

EX-SITU IR INVESTIGATION OF STRUCTURAL CHANGES IN SOL-GEL V₂O₅ FILMS DURING CHARGING/DISCHARGING

A. Surca Vuk¹, B. Orel¹, M. Liberatore², F. Decker²

¹ National Institute of Chemistry, Hajdrihova 19, SI – 1000 Ljubljana, Slovenia

² Dipartimento di Chimica and INFM, Università degli Studi di Roma “La Sapienza”, Piazzale Aldo Moro 5, I – 00186 Roma, Italy

Vanadium pentoxide is one of the most extensively studied intercalation compounds mainly because of its potential use as an ion-storage electrode films in electrochromic devices (ECDs) or, in a bulk powder form, as a cathode material for rocking-chair lithium batteries. Charging/discharging properties of V₂O₅ films have been studied with various electrochemical techniques and electrochromic properties established with in-situ UV-visible spectroelectrochemical techniques. In this work we focus on ex-situ IR spectroelectrochemical studies of the crystalline V₂O₅ films made from V-isopropoxide sols deposited with a dip-coating deposition technique. Such measurements are scarce in spite of the fact that vibrational bands reflect short-order interactions between the inserted Li⁺ ions and the film matrix and at the same time give information of the electrochemical changes that occurred in the V₂O₅ structure. The main aim of the present work was to follow step-by-step the vibrational spectra changes of V₂O₅ as a function of the inserted/extracted charge.

Films were galvanostatically charged/discharged in 1M LiClO₄ in propylene carbonate (PC) and after each charging/discharging the IR spectra (4000 – 400 cm⁻¹) were recorded. The intercalation coefficient (x) was gradually increased in steps of x = 0.25 from x = 0 to x = 3.5 (in Li_xV₂O₅). Figure 1 shows the changes of the V_A-O, V-O_B-V and 3V-O_C modes (stretchings and deformations) in the range 4000 – 400 cm⁻¹ and the evolution of the tail of the polaron absorption extending from the visible and near spectral range to the 4000 – 2000 cm⁻¹ spectral region.

Detailed examination of the vibrational bands using deconvolution technique revealed the co-existence of various phases formed electrochemically. Diversibility of the phase formation (α , ϵ , δ and γ) was confirmed from the electrochemical techniques (slow-scan CV), showing the reversibility of the $\alpha \leftrightarrow \epsilon$ phase at x up to 0.5, the insertion of the additional x = 0.5 led to the formation of δ phase while discharging brought about the α phase again without retained Li⁺ ions.

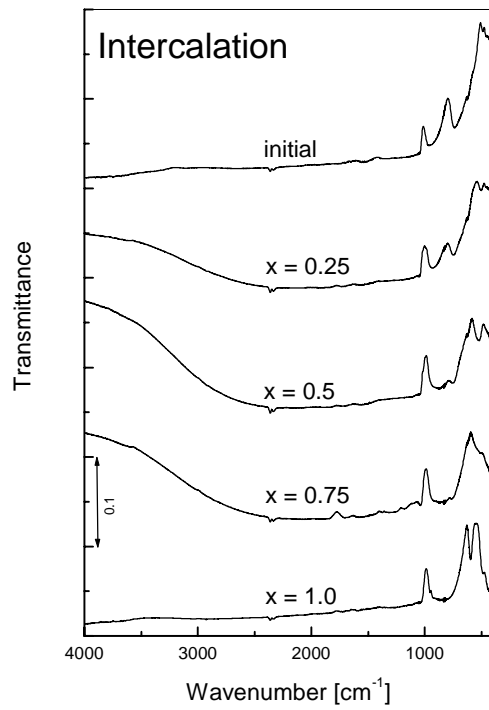


Fig. 1 *Ex-situ* IR transmission spectra of V_2O_5 : initial state and charged to intercalation coefficient $x = 0.25$, 0.5, 0.75 and 1.0 (in $Li_xV_2O_5$).

Diffusion coefficient measurements made with a PITT were followed during the evolution of the CV peaks in SS-CV; the minimum of D 's coincided with the changes of $\alpha \rightarrow \epsilon$ and $\epsilon \rightarrow \delta$ phase. SEM measurements of charged/discharged films were recorded and the morphology changes correlated with the CO_3^{2-} species determined from the IR spectra measurements of the films.