Operando X-ray absorption tomography for the characterization of lithium metal electrode morphology and heterogeneity in a liquid Li/S cell

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The brighter regions correspond to pits formed in the lithium layer. For better visualization, the volume representation of the pits has been reversed, meaning that pits formed in the lithium volume appear as hills in Figure .

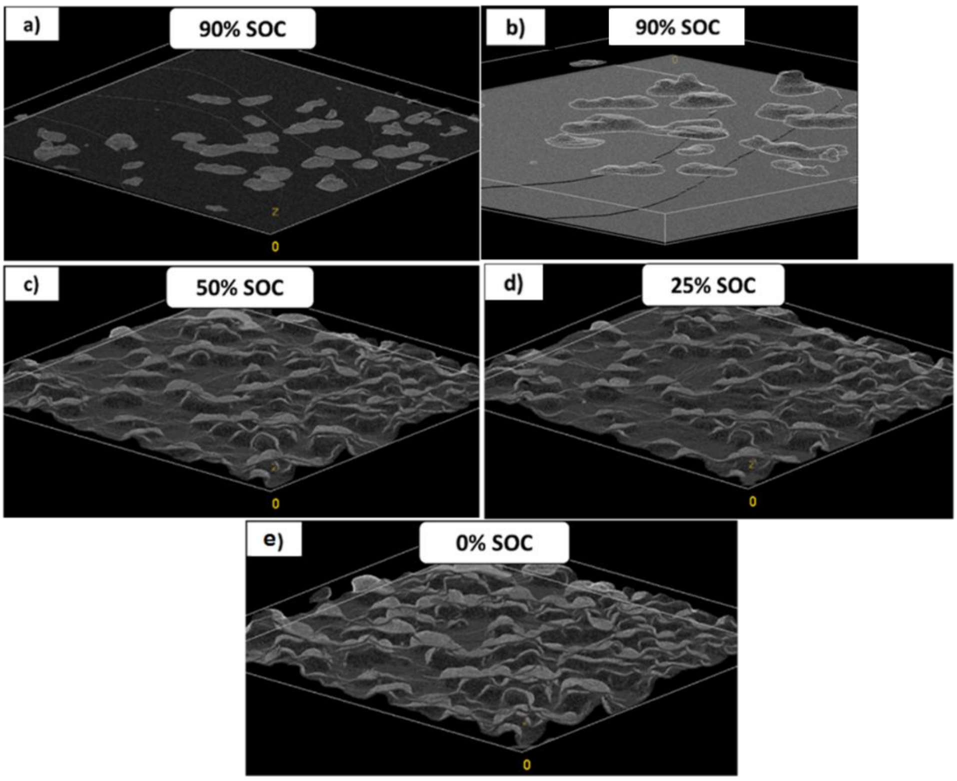

Figure S1: Volume representation of the pits formed at the lithium/electrolyte interface (a) at 90% SOC with (b) a zoom for better visualization of the first pits, (c) at ~50% SOC, (d) at ~25% SOC and (e) at 0% SOC (end of discharge). For better visualization, the volume representation of the pits has been reversed, meaning that pits formed in the lithium volume appear as hills.

Calculation of local current density maps

In order to draw a local current density map, a short automatic code has been written. The back face of the lithium was taken as a reference (**Erreur ! Source du renvoi introuvable.**) to calculate the local thickness of the lithium foil, which corresponds to the altitude of the Li/electrolyte interface.

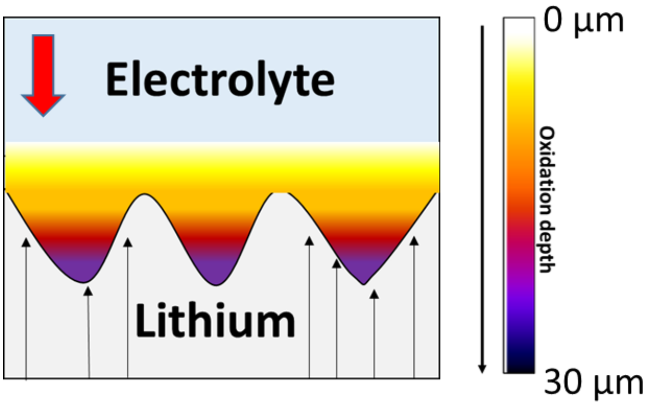

Figure S2: Schematic representation of the electrolyte/lithium interface, with the colormap corresponding to the lithium oxidation depth.

From each pixel of the back surface of the lithium, the distance to the lithium/electrolyte interface was determined. Then a colormap was used to show the distribution of these distances in the 2D (x,y) plane view. These distances compared to the initial thickness represent the amount of lithium that has been oxidized (resp. reduced) at the position (x,y) of the lithium surface. Using the faradays law for lithium stripping reaction (1 electron per lithium), one can deduce the local current density [1]. The average current density (0.55 mA cm^{-2}) is represented in orange and corresponds to the mean lithium oxidation thickness, while yellow pixels correspond to areas where lithium has been less oxidized than expected (based on coulometry), and the purple pixels to areas where lithium has been more oxidized than expected. In this way, 2D maps of the heterogeneity (thickness/current density) of the lithium/electrolyte interface could be drawn (Figures 3 and 4), as well as 3D stacks in order to better see the zoology of the objects (Figure 6, Figure S3).

Definition of the different lithium thicknesses

Two methods for the calculation of the lithium thickness reduction have been done, as detailed here. The first method was based on the average reduction of the lithium thickness (labelled "Averaged") taking into account the homogenous and heterogeneous oxidation (in orange, Figure S3). The second one was solely based on the thickness reduction corresponding to the complete oxidation of the lithium (labelled "Complete"), i.e. not taking into account the heterogeneity formed along the interface (in green, Figure S2).

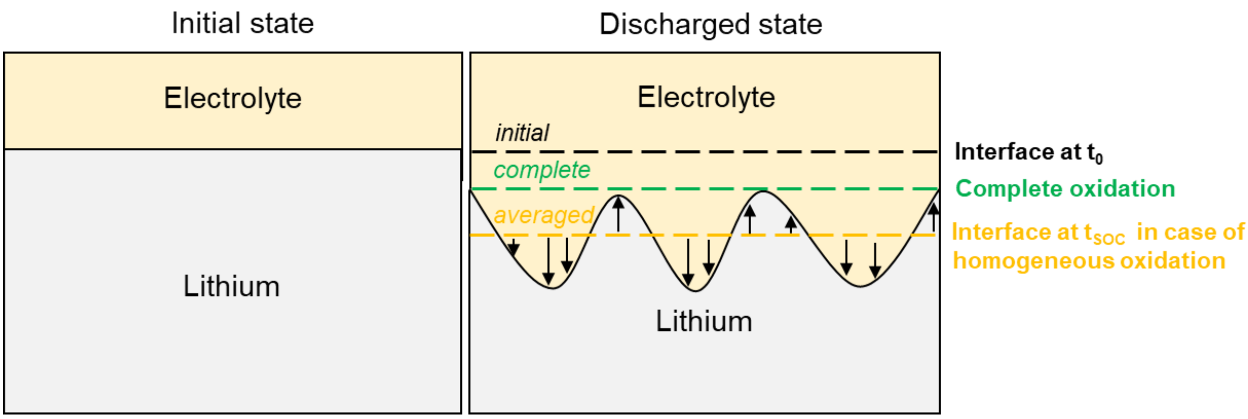

Figure S3: Schematic representation of the evolution of lithium/electrolyte interface during stripping, indicating the initial interface position (in black), the thickness change corresponding to "complete" oxidation (lithium homogeneously stripped, in green) and the thickness change corresponding to the averaged lithium stripping (in orange).

3D representation of the lithium/electrolyte interface after the second discharge

In order to study the effect of the heterogeneity of the lithium interface after two cycles, the 3D representation of the interface at the end of the second discharge is shown in Figure S4. For better visualization, the volume representation of the pits has been reversed, meaning that pits formed in the lithium volume appear as hills.

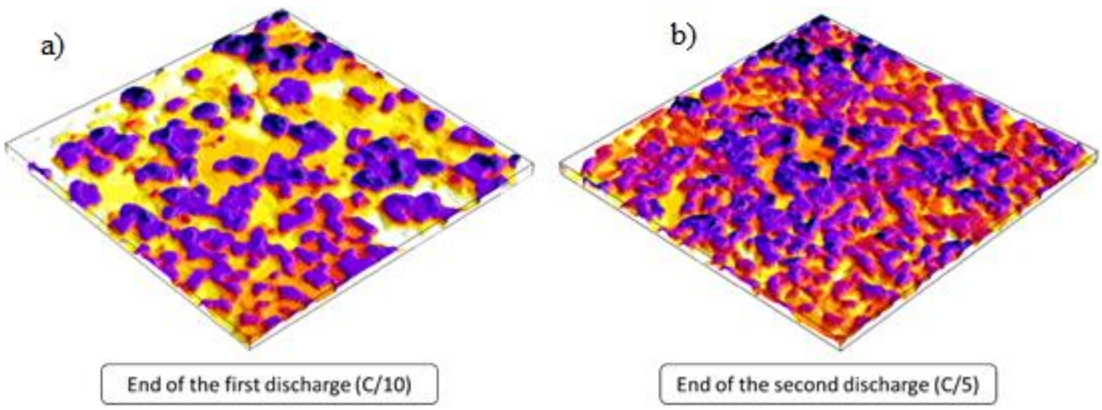

Figure S4. 3D representations of the lithium/electrolyte interface a) at the end of the first discharge (0.55 mA cm^{-2}) and b) the end of the second discharge (1.1 mA.cm^{-2}). For better visualization, the volume representation of the pits has been reversed, meaning that pits formed in the lithium volume appear as hills.

REFERENCES

[1] Magnier, L. et al., ACS Appl. Mater. Interfaces 12, 41390–41397 (2020)