

**FIRST PRINCIPLES STUDY ON NOVEL CATHODE
MATERIAL NaFeSO_4OH FOR SODIUM ION
BATTERY**

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MASTER OF SCIENCE (PHYSICS)

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**FIRST PRINCIPLES STUDY ON NOVEL CATHODE MATERIAL NaFeSO_4OH
FOR SODIUM ION BATTERY**

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ABSTRACT

This research sought to investigate via calculations from first principles based on the density functional theory (DFT), various properties of a novel cathode material (positive electrode) for secondary/rechargeable sodium ion battery (SIB), namely sodium iron(II) hydroxysulphate, NaFeSO_4OH . Today lithium ion batteries (LIBs) dominate portable electronics and are currently making inroads into electric vehicle and grid energy storage sectors. Its main attraction over the other energy storage technologies is its high energy density. Nevertheless, lithium suffers from natural abundance problem, hence the idea to replace it with sodium, which is far more abundant and shares similar structure as lithium, making SIBs a promising prospect as next-generation technology. The key component of the battery is the cathode, and there have been several candidates proposed, yet none has reported on NaFeSO_4OH . In this research, NaFeSO_4OH was virtually built from the crystallographic data of layered lithium iron(II) hydroxysulphate, LiFeSO_4OH through *in situ* substitution of lithium with sodium. Before that, the experimentally measured lattice parameters and redox voltage of layered LiFeSO_4OH were reproduced, as the computational parameters used to achieve those are said to describe the layered FeSO_4OH host structure well, thus giving confidence when applying them to NaFeSO_4OH . Some traits were expected beforehand and indeed confirmed from the calculations made. In particular, NaFeSO_4OH should have lower redox voltage than layered LiFeSO_4OH and this was confirmed (3.23 V versus 3.60 V), which is still acceptable for a Na-based cathode. Besides that, its positive attributes include robust host structure due to strong S-O and Fe-O bonds (maximum bond order, BO_{max} values 0.27 and 0.64 respectively), thereby promising thermal and cycling stabilities. It also possesses a high theoretical capacity (140 mAh/g) while being made up of abundant constituent elements. Its disadvantages include large unit cell volume change (13.10%) and strong Na-O bond (BO_{max} 0.24) which may affect electrochemical activity, and large electronic band gap (3.46 eV) which implies low electronic conductivity. Considering the overall results with some insight from experiments on other related cathodes, it was concluded that NaFeSO_4OH is still a viable cathode candidate for SIB, keeping in mind that its performance could yet be enhanced for which various techniques were suggested.

ABSTRAK

Matlamat penyelidikan ini adalah untuk mengkaji pelbagai ciri suatu katod (elektrod positif) baru untuk bateri sodium ion (SIB) sekunder / boleh dicas semula melalui pengiraan dari prinsip-prinsip pertama berdasarkan kepada teori fungsi ketumpatan (DFT), iaitu *sodium iron(II) hydroxysulphate*, NaFeSO_4OH . Dewasa ini bateri ion lithium (LIB) mendominasi sektor alatan elektronik mudah alih, dan kini dalam fasa menembusi sektor kenderaan elektrik dan penyimpanan tenaga grid. Tarikan utamanya berbanding teknologi penyimpanan tenaga yang lain adalah ketumpatan tenaganya yang tinggi. Walaubagaimanapun, kuantiti lithium di alam adalah terhad, maka dicadangkan agar digantikan dengan sodium yang jauh lebih banyak dan ia pula memiliki struktur yang serupa dengan lithium, menjadikan SIB suatu prospek cerah sebagai teknologi masa hadapan. Dalam bateri, komponen mustahak adalah katod, dan beberapa calon katod telah pun disyorkan, namun sehingga kini masih tiada laporan untuk NaFeSO_4OH . Dalam kajian ini, NaFeSO_4OH telah dibina secara maya berdasarkan data kristallografi lapisan *lithium iron(II) hydroxysulphate* LiFeSO_4OH melalui penggantian setempat lithium dengan sodium. Sebelum itu, parameter kekisi dan voltan lapisan LiFeSO_4OH telah dihasilkan semula, kerana parameter perkomputeran yang digunakan untuk mencapai tujuan itu dikatakan mampu menerangkan rangka struktur lapisan FeSO_4OH dengan baik, maka ia boleh diaplikasikan dengan yakinnya kepada NaFeSO_4OH . Beberapa hasil telah dijangka sebelum pengiraan dilakukan, dan memang terbukti hasilnya. Khususnya, NaFeSO_4OH dijangka memiliki voltan yang lebih rendah dari lapisan LiFeSO_4OH dan ini telah terbukti (3.23 V berbanding 3.60 V), namun dikira boleh diterima untuk katod berasaskan Na. Selain itu, kelebihan NaFeSO_4OH termasuklah rangka struktur yang tegap disebabkan oleh ikatan S-O dan Fe-O yang kuat (nilai susunan ikatan maksima, BO_{max} masing-masing adalah 0.27 dan 0.64), maka menjanjikan kestabilan haba dan jangka hayat yang panjang. Ia juga memiliki kapasiti teori yang tinggi (140 mAh/g) sambil terdiri daripada unsur-unsur yang berkuantiti tinggi. Kekurangannya termasuklah perubahan isi padu sel unit yang besar (13.10%) dan ikatan Na-O yang kuat (BO_{max} 0.24) yang boleh mempengaruhi aktiviti elektrokimia, dan jurang jalur elektronik yang besar (3.46 eV) yang menandakan konduktiviti elektronik yang rendah. Berdasarkan hasil kajian secara keseluruhannya berserta pemahaman daripada eksperimen terhadap katod lain yang berkaitan, telah disimpulkan bahawa NaFeSO_4OH adalah calon katod yang masih baik untuk SIB, dengan mengambil kira faktor bahawa terdapat potensi untuk prestasinya dipertingkatkan lagi, dan beberapa kaedah untuk tujuan ini dicadangkan.

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APPROVAL

The Examination Committee has met on **11th August 2020** to conduct the final examination of **Aqeel Bin Idrus** on his degree thesis entitled '**First Principles Study on Novel Cathode Material NaFeSO₄OH for Sodium Ion Battery**'.

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LIST OF ABBREVIATIONS

1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
AC	Alternating current
AFM	Antiferromagnetic
BFGS	Broyden-Fletcher-Goldfarb-Shanno
BG	Band gap
BL	Bond length
BO	Bond order
BZ	Brillouin Zone
CA-PZ	Ceperley, Alder-Perdew, Zunger
CASTEP	Cambridge Serial Total Energy Package
CBM	Conduction band minimum
DC	Direct current
DFT	Density Functional Theory
DFT-D	Dispersion-corrected density functional theory
DFT+U	Density functional theory with Hubbard U correction
DOS	Density of states
ESS	Energy storage system
EVGGA	Engel-Vosko Generalized Gradient Approximation
FB	Flow battery
FPC	First principles calculations
FM	Ferromagnetic
G06	Grimme-2006
GGA	Generalized gradient approximation
GGA+U	Generalized gradient approximation with Hubbard U correction
IBZ	Irreducible Brillouin Zone
IL	Ionic liquid

LDA	Local density approximation
LIB	Lithium ion battery
MD	Molecular dynamics
OBS	Ortmann-Bechstedt-Schmidt
OCV	Open circuit voltage
optPBE-vdW	Optimized Perdew-Burke-Ernzerhof for van der Waals interaction
PBE	Perdew-Burke-Ernzerhof
PDOS	Partial density of states
ppm	Parts per million
SG	Space group
SHE	Standard hydrogen electrode
SIB	Sodium ion battery
SRP	Standard reduction potential
TEG	Tetraethylene glycol
TGA	Thermogravimetric analysis
TM	Transition metal
TS	Tkatchenko-Scheffler
U	Hubbard U correction
USGS	United States Geological Survey
UV-Vis-NIR	Ultraviolet-Visible light-Near Infrared
VBM	Valence band maximum
vdW	van der Waals
VFRB	Vanadium redox flow battery
XC	Exchange-correlation (or exchange and correlation)
XRD	X-ray diffraction
ZEBRA	Zero Emission Battery Research Activity

CHAPTER 1

INTRODUCTION

1.1 Research background

Continuous consumption of fossil fuels which are non-renewable, and the subsequent pollution produced have contributed to the constant increase in greenhouse gases emissions. These emissions are the root cause of the climate crisis the world is experiencing today in the form of global warming as we know them [1]. This has made it even more critical to develop electrical-based transportations that emits very little or no unwanted polluting gases at all, as well as secondary or rechargeable battery to power them, with the latter akin to a renewable energy source. Ideally, such technology requires the storage of large amount of energy to enable long traveling distances as well as quick recharge [2]. Meanwhile, when one speaks of renewable energy resources, one is drawn to think about how the energy generated from intermittent sources such as solar and wind can be efficiently stored so that they do not go to waste when there are plenty of them, and be able to utilize them as additional support for when electricity demands exceed supply [3,4]. Presently, lithium ion battery (LIB) is the preferred choice as energy storage

device in general due to its high energy density and longer cycle life [5]. Nevertheless, scientists are always on the lookout for further improvements, hence research are continuously conducted to develop even better batteries.

Since the commercialization by Sony in 1990s [6], layered lithium cobalt(III) oxide LiCoO_2 has been the cathode of choice due to its high theoretical gravimetric capacity of 294 mAh/g and practical voltage of 4.2 V [7]. On the downside however, it contains toxic cobalt which makes it costly to handle. In addition, fully charged $\text{Li}_{1-x}\text{CoO}_2$ loses oxygen O_2 at above 180 °C [8], rendering it thermally unstable and thus posing the risk of explosion if used for high power application such as electric vehicle [9,10]. Subsequently, this raised interest in polyanionic materials under the presumption that the strength of X–O bond (X = ligand) would provide a robust structure capable of sustaining large amount of Li (de)intercalation processes without safety concerns [5]. In 1997, Padhi *et al.* [11] synthesized what is now a widely accepted and commercially successful polyanionic cathode material, lithium iron(II) phosphate LiFePO_4 . It is made up of abundant component elements leading to its low cost, and it has better thermal stability compared to LiCoO_2 albeit at the expense of lower voltage of 3.5 V [12], which is still fairly attractive, as is also its theoretical gravimetric capacity 170 mAh/g [13]. However, LiFePO_4 suffers from poor ionic and electronic conductivities [7] and requires modification and treatment such as nano-sizing and carbon coating [14,15] which increase its synthetization cost.

To improve the voltage, Recham *et al.* [16] replaced the phosphate ion PO_4^{3-} with the more electronegative sulphate ion SO_4^{2-} and further joining it with the fluoride ion F^- to synthesize lithium iron(II) fluorosulphate LiFeSO_4F . This cathode material exhibits slightly higher voltage of 3.6 V but a lower gravimetric capacity at 140 mAh/g. However, it is capable of 85% capacity retention at C rate (discharge rate of 1 Li ion in 1 hour) which means fast ionic diffusion. Consequently, it does not require nano-sizing or carbon coating while sharing the same cost advantage, thereby making it a promising contender to LiFePO_4 . Still, it was argued that the use of hazardous F^- in the material may not be ideal [17]. Therefore, attempts were made to replace F^- with the more environmentally friendly hydroxyl group OH^- . Three separate groups successfully synthesized lithium iron(II) hydroxysulphate LiFeSO_4OH via two different methods resulting the material being reported to crystallize in two polymorphs: tavorite and layered. Tavorite LiFeSO_4OH was obtained by electrochemically inserting lithium (Li) into the iron(III) hydroxysulphate FeSO_4OH host structure, and it exhibits a voltage of 3.2 V and gravimetric capacity of 110 mAh/g [18,19]. Meanwhile, direct synthesis of LiFeSO_4OH was achieved by Subban *et al.* [17] through mechanochemical synthesis approach (via ball milling) which resulted in the layered polymorph with a voltage of 3.6 V and similar capacity as the tavorite phase.

In tandem with the rapid progress made in the research for better LIBs, scientists are also exploring the possibility of using sodium (Na) in cathode material for sodium ion batteries (SIBs). This is because Na has a much greater abundance of 2.3% in the Earth's crust, compared to Li at 0.0017%. Geographical abundance is crucial considering the increasing demand for rechargeable battery, and clearly research into SIB is needed as the

next generation energy storage technology. Moreover, Na is the next member after Li in Group 1 of the periodic table of elements, meaning that the two share similar structure and properties. This is important because fundamentally it means SIB can have the same working mechanism as the extensively researched and developed LIB [20].

To that end, various Na-based cathodes have been explored both experimentally and computationally, but a gap in literature was found in which one variant has yet to be reported. For all but one of the Li-based cathode materials mentioned above, there have been experimental and computational work performed on their respective Na counterparts: sodium cobalt(III) oxide NaCoO_2 [21,22], sodium iron(II) phosphate NaFePO_4 [23,24] and sodium iron(II) fluorosulphate NaFeSO_4F [25,26]. Curiously, there is still no report thus far, either experimentally or computationally, on sodium iron(II) hydroxysulphate NaFeSO_4OH . Researchers have instead focused on increasing the population of SO_4^{2-} polyanionic group. Singh *et al.* [27] for instance, synthesized sodium iron(III) bisulphate $\text{NaFe}(\text{SO}_4)_2$ which delivers a redox potential of 3.3 V with a reversible gravimetric capacity of 78 mAh/g. Regardless of the shift in direction, the gap in information on NaFeSO_4OH presents a clear research opportunity which should be grabbed. In this work, first principles study on the novel cathode material NaFeSO_4OH were carried out and the findings were compared to layered LiFeSO_4OH from which it was based on. This was a fully computational research, and no experimental work was involved.

1.2 Research problems

Commercially successful lithium ion batteries (LIBs), as its name suggests, are made up of lithium-based cathode. However, lithium (Li) is of limited amount in nature (17 parts per million, ppm = 0.0017% in Earth's crust) and is not renewable. Thus, alternative to Li-based cathodes must be explored. Sodium (Na) comes to mind due to its abundance (23 000 ppm = 2.3 % in Earth's crust) and it is in the same group in the periodic table (Group 1) as Li i.e. atomically both share relatively similar structure with one valence electron, although Na is larger in size (averaged atomic radius, $\bar{r}_{\text{Na}} = 187$ pm) compared to Li (averaged atomic radius, $\bar{r}_{\text{Li}} = 156$ pm). Theoretically, this means Na can replace Li as the guest ion to form Na-based cathodes to be employed in the next generation rechargeable battery technology in the form of sodium ion batteries (SIBs). The material of interest is NaFeSO₄OH which has no scientific report thus far, be it from experiment or from first principles calculations (FPC). This research will explore the said material exclusively via the latter route. This however pose an additional problem that precede everything else: how to ensure the validity of the calculations.

Having specified the material of interest for investigation, and suppose that some of its properties have been predicted, the next challenge would be to study the feasibility of NaFeSO₄OH as a cathode. Thanks to theoretical and technological advances, such endeavour can also be achieved via FPC in lieu of experimental characterization. The knowledge gained from this *ab initio* technique saves valuable things such as time, energy and cost.

1.3 Research objectives

Based on the research problems posed above, this study thus seeks to fulfil the following objectives:

1. To identify first principles computational settings that best reproduce the experimental observations for layered LiFeSO_4OH and layered FeSO_4OH with respect to lattice parameters and redox voltage.
2. To investigate the structural, electrochemical and electronic properties of layered NaFeSO_4OH via first principles calculations.
3. To gauge the feasibility of layered NaFeSO_4OH as a cathode for SIB.

1.4 Significance of research

This research adds a new entry to the database on Na-based cathodes in the global effort to discover and explore practical alternatives to Li-based cathodes for the rechargeable battery technology. This is a first ever study on NaFeSO_4OH as a cathode for SIB, which (partly) closes another gap in literature on the family of FeSO_4 -based cathodes, thereby providing reference to other researchers who could be interested in synthesizing this material. Furthermore, the information obtained from this study could serve as a basis for further research on how the properties and performance of NaFeSO_4OH can be optimized.

1.5 Scope and limitations of research

First and foremost, this research is fully computational and predictive in nature – no experimental work will be involved. The calculations will be based on the plane wave basis set of the density functional theory (DFT). As mentioned earlier in the research background section, LiFeSO_4OH had been found experimentally to crystallise in two polymorphs: tavorite and layered. This research will only study NaFeSO_4OH as virtually built from the crystallographic data of the layered LiFeSO_4OH polymorph through *in situ* substitution of Li with Na. The preference has to do with the higher redox voltage of the layered polymorph compared to the tavorite phase. If NaFeSO_4OH has much in common with layered LiFeSO_4OH or if it at least is not far off performance-wise, then NaFeSO_4OH should be considered as a good cathode candidate.

However, the possibility of structural change (crystal system, space group) as a result of the substitutions made will not be explored because it would require high computational cost, for which the necessary infrastructure is simply not available. Furthermore, the findings of this computational work for a novel material which has not been synthesised can only be validated through experimental work. But it is hoped that any findings on NaFeSO_4OH can be agreed to be acceptable provided that the experimental findings for layered LiFeSO_4OH can be satisfactorily replicated via FPC. This would then be considered to have validated the research method and subsequently allow it to be applied with confidence to layered NaFeSO_4OH .

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter provides the background information that may be useful later during analysis and discussion of research results. Firstly, in section 2.2 the various type of electrochemical energy storage technologies that are available in the world today are reviewed very briefly as an introduction. In the next section, the basic components and working mechanism of lithium ion battery are described, while the definitions of a few key parameters are given. Within it, subsection 2.3.1 addresses the issue pertaining to the availability of lithium – is the world facing shortage of Li? The core part of this chapter is section 2.4 where Li-based cathodes are compared to Na-based cathodes. Specifically, LiFePO_4 and NaFePO_4 (section 2.4.1), and LiFeSO_4F and NaFeSO_4F (section 2.4.2). In section 2.4.3, the polymorphs of LiFeSO_4OH are reviewed while in section 2.4.4, brief reviews on cathode materials which are constituted of the elements Na, Fe, S, O and H are presented. In section 2.5, the interesting phenomenon of why Na-based cathode has a