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Preparation and characterization of nanometric-sized $LiCoO_2$ cathode materials for lithium batteries by a novel sol–gel method

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Abstract

Nanometric-sized $LiCoO_2$ powders were obtained from a novel sol–gel method, in which the gels were synthesized by the polymerization of citric acid and hydroxypropyl cellulose. Molar ratios of citric acid to metal ions were varied, and the resulting effects on the properties of powders were studied using Fourier transfer infrared spectroscopy (FTIR), Raman spectroscopy, X-ray diffraction (XRD), and scanning electron microscopy (SEM). The results indicate that with a molar ratio of citric acid/metal ions = 1, the resin contains a number of bidentate ligand fractions and higher portion of C–C–O structure, which makes it possible to synthesize the low temperature phase of $LiCoO_2$ at a temperature as low as 300 °C. The powder calcined at 600 °C exhibits a pure high temperature phase of $LiCoO_2$ (HT-$LiCoO_2$) with a particle size of about 40–60 nm and a specific surface area of 25.24 m^2/g. The electrode prepared at 600 °C exhibits a better HT-$LiCoO_2$ structure and demonstrates a higher first run charge/discharge capacities at 186 and 168 mAh/g, respectively.

Keywords: A. Sol–gel process; Nanometric-sized; $LiCoO_2$; Charge/discharge capacity

1. Introduction

Layered oxides of $LiCoO_2$ have been extensively studied for use as cathode materials in lithium batteries [1]. It has been reported that a low temperature phase of $LiCoO_2$ (LT-$LiCoO_2$) prepared at 400 °C is significantly different from the high temperature phase of $LiCoO_2$ (HT-$LiCoO_2$) obtained at 850 °C in the electrochemical behavior of the Li/$LiCoO_2$ cells [2]. The HT-$LiCoO_2$ phase demonstrates its capacity to produce about 0.5 V higher than the LT-$LiCoO_2$ phase in lithium batteries [3].

The low temperature wet chemical methods, particularly the sol–gel process, to synthesize the cathode materials is recommended, because those methods can produce finer particles with homogeneous distribution and high surface area, and demonstrates better cell performance [4]. It is believed that good crystallinity, homogeneity, uniform particle morphology with narrow size distribution, and fine particle sizes are important parameters to achieve a higher electrode activity [5]. Among the low temperature solution methods, a sol–gel method can produce highly homogeneous powders having increased surface area and thus enhanced electrode reactivity [6,7]. This simple method also has some advantages, such as good stoichiometric control and the production of active finer particles in a relatively shorter processing time at a lower calcination temperature.

A simple powder preparation method was developed by Pechini [8], in which citric acid was used to chelate metal ions and ethylene glycol was used as solvent to obtain an intermediate of polyester-type resin. Ethylene glycol greatly inhibits metal ions segregation and achieves a homogeneous precursor in the polymerization of citric acid–metal complexes [9,10]. In the process, the properties of the synthesized product were crucially affected by the molar ratio of citric acid/metal ions [11,12]. In addition, Shao et al. [13] utilized citric acid and cellulose to synthesize $La_{1-x}Sr_xBO_3$ (B = Co, Fe, Mn), and showed that cellulose could improve the mixing homogeneity of cations effectively causing the decomposition of resin easily at a lower temperature to obtain a finer and high quality $La_{1-x}Sr_xBO_3$ powder. The use of hydroxypropyl cellulose provides steric stabilization during the precipitation of particles, and a monodispersed powder can be obtained. However, to the best

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of our knowledge, a novel sol–gel method utilized the combination of citric acid and hydroxypropyl cellulose to prepare nanometric-sized HT-$LiCoO_2$ cathode materials for lithium battery is not yet available.

In this study, a novel sol–gel method were proposed and a complex route based on polyesterification between citric acid and hydroxypropyl cellulose has been successfully used to synthesize nanometric-sized HT-$LiCoO_2$ powders. The molar ratio of citric acid/metal ions had been studied for its effects on the powder properties and microstructure of $LiCoO_2$ powders. In addition, the charge/discharge property of the as-prepared $LiCoO_2$ cathode was also investigated.

2. Experimental

2.1. Preparation of nanometric-sized $LiCoO_2$ powders

Layered $LiCoO_2$ powders were prepared according to the procedure shown in Fig. 1. First, analytical grade $LiNO_3{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ were weighed accurately in a certain molar ratio, Li:Co = 1.0:1.0, then dissolved in deionized water to obtain a clear solution in order to prepare $LiCoO_2$.

In the preparation of nanometric-sized $LiCoO_2$ powders, the effect of molar ratio of citric acid/metal ions was investigated. Various amounts of citric acid ($HOOCCH_2C(OH)(COOH)CH_2$-COOH) were weighed, the molar ratios of citric acid/total metal ions (defined as R) being varied from 1 to 7, and mixed with a certain weight of hydroxypropyl cellulose to produce various citric acid–cellulose solutions. Then, the citric acid–cellulose solution was mixed with the above solution containing metal ions and agitated vigorously to obtain a homogeneous clear solution. After achieving complete dissolution, the resultant solution was heated with continuous stirring at 60 °C for 2 h in order to promote the polymerization. After being heated at 85 °C for several hours, the solution became highly viscous, and finally gelled to a glassy resin. The gels prepared at various molar ratios of citric acid/metal ions (1–7) were dried and calcined to obtain powders at various temperatures.

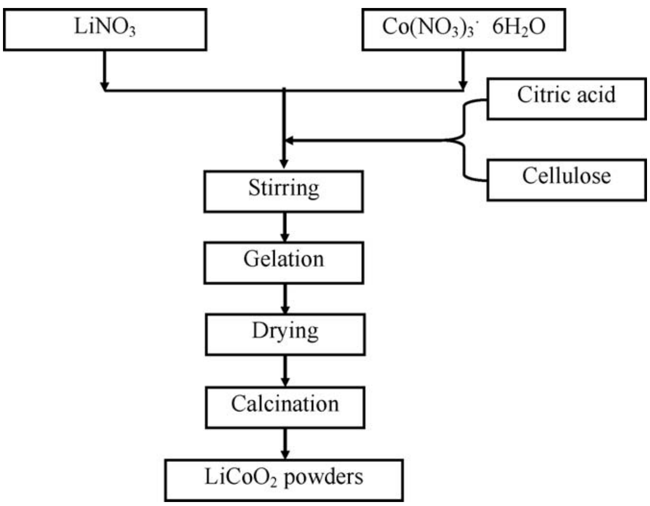

Fig. 1. Schematic illustration of the preparation of $LiCoO_2$ by the sol–gel process.

2.2. Characterization

Physical properties of dried citric acid–cellulose–metal ion gels were investigated by Fourier transform infrared spectroscopy (FTIR) (BIO, FIS-165), Raman spectroscopy (Renishaw), X-ray powder diffraction (XRD) (RIGAKU, Rint-2000) and scanning electron microscopy (SEM) (JEOL-5610). Furthermore, the characteristics of calcined $LiCoO_2$ powders were analyzed: the crystalline phase was identified by an X-ray diffractometer (XRD), the surface area was determined by a BET analyzer (Micromeritics, ASAP 2101), and the surface structure and particle morphology were examined by a scanning electron microscope (SEM).

2.3. Charge/discharge test

The mixture containing 85 wt% $LiCoO_2$ powder, 10 wt% carbon black, and 5 wt% poly(vinylidene fluoride) (PVDF) were well mixed with appropriated amount of alcohol, and then pressed onto a aluminum foils calcined at 250 °C for 4 h served as the cathode. The electrochemical cells were then assembled in Ar filled glove box using foils of Li metal as counter electrodes. Additionally, 1 M $LiPF_6$ (electrolyte) containing a solution of ethylene carbonate (1:1 in weight) was utilized as an electrolyte. The cells were examined in the voltage range 3.0–4.2 V with constant current density using a galvanostatic charge/discharge cycler.

3. Results and discussion

3.1. Effect of molar ratio of citric acid/metal ions on $LiCoO_2$ powders

3.1.1. FTIR analyses

The FTIR spectra of resin prepared from various molar ratios of citric acid/metal ions and dried at 120 °C are shown in Fig. 2. A broad adsorption band around 3400 cm^{-1} for all citric

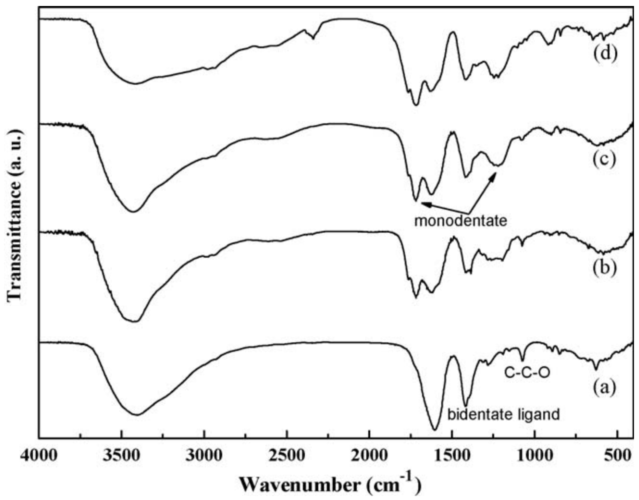

Fig. 2. FTIR spectra of Li–Co-resins prepared from various molar ratios of citric acid/metal ions and dried at 120 °C for 24 h. Molar ratio of citric acid/metal ions at: (a) 1; (b) 3; (c) 5; and (d) 7.

acid–cellulose–salt resins are the characteristic of absorbed water or hydroxyl group in the resin. The sharp absorption bands at the vicinities of 1717 and 1220 cm^{-1} are attributed to the monodentate ligand of metal ion with carbonyl groups (COO^-) [14,15]. There are also two absorption bands around 1624 and 1418 cm^{-1}, which are due to asymmetric and symmetric vibration of the carbonyl groups. Furthermore, an absorption band observed at around 1180 cm^{-1} has been identified as due to the C–C–O structure from cellulose [16].

According to the FTIR analysis in Fig. 2(a), the resin prepared at $R = 1$ contains only a trace of monodentate ligand but lot of bidentate ligand and a relatively high fraction of C–C–O structure. In contrast, the gels prepared at higher molar ratio of citric acid/metal ions were characterized to have both monodentate and bidentate ligand of carbonyl group, as shown in Fig. 2(b)–(d), which may be due to the fact that the resin contains the ligand of carbonyl group with metal ions.

It showed that the lower decomposition temperature of monodentate ligand makes the chelating of metal ions with carbonyl group to collapse easily. Hence, the metal ions ligand with monodentate COO^- would be much easier to segregate with the heating process. Furthermore, the lower decomposition temperature of C–C–O structure, which is constituted in the resin obtained from the raw material of cellulose, makes it possible for the formation of much smaller fractional pieces in the resin during the heat treatment process [16]. Thus, it could be predicted that a small and chemically homogeneous $LiCoO_2$ powder could be prepared in the presence of increased fraction of bidentate ligand, *i.e*. lower fraction of monodentate ligand, and the existence of more C–C–O structure. It could also be inferred that the $LiCoO_2$ powders, prepared from $R = 1$, should have a smaller size and homogeneous chemical composition, and these results are also in agreement with the results of BET and SEM (not shown).

It was reported that the electrochemical behavior of $LiCoO_2$ is related to the preparation temperature, which affects the phase formation of LT-$LiCoO_2$ or HT-$LiCoO_2$. However, the LT-$LiCoO_2$ and HT-$LiCoO_2$ can be identified from their FTIR spectra. The FTIR spectra of $LiCoO_2$ samples calcined at various temperatures for 4 h are shown in Fig. 3.

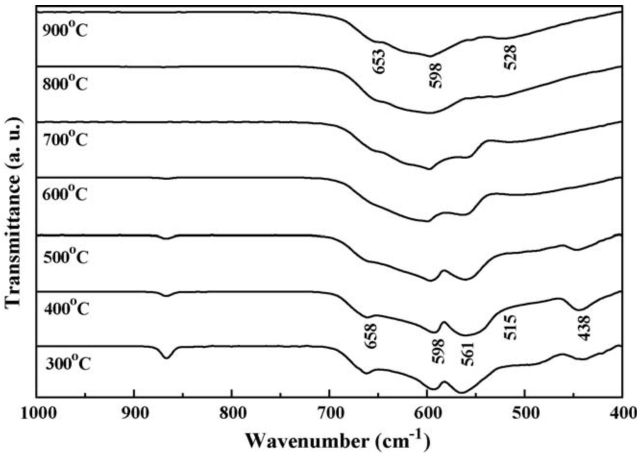

Fig. 3. FTIR spectra of Li–Co-resins prepared from molar ratio of citric cid/ metal ions at 1 and calcined at various temperatures.

At lower calcination temperatures, some distinct FTIR bands at 658, 598, 561, 515 and 438 cm^{-1} are observed for the identification of spinel LT-$LiCoO_2$. Particularly, for the sample calcined at 300, 400 and 500 °C, respectively, the weak absorption around 438 cm^{-1} due to the Li–O stretching motion is observed, which indicates that it contains the LT-$LiCoO_2$ phase [17]. The absorption band exists until the calcinations of $LiCoO_2$ powder at 500 °C, revealing that the $LiCoO_2$ powder prepared below 500 °C is the LT-$LiCoO_2$ phase.

For the $LiCoO_2$ prepared at higher calcination temperatures (600–900 °C), the absorption bands at 653, 598, 528 cm^{-1}, and a very weak feature at 550 cm^{-1} agree very well with the reported value for HT-$LiCoO_2$ [18], indicating that it is a typical high temperature $LiCoO_2$ phase. However, the two higher frequency bands at 653 and 598 cm^{-1} may be attributed to Co–O stretching and O–Co–O bending vibrations, respectively, whereas the lower frequency bands at 528 cm^{-1} is attributed to the Li–O stretching motion in the HT-$LiCoO_2$ phase. The $LiCoO_2$ obtained at 600 °C basically belonged to the high temperature phase because the absorption band at 438 cm^{-1} (Li–O stretching) is not observed. In addition, the absorption band at 865 cm^{-1} is the characteristic of carbonate (CO_3^{2-}). The carbonate decreased upon increasing the calcination temperature, and disappeared at 600 °C.

3.1.2. Raman analyses

The Raman spectra of the dried gel prepared from various molar ratios of citric acid/metal ions and dried at 120 °C are shown in Fig. 4. As shown in Fig. 4, the Raman peaks observed at around 495 and 601 cm^{-1} in the powder are attributed to the Raman active modes E_g and A_{1g}, due to the space group $R3m$, which demonstrate that the powders consist of the layered-hexagonal structure (HT-$LiCoO_2$) [19]. In Fig. 4(a), the $LiCoO_2$ powder exhibits two main characteristic bands of E_g and A_{1g} at 481 and 591 cm^{-1}, and small bands around 523 and 678 cm^{-1} originating from $Fd3m$ symmetry.

It reveals that the layered-hexagonal phase (HT-$LiCoO_2$) appears to change to the cubic spinel phase (LT-$LiCoO_2$) at a

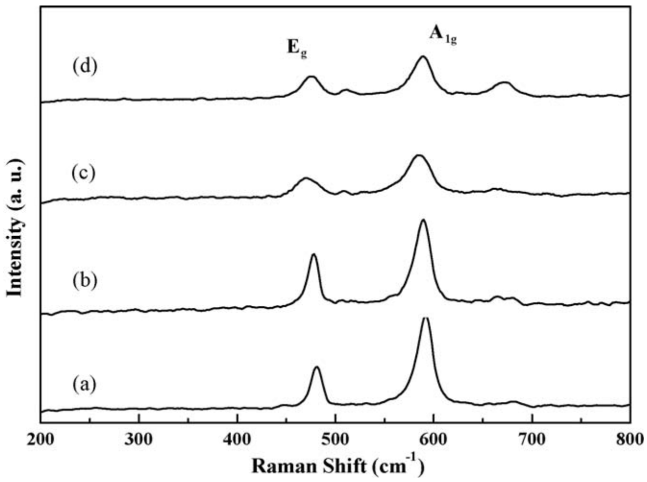

Fig. 4. Raman spectra of Li–Co-resins prepared from various molar ratios of citric acid/metal ions and dried at 120 °C for 24 h. Molar ratio of citric acid/ metal ions at: (a) 1; (b) 3; (c) 5; and (d) 7.

higher molar ratio of citric acid/metal ions. Two big Raman bands attributed to the layered-hexagonal phase are softened accompanying the broadening of bands and the intensity decreased upon increasing the molar ratios of citric acid/metal ions, while two other bands near 523 and 678 cm^{-1} corresponding to cubic spinel phase are enhanced [20]. Such a phenomenon is certainly associated with the phase change in $LiCoO_2$ from layered-hexagonal structure to cubic spinel structure.

Obviously, as R increases, a small peak appeared at around 460 cm^{-1} in addition to the two peaks observed in the layered-hexagonal structure, indicating the mixed structure of the layered-hexagonal and the cubic spinel structures. These results also suggest the powder contain relatively lower fraction of layered-hexagonal structure, because of a few spinel existed. Therefore, these Raman scattering data support the XRD data for each annealing sample.

In addition the studies of Raman spectra are in good agreement with the studies of FTIR, revealed that the lower R ($R = 1$ or 2) exhibits the precursor obtained in less crosslinking structure and with much more homogeneity of metal ions chelated, resulting in a finer particle size of $LiCoO_2$ powders.

3.1.3. XRD analyses

X-ray diffraction patterns for powders calcined at various temperatures for 4 h are shown in Fig. 5. As the dried gel calcined at 300 °C, some additional peaks are also observed between the 2θ values of 20° and 40° is attributed to the presence of both $LiNO_3$ and Li_2CO_3 [21]. The XRD pattern for the sample calcined at 600 °C shows all the peaks, which indicates the development of crystallization behavior at this temperature. Furthermore, the XRD pattern is well defined and displays the hexagonal doubles (0 0 6)/(0 1 2) and (1 0 8)/(1 1 0) with a clear splitting, which indicates that samples have a high degree of crystallinity, good hexagonal ordering, and greater layered characteristics [22]. Based on the above results, it can be concluded that the minimum temperature required for the complete hexagonal ordering is 600 °C.

As seen from this figure, all the X-ray patterns have sharp peaks, which indicate a high degree of crystallinity. The intensity ratio $I_{(0\ 0\ 3)}/I_{(1\ 0\ 4)}$ increases from 1.33 to 1.50 for the $LiCoO_2$ powder obtained by changing the temperature from 300 to 900 °C. Obviously, the intensities of the (0 0 3) reflections are higher than those for the corresponding (1 0 4) reflection, which indicates that these samples have good cations ordering.

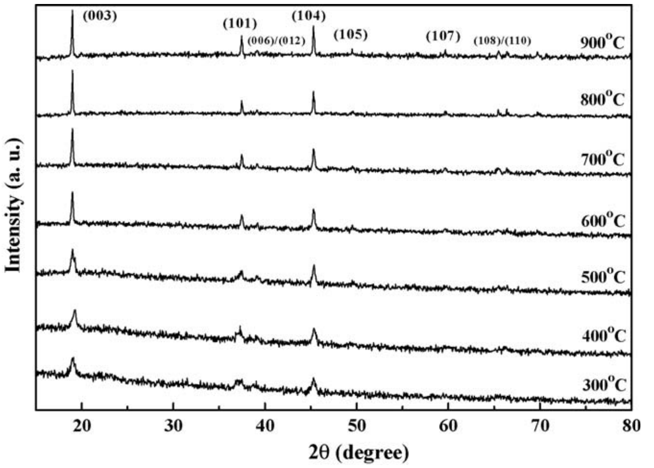

Fig. 5. The XRD patterns of Li–Co-resins prepared from molar ratios of citric acid/metal ions at 1 and heat-treated at various temperatures.

The XRD patterns reveal that there is a little amount of Li_2CO_3 and trace amounts of Co_2O_3 and $LiNO_3$ as intermediate phases prior to the formation of $LiCoO_2$ phase during the calcination of the dried gel. Only trace amounts of the intermediate phases are expected in the case of perfect mixing of constituent cations in the resin. This would be understood to mean that $LiCoO_2$ phase prepared from this route, in which the metal ions are not significant segregation that leading a homogeneous $LiCoO_2$ powder obtained.

3.1.4. SEM analyses

The powders prepared from various molar ratios of citric acid/metal ions ($R = 1$, 3, 5 and 7) were heat-treated at 600 °C for 4 h and examined by SEM, as shown in Fig. 6. It is found that the morphology of powders is dependent on the molar ratio of citric acid/metal ions. The dependency of the obtained particle size is reciprocal to the molar ratio of citric acid/metal ions. The particle size of the powder made from $R = 1$ is the finest, which is about 40–60 nm, as shown in Fig. 6(a), and that of the powder formed from $R = 7$ is the largest (about 150–200 nm).

It is revealed that the ligand of citric acid to metal ion is influenced by the molar ratio of citric acid; therefore, the morphology of powder is changed depending on the amount of citric acid. A lower molar ratio of citric acid/metal ions ($R = 1$) contains a relatively higher fraction of bidentate ligand and C–C–O structures. The bidentate ligand makes the chelating of metal ions with carbonyl group to be less segregated (more homogeneous), resulting in the production of $LiCoO_2$ with finer particle sizes. It could be predicted that the $LiCoO_2$ powders, prepared at $R = 1$ should have a smaller size and homogeneous chemical composition. In contrast, at a higher ratio of citric acid/metal ions ($R = 5$ or 7), larger fraction of monodentate and less C–C–O structure are observed, revealing that excess amount of citric acid causes more segregation of metal ions, and results in the formation of larger particle size with less homogeneity (examined by XRD and SEM).

3.2. Charge/discharge properties of electrodes

The first run charge/discharge capacity of the electrodes manufactured from $LiCoO_2$ powders prepared by various molar ratio of citric acid/metal ions and calcined at 600 °C were measured as shown in Fig. 6. However, it is found that the particle sizes of $LiCoO_2$ powders prepared from various molar ratios of citric acid/metal ions ($R = 1$, 3, 5, and 7) were 40–60, 70–100, 120–150, and 150–200 nm, respectively. The discharge capacity obtained for the first cycle shows a highest value for the finest size of $LiCoO_2$ (obtained at a low molar ratio of citric acid/metal ions = 1). This high value could be related mainly to the nanometric-sized $LiCoO_2$ and more layered

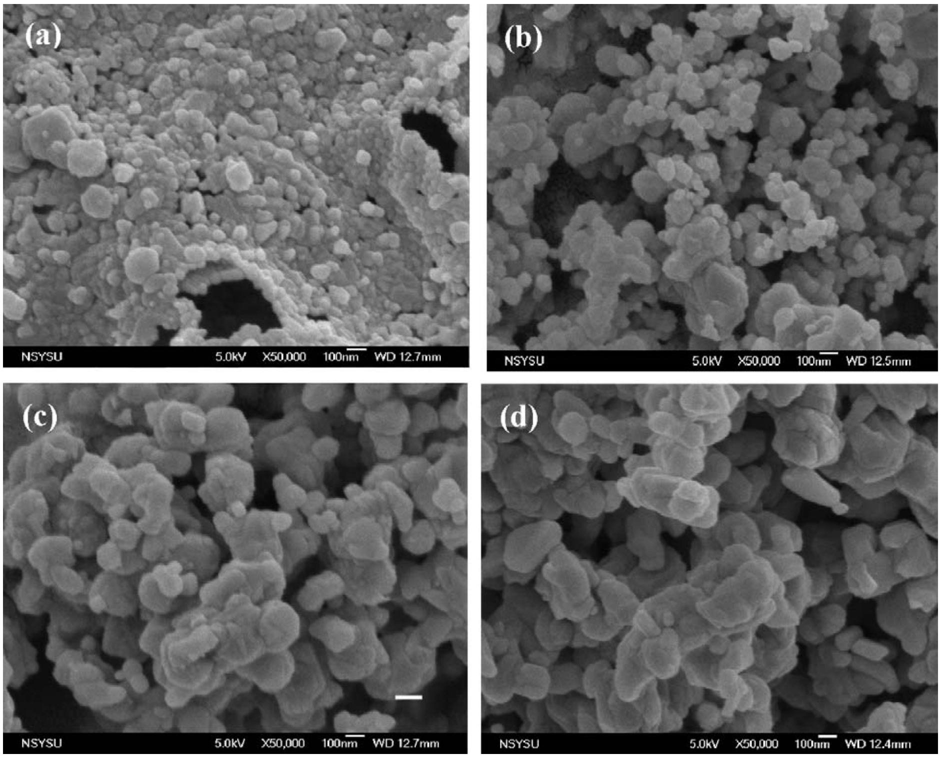

Fig. 6. SEM micrographs of $LiCoO_2$ powders obtained from various molar ratios of citric acid/metal ions and heat-treated at 600 °C for 4 h. Molar ratio of citric acid/metal ions at: (a) 1; (b) 3; (c) 5; and (d) 7.

structure and to the faster rate for the Li^+ insertion/deinsertion process [23].

The discharge capacity decreases with the increasing of $LiCoO_2$ particle size. The discharge capacity value is larger for the $LiCoO_2$ material at a nanometric-size of $LiCoO_2$ (Fig. 7(a) and (b)), but it is lower observed from this figure for the larger sized $LiCoO_2$ obtained (Fig. 7(c) and (d)). This higher discharge capacity could be associated to the nanometric-sized effects and the presence of larger portion of the layered structure, which were revealed by the studies of Raman and SEM stated previous. Clearly a finer particle size of $LiCoO_2$ powders results in a higher charge/discharge capacity. The maximum value of the charge/discharge capacity at the first discharge capacity of the electrode prepared by $LiCoO_2$ powder obtained from the molar ratio of citric acid/metal ions = 1 and calcined at 600 °C was 186 and 168 mAh/g, respectively.

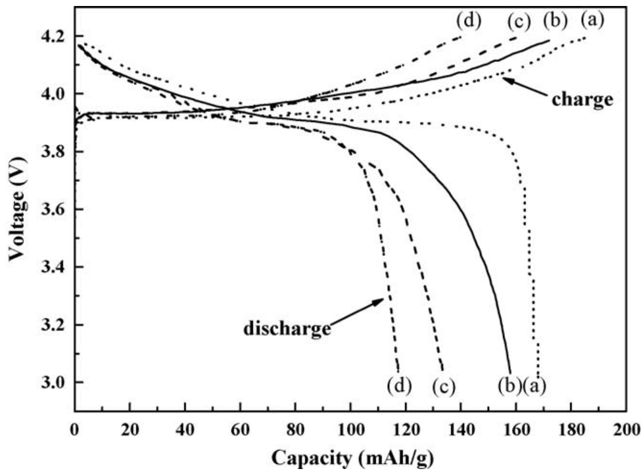

Fig. 7. The first run charge/discharge capacity of the electrodes manufactured from $LiCoO_2$ powders prepared by various molar ratios of citric acid/metal ions and calcined at 600 °C. Molar ratio of citric acid/metal ions at: (a) 1; (b) 3; (c) 5; and (d) 7.

4. Conclusions

The nanometric-sized $LiCoO_2$ powders have been synthesized successfully through the polymerized complex technique based on a novel sol–gel method. An aqueous solution containing mixtures of nitrates is chelated with the resin, which contains citric acid and hydroxypropylcellulose to produce the resin of chelate from polyesterification. Molar ratios of citric acid to metal ions were varied in the range of 1–7, and the resulting effects on the properties of powders were studied using FTIR, Raman spectroscopy, XRD and SEM. The results of the present study indicate that at a molar ratio of citric acid/metal ions = 1, the resin contains a higher fraction of bidentate ligand and a higher portion of C–C–O structure, and obtain a small size LT-$LiCoO_2$ phase synthesized at temperature as low as 300 °C. The powder was calcined at 600 °C to obtain a pure HT-$LiCoO_2$ phase, which exhibited a particle size of about 40–60 nm.

Furthermore, the charge/discharge properties of the cathodes are influenced by the morphology and phase structure of the prepared $LiCoO_2$ powders. The first run charge/discharge capacity of the electrode prepared by $LiCoO_2$ powder obtained from the molar ratio of citric acid/metal ions at 1 and calcined at 600 °C was 186 and 168 mAh/g, respectively.

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