

Lithium/electrolyte interface in Li/S₈ batteries conditions: passivation and dendritic growth

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Ecofriendly, cheap and widely available, sulfur allows to reach high theoretical energy density (~2600 Wh.kg⁻¹)^[1] when it faces to lithium. Li/S is therefore a very promising technology in the perspective of replacement of classical Li-Ion batteries, especially for the large markets of electric transport and stationary applications.

Beside the very complex discharge mechanism^[1] of the positive sulfur electrode, which focuses most of the research, the dendritic growth of the lithium at the negative electrode during charging is one of the stumbling blocks of this technology. However, the electrodeposition of lithium is still little studied even though the high current densities involved in this technology would lead to an exacerbation of this phenomenon. The mitigation of dendritic growth would be a great step forward in the development of safe and reliable Li/S₈ batteries.

Therefore, the aim of this work is the study of the lithium metal/electrolyte interface both in equilibrium and under current conditions.

First, the lithium passivation and ageing is monitored in Li/El/Li symmetric cell by impedance spectroscopy and correlated to chemical surface analysis by XPS measurement. Then, the dendritic growth is systematically studied in galvanostatic experiments as function of both the current densities and electrolyte additives (Polysulfides Li₂S_x and LiNO₃). The morphology of the dendrites is determined by *post-mortem* SEM imaging (cf. figure 1). Eventually, to separate dendrites nucleation and growth processes, we performed *operando* optical analysis. Our methodology allows determining unambiguously the impact of the different additives that are classically used in this technology.

Furthermore, our results are analyzed in the framework of classical models for dendrite formation (Yamaki, Chazalviel, Newman...)^{[2], [3], [4]}.

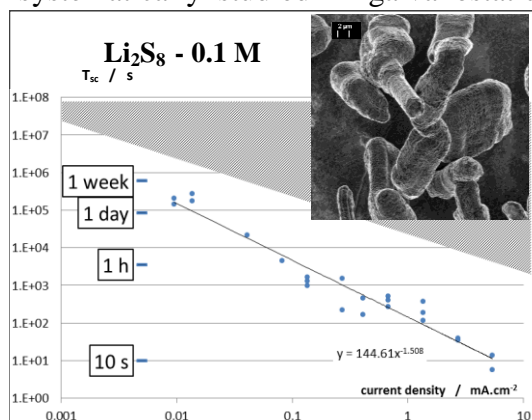


Figure 1 : two ways to understand dendrites : the time of short-circuit plotted in function of the current density and SEM images of dendrites (the hatched area represents the part of the graph that is beyond the total capacity of the Li⁰ electrode)

- [1] C. Barchasz, F. Molton, C. Duboc, J.-C. Leprêtre, S. Patoux, and F. Alloin, "Lithium/sulfur cell discharge mechanism: an original approach for intermediate species identification," *Analytical chemistry*, vol. 84, May 2012, no. 9, pp. 3973–80.
- [2] J. Yamaki, S. Tobishima, K. Hayashi, and K. Saito, "A consideration of the morphology of electrochemically deposited lithium in an organic electrolyte," *Journal of Power Sources*, 1998, vol. 74, pp. 219–227.
- [3] C. Brissot, M. Rosso, J. Chazalviel, P. Baudry, and S. Lascaud, "In situ study of dendritic growth in lithium / PEO-salt / lithium cells," *Electrochimica Acta*, vol. 1998, 43, pp. 1569–1574.
- [4] C. Monroe and J. Newman, "Dendrite Growth in Lithium/Polymer Systems," *Journal of The Electrochemical Society*, 2003, vol. 150, no. 10, p. A1377.