Lithium/Sulfur Batteries upon cycling: Application of Electrochemical Impedance Spectroscopy, *in situ* X-Ray Diffraction and tomography.

Sylwia Waluś[a,b,c], Alice Robba[a,b,c], Guillaume Tonin[a,b,c,d], Céline Barchasz[c], Jean-Claude Leprêtre[a,b,e], Renaud Bouchet[a,b,e], Gavin Vaughan[e], Jean-Francois Colin[c], Erik Elkaïm[f], Fannie Alloin[a,b,e]

[a] *Univ. Grenoble Alpes, LEPMI, F-38000 Grenoble, France*
[b] *CNRS, LEPMI, F-38000 Grenoble, France*
[c] *CEA, LITEN – 17 Rue des Martyrs – F-38054 Grenoble, France*
[d] *Synchrotron ESRF – 6 Rue Jules Horowitz – 38000 Grenoble, France*
[e] *Réseau sur le Stockage Electrochimique de l'Energie (RS2E), CNRS, FR3459, 33 Rue Saint Leu, 80039 Amiens Cedex, France*

Lithium/Sulfur batteries, due to their high theoretical values of gravimetric (2500 Wh kg^{-1}) and volumetric (2800 Wh L^{-1}) energy densities, became one of the most popular candidates for next-generation energy storage system[1]. However, the practical discharge capacity and cycle life of Li/S cells are still below expectation despite of many efforts which has been done during last three decades. The understanding of the working mechanism is an essential point in order to help to improve the electrochemical performances. This presentation will be an overview of our recent studies conducted in this goal.
It is well known that structural and morphological changes occur inside the Li/S cell upon cycling, since the redox reaction is accompanied by phase transformation of active material (solid/soluble phases), in that context, *in situ* and *operando* synchrotron-based XRD was applied, this investigation permitted us to define precisely the moment of liquid/soluble phase transitions and to propose electrochemical process[2,3]. In parallel, electrochemical impedance spectroscopy study was perform upon cycling and give complementary information on both transfer reactions, electrolyte conductivity evolution, electrode morphology and passivation layer formation.
Recently, coupled X-ray absorption and diffraction tomography preliminary results were obtained at ID15a at the ESRF. This powerful technic is used to characterize the batteries on length scales from the atomic to the microscopic. Sequential X-ray absorption tomography and X-ray diffraction measurements allowed different mechanisms within a Li/S cell to be observed, such as sulfur reduction/formation, polysulfide dissolution and Li_2S deposition/dissolution.
Another important issue of a Li-S cell lies in the fact of using metallic lithium as negative electrode, which leads to serious safety hazards (dendrites formation, reactivity). Some investigations have been focused on the development of lithium sulfide (Li_2S) positive electrode, as an alternative solution to sulfur electrodes, which could lead to metallic lithium-free Li-ion/S batteries. By applying GITT and *operando* XRD measurements, an electrochemical mechanism was proposed to explain the initial charge profile, in terms of equilibrium potential and polarization phenomenon[4].

[1] N. -S. Choi, Z. Chen, S. A. Freunberger, X. Ji, Y. -K. Sun, K. Amine, G. Yushin, L. F. Nazar, J. Cho, P. G. Bruce, *Angew. Chem. Int. Ed.* 51 (2012) 9994.
[2] S. Waluś, C. Barchasz, J. -F. Colin, J. -F. Martin, E. Elkaïm, J. -C. Leprêtre, F. Alloin, *Chem. Commun.* 49 (2013) 7899.
[3] S. Waluś, C. Barchasz, R. Bouchet, J.-C. Leprêtre, J.-F. Colin, J.-F. Martin, E. Elkaïm, C. Baehtz, F. Alloin Advanced Energy Materials, 1500165, 2015
[4] S. Waluś, C. Barchasz, R. Bouchet, J.-F. Martin, J.-C. Leprêtre, F. Alloin, Electrochimica Acta, 180, 178-186, 2015