Glycerol Assisted Polymeric Precursor Route for the Synthesis of Nanocrystalline $LiCoO_2$ Powders

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ABSTRACT

Glycerol assisted polymeric precursor route was investigated for the synthesis of nanocrystalline layered $LiCoO_2$ powders using metal nitrates as metal ion sources, citric acid and glycerol as fuels as well as polymerizing agents. The synthesis process was investigated through TG/ DTA, FTIR, XRD, and SEM analysis. It is observed that the addition of glycerol to citric acid caused the formation of foamy porous intermediate. From FTIR and XRD analysis, it was found that the ethylene glycol assisted polymeric precursor process lead to the formation of organic free single phase crystalline $LiCoO_2$ powder at 600 ^oC for 12 hours and the crystallite size is found to be 45 nm.

Keywords: nanocrystalline $LiCoO_2$, citric acid, glycerol, XRD, FTIR, TG/DTA, SEM.

1 INTRODUCTION

$LiCoO_2$ with Layer structure has been widely used as a cathode material in lithium batteries [1, 2]. Recently, it is found that the nanostructured $LiCoO_2$ powders exhibit an enhanced electrochemical performance compared to their bulk. Physiochemical properties of the nanocrystalline $LiCoO_2$ powders like crystallite size, homogeneity, chemical stability etc., are mainly depending on the synthesis process [3-5]. A number of wet chemical routes such as sol-gel, combustion, polyol, hydrothermal, etc., were investigated for the synthesis of nanocrystalline metal oxides including $LiCoO_2$ powders [6-9].

Among them, polymeric precursor route is found to be a simple and effective soft combustion process for the synthesis of nanocrystalline multi-component oxide powders relatively at lower temperatures [10]. Selection of suitable fuel is an important issue in combustion process. Carboxylic acids like citric acid, tartaric acid, etc., have been extensively investigated for these propose [10, 11]. Apart from that, poly hydroxyl alcohols such as ethylene glycol, polyvinyl alcohol, etc., are used as polymerizing agent (Pechini process) in order to enhance the uniform distribution of metal ions and avoid their precipitation during evaporation [12]. Recently, we have investigated a novel process based on glycerol as polymerizing agent along with citric acid for the successful synthesis of nanocrystalline $LiNiVO_4$ powders relatively at lower temperature [13].

Hence, in the present work, glycerol assisted polymeric precursor route was investigated for the synthesis of nanocrystalline layered $LiCoO_2$ powders using citric acid and glycerol as polymerizing and chelating agents. The complete process was investigated through TG/DTA, FTIR, XRD and SEM techniques.

2 EXPERIMENTAL TECHNIQUES

Fig. 1 shows the schematic of polymeric precursor route for the synthesis of nanocrystalline $LiCoO_2$ powders. Required stoichiometric amounts of lithium nitrate (99.8 %, S. d. Fine-Chem. Ltd.) and cobalt (GR grade, Merck, India) nitrate solutions were made and mixed with citric acid (GR grade, Merck) and glycerol (SQ grade, Qualigens) solutions. Resulting transparent clear pink colour solution was evaporated at 80 ^oC under constant stirring. Continuous evaporation lead to the formation of polymeric resin and it was further dried at 150 ^oC for 12 hours for the removal of excess water. During the drying process the resin has expanded upto 30 times and caused the formation of high foamy nature. Further, the intermediate was calcined at 600 ^oC in order to get nanocrystalline $LiCoO_2$ powders.

FTIR spectra were recorded using FTIR - 8000 spectrometer of Shimadzu, Japan. The measurement was carried out between 400 and 4000 cm^{-1} with KBr diluter. X-ray diffraction (XRD) experiments were carried out using a Panalytical, X-ray powder diffractometer, with Cu Kα radiation. The average crystallite size was calculated from the Scherrer's formula employing line – broadening technique. NBS standard silicon was used for estimation of instrumental broadening [14]. Thermal behavior of the polymeric intermediates was investigated by simultaneous TG/DTA using Labsys thermal analyzer, Setaram, France. Approximately, 3mg of polymeric intermediate was heated at a rate of 10 ^oC min^{-1} between 30 – 600 ^oC. All thermal studies were performed in flowing oxygen. Microstructure of the polymeric intermediates was taken using scanning electron microscope, Jeol, Japan.

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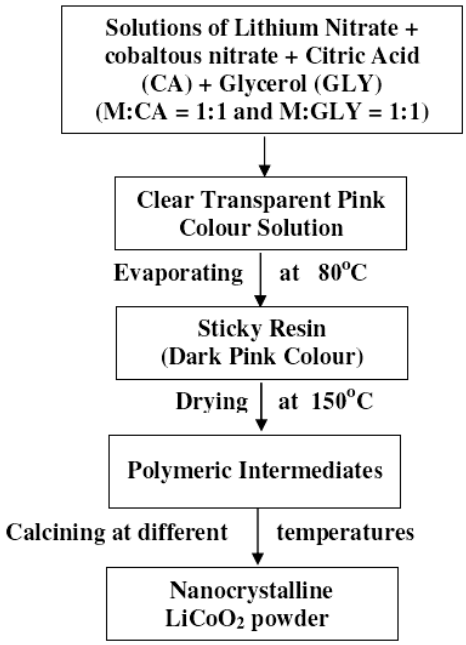

Fig. 1 Flow chart for the synthesis of nanocrystalline $LiCoO_2$ powder by Polymeric precursor route

3 RESULTS AND DISCUAAION

Fig 2a shows the photograph of synthesized foamy polymeric intermediate and the respective microstructure obtained from SEM is shown in fig. 2b. SEM image shows the porous structure with large size of voids. Fig. 3a and 3b are the FTIR and XRD results of polymeric intermediate respectively. From fig. 3a the observed peaks at 3417-3444 cm^{-1} and 2926-2974 cm^{-1} are respectively due to the stretching frequencies of OH (due to the adsorbed moisture) and aliphatic CH groups from citric acid and glycerol [15]. The shoulder band at 1725 cm^{-1} observed in citric acid derived intermediate is corresponds to the asymmetric vibration of bridging COO^- group and the respective symmetric vibration is observed at 1314 cm^{-1}. From fig. 3a, the IR peaks observed at 1608-1632 cm^{-1} and 1400-1415 cm^{-1} region for all the intermediates are respectively due to the asymmetric and symmetric stretching vibration of COO^- groups, which confirm the chelation of metal ions by citric acid [15]. The observed peak free XRD patterns for the intermediates confirm their amorphous nature of the polymeric structure.

The TG/DTA thermogram of the polymeric intermediate is shown in fig. 4. Initial weight loss about 3%, observed between 75 and 100 °C is due to the removal of absorbed moisture. The major weight loss observed in TG curve between 250 and 415 °C is responds to the decomposition of organic derivatives and the respective exothermic peak was observed in DTA curve. Though the combustion reaction completes at 410 °C, there is a gradual weight loss in TG curve up to 500 °C, which indicates the presence of un-decomposed organic residuals even after the completion of combustion reaction. Hence, 600 °C is optimized for the calcinations of polymeric intermediate in order to get organic free $LiCoO_2$ powder.

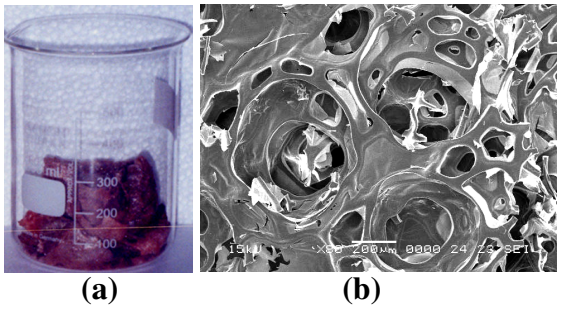

Fig. 2. Photograph (a) as well as scanning electron micrograph (b) of polymeric intermediate

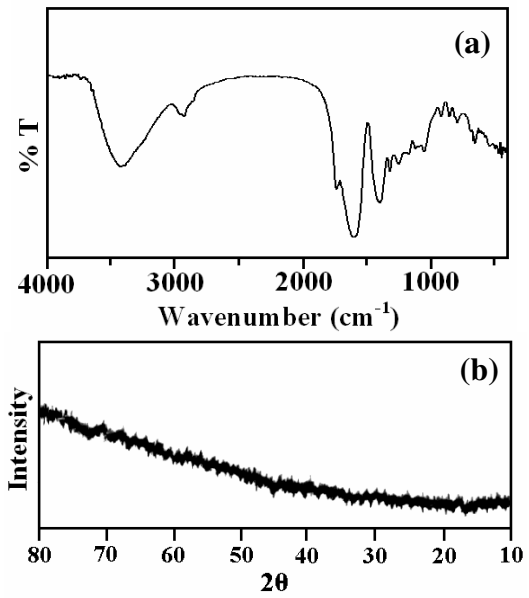

Fig. 3 FTIR (a) and XRD (b) analysis of polymeric intermediate

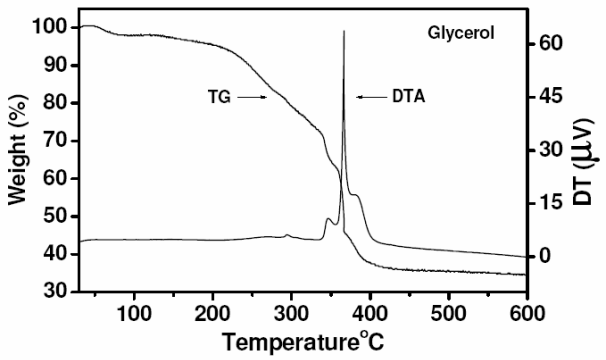

Fig. 4 TG/DTA thermograms of polymeric intermediate

FTIR, XRD and SEM analysis of the synthesized $LiCoO_2$ powders are respectively shown in fig 5a, 5b and 5c. In FTIR spectra, absence of peaks, which are belongs to organic derivatives, indicate their complete decomposition during the calcinations process at 600 ^oC. The observed new peaks at 510- 520 cm^{-1} and 580-610 cm^{-1} region are attributed to the asymmetric stretching modes of $[CoO_6]$ group, which confirms the formation of $LiCoO_2$ structure [16, 17]. From fig. 5b, the observed major peaks at 45^o, 38^o and 19^o respectively for (104), (101) and (003) planes confirm the formation of $LiCoO_2$ phase. Further, it was confirmed by comparing their XRD pattern with JCPDS data and the crystallite size calculated using XRD data is found to be 45nm. The cell parameters obtained for the $LiCoO_2$ powders prepared by citric acid assisted process are a = 2.807 Å, c = 14.028 Å and c/a = 4.998, which are very much comparable with reported values of hexagonal cell in the literature [18, 19]. SEM image of $LiCoO_2$ powder exhibit an agglomeration of fine $LiCoO_2$ particles.

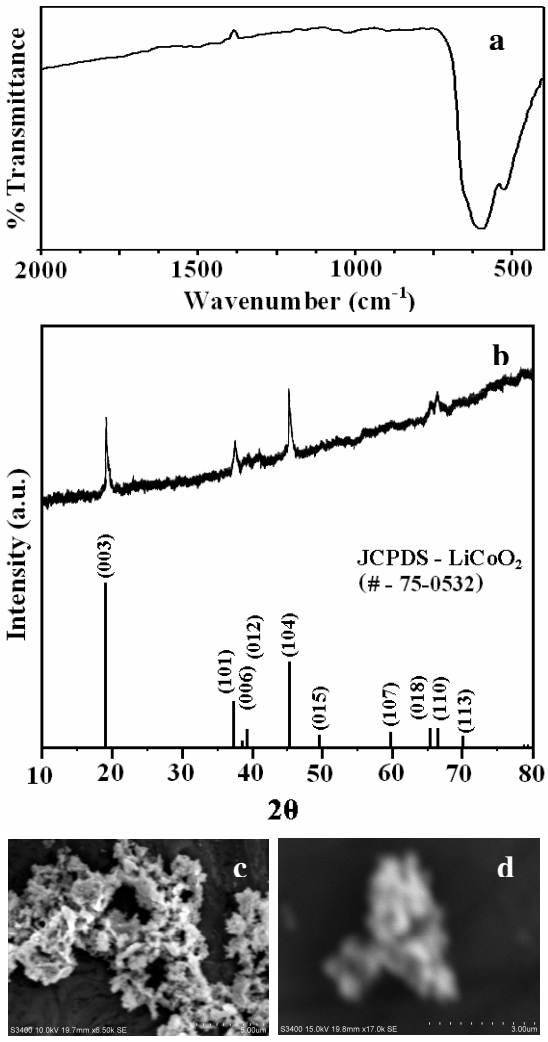

Fig. 5 FTIR (a), XRD (b) and SEM (c & d) analysis of Synthesized $LiCoO_2$ powder

4 CONCLUSIONS

Glycerol assisted polymeric precursor route has successfully investigated for the synthesis of nanocrystalline $LiCoO_2$ powders. Addition of glycerol to citric acid in the precursor solution caused formation of the porous foamy polymeric intermediate. From, TG/DTA, FTIR and XRD analysis, it is confirmed that the decomposition of synthesized foamy intermediate at 600 ^oC results ultra fine nanocrystalline $LiCoO_2$ powders. Crystallite size of the $LiCoO_2$ powders prepared by glycerol assisted polymeric precursor process is found to be 45 nm. Scanning electron micrograph of synthesized $LiCoO_2$ powders exhibits the agglomeration of fine particles.

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