# Experimental report

03/08/2022

**Proposal:** UGA-125 **Council:** 10/2020

**Title:** Lithium dendrites analyzed by neutron tomography technique

**Research area:**

**This proposal is a new proposal**


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**Samples:** Lithium symmetric cell with a liquid electrolyte. The chemical within the cells are: Lithium metal, Lithium salt dissolved in a deuterated liquid electrolyte (Lithium bis(trifluoromethanesulfonyl)) in deuterated dimethyl carbonate)

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D50 T | 2 | 2 | 20/03/2021 | 22/03/2021 |

**Abstract:**

# Experimental Report
## UGA-125: Lithium deposits analyzed by Neutron tomography technique


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| **Number of days** | 2 | **Date** | 20/03/2021 – 22/03/2021 |
| **Research field:** | Electrochemistry<br>Lithium Battery | **Sample material:** | Li symmetric cylindrical cells. Cell casing in Teflon. |
| **Testing conditions:** | Room temperature<br>Post-mortem analysis | **Temporal res:** | 18 h |
| **Min. spatial res:** | 15 µm | **Field of view:** | 3 mm x 3 mm |

- **Goal of proposal**

Lithium metal anode can offer superior electrochemical performance such as very high theoretical capacity (3860 mAh/g), very low electrochemical potential (-3.04 V *vs*. standard hydrogen electrode). During cell operation in a typical lithium battery, Li is stripped and plated alternatively during charge and discharge steps. Nonetheless, the stripping/plating of Li is non-uniform due to potential gradients that build-up in the cell and impurities on the Li surface. This might lead to the growth of undesirable dendrites of uncontrollable forms which could lead to short-circuiting and eventual cell failure.

Therefore, several techniques have been used in the past to fully understand the different phenomena at stake during the nucleation, growth, and propagation of dendrites at the Li/electrolytes interface. This is because, such an understanding will be beneficial to the design of appropriate electrolytes to be used in the next generation of Li batteries, that can mitigate or suppress dendritic growth since the nature of the electrolytes and the passive layer it forms with the Li play a leading role in the stripping/ plating process. To separate the phenomena that drive the oxidation and reduction of Li we proposed to carry out experiments to image both the plating and stripping on Li metal electrodes at the same time via model Li symmetric cell. For this, non-invasive techniques such as X-ray tomography are well-suited to probe soft material interfaces such as those encountered between Li metal and the electrolyte. **The originality of this work is to take advantage of the opacity of Li and Li isotope sensitivity to move toward a new methodology to precisely image the Li dendrite volume by Neutron tomography.**

- **Sample details and experimental conditions**

Specifically designed symmetrical cells were assembled in an Argon-filled glovebox prior to the beamtime (see **Figure 1**). The cells are based on conventional airtight Swagelok polytetrafluoroethylene (PTFE) straight union. The cell design was established thanks to results acquired during the UGA-91 beamtime at NeXT beamline. The inner diameter of the cell was 1/8" (~ 3.2 mm). The electrochemically active Li symmetrical cell was placed on top of an Al shim, which was seated on top of a stainless-steel compression spring. The spring was used to ensure a constant contact pressure in the cell during cycling. Due to the strong degradation of the Al shim when in contact with Li metal (exp. report UGA-91, see also L. Magnier *et al.*, *Front. Energy. Res.*, 9 (2021) 266), a titanium (Ti) layer was placed between the Li and the Al to act as a buffer. The current was transmitted through the cell via Al plungers located at both ends of the assembly and collected with crocodile clips when connected to a potentiostat.

The Li symmetric cells consisted of $^{6}$Li electrode and a natural Li electrode (92.4% $^{7}$Li and 7.6% $^{6}$Li), each having a 3 mm diameter, and separated by perfluoroalkaoxy alkane (PFA) tube (2.5 mm height x 3.2 mm outer diameter). The PFA tube was filled with a conventional deuterated liquid electrolyte, *i.e.*, 1M LiTFSI in deuterated dimethyl carbonate. After assembly, the cells were cycled at room temperature by passing a constant current up to 0.6 mA/cm$^2$ in one direction so that the $^{6}$Li is stripped and then plated onto the natural $^{7}$Li opposite electrode inducing the formation and growth of $^{6}$Li deposits. A typical cycling profile of a Li symmetric cell, potential ($E$) as a function of time ($t$), is shown in **Figure 2**. After cycling the cells, they were brought to the beamline to be imaged. The beamtime occurred remotely with the beamline scientist at ILL and the other users connected online.

At the beamline, the cells were first radiographed to select the best sample for a high-resolution tomographic acquisition. To get the best resolution possible from the Swagelok cell, a 18 h acquisition time was chosen in order to image up to 3 samples. The selected cell ends up with a 15 µm resolution.

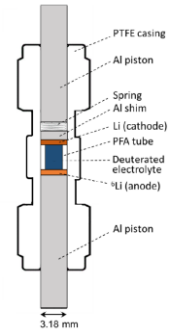


**Figure 1**. Design of the electrochemical cell.

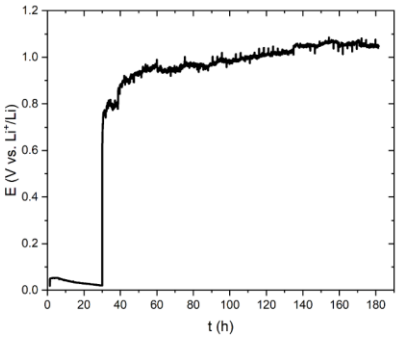


**Figure 2.** Stripping and plating of $^6$Li as shown by potential (*E*) vs. time (*t*) for a typical cell. The current density was 0.1 mA/cm$^2$.

- **Initial results**

Analysis of all of the stack of data obtained during the UGA-125 experiment is still ongoing. Meanwhile, **Figure 3** represents a typical radiography of the $^6$Li/Li cell. The residual $^6$Li located at the bottom of the image is still present on top of the Ti buffer layer. It can be seen that the electrodes are not flat but are rather parabolic in shape. This is due to the Li being too smooth when pressed with the PFA tube during cell. In between the electrodes, the deuterated electrolyte within the PFA tube is highly transparent and the black/dark gray parts correspond to $^6$Li deposits on the top electrode. Indeed, the $^6$Li isotope has a stronger Neutron absorption than natural Li (or $^7$Li). From **Figure 4** (right) it can clearly be seen that non-uniform of $^6$Li dendrites with preferential orientation along the walls of the PFA tube have been deposited. A first 3D rendering of this volume is proposed in **Figure 4**. This cell design is optimized compared to the initial one when imaged during UGA-91 beamtime as it helps to remove two type of artefacts: i) presence of bubble within the electrolyte and ii) degradation of the Al parts thanks to the use of Neutron-transparent and Li-stable Ti materials.

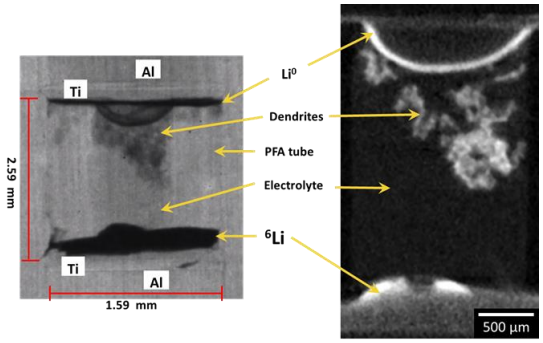


**Figure 3.** Neutron radiography of a $^6$Li/Li cell. Al metal parts showed strong degredation due to instability towards Li.

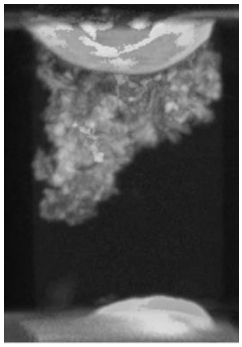

**Figure 4.** 3D rendering of the $^6$Li deposits.

- **Conclusion, future work, and publication**

A first $^6$Li image of dendrite was obtained during UGA-125 beamtime which was possible only thanks to results acquired during UGA-51 and UGA-91 beamtime (see L. Magnier *et al.*, *Front. Energy. Res.*, 9 (2021) 266). This study clearly shows the capability of Neutron tomography as a new tool to study the deposition of Li to form dendrites as well as its quantification. In addition, this technique is very promising to dissociate the process during plating and stripping by taking advantage of the Li isotope sensitivity. The knowledge acquired during this beamtime will be used to study the ionic transport properties in the electrolyte and their stability with Li metal (dendrite formation). We hope to publish a paper related to this study in the upcoming year.