COMBINED *OPERANDO* STUDIES OF NEW ELECTRODE MATERIALS FOR Li-ION BATTERIES

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The development of high energy and power Li-ion batteries for portable power tools applications, automotive electric transportation (hybrid and electrical vehicles), electrical storage of renewable energies (small and medium size outfits), leads to intensive world-wide research on new electrode materials and electrolytes [1]. The performances of Li-ion batteries depend on many factors amongst which the important ones are the electrode materials and their structural and electronic evolution upon cycling. Fundamental studies are necessary for a better understanding of lithium reactivity mechanism by means of experimental techniques providing both structural and electronic information during the electrochemical cycles as X-Ray Powder Diffraction (XRPD) and Transmission Mössbauer Spectroscopy (TMS). A specific test cell [2], derived from a conventional Swagelok (Figure 1) cell was designed to allow measurements both in reflection mode (XRPD) or transmission mode (TMS) (Figure 2). Thanks to these two complementary techniques it is now possible to follow *in situ* and from *operando* mode the electrochemical behaviour of promising new Sn or Fe-based electrode materials.

XRPD spectra provide valuable information about the structural change behaviour and different contributions of each individual crystallized component during the charge/discharge process.

From TMS spectra the hyperfine parameters, δ (isomer shift) and Δ (quadrupole splitting), respectively proportional to the *s electronic density* at the nucleus and to the *electric field gradient*, make it possible to characterize the oxidation state and coordination of the probed element. The *f* recoil-free fraction which governs the intensity of the Mössbauer absorption gives information about the network rigidity and bonding and allows us to determine the relative proportions of each individuals species (crystallized, amorphized, nanosized).

Several examples will be presented to illustrate the greatness of combining XRPD and TMS for the study of Fe or Fe,Mn-based phosphates [3] as positive electrodes and Sn-based intermetallics [4] or composites [5] as negative electrodes. Different kind of reactions have been identified (insertion, phase transition, conversion) and in all cases understanding of such mechanisms is essential to optimize existing materials or to create new materials.

With the massive arrival of Sn-based nanocomposite electrodes joined with the advent of new Fe-based electrodes, the combination of XRPD and TMS has a bright future within the field of Li-ion batteries.

Acknowledgements

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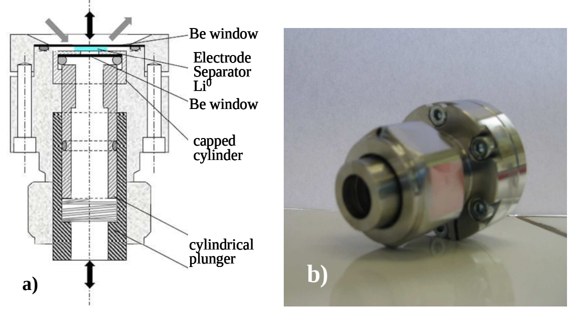

Figure 1. Electrochemical cell for *operando* measurements: a) schema from [2], b) photo

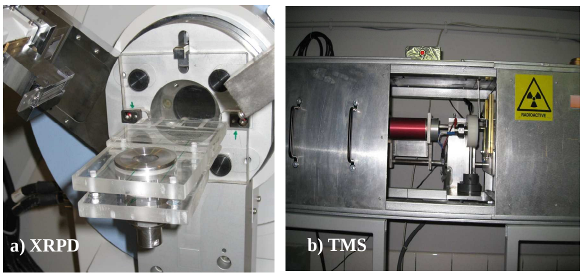

Figure 2. Experimental setup : a) XRPD, b) TMS

[1] 16th International Meeting On Lithium Batteries, IMLB-16, Jeju, Korea, June 17th– 22th, 2012.
[2] J.B. Leriche et al., J. Electrochem. Soc., 157 (2010) A606.
[3] A. Perea et al., RSC Advances 2 (2012) 2080.
[4] M. Chamas et al., J. Power Sources, 196 (2011) 7011.
[5] D.E. Conte et al., J. Power Sources, 196 (2011) 6644.