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The effect of firing temperature, preparation technique and composition on the electrical properties of the nickel cobalt oxide series $Ni_xCo_{1-x}O_y$

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The spinel $NiCo_2O_4$ and the materials within the Ni-Co oxide series have well established applications in electrochemistry. However, the importance of the electrical conductivity of these materials and the consequences of the choice of preparation technique and firing regime are often overlooked.

In this paper the effect of thermal treatment on the formation of the $NiCo_2O_4$ phase, its structure and electrical properties are investigated. Given the selection of an appropriate firing regime, a range of preparation techniques (thermal decomposition, cryochemical, spray pyrolysis and several precipitation methods) are investigated for the resultant electrical, structural and morphological properties. Finally, having selected an appropriate preparation procedure, the entire range of Ni-Co compositions is investigated with respect to the phases formed and their electrical properties.

The formation of pure $NiCo_2O_4$ in a narrow range of firing temperatures is highlighted and the temperature of 375°C is identified as being the most suitable. Besides morphological and granular concerns regarding the selection of the preparation procedure, the importance of the formation of the $NiCo_2O_4$ phase for the attainment of high electrical conductance is illustrated. Furthermore, the existence of the $NiCo_2O_4$ phase in compositions considerably outside of this stoichiometry is noted, and the presence of this phase in the attainment of high electrical conduction is highlighted.

1. Introduction

The solid solutions of the nickel cobaltite system, represented as $Ni_xCo_{1-x}O_y$, and more commonly the spinel oxide $NiCo_2O_4$, have well documented and established applications in electrochemistry. It is well known that this series of solid solutions have exceptionally high activity with regard to the reduction of oxygen and the oxygen evolution reaction (OER) [1–6]. Alternative electrochemical reactions to which this system of metal oxides has been applied include the oxidation of alcohols and amines [7, 8], the decomposition of hydrogen peroxide [9] and the indirect oxidation of ethylene glycol [10]. With specific regard to these reactions, most authors conclude that the spinel $NiCo_2O_4$ yields the highest activity of the compounds within this system, the activity exceeding that for the individual oxides Co_3O_4 and NiO. More recently, the nickel rich cobaltite solid solutions have been reported as being potentially successful cathode materials for the application to lithium-ion rechargeable batteries [11]. For this application the nickel rich compositions of 75 mol% Ni [12] and 85 mol% Ni [13] have been suggested, which offer a high battery performance whilst significantly reducing the material costs through partial replacement of the expensive cobalt constituent.

The spinel $NiCo_2O_4$ possesses a high electrical conductivity, antiferromagnetic properties but a low thermal stability. The distribution of the cations within the spinel unit cell of $NiCo_2O_4$ is well documented and, although some reports detail an perfectly inverse spinel [14–16], it is generally agreed that the distribution of cobalt and nickel ions about octahedral and tetrahedral sites is random and the general configuration $(Co)_{tet}[Ni\text{-}Co]_{oct}O_4$ is most commonly postulated.

However, opinions as to the qualitative distribution remain different. Some examples are detailed

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below.

$(Co^{2+}_{0.875}Co^{3+}_{0.125})_{tet}[Ni^{2+}_{0.875}Ni^{3+}_{0.125}Co^{3+}]_{oct}O_4$ King [17]

$(Co^{2+}_{1-y}Co^{3+}_{y})_{tet}[Ni^{2+}_{y}Co^{3+}_{1-y}]_{oct}O_4$ Kovalenko [18]

$(Ni^{2+}_{1-x}Co^{3+}_{x})_{tet}[Ni^{2+}_{x}Co^{3+}_{2-x}]_{oct}O_4$ Tarasevich [9]

Deviancies in the precise quantitativity of the cationic distributions are likely to be attributable to both the preparation technique and the firing regime employed, these differing substantially in many publications. The low thermal stability of the spinel structure is observed by decomposition through the loss of NiO from the bulk to the surface, which commences at about 400°C. Since the majority of preparations involve firing the material at around 400°C the thermal history of the spinel is likely to profoundly effect the cationic distribution within the bulk material, and therefore the physical and structural properties.

Indeed the low thermal stability of the nickel cobaltite system and in particular the spinel $NiCo_2O_4$ is well documented and is discussed within this paper. It is clear from literature that consideration of this in the selection of preparative procedures for pure $NiCoO_4$ is often lacking. Furthermore the analysis of the products obtained over a wide range of firing temperatures appears scant. The formation of the lower cobaltite, $NiCo_2O_2$, at approximately 600°C is also reported in this paper. The requirement to maintain the temperature of thermal treatment at a suitably low level in order to reduce the effects of sintering is generally realised and, furthermore, the necessity of maintaining that temperature for a minimal duration is also recognised.

Several preparation techniques have been applied to the cobaltite series. The most common method employs the thermal decomposition of metal nitrate precursors either to form bulk powders or directly on the surface of an electrode support. Some authors report data obtained using electrodes fabricated from $NiCo_2O_4$ powder with the addition of a binder and, occasionally, graphite. Alternative preparation techniques include cryochemical [19, 20], coprecipitation of metal hydroxides [18], oxalates [21] and hydroxide carbonates [22], spray pyrolysis [5, 23–26] and sol-gel [27].

Studies of the bulk and surface compositions of the spinel $NiCo_2O_4$ are widespread and the methods for the preparation of this and the materials in the entire range of solid solutions are diverse. More recently studies pertaining to the surface species present within the nickel cobaltite system have been undertaken. For example, Kim and co-workers [28] prepared $NiCo_2O_4$ through a sol-gel method and by thermally decomposing the metal nitrates. They concluded that the surface was somewhat deficient in oxygen when prepared by the thermal decomposition route and that Ni^{2+} was octahedrally coordinated whilst Co ions assumed both octahedral and tetrahedral coordinations. Furthermore, hydroxylation effects were concluded to be minimal. Contrary to this, Roginskaya [3] indicated that considerable hydroxylation occurs on the surface of $NiCo_2O_4$ prepared by thermal decomposition. Haenen and co-workers [29], prepared $NiCo_2O_4$ by the thermal decomposition of metal nitrates and noted that the surface contained both Ni^{2+} and Co^{2+} species. De Faria and co-workers [30] investigated the entire range of the nickel cobaltite system and concluded that the surface exhibited nickel enrichment at nickel concentrations exceeding 20 mol%.

Furthermore, the characterisation of the surface is often undertaken, with particular respect to the surface area, morphology and, less frequently particle size. Characterisation of the activity of these materials is invariably undertaken by electrochemical methods pertaining to the reaction being investigated. However, the diverse preparation methods, the addition of binders and graphite during electrode preparation and their subsequent characteristics and the analytical methods employed, makes the direct comparison of the electrochemical activities impossible.

An additional problem is that the focus of attention is often placed on the cobalt rich end of the $Ni_xCo_{1-x}O_y$ series extending to the stoichiometric composition $NiCo_2O_4$ [4, 6, 7, 10, 25, 31]. Studies of the entire range of compositions are less common. Roginskaya and co-workers [3] detailed the structure and surface properties of the full range of compositions together with some electrochemical data. Kovalenko [18] reported data concerning the structure (unit cell parameter) and electrochemical activity for all Ni-Co ratios in the system. However, the materials were thermally treated at temperatures in excess of 500°C and therefore conclusions regarding the effect of composition are unreliable due to the formation of the thermally derived NiO phase. Hu and co-workers [32] reported a range of solid solutions, although the cobalt rich end of the series was not well represented. The study involved the characterisation of the materials electrochemically with respect to the oxygen evolution reaction and detailed the phases present. It was concluded that the solid solution comprising equal amounts of nickel and cobalt yields better performance than $NiCo_2O_4$. Trunov [16] detailed the structure, electrochemical properties and conductivity of the entire range of compositions. However these were prepared by a route of hydroxide precipitation using ammonia, and current investigations have shown that rather than causing precipitation, the metals become involved in complex formation. These articles are discussed in detail within this paper.

It is clear, however, that consideration of the bulk conductivity of the materials is often neglected, and is limited to a few firing temperatures of a few different compositions, normally of the cobalt rich end of the above series. However, it is inappropriate to make comparisons between these reports primarily due to the differences in preparation techniques. Furthermore, it is considered inappropriate in many cases to detail conductivity values since the precise geometry of the material being investigated is often poorly understood. A more accurate measure would therefore be conductance, which is employed in this paper.

It is imperative to consider the surface (geometric) properties, the bulk composition and the electrical conductivity of a given electrocatalyst in order to interpret the degree of activity and to enable the selection of the optimum formulation and preparative procedure. The importance of the conductivity of the bulk material was highlighted by Trasatti [33, 34] in review articles concerning the development and production of effective electrocatalysts. Indeed for all electrochemical applications, and especially for lithium-ion batteries, bulk conductivity is an essential prerequisite to the selection of materials.

In this paper, the effect of a wide range of firing temperatures on the conductance of $NiCo_2O_4$ is analysed and the importance of the spinel structure is highlighted. Given suitable thermal treatment the comparison of several preparation techniques and the effect on the conductance and surface area of the products is discussed. Given a suitable preparation technique, this is extended to the investigation of the conductivity and structure of the entire range of the $Ni_xCo_{1-x}O_y$ series. The dependence of high electrical conductance on the formation of the spinel $NiCo_2O_4$ is highlighted and the most suitable preparation procedure for the attainment of this is identified. Given such data the preparation of materials within this system for electrocataylitic applications, having high activity, may be obtained.

2. Experimental

2.1. Methodology

First the effect of the firing temperature on the formation of the stoichiometric spinel $NiCo_2O_4$ was investigated through the preparation of the spinel by thermally decomposing nickel and cobalt nitrates. This method of preparation owes its popularity to its ease of use and its appropriateness for the direct deposition of electrode materials. The later point is of particular importance to this system given that the low thermal stability precludes many procedures that require high temperature treatments. This was conducted over a wide range of temperatures and the phase purity, surface area and conductance of the materials were analysed. Once the optimum firing conditions had been established a range of preparation techniques were assessed, undertaken according to the thermal treatment identified. These included co-precipitation under several different conditions of pH control, cryochemical (freeze drying) and spray pyrolysis. It is submitted that attaining high conductance is largely dependant on the formation of the $NiCo_2O_4$ phase. Therefore, given the most appropriate method of preparation, that is to say the method deriving the highest purity of the spinel phase, the entire range of nickel cobaltites were prepared and analysed.

2.2. Experimental procedures—preparation techniques

2.2.1. Thermal decomposition of common salts

In order to evaluate the effects of the temperature of thermal treatment, $NiCo_2O_4$ was prepared by the thermal decomposition of the metal nitrates. $Ni(NO_3)_2{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ (Analar grade, Aldrich) were dissolved in methanol in the appropriate quantities and the methanol evapourated. The mixed nitrates were either transferred to a crucible (for preparation of samples for XRD and BET analysis) or spread to a piece of alumina (samples for the conductance measurements). These were dried at 110°C and then heated at temperatures in the range 250 to 700°C, in 50°C increments, for 2 h. Samples were generally heated from room temperature to that required for the thermal treatment at 5°C/min, although the effect of the ramp rate was investigated through the preparation of $NiCo_2O_4$ thermally treated at 400°C with a ramp rate of 2°C/min. The optimum temperature for firing was identified as 375°C and was subsequently used throughout the further investigations. This was confirmed by thermal analysis conducted on the mixture of the metal nitrates. Three coatings were applied to the alumina and were gently pressed at 1 ton for 2 min before drying to ensure that the oxide loadings of the samples and the morphologies were comparable. To enable the complete assessment of the conductance of this series, the individual oxides of cobalt and nickel were prepared in the same manner on the alumina substrate and fired at 400°C.

2.2.2. Co-precipitation

Co-precipitation offers a convenient method for the preparation of mixed metal salts and incorporates a high degree of mixing, the only concern being the purification from any impurities incurred from the precipitating agent. It is well known that transition metal salts undergo alkaline precipitation, furthermore nickel and cobalt hydroxides are observed to precipitate from metal nitrates in similar pH ranges 6.6–8.1 and 6.8–8.6 respectively.

Ammonia or ammonium hydroxide are unsuitable precipitating agents due to water-soluble chloroaquotetra-ammine cobalt (III) and chloroaquotetra-ammine nickel (III) complexes that form.

Three co-precipitation routines were followed; The addition of NaOH to a solution of the metal nitrates, the addition of a solution of the nitrates to NaOH and the addition of each of the reagent separately to a buffer solution of a suitable pH.

A buffer solution was prepared from 50 ml 0.2 M imidazole and 62.8 ml 0.1 N HCl diluted with distilled water to 200 ml and the pH found to be 7.0. Aqueous solutions of 0.5 M NaOH and metal nitrates (0.07 M Ni and 0.14 M Co) were slowly added to the buffer at a rate so that the pH remained as close to 7.0 as possible, a deviance of 0.2 pH units being controlled. After the complete addition of metal nitrates further alkali was added until pH 10 was obtained, this being found to be the lowest pH at which further precipitation of cobalt hydroxide ceased in the filtrate. The precipitate was stirred for a further hour before being filtered. The filtrate was tested with 1 M NaOH for complete precipitation of hydroxides before washing with 250 ml portions of distilled water. The washing was continued until the filtrate showed no reaction with 0.5 M $AgNO_3$

(chloride ion purity) and pH and a platinum wire flame test matched that of the distilled water used. The residue was then dried in air at 110°C and fired in air at 375°C for 2 h.

2.2.3. Cryochemical

A 0.1 M aqueous solution of nickel and cobalt nitrates in the required proportions was frozen in liquid nitrogen and transferred to a freeze drying apparatus. The system was isolated from the atmosphere and a vacuum applied with the flask seated in a dry ice bath, this being removed after 12 h and the vacuum sublimation continued for a further 12 h. The metal nitrates were then heated at 300°C for 6 h under vacuum and the resultant powder was then heated in air at 375°C for a further 2 h.

2.2.4. Spray pyrolysis

$NiCo_2O_4$ was directly deposited to a glass slide by spray pyrolysis. An alcoholic solution comprising 0.14 M $Co(NO_3)_2 \cdot 6H_2O$ and 0.07 M $Ni(NO_3)_2 \cdot 6H_2O$, in accordance with the precursors discussed by Tiwari and co-workers [25] was deposited onto a thermostatically controlled heated substrate at 375°C in a vertical arrangement as an aerosol generated by a nebulizer (Hudson disposable). This was continued for 5 h, the material being removed from the glass slide at 30 min intervals and collected for subsequent analysis.

2.3. Analytical techniques

Due to the uncertainty of the precise path length and the area of electrical conduction, the measurement of resistivity was not undertaken due to the likely errors and poor comparability of samples. Instead measurements of resistance and conductance were made. For the studies of thermal treatment and compositions, the resistance of samples coated to alumina were measured between gold tracts screen printed on alumina substrates. The dimensions of the substrates were, in all cases, 8 mm by 12 mm 96% alumina with two screen printed gold tracts of 1.5 mm width and 2 mm spacing (Du-pont). A Hewlett-Packard model 3478 A digital multimeter was used to measure resistance at 25°C.

Although the thermal decomposition of the metal nitrates and precipitated hydroxides and spray pyrolysis can be undertaken directly on alumina to yield films of good adhesion, the cryochemically prepared powder could not be coated without the addition of binding agents. The resistance measurements of $NiCo_2O_4$ prepared by the different methods were therefore undertaken using pressed pellets of the powders. These were pressed as discs of 10 mm diameter under a pressure of 20 tons/cm^2 for 5 min from 0.5 g of the respective powders. The conductance values reported in Table III were corrected for variances in disc thickness. Silver paste was applied to both surfaces to make electrical contacts and the resistance through the pellets was measured. Such a method was not favoured for all investigations since the degree of penetration of the conductive paint, necessary to achieve reliable electrical contacts, was uncertain. The reproducibility of the path length of electrical conduction through each pellet was, therefore, to some extent uncontrollable and lower resistance values may have been incurred given the incidence of greater diffusion of the conductive layer.

X-ray powder diffraction (XRD) was undertaken on a Philips PW1850 powder diffractometer using Cu K_α radiation operated at 35 kV and 40 mA with a Ni filter. The average wavelength of the radiation was given as 1.54186 Å. Samples were mounted on an aluminium/silica slide and angles from 5° to 90° were measured in 0.02° steps at 0.01°/s. Average crystallite sizes for $NiCo_2O_4$ prepared by different techniques were calculated using the Scherrer equation with a shape factor of 0.9. Calculations were performed using the [311], [440] and [511] diffraction lines. Instrumental broadening was measured using a standard sample of high crystallinity Co_3O_4 having a known distribution of crystallite sizes.

Du-Pont models 910 1600DTA and 951TGA were used for differential thermal analysis (DTA) and thermogravimetric analysis (TGA) respectively. Analysis was undertaken under static air in the temperature range 10–1000°C at a heating rate of 5°C/min.

The surface areas of the powders were measured by the BET method using a Micrometrics Gemini instrument with nitrogen adsorption under isothermal conditions. 20 points were measured and STAR software was used for data analysis.

Scanning Electron Microscopy (SEM) was undertaken on several samples, as detailed in the results and discussion sections. This was conducted on a Cambridge Instruments Spectroscan model 90 Scanning Electron Microscope operated at 25 kV and 100 mA with an X-ray detector. The samples were of sufficient electrical conductivity so as to alleviate the necessity of coating with gold prior to analysis.

3. Results and discussion

3.1. Effects of firing temperature

The conductance of the samples and the sample loadings are given in Table I, selected XRD patterns are given in Fig. 1 whilst the XRD results are summarised for all of the samples in Table II.

TABLE I Resistance values, surface areas and sample loadings for $NiCo_2O_4$ samples fired at varying temperatures

Temperature of thermal treatment (°C)	Conductance (S) at 25°C	Sample loading (mg/cm^2)	Surface area (m^2/g)[a]
250	2.69×10^{-4}	9.94	2.80
300	0.0475	8.22	12.05
350	0.0499	9.67	16.77
400	0.0389	8.25	17.05
450	0.0360	9.17	10.41
500	0.0421	8.20	4.32
550	0.0409	8.11	3.19
600	0.0143	10.10	2.93
650	4.75×10^{-4}	8.52	3.03
700	1.90×10^{-4}	9.42	2.78
NiO @ 400	1.54×10^{-4}	8.99	9.76
Co_3O_4 @ 400	2.09×10^{-4}	9.86	2.22

[a] Assessed with powder samples.

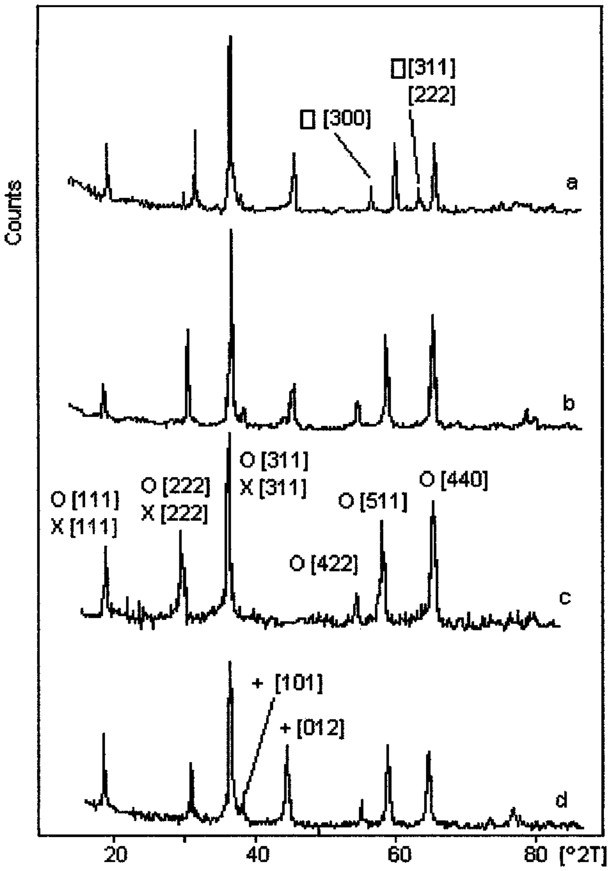

Figure 1 Selected XRD patterns of $NiCo_2O_4$ fired at various temperatures: (a) 650°C, (b) 400°C, (c) 350°C, and (d) 300°C. Common lines labelled on single patterns for clarity: O = $NiCo_2O_4$, X = Co_3O_4, + = NiO, □ = $NiCoO_2$.

The method of thermal decomposition of the metal nitrates, mixed through recrystalisation from an alcoholic solution was chosen due to the simplicity of the technique and its common occurrence in the literature. Furthermore, the technique offers a facile means of preparing the spinel material directly on a substrate, an operation that poses difficulties when starting with the pre-fired powder due to the low thermal stability.

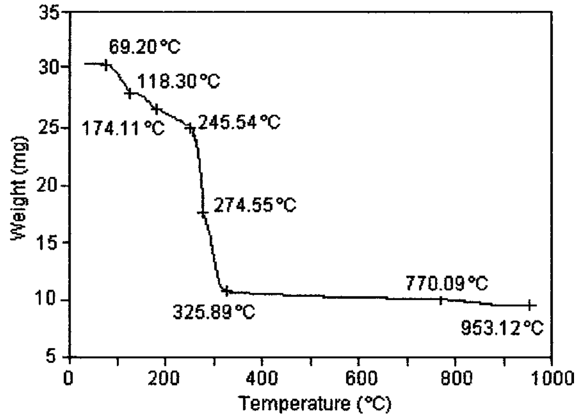

Figure 2 TGA profile of mixed nickel and cobalt nitrates.

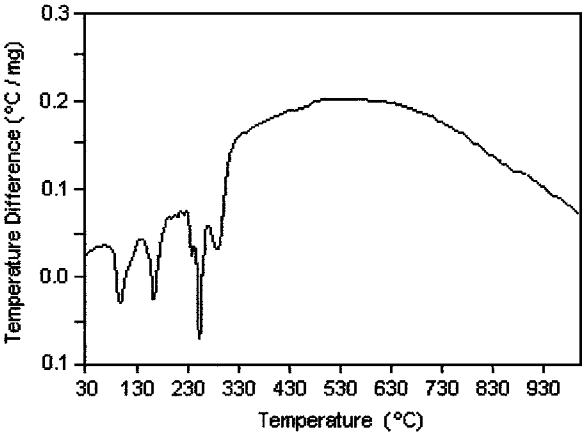

Figure 3 DTA profile of mixed nickel and cobalt nitrates.

X-ray diffraction data showed that the spinel $NiCo_2O_4$ is scarcely formed below 350°C, this was confirmed by thermal analysis (TGA and DTA), Figs 2 and 3, which indicated that the metal nitrates had almost fully decomposed at 325°C. The profiles showed that, after initial melting of the nitrates at 97°C, the loss of waters of hydration occurred to yield distinct tetra and di-hydrated salts. This is common with $Ni(NO_3)_2 \cdot 6H_2O$ but not the cobalt analogue [35] and was therefore due to the nickel precursor alone.

TABLE II Summary of XRD phases for $NiCo_2O_4$ fired at varying temperatures

Temperature of thermal treatment (°C)	Phases present	Cell parameter (Å)
250	Some $NiCo_2O_4$, and Co_3O_4, mainly nickel and cobalt salts	$NiCo_2O_4 = 8.1462$, $Co_3O_4 = 8.0470$
300	$NiCo_2O_4$, NiO and Co_3O_4	$NiCo_2O_4 = 8.1221$, $Co_3O_4 = 8.1094$, $NiO = 4.1382$
350	$NiCo_2O_4$ only	$NiCo_2O_4 = 8.1185$
400	$NiCo_2O_4$ and NiO	$NiCo_2O_4 = 8.1182$, $NiO = 4.1706$
450	$NiCo_2O_4$ and NiO	$NiCo_2O_4 = 8.1185$, $NiO = 4.1705$
500	$NiCo_2O_4$ and NiO	$NiCo_2O_4 = 8.1197$, $NiO = 4.1700$
550	$NiCo_2O_4$ and NiO	$NiCo_2O_4 = 8.1183$, $NiO = 4.1708$
600	$NiCo_2O_4$, Co_3O_4 and trace NiO	$NiCo_2O_4 = 8.1151$, $NiO = 4.1755$, $Co_3O_4 = 8.0624$
650	Co_3O_4, NiO and some $NiCo_2O_4$, $NiCoO_2Co_3O_4$, NiO	$NiCo_2O_4 = 8.2562$, $NiO = 4.1782$, $Co_3O_4 = 8.0876$, $NiCoO_2 = 4.2488$
700	NiO, Co_3O_4 and trace $NiCo_2O_4$ and $NiCoO_2$	$NiO = 4.1964$, $Co_3O_4 = 8.0894$, $NiCoO_2$, $NiCoO_2 = 4.2480$

Following decomposition a constant weight loss occurred due to the loss of excess oxygen from the spinel. The final weight loss to occur was observed at 953°C (evident as the endotherm at 956°C on the DTA trace) and was due to the $Co_3O_4 \rightarrow CoO$ transition. This indicates that the $NiCo_2O_4$ phase had become totally decomposed to Co_3O_4 and NiO at this temperature. This is in contradiction to that reported by Haenen [20] who suggested that these precursor materials were decomposed at approximately 250°C and that the $NiCo_2O_4$ phase was evident at this temperature. This may, however, be explained by the greater duration of heat treatment by Haenen (10 h). Furthermore the cobalt oxide transition at approximately 950°C was absent from the profiles reported by Haenen. The sample fired at 350°C showed only $NiCo_2O_4$ to be present with a cell parameter of 8.1185 Å, this being in agreement with the literature value 8.1140 Å [36]. It should be noted, however, that the difference between powder diffraction patterns for $NiCo_2O_4$ and Co_3O_4 is, unsurprisingly, very slight and the close inspection of high angle diffraction lines is often necessary in order to assess the presence of small quantities of Co_3O_4.

The presence of the cubic NiO phase initially appeared in the sample fired at 400°C and co-existed with the $NiCo_2O_4$ in greater quantities, but with the exclusion of Co_3O_4, up to the firing temperature of 550°C. The cell parameter of the NiO within this temperature range changed little and remained close to the literature value of 4.1780 Å [37], indicating little structural interaction between the two phases. Therefore the NiO must be considered as a separate entity to $NiCo_2O_4$ and not merely a surface species, furthermore, the existence of a solid solution of the form NiO—Co_3O_4 can be excluded. The surface coverage of $NiCo_2O_4$ by NiO for the materials fired at higher temperatures would then explain the loss of electrochemical performance evident from literature reports. The loss of activity may also be due to the reduction in the surface area associated with the formation of the NiO layer.

At a firing temperature of 600°C some $NiCo_2O_4$ was observed together with some NiO, indicating that Ni preferentially formed the spinel $NiCo_2O_4$ but presented the same separate NiO phase as was common with all temperatures above 400°C. The cause for the incomplete formation of $NiCo_2O_4$ would then appear to be the cobalt constituent, this forming Co_3O_4 with a cell parameter of 8.0624 Å, slightly smaller than the literature value of 8.084 Å [38]. This was evident at higher firing temperatures, and at 650°C the cell parameter for Co_3O_4 became very close to that quoted (8.0876 Å). An interesting phase apparent at 650 and 700°C is the lower cobaltite $NiCoO_2$, having a cell parameter of 4.2488 Å and 4.2480 Å at these temperatures and in excellent agreement with the literature value of 4.248 Å [39]. At 700°C no $NiCo_2O_4$ was formed.

The surface areas of the powder samples were observed to increase to a maximum value of 17.05 m^2/g for the powder treated at 400°C and fall sharply to 4.32 m^2/g at 500°C, from whereon they remained fairly constant. The surface areas are lower than reported elsewhere for powders treated at lower temperatures (250 to 300°C) [20, 40], however, in both of these studies the surface area of powders fired at temperatures higher than 400°C were not detailed and therefore this significant decrease was omitted. Such a sudden and significant decrease in surface area must have been due to the formation of a NiO surface layer, the surface area of which was found to be significantly less than that of $NiCo_2O_4$.

Observations by SEM indicated that, providing the temperature was increased gradually, the particle and agglomerate sizes did not become significantly enlarged at successively higher temperatures. SEM pictures of the samples heated at 400, 500 and 600°C are given in Figs 4–6. Between 400 and 500°C the degree of agglomeration was very similar and the particle sizes remained at 0.5–1 μm. The degree of agglomeration of the particles did, however, become somewhat more pronounced at 600°C, although the particle sizes were not observed to change significantly. The profound changes in conductance were, therefore, due to the presence of the $NiCo_2O_4$ and not to changes in the surface morphology. Since it is unlikely that changes in the size of the crystallites would have contributed to the observed

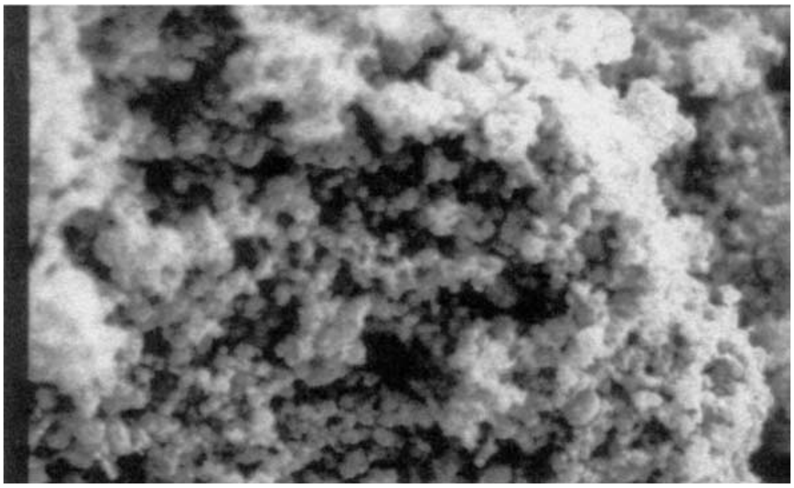

Figure 4 SEM image of $NiCo_2O_4$ from metal nitrates fired at 400°C.

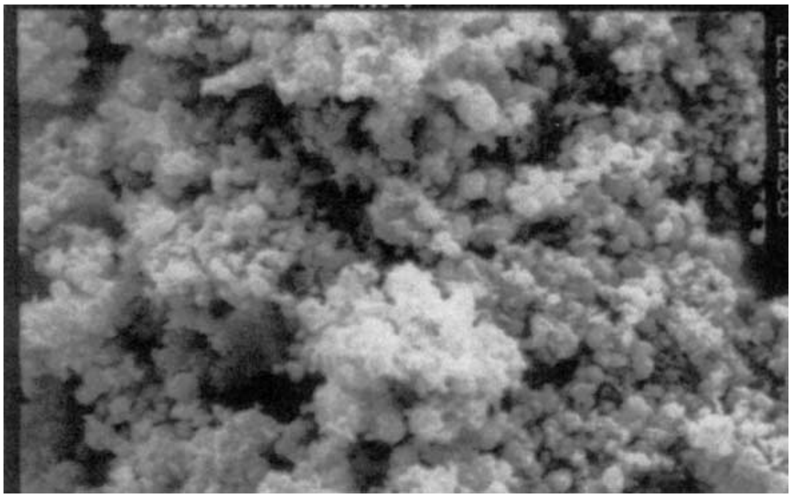

Figure 5 SEM image of $NiCo_2O_4$ from metal nitrates fired at 500°C.

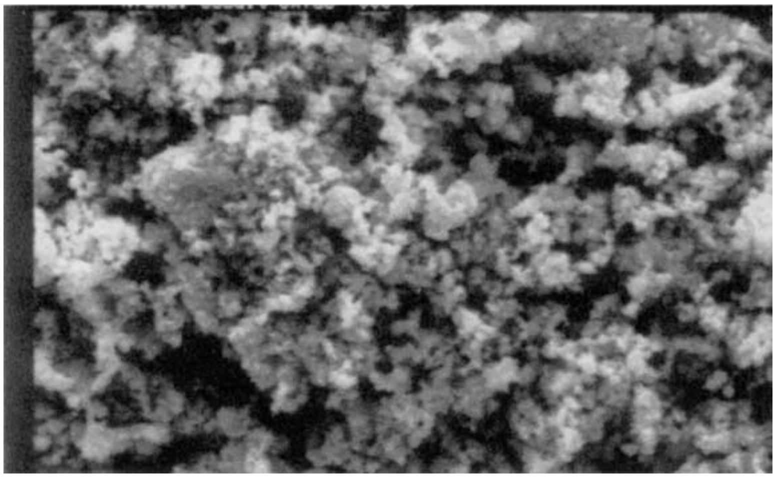

Figure 6 SEM image of $NiCo_2O_4$ from metal nitrates fired at 600°C.

conductance changes. Indeed no significant changes in the broadness of powder diffraction lines were observed throughout the range of firing temperatures. The lack of changes in the crystallite sizes for Co_3O_4 throughout a similar range of firing temperatures has also been reported for Co_3O_4 powders prepared by the same method [41].

The variance in sample conductance throughout the range of firing temperatures was dependant on the formation of the spinel $NiCo_2O_4$ and due to the semiconducting nature of this compound, this exceeding the bulk conductance of the individual metal oxides alone. It should be noted that the sample loading was observed to exert no significant interaction with the overall trend of the conductance values throughout this series. This is shown in Fig. 7, which illustrates the fluctuations in conductance to be independent of changes in loading.

The initial increase in conductance from firing temperatures of 250°C to 300°C was largely due to the formation of the spinel and the conductance maintained the highest values at firing temperatures of 300°C and 350°C, at which the purest spinel phase was identified by XRD. This inverse correlation between conductance and NiO content (and therefore firing temperature above 400°C) continued as the temperature was further increased and the $NiCo_2O_4$ phase became less pure with respect to the formation of NiO on the surface and therefore the loss of Ni from the bulk material, presumably as Ni^{2+} species. The sudden decrease in conductance at 650°C was then due to the more complete decomposition of $NiCo_2O_4$. The fluctuations in conductance values between firing temperatures of 300°C and 550°C may have been due to the differences in the grain structure, and hence the nature of the grain boundaries caused by progressively higher temperatures. Indeed it is realised that such phenomena exert profound

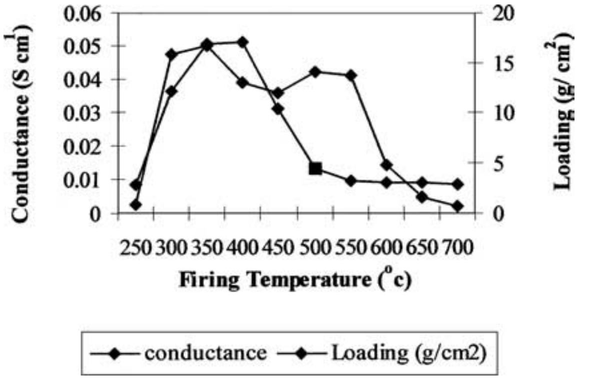

Figure 7 Sample conductance and loading for $NiCo_2O_4$ samples prepared from thermally decomposed metal nitrates.

influences on the conducting nature of such materials. Although, with respect to the importance of $NiCo_2O_4$ formation, this was minimal and the changes in the crystallite sizes have been shown to be negligible, the effects may be amplified due to the particularly low resistance of the $NiCo_2O_4$ phase.

Comparisons of the electrical properties of these materials with literature reports can only be made with difficulty. Indeed very few details are to be found in the literature and these represent only a narrow range of firing temperatures, furthermore figures are invariably quoted as resistivity or conductivity values which can only be accurately measured given detailed knowledge of the geometry of the sample and the pathway of electrical conduction. Carapuca [40] detailed the resistivity of $NiCo_2O_4$ electrodes fired at three temperatures (300, 350 and 400°C) and indicated the same trend as observed in the present study. Tarasevich [9] detailed the conductivity of pressed pellets formed by the same method and treated to 600°C at a range of measurement temperatures. The firing temperatures above 350°C were, however, only sparsely covered and therefore the significant fluctuations caused by the loss of nickel species from the bulk were missed. Again the same trend at lower temperatures was observed, although the conductivity of the material fired at 250°C was significantly higher whilst the materials were prepared by the same method as detailed in this paper. Furthermore the authors suggested the fall in conductivity at firing temperatures above 450°C to be due to the formation of separate NiO and CoO oxides. However, no XRD data was given to support this and the oxide CoO, which, for the materials fired in air, only forms when cobalt oxides are heated above 950°C, has not be observed in powder diffraction patterns. Another difference in conclusions is the mechanism for conduction, the authors suggesting the novel cationic distribution as outlined above.

Given the XRD, conductance and surface area results, and consideration of previous investigations, the optimum temperature for the preparation of $NiCo_2O_4$ may be selected. Such a temperature should not only result in the production of phase pure $NiCo_2O_4$, that is to say with the absence of the oxides of the nickel and cobalt, but also seek to maximise both surface area and conductance. It is therefore suggested that 375°C should be selected, and is indeed applied throughout the following investigations.

3.2. Effects of preparation technique

Given the identification of the optimum calcination temperature as being 375°C for the preparation of the purest $NiCo_2O_4$ phase, this was subsequently applied to the following investigations to preparation techniques.

Table III details the surface area and conductance of the samples prepared by the various techniques and Table IV summarises the phases present on the powder diffraction patterns. A selection of the powder diffraction patterns is given in Fig. 8.

From the powder diffraction patterns it is clear that the formation of $NiCo_2O_4$ with the absence of the individual oxides was dependant on the preparation

TABLE III Resistance values, crystallite sizes and surface areas for $NiCo_2O_4$ prepared by alternative methods and fired at 375°C

Preparation technique	Conductance (S) at 25°C	Average crystallite size (Å)	Surface area (m^2/g)[a]
Thermal decomposition	0.083	120–140	17.05
Temperature ramped thermal decomposition	0.071	135–160	18.73
Spray pyrolysis	0.039	80–100	32.75
Cryochemical	0.042	50–60	63.45
Co-precipitation @ pH 7.0	0.027	60–80	47.04
Co-precipitation into nitrates	0.031	55–65	42.58
Co-precipitation into NaOH	0.053	50–60	51.01

[a] Obtained from powder samples.

TABLE IV Summary of XRD phases for $NiCo_2O_4$ prepared by different techniques and fired at 375°C

Preparation technique	Phases present	Cell parameter (Å)
Thermal decomposition	$NiCo_2O_4$	$NiCo_2O_4 = 8.1165$
Temperature ramped thermal decomposition	$NiCo_2O_4$, NiO and some Co_3O_4	$NiCo_2O_4 = 8.1160$, $NiO = 4.1531$
Spray pyrolysis	$NiCo_2O_4$ only	$NiCo_2O_4 = 8.1173$
Cryochemical	$NiCo_2O_4$ only	$NiCo_2O_4 = 8.1146$
Co-precipitation @ pH 7.0	$NiCo_2O_4$ and some NiO	$NiCo_2O_4 = 8.1161$, $NiO = 4.1812$
Co-precipitation into nitrates	$NiCo_2O_4$, NiO and some Co_3O_4	$NiCo_2O_4 = 8.1155$, $NiO = 4.1870$ $Co_3O_4 = 8.0851$
Co-precipitation into NaOH	$NiCo_2O_4$	$NiCo_2O_4 = 8.1144$

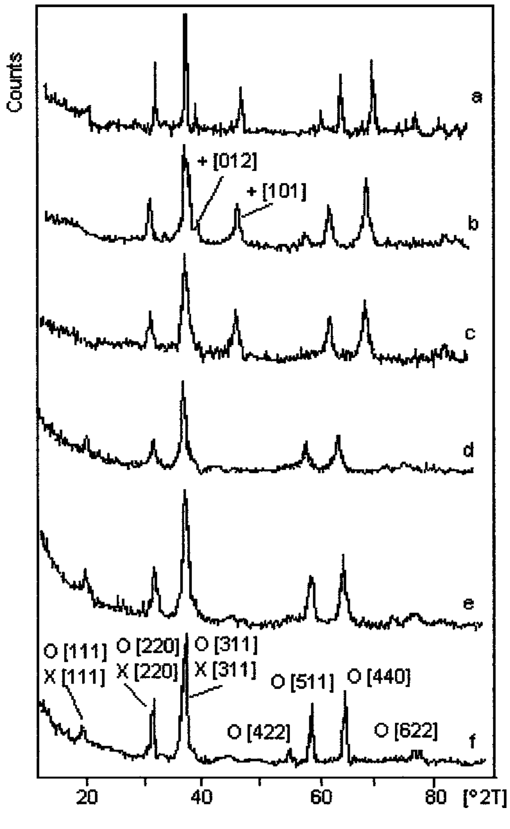

Figure 8 Selected XRD patterns of $NiCo_2O_4$ prepared by various techniques: (a) Thermal decomposition, (b) Co-precipitation at pH 7.0, (c) Co-precipitation of NaOH into metal nitrates, (d) Co-precipitation of metal nitrates into NaOH, (e) Cryochemical, and (f) Spray pyrolysis. Common lines labelled on single patterns for clarity.

technique employed, the spray pyrolysis, cryochemical and co-precipitation into NaOH techniques forming only $NiCo_2O_4$. It is suggested that the differences in the phase purity obtained by these techniques was due to the degree of mixing of the precursors obtained and the extent to which this was maintained during the decomposition step.

The simplest technique, that is to say thermal decomposition of the metal nitrates, when undertaken at 375°C, formed $NiCo_2O_4$ with a cell parameter close to the literature value. However some NiO and Co_3O_4 were also observed on the powder diffraction pattern of the sample fired under conditions of low thermal ramping up to a final temperature of 375°C. This was probably due to the slight separation of the materials when heated due to the slight differences in their melting points, and made apparent due to the increased time available for the separation of the nitrates before the solid state reaction occurred.

The spray pyrolysis and the cryochemical techniques yielded $NiCo_2O_4$ with no detectable NiO or Co_3O_4 phases. It is documented that this may be achieved for the compound $NiCo_2O_4$ by these techniques [22, 23, 29], although the importance of the intimacy of mixing and the maintenance of this was only noted for the cryochemical technique [22, 23].

Of the methods of co-precipitation investigated, the addition of a solution of the mixed nitrates to a slight excess of NaOH yielded the purest phase of $NiCo_2O_4$, this being with the total absence of NiO and Co_3O_4. The addition of NaOH to the nitrates caused the appearance of a considerable quantity of NiO and was due to the precipitation of $Ni(OH)_2$ before $Co(OH)_2$, the latter occurring at a higher pH [42], and the subsequent continued separation of the materials throughout the procedure. Controlling the pH of the precipitation close to the values observed for the alkaline hydrolysis of the metal nitrates was also observed to be of little merit since small quantities of NiO were again observed, and due to the same preferential precipitation of $Ni(OH)_2$.

The surface areas of the powders prepared by these methods reflected the crystallite sizes produced, these being calculated from the XRD data. The thermal decomposition techniques yielded the lowest surface areas due to the melting of the nitrate precursors and, therefore, the formation of a dense material before decomposition occurred. This was also indicated by the large crystallites formed, indeed those for the sample prepared under conditions of slow thermal ramping (135–160 Å) were larger than those from the normal heat treatment (120–140 Å) due to the increased time for agglomeration under melting to occur before decomposition. The cryochemical technique produced the highest surface area powder, comparable to that previously obtained [22, 23], as is unsurprising since the particle sizes obtained during the initial freezing step would have been maintained throughout the entire process. Co-precipitation also yielded powers of high surface area, and small crystallite size (50–80 Å) and this reflected the very fine nature of the precipitates obtained. Furthermore since the metal hydroxides were considerably less hydroscopic than the nitrates, less separation of the nickel and cobalt constituents could occur during the firing step because of considerably less melting through the loss of the waters of hydration. The surface area obtained for the powder produced by spray pyrolysis was rather low and the crystallites a little larger than for alternative techniques due to the spreading of the deposition on the substrate and the subsequent agglomeration of the particles. This was due to the impinging spray being too wet due to either the substrate being too cool or the flow rate being too high. A similar morphological effect has also been reported for $NiCo_2O_4$ prepared through this method [27, 28].

The conductance of the pressed pellets formed from the powders indicated that the thermal decomposition technique was particularly suitable to the preparation of $NiCo_2O_4$ of high conductance. However XRD analysis showed that these techniques were unsuitable for the preparation of high purity $NiCo_2O_4$ due to the presence of NiO and Co_3O_4, and, therefore, this appears to be in contradiction. It is unlikely that the applied conductive paint would have diffused into these pellets significantly more than with the other pellets as very similar conductance values for several other pellets were also attained. The more likely cause for the high conductance is a combination of two factors. Firstly larger grain sizes were derived from the thermally decomposed nitrates, evident in the low surface area and large crystallite sizes. Secondly the thermally decomposed nitrates were of greater compressibility than those of the alternative techniques, evident by the formation of thinner pressed discs. These factors therefore combined to yield pellets having larger intergranular contacts and therefore greater conducting pathways than was present in the discs of the powders prepared by the alternative techniques. Therefore, in this case, the nature of the particles and their contacts was significant, although this only became evident due to the nature of the pressed pellet technique.

The other preparation techniques identified by XRD as deriving $NiCo_2O_4$ of low phase purity were the precipitation methods involving the buffer solution and the addition of NaOH to the metal nitrates. These yielded lower conductance due to the degree of formation of the $NiCo_2O_4$ phase whereas the morphology of the powders was similar. This is shown by the similarity in crystallite size (60–80 Å) and surface area, for both powders. The methods by which the purest $NiCo_2O_4$ phase was prepared yielded appreciably higher conductance values due to the greater formation of the spinel phase. Again the particle sizes, typically 50–60 Å for the cryochemical and co-precipitation into NaOH techniques, and 80–100 Å for the spray pyrolysis technique. The differences in the surface areas of the powders were not found to influence conductance as this was quite similar, whilst the surface area of the spray pyrolysed sample was significantly lower than for the other techniques.

Although a wide range of preparation techniques are reported in the literature, details pertaining to the surface area and crystallite sizes produced are scarce. Krezhov [31] prepared $NiCo_2O_4$ by the thermal decomposition of the metal hydroxides and reported a surface area of 50 m^2/g with 150 Å crystallite sizes. Klissurski [22] precipitated metal hydroxycarbonates from the metal nitrates and reported surface areas of up to 90 m^2/g and crystallite sizes of 80–120 Å. Peshev [21] obtained a similarly high surface area of 94 m^2/g through the precipitation of metal oxalates. De Faria [30] produced the oxides through the thermal decomposition of the metal nitrates and recorded the same low surface area (32 m^2/g) and large crystallites (>200 Å). Carapuca [40] investigated several different procedures for the thermal decomposition of the metal nitrates and reported very low surface areas, typically 10–18 m^2/g. The same trends have, therefore, been observed, although the precise figures are quite different due to the precise nature of the preparation technique employed.

With respect to electrochemical performance, Bocca and co-workers [43] have explicitly investigated the effects of preparation procedure. A similar range of techniques were investigated by electrochemical means, although Teflon bonded electrodes were used. It was shown that the method of hydroxide precipitation gave optimum performance and greatest stability, although electrodes prepared from thermally decomposed powders improved on ageing, presumably as the active surface area became increased. The authors indicated the surface area and morphology as being of fundamental importance, although no measures of these were given.

3.3. Effect of composition

Results from the investigations concerning the optimum firing temperature and preparation technique were applied to the selection of the preparation method for the generation of materials in the series $Ni_xCo_{1-x}O_y$. The co-precipitation of metal hydroxides from their respective nitrates, and introduced to NaOH as outlined in Section 2.2 was selected as the preparation technique. This selection was made by virtue of the phase purity of $NiCo_2O_4$ formed during the previous investigations into techniques and the smaller crystallite size produced. This in turn would then be of interest to the generation of higher surface area powders pertinent to subsequent applications. The precipitates were then thermally treated at 375°C.

Table V details the conductance and surface areas of powders in the composition range $Ni_xCo_{1-x}O_y$ $(0 < x < 1)$ and the XRD patterns are summarised in Table VI. A selection of the patterns in shown in Fig. 9.

The spinel $NiCo_2O_4$ was found to be formed, at least in the minority, for all compositions within the range 10–80 mol% Ni inclusively. The unit cell parameter was observed to increase from the value of pure Co_3O_4 (8.0821 Å) with the initial introduction of nickel and then fall from the value at 10 mol% Ni to that at 33 mol% Ni, this being the spinel $NiCo_2O_4$. The large cell parameter at 10 mol% Ni may have been due to more Co^{2+} or Ni^{2+} assuming tetrahedral coordination, in which they are unstable with respect to octahedral coordination, than is common in the stoichiometric spinel. Immediately following the spinel composition the unit cell parameter again increased but remained fairly stable as the system became rich in Ni up to the composition of 75 mol% Ni, at which the major constituent in the XRD pattern became NiO. This increase was probably due to the replacement of the Ni^{2+} species, lost as NiO with the larger Co^{2+} ion in order to maintain the charge neutrality of the spinel species. At 90 mol% Ni only Co_3O_4 and NiO were observed, the Co_3O_4 having a larger cell parameter than quoted in literature. The cell parameter of the cubic NiO phase was not observed to change as the compositions became richer in Ni, and since these were very close to the literature value, Ni-Co oxide solid solutions were not formed. If such solutions were formed, then the cell parameter would be expected to change as the larger cobalt ions became introduced to NiO.

The agreement of XRD patterns of the standard samples of NiO and Co_3O_4 with those prepared through the thermal decomposition method was very good. Indeed the prepared Co_3O_4 sample had a cell parameter (8.0821 Å) in closer agreement with the literature value (8.084 Å) than the purchased standard sample

TABLE V Resistance values and sample loadings for materials in the series $Ni_xCo_{1-x}O_4$, prepared by co-precipitation into NaOH and fired at 375°C

X	Conductance (S) at 25°C	Sample loading (mg/cm^2)
0	2.35×10^{-4}	4.21
0.1	2.97×10^{-4}	3.98
0.2	4.08×10^{-4}	4.45
0.33	0.0460	4.02
0.4	0.0195	3.88
0.5	0.0105	3.92
0.67	8.25×10^{-4}	4.31
0.75	5.94×10^{-4}	4.22
0.8	5.12×10^{-4}	3.89
0.9	4.45×10^{-4}	4.08
1.0	3.94×10^{-4}	4.01

TABLE VI Summary of XRD phases for the series $Ni_xCo_{1-x}O_y$ prepared by co-precipitation into NaOH and fired at 375°C

X	Phases present	Cell parameter (Å)
Co_3O_4	Co_3O_4	8.0662
0	Co_3O_4	8.0821
0.1	$NiCo_2O_4$, Co_3O_4 and trace NiO	$NiCo_2O_4 = 8.1187$, $Co_3O_4 = 8.0511$
0.2	$NiCo_2O_4$, and trace Co_3O_4 and NiO	$NiCo_2O_4 = 8.1121$
0.33	$NiCo_2O_4$	$NiCo_2O_4 = 8.1144$
0.4	$NiCo_2O_4$ and NiO	$NiCo_2O_4 = 8.1125$, $NiO = 4.1880$
0.5	$NiCo_2O_4$ and NiO	$NiCo_2O_4 = 8.1125$, $NiO = 4.1895$
0.67	$NiCo_2O_4$ and NiO (approximately equal quantities)	$NiCo_2O_4 = 8.1128$, $NiO = 4.1807$
0.75	$NiCo_2O_4$ and NiO (NiO major constituent)	$NiCo_2O_4 = 8.1167$, $NiO = 4.2011$
0.8	$NiCo_2O_4$ and NiO (NiO in majority)	$NiCo_2O_4 = 8.1215$, $NiO = 4.1926$
0.9	NiO and Co_3O_4	$Co_3O_4 = 8.1031$, $NiO = 4.2025$
1.0	NiO	4.1921
NiO	NiO	4.1792

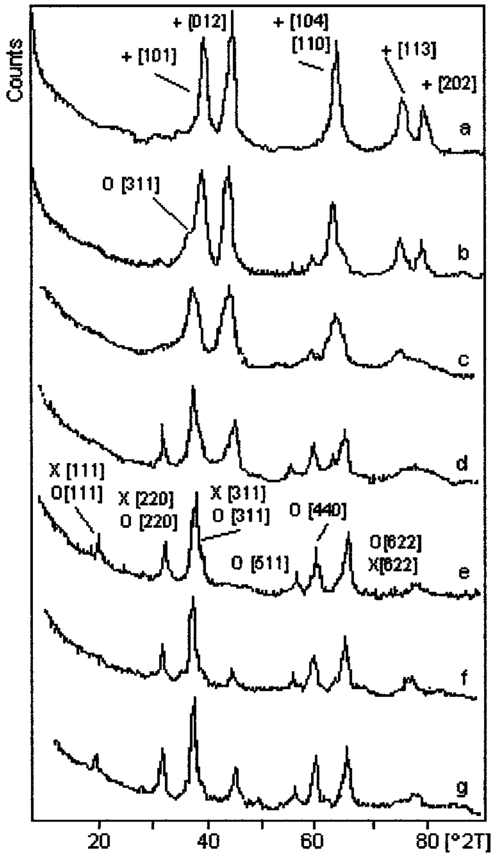

Figure 9 Selected XRD patterns of the series $Ni_xCo_{1-x}O_y$: (a) = 10 wt% Ni, (b) = 20 wt% Ni, (c) = 33 wt% Ni, (d) = 50 wt% Ni, (e) = 67 wt% Ni, (f) = 75 wt% Ni, and (g) = 90 wt% Ni. Common lines labelled on single patterns for clarity.

(8.0662 Å). The lines for the NiO sample were however slightly shifted to higher diffraction angles.

It is interesting to note that, even with the composition of 50 mol% Ni and 50 mol% Co, the lower cobaltite, $NiCoO_2$ observed earlier was absent and therefore the formation of this material is dependant on higher temperatures as opposed to the correct stoichiometry.

As noted previously the occurrence of reports pertaining to the entire range of Ni-Co compositions are rather scant and, more typically, only the cobalt rich end of the system is investigated. Krezhov [31] reported some XRD data for the cobalt rich range and the results are in good agreement with those presented in this paper. Likewise Singh and co-workers [16] analysed the cobalt rich system having used sol-gel as the preparation technique. However, besides the oxides their XRD data showed a mixture of hydroxides which, since these have not be identified by studies using alternative preparative procedures, must have been due to the alkoxides formed during the sol-gel process.

Kovalenko [18] reported the entire composition range and noted that NiO was present in all compositions from $x = 0.33$ ($NiCo_2O_4$). The presence of NiO in the sample that should have been $NiCo_2O_4$ can be explained by the high firing temperature of the materials (500°C). Since the temperature of heat treatment employed was prohibitively high so as to preclude the formation of pure $NiCo_2O_4$ the cell parameter and phase purity details presented can not be accurately relied upon.

De Faria and co-workers [21] studied bulk and surface composition of the entire range of materials prepared by thermal decomposition of the metal nitrates at 400°C. The current XRD results are generally in good agreement although they did not detect NiO below compositions containing 60 mol% Ni, and this was attributed to its smaller particle size. Furthermore the cell parameters of the $NiCo_2O_4$ phase were found to fluctuate, although generally increased, as the nickel rich compositions were considered. However the results in this paper indicate that the cell parameter of $NiCo_2O_4$ increased only very gradually up to a composition of 75 mol% Ni. This may be attributable to the greater degree and intimacy of mixing of the precursors by the current co-precipitation technique and therefore the more complete formation of the spinel phase.

Roginskaya and co-workers [3] presented XRD data pertaining to the entire composition range, again prepared by thermal decomposition of metal nitrates. The presence of γ-NiOOH in the XRD pattern of the pure NiO sample was noted but the cobalt analogue was not found, the absence of Co_3O_4 in the composition of 90 mol% Ni was ascribed to the imbedding of cobalt oxide species in the amorphous NiOOH phase. The NiOOH phase was shown to be present up to a firing temperature of 500°C, beyond which $NiCo_2O_4$ would have been thermally decomposed. The absence of Co_3O_4 for the formulation of 20 mol% Ni was also noted, the formation of only $NiCo_2O_4$ being suggested. NiO was, however, detected by infrared spectroscopy, confirming the deficiency of the thermal decomposition technique in the preparation of pure $NiCo_2O_4$ as discussed above. However, the same gradual increase in the unit cell parameter of $NiCo_2O_4$ was observed with increasing Ni content in the formulation, and the cell parameter of the cubic NiO phase was not observed to change appreciably.

Trunov and co-workers [16] prepared the entire range of compositions by the precipitation of the metal hydroxides, although they favoured the use of ammonia as the precipitating agent. Although many transition metal salts undergo alkaline hydrolysis, if ammonia or an ammonium salt is used, complexation of the form detailed in the discussion above often occurs [44]. This is certainly true of nickel and cobalt salts and was confirmed during the current investigations. No further details of the preparation technique beyond the identity of the precipitation agent were, however, stated and a brief consideration of the XRD patterns indicated similar results to those presented in this communication.

Hu and co-workers [32] reported a series of primarily Ni rich cobaltite systems beyond $NiCo_2O_4$ prepared by the thermal decomposition of the metal nitrates on titanium and fired for very short periods (10 min). At the composition relating to stoichiometric $NiCo_2O_4$ the authors indicated the additional presence of Co_3O_4, whilst NiO appeared on XRD patterns at compositions above 40 mol% Ni. At higher nickel contents NiO became the majority phase and very little $NiCo_2O_4$ appeared to form above 70 mol% Ni, no details of cell parameters were given. The lower degree of $NiCo_2O_4$ formation and the narrower composition range in which this phase was evident, further indicates the deficiency in precursor mixing, and may have been exacerbated further by the short firing time.

It is clear, therefore, that the spinel $NiCo_2O_4$ forms preferentially to the individual metal oxides at compositions outside of the stoichiometry for $NiCo_2O_4$. For such mixtures the excess of either metal will form the oxide of that metal in addition to $NiCo_2O_4$, and with the absence of NiCo solid solutions.

The conductance of the films supports the supposition that, $NiCo_2O_4$ being the most conducting constituent identified by XRD, the electronic conductance of the films should increase as more $NiCo_2O_4$ was formed. Indeed conductance increased from the value of Co_3O_4, this being a semiconductor having low conductivity due to the inverse spinel structure and the subsequently low concentration of conducting chains. The maximum conductance was then obtained for the stoichiometric composition giving rise to $NiCo_2O_4$ and then decreased as the composition became richer in Ni. The decrease in conductance with added Ni was, initially, gradual as $NiCo_2O_4$ remained the majority constituent but decreased abruptly as NiO, again a semiconductor of low conductivity which relies on oxygen deficiency for conduction, became the majority constituent. The variance in the sample loading again had little effect on the conductance values and this is plotted in Fig. 10.

Trunov [16] measured the conductance of pressed pellets of the oxides formed in the series detailed above, although no figures are quoted. It is, however, stated that the highest conductance corresponded to the composition range between x values of 0.2 and 0.4. This is extended to include $x = 0.5$ in the present study and is probably attributable to the method of preparation.

It is realised that changes in the morphology of the films, and the subsequent differences in inter-granular contacts, cause changes in the electrical conductance of the materials. However it is considered that such pronounced changes and of such magnitudes can not be due entirely to these factors. Moreover the trend of conductance with varying composition within this system relates well to the established values for these oxides, that is to say $NiCo_2O_4$ being more conducting than the individual oxides NiO and Co_3O_4.

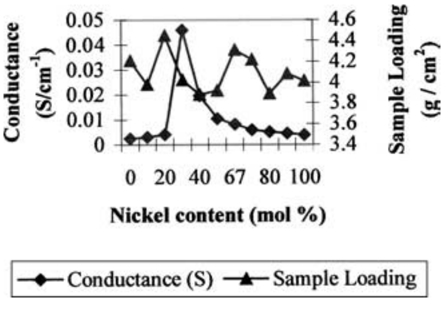

Figure 10 Conductance and sample loading of the series $Ni_xCo_{1-x}O_y$.

4. Conclusions

The investigations of the firing temperature show that, for the thermal decomposition of the metal nitrates, the $NiCo_2O_4$ phase with the exclusion of the individual oxides of nickel and cobalt is only formed within a narrow range of firing temperatures. Below 350°C the nitrates are not fully decomposed and the solid state reaction to form $NiCo_2O_4$ is, therefore, incomplete. Above 400°C the spinel decomposes with the loss of NiO, the unit cell parameter of which remained fairly constant and suggested that solid solutions of the form $NiO{-}Co_xO_y$ were not formed.

The abrupt and significant changes in conductance, and moreover the strong correlation with the formation and decomposition of the spinel $NiCo_2O_4$ phase, show that the maximisation of the electrical conductivity of these materials is entirely dependant on the formation of the spinel.

The decrease in conductance as the firing temperature was increased from 450°C was therefore due to the loss of NiO from the $NiCo_2O_4$ bulk. This decrease may then be due to either the formation of a less conducting NiO surface layer or the loss of nickel species from the bulk material. The introduction of a less conducting material on the surface must cause a decrease in conductance. However, the surface coverage of NiO at 400°C is likely to be low, whereas the conductance of the material decreased by approximately 22%, and, therefore, the loss of nickel species from the bulk had the more profound effect. This supports the conductance model of electron hopping of octahedrally coordinated nickel species and, therefore, the cationic distribution $(Co_{1-x}{}^{2+}\ Co_x^{3+})_{tet}[Ni_{1-y}^{2+}Ni_y^{3+}Co^{3+}]_{oct}O_4$. The loss of electrochemical activity for $NiCo_2O_4$ fired in excess of 400°C may be attributable to three factors, namely; the lower conductance of the material, the coverage of the surface with NiO and the lower surface area of the NiO surface layer.

The firing temperature of 375°C maintained for a period of 2 h is therefore suggested for the formation of $NiCo_2O_4$ from thermally decomposed metal nitrates.

Of the preparation techniques investigated, spray pyrolysis, co-precipitation of the metal nitrates into NaOH and freeze drying formed the most pure $NiCo_2O_4$, with the exclusion of the individual metal oxides. The alternative co-precipitation techniques and the thermal decomposition of the metal nitrates formed impure $NiCo_2O_4$ and the importance of obtaining a high degree of mixing of the precursors and maintaining this during firing is therefore highlighted.

Whilst the conductance of the thermally decomposed nitrates was high, the surface area was low due to the large crystallites formed due to the spreading of the materials as they melted. Of the other techniques the attainment of high conductance was dependant on the formation of the $NiCo_2O_4$ phase, with higher values being obtained for the techniques yielding higher surface area and smaller crystallites. High electrical conductance is, therefore, primarily due to the degree to which $NiCo_2O_4$ is formed, the nature of the morphology having a less pronounced effect.

Whilst the firing temperature of 375°C was adequate for the complete formation of $NiCo_2O_4$, this may be reduced for the co-precipitation technique for which the thermal decomposition of the metal hydroxides is considered.

The selection of preparation technique depends on the required use of the powder and therefore the nature of its format. Whilst the cryochemical technique provides for high surface area $NiCo_2O_4$ having high electrical conductance and small crystallites, the subsequent formation of films on a support material can only be made with the addition of a binder material. The precipitation of metal hydroxides, which may then be coated to a support medium before decomposition would, therefore, become the favoured technique. Nevertheless the thermal decomposition of the metal nitrates provides for a very simple means of attaining well adhered films, although electrochemical performance would consequently be lower due to the low surface area.

For the application to lithium-ion batteries the cryochemical and precipitation techniques would be particularly suitable since the use of binding agents are routinely included during the formation of large area films.

The details of the phases present with changing composition show that, as is stated in the literature cited, the spinel $NiCo_2O_4$ phase may be obtained outside the stoichiometric composition. Furthermore these results highlight the relationship between the purity of the $NiCo_2O_4$ and the preparation technique employed. Through using the co-precipitation technique, which derives better mixing of the nickel and cobalt species before firing and considerably lower particle sizes, the range of compositions in which $NiCo_2O_4$ is produced has been extended considerably. It follows that the technique of freeze drying may also derive these benefits due to the low particle size and the intimacy of mixing obtained. The additional consideration of conductance shows that the attainment of high electrical conductivity depends on the purity of the $NiCo_2O_4$ phase and that higher conductance than the individual oxides can be obtained outside the stoichiometric composition.

This is of particular importance to the application to lithium-ion battery technology, in which the attainment of high conductivity of the cathode materials is of fundamental importance. These compositions, which are nickel rich, maintain a high conductivity due to the inclusion of $NiCo_2O_4$ in the mixed oxide phases. This, therefore, allows for the inclusion of large proportions of Ni into the Co_3O_4 host material without the necessity for the inclusion of increased conducting additive over the pure Co_3O_4 system. Electrochemical performance would not be compromised through the reduction of the amount of active material.

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