

## Site Occupancy and Auger Parameter

J.E. Castle\*, A.M. Salvi<sup>o</sup>, A. DeBonis<sup>o</sup>, F.Decker<sup>+</sup>  
and A. Surca<sup>#</sup>

\* University of Surrey, Guildford GU2 7XH, UK

<sup>o</sup> Università degli Studi della Basilicata, Via N.Sauro  
85, 85100, Potenza, Italy

<sup>+</sup> Università degli Studi 'La Sapienza' P.le Aldo Moro  
5, 00185, Roma, Italy

<sup>#</sup>National Institute of Chemistry, Hajdrihova 19, SI -  
1000 Ljubljana, Slovenia

### ABSTRACT

Chemical shifts in the X-ray photoelectron spectrum (XPS) are sensitive to changes in the dielectric properties of the material under observation. A well established method for the correlation of these changes is based on the direct relationship between the Auger parameter, derived from the spectrum, and the electronic polarisability of the ionic lattice.

In prior publications<sup>1,2</sup> we showed that intercalation of lithium ions in an oxide lattice gives rise to a shift in the Auger parameter, and that this can be correlated with other changes in dielectric properties, such as refractive index. There is potential, in correlations such as these, for the development of a powerful method for the characterization of electrochromic, thin films, particularly for measurement of their response to different degrees of lithium ion intercalation. By this method, the composition, chemical state, and dielectric condition can be measured simultaneously, an important consideration given the sensitivity of intercalated thin films to air exposure. In this presentation we extend our previous investigation of the method in two respects. Firstly, we investigate the possibility that the Auger parameter is sensitive to the lattice site of the intercalated ion; and secondly, we present a direct comparison of results from direct transfer, and indirect transfer, between the intercalation cell and the spectrometer.

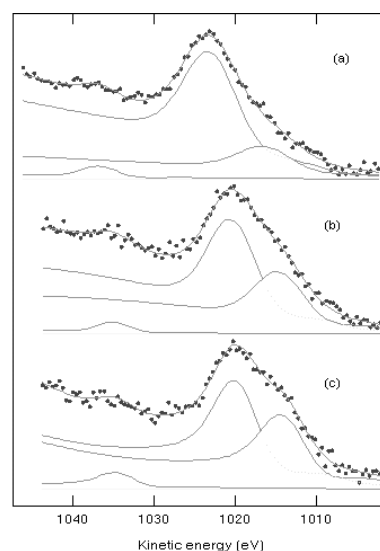
Electrochromic materials such as  $V_2O_5$  undergo phase changes during the course of intercalation. The Auger parameter is not normally sensitive to crystalline phase. However the phase change arises because intercalation occurs in stages, corresponding to the sequential filling of specific sites. Therefore a clear difference might be expected in the AP for vanadium ions in the cells occupied by lithium, in comparison with those that have not been occupied. This would not be observable if the lithium ions were random in occupation sites since the shifts would then be averaged across all possible sites. Preliminary results give strong evidence for a double AP in partially intercalated  $V_2O_5$ , as shown in Figure 1. The observation of a marker for intercalation into specific sites will be of importance in studies of degradation on the crystalline lattice as a result of intercalation/deintercalation cycles.

The second part of the work, comparison between direct transfer and indirect transfer of test pieces is important because of the need, occasionally for very long transfer paths between the electrochemical laboratory and the analytical facility, for example in the context of work undertaken on National or International synchrotron facilities. In the work to be described, samples have been intercalated in argon-filled glove boxes, sealed in the transfer cavity of a purpose-made sample holder, and inserted directly into the XPS spectrometer standing adjacent to the glove box. These then have been compared with samples intercalated in the other laboratory of this collaboration using a similar glove box

facility but with the need to transfer samples in argon filled bags over a distance of some 350km prior to analysis. A discussion will be given of the best-practice for such transfer.

### References

1. A.M.Salvi, F.Decker, F.Varsano.  
and G.Speranza. Surf.Interface Anal., **31**, 255-264  
(2001)
2. J.E.Castle, A. M. Salvi, F. Decker and G.Moretti.  
'Surf.Interface Anal., **33**, 533-538 (2002)



**Figure 1**

- a) Vanadium LMM Auger peak prior to intercalation;
- b) after intercalation at 2.1volts and
- c) after intercalation at 3.5volts (with reference to  $Li^+/Li$ ).

*Note the growth of the second Auger peak.*