

Temperature Dependent Surface Morphology and Lithium Diffusion Kinetics of LiCoO₂ Cathode

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In an attempt to understand the effect of synthesis temperature upon surface morphology and lithium diffusion kinetics of LiCoO₂, the compound was synthesized at four different temperatures, viz., 600, 700, 800 and 900 °C using a novel gelatin-assisted combustion method. LiCoO₂ synthesized at 800 °C is found to be a mixture of rhombohedral and cubic LiCoO₂ and a temperature of 900 °C leads to the formation of cubic LiCo₂O₄ compound, thus favoring lower temperatures such as 600 and 700 °C to prepare phase pure rhombohedral LiCoO₂. Cyclic voltametry and impedance spectral studies evidence that LiCoO₂ synthesized at 600 °C exhibits better electrochemical cycling behavior and considerably reduced internal resistance upon cycling, which are substantiated further from the higher lithium diffusion coefficient value. The study demonstrates the possibility and superiority of synthesizing electrochemically active LiCoO₂ with preferred surface morphology and better lithium diffusion kinetics at a relatively lower temperature of 600 °C, using a gelatin-assisted combustion method.

Key words: energy storage materials, self-propagating synthesis, electrochemistry, scanning electron microscopy, X-ray diffraction

1. INTRODUCTION

Layered LiCoO₂ is a two-dimensional (2D) system that adopts a α -NaFeO₂ type of structure, which can be regarded as a distorted rock salt structure [1]. It is well known that even with the same chemical composition and crystal structure, small variations in physical properties of cathode materials, such as surface morphology and size of the particles are reported to influence the performance of the battery to a noticeable extent [2]. Particularly, the capacity of lithium intercalating oxides is reported to enhance [3,4] with a decrease of average grain size of the oxides. In other words, solid-state diffusion of lithium ions, being the rate-determining step of intercalation and de-intercalation processes, prefers a smaller particle size with a shorter diffusion length to aid faster lithium diffusion kinetics [5,6].

To understand the effect of particle size upon diffusion kinetics, one needs to prepare the title compound containing different particle sizes individually. Herein, instead of preparing LiCoO₂ using different synthesis methods, the compound has been prepared at different temperatures by adopting a select synthesis approach, in order to avoid the problem of

comparison of powder obtained by different synthesis methods, which would not be a fairly correct measure due to the simultaneous influence on the crystallographic ordering type of dominating defects [7]. In addition, it is reported that suitable variation in the reaction parameters of the synthesis approach to obtain preferred surface morphology and reduced particle size could significantly influence the electrochemical properties [8–10] of lithium intercalating cathode materials. As a result, synthesis of LiCoO₂ at four different temperatures in the range 600–900 °C has been attempted in the present study using a novel gelatin assisted combustion method.

Literature is replete with reports on the solid-state synthesis of LiCoO₂ that requires 850 °C (20 h) [11] or solution assisted synthesis methods that require temperatures such as 700 °C (12 h) and 900 °C (10 h) respectively for pechini and sol-gel methods. On the other hand, the currently adopted gelatin-assisted combustion synthesis requires a temperature as low as 600 °C, thus leading to the identification of an energy saving synthesis approach to prepare phase pure LiCoO₂. Further, the currently deployed 600 °C is found to be lower than the temperature reported in the literature (800 and 900 °C) for a combustion method [12,13] to prepare electrochemically active LiCoO₂ compound, which is the highlight of the present study and thus assumes importance.

The focal theme of this study is to understand the variation

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of physical properties such as phase purity, particle size, shape, surface morphology and related electrochemical properties of synthesized LiCoO_2 as a function of synthesis temperature with a special reference to a gelatin-assisted combustion method. Comparison of aforesaid properties investigated at four different temperatures such as 600, 700, 800 and 900 °C has clearly indicated two factors viz., synthesis temperature plays a vital role in deciding the physical as well as electrochemical properties of LiCoO_2 and the optimum synthesis temperature is 600 °C with regard to the gelatin-assisted combustion method to prepare phase pure and better performing LiCoO_2 with desirable surface morphology and enhanced lithium diffusion kinetics.

2. EXPERIMENTAL PROCEDURES

2.1. Synthesis Procedure

In the gelatin-assisted combustion method, a mixture consisting of stoichiometric amounts of lithium nitrate ($\text{LiNO}_3 \cdot \text{H}_2\text{O}$, Merck) and cobalt nitrate $\{\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}\}$ was dissolved in hot water while stirred to get a homogenous solution. To the solution, 3 g of gelatin was added and the process of stirring and heating was continued to get a dried, foamy mass. The same was furnace-heated to 300 °C for about 12 h followed by an intermittent grinding and subjected to further calcination at temperatures such as 600, 700, 800 and 900 °C for about 12 h individually in air using alumina crucibles. The ultrafine LiCoO_2 powders obtained after grinding were collected and subjected to systematic characterization studies.

2.2. Physical and Electrochemical Characterizations

Phase characterization was done by powder X-ray diffraction technique on a Philips 1830 X-ray diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda=1.54\text{\AA}$) in the 10-90° range at a scan rate of 0.04°/s. Surface morphology of synthesized samples was examined by scanning electron microscopy (SEM, Hitachi S-3000 H, Japan) and particle size analysis was carried out on a Malvern particle size analyser. Fourier transform infrared spectroscopy (FT IR) was performed on a Perkin-Elmer Paragon-500 FT IR spectrophotometer using a pellet containing a mixture of KBr and the response of active material in the region 400-1200 cm^{-1} has been noted. Room temperature electrochemical studies, such as cyclic voltametry (CV) and Electrochemical Impedance Spectroscopy (EIS) measurements, were performed using an Auto lab electrochemical workstation, wherein the CV scan rate was fixed as 0.2 mV/s and the impedance analysis was done over a frequency range of 100 KHz-100 mHz.

2.3. Electrode Preparation and Coin Cell Fabrication

Prior to electrochemical studies, 2032 coin cells were assembled with lithium anode, synthesized cathode material and a non-aqueous electrolyte containing 1 M LiPF_6 dis-

solved in 1:1 v/v EC:PC with a celgard separator. To prepare the cathode electrode, the synthesized powder was first mixed intimately with super P carbon black (additive) and polyvinylidene fluoride (binder) in an 80:10:10 ratio respectively, and the same was treated with N-Methyl pyrrolidin-2-one (solvent) to form a slurry. The slurry was cast uniformly on a thin aluminum foil and then dried for about 2 h at 110 °C. The dried foil was hot pressed (under 5 tons of pressure) and the circular electrodes were punched out from the coated foil. Using such cathodes, 2032 coin cells were assembled in an Argon-filled glove box and crimp sealed.

3. RESULTS AND DISCUSSION

3.1. Phase Analysis-XRD

The XRD pattern recorded for LiCoO_2 synthesized at different temperatures is appended in Fig. 1. The diffraction patterns indicate that the crystal structure is identified to that of single-phase rhombohedral LiCoO_2 for temperatures such as 600 and 700 °C (JCPDS File No.: 75-0532). On the other hand, LiCoO_2 synthesized at 800 °C corresponds to a mixture of rhombohedral and cubic LiCoO_2 , as understood from the reduced intensity of doublets corresponding to hexagonal ordering [14]. LiCoO_2 synthesized at 900 °C matches exactly with the cubic structure of LiCo_2O_4 , as understood from a striking similarity to JCPDS No: 82-0330. The Bragg peaks

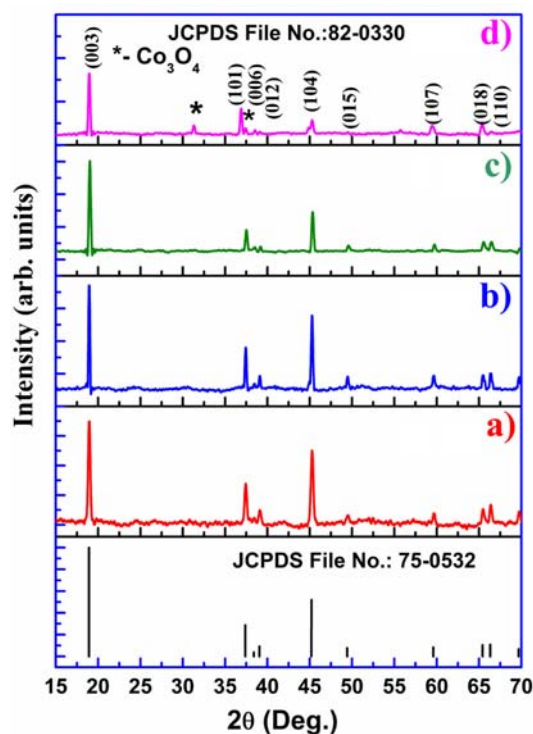


Fig. 1. XRD patterns of LiCoO_2 synthesized by gelatin-assisted combustion method using different temperatures: (a) 600 °C, (b) 700 °C, (c) 800 °C, and (d) 900 °C.

Table 1. Calculated physical parameters of LiCoO₂ prepared at different temperatures

| Compound | a (Å) | c (Å) | c/a | V (Å ³) | Stokes strain $\times 10^{-3}$ m | $I_{(003)}/I_{(104)}$ | $\theta_{(012)}-\theta_{(006)}$ | $\theta_{(110)}-\theta_{(018)}$ |
|----------------------------|-------|--------|-------|---------------------|----------------------------------|-----------------------|---------------------------------|---------------------------------|
| LiCoO ₂ -600 °C | 2.807 | 14.030 | 4.990 | 95.72 | 7.213 | 1.316 | 0.338 | 0.457 |
| LiCoO ₂ -700 °C | 2.871 | 14.021 | 4.883 | 96.37 | 6.12 | 1.270 | 0.317 | 0.450 |

of Fig. 1(a-d) are indexed accordingly and the calculated lattice parameter values using the iterative least square method are given in Table 1.

Formation of rhombohedral LiCoO₂ with R-3 m symmetry is understood from the observed XRD pattern, especially at 600 and 700 °C. Presence of sharp Bragg peaks confirms the crystallinity of the synthesized LiCoO₂ compound and the calculated integrated intensity value of I_{003}/I_{104} , which is found to be greater than 1, is attributed to the perfect arrangement of LiO₆ and CoO₆ octahedra [12]. In addition, presence of clear doublets (012) (006) and (110) (018), as understood from Fig. 1 and Table 1 corresponding to 600 and 700 °C, are in favor of ordered distribution of lithium and cobalt ions that exist in a perfect layered structure [12]. Based on the higher integrated intensity (1.316) and c/a (4.99) values, it is understood that a minimum of 600 °C is sufficient to prepare phase pure LiCoO₂, which is lower than the temperature reported in literature [12,13] to synthesize LiCoO₂ using combustion method. Hence, the present study is bestowed with the identification of a novel and low temperature gelatin-assisted combustion method to prepare phase pure LiCoO₂, which is noteworthy.

It is reported that a mixture of rhombohedral (layered) LiCoO₂ and cubic (spinel) LiCo₂O₄ [14] structures is obtained with low temperature (400 °C) synthesized LiCoO₂, wherein concentration of undesirable spinel structures of LiCo₂O₄ is found to decrease as a function of increased synthesis temperature. On the other hand, the present study infers that a possible co-existence of rhombohedral and cubic structures occurs at 800 °C. More interestingly, complete formation of cubic LiCo₂O₄ is found to be present at 900 °C. This could be understood from the diminished intensity of doublets at $2\theta=65.5$ and 66.4° (Figs. 1(c) and (d)) observed with LiCoO₂ synthesized at higher temperatures such as 800 and 900 °C. Particularly, LiCoO₂ synthesized at 900 °C corresponds to the (Fig. 1(d)) presence of two additional peaks at $2\theta=32^\circ$ and $2\theta=37.5^\circ$ at the expense of doublet disappearance at $2\theta=65.5$ and 65 into a singlet, thus confirming the complete formation of cubic structures [14]. Presence of additional peaks at $2\theta=32^\circ$ and $2\theta=37.5^\circ$ may also be attributed to the co-existence of Co₃O₄ impurity, which is common with high temperature synthesized LiCoO₂ [15].

3.2. Surface Morphology-SEM Studies

Presence of perfectly formed hexagonal particles with definite grain boundaries are seen for LiCoO₂ synthesized at 600 °C (Fig. 2a). On the other hand, closely arranged spherical grains of LiCoO₂ are seen from the SEM images of

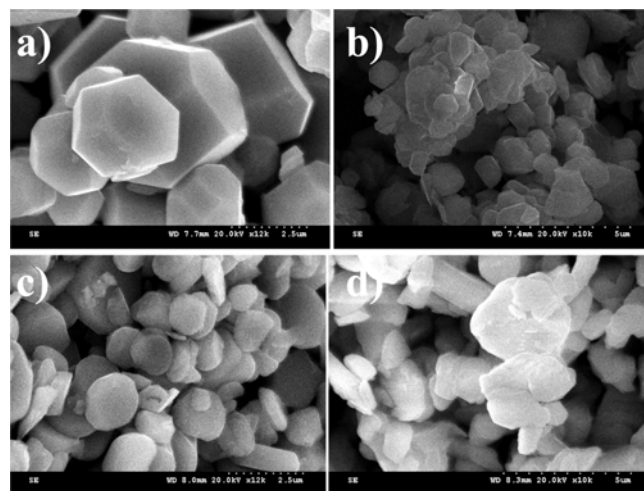


Fig. 2. SEM images of LiCoO₂ synthesized at temperatures: (a) 600 °C, (b) 700 °C, (c) 800 °C, and (d) 900 °C.

LiCoO₂ synthesized at higher temperatures such as 700, 800 and 900 °C (Fig. 2(b-d)). More specifically, co-existence of Co₃O₄ (as indicated by XRD) is evident from the bright secondary particles formed with the desired LiCoO₂ compound synthesized at 900 °C.

Despite the fact that preferred surface morphology is observed only for LiCoO₂ synthesized at 600 °C, formation of reduced grain size is understood from the SEM images recorded for LiCoO₂ synthesized at different temperatures such as 600~900 °C individually. Interestingly, possible agglomeration of particles at higher sintering temperatures is found to be missing, thus endorsing the significance of a gelatin-assisted combustion process in controlling the growth and wider distribution of particles via multiple steps and a controlled heat rate (2 °C/min.) along with the process of intermittent grinding.

3.3. Particle Size Analysis

The particle size analysis of LiCoO₂ synthesized at different temperatures clearly evidences the presence of nano crystalline particles with <100 nm particle size at 600 °C (Fig. 3a) and the high temperature synthesized LiCoO₂ at 700, 800 and 900 °C corresponds to large particle size (>100 nm), as understood from the graph (Fig. 3b-d).

3.4. FTIR Study

Figure 4 shows that characteristic vibrational peaks at 602 and 520 cm⁻¹ corresponding to the stretching Co-O bonds and bending O-Co-O bonds in CoO₆ octahedral moiety of

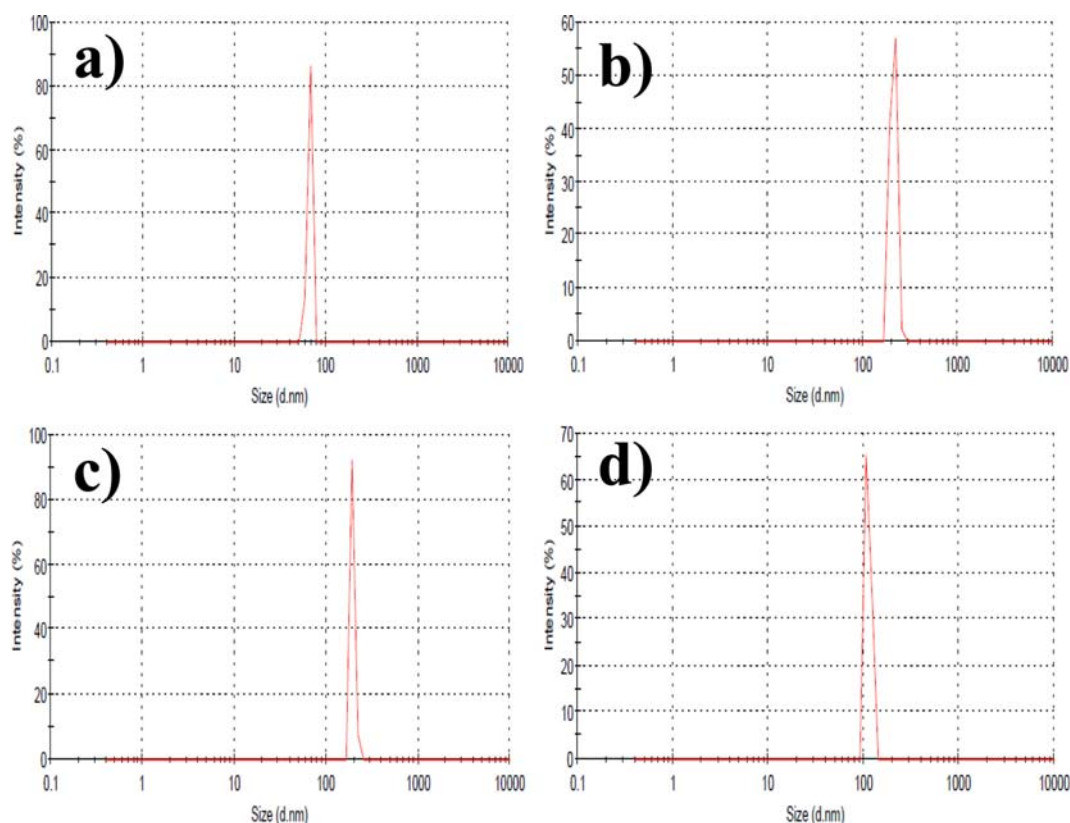


Fig. 3. Particle size distribution of LiCoO_2 synthesized by gelatin-assisted combustion method at temperatures: (a) 600 °C, (b) 700 °C, (c) 800 °C, and (d) 900 °C.

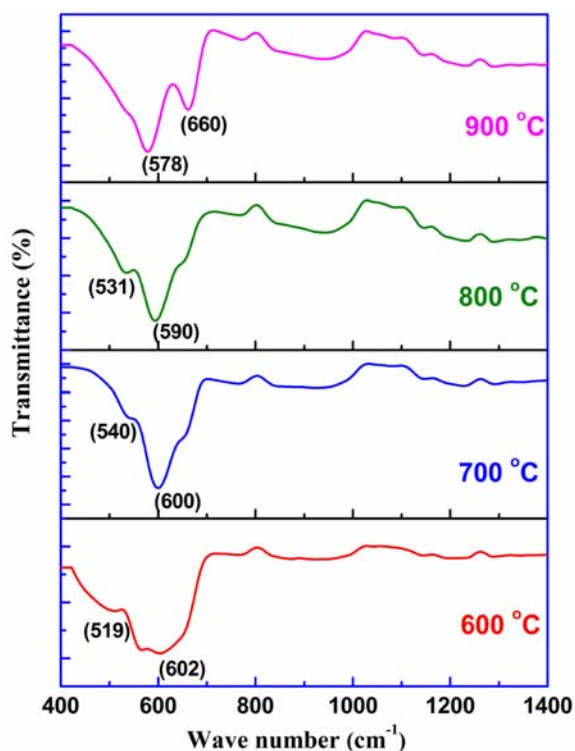


Fig. 4. FTIR spectra of gelatin-assisted combustion synthesized LiCoO_2 .

LiCoO_2 are found with samples synthesized using 600, 700, and 800 °C [16–18]. On the other hand, significant shift in FT-IR frequencies of Co-O and O-Co-O bonds observed with LiCoO_2 prepared at 900 °C indicates the presence of cubic structures instead of the preferred rhombohedral LiCoO_2 .

3.5. Cyclic Voltammetry Studies

The electrochemical cycling behavior of LiCoO_2 synthesized at different temperatures has been investigated by subjecting Li/LiCoO_2 half cells to cyclic voltammetry studies performed at a scan rate of 0.2 mV/sec. in the potential range of 2.5–4.5 V. For LiCoO_2 synthesised at 600 °C, two significant oxidation peaks (4.03 and 4.20 V) are observed with corresponding reduction peaks (4.14, 4.03 and 3.83 V) for the first cycle. Similarly, highly pronounced red-ox peaks at 4.0/3.83 4.1/4.04 and 4.19/4.14 V are observed for the same after completing 5 cycles (Fig. 5), wherein no significant change in peak position is observed.

For LiCoO_2 synthesized at 700 °C, characteristic red-ox peaks are observed wherein the oxidation peak at 4.2 V and the reduction peak at 4.14 V are less pronounced. In addition, red-ox peak positions upon progressive cycling change slightly along with considerable reduction in peak currents, which is noteworthy. Basically, the CV behavior of LiCoO_2 synthesized at 600 °C corresponds to no significant change

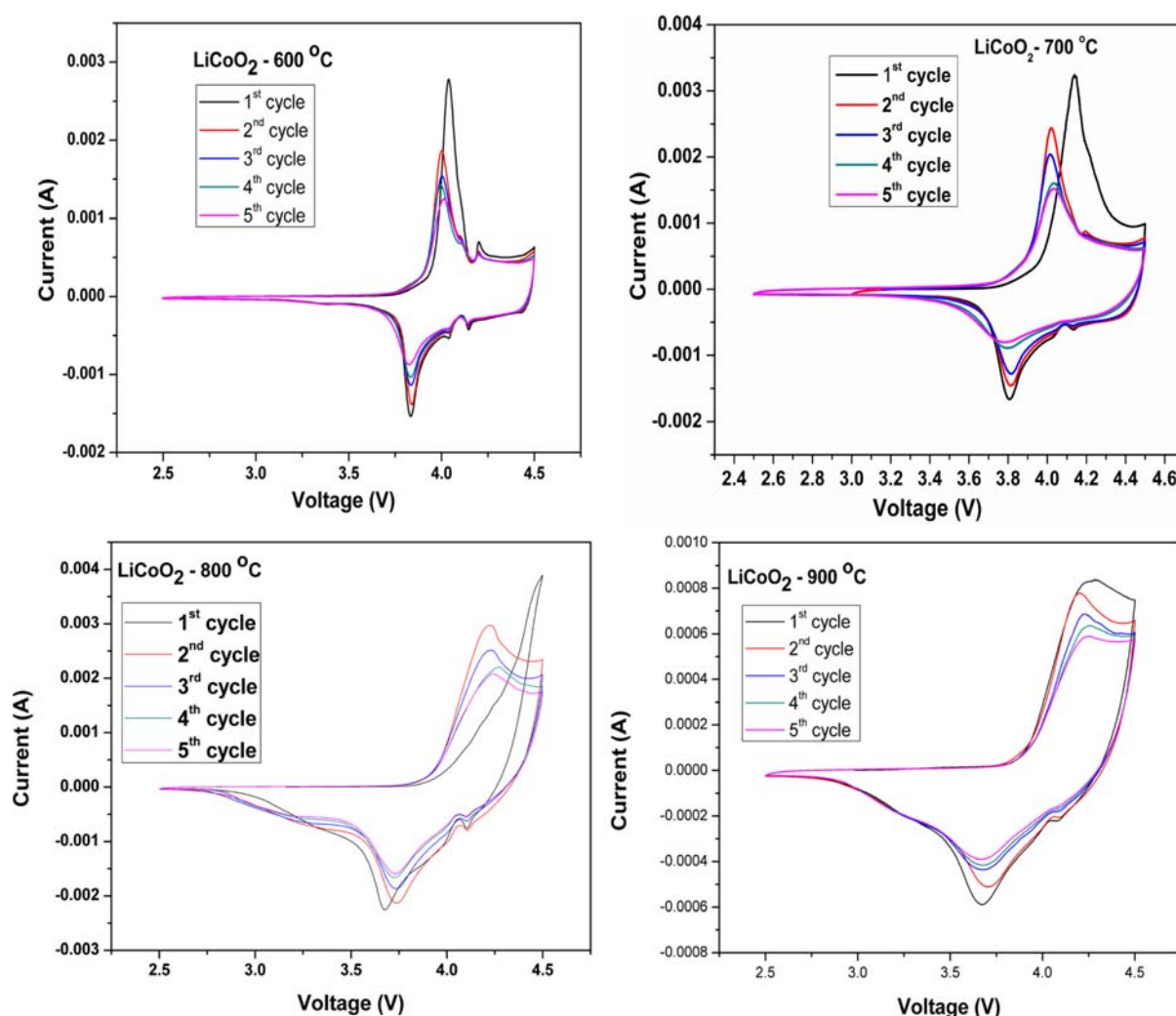


Fig. 5. Cyclic voltammograms of LiCoO₂ synthesized with different temperature.

in peak current values, especially after the stabilization of SEI from the formation cycle, based on which the cycling stability of low temperature (600 °C) synthesized LiCoO₂ cathode could be understood. In addition, an enhanced peak current value is observed for LiCoO₂ synthesized at 600 °C, thus substantiating the superiority of 600 °C over 700 °C in producing LiCoO₂ with desired electrochemical intercalation/de-intercalation behavior of lithium ions, as derived from physicochemical properties.

LiCoO₂ synthesized at 800 °C exhibits one visible oxidation and two reduction peaks at 4.2 and 4.1, 3.7 V respectively corresponding to the first cycle. Similarly, an oxidation peak at 4.2 V and two reduction peaks at 4.0 and 3.7 V are observed after the 5th cycle, thus demonstrating the intercalation and de-intercalation of LiCoO₂ cathode synthesized at 800 °C. On the other hand, LiCoO₂ synthesized at 900 °C exhibits an oxidation peak at 4.27 V and two reduction peaks at 4.08 and 3.68 V for the first cycle, whereas the reduction peak at 4.08 V is found to be missing after 2 cycles. Further,

LiCoO₂ synthesized at 800 and 900 °C are expected to suffer from poor cycling stability and capacity fade related issues, as evidenced from the inferior CV behavior. The disappearance of a characteristic major oxidation peak at 4.0 V and the appearance of a pronounced oxidation peak at 4.2 V found with 800 and 900 °C samples are in favor of the fact that LiCoO₂ synthesized at such higher (800 and 900 °C) temperature is not phase pure or rhombohedral LiCoO₂ cathode. Hence, the formation of a mixture of rhombohedral and cubic forms of LiCoO₂ at 800 °C, and the complete formation of cubic LiCo₂O₄ at 900 °C as indicated by XRD, are also substantiated by CV studies. The same is further authenticated from the chemical diffusion coefficient values calculated from CV studies.

The chemical diffusion coefficient of Li⁺ ions is found to be higher ($2.2 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$) for LiCoO₂ synthesized at 600 °C and lower ($2.0 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$) for LiCoO₂ synthesized at 900 °C [19–20]. In other words, the chemical lithium diffusion coefficient is found to be enhanced by one fold when

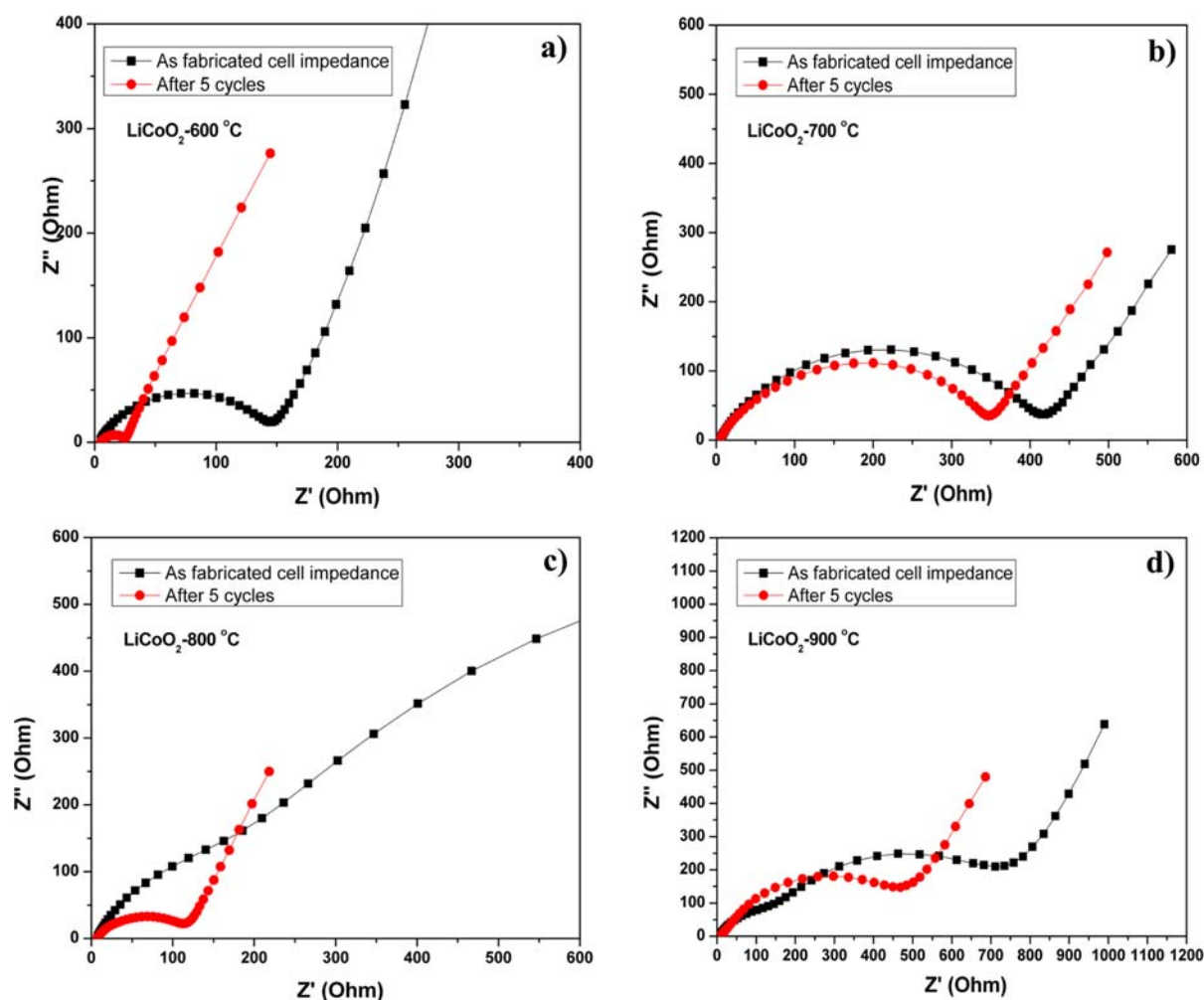


Fig. 6. Impedance spectra of different temperature synthesized LiCoO_2 : (a) 600°C , (b) 700°C , (c) 800°C , and (d) 900°C .

the synthesis temperature is reduced from 900 to 600°C . Such an encouraging lithium diffusion kinetics observed at 600°C is in accordance with the comparably better physical properties, especially in terms of phase purity, perfect layeredness, particle size reduction and preferred surface morphology observed with LiCoO_2 synthesized at 600°C . Hence, the role of synthesis temperature in improving the lithium diffusion properties can be understood.

3.6. Electrochemical Impedance Analysis

The extent of formation of internal resistance upon cycling and the Nyquist behavior of LiCoO_2 cathode synthesized at different temperatures is shown in Fig. 6. Each Nyquist plot consists of a semicircle corresponding to a charge-transfer controlled reaction and a Warburg behavior corresponding to a diffusion-controlled lithium intercalation - de-intercalation process [21]. The internal resistance of the cell is found to decrease after 5 cycles for LiCoO_2 synthesized at 600 and 700°C whereas the same is found to be increased upon progressive cycling for LiCoO_2 synthesized at 800 and 900°C .

Hence, it is understood that the process of intercalation and de-intercalation gets stabilized with LiCoO_2 synthesized at lower temperatures, thus ensuring better electro-chemical cycling behavior without considerable fade in capacity. More specifically, LiCoO_2 synthesized at 600°C has exhibited considerably reduced internal resistance ($25\ \Omega$) upon cycling, corresponding to improved lithium diffusion kinetics and electrochemical cycling behavior. A comparison of initial (Fig. 7(a)) and final impedance values after 5 cycles (Fig. 7(b)) evidences that low temperature synthesized (600°C) LiCoO_2 corresponds to the lowest initial ($150\ \Omega$) as well as final impedance ($25\ \Omega$) values. Such an encouraging impedance behavior exhibited by LiCoO_2 synthesized at 600°C could be understood as a function of perfect formation of individually seen hexagonal particles (SEM) and enhanced chemical lithium diffusion coefficient values calculated from CV. Hence, it is understood from the impedance study that LiCoO_2 synthesized at 600°C exhibits superior electrochemical performance over the rest of the samples synthesized at temperatures such as 700 , 800 and 900°C .

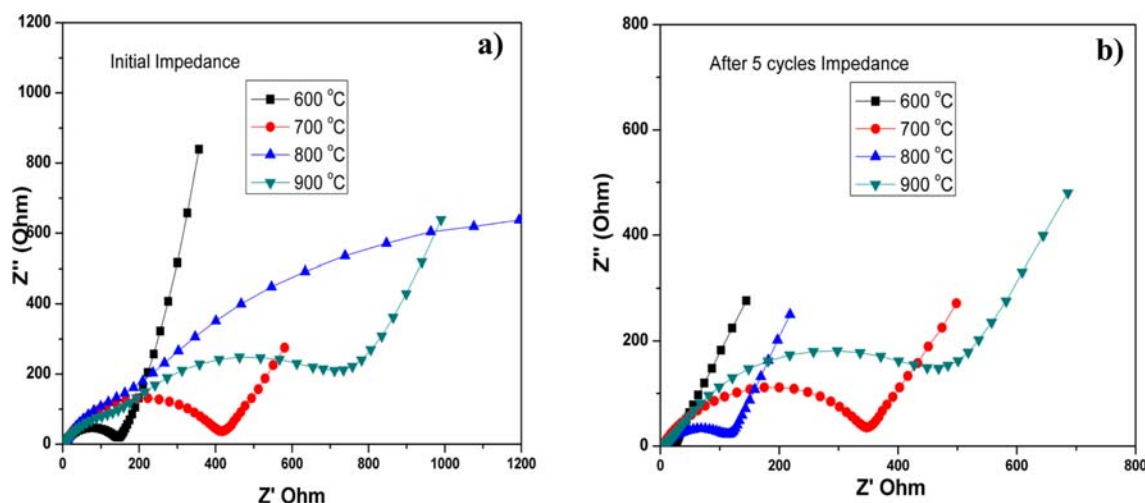


Fig. 7. Comparison of impedance behavior exhibited by (Li/Li⁺ cells containing LiCoO₂ cathode): (a) As fabricated and (b) cells completing 5 cycles.

4. CONCLUSIONS

By adopting a novel gelatin-assisted combustion method, LiCoO₂ has been prepared at different temperatures ranging from 600 to 900 °C, in an attempt to understand the effect of synthesis temperature upon electrode properties. Interestingly, a temperature as low as 600 °C is found to be sufficient to prepare phase pure and rhombohedral LiCoO₂, which is lower than the temperatures reported in the literature on the same topic. Presence of hexagonal particles with definite grain boundaries, possessing an average particle size of ~100 nm is obtained at 600 °C. Further, an enhanced lithium diffusion coefficient value ($2.2 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$) and the lowest impedance value (25 Ω) are exhibited by LiCoO₂ synthesized at 600 °C compared with the same prepared at 700, 800 and 900 °C. The study demonstrates the feasibility of deploying a novel and low temperature, gelatin-assisted combustion method to prepare phase pure and better performing LiCoO₂ besides evidencing the variation of electrode properties such as phase purity, surface morphology, particle size and diffusion kinetics as a function of temperature involved in the synthesis approach.

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