

**FIRST PRINCIPLES STUDY OF POLYANIONIC
CATHODE MATERIALS LiFeSO_4F AND LiFeSO_4OH
USING DENSITY FUNCTIONAL THEORY**

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**DOCTOR OF PHILOSOPHY
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ABSTRACT

In this research, first principles techniques have been leveraged to thoroughly understand on the fundamental knowledge of Li-ion batteries. Computational materials design demonstrated that the modern modelling techniques play a valuable role that can help to achieve deeper fundamental insight into novel materials for rechargeable lithium ion batteries by computing key relevant properties. The effect of DFT + U method was investigated on the properties of cathode materials such as structural properties, electronic properties and voltage of the cathode. It is found that the electronic properties and voltage calculation are improved upon the addition of U value to the iron atom. However, the addition of U value on the structural properties calculation is not necessary as it has overestimated the data. To understand the difference of voltage between LiFeSO_4F and LiFePO_4 , the Mulliken population analysis calculation was conducted. The result shows that the increase of voltage of LiFeSO_4F compared to LiFePO_4 which is due to the inductive effect. However, the difference of voltage between tavorite and layered LiFeSO_4OH could not be explained using this inductive effect. The best explanation to this phenomenon, the difference between the polyhedral connectivity of the tavorite and layered LiFeSO_4OH structure is taken into account. It is found that the layered LiFeSO_4OH produces the overestimated result on lattice parameter using the conventional exchange correlation functional. To improve the result, the van der Waal dispersion correction was applied to the GGA-PBE and GGA-PBESol exchange correlation functional. Upon the addition, the structural properties and the calculated voltage of the layered LiFeSO_4OH have been improved near to experimental values. The density of states of LiFePO_4 , LiFeSO_4F and LiFeSO_4OH cathode materials were calculated to investigate their rate capability. It is found that those cathode materials possess low rate capability as the lithiated and delithiated states behave as n-type and p-type semiconductor respectively. Furthermore, the effect of Vanadium substitution on the layered LiFeSO_4OH was also investigated. Based on the formation energy calculation, vanadium substitution in LiFeSO_4OH tends to reside at the Fe site because of it more energetically stable compared to S site. The high volume of $\text{LiFe}_{0.75}\text{V}_{0.25}\text{SO}_4\text{OH}$ facilitates lithium ion to move easily and hence enhancing the rate number of lithium ion to channel in and out from the cathode. Thus, this contributes in increasing the ionic conductivity of such cathode material. The reduced band gap upon the vanadium substitution could improve the electronic conductivity of the cathode material. The calculated bond order values obtained upon delithiation process showing that the changes of S-O bond in $\text{LiFe}_{0.75}\text{V}_{0.25}\text{SO}_4\text{OH}$ are more uniform resulting the volume shrinking after the removal of lithium ion is lower compared to the pristine compound. Thus, it could improve the cycle life of the battery and could make this new $\text{LiFe}_{0.75}\text{V}_{0.25}\text{SO}_4\text{OH}$ as a promising cathode material candidate in lithium ion batteries.

ABSTRAK

Penyelidikan dalam bidang ini telah memanfaatkan kaedah prinsip pertama secara menyeluruh bagi meningkatkan kefahaman secara mendalam terhadap teknologi bateri Li-ion. Rekabentuk bahan berkomputeran menunjukkan bahawa kaedah pemodelan moden memainkan peranan yang bernilai untuk mencapai pemahaman fundamental secara terperinci terhadap bahan novelti untuk aplikasi bateri lithium berdasarkan pengiraan sifat-sifat bahan yang berkaitan. Kesan kaedah DFT + U terhadap sifat-sifat bahan katod seperti sifat struktur, sifat elektronik, dan voltan katod telah diselidik. Berdasarkan penyiasatan tersebut, sifat elektronik dan pengiraan voltan telah bertambah baik selepas penambahan nilai U di dalam atom ferum. Walaubagaimanapun, penambahan nilai U terhadap sifat struktur adalah tidak diperlukan kerana akan menyebabkan anggaran nilai yang berlebihan. Untuk memahami perbezaan voltan antara LiFeSO_4F dan LiFePO_4 , pengiraan analisis populasi Mulliken telah dilakukan. Hasil menunjukkan, peningkatan voltan LiFeSO_4F berbanding LiFePO_4 adalah disebabkan oleh kesan induktif. Walaubagaimanapun, perbezaan antara LiFeSO_4OH *tavorite* dan berlapis tidak dapat dijelaskan menggunakan kesan ini. Penjelasan terbaik terhadap fenomena ini adalah dengan mengambil kira perbezaan antara sambungan polihedra struktur *tavorite* dan berlapis. Selain itu, apabila fungsi kolerasi pertukaran konvensional digunakan, anggaran yang berlebihan terhadap sifat parameter kekisi struktur LiFeSO_4OH berlapis akan terjadi. Untuk memperbaiki hasil tersebut, pembetulan serakan van der Waals telah digunakan terhadap fungsi kolerasi pertukaran GGA-PBE dan GGA-PBEsol. Setelah penambahan tersebut, penambahbaikan terhadap sifat struktur dan pengiraan voltan LiFeSO_4OH berlapis menghampiri keputusan nilai eksperimen. Ketumpatan keadaan bagi bahan katod LiFePO_4 , LiFeSO_4F dan LiFeSO_4OH telah dikira untuk mengetahui kadar keupayaan mereka. Ia didapati bahawa, bahan-bahan tersebut mempunyai kadar keupayaan yang rendah kerana keadaan berlitium yang bersifat sebagai semikonduktor jenis-n dan keadaan tidak berlitium yang bersifat sebagai semikonduktor jenis-p. Selain itu, kajian kesan penggantian vanadium di dalam LiFeSO_4OH berlapis turut dijalankan. Berdasarkan pengiraan tenaga pembentukan, penggantian vanadium di dalam LiFeSO_4OH lebih cenderung berada di tempat Fe kerana tenaganya lebih stabil berbanding di tempat S. Isi padu $\text{LiFe}_{0.75}\text{V}_{0.25}\text{SO}_4\text{OH}$ yang lebih besar memudahkan pergerakan ion litium dan seterusnya meningkatkan kadar pergerakan ion masuk dan keluar di dalam katod. Oleh yang demikian, ini akan menyumbang kepada peningkatan kekonduksian ion di dalam bahan katod. Pengurangan jurang jalur selepas penggantian vanadium boleh meningkatkan kekonduksian elektronik bahan katod. Nilai susunan ikatan yang dikira selepas proses pembuangan litium menunjukkan kepada perubahan ikatan S-O di dalam $\text{LiFe}_{0.75}\text{V}_{0.25}\text{SO}_4\text{OH}$ adalah lebih seragam, menghasilkan pengecutan isipadu selepas pembuangan litium yang lebih rendah berbanding bahan asal. Ini boleh meningkatkan jangka hayat sesuatu bateri dan boleh menjanjikan $\text{LiFe}_{0.75}\text{V}_{0.25}\text{SO}_4\text{OH}$ yang baharu sebagai calon bahan katod kepada bateri litium ion.

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APPROVAL

I certify that an Examination Committee has met on **29 August 2016** to conduct the final examination of **Fadhlul Wafi bin Badrudin** on his degree thesis entitled “First Principles Study of Polyanionic Cathode Materials LiFeSO_4F and LiFeSO_4OH Using Density Functional Theory”. The committee recommends that the student be awarded the Degree of Doctor Philosophy (Physics).

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LiFeSO₄F and LiFeSO₄OH Using Density Functional Theory
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LIST OF ABBREVIATIONS

AFM	Antiferromagnetic
BFGS	Broyden–Fletcher–Goldfarb–Shanno
BG	Band Gap
BL	Bond Length
BO	Bond Order
CASTEP	Cambridge Serial Total Energy Package
CB	Conduction Band
CD	Charge Density
CT	Charge-Transfer
DFT	Density Functional Theory
DFT-D	Density Functional Theory Dispersion
DFT+U	Density Functional Theory plus Hubbard U Parameter
DOS	Density of States
FM	Ferromagnetic
G06	Grimme
GGA	Generalized Gradient Approximation
GWA	GW approximation
HF	Hartree-Fock
LDA	Local Density Approximation
LIB	Lithium ion Battery
MH	Mott-Hubbard
OCV	Open Circuit Voltage
PBE	Perdew-Burke-Ernzerhof Scheme
PBEsol	Perdew-Burke-Ernzerhof Scheme for Exchange in Solid and Surface
SIC	Self-interaction correction
TS	Tkatchenko–Scheffler
VB	Valance Band
vdW	Van der Waals

CHAPTER ONE

INTRODUCTION

1.1 Background

Nowadays, the fully harness renewable energy and ideal electrical transportation become the urge factor to researchers to face the global warming, depletion of fossil fuels and pollution. Many scientists across the globe have conducted many researches in order to achieve the green technology. To realize it, large enough of electrical energy storages are required to make sure they operate for the reasonable amount of time and able to deliver demanded power. The best available option to meet this demand is using battery which can convert the electrical energy to the chemical energy or vice versa.

So far, Li-ion battery is still the best offered technology considering of its high energy density [1]. This is because of high energy density that could be provided by lithium ion batteries make them as the most suitable candidate for the application. However, other issues such as safety and cost of the batteries are also crucial to be concerned particularly for high power application such as electric vehicle (EV) and plug in hybrid electric vehicle (PHEV) [2,3]. Since the commercialization of the layered LiCoO_2 by Sony in 1990 [4,5], therefore it has become the world attention due to its high theoretical gravimetric capacity ($273.84 \text{ mAh g}^{-1}$) [6]. However, its large volume production has been hampered by high cost and toxicity of cobalt (Co)[7–9]. Additionally, the pristine LiCoO_2 are thermally unstable and can cause

thermal runaway, thus the battery potentially to explode when used for high power application [10,11].

Besides layered oxide materials, most researches are now focusing in finding new high performance electrode materials particularly in polyanionic material. In 1997, Padhi et al. [12] have successfully synthesized a widely accepted polyanionic cathode material, LiFePO_4 . This cathode material possesses reasonable specific capacity, improved safety, low cost, high stability and environmentally benign properties, subsequently leads to its commercialization [13–15]. It also has a high theoretical capacity (170 mAh g^{-1}) and high reversible voltage (3.5 V) [15]. However, this LiFePO_4 suffers poor electronic and ionic conductivity which requires further modification and treatment such as nano-sizing, carbon coating and material doping [16,14,17], thus increases the synthesization cost.

In recent past, Recham et al. [18] revealed a new fluorosulphate cathode material viz. LiFeSO_4F that crystallized in space group of P-1 with favorite structure. This material was designed by replacing the PO_4^{3-} with SO_4^{2-} and co-joining the F^- atom to increase the electronegativity. It has shown slightly increasing redox potential 3.6 V vs. Li^0/Li^+ which is higher than LiFePO_4 (3.45 V). Its ionic conductivity is found to $\sim 10^3$ higher than that of LiFePO_4 : $\sim 4 \times 10^{-6} \text{ Scm}^{-1}$ for LiFeSO_4F and $2 \times 10^{-9} \text{ Scm}^{-1}$ for LiFePO_4 at $147 \text{ }^\circ\text{C}$ [18]. This could obviate the need of carbon coating or nano-sizing that eventually lowering the cost and density of the material.

Moreover, in the polyanionic electrode such as LiFeSO_4F , the iono-covalency of the M-X bond plays an important role in determining the redox potential. The higher electronegativity of SO_4^{2-} compared to the PO_4^{3-} possesses the higher inductive effect that draws more electrons near the SO_4^{2-} and thus decreases the covalency of the M-X (M = transition metal, X = ligand) bond. However, there is little report on the

ionic and covalent characters of the LiFeSO_4F by means of the first principles approach. Previous studies [17,19] revealed that the first-principles method using the density functional theory (DFT) is a powerful tool to study the electronic structures of cathode materials and even novel materials that have not been synthesized such as GeTiO_3 [20–22] and SnTiO_3 [23–25]. Using this method, the ionic and covalent character of the materials can easily be monitored using bond length (BL) and bond order (BO) calculation and can also be supported by effective charge Q^* calculation. Therefore, in this thesis the electronic and structural properties of LiFeSO_4F have been investigated using DFT implemented in the Cambridge Serial Total Energy Package (CASTEP) computer code.

The work is then continued by computationally investigating and comparing the properties between hydrosulphate, LiFeSO_4OH and fluorosulphate, LiFeSO_4F cathode materials. This hydrosulphate, LiFeSO_4OH cathode material is hypothesized to be sustainable alternative because of the F^- ion is replaced with OH^- ion. This material crystallized into two types of polymorph: one is a layered structure which was recently discovered by Subban et al. [26], and the other is a tavorite structure [27]. Both structures were synthesized via different experimental processes. The layered structure was synthesized using the ball-milling approach, whereas the tavorite structure was synthesized using the electrochemical lithiation of FeSO_4OH [28]. The tavorite LiFeSO_4OH was reported to exhibit only 3.2 V vs. Li^+/Li^0 which is lower compared to tavorite LiFeSO_4F . The new layered phase of LiFeSO_4OH was synthesized from caminite related mineral. This cathode material showed reversibly 0.7 Li^+ with an average voltage of 3.6 vs. Li^+/Li^0 which is the same with tavorite LiFeSO_4F . However, the difference of voltage between these cathode materials is still unclear [29]. Therefore, this thesis focuses on the investigation of the factors that

lead to the difference of voltage between tavorite LiFeSO_4OH and layered LiFeSO_4OH and also the similarity of voltage between layered LiFeSO_4OH and tavorite LiFeSO_4F .

As well known, calculations using conventional exchange correlation in DFT have faced several problems to generate the experimental structure of the layered LiFeSO_4OH . Therefore, previous works [30,31] have proved to improve the experimental structure and voltages using van der Waals (vdW) dispersion correction on the layered cathode materials such as LiCoO_2 and LiV_2O_5 . With the same motivation, in this thesis, the vdW dispersion correction has been applied to the exchange correlation GGA-PBE to comprehend the effect of the implementation of the correction.

According to Subban et al. [26], the layered LiFeSO_4OH was able to deliver $\sim 100\text{-}110 \text{ mAh g}^{-1}$ at C/20 rate. However, this is still far from the theoretical capacity and it also then dropped to 93 mAh g^{-1} at C rate. Therefore in this thesis, enhancement of the performance of LiFeSO_4OH cathode material was performed by substituting vanadium on the LiFeSO_4OH . In this work, structural and electronic properties such as the lattice parameter, density of state (DOS), bond length (BL), bond order (BO) and charge density were determined using the first principles approach. In addition, van der Waals (vdW) dispersion correction has been taken into account for calculating the structural parameter.

1.2 Challenges and Motivation

A layered LiFeSO_4OH cathode material offers greener approach compared to fluorosulphate-based because the absence of hazardous fluorine, F^- , thus it is worthy to be further investigated. To date, there is very little study on a new phase of

LiFeSO₄OH has been reported and hence, there is not much reliable information could be retrieved about it. Moreover, Subban et al. [26] reported that using traditional DFT method has encountered difficulties in simulating the layered LiFeSO₄OH cathode material and suggested a need for new methods to reliably predict the structure and electrochemical properties of the material. Therefore in this thesis, different with literatures, the challenge has been taken to simulate this material using DFT treated by van der Waals dispersion correction method (G06 and TS scheme). However, in enhancing specific capacity of this layered material, substitution of vanadium into layered LiFeSO₄OH has been conducted. To the best of knowledge, this is the first study on the properties of a new LiFe_{0.75}V_{0.25}SO₄OH cathode material using first principles method. Based on its properties, thus, this new material could be a promising candidate as a cathode material in lithium ion batteries.

1.3 Problems Statement

To correctly obtain electronic properties of cathode materials, the DFT + U method is very essential to be performed especially for the compounds containing transition metal or rare earth material. This is because the calculated results using conventional DFT method always fails to reach agreement with the experimental electronic properties values [32,33]. In the cathode material, the electronic properties such as band gap, density of state and voltage are always underestimated without U value applied to the d orbital of the transition metal [34–38]. Therefore, the DFT + U method is barely suitable to be used in calculating the electronic properties of cathode materials.

The layered LiFeSO₄OH has just been discovered in 2013 [26] as an alternative cathode material. However, to date there is very little information reported on this

cathode material and thus providing opportunities for further exploration. Moreover, this layered cathode material has been reported to have problem to be simulated using traditional DFT (GGA, LDA) which required another approaches [39]. This problem is also similar to other layered compounds such as LiCoO_2 and LiV_2O_5 [30,31]. This shows that the exchange correlation functional such as GGA or LDA needs a treatment to improve the description of the properties such as structural and electronic properties of the layered compound. Therefore, to overcome this problem, the van der Waals dispersion correction has been adopted.

The hydrosulphate system LiFeSO_4OH has two types of polymorph which crystallized in tavorite and layered structure depending on the synthesization method. The tavorite and layered structure exhibited 3.2 V and 3.6 V of redox potential, respectively. Until now, the fundamental reason on why differences between the redox potential of both structures happened are still unclear [29]. Moreover this also raises a question why the layered LiFeSO_4OH has the same voltage with the tavorite LiFeSO_4F . However, the experimental value of specific capacity of the layered LiFeSO_4OH [26] has still far from the theoretical capacity. Therefore, efforts to seek a new promising cathode material that could possess a higher specific capacity are necessary. In this thesis, substitution of vanadium into LiFeSO_4OH has been conducted.

1.4 Research Objectives

Objectives of this research can be described as follows:

1. **To elucidate** the effects of addition of Hubbard U parameter to DFT on the calculation of structural and electronic properties of LiFePO_4 and LiFeSO_4F .