

A NEW ELECTRODE BASED IN ANTIMONY OXIDE FOR LITHIUM ION BATTERIES

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Since the announcement in 1994 by Fuji Film Co[1] of an amorphous tin oxide based anode for rechargeable lithium batteries, there was an increasing interest on tin based systems, especially tin oxides. In these cells, working voltage range is sufficiently low to compete with lithium or graphite based negative electrodes. Moreover, the reversible specific capacities delivered by tin dioxide electrodes are respectively $790 \text{ mAh}\cdot\text{g}^{-1}$ and $5465 \text{ Ah}\cdot\text{L}^{-1}$. These values are two and six times higher than those found for the graphite electrode.

The success of tin oxides electrodes have arose an interest on other metal or metalloid oxides where electrochemical reaction with lithium have analogous mechanism to which of tin oxides, it means, irreversible oxide dissociation to yield Li_2O and metal or metalloid, followed by the reversible electrochemical alloying between lithium and the metal or metalloid particles. One of these systems is the Sb_2O_3 senarmontite polymorph studied by Li et al.[2] in powder form. In their work, the sequential formation of Sb and Li_3Sb is detected by X-rays diffraction. Sb_2O_3 cell delivered $780 \text{ mAh}\cdot\text{g}^{-1}$ in the first discharge, which is only 70% of the theoretical capacity according to the formation of Li_3Sb in the final antimony phase. More recently, our group has prepared Sb_2O_4 cervantite thin film electrodes [3] which mechanism of reaction with lithium is similar to senarmontite. However, the delivered capacity of this cell was less than the theoretical one since cervantite is not completely decomposed by lithium in the first discharge.

In this context, valentinite, the other Sb_2O_3 polymorph has not been studied as negative electrode in lithium ion cells. In contrast to the 3D network of senarmontite, valentinite is a layered oxide. For an electrode based on this polymorph, the diffusion of lithium ions should be enhanced and the efficiency of the electrochemical reaction should be improved. Keeping that in mind, we prepared some samples of valentinite to analyse how the dimensionality of the antimony (III) oxide influences its electrochemical performance in lithium batteries.

Sb_2O_3 samples were prepared from the hydrolysis of SbCl_3 . Different media (water or ethanol), temperatures and times of reaction and the presence/absence of directing agents (CTABr, Pluronic) were evaluated in order to reach highly pure valentinite crystals with small size (figure 1). Also, pH was monitored for avoiding the occurrence of cervantite phases.

Pure valentinite phases were mixed with some additives (carbon black and binder) to prepare the electrodes. In this communication, the performances of these electrodes in lithium batteries are reported and compared to the previously tested senarmontite electrodes.

References

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2. H. Li, X. Huang and L. Chen, *Solid State Ionics*, 1999, **123**, 189.
3. J. Santos Peña, T. Brousse and D.M. Schleich, submitted to *Journal of Materials Chemistry*.

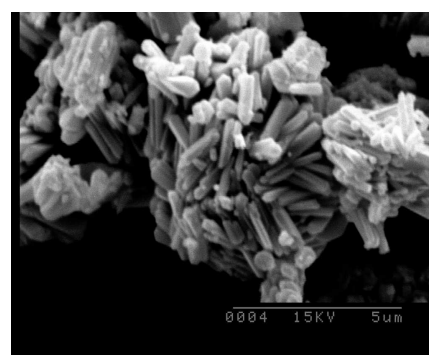


Figure 1. Valentinite crystals obtained after hidrothermal treatment of SbCl_3 at 100°C . Bar indicates 5 micron.

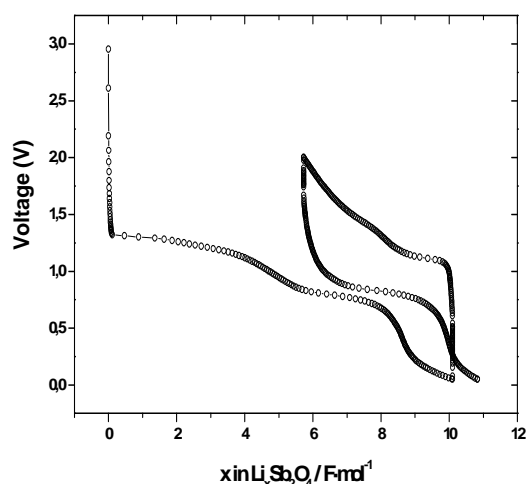


Figure 2. First galvanostatic cycles [C/10, 50 mV-2000mV] of a lithium cell with negative electrode based on a Sb_2O_4 thin film.