Interfaces analysis in lithium solid-state batteries using *operando* Auger, XPS

J. Morey[1], J.-B. Ledeuil[1], H. Martinez[1,2,3], L. Madec[1,2]

[1] *Universite de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IPREM, Pau, France*
[2] *Réseau sur le Stockage Electrochimique de l'Energie, CNRS FR3459, Amiens, France*
[3] *Ecole Centrale Casablanca, Centre de Recherche Systèmes Complexes et Interactions ; Ville Verte Bouskoura, Maroc*

Contact: lenaic.madec@univ-pau.fr

Introduction

Interfaces and their electro-chemo-mechanical evolution upon cycling/storage are the key to solid-state batteries (SSBs) performance.[1][2] However, these interfaces are buried in battery stacks so that their analysis remains a challenge. While cross-sectioning is mandatory to reveal these buried interfaces, it is not a trivial task.[2] Moreover, *in situ* (*i.e.* sequential analysis and electrochemical cycling) and *operando* (*i.e.* analysis during cycling) analysis are of high interest but remain to be developed.[2]

This work is part of the ''Towards All solId State battery'' project (RAISE2024).

- In this work, the cross-sectioning challenge of a model polymer-based SSBs is presented.

- Moreover, the high interest of *operando* Auger is highlighted for a model Li/Li_6PS_5Cl stack and compared to *operando* XPS.

The RAISE2024 project

The project is funded by E2S-UPPA (2M€, 6 PhD, 20 years of Postdoc)

3 academic labs: D-MEX Centre for X-ray Imaging; IPREM; PAU DROITPUBLIC

2 international companies: ARKEMA; SAFT a company of TOTAL

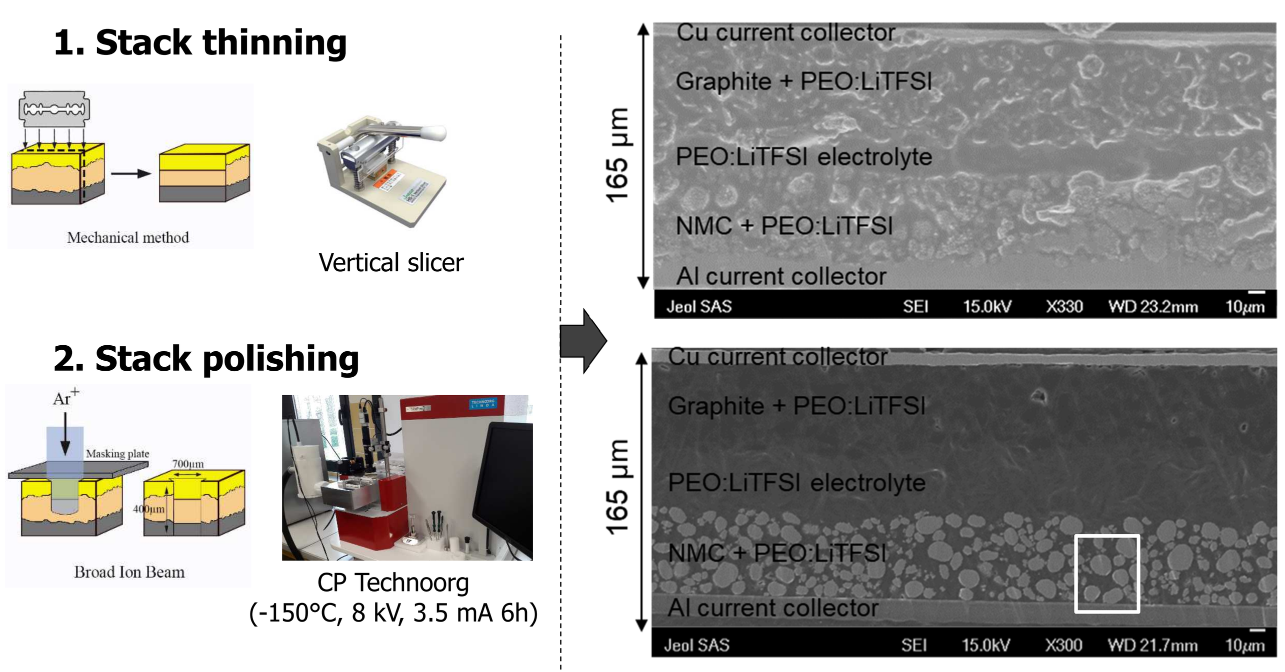
The aims are to:

→ develop a polymer-based SSB at TRL 6

→ **develop cross-section preparation to reveal buried interfaces in SSBs**

→ **develop *in situ* / *operando* methods to analyse these interfaces**

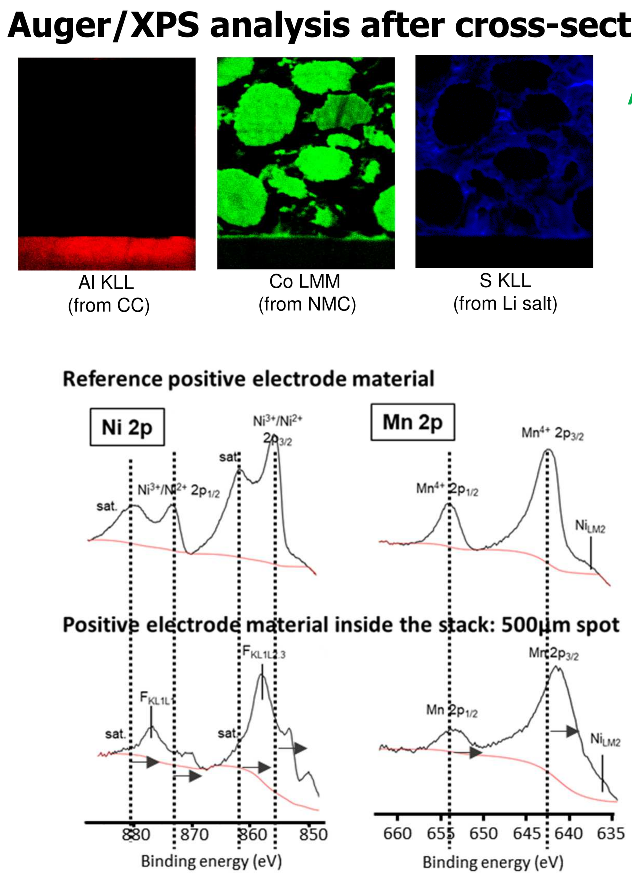
Cross-section of a model polymer-based SSB stack



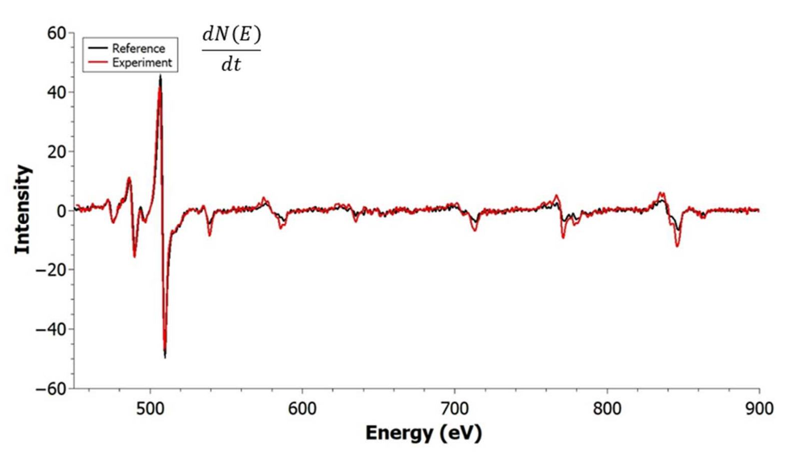
→ Rough surface

→ Flat surface
→ No delamination
→ No flowing (polymer)

Auger/XPS analysis after cross-sectioning

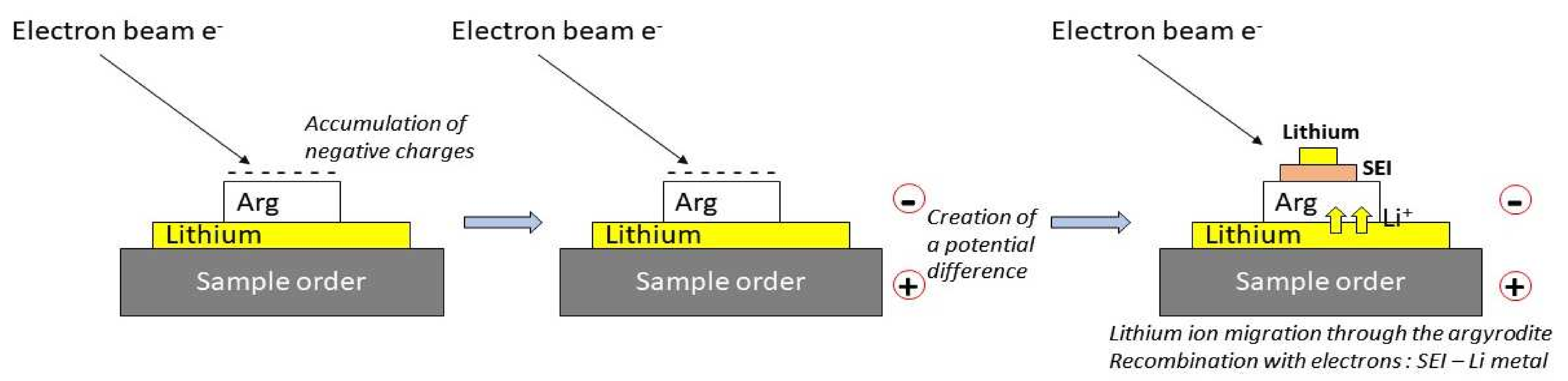


Remark: perfect filling of the electrode porosity by the electrolyte



→ **No chemical change** despite the highly sensitive polymer-based SSB stack
= **validation of the cross-sectioning method**

Operando approach



- **Li_6PS_5Cl** (Arg, 99.9%, Ampcera, 120 mg, 10 mm diameter pressed at 375 Mpa (3T)
- **Li** (GoodFellow, 99.9 %, thickness of 0.2
- Grounded **Auger/XPS sample holder**

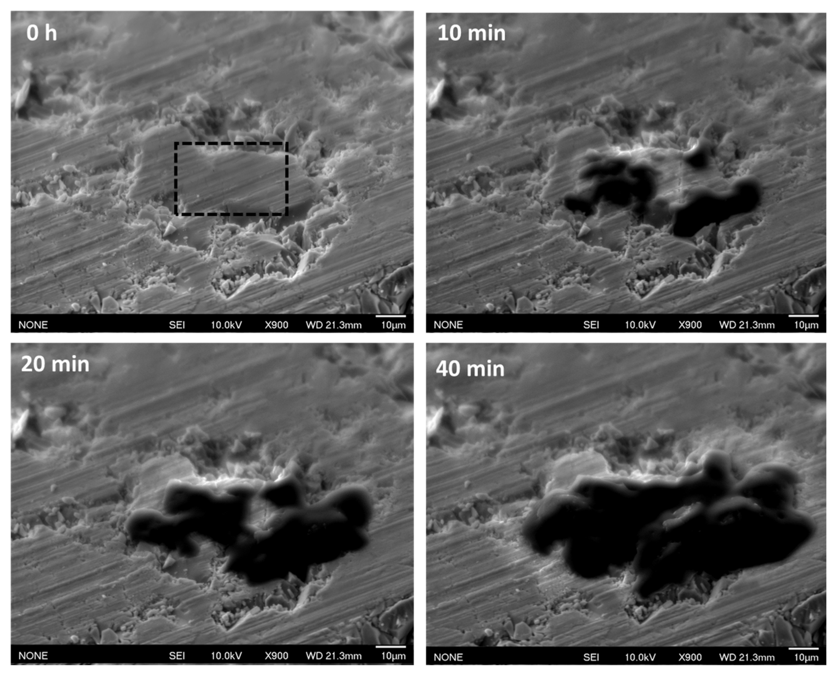
***Operando* Auger**
JEOL JAMP95000F, 1.5 x 10^{-9} mbar
***Operando* XPS**
THERMO ESCALAB 250 Xi, 9 x 10^{-9} mbar

References

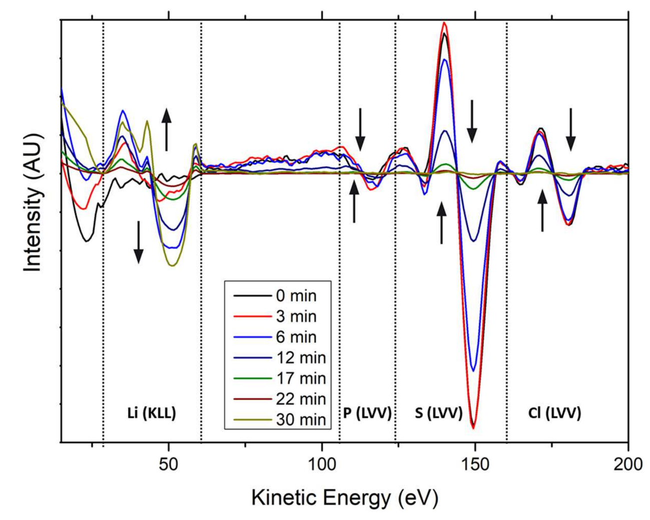
[1] T. Krauskopf, F.H. Richter, W.G. Zeier, J. Janek, *Chem Rev.*, 120, 7745-7794 (2020).
[2] I. López, J. Morey, J.-B. Ledeuil, L. Madec, H. Martinez, *J. Mater. Chem. A.*, 9, 25341-25368 (2021).

Operando Auger analysis of LI/Li_6PS_5Cl stack

→ **Sequential SEM images / Auger spectra (area scan)**



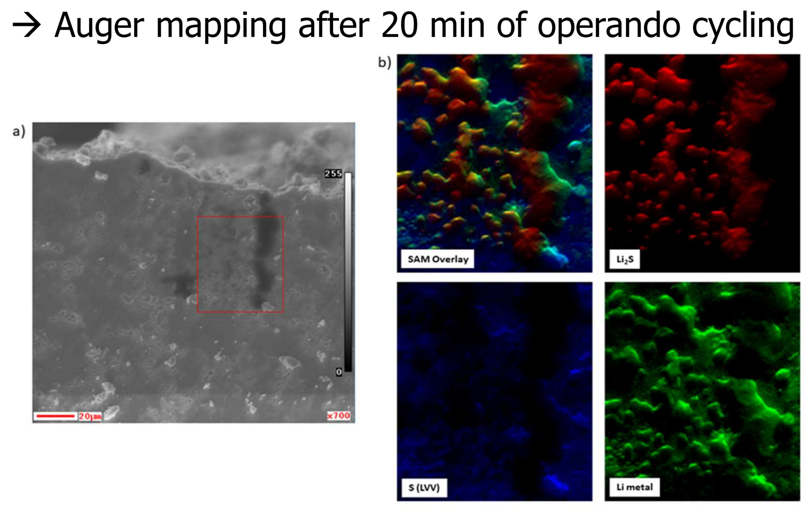
→ Covering of the Arg pellet over cycling by a non-uniform and thick layer (Li plating)

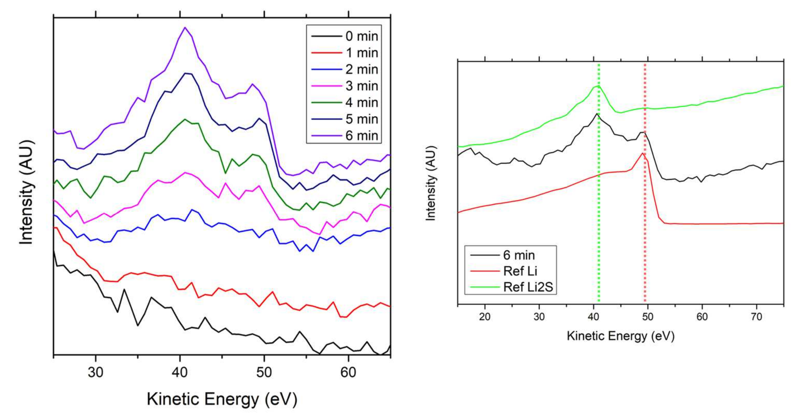


- decrease of Auger transition from Arg
- increase of the Li KLL transition

→ **Covering of Arg by Li plating.**

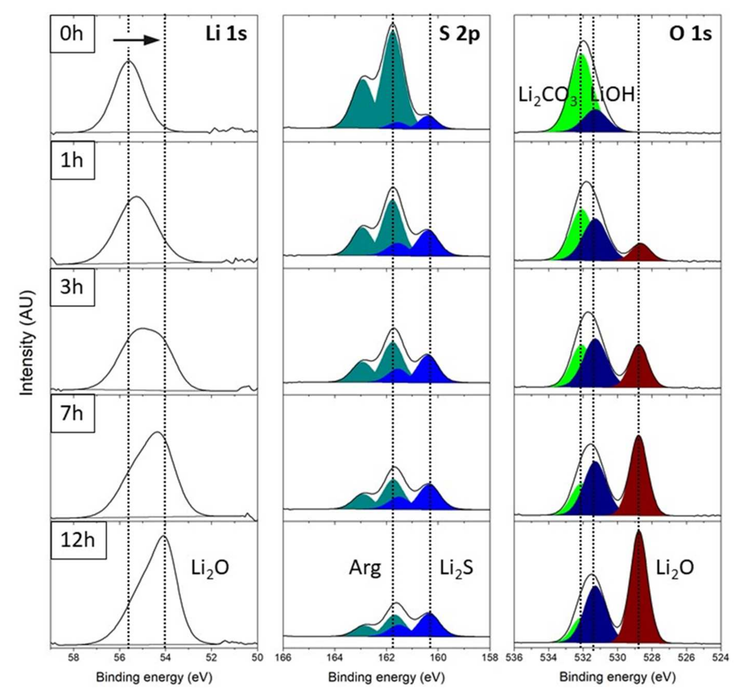
→ Auger mapping after 20 min of operando cycling





→ **Li_2S is formed while Li plating occurs**

Comparison with *operando* XPS



Compounds	0h	1h	3h	7h	12h
Li_6PS_5Cl	37.2	21.6	14.4	10.8	7.2
Li_2S	5.1	10.8	10.8	9	7.8
LiCl	2.2	2.6	2.6	2.2	1.8
Li_2O	-	9.9	21.6	35.7	45.3
Li_xP	-	3.0	3.0	2.8	2.1
Li_2CO_3	24	16.8	13.8	10.8	7.8
P_2S_5	2.1	1.1	1.1	0.7	0.4
Li_xSO_3	7.5	3.5	3	1.5	1.5

Similar results *vs.* Auger

1° Li_6PS_5Cl is reduced into Li_2S, LiCl and Li_3P
2° Li plating occurs almost concomitantly
3° Li plating proceeds until the end

Remark: Li_2O is formed instead of Li metal due to the chamber pressure and analysis time compared to operando Auger

Conclusion

Cross-sectioning of a model polymer-based SSB

Reliable/reproducible method obtained using Ar^+ milling at -150°C.

Operando analysis of a model Li/Li_6PS_5Cl

Overall: (i) Li_6PS_5Cl is first reduced into Li_2S, LiCl and Li_3P while (ii) Li platting occurs almost concomitantly and (iii) proceeds until the end of the *operando* cycling. Importantly, *operando* Auger provides visual observation of the dynamics/morphology of both Li/solid electrolyte interphase formation and Li plating together with reliable chemical information.

This study thus opens the door for future development of cross-sectioning by Ar^+ milling and *operando* Auger cycling as powerful approaches to reveal/analyze buried interfaces in solid-state batteries.

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