CHAPTER IV
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SYNTHESIS AND CHARACTERIZATION OF NANOCRYSTALLINE SPINEL 
LiMn\(_2\)O\(_4\) AND INVERSE SPINEL LiNi\(_{0.5}\)Co\(_{0.5}\)VO\(_4\) POWDERS BY 
COMBUSTION PROCESSES

4.1 Introduction

Spinel LiMn\(_2\)O\(_4\) powders have been receiving a special attention for rechargeable lithium batteries due to their better electrochemical performance (high discharge voltage), environment compatibility (non-toxicity), lower cost, etc. [1-5]. Moreover, these spinel structures are more stable under electrochemical cycling, since the volume variation in the cubic unit cell is less than 1% with in the controlled composition limits [6, 7]. Recently, another new class of compounds called inverse spinel lithiated transition metal vanadium oxides (LiMVO\(_4\), where M = Co, Ni) also received the attention due to their high voltage versus the Li [8-12]. However, high voltage cathode materials are strong oxidizers, which may create electrolyte degradation problems. In order to overcome such problems and to understand the effects of replacing nickel by cobalt in LiNiVO\(_4\), the mixed vanadium oxides were prepared and characterized [13]. The general formula of the mixed vanadium oxide is LiNi\(_{(1-x)}\)Co\(_{x}\)VO\(_4\). The enhanced electrochemical performance was observed in LiNi\(_{0.5}\)Co\(_{0.5}\)VO\(_4\) powders [14-17].

It should be noted that the charge – discharge characteristics of lithium cells are mainly depend on the physical and chemical properties of the cathode material, such as, particle size, purity of the phase, homogeneity, etc. [18-21]. Electrochemical properties of any cathode materials vary greatly with the synthesis processes, since it plays major role on the physiochemical properties of their final products [22-24]. In recent years, there is a
great interest in the synthesis of nanocrystalline cathode materials, which exhibit an improved electrochemical performance [25-30]. Synthesis process plays a major role to obtain the nanocrystalline cathode materials with desired properties [31, 32]. Synthesis of LiMn$_2$O$_4$ and LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powders by conventional solid state reaction method, which involves high temperature heating of oxide and / or carbonate precursors, exhibits disadvantages such as abnormal grain growth, poor stoichiometry, inhomogeneity etc. and lead to the poor electrochemical performance [33-35]. Hence, wet chemical techniques such as, sol-gel, co-precipitation, hydrothermal, combustion, Pechini process, etc., have been investigated for the synthesis of wide ranges of nanocrystalline metal oxides including the cathode powders for lithium battery application [36-45].

Polymeric citrate process is one of the combustion processes using citric acid, as a fuel as well as chelating agent, which is simple, cost effective and versatile for the preparation of multicomponent metal oxides [46, 47]. Also, it has been used for the synthesis of nanocrystalline LiMn$_2$O$_4$ and LiCoVO$_4$ powders [48, 49]. However, the metal oxides prepared by polymeric citrate processes exhibit disadvantages such as impurity phase as well as residual organics due to the prolonged multi step combustion mechanism [15]. In order to overcome these disadvantages, the prepared powders were sintered at higher temperatures, which resulted bigger crystallite size [28]. Hence, there is a need to modify the polymeric citrate process for the synthesis of phase pure organic free nanocrystalline materials at lower temperature.

In addition to the above, Pechini process is also one among the combustion process, where the polyhydroxy alcohols are used alongwith citric acid as the polymerizing agent [48-50]. Wide ranges of metal oxides were synthesized using Pechini process relatively at lower temperatures. However, the formation of hard crystalline agglomerates is a problem for the Pechini approach. Evidence indicates that the property
of the final product made by Pechini process is mainly depending on the microstructure of its resin intermediates [51]. Hence, it is necessary to optimize the suitable polymeric precursors as well as experimental conditions for the synthesis of metal oxides with desired properties by both polymeric citrate and Pechini process.

Hence, in the present chapter, we have carried out a systematic study of two different combustion processes for the synthesis of nanocrystalline LiMn$_2$O$_4$ powders which are,

- Urea assisted polymeric citrate process (where the fuels are citric acid and urea under acetic condition)
- Nitric acid assisted Pechini process (where the fuels are citric acid and ethylene glycol- effect of the nitric acid addition was investigated)

Also, the following two different combustion processes were investigated for the synthesis of nanocrystalline LiNi$_{0.5}$Co$_{0.5}$O$_4$ powders,

- Citric acid assisted sol-gel combustion process (investigate the effect of citric acid amount for the synthesis of nanocrystalline LiNi$_{0.5}$Co$_{0.5}$O$_4$ powders)
- Effect of various ethylene glycol precursors on Pechini process (the fuels are citric acid and different ethylene glycols such as ethylene glycol, polyethylene glycol-400 & polyethylene glycol-4000)

Thermal behavior of the polymeric intermediates was studied by thermogravimetric and differential thermal analyzer (TG/DTA). Approximately 15 mg of polymeric intermediate was heated at the rate of 10 °C per minute from room temperature to 750 °C in a flowing air ambient and recorded the TG / DTA curves using M/S Rheometric Scientific Co., UK instrument. Also, DSC measurement was carried out for the polymeric intermediate using a DSC 821e/500/575/414183/578. The FTIR spectra were recorded using Shimadzu FTIR/8300/8700 spectrometer. All samples were examined
between 400 and 4000 cm$^{-1}$ and KBr was used as diluter. Powder XRD patterns were recorded using X’ Pert PRO MPD, PANalytical (Philips) X-ray powder diffractometer employing Cu Kα radiation. The crystallite size of the cathode powders was calculated using the Scherrer’s formula [52] and NBS silicon standard was used for the estimation of instrumental broadening. Microstructure of the polymeric intermediates as well as synthesized powders was identified using scanning electron microscope, Hitachi, S-3400N, Japan.

4.2 Urea Assisted Polymeric Citrate Process for the Synthesis of Nanocrystalline LiMn$_2$O$_4$ Powders

Among the combustion processes, polymeric citrate process (where the citric acid is used as a fuel as well as chelating agent for metal ions) has been used for the synthesis of wide range of metal oxides. However, it exhibits some disadvantages like phase impurities, organic residuals, etc., which are due to the prolonged combustion reaction. Recently, we have investigated an interesting new combustion process by adding urea to citric acid alongwith the presence of nitric acid as catalyst, which decreases the ignition temperature as well as duration of combustion process and yields phase pure organic free nanocrystalline oxide powders. Hence, in the present investigation, the effect of urea addition to citric acid in the polymeric citrate process for the synthesis of nanocrystalline LiMn$_2$O$_4$ powders was studied systematically and an optimum total metal ions to urea ratio was identified.

4.2.1 Synthesis

Lithium nitrate (99.8%, Loba Chemic), manganese acetate (99.9 %, Qualigens), citric acid (SQ grade, Qualigens), nitric acid (SQ grade, Qualigens) and urea (SQ grade,
Qualigens) were used for the synthesis of nanocrystalline LiMn$_2$O$_4$ powders by urea assisted polymeric citrate process.

Stoichiometric amounts of lithium nitrate and manganese acetate solutions were mixed with aqueous citric acid and urea. The molar ratio of total metal ions to citric acid (M / CA) was kept constant as 1:2 in the starting solution. Different amount of urea was added, in order to maintain the molar ratio of metal ions to urea as 1:1 and 1:2. LiMn$_2$O$_4$ powders were also prepared without urea (M/ U= 1:0), for comparison to investigate the role of urea in the synthesis process. Concentrated nitric acid was added to the starting solution in the volume ratio of 1: 0.1. Resulting solutions were evaporated at 80 °C for 4 to 6 hours under continuous stirring to remove the water. The viscous of solutions gradually increased and the colour of solution turned in to dark yellow. The evaporation leads the resin formation and the resulting resin was dried at 170 °C for 12 hours. Volume of the resin was expanded and the black coloured bread like porous polymeric intermediates were formed. Further, it was calcined at various temperatures to get nanocrystalline LiMn$_2$O$_4$ powders. Flow chart of the synthesis of nanocrystalline LiMn$_2$O$_4$ powders by urea assisted polymeric citrate process is shown in fig. 4.1. Various stages involved in the formation of polymeric intermediates by urea assisted polymeric citrate process (M: U= 1:2) is shown in fig. 4.2. Photograph of the polymeric intermediates prepared with three different fuel conditions are shown in fig.4. 3. From fig. 4.3, the foamy intermediate was observed only for the polymeric intermediate prepared with the total metal ions to urea ratio of 1:2, which may be due to the better polymerization.
Mixing of Citric acid, Urea and Aqueous Metal nitrate/Metal Acetate solutions
\((M/CA = 1:2)\)
\((M/ U) = 1:0, 1:1 \text{ and } 1:2\)

\[
\begin{align*}
\text{Transparent yellow solution} & \\
\text{Evaporating at } 80 ^\circ C \text{ for 4 to 6 hours} & \\
\text{Yellowish Gel} & \\
\text{Drying at } 170 ^\circ C \text{ for 12 hours} & \\
\text{Porous bread like black colour powders} & \\
\text{Calcining at different temperatures for 12 hours} & \\
\text{Nanocrystalline LiMn}_2\text{O}_4 \text{ powders} &
\end{align*}
\]

Fig. 4.1 Flow chart of urea assisted polymeric citrate route for the synthesis of nanocrystalline LiMn$_2$O$_4$ powders.
Fig. 4.2 Photographs of various stages for the synthesis of polymeric intermediate prepared with M/U ratio of 1:2.

(a) – Starting solution.

(b) – Polymeric resin.

(c) to (e) – Expansion of polymeric resin during drying process.

(f) – Foamy polymeric intermediate after the completion of drying process.
Fig. 4.3 Photograph of the polymeric intermediates prepared with three different M/U ratios.
4.2.2 Proposed Chemical Reaction

During the evaporation of starting solution, urea (NH$_2$-CO-NH$_2$) was hydrolyzed in the presence of H$^+$ ions (from nitric as well as citric acids) and converted into NH$_4^+$ ions by releasing CO$_2$ gas, as given in the following chemical equation.

\[
\text{NH}_2\text{- CO - NH}_2 + 2\text{H}^+ + \text{H}_2\text{O} \rightarrow 2\text{NH}_4^+ + \text{CO}_2
\] (1)

The ammonium ions resulted from the above reaction could react with carboxylate (in citric acid) and NO$_3^-$ (from metal nitrate and nitric acid) ions and respectively forms the ammonium carboxylates as well as ammonium nitrate as follows,

\[
\text{NH}_4^+ + \text{R-COO}^- \rightarrow \text{R- COONH}_4
\] (2)

\[
\text{NH}_4^+ + \text{NO}_3^- \rightarrow \text{NH}_4\text{NO}_3
\] (3)

The above proposed mechanism of chemical reactions, equation 1, 2 and 3, were confirmed through FTIR analysis and explained in section 4.2.3.

Ammonium salt of citric acid acts as a combustion aide and ignites at lower temperature. Heat produced by the ammonium citrate explosion lowering the combustion duration. The total reaction for the formation of LiMn$_2$O$_4$ powders using M/CA ratio of 1:2 and M/U ratio of 1:1 could be written as,

\[
\text{LiNO}_3 + 2\text{C}_4\text{H}_6\text{OMn.6H}_2\text{O} + 6\text{C}_6\text{H}_8\text{O}_7 + 3\text{NH}_2\text{-CO-NH}_2 + 6\text{HNO}_3 + 34\text{O}_2 \rightarrow
\]

\[
\text{LiMn}_2\text{O}_4 + 47\text{CO}_2 + 7\text{NO}_2 + 6\text{NH}_3 + 38\text{H}_2\text{O}
\] (4)

The above proposed chemical reaction in equation 4 is investigated through FTIR, XRD and TG/DTA analysis.

4.2.3 Characterization of Polymeric Intermediates by FTIR, XRD and SEM

Fig. 4.4 shows the FTIR spectra of polymeric intermediate synthesized with three different total metal ions to urea ratios. From fig. 4.4, the broad peak observed at ~3496 cm$^{-1}$ region for all the samples is associated with the OH stretching, indicates the adsorbed
moisture, further, it is confirmed by TG/DTA analysis [53]. The FTIR spectra for polymeric intermediates prepared with three different experimental conditions show the IR peaks at 1384 cm\(^{-1}\) - 1433 cm\(^{-1}\) and 1597 cm\(^{-1}\) - 1603 cm\(^{-1}\) regions are respectively indicate the symmetric and asymmetric stretching of C=O bond in metal carboxylates, which confirm the chelation of metal ions by citric acid [53, 54]. The IR peak observed at 1723 cm\(^{-1}\) is due to presence of carbonyl groups in the polymeric intermediates, which increases with the urea addition. The observed peak at 1354 cm\(^{-1}\) for the polymeric intermediates prepared with urea addition is due to the asymmetric stretching of H-N-H groups, which indicates the presence of ammonium and / or urea derivatives. The intensity of this peak is high in the polymeric intermediates prepared with M/U=1:2 due to the addition of more amount of urea. Also the observed peak at 1385 cm\(^{-1}\) for all the intermediates is due to the presence of \(\text{NO}_3^-\) groups. In addition, the observed broad peak at 3250 cm\(^{-1}\) for the polymeric intermediates prepared with urea addition is assigned to the NH stretching in ammonium group, which may confirms the presence of ammonium salts in the form of ammonium citrate as well as ammonium nitrates. Addition of urea (M/U=1:1 and 1:2) increases the intensity of the peak at 1720 cm\(^{-1}\), which may be due to the formation of alkyl urethanes (=NCO-O-) and lead to the formation of porous polymeric intermediates as shown in fig. 4.4 [53].

Fig. 4.5 shows the XRD patterns of polymeric intermediates obtained from different total metal ions to urea ratios of 1:0, 1:1 and 1:2. From fig.4.5, the observed peaks in the XRD patterns for the polymeric intermediates prepared with M/U = 1:0 indicate the existence of metal nitrates due to the poor polymerization. Whereas, the polymeric intermediate prepared with M/U=1:1 exhibits low intense peaks, which is due to the formation of polymeric network between citric acid derivatives and urea. These peaks are not observed clearly in the XRD pattern of polymeric intermediates prepared with M/U
Fig. 4.4 FTIR spectra of polymeric intermediates prepared with three M/U ratios.

Fig. 4.5 XRD patterns of polymeric intermediates with three different M/U ratios.
of 1:2, which may due to the formation of highly polymerized foamy structure as shown in fig. 4.3, further, it was confirmed by SEM analysis.

Fig 4.6 shows the scanning electron micrographs of polymeric intermediates prepared with three different metal ions to urea molar ratios. SEM image of the polymeric intermediate prepared with out urea (fig. 4.6a) exhibits non porous hard mass (arrow mark indicates the metal citrate precipitates) whereas, the polymeric intermediate prepared with urea addition (fig. 4.6b and 4.6c) exhibits porous structure. Formation of porous structure may be due to the gas (NO₂, COₓ and NH₃) generation during the drying process. High porous polymeric flakes with large voids are observed for the polymeric intermediate prepared with the total metal ions to urea ratio of 1:2. SEM analysis indicates that the porosity of the polymeric intermediate increases with urea concentration.

4.2.4 Thermal Analysis of Polymeric Intermediates by TG/DTA

TG/DTA thermograms of polymeric intermediates synthesized by urea assisted polymeric citrate process with three different total metal ions to urea ratio are shown in fig 4.7. For all the thermograms, the observed weight loss between 75 and 100 °C alongwith endothermic peak is attributed to the removal of adsorbed moisture, which indicates the hygroscopic nature of polymeric intermediates. From fig 4.7, the exothermic peaks that correspond to the combustion process accompanied by major weight loss observed in TG thermograms of all the intermediates. Gradual weight loss was observed for the intermediates obtained from M / U = 1:0 and 1:1 with wide exothermic peaks and a sudden weight loss were observed, for the intermediate obtained from M /U = 1:2, at 255 °C with narrow exothermic peak indicates the vigorous combustion. A very long duration of combustion process is observed up to 400 °C for the polymeric intermediates obtained from M / U = 1:0 and 1:1, whereas the combustion was completed within 300 °C
Fig. 4.6 Scanning electron micrographs of polymeric intermediates prepared with three different M/ U ratios (a = M/ U = 1:0, b = M/ U = 1:1 and c = M/ U = 1:2).
Fig. 4.7 TG/DTA thermograms of polymeric intermediates prepared with three different M/U ratios.
for the polymeric intermediate obtained from M/U = 1:2. From fig. 4.7, it was found that
the ignition temperature decreases with increasing the urea concentration and it is found to
be 300, 270 and 255 °C respectively for the total metal ions to urea ratios of 1:0, 1:1 and
1:2, which is due to the formation of ammonium derivatives (ammonium nitrate and
ammonium citrate) that acts as an oxidizer. After the combustion process, no more weight
loss was observed in the TG curves for all the intermediates, which indicates the complete
decomposition of organic derivatives and the formation of LiMn\textsubscript{2}O\textsubscript{4} structure. From FTIR,
SEM and TG/DTA analysis, it is found that the addition of urea to polymeric citrate
process not only caused the formation of ammonium derivatives, such as, ammonium
nitrate and ammonium citrates but also leads to the formation of highly polymerized
intermediates, which increases with the urea concentration. Also, the foamy polymeric
intermediate observed for the M/U ratio of 1:2 caused better combustion during the
calcinations, which is confirmed by TG/DTA analysis. Combustion of the polymeric
intermediate prepared with the M/U ratio of 1:2 is shown in fig. 4.8.

Typical FTIR spectra of the polymeric intermediate (prepared with M/U = 1:2)
calcined at different temperatures are shown in fig. 4.9. The FTIR peaks related to the
organic derivatives are begins to disappear at 200 °C and completely disappeared when the
intermediate is calcined at 300 °C and above, which confirms the complete decomposition
of organic derivatives at 300 °C as observed in TG/DTA analysis. The newly observed
FTIR peaks at 612 cm\textsuperscript{-1} and 510 cm\textsuperscript{-1}, which are attributed to the O-Mn-O vibrations in the
LiMn\textsubscript{2}O\textsubscript{4} structure [55, 56].

Fig. 4.10 shows the typical XRD patterns of the polymeric intermediate prepared
with M/U = 1:2 calcined at different temperatures. From fig. 4.10, the XRD patterns show
that the spinel LiMn\textsubscript{2}O\textsubscript{4} phase begins to form at very low temperature i.e., 200 °C and the
complete phase were obtained at 300 °C and above, which is consistence with TG/DTA
Fig. 4.8 Photograph of the combustion of polymeric intermediate prepared with M/U ratio of 1:2.
Fig. 4.9 FTIR spectra of Polymeric intermediate (Prepared with M:U = 1:2) calcined at different temperatures.
Fig. 4.10 XRD patterns of the Polymeric intermediate (Prepared with M:U = 1:2)
calcined at different temperatures.
and FTIR results. Also, the observed increment in the intensity of the peaks as a function of calcining temperature indicates the increment in crystallinity.

### 4.2.5 Characterization of LiMn$_2$O$_4$ Powders by FTIR, XRD and SEM

Fig. 4.11 shows the FTIR spectra of LiMn$_2$O$_4$ powders prepared by urea assisted polymeric citrate process with three different M/U ratios at 300 °C for 12 hours. From fig. 4.11, the observed low intense IR peaks at ~1384 and ~1080 cm$^{-1}$ for the LiMn$_2$O$_4$ powders prepared with the M/U ratios of 1:0 and 1:1 are respectively assigned to the nitrate and carbonate derivatives, which indicates the incomplete decomposition of polymeric intermediates during the combustion process as observed in TG/DTA thermograms. Whereas the LiMn$_2$O$_4$ powder prepared with M/U ratio of 1:2 does not exhibit any peaks related to the organic derivatives and it is confirmed the complete decomposition of organic intermediates at 300 °C, which may be due to the porous foamy structure of the intermediates as observed in fig. 4.3 and fig 4.6c. Also, the FTIR spectra showed two new peaks at 612 and 510 cm$^{-1}$, which are attributed to the O-Mn-O vibrations in the LiMn$_2$O$_4$ structure [55, 56]. The simultaneous disappearance of the ~1723, ~1398 and ~1587 cm$^{-1}$ peaks and appearance of two new peaks at 612 and 510 cm$^{-1}$ for the calcined polymeric intermediates at 300 °C, indicated the formation of LiMn$_2$O$_4$ structure, which is further confirmed by XRD analysis. The organic free pure LiMn$_2$O$_4$ structure was observed for the polymeric intermediate prepared with the total metal ions to urea ratio of 1:2 confirms the better combustion, which is consistent with TG/DTA results.

XRD patterns of LiMn$_2$O$_4$ powders prepared by urea assisted polymeric citrate process at 300 °C for 12 hours are shown in fig. 4.12 alongwith the JCPDS data. The phase purity of the obtained LiMn$_2$O$_4$ powder was confirmed by comparing its XRD
Fig. 4.11 FTIR spectra of LiMn$_2$O$_4$ powders synthesized by urea assisted polymeric citrate route with three different M/ U ratios (1:0, 1:1 and 1:2) at 300 °C.
pattern with JCPDS data (35-0782). The crystalline LiMn$_2$O$_4$ phase was clearly observed for all the powders. Also, the obtained XRD patterns for all the samples do not show any impurity phase. Though the polymeric citrate process with M/U = 1:0 and 1:1 forms the LiMn$_2$O$_4$ phase at 300 °C, but also exhibit residual organic impurities in their respective FTIR spectra. Hence, from FTIR, and XRD results, the total metal ions to urea ratio of 1:2 is optimized for the synthesis of organic free phase pure nanocrystalline LiMn$_2$O$_4$ powder relatively at lower temperature (300 °C for 12 hours). The lattice parameter calculated for the LiMn$_2$O$_4$ powder prepared with M/U = 1:2 is a = 8.17960 Å, which is very much comparable with the reported value [57]. Crystallite size of the synthesized LiMn$_2$O$_4$ powders is calculated by Scherrer’s formula with the FWHM data of the (111) plane observed at 18.8° of $2\theta$ value obtained from the Lorentz fit of observed XRD peak. Table-4.1 shows the FWHM and the crystallite size of the LiMn$_2$O$_4$ powders prepared with three different M/U ratios. The crystallite size was found to be 33, 36 and 19 nm respectively for the LiMn$_2$O$_4$ powders prepared with M/U of 1:0, 1:1 and 1:2. From the obtained crystallite size, it is found that increasing of exothermicity caused the increment in crystallite size. However, the observed lowest crystallite size (19 nm) for the LiMn$_2$O$_4$ powder prepared with M/U of 1:2 is may be due to the formation of porous foamy polymeric intermediate, which inhibits the rapid nucleation of LiMn$_2$O$_4$ structure during the combustion. Fig. 4.13 shows the typical SEM micrograph of the LiMn$_2$O$_4$ powder prepared with the total metal ions to citric acid ratio of 1:2 at 300 °C for 12 hours. From fig. 4.13, the SEM image of the synthesized LiMn$_2$O$_4$ powder showed an agglomeration of fine nanocrystalline LiMn$_2$O$_4$ particles.
Fig. 4.12. XRD patterns of LiMn$_2$O$_4$ powders synthesized by urea assisted polymeric citrate process with three different M/ U ratios (1:0, 1:1 and 1:2) at 300 °C.

Fig. 4.13 Scanning electron micrograph of LiMn$_2$O$_4$ powder synthesized by urea assisted polymeric citrate process with M/U = 1:2.
Table – 4.1

Lorentz fit data and the crystallite size of nanocrystalline LiMn$_2$O$_4$ powders prepared with M/U ratio of 1:0, 1:1 and 1:2 at 300 °C for 12 hours

<table>
<thead>
<tr>
<th>S No.</th>
<th>Name of the Process</th>
<th>2θ (Degree)</th>
<th>FWHM* of the 100% Peak (Degree)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>M/U = 1:0</td>
<td>18.83</td>
<td>0.2629</td>
<td>33</td>
</tr>
<tr>
<td>2</td>
<td>M/U = 1:1</td>
<td>18.82</td>
<td>0.2441</td>
<td>36</td>
</tr>
<tr>
<td>3</td>
<td>M/U = 1:2</td>
<td>18.81</td>
<td>0.4497</td>
<td>19</td>
</tr>
</tbody>
</table>

* FWHM = Full Width Half Maximum

Instrumental broadening obtained using NBS standard silicon = 0.09470 (degree)
4.3 Novel Nitric Acid Assisted Pechini Process for the Synthesis of Nanocrystalline LiMn$_2$O$_4$ Powders

Pechini process is a simple preparative method, which has been used for the synthesis of ultra fine particles of multicomponent oxide powders using metal nitrates, citric acid (CA) and ethylene glycol (EG) [48-50]. In Pechini process, foaming of polymeric intermediate is a major factor for the synthesis of non-agglomerated as well as fine ceramic powders [51]. Sub micron size (0.2–0.5 μm) of LiMn$_2$O$_4$ powders were synthesized using Pechini process, where foaming effect was not observed [50]. Hence, proper synthesis condition should be designed not only to get the better foaming polymeric intermediates but also to get the phase pure nanocrystalline powders at lower temperature.

Hence, in the present work, we have investigated an interesting new finding by modifying the synthesis conditions, in the form of adding nitric acid to the precursor solutions. Addition of nitric acid to the starting solution inhibits the precipitation of metal citrates and motivates the better polymerization reaction between citric acid and ethylene glycol, resulted high porous foam like polymeric intermediate, which yields an organic free phase pure LiMn$_2$O$_4$ powders with smaller crystallite size. A systematic comparative study was made on two different synthetic conditions, with and without nitric acid for the synthesis of nanocrystalline LiMn$_2$O$_4$ powders.

4.3.1 Synthesis

LiNO$_3$ (99.8 %, S. d. Fine-Chem. Ltd.) and manganese acetate (AR grade SD-Fine Chem. Ltd.) were used as sources of metal ions. Citric acid (SQ grade, Qualigens) and ethylene glycol (SQ grade, Qualigens) were used as fuels as well as polymerizing agent alongwith nitric acid (AR grade, SRL).
Lithium nitrate and manganese acetate were used as sources of metal ions. The lithium and manganese salts with a cationic ratio of Li: Mn = 1:2 were dissolved in citric acid and ethylene glycol solution. The molar ratio of total metal ions to citric acid ratio was kept as 1:1 and the molar ratio of total metal ions to ethylene glycol was set as 1:2. Concentrated 16N nitric acid (NA) was added to starting solution (SS) by keeping the volume ratio of SS: NA = 5:1. The resulting transparent yellow colour solutions were evaporated at 80 °C under constant stirring condition. Continuous evaporation of the starting solution with nitric acid caused the formation of dark yellowish resin. Whereas, the starting solution without nitric acid turns into white colour paste like precipitate, which may indicate the formation of metal citrates due to the poor polymerization. In order to obtain the dried intermediates, the resulting products (resin and paste) were heated at 170 °C in air. On heating, resin expanded 40 times of its original volume and resulted high porous polymeric intermediate, whereas, heating of paste formed the solid mass. Flow chart of the nitric acid assisted Pechini process for the synthesis of nanocrystalline LiMn$_2$O$_4$ powders is shown in fig. 4.14.

4.3.2 Characterization of Polymeric Intermediates by FTIR, XRD and SEM

Three types of reactions (esterification, polymerization and chelation) involved in the nitric acid assisted Pechini process for the synthesis of nanocrystalline LiMn$_2$O$_4$ powders are schematically shown in fig. 4.15. Photograph of the polymeric intermediates prepared by Pechini process with and without nitric acid addition is shown in fig 4.16. From fig. 4.16, the foamy nature is observed only for the polymeric intermediate prepared with nitric acid addition, whereas the polymeric intermediate prepared without nitric acid addition exhibits solid mass. From fig. 4.16, it is clearly observed that the addition of nitric acid lead to the formation of porous foamy intermediate.
Mixing of Citric acid, Ethylene glycol and Aqueous Metal nitrate/Metal Acetate solutions (M/CA = 1:1) 
(M/EG) = 1:2)

- Transparent yellow solution
- Evaporating at 80 °C for 4 to 6 hours
  - Yellowish resin
- Drying at 170 °C for 12 hours
  - Porous bread like black colour powders
- Calcining at different temperatures for 12 hours
  - Nanocrystalline LiMn$_2$O$_4$ powders

Fig. 4.14 Flow chart of the nitric acid assisted Pechini process for the synthesis of nanocrystalline LiMn$_2$O$_4$ powders.
Fig. 4.15 Reactions involved in the nitric acid assisted Pechini process for the synthesis of nanocrystalline LiMn$_2$O$_4$ powders.
Fig. 4.16 Photograph of polymeric intermediate prepared by Pechini process with two different synthesis conditions (without (A) and with (B) nitric acid).
Fig. 4.17a shows the FTIR spectra of the polymeric intermediates obtained from two different synthetic conditions. From fig. 4.17a, the peak observed at 3410 cm\(^{-1}\) for all the polymeric intermediates is attributed to OH stretching due to the adsorbed moisture as well as OH group present in the citric acid derivatives [53]. The IR spectra for all the intermediates showed two bands at 1595 and 1390 cm\(^{-1}\) are assigned to asymmetric and symmetric vibrations of the COO\(^{-}\) ions respectively, which confirm the chelation of metal ions [53, 54]. The new band observed at 1300 cm\(^{-1}\) for the intermediate prepared with nitric acid confirms the presence of bridging COO\(^{-}\) groups, which shows a clear evidence for the formation of polymeric network between citric acid and ethylene glycol [53]. The intensity of the IR peak at 1070 cm\(^{-1}\)corresponds to NO\(_3\)\(^{-}\) and the intensity of the peak increases for the intermediate prepared with nitric acid. XRD patterns of the polymeric intermediates prepared with two different synthesis conditions are shown in fig. 4.17b. From fig. 4.17b, the observed peaks for the polymeric intermediate prepared without nitric acid indicates the formation of crystalline metal citrates and the peak free XRD pattern for the polymeric intermediate prepared with nitric acid addition confirms the amorphous nature polymeric structure, which are further confirmed by SEM results.

Fig. 4.18 shows the scanning electron micrographs (SEM) of polymeric intermediates obtained from two different starting solutions. From fig.4.18a, the SEM picture for the polymeric intermediate synthesized without nitric acid showed the precipitation, which may be due to the formation of crystalline metal carboxylates, which are consistence with XRD results. From fig. 4.18b, the SEM picture for the intermediate synthesized with nitric acid showed the polymeric structure with high porosity, which may be due to the addition of nitric acid to starting solution.
Fig. 4.17 FTIR and XRD analysis of polymeric intermediates prepared by Pechini process with two different conditions (without and with nitric acid addition).
Fig. 4.18 SEM micrographs of polymeric intermediate prepared by Pechini process with two different conditions (without and with nitric acid addition).
4.3.3 Thermal Analysis of Polymeric Intermediates by DSC

Fig. 4.19 shows the DSC thermograms of polymeric intermediates obtained from two different synthesis conditions, i.e., with and without nitric acid. From fig. 4.19, DSC curves for the polymeric intermediate, prepared without nitric acid, showed wide exothermic peak between 300 °C and 375 °C in three steps and the polymeric intermediate prepared with nitric acid showed single sharp exothermic peak between 310 °C to 400 °C with large heat generation. From fig. 4.19, the DSC curves of polymeric intermediates clearly showed that the addition of nitric acid to the starting solution increases the ignition temperature as well as the exothermicity of combustion reaction. polyesterification between CA and EG in nitric acid assisted process results the highly polymerized intermediate, which increased the ignition temperature. Similarly, the increased exothermicity of combustion reaction for the intermediate prepared with nitric acid addition is due to the formation of high porous foam like polymeric intermediates.

4.3.4 Characterization of LiMn$_2$O$_4$ Powders by FTIR, XRD and SEM

Fig 4.20a shows the FTIR spectra LiMn$_2$O$_4$ powders prepared by Pechini process with and without nitric acid at 450 °C for 12 hours. From fig. 4.20a, the FTIR spectra for the LiMn$_2$O$_4$ powders showed two peaks at 612 cm$^{-1}$ and 510 cm$^{-1}$, which are attributed to the O-Mn-O vibrations indicate the formation of LiMn$_2$O$_4$ structure, further it is confirmed from XRD analysis [55, 56].

Fig. 4.20b shows the XRD patterns of crystalline spinel LiMn$_2$O$_4$ powders obtained by calcining the polymeric intermediates at 450 °C alongwith JCPDS standard. Formation of spinel LiMn$_2$O$_4$ phase was confirmed by comparing their respective XRD pattern with the JCPDS standard. From fig. 4.20b, the XRD peaks correspond to the Mn$_3$O$_4$ impurity phase was observed only for the LiMn$_2$O$_4$ powders prepared without nitric acid, which
Fig. 4.19 DSC thermograms of polymeric intermediates prepared with two different conditions (without and with nitric acid).
Fig. 4.20 FTIR and XRD analysis of the synthesized LiMn$_2$O$_4$ powders prepared by Pechini process with two different conditions (without and with nitric acid addition).
may be due to the multi step combustion mechanism as observed in DSC thermogram. The crystallite size of LiMn$_2$O$_4$ powders is calculated using the broadening of the (111) peak (recorded at the scanning rate of $1/2$ ° per min) through Lorentz fitting method and the Scherrer's formula. Table - 4.2 shows the FWHM and the crystallite size of the LiMn$_2$O$_4$ powders prepared by Pechini process without and with nitric acid addition. The lowest crystallite size is found to be 16 nm for the organic free phase pure LiMn$_2$O$_4$ powders prepared by combustion process with nitric acid addition. Also, the calculated lattice parameter for the LiMn$_2$O$_4$ powder prepared with nitric acid addition is $a = 8.1852$ Å, which is very much comparable with the reported value [57, 58]. DSC, FTIR, SEM and XRD results confirm that the addition of nitric acid to Pechini process results in the formation of high porous foam like polymeric intermediate, which lead to the better combustion and also lead to the formation of smaller crystallite size. Table - 4.3, shows the comparison of the nature of intermediates and LiMn$_2$O$_4$ powders prepared by Pechini process under various experimental conditions alongwith the present investigation [42, 43, 50]. From the table, it is found that the Pechini process with nitric acid addition showed lowest crystallite size so far reported in the literature by different method including Pechini process. Fig. 4.21 shows the SEM micrograph of the LiMn$_2$O$_4$ powder prepared by Pechini process with nitric acid addition at 450 °C for 12 hours. From fig. 4.21, the SEM image of the synthesized LiMn$_2$O$_4$ powder showed an agglomeration of fine nanocrystalline LiMn$_2$O$_4$ particles. Hence, the newly developed modified nitric acid assisted Pechini process is useful for the synthesis of smaller size nanocrystalline multicomponent oxide powders at lower temperature.
Table – 4.2

Lorentz fit data and the crystallite size of nanocrystalline LiMn$_2$O$_4$ powders prepared by Pechini process with two different conditions (with out and with nitric acid addition) at 450 °C for 12 hours

<table>
<thead>
<tr>
<th>S No.</th>
<th>Name of the Process</th>
<th>$2\theta$ (Degree)</th>
<th>FWHM$^*$ of the 100% Peak (Degree)</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Without nitric acid</td>
<td>18.80</td>
<td>0.17865</td>
<td>53.20</td>
</tr>
<tr>
<td>2</td>
<td>With nitric acid</td>
<td>18.78</td>
<td>0.51242</td>
<td>16.00</td>
</tr>
</tbody>
</table>

* FWHM = Full Width Half Maximum

Instrumental broadening obtained using NBS standard silicon = 0.09470 (degree)
<table>
<thead>
<tr>
<th>S. No</th>
<th>Fuel Conditions</th>
<th>Nature of the Intermediate</th>
<th>Crystallite Size of the LiMn₂O₄ Powders</th>
<th>Remarks</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CA/ EG = 1:x, Where x = 0,1,2 and 4</td>
<td>Puffed char</td>
<td>Micro meter range at 800°C (as shown in the SEM images)</td>
<td>Increasing the x value decreases the particle size</td>
<td>Yi-Sup Han et.al [42]</td>
</tr>
<tr>
<td>2</td>
<td>CA/ EG = 1:4</td>
<td>Polymeric gel</td>
<td>0.2–0.6 μm (powders calcined at 600-800°C)</td>
<td>LiMn₂O₄ powders prepared below 700°C exhibits Mn₃O₄ impurities</td>
<td>She-huang Wu, et. Al [43]</td>
</tr>
<tr>
<td>3</td>
<td>CA/ EG = 1:4</td>
<td>Glass like Solid with out precipitate</td>
<td>0.2–0.5 μm (powders calcined at 800°C) Crystallite size at lower temperatures are not calculated</td>
<td>LiMn₂O₄ phase was obtained at as low as 250°C but the undecomposed organic residual was not discussed</td>
<td>W. Liu et.al [50]</td>
</tr>
<tr>
<td>4</td>
<td>CA/ EG = 1:2 Under concentrated nitric acid</td>
<td>High Porous foam</td>
<td>16 nm (LiMn₂O₄ powders prepared at 450°C)</td>
<td>No organic residuals as well as Mn₃O₄ impurities were observed in the LiMn₂O₄ prepared at 450°C</td>
<td>Present Investigation</td>
</tr>
</tbody>
</table>
Fig. 4.21 SEM micrograph of the nanocrystalline LiMn$_2$O$_4$ powder prepared by nitric acid assisted Pechini process.
4.4 Citric Acid Assisted Sol-Gel Combustion Process for the Synthesis of Nanocrystalline LiNi_{0.5}Co_{0.5}VO_{4} Powders

Among the available wet chemical processes, citric acid assisted sol-gel combustion process has been used for the preparation of nano sized multicomponent oxide powders with required properties at a lower calcination temperature in shorter period. The formation of viscous liquid or gel is a primary factor, which can prevent the precipitation of metal ions. In this process, citric acid plays a major role in the chelation of metal ions and also in the formation of polymeric network through esterification, which may lead to the sol formation [16, 17]. The nature of the fuel, its amount and pH of the starting solution are some of the important parameters for obtaining the polymeric gel. Total metal ions to fuel ratio, which also called as fuel to oxidant ratio, is an important key parameter in this process. Also, it is necessary to optimize the metal ions to fuel ratio for the better combustion, which yields organic free phase pure nanocrystalline final products. Hence, in the present investigations, the advantage of the citric acid assisted sol-gel combustion process is utilized to synthesize the organic free phase pure nanocrystalline LiNi_{0.5}Co_{0.5}VO_{4} powders. Also, the systematic study was carried out to investigate the effect of citric acid amount (different total metal ions to citric acid ratios such as 1:1, 1:2 and 1:3) for the synthesis of nanocrystalline LiNi_{0.5}Co_{0.5}VO_{4} powders.

4.4.1 Synthesis

LiNO_{3} (99.8%, Loba Chemic), Co(NO_{3})_{2}.6H_{2}O (GR grade, Merck, India), Ni(NO_{3})_{2}.6H_{2}O (AR, Merck, India) and NH_{4}VO_{3} (AR grade, TRAC) were used for the sources of metal ions. Citric acid anhydrous (SQ grade, Qualigens) was used as chelating agent as well as fuel for the synthesis of LiNi_{0.5}Co_{0.5}VO_{4} powders.
Nanocrystalline LiNi_{0.5}Co_{0.5}VO_{4} powders were synthesized by sol-gel process according to the flow chart shown in fig. 4.22. Required amount of LiNO_{3}, Co(NO_{3})_{2}\cdot6H_{2}O, Ni(NO_{3})_{2}\cdot6H_{2}O, ammonium meta vanadate were dissolved in distilled water and mixed with citric acid solution. The pH of the solution was uniformly maintained for all the three starting solutions by adding concentrated nitric acid. The resulting blue colored solution was evaporated at 60 °C for 2 hours to form the sol. Obtained transparent sol was heated at 50 °C for 48 hours to remove the remaining excess water, which lead to the formation of high viscous sticky brown colour gel. The gels were prepared with different molar ratios of the total metal ions to citric acid as (M/CA) 1:1, 1:2 and 1:3 and these were dried at 150°C for 12 hours. The dried gels exhibit 15 to 30 times of expansion to its original volume, with the citric acid concentration. The resulting high porous bread like material was grounded and calcined at different temperatures for 12 hours to obtain the nanocrystalline LiNi_{0.5}Co_{0.5}VO_{4} powders.

4.4.2 Characterization of Polymeric Intermediates by FTIR, XRD and SEM

Different stages involved in the formation of dried gels (polymeric intermediates) by citric acid assisted sol-gel combustion process (M: CA = 1:2) is shown in fig. 4.23. Fig. 4.24 shows the photograph of the dried gels prepared with three different total metal ions to citric acid ratios (M/CA = 1:1, 1:2 and 1:3). From fig. 4.24, it is observed that the increment of citric acid addition increases the foamy nature of the dried intermediates.

Fig. 4.25 shows the FTIR spectra of the dried gels prepared with three different M/CA ratios. From fig. 4.25, the broad band observed, in all the dried gels, at around 3430 cm^{-1} is assigned to OH stretching of the adsorbed moisture [53]. The band at 3226 cm^{-1} for the dried gels prepared with M/CA 1:2 and 1:3 is due to the presence of OH group in citric acid derivatives and it was not observed for the dried gels prepared with M/CA= 1:1,
Mixing of aqueous citric acid, aqueous metal nitrate solutions and nitric acid (M/CA = 1:1, 1:2 and 1:3)

Transparent blue colour solution

Heating at 60°C for 2 to 3 hours

Dark Blue coloured Sol

Evaporating at 50°C for 48 hours

Black colour viscous Gel

Drying at 150°C for 12 hours

Porous polymeric Dried Gel

Calcining at different temperatures

Nanocrystalline LiNi_{0.5}Co_{0.5}VO_{4} powders

Fig. 4.22 Flow chart of sol-gel combustion process for the synthesis of nanocrystalline LiNi_{0.5}Co_{0.5}VO_{4} powders.
Fig. 4.23 Photographs of various stages for the synthesis of dried gel prepared with M/CA ratio of 1:2.

(a) – Sol
(b) – Gel
(c) to (e) – Expansion of gel during drying process.
(f) – Foamy dried gel after the completion of drying process.
Fig. 4.24 Photograph of dried gels prepared with three different M/CA (1:1, 1:2 and 1:3) ratios.
which may be due to the lower citric acid content. The peaks at 2916 and 2857 cm\(^{-1}\) are respectively attributed to asymmetric and symmetric vibrations of CH\(_2\) groups in citric acid derivatives [53]. The IR spectra of all the dried gels showed two bands at 1587-1594 cm\(^{-1}\) and 1398-1401 cm\(^{-1}\) region are respectively assigned to the asymmetric and symmetric vibrations of the COO\(^-\) ions from metal carboxylates, which confirm the chelation of metal ions [53, 54]. The IR peaks observed at 1245-1255 cm\(^{-1}\) and 1098-1087 cm\(^{-1}\) are respectively due to the asymmetric and symmetric stretching vibration of the C-O-C groups, which confirmed the esterification [53]. The peak observed at 780-550 cm\(^{-1}\) region is due to the in-plane and out-plane deformation vibrations of the carboxylic ion. The observed band positions at 1700 and 1300 cm\(^{-1}\) in M/CA-1:3 are due to the formation of bridging coordination between carboxylic groups in citric acid, which caused the high order polymerization, further it is confirmed by SEM images [22].

Fig 4.26 showed the XRD patterns of the dried gels prepared with M/CA 1:1, 1:2 and 1:3. From, fig. 4.26 the observed peak free XRD patterns for the dried gels prepared with M/CA ratio of 1:2 and 1:3 confirmed the amorphous nature. Whereas the dried gel prepared with M/CA ratio of 1:1 exhibits the low intense peaks, which may be due to the existence of metal citrate precipitation. Formation of polymeric network due to the esterification between OH and COOH groups in citric acid may cause the amorphous nature, which consistent with the FTIR and SEM results. Scanning electron micrographs of the dried gels prepared with different citric acid amounts (M/CA= 1:1, 1:2 and 1:3) are shown in fig. 4. 27. The SEM image showed that the dried gel prepared with M/CA= 1:1 exhibits high porous microstructure with large voids, whereas the dried gel prepared with M/CA= 1:2 and 1:3 exhibit highly polymerized microstructure (which is also consistent with FTIR results) with less voids. Increasing the citric acid concentration in the starting solution increases the order of polymerization, which is confirmed by SEM images.
Fig. 4.25 FTIR spectra of dried gels prepared with three different total metal ions to citric acid ratios (M/CA = 1:1, 1:2 and 1:3).

Fig. 4.26 XRD patterns of dried gels prepared with three different total metal ions to citric acid ratios (M/CA = 1:1, 1:2 and 1:3).
Fig. 4.27 Scanning electron micrographs of the dried gel prepared with M/CA = 1:1, 1:2 and 1:3.
4.4.3 Thermal Analysis of Polymeric Intermediates by TG/DTA

Thermal behavior of the dried gels prepared with three different citric acid amounts is investigated by TG/DTA measurements and the obtained thermograms were shown in fig.4.28a, 4.28b and 4.28c. The observed endothermic peak between 75 and 100°C with respective weight loss for all the dried gels indicates the removal of adsorbed moisture. From fig. 4.28a, the observed second endothermic peak at 245 °C without weight loss is due to the melting process of polymeric intermediate. The major weight loss about ~30% was observed between 360 °C and 410 °C with mild exothermic peak is due to the decomposition of dried intermediate. TG/DTA curve of the dried gel prepared with M/CA = 1:2 shows a single step exothermic decomposition between 300 °C and 415 °C with the major weight loss about ~20% and no more weight loss was observed beyond 415 °C, which indicates the complete decomposition of organic derivatives. From fig. 4.28c, decomposition of the dried gel prepared with M/CA = 1:3 is observed as two step broad exothermic peak between 320 °C and 445 °C with the major weight loss about ~27%. From TG/DTA analysis of dried gels, it is found that the exothermicity of the combustion reaction increases with increasing M/CA ratio and all the combustion reactions are completes before 415 °C.

Fig. 4.29 shows the typical FTIR spectra of the calcined dried gels, prepared with metal ion to citric acid ratio of 1:1, at different temperatures. From fig. 4.29, the IR peaks at 1589 cm⁻¹ and 1389 cm⁻¹, due to organic derivatives, are disappeared only the dried gels calcined at 450 °C and above. Simultaneously, two new IR peaks observed at 815 cm⁻¹ and 710 cm⁻¹ are respectively attributed to asymmetrical stretching vibrations of VO₄ tetrahedron [59], and bending vibrations of NiO₆ /CoO₆ octahedral [17] for the dried gels calcined at 300 °C and above, which may indicate the formation of LiNi₀.₅Co₀.₅VO₄ structure, further, it is confirmed by XRD results. Fig. 4.30 shows the typical XRD patterns.
Fig. 4.28 TG/DTA thermograms of the dried gel prepared with three different total metal ions to citric acid ratios (M/CA = 1:1, 1:2 and 1:3).
Fig. 4.29 Typical FTIR spectra of the dried gel prepared with the total metal ion to citric acid ratio of 1:1 calcined at different temperatures.
Fig. 4.30 Typical XRD patterns of the dried gel prepared with the total metal ion to citric acid ratio of 1:1 calcined at different temperatures.
of the calcined dried gels, prepared with M/CA - 1:1, at different temperatures for 12 hours. From fig. 4.30, the crystalline phase of LiNi$_{0.5}$Co$_{0.5}$VO$_4$ began to form when the polymeric intermediate calcined at 300 °C and the complete phase was observed at 450 °C and above.

4.4.4 Characterization of LiNi$_{0.5}$Co$_{0.5}$VO$_4$ Powders by FTIR, XRD and SEM

Fig. 4.31 shows the FTIR spectra of the synthesized LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powders prepared with three different metal ions to citric acid ratios (M/CA = 1:1, 1:2 and 1:3) at 450 °C for 12 hours. From fig. 4.31, it is clearly observed that the peaks due to organic derivative are completely disappeared for the LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powders prepared with M/CA 1:1, whereas LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powder prepared with M/CA = 1:2 and 1:3 exhibits the IR peaks corresponds to the organic derivatives with reduced intensities. This is due to the presence of residual organics, which indicate the incomplete decomposition of dried gels.

Fig. 4.32 shows the XRD patterns of LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powders prepared with three different metal ions to citric acid ratios (M/CA = 1:1, 1:2 and 1:3) at 450 °C for 12 hours. The formation of crystalline LiNi$_{0.5}$Co$_{0.5}$VO$_4$ phase was confirmed by comparing the observed XRD pattern with JCPDS standards of LiNi$_{0.5}$Co$_{0.5}$VO$_4$. The intensity of the XRD patterns decreases with increasing citric acid concentration, which may be due to the reduction of crystallinity of the obtained LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powders. From fig. 4.32, the XRD pattern does not show any peaks related to undecomposed organic derivatives, whose structure is observed in the FTIR spectra for M/CA = 1:2 and 1:3 powders since the organic derivatives are in the amorphous phase. Crystallite size for the LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powders was calculated using the Sherrer’s formula and the FWHM data obtained by Lorentz fit for the observed XRD peak at 36.2° corresponds to the (311) plane. Table-4.4
Fig. 4.31 FTIR spectra of the synthesized LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powders at 450 °C by sol-gel combustion process with M/CA ratio of 1:1, 1:2 and 1:3.
Fig. 4.32 XRD patterns of the LiNi<sub>0.5</sub>Co<sub>0.5</sub>VO<sub>4</sub> powders synthesized by sol-gel process with three different M/CA ratios (1:1, 1:2 and 1:3) at 450 °C.
Lorentz fit data and the crystallite size of nanocrystalline LiNi_{0.5}Co_{0.5}VO_4 powders prepared by sol-gel combustion process with different total metal ions to citric acid ratios (M/CA = 1:1, 1:2 and 1:3) at 450 °C for 12 hours

<table>
<thead>
<tr>
<th>S No.</th>
<th>Name of the Process</th>
<th>2θ (Degree)</th>
<th>FWHM* of the 100% Peak (Degree)</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>M/CA = 1:1</td>
<td>36.17</td>
<td>0.13334</td>
<td>89.11</td>
</tr>
<tr>
<td>2</td>
<td>M/CA = 1:2</td>
<td>36.20</td>
<td>0.15243</td>
<td>70.03</td>
</tr>
<tr>
<td>3</td>
<td>M/CA = 1:3</td>
<td>36.20</td>
<td>0.18709</td>
<td>51.84</td>
</tr>
</tbody>
</table>

* FWHM = Full Width Half Maximum

Instrumental broadening obtained using NBS standard silicon = 0.09470 (degree)
shows the FWHM and the crystallite size of the LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powders prepared by citric acid assisted sol-gel combustion process with three different total metal ions to citric acid ratios. The calculated crystallite size is 89, 70 and 52 nm respectively for the LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powders prepared with M/CA = 1:1, 1:2 and 1:3. Though, the crystallite size of LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powders prepared with M/CA = 1:2 and 1:3 is lower than M/CA = 1:1, it exhibits organic impurity, which is observed in FTIR analysis. Also, the calculated lattice parameter for the LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powder prepared with M/CA = 1:1 is $a = 8.2293$ Å, which is very much comparable with the reported value [59]. Fig. 4.33 shows the SEM image of the synthesized LiNi$_{0.5}$Co$_{0.5}$VO$_4$ Powders at 450 °C for 12 hours prepared with the total metal ions to citric acid ratio of 1:1. From fig. 4.33, the SEM image showed agglomeration of fine LiNi$_{0.5}$Co$_{0.5}$VO$_4$ particles. From the above analysis total metal ions to citric acid ratio of 1:1 is optimized for the synthesis of organic free nanocrystalline LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powder with lowest crystallite size.

4.5 Pechini Process Using Different Ethylene Glycol Precursors for the Synthesis of Nanocrystalline LiNi$_{0.5}$Co$_{0.5}$VO$_4$ Powders

The Pechini process has been used for the preparation of variety of ultra fine oxide ceramic powders relatively at lower calcining temperature using carboxylic acids and polyhydroxyl alcohols as fuels as well as chelating agents [18, 19]. The physiochemical properties of ceramic powders prepared by Pechini process are mainly depend on the properties of their respective polymeric intermediates (dried resin). Nature of polyhydroxy alcohols plays an important role in the formation of polymeric intermediates, which can modify the physiochemical properties of oxide powders. Among the available polyhydroxy alcohols (ethylene glycol) is found to be an effective for the synthesis of organic free, phase pure oxides materials.
Fig. 4.33. Scanning electron micrograph of the nanocrystalline LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powder prepared by sol-gel combustion process with M/CA = 1:1.
Hence, in the present work, we have carried out a systematic study on Pechini process using three different ethylene glycol precursors named ethylene glycol (EG), polyethylene glycol- 400 (PEG-400) and polyethylene glycol- 4000 (PEG-4000) with citric acid for the synthesis of nanocrystalline LiNi_{0.5}Co_{0.5}V_{0.4} powders. The effect of different ethylene glycols on the structural coordination, thermal decomposition, microstructure and the crystallinity were investigated and the suitable ethylene glycol precursor was identified.

4.5.1 Synthesis

LiNO₃ (99.8%, Loba Chemie), Co(NO₃)₂.6H₂O (GR grade, Merck, India), Ni(NO₃)₂.6H₂O (AR, Merck, India), NH₄VO₃ (AR grade, TRAC), citric acid anhydrous (SQ grade, Qualigens), ethylene glycol (EG) (SQ grade, Qualigens), polyethylene glycol-400 (PEG- 400) (SQ grade, Qualigens), polyethylene glycol 4000 (PEG- 4000) (SQ grade, Qualigens) were used for the synthesis of LiNi_{0.5}Co_{0.5}V_{0.4} powders.

The synthesis procedure adopted for the preparation of nanocrystalline LiNi_{0.5}Co_{0.5}V_{0.4} powders is shown in fig. 4.34. The required stoichiometric quantities of metal nitrate solutions were mixed with citric acid solution by keeping metal ion to citric acid ratio of (M/CA) 1:1 under stirring condition. Different ethylene glycols were added to metal nitrates and citric acid solution by maintaining the molar ratio of citric acid to ethylene glycol as 1:1 and respectively denoted as EG, PEG – 400 and PEG - 4000. The resulting blue colored solution was evaporated at 90 °C for 6 hours and it turned into a viscous brown colour resin. Further, the resin was dried at 150 °C for 24 hours and obtained the porous polymeric intermediates. The resulting porous material was grounded and calcined at various temperatures as 300, 450, 600 and 750 °C to obtain nano sized LiNi_{0.5}Co_{0.5}V_{0.4} powders.
Mixing of Metal nitrate solutions with Aqueous Citric acid and different ethylene glycols (EG, PEG-400 and PEG-4000) M/CA = 1:1 and M/EG = 1:1

- Transparent Blue colour solution
  - Evaporating at 90°C for 6 hours
  - Brown Colour Resin
  - Drying at 150°C for 24 hours
  - Porous black colour powders (Polymeric intermediate (PI))
  - Calcining the PI at different temperatures
  - Nanocrystalline LiNi_{0.5}Co_{0.5}VO_{4} powders

Fig. 4.34 Flow chart of the EG, PEG-400 and PEG-4000 assisted Pechini process for the synthesis of nanocrystalline LiNi_{0.5}Co_{0.5}VO_{4} powders.
4.5.2 Characterization of Polymeric Intermediates by FTIR, XRD and SEM

Fig. 4.35 shows the photograph of polymeric intermediates prepared using three different ethylene glycol precursors. From fig 4.35, it is observed that the increment of ethylene glycol molecular weight decreases the foamy nature of the dried intermediates, which may be due to the poor polymerization between polyethylene glycol precursors (PEG-400 and PEG-4000) and citric acid.

Fig. 4.36 shows the FTIR spectra of polymeric intermediates prepared with three different ethylene glycols (EG, PEG-400 and PEG-4000). From fig.4.36, the peak observed at 3410 cm⁻¹, for all the three polymeric intermediates, is due to the presence of OH groups in the citric acid and ethylene glycol derivatives [53]. Two small peaks observed at 2923 and 2848 cm⁻¹ for all the polymeric intermediates are respectively attributed to the asymmetric and symmetric stretching of CH₂ group present in the organic derivatives [53]. Similarly, the IR peak observed at 1622 cm⁻¹ for all the polymeric intermediates is due to the asymmetric vibrations of COO⁻ groups with the metal ions [53, 54]. Hence, the IR spectra of polymeric intermediates obtained with three different ethylene glycols showed the presence of metal carboxylates, which confirmed the chelation of metal ions by citric acid. The IR peaks observed at 1314 and 1074 cm⁻¹ are respectively due to the presence of asymmetric stretching of =C-O-C and C-O-C groups. The intensity of the above peaks is high in ethylene glycol assisted polymeric intermediate, which indicates the presence of more ester groups [53]. More ester groups observed in the polymeric intermediate prepared with ethylene glycol, indicates the better polymerization occurred between ethylene glycol and citric acid and hence, formed the highly branched polymeric network. Whereas, the addition of polyethylene glycols (PEG-400 and PEG-4000) to citric acid reduced the formation of branched network, which lead to the
Fig. 4.35 Photograph of the polymeric intermediates prepared by Pechini process using three different ethylene glycol precursors (EG, PEG-400 and PEG-4000).
formation of polymeric intermediates as solid mass. Further, the polymeric phase and its microstructure are confirmed respectively from XRD and SEM results.

Fig. 4.37 shows the X-ray diffraction patterns of the polymeric intermediates prepared with three different ethylene glycols. From fig. 4.37, observed peak free XRD patterns indicate the absence of crystalline nature, which confirm the formations of amorphous phase in all the intermediates and it may be due to the formation of polymeric network between ethylene glycols and citric acid.

The scanning electron micrographs (SEM) of polymeric intermediates prepared with three different ethylene glycols are shown in fig. 4.38a, 4.38b and 4.38c. From fig. 4.38a, the SEM image for the polymeric intermediate prepared with ethylene glycol shows the polymer structure with large voids, which confirms the high porous nature. Whereas, the polymeric intermediates prepared with polyethylene glycols showed the void less cluster type of solid compound, which may be due to the poor polymerization between citric acid and polyethylene glycols.

4.5.3 Thermal Analysis of Polymeric Intermediates by DSC

DSC thermograms of the polymeric intermediates are shown in fig. 4.39. The observed exothermic peak between 335 °C and 440 °C, for all the polymeric intermediates, indicates the decomposition of organic derivatives. The sharp exothermic peak observed for the polymeric intermediate prepared with ethylene glycol indicates the better combustion compared to others. Observed broad exothermic peak with lower heat generation in DSC thermograms for the polymeric intermediates prepared with PEG- 400 and PEG-4000 indicate the poor combustion, which may lead to leave the residual organics, as impurities, in the prepared LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powders, further it is confirmed by FTIR spectral analysis.
Fig. 4.36 FTIR spectra of the polymeric intermediates prepared with different ethylene glycols (EG, PEG-400 and PEG-4000).

Fig. 4.37 XRD patterns of polymeric intermediates prepared with different ethylene glycols (EG, PEG-400 and PEG-4000).
Fig. 4.38. Scanning electron micrographs of polymeric intermediates prepared with different ethylene glycols (EG, PEG-400 and PEG-4000).
Fig. 4.39 DSC thermograms of the polymeric intermediates prepared with different ethylene glycols (EG, PEG-400 and PEG-4000).
The typical FTIR spectra of calcined polymeric intermediate at different temperature prepared with EG are shown in fig. 4.40. From fig 4.40, the intensity of the observed peaks, correspond to the organic derivatives, were begun to decrease at 300 °C and complete disappearance of IR Peaks was observed at 450 °C and above, which indicate the complete decomposition of organic derivatives. Simultaneously, two new IR peaks observed at 811 and 690 cm⁻¹ were respectively attributed to asymmetrical stretching vibrations of VO₄ tetrahedron [59], and bending vibrations of NiO₆/CoO₆ octahedral [17] for the dried gels calcined at 300 °C and above, which may be due to the formation of LiNi₀.₅Co₀.₅VO₄ structure and further, it is confirmed by XRD results. Typical XRD patterns for the calcined polymeric intermediates at different temperature prepared with ethylene glycol (EG) are shown in fig. 4.41. From fig. 4.41, crystalline phase of LiNi₀.₅Co₀.₅VO₄ was begun to form at 300 °C and the complete phase was observed at 450 °C and above, which is consist with FTIR results.

4.5.4 Characterization of LiNi₀.₅Co₀.₅VO₄ Powders by FTIR, XRD and SEM.

Fig. 4.42 shows the FTIR spectra of the LiNi₀.₅Co₀.₅VO₄ powders prepared by EG, PEG-400 and PEG-4000 assisted Pechini process at 450 °C for 12 hours. From fig 4.42, the FTIR spectra for the LiNi₀.₅Co₀.₅VO₄ powders prepared with PEG- 400 and PEG- 4000 showed the low intense peak around 1600 cm⁻¹, due to the presence of carboxylates, which indicates the poor combustion and it is consistence with DSC results. Also the observed IR peaks observed at 811 and 690 cm⁻¹ may be confirmed the formation of LiNi₀.₅Co₀.₅VO₄ structure.

Fig. 4.43 shows the XRD patterns of LiNi₀.₅Co₀.₅VO₄ powders prepared by EG, PEG-400 and PEG-4000 assisted Pechini process alongwith JCPDS standard of LiNi₀.₅Co₀.₅VO₄. The crystallite size of LiNi₀.₅Co₀.₅VO₄ powders, obtained by calcining the
Fig. 4.40 Typical FTIR spectra of as prepared and calcined polymeric intermediate at different temperatures prepared with EG.
Fig. 4.41 Typical XRD patterns of as prepared and calcined polymeric intermediate at different temperatures prepared with EG.
Fig. 4.42 FTIR spectra of LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powders prepared by Pechini process with different ethylene glycols at 450 °C.
Fig. 4.43 XRD patterns of LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powders prepared by Pechini process with different ethylene glycols at 450 °C.
polymeric intermediates at 450 °C, is calculated using the broadening of the (311) peak (recorded at the scanning rate of \( \frac{1}{2} \)° per min) obtained through Lorentz fitting method and the Scherrer's formula \([52]\). Table- 4.5 shows the FWHM and the crystallite size of \( \text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4 \) powders. Crystallite size of the \( \text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4 \) powders obtained by calcining the polymeric intermediates prepared with ethylene glycol, polyethylene glycol-400 and polyethylene glycol-4000 are respectively found to be 49, 71 and 76 nm. The lowest crystallite size is found to be 49 nm for the \( \text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4 \) powders prepared by Pechini process using ethylene glycol. The lattice parameter calculated for the \( \text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4 \) powder prepared with ethylene glycol is \( a = 8.2471 \) Å, which is very much comparable with the reported value in the literatures \([11]\). Hence, from the FTIR and XRD results ethylene glycol assisted Pechini process has optimized for the synthesis of organic free nanocrystalline \( \text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4 \) powders. Fig. 4.44 shows the typical SEM micrograph of the synthesized nanocrystalline \( \text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4 \) powder by Pechini process using ethylene glycol at 450 °C for 12 hours. From fig. 4.44, the SEM image of the synthesized \( \text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4 \) powder shows the agglomeration of fine nanocrystalline \( \text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4 \) particles.

### 4.6 Conclusions

Effect of various fuels and experimental conditions were investigated for the synthesis of nanocrystalline \( \text{LiMn}_2\text{O}_4 \) and \( \text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4 \) powders. A systematic study was carried out through FTIR, XRD, TG/DTA and SEM analysis and the following conclusions were made.

TG/DTA results of polymeric intermediates showed that the ignition temperature and duration of combustion reaction were decreased with increase of urea content. Lowest ignition temperature was observed as 255 °C for polymeric intermediates prepared with
Table – 4.5

Lorentz fit data and the crystallite size of nanocrystalline LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powders prepared by Pechini Process using different ethylene glycol precursors (EG, PEG-400 and PEG-4000) at 450 °C for 12 hours

<table>
<thead>
<tr>
<th>S No.</th>
<th>Name of the Process</th>
<th>2θ (Degree)</th>
<th>FWHM* of the 100% Peak (Degree)</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EG</td>
<td>36.12</td>
<td>0.24024</td>
<td>49</td>
</tr>
<tr>
<td>2</td>
<td>PEG – 400</td>
<td>36.20</td>
<td>0.20600</td>
<td>71</td>
</tr>
<tr>
<td>3</td>
<td>PEG – 4000</td>
<td>36.15</td>
<td>0.20223</td>
<td>76</td>
</tr>
</tbody>
</table>

* FWHM = Full Width Half Maximum

Instrumental broadening obtained using NBS standard silicon = 0.16924 (degree)
Fig. 4.44 Scanning electron micrograph of the LiNi_{0.5}Co_{0.5}VO_{4} powder prepared by Pechini process with ethylene glycol at 450 °C.
From FTIR and TG/DTA analysis, it is confirmed that the addition of urea to citric acid under acidic condition lead to the formation of ammonium carboxylates as well as ammonium nitrates in the polymeric intermediates and reduced the ignition temperature and also combustion duration. Also, FTIR and XRD studies, confirmed that the phase pure organic free nanocrystalline LiMn$_2$O$_4$ powder of 19 nm size was synthesized by calcining the polymeric intermediate at 300 °C prepared with M/ U = 1:2 and hence it is optimized.

Effect of nitric acid addition to the precursor solution was investigated in the Pechini process for the synthesis on nanocrystalline LiMn$_2$O$_4$ powders. XRD, FTIR and SEM results clearly showed that the addition of nitric acid to the starting solution inhibits the precipitation of metal citrates and motivated the better polymerization through the esterification between citric acid and ethylene glycol. Large expansion of the polymeric resin was observed for the Pechini process with nitric acid addition, whereas Pechini process without nitric acid addition results hard solid mass. From DSC analysis, the polymeric intermediate prepared with nitric acid addition caused more heat generation, during the combustion, which is due to the better combustion causes by the porous foamy intermediates. The phase pure nanocrystalline LiMn$_2$O$_4$ powders were obtained at 450 °C and the smallest crystallite size is found to be 16nm for the Pechini process with nitric acid addition, hence it is optimized. Though the heat generation is high for the polymeric intermediates prepared with nitric acid addition, the obtained crystallite size is smaller than other process, since the foamy porous microstructure of the polymeric intermediate inhibits the rapid nucleation of metal oxides during the combustion.

The effect of citric acid amount in citric acid assisted sol-gel combustion process was investigated for the synthesis of nanocrystalline LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powders relatively at lower temperature (450 °C). Addition of more citric acid (M/CA = 1:2 & M/CA = 1:3) caused the porous foamy intermediates (dried gels). However, from FTIR results, the
LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powders prepared with M/CA = 1:2 and 1:3 exhibits organic residuals due to the poor decomposition of organic derivatives. Hence, the sol-gel combustion process with M/CA = 1:1 has optimized for the synthesis of phase pure organic free nanocrystalline LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powder. The crystallite size of the LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powder is found to be 89 nm for the sol-gel process with M/CA ratio of 1:1.

The effect of various ethylene glycol precursors (EG, PEG-400 and PEG-4000) on the Pechini process was investigated for the synthesis of nanocrystalline LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powders. FTIR, XRD, DSC and SEM results confirmed that an addition of polyethylene glycols (PEG-400 and PEG-4000) to citric acid decreases the porosity of polymeric intermediates, which caused the poor combustion with long duration and leaves organic impurities in the prepared LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powders. Whereas, complete organic free phase pure nanocrystalline LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powders were obtained using the EG assisted process. The lowest crystallite size was found to be 49 nm for LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powders prepared by EG assisted process at relatively lower temperature (at 450 °C for 12 hours), hence it is optimized.

Among the above optimized processes nitric acid and ethylene glycol (EG) assisted Pechini processes are optimized respectively for the synthesis of nanocrystalline LiMn$_2$O$_4$ and LiNi$_{0.5}$Co$_{0.5}$VO$_4$ powders for further studies (surface modification), since they have resulted organic free phase pure powders with lower crystallite size.
References


