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Room-temperature synthesis of monodisperse mixed spinel $(Co_xMn_{1-x})_3O_4$ powder by a coprecipitation method

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Spinel oxide Co_3O_4 has traditionally been synthesized by thermal decomposition of cobaltous salts at temperatures of 250–900 °C under oxidizing conditions. Here, we report a solution synthesis route that yields mixed spinel oxide $(Co_xMn_{1-x})_3O_4$ at room temperature in air. $(Co_{0.75}Mn_{0.25})_3O_4$ solid solutions were synthesized by coprecipitation and oxidation of $Co(OH)_2$ and $Mn(OH)_2$ from mixed aqueous solutions of Co- and Mn-salts. The spinel oxide phase was stabilized by crystallization of Mn_3O_4 resulting from the oxidation of $Mn(OH)_2$ in the mother liquor. While undoped Mn_3O_4 is tetragonal, the $(Co_{0.75}Mn_{0.25})_3O_4$ solid solution has a cubic symmetry due to the reduced Mn^{3+} concentration. The resulting powder is spherical with an average particle diameter of *ca.* 0.1 μm and a narrow size distribution. Transmission electron microscopy (TEM) showed that individual particles are nearly single crystalline but consist of a mosaic of multiple nanocrystallites. This observation supports an aggregation mechanism of formation for the nearly monodispersed particles.

Introduction

Co_3O_4 has extensively been investigated as an electrocatalyst for both O_2[1–4] and Cl_2 evolution.[5] Although it has the drawback of lower long-term stability compared to recently developed RuO_2 catalysts,[6] Co_3O_4 has the advantage of lower cost while retaining adequate performance. This spinel compound is also receiving wide attention as a promising electrochromic material.[7] There are numerous reported procedures for the preparation of Co_3O_4, all essentially based on the thermal decomposition of cobaltous salts at temperatures varying between 250 and 900 °C under oxidizing conditions as reviewed by Sugimoto and Matijevic.[8] High temperature firing typically results in oxides with surface area of only a few square meters per gram.[9] Because oxides are used in finely divided form, electrocatalytic properties often depend strongly on morphological as well as electronic factors. Therefore, particles of uniform shape with a large surface area and a narrow size distribution are generally required.[10]

Efforts have previously been made to synthesize fine Co_3O_4 powder at low temperatures by solution methods. Sugimoto and Matijevic[8] obtained Co_3O_4 particles of cubic shape with uniform edge length (*ca.* 0.1 μm) by heating cobalt acetate solution at 100 °C in the presence of O_2 gas. Recently, Furlanetto and Formaro[10] reported that mixtures of Co_3O_4 and CoOOH can be obtained by mixing $Na_3Co(NO_2)_6$ solution with NH_4NO_3 solution while purging with N_2 gas. Upon heating at 70–100 °C, they observed that CoOOH transformed to Co_3O_4, resulting in spherical particles with diameter of 0.2–0.3 μm.

The present work describes a novel room-temperature coprecipitation synthesis method which yields mixed spinel $(Co_xMn_{1-x})_3O_4$. This composition is of interest for several reasons. Like the endmembers Co_3O_4[1–5] and Mn_3O_4,[11,12] $(Co_xMn_{1-x})_3O_4$ solid solutions can be applied as catalysts for oxygen reduction,[13] and considered to be amongst the mixed-spinel candidates for active catalysts.[4,14–18] Like Co_3O_4, Mn_3O_4 can easily be obtained by thermal decomposition of manganous salts.[19] However, this compound can also be prepared by the so-called 'autoxidation' of $Mn(OH)_2$ in alkaline aqueous solution. It is known that mixtures of MnO_2, Mn_2O_3 or Mn_3O_4 can be obtained by oxidation of $Mn(OH)_2$, depending on many factors such as temperature, pH, nature of ions in the solution, and the rate of air or oxygen flow.[20] We therefore anticipated that under autoxidation conditions where Mn_3O_4 is favored, a predominantly $Co(OH)_2$ material doped with $Mn(OH)_2$ would exhibit enhanced autoxidation of $Co(OH)_2$ to Co_3O_4 spinel. The Mn_3O_4 was expected to act as a stabilizer for Co_3O_4 formation. The direct precipitation of mixed metal spinel oxides has previously been reported for ferrites,[21] including those doped with Co,[22] Mn,[23] and Ni.[24]

Experimental

$Co(NO_3)_2\cdot6H_2O$ (Alfa Aeasar, 99.5%), $Mn(NO_3)_3\cdot6H_2O$ (Aldrich, 98%) and $LiOH\cdot H_2O$ (Alfa Aeasar, 98%) were used for preparing the starting aqueous solutions. A special aspect of our synthesis procedure is the use of LiOH as precipitating reactant rather than previously used reactants such as NH_4OH. The ammonium ion is known to retard the rate of autoxidation of $Mn(OH)_2$,[20] mitigating against use of NH_4OH. Preliminary examinations to determine appropriate autoxidation conditions for Mn_3O_4 were performed with a 0.1 M $Mn(NO_3)_3$ solution at room temperature in ambient air atmosphere. Results from these experiments were used to determine the reaction conditions for obtaining $(Co_{0.75}Mn_{0.25})_3O_4$.

0.1 M aqueous solutions of $Co(NO_3)_2$ and $Mn(NO_3)_3$ in a Co : Mn = 3 : 1 atomic ratio were added dropwise to a LiOH solution that was vigorously stirred and monitored to keep the pH at *ca.* 11. This is near the minimum solubility conditions for both $Co(OH)_2$ and $Mn(OH)_2$.[25] For comparison, the precipitation of Co_3O_4 was also attempted from 0.1 M $Co(NO_3)_2$ solution under the same conditions. In each instance, the precipitate was aged in the mother solution for 12 h at room temperature in air with continuous stirring, followed by rinsing to remove Li^+ and NO_3^- species with distilled water as described in ref. 26. Finally the precipitate was atomized into liquid nitrogen, and the frozen droplets were freeze-dried (VirTis Consol 12LL, Gardiner, NY).

The present synthesis method has also been used to prepare lithium intercalation compounds, in which case LiOH solution is added after the rinsing step and before freeze-drying.[26–29] The effect of residual LiOH on the present materials was also studied, as an extreme case where the precipitating reactant is not completely removed. The powders were characterized by X-ray diffraction (XRD) using a Rigaku diffractometer

(RTP500RC) with Cu-Kα radiation and by transmission electron microscopy (TEM) using a JEOL-200CX instrument.

Results and discussion

The XRD pattern of the oxide precipitated from $Mn(NO_3)_3$ solution is shown in Fig. 1. Mn_3O_4 appears as the predominant phase after freeze-drying with no other Mn-containing minor phases being detectable. Miller indices (*hkl*) are indexed for the tetragonal phase (space group $I4_1/amd$) in Fig. 1. Lattice parameters calculated from the XRD data using Cohen's least squares method[30] are: $a = 5.764$ Å, $c = 9.452$ Å. These values agree well with the data in JCPDS (#24-734).[31] The tetragonal symmetry of Mn_3O_4 spinel is known to result from the cooperative Jahn–Teller distortion of Mn^{3+} ions in octahedral sites.[32] According to ref. 32, the c/a ratio decreases from 1.64 to 1.50 (equivalently from 1.157 to 1.054 in space group $F4_1/ddm$) when Mn_3O_4 is lithiated to $LiMn_3O_4$, indicating that the degree of tetragonal symmetry decreases when lithiation reduces Mn^{3+} to Mn^{2+}. Since the Mn_3O_4 obtained in this study has a c/a ratio of 1.64, it appears to be largely unlithiated after freeze-drying. This is consistent with TEM results on $LiCoO_2$ produced by the same method,[26] where the LiOH remains as a separate amorphous phase after freeze-drying. One can notice from Fig. 1 that Li_2CO_3 exists as a minor phase. This is due to minor reaction of residual LiOH with CO_2 to form the carbonate phase during sample handling; LiOH is a well-known CO_2 absorbent.[33] However, the residual lithium salts LiOH or Li_2CO_3 are easily removed from the present powder by washing as they are water soluble.

Having confirmed that Mn_3O_4 is obtained under the present precipitation and autoxidation conditions, we employed the same experimental conditions to synthesize $(Co_{0.75}Mn_{0.25})_3O_4$. Fig. 2 shows the XRD pattern of powder obtained by co-precipitation and autoxidation of $Co(OH)_2$ and $Mn(OH)_2$ from their mixed nitrate solution. The diffraction peaks match very well with the XRD patterns of either Co_3O_4 or $MnCo_2O_4$ as reported in JCPDS (#43-1003 and #23-1237).[34,35] Considering the fact that $MnCo_2O_4$ in ref. 35 was synthesized by heating Co- and Mn-nitrate precursors at 760 °C, one can conclude that the present oxide obtained at room temperature is nearly as well crystallized as high temperature fired materials. The slight peak broadening in Fig. 1 and 2 is consistent with fine crystallite size, as discussed later. Note that $(Co_{0.75}Mn_{0.25})_3O_4$ has a cubic symmetry (space group $Fd\bar{3}m$), indicating that the concentration of Mn^{3+} is lower than the critical concentration for the cooperative Jahn–Teller distortion to a tetragonal symmetry.

The formation of Co_3O_4 spinel was not observed in precipitation experiments with $Co(NO_3)_2$ solution alone under the same conditions. As shown in Fig. 3, $Co(OH)_2$ appears as the major phase (space group $P3m1$), and CoOOH as a minor phase (space group $R\bar{3}m$). It is thus clear that when $Co(OH)_2$ is coprecipitated with $Mn(OH)_2$, the spinel phase is stabilized by Mn_3O_4 resulting from the autoxidation of $Mn(OH)_2$.

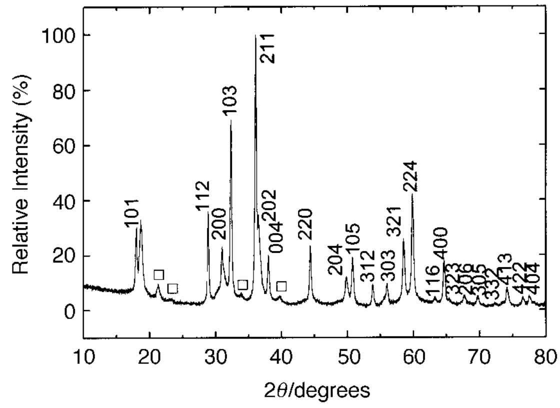

Fig. 1 Powder XRD pattern of Mn_3O_4 (with *hkl* in $I4_1/amd$) obtained by precipitation from $Mn(NO_3)_3$ solution mixed with LiOH solution (□: Li_2CO_3).

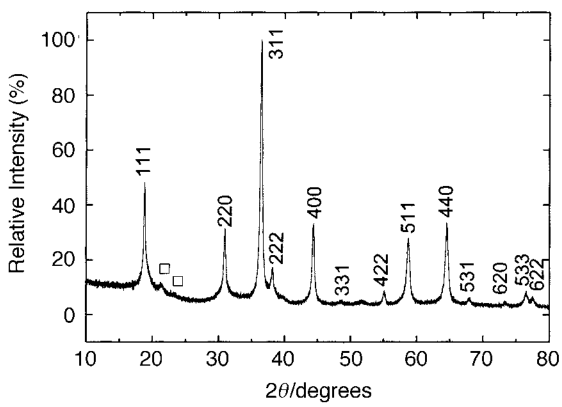

Fig. 2 Powder XRD pattern of $(Co_{0.75}Mn_{0.25})_3O_4$ (with *hkl* in $Fd\bar{3}m$) obtained by coprecipitation from $Co(NO_3)_2$ and $Mn(NO_3)_3$ solution mixed with LiOH solution (□: Li_2CO_3).

Miller indices (*hkl*) are indexed in Fig. 2 for the cubic mixed-spinel phase. The lattice parameter calculated from the XRD data is $a = 8.168$ Å, inbetween that of Co_3O_4 (8.084 Å)[34] and $MnCo_2O_4$ (8.226 Å),[35] as is expected from its intermediate Mn concentration. Fig. 4 shows that the variation in cubic spinel lattice parameter is approximately linear (Vegard's law) with Mn concentration, increasing upon substituting the larger Mn ions for Co ions.[36]

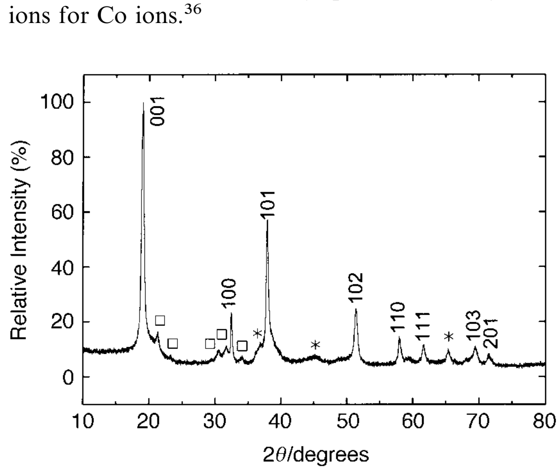

Fig. 3 Powder XRD pattern of $Co(OH)_2$ (with *hkl* in $P3m1$) obtained by precipitation from $Co(NO_3)_2$ mixed with LiOH solution (□: Li_2CO_3; *: CoOOH).

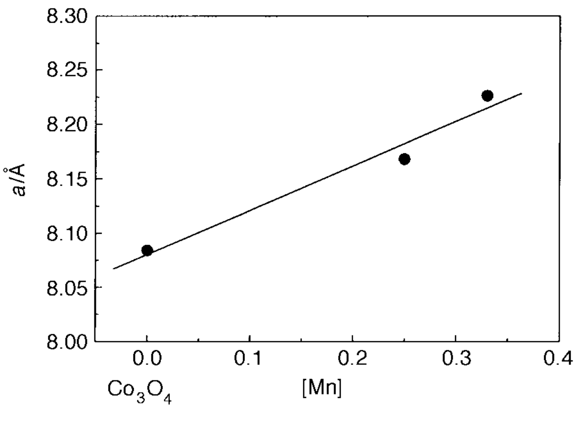

Fig. 4 Lattice parameter of $(Co_{0.75}Mn_{0.25})_3O_4$ in comparison with Co_3O_4[34] and $MnCo_2O_4$.[35]

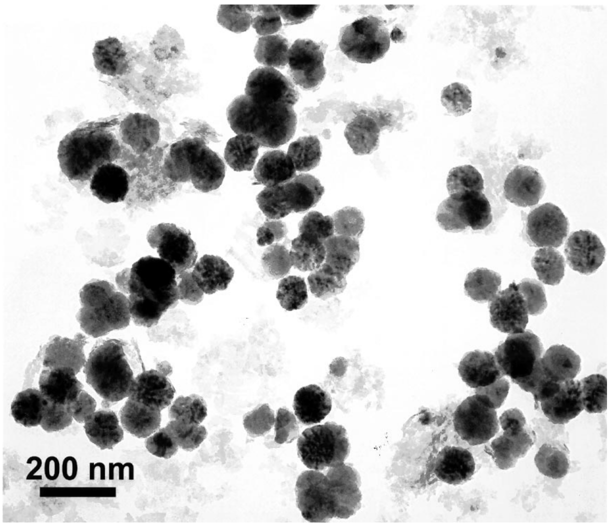

Fig. 5 TEM micrograph of $(Co_{0.75}Mn_{0.25})_3O_4$ particles obtained by coprecipitation from $Co(NO_3)_2$ and $Mn(NO_3)_3$ solution mixed with LiOH solution.

Fig. 5 shows a TEM bright-field image of the $(Co_{0.75}Mn_{0.25})_3O_4$ obtained in this study. Spherical particles of *ca.* 0.1 μm with a narrow particle size distribution are observed. The uniform particle size obtained in this study is noteworthy because it has generally been believed that it is difficult, if not impossible, to obtain monodispersed metal (hydrous) oxide colloids by the reaction of a strong base with a metal salt solution.[37] The much smaller particle size that we obtained compared to that of the Co_3O_4 of ref. 10 (0.2–0.3 μm) is probably due to our lower synthesis temperature (25 °C *vs.* 70–100 °C). The Li_2CO_3 and LiOH phases resulting from LiOH added after the rinsing step and before freeze-drying are seen surrounding the spherical particles. However, without addition of LiOH after rinsing, those lithium-containing phases were rarely observed with TEM.

In order to explain the formation of precipitates with uniform size, the LaMer model,[38,39] based on a short single burst of nucleation followed by uniform growth has been previously used. However, more recently, an aggregation mechanism in which each particle forms a large number of smaller subunits has been proposed by Matijevic, as reviewed in refs. 37 and 40. In order to address this matter, we have conducted direct observations with higher resolution of a single particle using TEM. Fig. 6 shows a bright field TEM image of a single oxide particle and corresponding selected area diffraction pattern. We observe diffraction contrast variations within each particle showing clearly that each particle is composed of much smaller nanocrystallites. However, sharp crystalline diffraction spots are observed in the selected area diffraction pattern in Fig. 6, indicating that each particle is overall single-crystalline. It appears that the nanocrystallites have aggregated to form a particle in which the crystallites are sufficiently misoriented with respect to one another to provide diffraction contrast, yet are well aligned enough to yield sharp reflections in the selected area diffraction pattern (mosaic structure). These results strongly support the aggregation mechanism for the present system.

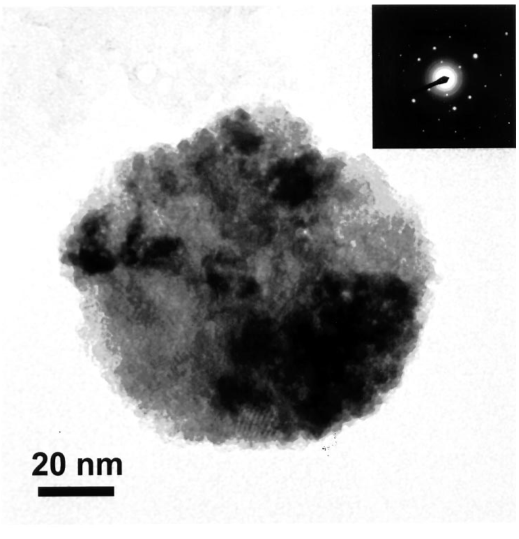

Fig. 6 Bright field TEM image and corresponding selected area diffraction pattern of a $(Co_{0.75}Mn_{0.25})_3O_4$ particle obtained by coprecipitation from $Co(NO_3)_2$ and $Mn(NO_3)_3$ solution mixed with LiOH solution.

Conclusion

A cobalt-rich mixed spinel oxide $(Co_{0.75}Mn_{0.25})_3O_4$ has been synthesized at room temperature by the coprecipitation of Mn and Co hydroxides from mixed nitrate solutions. Mn_3O_4 resulting from the autoxidation of $Mn(OH)_2$ stabilizes the mixed spinel phase under conditions where the undoped Co precursor produces $Co(OH)_2$. The resulting particles are nearly single-crystalline spheres (diameter *ca.* 0.1 μm), and have a narrow size distribution. Each particle is composed of nanometer-scale crystallites, supporting an aggregation mechanism of particle formation. This new route is simple and cost-effective, and is suitable for the synthesis of chemically homogeneous mixed cobalt spinel oxides of high surface area and uniform particle size distribution for such applications as catalysis and electrochromic materials.

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