

STRUCTURE AND ELECTROCHEMICAL PROPERTIES OF VANADIUM
DOPED FOR LITHIUM IRON PHOSPHATE CATHODE

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This thesis is dedicated to my supportive family and friends.

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ABSTRACT

LiFePO_4 and vanadium doped LiFePO_4 were successfully prepared by sol- gel method. The concentrations of vanadium were varied by 0.01, 0.03, 0.05, 0.10, 0.15, and 0.2 wt %. Both doped and pure LiFePO_4 were calcined at 400 and 600°C. XRD results showed that by changing the dopant concentration and calcination temperature, the crystallinity changed. As the concentration of dopant increased the size of crystallite size become larger. The peaks pattern shows orthorhombic structure for LiVFePO_4 upon incorporation of vanadium, and changed to hematite at low calcination temperature. As the calcination temperature increase the size of particle become larger while smaller particle were obtained at low temperature. FESEM analysis showed that at low temperature, smaller particles tend to agglomerate. Agglomeration of several grains produced larger particles which might be due aggregation of very small crystal grains during calcinations. Upon addition of vanadium to LiFePO_4 , larger particles size was obtained. Similar ionic radius of vanadium with iron may cause the expansion of crystal lattice, resulting in larger particle size. EDX analysis confirmed the existence of each element in the samples except for Li which cannot be detected as the atomic number is less than five. In charge/discharge electrochemical test, the obtained discharge capacities were far from the theoretical value and not suitable for commercialization of lithium ion batteries. Poor performance of the prepared samples may be due to the formation of solid electrolyte interface layer and cracking causes the loss of lithium and active materials from the sample.

ABSTRAK

Penyediaan LiFePO_4 dan LiFePO_4 didopkan vanadium telah dilakukan melalui kaedah sol-gel. Kepekatan vanadium yang didopkan mengikut peratusan berat bermula daripada 0.01, 0.03, 0.05, 0.10, 0.15, dan 0.2. Kedua-dua LiFePO_4 tulen dan LiFePO_4 terdop telah dikalsinkan pada suhu 400 dan 600°C. Keputusan XRD menunjukkan kehabluran berubah apabila kepekatan dop dan suhu pengkalsinan diubah. Apabila kepekatan pendopan bertambah, saiz hablur akan menjadi lebih besar. Corak puncak pembelauan sinar - X menunjukkan struktur otorombik setelah LiFePO_4 bergabung dengan vanadium, dan berubah kepada hematit pada suhu pengkalsinan rendah. Apabila suhu pengkalsinan meningkat, saiz zarah menjadi besar manakala saiz zarah menjadi lebih kecil pada suhu rendah. Analisis FESEM menunjukkan pada suhu yang rendah, zarah yang lebih kecil cenderung untuk menggumpal. Penggumpalan beberapa zarah menghasilkan zarah yang lebih besar mungkin disebabkan oleh pengumpulan partikel kristal semasa pengkalsinan. Apabila kepekatan vanadium kepada LiFePO_4 bertambah, saiz zarah yang lebih besar akan diperolehi. Saiz jejari ion vanadium yang hampir sama dengan ion besi menyebabkan pengembangan kekisi kristal sehingga menghasilkan saiz zarah yang lebih besar. Analisis EDX mengesahkan kewujudan setiap unsur dalam sampel kecuali Li yang tidak boleh dikesan kerana nombor atom kurang daripada lima. Dalam ujian elektrokimia cas/nyahcas, kapasiti nyahcas yang diperolehi jauh berbeza daripada nilai teori dan tidak sesuai untuk dikomersialkan sebagai bateri ion litium. Keberkesanan sampel yang lemah mungkin disebabkan oleh pembentukan lapisan elektrolit pepejal dan keretakan yang menyebabkan kehilangan litium dan bahan aktif daripada sampel.

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LIST OF ABBREVIATIONS AND SYMBOLS

d	-	distance between atomic layers
D	-	Crystallite size
DMC	-	Dimethyl carbonate
EC	-	Ethylene carbonate
HEDP	-	1-hydroxy ethylidene-1,1-diphosphonic
k Ω	-	Kilo Ohm
LFP	-	Lithium iron phosphate, LiFePO ₄
LFP/PC	-	Lithium iron phosphate/polycarbonate (LiFePO ₄ /polycarbonate)
m	-	Metre
M	-	Molar (mole per volume)
mA h g ⁻¹ or mA h/g	-	Capacity unit (milliampere-hour per gram)
m Ω	-	Mili Ohm
n		A small integer, usually 1
nm	-	nanometer
PAS	-	Polyacenic semiconductor
S		Siemens (= reciprocal ohms)
Å	-	Angstroms
β	-	Beta (Full Width Half Maximum value)
λ	-	Radiation wavelength
θ	-	Glancing angle or Bragg angle
V _m	-	Volume of the adsorbed monolayer
1D	-	One dimension

CHAPTER I

INTRODUCTION

1.1 Background of Research

Rechargeable lithium ion batteries have been considered as an attractive power source for a wide variety of applications, such as cellular phones, notebook computers, camcorders and hybrid electric vehicles (HEV) due to the high energy density, high working potential and long life (Mi *et al.*, 2007). In various aspects, this kind of lithium secondary battery has many advantages over the traditional rechargeable systems like lead acid and Ni-Cd, for example, a high energy density, a high average output voltage (3.6 or 3.7 V), a low self-discharge (<5 % per month), no memory effect like that of Ni-Cd and Ni-MH, an excellent cycling behaviour (its cycle number can be >1200), a high rate capability like 1C, a high coulomb efficiency (near to 100 % except in the first cycle), a wide work temperature range (ranging from -25 to +45°C, expected to be +70°C), an easy measurement of the residual capacity, maintenance free and very few adverse effects on the environment (it can be called a green battery) (Takahashi *et al.*, 2005). As a result, its development has been very rapid, and now it has been widely applied in a lot of light electronics with high value, e.g., portable telephones and computers, digital cameras and videos (Fu *et al.*, 2005). The cathode is particularly critical in determining the capacity of the lithium battery, as it is the heaviest component, and has the greatest

potential for improvement (Yang *et al.*, 2003). In the lithium-ion battery, lithium ions shuttle between cathode and anode hosts via intercalation and de-intercalation. The cathode host provides lithium ion sources for battery operation (Wang *et al.*, 2006). The common cathode materials are oxide and phosphate based.

Several types of cathode materials have been introduced for lithium-ion batteries, such as LiCoO_2 , LiNiO_2 , LiMn_2O_4 , $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, and LiFePO_4 (Fergus 2010). Among the cathode materials, LiFePO_4 has been recognized as one of the most promising cathode materials for large format lithium batteries because of its high theoretical capacity of 170 mA h g^{-1} , environmental benign, and high thermal stability since the report done by researcher was published in 1997 (Nanjundaswamy *et al.*, 1996). The three-dimensional framework structure of LiFePO_4 is not built on close packing of oxygen anions, but built on PO_4^{3-} polyanions and octahedral MO_6 groups ($\text{M} = \text{Fe, Li}$) that make the cells comprised with this material manifest higher thermal stability than others (Wu *et al.*, 2009).

However, it is known that the high-rate performances of pure LiFePO_4 are rather poor due to the low intrinsic electrical conductivity (Nanjundaswamy *et al.*, 1996; Fu *et al.*, 2005; Zhang 2011) and the sluggish Li^+ diffusion in the bulk of the materials (Sun *et al.*, 2010). The low conductivity of LiFePO_4 is because it has only one oxidation state of +2 or +3. The development of the nanostructure materials have become of great interest to replace the micron-sized materials (Rui *et al.*, 2011). These nanostructured materials have high possibility for high power operation. This is due to their function in controlling the charge/discharge process which is attributed by the rate of lithium ion transport across the electrode-electrolyte interface. It is advantageous in terms of fast ions conduction and electron transport over shorter distance. Therefore, more active materials will be utilized to give higher capacity for the batteries.

LiFePO_4 powders can be prepared by both solid state and solution based methods. Solid state techniques are carried out at high temperatures without any solvent addition. On the other hand, solution based methods are based on reactions that take place with the presence of appropriate solvent systems. Solid state

synthesis, mechanochemical activation, carbothermal reduction and microwave heating are based on solid state chemistry and are the most common solid state methods for preparing LiFePO_4 powders. Solution based methods are of increasing importance since they often result in smaller and more uniform particle size, higher purity, more homogeneous carbon coating, and higher electrochemical capacity. Hydrothermal synthesis, sol-gel synthesis, spray pyrolysis, coprecipitation, and microemulsion drying are common solution based methods used for the preparation of LiFePO_4 powders.

In recent years, the development of LiFePO_4 nanostructure cathode materials with improved electrochemical properties increase rapidly (Li *et al.*, 2007; Chang *et al.*, 2009). Based on their studies, this is because the capacity of the electrode material is significantly affected by the morphology of the materials. The morphology of the materials can influence the diffusion of mechanism of lithium ions as well as electrons transport throughout the material.

1.2 Statement of Problems

More recently, LiFePO_4 has become one of the most promising compounds to replace the cathode candidates such as LiCoO_2 , LiMn_2O_4 and LiNiO_2 due to the relative lack of toxicity and inexpensive and abundant raw materials (Zhang *et al.*, 2012). However, there are major drawbacks for the use of LiFePO_4 as a commercial cathode material which is its poor electronic conductivity resulting from the low lithium ion diffusion rate and the low tap density ($1.0 - 1.3 \text{ g cm}^{-3}$) which results in a low volumetric specific capacity of the material (Chang *et al.*, 2010). There are a lot of approaches have been attempted to overcome these problems either by coating with carbon or metal powders, nanostructure designs, optimizing preparation procedure, or doping. Carbon or metal powder coating and doping were introduced to overcome the conductivity problem LiFePO_4 . This is because carbon can control the particle growth and provides better electronic contact between particles. A thin carbon layer can provide a path for electrons without blocking access for lithium

ions. However, these approaches still could not fully improve the intrinsic conductivity of LiFePO_4 because the diffusion coefficient of electrons does not influence the ionic conductivity (Liu *et al.*, 2008). Optimization of the synthesis routes and parameters need to be explored by researcher to obtain the most suitable conditions for synthesizing the high performance LiFePO_4 .

1.3 Research Objective

Therefore, the research embarks on the following objectives:

- i. To synthesize vanadium doped for lithium iron phosphate by sol gel method.
- ii. To determine the structural properties characterizations in terms of structure and morphology.
- iii. To study the electrochemical performance of prepared samples using charge-discharge test.

1.4 Scope of Study

In this work, the sol-gel method is selected to synthesize vanadium doping LiFePO_4 for lithium ion batteries. The parameters involve are calcination temperature and dopant concentration. The LiFePO_4 sample undergoes heat treatment reaction at 400°C and 600°C for 4 hours before being optimized. The X-ray diffractometer (XRD), field emission scanning electron microscopy (FESEM) with Energy-dispersive X-ray spectroscopy (EDX) and The Brunauer, Emmett, and Teller (BET) will be used to identify the structure, morphology and surface area of the samples. Besides, the electrochemical characterization will be carried out by means of charge discharge test between 2.5 and 4.5V.

1.5 Significance of Study

A good cathode material for lithium ion batteries should have large capacity, good cycling performance, high stability, low toxicity, and high purity, and it should be easily produced and affordable. In order to obtain these features, small particle size, narrow size distribution, uniform morphology, optimum crystallinity degree, high specific surface area, minimum defects and agglomeration, and homogeneous carbon coating or metal doping are required for the practical application of LiFePO_4 powders in lithium ion batteries. Sol-gel method is more advantageous over solid state to produce higher purity and homogeneity materials. It also formation of porous structure which favourable for electrolyte immersion and reduces the diffusion distance for lithium ions (Fu *et al.*, 2005). The vanadium doping was selected due to stability at high temperature and in organic solvents. By adding the vanadium, Fe site will be replaced and the electrochemical performances suggested to be greatly improved (Hua *et al.*, 2010). Once the results obtained shows the positive improve regarding to the physical and electrochemical properties, the vanadium doped LiFePO_4 can be a promising candidate for cathode materials.

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