

A new rapid synthesis technique for electrochemically active materials used in energy storage applications

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Abstract

LiFePO₄ is a promising environmentally friendly and low cost alternative cathode material for use in lithium-ion batteries. The most common materials production process used to manufacture LiFePO₄ is solid-state synthesis which entails several grinding and recalcination steps, occurring over many hours. We report on the synthesis of crystalline LiFePO₄ in only 10 min via a versatile process of Electric discharge assisted mechanical milling (EDAMM). Preliminary electrochemical testing of the synthesized powder demonstrates good capacity and excellent cyclability. The EDAMM technique offers an exciting opportunity to synthesize a range of new and existing materials to be used in a variety of energy storage applications that include rechargeable lithium batteries, hydrogen fuel cells, and supercapacitors.

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1. Introduction

Lithium-ion batteries have become the battery of choice for powering popular consumer goods such as mobile phones, laptop computers, and digital cameras. The reason for this choice from a consumer perspective is the convenience of being able to recharge these lightweight powerful cells over 1000 times without having to repurchase batteries. There is currently a race among battery companies and research organizations to apply the basic advantages of the Li-ion rechargeable system to large scale applications such as hybrid electric vehicles (EVs). The basic premise of striving to improve the energy storage capacity while enhancing the cycle life of the battery will also allow Li-ion batteries to be integral in the ongoing push for miniaturization of medical and consumer electronics. To remain at the fore-

front of energy storage technology, Li-ion battery designs must be cost effective and meet the pressing environmental and ecological concerns of modern society.

One such material that shows promise as a cathode in Li-ion batteries is lithium iron phosphate (LiFePO₄), which belongs to the mixed olivine-type orthophosphate family LiMPO₄, where M = Mn, Fe, Co. LiFePO₄ was originally proposed as a potential commercial replacement to existing cathode materials due to its high theoretical specific capacity (170 mAh g⁻¹) and a flat potential plateau of around 3.4 V vs. Li/Li⁺ [1]. Furthermore, the use of a compound that contains iron is attractive for large-scale battery applications due to its abundance, relatively low cost, and low toxicity when compared to other transition metals. Conventional cathode materials used in Li-ion batteries such as LiCoO₂, LiNiO₂, and LiMn₂O₄ suffer one or more of a number of drawbacks including high cost, toxicity, and chemical instability.

A primary challenge to the commercial use of LiFePO₄ is that the synthesis routes are often difficult and time

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consuming. This is due to the requirement to maintain an iron (II) oxidation state, which is usually achieved by inert or reductive gas flow during formation of LiFePO_4 . In most previous studies, solid-state synthesis has been the chosen method of preparation [2–4], although more recent investigations have used hydrothermal synthesis [5], pulsed laser deposition (PLD) [6], sol-gel [7], and mechanical milling [8]. Regardless of the route chosen to synthesize LiFePO_4 , almost all require lengthy heat treatment schedules that usually exceed 10 h as well as multi-stage processing steps [9]. We report on a rapid route to form pure LiFePO_4 phase by Electric discharge assisted mechanical milling (EDAMM). EDAMM combines the benefits of producing fine, highly reactive particles via mechanical milling [10], with the accelerated sintering characteristics afforded by the use of electric discharges [10–12]. During EDAMM, powders are subjected to a localised and intense reaction area characterised by the formation of an electrical discharge and/or plasma [13]. This process is different from mechanical alloying processes which have been employed unsuccessfully in the past in an attempt to directly synthesize LiFePO_4 [8,14]. EDAMM is also different from the popular Spark plasma sintering (SPS) used to rapidly sinter and densify ceramic materials [15–17] and other thermal plasma techniques that have used high-intensity arcs (ac or dc) and high-frequency discharges (RF and microwave) to synthesize various materials [18]. The benefits of using plasmas for materials synthesis have only been realized by the use of novel reactor designs such as the RF-dc hybrid reactor [19], the reactive submerged arc (RSA) [20], multiple plasma jets, and counterflow liquid-injection plasma reactors. It is apparent that the greatest advantage of EDAMM is that the morphology of the synthesized powder can be made to order in a matter of minutes by simply adjusting the processing parameters. Work is ongoing into the nature of the mechanism(s) responsible for these results.

2. Experimental

Stoichiometric amounts of Li_2CO_3 (99%, Aldrich), $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (99%, Aldrich), and $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ (97%, Aldrich) powders were first premixed with a mortar and pestle for 15 min. The mixed precursor powders were then fed into the reaction vessel between two stainless steel electrodes with curved ends. One electrode acted to contain

the powders while the other rod-shaped electrode was vibrated at 10 Hz to pulverize the powders. A power supply was connected to these electrodes through an alternating current (ac) high voltage transformer that generated 0.1–1 kV, 70 Hz impulses at 100–300 mA. During vibration, gaps between the stainless steel rod and the chamber wall caused the formation of an electric discharge. The localized temperature of the reacting precursor powders rapidly increased due to the concurrent effects of the electric discharge and fracture-mixing mechanism of the vibrating electrode, enabling the formation of LiFePO_4 . The reaction vessel was sealed, apart from a gas inlet valve that supplied $0.3 \text{ L min}^{-1} \text{ N}_2 + 3\% \text{ H}_2$ and a gas outlet valve to extract reaction gases. Depending upon the powder species present in the mill, the vibration frequency of the plunger and the electrical parameters selected, we were able to promote the formation of a low energy (10–50 W) or high energy (>50 W) thermal arc discharge as shown in Fig. 1(a). A schematic of the interaction between an electric discharge and precursor powder particles is shown in Fig. 1(b).

Analysis of the composition and structure of the powders was conducted using a Philips PW1730 X-ray diffractometer with monochromatised $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at a scan rate of 1° min^{-1} . The carbon content of LiFePO_4 powder derived from the iron oxybate precursor was analysed by the Thermogravimetric (TG) method performed on a SPT Q600 TG–Differential Thermal Analysis (DTA) apparatus at a heating rate of $10^\circ \text{ min}^{-1}$ in air. Reference TG curves were first obtained by analyzing powders with the following LiFePO_4 : C proportions; 0:100, 20:80, 40:60, 60:40, 80:20, 100:0. The mass change was plotted against known carbon content for these reference powders. For the LiFePO_4 powder synthesized at 10 min reaction time, the mass change from the TG experiment corresponded to 4 wt% carbon on the reference curve. The morphology of the powders was observed by a JEOL JSM-6460A Scanning electron microscope (SEM). The distribution of iron and phosphorus in mixed precursor powders was investigated by firstly preparing pellets by cold pressing 50 mg of powder uniaxially in a hydraulic press at 500 kg cm^{-2} for 5 min. Elemental maps were obtained by using an Energy dispersive X-ray spectroscopy (EDXS) instrument attached to the abovementioned SEM. Gas sorption experiments were conducted with an Autosorb-1 Gas Sorption system (Quantachrome,

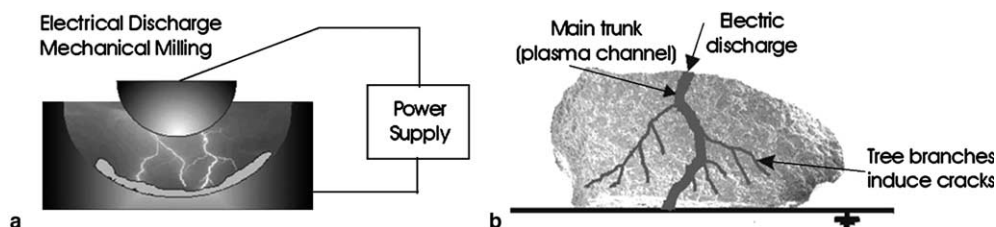


Fig. 1. Schematic of EDAMM reaction vessel detailing how an electric discharge is produced between the vibrating stainless steel plunger and mill floor (a) and the interaction of an electric discharge with a powder particle (b).

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