

## SUPPORTING INFORMATION

### Operando Auger/XPS using electrons beam to reveal the dynamics/morphology of Li plating and interphase formation in solid-state batteries

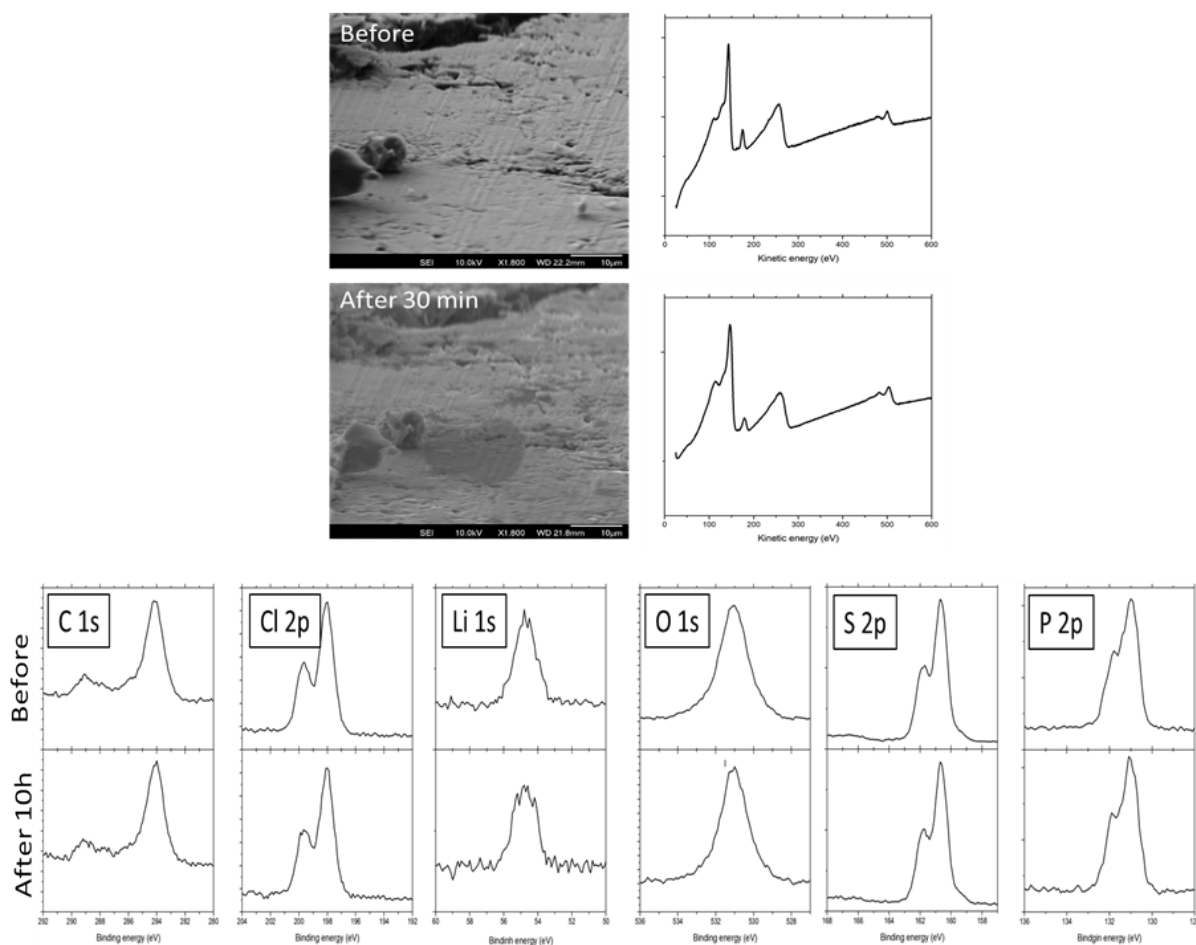
Julien Morey<sup>1</sup>, Jean-Bernard Ledeuil<sup>1</sup>, Hervé Martinez<sup>1,2,3</sup>, Lénaïc Madec<sup>1,2,\*</sup>

<sup>1</sup> Université de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IPREM, Pau, France

<sup>2</sup> Réseau sur le Stockage Electrochimique de l'Énergie, CNRS FR3459, Amiens, France

<sup>3</sup> Ecole Centrale Casablanca, Centre de Recherche Systèmes Complexes et Interactions, Bouskoura (Maroc)

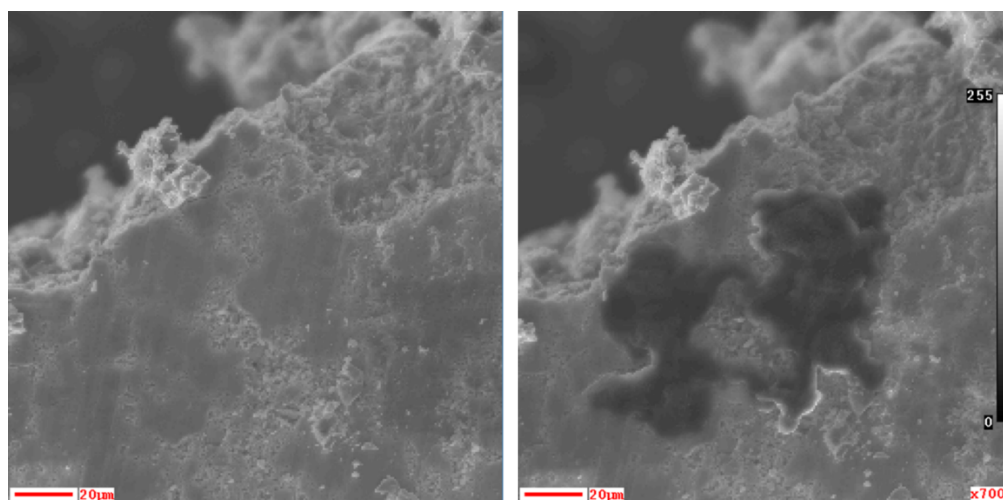
\* Corresponding author: [lenaic.madec@univ-pau.fr](mailto:lenaic.madec@univ-pau.fr)



**Figure S1.** top) SEM images and Auger survey spectra for an Arg pellet surface with no Li electrode below, before and after 30 min of exposure to the electron beam. bottom) XPS core level spectra for an Arg pellet surface with no Li electrode below, before and after 10h of exposure to the electron beam.

<https://filesender.renater.fr/?s=download&token=1faff5b5-bfa1-4d9c-af21-3aa4b03e4ab7>

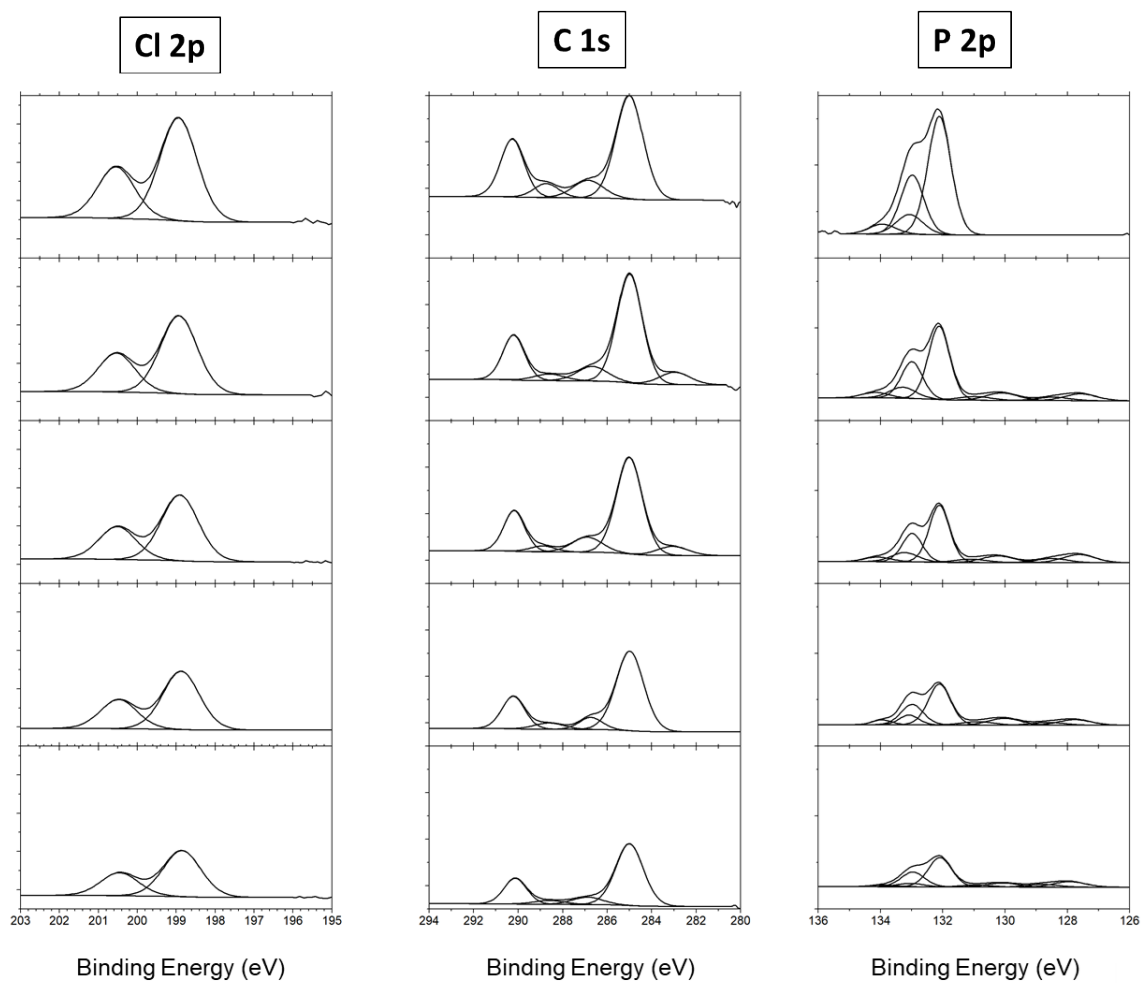
**Figure S2.** Video of full evolution of the SEM images recording during the *operando* Auger cycling of a Li/Arg stack using electrons beam.



**Figure S3.** SEM images of an Arg pellet surface a) before the operando Auger cycling and b) after 30 min of operando cycling using electrons beam.

**Table 1.** Full XPS quantification table (in at.%) as obtained from the XPS analysis of the Arg pellet surface during the *operando* XPS cycling using electrons beam.

		B.E. (eV)	0h	1h	3h	7h	12h
<b>C 1s</b>	C=C (carbon)	<284.6		1.1	0.7		
	C-C, C-H	285	8.1	7.7	6.8	5.4	3.9
	-CO	286.8	1.5	1.3	1.2	0.7	0.5
	-CO <sub>2</sub>	288.7	1	0.6	0.4	0.5	0.5
	-CO <sub>3</sub>	290.3	4	2.8	2.3	1.8	1.3
<b>O 1s</b>	Li <sub>2</sub> O	528.7	-	3.3	7.2	11.9	15.1
	LiOH	531.3	5.5	10	10.6	10.4	10
	-CO <sub>2</sub> , -CO <sub>3</sub>	532.1	17.9	11.2	8.3	5.6	3.8
<b>Cl 2p</b>	Arg, LiCl	198.9-200.6	4.2	3.1	2.5	2	1.5
<b>P 2p</b>	Arg	132.1-133	3	1.8	1.2	0.9	0.6
	P <sub>2</sub> S <sub>5</sub>	133.1-133.9	0.6	0.3	0.3	0.2	0.1
	Li <sub>x</sub> P	>130.0 eV	-	0.6	0.6	0.5	0.3
<b>S 2p</b>	Arg	161.7-162.9	13.4	7.4	5.4	3.5	2.4
	Li <sub>2</sub> S	160.4-161.6	1.7	3.6	3.6	3	2.6
	-SO <sub>3</sub>	167.3-168.5	1.5	0.7	0.6	0.3	0.3
<b>Li 1s</b>		54-55.6	37.5	44.6	48.3	53.4	57.3



**Figure S4.** XPS core level spectra of Li 1s, S 2p and O 1s as recorded at the Arg pellet surface during operando XPS cycling using electrons beam.