

## EXAFS operando study of TiO<sub>2</sub>(b) as active insertion material for lithium ion batteries

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Titanium dioxide is an attractive candidate to replace today's commercially established graphite as electrode material in Lithium ion batteries. Its abundance, its benignancy for nature and human beings, its cost effectiveness and especially its good lithium insertion properties put it in a sublime position [1]. The most intensively studied polymorph is the tetragonal anatase phase which features a flat plateau of Li insertion followed by a slope like Li insertion which corresponds to a biphasic and subsequent monophasic Li insertion reaction respectively, see Fig. 1 b).

The monoclinic TiO<sub>2</sub>(b) phase has gained attention as superiority of electrochemical cycling was claimed [2,3]. Although chemically equivalent to the anatase phase, TiO<sub>2</sub>(b) reveals a very distinct lithium insertion mechanism in its electrochemical cycling curve, see Fig. 1a). This is attributed to the differences in electronic and crystal structure [4], however exact information on the mechanism of Li<sup>+</sup> insertion and de-insertion into TiO<sub>2</sub>(b) is still insufficient. In their ex situ XAS study on TiO<sub>2</sub>(b), Okumura *et al.* claim a two regime process of Li<sup>+</sup> insertion. However the number of points in the discharge curve that were investigated is scarce and hence the picture provided remains still incomplete [5].

To better understand the mechanisms during electrochemical cycling we have developed a real time in situ x-ray absorption spectroscopy set-up, allowing us to study structural and electronic modifications during the insertion and de-insertion of lithium ions. While a steady shift of the Titanium k-edge along with changes in the shape of the pre-edge reflects the change in oxidation state from Ti<sup>IV+</sup> to Ti<sup>III+</sup> the modification of the coordination shells around the Ti centres allows us to identify the probable lattice sites that are occupied by the Li ions during insertion. Comparing this to the changes occurring during Li de-insertion gives us evidence of reversibility of the mechanisms and processes.

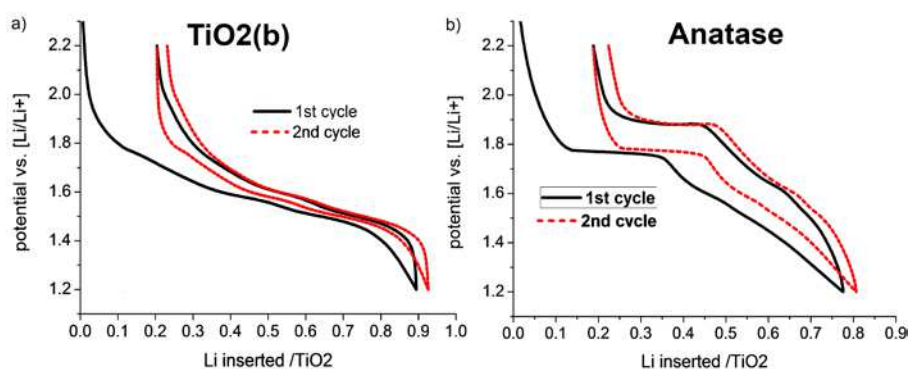


Fig. 1: Galvanostatic cycling curve of first two cycles of a) TiO<sub>2</sub>(b) and b) Anatase.

- [1] Ren *et al.* *Angew. Chem.* 124 (2012) 2206
- [2] Brousse *et al.* *Journal of Power Sources*, 158 (2006) 571
- [3] Zúkalová *et al.* *Chemical Materials*, 17 (2005) 1248
- [4] Nusz *et al.* *J. Material Chemistry* 7 (1997) 2529
- [5] Okumura *et al.* *J. Material Chemistry* 21 (2011) 15369