JOURNAL OF Materials CHEMISTRY

Electrochemical deposition of the hydroxide precursors to $YBa_2Cu_3O_{7-\delta}$ and related phases

Paul M. S. Monk,*† Robert Janes and Robert D. Partridge

Department of Chemistry and Materials, Manchester Metropolitan University, Chester Street,
Manchester, UK M1 5GD

Thin films of hydroxide precursors of $YBa_2Cu_3O_{7-\delta}$ (YBCO) have been electrodeposited from aqueous solution. The compositions of the films were tailored in two ways: firstly by adjusting the deposition voltage, and secondly by varying the relative amounts of precursor solutes in solution. The desired hydroxide precursor to $YBa_2Cu_3O_{7-\delta}$ having the correct ratios of cation can be formed by electrodeposition at a potentiostatic voltage of -1.4 V (*vs.* SCE) at a silver electrode immersed in an aqueous solution of composition $Y(NO_3)_3 = 0.0125$ mol dm^{-3}; $Ba(NO_3)_2 = 0.150$ mol dm^{-3} and $Cu(NO_3)_2 = 0.025$ mol dm^{-3}.

Introduction

We have shown recently that films of rare-earth cuprates and nickelates can be prepared by electrodeposition from aqueous solution.[1–3] The end application envisaged for our materials is in electrochromic or semiconductor devices. Since many of these semiconductors can be regarded as precursors to superconducting phases, it is reported here that the well known high T_c superconductor yttrium barium cuprate $YBa_2Cu_3O_{7-\delta}$ can also be formed by electrodeposition from an aqueous system comprising wholly inorganic solution-phase solutes.

The form of electrodeposition mechanism seen in this study involves the electrochemical formation of hydroxide ion by electron transfer to aqueous nitrate ion, with subsequent formation of solid (insoluble) films of metal hydroxide:[4]

$$NO_3^- + 7\ H_2O + 8\ e^- \rightarrow NH_4^+ + 10\ OH^- \qquad (1)$$

$$5\ M^{2+} + 10\ OH^- \rightarrow 5\ M(OH)_2 \qquad (2)$$

The oxide end-product(s) are formed during annealing of the precursor. The literature on nitrate reduction is now vast; so we consider it reasonable, therefore, to assume that hydrogen formation is most unlikely except when mass transport of NO_3^- is insufficient at very negative applied potentials, V_a (when bubbles of gas are seen to form at the working electrode).

YBCO, or its precursors, have been prepared previously by electrodeposition from solution (refs. 4–8 are but a selection), the methods falling into two broad categories: formation of metal alloys or metal oxyhydroxides; however, it is believed that the work here represents the first to successfully prepare an YBCO precursor *via* aqueous solutes using other than a limiting current.

The preparation of $YBa_2Cu_3O_{7-\delta}$ requires the electrodeposition of $Y(OH)_3$, $Ba(OH)_2$ and $Cu(OH)_2$ with the respective stoichiometric ratios of 1:2:3. Thus the compositional variations of all three metal hydroxides need to be studied as a function of deposition conditions in order to 'tailor' the stoichiometry of the desired product.

Experimental Details

Electrodeposition

Deposition solutions were prepared by using aqueous metal nitrate mixtures. The concentration of each cation was 0.025 mol dm^{-3}, unless otherwise stated. The temperature of bath solutions was maintained at 298 K. All solutions were purged with N_2 gas prior to electrodeposition.

Electrodeposition was performed using a PAR 273A potentiostat interfaced to a PC running PAR 270 electrochemistry software. Solutions were gently agitated by stirring slowly during deposition to maintain convective control unless stated otherwise. The rate of solution flow was optimised to facilitate ion replenishment at the electrode without causing film disruption or streaking, as determined using a chronoamperometric system and determining the slowest stirring rate which would still prevent the current drop caused by ion depletion.[2]

Electrodeposition was performed potentiostatically with a 3-electrode configuration. The working electrode was silver foil of area 4.8 cm^2, the counter electrode was a platinum mesh of large surface area, and the reference electrode was a saturated calomel electrode (SCE). The silver electrode was cleaned electrochemically by stepping the potential in a cathodise–anodise–cathodise sequence, with the electrode immersed in dilute sulfuric acid. The silver was rinsed in deionised water after the final cathodise step. All potentials are cited with respect to the SCE. The deposition current was typically in the range 10–50 mA cm^{-2}, the value depending on the deposition conditions. The deposition time was 120 seconds unless stated otherwise. This duration was chosen since it yielded films thick enough for reliable ICP determinations, yet thin enough that films were not flocculent.

Elemental analysis of films

Elemental compositions of deposited films were determined with a Philips PU 7450 inductively coupled plasma (ICP) spectrometer. Films were rinsed with de-ionised water following deposition, and dissolved in 2 mol dm^{-3} nitric acid prior to ICP analysis. There is no evidence for silver doping of these films.

Films were dried thoroughly in a desiccator prior to sintering on the electrode substrate. Sintering conditions were typically 1223 K for 15 minutes in air. Sintered films were analysed by XRD and EDS whilst still on the electrode substrate, and were dissolved in nitric acid for elemental analysis.

X-Ray powder diffractograms (XRDs) were obtained with a Philips PU 3020 diffractometer operating with Cu-Kα radiation. Measurements of energy dispersion by X-rays (EDS) were obtained using a Cambridge 250 electron microscope.

Results and Discussion

All films were amorphous as deposited, or insufficiently crystalline to allow an X-ray diffractogram to be obtained. EDS was

---

†E-mail: p.monk@mmu.ac.uk

unable to detect any material segregation, indicating that there are no 'clusters' of either metal in the deposited solid, *i.e.* that mixing of the two component metals was always complete (certainly, mixing in the deposition solution occurs at the atomic level). In a related study, films of La_2CuO_4 or Nd_2CuO_4 having varying thicknesses were dissolved[2,3] to show that the films were homogeneous as deposited.

Effect of deposition voltage, V_a

Initial experiments investigated the effect of varying the deposition voltage. As with previous work,[1–3] the mole fractions of the three constituent hydroxides varied dramatically as a function of the potential applied to the working electrode, see Fig. 1, which shows diagrammatically the variations found. The concentrations of precursor nitrate salts were each the same at 0.025 mol dm^{-3}. The mole fractions converge with increases in the amount of hydroxide formed, *i.e.* x converged as V_a became more negative. There is no theoretical reason why graphs of mole fraction x *vs* V_a should be linear and, indeed, in other systems such as La_2CuO_4 the non-linearity can be modelled and thence explained *via* computer speciation methods.[2,3]

Effect of relative solute concentration

It is clear from Fig. 1 that the mole fraction x of Ba in the electrodeposited product is woefully lower than the $x=0.33$ desired for YBCO, almost certainly because the solubility of $Ba(OH)_2$ is so high, *i.e.* any ion-associated $Ba(OH)_2$ product is not solid; or perhaps the $Ba(OH)_2$ that does remain is occluded within the $Y(OH)_3$ and $Cu(OH)_2$ that is truly solid. Accordingly, the amount of $Ba(NO_3)_2$ precursor in the initial deposition solution was increased. Fig. 2 shows a ternary diagram to represent the way that the proportion of $Ba(OH)_2$ in the product increases as a function of increasing $[Ba^{2+}]$ in the deposition solution.

We chose to represent the data on ternary diagrams of this type for clarity: each point '●' represents a film composition obtained at the deposition conditions cited; and the point '×' indicates the target stoichiometry of Y : Ba : Cu of 1 : 2 : 3. The solute ratios in our figures employ a 'baseline unit' of $[Cu^{2+}] = 0.025$ mol dm^{-3}. It is clear from Fig. 2 that the mole fraction of barium in the product rises as the mole fraction of Ba^{2+} in solution rises, as expected from speciation considerations. It is always found that as $[M^{n+}]$ in solution increases, so the mole fraction of M in the solid hydroxide product also increases.

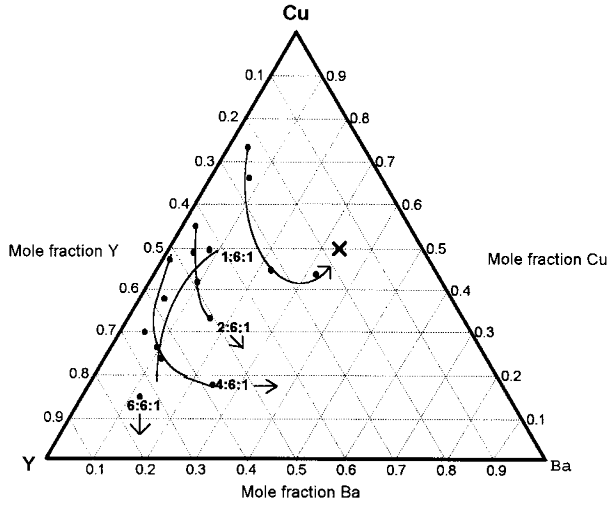

Fig. 2 Phase diagram showing mole fractions of Y, Ba and Cu in electrodeposited solid thin films as a function of applied potential V_a. The point '×' represents the target stoichiometry of $YBa_2Cu_3(OH)_n$. Each experiment commenced at $V_a = -1.0$ V *vs.* SCE, the potential becoming more cathodic in the direction of the arrow, in increments of 0.2 V. The solutes were $[Y(NO_3)_3]$, $[Ba(NO_3)_2]$ and $[Cu(NO_3)_2]$ in the ratios indicated (and cited in the order Y : Ba : Cu). The concentration increment was 0.025 mol dm^{-3}; $T = 25$ °C.

From Fig. 2, it can also be seen that the closest composition to the target stoichiometry of 1 : 2 : 3 occurred when Y : Ba : Cu = 1 : 6 : 1. As the ratio of yttrium to copper increased, so the composition of the electrodeposited product deviates from the target (as represented on the figure by '×'). In fact, it is found that the target composition cannot be attained if equal concentrations of yttrium and copper are in solution. Fig. 3 shows the effect of decreasing the amount of yttrium in solution, while maintaining 6 $[Cu^{2+}] = [Ba^{2+}]$. The best experimental fit to the desired YBCO stoichiometry occurs when Y : Ba : Cu is 0.5 : 6 : 1.

With these electrodeposition conditions, a small quantity of YBCO precursor was harvested (*ca.* 0.8 g) and fired using the conditions cited above. The XRD pattern of our YBCO was

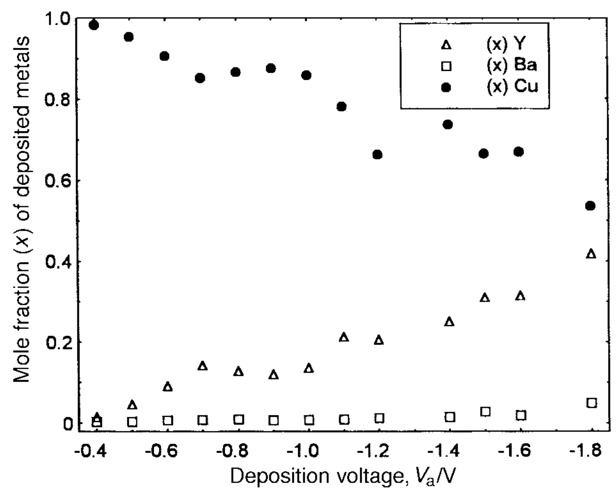

Fig. 1 Mole fractions of Y, Ba and Cu in the electrodeposited solid as a function of applied potential V_a (*vs.* SCE). Mole fractions were determined by ICP, the solid being removed from the metallic silver electrode by digesting the hydroxide mixture in HNO_3 (2 mol dm^{-3}), and analysing by matrix-matched ICP. The initial voltammetry solution comprised $[Y(NO_3)_3] = [Ba(NO_3)_2] = [Cu(NO_3)_2] = 0.025$ mol dm^{-3}; and $T = 25$ °C.

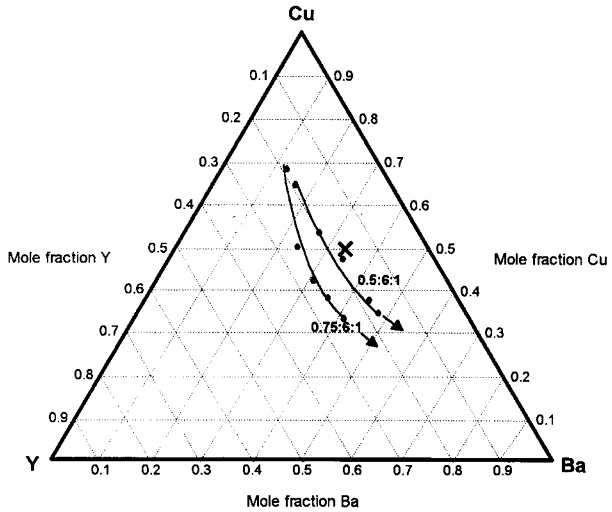

Fig. 3 Phase diagram depicting mole fractions of Y, Ba and Cu within electrodeposited solids as a function of applied potential V_a: the effect of decreasing the yttrium precursor concentration in solution. Solute ratios are indicated in the order Y : Ba : Cu, the concentration increment being 0.025 mol dm^{-3}. Each experiment commenced at $V_a = -1.0$ V *vs.* SCE, the potential becoming more cathodic in increments of 0.2 V, in the direction indicated. $T = 25$ °C.

Table 1 Thermodynamic formation constants[10] (cited as logβ) of the formation of solid metal hydroxide species from aqueous solution

solid hydroxide	logβ
$Ba(OH)_2$	-31.8^a
$Ba(OH)_2 \cdot 8H_2O$	-24.4^a
$Cu(OH)_2$	-9.0
$La(OH)_3$	-19.4
$Nd(OH)_3$	-24.4
$Ni(OH)_2$	-12.8
$Y(OH)_3$	-22.2

[a] Estimated values.

identical with that in the literature.[9] It is easier, experimentally, to fire the YBCO precursor while still adhering to the silver substrate. After firing, such thin-film YBCO had the same XRD pattern as the harvested material, albeit with additional peaks owing to the Ag of the substrate.

Physical properties of electrodeposited mixtures

At no time did YBCO and the ternary hydroxides of general composition $Y_xBa_yCu_z(OH)_n$ adhere well to the silver of the electrode. The adhesivity of the product decreased as the proportion of Ba in the product increased.

Prior to firing, films having a high barium content were pale blue and appeared gelatinous and flocculent. Deposits obtained with still (*i.e.* unstirred) solutions were extremely flocculent and could not be collected readily. The electrodeposited product obtained in a solution that was stirred gently did have a greater mechanical strength, but even with a moderately fast stirring rate, the force exerted by laminar solution flow was sufficient to rip the deposit from the electrode. No stirring method was fail-safe: eventually, we chose to agitate the solution *via* a gentle N_2 gas flow (*ca.* 1 bubble per second through an aperture of diameter 1 mm adjacent to the working electrode).

Film stability

A further difficulty arose: owing to the relatively high solubility of $Ba(OH)_2$, deposits of $Y_xBa_yCu_z(OH)_n$ lost barium when digested in water, or even in the deposition solution. For this reason, all analyses represent deposited films (on silver) which were removed from the deposition solution immediately following formation. Such films were rinsed and dried as soon as was practicable.

Table 1 cites logβ‡ values for constituent solid metal hydroxides in YBCO;[10] and a few other values of β are included for comparative purposes. It is clear that the formation of $Ba(OH)_2$ is not viable since $\beta = 10^{-31.8}$, although an octahydrate species $Ba(OH)_2 \cdot 8H_2O$ also forms with a much higher β value of $10^{-24.4}$; and such highly hydrated hydroxide species are often gelatinous.

Even if $Ba(OH)_2$ and $Ba(OH)_2 \cdot 8H_2O$ do form as solids, most of the barium dication will reside at the electrode interface as a free ion, *i.e.* remaining as unassociated Ba^{2+}. Such free Ba^{2+} will block the electrode, screening it from incoming Cu^{2+} and Y^{3+} ions, thus restricting the consumption of electrogenerated OH^-. Following directly from this restriction, the interfacial pH will increase such that the reaction front becomes broader, extending further into solution, with a shallower pH–distance gradient. Note that a gradient of $d(pH)/dx$, rather than a concentration step function, causes any speciation analysis of the electrode–solution interface to be extremely difficult.

The broadness of the reaction front is also our preferred explanation for poor film adhesivity on silver, and the worse than usual[1–3] scatter in graphs of mole fraction x against deposition voltage V_a. Adhesivity of the YBCO precursor (and related phases) was better on silver than on other substrates—other substrates investigated to this end were Pt, indium-tin oxide, brass. The optimum exchange current density for preparing these barium-containing precursors is best achieved by electrodepositing at a silver electrode.

Conclusion

Thin films of $YBa_2Cu_3(OH)_n$ have been electrodeposited from aqueous solution at a potentiostatic voltage of -1.4 V (*vs.* SCE) at a silver electrode immersed in an aqueous solution of composition $Y(NO_3)_3 = 0.0125$ mol dm^{-3}; $Ba(NO_3)_2 = 0.150$ mol dm^{-3} and $Cu(NO_3)_2 = 0.025$ mol dm^{-3}. The barium hydroxide component in the precursor films is insufficiently insoluble for this method to satisfactorily yield completely reproducible films.

We thank the EPSRC materials panel for a studentship (for R.D.P.).

References

1 R. Janes, P. M. S. Monk, R. D. Partridge and S. B. Hall, *J. Mater. Chem.*, 1996, **6**, 183.
2 P. M. S. Monk, R. Janes and R. D. Partridge, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 3985.
3 P. M. S. Monk, R. Janes and R. D. Partridge, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 3991.
4 D. A. Corrigan and R. M. Bendert, *J. Electrochem. Soc.*, 1989, **136**, 723.
5 C. T. Chu and B. Dunn, *Appl. Phys. Lett.*, 1989, **55**, 492.
6 M. Hein, G. Muller, H. Piel, L. Ponto, M. Becks, U. Klein and M. Pieniger, *J. Appl. Phys.*, 1989, **66**, 5940.
7 N. Casan-Pastor, P. Gomez-Romero, A. Fuertes and M. Brossa, *Solid State Ionics*, 1993, **66**, 241.
8 S. H. Pawar, M. M. Tonape and V. N. Shinde, *Mater. Chem. Phys.*, 1993, **35**, 86.
9 R. M. Hazen, L. W. Finger, R. J. Angel, C. T. Prewitt, N. L. Ross, H. K. Mao, C. G. Hadidiacos, P. H. Hor, R. L. Meng and C. W. Chu, *Phys. Rev. B*, 1987, **35**, 7238, erratum 1987, **36**, 3966.
10 C. F. Baes Jr. and R. E. Mesmer, *The Hydrolysis of Cations*, John Wiley and Sons, New York, 1976.

Paper 8/02496K; *Received* 1*st April*, 1998

---

‡ β = overall formation constant for $M(OH)_n \rightleftharpoons M^{n+} - nOH^-$.