

## A Study of the Electrochemical Mechanisms Involved During Lithium Insertion into $\text{TiO}_y\text{S}_z$ Thin Films used as Positive Electrode in Lithium Microbatteries

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Intensive efforts are currently performed with regard to technical microequipment, which also involves the miniaturisation of power sources. The ICMCB/ENSCP group has patented the following all solid state microbattery:  $\text{TiO}_y\text{S}_z$  / borate glass / lithium [1]. The French company HEF is currently developing a multilayer semi-industrial vacuum deposition equipment for producing ultra thin batteries [2]. To improve the electrochemical properties of our microbatteries, we have investigated the local structure and electrochemical processes occurring during the cycling. Two complementary techniques have been used: X-ray absorption spectroscopy (XAS) in the total electron-yield detection mode and X-ray photoelectron spectroscopy (XPS).

Amorphous  $\text{TiO}_y\text{S}_z$  thin films were prepared by r.f. magnetron sputtering under argon atmosphere using pressed  $\text{TiS}_2$  polycrystalline powder (Aldrich) as target.

**As prepared sample analysis:** The composition  $\text{TiO}_{0.6}\text{S}_{2.8}$  is determined by RBS. XPS Ti2p core peak analyses have evidenced a predominant sulphur environment for  $\text{Ti}^{4+}$  ions. Concerning sulphur S2p XPS analysis,  $\text{TiO}_{0.6}\text{S}_{2.8}$  thin film exhibits two kinds of sulphur atoms:  $\text{S}^{2-}$  and  $\text{S}_2^{2-}$  in the same proportions as in bulk  $\text{TiS}_3$ . Therefore, the obtained thin films are very close to bulk  $\text{TiS}_3$  with regard to the composition and the XPS core peak analysis. This is also confirmed by the valence band analysis. Furthermore, this analogy is emphasized by the XANES spectra at S K-edge (Fig. 3a), which proves that the sulphur local environment in the thin film is close to the one of bulk  $\text{TiS}_3$ .

**First cycle study:** The electrochemical characterisation was carried out galvanostatically in the  $\text{Li} / \text{LiAsF}_6, \text{EMC} (1\text{M}) / \text{TiO}_{0.6}\text{S}_{2.8}$  cell with a current density of  $3 \mu\text{A}\cdot\text{cm}^{-2}$  between 0.5 and 3.3 V/Li (Fig. 1a). Local structure modifications and redox processes occurring during the first cycle were investigated using XPS (Fig. 2a and 2b) and XAS (Fig. 3b). At the end of the discharge,  $\text{S}_2^{2-}$  pairs are totally reduced to  $\text{S}^{2-}$  ions and  $\text{Ti}^{4+}$  is partially reduced to an oxidation state quite close to the one encountered in metallic titanium. At the end of the charge, XPS spectra are very similar to the as prepared samples. Therefore, these results evidence that titanium and sulphur are completely oxidised to their pristine oxidation state. As a consequence, this XPS study has highlighted the sulphur contribution to the electrochemical processes, which has also been confirmed through a XAS study at the sulphur K-edge. Fig. 3b represents the XANES spectra of the as prepared thin film and at the end of the discharge. The pre-peak intensity decreases and the main peak energy shifts towards lower energies with lithiation, which is consistent with sulphur reduction.

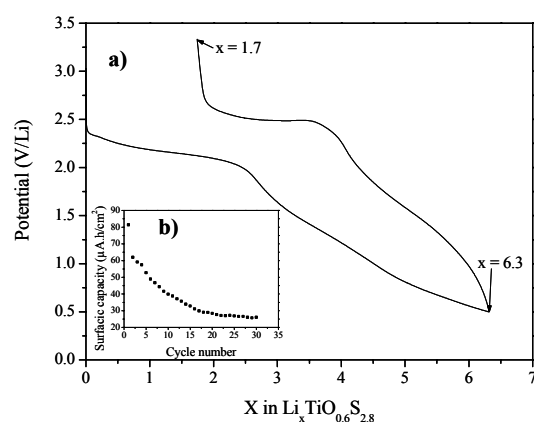
All the previous mentioned XPS analyses were performed after mechanical erosion to probe the electrochemical

mechanisms occurring inside the thin film. Anyway, analyses were also systematically carried out before the erosion to study the cathode/liquid electrolyte interface. The results seem to evidence the growth of a Solid Electrolyte Interphase (SEI) layer with lithium insertion. However, this layer seems to undergo a partial dissolution during the charge. Owing that 1.7 Li are trapped in the cathode and that the XPS spectra (after erosion) are similar to the as prepared samples, SEI layer is believed to be mainly responsible for the irreversibility observed at the first cycle.

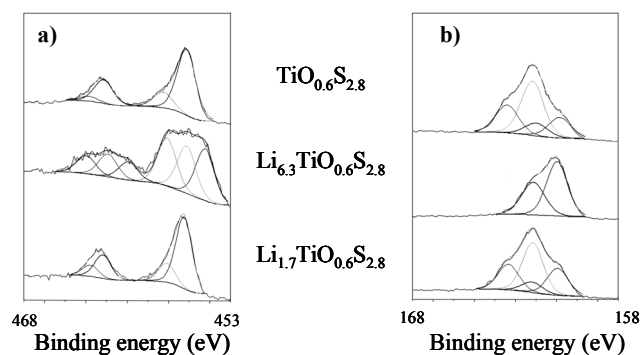
**Study after 30 cycles:** A sample was cycled within the 1.6-3.3 V/Li potential window at a current density of  $3 \mu\text{A}\cdot\text{cm}^{-2}$  (Fig. 1b). XPS analyses (after erosion) were performed at the end of the 30<sup>th</sup> charge. The proportion of  $\text{S}_2^{2-}$  disulfide ions is reduced by half, which means that the reduction to  $\text{S}^{2-}$  becomes less reversible with cycling. As a consequence, the latter is supposed to be responsible for the capacity fading observed during cycling.

### References:

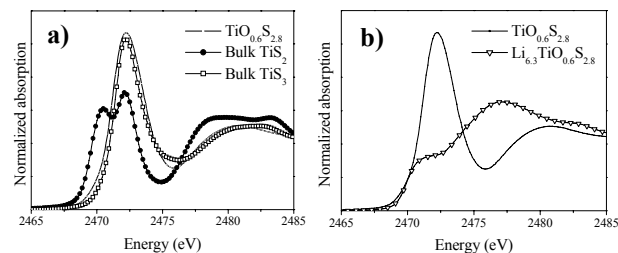
- [1] G. Meunier, R. Dormoy, A. Levasseur, *CNRS Patent*, WO9005387 (1988).
- [2] M. Martin, F. Faverjon, *Thin Solid Films*, 398-399, 572 (2001).



**Figure 1 :** a) Voltage-composition curve corresponding to  $\text{TiO}_{0.6}\text{S}_{2.8}$  thin film, b) Surface capacity evolution with cycling ( $j=3 \mu\text{A}\cdot\text{cm}^{-2}$ , potential window: 1.6-3.3 V/Li).



**Figure 2:** a) Ti2p core peak and b) S2p core peak XPS analysis of  $\text{Li}_x\text{TiO}_{0.6}\text{S}_{2.8}$  ( $x=0, 6.3$  and  $1.7$  after charge).



**Figure 3:** XANES spectra at S K-edge a) for the as prepared  $\text{TiO}_{0.6}\text{S}_{2.8}$  thin film and b) for  $\text{Li}_{6.3}\text{TiO}_{0.6}\text{S}_{2.8}$ .