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Lucile Magnier, Lauréline Lecarme, Fannie Alloin, Andrew King, Renaud Bouchet, et al.. Tomography Imaging of Lithium Electrodeposits Using Neutron, Synchrotron X-ray, and Laboratory X-ray sources: A Comparison. *Frontiers in Energy Research*, 2021, 9, 10.3389/fenrg.2021.657712 . hal-03262977

HAL Id: hal-03262977

<https://hal.science/hal-03262977v1>

Submitted on 16 Jun 2021

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Tomography Imaging of Lithium Electrodeposits Using Neutron, Synchrotron X-ray, and Laboratory X-ray sources: A Comparison.

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Keywords: lithium metal, electrodeposit, dendrite, neutron tomography, X-ray tomography, synchrotron

Abstract

X-ray and neutron imaging are widely employed for battery materials thanks to the possibility to perform non-invasive *in situ* and *in operando* analyses. X-ray tomography can be performed either in synchrotron or laboratory facilities and is particularly well-suited to analyze bulk materials and electrode/electrolyte interfaces. Several post Lithium-ion (Li-ion) devices, such as Li-sulfur, Li-O₂, or all-solid-state Li batteries, have in common an anode made of metallic Li. The main failure mode of Li batteries is the inhomogeneity of the Li electrodeposits onto the Li anode during charge steps leading to dendrite growth and low Coulombic efficiency. X-ray tomography is a powerful tool to study dendrites as it provides useful information about their locations, dynamics, and microstructures. So far, the use of neutron tomography is scarcely reported for Li deposit analysis due to the difficulty to reach sufficient image resolution to capture the deposit microstructure, *i.e.* typically below 10-20 μm . The very different interactions of X-rays and neutrons with Li, which has significantly different opacity in the two cases, make the two techniques highly complementary. Notably, the capacity of neutrons to discern different Li isotopes is pivotal to get an insight on the composition of Li deposits by

distinguishing between Li originating from an electrode (^6Li in this study) to that from the Li salt electrolyte (mainly in ^7Li here). Indeed, the theoretical linear neutron attenuation coefficient of ^6Li is about 15 and 2000 larger than that of natural Li and ^7Li , respectively. Therefore, high imaging contrast difference is obtained between ^6Li (high attenuation) and natural Li and ^7Li (lower attenuations) which could allow a better understanding of the origin of the Li comprising the electrodeposits. In this work, we report, as a proof-of-concept, an *in situ* neutron tomography imaging of Li electrodeposits in a cycled Li symmetric cell. The electrochemical cell comprises a natural Li electrode, a ^6Li electrode, and a deuterated liquid electrolyte. The neutron tomographies are compared with X-ray tomography images of the same electrochemical cell acquired both at an X-ray synchrotron beamline and at a laboratory X-ray tomograph. Neutron tomography is shown to be compatible with *in situ* analysis and capable to capture the overall morphology of the Li deposits in good accordance with X-ray tomography analyses.

1 Introduction

In the journey to develop safe high energy density batteries many systems are currently studied such as Li-sulfur, Li- O_2 , or all-solid-state Li devices (Whittingham 2004; W. Li, Song, and Manthiram 2017; Bruce et al. 2012). A common feature for those batteries is the use of a lithium (Li) metal negative electrode. Indeed, Li metal is one of the most promising electrode materials thanks to its high capacity (3860 mAh.g^{-1}), low density (0.534 g.cm^{-3}), and low electrochemical potential (-3.04 V vs. standard hydrogen electrode) (X.-B. Cheng et al. 2017a). The industrialization of Li metal electrodes with a conventional liquid electrolyte has been hindered by the heterogeneities of the Li electrodeposit onto the Li surface, which limits the Coulombic efficiency (ratio between the discharge and charge capacity), battery cycle life, and may grow sufficiently in the form of dendrite to induce a short-circuit (Aurbach et al. 2000; Z. Li et al. 2014).

To move toward an optimized Li-electrolyte interface, understanding the origin and growth of dendrites is of the utmost importance (Z. Li et al. 2014b). Indeed, depending on the nature of the electrolyte and the passive layers (X. B. Cheng et al. 2016a). formed onto the Li metal, different families of dendrite morphologies are observed such as mosses, needles, and globules (Harry et al. 2014; K. N. Wood et al. 2016; X.-B. Cheng et al. 2017). Furthermore, the dendrite microstructure depends on the operating and cycling conditions such as temperature or current density (Bai et al. 2016a).

The most usual techniques to study dendrites are based on optical microscopy (Brissot et al. 1999a), electron microscopy (Gireaud et al. 2006), atomic force microscopy (Morigaki and Ohta 1998), or magnetic resonance imaging (Illott et al. 2016) to name a few. However, most of them are two-dimensional and invasive by nature and may alter the probed materials and interfaces. Non-invasive technique based on X-ray imaging which takes advantage of the prevalent interaction of X-ray with the outer electron shell of the atoms are now more accessible thanks to the development of dedicated synchrotron X-ray beamlines and widespread diffusion of laboratory tomographs (Maire et al. 2001; Pietsch and Wood 2017). X-ray tomography is well-suited to study, qualitatively and quantitatively, soft material interfaces. As an example, Balsara *et al.* studied model Li symmetric cells and Li based batteries using synchrotron hard X-ray to report on dendrite growth and volume (Devaux et al. 2015;

Harry et al. 2014b). Therefore, X-ray tomography is widely reported to study battery materials (V. Wood 2018; Vanpeene et al. 2020; Magnier et al. 2020). In addition, the temporal and spatial resolution obtained from synchrotron sources are high enough to be compatible with electrochemical processes leading to the development of *in operando* imaging via dedicated electrochemical cells (Schröder et al. 2016; Grey and Tarascon 2017; Sun et al. 2016; Foroozan, Sharifi-Asl, and Shahbazian-Yassar 2020).

Despite the high spatial and temporal resolution of X-ray imaging techniques, some limitations arise due to the low sensitivity towards light Li compared to materials with high atomic number atoms typically encountered in current collectors (Al, Cu) or active materials (Co, Fe, Mn, Ni). As a complementary non-invasive technique, neutron imaging, which is based on the specific interactions of atomic nuclei with a neutron beam, gives useful additional information thanks to a high penetration depth capability into materials comprising high atomic number elements as well as high Li visibility and sensitivity to its isotopes (Strobl et al. 2009; Banhart et al. 2010). The theoretical linear neutron attenuation coefficient comprising of ^6Li is about 15 and 2000 times larger than that of natural Li and ^7Li , respectively (Sears 1992). As an example of *in operando* neutron radiography, Wang *et al.* imaged at a 50 μm resolution a planar battery made of a highly oriented pyrolytic graphite electrode and ^6Li as counter electrode (Wang et al. 2012). By taking advantage of the beam attenuation induced by ^6Li atoms, the graphite electrode areas enriched with ^6Li were followed over the course of a galvanostatic experiment.

Neutron tomography was first applied to commercial batteries to either quantify gas in an alkaline cell or to probe the internal volume modification of battery cell upon cycling (Manke et al. 2007; Butler et al. 2011; Senyshyn et al. 2012). So far, neutron tomography remains an *ex situ* and *in situ* technique as multiple hours are needed to perform a sample acquisition. The Li spatial distribution is typically quantified within cathode (Nanda et al. 2012; Ziesche, Arlt, et al. 2020), anode (Zhang et al. 2017), and battery cell (Ziesche, Robinson, et al. 2020) by neutron tomography. Riley *et al.* performed *in situ* neutron tomography at a 150 μm resolution to report on the jellyroll volume change in Li primary cell (Riley, Hussey, and Jacobson 2010). To get better quantitative data several optimization strategies were proposed by the authors such as designing specific electrochemical cell comprising deuterated electrolytes and isotope enriched Li electrodes. Indeed, ^6Li and ^7Li are strongly attenuating and almost transparent to the neutron beam, respectively.

To get specific information within a battery by neutron imaging, dedicated cells and setups (Owejan et al. 2012) are thus needed to increase the spatial and temporal resolution, *i.e.* get information in times compatible with typical beamtime allocations to move toward *in operando* analysis. Several strategies have already been explored such as an electrochemical cell casing made of a neutron transparent polytetrafluoroethylene (PTFE) casing (Owejan et al. 2012), an adapted pouch bag cell (Knoche et al. 2016), or a coin cell (Sun et al. 2017).

To combine X-ray and neutron information, Sun *et al.* designed a cylindrical polyamide-imide cell casing having an inner and outer diameter of 3 mm and 6 mm, respectively. The cell is optimized to image Li-air batteries for *in operando* synchrotron X-ray ($\sim 1.2 \mu\text{m}$ resolution) and *in situ* neutron ($\sim 13 \mu\text{m}$ resolution) tomography experiments (Sun et al. 2019). The complementarity of the two techniques revealed the degradation mechanisms at play at the Li/separator interface. Moreover, Song

et al. (Song et al. 2019) performed *in operando* neutron radiography and *in situ* tomography on a Li/LiMn₂O₄ battery using a TiZr based cell to study the Li dynamic distribution upon dendrite short-circuit. The electrochemically active assembly was made of a neutron transparent ⁷Li metal and deuterated electrolyte in order to enhance the contrast between the Li electrodeposits and the ⁷Li electrode and to reduce the scattering of hydrogen, respectively.

In this work, by taking advantage of the capability of a neutron imaging beamline and of the Li isotope sensitivity, we report an *in situ* neutron tomography analysis of Li electrodeposits. A Swagelok-type electrochemical cell with a PTFE casing specifically designed for neutron imaging comprises a Li symmetric cell made of a natural Li (92.4 wt.% ⁷Li and 7.6 wt.% ⁶Li) electrode, a ⁶Li (95 wt.% ⁶Li and 5 wt.% ⁷Li) electrode, and a deuterated liquid electrolyte. ⁶Li was selected to increase the contrast of the deposits from the deuterated electrolyte. The ⁶Li electrode (anode) was oxidized and ⁶Li was plated onto the opposite natural Li electrode (cathode) to induce dendrite growth. The neutron images are then compared to X-ray tomography analysis of the same cell acquired both at an X-ray synchrotron beamline and in a laboratory X-ray tomograph with a voxel size of 0.64 and 2.0 μm, respectively. In addition, the deposit volume is here quantified and positively compares to the measurement obtained by X-ray techniques. Despite the needed optimization to get further image quality and accelerated acquisition time, this *in situ* neutron tomography experiment is a proof-of-concept showing the possibility to study battery failure modes via neutron imaging.

2 Material and Methods

2.1. Li symmetric cell assembly

To minimize neutron or X-ray absorption of the casing, a dedicated electrochemical cell was developed. **Figure S1** (see supplementary file) shows a schematic of the electrochemical cell comprising, as main components, a casing made of polytetrafluoroethylene (PTFE) and current collectors in aluminum (Al). The active cell composed of the ⁶Li/electrolyte/Li assembly is located in its middle. PTFE was selected for its high neutron transparency, allowed by its macromolecular structure made of fluorine and carbon atoms, which have a small neutron cross section. In addition, PTFE based electrochemical cells are known to be suitable for X-ray based techniques (Tan et al. 2018). A PTFE Swagelok straight union with a 1/8 inch (~ 3.18 mm) inner diameter was selected to ensure a proper sealing and airtight conditions of the assembly. In addition, the outer part of the straight union was machined at its center, where the active cell is located, to reduce the wall thickness leading to an outer diameter of about 8 mm thus facilitating X-ray transmission. Despite the better corrosion resistance of stainless-steel, Al current collectors were selected because of its neutron transparency and low radioactive activation under a neutron beam (Girardi and Pietra 1963). To assemble the cell, a first Al piston is inserted followed by the active cell and an Al shim. Then, a stainless-steel spring and a second Al piston conclude the assembly. The spring allows the imposition of a constant load to the active cell while all the Al and stainless-steel parts ensure electronic conduction from the active cell to a potentiostat via conventional ‘crocodile’ clips.

The active cell consists in Li symmetric cell assembled in an argon (Ar) filled glovebox (Campus, Jacomex) with sub-ppm values of oxygen and water. For each cell, one electrode is made of natural Li

(92.4 % ^7Li and 7.6 % ^6Li) while the other is in ^6Li (95 atom % chunk in mineral oil, Sigma Aldrich). The deuterated liquid electrolyte is formulated in the Ar glovebox by mixing lithium bis-trifluoromethanesulfonimide (LiTFSI) with deuterated dimethyl carbonate (*d*-DMC, Sigma Aldrich, used as received) to attain a 1 M concentration. First, a layer of ^6Li was cut from a larger piece, manually flattened using a roll, and 3 mm diameter disks were punch out. The average thickness of ^6Li electrode is $145 \pm 10 \mu\text{m}$ based on the series of cell replicates. Similarly, 3 mm diameter disks of natural Li were punched out from a Li foil. The PTFE cell were assembled halfway by inserting a first Al piston (see **Figure S1**). The ^6Li electrode was placed inside the cell followed by a 2 mm long perfluoroalkoxy alkane (PFA) tube with a 1/8 inch ($\sim 3.18 \text{ mm}$) outer and 1/16 inch ($\sim 1.59 \text{ mm}$) inner diameter to confine the liquid electrolyte and separate the two electrodes. The tube is filled with the deuterated liquid electrolyte (1M LiTFSI in *d*-DMC) and the natural Li electrode placed on top of the tube. Then, an Al shim, the spring and a second Al piston is inserted and the cell closed. Four cell replicates were assembled and cycled for the purpose of this study.

2.2. Cell cycling

The cell replicates were taken out of the glove box, placed in an oven (UN30, Memmert) held at 25°C , and connected to a single-channel potentiostat (SP200, BioLogic) with impedance capability. Then, a constant current of $8.4 \mu\text{A}$ was applied to each cell up to 72.5 h in one direction. During the galvanostatic step, the ^6Li is stripped and plated onto the opposite natural Li electrode. The cell impedances were recorded before and after the galvanostatic step via potentiostatic electrochemical impedance spectroscopy. At the open circuit voltage, an excitation signal of 40 mV is applied to the cell in a frequency range in between 7 MHz and 1 Hz. The impedance spectra were fitted using the Zfit module included in the EC-lab software.

2.3. Electrolyte conductivity

The ionic conductivity of the sole deuterated liquid electrolyte (1M LiTFSI/*d*DMC) was determined as a function of temperature. Inside the Ar glovebox, a conductivity cell for microsample (Hach Co.) was inserted into a test tube filled with the electrolyte and hermetically sealed. The cell was taken out of the glove box and placed in an oven (VTM 4004, Vötsch) to perform impedance measurements at temperature ranging from 25 to 60°C in steps of 10°C , then cooled down to -25°C before a final heating scan up to 60°C in steps of 5°C . The impedance spectra were fitted using a similar electrical equivalent circuit detailed in a previous report (Devaux et al. 2012) to extract the electrolyte resistance (R_{el}). In addition, the electrode cell constant (k) was determined beforehand via a 0.01 M KCl aqueous solution.

2.4. Neutron tomography

Neutron tomography was performed at the NeXT beamline at the Institut Laue-Langevin (ILL, Grenoble, France) (Tengattini et al. 2020). The cells were mounted on a rotation platform and imaged at room temperature. There, cold neutrons reach the cell after going through a 15 mm diameter pinhole collimator (D), placed at 10 m from the sample (L) without any filter. Given this collimation ratio $L/D = 667$ and an effective 12 mm cell diameter placed close to the detector, the neutron penumbra

(blurring) is estimated to be around 10 μm , close to the pixel size. To detect neutrons a typical scintillator-mirror-camera as well as an infinity-corrected optical system are employed (Tengattini et al. 2020). The Hamamatsu Orca Flash 4V2 equipped with Canon 100 mm f./2.0 optics with a 50 μm thick LiF ($^6\text{LiF}/\text{ZnS}:\text{Cu}$) scintillator was firstly employed to gather rough estimates of the geometry of the different cells over a large field of view set at 40 x 40 mm leading to a 20 μm spatial resolution. Once a cell was selected, a second, infinity corrected setup, composed of a 5 μm Gadolinium ($\text{Gd}_2\text{O}_3\text{S}:\text{Tb}/^6\text{LiF}$) scintillator and a combination of a 50 mm f./1.2 Canon lens and a 55 mm Heliflex lens was employed to achieve a 7.4 μm pixel size over a 14 mm field of view. A series of 2600 projections, each 25 seconds long were acquired over a 360° rotation, leading to a total acquisition time of 18 h. In the 32 bits reconstructed images via the RX Solutions software which employs a Feldkamp (FDK) filtered back projection algorithm, the grayscale value represents the attenuation coefficient, so more attenuating regions are brighter. The volume obtained was 2575 x 2538 x 3397 μm^3 . Further image analysis was performed using the Fiji software (Schindelin et al. 2012).

2.5. Synchrotron X-ray tomography

Synchrotron X-ray computed tomography (XRCT) using phase contrast was performed at the PSICHE beamline at the Soleil Synchrotron (Gif-sur-Yvette, France) (King et al. 2016). At the beamline, the cell was mounted on a rotating plate and illuminated at room temperature with a pink X-ray beam set at an average energy of 25 keV. A series of 1500 projections along a 180° rotation with an exposure time of 40 ms per projection was acquired. The field of view was restricted to 1.3 x 1.3 mm with a 0.64 μm voxel size. The collected radiographs were reconstructed using the PyHST2 software (Mirone et al. 2014). Given that the Li cell height comprising the 2 mm long PFA tube is larger than the field of view, two tomographic acquisitions were performed on the cell; one focusing on the top of the active cell to image the natural Li electrode and another one focusing on the lower half of the active cell to image the ^6Li electrode. Each image stack reconstructed in 32 bits floating-point were subsequently merged into a single one. The volume obtained 2510 x 1313 x 1313 μm^3 . The analysis of the images was also performed with the Fiji software.

2.6. Laboratory X-ray tomography

A laboratory X-ray tomograph (EasyTom, RX Solutions) with a LaB_6 cathode source and a Paxscan 2520DX (Varex Imaging) amorphous silicon flat panel detector located at MATEIS laboratory (Villeurbanne, France) was employed to image the cells at room temperature. The detector has 1920 rows and 1536 columns of square pixels (each 127 x 127 μm^2 in size) with a CsI scintillator and provides the value of the attenuation with a 16 bits gray level. Each cell was fixed to the scanner rotation platform and a tension of 50 kV was used to acquire the scan. The tomography was acquired over four 360° rotations plus references (for alignment in case of thermo-mechanical misalignments along the test) comprising 1184 images. Each projection was the result of the average of 3 frames at 0.70 frames per second, optimized to ensure sufficient X-ray flux to have good signal to noise ratio. The volume obtained was 3422 x 3422 x 2614 μm^3 with an isotropic voxel size of 2 μm . The collected radiographs were reconstructed to produce a 3-dimensional (3D) stack via the RX Solutions software without correction of beam hardening and Fiji software was used for image analysis.

3 Results and Discussion

To validate the design of the electrochemical cell, a series of uncycled electrochemical cells was imaged by X-ray tomography at the laboratory source to get insight on the quality of the active cell assembly (^6Li /electrolyte/Li). **Figure 1** shows a tomography of a cell cross-section acquired at room temperature. In this figure, the grayscale value for each pixel is the attenuation coefficient of the corresponding portion of space. So, for example, heavy elements such as Al that strongly absorbs X-rays appear brighter. The cell casing made of PTFE is transparent enough to the X-ray so that the active cell and the Al parts (piston or shim) can be distinguished. Due to the slightly higher absorption of PFA compared to Li and to the polychromatic nature of the laboratory X-ray source, reconstruction artefacts likely due to the cone beam or beam hardening (Maire and Withers 2014) are observed. Indeed, the upper Li electrode seems to exhibit two different attenuation values, *i.e.* the pixels corresponding to the Li electrodes close to the Al materials appear more attenuating than they should be. In addition, the natural Li electrode located on top of **Figure 1** has similar gray values than the bottom one made of ^6Li . As expected, X-ray imaging is not sensitive to the Li isotopes making it impossible to distinguish between these two electrodes (^6Li vs. natural Li). It can also be noticed the presence of two domains located within the PFA tube, one with grey values close to those of the PFA, and ascribed to the liquid electrolyte, while the other one presents grey values similar to those of the Li electrodes suggesting the presence of an Ar bubble. This is explained by the delicate cell assembly that may entrapped Ar bubble in the liquid electrolyte. Despite the presence of a bubble in **Figure 1**, the Li electrodes are not perfectly flat as the surface of both Li electrodes facing the liquid electrolyte tends to adopt a spherical cap shape. This feature observed on all cell replicates is probably due to the softness of Li compressed within the PFA tube due to the spring pressure and to a mediocre adhesion of Li with the Al parts. The study of the uncycled cells by X-ray tomography highlights the importance of the 3D nature of these analyses, as the inner cell geometry must be accounted for electrochemical and impedance studies. Indeed, the dome surfaces lead to an effective surface and an effective cell constant that will differ from the geometrical ones. We can consider that the two electrodes formed equivalent spherical cap spheres within the PFA tube having a radius (r) equivalent to the PFA inner tube radius, a height (h), and separated by a distance (l) equivalent to the PFA tube height. In such configuration, the effective cell constant (k) is estimated using the equipotential current line (Hong, Chong, and Cho 2019) between two domes given by:

$$k = \int_h^{l-h} \frac{1}{\pi \cdot r} \cdot \frac{dx}{x} = \frac{1}{\pi \cdot r} \cdot \ln\left(\frac{l}{h} - 1\right) \quad (1)$$

By measuring the distance r , h , and l by laboratory X-ray tomography imaging on a series of four uncycled cell replicates, the average effective cell constant k is 6.9 ± 0.1 . Impedance spectroscopy was then performed on the uncycled cell replicates at 25 °C. Considering the effective surface, **Figures 2a** and **2b** show the impedance spectra in Nyquist coordinates along with the characteristic frequencies of two typical cells, denoted cell_A and cell_B, respectively. Each spectrum presents two semi-circle loops, one in the high frequency range between 7 MHz and 100 kHz and another one at lower frequencies. The high and low frequency loops are ascribed to the electrolyte (R_{el}) and Li/electrolyte

interface resistances, respectively (Bouchet, Lascaud, and Rosso 2003). The spectra were fitted with an electrical equivalent circuit composed of elements in series corresponding to the cable resistance and inductance, the electrolyte response as R_{el} in parallel with a constant phase element followed by another resistance in parallel with a constant phase element corresponding to the Li/electrolyte interfaces. The equivalent circuit is displayed in the inset of **Figure 2a**. The electrolyte and interface resistances of cell_A are higher than that of cell_B by a factor of 7 and 2, respectively. These higher resistances are ascribed to the presence of an Ar bubble entrapped within the PFA tube due to a contact surface reduction which also induces a frequency dispersion as the bubble possesses different dielectrical properties. Regarding the electrolyte resistance of cell_B, the ionic conductivity (σ) at given temperature (T) is calculated using the following equation:

$$\sigma(T) = \frac{k}{R_{el}(T)} \quad (2)$$

By combining equation (1) and (2), the ionic conductivity of cell_B at 25 °C is $6.6 \cdot 10^{-3} \text{ S.cm}^{-1}$. For comparison, the conductivity of the sole deuterated liquid electrolyte (1M LiTFSI/dDMC) was determined using the conductivity cell for microsample (see electrolyte conductivity in the experimental section). **Figure S2** shows σ of the deuterated electrolyte as a function of the inverse of the temperature in between -25 and 60 °C. In the temperature range explored, the conductivity presents two different domains with a transition at about -5 °C corresponding to the electrolyte crystallization. At 25 °C, the conductivity is $6.6 \pm 0.2 \cdot 10^{-3} \text{ S.cm}^{-1}$. This value is consistent with the one reported by Dahbi *et al.* of about $7.0 \cdot 10^{-3} \text{ S.cm}^{-1}$ for a non-deuterated 1M LiTFSI/DMC electrolyte at 24.8 °C (Dahbi *et al.* 2011). Therefore, the conductivity at 25 °C of cell_B lies within the error bar of the value measured by the conductivity cell. Consequently, the analysis of the electrolyte conductivity of uncycled ^6Li -Li cell by impedance spectroscopy in combination with X-ray tomography validates the design of electrochemical cell and allow the identification of assembly defects (deformed electrodes and entrapped gas bubble) that should be taken into account for a future cell assembly optimization.

The cell replicates were then cycled at a constant low current of 8.4 μA in order to move ^6Li (anode) onto the natural Li electrode (cathode). Considering the effective surface, cell_B was cycled at 0.53 mA.cm^{-2} . For cell_A, the bubble within the liquid electrolyte induces complex current lines between the two electrodes, and thus an uncertain current density value. The result of the galvanostatic step performed on cell_A and cell_B is provided in **Figure 3** showing the cell voltage (E in V vs. Li^+/Li) as a function of time (t). The voltage profile of cell_B is almost constant at 0.1 V vs. Li^+/Li for 16 h then increases until a plateau at about 0.45 V vs. Li^+/Li . For cell_A, the voltage profile presents first a sharp increase after 5 h with a peak at about 1.7 V vs. Li^+/Li at $t = 15 \text{ h}$, before decreasing to 0.2 V vs. Li^+/Li at $t = 27.5 \text{ h}$. For $t > 27.5 \text{ h}$, the cell voltage becomes similar to that of cell_B with E being constant at 0.2 V vs. Li^+/Li followed by a slight increase up to a final value of about 0.53 V vs. Li^+/Li , in the same range than the one reached by cell_B. The voltage fluctuation and high polarization of cell_A during the first 27.5 h is attributed to the presence and the movement of the Ar bubble within the PFA tube during the electrochemical step leading to a geometrical factor modification coupled with an increase of the Li/electrolyte interface due to heterogeneous electrodeposits (K. N. Wood *et al.* 2016).

A similar cell voltage behavior than the one observed for cell_B was reported in the works of Brissot *et al.* (Brissot *et al.* 1999b) and Rosso *et al.* (M. Rosso *et al.* 2001) focusing on the study of Li dendrite growth mechanisms in Li symmetric cells comprising a polymer electrolyte. The authors show that below a critical current density (J^*) the ionic concentration profile, and thus the concentration gradient, throughout the cell evolves to a steady state. The cell voltage attains a constant value which eventually drops to zero when a dendrite makes a contact between the two electrodes. For $J < J^*$, the morphology of the electrodeposits observed by Brissot and coworkers (Brissot *et al.* 1999c) is tortuous, forming mostly mossy Li with the presence of needle-like dendrites. This behavior was partly confirmed by Bai *et al.* on Li symmetric cell comprising a liquid electrolyte with an electrode inter-distance in the range of several millimeters where the electrodeposited Li morphology remains mostly mossy if the current density is below J^* (Bai *et al.* 2016). Based on the work of Brissot and coworkers (Brissot *et al.* 1999c), J^* is defined as:

$$J^* = \frac{2.F.C.D}{(1-t^+).l} \quad (3)$$

with F the Faraday constant, C the concentration of salt in the electrolyte, D the ambipolar diffusion coefficient, and t^+ the cationic transference number.

By considering that the ionic transport properties of the deuterated liquid electrolyte are similar to that of its non-deuterated counterpart, we can take C , t^+ , and D values equal to 1000 mol.m⁻³, 0.46, and 3.46 10⁻⁶ cm².s⁻¹, respectively (Borodin and Smith 2006). Using equation 3 and considering a distance l equal to the typical PFA tube length of 2 mm, then J^* is 5.8 mA.cm⁻². Consequently, the imposed current density of cell_B corresponds to 9 % of J^* and the voltage behavior falls within the $J < J^*$ case. For cell_A, despite of the effect of the Ar bubble, its cell voltage profile corresponds also to the $J < J^*$ case. Indeed, even by considering an active surface being a minor fraction of the effective surface, the current density remains below the J^* value. Moreover, for cell_B, the total amount of charges passed during the 54.7 h of the galvanostatic step corresponds to a theoretical displacement of 139 µm of ⁶Li based on the Faraday law and considering the effective surface. This value is close to the ⁶Li electrode thickness used in cell_B of 145 µm which means that a quasi-total ⁶Li oxidation was performed during current imposition. Therefore, for both cells their current densities used for the Li transfer from the anode to the cathode lies in the $J < J^*$ case and the length of the PFA tube permit to oxidize most of the anode (⁶Li) onto the cathode (natural Li) without dendrite short-circuit.

At the end of the galvanostatic step, a final impedance measurement was performed on cell_A and cell_B, and the corresponding spectra are added in **Figure 2a** and **2b**, respectively. For cell_A, the total cell resistance is diminished by a factor 3 compared to its initial state with a strong reduction of the interface resistance by a factor 18 in the lower frequencies range. This situation is certainly due to an increase in the active surface on the cathode by the growth of mossy or dendritic electrodeposits (as shown later by Neutron imaging in **Figure 4**) as well as a modification of the solid electrolyte interphase (X. B. Cheng *et al.* 2016) on the anode (M. Rosso *et al.* 2006). In addition, the electrolyte loop is depressed with a resistance value similar to the initial one which is ascribed to the presence of

both Li deposits and bubble within the liquid electrolyte inducing a strong dispersion in the characteristic frequencies. For cell_B, the total cell resistance increased by a factor 1.4 with the main change observed for the electrolyte resistance (high frequency loop) while the characteristic frequencies of the two loops are modified. This behavior may be due to a cell constant modification during the galvanostatic step. Based on **Figure 1**, the ^6Li takes the form of a dome on top of the Al current collector, so the cell constant will gradually change towards a higher constant value while the anode (^6Li) is oxidized, and conversely, electrodeposits formed onto the cathode, until most of the ^6Li is consumed inducing a hole in the anode.

After the galvanostatic step, the electrochemical cells were taken to the neutron tomography beamline for an *in situ* imaging at room temperature. There, a series of radiographies was first acquired at a large field of view and at different rotation angles in order to quickly inspect each cell. Except cell_A, the radiographies of cell_B and other replicates revealed a damaged assembly and thus were discarded for further tomography imaging. For cell_A, a typical radiography is reported in **Figure 4a** where at each pixel, the gray value is proportional to the neutron attenuation of the corresponding region of space. In this image, neutron transparent materials such as Al (piston and shim) and PTFE (cell casing) appear brighter (given that most of the neutrons are transmitted to the detector) than material with stronger neutron attenuation such as the stainless steel spring or Li electrodes (Sears 1992). As expected, the Al and PFA materials are suitable for neutron imaging as their attenuation is essentially negligible. The top and bottom Li electrodes appear black in between the Al parts and PFA tube. In addition, the PFA inner surface is visible from the overall background because of the presence of absorbent materials within the deuterated electrolyte, with from top to bottom as detailed in **Figure 4a**: the natural Li electrode (the cathode in the galvanostatic step) with a spherical cap shape as observed in the uncycled cell through X-ray tomography (see **Figure 1**), the ^6Li deposits in the electrolyte, and a less attenuating portion at the bottom suggesting the presence of a bubble. It can be noted that at the bottom of the PFA tube, the ^6Li electrode is almost absent from the radiography in agreement with its quasi-total oxidation during the electrochemical step (see **Figure 3**). Moreover, at the interface between the PFA tube and the Al parts on both side of the cell, a highly attenuating material is covering the Al surface as well as on its edges. This is attributed to a chemical and electrochemical degradation of Al areas in contact with Li metal. Tahmasebi *et al.* recently reported on the degradation of Al surface associated with the formation of the LiAl (β) phase either during electrochemical lithiation or by simple contact between Al and Li metal (Tahmasebi et al. 2019). Cell_A was subsequently imaged in tomography for 18 hours. **Figure 4b** shows a typical vertical slice of the tomography, showing a cross-section of cell_A. The values of the voxels in a tomography are related to the attenuation coefficients of the corresponding volume of space with higher values for highly attenuating materials which is the opposite to the radiography images. As observed in the radiography, both Al parts in contact with Li are highly attenuating, indicating the presence of the LiAl phase. At the bottom part, the few ^6Li anode remainders appear in bright white. The gray values of the ^6Li throughout the reconstructed volume are the highest of all observed materials in the active cell with some gray saturation at some voxels as shown in the bottom right corner. As expected, the gray values associated to the natural Li electrode (the bended electrode at the top of **Figure 4b**) are lower than that of the ^6Li , as its theoretical neutron attenuation coefficient is 15 times lower (Sears 1992). This result

shows that the Li isotope sensibility to neutron is an effective tool to differentiate between Li electrodes (^6Li vs. natural Li) after an electrochemical step. Moreover, inside the electrolyte volume in **Figure 4b**, a highly neutron attenuating, irregularly shaped domain is observed and attributed to ^6Li deposits, appearing in light-gray and white, originating from the natural Li electrode and spreading throughout the electrolyte. In this experiment, the attenuation values from the ^6Li deposits are in the same range as that of the natural Li electrode and of the Li reacted with Al leading to difficulties in distinguishing between each of these domains. Indeed, even if the voxel size is larger than the characteristic diameter of mossy Li or Li dendrites (Bai et al. 2016), the ^6Li deposits are visible because of the partial volume effect (Santago and Gage 1995; Kaestner et al. 2013). Typically, the attenuation coefficient of voxels partially occupied by both deposits and electrolyte will be intermediate between the attenuation of the individual components. The ^6Li deposits are also surrounding a dark-gray black volume with gray values close to that of the background air, and having a bulb shape confirming to the presence of a bubble.

From the tomography imaging, the active cell volume can be segmented in different components, based on their gray level. The Al domain can be easily segmented as it has significantly lower attenuation values. The segmentation of the other domains containing Li (deposits, cathode and the LiAl alloy) is more delicate, given the comparable attenuation values. The thresholding limits between these is therefore more arbitrary. **Figure 4c** corresponds to the segmentation of the slice shown in **Figure 4b** while a 3D volume rendering is shown in **Figure 4d**. The ^6Li deposits within the electrolyte take the form of a heterogeneous ramified structure. Beside this graphical representation, the segmentation allows a quantitative analysis. The overall deposits volume can be calculated by summing all the voxels attributed to this material. The result of $0.48 \pm 0.10 \text{ mm}^3$ is given in **Table 1**. This value is overestimated as the image resolution is larger than typical electrodeposits dimensions (Bai et al. 2016). It follows that, depending on the threshold value chosen for the segmentation, an overestimation of the deposit volume is probable which tends to increase with the amount of porosity. So, even if the microstructure has typical dimensions smaller than that of the tomography resolution, this proof-of-concept experiment highlights the potential of neutron imaging in determining the overall shape and nature of heterogeneous electrodeposits as well as cell assembly defects within electrochemical cell comprising X-ray attenuating materials.

To get further insight on the fine structure of the deposits, cell_A was then imaged at a synchrotron X-ray tomography beamline. A typical tomography image of the entire cross-section of the active cell is shown in **Figure 5a**. Thanks to the voxel size of $0.64 \mu\text{m}$, the ^6Li deposits are clearly seen as they attenuate less X-rays than the liquid electrolyte. The ^6Li deposits develop a needle-like dendritic morphology in accordance with the finding of Brissot and coworker (Brissot et al. 1999c). In addition, the LiAl domain is easily discernable at the top and bottom part of the cell showing interface degradation. A segmentation process was then performed on the X-ray images and the dendrites in the electrolyte were segmented based on their gray level (very dark dendrites). However, synchrotron tomography has a very coherent X-ray source leading to dark/light fringes due to phase contrast (Vanpeene et al. 2020). As seen in **Figure 5a**, the interfaces of the curved Li foil have different gray levels. An automatic grayscale segmentation of the curved foil was therefore unsatisfactory and thus

manually corrected. An illustration of this process is provided in **Figure 5b** and the resulting 3D rendering volume in **Figure 5c**. From this segmentation process, the dendrite volume was calculated to be $0.14 \pm 0.01 \text{ mm}^3$, a value also included in **Table 1**. A factor of 3.4 separates the dendrite volume measured by neutron and synchrotron X-ray analysis which is mainly due to the difference in imaging resolution.

For completeness, cell_A was imaged at the laboratory X-ray tomograph with a $2.0 \text{ }\mu\text{m}$ voxel size. In **Figure 6a**, a cross-section image corresponding to the same area as the one reported in **Figure 5a** is shown. Similar observations of the cell can be made compared to the synchrotron X-ray and neutron based images. It should also be noted that the cell was imaged at the neutron and X-ray beamlines, and laboratory tomograph within few weeks. The morphology of the electrodeposit is then preserved over time. Therefore, post-cycling analyses can be performed with confidence several days or weeks after the electrochemical experiment. After the scan, the segmentation process was performed and the dendrite volume was reconstructed in 3D as depicted in **Figure 6b** and **6c**, respectively. A Li dendrite volume of $0.15 \pm 0.02 \text{ mm}^3$ was calculated, a value also reported in **Table 1** which is in the same range than the one obtained from synchrotron X-ray imaging. This result is in agreement with the fact that the signal-to-noise and contrast-to-noise ratios of a laboratory tomograph is lower than for synchrotron beamlines leading to lower resolution images with lower contrasts (Vanpeene et al. 2020b). The dendrite volumes measured with the X-ray sources are similar while at larger voxel size by neutron tomography the measured dendrite volume is higher by at least a factor 3 with higher uncertainty. This difference is attributed to lower resolution of the neutron tomography images leading to the selection of voxels comprising a mixture of Li dendrite and electrolyte (partial volume effect) during the segmentation process. While the neutron imaging resolution is unavoidably lower because of the technical constraints of the technique, the capacity of neutrons to discern different isotopes can be exploited to pinpoint the origin and the composition of the Li comprising the dendrites. It would then be of interest to discern the chemical composition within dendrites between Li originating from the anode (^6Li in this study) to that from the Li salt of the electrolyte (mainly in ^7Li here).

4 Conclusion

We report an *in situ* neutron tomography imaging of Li electrodeposits in a cycled ^6Li -Li cell by taking advantage of the capability of the neutron imaging beamline and the intrinsic contrast of Li isotopes to neutron. This proof-of-concept experiment shows that the overall morphology of the deposits can be captured by neutron tomography. The deposit volume could be measured and compared to those obtained by X-ray techniques. To go further, several experimental parameters need to be optimized to move towards higher resolution and contrast in shorter acquisition times. For the proposed electrochemical cell, the use of neutron transparent buffer metal layer in between Al parts and Li metal while being chemically and electrochemically stable is a necessity as is the reduction of the cell diameter. As for the beamline, the foreseen increase in capabilities will permit to close the resolution and contrast gap between neutron and laboratory X-ray tomograph. In addition, the study of uncycled cell also highlights the importance of 3D analyses in order to validate the design of electrochemical cell as it allows the identification of assembly defects such as deformed electrodes or entrapped gas bubble that must be taken into account for electrochemical and impedance measurements. *In situ*

neutron tomography permits to envision the thorough study of battery failure modes in electrochemical cells comprising X-ray attenuating materials. The capacity of neutrons to discern different isotopes can be then a tool get insight on the origin and the composition of the Li deposits by distinguishing between Li from the anode (^6Li is this study) to that from the Li salt electrolyte (mainly in ^7Li here).

5 Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

6 Author Contributions

DD, AT, FA, RB, and LL designed the project study. LM, LL, EM, AK, RB, AT, and DD conducted the experiments. LM, LL, EM, RB, AT, and DD analyzed the data. LM, FA, EM, RB, AT, and DD wrote the manuscript. All the authors commented on the manuscript.

7 Funding

This work was supported by the French Agence Nationale de la Recherche ANR grant SHUTTLE (ANR-19-CE05-0023).

8 Acknowledgments

We acknowledge the French Agence Nationale de la Recherche ANR for its financial support. A portion of this work was performed through beamtime proposal to the NeXT beamline at ILL (beamtime no. UGA-52 and UGA-91) and PSICHE beamline at the SOLEIL synchrotron (beamtime no. 20190532)

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10 Table

Tomography	Synchrotron X-ray	X-ray laboratory	Neutron
Voxel size (μm)	0.64	2.0	7.4
^6Li deposit volume (mm^3)	0.14 ± 0.01	0.15 ± 0.02	0.48 ± 0.10

Table 1. Comparison of the ^6Li deposit volume from the volume segmentation process depending on the tomography techniques and their voxel size.

11 Figure captions

Figure 1. X-ray tomography image of an uncycled ^6Li -Li cell using a laboratory scanner and recorded at room temperature.

Figure 2. Impedance spectra recorded at 25 °C of the electrochemical cells (filled symbols) before and (open symbols) after cycling for (A) cell_A and (B) cell_B. The inset in (A) shows the electrical equivalent circuit used to fit all the spectra.

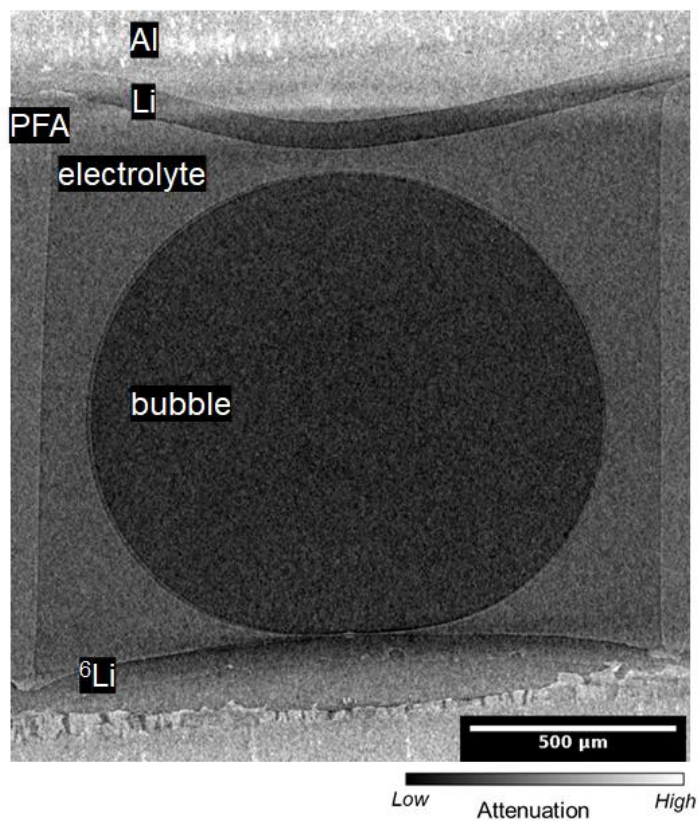
Figure 3. Cell voltage at 25 °C during the galvanostatic step for (solid curve) cell_A and (dotted curve) cell_B.

Figure 4. Typical image of the cycled ^6Li -Li Cell_A recorded at room temperature from (A) neutron radiography (transmission contrasts), (B) slice of the reconstructed 3D stack obtained by neutron tomography (absorption contrasts), (C) result of the segmentation process performed on the slice shown in (B), and (D) volume rendering from the segmentation process.

Figure 5. Typical image of the cycled ^6Li -Li Cell_A recorded at room temperature from (A) synchrotron X-ray tomography imaging, (B) the segmented slice and (C) volume rendering from the segmentation process.

Figure 6. Typical image of the cycled ^6Li -Li Cell_A recorded at room temperature from (A) laboratory X-ray tomography imaging, (B) segmented slice and (C) volume rendering from the segmentation process.

722 12 Figures



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724 **Figure 1.**

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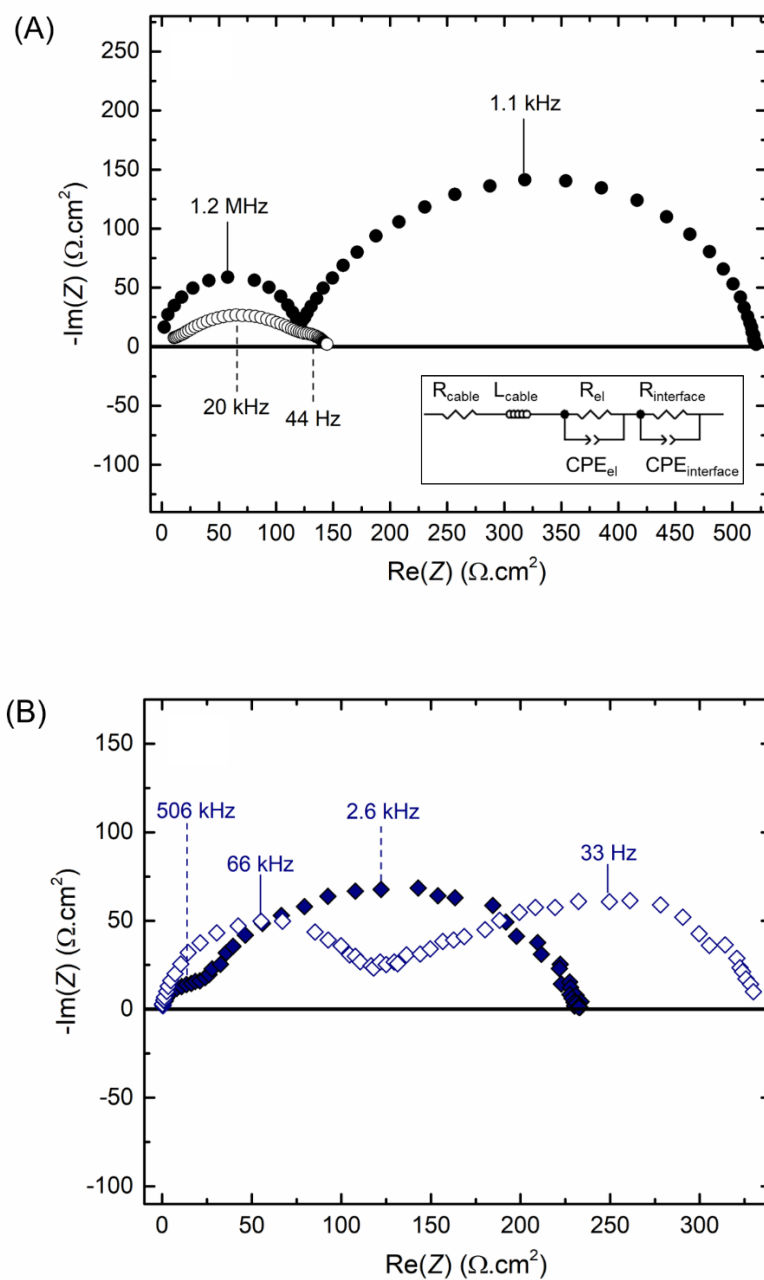
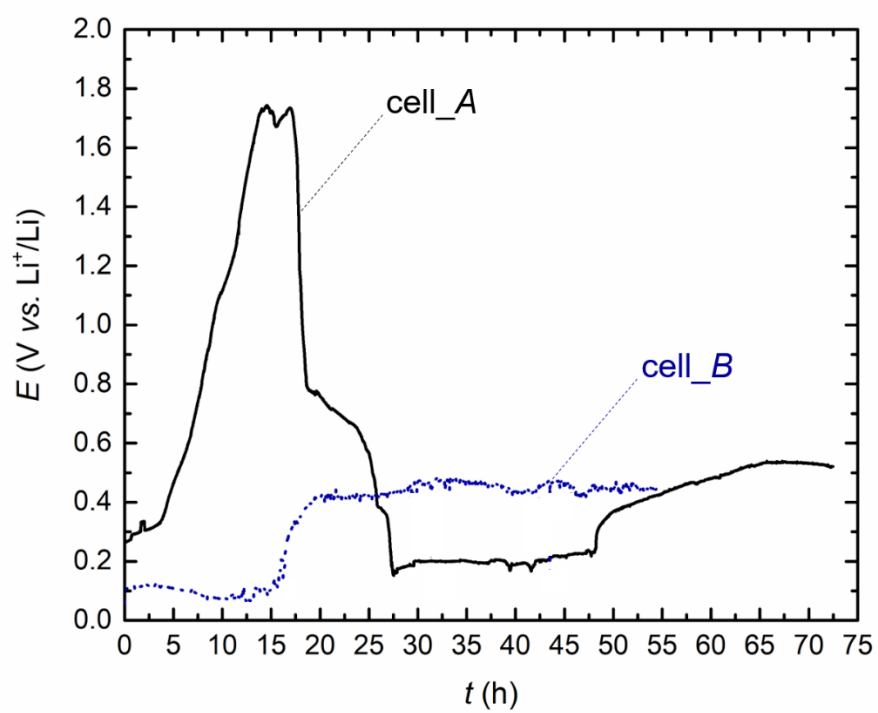


Figure 2.



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732 **Figure 3.**

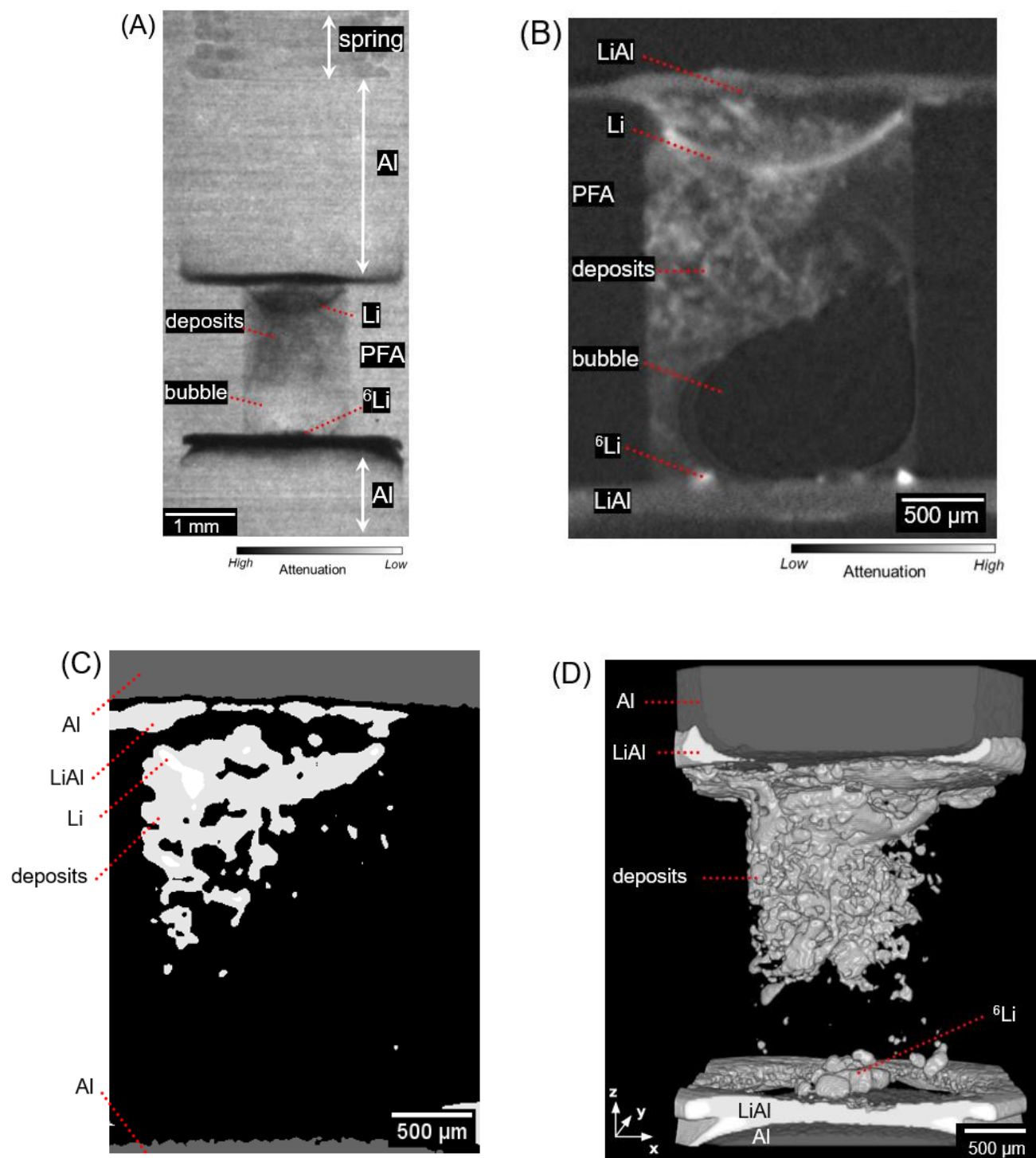
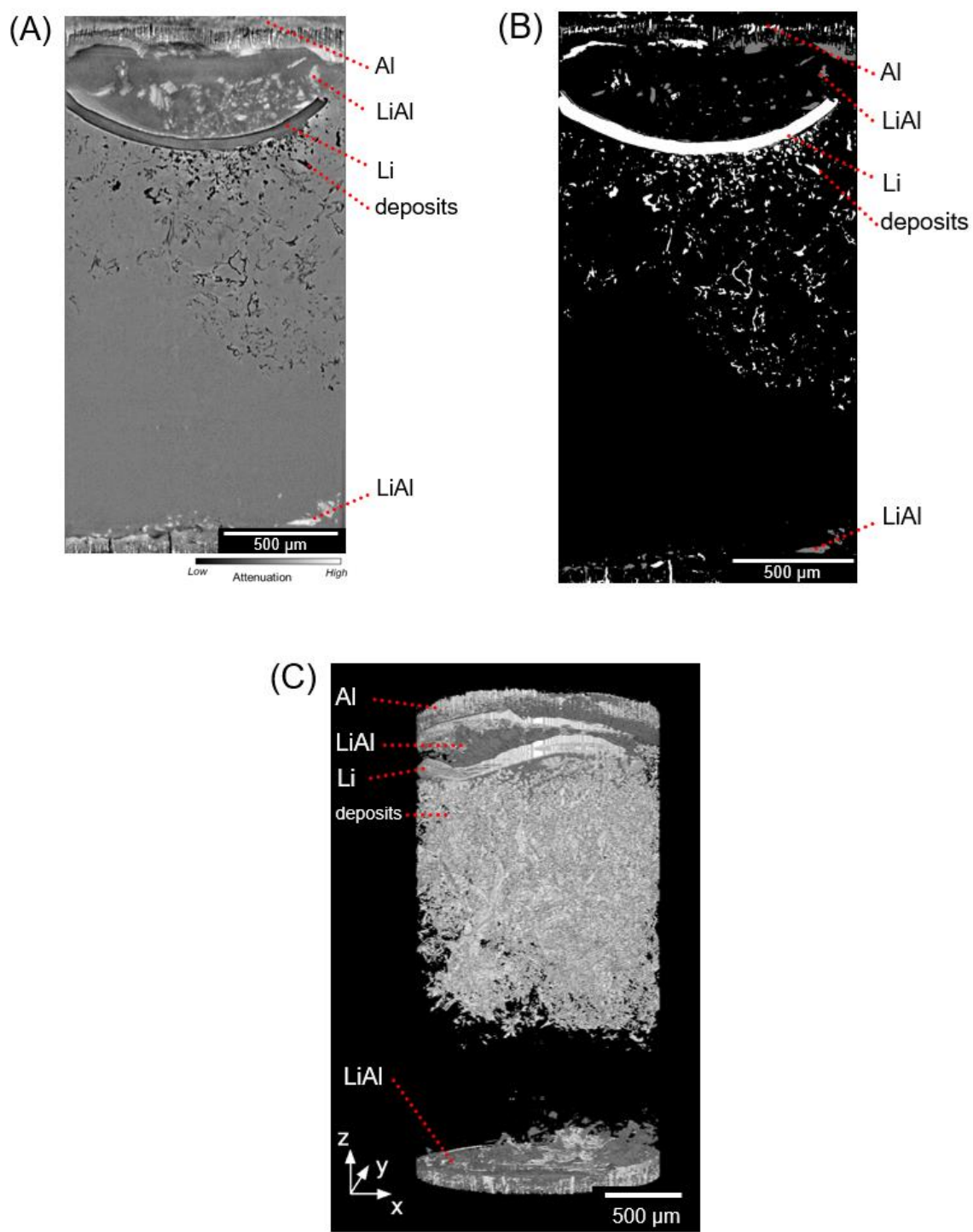


Figure 4.

**Figure 5.**

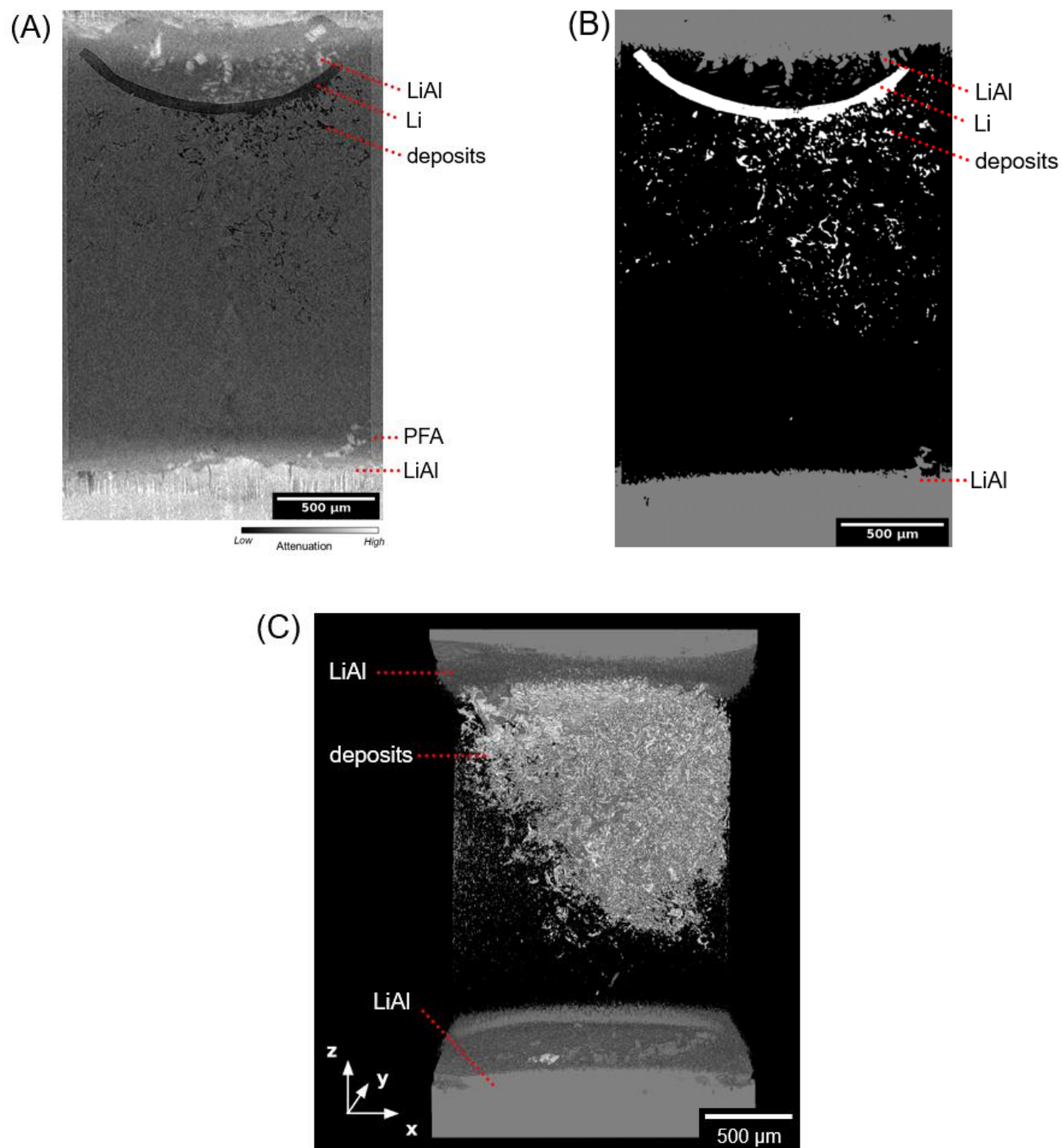


Figure 6.