PERCEPTIBLE OUTPUT BASED ON THIS RESEARCH WORK
Papers published in International Journals…


7. M. Sivakumar, **R. Muruganantham**, R. Subadevi, “Investigation on polyol technique developed LiFePO$_4$/CeO$_2$ composite positive electrode materials for Rechargeable Lithium batteries”, *(under revision, RSC advances)*
8. **R. Muruganantham**, M. Sivakumar, R. Subadevi, “Polyol technique used Nb$_2$O$_5$ treated lithium iron-phosphate cathode materials for rechargeable Lithium-ion batteries”, *(To be submitted)*


**Papers presented/accepted in International and National conferences/symposium…**


2. M. Sivakumar, **R. Muruganantham**, R. Subadevi and F.M. Wang, “**Structural Investigations on Ag-Doped LiFePO$_4$ Composite Cathode Materials For Li-Batteries**”, Paper accepted in 16$^{th}$ International **Meeting on Lithium Batteries (IMLB-2012)** to be held at the ICC Jeju, Korea during 17 & 22, June 2012. Abstract No. **AF0760**.


4. M. Sivakumar, R. Muruganantham, R. Subadevi, “A Venture to Prepare Nano Sized LiFePO$_4$ by Low Temperature Method”, Paper accepted in National Conference on Nanomaterials-2010 to be held at Department of Physics, Karunya University, Tamil Nadu, India, during 3$^{rd}$ & 4$^{th}$ December, 2010.


**Workshops Participated in National/International levels…**

1. One day Workshop on “Materials Characterization Techniques-AFM & XRD” on 19$^{th}$ November 2014 at School of Physics, Madurai Kamaraj University, Madurai-24, Tamil Nadu, India.
2. One Day Acquaintance Programme on **Experimental Facilities at Inter University Accelerator Centre**, New Delhi held on 15 November 2013 organized by School of Physics, Madurai Kamaraj University, Madurai-24, Tamil Nadu, and IUAC New Delhi.

3. Workshop on **“Computational Physics”** held on 30\(^{th}\) and 31\(^{st}\) August 2013 at School of Physics, Madurai Kamaraj University, Madurai-24, Tamil Nadu, India.

4. National Workshop on **“Innovative and Creative Approaches for Sustainable Development of India”** held on 30\(^{th}\) April 2013, organized by Industry and Consultancy Cell, Alagappa University, Karaikudi-03, Tamil Nadu, India.

5. National Workshop on **“Characterization Techniques-II (NWCT-II)”** during 21-23, March 2013 at School of Physics, Alagappa University, Karaikudi-04, Tamil Nadu, India.

6. National Workshop on **“Characterization Techniques-I (NWCT-I)”** during 24 & 26 March 2012 at School of Physics, Alagappa University, Karaikudi-04, Tamil Nadu, India.

7. International Workshop on **“Advanced Energy Materials (IWAEM-2012)”** held on 9 & 10, February 2012 organized by School of Physics, Alagappa University, Karaikudi-04, Tamil Nadu, India.

8. State level Workshop on **“Structure Solving by Powder X-Ray Diffraction (SLWSSPXRD-2011)”** on 26 & 27 July 2011, organized by School of Physics, Alagappa University, Karaikudi-03, Tamil Nadu, India.

9. International Workshop on **“Advanced Functional Nanomaterials”** organized by Centre of Nanoscience and Technology, Crystal Growth Centre & Centre for International Affairs held at Anna University, Chennai, Tamil Nadu, India during 21-24, February, 2011.
10. International Workshop on “Advances in Nanoscience and Technology” organized by Crystal Growth Centre, Anna University Chennai, Tamil Nadu, India during 28-30, October 2009.

11. National Workshop on “Crystal Growth and Characterization (NWCGC 09)” on 16th March 2009 organized by School of Physics, Alagappa University, Karaikudi-03, Tamil Nadu, India.

12. National Workshop on “Recent Advancement in Material Science (NWRAMS)” on 7th March 2008 at School of Physics, Alagappa University, Karaikudi-03, Tamil Nadu, India.

13. Workshop on “Nano Structures and Devices” (under TEQIP Community Services) on 23rd Feb. 2008, held at Department of Physics, NIT, Trichy-15, Tamil Nadu, India.

Seminars Participated…


2. State Level Seminar on “Recent Trends in Condensed Matter Physics (RTCMP-2010)” under UGC-DRS-Phase III program, during 15-16, Feb. 2010 at School of Physics, Madurai Kamaraj University, Madurai-24, Tamil Nadu, India.

3. National Conference on “Renewable Energy Sources and Technology (REST)” during 21- 23 January 2010 organized by Department of Physics, VHNSN College, Virudhunagar, Tamil Nadu, India.
4. National Symposium on “Importance of Nanoscience and Nanotechnology (INT 09)” on 14 & 15 March 2009 conducted by Department of Nanoscience and Nanotechnology, Alagappa University, Karaikudi-03, Tamil Nadu, India.

5. National Seminar on “Differential Equations (NSDE 09)” on 6 & 7 March 2009 at Department of Mathematics, Alagappa University, Karaikudi-03, Tamil Nadu, India.

**Participated on Short-Term Certificate Course…**

- Certificate Course on “Materials Characterization” has been completed at IIT Madras, Chennai, Tamil Nadu, India during December 16-19, 2013.
A facile synthesis and characterization of LiFePO$_4$/C using simple binary reactants with oxalic acid by polyol technique and other high temperature methods

R. Muruganantham, M. Sivakumar, R. Subadevi & N.-L. Wu
A facile synthesis and characterization of LiFePO$_4$/C using simple binary reactants with oxalic acid by polyol technique and other high temperature methods

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Abstract An attempt has been made to synthesize the carbon coated Fe-based phospho-olivine nano-crystalline cathode materials using simple binary sources via polyol method. Also, a curious attempt has been made to compare the material with the high temperature methods, viz., hydrothermal and solid state method with the same binary sources as raw materials and oxalic acid as a carbon source. The thermal behaviour of the mixed raw materials of LiFePO$_4$ and thermal stability of the final prepared materials were characterized by TGA. The prepared materials were confirmed as orthorhombic olivine structure with Pnma space group. LiFePO$_4$/C material prepared by Polyol method exhibits an initial reverse capacity of 150 mAh g$^{-1}$ at 0.1 C rate under room temperature. Also, stable capacity of 143 mAh g$^{-1}$ has been observed over 50 cycles at 0.1 C rate at room temperature among the other methods studied. It may be due to the coverage of tiny particles by carbon and it leads to provide better electronic conductivity and thereby provides good electrochemical performances.

1 Introduction

Nowadays, Lithium batteries are suitable power sources for portable electronics and electric vehicles (EVs), but, further improvements are going to use the hybrid electric vehicles (HEV), plug-in hybrid electric vehicle (PHEV) and space application respectively. In the past decade, most of the researchers are investigating LiFePO$_4$ cathode material, because it exhibits various advantages such as low cost, eco-friendly, low toxicity, high thermal and chemical stability in fully charged state. It can be attained its maximum theoretical specific capacity (170 mAh g$^{-1}$) and good flat discharge potential at 3.4 V versus Li/Li$^+$ [1-4].

However, the low electronic conductivity and lithium diffusivity significantly restrict the rate performance of LiFePO$_4$. To overcome these problems, many efforts have been taken including reduction of the particle size [5], surface modification using metal oxide, [6] or carbon coating, [7, 8] and lattice modification via doping of other cation [9, 10], etc. For better realization, the synthesis method affects the particle size and morphology. The decrease of particle size will not improve the electronic conductivity, but, can obviously reduce the diffusion distance of lithium ions. This indicates that the particle size and morphology play an important role on electrochemical performances of the material. However, the carbon coating is one of the best method to enhance the electronic conductivity [7]. In this view point, LiFePO$_4$ cathode materials have been prepared via three different methods such as polyol, [11-13] hydrothermal, [14] and solid state reaction methods [15]. Due to its simplicity and controllability, the cost-effective method like polyol process is one of the suitable technique for the production of LiFePO$_4$ in nanoscale without inert atmosphere and post heat treatment.

Kim and Kim [11] introduced the polyol process prepared LiFePO$_4$ using three raw materials with tetra ethylene glycol (TTEG) as a polyol solvent. They controlled particle size using modified reaction time [16]. They obtained an initial capacity of 166 mAh g$^{-1}$ at a current density of 0.1 mAcm$^{-2}$ with utilization efficiency of 98% and 168 mAh g$^{-1}$ at the 0.1 C rate in the voltage range of 2.5-4 V with well-formed plateau. Munichandraiah et al. [17] reported nanoplate LiFePO$_4$ was synthesized by
Studies on Graphene Enfolded Olivine Composite Electrode Material via Polyol Technique for High Rate Performance Lithium-Ion Batteries

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The graphene enfolded LiFePO4/C composite cathode material has been prepared via low temperature polyol process, followed by a simple chemical reaction method. The low viscous polyol solvent (DEG) (3.57 mPa s at 25°C) and usage of low temperature process (below 245°C) aid the graphene tightly encapsulated on the LiFePO4 surface that plays an important role, especially in the high rate performances over long cycles, efficiently preventing the separation of the graphene and LiFePO4 during the reaction processes, hence realizing the full potential of the active materials. The graphitization on LiFePO4/C remarkably increased the electronic conductivity of LiFePO4. The layered sheets of graphene wrapped on LiFePO4 particles provide void between graphene sheets and LiFePO4 surfaces, which facilitate the diffusion of Li+. This approach opens up a method to attain the theoretical capacity of LiFePO4. The material exhibits a superior electrochemical performance such as initial discharge capacities of 169.6 and 92 mAhg-1 at 0.1 and 30 C rates, respectively. It has an excellent capacity retention and diminutive capacity fading. The narrow size of LiFePO4 particle causes a shorter diffusion path, which reduce the time for Li+ migration between cathode and electrolyte.

Keywords: polyol process, LiFePO4, graphene, electrochemical performance, capacity fading

1. INTRODUCTION

The Lithium-ion batteries are a suitable power source of high-energy applications. The electrode materials determine the operating voltage and electrochemical performance of a battery.21 The positive electrode (cathode) material plays a vital role in Lithium-ion batteries; they are classified into three categories based on their structure, such as layered, spinel and olivine types. Among these, olivine type LiFePO4 cathode material has attractive advantages such as low cost, eco-friendly, low toxicity, and high thermal and chemical stability in fully charged state. It can be attained its maximum theoretical specific capacity (170 mAhg-1) and good flat discharge potential of 3.4 V versus Li/Li+. However, the drawbacks of LiFePO4 are its low electronic conductivity (10-10 to 10-12 S cm⁻¹) and low diffusion of Li+ ions across the LiFePO4/FePO4 boundary, which leads to low capacity and poor rate capability.12 To overcome the drawbacks and to enhance the electrochemical performance
Synthesis of surface modified LiFePO₄ cathode material via polyl technique for high rate lithium secondary battery

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ABSTRACT

The NIO-coated LiFePO₄ composite cathode materials were prepared by simple tailored polyl technique, which has orthorhombic olivine structure without NIO phase. It delivers the reversible capacity of 164 mAh g⁻¹ at 0.1 C rate at ambient temperature. The material exhibits stable reverse capacity for several cycles even for the higher C-rates. Increasing the rate, the reverse capacity is almost stable over several cycles. Furthermore, at a high rate viz., 10, 20 and 30 C, the discharge capacity has been observed for the optimised NIO-coated LiFePO₄ at 135, 120 and 93 mAh g⁻¹, which demonstrates the excellent rate performance that can be useful for high power lithium secondary battery.

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1. Introduction

Day by day, our society meets two major challenging issues, such as energy crisis and environmental issues. Hence, a safe, low-cost, high efficiency and environmentally benign alternative power sources have become a most urgent need. For decades, lithium battery has been fulfilled the requirement and played a key role in the consumer electronic market. Nowadays, it is moving towards electronic automotive transportation (electric vehicles, full hybrid electric and plug-in electric vehicles) [1,2]. Electrode plays a crucial role in electrochemical performance of batteries and ion transport between positive and negative electrode. It holds an important implication for battery capacity, circulation, and security properties. At present, thermal stability of LiFePO₄ enables the safety of the batteries especially for large-scale applications. It has a highly stable three-dimensional frame work due to strong N-O covalent bonds in the PO₄³⁻ polyanion, which prevents the liberation of oxygen and keeps the stable framework during the charge and discharge processes [3]. This property provides an excellent stability, stable operation of lithium batteries even under unusual conditions. Recently, some approaches have been explored to enhance the electrochemical performances of LiFePO₄ through particle size reduction, conductive elements or metal oxide modification on the surface of LiFePO₄ and lattice modification with other metals [4-7]. Among these, few works have been established to develop the LiFePO₄ via coating with oxide materials, such as RuO₂ [8], ZrO₂ [9], TiO₂ [10], CaO [11], SiO₂ [12], Al₂O₃ [13], V₂O₅ [14], Cr₂O₃ [15], SnO₂ [16], Sn₂O₃ [17], MoO₃ [18] and WO₃ [19] and improved its electrochemical performances. In connection, NIO is one of the suitable materials for energy storage applications owing to its high theoretical capacity, low cost, and high chemical and thermal stability [20]. The NIO nanotubes enhance the diffusion of electrolyte and provide more paths for diffusion of ions leading to improvement in the performance of the electrode material [21]. The NIO-coated LiFePO₄ active material provides a better channel for the Li⁺ diffusion from the electrolyte to the surface of the active materials during intercalation and deintercalation. Ge et al. [22] and Qing et al. [23] reported that the Ni-doped LiFePO₄/C by solid state reaction method; also Novikova et al. [24] proposed Ni, Co and Mg doped LiFePO₄ using sol-gel method. They have obtained an excellent rate capability and cycling performance. The first polyl technique prepared LiFePO₄ has been reported by Kim and Kim [25] and recently carbon nanotubes and graphene nanosheet comodified LiFePO₄ via polyl process reported by Wu et al. [26].

To the best of our knowledge, no reports are available in the literature about the NIO-coated LiFePO₄ prepared via polyl technique. Hence, in the present investigation, an effort has been made to prepare NIO-coated LiFePO₄ composite and to scrutinize their structural, morphological and electrochemical performances.
Structural and magnetic properties of LiFePO₄ cathode material prepared by polyol technique

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ABSTRACT
Nano-crystalline LiFePO₄ cathode material has been prepared by polyol technique. The crystalline structure, functional group vibration analyses of the prepared cathode material were characterized by X-ray diffraction (XRD), Fourier transfer infrared spectroscopy (FT-IR) and Raman Studies. The surface morphology of synthesized material has been studied by scanning electron microscopy (SEM) and the compositional analysis has also been carried out through EDX analysis. It is inferred from XRD result that LiFePO₄ powder have an orthorhombic structure with a space group of Pnma. The magnetic properties of the fine particles of LiFePO₄ were examined by vibrating sample magnetometer (VSM) at room temperature, which showed that the prepared sample exhibited a tiny hysteresis loop with the coercivity of 400 G.

Introduction
Since Goodenough et al. [1] first reported lithium iron phosphate (LiFePO₄) with olivine structure as a new cathode material for rechargeable lithium-ion batteries, LiFePO₄ has become one of the most promising cathode materials for application in electric vehicles (EV) and hybrid electric vehicles (HEVs) because of its high theoretical capacity (170 mAh/g), safety, environmental benignity and low raw materials cost, which can be fairly implemented in practice. It consists of polyanionic framework where LiOₓ, FeO₅, octahedra and PO₄ tetrahedra are present, and Li, Fe and P atoms occupy octahedral 4a, octahedral 4c and tetrahedral 4c sites, respectively. The strong P-O covalence, stabilizes the anti-bonding Fe-³⁺ state through the Fe-O-P inductive effect to generate high operating potential (3.4-3.5 V vs Li/Li⁺). However, one of the main problems of Olivine LiFePO₄ materials lies in its poor rate capability, which is attributed to its low electronic conductivity and slow kinetics of lithium ion diffusion through the LiFePO₄ - PO₄ interfaces [2]. One of the approach is to improve the intrinsic electronic conductivity by cation doping [3]. The other one is to synthesize LiFePO₄ with small particle size [4, 5] and also add additive content to modify the particle size [6, 7] and also improve toughness properties [8]. The reason is that a small particle size of LiFePO₄ could shorten the diffusion length of lithium ion while the electronic conductive phase coating would increase the surface electronic conductivity.

Based on the concept, currently many of the synthetic routes are both time and energy consuming also need for an inert or reducing atmosphere to enhance crystallinity and avoid the oxidation of Fe²⁺ state. Driven by the energy crisis, researchers presently focused on low-temperature synthesis methods, such as hydrothermal process [9], ionothermal synthesis [10], solvothermal technique [11] and polyol process [12] are low-temperature effective method to prepare materials with well-defined morphology, rarely used in the synthesis of LiFePO₄ particles. Among those, polyol process is a versatile chemical approach, which refers to the use of polyol (for example ethylene glycol, diethylene glycol and TEG) to reduce metal salts to metal particles, that has been successfully used to prepare a great variety of inorganic compounds. The polyol medium itself not only acts as a reducing agent and dissolving medium but also as a stabilizer and controls the particles growth [13].

Experimental
Synthesis of LiFePO₄
LiFePO₄ material was synthesized via polyol process. Iron (II) sulphate (99.9% purity, FeSO₄·7H₂O), Lithium hydroxide (LiOH·H₂O) (99.9% of SRL, India) and Ammonium dihydrogen phosphate (NH₄H₂PO₄) (98.9% of Alfa-Aesar) were taken in stoichiometric amount, which were dissolved in tetra ethylene glycol (TEG) and heated in a reflux condenser near to the boiling point of the polyol solvent (320°C) for 12 h. In order to remove the TTEG and partial organic components, the resulting solution was washed several times with acetone and ethanol. The resulting particles were separated and dried in a vacuum oven at 150°C for 24 h and finally the LiFePO₄ fine particles were obtained [12].

Characterization of LiFePO₄
The Powder X-ray diffraction (PXRD) patterns of LiFePO₄ samples were obtained using a PANalytical X-pert diffractometer with a Cu Kα radiation operated at 40 kV and 30 mA. The radiation wavelength = 1.5406 Å in the range of 15-60° was used to determine the crystal structure of the prepared material. The functional group vibration was analyzed using thermos Nicolet 380 FT-IR spectrophotometer by preparing KBr pellets technique. The surface morphology of the...
A Polyol Route LiFePO₄ Cathode Material For Li-Batteries

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Keywords: Lithium rechargeable battery, X-ray diffraction, LiFePO₄, polyol process.

Abstract. Lithium ion battery technology has played a key role in portable electronics revolution, and it is vigorously pursued for electric vehicle applications. LiFePO₄ has recently received a great deal of attention due to its potential usage as a next-generation cathode material for lithium-ion batteries such as power tools, electric vehicles (EVs) and hybrid electric vehicles (HEVs), etc. LiFePO₄ is advantageous when comparing other conventional cathode materials such as LiCoO₂, LiNiO₂, and LiMn₂O₄, namely, it is inexpensive, environmentally benign and thermally stable, etc. In the present work, LiFePO₄ has been prepared using polyol method and its crystal structure has been confirmed by powder X-ray diffraction. The as-prepared LiFePO₄ has olivine structure with space group Pnma and orthorhombic lattice parameters calculated as a=10.3999Å, b=6.0070Å, and c=4.6388Å. The functional group vibrations have been analyzed using Fourier Transform Infrared Spectroscopy (FT-IR). The surface morphology of synthesized material have been studied by scanning electron microscopy (SEM) and the compositional analysis were also carried out through EDX analysis.

Introduction

Recently, olivine structure LiMPO₄ (M=transition metal) is attracted as alternative cathode materials for lithium rechargeable batteries because of its excellent cycleability, thermal stability, low cost and environmental benefits [1]. Among these Lithium iron phosphate (LiFePO₄) cathode materials gave relatively high theoretical capacity of 170 mAhg⁻¹ and has a suitably flat voltage-region (3.4 V) vs. Li/Li⁺ [2]. One of the major drawbacks of using LiFePO₄ is its low intrinsic electronic conductivity. Various synthesis and processing approaches have been employed to overcome this problem, which include the reduction of particle size, doping with other metal ions and coating of conductive element [3]. Particle size, morphology, crystallinity, and electrochemical properties of LiFePO₄ are strongly dependent on preparation methods and conditions.

Several methods have been proposed for the synthesis of olivine structure LiFePO₄, including solid-state, sol-gel, spray pyrolysis, mechano-chemical, and emulsion drying [4]. These methods often suffer from generation of large chemicals, requirement of high temperatures under an inert or reductive atmosphere to enhance crystallinity and avoid the oxidation of Fe²⁺ state. Therefore, there are still considerable efforts underway to develop more reliable, simpler, less chemical intensive and less expensive techniques that can produce high quality LiFePO₄ for ultimate large-scale battery applications [5, 6]. In this regard, an innovative method to obtain nanoparticles has been conducted via the polyol process. The polyol process consists of the reduction of metallic compounds such as oxides and salts in a liquid alcohol medium maintained at its boiling point. The polyol medium itself acts as a reducing agent as well as dissolving medium and also acts as a stabilizer, limiting particle growth and prohibiting agglomeration [7].

In this work, LiFePO₄ cathode material has been synthesized via polyol method. The structure and functional group vibrations of the prepared samples have been analyzed using XRD and FT-IR analyses, respectively. The surface morphology of synthesized material was studied by scanning electron microscopy (SEM).