Studies on LiCr$_x$Ni$_y$Mn$_{2-x-y}$O$_4$ spinels synthesized by sol-gel method as 5V cathode materials for lithium rechargeable batteries
Summary

Glycine assisted spinel LiCr$_x$Ni$_y$Mn$_{2-x-y}$O$_4$ (0 ≤ $x$ ≤ 0.4 and 0 ≤ $y$ ≤ 0.4) has been synthesized. Thermal study of the precursor was carried out by thermo-gravimetric and differential thermal analysis. Further, the material has been subjected to x-ray diffraction, scanning electron microscopy and Fourier transform infrared spectroscopy analysis. X-ray diffraction patterns of LiCr$_x$Ni$_y$Mn$_{2-x-y}$O$_4$ matches well with the Joint Committee on Powder Diffraction Standard card No. 35-782 confirming the formation of single phase spinel. Charge/discharge studies were carried out between 3 and 5V to understand the electrochemical behaviour of the undoped and doped spinels. LiCr$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ calcined at 850°C possesses a particle size of around 70 nm and exhibiting an initial discharge capacity of 105 mAh g$^{-1}$ stabilizing at 98 mAh g$^{-1}$ over the investigated 20 cycles. However, maleic acid derived LiCr$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ delivers a stable higher discharge capacity of ~115 mAh g$^{-1}$ over the investigated 20 cycles and is a promising 5V cathode material.
3.1 Introduction

The technological escalation in the microelectronics zone and the onset of applications ranging from toys to missiles necessitate low cost, environment friendly and thermally stable lithium batteries with high power and energy densities. To cater to these requirements, the spinel LiMn$_2$O$_4$ has been focused with intense research as a prospective cathode material in lithium secondary batteries due to its low toxicity, easy availability, environmental benign nature, facile synthesis of this phase and also the low cost of lithium manganese oxide compared to other transition metal oxides such as LiCoO$_2$ and LiNiO$_2$ [279,280]. Recent trends in lithium batteries have been focused on the development and characterization of enhanced performing high voltage cathode material operating in the 5V regions [206]. Researchers revealed that partial substitution of manganese in LiMn$_2$O$_4$ with 3d transition metals renders it as a high voltage material with improved cyclability. Extending this concept of replacing of Mn atoms by 3d transition metal atoms in LiMn$_2$O$_4$, Zhang et al. [281] substituted Cr while Amdouni et al. [282] and Wu et al. [283] substituted Ni in LiM$_x$Mn$_{2-x}$O$_4$ (M= Cr, Ni) and concluded that the lost capacity at 4V plateau reappears in the higher voltage plateau (> 4.5V for M=Cr and > 4.7 for M= Ni) [284,285]. Several papers reported that single/multi doped cubic spinels and layered compounds were charged up to 5V to reduce the capacity fade upon repeated cycling [286-288].

The Ni substitution leads to higher discharge plateaus around 5V and in turn to high power density. The structural disintegration upon cycling can be prevented by
substituting metal with higher bonding energy. Towards this goal, Cr is substituted to maintain the spinel structure during cycling as the bonding energy of Cr-O is stronger than that of Mn-O and Ni-O [289].

In this present study, LiCr$_x$Ni$_y$Mn$_{2-x-y}$O$_4$ ($0 \leq x \leq 0.4$ and $0 \leq y \leq 0.4$) using glycine or maleic acid as chelating agent has been synthesized by sol-gel technique. The physical and electrochemical studies of the synthesized material have been done and the experimental results are discussed.

### 3.2 Experimental

Fig.3.1 shows flow chart for the synthesis of LiCr$_x$Ni$_y$Mn$_{2-x-y}$O$_4$ by a sol-gel method using glycine or maleic acid as chelating agents. Stoichiometric amounts of nitrates of lithium, manganese, chromium and nickel were uniformly mixed and dissolved in triple distilled water. This solution was stirred continuously for some time with mild heating to obtain a homogeneous solution. The solution was added drop by drop into an aqueous solution of 3 M glycine or maleic acid solution which is used as a chelating agent. The pH of the solution was adjusted between 5 and 7.5. The process of stirring and heating was continued until a solid gel was obtained. Further, the gel was initially heated overnight at 110°C. The thermal behaviour of the gel precursors was characterized by thermo-gravimetric and differential thermal analysis (TG/DTA) in a PL Thermal
Fig. 3.1 Flow chat for the synthesis of LiCrₓNiᵧMn₂₋ₓ₋ᵧO₄ by a sol-gel method using glycine/maleic acid chelating agents.
Sciences Instrument, model STA 1500. All experiments were carried out in air at a heating ramp of 20°C/min with typically 50mg samples. Furthermore, this gel mass was calcined at different temperatures viz., 250, 400, 600 and 850°C for 8 h in alumina crucibles. The resulting calcined samples are physically characterized using XRD, (JEOL 8030 X-ray diffractometer) with nickel filtered Cu-Kα radiation, scanning electron microscope, (SEM, Hitachi S-3000 H) and Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer, model paragon-500 spectrophotometer).

3.3 Electrochemical Studies

The electrochemical cell was a typical 2016 type coin cell (Hohsen Co., Japan) assembled using lithium metal as anode, Celgard 2400 as separator, and 1 M solution of LiPF$_6$ in a 50:50 (V/V) mixture of ethylene carbonate/diethylene carbonate [EC/DEC] as electrolyte and the synthesized material as cathode active material. The cathodes were prepared using a slurry coating procedure over an aluminum foil of 18 mm diameter. The slurry is a 85:10:5 mixture of respective cathode active material, acetylene black and polyvinylidene fluoride in N-methyl-2-pyrrolidone. Battery cycling tester unit has been employed for the evaluating the charge/discharge characteristics in the voltage range (3.0-5.0V) at C/10 rate.
3.4 Results and discussion

3.4.1 Thermal Studies

Fig. 3.2 shows TG/DTA curves of the Glycine and maleic acid assisted sol-gel derived LiCr$_x$Ni$_y$Mn$_{x-y}$O$_4$. The TG curves of all dual doped spinel depict two weight loss zones. Ab initio, a weight loss of ~ 15% in LiCr$_{0.1}$Ni$_{0.4}$Mn$_{1.5}$O$_4$ is obtained up to 152°C and may be due to loss of water molecule. Subsequently, another weight loss zone is seen between 152–300°C corresponding to 50% which could be ascribed to the decomposition of glycine or maleic acid as chelating agent and nitrate precursors. DTA curves show a sharp and shallow exothermic peaks at two different stages at the temperatures between 235 – 272°C and 300 – 400°C ascertaining the formation spinel compound. The formation temperature of LiCr$_{0.3}$Ni$_{0.2}$Mn$_{1.5}$O$_4$ is low ie., ~ 257.04°C in view of the higher specific heat of nickel (444 KJ/mole) as compared to chromium (397 KJ/mole). Furthermore, the formation temperatures with two exothermic peaks at all dual doped spinel compounds are seen between 257–272°C without much variation. However, in the case of maleic acid as chelating agent, the formation temperature is much lower (236°C) and could be due to the higher combustible nature associated with two carboxylic acids. Finally, all the sol-gel synthesized nitrate precursors confirm no weight loss beyond ~350°C suggesting the completion of thermal events.
Fig. 3.2  TG/DTA curves of the Glycine assisted LiCr$_x$Ni$_y$Mn$_{3-x}$O$_4$ (a) Cr–0.1; Ni–0.4, (b) Cr–0.2; Ni–0.3, (c) Cr–0.25; Ni–0.25, (d) Cr–0.3; Ni–0.2, (e) Cr–0.4; Ni–0.1, (f) Cr–0.25; Ni–0.25 (maleic acid assisted).
Fig. 3.3  XRD patterns of the sol-gel derived LiCr$_x$Ni$_y$Mn$_{2-x-y}$O$_4$ calcined at 850°C.  
(a) Cr–0.1; Ni–0.4, (b) Cr–0.2; Ni–0.3, (c) Cr–0.25; Ni–0.25, (d) Cr–0.3; Ni–0.2, 
(e) Cr–0.4; Ni–0.1.
3.4.2 X-Ray Diffraction

Fig.3.3 shows XRD patterns of the sol-gel derived LiCr$_x$Ni$_y$Mn$_{2-x-y}$O$_4$ calcined at 850°C. The high intensity peaks such as (111), (311), (222), (400), (331), (551), (440) and (351) obtained for the samples calcined at 850°C shows the high degree of crystallinity with phase pure structure and formation of the spinel compound, which is in agreement with previous researchers [290, 291]. It is well known that the pristine spinel has an Fd3m space group wherein the lithium occupies the 8a tetrahedral sites, and the manganese ions (Mn$^{3+}$ and Mn$^{4+}$) occupy the 16d sites and O$^{2-}$ occupies 32e sites [292]. However, when it is heated above 900°C, some impurities additional peaks are observed such as Mn$_3$O$_4$ and Li$_2$MnO$_3$. In other words, when the spinel structure is calcined to 900°C, it transforms to layered structure of LiMnO$_2$ which is not stable below 900°C and it will be oxidized in air to form LiMn$_2$O$_4$ [293]. All the peak signatures of spinel are in good agreement with the Joint Committee on Powder diffraction Standard (JCPDS card No.35-782). Glycine or maleic acid as chelating agent in sol-gel synthesis is beneficial for favouring metal ligand chain between Mn–O and COO$^-$ resulting in the formation of spinel product. Finally, the highly crystalline compounds were subjected to electrochemical charge-discharge studies.

3.4.3 FTIR Spectroscopy

Fig.3.4 shows FTIR spectra of the glycine or maleic acid assisted LiCr$_x$Ni$_y$Mn$_{2-x-y}$O$_4$ calcined at 850°C. The synthesized sample was ground, mixed with KBr and pressed
Fig. 3.4 FTIR spectra of the Glycine assisted LiCr$_x$Ni$_y$Mn$_{x-y}$O$_4$ calcined at 850°C. (a) Cr–0.1; Ni–0.4, (b) Cr–0.2; Ni–0.3, (c) Cr–0.25; Ni–0.25, (d) Cr–0.3; Ni–0.2, (e) Cr–0.4; Ni–0.1.
10mm diameter pellets. The FTIR spectra reveal asymmetric stretching and asymmetric bending vibrations for the spinel lithium manganese oxide. The high frequency bands of the FTIR absorption spectrum of LiMn$_2$O$_4$ located at approximately 615 and 513 cm$^{-1}$ are attributed to the asymmetric stretching modes of MnO$_6$ octahedra, whereas the low-frequency bands at approximately 225, 262, 355 and 420 cm$^{-1}$ have a mixed character due to the presence of the bending modes of O$^-$ Mn O bonds and modes of LiO$_4$ tetrahedra in the spinel structure. FTIR study on chromium and nickel doped spinel had been investigated by several authors [282,294]. The IR spectral band is seen at lower wave length around 614 cm$^{-1}$ may be assigned to Cr–O stretching vibration band and another band is shown at higher wave number around 512 cm$^{-1}$ due to Ni–O. These observations are in good accordance with the previous researchers. Further, it is ascertained that there is no significant spectral reflections as all sample were calcined at 850$^\circ$C except a slight shift for nickel dopant towards the lower wave number.

3.4.4 Scanning Electron Microscopy

Fig.3.5 shows SEM images of different dopant levels of the glycine or maleic acid assisted LiCr$_x$Ni$_y$Mn$_{x+y}$O$_4$ calcined at 850$^\circ$C. The surface morphology of LiCr$_{0.1}$Ni$_{0.4}$Mn$_{1.5}$O$_4$ calcined at 850$^\circ$C (Fig. 3.5a) clearly illustrates an average particle size of 0.5$\mu$m while in other two doped samples (LiCr$_{0.2}$Ni$_{0.3}$Mn$_{1.5}$O$_4$; LiCr$_{0.3}$Ni$_{0.2}$Mn$_{1.5}$O$_4$) the average spherical grain size is around 0.5$\mu$m.. Furthermore, it is quite interesting to note that LiCr$_{0.4}$Ni$_{0.1}$Mn$_{1.5}$O$_4$ depicts small particles size (0.3$\mu$m) with small grains as compared to other dopants. However, in the case of maleic acid derived
Fig. 3.5  SEM images of different dopant levels of the Glycine assisted LiCr$_{x}$Ni$_{y}$Mn$_{z}$O$_{4}$ calcined at 850°C. (a) Cr–0.1; Ni–0.4, (b) Cr–0.2; Ni–0.3, (c) Cr–0.25; Ni–0.25, (d) Cr–0.3; Ni–0.2, (e) Cr–0.4; Ni–0.1, (f) Cr–0.25; Ni–0.25 (maleic acid assisted).
LiCr$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ calcined at 850°C, the average particle size of ~0.25μm is reflected in the charge-discharge studies for obtaining high electrochemical activity and columbic efficiency. The above preliminary observations suggest that equal ratio of Cr and Ni dopant (LiCr$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$) in the pristine spinel is beneficial for enhancing the electrochemical performance.

### 3.4.5 Galvanostatic Charge-discharge and Cycling Studies

Fig.3.6 (a-e) show the first charge/discharge behaviour of different dopant levels of the glycine assisted LiCr$_x$Ni$_y$Mn$_{x-y}$O$_4$ calcined at 850°C. LiCr$_{0.1}$Ni$_{0.4}$Mn$_{1.5}$O$_4$ compound calcined at 850°C delivered a discharge capacity of 64 mAh g$^{-1}$ against the charging capacity of 95 mAh g$^{-1}$ corresponding to 75% columbic efficiency. It is evident that all other cells comprising the cathode materials viz., LiCr$_{0.2}$Ni$_{0.3}$Mn$_{1.5}$O$_4$, LiCr$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$, LiCr$_{0.3}$Ni$_{0.2}$Mn$_{1.5}$O$_4$, LiCr$_{0.4}$Ni$_{0.1}$Mn$_{1.5}$O$_4$ delivers first discharge capacities of ~ 82, 100, 72 and 65 mAh g$^{-1}$ respectively. Among all the investigated cells, the equal ratio of dopants in LiCr$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ with glycine as chelating agent exhibits better electrochemical performance (~100 mAh g$^{-1}$) with high columbic efficiency of ~85%.

It is interesting to note Fig.3.6 (f) that higher first charge/discharge (~115 mAh g$^{-1}$) is obtained in the case of maleic acid assisted synthesis of LiCr$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ calcined at
Fig. 3.6 Charge-discharge behaviour of different dopant levels of the Glycine assisted LiCr$_x$Ni$_y$Mn$_{1-x-y}$O$_4$ calcined at 850°C. (a) Cr–0.1; Ni–0.4, (b) Cr–0.2; Ni–0.3, (c) Cr–0.25; Ni–0.25, (d) Cr–0.3; Ni–0.2, (e) Cr–0.4; Ni–0.1, (f) Cr–0.25; Ni–0.25 (maleic acid assisted).
Fig. 3.7 Cycling behaviour of different dopant levels of the Glycine assisted LiCr$_x$Ni$_y$Mn$_{x-y}$O$_4$ calcined at 850°C. (a) Cr–0.1; Ni–0.4, (b) Cr–0.2; Ni–0.3, (c) Cr–0.25; Ni–0.25, (d) Cr–0.3; Ni–0.2, (e) Cr–0.4; Ni–0.1, (f) Cr–0.25; Ni–0.25 (maleic acid assisted).
850°C. This observation could be assigned to the two COOH groups present in maleic acid as compared to one in glycine thereby facilitating the formation of metal ligand chains between Mn–O and two COOH- groups resulting in the formation of sub-micron sized particles and resulting in stabilizing the spinel structure. However at unequal dopant concentrations there are much fall in discharge capacities owing to high density of cation distribution.

Fig. 3.7(a-e) illustrates the cycling behaviour of the investigated 20 cycles and corresponding columbic efficiencies for different dopant levels of the glycine assisted LiCr$_x$Ni$_y$Mn$_{x-y}$O$_4$ calcined at 850°C. LiCr$_{0.1}$Ni$_{0.4}$Mn$_{1.5}$O$_4$ compound calcined at 850°C shows initial discharge capacity of 64 mAh g$^{-1}$ but the capacity fades drastically up to 10 cycles and finally stabilizing at around 45 mAh g$^{-1}$ over the investigated 20 cycles. In the case of LiCr$_{0.2}$Ni$_{0.3}$Mn$_{1.5}$O$_4$, very low capacity fade has been observed i.e., 0.01 mAh (g$^{-1}$cycle$^{-1}$) vindicating the better capacity retention with a discharge capacity of 81 mAh g$^{-1}$ corresponding to a columbic efficiency of 85%. Furthermore, in the case of other two compositions (LiCr$_{0.3}$Ni$_{0.2}$Mn$_{1.5}$O$_4$, LiCr$_{0.4}$Ni$_{0.1}$Mn$_{1.5}$O$_4$) it is well known that the discharge capacities of 75 and 65 mAh g$^{-1}$ respectively are delivered in the 20$^{th}$ cycle corresponding to a capacity fade of 0.12 and 0.04 mAh(g$^{-1}$cycle$^{-1}$) with a columbic efficiency of ~85%. It is very exciting to see that the equal doping ratio of LiCr$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ with maleic acid as a chelating agent delivers the maximum capacity of ~115 mAh g$^{-1}$ with a capacity fade of only 0.01mAh(g$^{-1}$cycle$^{-1}$) corresponding to a columbic efficiency of 92% and exhibits higher capacity with very low capacity fade than glycine assisted spinel. The observations vindicate that the equal
doping ratio of LiCr$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ with maleic acid as chelating agent, exhibits higher discharge capacity and good columbic efficiency as compared to other doped spinels using glycine.

LiCr$_{0.1}$Ni$_{0.4}$Mn$_{1.5}$O$_4$ had been reported recently by Liu et al. [235] using citric acid as chelating agent to obtain high discharge capacity of the spinel. In his report only one composition i.e., LiCr$_{0.1}$Ni$_{0.4}$Mn$_{1.5}$O$_4$ synthesized by sol-gel method having low concentration of chromium and high concentration of nickel delivered a discharge capacity of $\sim$110mAh g$^{-1}$. Further, Yucheng Sun et al. reported the electrochemical performance of LiCr$_{0.4}$Ni$_{0.2}$Mn$_{1.4}$O$_4$ obtained by solution method after heating for 18h to use as cathode material for lithium rechargeable batteries [295]. In our present study, an attempt has been made to use either glycine or maleic acid as chelating agents so as to enhance the electrochemical performance of the spinel. However, our results are superior than that of maleic acid assisted equal doped ratio of chromium and nickel in the manganese spinel (LiCr$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$) exhibits very stable discharge capacity of $\sim$115 mAh g$^{-1}$ with very low capacity fade (0.01mAh/g$^{-1}$cycle$^{-1}$) up to 20 cycles.

3.5 Conclusions

LiCr$_x$Ni$_y$Mn$_{2-x-y}$O$_4$ ($0 \leq x \leq 0.4$ and $0 \leq y \leq 0.4$) has been synthesized using either glycine or maleic acid via sol-gel method to obtain sub-micron sized particles to enhance the electrochemical stability of the spinel. XRD and SEM studies show the formation of single phase compound with spherical grains of surface morphology having an average
particle size of 0.5μm. The synthesized spinel has been ascertained by XRD and FT-IR studies. Charge-discharge studies confirm that among all the investigated cells, the equal ratio of dopants with maleic acid assisted LiCr$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ exhibits maximum superior performance (~115mAh g$^{-1}$) with capacity of 0.01 mAh(g$^{-1}$cycle$^{-1}$) corresponding to a cumbic efficiency of 92% than that of glycine assisted LiCr$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ in the investigated 20 cycles which may be due to equal ratio of both dopants causing low cation mixing at the manganese site without any structural distortion. Finally, LiCr$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ with maleic acid as chelating agent seems to be an apt positive material to deliver high capacity for use in lithium rechargeable batteries.
Summary

Duo doped spinel LiCo$_x$Ni$_y$Mn$_{2-x-y}$O$_4$ (0 < $x$ ≤ 0.4 and 0 < $y$ ≤ 0.4) have been synthesised via sol-gel method using acetic acid, as chelating agent to obtain 5V positive electrode material for use in lithium rechargeable batteries. The sol-gel route endows lower processing temperature, lesser synthesis time, high purity, better homogeneity, good control of particle size and surface morphology. The optimized stoichiometric proportion is compared with maleic acid and oxalic acid as chelating agents. Physical characterizations of the synthesized powder were carried out using thermo-gravimetric and differential thermal analysis (TG/DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The electrochemical behaviour of the calcined samples have been carried out by galvanostatic charge/discharge cycling studies in the voltage range 3 to 5V. The XRD patterns reveal crystalline single-phase spinel product. SEM photographs indicate micron sized particles with good agglomeration. The charge-discharge studies show LiCo$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ synthesized using oxalic acid to be as a promising cathode material as compared to other two chelating agents and delivers average discharge capacity of 110 mAh g$^{-1}$ with low capacity fade of 0.2 mAh g$^{-1}$ (per cycle) over the investigated 15 cycles.