VIBRATIONAL MODIFICATIONS DURING ELECTROCHEMICAL LITHIUM INSERTION IN V_2O_5 THIN FILMS DEPOSITED BY ATOMIC LAYER DEPOSITION (ALD)

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Vanadium pentoxide V_2O_5 exhibits attractive properties as cathodic material for secondary lithium batteries because of its relatively high specific energy density. However, the efforts devoted to the $Li_xV_2O_5$ system have not resulted in a complete and established picture of all its properties, owing partly to the complicated structural behaviour which occurs as lithium intercalation proceeds.

Raman spectroscopy is unique as it can bring information about local disorder and changes in bond lengths and coordination environments during lithium intercalation. However, Raman data available in the literature come mainly from chemically lithiated samples and do not lead to reliable conclusions[1,2]. A previous Raman study during electrochemical lithium insertion concludes to a fast amorphization of the oxide[3]: the V_2O_5 lines vanish nearly completely from the early lithium contents and only weak intensities are recovered during the charge.

We report here a Raman microspectrometry study of electrochemical lithium intercalation in V_2O_5 thin films prepared by Atomic Layer Deposition. As shown in **fig. 1**, we observe the two well known defined steps in the voltage range 3.8V/3V ($0<x<1$) as well as an excellent reversibility whatever the C rate.

The good homogeneity and cristallinity of the films compared with usual conventional composite electrodes has allowed to obtain high resolution spectra in a wide lithium composition range. Spectral changes as lithium insertion proceeds are discussed in relation with structural data drawn from X-ray diffraction. As a result, specific Raman fingerprints are evidenced during the formation of the successive α, ε, δ and γ $Li_xV_2O_5$ phases ($0\leq x\leq 1.8$) related to the first three lithium insertions steps at 3.4, 3.2 and 2.8V vs Li/Li^+ (**fig. 2**). Moreover, structural reversibility has been evidenced for lithium uptake>1[4].

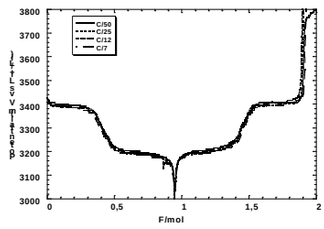

Fig 1. Chronopotentiometric curves for the reduction and oxidation of ALD V_2O_5 thin film deposited on titanium plate at various current densities

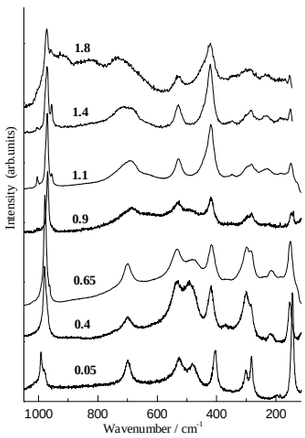

Fig 2. Raman spectra of the electrochemically produced $Li_xV_2O_5$ phases, $0.05<x<1.8$

References

1. C. Julien, I. Ivanov and A. Gorenstein, *Mat. Science and Eng.* B33 (1995) 168.
2. X. Zhang, R. Frech, *Electrochim. Acta*. 42 (1997) 475.
3. E. Cazzanelli, G. Mariotto, S. Passerini, F. Decker, *Solid State Ionics*, 70/71 (1994) 412.
4. R. Baddour-Hadjean, V. Golabkan, J. P. Pereira Ramos, A. Mantoux and D. Lincot, *J. Raman Spectrosc*. 33 (2002) 631.