

Metal Site Determination in Doped V_2O_5 ARG-like Cathodes for Lithium Battery

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The preparation of vanadium pentoxide via sol-gel processes has been extensively reported and comprehensive reviews are available [1,2]. This class of materials shows exceptional stability, intercalation capacity, and reversibility allowing application as cathodes for lithium batteries. The electrochemical properties of vanadium oxide electrodes prepared by sol-gel processes have been shown to depend on the structural and morphological characteristics that are quite sensitive to the preparation method. Following this route, a number of pillared and pristine nanocomposites of vanadium oxide have been studied and characterised [3,4]. The materials are amorphous and have intercalation capacity as high as 650 Ah/kg with corresponding specific energies exceeding 1600 Wh/kg.

Previous studies by XAS techniques of the V_2O_5 based compounds have allowed us to determine fundamental structural information on a wide variety of native and pillared nanocomposites [5-7], using both ex-situ and in-situ techniques.

To enhance the rate of insertion, the electronic conductivity of amorphous V_2O_5 was increased by doping. Ag, Cu and eventually Zn was used to the level of 0.25 mole/mole of V_2O_5 , showing the increase of the conductivity by three orders of magnitude. Subsequent intercalation of Li^+ into the doped materials was very facile and highly reversible. Nanocomposites of the Cu doped sample are able to support high rates for lithium intercalation. Previous XAS study [7] showed that the copper ion was reduced to the metallic state in a parallel process during lithium intercalation, and was re-oxidised and returned to the same site in the lattice upon lithium release. Thus, not only is the intercalation reversible for guest species like Li^+ , but doping species are not lost into the solution upon electrochemical cycling.

The XAFS technique has been used to study the site and the local structure of the selected atom. Measurements have been done either in-situ and ex-situ. The strategy in determining the local structure around the vanadium site as well as the doping metal will be discussed. In this case, the reliability of the analysis is enhanced because the presence of the two metals gives independent absorption signals, for the same compound. A general discussion of intercalation and the analysis of XANES curves is also presented.

Fig. 1 shows the comparison of the XANES k-edge spectra of V_2O_5 crystalline, aerogel (ARG) and xerogel (XRG) pristine materials. The vanadium k-edge is very sensitive to the local symmetry of the vanadium site. Analysis of the pre-edge peak (A) is very useful for the determination of the effective charge of vanadium.

Fig. 2. shows the comparison of the experimental and theoretical k-weighted EXAFS spectrum at the copper k-edge of $Cu_{0.1}V_2O_5$ aerogel like (ARG-like) sample.

Measurements have been made using several synchrotron radiation facilities (NSLS of the Brookhaven National Laboratory; LURE, Paris and SLS at Daresbury Laboratory).

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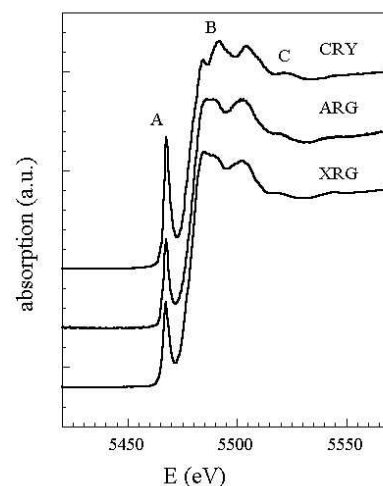


Fig 1. XANES spectra at the vanadium k-edge of V_2O_5 crystalline, ARG and XRG.

Fig. 2. experimental and theoretical k-weighted EXAFS spectrum at the Cu k-edge of $Cu_{0.1}V_2O_5$ ARG-like.

