Supplementary Information: Monitoring Lithiation Gradients in Solid-state Batteries Using *Operando* Neutron Radiography

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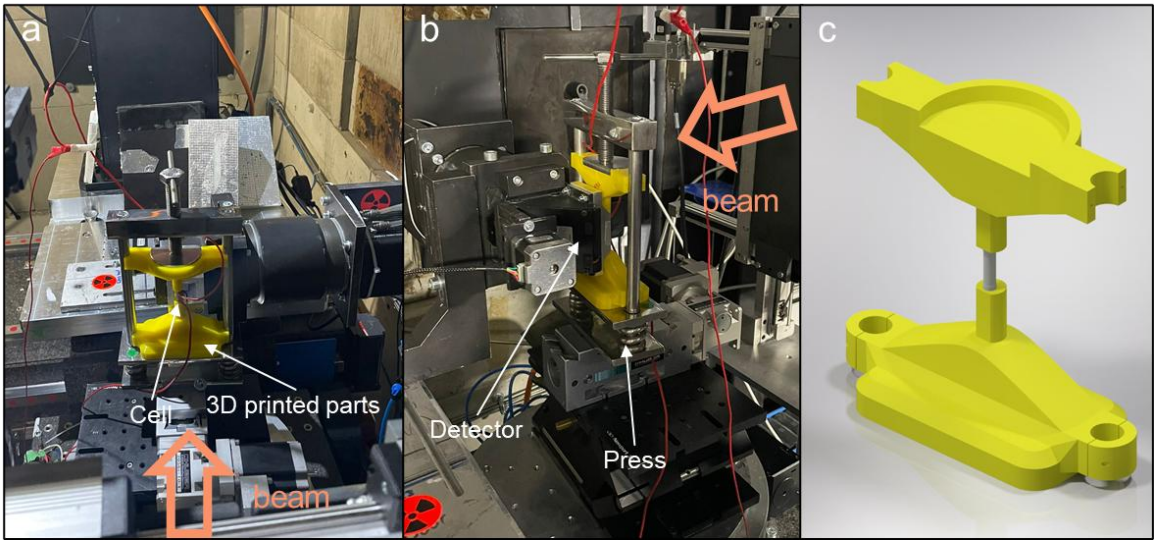


Figure S1: Pictures of the experimental setup at NeXT instrument in a) the same direction of the beam and b) a side view. c) the 3D printed frame that it fixed in the modified dental press, which allowed high spatial resolution neutron radiography imaging.

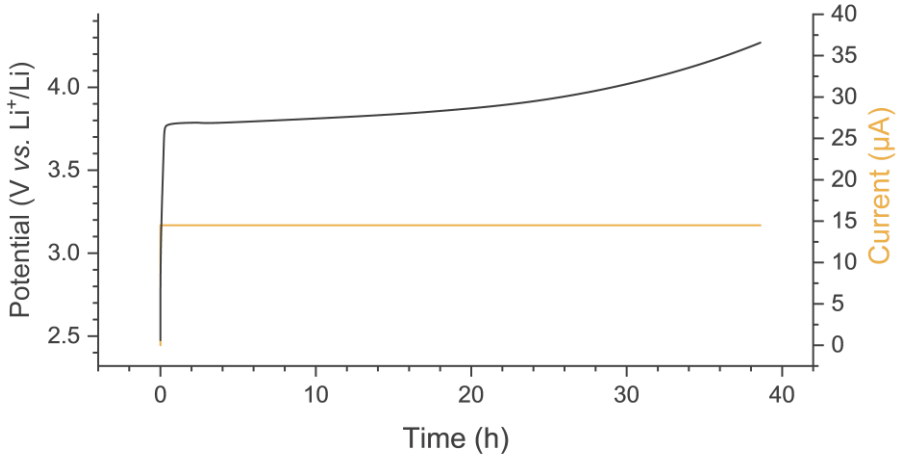


Figure S2: First charge of the cell (NMC532 vs. $In^{6}Li_{0.3}$, with LPSCl as a solid electrolyte) cycled at a C/40 rate and 25°C in the laboratory between 2.5 to 4.3 V vs Li^{+}/Li.

Note S1. Concentration calculations

a. Pristine state

Since the composite electrode is made of natural Li as well as the solid electrolyte, we can expect to have a natural $^{6}Li/^{7}Li$ exchange between the counter electrode made of In^{6}Li and the rest of the cell made of natural Li (considering that natural Li is made of 92.6% of ^{7}Li and 7.4% of ^{6}Li). Thus, when starting the *operando* imaging measurement, we can "easily" calculate the ^{6}Li concentration of the CE since (i) the concentration is known from the weighed cell fabrication, (ii) it has been enriched to an exact concentration of ^{6}Li, and (iii) that the self-diffusion from the In^{6}Li to the positive electrode through the thick electrolyte is neglectable at the pristine state (initial time t_0) and that the cell was also charged without being set to rest for a long period.

The quantity of lithium has been calculated from the weights during the sample fabrication ($n_{Li\ tot}$). The volume occupied by the cell components, and in particular the CE, has been measured on the images, as a clear distinction between the CE and the separator can be seen. The projection area of the composite electrode has been measured using Fiji software[39] as follows:

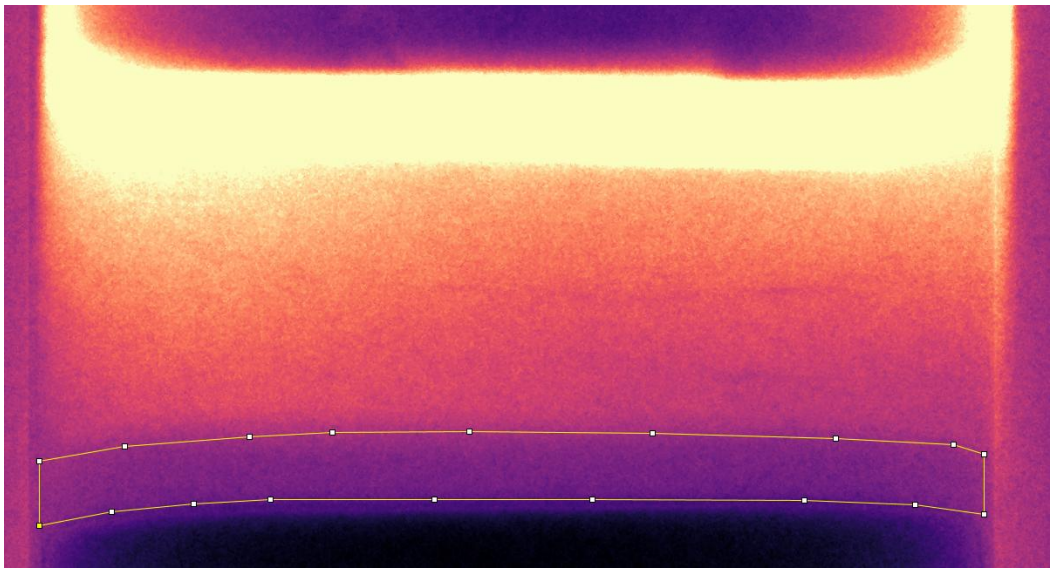


Figure S3: Measurement of the projected area (highlighted in yellow) of the positive electrode by image analysis at the charged state.

Then, the volume occupied by the CE has been calculated with the following formula:

$$V = \frac{\pi D}{4} \times A \qquad (1)$$

With V the volume in cm^3, D the diameter in cm, and A the projected surface area in cm^2 (highlighted in yellow in **Figure S3**).

Taking the lithium natural abundance ($^6Li/^7Li$) at 7.4 %/92.6 % and knowing the quantity of lithium inside the composite electrode, the concentration can be calculated. The same calculation can be obtained with the separator and the negative electrode. The values are summed up in **Table S1**.

Table S1: Concentration calculation of the pristine state of the composite electrode (CE), the separator, and the negative electrode.

Metrics in pristine state	**Composite electrode (70%w NMC + 30%w LPSCl)**	**Separator (LPSCl)**	**Negative electrode (In^6Li)**
Mass $m_{Li\ LPSCl}$ (g)	1.60×10^{-3}	1.16×10^{-2}	/
Molar mass $M_{Li\ LPSCl}$ (g/mol)	2.68×10^{2}	2.68×10^{2}	/
Amount of substance n_{LPSCl} (mol)	5.96×10^{-6}	4.32×10^{-5}	/
Amount of substance $n_{Li\ LPSCl}$ (mol)	3.58×10^{-5}	2.59×10^{-4}	/
Mass m_{AM} (g)	3.80×10^{-3}	/	7.50×10^{-1}
Molar mass M_{AM} (g/mol)	9.66×10^{1}	/	6.02
Amount of substance $n_{Li\ AM}$ (mol)	3.94×10^{-5}	/	1.25×10^{-1}

Pixel size (cm)	2.65×10^{-4}	2.65×10^{-4}	2.65×10^{-4}
Horizontal area A (from image) (pix²)	96714	354429	109017
Horizontal area A (from image) (cm²)	6.79×10^{-3}	2.49×10^{-2}	7.66×10^{-3}
Height h (cm)	2.26×10^{-2}	8.30×10^{-2}	2.55×10^{-2}
Volume V (from image) (cm³)	1.60×10^{-3}	5.86×10^{-3}	1.80×10^{-3}
Amount of substance $n_{Li\ tot}$ (mol)	7.51×10^{-5}	2.59×10^{-4}	1.25×10^{-1}
Concentration Li_{tot} (at/cm³)	2.83×10^{22}	2.66×10^{22}	4.16×10^{22}
Concentration ^{6}Li (at/cm³)	**2.15×10^{21}**	**2.02×10^{21}**	**3.95×10^{25}**
Concentration ^{7}Li (at/cm³)	2.61×10^{22}	2.46×10^{22}	2.08×10^{22}

b. Infinite time diffusion

To calculate the infinite time diffusion concentration in each component, the total amount of substance of ^{6}Li and ^{7}Li is calculated in the entire cell based on the previous calculation in **Table S1**. The average content of ^{6}Li in the entire cell is calculated, and the final ratio of abundance to infinite time diffusion is determined. This ratio is then used on the amount of substance of the total Li content in each component. The results, presented in **Table 1**, will also be shown in the scheme in **Figure 3**.

c. Charged state

The cell has then been charged in the laboratory, and the composite electrodes have been delithiated. Assuming that every coulomb exchanged during charging is caused by the delithiation of the active materials, and that only Li^+ can move in the cell, we can determine the quantity of lithium "plated" at the negative electrode ($n_{Li\ electrochem\ plated}$) using the Faraday's law. As the composite electrode is being delithiated, this amount can be subtracted from the previous

amount of lithium $n_{Li\ AM}$ calculated in **Table S1** for the composite electrode to obtain the lithium concentration after the first charge.

Table S2: Concentration calculation at the delithiated state of the composite electrode.

Charged composite electrode (CE): delithiated state (70%w NMC + 30%w LPSCl)	
Metrics	Value
$n_{Li\ electrochem\ plated}$ (mol)	2.19×10^{5}
$n_{Li\ CE\ delithiated}$ (mol)	5.32×10^{5}
$at_{Li\ CE\ delithiated}$ (at)	3.20×10^{19}
Concentration $Li_{CE\ delithiated}$ (at/cm^3)	2.00×10^{22}
Concentration $^6Li_{CE\ delithiated}$ (at/cm^3) (7.4 %)	1.50×10^{21}
Concentration $^7Li_{CE\ delithiated}$ (at/cm^3) (92.6 %)	1.85×10^{22}

d. Charged state (beginning of the neutron experiment)

The cell has then been placed in the beam line. The dark and flat field images have been taken, and the neutron radiography acquisition has been started while the cell is being discharged. Once again, considering that every coulomb is only dedicated to the lithiation/delithiation of the composite electrode, we can determine the quantity of lithium reinserted in the composite electrode ($n_{Li\ electrochem\ stripped}$). Hence, this amount can be added to the previous amount of lithium $n_{Li\ CE\ delithiated}$ corresponding to the delithiated state, calculated in **Table S2**. However, in the relithiation, due to the enriched negative electrode with ^6Li and the exchange of $^6Li/^7Li$ that could have happened between the negative electrode and the separator, the reinserted Li^+ in the NMC may not be in the same ratio as the natural abundance of lithium isotopes.

Table S3: Concentration calculation at the relithiated state of the composite electrode.

Recharged composite electrode: relithiated state (70%w NMC + 30% w LPSCl)	
Metrics	Value
$\mathbf{n_{Li\ electrochem\ discharge}}$ **(mol)**	1.81×10^{5}
$\mathbf{n_{Li\ CE\ relithiated}}$ **(mol)**	8.89×10^{5}
$\mathbf{at_{Li\ WE\ relithiated}}$ **(at)**	5.35×10^{19}
Concentration Li $_{\mathbf{WE\ lithiated}}$ **(at/cm^3)**	3.35×10^{22}
Concentration ^{6}**Li**$_{\mathbf{WE\ lithiated}}$ **(at/cm^3) (7.4 %)**	2.51×10^{21}
Concentration ^{7}**Li**$_{\mathbf{WE\ lithiated}}$ **(at/cm^3) (92.6 %)**	2.32×10^{21}

Note S2. Quasi-stationary state of transport during charging through the separator

The majority of ^{6}Li in the system is present in the In^{6}Li negative electrode at the pristine ($n_{6Li\ neg.\ elec.}$), as opposed to the natural abundance in the rest of the cell. When a gradient of concentration is present, ^{6}Li will diffuse in different ^{nat}Li materials[40,41]. During the charge, when transport processes are in opposite direction, the ^{6}Li concentration along the separator is at a quasi-stationary state (Figure 5). In other words, the total ^{6}Li flux is equal to zero indicating that the flux of isotopic diffusion and of the electrochemical migration are counterbalancing each other and can be considered as equal during the charge. The following equation describe this state:

$$J_{diff} = -J_{migr} \qquad (2)$$

Conduction associated to ^{6}Li in the separator

As we are only following the ^{6}Li isotope with the neutron radiography, we need to determine the associated average enrichment of ^{6}Li along the separator.

The average ^{6}Li concentration during the charge is measured along the separator at 3.28 x10^{21} at/cm^3. Compared to the initial calculated value of ^{6}Li concentration in the separator (2.02 x10^{21} at/cm^3), this corresponds to an average 12% of ^{6}Li enrichment.

The electrochemical migration flux is defined by the equation that follows:

$$J_{migr} = \frac{Z_{^{6}Li} F}{RT} D_{^{6}Li} C_{^{6}Li} \frac{\partial \varphi(x)}{\partial x} = \mu_{^{6}Li} C_{^{6}Li} \frac{\Delta E}{L} = \frac{\sigma_{LPSCl} \times x_{^{6}Li}}{e} \frac{\Delta E}{L} \quad (3)$$

With σ_{LPSCl} the ionic conductivity of LPSCl (S/cm), x_{6Li} the fraction of ^{6}Li enrichment, e the elementary charge (in C), ΔE the potential difference between the positive and negative electrode (in V) and L the length of the separator (in cm).

Based on equations (2) and (3), the following equality can be written:

$$J_{diff} = D_{^{6}Li} \frac{\partial C}{\partial x} = -J_{migr} \quad (4)$$

By ordering equation (4), the diffusion coefficient can be calculated as follows:

$$D_{^{6}Li} = -J_{migr} \times \frac{\partial x}{\partial C} \quad (5)$$

The data are available in **Table S4**.

Table S4: Diffusion coefficient calculation based on the equivalent electrochemical migration.

Diffusion calculation	
Metrics	Value
x_{6Li}	12 x10^{-2}
σ_{6Li} (S/cm)	2 x10^{-3}
e (C)	1.602 x10^{-19}
ΔE (V)	3.26
L (cm)	8.3 x10^{-2}

J_{migr} (at/cm²·s)	5.88 x10^{16}
$\partial C/\partial x$ (at/cm^4)	2.43 x 10^{22}
$D_{6Li\ in\ 7LiPSCl}$ (cm²/s)	2.42 x10^{-6}

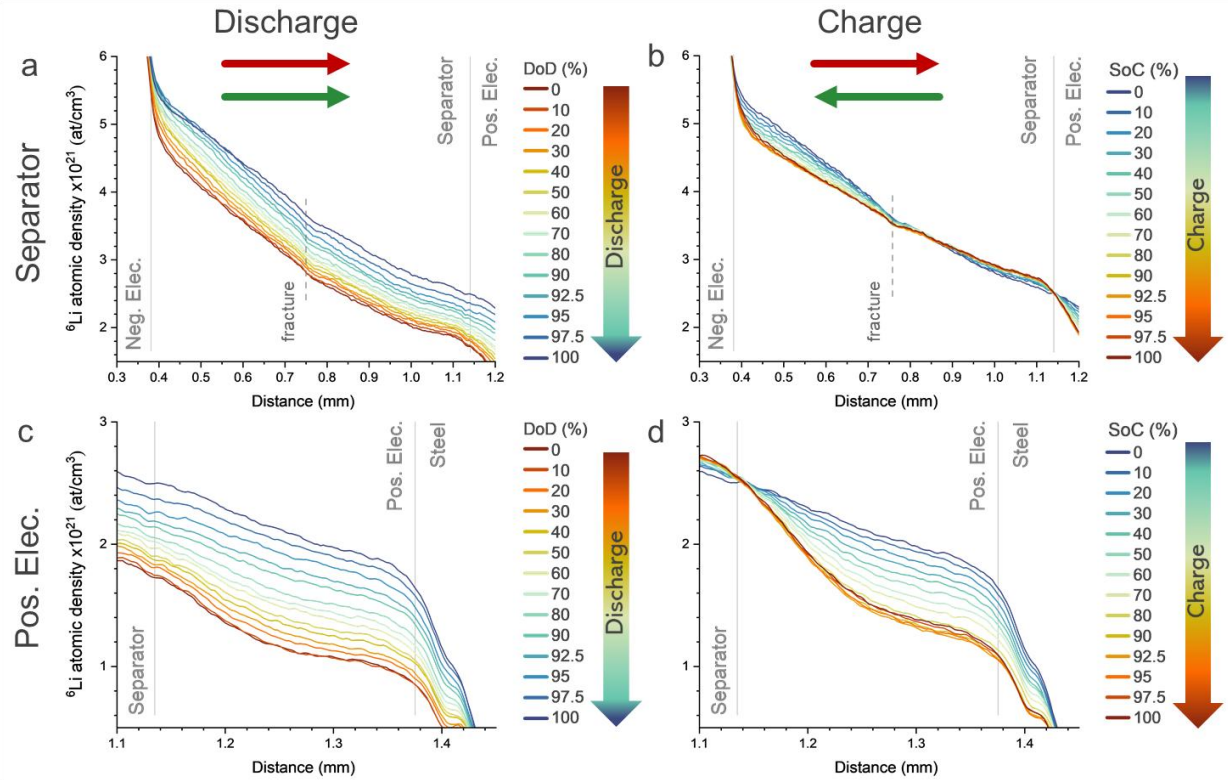


Figure S4:Profiles of ^{6}Li content along the cell components at different DoD and SoC during a, c) discharge and b, d) charge, averaged over the entire width of the sample. The top panels focus on the separator and the bottom panels focus on the positive electrode, respectively. The red and green arrows highlight the direction of the isotopic diffusion and the electrochemical migration, respectively. The dashed line indicates the position of an identified fracture. The arrows on the right help visualize the curves' evolution during cycling.

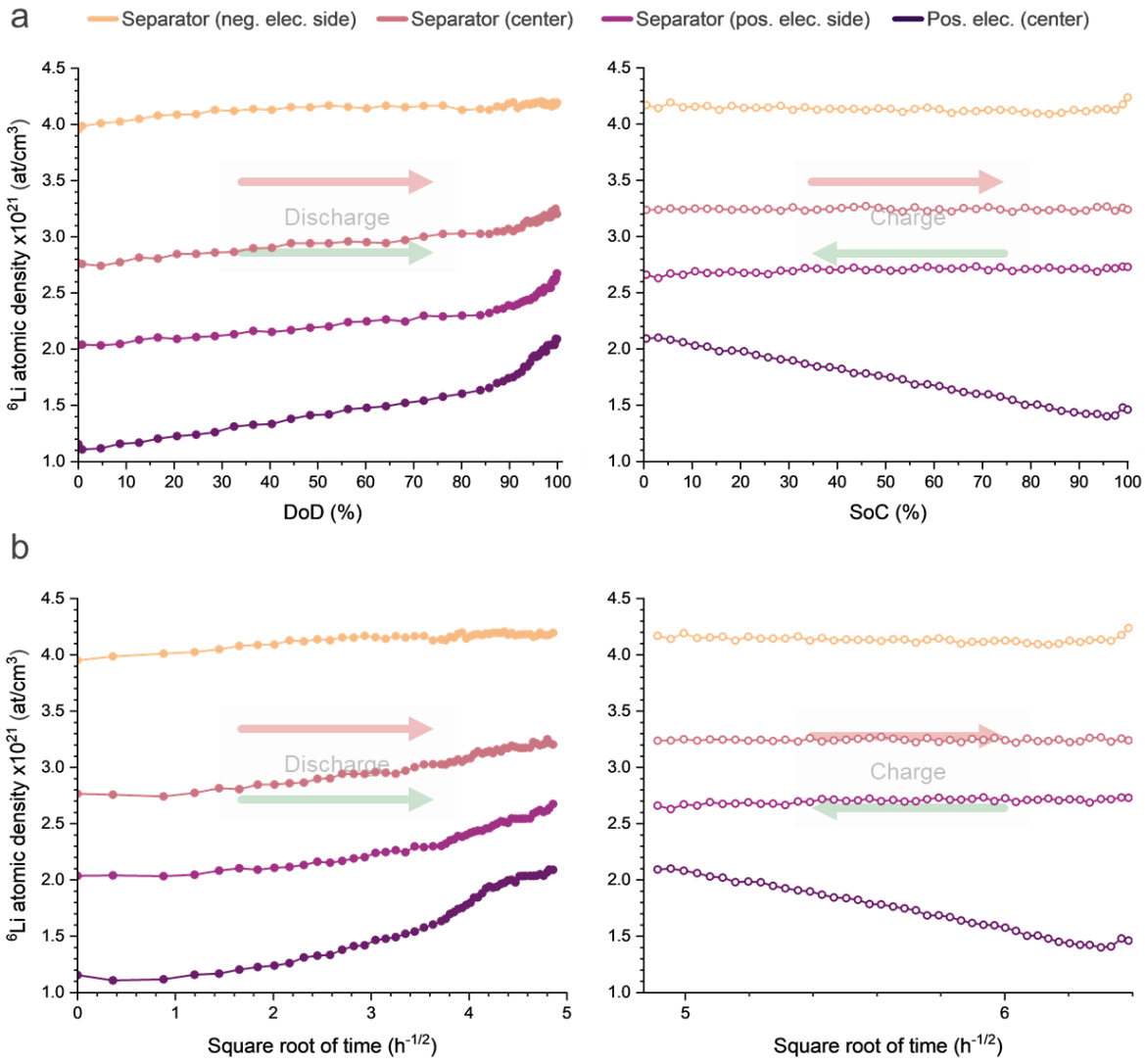
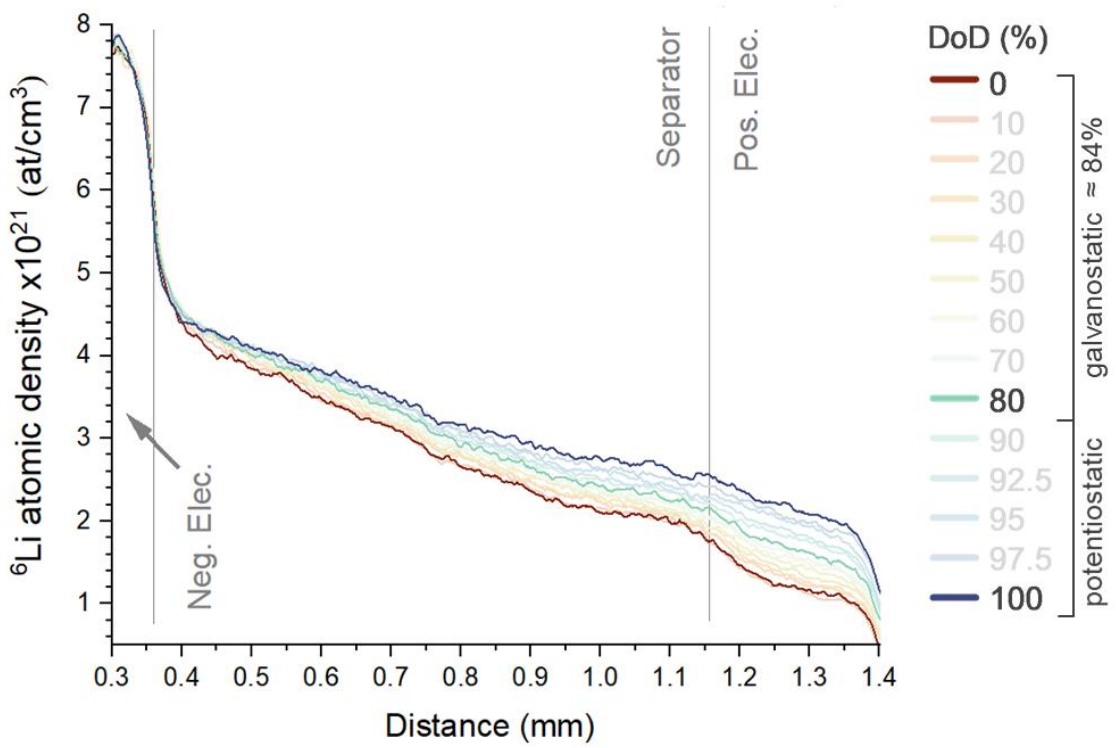


Figure S5: ^{6}Li atomic density as function of a) DoD and SoC and b) the square root of time at various height in the separator and in the positive electrode, measured in the center over a width of 265 µm, highlighting diffusion-driven transport. The red and green arrows refer to the direction of the isotopic diffusion and the electrochemical migration, respectively. These concepts are further explained in "Isotopic diffusion vs. electrochemical migration".



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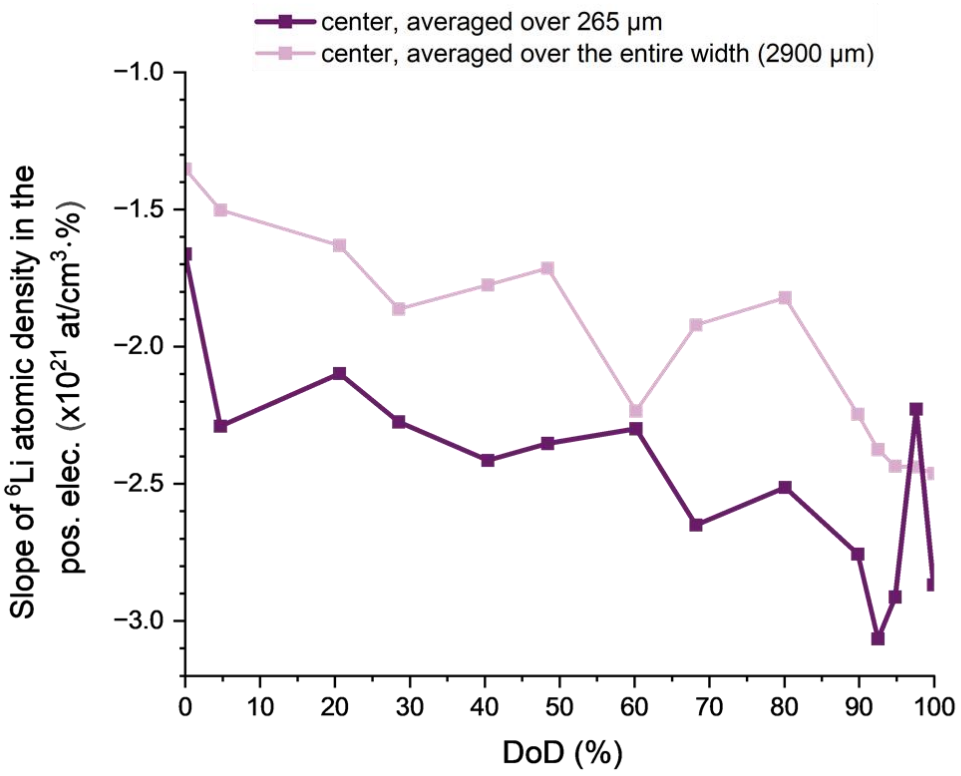
116 **Figure S6**: Profiles of lithium content along the cell components at different DoD, averaged over the

117 width of the 265 µm, with the highlight of the switch from galvanostatic to potentiostatic regime (at DoD

118 84%).



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120 **Figure S7**: Slope of the linear fit in the positive electrode of the ^{6}Li atomic density in function of the DoD,

121 extracted from **Figure 4** and **Figure S4**.

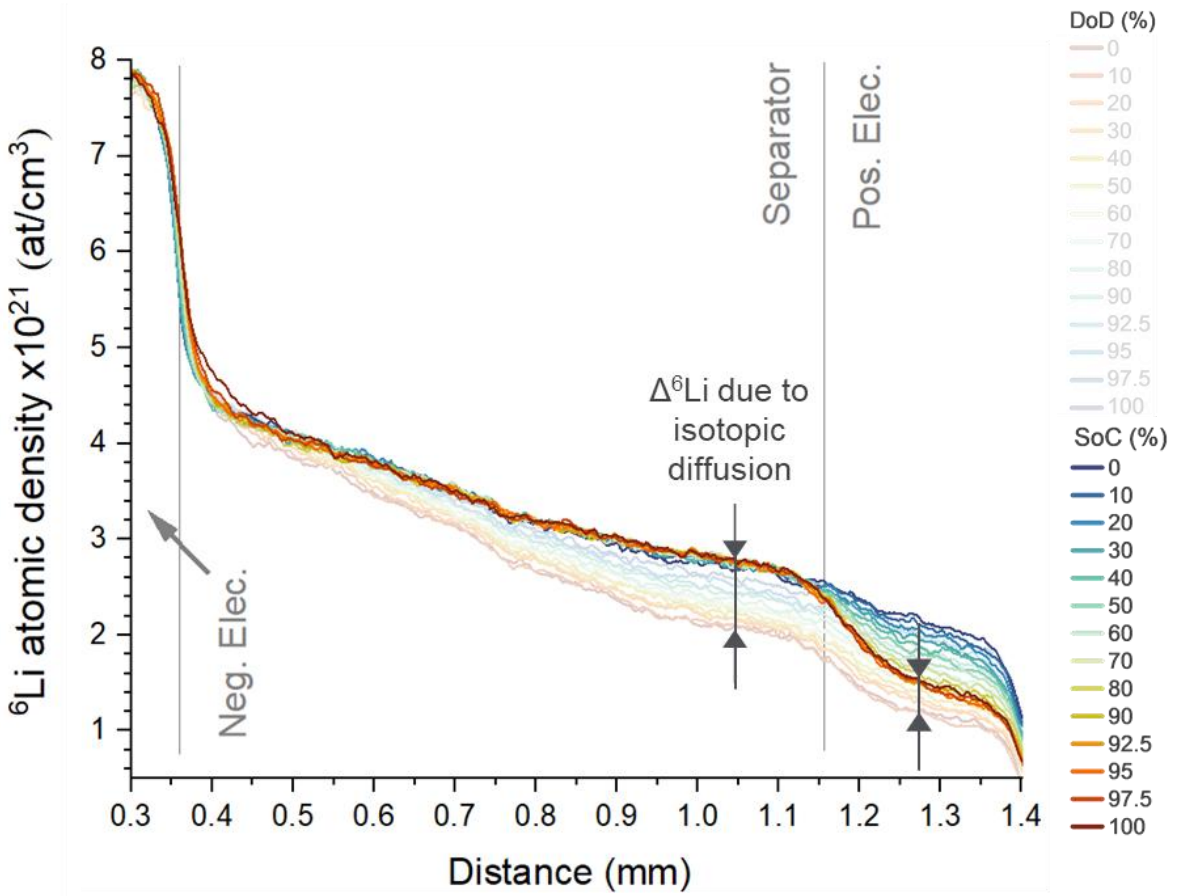
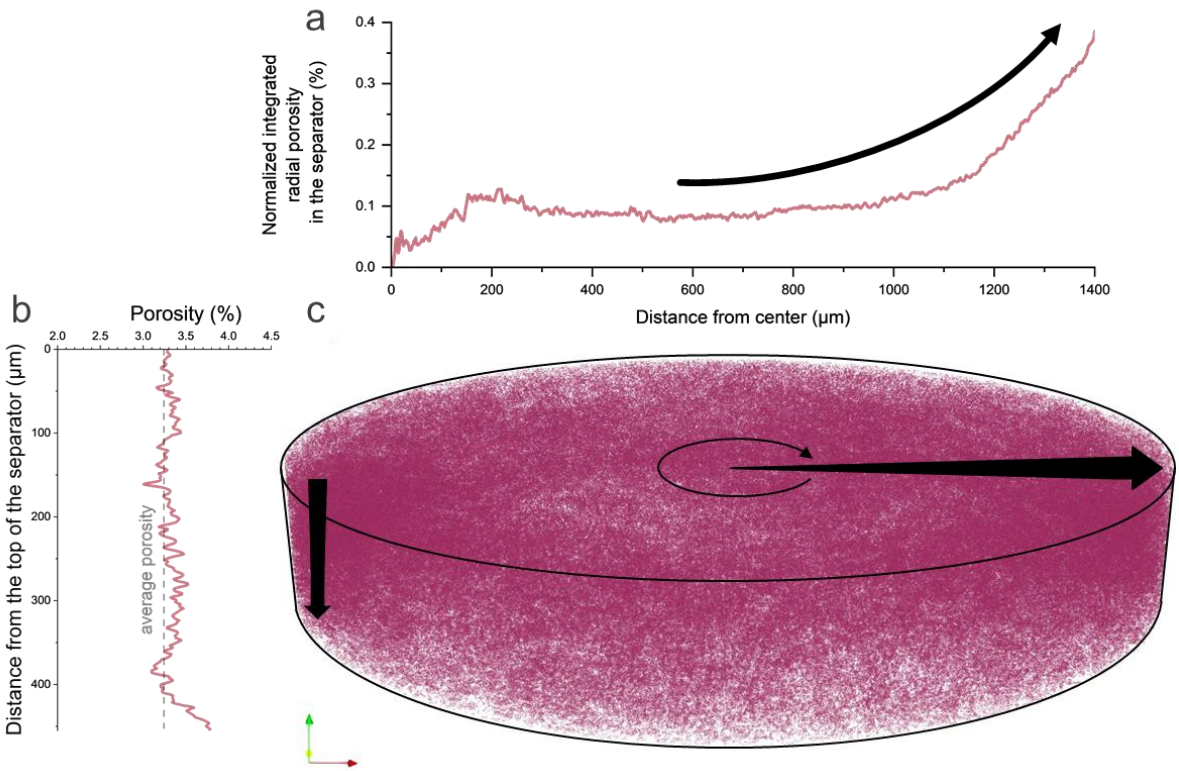


Figure S8: ^{6}Li profiles of lithium content at different DoD and SoC, averaged over the width of the sample, highlighting the evolution of ^{6}Li due to isotopic diffusion in the separator and the positive electrode as the cell come back to its original state of SoC 100%.



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127 **Figure S9**: Spatial distribution measurement of porosity made at ID19 (ESRF) on LPSCl separator. a) the
128 integrated radial distribution of porosity, highlighting higher porosity on the edge of the sample. b) the
129 height-wise distribution per slice of porosity, showing homogeneous porosity along the height of the
130 separator. c) 3D representation of the porosity in the LPSCl separator with the pellet diameter of 3 mm with

the arrows in the center showing the radial integration and the arrow on the side showing the height-wise measurement.

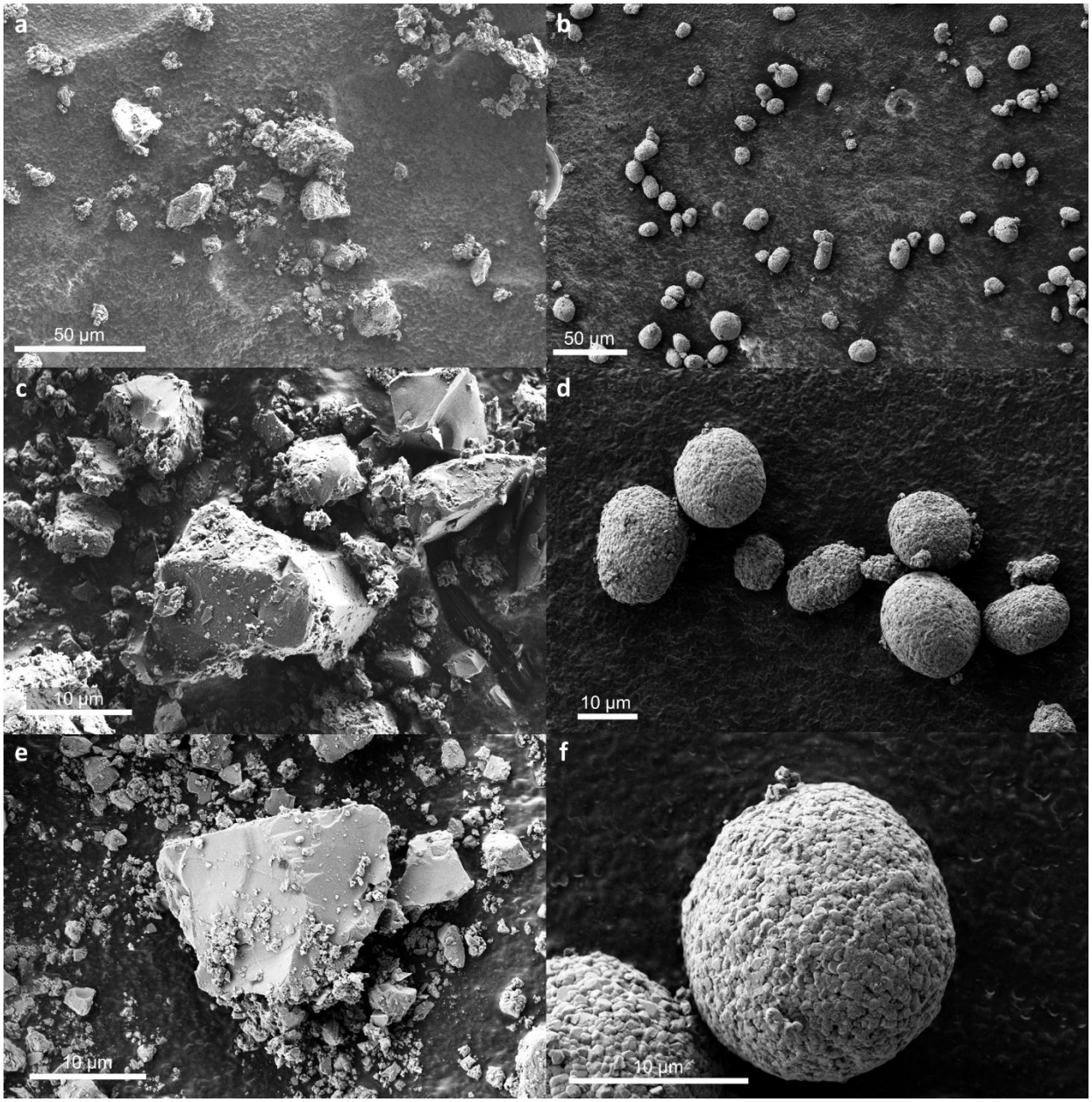

Figure S10: Secondary electrons images of a), c), e) the LPSCl powder and b), d), f) the NMC532 powder.