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Two-Step Electrochromism in Chemically Bath-Deposited V_2O_5 Thin Films: Thickness Control of the Optical Modulation

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Abstract

The electrochromic behaviour of ammonium-intercalated vanadium(V) oxide xerogel thin films has been examined as a function of film thickness. Films with 70 to 440 nm thickness, were grown on fluorine-doped tin oxide glass from a chemical bath in which diethyl sulfate is hydrolysed to acidify an ammonium metavanadate solution. Cyclic voltammetry in 1 M $LiClO_4$ in propylene carbonate reveals two reduction and two oxidation peaks, at −0.10 and −0.46 V and at 0.11 and −0.12 V versus Ag/AgCl, which are assigned to successive lithium intercalation steps between V(V) and V(IV) and to the corresponding $Li_xV_2O_5$ phases. The voltammograms are stable over repeated cycling. In situ absorbance measurements at 900 nm show that switching is complete within two minutes at ±2.5 V, and that the modulation depth increases with the magnitude of the applied voltage. Under these conditions the films colour reversibly in two steps, from yellow to green and then to blue, in agreement with the two redox pairs observed voltammetrically. The transmittance variance depends strongly on both wavelength and thickness: at 400 nm it falls from 45% for the thinnest film to 6% for the thickest, whereas at 900 nm it rises from 13% to 48%, the two becoming equal near 200 nm. The crossover is attributed to saturation of the absorption of the oxidised film in the blue and to the growth of the intervalence absorption of the reduced film in the near infrared.

Keywords: *Electrochromism, Vanadium(V) Oxide Xerogel, Thin Films, Lithium Intercalation, Transmittance Variance, Chemical Bath Deposition.*

I. INTRODUCTION

Electrochromic materials change colour reversibly when charge is inserted into or removed from them, and they underpin a range of devices in which transmittance must be controlled electrically — smart windows, displays, variable-reflectance mirrors and optical shutters.[1]

The origin of this behaviour lies in the layered structure of $V_2O_5{\cdot}nH_2O$.[2] Sheets built from VO_5 square pyramids enclose an interlayer region occupied by water molecules, and this region accepts guest cations readily. Insertion of lithium reduces part of the vanadium from the +5 to the +4 oxidation state, and the resulting mixed-valence material absorbs light through intervalence charge transfer between neighbouring V(IV) and V(V) centres. Because the reduction proceeds in discrete stages, the colour passes through a sequence — yellow, green, blue and, at deep reduction, violet — rather than changing in a single step.[3] The capacity of the interlayer region for guest species also depends on how much water it contains, so the hydration state of the oxide influences its electrochemical response directly.[4]

The same intercalation chemistry has made these materials attractive as cathodes for lithium batteries,[5] as electrodes in supercapacitors[6] and as the active layer in electrochromic mirrors.[7] For optical applications, the practical figure of merit is the transmittance variance ΔT, the difference in transmittance between the coloured and bleached states at a given wavelength. Maximising ΔT is not simply a matter of depositing more material: a thicker film inserts more lithium and therefore absorbs more strongly when reduced, but it also absorbs more strongly when oxidised, and at wavelengths where the oxidised film is already opaque there is no modulation left to exploit.

Chemical bath deposition is well suited to producing the graded thickness series needed for such a study. The technique operates at atmospheric pressure and modest

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temperature, coats large and irregular substrates uniformly, and allows thickness to be varied simply by changing the immersion time.[8] It has been applied to nickel oxide[9] and vanadium(V) oxide xerogels, for which deposition conditions have been systematically optimised. For vanadium(V) oxide itself, sol–gel chemistry remains the most common route,[10,11] generally through acidification of a metavanadate solution,[12,13] hydrolysis of an alkoxide[14,15] or the reaction of hydrogen peroxide with the oxide,[16] while hydrothermal synthesis,[17] sputtering,[18,19] spray pyrolysis,[20] pulsed laser deposition[21] and spin coating[22] have all been used to make films.

In this work we report the electrochemical and optical characterisation of a series of ammonium-intercalated vanadium(V) oxide xerogel films of composition $(NH_4)_{0.15}V_2O_5{\cdot}H_2O$, deposited from a chemical bath in which the acid is generated internally by the hydrolysis of diethyl sulfate. Films between 70 and 440 nm in thickness were prepared and examined by cyclic voltammetry and by in situ ultraviolet–visible spectroscopy.

II. MATERIAL AND METHODS

➢ *Preparation of the Films*

Films were grown on commercial glass substrates coated with fluorine-doped tin oxide (SnO_2:F, FTO), of transmittance about 80% in the visible range and sheet resistance 10–20 Ω/cm². Immediately before deposition the substrates were treated in sequence with aqueous detergent, alkaline solution, hydrochloric acid, hexane and acetone, rinsed with deionised water and dried in air.

The bath was made by dissolving 0.1 g of ammonium metavanadate (NH_4VO_3, Riedel-de Haën) in 90 ml of deionised water, giving a solution of pH 6, to which 0.5 ml of diethyl sulfate ($(C_2H_5)_2SO_4$, Aldrich) was added. The bath was held at 90 °C with stirring, the substrates standing vertically against the wall of the beaker. At this temperature the diethyl sulfate hydrolyses and releases acid, so that the pH of the bath falls to 2 without any acid being added from outside. A yellow-brown precipitate appears in the bath after about 50 min, and this marks the start of deposition; immersion times quoted below are measured from that moment. Films were withdrawn after 10, 15, 20, 25 or 30 min, washed with ethanol and dried in air at room temperature. The resulting films are transparent and yellow, the colour deepening with immersion time.

➢ *Electrochemical and Optical Measurements*

Cyclic voltammetry was carried out with a micro AUTOLAB II instrument (Eco-Chemie, Utrecht) in a conventional three-electrode cell, using the coated FTO as working electrode, Ag/AgCl in 3 M KCl as reference and a platinum wire as auxiliary electrode. The electrolyte was 1 M $LiClO_4$ in propylene carbonate (PC), the potential was swept between −1 and +1 V, and the exposed film area was 0.40 cm².

In situ optical spectra were recorded between 350 and 900 nm on a Varian Cary 50 Scan spectrophotometer with the film mounted in an electrochromic cell containing the same electrolyte, the applied voltage being switched between −2.5 and +2.5 V. The spectrum of an uncoated FTO substrate was used as background. Film thickness was determined with an Alpha Step D-100 profilometer (stylus force 5 mg, scan length 8 mm, range 10 µm, speed 0.07 mm s^{-1}). The composition and structure of the deposits were established by X-ray diffraction (Rigaku Ultima IV, CuKα), infrared spectroscopy (Perkin-Elmer System 2000, KBr discs) and thermal analysis (LABSYS™ Evo, SETARAM, to 500 °C at 10 °C min^{-1} in air).

III. RESULTS AND DISCUSSION

➢ *Composition, Structure and Thickness of the Films*

Diffraction from both the deposited films and the solid recovered from the bath gives only the 00l series of a layered hydrated vanadium(V) oxide, in close correspondence with the reference pattern of $V_2O_5{\cdot}nH_2O$ xerogel (PDF 40-1296); apart from the reflections of the FTO substrate (PDF 46-1088), the two patterns coincide, so film and precipitate are the same phase. The first 00l reflection places the V–O layers 11.0 Å apart, a spacing that corresponds to fewer than 1.5 water molecules per formula unit.[23]

Infrared spectra of both samples carry the three bands characteristic of the xerogel framework[24,25,26] — the terminal V=O stretch near 1011 cm^{-1}, the asymmetric V–O–V stretch at 762 cm^{-1} and the mixed symmetric stretching and bending mode at 513 cm^{-1} — together with absorptions of water at 3600–3400 cm^{-1} and 1630 cm^{-1}. Bands at 3140 and 1400 cm^{-1} show that ammonium ions are present in the interlayer region; since none of the three framework bands is displaced, the amount intercalated must be small. Thermal analysis gives a total mass loss of 9.61 wt% in two stages, which after allowance for the ammonia released corresponds to approximately one water molecule per formula unit. Taken with an ammonium content of about 0.15 mol determined by elemental analysis, these data give the composition $(NH_4)_{0.15}V_2O_5{\cdot}H_2O$.

Film thickness is governed by immersion time, the five films used in this study measuring 70, 110, 160, 320 and 440 nm for immersion times of 10, 15, 20, 25 and 30 min respectively.

➢ *Cyclic Voltammetry*

Figure 1 shows five successive voltammograms of an as-deposited film of 110 nm thickness, recorded at 10 mV s^{-1} in 1 M $LiClO_4$/PC.

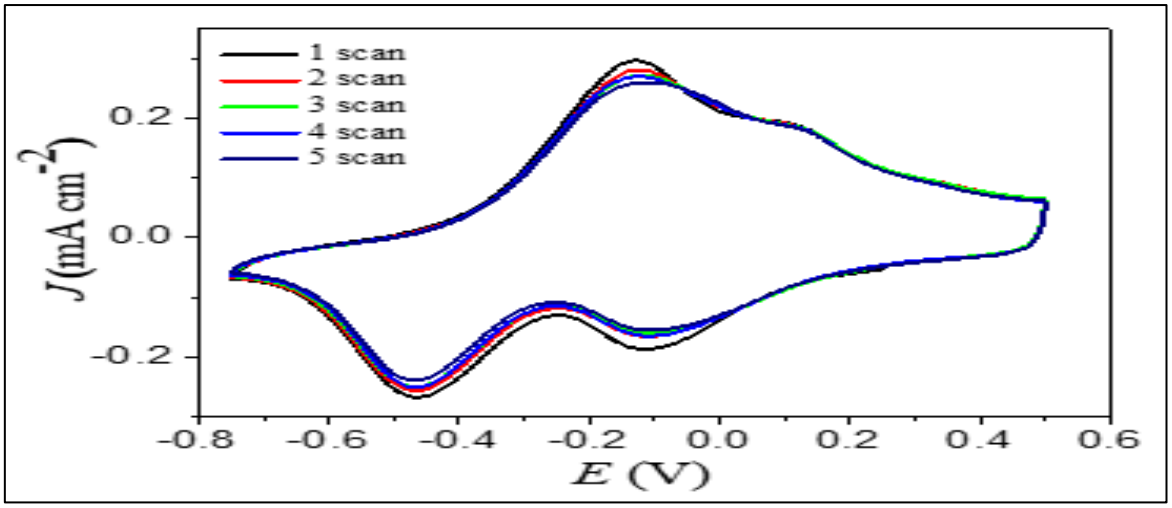


Fig 1 Cyclic Voltammograms of the $(NH_4)_{0.15}V_2O_5 \cdot H_2O$ Thin Film with 110 nm Thickness.

Two cathodic and two anodic peaks are resolved. The cathodic peaks lie at −0.10 and −0.46 V and the anodic peaks at 0.11 and −0.12 V versus Ag/AgCl, giving peak separations of 0.21 V for the first redox pair and 0.34 V for the second. Both processes are therefore quasi-reversible rather than fully reversible, the second more so than the first, which is consistent with the slower kinetics expected once lithium has already been inserted and the host lattice has been distorted. Vanadium(V) oxide films have been reported to show one, two or three pairs of peaks,[3,8,10] and the distinction is generally attributed to the degree of order in the film: a single broad pair is characteristic of amorphous material,[8] in which the insertion sites form a continuous distribution of energies, whereas resolved pairs indicate that lithium occupies distinct, well-defined sites.[10].

Both processes correspond to the reduction of V(V) to V(IV) accompanied by insertion of lithium into the interlayer region, and to the reverse on oxidation. That they occur at two distinct potentials reflects the stepwise nature of the intercalation: the lithiated material passes through a succession of $Li_xV_2O_5$ phases, conventionally labelled α, ε and δ, whose stability ranges are set by the lithium content,[10,27] so that each stage of filling has its own characteristic potential.

➢ *Switching Kinetics and Choice of Operating Voltage*

Before the spectra could be recorded it was necessary to establish how long the films take to switch and what voltage is required, since an in situ measurement made before the film has reached its final state underestimates the modulation. The kinetics were followed on the thickest film in the series, 440 nm, by monitoring the absorbance at 900 nm while the polarity was reversed; Figure 2 shows the response at three applied voltages between ±1.5 and ±2.5 V.

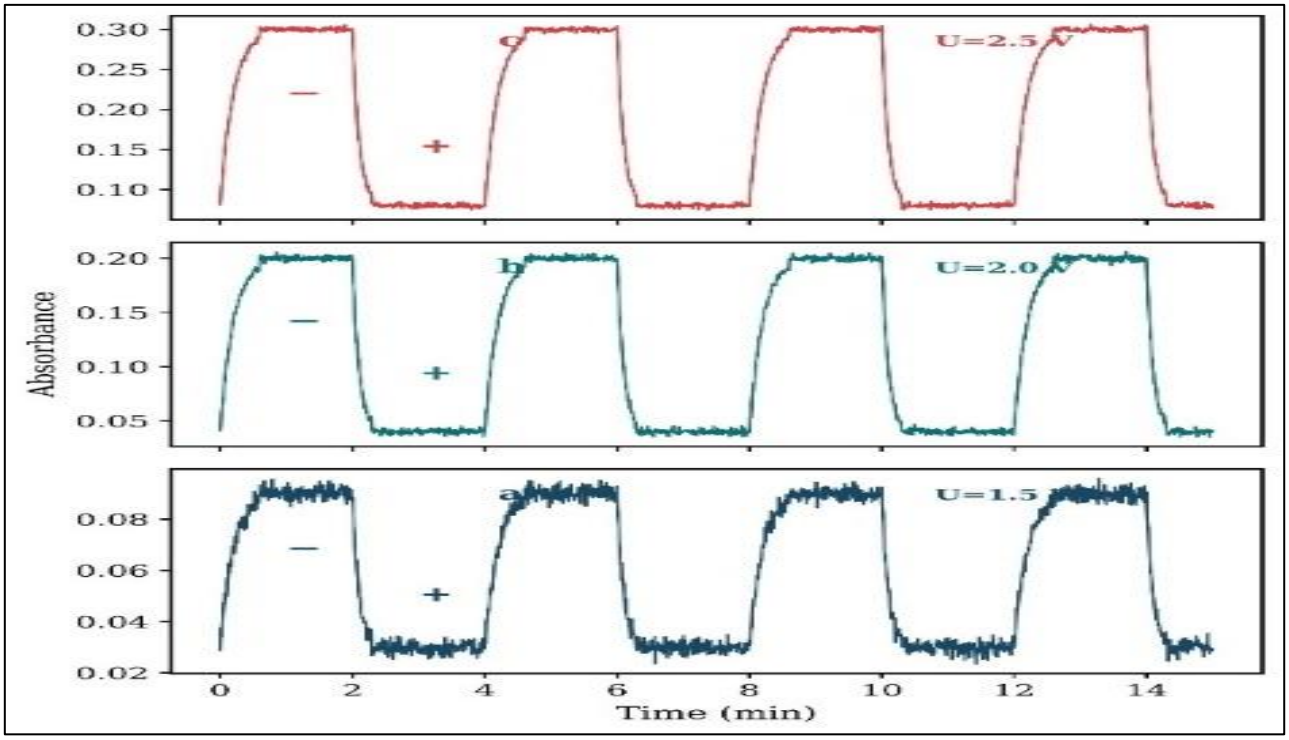


Fig 2 Optical absorbance at 900 nm vs. time of $(NH_4)_{0.15}V_2O_5 \cdot H_2O$ thin films with 440 nm thickness.

Two results follow from these measurements. First, two minutes is sufficient for the absorbance to reach a steady value at ±2.5 V (Figure 2a–c). Since the 440 nm film is the thickest prepared, and since the time required for switching increases with the amount of material through which lithium must diffuse, two minutes is sufficient for every film in the series. Second, the change in absorbance between the two states grows as the applied voltage is raised from ±1.5 to ±2.5 V, which indicates that the lower voltages do not drive the intercalation to completion within the measurement window.

- *In Situ Transmittance and the Two-Step Colour Change*

Transmittance spectra of the films between 350 and 900 nm, are shown in Figure 3.

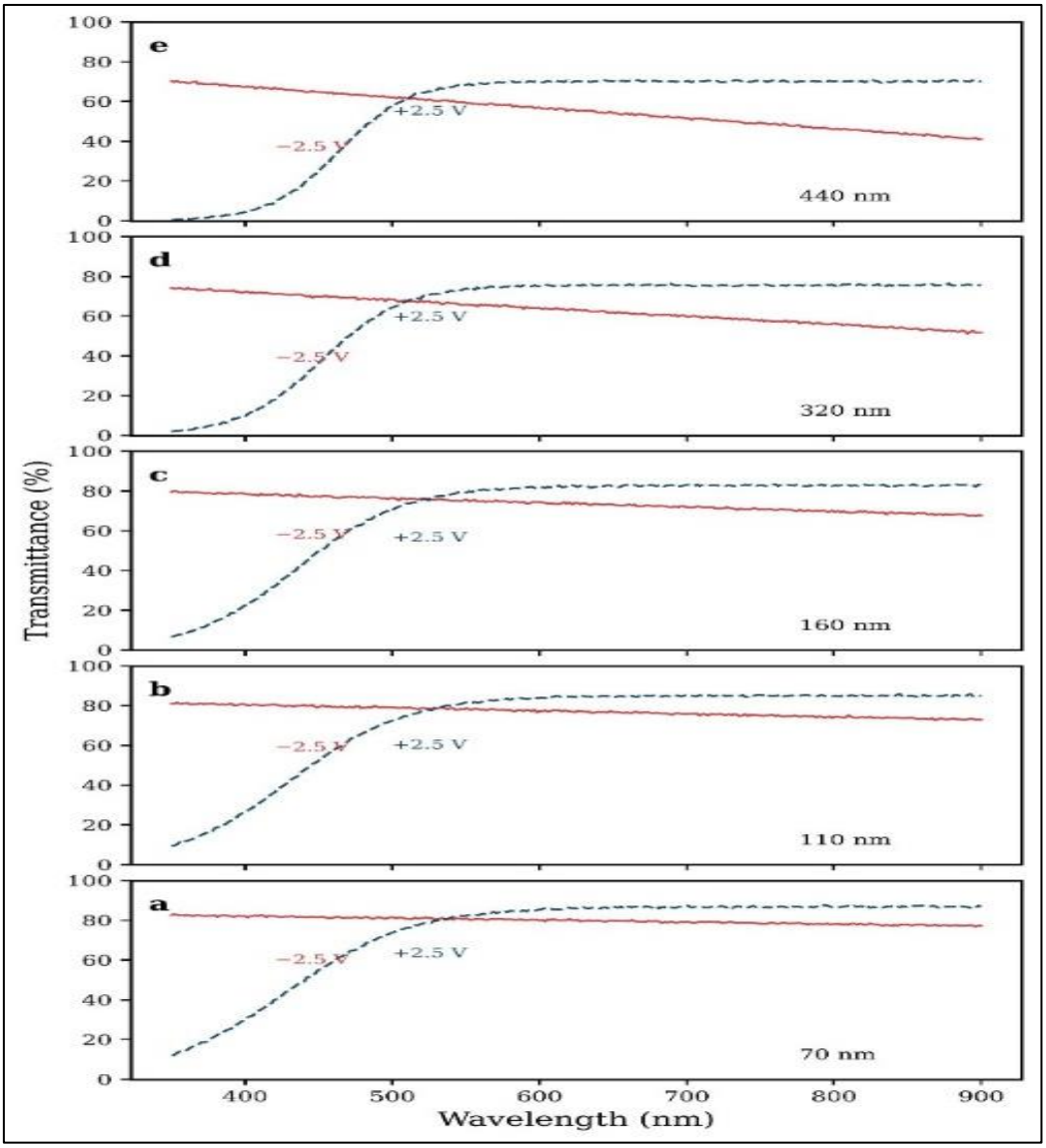


Fig 3 In Situ Optical Transmittance Spectra of $(NH_4)_{0.15}V_2O_5 \cdot H_2O$ Thin Films with Different Thickness.

On switching, the films change colour reversibly in two stages, passing from yellow to green and then from green to blue. The number of stages matches the number of redox pairs resolved voltammetrically in Section 3.2, which is what one expects if each intercalation step produces its own absorbing species: the first reduction generates a modest population of V(IV) centres and a correspondingly weak intervalence absorption, which combines with the residual yellow of the oxidised film to give green, while the second reduction raises the V(IV) content far enough for the intervalence band to dominate and the film to appear blue.

The spectra also show that the two states differ in opposite senses at the two ends of the range. In the oxidised state the films transmit well in the red and near infrared and absorb in the blue, as expected for a material whose absorption edge lies in the visible. Reduction raises the transmittance somewhat at the short-wavelength end while lowering it substantially at long wavelengths, because the intervalence absorption of the mixed-valence material grows towards the near infrared. The consequence is that the position of maximum modulation depends on thickness, which is examined next.

- *Dependence of the Transmittance Variance on Thickness*

Values of the transmittance variance ΔT at 400, 700 and 900 nm are collected in Table 1 for the five deposition times, and the dependence on film thickness is plotted in Figure 4.

Table 1 ΔT Values of $(NH_4)_{0.15}V_2O_5 \cdot H_2O$ Thin Films at Different Deposition Times.

λ (nm)	10 min	15 min	20 min	25 min	30 min
400	45	39	25	18	6
700	14	15	13	33	35
900	13	16	14	37	48

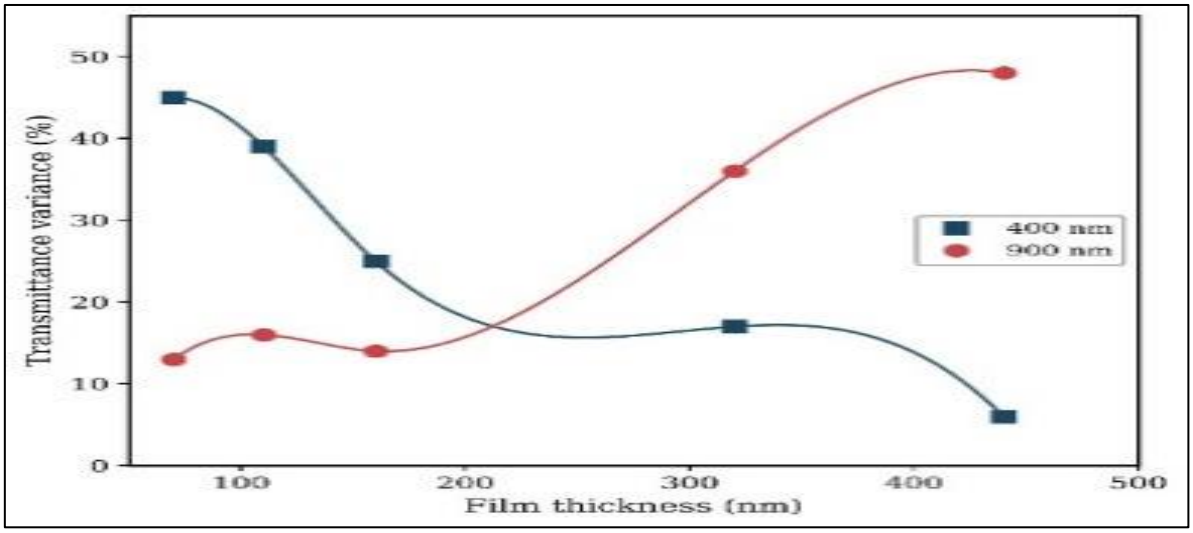


Fig 4 The Dependence of Transmittance Variance on the Film Thickness.

The two ends of the spectral range behave in opposite ways. At 400 nm, ΔT is largest for the thinnest film, 45% at 70 nm, and falls steadily as the film thickens, reaching 6% at 440 nm. At 900 nm the trend is reversed: ΔT remains between 13 and 16% for the three thinnest films, then rises sharply to 37% at 320 nm and 48% at 440 nm. The behaviour at 700 nm follows that at 900 nm but saturates, increasing from 13% at 160 nm to 33% at 320 nm and then only to 35% at 440 nm. The two curves cross at a thickness of roughly 200 nm, where the modulation is around 20% at both wavelengths.

The decline at 400 nm is a consequence of the absorption of the oxidised film. The xerogel absorbs strongly in the blue even in its fully oxidised state, so the transmittance of the bleached film at 400 nm falls as the film thickens; once the oxidised film transmits little at this wavelength there is no range left over which the reduced state can differ from it, and ΔT must approach zero. The modulation at 400 nm is thus limited not by how strongly the film colours but by how transparent it can be made.

At 900 nm the situation is the opposite. The oxidised film transmits well there, so the bleached state imposes no ceiling, and the modulation is set instead by how much the reduced state absorbs. A thicker film accommodates more lithium and therefore develops a stronger intervalence absorption, so ΔT increases with thickness. The saturation evident at 700 nm but not at 900 nm reflects the shape of that absorption band, which continues to rise towards the near infrared.

The largest values obtained in this series are 45% at 400 nm, for the 70 nm film, and 48% at 900 nm, for the 440 nm film. Taken together, the results indicate that thickness can be used to tune the spectral region over which these films modulate most strongly: films below about 100 nm are the better choice where modulation in the blue is wanted, while films of 300 nm and above are preferable for applications operating in the near infrared.

IV. CONCLUSION

The electrochromic behaviour of chemically bath-deposited $(NH_4)_{0.15}V_2O_5 \cdot H_2O$ films has been characterised over a thickness range of 70 to 440 nm.

Cyclic voltammetry in 1 M $LiClO_4$/PC resolves two cathodic peaks, at −0.10 and −0.46 V, and two anodic peaks, at 0.11 and −0.12 V versus Ag/AgCl. The peak separations of 0.21 and 0.34 V indicate quasi-reversible behaviour, and the voltammograms are stable over repeated cycling. The two redox pairs are assigned to successive stages of lithium insertion accompanying reduction of V(V) to V(IV), and correspond to the two-step colour change from yellow to green and then to blue observed optically.

Switching is complete within two minutes at ±2.5 V even for the thickest film, and the modulation depth increases with applied voltage over the range examined, which establishes ±2.5 V and a two-minute interval as adequate operating conditions for the whole series.

The transmittance variance depends jointly on wavelength and thickness, and in opposite senses at the two ends of the spectral range: at 400 nm it falls from 45% to 6% as the thickness increases from 70 to 440 nm, while at 900 nm it rises from 13% to 48% over the same range, the two becoming comparable near 200 nm. The decline in the blue is attributed to the absorption of the oxidised film and the rise in the near infrared to the intervalence absorption of the reduced film.

Thickness therefore provides a direct means of selecting the spectral region in which these films modulate

most strongly, which is a useful degree of freedom in designing electrochromic devices for a specified operating range.

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