Conversion type materials have recently been considered as a plausible alternative to conventional electrode materials, owing to their strong gravimetric and volumetric energy densities. The ternary alloy TiSnSb was recently proposed as being a suitable negative electrode material in Li-ion batteries owing to its excellent electrochemical performance. Using complementary \textit{in situ operando} X-ray diffraction (XRD) and \textit{in situ operando} $^{119}$Sn Mössbauer spectroscopy, it was determined that during the first discharge, TiSnSb undergoes a conversion process leading to the simultaneous formation of Li-Sb and Li-Sn intermetallic compounds. However, some ambiguities remain: A shifted, group of resonances appear in the $^7$Li NMR spectra at approx. 20 ppm, in addition to a contribution from Li$_3$Sb at 3.5 ppm and a resonance at 8.5 ppm (assigned to Li$_2$Sn$_2$), and could correspond to intermediate phases. In addition, changes in the local environments of Sn and Li nuclei have been detected upon OCV relaxation after the lithiation process, using $^{119}$Sn Mössbauer and $^7$Li NMR spectroscopies, respectively. These results suggest an intrinsic instability of the phases formed at the end of the lithiation process. \textit{Ex situ} $^7$Li NMR indicates that this evolution is stopped or at least slowed down when the active material is in contact with the electrolyte. Both "\textit{in situ}" and "\textit{ex situ}" type experiments have been completed using the two techniques in order to understand the influence of small changes in composition on Mössbauer signal and $^7$Li NMR shifts. Following this approach, the ternary alloy NbSnSb was investigated and directly compared to TiSnSb to determine the influence of the inactive metal on the $^7$Li NMR shift. The obtained results highlight the sensitivity of $^7$Li NMR to the chemical or electronic environment around the Li$_3$Sb phase or clusters and not only to the direct local environment (Li$_3$Sb). This result shows the crucial importance of interfaces between the phases formed along the redox processes in the case of conversion materials. A systematic study using both Mössbauer spectroscopy and NMR the phases formed during discharge and subsequent relaxation will be presented and discussed.

References