

Distribution of intercalated lithium in V₂O₅ thin films determined by SIMS depth profiling

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The distribution of Li in the V₂O₅ films was determined before and after intercalation/deintercalation electrochemical cycles by time of flight secondary ion mass spectroscopy (ToF-SIMS) depth profiling. On deintercalation most of the inserted Li is removed except in the vicinity of the interface with the fluorine-substituted tin oxide, used as a conducting substrate. More surprisingly, Li was also found in the interface region of the part of the film that has not been immersed in the electrolyte and that had thus not been electrochemically controlled. This finding suggests that Li diffuses through the interface, in the plane of the electrode surface, during intercalation of the main body of the film. The SIMS results have been confirmed by proton beam analysis using the nuclear reaction between H and Li to produce characteristic alpha particles that reveal the distribution of Li, both inside and outside the electrochemically treated area of the electrode. The energy loss of the alpha particles on their way through the sample to the detector also reveals the Li concentration distribution inside the V₂O₅ films. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: vanadium pentoxide; fluorine tin oxide; lithium intercalation; SIMS; lithium depth profiling; proton microbeam

INTRODUCTION

V₂O₅ thin films provide good host lattices for Li ions in electrochromic devices and for charge storage in batteries. A few papers have reported on lithium depth profiling in WO₃ layers using SIMS,^{1,2} demonstrating that the technique has an excellent sensitivity to lithium and yields a very good depth resolution. Here, SIMS depth profiling of Li ions is reported upon, after electrochemical intercalation/deintercalation cycles of V₂O₅ films, of *ca* 400 nm in thickness. These particular films were modified during the course of the sol-gel preparation by incorporation of the substituted silane 3-isocyanatopropyltriethoxi silane-poly (propyleneglycol)-bis-2-amino-propylether (ICS-PPG) to improve the film compactness and reduce optical defects. SIMS has also been used to identify silicates that might have been formed from the ICS-PPG.

As a result of depth profiling, Li was found in the interface region of the part of the film that had not been immersed in the electrolyte and that had thus not been electrochemically controlled. Because of the potential importance of this interface mobility to the operation of devices, the SIMS results need to be validated. Only a few methods could be used to assess the Li distribution: neutron² or proton³ microbeam analysis using the energy loss of emitted alpha

particles, elastic recoil detection³ and electron energy loss spectroscopy (EELS) analysis of the cross section. Here, a proton microbeam analysis was performed using the nuclear reaction between H and Li to produce characteristic alpha particles. This analysis has the advantage of being quantitative.

EXPERIMENTAL

Sample preparation

The V₂O₅ thin films were prepared by a sol-gel technique modified by the addition of an organic–inorganic hybrid gel, ICS-PPG, prepared from 3-isocyanatopropyltriethoxysilane poly(propyleneglycol) bis-2 aminopropylether added in molar percentages of 1, 2 or 5. Films were deposited on fluorine-doped tin oxide-(FTO-) coated glass substrates by dip coating using a pulling velocity of 10 cm min⁻¹ and followed by heating for one hour at 400 °C. The thickness of the V₂O₅ was 400 nm and that of the FTO *ca* 250 nm, measured in cross section in the SEM after the focused ion beam (FIB) sections were cut.

Lithium intercalation/deintercalation was carried out in three-electrode cells, hermetically sealed under argon. Lithium foils were used as counter and reference electrodes and the V₂O₅ film as the working electrode. The electrolyte was 1:1 M LiClO₄/propylene carbonate (PC) solution. A Potentiostat/Galvanostat (ECOCHIMIE AUTOLAB 12) was used to measure cyclic voltammograms (CV) during intercalation/deintercalation cycles running at 0.5 mV/s.

Three samples were studied: one as deposited with 1% ICS-PPG (sample 1), another with 2% ICS-PPG, after 10 CV

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cycles (sample 2), and the last with 5% ICS-PPG, after 300 CV cycles (sample 3). The last two had been cut at the boundary between the intercalated part (between blue and colorless for 10 CV and fading yellow for 300 CV) and the nonintercalated (dark yellow).

Experimental set-up

Time of flight secondary ion mass spectroscopy (ToF-SIMS) analysis was performed with a VG Scientific Type 23 System equipped with a two-stage reflectron type analyzer with a MIG300PB pulsed liquid metal ion source. The spectrometer was run at an operating pressure of 10^{-9} mbar. The primary ion beam used was a 16-keV $^{69}\text{Ga}^+$ ion beam rastered over an analysis area of $65 \times 65 \mu\text{m}^2$ at a rate of 5 kHz. The system was operated with a pulse width of 50 ns and with a beam current of 1 nA, resulting in a primary ion dose $<10^{13}$ ions/cm² during analysis. SIMS spectra were acquired over a mass range of $m/z = 0 - 200$ Da in positive and negative mode. The spectrometer was controlled by a VG Scientific Type 23 data system based on a DEC PDP11/73 computer running the microRSX operating system. The SIMS etching was carried out over an area of $162.5 \times 162.5 \mu\text{m}^2$ in a continuous mode. The depth profiling is performed by measuring the intensity of significant peaks in the spectrum as a function of time. The intensities are cited as a percentage of the summed intensity of the measured peaks: no correction was made for the differing relative sensitivities of the secondary ions.

A proton microbeam ($\sim 5 \mu\text{m}$ diameter) was used to validate the Li distribution shown by SIMS. Lithium is identified by the alpha particles emitted from the ^7Li (p, α) reaction.⁴ A proton impact energy of 1.2 MeV is chosen, which is below the maximum of the reaction cross section but avoids possible interferences with the fluorine coming from the underlayer, since at this energy, the ^{19}F (p, α) reaction cross section is very low. The energy of the alpha particles is measured with an annular silicon surface barrier detector. Following the geometric arrangement of the detectors relative to the samples, the energy of alpha particles amounts to $E_\alpha = 7.68$ MeV

RESULTS AND DISCUSSION

SIMS depth profiling

Sample 1

The SIMS measurements, Fig. 1, show that both vanadium and vanadium oxide (mass 67) ions are found as signatures for V_2O_5 but during the first minutes of etching, the oxide ion decreases quickly while vanadium increases and is then steady. The analysis shows the presence of sodium and potassium, uniformly distributed through the V_2O_5 layer. The readers are reminded that only a qualitative estimation of elements can be done from the data because of the different sensitivity factors that SIMS has for different elements and different matrixes. The Na and K could have come from the glass of the substrate, which means that they diffused inside the vanadium layer during the synthesis of the film, or they could have come from the glassware that is also used during the synthesis of the film; in any case, they probably make a very minor contribution to the film.

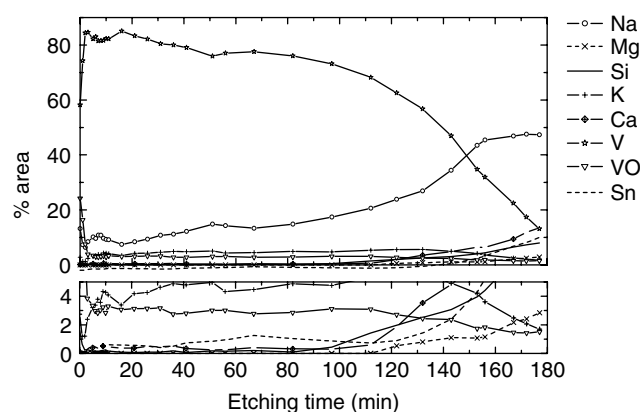


Figure 1. SIMS depth profiles for sample 1 (V_2O_5 as deposited with 1% mol ICS-PPG). The scale of the lower graph is magnified by ~ 5 .

After around 120 min of etching, the vanadium fragments decrease while calcium, silicon, sodium, magnesium and tin elements increase. Only potassium decreases. All the elements showing an increase could come from the substrate (glass) except Sn, which comes from the FTO interlayer (between the V_2O_5 layer and the glass). So this point certainly represents the far side of the V_2O_5 layer.

Sample 2

Intercalated part. Figure 2(a) indicates that the top layer mainly contains lithium. A few minutes of etching reveals the vanadium layer and, from that point, the sample has homogenous Li^+ and V^+ depth distributions. After 55 min of etching, the percentage areas of Li^+ and V^+ ions decrease while those of the elements from the substrate increase. An idea of the relative sensitivities for Li and V ions can be obtained from this plot; For a Li/V atomic ratio of 0.5:1, the intensity ratio is 9:1, indicating that Li is approximately 18 times more sensitive than V in the ToF-SIMS.

Nonintercalated part. Positive ions depth profiling. On the surface of the electrode, the analysis (Fig. 2(b)) looks like that of the first sample: detection of vanadium fragments and those from glass (Na^+ , K^+ and Si^+) but the analysis also detects the presence of lithium. Then during the first minutes, the percentage areas of all the elements decrease, except that of vanadium which increases. Throughout the V_2O_5 layer, the Na and K concentrations are noticed to be lower than those for the first sample. Approximately, after 60 min of etching, the percentage of Li^+ ions increases and then reaches a maximum at the V_2O_5 /FTO interface: vanadium drops and elements from the substrate (Na, Ca, Si, Mg, K and Sn) increase. Bearing in mind the relative sensitivity of Li and V, the lithium ion concentration at the interface is ca 6% of vanadium. However, the presence of any lithium in this part of the electrode is unexpected since this part has not been subjected to electrochemical cycling in the lithiated electrolyte. This finding seems to prove the diffusion of lithium through the plane of the electrode surface, following the interface between the vanadium layers and the FTO.

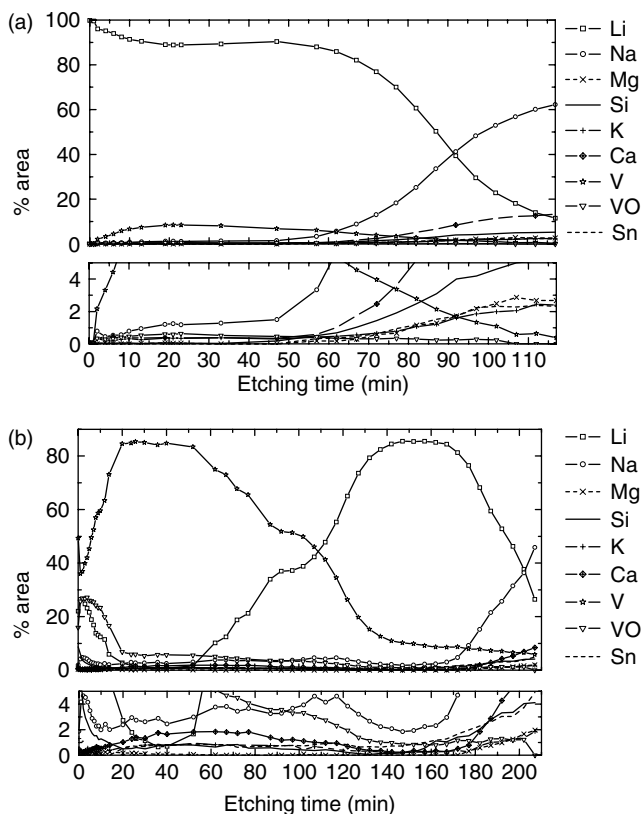


Figure 2. (a) SIMS depth profile for sample 2 (V₂O₅ with 2% mol ICS-PPG, after 10 CV cycles), the cycled part. The scale of the lower graph is magnified by ~5. (b) SIMS depth profile for sample 2 (V₂O₅ with 2% mol ICS-PPG, after 10 CV cycles), not the intercalated part. The scale of the lower graph is magnified by ~5.

Negative ions depth profiling. Negative ions spectra were also examined between each sputtering, just after the acquisition of positive ions. The resulting depth profiles have shown a homogenous distribution of mainly oxygen, as well as VO₃⁻, SiO_x⁻ and Cl⁻. The SiO_x⁻ ions come from the ICS-PPG components added into the V₂O₅ gel. As the interface is approached, fluorine ions increase exactly where Li⁺ increased on the positive ion depth profile; chlorine ions also increase, but in less quantity. Then SnO₂⁻ starts to increase. This means that there is certainly a LiF layer just between the V₂O₅ film and the FTO interlayer.

Sample 3

Intercalated part. Figure 3 indicates that the top layer mainly contains lithium. But after a few minutes of etching, the percentage falls (it was not the case for this same part of sample 2) while those of V⁺, Na⁺ and Ca⁺ increase. Compared to the second sample, in sample 3 the percentages of the elements from glass are much higher. After going through the vanadium layer, a peak of lithium was obtained and then the substrate was reached. Here, there is a peak for Sn⁺ ion. (This part is more similar to the nonintercalated parts).

Nonintercalated part. The evolution (not reported) is similar to the same part of sample 2. The only differences are:

- the percentage area of Na⁺ ion is higher all along the vanadium pentoxide layer
- the profiling has been performed deeper, through the tin oxide underlayer into the glass substrate.

The generation of a Li depth profile similar to that shown in Figs 2(b) and 3 has already been reported in the case of the WO₃ layer with a small peak at the WO₃/ITO interface developing with the aging time² (first hours after the loading of the WO₃ layer). Similar results obtained with neutron depth profiling had excluded the effect of primary ion beam. The plausible explanation suggested was the great mobility of the Li atoms, which slowly redistributes over the WO₃ layer as a function of the time.

Proton microbeam analysis

Figure 4 shows the summed alpha particle energy spectra for three different areas of sample 2, after 10 CV cycles. For all

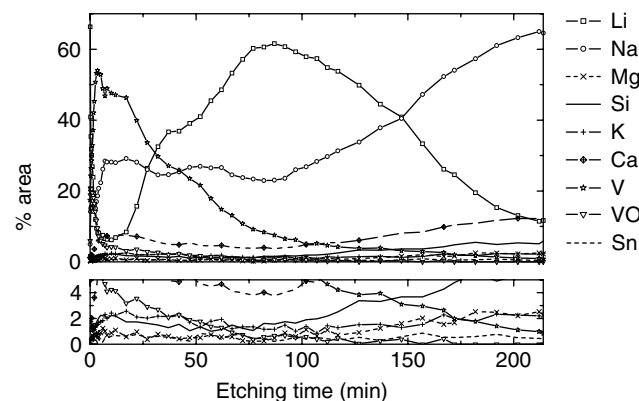


Figure 3. SIMS depth profile for sample 3 (V₂O₅ with 5% mol ICS-PPG, after 300 CV cycles), intercalated part. The scale of the lower graph is magnified by ~5.

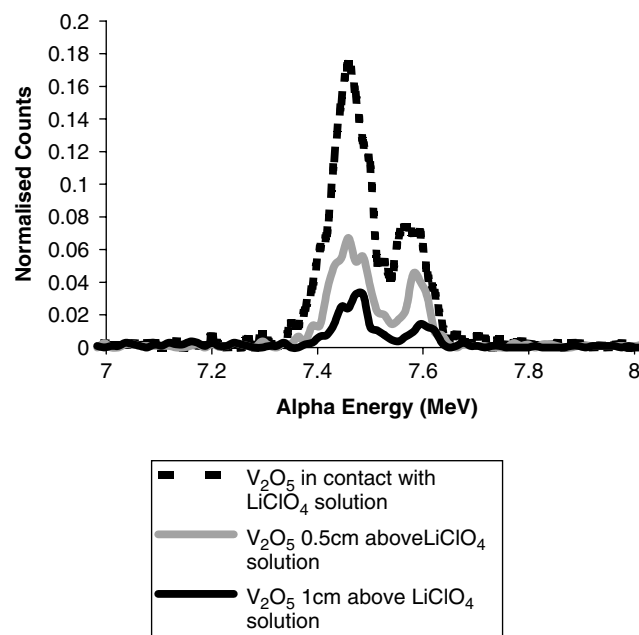


Figure 4. Alpha particles peaks produced from ⁷Li(p, α)⁴He reaction for sample 2, (V₂O₅ with 2% mol ICS-PPG, after 10 CV cycles).

areas, two peaks are displayed around 7.5 MeV, peaks which were not seen on the sample before intercalation (sample 1). The intensities of these peaks are higher for the part of the film, which has been immersed in the electrolyte, and decrease especially as one moves away from this part of the film. From these two peaks, it can be inferred that lithium was not only located at the surface but also distributed in depth. The lower energy peak certainly comes from the deeper reaction site as the alpha particles lose energy on their way to the surface of the sample towards the detector, and hence have a lower energy with increasing depth of the reaction site.³ However, further investigations are needed because, among other competitive phenomena, the alpha particle energy increases when generated from protons that, having lost energy along their path to the reaction site, have an energy of less than 1 MeV.

CONCLUSION

It has been shown that Li depth profiles can be determined using different techniques. SIMS and nuclear reaction analyses have been performed on thin modified V₂O₅ films before and after Li intercalation/deintercalation cycles in

order to study the distribution of lithium inside the vanadium oxide films. It has been determined that on deintercalation, lithium is mainly removed after long cycling, except in the vicinity of the FTO interlayer. It has also been pointed out that lithium is irreversibly inserted into the interface region of the part of the film that has not been immersed in the electrolyte, suggesting that Li diffuses through the interface, in the plane of the electrode surface.

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