EX-SITU IR STUDY OF THE STRUCTURAL CHANGES IN V_2O_5 AND OTHER VANADATE FILMS DURING CHARGING/DISCHARGUNG

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In our study of the structural changes caused in V_2O_5 and other vanadate films by charging/discharging we used ex-situ IR transmission spectroelectrochemical technique. The ex-situ IR technique was successfully applied to thin films that retain their charge after being removed from the electrochemical cell. Cleaning of the films removes the traces of the electrolyte and high-quality IR spectra can be obtained. Carbonate surface species may form during manipulation of the films but can be easily identified in the ex-situ IR spectra. By measuring the IR spectra of initial, charged and discharged states of the films one can follow the phase modification or even amorphisation of the film structure, retention of Li^+ ions in thin films and, in some cases, identify the reduced metal species.

V_2O_5 is suitable for IR spectroscopic study since the vibrational bands are assigned on the basis of the symmetry group analysis[1,2]. V_2O_5 films were deposited from V-oxoisopropoxide sols by dip-coating technique. Films were galvanostatically charged/discharged in 1M $LiClO_4$ in propylene carbonate and after each charging and discharging the IR spectra were measured. The intercalation coefficient was gradually increased in steps of x = 0.25 from x = 0 to 3.5 (in $Li_xV_2O_5$). The ex-situ IR spectra of intercalated states corresponded to the current waves of the first cyclovoltammetric curve of V_2O_5. For example, the polaron absorption of V^{4+}/V^{5+} pairs above 2000 cm^{-1} is maximal at x = 0.5, while it is no more visible at x = 1 (Fig. 1). Results revealed the systematic changes in the IR spectra (Fig. 2) that can be ascribed to the formation of various lithiated phases (α, ε, δ, γ-$Li_xV_2O_5$)[3-5] and finally, to the amorphisation of the structure.

The structural transformations of the V_2O_5 films during electrochemical charging/discharging will be compared with those that occur in various vanadate films, including orthovanadates ($M^{3+}VO_4$, M = In, Fe,…)[6] and $M^{5+}VO_5$ (M = Nb, Ta)[7].

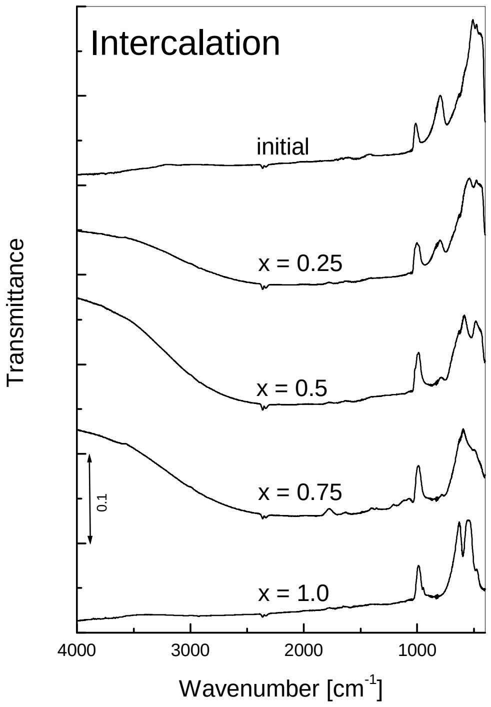

Fig. 1 Ex-situ IR transmission spectra of V_2O_5: initial state and charged to intercalation coefficient x = 0.25, 0.5, 0.75 and 1.0 (in $Li_xV_2O_5$).

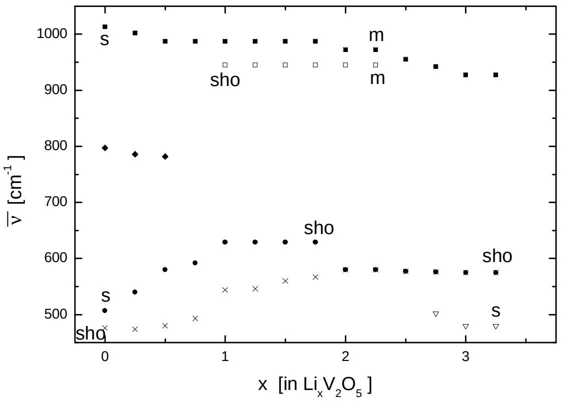

Fig. 2 Changes in the IR band positions (in cm^{-1}) of a crystalline V_2O_5 film (300 °C) with intercalation coefficient x (in $Li_xV_2O_5$). 1025 – 900 cm^{-1}: V=O vanadyl stretching, 800 – 750 cm^{-1}: bridging V-O_B-V stretching, below 650 cm^{-1}: 3V-O_C stretching and V-O deformations.

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[1] P. Clauws, J. Broeckx, J. Vennik, Phys. Stat. Sol. (b) 131, 459 (1985).
[2] L. Abello, E. Husson, Y. Repelin, G. Lucazeau, Spectrochim. Acta 39A, 641 (1983).
[3] Galy, J. Solid State Chem. 100, 229 (1992).
[4] P. Rozier, J. M. Savariault, J. Galy, Solid State Ionics 98, 133 (1997).
[5] E. A. Meulenkamp, W. van Klinken, A. R. Schlatmann, Solid State Ionics 126, 235 (1999).
[6] S. Denis, E. Baudrin, M. Touboul, J. M. Tarascon, J. Electrochem. Soc. 144, 4099 (1997).
[7] J-M. Amarilla, B. Casal, J-C. Galvan, E. Ruiz-Hitzky, Chem. Mater. 4, 62 (1992).