

## On the electrode behavior of $\text{Li}_{1.2}\text{V}_3\text{O}_8$

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The lithium trivanadate  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  ( $x=0.1-0.2$ ) is one of the most promising electrode materials for rechargeable lithium batteries [1] due to its layered structure [2, 3] which can reversibly insert up to about 3.8 Li per formula unit [4] with fair cyclability. It is presently used as the cathode material of Li-polymer rechargeable batteries commercialized by Avestor (Canada) and industrially developed by Batscap (France). The electrochemical behavior of such compounds has already been studied in polymer [4-6] or liquid electrolyte [5-10], at 90-120°C or at room temperature, respectively. The synthesis conditions of  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  samples were shown to induce important differences in reversible capacity and cycling behavior.

In a previous work, we have put into evidence the main role played by different aspects of the grain morphology and texture on the Li insertion performance of such materials. The aim of our on-going work is to deeply understand the lithium insertion mechanism and to find the factors responsible for the difference in the electrochemical behaviors.

In this presentation, we will focus on two  $\text{Li}_{1.2}\text{V}_3\text{O}_8$  compounds, prepared at different temperatures and displaying different electrochemical behaviors. We will study their cycling behavior over the different Li insertion processes in order to find the origin of the capacity fading. We have also applied several techniques to characterize in depth the Li insertion mechanism during the first cycle : slow rate Potentiostatic Intermittent Titration Technique (PITT) and two complementary spectroscopies probing the material bulk (XAS) and the surface (XPS). Furthermore, the insight of DFT calculations with geometry relaxation to further understand the origin of the structural two-phase transformation  $\text{Li}_3\text{V}_3\text{O}_8/\text{Li}_4\text{V}_3\text{O}_8$  will be demonstrated.

We have synthesized and studied two materials, called SD580 and S350G, with the formulation  $\text{Li}_{1.2}\text{V}_3\text{O}_8$ . Figure 1 shows the electrochemical behavior of both compounds. The SD580 material is prepared by solid state synthesis at 580°C. It is made of 5 to 10  $\mu\text{m}$  long sticks and shows a 190mAh/g capacity, stable on cycling. S350G is synthesized by heating a gel precursor [4] at 350°C. This compound is made up of agglomerates of small sized sticks (0.1-0.3  $\mu\text{m}$  long). The very large capacity for the first cycle decreases rapidly on cycling. No difference between the two starting compounds has been found by X-Ray diffraction, neutron diffraction or chemical analysis.

Slow rate PITT is a useful technique to thoroughly characterize the different Li insertion processes. It has been used for Li deinsertion to the composition  $\text{LiV}_3\text{O}_8$  and for Li insertion to the composition  $\text{Li}_{4.6}\text{V}_3\text{O}_8$ . We will show that the Li insertion mechanism is very complex, with 9 different processes evident over the total Li composition range.

Cycling the S350G compound over some selected Li insertion processes demonstrates that the capacity fading upon cycling S350G sample mainly comes from the two-phase transformation  $\text{Li}_3\text{V}_3\text{O}_8/\text{Li}_4\text{V}_3\text{O}_8$ , which had already been proposed by Thackeray [3]. DFT calculations with geometry relaxation have been developed in order to shed

some light on the origin of this phase transformation. Results show that it originates from geometric factors (Li crystallographic sites) and not from electronic factors.

The evolution of the absorption pre-edge and edge and of the local environment of the vanadium in the bulk SD580 and S350G materials, has been examined by ex-situ X-ray absorption spectroscopy at the V edge, during the first discharge-charge cycle. The results show a regular and reversible evolution of the pre-edge area, the edge position and the vanadium environment toward nearly perfect octahedral  $\text{VO}_6$ , for both materials.

XPS experiments probe the material surface and allow one to follow the surface composition and the vanadium surface oxidation states. Results show the appearance of the 3 oxidation states  $\text{V}^{\text{V}}$ ,  $\text{V}^{\text{IV}}$  and  $\text{V}^{\text{III}}$ , simultaneously, which will be discussed.

The PITT, XAS and XPS tools will be further applied to SD580 and S350G samples after 50 cycles in order to detect and characterize any possible bulk and/or surface evolution.

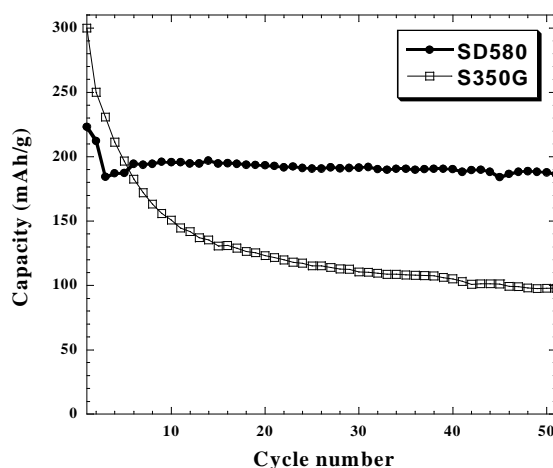


Figure 1 : Capacity versus cycle number for the two materials studied (S350G and SD580).

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