Research Article

SURFACE and INTERFACE ANALYSIS

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XPS and TOF-SIMS study of the distribution of Li ions in thin films of vanadium pentoxide after electrochemical intercalation

James E Castle,[a]* Franco Decker,[b] Anna Maria Salvi,[c] Frantz A Martin,[a] Frederique Donsanti,[b] Neluta Ibris[c] and David Alamarguy[a]

The intercalation of vanadium pentoxide by lithium ions leads to a change in optical properties, a process that is of value in thin-film electrochromic devices. The extent of intercalation can be measured, electrochemically, from the charge capacity of the film and, is in good agreement with that determined in the outermost layers by X-ray photoelectron spectroscopy (XPS), when intercalation occurs homogeneously through the film thickness. SIMS profiles of V_2O_5-deposited on ITO-glass coupons have allowed examination of the interface between these layers and in prior work showed a marked build up of Li in this interphase. Investigation of the distribution of lithium within the interphase showed it to be present in parts of the testpiece that were not immersed in the electrolyte used for Li insertion. In this work we have tested the suggestion that the lithium found in the interface can be introduced, during intercalation, via the exposed edge of the V_2O_5/ITO interface at the periphery of the sample. A series of intercalation cycles using modified cells to expose either: a) the periphery; or b) the centre; of the thin film have been carried out. The distribution of lithium after intercalation has been examined using a combination of ToF-SIMS and XPS. XPS showed lithium in the film to be related only to the immersed regions of the testpiece whilst SIMS profiles confirmed the widespread distribution of Li through the interface, only when an edge was exposed. We work confirms an important influence of an unsealed edge when samples are produced by cutting from larger glass plates.

Keywords: Li ion intercalation; SIMS; vanadium pentoxide; electrochromism

Introduction

The intercalation of some oxides by lithium ions leads to a change in transparency, a process that is of value in thin-film electrochromic devices. In these devices the intercalation is controlled by an applied electropotential so that the lithium ions can be introduced or withdrawn at will – a process that is exactly similar to the operation of lithium-ion batteries. A requirement of such devices is that the oxide is transparent when deintercalated and sufficiently conducting for controlled potential. Vanadium pentoxide meets these requirements and can be deposited as a thin film on a suitably prepared substrate by a sol-gel process followed by annealing at 400 °C.[1] A complete device required an assembly of five separate layers to be built up on a glass or polymer substrate. Typically these layers are: (i) indium tin oxide (ITO), to give a conducting base to the films; (ii) the cathodic layer, vanadium pentoxide; (iii) a solid electrolyte; (iv) an anodic layer, often tungsten oxide; and finally, (v) ITO to provide the conducting contact with the stack.[2] Such a stack has four distinct interfaces and problems associated with charge transport across any one of them can have a deleterious influence on performance. The interface in all fields of materials science is difficult to study, mainly because it is hidden from view by the techniques of surface analysis. The study of lithium-ion chemistry at the buried interface is made difficult by its lack of an Auger electron emission and its weak signal in x-ray photoelectron spectroscopy (XPS). Secondary ion mass spectrometry (SIMS), however, has an excellent sensitivity to Li[3,4] and this article reports on an investigation of the behaviour of lithium ions at the ITO/V_2O_5 interface using SIMS-depth profiling. The lithium ions were introduced by the widely used technique of electrochemical insertion from a non-aqueous electrolyte and continues an investigation of the Li-V_2O_5 system by electrochemical and XPS characterisation.[5]

Li^+ insertion is accompanied by the reversible reduction of V^{5+} to V^{4+}: oxidation states which are readily distinguished by XPS. Thus XPS enables correlation of the film composition with the electrochemical insertion of charge. XPS has also enabled measurement of the thickness and composition of the V_2O_5-electrolyte interface and provided evidence of a small concentration of non-reactive V^{4+} within the top few nanometres (*ca* 3 nm) of the surface, possibly associated with trapped lithium ions.[6] SIMS-depth profiling gave evidence of diffusion of Li ions through the ITO/V_2O_5 interface and showed that lithium was present in the interface region of the part of the sample that was

* *Correspondence to: James E Castle, Emeritus Professor of Materials Science, Faculty of Engineering and Physical Science, Mail Drop A1, University of Surrey, Guildford GU2 7XH. E-mail: j.castle@surrey.ac.uk*

a *Surface Analysis Laboratory, Faculty of Engineering and Physical Science, University of Surrey, Guildford, GU2 7XH, UK*

b *Dipartimento di Chimica, Università La Sapienza, Piaza A.Moro, 00185 Roma, Italy*

c *Università degli Studi della Basilicata, Dipartimento di Chimica, Potenza, Via N. Sauro, 85-85100, Italy*

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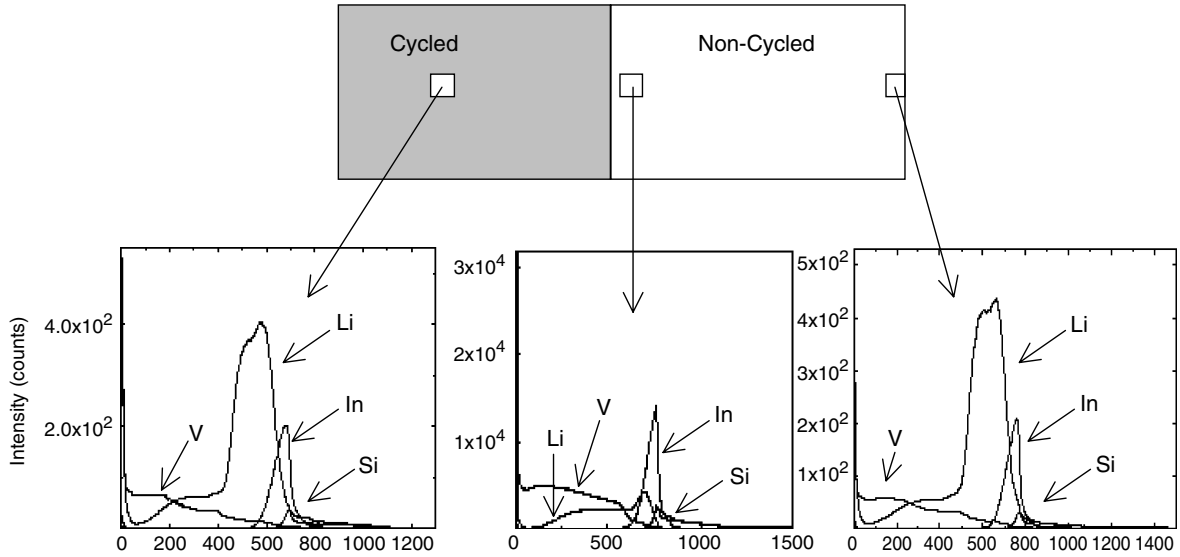

Figure 1. SIMS profiles through different areas of a deintercalated sample, as shown in the key.

not immersed in the electrolyte.[4] The SIMS profiling was validated by the non-invasive technique of proton-beam reaction profiling: Lithium is identified by the alpha particles emitted from the ^{7}Li (p, α) reaction[7] and had a bimodal energy distribution corresponding to Li at the surface and the interface. This technique also confirmed the finding of Li in the interface of the non-immersed region of the test piece.

In subsequent work SIMS-depth profiling has been used extensively to examine the distribution of Li in depth and at different regions of the sample surface.[6] Figure 1 summarises the findings that are pertinent to this study. The sample was intercalated and deintercalated through 598 cycles and removed for examination in the deintercalated state. The sample was then transferred, in the deintercalated state for SIMS profiling. The profiles are shown in Fig. 1, keyed to the position on the test piece from which they were obtained. The lithium profile from the intercalated region is notable for the broad peak at the interface with ITO. This distribution was found on all samples after deintercalation. It points to a region in which the insertion of charge and consequential electrochromic action is blocked by trapped lithium. Typically, this interphase zone had a thickness of *ca* 27 nm. The profile a few mm outside the electrolyte-wetted region is also shown. The interface lithium is not as prominent but has the same distribution. Finally, a profile taken from an edge of the sample, far from the electrolyte is remarkable for its similarity to that of the immersed region. XPS showed that there was no Li present on the outer surface beyond the region wetted by the electrolyte and thus it was concluded that the Li had diffused to the non-wetted regions by diffusion through the ITO/V_2O_5 interface.

As a result of these findings we speculated that the exposed edge formed when cutting out coupons from the coated glass plate might have played a significant role. The immersed part of this edge provides a ready access to the interface for the electrolyte and, by this route, lithium ions might redistribute throughout the entire interface. In this article, we describe results from work carried out to test this hypothesis. Since test coupons are often cut from large plates, in the manner that was used in our work, the results will be of general interest.

Experimental

The films of V_2O_5-deposited on ITO-glass plates measuring 100 mm square were produced by a sol/gel process as previously described.[1,8] All the experiments were done into a dry box, under Argon. Intercalation was carried out, electrochemically, as in prior work, using lithium perchlorate in propylene carbonate as the electrolyte, but using two specially designed electrochemical cells; (i) a conventional cell in which the sample was lowered on a micrometer screw until the lower edge made contact and formed a meniscus with the electrolyte and (ii) a cell that intercalated the centre of the coupon through contact with a droplet at the end of a capillary. These cells are illustrated in Fig. 2 and of the two the droplet cell is particularly novel. The cell, shown in Fig. 2(b), is based on a Pasteur pipette modified with side tubes for the counter and reference electrodes (Lithium). These electrodes, in the form of wires, are sealed into the side tubes using bungs and parafilm so that electrolyte droplets would be released, only on demand, by slight pressure on the syringe. The whole arrangement was carefully lowered, bringing the capillary opening into close proximity to the V_2O_5 thin film. Once the gap was bridged by an electrolyte droplet, Li intercalation could be carried out electrochemically using the classical, three-electrodes method. By this means lithium is introduced only through the part of the surface in contact with the electrolyte: a circular region of about 0.5 mm of diameter. In particular, any contact with the cut edge of the test piece is avoided and thus there is no direct entry to the interface zone.

After intercalation the samples were packaged in an argon atmosphere and transferred for SIMS analysis. Li distribution profiles were obtained using time-of-flight (TOF) SIMS with an IonTOF 5 spectrometer. The spectrometer was run at an operating pressure of 10^{-9} mbar. A pulsed 25 keV Bi^+ primary ion source was employed for analysis, delivering 1 pA of current over a 100 × 100 μm^2 area. Depth profiling was performed using a 3 keV Cs^+ sputter beam giving 20 nA target current over a 300 × 300 μm area. Data acquisition and post-processing analyses were performed using the IonSpec software. Results are based on the positive ion profile, Fig. 3 shows a typical depth profile from a

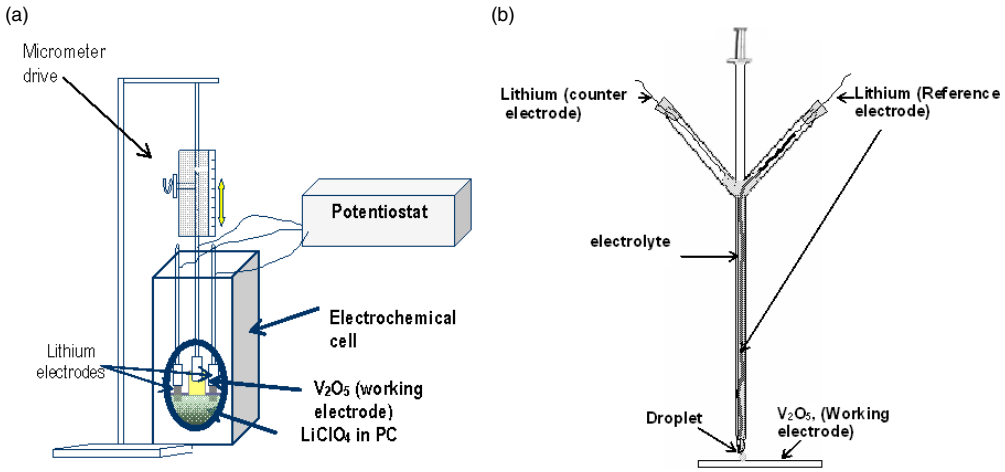

Figure 2. (a) Cell configured for meniscus-line contact with lower edge; (b) cell used for droplet intercalation. This figure is available in colour online at www.interscience.wiley.com/journal/sia.

droplet intercalated sample. A set of SIMS profiles were carried out at set intervals from the centre of the electrochemically treated regions of both types of sample. In the case of the cell shown in Fig. 2(a) the influence of the edge would be maximised whereas, in the droplet cell, (Fig. 2(b)) there was expected to be no edge effect. The location of the profiles is shown in Fig. 4. In addition to the SIMS analysis, a second set of samples were intercalated at the meniscus-line for XPS examination of the outer surface to confirm that the main body of the film remained free of Li and that the electrolyte had not crept across the outer surface. These spectra were acquired using a LH X1 Leybold instrument operating at 13 kV and 20 mA. The x-ray source was unmonochromatised Al Kα. The spectra were recorded in FAT operation mode with a pass energy of 50 eV and a channel width of 0.1 eV

Results

The outcome of the profiles taken as shown in Fig. 4 was assessed by means of the Li/V ratio obtained by integrating the signal for each ion over two regions of the profile. These relate to the interface region and to the main body of the film, as shown in Fig. 3. Comparison of the interface region in the profiles of Figs 1 and 3 shows that the interface is easily recognisable in the intercalated sample.

The results are given in Figs 5(a) and (b). Fig. 5(a) shows that there is no evidence of interface transport using the droplet intercalation. The interface distribution mirrors that of the film itself: both are high in the droplet region and fall rapidly outside the intercalated region. The absolute value of the ratio in the interface is larger than that in the film but this is largely because the signal for V is lower in the interface and not because the Li is greater there. Figure 5(b) shows the contrast in behaviour when the cut edge is in contact with the electrolyte. There is some intercalation of the film but the dominant feature is the presence of the Li within the interface region. The Li/V ratio in the interface remains high for a distance of more than 25 mm from the edge whereas this ratio in the film has dropped to a very low value after only 5 mm. Figure 6 shows the XPS spectra from this sample. Close to the edge lithium

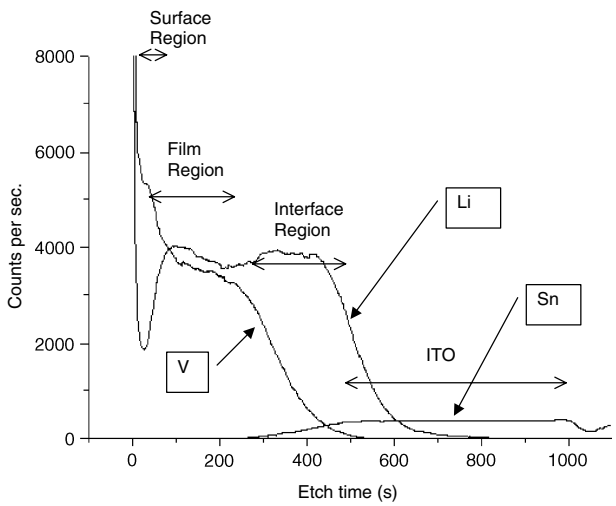

Figure 3. A SIMS depth-profile taken from a region intercalated by the droplet technique. The interface region and film regions used for assessing the Li/V intensity ratio are indicated.

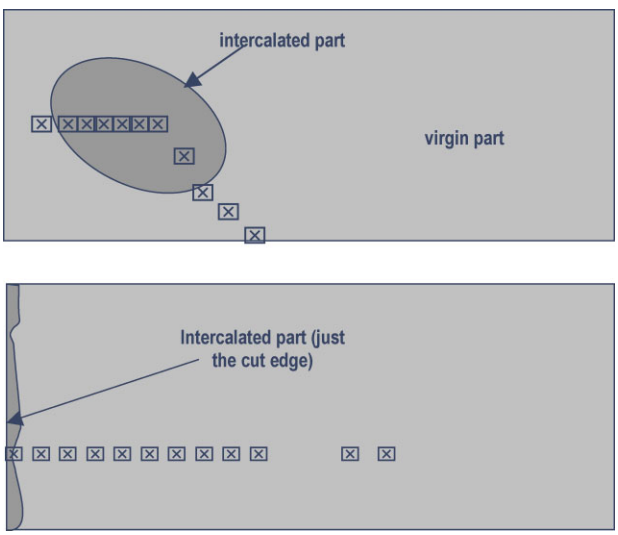

Figure 4. The positions of SIMS profiles for the droplet and edge intercalated samples. This figure is available in colour online at www.interscience.wiley.com/journal/sia.

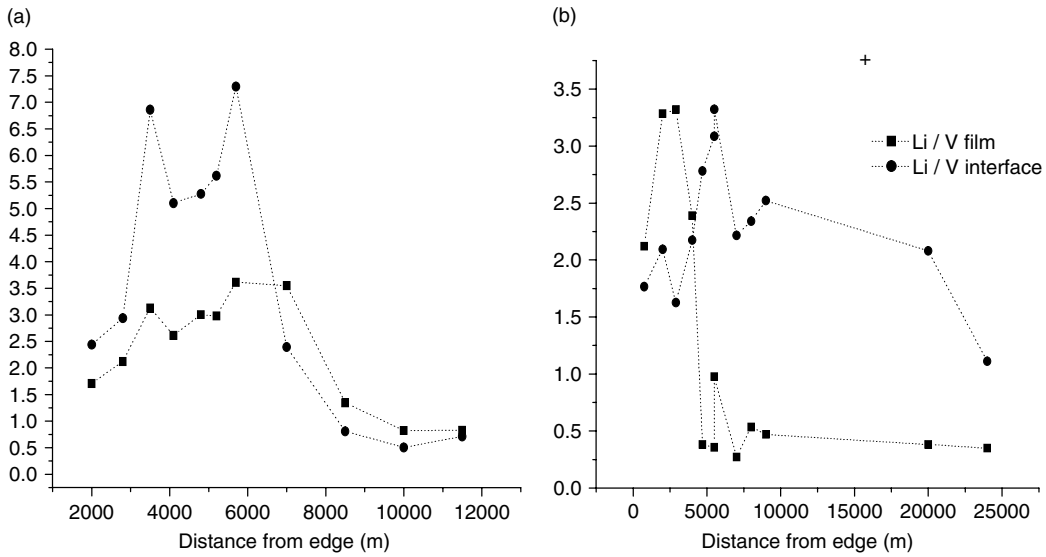

Figure 5. (a) The distribution of lithium, relative to vanadium after intercalation by the droplet method; (b) the distribution of lithium after intercalation at the cut edge of a sample.

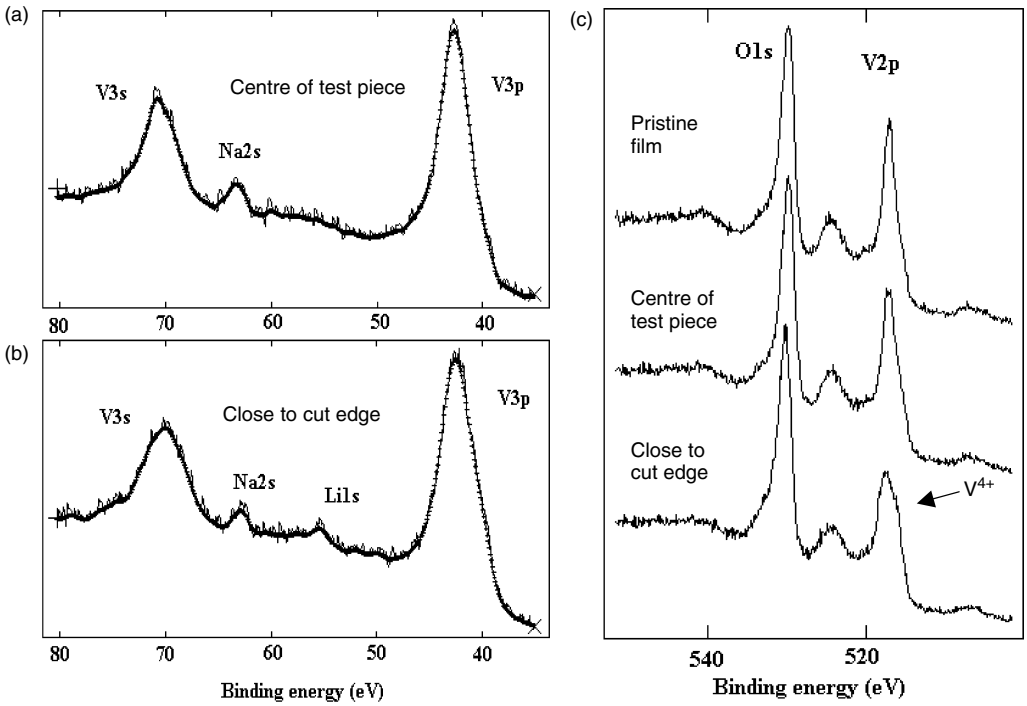

Figure 6. XPS Spectra, (a) The lithium 1s region, taken in the centre of the test piece and (b) taken close to the cut edge; (c) the vanadium 2p region, the shoulder from the spectrum close to the cut edge shows the presence of the V^{4+} ion. (N.B. The spectra taken close to the cut edge are from a sample that was immersed beyond meniscus-line contact in order for the Li and V^{4+} to be detectable).

is present (Fig. 6(b)) and, as would be expected, the vanadium is in the partly reduced (V^{4+}) state Fig. 6(c)). Away from the edge, but within the region where the interface is rich in lithium, the film contains no lithium, Fig. 6(a), and the V2p spectrum is identical to that of a pristine film used as a control sample.

Discussion

The combination of SIMS and XPS analysis has shown that Li ions are able to travel through the V_2O_5 interface for a great distance. The sequence of analysis also show that the entry point is the edge of the sample. The crucial points are: (i) that there was no lateral diffusion through the interface from the intercalated spot; (ii) lateral diffusion occurred throughout the test piece when only edge contact with the electrolyte was allowed; (iii) XPS showed no trace of intercalation over the region in which lateral diffusion through the interface was found using the edge specimen; and (iv) XPS showed the normal behaviour of intercalation (Li^+ plus V^{4+}) for the small amount of film that was submerged in the meniscus line formed at the contacting edge.

When the relative distances travelled by the ions in the main body of the film (*ca* 50 nm) and the interface (*ca* 25 mm) are scaled according to (distance)^2 as is usual in calculations of diffusion coefficients, the difference in diffusion rate is seen to be enormous. The absence of movement of lithium through the interface in the sample intercalated by way of the droplet shows that there is no easy contact with this fast transport route. There maybe a small amount of insertion of Li from the backside of the film, as evidenced by the shape of the profiles, as shown in Fig. 1, but it appears that the film itself is not easily intercalated by lithium transported through the inner interface. Thus the film and the interface transport route appear, perhaps, to be well insulated from each other. The interface lithium might be associated with the growth of a new phase. There is a clear reduction of the vanadium signal in this region, e.g. the profiles of Fig. 1. Whilst this could, in principle, be a SIMS artefact, resulting from a change in the ion-emission coefficient, nothing in the spectrum supports such a change. Thus the interface-Li may not be intercalated in vanadium oxide and a new phase might have formed as result of the electropotential applied to the ITO being directly visible to the electrolyte at the cut edge. Possibilities would include Li_2O but not Li_2CO_3 since no carbonate species are found in the negative-ion spectrum. Whilst there is a reduction in the vanadium signal, it is not zero and thus another possibility is the formation of a LiV oxide structure with highly reduced vanadium, possibly V(III) ions.

This study by SIMS of changes at an interface that is normally hidden from other surface analytical techniques shows that the use of coupons cut from larger plates should be undertaken with care. The very high mobility of the Li ion leads to its distribution throughout the test piece when the edge is exposed and thus introduces an uncontrolled element into the experiment. However, the work also shows that true intercalation from the front side of the test piece does not lead to further Li distribution via the interface, even though the same interface compound appears to form.

Conclusions

When a cut edge is exposed, an interface enrichment of Li occurs that extends more than 25 mm from the intercalated zone. There is virtually no extension of intercalation within the body of the film.

When a droplet is used to intercalate a region without exposing an edge there is no extension of the lithium in the interface beyond the region directly intercalated.

The edges of thin film samples when cut from a prior-prepared plate offer an easy route to the interfaces in layered samples. This offers the opportunity for direct insertion of Li ions to the interface and thence for lateral diffusion at a high rate throughout the test piece.

Acknowledgements

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