



Master of Science

# Synthesis and Electrochemical Performance of Lithium Vanadium Sulfate-based Polyanionic Compound for

## **Cathode Materials Li-ion Battery**

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## Synthesis and Electrochemical Performance of Lithium Vanadium Sulfate-based Polyanionic Compound for Cathode Materials Li-ion Battery

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#### Abstract

The development of polyanionic compound Li-ion batteries (LIBs) is rapidly growing to support green sustainable energy especially for electric vehicles (EVs). In this work, a double sulfate  $LiV(SO_4)_2$  material has been successfully synthesized, having high discharge potential and excellent stability. Our investigation shows that LiV(SO<sub>4</sub>)<sub>2</sub> has a crystal structure of trigonal rhombohedral which provides a two-dimensional framework parallel with ab-plane for Li-ion accommodation. LiV(SO<sub>4</sub>)<sub>2</sub> was synthesized by Li<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, V<sub>2</sub>O<sub>5</sub>, and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O as raw material. This material was synthesized by the water-based solution method at low temperature. Sintering temperature 350 °C, sintering time 1 h, and an additional 50% wt. excess oxalic acid dihydrate was obtained as an optimum condition for synthesis in inert argon gas atmosphere. Electrochemical performance of LiV(SO<sub>4</sub>)<sub>2</sub> as cathode material shows ~60% of lithium ions are extractable with 107 mA  $g^{-1}$  rate in ambient condition through potential range 1.0 V - 4.8 V for 50 cycles. The potential of discharge was observed at 3.9 V vs. Li<sup>+</sup>/Li in the 2016 type coin cell. Infrared spectroscopy and SEM-EDX were conducted. The charge-discharge phenomenon of this material was proposed as a pseudocapacitive mechanism related to the structure and cyclic voltammetry measurement. This discovery may lead to the potential base material to obtain a higher stoichiometric composition by accomodating more than one Li-ion, which will be valuable for the next high power density rechargeable battery generation.

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#### 1. Introduction

Recently, huge challenges to reaching environmentally friendly and renewable energy options associated with fossil fuels, global warming, and climate change.<sup>1</sup> As the global demand and societal dependency on fossil fuels increase, efforts to electrify the transportation industry are progressing rapidly.<sup>2</sup> Renewable energy sources, considering their rich natural resources, are inherently unreliable and largely scattered. Excellent energy-storage systems are needed to make the best use of these sources of energy.

Since the early 1990s, the recent global revolution in energy storage systems (ESSs), for Li-ion batteries (LIBs) and their applications, becomes popular.<sup>2-4</sup> Current technology can provide 260 Wh kg<sup>-1</sup> and 780 Wh L<sup>-1</sup> of gravimetric and volumetric energy density, respectively.<sup>2,3</sup> In terms of energy and power density, service life, and design versatility, Li–ion batteries (LIBs) are well–established, efficient energy storage technology.<sup>2</sup> The advantages of batteries include wide operating temperature range, versatile choice of chemical system and voltage, variable size and shape, and low cost (e.g. portable electronics, electric and hybrid vehicles). Li-ion batteries (LIBs) have been intensively investigated for grid-scale ESSs among various applicants because of their high energy density and mature chemistry with well–established industries.<sup>1</sup>

Li-ion batteries (LIBs) are the most exciting technology in this field so far, and they have rapidly dominated the market for portable electronics in recent decades and are now entering the automotive industry. Despite its tremendous success, to keep up with rapid technological advances, Li-ion batteries (LIBs) still need to be improved, particularly in terms of energy density. Since a battery's overall electrochemical efficiency depends on the favorable synergy of the anode, cathode, and electrolyte, the cathode is critical for high energy densities to be achieved.

The appeal of Li–ion batteries (LIBs) technology lies in its flexibility of broad application coverage for example portable electronics, electric vehicles, and grid applications, with design capabilities to meet the requirements of autonomy and control. In particular, the electric vehicle (EV) industry has recently grown. However, the production of Li–ion batteries (LIBs) to meet the fluctuating energy needs of various types of society, as well as to offer environmental benefits, is a formidable challenge, especially regarding material requirements. Electroactive materials are sought with high specific strength, energy density, long calendar life, high protection, and low cost. It is also important to explore environmentally friendly materials that use less energy and emit less  $CO_2$  during manufacturing. Then, batteries will only begin to have an environmental benefit beyond hundreds of cycles includes the optimization and revolution of a commercial electrode, as well as the innovative nature of novel Li–ion battery materials.



**Figure 1.1** Comparison of the energy density defines as the capacity to do work and the power density is the rate at which work is applied.<sup>5</sup>

The advantage of Li-ion batteries (LIBs) is upon lithium ions flowing between anode and cathode.<sup>6</sup> Battery–powered vehicles, which involve a set of stringent requirements as shown in Figure 1.1 including a range of duration, cost, and environmental capability. They are expected to reduce carbon footprint and air pollution from conventional petroleum-driven engines.<sup>2</sup> Li–ion batteries (LIBs) are a promising option for large–scale energy storage systems (ESSs).<sup>1</sup> The battery is consists of three main components, there are electrolyte, cathode, and anode. They are connected by an ionic conductive material called an electrolyte to maintain the charge balance.<sup>7</sup> In modern Li–ion batteries (LIBs), the vital component to determine the overall performance of the battery cell is cathode materials.<sup>3</sup> The quantity of battery energy storage content can be manipulated in different ways by:<sup>7</sup>

- a. Having a large chemical potential difference between a couple of electrodes;
- b. Reduce the mass or volume of material for each exchanged electrons;

Ensure that the electrolyte is not participating in a reaction during the charge/discharge process of the battery. The term "battery" refers to a stack of cells or a single cell. In this electrochemical reactor, the nature of different redox reactions in the electrolyte provides different electrochemical performance. The three main criteria to evaluate the performance of a battery includes the output voltage, the specific capacity (expressed in mAh g<sup>-1</sup> or Ah L<sup>-1</sup>), the energy density also known as "specific energy", expressed in Wh kg<sup>-1</sup> or Wh L<sup>-1</sup>) and the electrical power density expressed in W kg<sup>-1</sup> or W L<sup>-1</sup>).



**Figure 1.2** (a) Schematic of the first Li–ion batteries (LIBs).<sup>6</sup> (b) A scheme showing the working electrode *vs.* the reversible capacity of the two electrode materials with the energy levels of the electrolyte at an open–circuit state. Various emerging high–voltage cathode materials have their operating potentials in part or entirely below the highest occupied molecular orbital (HOMO) of state–of–the–art electrolyte systems.<sup>2</sup>

The electrochemical reactions continue on both sides when the electrodes are attached through an external circuit, as shown in Figure 1.2a, allowing the electrons (current) to flow from the negative to the more positive side. At the same time, ions that pass through the electrolyte in the opposite direction ensure electro–neutrality. When one of the redox reactions is complete, the current ceases, resulting in a complete battery discharge. The battery can be recharged and it is considered a secondary battery if this mechanism can be reversed by adding an external voltage. The open–circuit potential of the  $V_{oc}$  electrochemical cell is determined by the difference, divided by the elementary charge, between the  $\mu A$  and  $\mu C$  electrochemical potentials of the anode and cathode, respectively.

The voltage is limited by the energy gap illustrated in Figure 1.2b between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the electrolyte (voltage window).<sup>6</sup> In both electrodes, the cell voltage is regulated by the lithium chemical potential difference. Measuring the voltage is equal to measuring the chemical potential of lithium when charging and discharging a battery. The theoretical capacity of a cell is the amount of charge, usually defined in terms of ampere–hours, that can be produced. Based on theoretical chemistry, 26.8 Ah or 96,487 C is delivered by the molecular weight of active materials with one electron. The Li–ion cell capability is dependent solely on active materials involved in the electrochemical reaction and chemistry of the active material. In this research, we established new potential cathode material materials by exploring double sulfate–based polyanionic compounds.

#### 1.1 Cathode materials for Li–ion battery

Various 2D layered transition metal oxides and 3D polyanionic structure materials have been unraveled in the quest to create robust Li-ion batteries (LIBs). Three primary compounds include cathode material consisting of active material, conductive agent, and binder. Polyvinylidene fluoride (PVDF) binders are commonly used as the piezoelectric polymer in the commercial process of energy harvesting and composite electrodes, helping to retain structural integrity and ensure smooth transport of electron/ Li-ion between the active material, conductive agent, and current collector during cell operation.<sup>2</sup> With robust cycling stability, inert binders can be used to realize successful electrochemical efficiency. Although the battery core is the cathode, efforts are aimed at developing and implementing sufficient electrolytes with an ideal combination of salts and organic solvents.<sup>4</sup> Understanding the Li-ion transport and electrochemical reaction mechanism of the electrode materials is key to developing new and improved electrode materials. Another perspective is categorized based on four class compounds as shown in Figure 1.3 and it analyzes five parameters such as energy density, power density, cost production, thermal stability, and cyclability.



Figure 1.3 Comparison of various types of cathode materials for Li–ion batteries

(LIBs).<sup>2</sup>

Several methods for the successful design of new cathode materials are envisaged. One approach driven by Ceder et al. focused on computing high-throughput materials, but only limited performance has been achieved.<sup>8</sup> A second method, new materials is developed by spotting clusters compound with desirable structural characteristics, using conceptual methods such as acid-basicity, solvent dielectric constants, and solvent energies to establish new reaction paths. The goal is for stabilizing metastable phases, dealing with electronegativity, and chemical pressure to tune the redox potential of 3d-metal redox centers.<sup>8</sup>

Alongside the battery determines the electrode's complexity, electrochemical reactions occur primarily at the point of interaction with electrolytes, cathode–active materials, and electronic conductors. First, the requirements of cathode material for battery:<sup>8</sup>

- a. The material contained reducible/oxidizable ion like a transition metal;
- b. The material must react with lithium reversibly and without major structural change to give a rechargeable cell;
- c. The material must react with the high free energy for high voltage;
- d. The material should react with lithium very rapidly on both lithium insertion and removal to give high power;
- e. The material should ideally be a good electronic conductor to alleviate the need for a conductive additive;
- f. The material must be low-cost, environmentally benign, and plentiful elements.



Figure 1.4 Scheme of the dimensionality of Li–ion channel pathway based on the crystal structure.<sup>3</sup>

However, there are major stability issues with the electrolyte depends on the four types of cathode materials as mentioned in Figure 1.4 non-frame, one-dimension (1D), two-dimension (2D), and three-dimension (3D) based on the Li-ion transport mechanism.<sup>3</sup> Nowadays, the systems are not stable much beyond 4.8 V, with decomposition reactions occurring at higher voltages. Besides, the conductive carbon additives can react with the electrolyte salt at these potentials, forming intercalation compounds.

There is a considerable lack of knowledge at this time of the molecular interactions that occur within the electrolyte. Also, these interfaces may be found on the external surface of the electrodes or in the complex porous internal structure. Compared to today's systems, an advanced electrolyte, either for a battery or an electrochemical capacitor, will need the following characteristics and the proposed strategies are presented as shown in Figure 1.5:

- a. higher ionic conductivity for high cycling rates over a wide range of temperature;
- b. higher stability, both chemical and electrochemical for higher voltage systems and safety;
- c. higher compatibility for better wettability and lower reaction rates; and
- d. low-cost and decreased environmental impact.

Electrolytes containing  $\text{LiPF}_6$  salt dissolved in a mixed carbonate solvent are currently used in Li–ion batteries (LIBs), while high–voltage capacitors use quaternary ammonium salts dissolved in acetonitrile or organic carbonate.<sup>5</sup>



Figure 1.5 Strategy for improvement proposed in the development of cathode

materials.9

#### 1.1.1 Layered oxide materials

A cathode made from the cobalt analog of the layered transition metal oxides, general formula: LiMO<sub>2</sub> (M = Co, Ni, Mn, V), was found in the Sony cell produced in 1991. Alternating layers of interconnected CoO<sub>6</sub> octahedra and octahedrally coordinated lithium ions comprise the crystal structure of LiCoO<sub>2</sub> reported by Goodenough et al.<sup>10</sup> The layers are stacked in the c-direction and consist of octahedrally coordinated cobalt(III) ions with edge–sharing in the directions of the *a*–axis and *b*–axis. Delithiation from x = 0.21 to x = 0.51 in Li<sub>1-x</sub>[Co/Ni]O<sub>2</sub> results in a transformation from trigonal crystal symmetry to monoclinic in a reversible step. The structure is destabilized when x > 0.5 due to the high oxidation potential to increase the organic electrolyte reaction. If total delithiation is feasible, this decreases the capacity based on LiCoO<sub>2</sub> cathodes to about half the theoretical capacity.

By using a solid-state reaction process, the compound was synthesized and the  $\alpha$ -NaFeO<sub>2</sub> structure was adopted. As defined in Figure 1.6, both Co and Li atoms are octahedrally coordinated, Co<sup>3+</sup> resides at the 3a site, and Li<sup>+</sup> ions in the  $R\overline{3}m$  ccp packed O<sup>2-</sup> lattice at the 3b site. The O3 structure evolves towards an O1 structure at x  $\approx 0.5$  as increasing the amount of extracted Li-ion, thus showing an expansion of the c-axis interlayer as a result of electrostatic repulsion of the x  $\leq 0.5$  oxygen layers. Ultimately, at x  $\approx 0.05$ , there is a transformation of the O3 LiCoO<sub>2</sub> process into a stable O1 Li<sub>x</sub>CoO<sub>2</sub> phase (ABAB stacking sequence). P or O defines the form of alkali coordination (prismatic or octahedral) in terms of 'On' and 'Pn' (n = 1, 2, 3, etc.), and the number n indicates the number of sodium layers per unit cell.



Figure 1.6 Illustration of (a)  $A_xMO_2$  material that is classified as layered oxides with different sites and types of atomic arrangement.<sup>3</sup> Schematic diagram of (b) phase transition during the charge–discharge process of LiCoO<sub>2</sub>.<sup>11</sup>

#### 1.1.2 Spinel oxide materials

The natural progression from the two–dimensional layered oxides is to the three–dimensional spinel oxides, of general formula  $\text{Li}[M_2]O_4$  (M = Ti, Mn, Co, V). The LiMn<sub>2</sub>O<sub>4</sub> analog, due to environmental and economic perspectives as manganese is much more abundant than cobalt and non–toxic.<sup>12</sup> LiMn<sub>2</sub>O<sub>4</sub> crystallizes with cubic symmetry in the space group  $Fd\overline{3}m$ . The crystal structure of LiMn<sub>2</sub>O<sub>4</sub> with Li–ions occupying the tetrahedral holes in between the MnO<sub>6</sub> octahedra framework comprises a three–dimensional framework of edge–sharing MnO<sub>6</sub> octahedra.

LiMn<sub>2</sub>O<sub>4</sub> cathode charge-discharge profiles show two distinct plateaus around 4 V and 4.1 V (*vs.* Li<sup>+</sup>/Li) as illustrated in Figure 1.7 which is attributed to the two-step reversible lithium intercalation. At ambient temperature, the theoretical value of specific capacity based on intercalation of one lithium ion per formula unit is 148 mAh g<sup>-1</sup>, but LiMn<sub>2</sub>O<sub>4</sub> suffers from capacity fading at elevated temperatures on prolonged current discharge. This ability is due to structural changes occurring at the electrode surface, resulting in oxidation of Mn<sup>4+</sup> to Mn<sup>3+</sup> through lithiation, and subsequent distortion of Jahn–Teller, and reduction of crystal symmetry from cubic to trigonal. Numerous coatings include Al<sub>2</sub>O<sub>3</sub>, LiCoO<sub>2</sub>, and AlPO<sub>4</sub>, all showing improvement in capacity retention. Substituted manganese spinels have been widely investigated with the effects of both cationic and anionic substitution reported by Manthiram et al. who found that partial substitution of both Mn and O reduced capacity fade without sacrificing capacity values.<sup>13</sup>



Figure 1.7 Illustration (a) the crystal structure of spinel oxide and the charge–discharge curves of ordered and disordered  $LiMn_2O_4$ .<sup>2</sup> (b) The charge–discharge reaction mechanism of spinel oxide.<sup>3</sup>

#### 1.1.3 Polyanionic materials

Using various forms of polyanion units, the material discovery going to a step forward with polyanionic chemistry.<sup>4</sup> This problem can be circumvented by introducing polyanionic cathode materials with the tunable crystal structure, a stable system providing safe function, and greater redox potential due to the inductive effect. Following the inductive effect principle, a plethora of cathodes with polyanionic units  $[(XO_4)_m^{n-}: X = B, P, Si, S, W, Mo, As, Ti, V, etc.]$  have been discovered.<sup>4</sup> Principle of inductive effect is based on *Pauling* electronegativity of the following atoms:

**B** (2.09) < **C** (2.55) < **P** (2.19) < **S** (2.58) < **O** (3.44) < **F** (3.98)

Briefly speaking, the redox potential of electrode material is governed by the ion–covalency of the M–X bond (M = transition metal, X = ligand) with higher potentials for more ionic bonds and vice versa. More specifically, it consists of tuning the ion covalency of the M–O bonds by replacing  $O^{2-}$  anions with  $XO_4^{n-}$  polyanions (with X = Si, P, W, Mo, and S), that is by changing the electronegativity difference between M and the polyanion. Despite the "weight penalty" (low theoretical gravimetric capacity) listed in Table 1.1 arising from the presence of polyanion groups such as  $(PO_4)^{3-}$ ,  $(SiO_4)^{4-}$ , and  $(SO_4)^{2-}$ , the positive attributes of such materials are as follows:<sup>14</sup>

- a. Very stable frameworks for long-term stability, extensive cycling, and safety issues;
- b. The chemical nature of the polyanion allows the monitoring of a given  $M^{n+}/M^{(n-1)+}$  redox couple, through the inductive effect and rise to higher values;
- c. With extreme flexibility towards cation and anion substitutions for a given structural form, an enormous variety of atomic arrangements and crystal structures were adopted.

Dolyanion	Molecular Weight	Molecular Weight
1 olyanion	[g mol <sup>-1</sup> ]	per charge electron
BO <sub>3</sub> <sup>3-</sup>	59	19.67
CO3 <sup>2-</sup>	60	30.00
SiO44-	92	19.67
PO4 <sup>3-</sup>	95	31.67
SO4 <sup>2-</sup>	96	48

Table 1.1. Comparison of the most common polyanion.

These polyanionic combinations lead to rich structural diversity and numerous electron redox events, leading to robust electrochemical efficiency resulting in robust electrochemical performance.<sup>4</sup> Li–ion batteries (LIBs) performance are directly related to the crystal structure/electronic structure of electrode materials regulating the properties of electronic/ionic transport, cell potential, and the number of exchanged electrons. Intrinsic electrical conductivity information can be derived directly from the electronic structure of the electrode materials. Based on Figure 1.8, for the d<sup>n</sup>p<sup>m</sup> configuration of the transition metal–oxygen tetrahedral, the coulomb correlation, the charge transfer energy, the hybridization strength between the cation 3d and oxygen 2p states, and the crystal field splitting, control the electronic structure of the ground state, magnetic and transport properties of the cathode materials for Li–ion batteries (LIBs).<sup>15</sup>



**Figure 1.8** Illustration of inductive effect, (a) blue octahedral and pink tetrahedral represents transition metal and anion, respectively. (b) Electron delocalization in anionic structure.<sup>2</sup>

#### 1.1.3.1 Borates-based compounds

Instead of other polyanions, the borate anion represented the lightest anionic species, thus providing the ability to greatly increase the gravimetric potential in comparison to phosphates or silicates. It is important to explore borate-based materials because boron adopts planar or tetrahedral oxygen trigonal coordination.<sup>16</sup> LiMBO<sub>3</sub> cathode material M = Fe, Mn, and Co investigated for structural and electrochemical performances.<sup>17-19</sup> LiFeBO<sub>3</sub> and LiCoBO<sub>3</sub> have a crystal structure monoclinic with space group *C*2/*c* while LiMnBO<sub>3</sub> has a hexagonal and monoclinic crystal structure.<sup>20</sup> The high polarization cause low intrinsic conductivity.

Furthermore, exploration of pyroborate  $(B_2O_5)^{4-}$ -based materials need to be performed instead of the different borate polyanions shown in Figure 1.9, indicating an improved working capacity. The enhancement of the performance of borate-based cathode material usually aims at the preparation of moisture-resistant material and the choice of nanoparticles in size.<sup>19, 21</sup> LiFeBO<sub>3</sub> has discharge potential at 3.0 V *vs.* Li<sup>+</sup>/Li with reversible capacity 190 mAh g<sup>-1</sup>. LiMnBO<sub>3</sub> shows potential insertion for monoclinic structure and hexagonal structure each of them at 3.7 V and 4.1 V *vs.* Li<sup>+</sup>/Li, respectively.<sup>21</sup>



Figure 1.9 Different oxygen coordination and borate polyanions. Boron and oxygen atoms are drawn in red and green, respectively.<sup>16</sup>

#### 1.1.3.2 Phosphate–based and pyrophosphate–based compounds

Since iron phosphate is a possible cathode material invented by Padhi et al., the analog of the olivine structure  $\text{Li}_x\text{MXO}_4$  (M = Mn, Fe, Co, and Ni; X = P, S, and As) has garnered great interest.<sup>22</sup> LiFePO<sub>4</sub> is the most studied, fully developed, and generally considered to be the most promising plug–in hybrid electric vehicle/electric vehicle (PHEV/EV) batteries. For high–power Li–ion battery systems today, these factors make it an incredible cathode content. Therefore, investment in the research and development of LiFePO<sub>4</sub> has begun worldwide, and the production of LiFePO<sub>4</sub> batteries has increased significantly in recent years.

LiFePO<sub>4</sub> crystallizes in the space group *Pnma* and comprises a three-dimensional framework is built from layers of corner-sharing FeO<sub>6</sub> octahedral interconnected by edge and vertex sharing with PO<sub>4</sub> tetrahedra.<sup>15</sup> Electrochemical cycling revealed a voltage of 3.5 V (vs. Li<sup>+</sup>/Li) with approximately 0.6 lithium atoms per formula unit being reversibly deintercalated. Though the phase formed from delithiation (FePO<sub>4</sub>) has the same crystal symmetry as the lithiated phase, there is a small reduction in unit cell volume (~7%). LiFePO<sub>4</sub> has very low conductivity at room temperature, therefore, only achieves close to theoretical capacity at very low current density or higher temperatures. Cathodes produced from such material exhibited initial discharge capacities of 165 mAh  $g^{-1}$  with no capacity fading over advanced knowledge, various 100 cycles. With transition metals for phosphate-based cathode materials are depicted in Figure 1.10.



**Figure 1.10** Voltage *vs.* maximum gravimetric capacity achievable phosphate–based cathode material. The red dashed line is the decomposition of the electrolyte.<sup>23</sup>
#### 1.1.3.3 Silicate–based compounds

After active phosphate application in Li–ion batteries (LIBs), orthosilicates  $(Li_2MSiO_4, M = Fe, Mn, Co, Ni)$  are another high-potential class of polyanion–type cathode candidates. The production of materials that could afford more than one electron reversible exchange per metal transition is one of the methods for increasing cathode power. For these tetrahedral structures, as many as eight different polymorphs are known to date, and they occur in two main groups, classified as  $\beta$  and  $\gamma$ , according to the distribution of cations over the two possible sets of tetrahedral sites available.<sup>15</sup>

Despite the beneficial sustainability and safety properties of polyanionic materials, their main setback is the lower gravimetric potential inherent in relatively heavy polyanions. Li<sub>2</sub>FeSiO<sub>4</sub>, which, for instance, is also lighter than pyrophosphates, is commonly explored as a potential cathode material. The structural resolution of this compound turned out to be very complex as, depending on the sintering temperature conditions, Li<sub>2</sub>FeSiO<sub>4</sub> crystallizes in different polymorphic configurations. Li<sub>2</sub>FeSiO<sub>4</sub> displays low electronic conductivity, which is solved by nano–sizing and carbon coating. This, however, contributed only to modest electrochemical efficiency changes. Li<sub>2</sub>MnSiO<sub>4</sub> and Li<sub>2</sub>CoSiO<sub>4</sub> are isostructural, but they both have reversible basic capability limitations.

## 1.1.3.4 Sulfate–based compounds

Sulfate chemistry cathode material for Li–ion batteries (LIBs) have arisen when NASICON-type  $Li_2V_2(SO_4)_3$  was synthesized successfully by electrochemically lithiated of  $V_2(SO_4)_3$  from reflux method of  $V_2O_3$  in H<sub>2</sub>SO<sub>4</sub>. The other oxysulfate compound reported by Sun et al. is  $Li_2Cu_2O(SO_4)_2$  which was found as an impurity during the synthesis of LiCuSO<sub>4</sub>F.<sup>11, 24, 25</sup> Reynaud et al.<sup>26</sup> and Lander et al.<sup>27</sup> have reported  $Li_2M(SO_4)_2$  cathode materials for Li–ion batteries (LIBs) with transition metal M = Fe, Mn, Co, Ni, Zn, and Mg which summarized in Table 1.2. Then, the development of sulfate-based cathode material is expanded recently with electrochemical performances are shown in Table 1.3.

Compound	Crystal Structure	Space Group
Li <sub>2</sub> Fe(SO <sub>4</sub> ) <sub>2</sub>	Monoclinic	$P2_{1}/c$
Li <sub>2</sub> Mn(SO <sub>4</sub> ) <sub>2</sub>	Monoclinic marinite	$P2_{1}/c$
$Li_2Co(SO_4)_2$	Monoclinic	$P2_{1}/c$
Li <sub>2</sub> Ni(SO <sub>4</sub> ) <sub>2</sub>	Orthorhombic	Pbca
Li <sub>2</sub> Zn(SO <sub>4</sub> ) <sub>2</sub>	Orthorhombic	Pbca
Li <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub>	Monoclinic marinite	$P2_{1}/c$

Table 1.2 Summarized of Li<sub>2</sub>M(SO<sub>4</sub>)<sub>2</sub> structure.

Materials	Structure	Space group	Theoretical Capacity	Electrochemical activity (vs. Li/Li <sup>+</sup> )	Redox Potential (vs. Li/Li⁺)
Li <sub>2</sub> Fe(SO <sub>4</sub> ) <sub>2</sub>	Orthorhombic	Pbca	$100\mathrm{mAh}~\mathrm{g}^{-1}$	91 mAh g <sup>-1</sup>	3.73 V; 3.85 V
Li <sub>2</sub> Fe(SO <sub>4</sub> ) <sub>2</sub>	<i>Marinite</i> monoclinic	P21/c	100 mAh g <sup>-1</sup>	83 mAh g <sup>-1</sup>	3.83 V
LiFeSO <sub>4</sub> F	<i>Triplite</i> monoclinic	C2/c	151 mAh g <sup>-1</sup>	140 mAh g <sup>-1</sup>	3.9 V
LiFeSO4F	<i>Tavorite</i> triclinic	<i>P</i> -1	151 mAh g <sup>-1</sup>	105 mAh g <sup>-1</sup>	3.6 V
LiFeSO₄OH	Layered monoclinic	P2 <sub>1</sub> /c	159 mAh g <sup>-1</sup>	100 mAh g <sup>-1</sup>	3.6 V
LiFeSO₄OH	<i>Tavorite</i> monoclinic	P2 <sub>1</sub> /c	159 mAh g <sup>-1</sup>	140 mAh g <sup>-1</sup>	3.2 V
$Li_2V_2(SO_4)_3$	NASICON rhombohedral	R∃c	137 mAh g <sup>-1</sup>	$70 \text{ mAh g}^{-1}$	2.6 V
Li <sub>2</sub> Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	NASICON rhombohedral	R∃c	134 mAh g <sup>-1</sup>	100 mAh g <sup>-1</sup>	3.6 V
Li <sub>2</sub> Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	Monoclinic	$P2_{1}/a$	$134\mathrm{mAh}~\mathrm{g}^{-1}$	$100\mathrm{mAh}~\mathrm{g}^{-1}$	3.6 V
Li <sub>1.6</sub> Fe <sub>2</sub> O(SO <sub>4</sub> ) <sub>2</sub>	Monoclinic	I2/m	167 mAh g <sup>-1</sup>	120 mAh g <sup>-1</sup>	2.83 V; 3.00 V; 3.19 V
Li <sub>2</sub> Cu <sub>2</sub> O(SO <sub>4</sub> ) <sub>2</sub>	Monoclinic	I2/m	153 mAh g <sup>-1</sup>	20 mAh g <sup>-1</sup>	4.7 V
Li <sub>2</sub> VO(SO <sub>4</sub> ) <sub>2</sub>	Tetragonal	I4cm	98 mAh g <sup>-1</sup>	50 mAh g <sup>-1</sup>	4.7 V

 Table 1.3 Sulfate-based polyanionic cathode materials for Li-ion batteries (LIBs).<sup>28</sup>

The industrial catalyst used for the production of sulfuric acid, through oxidation of SO<sub>2</sub> by O<sub>2</sub> to SO<sub>3</sub> at 400 °C – 600 °C, is considered to be a molten salt gas system,  $M_2S_2O_7-V_2O_5/SO_2-O_2-SO_3-N_2$  (M = Na, K, Cs).<sup>29</sup> During industrial operation, the catalytically active vanadium oxo sulfate complexes are formed. The phenomenon occurs by the dissolution of V<sub>2</sub>O<sub>5</sub> in molten alkali pyrosulfates  $M_2S_2O_7$ .<sup>30</sup> Thus complexes of V(V) such as (VO)<sub>2</sub>O(SO<sub>4</sub>)<sub>4</sub><sup>4-</sup>, (VO<sub>2</sub>SO<sub>4</sub>)<sup>-</sup>, and polymeric (VO<sub>2</sub>SO<sub>4</sub>)<sub>n</sub><sup>n-</sup> seem to be formed while reduction by SO<sub>2</sub> leads to V(IV) complexes VO(SO<sub>4</sub>)<sub>2</sub><sup>2-</sup>, VO(SO<sub>4</sub>)<sub>3</sub><sup>4-</sup>, and polymeric forms.<sup>30</sup> Slow decomposition of pyrosulfate is based on reaction below:<sup>31, 32</sup>

$$S_2O_7^{2-} \rightleftharpoons SO_4^{2-} + SO_3$$
 (Equation 1.4.4.1)

In pure pyrosulfate, the loosely bound SO<sub>3</sub> is physically dissolved or present as higher pyrosulfate ions.<sup>31</sup>

$$S_3O_{10}^{2-} \rightleftharpoons S_2O_7^{2-} + SO_3$$
 (Equation 1.4.4.2)

The increased "solubility" of  $SO_3$  in the melt containing vanadium might be explained by an increase of the physical solubility or by the tendency to form higher pyrosulfates.<sup>31</sup>

$$(VO_2)_2(SO_4)_2S_2O_7^{4-} \rightleftharpoons (VO_2)_2(SO_4)_3^{4-} + SO_3$$
 (Equation 1.4.4.3)

Alkali pyrosulfates are molten at 450 °C.<sup>29</sup> During the dissolution in molten alkali pyrosulfate, pentavalent vanadium is reduced by sulfur dioxide to the trivalent state.

$$V_2O_5 + K_2S_2O_7 + 2SO_2 \rightarrow 2 \text{ KV}(SO_4)_2$$
 (Equation 1.4.4.4)

Silica has been used since the fifteenth century for decomposing sulfates such as those of calcium or iron, the silica displacing the more volatile sulfur trioxide. The displacement of sulfur trioxide by silica can be conveniently expressed.<sup>29</sup>

 $2KV(SO_4)_2 + 2SiO_2 \rightarrow V_2Si_2O_7 + K_2S_2O_7 + 2SO_3$  (Equation 1.4.4.5)

$$V_2Si_2O_7 + O_2 \rightarrow V_2O_5 + 2SiO_2 \qquad (Equation 1.4.4.6)$$

Concerning compounds of V(V), it has proven much more difficult to obtain suitable crystals for X-ray investigations, for example, because in cooling process the molten  $M_2S_2O_7-V_2O_5$  systems frequently form amorphous phases.<sup>30</sup> At lower temperatures, that is, below around 440 °C, V(IV) and, in cases, V(III) compounds start precipitating, leading to deactivation of the industrial catalyst. Formation of the  $VO_2(SO_4)_2^{3-}$  and  $VO_3^{-}$  units in 2:1  $M_2SO_4 - V_2O_5$  molten mixtures are accounted for by the reaction.<sup>33</sup>

$$V_2O_5 + 2SO_4^{2-} \rightarrow 2VO_2(SO_4)_2^{3-} + VO_3^{-}$$
 (Equation 1.4.4.7)  
 $V_2O_5 + S_2O_7^{2-} + 2SO_4^{2-} \rightarrow 2VO_2(SO_4)_2^{3-}$  (Equation 1.4.4.8)

The molten salt complex species  $VO_2(SO_4)_2^{3-}$  occurring in oligomeric or polymeric.<sup>34</sup> This is due to a change in the composition of the melt, e.g., following a shift of the temperature – sensitive equilibrium as previously described.<sup>32</sup>

$$2\text{HSO}_4^- \rightleftharpoons \text{S}_2\text{O}_7^{-2-} + \text{H}_2\text{O} \qquad (\text{Equation 1.4.4.9})$$

The chemistry of vanadium (V) oxide dissolved in molten mixtures has been investigated due to the importance of catalytic  $SO_2$  to  $SO_3$  commercial oxidation in the sulfuric acid's manufacture.<sup>34-38</sup>

The known structure of sulfate-based material are summarized in Table 1.4, especially three reported compounds that visualized in Figure 1.10:<sup>34, 39</sup>

- a. The trigonal (*P*321) KAl(SO<sub>4</sub>)<sub>2</sub> structure of many anhydrous alums, including RbV(SO<sub>4</sub>)<sub>2</sub> and CsV(SO<sub>4</sub>)<sub>2</sub>;
- b. The monoclinic (*C*2/*m*) KFe(SO<sub>4</sub>)<sub>2</sub> structure, represented by the mineral yavapaiite, including NaV(SO<sub>4</sub>)<sub>2</sub> and AgV(SO<sub>4</sub>)<sub>2</sub>;
- c. The rhombohedral (*R*32) RbTl(SO<sub>4</sub>)<sub>2</sub> type, including one modification of TlV(SO<sub>4</sub>)<sub>2</sub>;
- d.  $ARE(SO_4)_2$  in example  $LiPr(SO_4)_2$ ,  $NaNd(SO_4)_2$ ,  $NaEr(SO_4)_2$ , and  $CsLa(SO_4)_2$ .

Compound	Space group	Metal Monovalent	Metal Trivalent	Ratio of ionic radii M <sup>I</sup> /M <sup>III</sup>
RbTl(SO <sub>4</sub> ) <sub>2</sub>	R32	6+6	6 (Trigonal Prismatic)	0.64
KAl(SO <sub>4</sub> ) <sub>2</sub>	P321	6+6	6 (Trigonal Prismatic)	0.38
KFe(SO <sub>4</sub> ) <sub>2</sub>	C2/m	10	6 (Octahedral)	0.48
$KV(SO_4)_2$	<b>R-</b> 3	6+6	6 (Octahedral)	0.56
$NaV(SO_4)_2$	C2/m	8	6 (Octahedral)	0.60
$CsV(SO_4)_2$	P-3	6 + 6	6 (Octahedral)	0.39
$LiLu(SO_4)_2$	Pbcn	6 + 4	6 (Octahedral)	1.12
KPr(SO <sub>4</sub> ) <sub>2</sub>	P <b>-</b> 1	12	8 (polyhedral)	0.74
LiPr(SO <sub>4</sub> ) <sub>2</sub>	$P2_{1}/b$	4	9 (polyhedral)	1.77
CsPr(SO <sub>4</sub> ) <sub>2</sub>	Pnna	14	8 (polyhedral)	0.63
$CsLa(SO_4)_2$	$P2_{1}/n$	13	9 (polyhedral)	0.66
$\alpha\text{-NaTm}(\mathrm{SO}_4)_2$	$P2_1/m$	8	8 (polyhedral)	0.87
NaEr(SO <sub>4</sub> ) <sub>2</sub>	$P2_{1}/b$	8	8 (polyhedral)	0.88
$NaNd(SO_4)_2$	P <b>-</b> 1	8	9 (polyhedral)	0.97

 Table 1.4 Structural features of double-sulfate types and coordination number of the metal.<sup>34</sup>



Figure 1.11 Crystal structure of (a)  $KV(SO_4)_2$ ,<sup>34</sup> (b)  $CsV(SO_4)_2$ ,<sup>40</sup> and (c)  $NaV(SO_4)_2^{38}$  constructed by VESTA<sup>41</sup> program.

## 1.1.4 X-ray Diffraction (XRD)

X-ray diffraction is a high-tech, non-destructive process for the study of thin – film coatings, fluids, ceramics, metals, catalysts, minerals, polymers, plastics, pharmaceuticals, solar cells, and semiconductors through a broad variety of materials.<sup>42</sup> In different industries, including microelectronics, power generation, aerospace, and many more, the technique finds countless practical applications. The presence of defects in a particular crystal, its level of resistance to stress, its texture, its size and degree of crystallinity, and virtually every other variable relating to the basic structure of the sample can easily be identified by XRD analysis. X-ray is a type of electromagnetic radiation with a 0.01–10 nm wavelength.<sup>43</sup>

X-ray sources are usually divided into two categories based on energy: soft X-rays with < 2,000 eV and hard X-rays with > 4,000 eV. Soft X-rays energy requires less acquisition time and beam damage but penetrates less into the sample, and hard X-rays energy requires more acquisition time and beam damage and penetrates deeper into the sample.<sup>44</sup> There are typical materials such as crystalline structure, crystalline domain size, multiple crystalline phases, and possible preferred orientations.<sup>45</sup> In principle and theoretical of XRD measurement based on Figure 1.11, Bragg's law has foundation equation as follow:

$$n\lambda = 2d.\sin\theta$$
 (Equation 1.1.4.1)

With specialized techniques, X–ray diffraction (XRD) can be used to determine crystal structures by using Rietveld refinement as depicted in Figure 1.12, determine modal amounts of minerals (quantitative analysis), characterize thin film samples, and make textural measurements, such as the orientation of grains, in a polycrystalline sample. Sample preparation has a vital role in XRD measurement.

Preferred orientation or texture means that the powder particles, usually platelets or needles, do not have an arbitrary form but a highly normal anisotropic shape. These are then ideally oriented along the sample surface during preparation, adjusting the peak intensities massively. In a ball mill, the anisotropic particle shape can be reduced by grinding. As excessive grinding can easily break down to nanometer size and contribute to amorphization, this should be done with great care. Rietveld refinement can be used to assess the degree of texture in this scenario.<sup>42</sup>

Crystallite size and strain are reciprocally compatible with the mean crystallite size. The smaller size of the crystallite, it caused the lower the absolute intensity, and the larger the reflection.<sup>46</sup> This effect becomes evident below the average size of less than 200 nm crystallite. Strain broadening is correlated with crystallite size broadening. Owing to the presence of defects in crystals, strain broadening takes place. This strain can be added by replacement of the constituent atoms, but also by special thermal treatment. Strain broadening can be distinguished as the dependency of the angle is much greater than in the latter case. The sample height is considered by rotating sample holders and the best results are thus collected to boost the measurement statistics.



**Figure 1.12** The principle of X-ray diffraction (XRD) through the atomic scattering.



# **Table 1.5** The seven crystal classes and fourteen Bravais lattices.<sup>47</sup>

# 2. Experimental section

## 2.1 Synthesis of $LiV(SO_4)_2$

The low-temperature solution method was conducted since  $SO_4^{2^{\circ}}$  polyanions decompose with the evolution of SO<sub>2</sub> at temperatures T > 600 °C.<sup>48</sup> LiV(SO<sub>4</sub>)<sub>2</sub> was synthesized using Li<sub>2</sub>SO<sub>4</sub> (Sigma Aldrich;  $\geq$  99.7%), V<sub>2</sub>O<sub>5</sub> (Alfa Aesar;  $\geq$  99.0%), H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> · 2H<sub>2</sub>O (Trade SCl Mark;  $\geq$ 99.5%), and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (Junsei;  $\geq$  99.5%) without further purification. LiV(SO<sub>4</sub>)<sub>2</sub> was synthesized by a two-step solution procedure described in Figure 2.1, the formation of vanadyl oxalate as intermediate vanadium (IV) species and further reduction to build up LiV(SO<sub>4</sub>)<sub>2</sub>. First, VOC<sub>2</sub>O<sub>4</sub> was produced by mixing vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) and oxalic acid dihydrate (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> · 2H<sub>2</sub>O) in distilled water with magnetic stirring for 1 hour at 70 °C.<sup>49</sup>

$$V_2O_5 + 3H_2C_2O_4 \cdot 2H_2O \rightarrow 2VOC_2O_4 + 9H_2O + 2CO_2$$
 (Equation 2.1)

Color transformation of solution from bright orange to dark blue indicates the formation of vanadyl cation  $(VO)^{2+}$ . Then, Li<sub>2</sub>SO<sub>4</sub> and  $(NH_4)_2SO_4$  were added to the solution at the same temperature 70 °C on the hotplate magnetic stirring.

 $VOC_2O_4 + Li_2SO_4 + (NH_4)_2SO_4$ 

$$\rightarrow 2\text{LiV}(\text{SO}_4)_2 + 6\text{NH}_3 + 3\text{CO}_2 + \text{CO} + 3\text{H}_2\text{O}$$
 (Equation 2.2)

When the solution is slightly remained, dry inside oven 100 °C overnight. The dried precursor was pelletized and put into sintering for the designed conditions. To maintain the characteristic of precursor pre–sintering and post–sintering, all materials were kept with silica gel.



Figure 2.1 Scheme the synthesis of  $LiV(SO_4)_2$  by a low-temperature solution method.

#### 2.2 Structural characterization

X-ray diffractometry (Rigaku Ultima IV) with Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å) was used for structural analysis. Step size 0.01° from 10° until 80° and continuous scan rate mode 2° min<sup>-1</sup> were applied to the sample. Scanning electron microscopy (SEM) under 10.0 kV as accelerating operating voltage was used to identified morphology of LiV(SO<sub>4</sub>)<sub>2</sub> prepared by Pt-coating (Sputter Coater 108Auto) for reduction of the charge effect. Infrared measurement was conducted using a single beam IR Affinity–1S Shimadzu spectrometer with the accuracy of the peak was reached ~0.125 cm<sup>-1</sup>. Ge-coated on KBr and pyroelectric DLATGS were used as a beam splitter and detector with a temperature control system, respectively.

## 2.3 Electrochemical characterization

The electrode composite is made with N-methyl pyrrolidone (NMP) as a solvent medium. The three components as mentioned before are consist of active material powder, polyvinylidene fluoride (PVDF), and graphene nanoplatelet with a ratio of 70: 5: 25 in weight terms. The composite was mixed by planetary ball-mill Pulverisette 6 (Fritsch GmbH) and it coated onto Al foil. The cells were assembled inside an Ar-filled glove box after the slurry was dried at 100 °C in a vacuum oven overnight. The solution of ethylene carbonate and dimethyl carbonate 1:1 (v/v) together with lithium hexafluorophosphate (1 M) was used as an electrolyte. The coin cells measured in galvanostatic charge and discharge measurement using the WonATech Battery Cycler System (WBCS) instrument.

# 3. Results and discussions

## 3.1 Optimization synthetic condition

The double sulfate-type synthesized by a low-temperature solution method. After drying at 100 °C in an air oven, the precursor color changed from dark bluish solution to green emerald amorphous agglomerate. The amorphous precursor was pelletized with a hydraulic press to make denser powder and reduce the surface of air contact.<sup>50</sup> Moreover, pelletized powder decreases the distance between the solid particle thus facilitating the heat transfer. Sintering temperature variation is to observe the optimum condition of heating the precursor for less impurity and high crystallinity of LiV(SO<sub>4</sub>)<sub>2</sub> in the inert Ar atmosphere. To prevent the gas from SO<sub>4</sub><sup>2-</sup> derivative to be carried away by Ar gas flow the furnace boat was capped.



Figure 3.1 Variation of sintering temperature for 5 hrs sintering time in inert Ar gas atmosphere.



Figure 3.2 XRD pattern  $LiV(SO_4)_2$  250 °C for 5 hrs based on reference  $NH_4LiSO_4$ .

Preliminary identification is initialized by the variation of sintering temperature with constant time sintering for 5 hrs from Figure 3.1. In our experiments, we used a heating rate of 5 °C per minute with natural furnace temperature cooldown. We observed that at 250 °C, the precursor phase has matched with orthorhombic NH<sub>4</sub>LiSO<sub>4</sub> crystal structure and space group  $P2_1/b$  with the number of space group 33 based on Figure 3.2. The result is due to the amorphous phase of vanadium species in the sample mixed with NH<sub>4</sub>LiSO<sub>4</sub> and it means the ammonium is still contained at this sintering temperature.

When the sintering temperature reached 300 °C, the material of  $\text{LiV}(\text{SO}_4)_2$ started to crystallize into our target phase. However, the crystallinity of as-prepared  $\text{LiV}(\text{SO}_4)_2$  at 300 °C is not good because of more broad peaks and higher full–width at half maximum (FWHM) value than XRD patterns at 350 °C and 400 °C. The thermal stability of our phase target still stands out until 400 °C, but it varies the impurity and crystallinity of the phase. Sintering temperature at 450 °C is the maximum  $\text{LiV}(\text{SO}_4)_2$  for heating resistance. After sintering temperature over 450 °C,  $\text{LiV}(\text{SO}_4)_2$  likely going to decompose as oxide materials. Based on the observation, we have chosen 350 °C as the sintering temperature because of better crystallinity. The longer sintering time resulted in peak shift and the apparition of impurity peaks attributed to vanadium oxide species such as vanadium dioxide  $VO_2$  and vanadium trioxide  $V_2O_3$ . Time sintering from 2 hrs until 5 hrs is not significant except for the formation of a small impurity peak. However, when sintering time reaches 12 hrs, the XRD pattern starts to evolve into another compound and decomposes based on Figure 3.3.

After screening the sintering time at 400 °C, the optimization shift to a lower temperature at 350 °C. Our result showed that the XRD pattern of  $\text{LiV}(\text{SO}_4)_2$  synthesized at 350 °C for 1 h is a better result than 2 hrs, 4 hrs, and 5 hrs. XRD patterns as shown in Figure 3.4,  $\text{LiV}(\text{SO}_4)_2$  in higher sintering temperature and short sintering time has more impurity peak than material synthesized in low temperature for longer sintering time confirm between 20 at  $10^\circ - 24^\circ$ . The next step is to reduce the impurity peak at 20 between  $10^\circ - 24^\circ$  and  $25^\circ - 35^\circ$ . Driscoll et al.<sup>49</sup> reported that to decrease the impurity peak, one way to solve the problem is increased the amount of oxalic acid.



Figure 3.3 Variation of sintering time at 400 °C sintering temperature.

The addition of excess oxalic acid dihydrate was used for this compound with a sintering temperature of 350 °C for 1 h, the results are shown in Figure 3.5. In pristine condition, without additional oxalic acid dihydrate, the sharp impurity peaks are observed as consecutive triple peaks after  $25^{\circ}$  -  $35^{\circ}$ . When the amount of oxalic acid is more than 30% wt. excess, the impurity peaks are going disappeared at 50% wt. excess. It is due to the trivalent vanadium species has less chance to oxidize to a higher oxidation state caused by heat or redox reaction with sulfur oxide species. Unfortunately, the addition of 70% wt. oxalic acid dihydrate appears impurity peak at 20 around 20° and 100% wt. excess oxalic acid reduces almost the peak intensity. It is due to the participation of oxalic acid dihydrate as the reducing agent for vanadium.

When the reducing agent is exceeded, it is will occur further reduction reaction besides vanadium such as sulfate  $SO_4^{2-}$  will be reduced to  $SO_x$  such as  $SO_2$  and  $SO_3$ . Then, oxalic acid dihydrate is used as carbon sources because it will transform into carbon dioxide and there is a chance to carbon black. Generally, carbon sources are used to support the electrochemical performance of polyanionic cathode material in terms of increase electrical conductivity by carbon-coating.



Figure 3.4 Variation of sintering time for 1 h, 2 h, 4 h, and 5 h at 350 °C.



Figure 3.5 XRD patterns of  $LiV(SO_4)_2$  with synthesis condition by an additional amount of  $H_2C_2O_4 \cdot 2H_2O$  pristine, 30 wt.%, 50 wt.%, 70 wt.% and 100 wt.% excess at 350 °C for 1 h.

#### 3.2 Structural Identification

The value from conventional Rietveld  $R_p$ ,  $R_{wp}$ , and  $R_{exp}$  are 18.2, 13.3, and 5.56, respectively. Based on Rietveld refinement results in Table 2.1 and it is shown in Figure 3.6, the value of chi-square  $\chi^2 = 5.719$  and Bragg R-factor 1.05. This value confirmed that analysis of structural determination is acceptable because the statistical value of chi-square is less than 10.

**Table 3.1** Crystallographic data and atomic coordinates of LiV(SO<sub>4</sub>)<sub>2</sub> from XRD patterns used Cu K $\alpha$  ( $\lambda$  = 1.54056 Å) as a target. The calculated lattice parameter and volume of LiV(SO<sub>4</sub>)<sub>2</sub> based on Rietveld refinement are a = b = 4.8517 Å, c = 24.0686 Å, and V = 490.637 Å<sup>3</sup> with density 1.236 g cm<sup>-3</sup>.

Atom	Wyckoff	х	У	Z
Li	3a	0	0	0
V	3b	0	0	0.5
S	6c	0	0	0.2414
O1	6c	0	0	0.3053
02	18f	0.0539	0.2109	0.2138

The determined structural phase shown in Figure 3.7 indicates one unit cell of  $LiV(SO_4)_2$  contains three  $Li^+$  ions coordinated with 6+6 oxygen atoms. Lattice plane (001) is composed of three-layered  $[V(SO_4)^-]_n$ , while each layer of  $[V(SO_4)^-]_n$  is built from the connection between VO<sub>6</sub> octahedral and SO<sub>4</sub><sup>2-</sup> tetrahedral through the corner and edge type bridged by an oxygen atom. In most of the structures, transition metal cations exhibit octahedral environments of different degrees of distortions.



**Figure 3.6** Rietveld refinement of LiV(SO<sub>4</sub>)<sub>2</sub> at 350 °C with 1 h and excess 50 wt.% of oxalic acid.



**Figure 3.7** Structure of  $\text{LiV}(\text{SO}_4)_2$  with space group  $R \overline{3}$  (148) trigonal rhombohedral with different orientations.

There are two different oxygen positions in these structures, equatorial and axial conformation, depend on the atomic coordination of sulfur. Equatorial and axial oxygens denote by  $O_{eq}$  and  $O_{ax}$ , respectively. The bond length between  $S-O_{eq}$  and  $S-O_{ax}$  within the  $SO_4^{2-}$  ion is affected by the interaction of distorted vanadium oxygen bond. This phenomenon occurs due to the stronger interaction of the triply coordinated  $O_{ax}$  with vanadium (III) ions compared to the weaker interaction of the tetrahedrally coordinated  $O_{eq}$  with Li–ion.<sup>34</sup> This layer–like arrangement with the weakest bonds between Li–ion and the triple of  $[V(SO_4)_2]^-$  anion sheets reflects the plate-like habit of the crystals.

It is of interest also to compare variations in the AV(SO<sub>4</sub>)<sub>2</sub> (A = Cs, K, Na, Li) group from the viewpoint of structural complexity. The structure of LiV(SO<sub>4</sub>)<sub>2</sub> shows the Li–ion pathway is going through a horizontal (001) plane between  $[V(SO_4)^2]_n$  layers. The sensitivity of LiV(SO<sub>4</sub>)<sub>2</sub> to the surrounding humidity was confirmed by the formation of partial hydrogen bonds with oxygen atoms of SO<sub>4</sub> tetrahedral. These results are from previously reported research works, which have shown the susceptibility of transition metal sulfate compounds to moisture.<sup>30</sup> This is a remarkably close relationship between our KV(SO<sub>4</sub>)<sub>2</sub> structure and the former three types KAl(SO<sub>4</sub>)<sub>2</sub>, KFe(SO<sub>4</sub>)<sub>2</sub>, and RbTl(SO<sub>4</sub>)<sub>2</sub>. All four structures contain very similar triple sheets of composition  $[M^{III}(SO_4)_2^-]_n$  with  $M^{III} = Al$ , Fe, V, or Tl alternating with layers of alkali-metal ions. The determining factor for structure type is caused by different sizes, the ratio of the metal atom, ionic radius, and intermediate phase of the material.



**Figure 3.8** (a) Subgroup graph of the point group  $4/m\bar{3}2/m$   $(m\bar{3}m)$ . Order at the left side given a logarithmic scale. Graph of the translational subgroups of  $Pm\bar{3}m$ . (b) Every conjugacy class of maximal subgroups marked by one line. For example, there are three non-conjugate subgroups of *Pmmm* of the type *Pmm2*, namely *Pmm2*, *Pm2m*, and *P2mm*, commonly designated by the conventional setting *Pmm2*. These may be conjugate in groups of a higher order; in *Pm* $\bar{3}$  there is only one class of three conjugates of *Pmm2*. The trivial subgroup *P*1 is not mentioned.<sup>47</sup>

The explanation of this crystal structure comes from the connection between the space group of CsV(SO<sub>4</sub>)<sub>2</sub>, KV(SO<sub>4</sub>)<sub>2</sub>, and NaV(SO<sub>4</sub>)<sub>2</sub>. AV(SO<sub>4</sub>)<sub>2</sub> with A as alkali metal Cs, K, and Na have space group  $P\overline{3}$ ,  $R\overline{3}$ , and C2/m, respectively. The space group of  $P\overline{3}$  and  $R\overline{3}$  have similarities as trigonal crystal system with -3 geometric crystal class as depicted in Figure 3.8. The  $P\overline{3}$  has hexagonal lattice and the  $R\overline{3}$  has rhombohedral lattice. The material of LiV(SO<sub>4</sub>)<sub>2</sub> has similarities to KV(SO<sub>4</sub>)<sub>2</sub> is due to the relationship between C2/m,  $P\overline{1}$ , and  $R\overline{3}$  space groups.

The further investigation of  $\text{LiV}(\text{SO}_4)_2$  structure via FTIR spectroscopy techniques showed a good correlation of vibrational frequencies with  $\text{KV}(\text{SO}_4)_2$  double-sulfate compound.<sup>26</sup> For qualitative determination of sulfate anion in crystals by infrared analysis, the shift of peak's position means the degeneracy energy is split corresponding to the rigidity of the crystal structure.



Figure 3.9 Observation data for (a) IR spectra, (b) SEM images, and (c) EDX mapping of  $LiV(SO_4)_2$  at 350 °C for 1 h with 50% wt. excess  $H_2C_2O_4 \cdot 2H_2O$ .

Table 3.2 Assignment of infrared bands (cm<sup>-1</sup>) for LiV(SO<sub>4</sub>)<sub>2</sub> and KV(SO<sub>4</sub>)<sub>2</sub>.<sup>26</sup>

Material	$v_3$	$\nu_4^*$	$v_4$	$v_2$
$LiV(SO_4)_2$	1057 cm <sup>-1</sup>	663 cm <sup>-1</sup>	594 cm <sup>-1</sup>	470 cm <sup>-1</sup>
$KV(SO_4)_2$	1030 cm <sup>-1</sup>	662 cm <sup>-1</sup>	595 cm <sup>-1</sup>	466 cm <sup>-1</sup>

The following data are shown in Table 2.2 and visualized in Figure 3.9a, the bending vibrational of  $\text{LiV}(\text{SO}_4)_2$  denoted as  $v_2$ ,  $v_4$  and  $v_4^*$  mode detected in low-wavenumber, while  $v_3$  at high-wavenumber assigned as the anti-symmetric stretching vibrational mode.<sup>51</sup> Based on these results, the peak position of  $\text{LiV}(\text{SO}_4)_2$  is higher than  $\text{KV}(\text{SO}_4)_2$  in terms of wavenumber because Li-ion is smaller than K-ion. The polarizing power is inversely correlated with the radius of the ion.

Besides the crystal structure, the morphology of  $\text{LiV}(\text{SO}_4)_2$  will have an impact on the conductivity of electrochemical performances as a positive electrode. The morphology of  $\text{LiV}(\text{SO}_4)_2$  is shown in Figure 3.9b described the physical structure of  $\text{LiV}(\text{SO}_4)_2$  has a disordered surface. The result of the surface's visualization is due to the high temperature inside the tube furnace triggered the reduction reaction and the decomposition of oxalic acid dihydrate such as carbon dioxide and carbon monoxide gases. The data of electron dispersion X-ray spectrometer in Figure 3.9c the distribution of sulfur atoms, oxygen atoms, and vanadium atoms on the surface of  $\text{LiV}(\text{SO}_4)_2$  particles are homogeneous.

#### **3.3 Electrochemical Performances**

LiV(SO<sub>4</sub>)<sub>2</sub> showed redox activity at 4.4 V and 3.9 V in ambient conditions. These findings suggest that redox activity of LiV(SO<sub>4</sub>)<sub>2</sub> are comparable to the second stage of Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> cathode material where three Li–ion can be extracted by 3 step voltage at 3.0 V – 4.3 V.<sup>52</sup> During subsequent charge–discharge processes, this material contributes one site recyclable of Li–ion. The extraction of Li–ion tends to favor because the potential of charge is higher than the potential of discharge. The arrangement of atomic coordination built inside the crystal structure affects how affordable Li–ion to diffuse through the channel framework.<sup>31</sup>

Based on the long cyclability with rate 107 mA g<sup>-1</sup>, the specific capacity of the potential range 1.0 V – 4.8 V, 2.0 V – 4.8 V, and 3.0 V – 4.8 V as shown in Figure 3.10a are 13 mAh g<sup>-1</sup>, 28 mAh g<sup>-1</sup>, and 60 mAh g<sup>-1</sup>, respectively. These results indicate that a longer potential range increases the chance of  $\text{LiV}(\text{SO}_4)_2$  to extract more Li-ion to the negative electrode. The specific capacity of 60 mAh g<sup>-1</sup> reaches around 60% of the theoretical capacity applied by 107 mA g<sup>-1</sup>, equal to the 1C rate. When these results are related to the  $\text{LiV}(\text{SO}_4)_2$  structure, three–fifth of Li–ion is extractable.



Figure 3.10 Comparison (a) long cyclability and (b) cyclic voltammetry of  $LiV(SO_4)_2$  with different potential range start from 1.0 V – 4.8 V (black), 2.0 V – 4.8 V (blue), and 3.0 V – 4.8 V (red) by 0.10 mV/s. Note that \* mark is oxidation peak and | mark is reduction peak.

Focus on cyclic voltammetry data, Figure 3.10b explained the difference between the required potential to extract (charge) and insert (discharge) Li-ion through the crystal structure. The other words, extraction of lithium-ion is assigned by oxidation reaction going to the higher voltage, and insertion of lithium-ion is presented by reduction reaction going to the lower voltage. These data show the first charge peak around 3.5 V until 4.2 V is shifted to higher potential when the potential range is become narrow, in this case, the maximum operating voltage is kept constant at 4.8 V. This result indicates that long potential range will increase the extractable Li-ion.

The fact that there is a gap or area inside cyclic voltammetry, is due to the pseudocapacitive mechanism when the charge–discharge process of  $\text{LiV}(\text{SO}_4)_2$  occurs. From cyclic voltammetry with potential range 1.0 V – 4.8 V, it is confirmed that the second discharge's peak appears at less than 2.0 V and the second charge's peak is rise at 2.9 V. Possible reason is based on the dynamicity of crystal structure and reversibility of the compound. However, the discharge peak takes place small shift around 3.9 V and 4.1 V because the number of extractable Li–ions at the first site have exact energy.



**Figure 3.11** Electrochemical performance of LiV(SO<sub>4</sub>)<sub>2</sub> with (a) long cyclability over Coulombic efficiency and (b) charge-discharge curves from long cyclability 0.5C rate.
After optimization of the potential range, our work continues with long cyclability measurement with lower charge–discharge 0.5C rate in 1.0 V – 4.8 V. Figure 3.11a shows the specific capacity of  $\text{LiV}(\text{SO}_4)_2$  by 0.5C rate is produced 113 mAh g<sup>-1</sup> at 25<sup>th</sup> cycle. Its exceeded theoretical capacity of  $\text{LiV}(\text{SO}_4)_2$  107 mAh g<sup>-1</sup> is due to the participation of lithium from electrolyte that contained  $\text{LiPF}_6$ . However, the Coulombic efficiency is not reached around 90% caused by pseudocapacitive processes and additional case the formation of the solid–electrolyte interface (SEI). For the detail on how  $\text{LiV}(\text{SO}_4)_2$  charge–discharge curves produce specific capacity at 0.5C rate, it is shown in Figure 3.11b. The picture explained the first curves until the 25<sup>th</sup> curves are almost smooth and it proved that the pseudocapacitive occurs. The charge–discharge measurement is applied with a constant voltage at 4.8 V to ensure that the extractable Li–ions are done at that rate.

As shown in Figure 3.12, the position of  $\text{LiV}(\text{SO}_4)_2$  as the cathode material with discharge potential 3.9 V and theoretical capacity is 107 mAh g<sup>-1</sup> are shown in Figure 3.12. Further and more detailed investigation of this material is still going on to verify and fully understand the intrinsic properties based on the mechanistic diffusion pathway and substantial improvement of electrical performance.



**Figure 3.12** Vanadium-based polyanionic compounds with  $V^{4+}/V^{5+}$  redox activity, in terms of the experimental discharge voltage and theoretical specific capacity. The different polyanionic families are shown in different colors: red for  $SO_4^{2-}$ , green for  $PO_4^{3-}$ , blue for  $AsO_4^{3-}$ , and gold for  $SiO_4^{4-}$ .

## 4. Conclusion

The goal of this thesis was the development of the double sulfate type compound with general formula  $AM(SO_4)_2$ , A denoted as monovalent alkali metal and M denoted as a trivalent transition metal. Our work closed with a conclusion.

- a. The synthesis of LiV(SO<sub>4</sub>)<sub>2</sub> has been successfully synthesized by the solution method with the optimum condition for the sintering temperature of LiV(SO<sub>4</sub>)<sub>2</sub> is 350 °C for 1 hr and an additional 50 wt.% excess of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O.
- b. The double sulfate type  $\text{LiV}(\text{SO}_4)_2$  compound has a crystal structure trigonal rhombohedral with space group  $R\overline{3}$  (148)
- c. The double sulfate type  $\text{LiV}(\text{SO}_4)_2$  compound has a potential intrinsic character as a cathode material with the potential of discharge 3.9 V vs.  $\text{Li}^+/\text{Li}$  using operating voltage 1.0 V – 4.8 V, the observable discharge capacity of  $\text{LiV}(\text{SO}_4)_2$  is 60 mAh g<sup>-1</sup> by 107 mA g<sup>-1</sup> (1C) rate.

Finally, this work shows that the double sulfate materials are still not fully explored especially the different crystal structures and space groups. Although the theoretical capacity of developed material is limited, we believe that this work unveils a new class of sulfate cathode materials and the chemistry behind it.

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