ENERGY STORAGE
a global challenge

The development of energy storage solutions, especially for batteries, has been one of the most active industrial fields for many years. The stakes are getting higher to this day with the exponential growth of electric mobility, connected objects and means of communication.

The current context of energy storage

There is one basic principle when talking about electrochemical battery: transforming electrical energy into chemical energy during charging and conversely to restore electrical energy during discharge. This tenet has been used in lead batteries for 150 years. Designed more than 30 years ago, Lithium-ion batteries are as for today the most widespread solution in various sectors. Its very high efficiency (3 times more power than a lead battery of the same weight) and the large number of cycles make it the most efficient solution. Nevertheless, there are many issues to improve existing products: storage capacity, manufacturing cost, safety, ecological cost and of course life expectancy. The work detailed in this application note was focused on these last two points.

Introduction to *Lithium-ion batteries*

Li-ion batteries are made up of a multitude of cells, each one being able of generating a few volts. Every cell is formed of two electrodes that will exchange ions, lithium in Li-ion batteries. These ions come mainly from the electrolyte salts present in the cell.

The electrodes of Li-ion batteries consist of a porous network of active particles, a conductive additive and a binder. The 3-dimensional distribution of these 3 components plays a crucial role in the battery's charge capacity.

The Li+ ions migrate from the anode to the cathode during the discharge according to a reversible phenomenon that allows the battery to be recharged as shown in the diagrams below.

The analysis on a very small scale of the chemical components of the electrodes is then an essential key to improve the performance of the batteries.

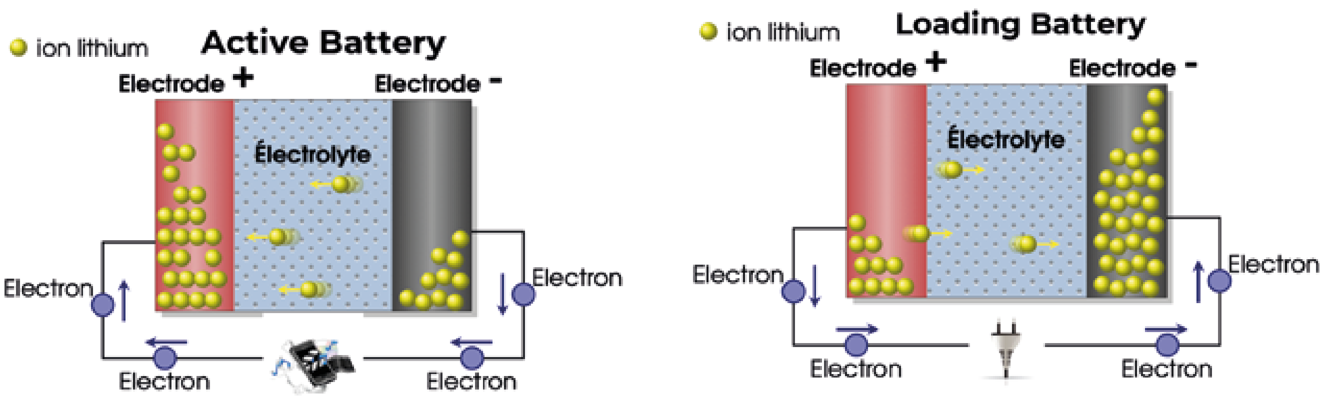

Diagram and principle of operation of a Li-ion battery

Conventional means of materials analysis often require the destruction of the sample and do not allow the evolution of a battery to be monitored over the charge and discharge cycles. In addition, these techniques provide two-dimensional information only, which is unsuitable for the analysis of a three-dimensional porous network.

X-Ray micro-tomography provides a technical solution to the challenge of understanding the mechanisms of electrode degradation over cycles:

- The acquisition method allows to set up "in situ" measurements to follow the phenomenon over time by subjecting the cell to charge/discharge cycles.

- The result is a volume of data that allows the three-dimensional analysis of the electrode on a sub-micron scale

The work carried out by *MATEIS lab of INSA Lyon*

The MATEIS laboratory of INSA Lyon (France) is a recognized research center in materials analysis. The team, led in particular by Eric Maire, was one of the pioneering laboratories in the use of X-Ray microtomography for the characterization of materials, via synchrotron sources and then with the help of lab equipment. The EasyTom 160 RX Solutions tomograph installed in Lyon in 2013 has made it possible to achieve laboratory resolutions close to those of synchrotron microtomography lines such as the ESRF in Grenoble, the SLS in Switzerland or Soleil in Paris, with wider access than in these large instruments.

Victor Vanpeene's doctoral work, conducted jointly with the Institut National de Recherche Scientifique (INRS) in Varennes (Canada), has led to advances in two different fields:

Electrode manufacturing process

Until now, the electrodes of Li-ion batteries use a formulation based on an organic binder (PVDF) soluble only in a solvent known to be highly carcinogenic and toxic (NMP). Much work has been done to replace the binder with a less polluting solution. In Victor Vanpeene's work, the binder used is a water-soluble compound: carboxymethyl cellulose or CMC.Results have shown that the performance obtained with active particles such as Silicon associated with CMC can be superior to current cells, in addition to being less polluting! However, a difficulty appears at the time of deposition on the porous carbonaceous substrate: the latter being hydrophobic, a classical process produces Silicon agglomerates which are very harmful to the efficiency of the cell. The analysis by X-ray micro tomography in the laboratory allowed to identify the best manufacturing process.

Electrode degradation during the charge/discharge cycle

As the operating characteristics of the cell are linked to the composition of the porous network of the electrode, the degradation of the electrode is observed by following the phenomena of expansion/contraction, degassing, crack formation and decohesion throughout the charge and discharge phases.

The tested material *Li-ion Cell*

The electrode analyzed is composed of 80% active silicon particles, 12% conductive additive and 8% binder. The active Silicon particles are obtained by grinding powder for 20 hours under a controlled atmosphere and then incorporated into a pasty solution with the binder and the conductive additive. The average diameter of the Silicon particles in the final mixture is 0.8 µm. The electrode is deposited on a carbon paper substrate instead of metal, mainly to avoid metallic artifacts that occur in tomography in the presence of a very dense material such as copper.

The counter electrode is composed of lithium metal and these two electrodes are separated by a fibrous separator soaked with an electrolyte which is a lithium salt (LiPF6) dissolved in an organic solution. The resulting assembly corresponds to a half cell.

The analyzed electrode is composed of :
- 80 % of active silicon particles
- 12% conductive additive
- 8 % binder

The operated equipment *EasyTom 160*

The EasyTom 160 microtomograph is the most resolute equipment in the RX Solutions range of machines. The X-Ray tube consists of an electric generator and an electron gun called "nanofocus". The very high level of electron beam focusing, and the fineness of the target allow to obtain a very small X-ray focus and to separate lines of the order of 300 nm. The tungsten target is deposited on a diamond window in order to obtain a focus of higher brilliance. The design of the tube provides the thermal and electrical stability required for submicron tomographic acquisitions.

The extremely precise air rotation stage and the use of different sensors allow to obtain very high-resolution tomographic reconstructions of excellent quality.

Microtomographe EasyTom 160

> ***The EasyTom 160 microtomograph is the most purposeful equipment in the RX Solutions range of machines***

The plane sensor produces remarkable images with relatively short acquisition times even at submicron resolutions but requires a sample size of a few millimeters at most to place the axis of rotation as close as possible to the tube.

The CCD camera allows, thanks to a pixel size of less than 10 µm, to reach voxel sizes of a few hundred nanometers, even with stronger constraints of sample dimensions as it is the case with an in-situ environment. The CCD camera is used for all the results presented in this paper.

The cabin of the EasyTom 160 is both compact for installation in a small laboratory and spacious to accommodate the sample environment. The wide access door facilitates installation operations.

Finally, the tomograph is controlled by the X-Act software, which provides the flexibility and fine-tuning needed to carry out experiments of this type.

Methodology *of the tomographic process*

The electrode is placed in an electrochemical cell in order to apply the charge/discharge cycles in place in the tomograph and to perform several acquisitions per cycle. The cell is held in a PTFE cylinder with an outer diameter of 1.2 mm. The small diameter allows the cell to be placed as close as possible to the tube in order to reduce scanning times and optimize the signal-to-noise ratio.

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The analysis of electrode degradation over the cycle requires a sufficiently short acquisition time to capture the degradation at time t and repeat the operation a large number of times. At the same time, the very small size of the desired phases, as well as the small absorption differences between these phases, require high resolution and sufficient contrast. Several scans were performed to identify the minimum scan conditions that would allow the segmentation of the different phases of the electrode.

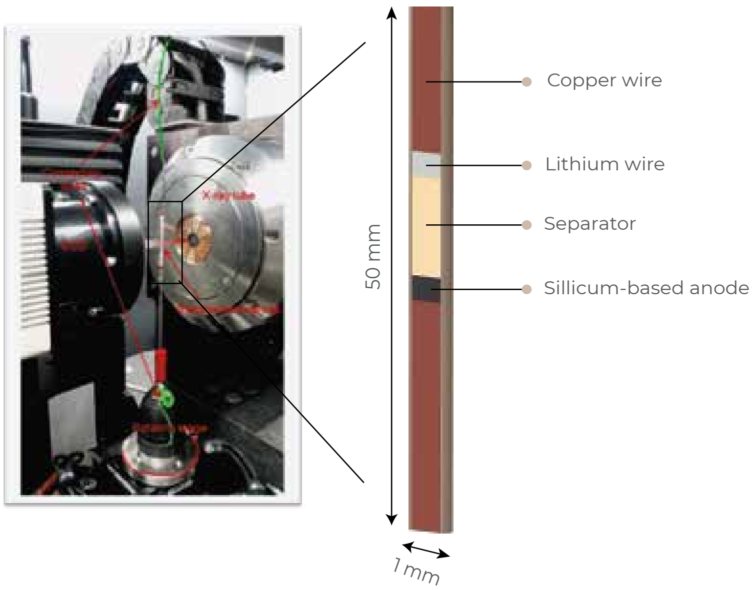
With the support of Jérôme Adrien and Joël Lachambre, engineers at the laboratory, Victor Vanpeene developed the conditions for acquisition and reconstruction on the EasyTom at the MATEIS laboratory.

The acquisition conditions chosen are as follows:

ID scan conditions	equipment	accelerating voltage	voxel size	acquisition time	reconstructed volume
#1	EasyTom 160	76 kV	700 nm	55 min	1358 x 1358 x 200 µm
#2	EasyTom 160	76 kV	800 nm	55 min	1358 x 1358 x 200 µm
#3	EasyTom 160	76 kV	800 nm	17 min	1358 x 1358 x 200 µm

The reconstruction algorithm used is a filtered back-projection implemented in the RX Solutions X-Act UniCT software.

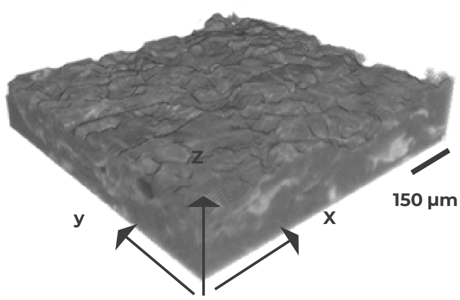
The cycling conditions used are set for a total cycle time of 18 hours, 9 hours for each phase (i.e. a so-called C/9 cycle). This kinetics should allow to perform several tomographies per cycle to observe the evolution of the electrode. Acquisition conditions #3 allowed to perform one measurement every hour, i.e. 18 scans over one cycle.



Scanning of the electrode in the X-ray tomograph. The electrode is placed in an electrochemical cell in order to apply charge & discharge cycles.

Results *of the tomographics process*

The tomographies obtained on the sample represent a volume of 1 mm x 1 mm x 0.16 mm. These consequent dimensions make it possible to carry out, on a representative volume, 3-dimensional analyses on the network formed by the 3 components of the electrode.



3D visualization of the volume obtained by X-Ray microtomography on the EasyTom 160 of MATEIS Laboratory .

3D visualization of the internal layers of a battery, with highlighting of the phenomenon of electrode swelling.

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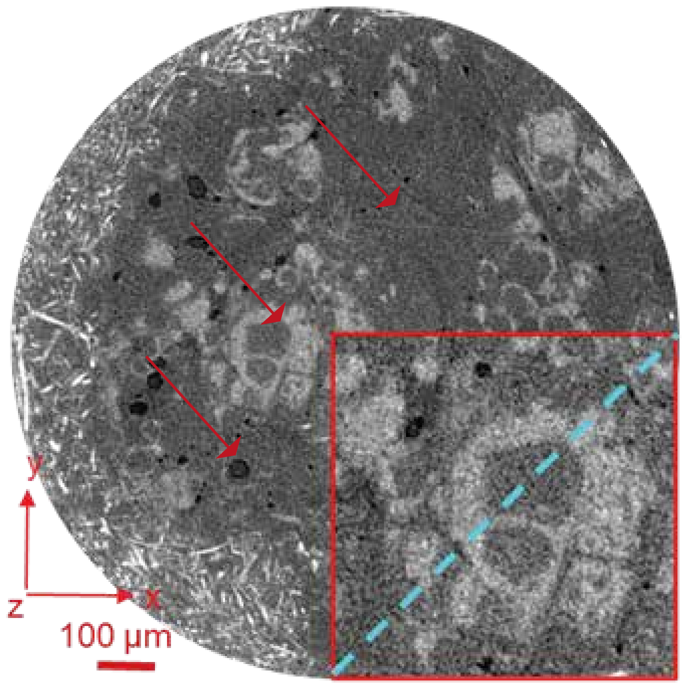
3D visualization of the volume obtained by X-Ray microtomography of a camera battery.

On the tomographic section opposite, we identify in the lighter regions the areas rich in Silicon, reflecting a higher attenuation to X-Rays.

The porosities, on the other hand, are the darkest areas, as the gas that composes them is very low in density and therefore has a very low attenuation. Some carbon fibers of the paper used for the substrate are visible but difficult to differentiate from the binder and the additive because of the very close value of the attenuation of these phases all composed of carbon.

The lightest areas correspond to the areas rich in Silicon. Conversely, the darkest areas indicate the presence of gas bubbles. The matrix composed of the binder, the additive and the substrate presents little contrast, as the X-Ray attenuation levels are very close.

The relatively high noise level in the image is due to the in situ test conditions and a relatively short time of exposure. acquisition deliberately kept short.

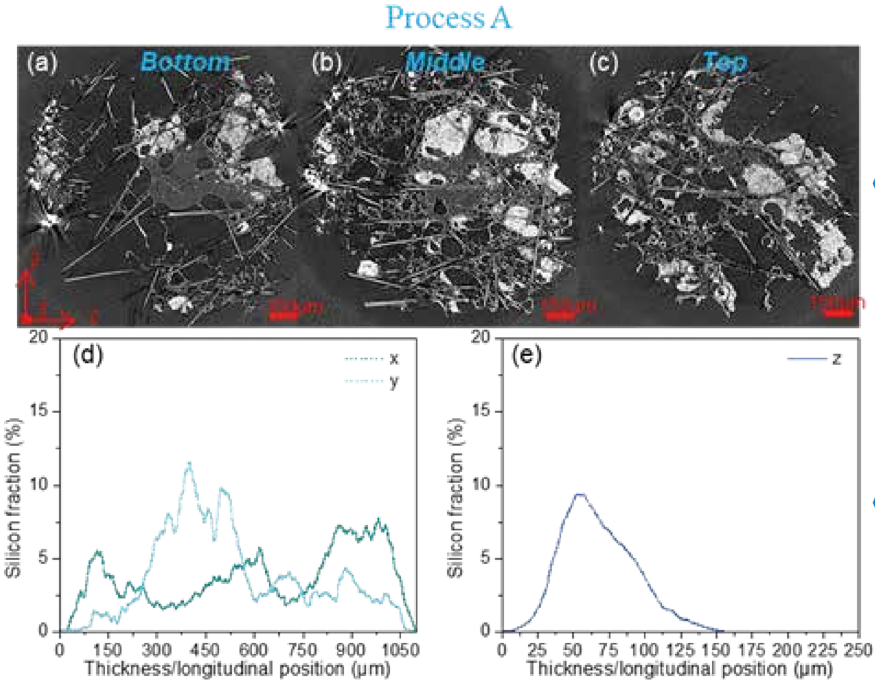


The lightest areas correspond to the areas rich in Silicon. The darkest areas indicate the presence of gas bubbles. The X-ray attenuation levels are very close. The relatively high noise level in the image is due to the "in situ" test conditions and a relatively long acquisition time deliberately short

Electrode manufacturing process

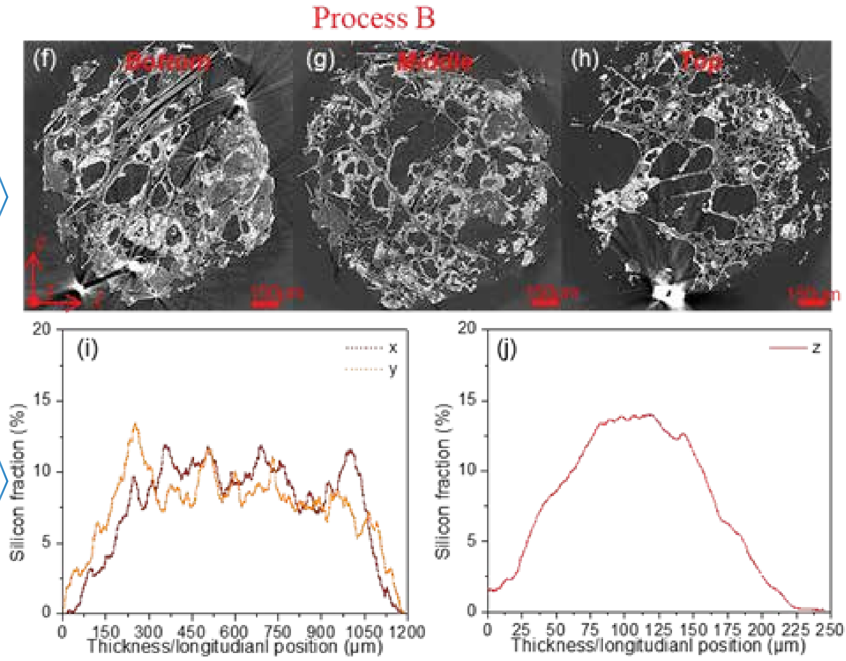
During the manufacture of the electrode, a homogeneous distribution of the active particles in the porous matrix offers better performance due to better ion circulation and reaction (swelling, etc.). This contributes to a more homogeneous electrode overall, which contributes to its proper functioning.The very high resolution scans obtained on the tomograph of the MATEIS laboratory have allowed to qualify different electrode manufacturing processes : after treatment and segmentation of the tomographic images, we extract the distribution of silicon in the volume.

Process A uses a purely aqueous solution when making the dough, while Process B uses a mixture of 10% isopropanol.



Transverse tomographic sections of the electrode obtained with the process A. Scan Condition #1. Silicon agglomerates are highly visible as large white grains.

Silicon fraction curve calculated from the volume tomographic tomography according to the position in the volume. The distribution is very heterogeneous especially in the thickness of the electrode



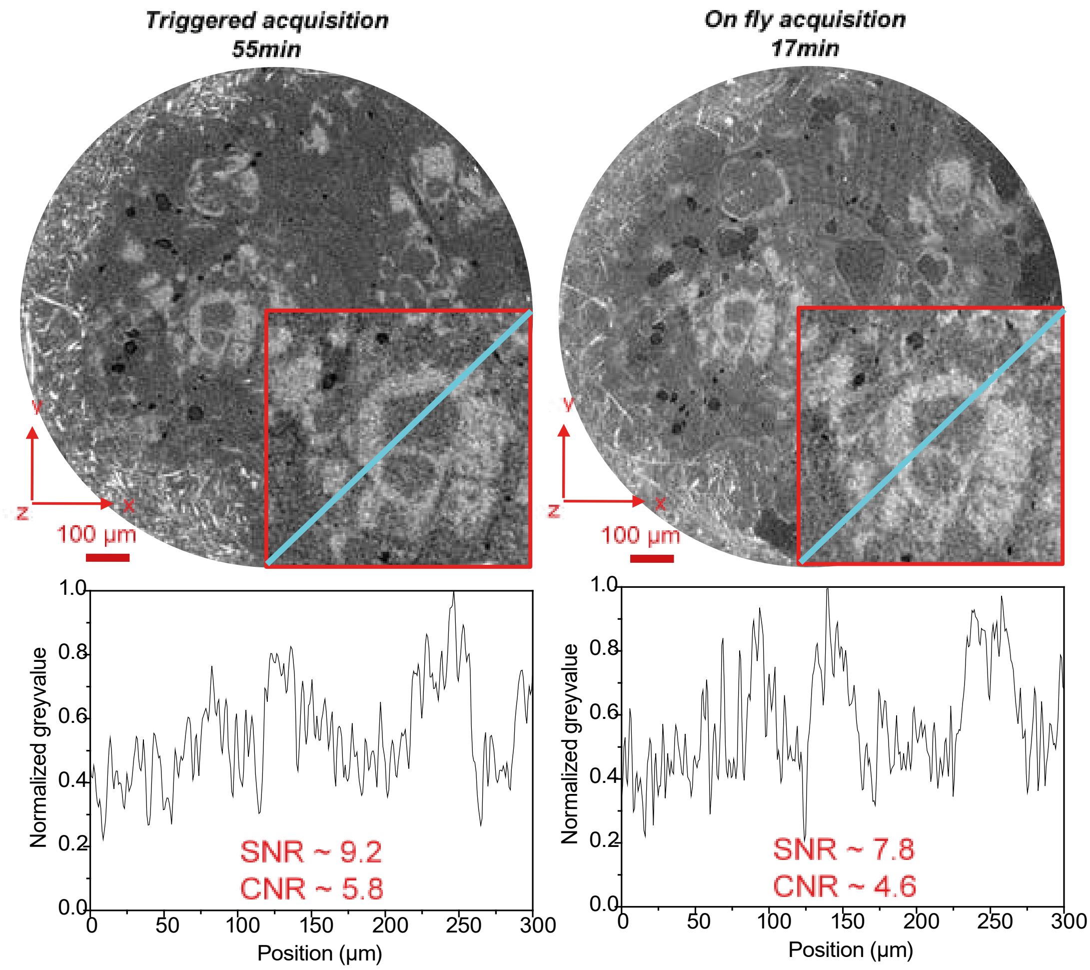
Transverse tomographic sections of the electrode obtained with the process B. Scan condition #1. Silicon is distributed in small white grains or around the porosities.

Silicon fraction curve calculated from the tomographic volume according to the position in the volume. The distribution is quite homogeneous in the 3 directions

Electrode degradation during the charge/discharge cycle

In order to reduce the acquisition time, the acquisition parameters were worked on by the team. The results presented in the following figure are obtained using an acquisition mode in continuous rotation instead of step-by-step mode and by suppressing the projection averaging. It is shown that a 17-minute acquisition has sufficient contrast levels for allow the segmentation of silicon-rich phases. Namely that 55 minutes is already an acquisition time low enough for a laboratory tomograph at sub-micron resolution.

The reduction to 17 minutes while maintaining sufficient acquisition quality is a step forward which opens the way to in situ analysis and characterization of the different stages of each charging and discharging phase. This type of analysis was until then almost exclusively reserved for synchrotron experiments.



Comparison of cross sections obtained with acquisition times of 55 and 17 min respectively. The analysis of the signal-to-noise ratio (SNR) and contrast-to-noise ratio (CNR) shows the small difference between the results of the two measurements. It is therefore possible to reduce the acquisition time to 17 min.

The following results are extracted from the in situ experiment carried out on the cell during the first cycle. A series of 18 CT scans were performed during the cycle. The sections below correspond to 5 phases of this first charge/discharge cycle.

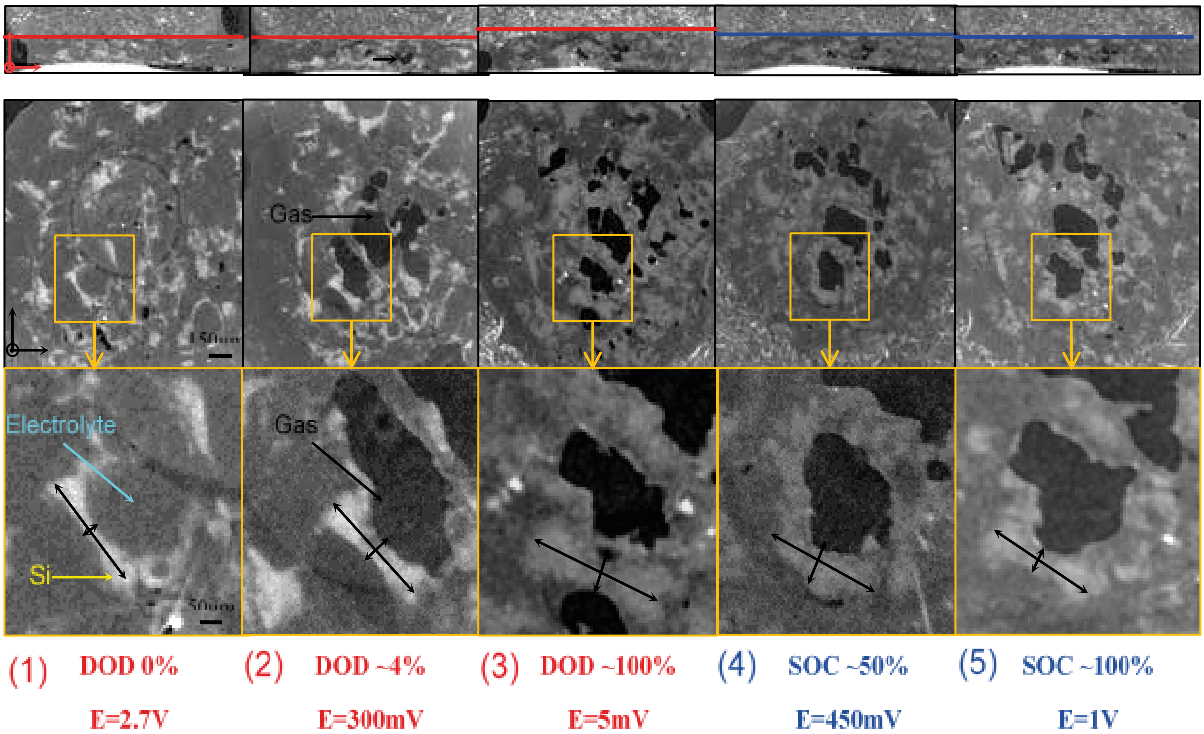
Electrode Swelling

The first cut made in the initial state shows little porosity and the presence of electrolytes. As the charge progresses, the quantity of porosities created by the degassing increases, increasing the volume of the electrode: we can thus see on the vertical section (line upper) the raise of the red dotted line of demarcation of the electrode with the separator.

The curve obtained from all the measurements shows that the increase in thickness is relatively linear and reaches 60% at the end of the charge (red curve). On the other hand, the contraction during discharge is not total: an irreversible expansion of 20% remains. Over the whole duration of the experiment the expansion is quantified in the 3 directions thanks to the 3D volume.

Lithiation

The first three acquisitions (columns 1 to 3) also show a decrease in the gray level of the Silicon particles. This corresponds directly to their chemical evolution: the lithiation phenomenon transforms Silicon into lithiated Silicon, 3 times less absorbent. We can directly observe the combination of Li+ ions with Silicon during the battery charging.



Tomographic sections obtained in situ on the EasyTom 160 microtomograph from the MATEIS laboratory in Lyon. Top line: vertical section in the cell. The dotted line locates the interface between the electrode and the separator. Next lines: horizontal section in the electrode. From left to right: First cycle of discharge/recharge of the cell to approximately 0%, 5% and 100% of the charge, 50% and 100% of the discharge.

On the slices obtained at the end of the cycle, a lower gray level is observed for the silicon particles. than in the initial state, which corroborates the total non-reversibility of the chemical phenomena.

Cracks

One can also guess delaminations between the Silicon and the rest of the matrix, but the quality of the images in in situ condition is insufficient for quantification. It would be interesting to redo an ex situ acquisition on the tomograph, to evaluate this aspect. Indeed, the solution in the cell reduces the phase contrast phenomena, which although weak on laboratory equipment are present and can allow to view such details.

The use of a laboratory microtomograph has been validated for the analysis of the microstructure. materials in Li-ion cells with Silicon electrode, both for ex situ analyses on an inert sample and for in situ experiments. It is thus possible to quantify with the EasyTom 160 the three-dimensional distribution of the Silicon in the electrode, and observe a number of degradation phenomena during a cycle.

This breakthrough enables laboratories and research centers to significantly accelerate their work while still relying on synchrotron sources when the limitations of the laboratory equipment are reached.

To go further:
https://www.researchgate.net/publication/326989238_Charactrza-tion_of_the_3D_microstructure_of_battery_electrodes_by_in_situ_X-ray_tomography_Application_to_a_Si-based_anode_for_Li-ion_batteries

INDUSTRIAL COMPUTED TOMOGRAPHY
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24 bis Rue Uranus - ZAC Altais
FR - 74650 Chavanod
+ 33 4 50 67 39 52
sales@rx-solutions.com
www.rx-solutions.com