ELECTROCHEMICAL STUDY OF THE ω-$Li_xV_2O_5$

C.Leger, P.Soudan, S.Bach, J.P.Pereira-Ramos
CNRS, LECSO, 2 rue Henri Dunant, 94320 THIAIS, France

Introduction

The structure changes induced by Li insertion into V_2O_5 are well known in the Li composition range $0 < x \leq 2$ with the successive appearance of α, ε, δ and γ phases, the working potential decreasing from 3.5 to 2 V. For larger Li contents, the electrochemical insertion in V_2O_5 down to a voltage smaller than 1.9 V has been reported to lead irreversibly to the formation of a new material ω-V_2O_5 [1, 2].

This ω 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 kwown 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 ω-$Li_xV_2O_5$ 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_2O_5 sample was prepared from a sol-gel process whose preparation has been extensively described [3].

Results and discussion

A typical chronopentiometric curve is shown Fig.1. Four steps appear during the first reduction, corresponding to the formation of α, ε, δ and ω-form for $Li_3V_2O_5$. A monotonous signal is observed during the first oxidation due to the irreversible structural change leading to the ω-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 $Li_3V_2O_5$ 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 ω-$Li_3V_2O_5$, ac impedance analysis has been performed ($0.3 \leq x \leq 3$). Fig.3 illustrated the D_{Li} vs x evolution in the ω-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 ω-phase with an improvment of the capacity by 10 %.

Reference

1. C. Delmas, S. Brethes and M. Menetrier, J. Power Sources, 1991, 34, 113.
2. H. Cognac-Auradou, Univ Bordeaux Thesis (1993)
3. P. Aldebert, N. Baffier, N. Gharbi and J. Livage, Mat.Res.Bull., 1981, 16, 669.

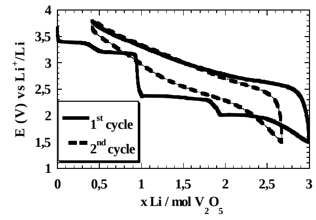

Fig.1 : Typical chronopotentiometric curve for a electrode of V_2O_5 between 3.5-.5V in 1M $LiClO_4$/PC.

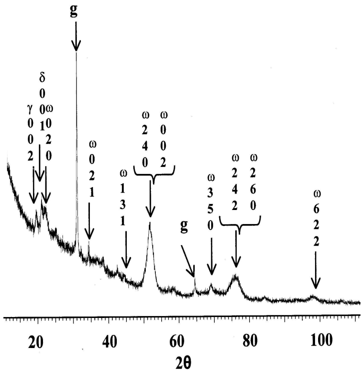

Fig.2 : X-ray diagram of ω-$Li_3V_2O_5$ (λCoKα) g : diffraction peaks of graphite.

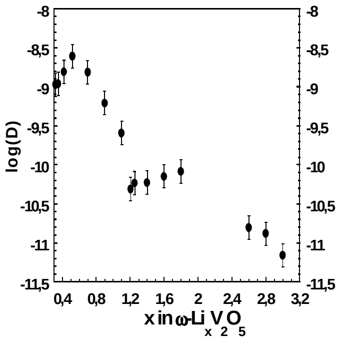

Fig 3 : Evolution of D_{Li} as a function of x in ω- $Li_xV_2O_5$.