Original Paper

Synthesis of Binary Component Metal Oxide Nanoparticles by Flame Spray Pyrolysis

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Abstract

Two component metal oxide nanoparticles such as lithium cobalt oxides (LiCoO₂), indium tin oxides (ITO) were synthesized from aqueous aerosol precursors by the flame spray pyrolysis. A high enough flame temperature was used for the complete thermal decomposition of the aerosol precursor. Molar concentration of the aqueous precursor solution, and the flow rate of combustion gas such as hydrogen are varied to control particle size, size distribution and crystal structure. Crystalline LiCoO₂ and ITO nanoparticles with the average particle diameter ranging from 11 to 35 nm and from 11 to 20 nm were synthesized, respectively.

Key words: Synthesis, Binary component, Metal oxide, Nanoparticles, Flame spray pyrolysis

Introduction

Nanoparticles are attracting increasing attention with the growth of interest in nano- technological disciplines. The dimensions of these particles make them ideal candidates for the nanoengineering of surfaces and the fabrication of functional nanostructures that are useful in optoelectronics, chemical and biosensors, drug delivery, and catalysis, etc^{1,2}.

Lithium cobalt oxide, LiCoO₂, has been considered one of the most suitable cathode materials in Li-ion secondary batteries³. The performance of the cathodes is affected by a number of factors such as particle size and crystalline phase. Smaller particle size distribution resulted in a better cycle stability⁴. This enhanced reactivity of the cathodes may be attributed to high specific surface area of nanoparticles smaller than 100 nm in diameter, resulting in higher activity as a catalyst and greater sensitivity as a sensor. The improvements in capacity and rechargeability still require development of a new process to synthesize LiCoO₂ nanoparticles with suitable characteristics.

Indium-Tin Oxide (ITO) is a wide bandgap material exhibiting high transmission in the visible and near-infrared region of spectrum. Further-

more, ITO is an n-type, highly degenerate semiconductor that has relatively low electrical resistivity. Due to these properties, ITO is used for wide range of optoelectronic applications and ITO films are becoming increasingly important in the production of electronic devices⁵. These films may also be prepared by dispersing ITO nanoparticles with desirable optical properties in a polymer binder.

Flame spray pyrolysis (FSP), a flame-assisted liquid droplet-to-particle conversion process, has been of interest to produce single and multi component nanoparticles with an advantage of starting with solution of precursors^{6–9}. A few studies have been reported on the synthesis of multi-component metal oxide nanoparticles by the FSP.

Given its characteristics and potential demonstrated by previous researchers, the FSP can be adopted to synthesize the binary metal oxide nanoparticles such as LiCoO₂ and ITO which is useful material for the cathode of rechargeable batteries and conductive coating, respectively.

In the present study, our goal was to generate crystalline metal oxide nanoparticles such as LiCoO₂ and ITO from aqueous precursor solution by the FSP. We examined the effects of precursor concentration on the particle properties, and also the effects of the flame temperature by varying flow rates of combustible gases such as hydrogen,

oxygen, or air.

Experimental

A schematic of the experimental apparatus for the preparation of metal oxide nanoparticles is shown in Fig. 1. The experimental apparatus consists of an ultrasonic atomizer for aerosol precursor, a diffusion flame burner, and a particle collector. The diffusion flame burner (36 mm in outer diameter and 300 mm in length) was designed that flame could form from the combustion of Ar+precursor, Ar, H₂, O₂, and air, separately introduced through five concentric stainless tubes. The aqueous precursor solution of the metal acetates was first atomized with an ultrasonic vibrator (1.7 MHz), and the atomized droplets of liquid precursor were subsequently carried into the central tube of the burner by flowing dry Ar gas. H₂ was used as a fuel while O₂ and air were used as oxidants. The temperature profile was obtained by moving the thermocouple in both axial and radial directions in the absence of precursor at the fixed gas flow rate (Ar(center): 2, Ar(2nd): 1, H₂(3rd): 6, O₂(4th): 6, air(5th): 15 l/min) (Fig. 2). The nanoparticles generated by the FSP were collected on the surface of a cold glass tube. The particles in the hot stream from the flame were deposited on the cold surface by thermophoresis.

The particle morphology and size were charac-

Fig. 1 A schematic of experimental apparatus for the synthesis of nanoparticles.

Fig. 2 Radial temperature profiles of the diffusion flame along the axial direction.

terized by a TEM (Philips Model CM12). The specific surface area of the particles was measured by nitrogen adsorption at -196°C using a BET (Micrometrics Model ASAP 2400). An X-ray diffractometer (Rigaku Co. Model RTP 300 RC) was used to obtain the X-ray diffraction patterns of the synthesized particles. The resistance of the ITO film was measured by a standard four-probe technique. A spectrophotometer (Minolta Model CM3500D) was used to measure the transparency of the ITO film.

Results and discussion

LiCoO₂ nanoparticles

The effect of precursor concentration on crystal structure and average particle size was investigated by varying molar concentration in the aqueous solution at the condition of Fig. 2. As precursor molar concentration increased from 0.5 to 1.4 mol/l at a fixed molar ratio 1.0 of Li to Co, average diameter increased from 11 to 28 nm while keeping their shape nearly spherical (Fig. 3). Fig. 4 shows the specific surface area with respect to the precursor feed rate. As the precursor feed rate into the flame increased from 1.08×10^{-4} to 3.3×10^{-4} mol/min, the specific surface area decreased from 101 to 60 m²/g, and in turn, average primary particle diameter calculated from the surface increased from 12 to 20 nm. The discrepancy might be attributed to the assumption in the BET analysis that the particles are smooth, uniform spheres. Figure 5 shows XRD patterns of all the particles corresponded to those of LiCoO₂, and the peak intensities increased with an increase in the precursor concentration mainly due to the growth of particle size.

The flow rates of combustible gases affect the

Fig. 3 TEM images of LiCoO_2 nanoparticles produced at precursor molar concentrations in the solution: (a) 0.5 mol/l and (b) 1.4 mol/l.

Fig. 4 Specific surface area and BET- equivalent particle diameter of LiCoO_2 with respect to the precursor feed rate.

flame temperature profile that plays a very important role in the determination of the particle size and crystal structure during the FSP.

The effects of the hydrogen gas flow rate on the particle size were investigated by varying the flow rate from 4 to 8 l/min. As the hydrogen flow rate increased, the maximum flame temperature increased from 1450°C up to over 1700°C. Higher flame temperature led to an increase in the average particle diameter from 16 to 35 nm, exhibiting coagulation and coalescence played a dominant role in the particle growth. The XRD pattern of the nanoparticles especially at H_2 flow rate of 8 l/min appeared to be nearly the same as that of a commercial sample powder of 6 μm in diameter (Fig. 6).

The oxygen flow rate was varied from 2 to 6 l/min with the molar precursor concentration in the solution of 1.0 mol/l. The increase in the oxygen flow rate also caused the flame temperature to rise.

Fig. 5 X-ray diffraction patterns of the particles produced at different precursor concentrations.

Fig. 6 X-ray diffraction patterns of the particles produced at different hydrogen gas flow rate.

The maximum flame temperature increased from 1420 to 1610°C to result in an increase in the average particle diameter from 11 to 18 nm, similar to the effect of the hydrogen flow rate on the particle size. Finally, the total gas flow rate was varied by controlling the air flow rate through the outermost tube of the burner holding the other gas flows at constant rates as given in Table 1 and the precursor feed rate at 1.08×10^{-4} mol/min. As the total gas flow rate decreased from 34.5 to 24.5 l/min, the maximum flame temperature increased from 1330 to 1680°C probably due to less convection energy loss to the air flowing around the outermost region of the flame. The reduced gas flow rate also led to the increase in precursor concentration in the flame. As a result, the average particle diameter increased from 13 to 28 nm, which is due to higher precursor concentration and coagulation rate with an additional effect of longer residence time in the flame.

Fig. 7 TEM micrographs of ITO nanoparticles (0.2 mol/l of precursor concentrations).

ITO nanoparticles

As the initial concentrations of In and Sn in the precursor solution increased from 0.05 to 0.2 M while the molar ratios of Sn/In was fixed at $1/9$, average particle diameter of ITO powder by the TEM analysis increased from 8 to 15 nm (Fig. 7). Fig. 8 shows the average particle diameter and the specific surface area obtained from TEM and BET analysis, respectively, with respect to the precursor feed rate. As the precursor feed rate into the flame increased from 2.5×10^{-5} to $1.0 \times 10^{-4} \text{ mol/min}$, the specific surface area decreased from 105 to $63 \text{ m}^2/\text{g}$. Crystal structures of the nanoparticles produced at different precursor concentrations showed nearly similar peak patterns corresponding to those of ITO (Fig. 9).

As the maximum flame temperature increased by increasing H_2 flow rates from 4 to 6 l/min , average particle diameter increased from 10 to 15 nm . O_2 flow rates were increased from 4 to 8 l/min to control flame temperature and oxidation rate, and then average particle diameter decreased from 13 to 11 nm .

In order to characterize the properties of ITO nanoparticles, the effect of average particle diameter on the transparency and the surface resistance of conductive films prepared with ITO nanoparticles were investigated. As the average particle diameter increased from 8 nm to 15 nm , the transparency and the surface resistance of conductive films decreased from 92 to 83% at the wavelength of 600 nm , and from 2×10^4 to $0.85 \times 10^4 \Omega/\square$, respectively. The transparency of the ITO film was

Fig. 8 Average particle diameter and specific surface area at the different precursor feed rate.

Fig. 9 X-ray diffraction patterns of the synthesized ITO nanoparticles.

quite acceptable but the higher conductivity was required for the industrial application.

Conclusion

The crystalline binary metal oxide nanoparticles such as LiCoO_2 and ITO were synthesized by the flame spray pyrolysis from the aqueous solution, respectively. Higher flame temperature profile obtained by controlling the gas flow rates caused the primary particle size to increase due to higher collision and coalescence in all the cases. In addition, it was also possible to increase the particle size by raising the molar concentration of the precursor in the aqueous solution while keeping the gas flow rates constant. The properties of nanoparticles such as particle size and crystalline phase can be controlled by the gas flow rates and precursor concentration. In the present study, crystalline LiCoO_2 nanoparticles with the average primary particle diameter ranging from 11 to

35 nm were synthesized. Crystalline ITO nanoparticles were also synthesized, and their average primary particle diameters ranged from 11 to 20 nm through the experiments

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