ELECTROCHEMICAL STUDY OF THE \(\omega\)-Li\(_x\)V\(_2\)O\(_5\)
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Introduction

The structure changes induced by Li insertion into V\(_2\)O\(_5\) are well known in the Li composition range 0 < x \(\leq\) 2 with the successive appearance of \(\alpha\), \(\epsilon\), \(\delta\) and \(\gamma\) phases, the working potential decreasing from 3.5 to 2 V. For larger Li contents, the electrochemical insertion in V\(_2\)O\(_5\) down to a voltage smaller than 1.9 V has been reported to lead irreversibly to the formation of a new material \(\omega\)-V\(_2\)O\(_5\) [1, 2].

This \(\omega\) phase has been found to exhibit a cubic structure maintained as Li insertion proceeds. From a structural and electrochemical point of view a solid solution behaviour characterized by a good reversibility of the intercalation process is reported [1]. However only a few is known on the structural evolution of this material during cycling and on the kinetics of insertion reaction.

In this paper, we report a detailed electrochemical and structural study of the \(\omega\)-Li\(_x\)V\(_2\)O\(_5\) form. Different techniques were used, X-ray diffraction analysis, a.c. impedance spectroscopy in order to provide new data on both the starting material and the intercalated compounds.

The V\(_2\)O\(_5\) sample was prepared from a sol-gel process whose preparation has been extensively described [3].

Results and discussion

A typical chronopotentimetric curve is shown Fig.1. Four steps appear during the first reduction, corresponding to the formation of \(\alpha\), \(\epsilon\), \(\delta\) and \(\omega\)-form for Li\(_3\)V\(_2\)O\(_5\). A monotonous signal is observed during the first oxidation due to the irreversible structural change leading to the \(\omega\)-form at 1.5V. 2.2 Li ions can be recovered during the second cycle.

XRD data experiments (Fig.2) indicate a quadratic symmetry for the Li\(_3\)V\(_2\)O\(_5\) phase with the following parameters a = b = 9.18 Å and c = 4.10 Å. This structure is maintained after each reduction.

After a first galvanostatic cycle allowing the formation of the new system \(\omega\)-Li\(_3\)V\(_2\)O\(_5\), ac impedance analysis has been performed (0.3 \(\leq\) x \(\leq\) 3). Fig.3 illustrated the \(D_{Li}\) vs x evolution in the \(\omega\)-phase. Two sets of data are obtained. From 0.3 < x < 1.2, \(D_{Li}\) was found to be relatively high (10\(^{-8}-10\(^{-10}\) cm\(^2\).s\(^{-1}\)) before to be almost constant (10\(^{-10}\) cm\(^2\).s\(^{-1}\)) for 1.2 \(\leq\) x \(\leq\) 2). A sharp decrease in \(D_{Li}\) occurs for larger Li contents (x > 2.4) The significant limitation of the specific capacity takes place for the higher Li contents, 2.7 \(\leq\) x \(\leq\) 3 is correlated with these kinetics data.

Optimization of cycling performances have led to a stable specific capacity around 320 Ah.kg\(^{-1}\) at C/20 rate in the voltage range 3.8-1.5 V.

We report also electrochemical features of new doped \(\omega\)-phase with an improvement of the capacity by 10%.

Reference