

Effect of Various Fuel Conditions on the Synthesis of Nano Crystalline LiNiVO₄ Powders for Lithium Battery Applications

S. Vivekanandhan, M. Venkateswarlu*, N. Satyanarayana[†]

Raman School of Physics, Pondicherry University, Pondicherry- 605 014, India

[†]Corresponding author: E-mail: nallanis2000@yahoo.com

*Present address: Department of Chemical Engineering, NTUST, Taipei, Taiwan

Abstract

Nano crystalline inverse spinel LiNiVO₄ powders were prepared by the gel combustion route with citric acid and glycerol under three different fuel conditions as (i) total metal ion to citric acid to glycerol ratio (M/CA/G) = 1:1:1 (ii) M/CA/G = 1:1:2 and (iii) M/CA/G = 1:2:1. Thermal behavior, structure and phase formation of the polymeric intermediates as well as LiNiVO₄ powders, were investigated by DSC, FTIR, SEM and XRD measurements. The pure crystalline phase of LiNiVO₄ powders with smallest crystallite size of 39nm were obtained from the polymeric intermediate, calcined at 450°C for 12 h, synthesized by Gel combustion route performed under the fuel condition of M/CA/G = 1:1:1.

Key words: Nano - crystalline LiNiVO₄, glycerol, polymeric gel, DSC, FTIR, SEM, XRD.

1. Introduction

Lithium nickel vanadate (LiNiVO₄), having inverse spinel structure, has been used as the cathode material for high voltage (4.8 V) lithium battery applications [1-4]. LiNiVO₄ type of high voltage cathode material offers a great promise for increasing the energy density of the lithium batteries. Better performance of the cathode material is due to its physical and chemical properties like crystallite size, homogeneity, stichiometry etc. which are mainly depend on the synthesis process [5]. Conventional solid state reaction method for preparing the LiNiVO₄ powders haven been reported, which showed the disadvantages as bigger grain size, high processing temperature, poor homogeneity etc [6,7]. In order to overcome these disadvantages, a variety of solution chemistry (wet chemistry) methods like sol- gel, hydrothermal, co-precipitation, gel combustion etc. have been developed and reported [8-12].

Among them, gel combustion method is a versatile, simple and cost effective process for the synthesis of multicomponent oxide powders in nano scale [13-17]. Some of the reports are available on the synthesis of LiNiVO₄ powders but smallest the reported grain size of LiNiVO₄ powders were found to be micro meter range only [2,7,13, 18]. Even the latest paper by Jina –Rui Liu et al

reported the particle size of as small as 0.5µm for the LiNiVO₄ powders prepared using citric acid at 500°C [18].

Recently, we have successfully developed a new gel combustion method using the combination of citric acid and glycerol (poly hydroxyl alcohol with three -OH groups in a molecule) for the synthesis of nano crystalline materials [20]. It is found that the fuel conditions can affect the formation of the polymeric network, which modifies the microstructure of the oxide powders. Hence, in the present work, gel combustion process was used, with three different fuel conditions as (i) M/CA/G = 1:1:1, (ii) M/CA/G = 1:1:2 and (iii) M/CA/G = 1:2:1, to synthesis nano crystalline LiNiVO₄ powders.

2. Experimental

Required stoichiometric amounts (metal ions to citric acid to glycerol ratio (M/CA/G) of 1:1:1, 1:1:2 and 1:2:1) of the lithium nitrate (SD-Fine, AR grade), nickel nitrate (MERCK India, Extra Pure) and ammonium vanadate (TRAC, AR grade) solutions (mole ratio of 1:1:1) were mixed together under the continuous stirring condition. Resulting transparent blue colour solutions were evaporated at 75°C under constant stirring condition and the continuous evaporation lead the formation of block colored gel (Stage-I). The block colored gel was then heated at 175°C for 12 hours to obtained polymeric intermediate (Stage-II). Thermal decomposition of the polymeric intermediates led to the formation of nano crystalline LiNiVO₄ powders, which were investigated using DSC, FTIR, SEM and XRD measurements.

3. Results and discussion

The DSC curves, measured between 30°C to 500°C, of the polymeric intermediates (Stage –II products) synthesized under three different fuel conditions are shown in fig. 1. From fig. 1, a single exothermic peak appears between 370 and 400°C for each sample indicates the combustion reaction of the polymeric intermediates. The combustion reaction observed at different temperatures is attributed to the nature of polymeric network exists in the intermediates, which was formed under different fuel conditions. The DSC thermogram of exothermic peak due to the combustion reaction indicate that the organic derivatives are decomposed at 400°C, which lead the

formation of crystalline LiNiVO_4 phase and it is further confirmed by FTIR and XRD analysis. DSC curve for the polymeric intermediate synthesized under the fuel condition of $M/CA/G = 1:1:2$ exhibits lower ignition temperature and high heat evaluation. The higher heat evaluation may cause the formation higher crystallinity as well as the formation of improper phase in LiNiVO_4 powders, which is confirmed by XRD spectra.

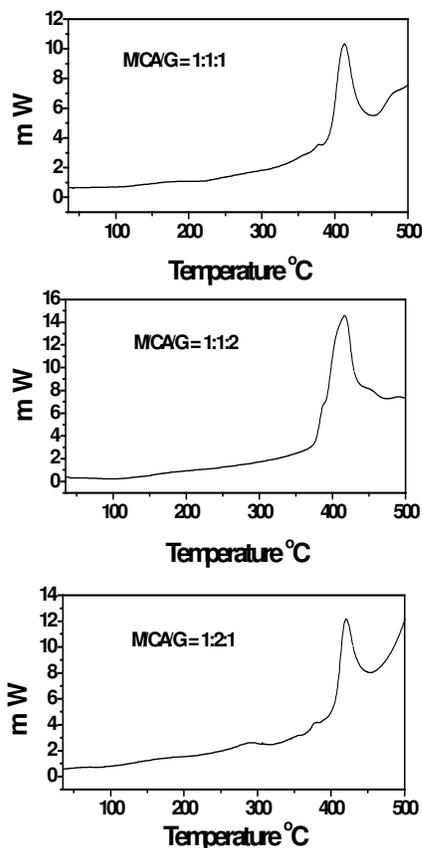
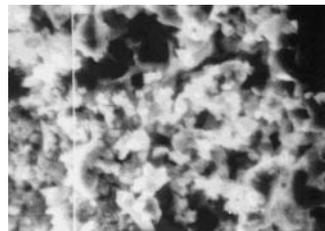
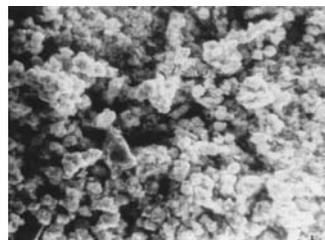


Fig. 1. DSC curves of the polymeric intermediates prepared with three different fuel conditions.

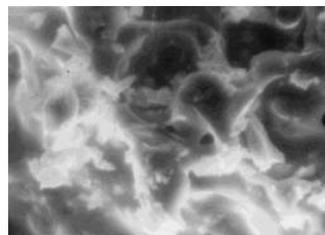
Fig 2 show the scanning electron micrographs of the polymeric intermediates. The SEM picture of fig. 2a and 2c showed the polymeric nature with large voids for the stage – II products prepared under the fuel conditions of $M/CA/G = 1:1:1$ and $1:2:1$. Increase of the glycerol over the citric acid ratio (i.e. $M/CA/G = 1:1:2$) lead the formation of the cluster structure as shown in fig. 2b, which indicates the poor polymerization due to the insufficient of the $-\text{COO}$ group (from the citric acid) to form the network through the esterification.



2a. $M/CA/G = 1:1:1$



2b. $M/CA/G = 1:1:2$



2c. $M/CA/G = 1:2:1$

Fig. 2. SEM images (2000 X) of the polymeric intermediates prepared with different fuel conditions.

FTIR spectra of the polymeric intermediates are shown in fig .3. From fig. 3, the IR peak at 3392 cm^{-1} for the polymeric intermediate is due to the O-H stretching associated with the hydroxyl group of the citric acid and the glycerol present in the polymeric intermediates. The peak at 1570 cm^{-1} is assigned to the asymmetric stretching of carboxylates ($-\text{COO}^-$), which confirms the chelation of metal ions through the formation of metal carboxylates [22]. The IR peak observed at 1255 cm^{-1} is due to the $-\text{C}-\text{O}-\text{C}-$ vibration shows the evidence for the esterification between the carboxylic and hydroxyl groups in citric acid and glycerol [23]. The intensity of the 1225 cm^{-1} peak decreases with increases of the glycerol amount ($M/CA/G = 1:1:2$) and the same peak was clearly observed for the stage- II product with $M/CA/G = 1:1:1$ and $1:2:1$. Thus, confirms the decrement of the ester formation between hydroxyl and carboxyl groups with increase of glycerol amount, which caused the poor polymerization and it is also clearly confirmed by SEM analysis. From fig. 4, FTIR spectra showed the formation of two new peaks at 811 cm^{-1}

and 690 cm^{-1} for the Stage – II powders calcined at 450°C , which are attributed to the stretching vibrations of V-O bonds of VO_4 tetrahedra in LiNiVO_4 [24, 25].

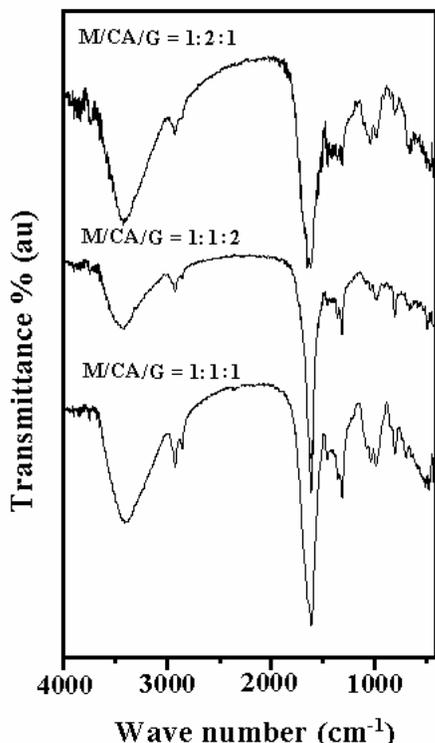


Fig. 3. FTIR spectra of the polymeric intermediates prepared with three different fuel conditions

Fig. 5 shows the typical XRD spectra for as prepared as well as calcined polymeric intermediates. From fig.5, the peak free XRD spectrum for the polymeric intermediates confirmed the amorphous/ polymeric nature. From fig.5 the crystalline LiNiVO_4 phase begun to form at 300°C and the complete phase was obtained 450°C and above. Fig 6 shows the XRD spectra of polymeric intermediates calcined at 450°C alongwith the respective JCPDS data. Crystallite size for the prepared crystalline LiNiVO_4 powders was calculated using the Scherrer's formula and the FWHM data obtained by Lorentz fit for the strongest XRD peak observed at $35^\circ 54'$. The crystallite size for the LiNiVO_4 powders obtained from the dried gels, calcined at 450°C , prepared with three different fuel conditions as M/CA/G = 1:1:1, 1:1:2 and 1:2:1 is 39, 55 and 40 nm respectively.

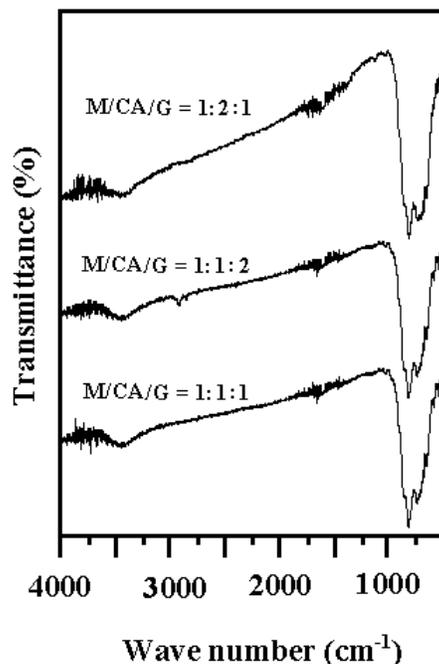


Fig. 4. FTIR spectra of the polymeric intermediates calcined at 450°C

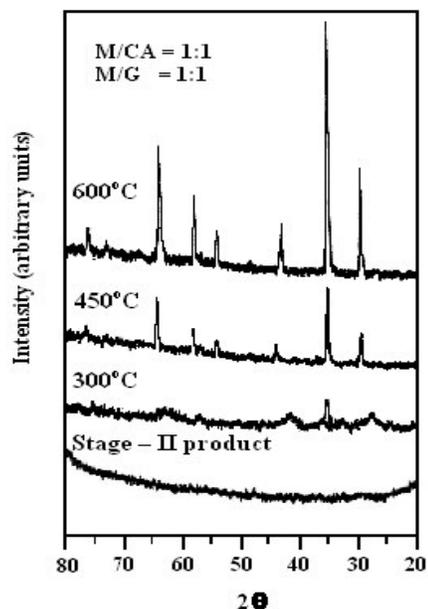


Fig. 5. Typical XRD spectra of the polymeric intermediates (M/CA/G/ = 1:1:1) calcined at different temperature:

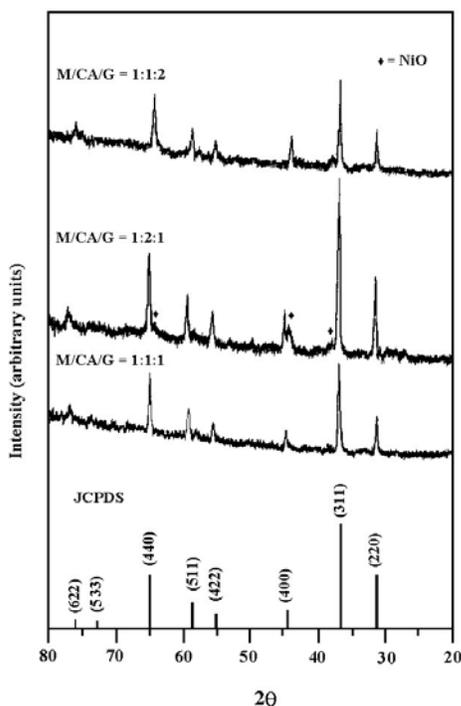


Fig. 6. XRD patterns of LiNiVO₄ prepared by calcining the polymeric intermediates at 450°C for 12 hours

4. Conclusions

Gel combustion process was systematically investigated for the preparation of nano crystalline LiNiVO₄ powders under three different fuel conditions. DSC, SEM, FTIR and XRD results confirm that the smallest crystallite size of 39 nm for LiNiVO₄ powders with pure crystalline phase obtained from the dried gels, calcined at 450°C for 12 hrs, synthesized using the gel combustion route with the fuel condition of M/CA/G= 1:1:1.

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