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Low-temperature preparation of ultrafine $LiCoO_2$ powders by the sol–gel method

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Ultrafine $LiCoO_2$ powders were prepared at lower temperatures by the sol–gel method using maleic acid as a chelating agent. The conditions of the sol formation from an aqueous solution of metal nitrates containing maleic acid, and the crystallization behaviour during the thermal decomposition of the gel precursors, were examined. The effect of the molar ratio of maleic acid to total metal ions, as well as the calcination temperature, on the physicochemical properties of the $LiCoO_2$ powders was also investigated. It was found that polycrystalline low- and high-temperature (LT- and HT-) $LiCoO_2$ powders could be obtained at calcination temperatures of 500 and 600 °C, respectively, with the calcination time of 1 h. They were found to be composed of very uniformly sized ultrafine particulates with an average particle size and a specific surface area of 30 nm and 12.4 $m^2 g^{-1}$ for LT-$LiCoO_2$ and 60 nm and 8.8 $m^2 g^{-1}$ for HT-$LiCoO_2$, respectively.

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1. Introduction

The layered oxides, $LiMO_2$ ($M = Co, Ni, V$), have been extensively studied as potential cathode materials for lithium batteries with high energy density [1–4]. In particular, research on $LiCoO_2$ has been most active on these materials because of not only the simple means of the materials preparation, but also its high potential for application [5]. Much attention also has recently been given to $LiCoO_2$ as the most promising alternative cathode material for molten carbonate fuel cells [6, 7].

The standard high-temperature $LiCoO_2$ powders (HT-$LiCoO_2$) have usually been prepared by the solid-state reaction in which hydroxides or carbonates such as $LiOH \cdot H_2O$, Li_2CO_3, and $CoCO_3$ are calcined at about 850–900 °C for a prolonged period [8, 9]. This method, however, has several disadvantages; inhomogeneity, irregular morphology, larger particle size ranging from 5–10 μm, broader particle-size distribution, higher calcination temperature, and longer calcination time. Recently, it was reported that a new phase of $LiCoO_2$ with modified structure prepared at the reduced temperature of 350 °C (LT-$LiCoO_2$) offered some promise in improving the cycle life of rechargeable lithium cells; and thus, several techniques based on solid-state reaction or spray-drying have been proposed to synthesize LT-$LiCoO_2$ powders with high surface area and low grain-size at low temperatures [10, 11]. However, these methods required a long calcination period ranging from 90 h to a week to form a single-phase product. Moreover, the electrode activity of such powders seemed to be not good enough to achieve a good performance. In Li_xMO_2 application, it is believed that good crystallinity, homogeneity, uniform particle morphology with narrow size distribution, and high surface area are important parameters to achieve a higher electrode activity. Considerable improvements have been made by using a solution method in obtaining high-performance cathode materials [12, 13]. Among the solution methods, a sol–gel method can produce highly homogeneous powders having increased surface area and thus enhanced reactivity of electrode. This simple method also has some advantages, such as good stoichiometric control and the production of active submicrometre-size particles in a relatively shorter processing time at a lower calcination temperature. For applications, the possibility of being able to take advantage of the wide heat-treatment ranges for such materials, is of particular interest. In spite of these advantages, there have been few reports on preparing $LiCoO_2$ powders by the sol–gel method. We have demonstrated that ultrafine HT-$LiCoO_2$ powders with an average particle size of 30–50 nm and a specific surface area of 2.3–17 $m^2 g^{-1}$ could be synthesized successfully at a calcination temperature of 550 °C and

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a calcination time of 1 h by the sol–gel method using polyacrylic acid (PAA) as a chelating agent [14].

In this study, ultrafine HT-$LiCoO_2$ powders with high surface area were prepared at lower temperatures by the sol–gel method using maleic acid, the cost of which is much cheaper than that of polyacrylic acid, as an alternative chelating agent. It was also shown that ultrafine LT-$LiCoO_2$ powders could be successfully prepared by the sol–gel method. Optimal synthetic conditions and the effect of the molar ratio of maleic acid to total metal ions, as well as the calcination temperature, on the physicochemical properties of $LiCoO_2$ powders were investigated.

2. Experimental procedure

$LiCoO_2$ powders were prepared according to the procedure shown in Fig. 1. A stoichiometric amount of lithium and cobalt nitrate (Junsei, EP grade) salts with the cationic ratio of $Li:Co = 1:1$ was dissolved in distilled water and mixed well with an aqueous solution of maleic acid. Maleic acid (Junsei, EP grade) was used as a chelating agent in making a gel. Ammonium hydroxide was slowly added to this solution with a constant stirring until the pH of 4.5–5.5 was achieved. The resultant solution was then evaporated at 70–80 °C with magnetic stirring for a day until a transparent pink sol was formed. As water evaporated further, the sol turned into a viscous transparent pink gel. For the preparation of gel precursors with different molar ratios of maleic acid to total metal ions, the same procedure was repeated with the molar ratio of maleic acid to total metal ions being varied to 0.75, 1, 1.5, and 2.0. The gel precursors obtained were then decomposed at 400 °C for 1 h in air to eliminate organic contents. The decomposed powders, which will be referred as precursor powders, were further heated to 500–700 °C to obtain single-phase polycrystalline $LiCoO_2$ powders.

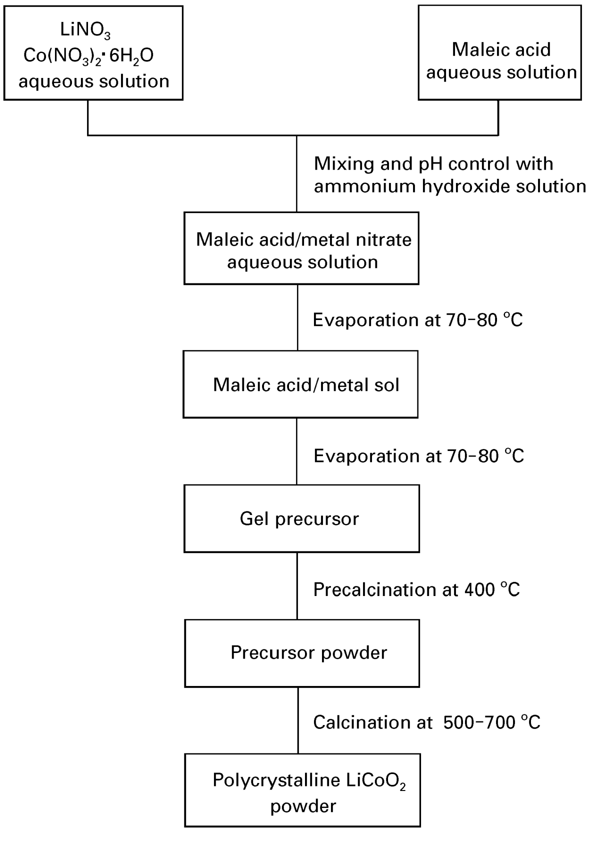

Figure 1 Flowsheet of the procedure for preparing polycrystalline $LiCoO_2$ powders by the sol–gel method.

The thermal decomposition behaviour of the gel precursor was examined by means of thermogravimetry (TG, Perkin–Elmer, TGA7) and differential thermal analysis (DTA, Perkin–Elmer, DTA1700). Powder X-ray diffraction (XRD, Rigaku, Rint-2000) with CuK_α radiation was used to identify the crystalline phase of the material calcined at various temperatures. The specific surface area of the material was determined by the BET method (Quantachrome, Autosorb-1) with nitrogen adsorption. For chemical analysis of the obtained powders, inductively-coupled plasma spectroscopy (ICP, Thermo Jarrel Ash, Poly-Scan61E) was adopted and the particle morphologies of the material were examined by scanning electron microscopy (SEM, Hitachi, S-4100).

3. Results and discussion

Gel formation was possible only within a limited pH range of the initial solution. A pink transparent gel was formed from the solution with the initial pH of 4.5–5.5 at all the ratios of maleic acid to total metal ions tested in this study. When the initial pH of the solution was lower or higher than this range, on the other hand, precipitation occurred during the vaporization of water in the solution. The transparency of the gel is an indication of compositional homogeneity. It is believed that the carboxylic groups on the maleic acid form a chemical bond with the metal ions and these mixtures develop the extremely viscous polymeric resins as the water evaporates. It was reported that the pH of the solution controlled not only the dissociation of carboxylic acid groups but also the formation of metal–acid complexes [15].

Fig. 2 shows TG and DTA of the gel precursors prepared when the molar ratio of maleic acid to total metal ions was 1.5. The weight loss of the gel precursors terminated at 454 °C and three discrete weight-loss regions occurred at 40–215, 215–276 and 276–454 °C. The weight loss in the temperature range 40–215 °C corresponded to the removal of superficial and structural waters in the gel precursor, which was accompanied by the endothermic peaks at 90 and 140 °C in the DTA curve. The weight loss in the temperature range 215–276 °C appeared to be the combustion of maleic acid and nitrate ions, which was indicated as an exothermic peak at 235 °C in the DTA curve. Half of the weight loss occurred during this stage because of a violent oxidation–decomposition reaction. It appeared that maleic acid functioned as a fuel in the pyrolysis of the gel precursors, accelerating the decomposition of nitrate ions. It was reported that chelating agents, such as polyacrylic acid, not only work as a chelating agent but also provides combustion heat for calcination in the synthesis of $LaMnO_3$ powders [16]. Polyvinyl alcohol, originally

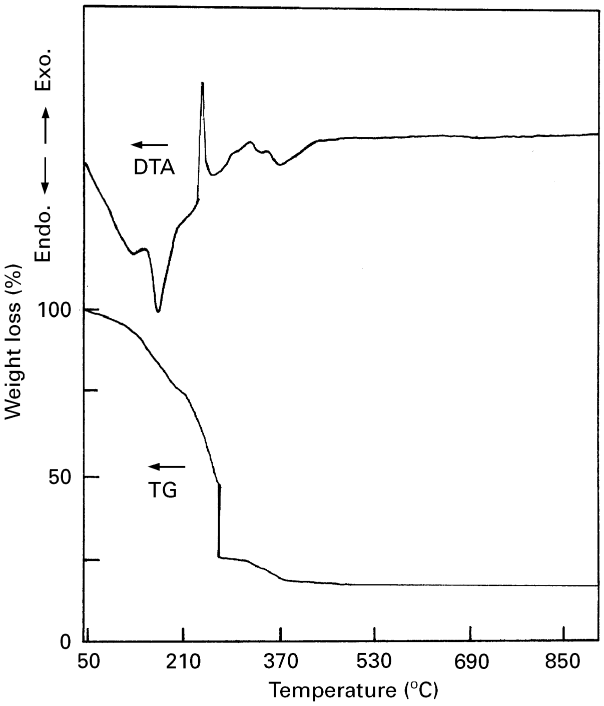

Figure 2 Thermogravimetric and differential thermal analysis of the gel precursors at an air flow rate of 40 cm^3 min^{-1} and a heating rate of 5 °C min^{-1}.

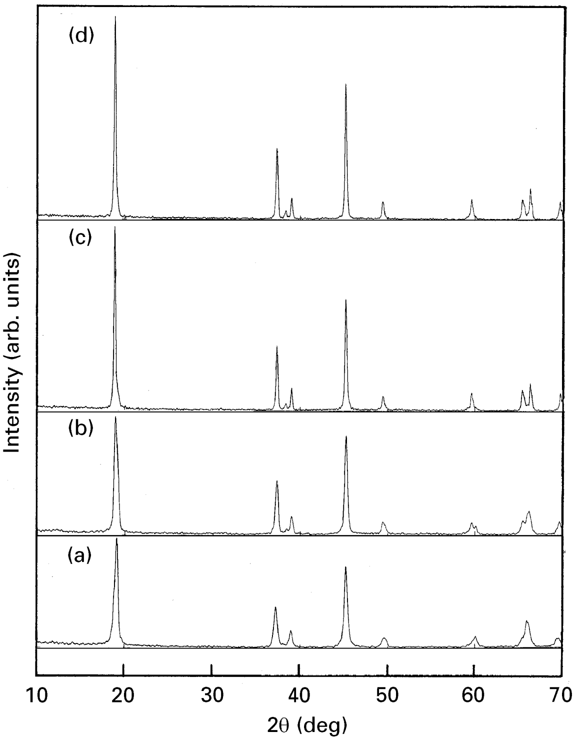

Figure 3 X-ray diffraction patterns of the gel-derived materials calcined at various temperatures: (a) 500 °C, (b) 600 °C, (c) 650 °C, and (d) 700 °C. The molar ratio of maleic acid to total metal ions was 1.5.

used to inhibit segregation and precipitation of the constituent metal ions from the solution during the sol–gel process, also provides heat and reduces the processing temperature for the preparation of fine particles of mixed oxide systems [17]. The gel precursors were self-burning once ignited, because the decomposed nitrate ions acted as an oxidizer [17]. It was observed during the pyrolysis experiment that the gel precursors turned into fluffy dark brown powders after being calcined at this stage. Similar behaviour was previously reported where nitrate decomposition in citrate–nitrate gels took place at around 230 °C together with violent gas evolution, such as NO_x and CO_2 [18]. The weight loss in the temperature range of 276–454 °C corresponded to the decomposition of the remaining organic constituents, which was accompanied by three exothermic peaks (290, 313, 345 °C). While the pyrolysis at this stage was very complicated, it could be presumed that the last endothermic peak at 370 °C in the DTA curve corresponded to the crystallization of the $LiCoO_2$ phase. Such an endothermic peak was also seen at 340 °C during the synthesis of HT-$LiCoO_2$ by the sol–gel method using polyacrylic acid in our previous study [14], and at about 380 °C during the synthesis of perovskite-type manganite by the sol–gel process using polyacrylic acid [19].

Fig. 3 shows the XRD patterns for the gel-derived materials calcined at various temperatures for 1 h in air, where the molar ratio of maleic acid to total metal ions was 1.5. When a material was precalcined at 400 °C, a significant amount of the LT-$LiCoO_2$ phase peaks and a small amount of the impurity peaks were detected (data not shown here). This is quite consistent with the result of DTA which shows the crystallization peak at 370 °C. For the material calcined at 500 °C, the LT-$LiCoO_2$ phase without any impurity was observed (Fig. 3a). A single-phase HT-$LiCoO_2$ formed when the material was calcined at 600 °C (Fig. 3b). It took less than 1 h to attain full crystallinity. As the material was further calcined to 650 and 700 °C, the crystallinity of HT-$LiCoO_2$ powders increased with increasing calcination temperature (Fig. 3c,d). Namely, with an increase in the calcination temperature there is a gradual increase in the peak intensities accompanied by sharpening of the peaks. This might be attributed to the gradual increase in the crystallite sizes with an increase in calcination temperature [17]. Compared with the solid-state reaction method, where the calcination temperature is almost 850–900 °C and the calcination time is longer than 24 h, the sol–gel method requires a much lower calcination temperature and shorter calcination time. This method is also superior to the ultrasonic spray decomposition method [13], where the calcination temperature for HT-$LiCoO_2$ is approximately 900 °C. Because the cross-linked gel may provide a more homogeneous mixing of the cations and less tendency for segregation during calcination, the use of maleic acid as a chelating agent greatly suppresses the formation of precipitates from which the heterogeneity stems. Thereby, the fine mixture state of calcined materials in the homogeneous composition makes it possible to form a single-phase of $LiCoO_2$ under the mild conditions. This may be ascribed to the fact that the materials derived from the gel precursor are of atomic scale and homogeneously mixed with each other, and thus have high sinterability. Also, the heat treatment of the precursor powders at decomposition temperatures and beyond results in the evolution of heat from the combustion of the residual carbonaceous material. This facilitates the reaction between the constituent metal ions and the formation of the oxide phase at a relatively low external calcination temperature [17].

Fig. 4 shows the dependence of the specific surface area of the polycrystalline $LiCoO_2$ powders on the calcination temperature when the molar ratio of maleic acid to total metal ions was 1.5 and the gel was calcined in air for 1 h. The specific surface area of the powders decreases almost linearly with the increasing calcination temperature. The specific surface area of the powders prepared in this study is seen to be quite larger than that of the commercialized product supplied by Cyprus Foote Mineral, which is typically of the order of $0.21\ m^2\,g^{-1}$. For example, the specific surface area of the LT-$LiCoO_2$ powders calcined at 500 °C and of the HT-$LiCoO_2$ powders calcined at 600 °C are 12.4 and $8.8\ m^2\,g^{-1}$, respectively, which are about 59 and 42 times larger than that of the Cyprus Foote Mineral $LiCoO_2$ powders. This result also clearly shows that the lower calcination temperature for the formation of a single-phase $LiCoO_2$ results in the larger surface area. Compared with the specific surface area range of the powders prepared by the sol–gel method using polyacrylic acid in our previous study ($2.3–17\ m^2\,g^{-1}$) [14], it is seen that both the chelating agents produce powders with comparable specific surface areas.

The XRD patterns for the materials calcined at 650 °C for 1 h in air at the various molar ratios of maleic acid to total metal ions are shown in Fig. 5. It was confirmed from the XRD patterns that a polycrystalline HT-$LiCoO_2$ phase could be formed, regardless of the molar ratio of maleic acid to total metal ions tested in this study. The molar ratio of maleic acid to total metal ions of 0.75 was the minimum amount of maleic acid needed to bind all metal ions under the assumption that metal ions replace the hydrogen from –COOH groups in the maleic acid molecule. However, as the molar ratio of maleic acid to total metal ions increased, the crystallinity of the materials was also found to increase. The more maleic acid is used in preparing gel precursors, the more the cross-linked gel precursors suppress cation mobility and the more combustion heat is generated from the maleic acid. It is, therefore, the reduced cation mobility by the cross-linked gel precursor and the evolution of heat from the combustion of the residual carbonaceous material that increase the crystallinity of HT-$LiCoO_2$ with higher amounts of maleic acid used in this process.

Table I summarizes the dependence of the chemical composition of $LiCoO_2$ powders on the calcination temperature when the molar ratio of maleic acid to total metal ions was 1.5. Lithium, cobalt, and carbon contents of the $LiCoO_2$ powders were measured by ICP. For the powders calcined at 400 and 600 °C, carbon residue was detected and the carbon content in the $LiCoO_2$ powders decreased with increasing calcination temperature. Carbon-doped $LiCoO_2$ powders may greatly enhance electronic conductivity. The molar ratio of lithium and cobalt in the $LiCoO_2$ powders

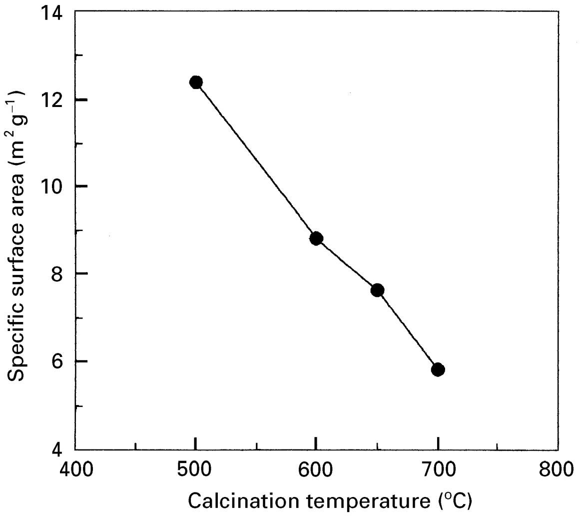

Figure 4 Dependence of the specific surface area of $LiCoO_2$ on the calcination temperature when the molar ratio of maleic acid to total metal ions was 1.5.

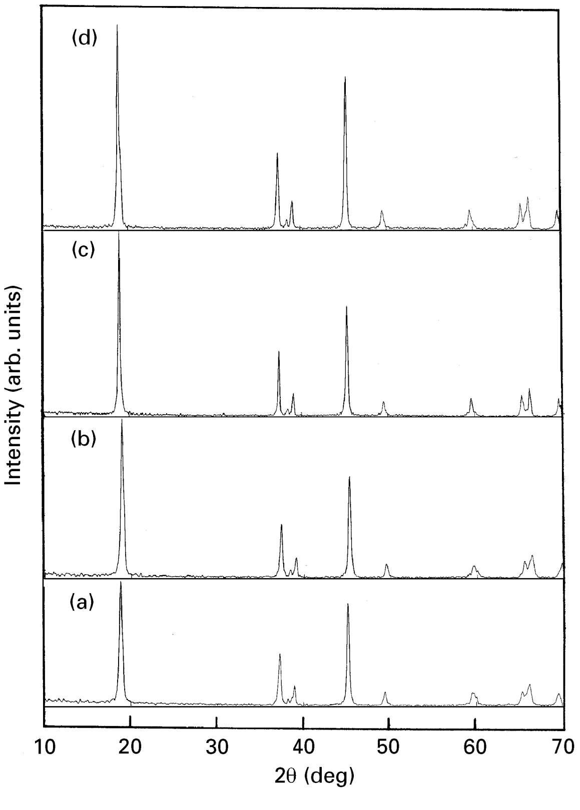

Figure 5 X-ray diffraction patterns of the gel-derived materials calcined at 650 °C at the various molar ratios of maleic acid to total metal ions of (a) 0.75, (b) 1.0, (c) 1.5 and (d) 2.0.

TABLE I Chemical analysis of the $LiCoO_2$ powders calcined at the various temperatures for 1 h in air

Temperature (°C)	Analytical value (wt %)			Approximate chemical composition (carbon)
	Li	Co	C	
400	6.82	56.6	0.83	$Li_{1.02}CoO_{2.01}$ ($C_{0.072}$)
600	7.05	57.8	0.54	$Li_{1.04}CoO_{2.02}$ ($C_{0.046}$)
650	7.21	58.4	–	$Li_{1.05}CoO_{2.03}$
700	7.10	60.0	–	$Li_{1.00}CoO_{2.00}$

calcined at different temperatures was very close to 1 : 1, and it was exactly 1 : 1 at 700 °C. It can be seen from Table I that stoichiometric $LiCoO_2$ powders are easily synthesized by the sol–gel method.

Fig. 6 shows scanning electron micrographs of the powders calcined at the various temperatures for 1 h in air when the molar ratio of maleic acid to total metal ions was 1.5. The LT-$LiCoO_2$ powders calcined at 500 °C are seen to contain monodispersed spherical ultrafine particulates with an average particle size of approximately 30 nm. When the precursor powders were heated at 600 and 700 °C to produce the HT-$LiCoO_2$ phase, it was observed that the particle size of the powders increased to approximately 60 and 100 nm, respectively. The particle sizes prepared using maleic acid are seen to be much smaller than those obtained from Cyprus Foote Mineral (about 3 μm) and to be comparable with those prepared using polyacrylic acid in our previous study (30–50 nm) [14].

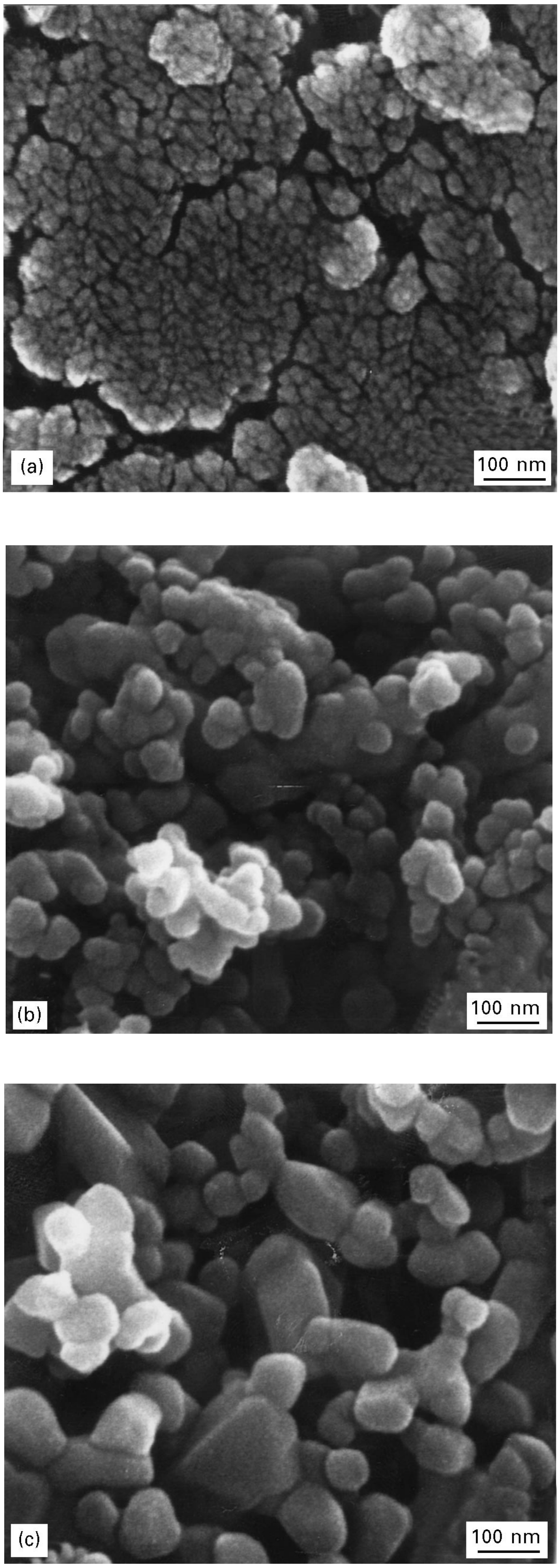

Figure 6 Scanning electron micrographs of the powders calcined at (a) 500 °C, (b) 600 °C and (c) 700 °C.

Compared with the sol–gel method using polyacrylic acid, the present method using maleic acid requires a slightly higher calcination temperature of 30 °C in preparing the $LiCoO_2$ powders with the same specific surface area and the particle size. This may be attributed to the combined effect of the cation mobility difference and the combustion heat difference, caused by the use of the different chelating agents. Actually, the crystallization of the $LiCoO_2$ phase started at 340 °C for polyacrylic acid, but at 370 °C for maleic acid. In spite of the slightly increased calcination temperature, maleic acid may have an advantage from the economic point of view. Because the cost of maleic acid is at least 70% cheaper than polyacrylic acid, the sol–gel method using maleic acid should be amenable to mass-production processes. For the practical application of the material as the cathode of lithium batteries and fuel cells, the powders with ultrafine particles and large specific surface area would be one of the major factors influencing the change in the electrochemical and mechanical properties. Although the physicochemical properties of the $LiCoO_2$ powders prepared in this study seem to be satisfactory, it will be necessary to study further the electrochemical characteristics for practical application.

4. Conclusions

Ultrafine $LiCoO_2$ powders were prepared at lower temperatures, by the sol–gel method which consisted of three steps: formation of transparent sols from the aqueous solution of metal nitrate containing maleic acid as a chelating agent; the formation of the gel precursor from sols; and its decomposition to the oxide powders. Transparent gel precursors could be obtained when the initial pH of the solution was 4.5–5.5 and the molar ratio of maleic acid to total metal ions was 0.75–2.0. During the thermal decomposition of the gel precursors, crystallization started at 370 °C and the polycrystalline LT- and HT-$LiCoO_2$ powders were obtained when the precursor was calcined at 500 and 600 °C for 1 h in air, respectively. It is concluded that the sol–gel method requires much lower calcination temperature and shorter calcination time than the solid-state reaction method. The crystallinity of HT-$LiCoO_2$ powders increased as the calcination temperature and the molar ratio of maleic acid to total metal ions increased. Polycrystalline LT- and HT-$LiCoO_2$ powders were found to be composed of very uniformly sized ultrafine particulates. Their average particle size and specific surface area were, respectively, 30 nm and 12.4 $m^2 g^{-1}$ for LT-$LiCoO_2$, and 60 nm and 8.8 $m^2 g^{-1}$ for HT-$LiCoO_2$. The chemical composition of the $LiCoO_2$ powders was very close to stoichiometry.

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