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A novel solid state reaction route to the preparation of LiCoO$_2$ using micro porous filter paper as scaffolds

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Abstract

A novel solid state reaction method has been followed to prepare LiCoO$_2$ (LCO) using micro porous filter paper as scaffolds. FT-IR spectroscopy confirms the vibration spectrum for the identification of CoO$_6$ as well as LCO. XRD diffraction analyses confirmed the formation rhombohedral crystal system of the prepared LCO materials with R-3m space group. The sharp XRD diffractogram of filter paper scaffold LCO demonstrate its crystallinity and purity. The presence of high intensity (003) plane, formation of Co–O–Co linkage with (104) plane and splitting of (006)/(012); (108)/(110) planes confirm layered structure of the prepared LCO. FESEM demonstrate that the presence of micropores in the cellulose backbone of filter played significant role for the solid state reaction and can be used as a scaffold to change the morphology of LCO in the microstructural aspect. UV-visible spectroscopy study reveals that the band gap energy of filter papers assisted LCO are less than the LCO prepared directly from raw materials.

Introduction

To power the world’s needs for portable energy storage system LCO has been emerged as the popular choice of cathode materials in rechargeable lithium ion batteries (LIBs) since its first introduction by Goodenough et al [1]. LCO has been used as cathode material by SONY Corporation, Japan in 1991 for first commercialized LIB. Since then despite of the huge development having been made in various cathode candidates, no one can deny the wide applicability and universality of LCO-based LIBs [2–5]. Still it has been considered as the leading cathode materials of LIBs [6–9]. High capacity, substantial specific energy and excellent cyclability epitomize its choice compared to other electroactive materials [10, 11]. Energy put in storage of a battery depends on the quantity of Li$^{+}$ in the structure of the cathode which is confined in octahedral sites. These sites must be interconnected with each other in order to permit mass transport. Consequently layered crystallographic geometry of electrode materials is preferred. LCO is the member of transition metal oxides family, exhibits the best properties in respect to these criteria. As a result surface of LCO leftovers renewed for Li transport. Nevertheless, LCO surface with cracked and nanowires form paved an effective way to develop the layer structure for the transportation of Li$^{+}$ ions through its structure [12, 13].

It is also well known that layered structure of LCO reveals two polymorphs depending on synthetic temperature and preparation method. LiCoO$_2$ produced at low temperature (∼400°C) (LT-LCO) has a cubic spinel structure with the space group Fd3 m [14–21]. HT-LCO prepared at high temperature (>850°C), has the same chemical formula as that of the LT phase but with a different cationic arrangement and possess rhombohedral layered structure [9]. LT-LCO exhibits a large hysteresis between charging–discharging process [22, 23] which is because of mixing Co$^{3+}$ and Li$^{+}$ in the structure, preventing the formation of layered conduits for Li$^{+}$ diffusion. Therefore material calcined at higher temperature to yield HT-LCO, that possesses alternating planes of Co$^{3+}$ and Li$^{+}$ in the hexagonal ABCABC oxygen packing [24] providing superior electrochemical properties in LIBs [25].
However, electrochemical performance of LiCoO$_2$ for use in LIBs greatly varies with the synthetic methods. Optimized synthetic conditions are necessary to improve the electrochemical behavior of the LCO materials. Various methods such as solid state reaction [26], sol–gel [27], oxalate [28], co-precipitation [29], molten salt [30], hydrothermal [31], template [32], spray pyrolysis [33], polymer pyrolysis [34], and starch assisted combustion [35] have been reported to prepare LCO. Solid state reaction route is commonly applied method to synthesize commercial LCO despite the success of other approaches for preparing LCO material with better homogeneity and finer particles [36]. Other methods require large quantity of solvent than the solid state reaction. Indeed, these methods sometimes require sophisticated instrumentation, difficult conditions and organic materials like citric acid, ethylene glycol, polyvinyl alcohol, etc [37]. The aforementioned limitations make them hard to be used in industrial production compare to the solid state reaction method. For example, complex processes and production cost impede sol–gel reaction process to be used in industry [38]. The synthesis parameters such as stirring, flow rate, temperature, pH and atmosphere of the co-precipitation method are practically difficult to control [39]. In contrast the commercial potentiality of LCO preparation via solid state reaction route is mainly due to the simplicity and cost-effectiveness of the process. The easy synthesis parameters of solid state reaction method retains its position in industry even though the requirement of high-temperature for heating the precursor materials over a long time and the formation of irregular morphologies and broad particle-sizes LCO materials [40]. In the consideration of commercial applications, it is hence necessary to develop an improved solid state reaction route for the preparation of regular morphologies and uniform particle sizes LCO materials. In this paper, LCO powders have been easily prepared from precursor materials and water via solid state reaction method at high temperature using filter paper as scaffolding. We have been employed soft template of cellulose filter paper as a scaffold for an improved solid state reaction route of the precursor’s material instead of ball milling process of the conventional method. Fourier-transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and UV-visible spectroscopy techniques were used to characterize the prepared LCO materials. To the best of our knowledge, this is the first attempt of preparing LCO materials in which filter paper has been taken as skeleton.

**Experimental**

Analytical grade LiOH.H$_2$O and (CH$_3$COO)$_2$Co.4H$_2$O were purchased from Loba Chemie Co. Ltd and Sisco Research Laboratories Pvt. Ltd (SRL), India respectively. Whatman filter paper (Cat no 1001125, Made in England) and double ring filter (Cat no 1102110, Made in China) were used in this study. Aqueous solution of LiOH.H$_2$O and (CH$_3$COO)$_2$Co.4H$_2$O were prepared by dissolving stoichiometric amount substances in deionized water using two separate measuring flasks. Then a certain amount of LiOH.H$_2$O solution was poured into a petri dish. Filter paper was immersed into the petri dish to absorb the solution. LiOH.H$_2$O solution-saturated filter paper was then placed in an electric oven and heated at 110 °C for 2 h to remove water. Li$^+$ grafted filter paper was cooled to room temperature and placed into a petri dish again. Then it was logged by (CH$_3$COO)$_2$Co.4H$_2$O solution and water part was removed in similar manner. Afterwards, calcination reaction of Li$^+$ and Co$^{2+}$ transfixed filter paper was carried out at 700 °C for 6 h in muffle furnace yielded LCO. Each of the filter paper was prepared in accordance with the aforementioned procedure to synthesize LCO. To compare the properties of prepared LCO another sample without filter paper via solid state method of same conditions was also prepared. LCO$_0$, LCO$_A$ and LCO$_{AL}$ terms are used for blank, Whatman and double ring filter paper assisted LCO materials. FTIR, FESEM, XRD and UV-visible spectroscopy techniques were applied for characterization of the prepared LCO materials.

**Fourier transform infrared spectroscopy (FT-IR)**

FT-IR measurements of prepared samples were carried out by IR Tracer-100 of Shimadzu Corporation, Japan. Prepared LCO materials were well mixed with KBr for FT-IR experiments. After that the mixture was pressed with a pressing machine to obtain a transparent pellet. Each LCO sample pellet was scanned in the wavenumber range of 400–4000 cm$^{-1}$ and data was recorded for analyses.

**Field emission scanning electron microscopy (FESEM)**

Prepared LCO sample was suspended in ethanol. 2–3 drops of the suspended LCO sample was added on the conductive carbon tape pasted on the alumina plate. Then it was dried and air blown to remove excess powder from the sample plate. After sputtering with gold the plate was mounted on the sample chamber for SEM.
operation. JSM-7610, Shimadzu, Japan, SEM machine was used to investigate the morphology of the prepared LCO materials.

**Powder x-ray diffraction (XRD)**

Bruker Advance D8 XRD diffractometer was used to investigate the phases present in the prepared LCO materials. Sample holder of the diffractometer was loaded with LCO material and mounted on the diffractometer. CuKα monochromatic beam (\(\lambda = 0.15406 \text{ Å}\)) produced at 40 kV and 40 mA was used to scan \((2\theta)\) the sample from 10 to 70°.

**Parameters such as x-ray density, bulk density, grain size and porosity**

X-ray density \(\rho_x\), bulk density \(\rho_b\), grain size \(D\) and percentage of porosity of the prepared LCO samples were theoretically calculated from x-ray diffractograms using the following equations.

X-ray density,
\[
\rho_x = \frac{ZM}{NV}
\]

where \(M\) is the molecular mass of the corresponding composition, \(N\) is the Avogadro’s number \((6.023 \times 10^{23} \text{ mole}^{-1})\), \(V\) is the volume of the unit cell and \(Z\) is the number of molecules per unit cell.

Bulk density,
\[
\rho_b = \frac{m}{V}
\]

where \(m\) is the mass of the sample, \(V\) is the volume of the sample.

Grain size,
\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]

where \(D\) is the crystal size; \(\lambda\) is the wavelength of the x-ray radiation \((\lambda = 0.15406 \text{ nm})\) for CuKα, and \(\beta\) is the line width at half-maximum height.

\[
\text{Porosity} = \left(1 - \frac{\rho_b}{\rho_x}\right) \times 100\%
\]

The measure of porosity in the prepared LCO sample was obtained from the difference of bulk density \(\rho_b\) and x-ray density \(\rho_x\).

**UV-visible spectroscopy**

Certain amount of LCO sample was dissolved in ethanol to prepare solution. Then solution was transferred in cuvette and it was placed into the cuvette holder of UV-visible spectrometer for measuring spectra. The absorption spectra of each LCO sample were obtained using UV-1800 spectrometer of Shimadzu Corporation, Japan, at the range 200–800 nm. Tauc plot was used to calculate the band gap energy for each LCO materials.

**Results and discussion**

A simple solid state reaction route followed to prepare lithium cobalt oxides (LCO). LCO materials were prepared in three steps as shown in figure 1. In the first step \(\text{Li}^+\) ions have been grafted from its solution by absorption into the pores of filter paper which is simply cellulosic materials. Upon evaporation the \(\text{LiOH.H}_2\text{O}\) solution-saturated filter paper \(\text{Li}^+\) ions together with \(-\text{OH}\) groups of cellulose entrapped into the pores. In the step two \(\text{Co}^{2+}\) ions have also been embedded from its aqueous solution in same technique. Finally, calcination reaction \(\text{Li}^+\) and \(\text{Co}^{2+}\) transfixed filter paper at 700 °C for 6 h in muffle furnace yielded black colored crystalline solids of LCO. For comparison a blank (without filter paper) reaction of same conditions was carried out and blackish colored LCO was obtained. A series of experiments such as FT-IR, FESEM, XRD and UV-visible techniques were applied for characterization of the prepared LCO materials.

\[
\text{O} = \text{Co} - \text{O} - \text{Li}^+\text{ bonds constitute the oxide network of LCO. The oxide network made of Co–O stretching vibration of CoO}_6\text{ octahedra. FT-IR spectroscopy has been used to investigate the presence of such vibrational peaks in the prepared LCO materials. Figure 2 shows the FT-IR spectrum of the prepared LCO}_0,
\]
LCO_A and LCO_AL materials. Bands in the frequency range from 570 to 600 cm$^{-1}$ are assigned for the Co–O stretching vibration of CoO$_6$ octahedra $^{[41]}$. While the lower frequency peaks appeared around 460 cm$^{-1}$ corresponding to the O–Co–O bending motions $^{[15, 42]}$. One peak observed around 1090 cm$^{-1}$ represents C=O vibration $^{[43]}$. In addition, bands of –OH group due to the absorption of water molecule has been observed at 1630 cm$^{-1}$ and 3400 cm$^{-1}$. It is thought that the appearance of C=O and –OH groups peak were due to the strong absorption of CO$_2$ and H$_2$O on LCO in the air. Results of FT-IR obtained in this study are in close agreement with other studies $^{[44]}$.

Surface morphologies of the prepared LCO materials were investigated by FESEM. Figures 3(a)–(c) represented the FESEM images of the LCO prepared without filter paper, using double rings filter paper and Whatman filter paper, respectively. It is clearly evident from figure 3 that the prepared LCO materials have distinct differences in their morphologies. In three cases the shape of the materials are different. LCO prepared without filter paper possessed polyhedral shapes (figure 3(a)) while LCO prepared with Whatman filter paper owned regular disc like shape and almost regular sizes (figure 3(c)). And double rings filter paper assisted LCO provided different shapes than the other two. Here micropores present in the cellulose backbone of filter paper might be acted as microreactor for the solid state reaction of preparing various morphologies LCO materials. Hence, filter papers may be used as a scaffold to change the morphology of LCO in the microstructural aspect. Its application as a structure directing soft template will be an effective method for the formation of LCO materials for use as cathode in Li-ion battery.

XRD diffraction analyses of the prepared LCO_0, LCO_A and LCO_AL materials are represented in figure 4. The diffraction peaks at 2θ of 18.977, 36.821, 38.519, 44.771, 59.294, 65.186 and 68.573 corresponding to the plane (003), (101), (006)/(012), (104), (015), (107)/(009), (018)/(110) and (113) confirmed the formation rhombohedral crystal system of the prepared LCO materials with R-3m space group $^{[45]}$. These peaks are in good agreement with the prepared LCO samples. However, a significant difference among the diffractogram of LCO_0, LCO_A and LCO_AL are observed. The diffractogram of LCO_A and LCO_AL are very sharp indicating that LCO materials prepared with the assistance of filter papers are highly crystalline nature. LCO_A and LCO_AL have no impurity peaks. In contrary, the diffraction pattern of LCO_0 has some addition Li$_2$CO$_3$ and Co$_3$O$_4$ impurities peak. Impurities of LCO_0 might have been resulted from the constituent metals strong tendency for the formation of their oxide particles. The fact of layered feature in the prepared LCO materials have
been identified by the presence of high intensity (003) plane and the formation of Co–O–Co linkage with (104) plane [46]. Indeed, the formation of layered structure of the prepared LCO compounds has been also confirmed from clear splitting (006)/(012) and (108)/(110) planes. The XRD information’s of the prepared LCO materials are given in table 1.

The Reitveld refinement method of Fullprof software has been employed to identify the exact crystalline phases present in the prepared LCO materials [47]. The Crystallographic Information Files (CIFs) used for the refinement and obtained from ICSD database under the code 1533825 [48]. The Reitveld plots are shown in figure 5. It can be seen that the filter paper assisted LCO materials have single phase (R3m) structure. However LCO_0 has multiphase structure. Values of Rp, Rwp, Rexp and \(\chi^2\) from the Reitveld plots are listed in table 2. The obtained values in table 2 indicate a good agreement between the calculated and observed diffractograms.

LCO crystallizes in the layer structure in which the Li\(^{+}\) ions as edge sharing octahedra lied between the extended anionic sheets of cobalt and oxygen atoms. All the atoms in each hexagonal close packed layer arranged in a regular triangular lattice. According to Bragg’s law [49].
\[ 2d \sin \theta = n \lambda \]  

(5)

where \( n \) is the order of diffraction (usually \( n = 1 \)), \( \lambda \) is the x-ray wavelength and \( d \) is the spacing between planes of given Miller indices \( h, k \) and \( l \). In the LCO hexagonal structure, the plane spacing \( d \) is related to the lattice constants \( a, c \) and the Miller indices by the following relation [49].

\[
\frac{1}{d_{hkl}^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}
\]

(6)

Lattice parameters of the prepared LCO_0, LCO_A and LCO_AL samples are calculated using equation (6) and given in table 3. The calculated \( a \) and \( c \) values of the prepared LCO can be compared with those reported by
Akimoto et al [50]. a and c values of the prepared LCO_0 sample are little bit higher than the LCO prepared using filter paper.

Increase of the lattice parameter a and c values of the LCO_0 can be attributed to the deficiency of Li^+ ion in their layer structure (x < 1 in Li_xCoO_2). This deficiency may be resulted from the formation of Li_2CO_3 and Co_3O_4 during the preparation of LCO without filter paper. The formation of those impurities can be also confirmed from the XRD spectrum (figure 4(c)) of LCO_0. On the other hand, a and c values of the prepared LCO_A and LCO_AL are close to the standard one [45]. It can be therefore concluded that a balanced electronic attraction exists between the CoO_2 layers with lithium ion in the hexagonal structure (x \approx 1 in Li_xCoO_2) of the prepared LCO_A and LCO_AL. The obtained lattice parameter values of the prepared LCO materials were used to calculate unit cell volume using the following equation [51].

\[
V = \frac{2}{\sqrt{3}} a^2 c
\]

Grain sizes were calculated using equation (3). The calculated values are listed in table 3. Figure 6 presented the variation of lattice parameter and volume of the prepared LCO samples with their grain size.

Then, equations (1) and (2) has been used to calculate the x-ray density (\( \rho_x \)) and bulk density (\( \rho_b \)) of the prepared LCO materials, respectively. The calculated values of \( \rho_x \) and \( \rho_b \) are given in table 4. The calculated value \( \rho_x \) of LCO_A and LCO_AL are higher than LCO_0 material. It may be resulted due to the balanced electronic attraction between the CoO_2 layers of LCO_A and LCO_AL crystal structure. In addition, \( \rho_b \) value of the prepared LCO materials has been also resulted from their lattice parameter (a and c) value and molecular weight (M). Similar pattern is obtained in the bulk density values of the prepared LCO materials. Thereafter, we calculated the percentage of porosity present in the prepared LCO materials from the obtained theoretical values of \( \rho_x \) and \( \rho_b \). The obtained values are given in table 4.

It is observed that the bulk density is lower than the x-ray density and relation among them for the prepared LCO samples are depicted in figure 7(a). It is also observed that \( \rho_b \) of LCO_A and LCO_AL are higher than

| Table 3. Calculated lattice parameter value, volume and grain sizes of LCO samples. |
|---|
| Sample | a (Å) | c (Å) | c/a | V (Å³) | Grain sizes (nm) |
| LCO_0 | 2.867 | 14.499 | 5.057 | 137.61 | 187 |
| LCO_A | 2.820 | 14.109 | 5.003 | 129.55 | 75 |
| LCO_AL | 2.818 | 14.094 | 5.001 | 129.23 | 68 |

| Table 4. X-ray density, bulk density and porosity of the prepared LCO samples. |
|---|
| Sample | X-ray density, \( \rho_x \) (g.cm\(^{-3}\)) | Bulk density, \( \rho_b \) (g.cm\(^{-3}\)) | Porosity (%) |
| LCO_0 | 2.361 | 1.786 | 24 |
| LCO_A | 2.508 | 1.899 | 24 |
| LCO_AL | 2.508 | 1.883 | 25 |

Figure 6. Variation of (a) lattice parameter with grain size (b) volume with grain size.
LCO_0. This may be due to the nucleation and growth of LCO in the defined pore of filter paper. However, a nonlinear relation between porosity and bulk density of the prepared LCO materials has been obtained. This relation is depicted in figure 7(b).

Next, we investigated the compositional analyses of the prepared LCO_A and LCO_AL materials. It is depicted in figure 8. The EDS spectrum has shown the presence of only Co and O elements in the prepared LCO_A and LCO_AL materials. Indeed, it clearly demonstrated the absence of other elements as an impurity in the prepared LCO_A and LCO_AL materials. Thus, laboratory grade filter paper may have a great potentiality for the preparation of LCO materials.

Electronic conductivity is a decisive factor to understand the performance of LCO material in rechargeable Li-ion batteries. Electronic structure of this compound has been previously studied by using several techniques such as first principle methods [52], x-ray photoelectron spectroscopy (XPS) [53] and x-ray absorption spectroscopy (XAS) [54]. Li (2s¹), Co (3d⁷, 4s²) and O (2s², 2p⁴) are the valence electron of LiCoO₂. The valence and conduction bands of this compound are mainly formed from the contribution of 2p state oxygen orbital and 3d state cobalt orbital [55]. The hybridized orbital of LCO has the corresponding electronic configuration as (t₂g){⁶–(e₅g)⁰}. Band gap values E_g of the prepared LCO materials are the function of electronic transition from (t₂g){⁶ orbital to (e₅g)⁰ orbital. Transitions of electron in the prepared LCO materials have been investigated from their UV-visible absorption spectra. The spectrum was recorded in the visible and UV region ranges from 200–800 nm. Figure 9 represents the obtained UV-visible absorption spectra of the prepared LCO_0, LCO_A and LCO_AL materials. It has been observed from the UV-visible spectra that the appearance of absorption hump occurred in the high frequency (lower wavelength) region.

Band gap values of different LCO samples have been determined using the Tauc equation [56].

\[ (\alpha h\nu)^{1/n} = A(E - E_g) \]

where \( \alpha \) is the absorption constant, \( A \) is a constant, \( E = h\nu / \) is the photon energy, \( E_g \) is the band gap energy, and \( n = 1/2 \) for direct transition of electron. The obtained Tauc plots of different LCO samples have been shown in the inset of figures 9(a)–(c). It is seen from Tauc plot that a tangent to the slope of \((\alpha h\nu)^2\) intersecting with x-axis gave band gap energy. Band gap values for LCO_0, LCO_A and LCO_AL are 5.4577, 5.0640 and 5.0937 eV,
respectively. The band gap energy of filter papers assisted LCO are less than the LCO prepared directly from raw materials. In case of LCO_A and LCO_AL the band gap energy decreased by 7% and 6%, respectively in compare to LCO_0 one. These results clearly indicate the effect of particle sizes (table 3) and cellulosic carbon on the obtained values. The calculated band gap energies of different LCO samples are depicted in figure 10.

**Conclusion**

A simple but improved solid state reaction method of preparing LiCoO_2 has been narrated. Li^+ and Co^{2+} have been grafted into the cellulose matrices of filter paper by absorption. FT-IR spectroscopy confirms the presence of O–Co–O bonding in CoO_6 octahedron as well as LiCoO_2. XRD diffraction analyses confirmed that filter
paper assisted LCO is pure crystalline solid and possesses rhombohedral layered crystal structure with R-3m space group. Filter paper assisted LCO has one major Li$_x$Co$O_2$ ($x \approx 1$) phases while that for without filter paper resulted the formation of second phases such as Li$_2$CO$_3$, Co$_3$O$_4$ in the prepared Li$_x$Co$O_2$ ($x < 1, y < 1$) compounds. Filter papers may be used as a scaffold to change the morphology of LCO in the microstructural aspect. Band gap energies reveal that filter papers assisted LCO are more conductive than LCO prepared directly.

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Conflict of interests

The authors declare that they have no conflict of interests.

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