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Chemical Bath Deposition of Vanadium(V) Oxide Xerogel Thin Films Through In Situ Hydrolysis of Diethyl Sulfate

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Abstract

Thin films of a hydrated, ammonium-intercalated vanadium(V) oxide xerogel were grown on fluorine-doped tin oxide glass by a modified chemical bath deposition route in which the acid required for condensation of the vanadate precursor is generated inside the bath itself. Heating a dilute aqueous solution of ammonium metavanadate containing diethyl sulfate to 90 °C hydrolyses the ester and lowers the bath pH from 6 to 2 without external addition of acid, so that acidification, nucleation and growth proceed as a single self-regulating process. Deposition begins after an induction period of about 50 min, marked by the appearance of a yellow-brown solid, and film thickness is then set by immersion time: films between 70 and 440 nm were obtained for deposition times of 10 to 30 min, growth being slow and almost linear over the first 20 min and faster thereafter. X-ray diffraction of both the film and the precipitate recovered from the bath shows only the 001 series of a layered xerogel with an interlayer spacing of 11.0 Å, which indicates a water content below 1.5 mol per formula unit. Infrared spectra confirm the V_2O_5 framework of the xerogel and reveal bands of intercalated ammonium ions that leave the V–O vibrations unperturbed. Thermal analysis gives a total mass loss of 9.61 wt%, consistent with the composition $(NH_4)_{0.15}V_2O_5{\cdot}H_2O$.

Keywords: *Chemical Bath Deposition, Vanadium(V) Oxide Xerogel, Diethyl Sulfate, Thin Films, Layered Structure, Ammonium Intercalation.*

I. INTRODUCTION

Chemical bath deposition (CBD) occupies an unusual position among thin-film techniques. It requires no vacuum, no elevated substrate temperature and no specialised apparatus, yet it coats large areas and awkwardly shaped substrates uniformly, because growth is governed by the chemistry of the solution rather than by a line-of-sight flux.[1] These features have made it an attractive route to a range of transition-metal oxide films, among them nickel oxide[2] and vanadium(V) oxide xerogels, for which deposition conditions have been systematically optimised.

For vanadium(V) oxide specifically, the sol–gel process remains the most frequently reported preparative approach.[3,4] Three synthetic routes have been developed within it: acidification of metavanadate solutions,[5,6] hydrolysis and condensation of vanadium alkoxides[7,8] and the reaction of hydrogen peroxide with vanadium(V) oxide.[9,10] Alongside these, hydrothermal synthesis,[11,12] sputtering,[13,14] pulsed spray pyrolysis,[15,16] pulsed laser deposition[17] and spin coating[18] have all been applied. Each offers a different balance of control and cost, and the acidification route in particular is attractive for its simplicity — but it normally requires an acid to be introduced from outside the system, by titration or by passage through an ion-exchange column, which makes the local pH history of the solution difficult to control and tends to produce rapid, poorly regulated precipitation.

The hydrated oxide $V_2O_5{\cdot}nH_2O$ crystallises in a layered structure in which ribbons built from VO_5 square pyramids are separated by a region containing water molecules. Because the interlayer separation and the intercalation capacity both scale with the amount of water held between the layers,[12] the properties of the material depend sensitively on its hydration state. Nanostructured forms — tubes,[4] belts,[19] fibres,[20] wires[20] and rods[21] — have accordingly attracted considerable attention. The ability of these hydrated phases to accommodate lithium ions reversibly underlies their use in humidity sensors and microbatteries,[22] as cathodes for

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lithium batteries,[15] as counter electrodes and components of electrochromic devices,[23] in supercapacitors[24] and in electrochromic mirrors.[25] The electrochromic response itself originates in reversible redox processes between vanadium oxidation states, accompanied by colour changes through yellow, green, blue and violet.[9]

In this paper we describe a chemical bath deposition method for vanadium(V) oxide xerogel thin films in which the acidification step is internalised. Diethyl sulfate is added to a dilute ammonium metavanadate solution and the bath is heated; hydrolysis of the ester then releases acid gradually and homogeneously throughout the solution, so that no external acid is added at any point and the pH falls under the control of the hydrolysis rate rather than the rate of mixing. The films that result have the composition $(NH_4)_{0.15}V_2O_5{\cdot}H_2O$. We report here the preparation, the structural and compositional characterisation by X-ray diffraction, infrared spectroscopy and thermal analysis, and the control of film thickness through deposition time.

II. MATERIAL AND METHODS

➢ *Deposition of the Thin Films*

The films were deposited on commercial fluorine-doped tin oxide (SnO_2:F, FTO) coated glass substrates, which have an optical transmittance of about 80% across the visible region and a sheet resistance of 10–20 Ω/cm². The substrates were cleaned immediately before use by successive treatment with aqueous detergent, alkaline solution, hydrochloric acid, hexane and acetone, then rinsed with deionised water and dried in air.

The deposition solution was prepared by dissolving 0.1 g of ammonium metavanadate (NH_4VO_3) in 90 ml of deionised water in a 100 ml beaker; the pH of this solution was 6. To it was added 0.5 ml of diethyl sulfate, $(C_2H_5)_2SO_4$.

The bath was heated to 90 °C with continuous stirring, the cleaned substrates being held vertically against the wall of the beaker. On heating, the diethyl sulfate hydrolyses and the pH of the solution falls to 2. The onset of deposition is marked by the appearance of a yellow-brown precipitate in the bath, which occurs approximately 50 min after the start of heating. The solution, initially yellow, becomes light brown as the reaction proceeds. The films obtained are transparent and range in colour from bright to dark yellow according to the deposition time. Deposition time was measured from the moment the precipitate first appeared until the substrates were withdrawn from the bath. The films were then washed with ethanol and dried in air at room temperature.

➢ *Characterisation*

X-ray diffraction patterns of the films and of the precipitate recovered from the bath were recorded on a Rigaku Ultima IV diffractometer using CuKα radiation. Infrared spectra were obtained with a Perkin-Elmer System 2000 interferometer using KBr discs. Thermogravimetric and differential thermal analysis of the precipitate was carried out on a LABSYS™ Evo instrument (SETARAM) up to 500 °C at a heating rate of 10 °C min^{-1} in flowing air. Film thickness was measured with an Alpha Step D-100 profilometer (stylus force 5 mg, scan length 8 mm, range 10 μm, speed 0.07 mm s^{-1}).

III. RESULTS AND DISCUSSION

➢ *Bath Chemistry and the Origin of the Deposit*

The distinguishing feature of the present route is that no acid is added to the bath. The acidity required to convert metavanadate into a condensed vanadium(V) oxide is produced in situ by the hydrolysis of diethyl sulfate.

The consequence for film growth is that protons are generated uniformly throughout the volume of the solution and at a rate set by the hydrolysis kinetics, rather than being introduced at a point of addition and dispersed by stirring. The pH of the bath falls from 6 to 2 over the course of the heating period. As it does so, the vanadate equilibria shift progressively from the monomeric and oligomeric metavanadate species that predominate near neutrality towards the protonated polyvanadates stable in acid solution, which subsequently condense through olation and oxolation into the layered hydrated oxide.[5,6]

This gradual acidification accounts for the induction period of roughly 50 min that precedes any visible deposition. During this interval the solution remains clear and its colour deepens only slowly, indicating that condensation is proceeding in solution but that the degree of polymerisation remains below the threshold for nucleation. The appearance of a yellow-brown solid marks the point at which that threshold is crossed, and it is from this moment that useful deposition on the substrate begins. Taking the appearance of the precipitate rather than the start of heating as the zero of deposition time is therefore not merely a matter of convention: it defines the start of the growth regime and makes the thickness reproducible between runs.

The ammonium ions present in the bath as the counter-ion of the metavanadate precursor are incorporated into the growing solid. Since no other cation is introduced at any stage, the composition of the deposit is fixed by the stoichiometry of the starting solution, and the dilute conditions used here (0.1 g NH_4VO_3 in 90 ml) limit the amount of ammonium available for intercalation.

It should be noted that the scheme above is a reasonable chemical account of the observed pH change and the observed induction period rather than one established by independent measurement in this work; the sulfate and ethanol products were not determined analytically, and the sequence of vanadate species was not followed spectroscopically.

➢ *Phase Composition and Layered Structure*

The X-ray diffraction patterns of the precipitate from the bath and of the as-deposited film are shown in Figure 1.

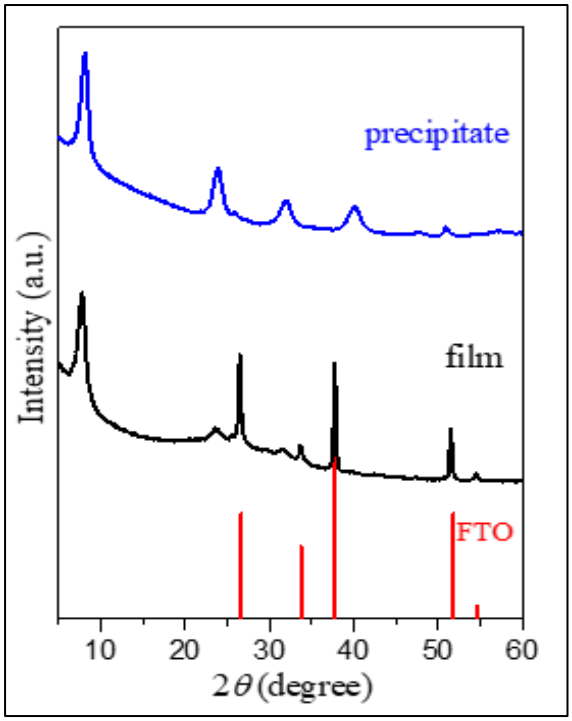


Fig 1 XRD Patterns of the Precipitate and of the Film of the Prepared Vanadium(V) Oxide Xerogel.

The pattern of the precipitate displays four to five broad reflections belonging to the 001 series, the 002 reflection being absent, and shows close similarity to the powder diffraction file of pristine $V_2O_5 \cdot nH_2O$ xerogel (PDF 40-1296). The breadth of the reflections and the absence of any hkl lines other than the 00l series are characteristic of a turbostratically disordered layered material: the stacking of the V–O layers is regular along the normal to the substrate but the layers are not registered with one another in the plane.

When the strong reflections of the FTO substrate (PDF 46-1088) are excluded, the pattern of the as-deposited film is indistinguishable from that of the precipitate, which establishes that the material growing on the substrate and the material precipitating in the bulk of the bath are the same phase. This is an important point for a chemical bath process, where film growth may in principle occur either by ion-by-ion condensation at the substrate or by adhesion of colloidal particles formed in solution; the identity of the two patterns is consistent with a cluster-by-cluster mechanism in which particles nucleated in solution attach to the substrate.

The position of the first and most intense 001 reflection gives the separation between the V–O layers directly. The value found here is 11.0 Å, which corresponds to a water content below 1.5 mol per formula unit.[26] This is a relatively contracted interlayer spacing for a vanadium(V) oxide xerogel and points to a comparatively dehydrated material, a conclusion tested independently by thermal analysis.

➢ *Infrared Spectra*

The infrared spectra of the precipitate and of material scraped from the film are shown in Figure 2 and confirm the xerogel framework inferred from diffraction.

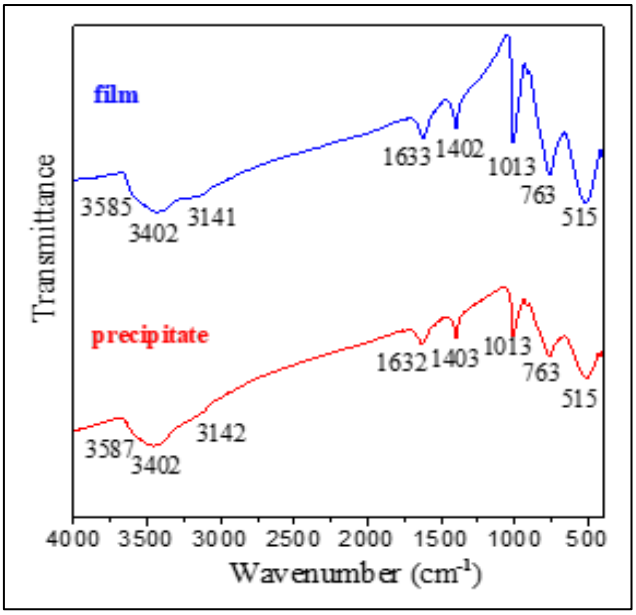


Fig 2 IR Spectra of the Thin Film and Precipitate from the Chemical Bath.

Both spectra display the three vibrational bands characteristic of the V_2O_5 framework of the xerogels:[27] a band at 1011 cm^{-1} assigned to the stretching vibration of the terminal V=O groups; one at 762 cm^{-1} assigned to the asymmetric stretching vibration of the bridging V–O–V units; and one at 513 cm^{-1} attributed to the symmetric V–O–V stretch mixed with bending V–O vibrations. The presence of water is evident from the broad absorption between 3600 and 3400 cm^{-1} (O–H stretching) and the band at 1630 cm^{-1} (H–O–H bending).

In addition, both spectra show bands that can only be attributed to ammonium ions: at 3140 cm^{-1} (N–H stretching) and at 1400 cm^{-1} (H–N–H bending). Their appearance in the spectrum of the washed, dried solid indicates that the ammonium is held within the material rather than adsorbed on its surface, and the layered structure established by diffraction provides the obvious site — the interlayer region, where the ammonium ions balance the negative charge of the V–O framework alongside the water molecules.

The positions of the three framework bands are worth examining for what they do not show. None of them is displaced relative to the values reported for ammonium-free vanadium(V) oxide xerogels. Intercalation of a cation into the interlayer region perturbs the V–O vibrations in proportion to the amount intercalated, and the absence of any measurable shift therefore indicates that the ammonium content is low. This is a qualitative argument and sets no numerical bound, but it is consistent with the dilute precursor solution used and with the formula derived below.

➢ *Thermal Behaviour and Composition*

The water content of the material was determined from the thermogravimetric and differential thermal analysis of the precipitate recovered from the bath (Figure 3).

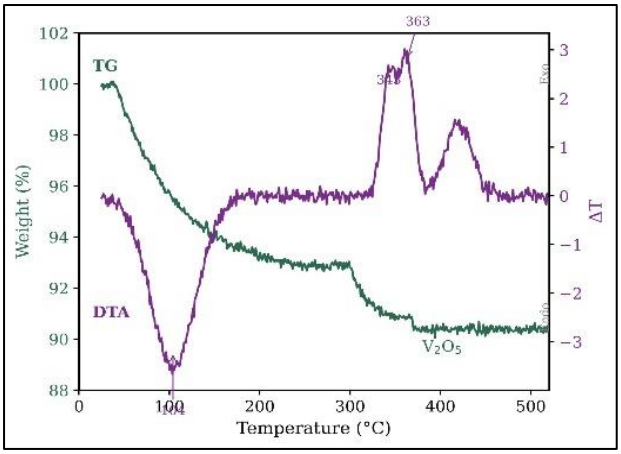


Fig 3 TG-DTA Curves for the $(NH_4)_{0.15}V_2O_5 \cdot H_2O$ Precipitate.

The TG curve shows mass loss in two stages, the first between 40 and 250 °C and the second between 300 and 370 °C. The total loss is 9.61 wt%. The low-temperature stage corresponds to the removal of water from the interlayer region, and the high-temperature stage to the decomposition of the intercalated ammonium with evolution of ammonia; the end product of the heating is V_2O_5.

Taken formally, a loss of 9.61 wt% corresponds to the evolution of 1.1 mol of water per formula unit. The total loss, however, includes both water and ammonia, so the water content proper is obtained by subtracting the contribution of the ammonium. Elemental analysis gave an ammonium content of about 0.15 mol per formula unit, and subtracting the corresponding 0.15 mol of NH_3 leaves approximately 1 mol of water. On this basis the composition of the xerogel may be written, $(NH_4)_{0.15}V_2O_5 \cdot H_2O$.

The water content obtained in this way — below 1.5 mol — agrees with the conclusion drawn independently from the interlayer spacing of 11.0 Å in Section 3.2. The two determinations rest on quite different measurements, and their agreement provides reasonable confidence in the formula.

➢ *Control of Film Thickness*

A series of $(NH_4)_{0.15}V_2O_5 \cdot H_2O$ films was prepared with deposition times between 10 and 30 min. The thickness increases monotonically with deposition time (Figure 4): 70 nm at 10 min, 110 nm at 15 min, 160 nm at 20 min, 320 nm at 25 min and 440 nm at 30 min.

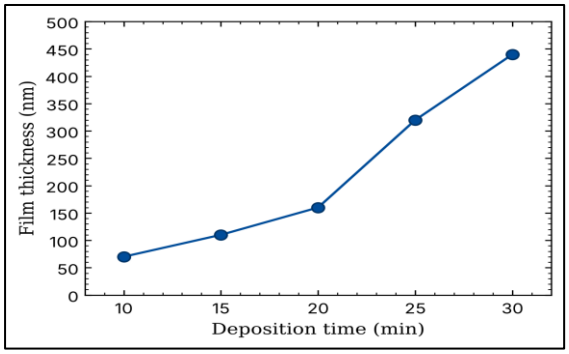


Fig 4 Film Thickness vs. Deposition Time.

The growth is not uniform in rate over this interval. Between 10 and 20 min the thickness increases by about 9 nm min^{-1} and the dependence is close to linear. Beyond 20 min the rate rises sharply, to roughly 32 nm min^{-1} between 20 and 25 min and 24 nm min^{-1} between 25 and 30 min. The change of regime near 20 min coincides with the point at which the substrate first becomes fully covered. Growth onto a partially covered substrate competes with growth onto bare FTO and is limited by the available nucleation sites, whereas growth onto a continuous xerogel layer has no such restriction; a faster rate once coverage is complete is therefore what one would expect. The slight decrease in rate in the final interval may reflect depletion of the bath, which is dilute and not replenished during deposition.

For practical purposes the useful consequence is that thickness over the technologically interesting range of roughly 100–400 nm is set simply by immersion time, with no change to the composition of the bath.

IV. CONCLUSION

A chemical bath deposition method has been developed for thin films of the vanadium(V) oxide xerogel $(NH_4)_{0.15}V_2O_5 \cdot H_2O$ in which the acid required for condensation of the vanadate precursor is generated within the bath by hydrolysis of diethyl sulfate, so that no acid is added externally at any stage. The pH falls from 6 to 2 under the control of the hydrolysis rate, and deposition begins after an induction period of about 50 min.

X-ray diffraction establishes that the films and the precipitate formed in the bath are the same layered phase, with an interlayer spacing of 11.0 Å. Infrared spectroscopy confirms the V_2O_5 framework and shows that ammonium ions are intercalated between the layers without perturbing the V–O vibrations, indicating a low level of intercalation. Thermal analysis gives a total mass loss of 9.61 wt%, which together with the elemental ammonium content corresponds to the composition $(NH_4)_{0.15}V_2O_5 \cdot H_2O$; the water content derived from this analysis agrees with that inferred independently from the interlayer spacing.

Films between 70 and 440 nm thick were obtained by varying the deposition time between 10 and 30 min, the growth rate increasing markedly once the substrate becomes fully covered at around 20 min.

The method is simple, requires no specialised equipment and gives controlled thickness from a single dilute bath, which makes it a convenient route to layered hydrated vanadium(V) oxide films for further study.

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