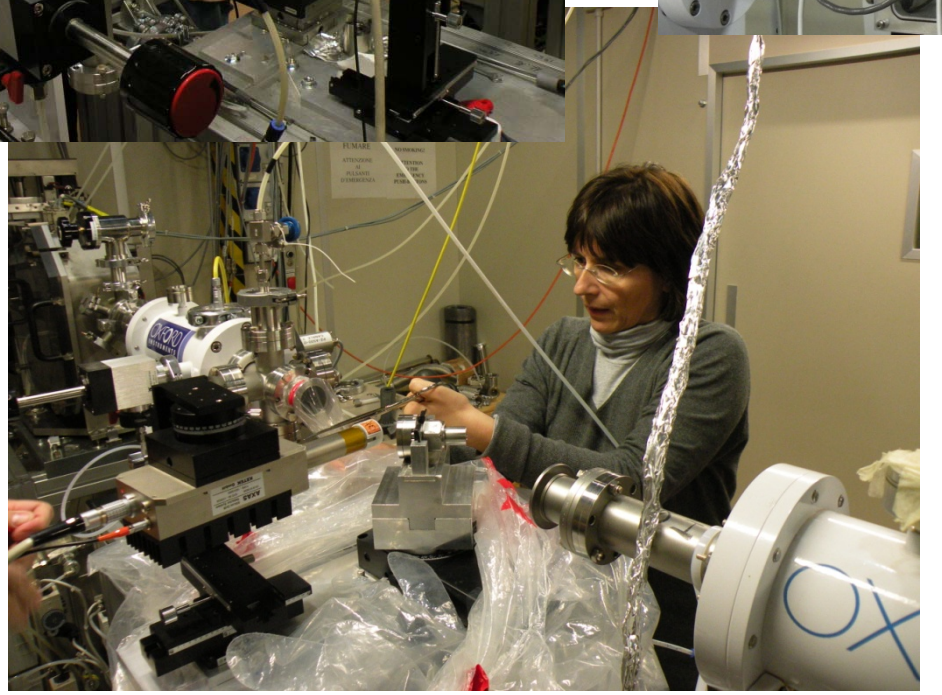
479nm

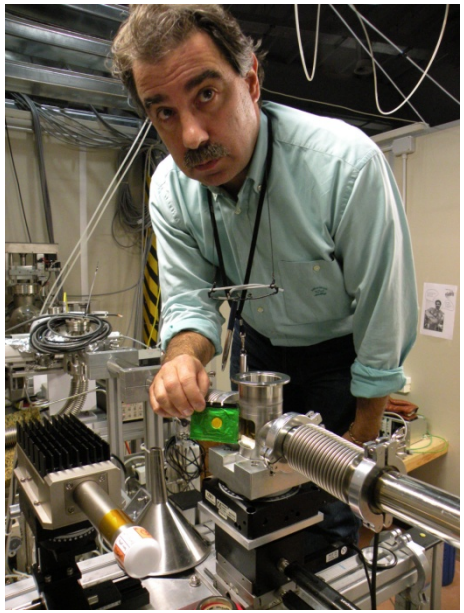
Chemically synthesized Li_2S_x dissoveld in 1M LiTFSI TMS electrolyte

In operando XAS measurements at XAFS beamline (ELETTRA)

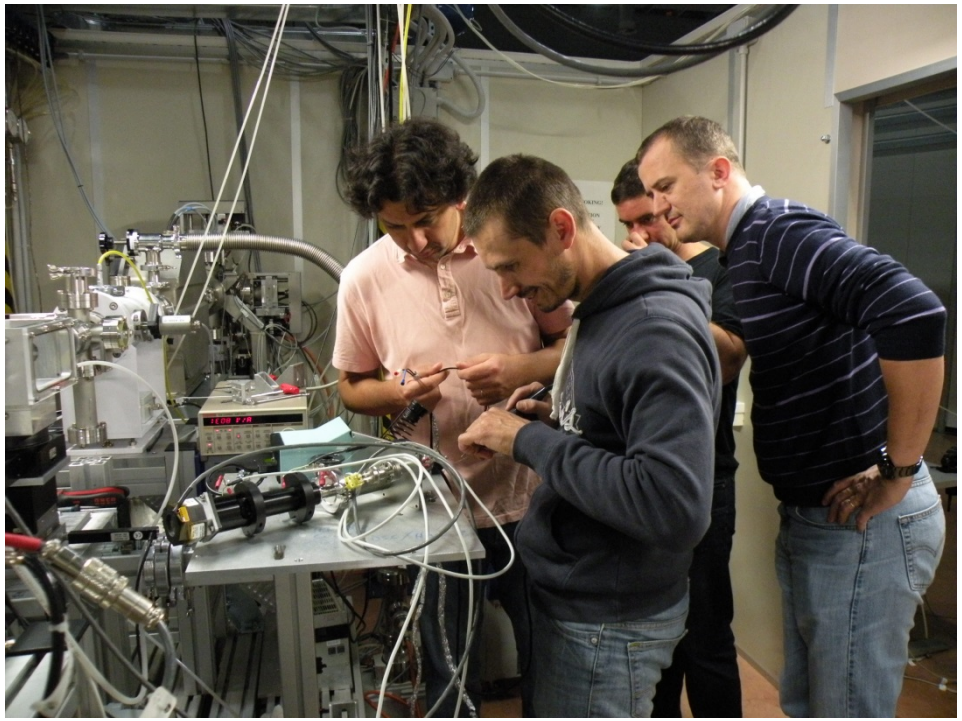


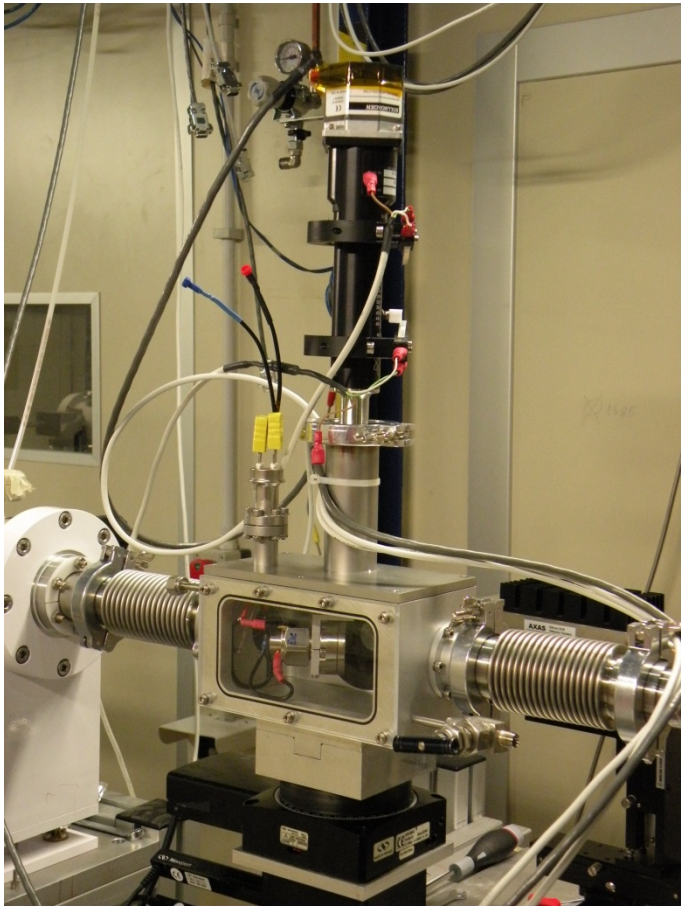


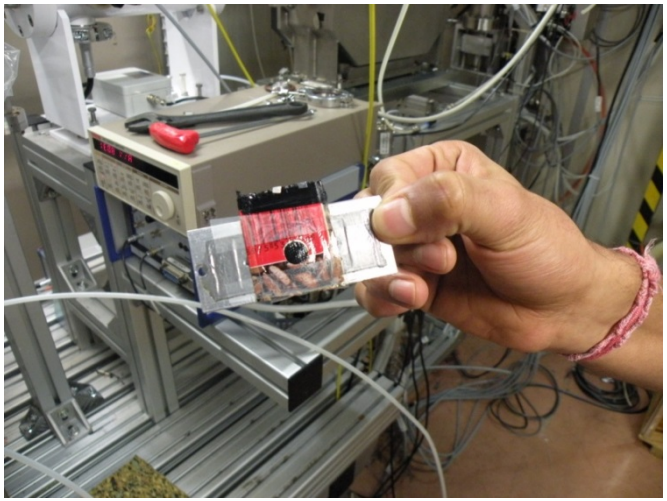


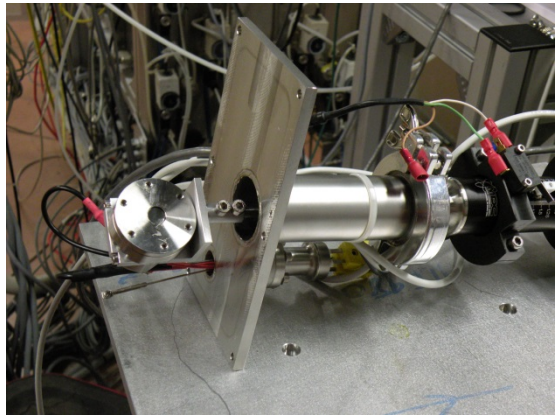


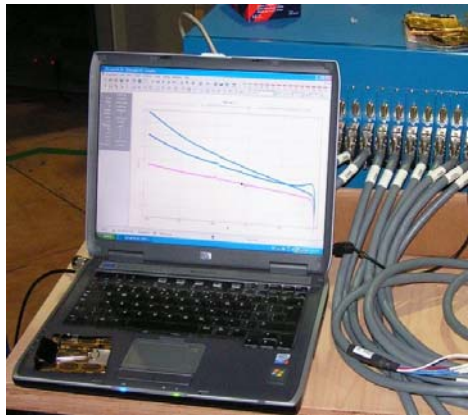
In operando XAS measurements at XAFS beamline (ELETTRA)





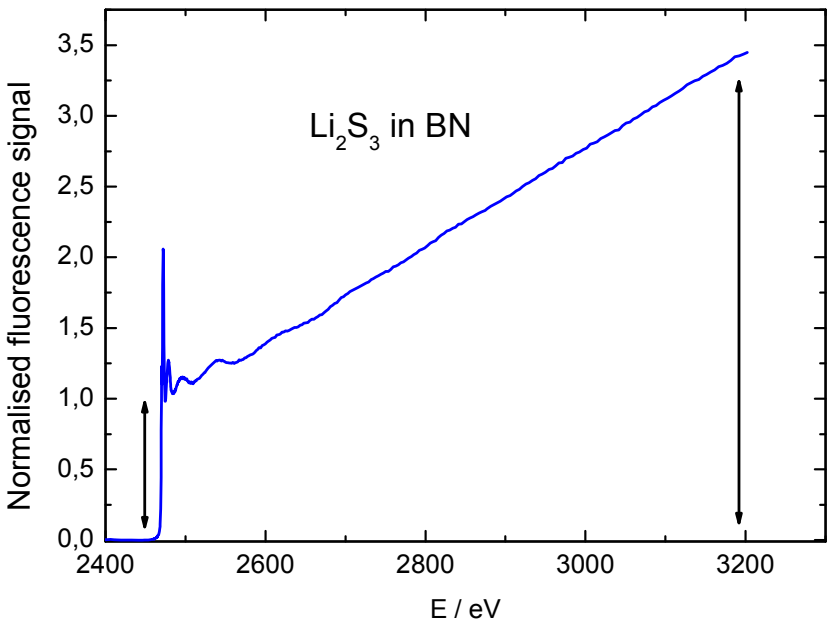






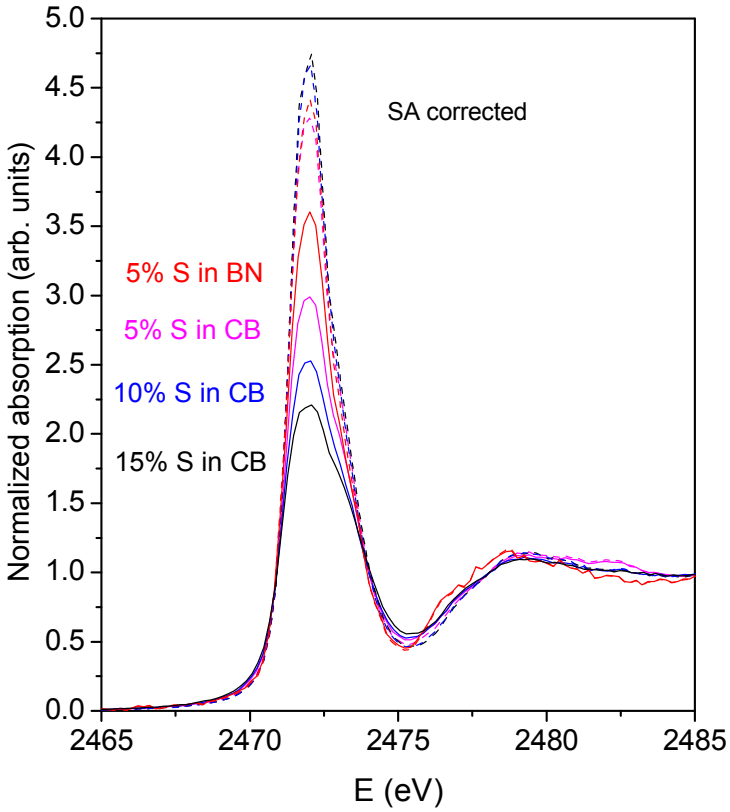
S K-edge XAS in fluorescence detection mode

Effect of strong energy dependent penetration depth in fluorescence detection mode.



Sulfur K edge fluorescence XAS spectrum measured on Li2S3 in carbon black normalised to unit K edge jump

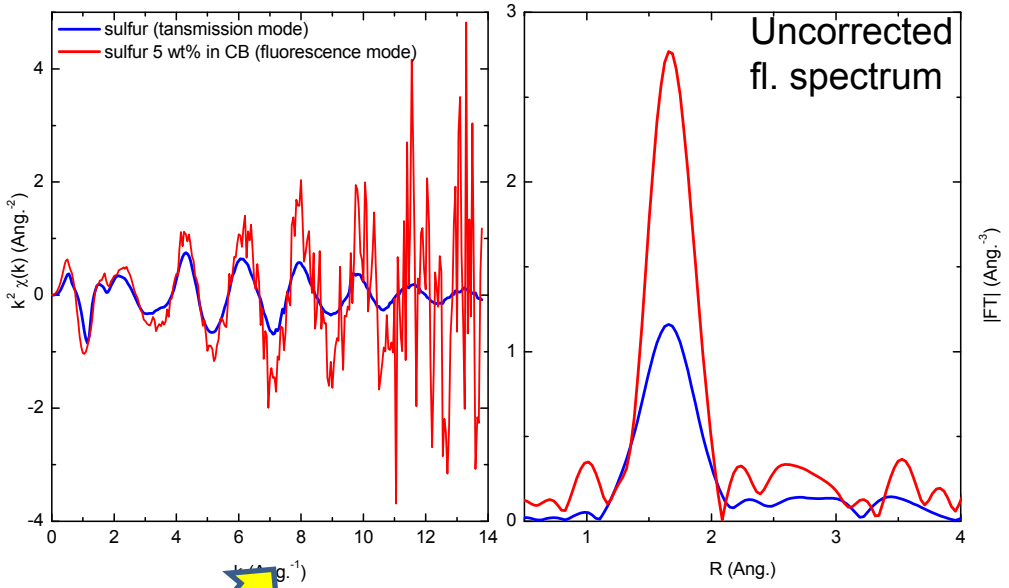
Self-absorption (SA) effect in fluorescence detection mode.

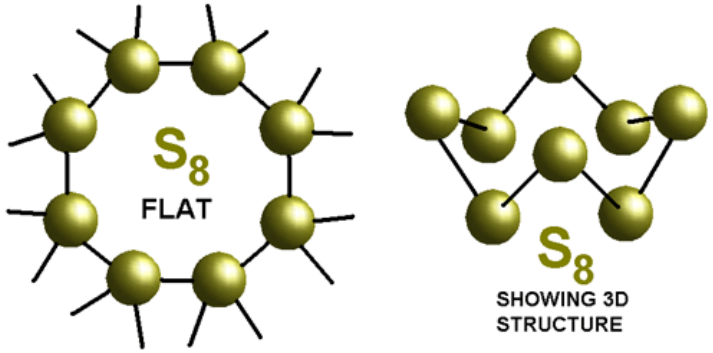


Sulfur K edge XANES spectra measured on samples with different concentrations of sulfur in carbon black or boron nitride before and after **(SA) correction**.

M. Patel, I. Arčon et al., ChemPhysChem 2014, 15, 894 – 904

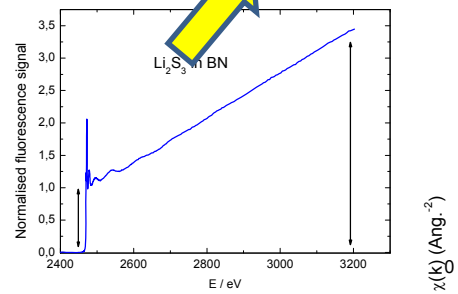
S K-edge EXAFS data normalization – fluorescence detection mode

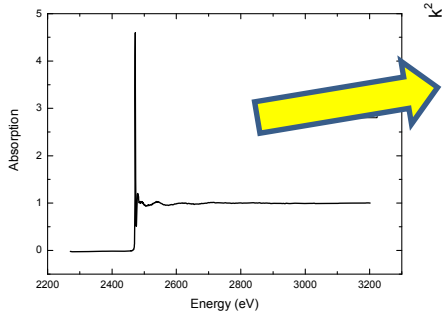


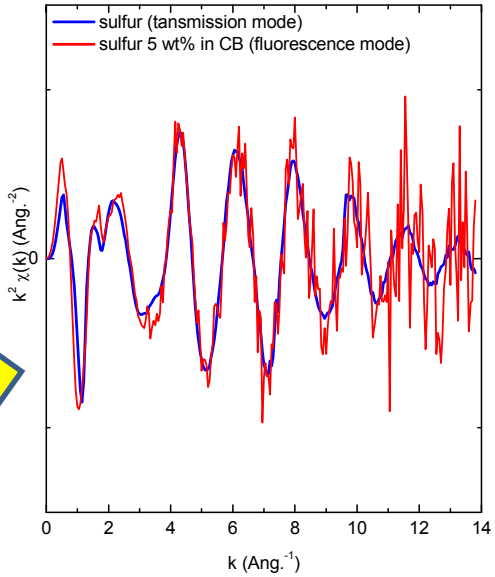


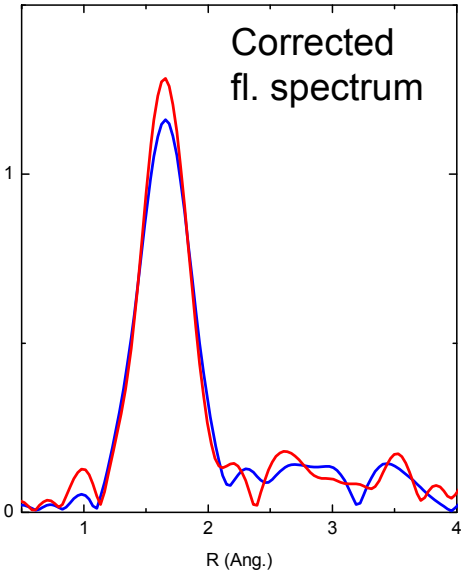
R = 2.04(1) Ang.
CN = 2
σ^2 =0.0034(6) Ang.^{2}

R = 2.03(1) Ang.
CN = 2
σ^2 = -0.0028(5) Ang.^{2}





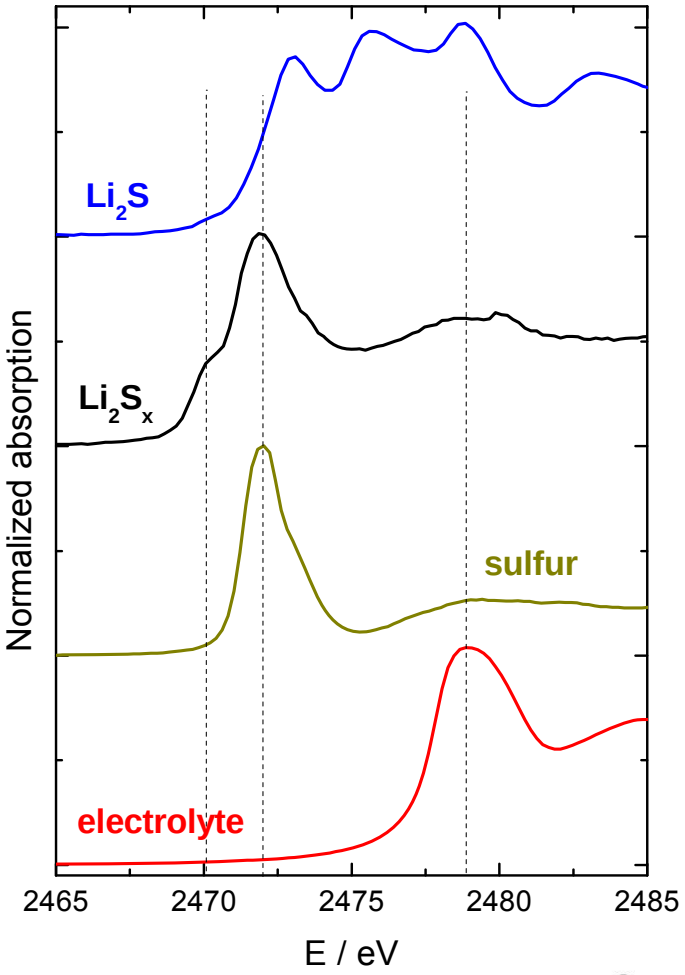


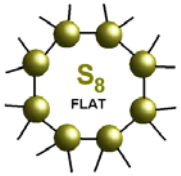


R = 2.03(1) Ang.
CN = 2
σ^2 = 0.0031(5) Ang.^{2}

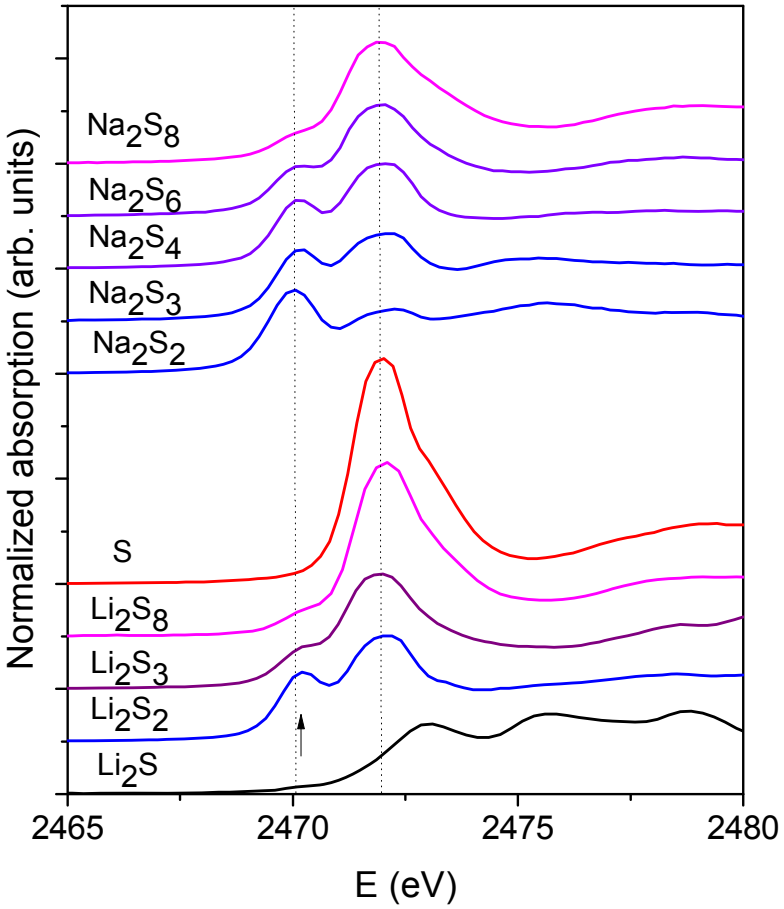
S K-edge XANES of reference compounds

Sulphur, polysulphides, electrolyte

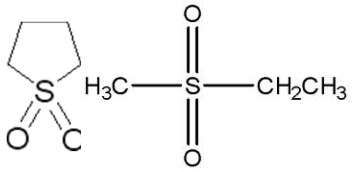




Li_2S_x and Na_2S_x in CB, S XANES



Electrolyte LiTFSI in TMS:



Li_2S_8 : Li—S-S-S-S-S-S-S-S—Li

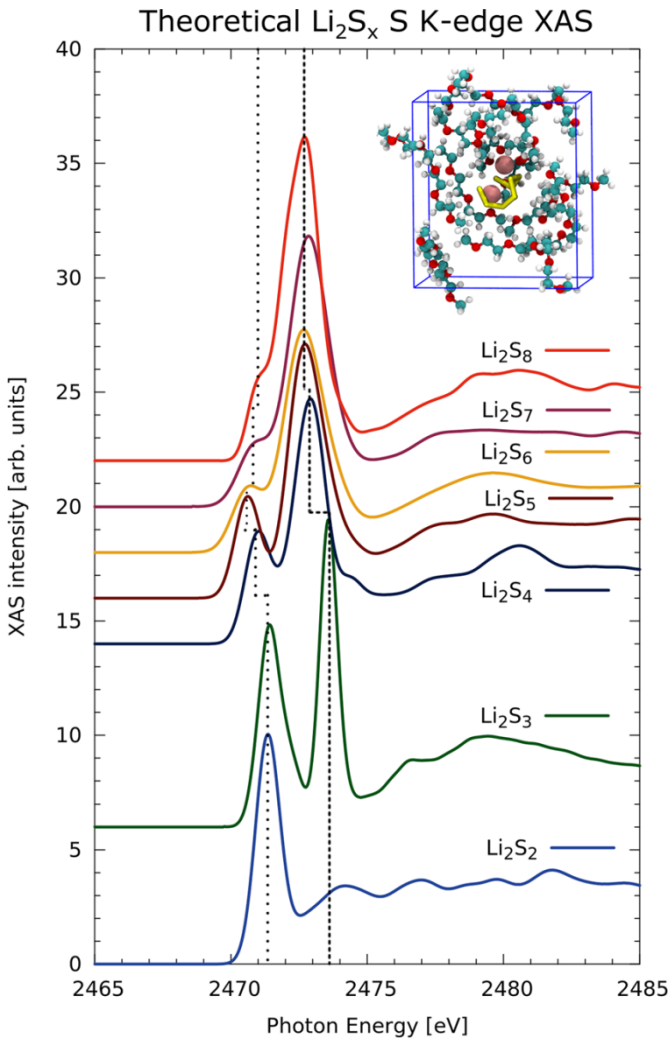
Li_2S_3 : Li—S-S-S—Li

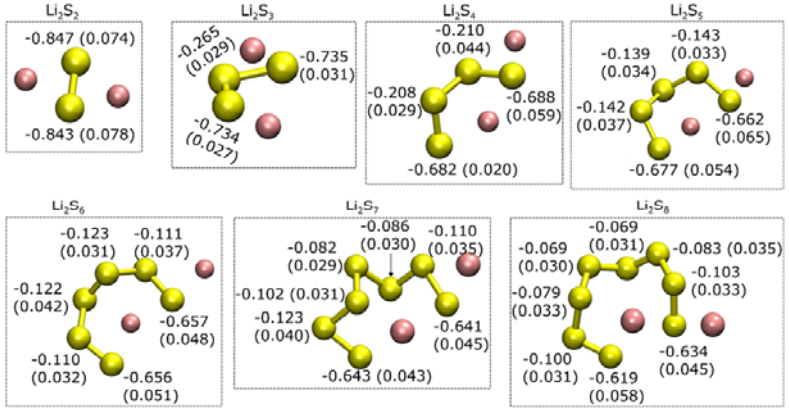
Li_2S_2 : Li—S-S—Li

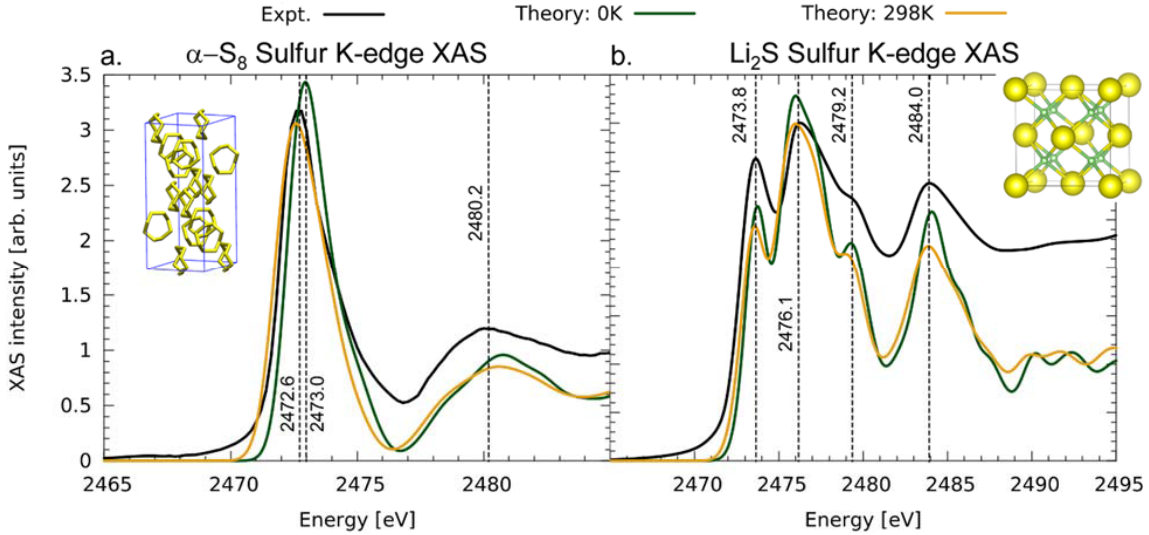
Li_2S : Li—S—Li

M. Patel, I. Arčon et al., ChemPhysChem 2014, 15, 894 – 904

Theoretical calculations







First-principles simulation of the sulfur K-edge XAS spectra of Li2Sx dissolved in TEGDME (x = 2−8) and crystaline Li2S, obtained from XCH-DFT calculations.

T. A. Pascal et al., J. Phys. Chem. Lett. 2014, 5, 1547−1551

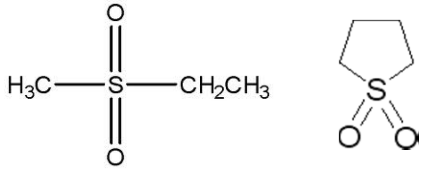
S K-edge XANES of as-prepared battery

Cathode composition: sulphur 20 wt.% 61.5% carbon black (Prx),

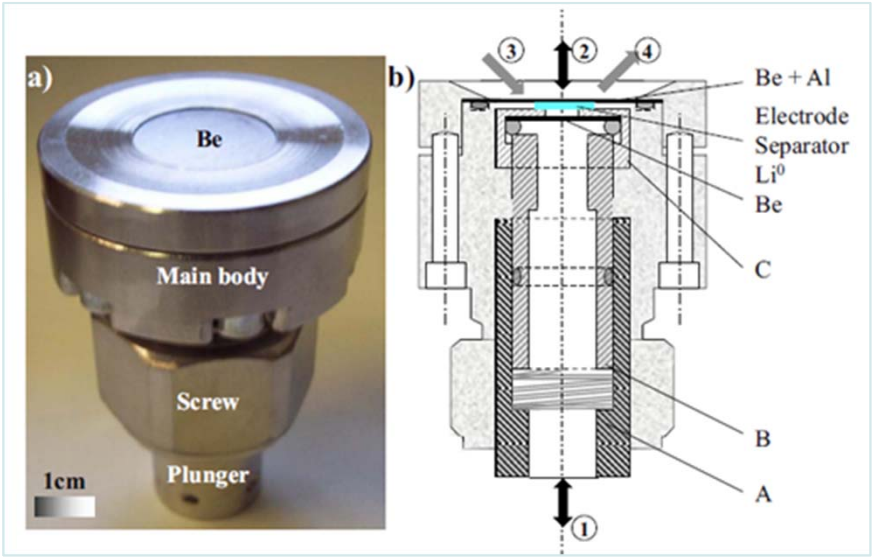
3.5% zeolite, and 15%Teflone. (density 1.2 g/cm3)

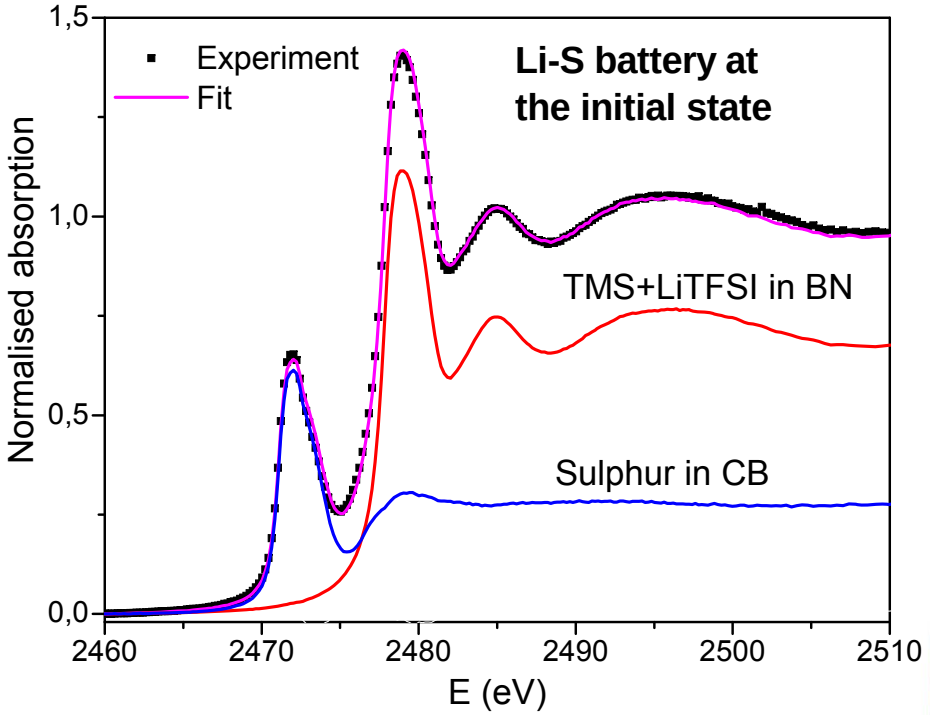
Electrolyte: 1M LiTFSI v TMS

1M LiTFSI in TMS



TMS: Tetra methylene sulfone





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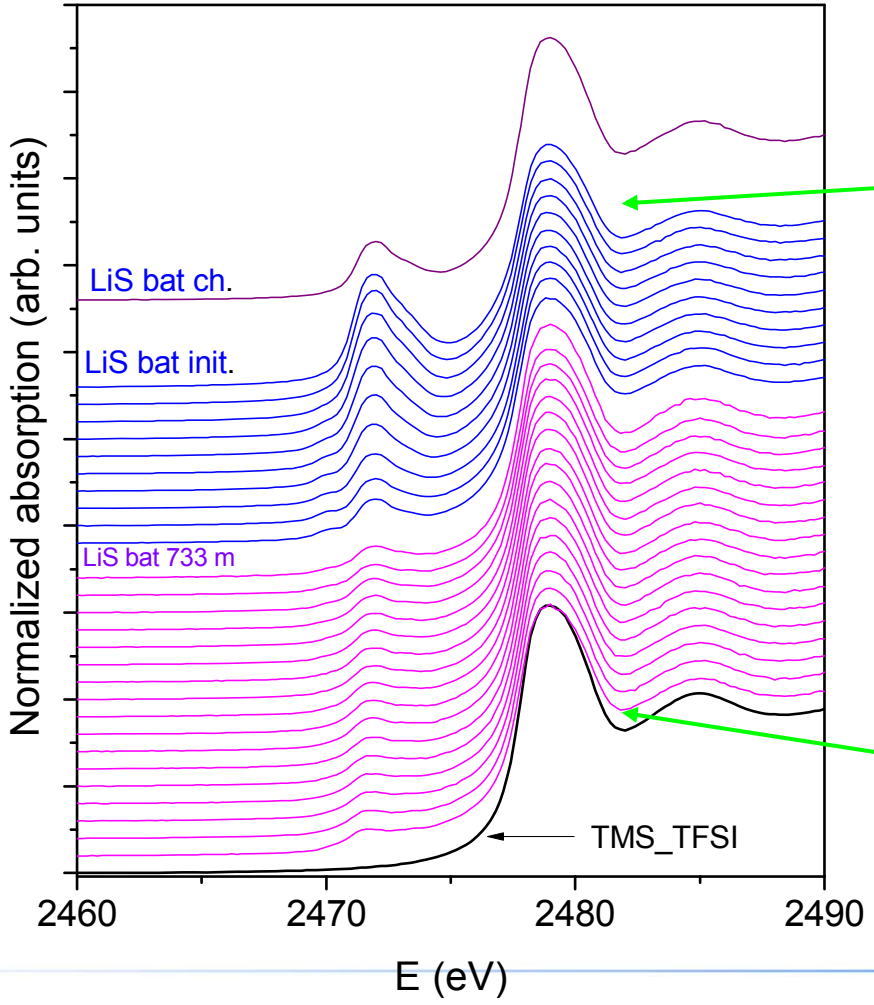
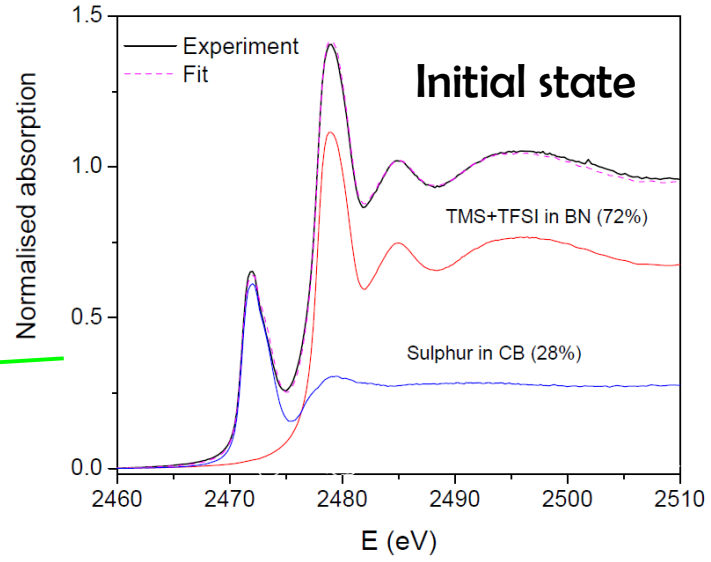
In operando S K-edge XANES eksperiment

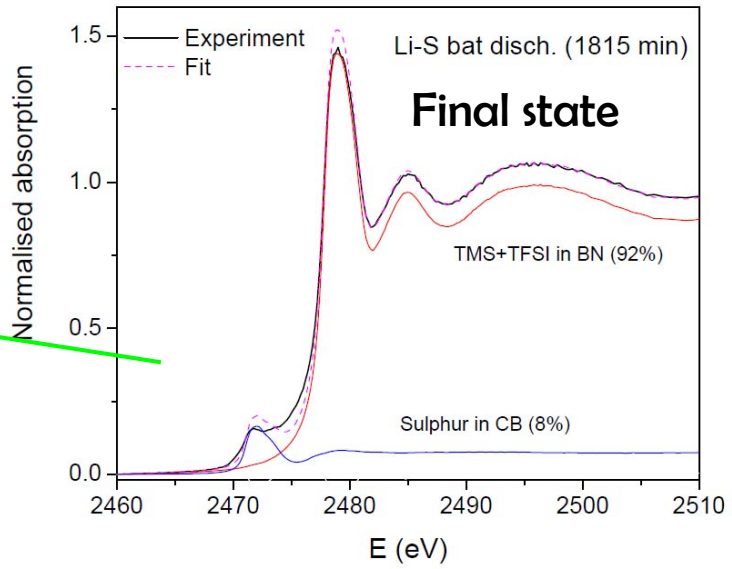
Discharging C/20, charging C/10

Cathode composition: sulphur 20 wt.% in carbon black,

Electrolyte: 1M LiTFSI v TMS







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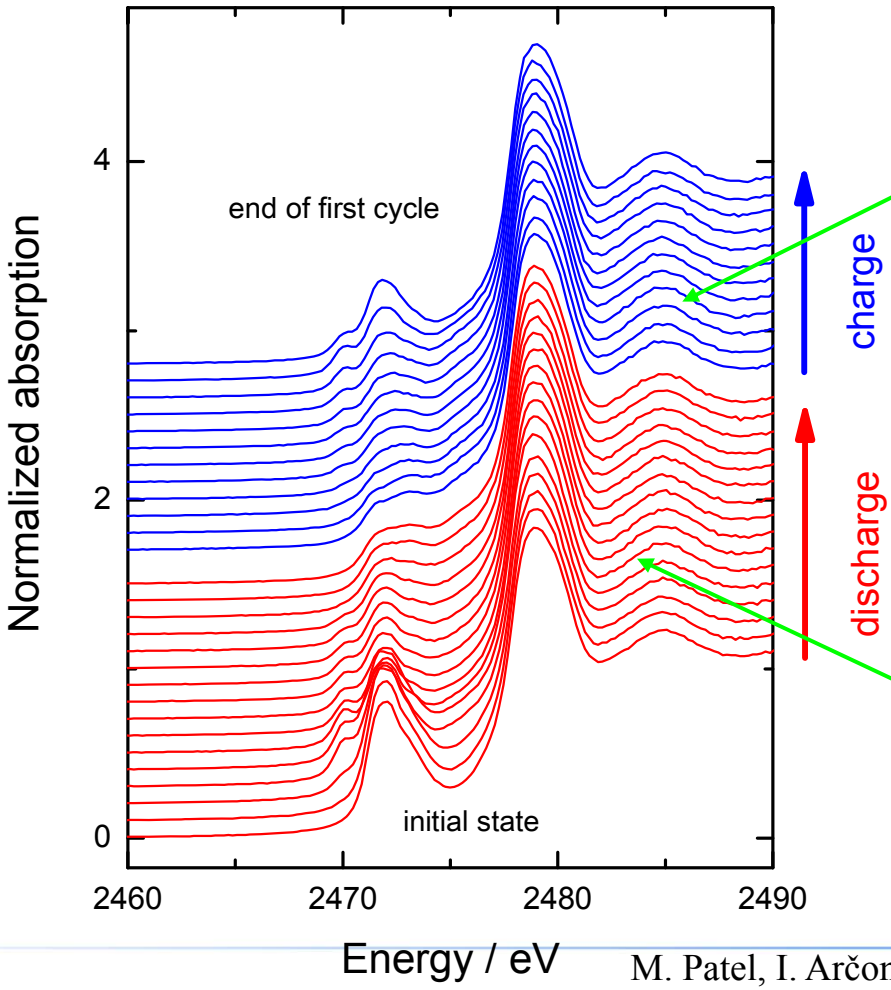
In operando S K-edge XANES eksperiment

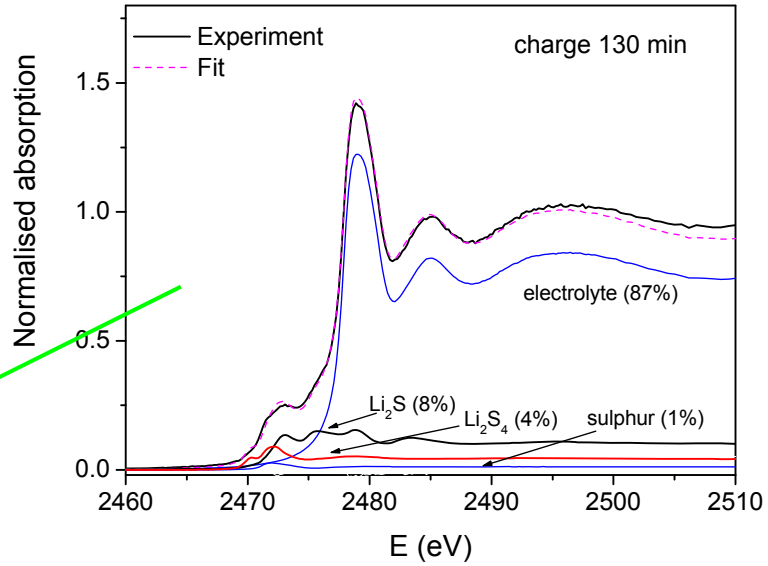
Discharging C/20, charging C/20

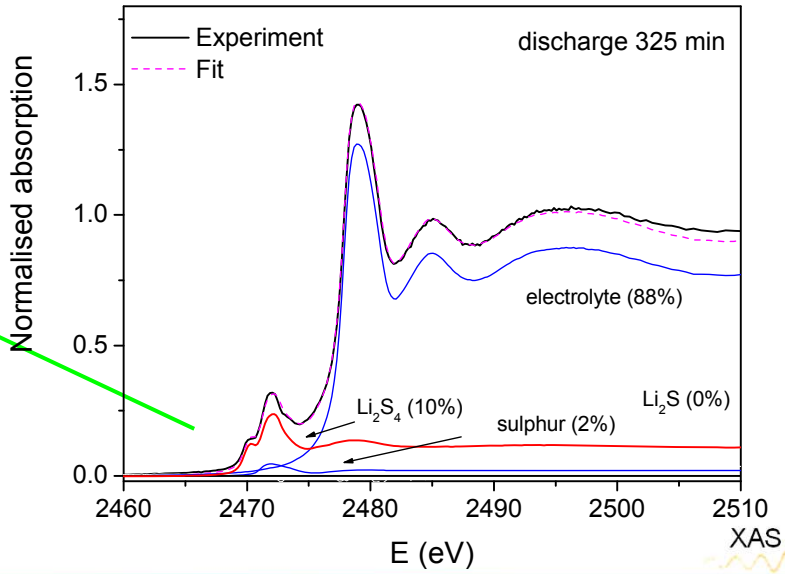
S K-edge XANES and EXAFS spectra continuously measured

(65 min per spectrum)



Intermediate states





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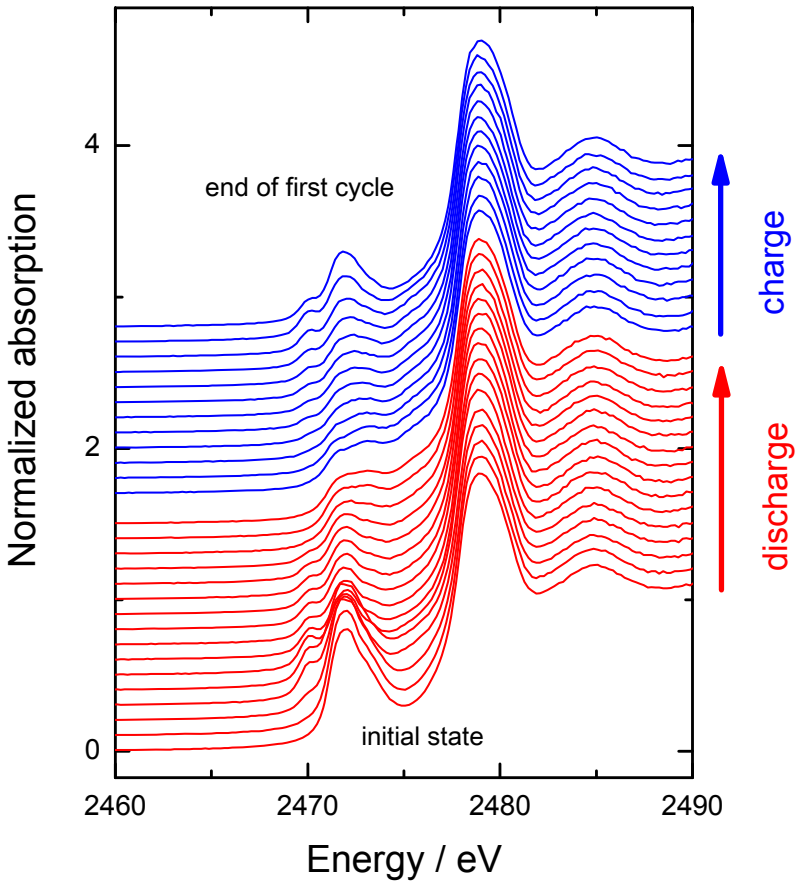
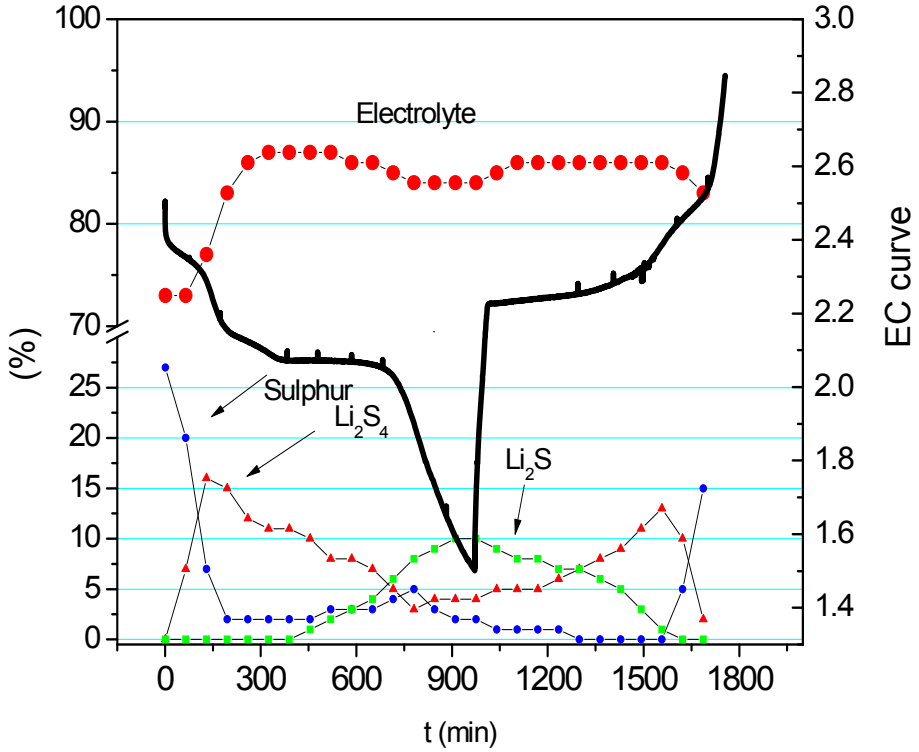
XAS

Iztok Arčon

In opearndo XAS measurement

Relative amount of different sulphur compounds in the cathode vs. electrolyte during 1st cycle ob battery opeartion





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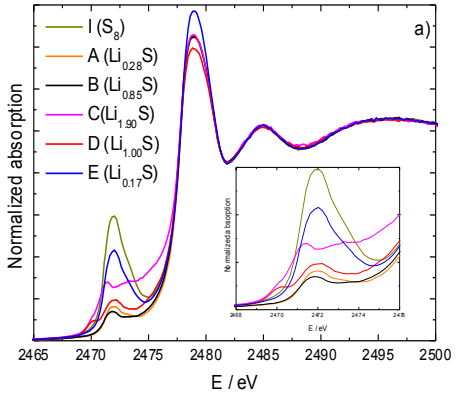
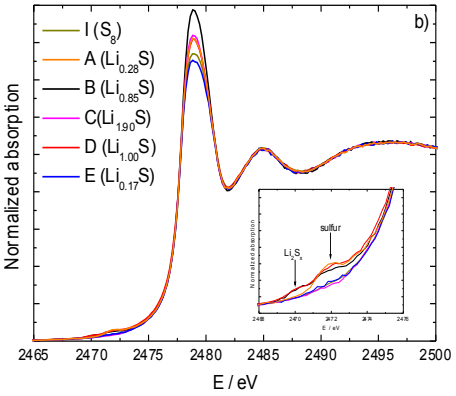
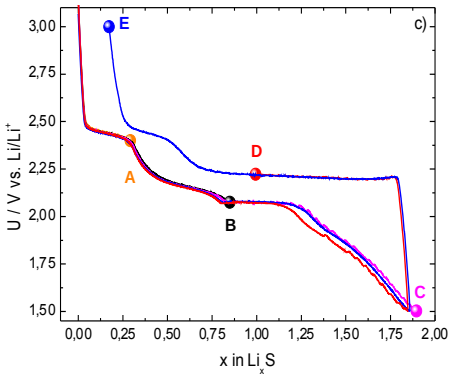
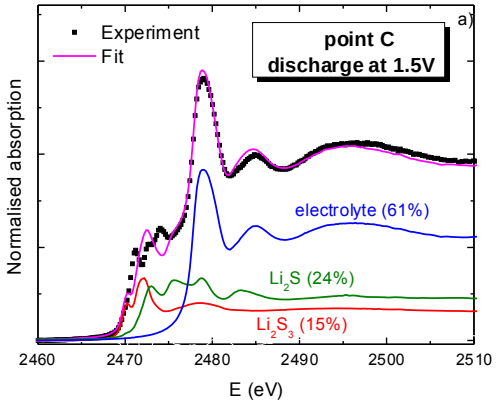
Post-mortem S K-edge XANES

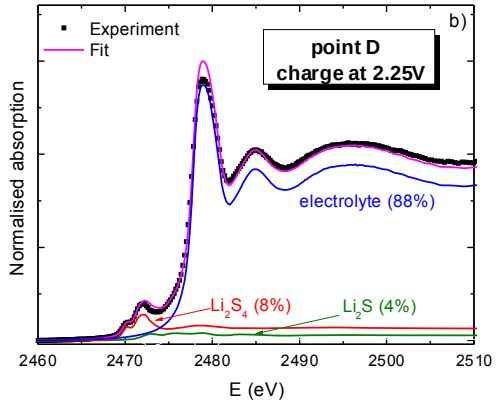


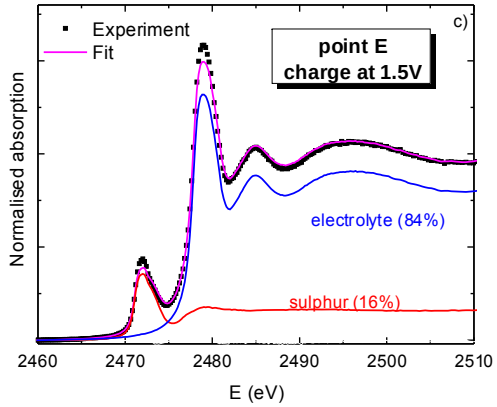




5 different batteries were galvanostatically charged to the characteristic points, stopped, transferred into glove box, opened, and the cathode and the separator were separately sealed into pouched cells with Mylar windows







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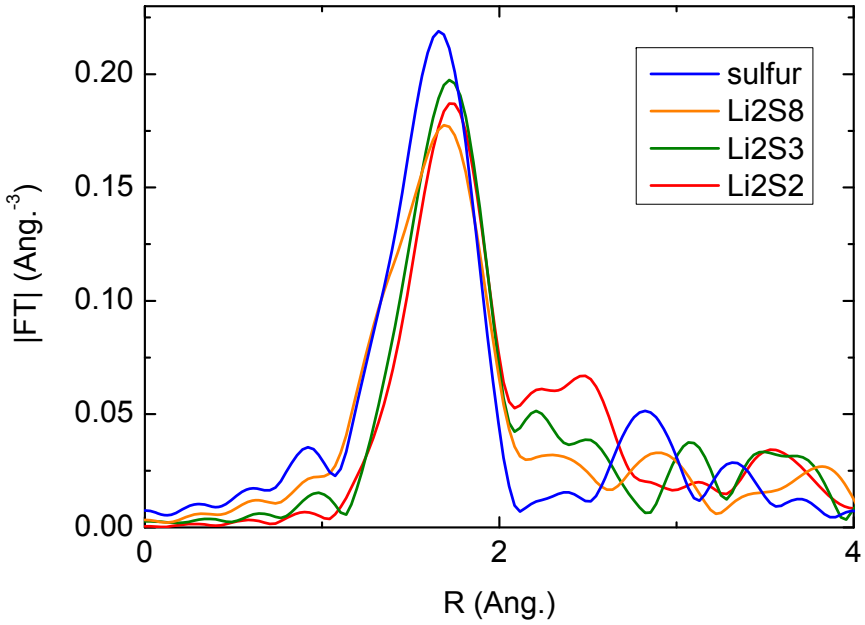
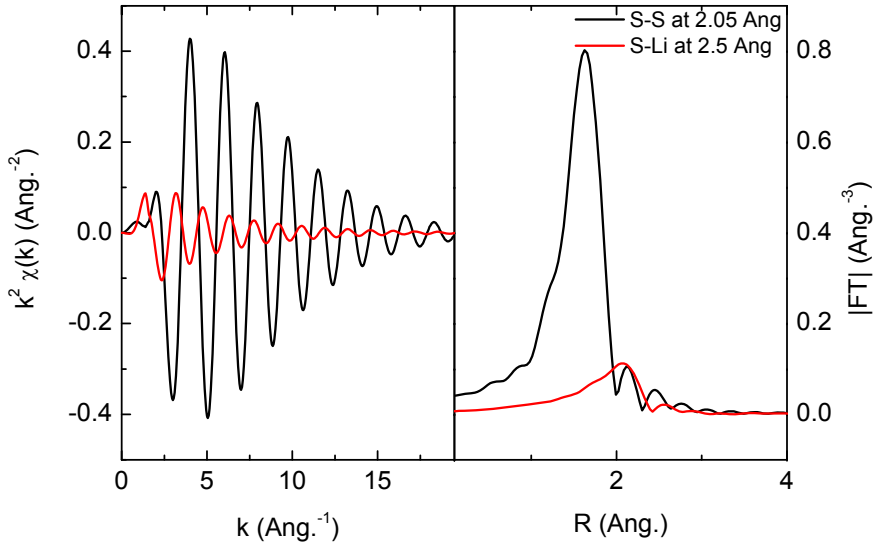
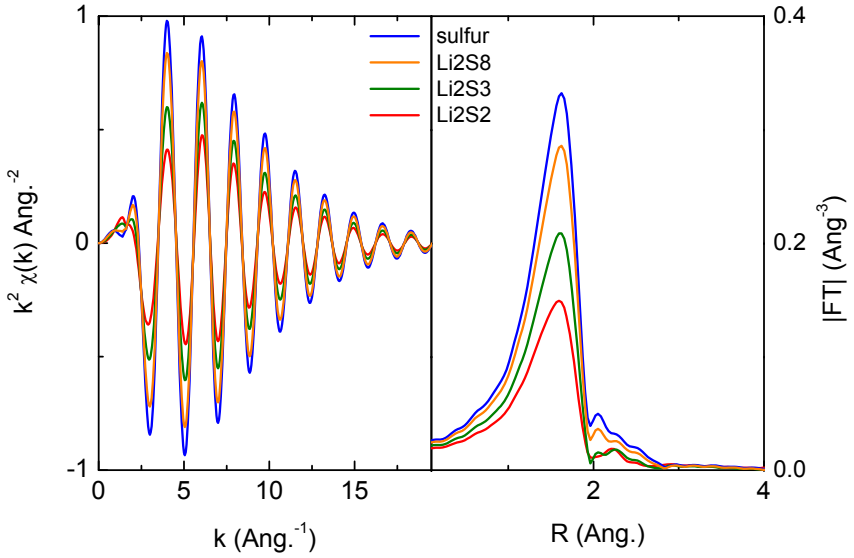
Li polysulphides: S K-edge EXAFS

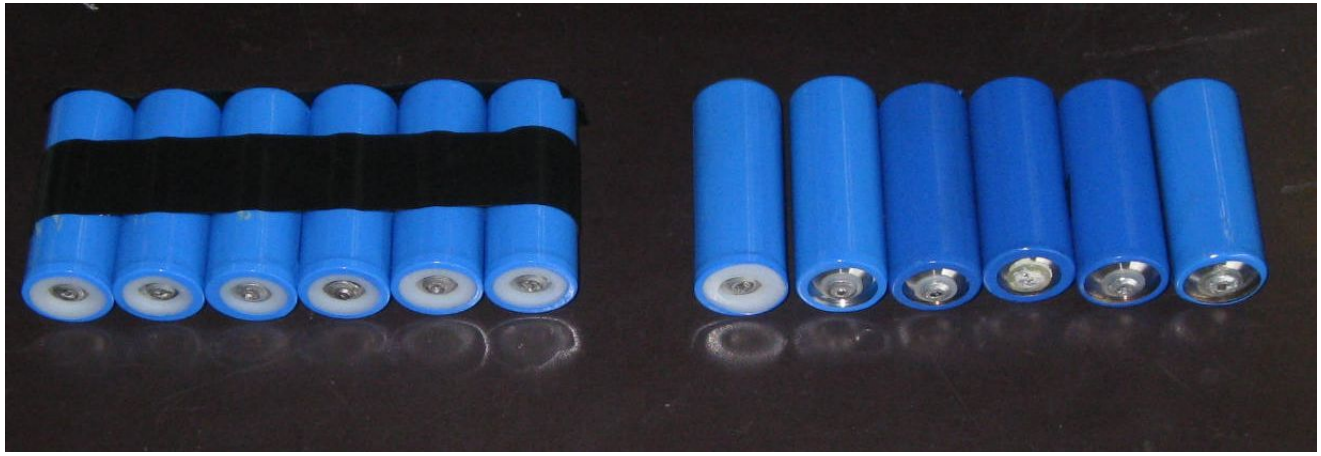
From the literature:
S-S bond length: 2.045 Ang.
S-Li bond length: 2.5 Ang







First large scale Li-S cells produced at SAFT



First large scale Li-S cells produced at SAFT in May 2014,
with the composition developed within EUROLIS project.

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- ✓ Manu Patel (Inst. Of Chemistry, Lj.)
- ✓ Lorenzo Stievano (Université Montpellier II)
- ✓ Luca Olivi (ELETTRA)
- ✓ Giuliana Aquilanti (ELETTRA)
- ✓ Antonella Iadecola (ELETTRA)
- ✓ Nicola Novello (ELETTRA)
- ✓ ...


ELETTRA, May 2014


ELETTRA, XAFS beamline, June 2013