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Metal and mixed-metal (oxy)-hydroxide ceramic precursor materials prepared by cathodically-induced precipitation using a hydrogen-sorbing palladium electrode

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Abstract

The electrochemical reduction of several metal and mixed-metal sulfate aqueous solutions at a palladium electrode has been studied. For magnesium, lanthanum, yttrium and scandium sulfates, metal (oxy)-hydroxide films are produced by cathodically-induced precipitation of the metal cations, following the local generation of hydroxide ions at the hydrogen-sorbing cathode. Mixed-metal (oxy)-hydroxide films are prepared from yttrium/lanthanum and yttrium/scandium sulfate solutions. For mixed yttrium/indium sulfate solutions, the amorphous yttrium/indium (oxy)-hydroxide films initially contain indium dendrites. On calcination, a metastable yttrium/indium oxide phase is observed between $600 - 1000°C$, followed by the separation of the indium and yttrium oxides above $1000°C$. No films are accessible from the sulfate solutions of electropositive metals such as sodium and potassium, where the corresponding metal oxides and hydroxides are highly soluble. Metals are electrodeposited from separate sulfate solutions of zinc, nickel and indium, in preference to the cathodically-induced precipitation of the metal (oxy)-hydroxide.

Keywords: Ceramic precursor; cathodically-induced precipitation; electrochemical; palladium; metal oxyhydroxide

1. Introduction

Electrochemical generation of base from aqueous metal salt solutions is a simple and inexpensive route to the synthesis of ceramic oxide thin films and powders [1]. Choice of electrolyte composition and electrochemical reduction regime provides a

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number of different base-generation mechanisms, including reactions that consume hydrogen ions, anion reduction reactions, and the electrolysis of water. All these reduction reactions cause a pH increase at the electrode/electrolyte interface, and, depending on the metal deposition potential, may compete with the metal ion reduction reaction. Applications of films prepared by cathodically-induced precipitation include the preparation of precursors to pre-shaped ceramic bodies [2], superconducting oxides [3-6], and electrochromic films [7-11].

For the preparation of aluminium (oxy)-hydroxide[†] films with humidity-sensing properties, we have described a cathodically-induced precipitation technique, where palladium is used as the cathode substrate [12, 13]. On electrolysis of aqueous aluminium sulfate solution, gaseous hydrogen evolution at the hydrogen-sorbing palladium cathode is eliminated and the local alkaline environment promotes the precipitation of aluminium (oxy)-hydroxide, which accumulates as an adherent surface film. Both porous and compact ceramic oxide precursor structures can be generated, depending on the electrode potential programme employed during deposition [14]. We now describe the investigation of the cathodically-induced precipitation technique to the preparation of other metal and mixed-metal (oxy)-hydroxide materials.

2. Experimental

2.1. Solution preparation and electrochemical procedures for investigation of cathodically-induced precipitation

Solutions were prepared by dissolution of the appropriate metal sulfate or mixed metal sulfates (Aldrich, >99%), each to 0.01 mol dm^{-3} in Milli-Q® deionised water (18.2 MΩ cm). No supporting electrolyte was used, as all investigated either co-precipitated or prevented metal (oxy)-hydroxide precipitate formation. Preliminary galvanostatic and cyclic voltammetric measurements were carried out using de-oxygenated solutions in a

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[†] The term 'oxyhydroxide' is often used to describe insoluble oxide/hydroxide mixtures of indeterminate ratio. In the work reported here, we use the term (oxy)-hydroxide to highlight the dominant species as hydroxide, as established in earlier studies [13] with aluminium (oxy)-hydroxide.

two-compartment glass electrochemical cell, with an EG&G Model PAR 273A potentiostat/galvanostat and associated computer software. The palladium wire (0.25 mm diameter and 2.5 cm length) working and platinum gauze counter electrodes were placed in the main electrochemical cell compartment, with a Luggin capillary linking to a Bioanalytical Systems RE-5B Ag|AgCl (3 mol dm^{-3} NaCl) reference electrode (+0.213 V versus SHE) in a separate compartment. For preparation of bulk metal (oxy)-hydroxide material for characterisation, a multi-channel galvanostat was designed and constructed, which could simultaneously produce a current of up to ±30 mA across 5 channels. Here, two-electrode circuitry was used, the horizontally mounted palladium flag (1.5 cm^2 exposed geometric surface area) being placed parallel to the platinum gauze counter electrode. Following application of -20 mA cm^{-2} for 40 min, precipitates were dried in air to produce films and then removed and collected to generate enough material for analysis. Deposit thickness could be controlled by varying deposition time, with a typical 40 min deposit having a thickness of 0.5 mm on the electrode surface.

2.2. Material characterisation techniques

A Leo 1530 Field Emission Gun Scanning Electron Microscope system was used for scanning electron microscopy (SEM), with an EDAX$^®$ detector attached for EDX analysis. Samples for analysis were mounted on SEM stubs using double sided carbon tape, before being coated with a thin layer of gold.

Powder X-ray diffraction data were collected on a Bruker D8 Advance powder diffractometer fitted with a PSD detector operating with monochromated Cu kα1 radiation (1.5406 Å). Samples were mounted on a silicon wafer (100, Aldrich). Temperature resolved powder X-ray diffraction experiments were carried out using an Anton Parr HTK 1200 heated sample stage. Data collection took place over 60 min, with XRD patterns being obtained for 2θ values between 15º and 70º using a 0.0147º 2θ step. All data collected were compared against patterns stored in the Joint Committee on Powder Diffraction Standards database.

3. Results and discussion

A selection of aqueous single metal sulfate and mixed metal sulfate solutions was examined to explore the range of accessible metal (oxy)-hydroxides that are available using the cathodically-induced precipitation technique. Table 1 summarises the appearance of the palladium cathode surface following electrolysis, together with relevant physico-chemical properties.
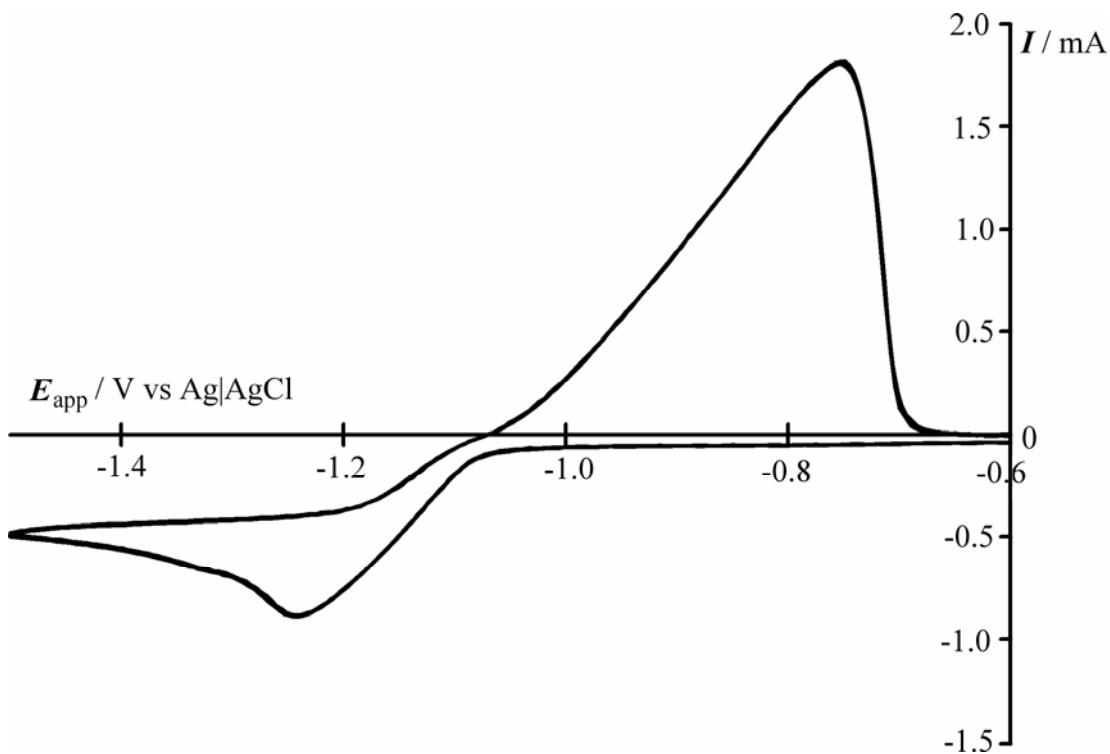
3.1. Sodium sulfate and potassium sulfate solutions

On electrolysis of separate sodium sulfate and potassium sulfate solutions, the palladium electrode surface did not change in appearance. Sodium and potassium have very negative reduction potentials (table 1), therefore the metal would not be expected to deposit on the palladium surface. However, no metal (oxy)-hydroxide precipitate or film will form as both sodium hydroxide and potassium hydroxide are very soluble (table 1) and the electrogenerated base and metal cations will remain in solution.

3.2. Zinc sulfate, nickel sulfate and indium sulfate solutions

On electrolysis of separate zinc, nickel and indium sulfate solutions, each metal was electrodeposited on the palladium surface. At the current density used here, metal deposition is favoured over metal (oxy)-hydroxide formation. The zinc formed as dendrites and the nickel and indium as uniform films. In each case, the cyclic voltammetric response shows a typical metal deposition peak, followed by a sharp stripping peak. An example cyclic voltammogram is that for zinc sulfate (Fig. 1), where the stripping peak is asymmetrical due to the lack of supporting electrolyte in solution.

Fig. 1

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2.0 I / mA

1.5

1.0

0.5

E_{app} / V vs Ag|AgCl

0

-1.4   -1.2   -1.0   -0.8   -0.6

-0.5

-1.0

-1.5

3.3. Magnesium sulfate, lanthanum sulfate, yttrium sulfate and scandium sulfate solutions

Electrolysis of separate magnesium, lanthanum, yttrium and scandium sulfate solutions generated insoluble metal (oxy)-hydroxide precipitates, which accumulate as white adherent films on the palladium surface. In each case, the metal ion reduction potential is sufficiently negative that hydrogen ion reduction, with the generation of a local high pH, occurs before metal plating. The hydrogen-sorbing palladium electrode was essential for successful metal (oxy)-hydroxide film formation. When each experiment was repeated using a platinum electrode, hydrogen evolution and gassing disrupted the forming precipitate, which then collected at the bottom of the cell.

3.4. Mixed metal sulfate solutions of yttrium/lanthanum and yttrium/scandium

Electrolysis of yttrium/lanthanum and yttrium/scandium sulfate solutions likewise generated insoluble metal (oxy)-hydroxide precipitates, which accumulate as white adherent films on the palladium surface. Following electrolysis from the mixed-metal sulfate starting solutions, EDX was used to confirm that a mixture of the two

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metal (oxy)-hydroxides was deposited, the data further confirming the purity of the films, with only sulfur being additional present, presumably as the sulfate.

3.5. Mixed metal sulfate solution of yttrium/indium

Electrolysis of a mixed yttrium/indium sulfate aqueous solution generated an adherent white film on the palladium surface. The morphology of the film was examined by SEM and for the majority of the material area, the image (Fig. 2 (a)) was typical of the other metal (oxy)-hydroxide films. However, in small regions, dendritic indium metal, was observed (Fig. 2 (b)). EDX measurements confirmed the presence of both yttrium and indium in the sample. XRD measurements (Fig. 3) at 80°C showed the material to be largely amorphous, indicating that film deposition is disordered. The only reflections observed at 80°C are due to the pure crystalline indium, with peaks due to sulfate, below $2\theta = 20°$.

Fig. 2



(a)   (b)
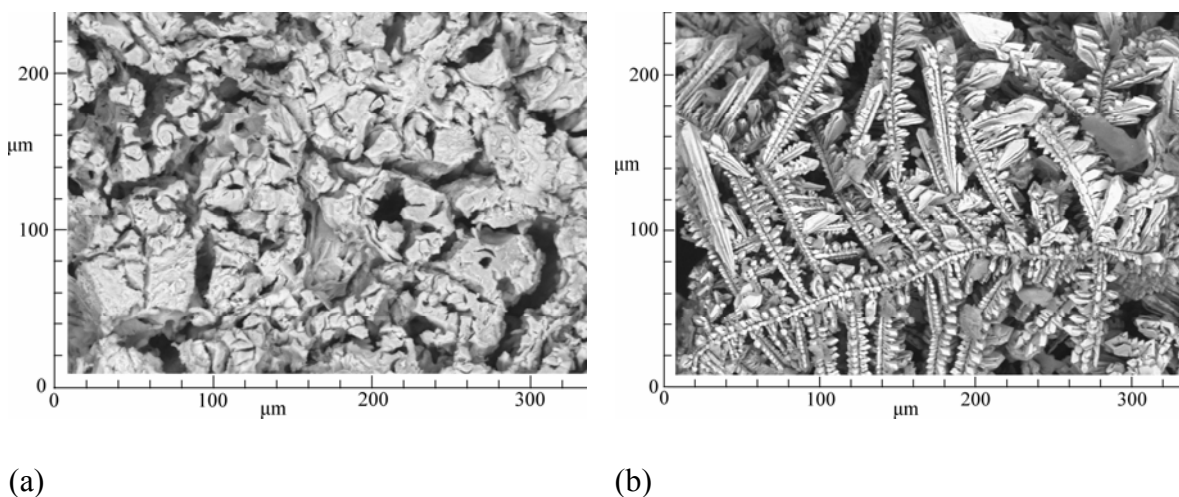
Calcination of the cathodically-precipitated film material was studied using temperature-resolved X-ray diffraction measurements (Fig. 3). By 200°C the indium reflections disappear. At higher temperatures, interestingly, a metastable yttrium/indium oxide phase is observed, which has a defect fluorite structure between the temperatures of 600 and 1000°C. Above 1000°C, a mixed phase system of yttrium and indium oxides

is observed. Following heating at 900°C for 3 h, upon cooling the metastable phase separates into a mixed phase system of indium and yttrium oxides.

Fig. 3
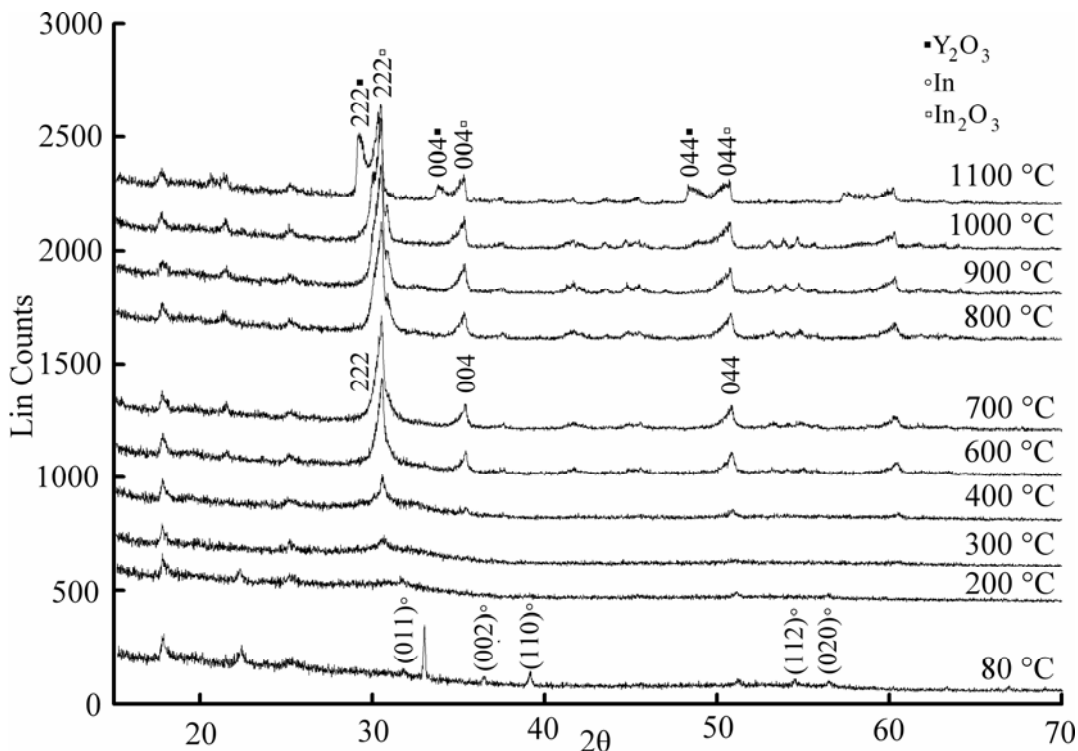
4. Conclusions

Several metal and mixed-metal (oxy)-hydroxide films are conveniently prepared by the electrolysis of aqueous metal sulfate solutions, using a hydrogen-sorbing palladium cathode. These materials are ceramic precursors, calcination allowing the preparation of a range of metal and mixed-metal oxides. The cathodically-induced precipitation method would be ideally suited to the production and testing of a range of metal oxides for various applications. The composition of the generated material may be tuned through the choice of the identity and concentrations of the metal sulfates in the starting solution. Metal oxides, for example, have long been used as gas sensing materials, with different mixtures allowing modification of selectivity and sensitivity [15]. With the method described here, rapid testing of materials is possible, using films grown as bridging precipitates between twin palladium electrodes, as we have earlier

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described in the study of humidity-sensing properties of aluminium (oxy)-hydroxide films [12, 13].

Acknowledgement

References

[1]   G.H.A. Therese, P.V. Kamath, Electrochemical synthesis of metal oxides and hydroxides, Chem. Mater. 12 (2000) 1195-1204.

[2]   P.J. Mitchell, G.D. Wilcox, An electrochemical route to pre-shaped ceramic bodies, Nature (London) 357 (1992) 395-397.

[3]   R.N. Bhattacharya, R. Noufi, L.L. Roybal, R.K. Ahrenkiel, YBaCuO superconductor thin films via an electrodeposition process, J. Electrochem. Soc. 138 (1991) 1643-1645.

[4]   P. Slezak, A. Wiechowski, Aqueous electrochemical synthesis of $YBa_2Cu_3O_{7-x}$ superconductors, J. Electrochem. Soc. 138 (1991) 1038-1040.

[5]   R. Janes, P.M.S. Monk, R.D. Partridge, S.B. Hall, Electrodeposition of thin-film rare-earth oxocuprates, J. Mater. Chem. 6 (1996) 183-186.

[6]   P.M.S. Monk, R. Janes, R.D. Partridge, Electrochemical deposition of the hydroxide precursors to $YBa_2Cu_3O_{7-\delta}$ and related phases, J. Mater. Chem. 8 (1998) 1779-1781.

[7]   P.M.S. Monk, S.L. Chester, D.S. Higham, R.D. Partridge, Electrodeposition of cobalt oxide doped with additional metal oxides, Electrochim. Acta 39 (1994) 2277-2284.

[8]   P.M.S. Monk, R.D. Partridge, R. Janes, M.J. Parker, Electrochromic tungsten oxide: doping with two or three other metal oxides, J. Mater. Chem. 4 (1994) 1071-1074.

[9]   P.M.S. Monk, T. Ali, R.D. Partridge, The effect of doping electrochromic molybdenum oxide with other metal oxides: correlation of optical and kinetic properties, Solid State Ionics 80 (1995) 75-85.

[10]   P.M.S. Monk, S. Ayub, Solid-state properties of thin film electrochromic cobalt-nickel oxide, Solid State Ionics 99 (1997) 115-124.

[11]   P.M.S. Monk, S.P. Akhtar, J. Boutevin, J.R. Duffield, Toward the tailoring of electrochromic bands of metal-oxide mixtures, Electrochim. Acta 46 (2001) 2091-2096.

[12]   P.J. Mitchell, R.J. Mortimer, A. Wallace, Evaluation of a cathodically precipitated aluminium hydroxide film at a hydrogen-sorbing palladium electrode as a humidity sensor, J. Chem. Soc., Faraday Trans. 94 (1998) 2423-2428.

[13]   R.J. Mortimer, R.J. Mayes, Characterisation and humidity-sensing properties of aluminium (oxy)-hydroxide films prepared by cathodically-induced precipitation, Sensors and Actuators B, Chemical, *submitted.*

[14]   P.J. Mitchell, R.J. Mortimer, A. Wallace, An in situ optical micrographic study of metal hydroxide film growth during potential controlled cathodic precipitation, 188th Electrochemical Society Meeting, 95-2, The Electrochemical Society, Chicago, Illinois, 1995, pp. 616-617.

[15]   P.T. Moseley, A.M. Stoneham, D.E. Williams, Oxide Semiconductors: Patterns of Gas Response Behaviour according to Material Type, in: Techniques and Mechanisms in Gas Sensing, ed. P.T. Moseley, J.O.W. Norris, D.E. Williams (Adam Hilger, IOP Publishing Ltd., Bristol, 1991) ch. 4.

Figure captions

Fig. 1

Zinc deposition/stripping cyclic voltammogram at 50 mV s^{-1} from a 0.01 mol dm^{-3} aqueous zinc sulfate solution at 20°C. Potential limits were -0.5 V and -1.5 V versus a Ag|AgCl (3 mol dm^{-3} NaCl) reference electrode. The working electrode was a palladium wire (0.25 mm diameter and 2.5 cm length), with a platinum gauze counter electrode.

Fig. 2

SEM images of the mixed yttrium and indium oxide film (a), and a region (b) within it where indium dendrites are evident

Fig. 3

XRD patterns for the mixed yttrium/indium oxides system

Table 1

Relevant physico-chemical data[‡] and observations at the palladium cathode, following electrolysis at -20 mA cm^{-2} from each 0.01 mol dm^{-3} metal sulfate solution

starting metal sulfate as 0.01 mol dm^{-3} aqueous solution	E°/V vs. SHE	metal oxide solubility at 25°C/g per 100 cm^3	metal hydroxide solubility at 25°C/g per 100 cm^3	observation at palladium cathode
Al$_2$(SO$_4$)$_3$	-1.68	insoluble	insoluble	white precipitate[§]
Na$_2$SO$_4$	-2.71	hydrolyses	114	no precipitate
K$_2$SO$_4$	-2.94	hydrolyses	119	no precipitate
ZnSO$_4$	-0.76	0.001	0.001	metal plates as dendrites
NiSO$_4$	-0.24	insoluble	0.001	metal plates
In$_2$(SO$_4$)$_3$	-0.34	insoluble	insoluble	metal plates
MgSO$_4$	-2.36	insoluble	0.0012	white precipitate
La$_2$(SO$_4$)$_3$	-2.38	0.0001	insoluble	white precipitate
Y$_2$(SO$_4$)$_3$	-2.37	insoluble	insoluble	white precipitate
Sc$_2$(SO$_4$)$_3$	-2.09	insoluble	insoluble	white precipitate

[‡] From G.H. Aylward, T.J.V. Findlay, SI Chemical Data, 4th edition, J. Wiley & Sons, Brisbane, 1998 and/or D.R. Lide (editor), CRC Handbook of Chemistry and Physics, 81st edition, CRC Press, USA, 2000.
[§] See references [12, 13]