

Nano Lithium – Ion Rechargeable Battery Materials

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ABSTRACT

Nano-crystallites of LTO (Lithium Titanium Oxide), LNP (Lithium Nickel Phosphate) type materials are prepared by means of ball milling methodology. High energy milling changes structural properties and morphological patterns. LTO and LNP have been investigated as prominent lithium-ion battery materials due to their excellent structural stability and safety. In this paper LTO and LNP nano particulates are characterized structurally and morphologically. Lithium-ion batteries, which are considered as promising power sources, have been extensively applied on electronic devices due to advantages such as high energy density, long cyclic life and no memory effect.

KEY WORDS: Nano Lithium-ion batteries, Ball milling method, LiNiPO₄, Li₄Ti₅O₁₂.

1. INTRODUCTION

Fossil materials causing global warming and atmospheric pollution, because they emit gases in to the ecosystem. Scientists working on clean energy sources (wind, solar, tidal) to reduce petrochemical pollution. We need to develop, better energy materials for the welfare of society. In human history energy storage has become more important. The present lithium ion batteries have proved themselves the most advanced electrochemical power sources for portable electronic devices (Robert F Nelson, 2000; Armand and Tarascon, 2008; Byoungwoo Kang and Gerbrand Ceder, 2009; Tarascon and Armand, 2001; Brian L. Ellis, 2010; Bruce Dunn, 2011; John B. Goodenough and Youngsik Kim, 2010; Vinodkumar Etacheri, 2011; Rui, 2010).

Lithium ion diffusion is important to achieve high power performance; due to this reason nanotechnology has paved the way for advanced electrode materials rather than the commercial lithium-ion battery electrodes. At present world, technological developments have increased the demand for nano bateries in high power applications. To achieve this goal, we have chosen the lithium transition metal phosphate, LiMPO₄ (M = Fe, Mn, Ni), potentials as cathode materials for rechargeable batteries (Padhi, 1997). Structural stability favors olivine-phosphates as next generation cathodes for high power Lithium ion batteries (Morgan, 2004). To improve the energy density, discharge rate and capacity retention, some of the scientific groups tried already with inert metals such as Al, Mg, Zn, Ti, Fe and Zr (Woo, 2009; Fu Zhou, 2009; Chen Yuhong, 2009; James Wilcox, 2009; Sivaprakash and Majumder, 2009; Bin Zhang, 2009; Ling Liu, 2009). Among cathode and anode candidates for high performance lithium-ion batteries, LNP, LTP have significant importance owing to its storage capacity. It is known that electrochemical performance of LTO is highly effected by its morphology and structure. We assume that these materials are highly discharge for electrochemical performance. Certainly we say that these materials good promising nano Lithium ion batteries of secondary electrode materials. Li₄Ti₅O₁₂, as a promising anode material for lithium ion batteries, it has many advantages compared to the conventional used graphite (Kingo Ariyoshi, 2005; Hongfa Xiang, 2011).

In the past decades, much effort has been devoted to the exploration of LTO with various particle sizes and morphological structures for enhancing rate capacities (Naiqing Zhang, 2011; Liang Zhao, 2011; Lijuan Wang, 2011; Mingdeng Wei, 2008). Extensive Studies on Li₄Ti₅O₁₂ nanoparticles, nanowires and nanotubes have been investigated (Zhaoyin Wen, 2005; Jie Shu, 2011). Li₄Ti₅O₁₂ have clearly indicated that the particle size and morphology play a prominent role in lithium intercalating activity and cycling stability of the material.

Synthesis of LTO and LNP: Stoichiometric quantities of precursor materials Li₂CO₃, TiO₂, NiO and NH₄H₂PO₄ were taken and intimately ball milled. After milling, the fine powder need to be calcined at 600°C 3h and sintered at 800°C 2h to effect solid state reaction among the reagents to form desired solid solution and to remove the gases of the reaction to form final powder. The ball mill was programmed to the respective milling time, with an interval period of 10 minutes for every one hour of milling at a speed of 400 rpm.

Characterization: The X-ray diffraction patterns of LTO, LNP were performed using D8 ADVANCE Diffractometer of BRUKER AXS with Cu K α radiation ($\lambda=1.5406 \text{ \AA}$). The data were collected using a step size of 4° min ranging from 0° to 90°. The morphology the samples were observed by Zeiss Ultra 55 FESEM, with oxford EDX system.

2. RESULTS AND DISCUSSION

Structure and morphology of LTO and LNP Materials: The X-ray diffraction patterns for LTO are shown in Fig.1. The LTO have confirms the formation of spinel cubic structure without any crystallographic defects. The well-defined reflections from the plains (1 1 1), (3 1 1), (4 0 0), (3 3 1), (3 3 3), (4 4 0) and (5 3 1) are observed. The Identified reflections from the plains closely correspond to the standard pattern for spinel LTO (JCPDS card 82-1616). This is an indication of the spinel cubic single-phase formation. The crystallite size calculated for the LTO from XRD data's are 54.31nm in size. X-ray diffraction patterns for LNP are shown in Fig.1a. After the analysis of XRD patterns, the LNP have confirms the formation of orthorhombic structure of lithium nickel phosphate in space group pnma without any crystallographic defects. The well-defined reflections from the plains (2 2 2), (1 0 1), (2 1 0), (0 0 1), (0 2 0), (3 0 1), (3 1 1), (1 2 1), (1 1 0), (2 2 1) and (2 2 2) are observed. The identified reflections from the plains closely correspond to the standard pattern for orthorhombic olivine-type structure of LNP (JCPDS card - 88-1297). The crystallite size calculated for the LNP from XRD data's is 47.34nm in size.

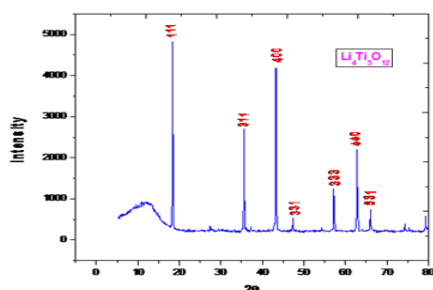


Fig.1. XRD Patterns of LTO

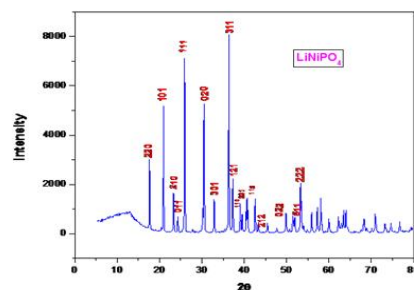


Fig.1a. XRD Patterns of LNP

Lattice constant: Lattice parameters of LTO, LNP are calculated using UNITCELL software (Unit-Cell software, 1995). These results agree reasonably well with previous crystallographic data. The results are tabulated below. The experimental results are good agreement with the reported values.

Table.1. Calculated lattice parameters and volume for LTO

S.No.	Lattice Constant & Cell Volume	Experimental	Reported (Gangulibabu, 2009)
1	a (Å)	8.36300	8.3420
2	V (Å ³)	584.9073	580.5113

Table.1a. Calculated lattice parameters and volume for LNP

	S.No.	Lattice Constant			Cell Volume (Å ³)
		a(Å)	b(Å)	c(Å)	
Experimental	1	9.39449	5.29470	5.21075	259.1875
Reported (Byung-Hyun Choi, 2010)	2	10.03	5.850	4.690	275.19

FE-SEM Studies: The morphology and particle size of LTO and LNP are examined by Field Emission-Scanning Electron Microscopy. The elemental composition also identified from EDS spectra. The size, shape and surface morphology of the LTP, LNO are clearly indicated FE- SEM image as shown in Fig.2 and Fig.2(a). The micrograph images of LTP, LNO prove that they have granular nano sized range and have a uniform distribution with agglomerated particles of spherical and rod shape [18]. The particle size ranges from 1μm to 100nm as shown in Fig.2 and Fig.2(a). Energy Dispersive X-ray (EDX) spectrometer analysis is confirmatory presence of elemental Phosphorous, Titanium, Oxygen signals in the LTO and Phosphorous, Nickel and Oxygen signals in LNP. The vertical axis displays the number of x-ray counts although the horizontal axis displays energy in KeV (Fig.3 and Fig.3a). The weight and atomic percentage of Phosphorous, Titanium, and Oxygen of LTO was to found in Table.2. Phosphorous, Nickel and Oxygen of LNO was found in Table.2a. These correspond, the spectrum without impurities peaks. EDS cannot detect the elements with atomic number less than four.

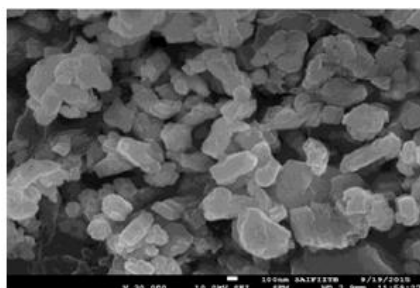


Fig.2. FE-SEM image of LTO

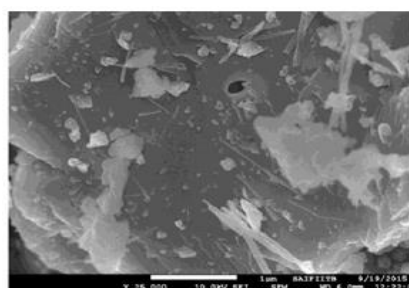


Fig.2a. FE-SEM image of LNP

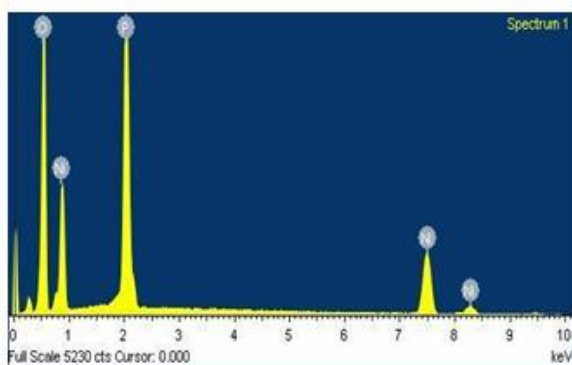


Fig.3. EDS patterns of LTO

Table.2. Elemental composition of LTO

Element	Weight %	Atomic%
O K	49.52	74.52
P K	0.42	0.33
Ti K	50.06	25.16
Total	100	

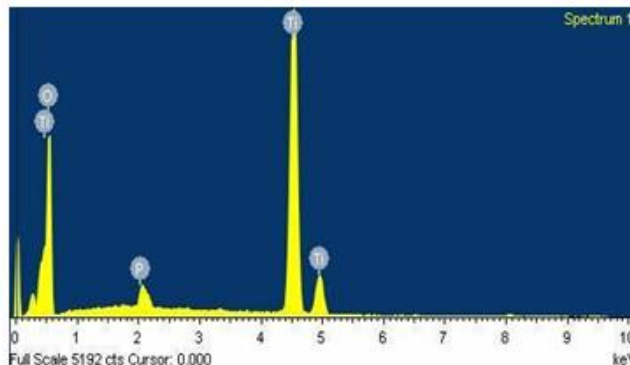


Fig.3a. EDS patterns of LNP

Table.2a. Elemental composition of LNP

Element	Weight %	Atomic%
O K	32.86	57.99
P K	22.56	20.56
Ni K	44.59	21.44
Total	100	

3. CONCLUSION

LTO and LNP materials are synthesized by Mechanical milling method. XRD patterns of these materials are shown the formation of phase and purity of the compounds. Field Emission - Scanning Electron Microscopy and Energy Dispersive Spectrum results shows that the average grain size is less than 100 nm. Energy dispersive spectroscopy revealed the elemental composition of these electrode materials.

Future Perspective: Development of new anode and cathode candidates as battery materials with transition and inert substituents. Impedance measurements and theoretical studies of LTO and LNP to be pursued. Furthermore, fabrication of these electrode materials is also to be investigated.

Conflict of Interest: The authors declare that there is no conflict of interest.

4. ACKNOWLEDGEMENT

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