RELAXATION EFFECTS OF THE NEGATIVE ELECTRODE TiSnSb USING ^{119}Sn MÖSSBAUER AND ^{7}Li MAS NMR SPECTROSCOPIES

Nicolas Dupré,[1,4] Karen E. Johnston,[1,3,4] Ali Darwiche,[2] Lorenzo Stievano,[2] Clare P. Grey[3,4] and Laure Monconduit[2,4]

[1]Institut des Matériaux Jean Rouxel (IMN), CNRS UMR 6502, Université de Nantes, France,
[2]Institut Charles Gerhardt Montpellier-UMR 5253 CNRS, Université Montpellier 2, 34095, Montpellier, France
[3]University of Cambridge, Department of Chemistry, Lensfield Road, CB2 1EW, UK
[4] *ALISTORE-ERI European Research Institute*

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 *in situ operando* X-ray diffraction (XRD) and *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_3Sb at 3.5 ppm and a resonance at 8.5 ppm (assigned to Li_7Sn_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. *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 "*in situ*" and "*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_3Sb phase or clusters and not only to the direct local environment (Li_3Sb). 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

[1]: M. Sougrati, et al. *J. Mater. Chem.* **2011**, *21*, 10069.
[2]: C. Marino et al. *Chem. Mater.* **2012**, *24*, 4735.
[3]: C. Marino et al. *J. Phys. Chem. C* **2013**, *117*, 19302.
[4] : H. Wilhelm, et al. *Electrochem. Commun*. **2012**, *24*, 89.