

Intercalation of polyelectrolytes into lamellar vanadium pentoxide

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Abstract – Layered vanadium oxide hybrids were prepared directly from commercial bulk V_2O_5 and poly(diallyldimethylammonium chloride) (PDDA) or alternatively, poly(alilamine chloride) (PAH). The materials thus produced, $[PDDACl]_{0.14}[PDDA]_{0.28}V_2O_5$ and $[PAHCl]_{0.34}[PAH]_{0.41}V_2O_5$, can be used as anion exchangers. On the basis of X-ray diffraction (DRX), elemental analysis (CHN), thermal analysis (TG/DTG) and spectroscopic results (FTIR and UV-Vis-NIR) the presence of the polycations in the interlayer space of V_2O_5 was confirmed. It emerged from this study that the intercalation of polyelectrolytes on V_2O_5 occurs only if some V^{5+} ions are reduced in V^{4+} .

Vanadium pentoxide (V_2O_5) has attracted special interest because of its lamellar structures. The layered structure is made of parallel ribbons of VO_5 pyramids and thus the interlayer space can be used to adequately host species to produce intercalation compounds [1]. Here, the intercalation of poly(diallyldimethylammonium chloride) (PDDA) and poly(alilamine chloride) (PAH) into the V_2O_5 matrix using only hydrothermal process is investigated. The objective is to simultaneously create layer charges in the V_2O_5 matrix and use the polyelectrolytes as locus to ultimately produce a novel material with anionic exchange sites. The synthesis of the hybrid materials was based on a very simple procedure: V_2O_5 was added to an aqueous solution of PDDA and PAH polyelectrolytes respectively, and stirred until a homogeneous suspension of the solid was obtained. The mixture was heated under hydrothermal conditions in a Teflon-lined stainless autoclave for 96 h at 150° C. The obtained green powders were filtered, washed with plenty of distilled water and ethanol and air dried at room temperature.

The insertion of PDDA and PAH into the interlayer space of the host oxide causes important changes in the structure of the material. Figure 1 shows XRD for the V_2O_5 matrix (Figure 1a) and for the intercalated compounds obtained with PDDA, $[PDDACl]_{0.14}[PDDA]_{0.28}V_2O_5$, and with PAH, $[PAHCl]_{0.34}[PAH]_{0.41}V_2O_5$ (Figure 1b and 1c). The first difference to call attention on the XRD profiles is that the polyelectrolytes intercalated causes the enlargement of the interlayer space, the original interlayer space of V_2O_5 (0.57 nm) increases to 1.40 nm after reaction with PDDA and to 1.80 nm upon intercalation with PAH. Those two materials $[PDDACl]_{0.14}[PDDA]_{0.28}V_2O_5$ and $[PAHCl]_{0.34}[PAH]_{0.41}V_2O_5$ still have exchangeable chloride ions, 33.3 and 45.0 % of total initial Cl^- respectively, as determined by the Mohr's method. The results of TG/DTG (not shown) presented weigh loss in the range of 250-550°C that are related with the decomposition of polycations inserted into V_2O_5 . The FTIR spectra (not presented) showed bands corresponding to PDDA and PAH as well as band in lower frequency range assigned to V_2O_5 vibration modes. The UV-Vis-Nir spectra (Figure 2) presented bands associated with $O \rightarrow V^{5+}$ charge transfer at 402 nm. After intercalation of polyelectrolytes (Figures 2b and c), new bands appear in near-infrared region, around 950 and 1400 nm, ascribed to an intervalence-transfer transition ($V^{4+} \rightarrow V^{5+}$) [2]. Therefore, V^{5+} ions are reduced to V^{4+} upon intercalation of polycations [2]. In summary, we have developed a novel and facile route for intercalation of polyelectrolytes into lamellar V_2O_5 in one single step. In comparison with the methods from the literature [3], the direct reaction and the hydrothermal treatment were straightforward procedures to create positive charges into the interlamellar space of V_2O_5 .

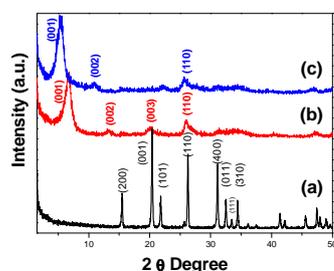


Figure 1: XRD of the V_2O_5 pristine (a), $[PDDACl]_{0.14}[PDDA]_{0.28}V_2O_5$ hybrid material (b) and $[PAHCl]_{0.34}[PAH]_{0.41}V_2O_5$ hybrid material (c).

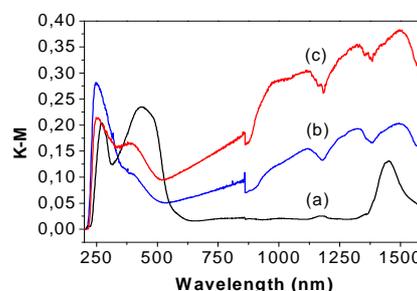


Figure 2: UV-Vis-Nir spectrum of V_2O_5 pristine (a), hybrid $[PDDACl]_{0.14}[PDDA]_{0.28}V_2O_5$ (b) and $[PAHCl]_{0.34}[PAH]_{0.41}V_2O_5$ (c).

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