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Synthesis and Stoichiometric Analysis of Glycine-Urea Assisted Synthesis of Nanoporous $LiFePO_4$ /C Composite Cathodes for EES Applications.

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Abstract**: *The present research work, An economical and novel method for synthesis of $LiFePO_4$/C Nano composite by glycine , urea assisted combustion method with fuel to oxidizer ratio Ψ = one .The average crystallite size of obtained $LiFePo_4$ /C composite from x-ray diffraction is 39-44nm. Morphological studies were done using scanning electron microscope the structure of the as synthesized nano material were investigated by Raman spectroscopy. The structure of the material at the molecular size scale has been investigated by FTIR transmittance and Thermal Analysis and stoichiometry analysis for Fuel to nitrate ratio for urea and glycine and for various molarities and there balancing equations and calculation for Enthalpy of combustion and adiabatic flame temperature results were presented in this paper.***

Index Terms**: *X-Ray Diffraction analysis (XRD), Solution Combustion Synthesis , Scanning Electron Microscopy (SEM), Raman spectrum .***

I. INTRODUCTION

Increased global demand for energy combined with the progressive depletion of natural energy resources; climate change related to carbon emissions turn saving energy as a global problem of our time and future. Nowadays, lithium-ion batteries are the most effective energy storage technology. They are characterized by high energy density, good cyclic resistance, long life, low self-discharge and low maintenance requirements. The varied use of lithium-ion batteries is narrow related to the development of electrode materials capable of interact reversibly with lithium at various potentials. Like most promising electrode materials for use in batteries electromobiles are the intercalation compounds of the base of lithium transition metal phosphates, LiMPO4 (M = Fe, Mn, Co, Ni) with an oval type structure. Studies on phospho- the Olives started in 1997, and 10 years ago it was commercialized and LiFePO4-based battery (Nanophosphate®Advantagene) [1-3].

Phospho-olivines are characterized by three-dimensional a crystal structure made of metal octahedra LiO6 and M 2 + O6 and tetraesters PO4, connected to the top and edge of the three crystallographic ones axes of orthorhombic crystal lattice. The presence of a margin connected LiO6 octahedrons creates a prerequisite for the most energy- beneficial transport of lithium on the b-axis of the olivine structure, which determines the intercalating properties of these compounds. The increased interest in phospho-olivines is determined by a number their advantages: high theoretical capacity (170 mAh / g), stability in multiple cycling, safety in full charged state and at higher temperature, low cost, especially for LiFePO4 and environmental compliance. Their shortcomings are low ion / electron conduction and diffusion-limiting transmission of lithium ions, which leads to a real decrease of capacity at high charge / discharge speeds of electrochemical cell [4-6]. To overcome these disadvantages is necessary synthesis of nano-sized powders and increase the conductivity of the phospho-olivines by obtaining composites with conductive phase and multi-ion treatment. The key to achieving that objective may lie on Stoichiometric optimization and synthesizing the cathode material using chemical methods for battery applications. Nanotechnology plays a vital role in the synthesize and designing of the material according to your requirements that is high energy density and high power density by controlling particle size and morphology of the as

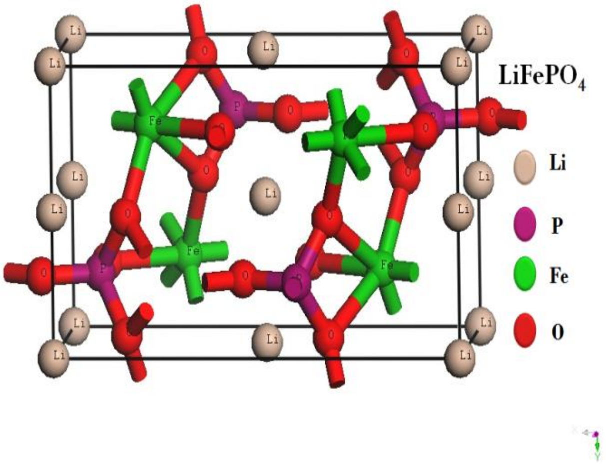

Fig. 1. Flowchart of various steps involved in Combustion synthesis for the preparation of $LiFePO_4$ Nanocomposite Material.

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synthesized material[3-6]. $LiFePO_4$ is one the high potential among the Fe related material. lattice parameter length is as follows a = 10.3290 (A°) , b =6.0065 (A°), and c = 4.6908 (A°) in the space group pnma (#62) and V= 291.2 A^3 respectively [7]. This paper reports economical route for the synthesis of $LiFePO_4$/C nano-composite cathode material for EES Application and further we can see the Stoichiometric analysis for Fuel to nitrate ratio for urea and glycine and for various molarities and there balancing equations and calculation for Enthalpy of combustion and adiabatic flame temperature (T_{ad}). Gaining pure, crystalline

A. Stoichiometric Analysis

To study the difference in (T_{ad}) with fuel/nitrate as well as nitrate/glycine molar ratio, were also calculated . T_{ad} is used to predict the accurate temperature at which the enthalpies of the synthesized nano end sample are equal to those of Precursors . If produced thermal energy generated heats up to the synthesized powder and no heat energy exchange takes place with the surrounding thenT_{ad} can be explained as

The Enthalpy of combustion synthesis can be defined as:

$$\Delta H^0_{reaction} = (\sum n\Delta H^0_f)\ \text{products} - \sum\ (n\Delta H^0_f)\ \text{reactants} \tag{1}$$

Adiabatic flame temperature can be calculated by using the equation:

$$Q = -\Delta H^0_{reaction} = \int_{298}^{T_{ad}} (\sum nC_p)_{products} dT \tag{2}$$

Where n = number of the moles

Thermodynamic calculation:

The sum of total reducing valencies in the fuel and total oxidizing valencies in the oxidizer is equal to zero.

$LiNO_3$ (C) +Fe $(NO_3)_3 \cdot 9H_2O$ (C) + $(NH_4)_2HPO_4$(C) +3.33 NH_2CONH_2 (C) (3)

From this chemical reaction nitrate to urea molar ratio is Nitrates have 3.33 Urea i.e.,

$$F/N = Fuel/Oxidant = Fuel/Nitrate = Urea/Nitrate = 3.33/4 = 0.8325 \tag{4}$$

Calculation of Fuel- to-Nitrate ratio for Glycine

The corresponding stoichiometric chemical reaction is as follows

⇒ $LiFePO_4$(C) + 2.22CO_2 (g) + (2 + 1.11) N_2 (g) + (13.5 + 2.22 × 2) H_2O (g) (5)

From this chemical reaction nitrate to urea molar ratio is **4** Nitrates have **2.22** Urea i.e.,

$$F/N = Fuel/Oxidant = Fuel/Nitrate = Glycine/Nitrate = 2.22/4 = 0.555 \tag{6}$$

Calculation of Urea-to-Nitrate molar ratio for different molarities and their balanced equations.

Metal Nitrate's-to-Urea molar ratio: (1:1:1)

$$Urea\ to\ .Nitrate\ \ ratio = 1/4 = 0.25 \tag{7}$$

Calculation of Enthalpy of combustion and T_{ad}:

$$\Delta H^0_{reaction} = (\sum n\Delta H^0_f)_{products} - \sum(n\Delta H^0_f)_{rectants}$$

=1034.57kcal/mol (8)

T_{ad} can be calculated by using the equation:

$$Q = -\Delta H^0_{reaction} = \int_{298}^{T} (\sum nC_p)_{products} dT \tag{9}$$

$$\Delta H^0_{reaction} = \int_{298}^{T} (\sum nC_p)_{products} dT \tag{10}$$

Metal Nitrate's-to-Urea molar ratio: (1:1:2)

$$Urea - to - Nitrate\ \ ratio = Urea/Nitrate = 2/4 = 0.50 \tag{11}$$

Calculation of Enthalpy of combustion reaction and T_{ad}:

The Enthalpy of combustion can be writen as:

$$\Delta H^0_{reaction} = 490.49\ Kcal/mol \tag{12}$$

T_{ad} calculation:

T_{ad}=1.277°K

Metal Nitrate's-to-Urea molar ratio: (1:1:3)

$$Urea - to - Nitrate\ \ ratio = 3/4 = 0.75 \tag{13}$$

Calculation of Enthalpy of combustion and T_{ad}:

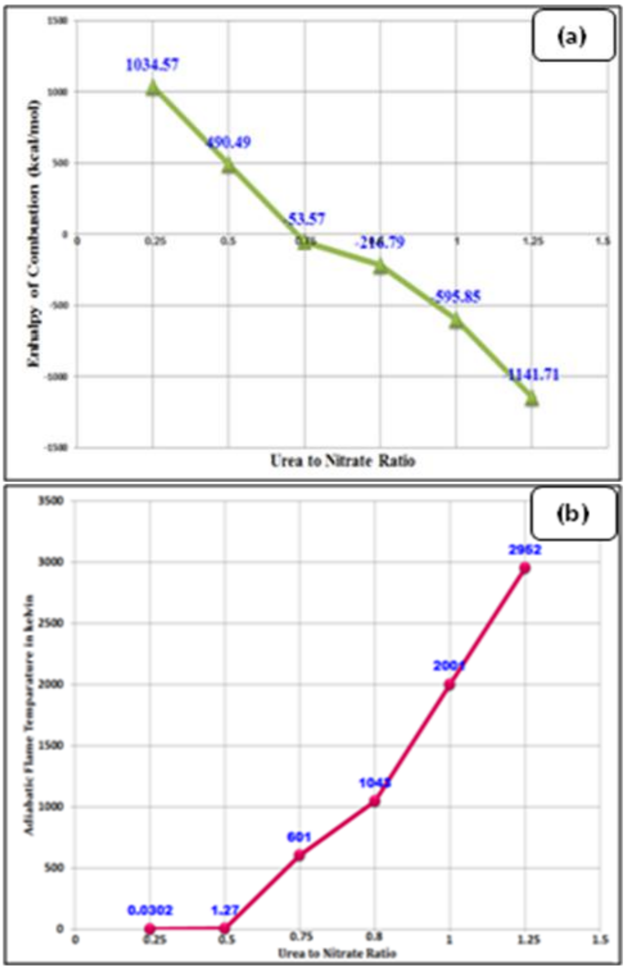


Fig. 2. (a) Enhalpy of combustion (Kcal/mol) Vs Urea / nitrate. (b) T_{ad} in Kelvin Vs urea to nitrate ratio of various steps involved in Combustion synthesis and Photographs of hotplate with stirrer

The Enthalpy of combustion can be expressed as:

$$\Delta H^0_{reaction} = -53.57kcal/mol \tag{14}$$

T_{ad}=601°K (15)

Metal Nitrate's-to-Urea molar ratio: (1:1:3)

This is Stoichiometric ratio calculated from valency method

$$\frac{Urea}{Nitrate} = \frac{3.3}{4} = 0.8250 \tag{16}$$

$$\Delta H^0_{reaction} = -216.79kcal/mol \tag{17}$$

T_{ad}=1043°K

Metal Nitrate's-to-Urea molar ratio: (1:1:3.3)

$$Urea\ to\ Nitrate\ \ ratio = 4/4 = 1 \tag{18}$$

$$\Delta H^0_{reaction} = -595.85kcal/mol \tag{19}$$

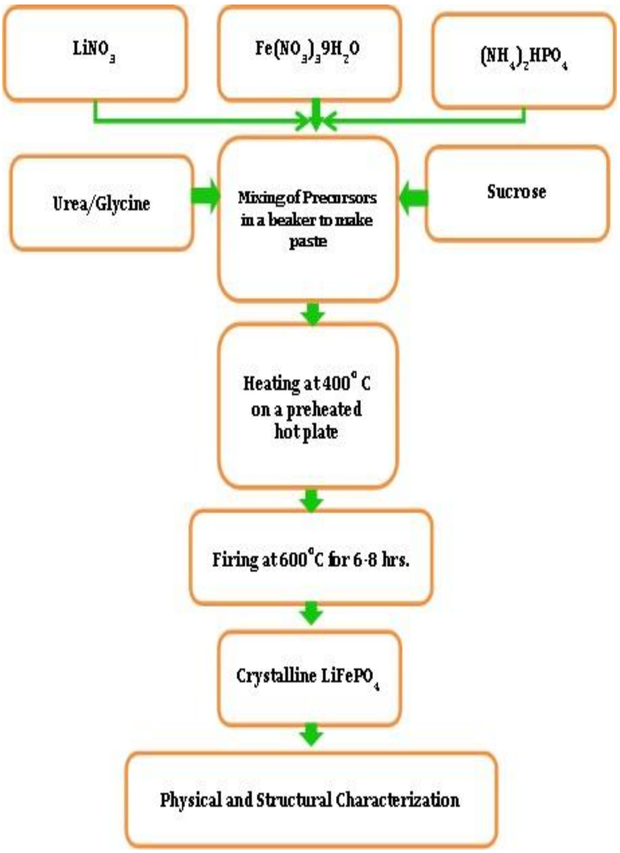
Adiabatic flame temperature calculation:

T_{ad}=2001°K

Metal Nitrate's-to-Urea molar ratio: (1:1:4)

$= 5/4 = 1.25$

$$\Delta H^0_{reaction} = -1141.71 kcal/mol \tag{20}$$



T_{ad}=2952°K

B. Synthesis

Nanoporous LiFePO$_4$ nanocomposite cathode material was synthesized glycine / urea assisted combustion method

All the reagents are analytical grade are taken in

Fig. 3. Flowchart of various steps involved in Combustion synthesis for the preparation of LiFePO$_4$ Nanopowder

the stoichiometric ratio Ψ=1 so that energy generated by the combustion is at a maximum.

I. Results and Discussion

A. X-Ray Diffraction analysis (XRD):

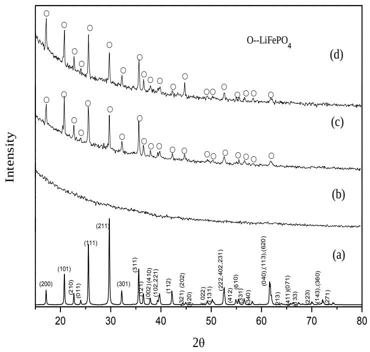
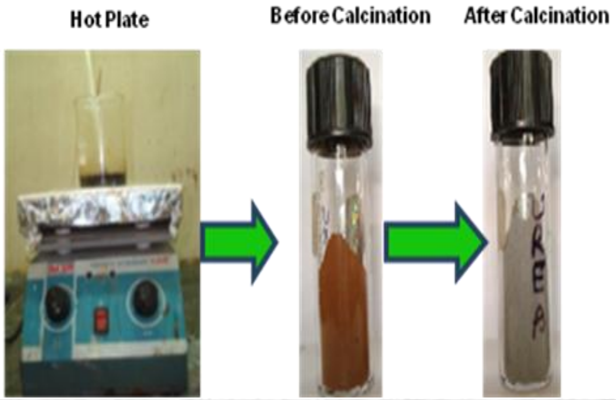


Fig. 4. XRD patterns of samples (a) standard LiFePO$_4$ with JCPDS card No:00-40-1499 (b) as synthesized powder(c) LiFePO4/C heat treated at 600°C for 6 hrs (d) 8hrs in vacuum furnace by filling 90% Ar+10%H$_2$

Fig.4 shows the X-Ray patterns of the as synthesized LiFePO$_4$/C nano composite calcinated at 600°C for different times.

B. Scanning Electron Microscope (SEM)



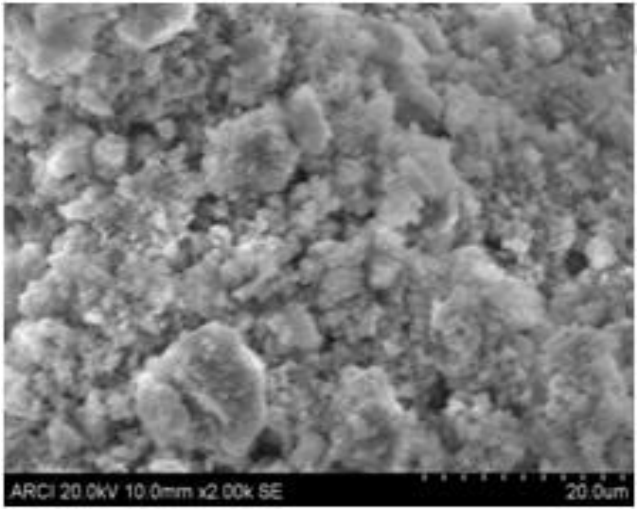


Fig. 5.SEM images of LiFePO$_4$/C composites containing samples (a) S1-Sample urea as fuel with 10% glucose and calcinated at 600C for 8 hrs in 90%Ar and 10% H2

The SEM (Hitachi s-3400E/N) micrograph of the typical LiFePO$_4$/C NanoComposite material obtained by the combustion process is shown in Fig. 4 which are calcinated 500^{o}Cat in vacuum for 7hrs. The SEM image shows the agglomeration of as synthesized sample with highly porous nature. From XRD the sample showing the nano sized crystallite sizes in the range of 39-44 nm.

C. Raman spectroscopy

The structure of the surface coated nano LiFePO$_4$/carbon and the material were investigated by Raman spectroscopy (Horiba Jobin-Yvon labram HR 800).

Table.I The relative intensities I_D/I_G disorder and graphitic carbon materials. The Raman spectra of as synthesized nano material shows two broad peaks at 1300-1480 and 1600-1625 cm^{-1}, both of which were attributed to the D band and the G band (graphite, sp^2) of Raman vibration modes for

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amorphous nature of carbon coating , respectively. Two broad peaks cantered at about 1345 and 1620 cm^{-1} corresponds to the D and G bands which show a breathing mode of rings and vibrations of sp^2 carbon atoms with dangling bonds, respectively.

Sample Name	D-Band	(I_D)	D-Band	(I_G)	I_D/I_G
(a)Gly+10% Glu HT600C6h	1327	145	1602	105	1.385
(b)Urea+10% Glu HT600C6h	1313	228	1603	164	1.391
(c)Urea+10% Glu VT600C6h	1346	350	1600	306	1.142
(d)Urea+20% Glu VT600C6h	1345	140	1623	123	1.138
(e)Gly+10% Glu VT600C6h	1373	144	1616	1370	1.050
(f)Gly+20% Glu VT600C6h	1353	264	1607	255	1.035

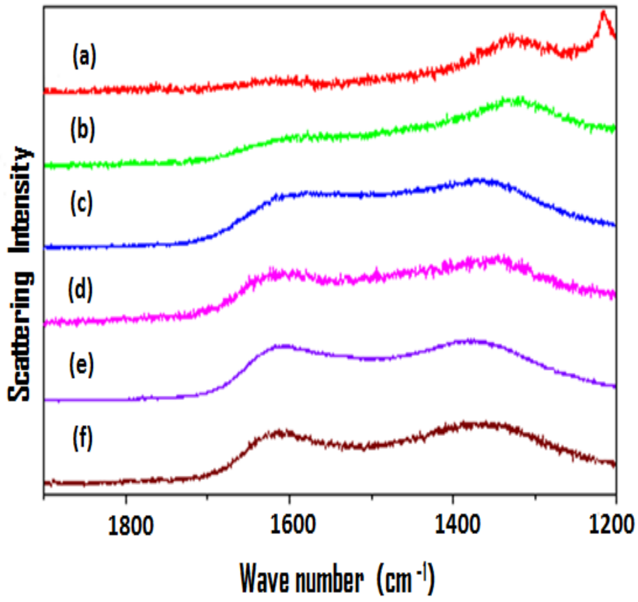

Fig. 6 Raman spectrum analysis of all samples (a)Glycine+10%Glucose+HT600°C 6h (b) U+10%G HT600°C 6h(c)Urea+10%Glucose+VT600°C7h (d) Urea+20%Glucose+VT600°C 7h (e) Glycine+10%Glucose+VT600°C 7h (f)Glycine+20%Glucose+VT600°C 7h Table.1. The relative intensities I_D/I_G disorder and graphitic carbon materials.

The relative intensities I_D/I_G can be used qualitatively to characterize the order of carbon materials. Higher ratios of I_D/I_G correspond to a lower degree of order in the graphite. The intensity ratio of D to G band is calculated to be varies from 1.392-1.035, which reflects the amorphous nature of carbon decreasing from sample (a-f) is shown in Table.1.

II. CONCLUSION

In In summary, we have demonstrated that the XRD peaks revels that by increasing the calcination time the amorphous powder achieves crystalline nature. All reflections of as synthesized powder reflect orthorhombic structure. noncrystalline part can be identified in the diffraction pattern of $LiFePO_4$, due to the existence of amorphous carbon coating on the sample. However main peaks broaden by increasing of calcinations temperature and time . SEM microstructure show the agglomerations of sample with highly porous nature and the crystalline size in the range of 40- 45nm.The ramanspectra of all samples displays disorderd carbon SP^3 and graphite sp^2 . The Raman spectra of carbon coated $LiFePO_4$ shows the group of peaks observed in the range of 1550–1660 cm−1 is called the graphite band (G-band), which is most pronounced for a high degree of symmetry and ordered structure in a carbon material.

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