Synthesis of nanocrystalline LiCoO$_2$ powders by polymeric combustion process: an investigation on the effect of different carboxylic acids as fuel

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Abstract Layer-structured nanocrystalline LiCoO$_2$ powders were prepared by polymeric combustion process using metal nitrates and different carboxylic acids as precursors. Three different carboxylic acids named citric, tartaric, and polyacrylic were experimented in order to synthesize ultrafine LiCoO$_2$ nanopowders. The combustion behavior of polymeric intermediates and the formation of LiCoO$_2$ structures were identified through thermogravimetry and differential thermal analyzer (TG/DTA), FTIR, XRD, SEM, and TEM investigations. The correlation between the microstructure of the polymeric intermediates and their thermal degradation profile was observed by their scanning electron micrographs and TG/DTA thermograms. The result found that the effective combustion was occurred only in citric acid (CA)-derived polymeric intermediate due to its porous microstructure, which leads to the formation of phase pure LiCoO$_2$ powders with no organic residual. The TEM analysis reveals that the particle size of the synthesized LiCoO$_2$ powders by the optimized CA-assisted combustion process at 450 °C existed in the range between 30 and 40 nm.

Keywords Combustion synthesis, Carboxylic acid, Nanocrystalline, Cathode materials, LiCoO$_2$

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Introduction

LiCoO$_2$ with layer structure has been widely investigated for the lithium battery application, as a cathode material, because of its excellent electrochemical performance including high specific capacity and durable cycle life compared to other lithium-based transition metal oxides.$^{1,2}$ Thus, it has been used in many of the commercial cells based on lithium ion technology.$^3$ However, the challenge is to increase their charge/discharge rate, which influences their commercial viability by meeting the future demand in mobile electronics and automotive transformation.$^4$ Electrochemical performance of cathode materials mainly depends on their physicochemical properties including their crystalline size, surface area, controlled stoichiometry/homogeneity, and other morphological features.$^4,5$ Recent developments in nanoscience and technology offer many advantages to lithium battery technology, which includes increased lithium insertion/removal rates, higher electrode–electrolyte contact area, significant change in electrode potential, and the structural stability of electrode materials against the wide range of lithium intercalation.$^4,5$ It is also proved that the nanocrystalline LiCoO$_2$ exhibits enhanced electrochemical performance such as specific capacity and cyclic ability due to their smaller particle size and larger surface area.$^7,8$ The challenging task is the effective synthesis of nanostructured electrode material with desired structural and morphological features, which lead to the expansion of a variety of synthesis routes.

Metal oxides were traditionally synthesized by employing solid-state method that involves mechanical mixing and high temperature heating of precursor chemicals.$^9,10$ This eventually leads to the formation of larger crystalline/particle size and poor in phase purity as well as composition homogeneity.$^9,11$ As the alternate, wet chemical processes such as solgel, hydrothermal, combustion, co-precipitation, and spray drying were reported for the synthesis of nanostructured metal oxides including LiCoO$_2$ cathode materials.$^{12–16}$ Among them, the combustion process is found to be simple and versatile one for the synthesis of nanostructured multi-component oxide materials relatively at lower temperatures.$^{16–19}$ A self-propagated exothermic reaction between the inorganic reagents (mostly metal nitrates) and the organic fuels (diformyl hydrazine, urea, glycine, citric acid (CA), tetraformal triazine, etc.) will be effectively used to form nanocrystalline metal oxides.$^{22,23}$ Carboxylic acids, including CA and tartaric acid (TA), play vital roles as a fuel during the combustion reaction, chelating agents for metal ions and the polymeric precursor that inhibits the
precipitation of metal ions. These result in their thermal behavior during the combustion reaction and affect the physiochemical properties such as crystallite size, phase purity, and morphology of the final products. Significant reports have been made on the combustion process based on different carboxylic acids for the synthesis of metal oxides individually.24–26 To the best of our knowledge, there is no report that has been made in order to compare the effect of different carboxylic acids on the structural features of polymeric intermediates and their thermal decomposition mechanism under uniform reaction conditions. This information is very much essential to select a suitable precursor for the synthesis of multicomponent metal oxide systems including LiCoO$_2$.

Hence, the present investigation deals with a systematic comparative study on the effect of various carboxylic acids such as CA, polyacrylic acid (PAA), and TA on the polymeric combustion process for the synthesis of residual organic-free phase pure LiCoO$_2$ nanopowders. Effects of different carboxylic acids on the structural and microscopic features of the polymeric intermediates and their thermal degradation profile in order to form nanocrystalline LiCoO$_2$ powders were investigated using thermogravimetry and differential thermal analyzer (TG/DTA), FTIR, XRD, SEM, and TEM analysis.

**Experimental**

LiNO$_3$ (99.8%, SD Fine Chemical) and Co(NO$_3$)$_2$·6H$_2$O (GR grade, Merck, India) were used as metal ions. CA anhydrous (GR grade, Merck), polyacrylic acid (AR grade, Qualigens), and TA (AR grade, Merck) were used as chelating agents for metal ions as well as fuel during the combustion reaction. All the precursors were used without further purification. The synthesis procedure for the preparation of nanocrystalline LiCoO$_2$ powders by the combustion of polymeric intermediate prepared with three different carboxylic acids (CA, TA, and PAA) is shown in Fig. 1. The calculated amount of metal nitrate and the carboxylic acid solutions were mixed by keeping metal ion to carboxylic acid ratio of 1:1, under constant stirring condition. The obtained clear transparent solution with pink color was evaporated at 80 °C for 6 h. Continuing the evaporation turned the liquid into a viscous resin. Further, the drying process of resin at 150 °C for 24 h caused the formation of dried polymeric intermediates. Figure 2 a–d shows the photographs of different stages involved in the synthesis of foamy polymeric intermediate with M/CA = 1:1. The drying process caused the generation of huge amount of gaseous molecules, which results in the expansion of polymeric resin and forms the foamy intermediate. The possible mechanism for the formation of foamy intermediate is schematically shown in

![Figure 1 Steps involved in the synthesis of nanocrystalline LiCoO$_2$ powders by polymeric combustion process](image-url)
Structural coordination of the dried polymeric intermediates as well as the synthesized LiCoO$_2$ powders was investigated using FTIR – 8000 spectrometer of Shimadzu, Japan, employing the wave number between 400 and 4000 cm$^{-1}$ with KBr diluter. The FTIR spectra were recorded employing 4 cm$^{-1}$ resolution with 40 scans per specimen. Powder X-ray diffraction patterns were recorded using PANalytical (Philips) X-ray powder diffractometer, model X Pert PRO MPD, employing Cu–K$_\alpha$ radiation. Scherer’s formula was used to calculate the average crystallite size of the synthesized LiCoO$_2$ powders employing line broadening profile. Instrumental broadening was taken into account, while calculating crystallite size, which was identified using NBS standard silicon.$^{27}$ Thermal degradation profile of the polymeric intermediates was identified using simultaneous TG/DTA instrument from Setaram, France. A total of 2–3 mg of dried intermediate samples were used for this analysis with the heating rate of 10 °C min$^{-1}$ from 30 to 600 °C under flowing oxygen atmosphere. Microscopic morphological features of the polymeric intermediates and synthesized LiCoO$_2$ powders were analyzed using Hitachi S-3400N scanning electron microscope, Japan. The samples were dispersed on the conducting tape pasted on the SEM sample holder and coated with carbon in order to create conducting surface. The partial size and their shape of the synthesized LiCoO$_2$ powders were further investigated by TEM characterization (JEOL-2010F) employing 100 k as electron beam accelerating voltage. The synthesized LiCoO$_2$ powders were well dispersed in acetone, and the dispersion was dropped on a copper grid coated with conducting carbon and allowed for room temperature drying prior to TEM analysis.

Results and discussion

Characterization of polymeric intermediates

Figure 3a shows the photograph of the polymeric intermediates obtained using three different carboxylic acids, CA, TA, and PAA. From Fig. 3a, the porous foamy structure was observed only for intermediate obtained using CA, whereas TA- and PAA-assisted processes resulted in the formation of solid masses. This is due to the effective polymerization, cross-linking, and chelation mechanism of CA, which completely inhibits the precipitation of metal ions as citrates. Further, the generation of gaseous molecules during the drying process expands the polymeric network and caused the formation of porous structure. In other cases, the poor polymerization as well as precipitation of metal carboxylates exhibits the poor expansion of polymeric matrix during the drying process and results in the formation of solid masses. Figure 3b–d shows the SEM images of dried intermediates prepared with CA, PAA, and TA respectively. From Fig. 3b, the SEM micrograph of polymeric intermediate prepared with CA showed the polymeric structure with large number of voids, which is caused by the evolved gases during the drying process and results in the formation of solid masses. Figure 3c for the intermediate prepared with PAA shows solid surface with big voids, which resulted in the smaller volume as observed in Fig. 3a. SEM image (Fig. 3d) of the intermediate...
Figure 3  (a) The photograph and (b–d) the SEM images of polymeric intermediates prepared with three different carboxylic acids [b – CA, c – PAA, and d – TA]

Figure 4  (a) FTIR spectra and (b) XRD patterns of the polymeric intermediates prepared with three different carboxylic acids
prepared with TA showed porous structure consisting clusters, which is confirmed as crystalline metal tartrate precipitation, and further it has been confirmed by XRD analysis.

The structural coordination of dried intermediates obtained by employing CA, PAA, and TA as chelating agents was investigated through FTIR analysis, and the obtained spectra are shown in Fig. 4a. The observed common peaks at 3417–3444 cm\(^{-1}\) and 2926–2974 cm\(^{-1}\) represent the stretching frequencies of OH (due to the adsorbed moisture) and aliphatic CH groups (from CA, PAA, and TA), respectively, that are present in intermediates.\(^\text{28}\) The observed common peaks at 3417–3444 cm\(^{-1}\) represent the stretching frequencies of OH (due to the adsorbed moisture) and aliphatic CH groups (from CA, PAA, and TA), respectively, that are present in intermediates.\(^\text{28}\) The shoulder band at 1725 cm\(^{-1}\) observed in CA-derived polymeric intermediate represents the asymmetric vibration of bridging COO\(^{-}\) group, and their respective symmetric vibration is observed at 1314 cm\(^{-1}\). Similar peaks are not observed in the FTIR spectra of intermediates prepared using TA and PAA. Hence, it confirms the better polymerization in CA-derived intermediates.\(^\text{28}\) The common peak observed at 1608–1632 cm\(^{-1}\) region, for all the intermediates, is assigned to the asymmetric stretching vibration of COO\(^{-}\) groups. Similarly, the observed medium intense band at 1417 cm\(^{-1}\) for all the intermediates (in PAA, it is observed as the shoulder band) indicates the symmetric stretching vibration of COO\(^{-}\) groups.\(^\text{28}\) The peak observed at 1254 and 1059 cm\(^{-1}\) are due to stretching vibrations of C–O groups, which confirm the formation of esters, whereas an esterification is not observed in PAA-assisted intermediates because PAA does not have OH group to form ester with COOH group.\(^\text{28}\) The intensity of these ester peaks is more in CA-assisted polymeric intermediates compared to others, which confirm that the CA has been effectively involved esterification reaction and lead to the formation of highly branched polymeric network.

Diffraction patterns of the powdered polymeric intermediates synthesized using three different carboxylic acids were recorded in order to identify their phase nature, and they are shown in Fig. 4b. The CA-assisted intermediate does not show any significant peaks, which confirms the amorphous nature of polymeric structure, whereas the polymeric intermediates prepared with PAA and TA exhibit small peaks, which are due...
to the formation of polycrystalline precipitates of metal carboxylates (in TA-assisted intermediate) and also unreacted metal nitrates (in PAA-assisted intermediate). XRD patterns confirm that polymeric intermediates prepared with PAA and TA exhibit poor polymerization, which are consistent with the results of FTIR and SEM analysis.

**Thermal analysis of polymeric intermediates**

Thermal decomposition mechanisms of the dried intermediates prepared using three carboxylic acid precursors are analyzed in a simultaneous TG/DTA, and the obtained thermograms are shown in Fig. 5. The thermogram of CA-assisted polymeric intermediate shows gradual weight increment up to 225 °C, which may be due to the trapped oxygen by carbon atoms present in the polymeric intermediates. Mechanism of carbon degradation was explained as follows,

$$\text{C} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} \text{ (entangled with sample)} \quad (1)$$

$$\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 \text{ (volatile gas)} \quad (2)$$

Further increase in the temperature caused weight loss of about 6% due to the removal of CO\(_2\) gas as mentioned in Equation (2). The sharp exothermic peak at 320 °C with major weight loss (about 33%) is due to the decomposition of polymeric intermediate through combustion, and it completes at 340 °C. Further weight loss was not observed after 350 °C, which confirms the complete decomposition of CA derivatives as well as the formation of LiCoO\(_2\) compounds, it is also confirmed by FTIR and XRD analysis. The TG/DTA thermogram for PAA-assisted polymeric intermediate showed the 15% weight loss between 50 and 100 °C with endothermic peak that highlights the effective removal of adsorbed moisture. The second weight loss occurred between 225 and 275 °C with exothermic peak due to combustion. The observed lower heat generation indicates the poor combustion, which caused gradual weight loss up to 420 °C.

From Fig. 5, the obtained TG/DTA thermogram of polymeric intermediate prepared with TA shows 5% weight loss between 40 and 70 °C with small endothermic peak (in box), which is due to the removal of absorbed moisture. The gradual weight increment up to 225 °C may be due to the trapped oxygen, which is also observed in CA-assisted intermediates. Rise in the temperature caused about 10% weight loss due to the removal of CO\(_2\) gas, as mentioned in Equation (2). The sharp exothermic peak at 318 °C with major weight loss (about 35%) is attributed to the decomposition of polymeric intermediate due to the combustion. Further heating to 600 °C caused slight weight loss which may be due to the removal of undecomposed organic residuals existing in the intermediates, and it is also confirmed from FTIR results.

**Characterization of synthesized LiCoO\(_2\) powders**

Figure 6 shows the FTIR spectra of LiCoO\(_2\) powders synthesized by CA-, PAA-, and TA-assisted combustion process at 450 °C for 12 h. The observed common FTIR peaks of the synthesized LiCoO\(_2\) using three different carboxylic acids at 510–520 cm\(^{-1}\) and 580–610 cm\(^{-1}\) indicate the asymmetric stretching modes of [CoO\(_6\)] octahedral and confirm the formation of LiCoO\(_2\) structure.\(^{9,10}\) From Fig. 6, the FTIR spectra of LiCoO\(_2\) powders prepared with PAA and TA showed low intense peaks at 1455–1553 cm\(^{-1}\) region, which is assigned to the organic residuals, due to the poor combustion of intermediate as observed in TG/DTA thermogram. The observed poor decomposition of polymeric intermediate prepared with PAA is due to the formation of rigid, nonporous structural features as observed in SEM images. Organic-free LiCoO\(_2\) compound was obtained only from the combustion process employing CA as fuel, which
are very much comparable with reported values of hexagonal cell in the literature.\textsuperscript{33, 34}

Figure 8\textsuperscript{a} and \textsuperscript{b} shows the SEM micrograph of the phase pure/organic-free LiCoO\textsubscript{2} powders prepared by the CA-assisted polymeric combustion process at 450 °C for 12 h. SEM image showed the agglomerated ultrafine LiCoO\textsubscript{2} particles. The detailed microscopic features of the LiCoO\textsubscript{2} particles have been indentified though TEM analysis. Figure 8\textsuperscript{c} and \textsuperscript{d} shows the TEM image of nanocrystalline LiCoO\textsubscript{2} powders at different magnifications. From Figs. 8\textsuperscript{c} and \textsuperscript{d}, it is observed that the synthesized LiCoO\textsubscript{2} powders exhibit sphere-like shape with the size of 30–40 nm, which is very much comparable with the crystallite size calculated from XRD analysis.

Conclusion

Nanocrystalline LiCoO\textsubscript{2} powders were successfully synthesized through polymeric combustion process using three different carboxylic acids named CA, TA, and polyacrylic acid relatively at lower temperature of 450 °C compared to traditional solid-state reaction method. FTIR, XRD, and SEM

**Table 1** Lorentz fit data and the crystallite size of nanocrystalline LiCoO\textsubscript{2} powders prepared with different carboxylic acids (CA, TA, and PAA) at 450 °C for 12 h

| S. No | Name of the process | 2θ (degree) | FWHM\textsuperscript{a} of the 100% peak (degree) | Crystallite size (nm) |
|-------|---------------------|-------------|-----------------------------------------------|---------------------|
| 1     | CA                  | 18.98       | 0.23205                                       | 38.05               |
| 2     | TA                  | 19.07       | 0.42884                                       | 19.28               |
| 3     | PAA                 | 18.99       | 0.17452                                       | 54.98               |

\textsuperscript{a}FWHM = Full width half maximum. Instrumental broadening obtained using NBS standard silicon = 0.09470 (degree).
results confirmed that the CA-assisted process exhibits better polymerization than others, which caused the formation of porous foam-type intermediate. Thermal analysis of polymeric intermediates indicates that the CA-assisted intermediates exhibit better combustion due to the porosity, which leads to the organic-free LiCoO$_2$ powders. Among the three different carboxylic acids, CA-assisted process leads to the synthesis of phase pure nanocrystalline LiCoO$_2$ powders without organic trace and the average crystallite size is found to be 38 nm. TEM analysis reveals that the synthesized nanocrystalline LiCoO$_2$ particles exist in the size between 30 and 40 nm.

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