LiFeSO$_4$F as a Cathode Material for Lithium-Ion Batteries

Synthesis, Structure, and Function

ADAM SOBKOWIAK
Abstract


In this thesis, two recently discovered polymorphs of LiFeSO$_4$F, adopting a tavorite- and triplite-type structure, were investigated as potential candidates for use as cathode materials in Li-ion batteries. The studies aimed at enriching the fundamental understanding of the synthetic preparations, structural properties, and electrochemical functionality of these materials.

By in situ synchrotron X-ray diffraction (XRD), the formation mechanism of the tavorite-type LiFeSO$_4$F was followed starting from two different sets of precursors, FeSO$_4$·H$_2$O + LiF, and Li$_2$SO$_4$ + FeF$_2$. The results indicated that the formation of LiFeSO$_4$F is possible only through the structurally related FeSO$_4$·H$_2$O, in line with the generally recognized topotactic reaction mechanism. Moreover, an in-house solvothermal preparation of this polymorph was optimized with the combined use of XRD and Mössbauer spectroscopy (MS) to render phase pure and well-ordered samples. Additionally, the triplite-type LiFeSO$_4$F was prepared using a facile high-energy ball milling procedure.

The electrochemical performance of as-prepared tavorite LiFeSO$_4$F was found to be severely restricted due to residual traces of the reaction medium (tetraethylene glycol (TEG)) on the surface of the synthesized particles. A significantly enhanced performance could be achieved by removing the TEG residues by thorough washing, and a subsequent application of an electronically conducting surface coating of p-doped PEDOT. The conducting polymer layer assisted the formation of a percolating network for efficient electron transport throughout the electrode, resulting in optimal redox behavior with low polarization and high capacity. In the preparation of cast electrodes suitable for use in commercial cells, reducing the electrode porosity was found to be a key parameter to obtain high-quality electrochemical performance. The triplite-type LiFeSO$_4$F showed similar improvements upon PEDOT coating as the tavorite-type polymorph, but with lower capacity and less stable long-term cycling due to intrinsically sluggish kinetics and unfavorable particle morphology.

Finally, the Li$^+$-insertion/extraction process in tavorite LiFeSO$_4$F was investigated. By thorough ex situ characterization of chemically and electrochemically prepared Li$_{1-x}$FeSO$_4$F compositions (0≤x≤1), the formation of an intermediate phase, Li$_{1/2}$FeSO$_4$F, was identified for the first time. These findings helped redefine the (de)lithiation mechanism which occurs through two subsequent biphasic reactions, in contrast to a previously established single biphasic process.

Keywords: Li-ion battery, cathode, LiFeSO$_4$F, tavorite, triplite, synthesis, performance, structure, coating, PEDOT, XRD, Mössbauer spectroscopy, SEM, TEM, electrochemistry

Adam Sobkowiak, Department of Chemistry - Ångström, Box 523, Uppsala University, SE-75120 Uppsala, Sweden.

© Adam Sobkowiak 2015

ISSN 1651-6214
ISBN 978-91-554-9344-8
urn:nbn:se:uu:diva-262715 (http://urn.kb.se/resolve?urn=nbn:se:uu:diva-262715)
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I  **Formation of Tavorite-Type LiFeSO₄F Followed by In Situ X-ray Diffraction**  
R. Eriksson, A. Sobkowiak, J. Ångström, M. Sahlberg, T. Gustafsson, K. Edström, F. Björefors  
*Journal of Power Sources* 298 (2015) 363-368

II  **A Mössbauer Spectroscopy Study of Polyol Synthesized Tavorite LiFeSO₄F**  
A. Sobkowiak, T. Ericsson, K. Edström, T. Gustafsson, F. Björefors, L. Häggström  
*Hyperfine Interactions* 226 (2013) 229-236

III  **Understanding and Controlling the Surface Chemistry of LiFeSO₄F for an Enhanced Cathode Functionality**  
*Chemistry of Materials* 25 (2013) 3020-3029

IV  **Insight into the Electrochemical Performance of PEDOT-coated Tavorite LiFeSO₄F for Li-ion Batteries**  
A. Blidberg, A. Sobkowiak, C. Tengstedt, M. Valvo, T. Gustafsson, F. Björefors  
*In Manuscript*

V  **Investigating the Electrochemical Performance of PEDOT-coated Triplite-Type LiFeSO₄F Cathode Material**  
A. Sobkowiak, A. Blidberg, C. Tengstedt, K. Edström, T. Gustafsson, F. Björefors  
*In Manuscript*

VI  **Identification of an Intermediate Phase, Li₁₂FeSO₄F, Formed during Electrochemical Cycling of Tavorite LiFeSO₄F**  
*Chemistry of Materials* 26 (2014) 4620-4628

Reprints were made with permission from the respective publishers.
Contributions to the papers

**Paper I.** Planned the experiments and prepared the studied precursors. Took part in the execution of the *in situ* XRD characterizations, as well as in the discussions of the results. Main author.

**Paper II.** Planned and executed the experimental work. Executed the materials characterization by XRD. Took part in the MS measurements and data analysis. Main author.

**Paper III.** Took a major part in planning and execution of the experimental work. Executed the materials characterization by XRD and electrochemical cycling. Took part in the materials characterization and data analysis by MS, FTIR, XPS, TGA, SEM and TEM. Main author.

**Paper IV.** Took part in the materials synthesis and in the planning of parts of the materials characterization. Participated in the discussions of the results and proof read the manuscript.

**Paper V.** Took a major part in planning and execution of the experimental work. Main author.

**Paper VI.** Planned and executed the experimental work. Executed the materials characterization by XRD and electrochemical cycling. Took a major part in the MS characterization and data analysis. Main author.
Other publications to which the author has contributed that are not included in the present thesis:

**Hydrogen Absorption and Desorption Properties of a Novel ScNiAl Alloy**
*Applied Physics A 104 (2011) 235-238*
Populärvetenskaplig sammanfattning ................................................................. 9

Introduction ........................................................................................................ 13

Li-ion batteries .................................................................................................. 15
  The early history in brief ............................................................................. 15
  The principles of modern Li-ion batteries ................................................. 15
  From oxide-based to polyanionic cathode materials ................................ 19
  LiFeSO₄F as a cathode material ................................................................. 21

Scope of the thesis ............................................................................................ 24

Methodology ...................................................................................................... 26
  Materials synthesis ..................................................................................... 26
    Solvothermal reaction ............................................................................ 26
    High-energy ball milling ...................................................................... 28
    Surface coatings of electronically conducting PEDOT ....................... 28
  Materials characterization ......................................................................... 31
    X-ray diffraction .................................................................................. 31
    Mössbauer spectroscopy ..................................................................... 32
    Electrochemical characterization ......................................................... 34
    Other characterization techniques ....................................................... 37

Results and discussion .................................................................................... 39
  Synthesis and structural characterization of pristine LiFeSO₄F materials .... 39
    The tavorite-type polymorph ............................................................... 39
    The triplite-type polymorph ............................................................... 48
  Understanding the electrochemical performance limitations of LiFeSO₄F ... 50
    The tavorite-type polymorph ............................................................... 50
    The triplite-type polymorph ............................................................... 61
  Structural changes in the tavorite-type LiFeSO₄F upon cycling .............. 64

Conclusions and outlook ................................................................................ 69

Acknowledgements .......................................................................................... 72

References ....................................................................................................... 74
Populärvetenskaplig sammanfattning

Den globala efterfrågan på energi är större än någonsin tidigare och beräknas öka med ytterligare 37% fram till år 2040. I takt med de stigande oljepriserna, samt den allmänt ökande miljömedvetenheten, läggs allt större fokus på att utnyttja förnybara energikällor som exempelvis vind-, sol- och vågkraft. Dessutom görs stora satsningar på att förbättra luftkaliteten i tätbebyggda områden genom ökad användning av eldrivna fordon. För att kunna nytta de ovan nämnda systemen (några exempel visas i Figur I) fullt ut måste möjligheten att lagra energi på ett effektivt och säkert sätt tillgodoses, och allra helst även vara ekonomiskt attraktivt. Detta eftersom vår energianvändning inte alltid sammanfaller med de mest gynnsamma väderförhållandena för elproduktion. För närvarande representerar uppladdningsbara litiumjonbatterier (Li-jonbatterier) ett av de mest lovande alternativen i detta sammanhang, bl.a. baserat på deras höga energiinnehåll i förhållande till den totala vikten och volymen för batteriet. Tack vare dessa egenskaper är Li-jonbatteriet redan idag ett väletablerat energilagringsmedium för portabel elektronisk utrustning (Figur I), och har i princip fullständigt konkurrerat ut äldre tekniker så som nickel-kadmium- (Ni-Cd) och nickel-metallhydrid- (Ni-MH) batterier.

I dagens kommersiella Li-jonbatterier utgörs den positiva polen, katodmaterialiet, av kemiska föreningar så som litium-(nickel, mangan, kobolt)-oxid (LiNi1/3Mn1/3Co1/3O2) eller litiumjärnfosfat (LiFePO4). Den negativa polen utgörs nästan uteslutande av rent kol i grafitform, vilket alltså är batteriets anodmaterial. Alla dessa elektrodföreningar besitter den säregna och nödvändiga egenskapen att kunna lagra Li-joner i sina kemiska strukturer. Detta utgör grunden för batteriets funktion, där Li-jonerna under

![Småskalig energilagring](#)  ![Storskalig energilagring](#)

*Figur I. Exempel på användningsområden för Li-jonbatterier.*
batterianvändning transporteras från anod- till katodmaterialet via en vätskebaserad elektrolyt, samtidigt som en motsvarande mängd elektroner transportereras i en yttre strömkrets och driver den tillkopplade elektroniska apparaturen. Vid återuppladdning av batteriet sker processerna i motsatt riktning, och dessa bör kunna upprepas i tusentals cykler (upp- och urladdningar) för en god livslängd.

Trots lovande utsikter lider Li-jonbatteriet fortfarande av en del förhindrande krav som förhindrar en snabb utveckling och effektiv användning av de ovan nämnda storskaliga applikationerna. Ännu längre livslängd, högre energilagringskapacitet, ökad användarsäkerhet och lägre produktionspris är exempel på eftersträvande förbättringar. Ett sätt att försöka förverkliga dessa mål på är att genom forskning utveckla nya materialkomponenter med bättre egenskaper än dagens konventionella alternativa, vilket studierna i denna avhandling ger ett exempel på.

Forskningen som presenteras i denna avhandling kretsar kring att utvärdera ett relativt nyupptäckt ämne, litiumjärnsulfatfluorid (LiFeSO₄F), för att få en uppfattning om det skulle kunna passa som katodmaterial för framtidens Li-jonbatterier. Eftersom den här kemiska föreningen upptäcktes så sent som år 2010, dvs ungefär samtidigt som det här doktorandprojektet startade, har de utförda studierna direkt bidragit till den grundläggande förståelsen kring materialets egenskaper. LiFeSO₄F är principiellt intressant av flera olika anledningar:

- det baseras på järn (Fe) som elektrokemiskt aktivt element, vilket innebär lägre materialkostnader och ökad miljövänlighet jämfört med många av dagens kommersiella material.
- det kan tillverkas på laboratorium (syntetiseras) på flera olika sätt, och beroende på tillvägagångssättet kan föreningen anta två olika kemiska strukturer som efterliknar de naturligt förekommande mineralen tavorit respektive triplit. En förståelse för hur olika tillverkningsparametrar påverkar vilken av strukturerna som erhålls är till stor nytta i sökandet efter nya typer av batterimaterial.
- dess strukturtyper (av tavorit- och triplit-typ) besitter vitt skilda, men på olika sätt lovande elektrokemiska egenskaper. Tavorit-strukturen är väldigt rymlig och ihålig, och erbjuder därav bättre transportegenskaper av Li-joner jämfört med många andra material. En snabb transport av Li-joner medför batterier som kan leverera en hög effekt. Triplit-strukturen å andra sidan besitter den högsta funktionella batteri- rispänningen som någonsin uppmått för ett järnbaserat katodmaterial (3,9 V, jämfört med 3,45 V för det kommersiella materialet LiFePO₄). Detta medför batterier med högt energiinnehåll.

För att utöka förståelsen kring hur tavorit- och triplit-strukturerna bildas, och hur olika tillverkningsparametrar påverkar materialens renhetsgrad, genomfördes omfattande syntesstudier där ett flertal analysmetoder användes.
**Figur II.** Figuren visar resultat erhållna från mätningar med analysmetoden in situ-röntgendiffraktion, där bildandet av LiFeSO₄F i tavorit-struktur studerades i realtid. Med denna metod får man upp en kombination av toppar som är unik för respektive kemisk förening, likt ett fingeravtryck, och kan på så sätt användas för att identifiera föreningarna som finns i det analyserade provet. I detta experiment studerades hur de kemiska föreningarna FeSO₄·H₂O och LiF med tiden övergår i LiFeSO₄F under högt tryck och hög temperatur. Adapterad från artikel I, Copyright 2015, med tillstånd från Elsevier.

**Figur III.** I (a) visas en optimerad batteriprestanda för LiFeSO₄F i tavorit-struktur efter beläggning med ett elektriskt ledande polymerskikt. Grafen visar hur batteripotentialen (y-axeln) varierar med mängden Li-joner i materialets kemiska struktur (x-axeln). Polymerskiktets tjocklek kunde uppskattas till ca. fem nanometer med elektronmikroskopi (den övre svartvita bilden). Den nedre bilden illustrerar schematiskt hur polymerskiktet underlättar elektrontransporten mellan materialpartiklarna. I (b) visas en uppladdningscykel av LiFeSO₄F i ett snävare potentialområde för att kunna granska finare detaljer av det elektrokemiska cyklingsbeteendet. I den övre delen av bilden visas de kemiska strukturer som materialet antar under de olika segmenten av uppladdningsförloppet. Adapterad med tillstånd från artikel III och VI. Copyright 2013, 2014 American Chemical Society.
för att få en så klar helhetsbild som möjligt. Ett exempel på detta visas i *Figur II* där analysmetoden *in situ*-röntgendiffraktion användes för att studera bildandet av *tavorit*-varianten av LiFeSO₄F i realtid. Informationen som erhölls är viktig för exempelvis batteriproducenter som skulle vilja tillverka materialet i stor skala.

Vidare genomfördes studier kring LiFeSO₄F-materialens elektrokemiska egenskaper, där en bättre förståelse erhölls för vilka materialparametrar som behöver optimeras för att uppnå en god batteriprestanda. En kraftigt förbättrad prestanda kunde exempelvis observeras då materialen belades med ett tunt skikt av ett elektriskt ledande polymermaterial, vilket underlättade elektrotransporten mellan materialpartiklarna vid den positiva batteripolen (visas i *Figur IIIa*).

I en annan studie undersöcktes även hur *tavorit*-strukturen av LiFeSO₄F påverkas av att Li-jonerna.transporteras in och ut ur materialet då batteriet utsätts för ur- respektive uppladdningar. Med hjälp av noggranna analyser kunde förekomsten av en tidigare okänd strukturförändring av materialet identifieras, vilken uppstår då batteriet är laddat till 50% (visas i *Figur IIIb*). Dessa observationer gav en djupare fundamental förståelse för hur LiFeSO₄F-materialet beter sig då det används i ett batteri, och upptäckten omdefinierade de tidigare formulerade teorierna kring detta fenomen.

Sammanfattningsvis har två kemiska strukturer av ämnet LiFeSO₄F studerats som bågge besitter både för- och nackdelar vid användning som katodmaterial i Li-jonbatterier. Huruvida de kan bli av kommersiellt intresse för nästa generations batterier kan endast avgöras genom fortsatt forskning och utveckling. Studierna i denna avhandling har dock bidragit till en allmänt djupare förståelse kring framställning, struktur och funktionalitet av dessa material. Den samlade kunskapen i detta arbete sträcker sig dock längre än till bara LiFeSO₄F, då de utvecklade teknikerna och förståelsen för de studerade fenomenen även är applicerbara på, och relevanta för, andra batteriamaterial.
Introduction

The continuous growth of both global population and global economy is contributing to a steady increase of the worldwide energy demand [1–4]. In the current scenario, the total energy demand is expected to grow by another 37% by the year 2040, with an average growth rate of 1.1% per year [3]. To date, energy needs have been met by a significant utilization of fossil fuels, such as oil, coal, and natural gas, which together account for well over 80% of the current total energy consumption [4,5]. Fossil fuels are, however, non-renewable energy sources and the global reserves are thus under constant depletion. More importantly, emissions produced from the combustion of these fuels are polluting the environment, and the release of greenhouse-gases, such as carbon dioxide (CO2), may have a negative impact on the future climate [6].

In an attempt to address these issues for future generations, considerable efforts are now focused on increasing energy conversion from renewable and clean sources through technologies such as solar, wind, and wave power. Electricity generation from these sources is, however, intrinsically intermittent due to the strong weather dependence. Thus, the energy harvested during favorable conditions must be accumulated and subsequently delivered as electricity to the power grid when needed. Moreover, reduction of air pollution in the most affected areas, the cities, is pursued by a shift towards electrified transportation, which has resulted in the emergence of zero/low-emission vehicle technologies, such as electric vehicles (EVs), hybrid electric vehicles (HEVs), and fuel cell vehicles (FCVs). The key to a successful breakthrough of the abovementioned applications lies in the development of efficient, safe, and cheap energy storage devices. Currently, one of the most promising and suitable technologies which is under intense consideration is that of rechargeable batteries.

A battery is a device that stores chemical energy and converts it to electrical energy on demand [7–10]. It usually consists of several individual cells that are electrically connected in series and/or in parallel to obtain the desired voltage and electrical current output, respectively. The energy conversion occurs through reduction and oxidation (redox) reactions at the cell terminals, the electrodes. During battery discharge, which is a spontaneous process, electrons flow from the negative to the positive electrode through an outer circuit, constituting the electrical current that is used to perform the desired work. The charge flow outside each cell is accompanied by conduc-
tion of the ionic species between the electrodes inside the cell through an electrolyte medium, which is also electronically insulating to prevent internal short circuit.

There is a wide range of commercially available battery technologies, mainly differing in the cell chemistry. Some of them only allow a single discharge before they are consumed, so called primary batteries. Some chemistries, however, enable reversible redox reactions, allowing the battery to be recharged by applying an external voltage across the electrodes, so called secondary batteries. The most widely employed secondary, or rechargeable, battery technologies are lead acid (Pb-acid), nickel cadmium (Ni-Cd), nickel metalhydride (Ni-MH), and lithium ion (Li-ion). While the use of Pb-acid is mainly restricted to SLI (starting, lighting, ignition) in automobiles [9], the other technologies have been extensively used in a variety of consumer electronics and power tools. The Li-based battery chemistry is relatively young compared to the more mature Ni-Cd and Ni-MH. However, the benefits in terms of lower weight and size provided by the state-of-the-art Li-ion batteries (Figure 1), as well as high energy efficiency and low self-discharge, have made them the primary choice for most portable, and also several large-scale, applications during the last decade. Further development is, however, constantly on-going to address the currently high production costs, and, in some instances, questionable safety performance and battery lifespan. This is partly addressed through research on new and improved material components, of which the studies presented in this thesis are one example. While the future for Li-ion batteries certainly looks promising, the forthcoming years of research and development will be decisive in whether or not they will be successfully integrated into the rapidly expanding renewable energy market.

![Figure 1. Comparison of the volumetric and gravimetric energy densities between several battery technologies, including lead acid (Pb-acid), nickel cadmium (Ni-Cd), nickel metalhydride (Ni-MH), and lithium ion (Li-ion). Redrawn from ref. [9].](image-url)
Li-ion batteries

The early history in brief

Even though lithium-based battery technology is considered to be relatively young, the very first work on utilizing metallic lithium (Li) in electrochemical cells dates back over 100 years, to 1912, and was carried out by G.N. Lewis [11]. The motivation for using Li as a negative electrode in batteries is the fact that it is the most easily oxidized metal, having a reduction potential of -3.04 V vs. the standard hydrogen electrode (SHE), as well as being the lightest metal and thus providing a high energy density [12]. It was, however, not until the 1970s that the first commercial Li-based batteries started to appear, initially as primary cells. Shortly thereafter, compounds that were able to reversibly intercalate lithium ions (Li-ions, Li⁺) into the structure were proposed as cathode materials, and in 1972, Exxon introduced the first commercial secondary (rechargeable) battery constituting of Li vs. TiS₂ [13]. However, the use of metallic Li in combination with a liquid electrolyte was quickly found to suffer from safety issues as the re-deposition reaction, during charging of the battery, resulted in Li-dendrite formation, which ultimately led to short circuit, thermal runaway, and eventually to explosion of the cells. This issue was addressed by replacing the Li anode with a second intercalation compound, initially demonstrated in research projects by Murphy et al. [14] and Lazzari et al. [15] during the late 1970s and early 1980s, respectively. This concept is usually referred to as “rocking-chair”, as the Li-ions are transported back and forth between the electrodes during charge and discharge, constantly remaining in the ionic state (Li⁺). In 1991, Sony Corporation commercialized the first rocking-chair cell utilizing carbon as the anode material and LiCoO₂ as the cathode material, and so, the rechargeable Li-ion battery was born [16–18]. Over two decades later, this chemistry is still widely used to power portable electronic devices.

The principles of modern Li-ion batteries

The basic cell operation mechanisms

Just as for any other battery type, a Li-ion battery cell comprises of a positive and a negative terminal, the electrodes. By convention, the active
Figure 2. Schematic of a Li-ion cell consisting of graphite and LiFePO$_4$ (a), and a typical galvanostatic cycling curve for this battery chemistry (b).

materials utilized at these terminals are referred to as the **cathode** (positive electrode) and the **anode** (negative electrode). A liquid electrolyte is employed as transportation medium for the Li-ions between the electrodes. Figure 2a illustrates the cell operation of a common commercial battery chemistry consisting of lithium iron phosphate, LiFePO$_4$, as the cathode and graphite, C, as the anode material. Typical performance of such a cell during constant current cycling is shown in Figure 2b. After assembly, this chemistry renders a discharged cell as all the Li-ion inventory is situated in LiFePO$_4$, while the graphite is empty on Li$^+$. The corresponding cell potential in this state is highlighted in Figure 2b. During charging, Li-ions are extracted from the LiFePO$_4$ host structure as charge compensation to the oxidation of the redox active transition-metal, in this case Fe (where the Fe$^{2+}$/Fe$^{3+}$ redox couple is utilized). Electrons and Li-ions are simultaneously transported to the negative electrode through the outer circuit and the electrolyte, respectively. At the negative electrode, Li-ions are inserted into the graphite structure synchronously with incoming electrons. During the charging process, the cell potential stays fairly constant (Figure 2b) due to the biphasic nature of the Li$^+$-insertion in the individual electrodes. The charging continues until practically all the Li-ion inventory is situated in the graphite electrode, whereupon the cell potential rises sharply until it reaches a preset cut-off voltage. On discharge, the reverse processes take place. The two individual half-cell reactions, and the resulting overall cell reaction, are presented in Equations 1-3, where the forward and backward reactions represent discharging and charging, respectively, of the cell. The oxidation state of the Fe in LiFePO$_4$ is given by roman numbers.

Negative electrode: \[ \text{LiC}_6 \rightleftharpoons \text{C}_6 + \text{Li}^+ + e^- \quad (1) \]

Positive electrode: \[ \text{Fe}^{II} \text{PO}_4 + \text{Li}^+ + e^- \rightleftharpoons \text{LiFe}^{II} \text{PO}_4 \quad (2) \]

Overall cell reaction: \[ \text{LiC}_6 + \text{Fe}^{II} \text{PO}_4 \rightleftharpoons \text{C}_6 + \text{LiFe}^{II} \text{PO}_4 \quad (3) \]
Besides the abovementioned examples, many other materials possess the ability to reversibly insert and extract Li-ions. Thus, commercial Li-ion cells come in a range of possible chemistries, and many new alternative electrode materials are under constant research and development. Moreover, other cell components, such as the electrolyte, are also being developed. Below follows a brief introduction to commonly employed materials for Li-ion batteries.

**Cathode materials**
The most commonly utilized type of cathode materials in commercial applications are transition metal oxides (TMOs), such as layer-structured LiMO$_2$ (M = Co, Ni, Mn) or the *spinel* LiMn$_2$O$_4$ [19–21]. However, today these compounds are commonly prepared in mixed cation arrangements, such as LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ [22,23], for improved stability. Recently, the polyanionic *olivine* LiFePO$_4$ [24,25] is also increasingly utilized in commercial applications. In general for secondary cells, the cathode material is the source of Li-ions as they are usually present in the structure of most as-synthesized compounds. The extraction/insertion process of Li$^+$ from these compounds usually occurs at high potentials, commonly ranging between 3 and 4.5 V vs. Li/Li$^+$, and most materials possess reversible specific capacities of 100-250 mAh/g. Since cathode materials are the major focus in this thesis, a more detailed coverage of the abovementioned, and other alternative compounds, is given in the section named *From oxide-based to polyanionic cathode materials*.

**Anode materials**
Anode materials used in Li-ion batteries have predominantly been carbonaceous, and in the early years a wide range of soft (readily graphitized) and hard (non-graphitized) carbons were employed in commercial cells [17]. Presently, the crystalline carbon allotrope graphite is almost exclusively utilized due to a much flatter cycling curve profile, and low operation voltage averaging *ca.* 0.125 V vs. Li/Li$^+$. Moreover, graphite anodes possess a high electronic conductivity and high practical capacity of approximately 350 mAh/g (theoretical capacity of 372 mAh/g for the end phase LiC$_6$) [26]. Nevertheless, many alternative non-carbon based anode materials are also being studied. The compound Li$_4$Ti$_5$O$_12$ possesses promising electrochemical behavior and undergoes practically no volume changes upon (de)lithiation, referred to as a “zero-strain” material, which facilitates a long cycle life time [27]. On the downside compared to the carbons, it has a lower theoretical capacity of 175 mAh/g and a fairly high Li$^+$-insertion potential (for an anode material) of 1.55 V vs. Li/Li$^+$. Other alternative materials that have attracted considerable attention recently are Li-alloys with different *p*-block elements, Li$_x$M, (M = Si, Sn, Sb, Al, etc.) [28–33]. These materials possess theoretical capacities of up to ten times higher than that of the carbon materials, but
suffer from significant volume expansions and contractions upon cycling, resulting in poor long term stability in full cells [28,34].

**Electrolyte components**

The electrolyte serves as a transportation medium for the Li-ions between the two electrodes during battery operation. It is usually composed of a Li-salt, such as lithium hexafluorophosphate (LiPF₆) or lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), dissolved in a mixture of organic carbonate solvents, such as ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), and propylene carbonate (PC). These solvents are unstable at potentials below 0.8 V vs. Li/Li⁺ where the majority of anode materials operate. Hence, during discharge, the electrolytes decompose into a passivating film on the electrode surface, commonly termed the solid electrolyte interphase (SEI). The SEI is essential to inhibit further rapid electrolyte decomposition, and to protect against co-intercalation of salt anions or solvent molecules which can cause exfoliation of the graphite [35,36]. However, the SEI formation also has negative consequences as it contributes to significant irreversible loss of the cell capacity during the initial cycle which needs to be accounted for. In commercial cells, various electrolyte additives are usually added to facilitate the SEI formation and improve its stability during ensuing cycles [37]. Moreover, other types of safety enhancing additives are also utilized to protect against overcharge and to reduce the solvent flammability [37–39]. Another strategy to improve the overall safety is to employ non-flammable solid polymer electrolytes, but they generally suffer from low ionic conductivities at ambient temperatures [40,41].

**Cell construction and architectures**

For conventional commercial Li-ion cells, the electrodes are usually prepared by casting the active materials as thin films onto metallic foils (aluminium-foil for cathode materials and copper-foil for anode materials) together with additive components; an amorphous carbon powder for enhanced electronic conductivity, and a polymer-based binder to facilitate adhesion and mechanical strength of the film. For power optimized cells, porous electrode films are usually targeted, while for cells where high energy density is required the electrode films are typically densified. For the cell assembly, the anode and the cathode films are aligned on top of each other, separated by a porous and electronically insulating film (to prevent short circuit) soaked with the electrolyte to allow for ionic conduction. Depending on the desired cell architecture, the electrodes are either stacked or wound, usually into prismatic or cylindrical designs.
From oxide-based to polyanionic cathode materials

As mentioned above, the cathode materials utilized in commercial Li-ion batteries have been dominated by different types of transition metal oxides over the last 25 years. It started with the layer-structured LiCoO$_2$ (Figure 3a) which was proposed [19] for use in batteries in the 1980s based on its high Li$^+$-insertion potential for the Co$^{3+}$/Co$^{4+}$ redox couple (around 4 V vs. Li/Li$^+$), promising ionic and electronic conductivities, and excellent cyclability. However, when extracting beyond 0.5 Li-ions per formula unit, the material undergoes structural rearrangements such as irreversible transition-metal migration to the Li-layers, resulting in significant performance degradation [25,42,43]. Moreover, at high temperatures, the material decomposes with release of oxygen from the structure, which in turn reacts exothermally with the electrolyte components and can trigger a thermal runaway [44–46]. The capacity of LiCoO$_2$ has thus in commercial applications been limited for safety reasons to ca. 150 mAh/g at a charging cut-off voltage of 4.2 V [17,47], compared to the theoretical value of 272 mAh/g obtained if completely removing all Li$^+$. Isostructural LiMO$_2$ compounds with M = Ni, Mn, Fe, have also been under consideration as a means to cut material costs and lower the toxicity [20,21,48]. Fe-based compounds are of particular interest in general due to the large elemental abundance in the earth crust. Stoichiometric LiNiO$_2$, LiMnO$_2$, and LiFeO$_2$ are, however, difficult to synthesize due to poor thermodynamic stability, and they tend to suffer from even more severe cycling and thermally induced structural rearrangements/decompositions compared to the Co counterpart [9,21,47–52]. Moreover, the energy of the Fe$^{2+}$/Fe$^{3+}$ and the Fe$^{3+}$/Fe$^{4+}$ redox couples in oxide compounds tend to lie too close and too far, respectively, from the Fermi level of Li/Li$^+$ for their potential to be of practical interest for cathode material applications [52]. Today, the chemical and electrochemical stability of the layered LiMO$_2$ structures is usually enhanced through cation mixing arrangements which enables higher reversible capacities and improves the safety performance, such as for the commercially successful Li-Ni$^{III}_{0.80}$Co$^{III}_{0.15}$Al$^{III}_{0.05}$O$_2$ (NCA) and Li-Ni$^{II}_{1/3}$Mn$^{IV}_{1/3}$Co$^{III}_{1/3}$O$_2$ (NMC), [22,53,54]. Another type of TMO material that has been extensively developed is the spinel LiMn$_2$O$_4$ (Figure 3b) [55]. However, it suffers from structural instability associated with a Jahn-Teller distortion of Mn$^{3+}$-octahedra in the composition range Li$_x$Mn$_2$O$_4$ (1 < x < 2) and with a slow dissolution of Mn$^{2+}$ (due to the disproportionation reaction 2Mn$^{3+}$ → Mn$^{2+}$ + Mn$^{4+}$) [56–58]. Just as for the layered materials, structural stabilization can be achieved through mono- or multivalent cation doping, LiMn$_{2-x}$M$_x$O$_4$ (M = Li, Mg, Zn, etc.) [58], and the dissolution can be alleviated by ceramic coatings [59].

Besides the oxides which are utilizing the O$^{2-}$ anion, a large academic effort has been devoted to research on materials consisting of polyatomic anion moieties (“polyanions”), XO$_4^m$ (X = Si, P, S, etc.), which provide
Figure 3. Crystal structures of (a) layered LiMO\(_2\) (M = Co, Ni, Mn, etc.), (b) spinel LiMn\(_2\)O\(_4\), (c) NASICON-type Li\(_2\)Fe\(_2\)(PO\(_4\))\(_3\), and (d) olivine LiFePO\(_4\). The transition metal octahedra, MO\(_6\), are represented in blue, while the polyanion tetrahedra, XO\(_4\), are represented in brown. Li-ions are shown in turquoise.

significantly enhanced structural stability [25]. Among the most studied polyanionic frameworks in the late 20th century is the NASICON (Na-superionic-conductors) structure (Figure 3c), A\(_x\)MM’(XO\(_4\))\(_3\) [60]. Compounds adopting this structure were initially considered primarily for use as solid electrolytes, but were later also proven viable as Li\(^+/-\)/Na\(^+/-\)-insertion electrode materials when incorporating redox active transition-metals [61,62]. More interestingly, this structure-type was used to demonstrate that the nature of the polyanion has a direct impact on the energetical position, and thus the redox potential, of the transition metal couple, M\(^{n+}/M^{(n+1)+}\), a phenomenon termed the “inductive effect” [25,63]. This opened a path for tuning the potential of the Fe\(^{2+}/Fe^{3+}\) redox couple to values useful for cathode materials, as evidenced by the isostructural compounds Li\(_x\)Fe\(_2\)(PO\(_4\))\(_3\), Li\(_x\)Fe\(_2\)(SO\(_4\))\(_2\)(PO\(_4\)), and Li\(_x\)Fe\(_2\)(SO\(_4\))\(_3\), which present a gradual increase in average operation voltage of 2.8, 3.4, and 3.6 V vs. Li/Li\(^+\), respectively, when substituting the PO\(_4^{3-}\) anion for the more electronegative SO\(_4^{2-}\) [64,65]. This inductive effect from the XO\(_4^{n-}\) moiety is rooted in the alternation of the covalent/ionic degree of the M-O bond in the M-O-X bonding sequence; a more electronegative species, X, causes a stronger polarization and reduces the covalent (increase the ionic) nature of the M-O bond. This results in a lowering of the anti-bonding states (e.g. the upper e\(_g\) orbitals of an octahedral
complex) and hence an increase in the difference between the $M^{n+}/M^{(n+1)+}$ and the Li/Li$^+$ redox couples [63].

The research on polyanionic frameworks eventually led to the discovery of the olivine-type LiFePO$_4$ (Figure 3d) [24], which showed a promising reversible electrochemical performance at 3.45 V based on the Fe$^{2+}$/Fe$^{3+}$ couple vs. Li/Li$^+$, and excellent attributes for safety [66]. The intrinsic limitations of one-dimensional Li$^+$-transportation and poor electronic conductivity can today be circumvented by nano-scaling of the particles and by applying electronically conducting surface coatings [67]. After several years of academic and industrial development efforts, LiFePO$_4$ now represents the state-of-the-art among Fe-based cathode materials and the material was introduced in commercial batteries by A123 Systems over the last ten years.

In light of the success of LiFePO$_4$, considerable effort has been devoted to find new polyanionic materials with similar or, preferably, improved properties. This has led to the identification of a wide range of novel and promising compositions/structures, such as pyrophosphates, Li$_x$MP$_2$O$_7$ (M = Ti, Fe, V, Mn) [68–71], silicates, Li$_x$MSiO$_4$ (M = Fe, Mn, Co) [72–76], borates, LiM$_x$BO$_3$ (M = Fe, Mn, Co) [77,78], and more recently, an extensive family of A$_x$MXO$_4$Y-type compounds (A = Li, Na; M = Fe, V, Mn, Ni, Co, Zn; X = P, S; Y = F, OH) [79–93]. Among these materials, the work in this thesis is focused around the polymorphs within the LiFeSO$_4$F system.

**LiFeSO$_4$F as a cathode material**

**The tavorite-type polymorph**

Electrochemically active lithium iron sulfate fluoride (LiFeSO$_4$F) was first reported in 2010 by the group of J.-M. Tarascon, prepared in the tavorite-type structure (named after the eponymous mineral with the composition LiFePO$_4$OH [94]) [86,91,92]. Their work was inspired by the promising Li-ion conductivities observed for the isostructural LiMgSO$_4$F by Sebastian et al. back in 2002 [95], who, however, failed to produce the Fe-based analogue using a classic high-temperature ceramic approach. The recent success in synthesizing the tavorite-type LiFeSO$_4$F, which is thermally unstable at temperatures just above 350 °C [86,91,96], was based on the use of a solution assisted, low-temperature, process using the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (abbreviated EMI-TFSI) [86]. The reaction between the precursors FeSO$_4$·H$_2$O and LiF is generally considered to proceed through a topotactic mechanism, where the water (H$_2$O) in the former precursor is exchanged for Li and F (OH$^-$ → F$^-$, and H$^+$ → Li$^+$) while the overall structural framework is preserved [86,87]. The structural relationship between the FeSO$_4$·H$_2$O precursor and the LiFeSO$_4$F product, as well as the rate at which the topotactic exchange takes
place, have been claimed to be the fundamental key parameters that render this synthesis feasible. Besides ionic liquids, more economic reaction media have also been demonstrated to be equally viable, such as glycols [87,97] and polymers [98]. A low-temperature solid-state synthesis has also been reported, but requires longer reaction times and a large excess of the LiF precursor [99].

The electrochemical activity for the tavorite-type LiFeSO₄F is centered around 3.6 V vs. Li/Li⁺ which is an increase of 0.15 V compared to that of LiFePO₄ and is due to the more electronegative SO₄²⁻/F⁻ anions (the inductive effect). However, the extra weight penalty from these anions results in a similar energy density for the materials [25]. The tavorite-type framework (Figure 4a) belongs to the triclinic crystal system, space group P⁻¹, and consists of FeO₄F₂ octahedra that are linked to each other through F-vertices, creating zigzag-type chains along the c-axis. The chains comprise of two crystallographically unique and periodically alternating iron sites, Fe(1) (Wyckoff position 1b with coordinates (0,0,1/2)) and Fe(2) (Wyckoff position 1a with coordinates (0,0,0)) [86]. All oxygen atoms are covalently bonded to sulfur in SO₄ tetrahedra which are bridging the Fe-chains together, while the Li-ions are situated in the channel-like voids in the resulting host framework. The Li⁺-conduction channels extend in the [100], [010], and [111] directions, among which the latter is the most energetically favorable [100]. This open framework, favorable for fast ionic transportation, enables a functional electrochemical performance without the need of nano-sizing the material particles, and practical reversible capacities of ca. 85% of the theoretical value (151 mAh/g) have been reported at modest cycling rates [86,92]. However, full delithiation can be achieved using the chemical oxidation agent NO₂BF₄ [86,87,91]. The (de)lithiation process has been claimed to proceed through a single biphasic reaction, accompanied by solid solution domains. Full Li⁺-removal from LiFeSO₄F leads to an increase in symmetry from the triclinic to a monoclinic FeSO₄F structure, space group C2/c, and this phase transition involves a decrease in cell volume (∆V/V) of ca. 10% [86,91,92,101,102].

The triplite-type polymorph

Through studies on 3d transition-metal substitutions on the Fe-sites, Li(Fe₁₋ₓMₓ)SO₄F (M = Mn, Co, Ni, Zn), it was shown that Mn facilitates a stabilization of a triplite-type structure (monoclinic, space group C2/c), even at substitution levels as low as x = 0.05 [83,89,102]. Later, this led to the understanding of how to prepare the purely iron-based LiFeSO₄F triplite-type polymorph [103–106]. In this structure, the Li⁺-insertion/extraction occurs at the highest potential ever reported for the Fe²⁺/Fe³⁺ redox couple, averaging 3.9 V vs. Li/Li⁺ [89,102,103,107,108], which makes it one of the few alternative Fe-based materials (along with LiFeBO₃) that can compete with the energy density of LiFePO₄ [25].
The structural framework of the *triplite* LiFeSO₄F (Figure 4b) consists of two crystallographically unique metal sites, Me(1) and Me(2), coordinated by four oxygen atoms and two fluorine atoms, forming MeO₄F₂ octahedra. The oxygen atoms are covalently bonded to sulfur in the SO₄ tetrahedra. In contrast to the *tavorite*-type structure, the MO₄F₂ octahedra in the *triplite*-type LiFeSO₄F are edge sharing rather than corner sharing, resulting in two crystallographically unique chains running along the [101] and [010] directions. Moreover, the fluorine ligands in the *triplite* lie in cis-orientation in respect to each other, rather than in trans-orientation, and the Fe and Li atoms are statistically distributed over the metal sites rather than occupying unique positions [102,104,106]. The structural framework of the *triplite* polymorph does not possess any clear Li⁺-transportation paths, and the six-fold coordination of the Li-ions stabilizes their position in the structure. This is well reflected in the electrochemical performance of the material which present sluggish kinetics as indicated by larger polarization and lower practical capacities compared to the *tavorite*-type polymorph [104,109].

Additionally, the *triplite*-type LiFeSO₄F shows indications of being the thermodynamically most stable between the polymorphs, as the *tavorite* LiFeSO₄F converts to the *triplite* structure through prolonged synthesis [89] or extensive annealing [106] while the opposite has not been reported.

![Figure 4. The crystal structures of (a) *tavorite*-type and (b) *triplite*-type LiFeSO₄F.](image)

Iron atoms are colored in blue, lithium in turquoise, oxygen in red, sulfur in yellow, and fluorine in green. The color of the polyhedra reflects the corresponding central atom.
Scope of the thesis

Aims of research
The work presented in this thesis is focused on investigations of two separate polymorphs of LiFeSO$_4$F (crystallizing in a tavorite- and a triplite-type structure) for the use as positive electrode materials in Li-ion batteries. This has involved the development of a fundamental understanding regarding several key aspects of these materials;

1. To understand how to synthesize pure and well ordered samples in a reproducible manner, *i.e.* to conceive how different synthesis conditions influence the properties of the products, and how this can be probed using appropriate characterization techniques.
2. To understand what material parameters that influence the electrochemical performance, and how these parameters can be controlled for an optimized result.
3. To understand how the Li$^+$-insertion/extraction processes in the host framework of the material affect the overall structural properties, *i.e.* to determine the Li$^+$-(de)insertion mechanisms in LiFeSO$_4$F.

Specific studies and their historical context
This PhD project started in 2011, *i.e.* the year after LiFeSO$_4$F was first reported. Hence, the presented studies in this thesis are part of the early development of this cathode material. Below follows a brief description of the specific studies conducted in this project, and attempts to put these in context of the state-of-the-art knowledge.

- The synthesis of the tavorite-type LiFeSO$_4$F is generally recognized to proceed through a topotactic reaction from the precursors FeSO$_4$·H$_2$O and LiF [86,87]. At one point, an alternative, non-topotactic, reaction route was proposed to be equally viable, based on a direct recrystallization from Li$_2$SO$_4$ and FeF$_2$ under solvothermal synthesis conditions [89]. To gain a better insight of the nature of the LiFeSO$_4$F formation, and to understand the order in which the involved phase transformations occur, both suggested reaction routes were studied by *in situ* X-ray diffraction in conditions mimicking a conventional autoclave synthesis (*paper I*).
In-house syntheses of both LiFeSO$_4$F polymorphs were optimized using appropriate reaction routes; a solvothermal (papers II-IV and VI) and a high-energy ball-milling (paper V) approach for the tavorite and triplite-type polymorphs, respectively. To be able to monitor the sample purities and atomic order with high precision, X-ray diffraction and Mössbauer spectroscopy were used in a complementary manner (paper II).

Despite the fact that the optimized syntheses in this work rendered phase pure materials, the electrochemical performance was significantly limited. Moreover, large variations in the cycling behavior of LiFeSO$_4$F were also spotted throughout the literature, despite similar degrees of purity and comparable morphologies [86,87,96–98,110]. Thus, in an attempt to better understand the parameters that limit the electrochemical performance, thorough studies were focused on controlling the surface chemistry of the material particles for an enhanced electronic conductivity. By coupling the changes of the surface chemistry to the electrochemical response, a better understanding was developed of the performance limiting factors for both LiFeSO$_4$F polymorphs (papers III-V).

The Li$^+$-extraction/insertion mechanism in the tavorite-type LiFeSO$_4$F has generally been recognized to proceed through a single biphasic reaction, directly from LiFeSO$_4$F to a fully delithiated FeSO$_4$F phase [86,91,92]. However, during the course of the electrochemical performance optimizations of this polymorph, indications of an intermediate phase were observed at Li$_x$FeSO$_4$F compositions of $x = 0.5$. This would imply a (de)lithiation process involving two subsequent biphasic reactions. To obtain a better understanding of the structural changes to the LiFeSO$_4$F framework during the Li$^+$-extraction/insertion, appropriate techniques were used to characterize chemically and electrochemically prepared Li$_x$FeSO$_4$F samples ($0 \leq x \leq 1$), (paper VI).
Methodology

The work in this thesis is based solely on experimental studies. To obtain a comprehensive understanding of the LiFeSO₄F materials, a wide range of different experimental techniques were employed. This includes application of suitable synthesis methods to produce the active battery materials and the performance enhancing surface coatings, followed by utilization of a range of materials characterization techniques to obtain information about structural properties, chemical compositions, and sample morphologies. Finally, the materials were subjected to electrochemical testing to evaluate their functionality in Li-ion battery applications.

The main techniques utilized throughout this work are individually introduced below, including brief descriptions of the employed experimental parameters. The less used techniques are only briefly mentioned at the end of this chapter. For further details regarding the experimental parameters for specific samples, information about the chemical suppliers, and the chemical purity grades, the reader is referred to the corresponding papers.

Materials synthesis

Solvothermal reaction

Many inorganic compounds cannot be synthesized under traditional high-temperature conditions in solid state, or from melts, due to a low thermal stability of the final product. This is also true for the LiFeSO₄F polymorphs which tend to decompose at temperatures above 350 °C [86,91,96]. In such cases, solvothermal techniques can serve as viable synthesis routes as they enable facile growth of crystals at low temperatures. In fact, nature serves as a good model for such processes as many geological minerals are grown in this way. A solvothermal reaction is, in its conventional meaning, a dissolution-precipitation process of solid materials in a liquid reaction medium, carried out above the boiling point of the liquid and above atmospheric pressure (the name of the process varies depending on the nature of the reaction medium, e.g. “hydrothermal reaction” when water is used). The liquid medium plays a central role as it acts both as a solvent and pressure-transmitter when heated in a closed vessel. At certain pressure-temperature conditions, the precursors are dissolved into ions, which are then intimately mixed
through convection and diffusion in the liquid-state, and subsequently recrystallized into the product, provided that it is stable under the given conditions. When it comes to the tavorite-type polymorph of LiFeSO₄F, however, as mentioned in the LiFeSO₄F as a cathode material section, its formation is claimed to rely on a kinetically controlled topotactic mechanism (Figure 5) rather than a typical dissolution-precipitation process [86,87,106]. Thus, in this scenario, the liquid medium is assisting the reaction on slightly different premises. It is important that the chosen medium does not dissolve the FeSO₄·H₂O precursor, as its structural framework makes the foundation for the LiFeSO₄F product. Moreover, the removal of water molecules from FeSO₄·H₂O should be controllable at modest temperatures, and at a rate which allows for a simultaneous incorporation of Li and F into the framework to crystallize the LiFeSO₄F, avoiding formation of anhydrous FeSO₄ [87]. Hence, the LiF precursor should be soluble to some extent. Among the various reaction media proven viable for this synthesis [86,87,97,98], tetraethylene glycol (TEG) was the medium of choice for the production of all tavorite-type LiFeSO₄F samples in this thesis. The hydrophilic nature of the TEG allows for dehydration of FeSO₄·H₂O at temperatures as low as 220 °C. Moreover, it is a far more economic alternative compared to the initially reported, but expensive, ionic liquids.

All the tavorite-type LiFeSO₄F samples presented in this thesis were produced using a similar procedure, inspired by the work of Tripathi et al. [87] and further optimized by our group (as described in the Results and discussion section and in paper II). In short, a FeSO₄·H₂O precursor was prepared by partial dehydration of commercially available FeSO₄·7H₂O under N₂ atmosphere. Then, the FeSO₄·H₂O precursor was thoroughly mixed with excess of commercially available LiF through planetary ball-milling in acetone. Next, the dried precursor mixture was dispersed in TEG, and the dispersion was then heated in a Parr Instruments autoclave using an optimized heating program to achieve a product of high purity and atomic order.

![Figure 5. Schematic highlighting the topotactic formation of LiFeSO₄F from the structurally related FeSO₄·H₂O when reacted with LiF.](image-url)
Typically, the heating consisted of a slow initial temperature ramp (RT-200 °C at 1.5 °C/min and 200-220 °C at 0.07 °C/min), followed by a dwell step at 220 °C for 50 h, and a final ramp to 230 °C (0.17 °C/min) before allowing for a slow cooling. The product, having an ivory white color, was separated from the TEG by centrifugation, washed several times with acetone, and subsequently dried at RT under N₂ flow. Usually, the amount of produced LiFeSO₄F per batch was ca. 1 g, and the final product was stored under an Ar atmosphere until further use.

High-energy ball milling

For commercial viability, materials synthesis should be kept as simple and efficient as possible. Regarding reactions directly between solids, high-energy ball milling has become an increasingly utilized method as it can produce materials during short time scales, using one single step, under rather mild conditions [111]. The method involves milling of a powder mixture of precursors in a jar containing heavy milling bodies (usually of spherical shape). In the milling apparatus, the jar is subjected to a motion along several axes, making the milling bodies traverse randomly inside the jar and crushing the powders via heavy impact against the walls. This action deforms and grinds the powder particles which creates new reactive surfaces, as well as bulk defects in the crystallites. Moreover, the energy release from the collisions result in locally elevated temperatures which further facilitate the solid-state mechanochemical reactions.

In this thesis, high-energy ball milling was used to produce LiFeSO₄F in the triplite-type polymorph, inspired by the work of Ati et al. [106]. In short, an anhydrous FeSO₄ precursor was prepared through dehydration of commercial FeSO₄·7H₂O under N₂ atmosphere. Then, an equimolar mixture of FeSO₄ and as-received LiF was sealed in the milling jar (including 4 milling balls) under Ar. The powder mixture was ball-milled for 2 h, with a 15 min pause for cooling after the first hour, using a Spex Mixer/Mill 8000M. The resulting product was then additionally annealed at 250 °C for 7 h under vacuum to allow for release of crystal strain, which resulted in a higher crystallinity as determined by XRD. Finally, the material was stored under an Ar atmosphere until further use.

Surface coatings of electronically conducting PEDOT

Electronically conductive coatings are commonly used as a way to circumvent the poor intrinsic electronic conductivity of many battery materials, usually resulting in enhanced battery performance. Typically, this involves carbon coatings produced by high-temperature pyrolysis of organic materials [67]. Such processes are, however, unsuitable for the LiFeSO₄F polymorphs due to their thermal instability at the required temperatures. An alternative
coating strategy is to use electronically conducting polymers, such as poly-
pyrrole (PPy), polyaniline (PANI), or polythiophene (PTP) [112,113], which
can be fabricated using facile low-temperature syntheses. While the neutral
form of these polymers is insulating, the introduction of charge carriers
along the polymer backbones through p-doping (electron removal, oxidation)
or n-doping (electron addition, reduction) renders the materials conducting.

In this thesis, a specific derivative of polythiophene, namely poly-3,4-
ethylenedioxythiophene (PEDOT), was used as coating material on the Li-
FeSO₄F polymorphs. The choice of this polymer was based on its reported
high electronic conductivity and Li-ion permeability [114], as well as on its
established usage within a wide range of commercial applications, such as
conducting layers in capacitors and printed circuit boards [113]. It has also
been extensively used specifically for battery applications where it has been
shown to improve the electrochemical performance of many materials [114–
120].

The LiFeSO₄F-PEDOT composites presented in this work were fabricated
using a two-step method, adopted from Lepage et al. [116] who used it to
coop LiFePO₄. In the first step, the LiFeSO₄F materials were chemically deli-
thiated using the oxidation agent NO₂BF₄, according to Equation 4 (also
shown schematically in Figure 6, step 1).

\[
LiFeSO₄F + xNO₂BF₄ \rightarrow Li_{(1-x)}FeSO₄F + xLiBF₄ + xNO₂ ↑ \tag{4}
\]

Here, “Li_{(1-x)}FeSO₄F” is a simplified notation referring to a degree of delithi-
ation corresponding to \(x\) Li-ions per formula unit of the compound. In the
second step, the intrinsic oxidizing power of the Li_{(1-x)}FeSO₄F material (owing
to the Fe²⁺/Fe³⁺ redox couple) during re-insertion of Li⁺ was utilized to
polymerize EDOT monomers directly on the surface of the LiFeSO₄F par-
ticles, resulting in the final composite material (denoted “LiFeSO₄F-
PEDOT”). The polymerization reaction step can be informally described by
the simplified reaction scheme in Equation 5 (also shown schematically in
Figure 6, step 2).

\[
Li_{(1-x)}FeSO₄F + LiTFSI + EDOT \rightarrow LiFeSO₄F-PEDOT \tag{5}
\]

With this method, the desired amount of PEDOT in the composite material
can be controlled by choosing an appropriate delithiation degree, \(x\), in the
first step, and matching it with a stoichiometric amount of EDOT monomers
in the second step. That might, however, render either a neutral and thus
highly insulating PEDOT coating, or result in a non-complete EDOT con-
sumption. To ensure a complete polymerization reaction and a certain degree
of p-doping of the polymer, less than a stoichiometric amount of EDOT must
be provided by appropriately balancing the delithiation degree, \(x\), with the
amount of added monomers, \(y\). Once all of the EDOT is consumed, the re-
remaining amount of oxidant (the Fe$^{3+}$ concentration in the LiFeSO$_4$F) is utilized to p-dope the PEDOT polymer, with subsequent attachment of TFSI$^-$ as counter ions. This is described by the more detailed reaction scheme in Equation 6, which is based on the well established mechanism of a two-electron polymerization reaction per EDOT monomer unit [113].

$$Li_{(1-x)}FeSO_4F + xLiTFSI + yEDOT \rightarrow LiFeSO_4F + PEDOT_{(3y-x)} + PEDOT^+_{(x-2y)} + 2yH^+ + xTFSI^- \quad (6)$$

Here, PEDOT$_n$ and PEDOT$_n^+$ refer to the neutral and p-doped parts of the polymer coating, respectively, with a total amount of $n$ repeating units. To end up with a complete consumption of EDOT monomers and a certain degree of p-doping of the final coating, $x$ must be chosen so that $x > 2y$. Further, for the equation to be balanced, the condition $x \leq 3y$ must be fulfilled, where $x = 3y$ corresponds to a doping degree of one electron per monomer unit in the polymer chain. In practice, however, PEDOT is assumed to have a maximum reversible doping level of one electron per every third monomer unit, and this level should thus not be exceeded. Optimization of the $x$ and $y$ values is necessary to obtain a high degree of relithiation of LiFeSO$_4$F and a suitable degree of p-doping of the PEDOT coating. The choice of the LiTFSI salt as Li$^+$-source during the relithiation step was based on the promising properties of the TFSI$^-$ molecule as counter ion to the oxidized PEDOT, including high chemical and electrochemical stabilities and a high conductivity of the final polymer coating [114,121,122].

Figure 6. Schematic describing the two-step process of coating the LiFeSO$_4$F materials with PEDOT. Adapted with permission from paper III. Copyright 2013 American Chemical Society.
Materials characterization

X-ray diffraction

Diffraction is a phenomenon that occurs when a set of obstacles individually scatter incoming waves or wave-like matter in all directions, whereupon the scattered waves undergo interference. In certain directions in the three-dimensional space, parallel waves will be in phase with each other, resulting in constructive interference, *i.e.* a diffracted beam. In all other directions, the interference will be partially or completely destructive due to the waves being more or less out of phase, resulting in virtually no intensity. By identifying the directions and intensities of the diffracted beams, information can be obtained about the relative positions and densities of the scattering obstacles.

By analogy, in X-ray diffraction (XRD), the wave-like property of X-ray radiation is utilized to study the atomic arrangement in crystals. For each type of inorganic crystalline material, the atomic arrangement is unique and periodically repeated in three dimensions. The way in which the arrangement of atoms is repeated is usually represented with an array of points called a lattice. Moreover, the smallest repeating unit of the atomic arrangement is termed the “unit cell”, which is represented in terms of the length of its edges \((a, b, c)\) and the angle between them \((\alpha, \beta, \gamma)\), while the atomic positions in the unit cell are given by fractional coordinates \((x, y, z)\) relative to a lattice point. When irradiating a crystal, the X-rays are scattered by the electrons surrounding the atomic nuclei, and the scattering power is proportional to the electron density, *i.e.* the atomic number. The condition under which diffraction occurs is given by Bragg’s law (Equation 7 and Figure 7), which correlates the radiation wavelength, \(\lambda\), with the interatomic distances, \(d\), and the angle, \(\theta\), between the incoming X-ray beam and the plane of diffracting atoms.

\[
n\lambda = 2d \sin\theta \quad (7)
\]

In a XRD experiment, the intensities of diffracted beams are collected as a function of the \(\theta\)-angle, resulting in a diffraction pattern. Since the employed radiation is of constant wavelength, the interatomic distances are directly obtained from Equation 7. From this data, the crystal structure of the irradiated compound can be determined.

In this thesis, *ex situ* powder XRD was mainly used as a tool to probe the phase purity of synthesized LiFeSO\(_4\)F materials and track their structural changes as a result of Li\(^+\)-insertion/extraction. The *ex situ* measurements were conducted on a Bruker D8 diffractometer using Cu K\(\alpha\) radiation, equipped with a Lynxeye linear detector with fluorescence suppression.
Additionally, *in situ* XRD was used to follow the formation mechanism of the *tavorite*-type LiFeSO₄F from different sets of precursor mixtures. This was performed at the I711 beamline [123] at the MAX II synchrotron, MAX IV Laboratory in Lund, Sweden. More detailed information about the employed setup is presented in paper I.

Crystal structure refinements were performed using the Rietveld method implemented in the software Fullprof [124].

It should be noted that XRD experiments on LiFeSO₄F materials only give structural information of the host framework. The actual Li⁺-positions cannot be reliably determined due to the low electron density of lithium in comparison to the heavier elements. Thus, the site coordinates of Li⁺ were usually not refined, but kept fixed according to reported neutron diffraction data [125].

**Mössbauer spectroscopy**

The Mössbauer effect is based on recoil-free emission and resonant absorption of γ-radiation by atomic nuclei (Figure 8). By modulating the energy of the radiation from the emitter (the source) through the Doppler effect, the absorption of the studied sample is monitored as a function of energy. The collected data is visualized as absorption peaks from which information about the studied sample can be obtained, such as the chemical environments, coordination numbers, and oxidation states.

The most commonly used isotope for Mössbauer spectroscopy (MS) studies is ^{57}Fe, which accounts for ~2% of the naturally occurring iron [126]. The natural abundance of this isotope in the studied material is sufficient to conduct a measurement, with no enrichment required. The γ-radiation from the source is produced by radioactive decay of ^{57}Co by electron capture to an excited state of ^{57}Fe, which in turn decays to the ground state while emitting photons (and electrons) of various discrete energies. The transition energy of 14.4 keV utilized in MS studies is extremely sharp as a result of the long mean-life of the excited level (as explained by Heisenberg’s uncertainty principle), having an energy spread (full width at half maximum, FWHM) of
only $4.7 \cdot 10^{-9}$ eV. With such well defined transition energy, the absorbing nucleus in the studied sample would have to be of the same type as in the source for resonance to occur. However, the nuclear energy levels of the iron atoms in the studied samples vary depending on e.g. the chemical state and environment, i.e. the hyperfine interactions. Thus, by moving the source back and forth along the direction of the $\gamma$-rays with constant acceleration, while the sample is held at a fixed position, the energy of the emitted photons is altered (the Doppler effect) and an absorption spectrum of the sample can be obtained.

In a conventional Mössbauer spectrum, the transmission of $\gamma$-radiation through the studied sample ($y$-axis) is plotted as a function of the radiation energy given as the velocity of the oscillating source in mm/s ($x$-axis). The velocity scale is relative, where 0 mm/s refers to the transition energy in $\alpha$-Fe in the stationary source, while positive velocities imply higher transition energies, and vice versa. Typically, a Mössbauer spectrum contains sets of one or several absorption peaks, one set for each unique Fe-environment within the studied sample. By isolating the spectral contributions through a least-square fitting procedure, several useful parameters for each Fe-environment can be obtained, among which the most important for the investigations in this thesis have been the center shift, CS, the quadrupole splitting, QS, and the peak width, W. The CS refers to the position of the peaks on the $x$-axis which correlates to the electron density at the nucleus. The CS parameter is mainly affected by the s-electrons, as they are the primary ones having a finite probability to penetrate into the nucleus, but it is also indirectly affected by the d-electrons due to the shielding effect. The QS parameter is seen as a split into two absorption peaks and is a result of an asymmetric distribution of positive charges in the nucleus in combination with an asymmetry of the electric field created at the nucleus by the surrounding electrons. These can be electrons from the absorbing atom itself, as well as from neighboring atoms. The peak width, W, is simply a measure of the local atomic order (crystallinity) of the studied sample.

![Figure 8. Schematic summarizing the principles of Mössbauer spectroscopy.](image)
A disordered crystal with a distribution of several different unique chemical/structural environments around the Mössbauer atom will result in an equal number of overlapping peaks, appearing as one broad peak.

Within the research field of iron-based cathode materials, $^{57}$Fe MS has become a very important and useful tool for quantifying sample purity of synthesized materials, and for retrieving qualitative information about the chemical environments and atomic order around the iron atoms. Moreover, the distinct differences of the Mössbauer hyperfine parameters for Fe$^{2+}$ and Fe$^{3+}$ in high spin states makes it possible to use MS to indirectly probe the Li content in this type of materials with high precision.

In this thesis, the LiFeSO$_4$F materials were analyzed by collecting spectra in transmission mode using a $^{57}$Co(Rh) source of constant acceleration, covering a velocity span of $\pm 5$ mm/s. The absorbers (the samples) were typically prepared by mixing 10-30 mg of the LiFeSO$_4$F material with boron nitride, BN, as an inert filler agent, and spread out evenly over a 13 mm in diameter absorber disc. Due to the moisture sensitivity of the LiFeSO$_4$F materials, the absorbers were kept under a constant flow of N$_2$ during the measurements. The recorded spectra were Lorentzian-line [127] least-square fitted using the software Recoil.

**Electrochemical characterization**

Electrochemistry involves the study of charge (electron) transfer coupled to chemical reactions. For battery materials, this implies studying the electrical to chemical energy conversion processes to obtain information on their thermodynamic and kinetic properties. Conventionally, electrochemical analysis is performed using a setup of three electrodes (a working, counter, and reference electrode) immersed in a liquid electrolyte. The working electrode (WE) is where the reaction of interest occurs. The potential at which this reaction takes place is measured against a reference electrode (RE), which itself has a stable and well-known potential. The counter electrode (CE) is closing the electrical circuit and balances the reactions occurring at the WE. However, within Li-ion battery research, in cases where the behavior of only one specific material is of interest, the employment of two-electrode setups is more common. This often involves using the Li$^+$-host material as WE, while employing metallic Li as a combined RE and CE due to the stable nature of the Li/Li$^+$ redox couple (such setups are often known as “half-cells”). Most electrochemical techniques are based on either monitoring the potential of the WE while controlling the current, or vice versa, using a potentiostat. In the studies presented in this thesis, conventional galvanostatic battery cycling (also known as chronopotentiometry) was almost exclusively used as a means to characterize the LiFeSO$_4$F materials.
Galvanostatic battery cycling

Galvanostatic battery cycling of a half-cell involves recording the potential, $U \ [V]$, of the WE as a function of time, $t \ [h]$, while applying a constant current, $I \ [A]$. The cycling continues until the potential of the WE reaches a predefined cut-off potential which is chosen with respect to the standard potential of the electrode reaction and the charging mode (charge or discharge). For the favorite-type LiFeSO₄F (working potential of 3.6 V vs. Li/Li⁺) as an example, cut-off potentials of 2.5 and 4.2 V were typically employed during discharge (lithiation) and charge (delithiation), respectively. A complete charge and discharge cycle results in a traditional “cycling curve” from which various types of information can be retrieved.

The practical capacity per mass unit of the studied material, $Cap \ [Ah/g]$, is retrieved by the following equation, where $m \ [g]$ is the mass loading of active material in the cell.

$$Cap = \frac{I \cdot t}{m} \ (8)$$

The degree to which Li-ions can be extracted/inserted in the host structure is obtained by comparing the practical capacity to the theoretically maximum capacity of the material. The theoretical capacity per mass unit, $Cap_{theo} \ [Ah/g]$, is in turn calculated by the following equation, where $M_{fw}$ is the formal weight of the studied material, $n$ is the number of electrons involved in the reaction per formula unit, and $F$ is Faraday’s constant.

$$Cap_{theo} = \frac{\left( \frac{1}{M_{fw}} \right) \cdot nF}{3600} \ (9)$$

Within battery research, the rate at which the cell is cycled is conventionally presented in the format $C/t$ (usually termed C-rate), where $t$ is the time in hours it should take to complete a full charge or discharge step corresponding to the theoretical capacity, $C \ [Ah]$, of the cell ($C = Cap_{theo} \cdot m$). For example, $C/10$ means a cycling rate where one full charge (or discharge) step should take 10 hours. The current corresponding to a certain cycling rate can be calculated by modifying Equation 8, as follows.

$$I = \frac{Cap_{theo} \cdot m}{t} = \frac{C}{t} \ (10)$$

By monitoring the discharge capacity as a function of cycle number using a constant C-rate, the long-term cycle life-time of the material is retrieved. Moreover, the rate capability of a material is obtained by comparing the delivered discharge capacities recorded for a series of different C-rates.
Additionally, a lot of information can be extracted from the voltage profile in the cycling curve. The average potential of the charge and discharge steps reflect the thermodynamic potential at which the reaction should take place, i.e. the standard potential. The deviation of the measured potential from the standard potential can be divided into different contributions; i) ohmic polarization (also referred to as overpotential or \( iR \)-drop) which is proportional to the applied current and is a measure of the internal resistances of the cell, and ii) concentration polarization which arises from mass transport limitations of Li-ions, usually in the solid state, and is most distinct towards the end of the charge/discharge steps. The integrated area between the charge and the ensuing discharge cycle gives a measure of the energy efficiency of the cell, where the lost energy for each complete cycle is due to resistive heat generation.

**Cell assembly**

Most of the electrochemical studies were conducted using Swagelok™-type cells. This cell type was chosen mainly for two reasons; i) it enables testing of the active material in a system kept as simple as possible, without the need of components such as binder materials which could influence the results, and ii) it enables testing of small material batches when the amount of synthesized product is insufficient for fabrication of cast electrodes (as usually employed in pouch cells). To be able to isolate the electrochemical performance of the LiFeSO₄F materials, evaluations were performed in half-cell configurations using metallic Li as a combined reference and counter electrode effectively constituting an infinite source of Li-ions and electrons. The Swagelok cells were typically loaded with 8-12 mg of LiFeSO₄F composite powder (however, around 30 mg was used if post-cycling characterizations were to be performed), which constituted the positive electrode of the cell. The composite powders usually consisted of 15 wt% carbon black powder mixed with either non-coated or, to different extents, PEDOT-coated LiFeSO₄F. Two glass fiber sheets were used as a separator, and the commercial electrolyte LP40 was employed, consisting of 1M LiPF₆ dissolved in equal volumetric amounts of ethylene carbonate (EC) and diethylene carbonate (DEC). As current collectors, Ni and Al were used on the negative and positive terminal of the cell, respectively, and a spring mechanism was employed inside the cell body to put a stack pressure over the cell components.

A few experiments were also conducted using pouch cells, which to a far greater extent resemble the design utilized in commercial Li-ion batteries. The electrode fabrication and cell assembly is described in greater detail in paper IV. In short, an electrode “slurry” was prepared by mixing the LiFeSO₄F-PEDOT composite powder, carbon black and poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) binder in a N-methyl-2-pyrrolidone (NMP) solvent. The resulting weight ratio of the electrode mixture was LiFeSO₄F/PEDOT/PVdF-HFP/carbon black (80/7/8/5 wt%). The
slurry was cast onto an Al-foil, from which ca. 30 μm thick, circular, electrodes were cut with a mass loading of 2-4 mg/cm² and a porosity of approximately 55% (estimated by comparing the real volume of the electrode to the theoretical volume of a dense electrode [128]). To investigate the influence of the porosity on the electrochemical performance, a series of electrodes were densified to different degrees by calendering. The electrodes were then vacuum sealed into pouch cells using a polymer coated Al-foil packaging material. Al and Ni tabs were employed as current collecting tabs for the positive and negative cell terminals, respectively, and porous polyethylene sheets were used as separator, soaked in the abovementioned LP40 electrolyte.

Other characterization techniques

**Thermal gravimetric analysis**
In thermal gravimetric analysis (TGA), the weight loss of a sample is recorded as function of temperature during a linear temperature ramp. The technique was used mainly to get a quantitative estimate of the polymer amounts in the LiFeSO₄F-PEDOT composite materials. Typically, the analysis was performed by comparing the weight loss of a coated sample to that of a non-coated reference sample, from which the amount of the PEDOT coating could be calculated, as described in *papers III-V*.

**Fourier transform infrared spectroscopy**
In fourier transform infrared spectroscopy (FTIR), the sample is irradiated with infrared radiation while an absorption spectrum is recorded. From the spectrum, the chemical components in the sample can be identified by their characteristic absorption energies. In this thesis, the technique was used in the attenuated total reflection (ATR) mode to probe chemical differences between pristine, washed, and polymer coated LiFeSO₄F powders, where the identification of surface confined species was of particular interest, as described in *papers III-V*.

**X-ray photoelectron spectroscopy**
X-ray photoelectron spectroscopy (XPS) is a highly surface sensitive technique often used for analysis of material interfaces in battery cells. The measurement is performed under ultra-high vacuum, and the sample is irradiated with X-ray radiation of a suitable energy to eject core or valence electrons from the surface confined species. By analyzing the kinetic energy of the ejected electrons and by knowing the energy of the incident X-rays, the binding energy can be determined which allows for identification of the irradiated species. In this thesis, XPS was used in *paper III* and *IV* as a tool to
analyze the surface chemistry of pristine, washed, and polymer coated LiFeSO₄F samples.

**Electron microscopy**

Scanning electron microscopy (SEM) and/or transmission electron microscopy (TEM) were used to get a better insight into the morphological aspects of the LiFeSO₄F materials before and after polymer coating, as well as of cast electrodes before and after cycling and/or calendering. In SEM, the sample is scanned with a focused electron beam under vacuum, whereupon signals such as secondary electrons are emitted and can be used to produce a topographic image of the surface. In TEM, the principles are similar, but here, however, the transmitted electrons through the sample are analyzed to produce the image. More detailed information on the experimental setups is presented in *papers III-IV.*
Results and discussion

In this chapter, a concise summary of the main findings from the appended papers and some additional unpublished work is presented, divided into three main subsections;

The first section addresses the synthesis and structural characterization of the LiFeSO₄F materials, individually presented for the tavorite- and triplite-type polymorphs. First, an investigation is presented regarding the formation mechanism of the tavorite-type LiFeSO₄F where the involved phase transformations were followed using in situ X-ray diffraction. Moreover, results from ex situ structural characterizations are presented for both polymorphs, synthesized “in-house”. This includes discussions of how the phase purity and the structural properties of the produced samples relate to, and to some extent were controlled by, the applied synthesis conditions.

In the second section, studies on the electrochemical functionality of the LiFeSO₄F polymorphs are presented. This includes discussions on how a fundamental understanding was developed regarding the factors that limit the electrochemical performance of these materials. In particular, the role of the surface chemistry of the material particles was in focus.

In the final section, a study on the structural changes as a function of the lithium content (i.e. state of charge) is presented for the tavorite-type LiFeSO₄F, shedding new light on the intercalation mechanism for this polymorph.

Synthesis and structural characterization of pristine LiFeSO₄F materials

The tavorite-type polymorph

Following the formation mechanism using in situ X-ray diffraction

As mentioned in the LiFeSO₄F as a cathode material and Methodology sections, the synthesis of the metastable tavorite-type LiFeSO₄F is considered to proceed through a topotactic mechanism when starting from the precursors FeSO₄·H₂O and LiF [86,87], as summarized by the following reaction scheme.

\[
\text{FeSO}_4 \cdot H_2O + \text{LiF} \rightarrow \text{LiFeSO}_4F + H_2O \quad (11)
\]
The feasibility of this reaction is claimed to be rooted in the strong structural resemblance between FeSO₄·H₂O and the LiFeSO₄F product, where the structural framework of the former is preserved only with a good control over the topotactic exchange rate of H₂O for Li and F [87]. During the early development following the discovery of the tavorite LiFeSO₄F, this reaction was recognized as the only possible synthesis route.

In 2012, however, an alternative route was reported to be equally feasible, based on a dissolution-precipitation mechanism [89]. In this reaction, LiFeSO₄F was suggested to crystallize directly from the precursors Li₂SO₄ and FeF₂ in tetraethylene glycol (TEG) as reaction medium, according to the following equation.

\[
\text{Li}_2\text{SO}_4 + \text{FeF}_2 \rightarrow \text{LiFeSO}_4\text{F} + \text{LiF} \quad (12)
\]

It was claimed that there can be no role of water involved in this alternative reaction path, in contrast to the profound role it plays in the topotactic counterpart [87,89]. The dissolution-precipitation mechanism was, however, later questioned as \textit{ex situ} XRD measurements enabled the identification of FeSO₄·H₂O and LiF to be formed as intermediate phases during attempts to reproduce this reaction [106]. It was thus suggested that Equation 12 should instead be described by the following reaction scheme (Equation 13), where the water was proposed to be introduced to the reaction mixture through the highly hygroscopic precursors and/or TEG medium.

\[
\text{Li}_2\text{SO}_4 + \text{FeF}_2 + \text{H}_2\text{O} \rightarrow \text{FeSO}_4 \cdot \text{H}_2\text{O} + 2\text{LiF} \rightarrow \text{LiFeSO}_4\text{F} + \text{LiF} + \text{H}_2\text{O} \quad (13)
\]

In light of these opposing discussions in the literature, the formation of the tavorite-type LiFeSO₄F was probed in real-time using \textit{in situ} XRD to obtain a more detailed picture of the phase transitions involved, as presented in paper I. This was carried out by reacting the proposed precursor-mixtures, FeSO₄·H₂O + LiF, and Li₂SO₄ + FeF₂, respectively, in a setup aimed to mimic the conditions of a solvothermal autoclave synthesis.

The result from the conventional synthesis route, using FeSO₄·H₂O + LiF, is presented in Figure 9 which shows the complete reaction progress by diffraction patterns spaced in 20 minute intervals. The reaction mixture was initially heated to a dwelling temperature of 230 °C whereupon no reaction could be observed during the first 200 min. Due to the time constraints at the beamline, the temperature was later increased to 260 °C at 220 minutes and
280 °C at 295 minutes in an attempt to speed up the reaction process. From the 220 minute mark and onwards, a clear decrease in intensity was observed for the diffraction peaks appertaining to the precursors, while a set of new peaks was identified which grew incrementally until the end of the experiment. These new peaks were found to correspond well to the expected diffraction pattern of the tavorite-type LiFeSO₄F which accounted for 92 wt% of the final sample composition. No other crystalline phases could be detected at any point of the reaction, as determined by sequential refinements.
The direct formation of LiFeSO₄F from FeSO₄·H₂O and LiF is in accordance with the previously proposed topotactic mechanism, and is thus in line with the reaction scheme presented in Equation 11.

The result from the alternative reaction route, between Li₂SO₄ + FeF₂, is presented in Figure 10, showing diffractions patterns spaced in 15 min intervals. It should be noted that the as-received powders of Li₂SO₄ and FeF₂ were found to contain hydrated impurity phases, the major one being Li₂SO₄·H₂O, while Fe₂F₅·2H₂O was present in trace amounts (see Table 1 in paper I for full details on the refined phase fractions). These impurity phases seemed, however, to disappear by dehydration during the initial heating of the system, starting already below 145 °C during the ramping up to the dwelling temperature at 230 °C. This is particularly noticeable by the significant decrease in the diffracting intensity of Li₂SO₄·H₂O and evident increase of intensity from the anhydrous Li₂SO₄ phase. More interestingly, together with the dehydration of the precursors, a decrease of the total amount of starting precursors (Li₂SO₄, Li₂SO₄·H₂O, FeF₂, and Fe₂F₅·2H₂O) was observed with a synchronized appearance of FeSO₄·H₂O and LiF. This transformation, presumably proceeding through a dissolution-precipitation mechanism, ran to completion rather quickly, whereupon no further reactions could be spotted during the following 180 minutes. Thereafter, however, a sudden nucleation of the tavorite-type LiFeSO₄F phase was identified, which continued to grow at the expense of the FeSO₄·H₂O and LiF precursors until the end of the experiment. The observations strongly indicate that the total reaction, when starting from Li₂SO₄ and FeF₂, proceeded as described by Equation 13, where the TEG reaction medium was found to be the main source of water, as discussed in more detail in paper I.

The findings from the in situ XRD experiments highlight the importance of the FeSO₄·H₂O precursor in the formation of the LiFeSO₄F as it was identified in both reaction routes. Moreover, since the LiFeSO₄F could not be crystallized directly from the dissolution of Li₂SO₄ and FeF₂, the results are in line with the reports claiming that the formation of tavorite-type LiFeSO₄F can only be achieved through a topotactic reaction.

**Structural characterization using ex situ techniques**

All samples in the tavorite-type structure presented from here on in this thesis were produced in a similar manner; by a solvothermal autoclave synthesis between FeSO₄·H₂O and LiF, using TEG as the reaction medium (a detailed description is given in the Methodology section).

Ex situ X-ray diffraction (XRD) was the main characterization technique used to probe the phase purity of the synthesized products. A representative diffraction pattern, collected in connection to the studies in paper VI, is presented in Figure 11. A structural refinement using the Rietveld method confirmed that the desired tavorite-type polymorph was obtained as the main phase, with weak reflections from the LiF precursor which was used in slight
excess to ensure a complete reaction. No other crystalline phases could be identified, indicating a highly pure sample. The LiFeSO$_4$F structure was refined within the triclinic crystal system, space group $P\overline{1}$, resulting in unit cell parameters of $a = 5.1754(1)$ Å, $b = 5.4896(2)$ Å, $c = 7.2216(2)$ Å, $\alpha = 106.514(3)^\circ$, $\beta = 107.191(3)^\circ$, $\gamma = 97.843(3)^\circ$, giving a cell volume of $V = 182.395(9)$ Å$^3$, in good agreement with literature reports [86,87] (full refinement outputs for this batch are presented in the Supporting Information of paper VI). Usually, the coordinates were refined for all atoms except for Li, as its relatively weak X-ray scattering power makes it difficult to acquire a reliable position. Thus, the Li-coordinates presented in the refinement outputs in the appended papers were kept constant according to the structural models reported in literature, which, however, have varied somewhat over the years. In early reports, as deduced from XRD experiments, a model with two partially occupied Li-sites was usually presented [86] and was hence adopted in the structural refinement presented in paper III. Later, results from neutron diffraction studies suggested only one, fully occupied, Li-site, situated at an average position of the two previously reported ones [125]. This structural model was used as the basis for the remaining structural refinements and scientific discussions in papers I, II, IV, and VI, and can be expressed in terms of Wyckoff positions as $(\text{Fe}(2))_{1a}(\text{Fe}(1))_{1b}\{\text{S}_2\text{[O}_2\text{]}\}_4\text{F}_2\text{Li}_2$.

Figure 11. XRD pattern and Rietveld refinement of pristine LiFeSO$_4$F. The red circles represent the experimental data, the black line is the calculated fit, the blue line shows the difference curve between the experimental and calculated data. The green bars show the Bragg positions for LiFeSO$_4$F and LiF. Adapted with permission from paper VI. Copyright 2014 American Chemical Society.
Although powder XRD is an excellent tool for probing phase purity of crystalline materials, it provides an average view of the overall structure. Within this average picture, there might be significant variations in the local structure. An excellent technique for examining the local structure around Fe is Mössbauer spectroscopy (MS) which can provide a measure of the sample purity and atomic order. In particular, MS was used to empirically find an optimal synthesis heating program, of which the final result is described in the Methodology section. Among the different steps, the heating procedure during the final 10 hours of the synthesis was found to be of particular importance to obtain pure and well ordered materials in a reproducible manner. This is evident in a comparison of three different LiFeSO₄F samples produced from the same batch of precursors for which the final heating was chosen slightly differently. Even though the diffraction patterns of the three samples did not show any significant differences (Figure 12b, d, and f), the corresponding Mössbauer spectra (Figure 12a, c, and e, respectively) revealed marked variations in the Fe-environments. Only a temperature ramp up to 230 °C during the final 10 h resulted in consistently well resolved Fe²⁺-signals (Figure 12c), corresponding to the two crystallographic Fe-sites, Fe(1) and Fe(2) [99,102]. If the temperature during this step was instead kept at 220 °C or ramped up to 240 °C, the signal resolution was often far less distinct, as presented in Figure 12a and 12e, respectively. Such peak broadening, compared to the spectrum in Figure 12b, is indicative of additional Fe-environments, which can either be explained by local atomic disorder around the Fe in the tavorite-type LiFeSO₄F phase, or by the presence of impurity phases (possibly amorphous and thus undetectable by XRD). Hence, the results highlight the importance of using MS as a complementary technique to XRD in ensuring high phase purity and/or atomic order of synthesized LiFeSO₄F samples.
Figure 12. Mössbauer spectra (a, c, and e) and corresponding diffraction patterns (b, d, and f) of tavorite-type LiFeSO₄F prepared solvothermally in TEG by using slightly different temperature programs. The results in the upper (a and b) row correspond to a sample that was kept at a dwelling plateau of 220 °C throughout the synthesis. The middle (c and d) and lower (e and f) row correspond to samples that were subjected to an additional temperature ramp to 230 °C and 240 °C, respectively, during the final 10 h of the heating program. The total synthesis time was identical for all samples.
Detailed structural characterization using Mössbauer spectroscopy

Using the optimized heating program finishing with the ramp to 230 °C, many samples could be reproducibly synthesized resulting in very similar Mössbauer spectra, well represented by the ones shown in Figure 12c and 13a. Peak fitting of the spectrum in Figure 13a shows two sharp doublets with hyperfine parameters (presented in Table 1 in *paper II*) corresponding well to Fe$^{2+}$ in a high spin configuration, as expected for LiFeSO$_4$F [99,102]. No traces of Fe$^{3+}$ impurities were detected. While the overall characteristics of the spectrum are in good agreement with previously reported data, a few details were noticed which have not been observed or discussed previously in the literature, as described briefly below and in greater detail in *paper II*.

Interestingly, all acquired spectra from the samples produced by the optimized synthesis consistently showed higher intensities for the inner doublet, accounting for ~52.5% of the total spectral intensity. The outer doublet consequently accounted for ~47.5%. Since the occupation of the two crystallographic Fe-sites is expected to be equal [100], this intensity divergence was attributed to the difference in isotropic displacement factors, $B$, which have been reported to be 0.66(5) and 0.77(4) Å$^2$ for Fe(2) and F(1), respectively [125]. This attribution was based on the fact that the atomic vibration magnitude affects the recoil-less fraction, i.e. the f-factor, of the absorbing atoms, which describes the probability of a resonant Mössbauer interaction to occur according to the following equation.

$$f = e^{-\frac{B}{2\lambda^2}} \quad (14)$$

Here, $\lambda$ represents the wavelength of the utilized radiation. The expected f-factor ratio between the two Fe-sites could thus be calculated by the following modification of Equation 14.

$$\frac{f_2}{f_1} = e^{-\frac{B_2 - B_1}{2\lambda^2}} \quad (15)$$

Given the reported values of $B$ and the employed radiation wavelength of $\lambda = 0.8616$ Å (14.4 keV), the calculation results in $f_2/f_1 = 1.077$. From this ratio, the atoms at the Fe(1) and Fe(2) sites could thus be predicted to contribute by 48.1% and 51.9%, respectively, to the spectral intensity, in very good agreement with the experimental values presented above. Thus, this analysis presented another approach of assigning the Mössbauer doublets to the crystallographic Fe-sites in LiFeSO$_4$F; the inner doublet to the Fe(2)-site, and the outer doublet to the Fe(1)-site, which is consistent with previously reported assignments deduced by other methods [99].
Another observed feature of the recorded spectra was a significant asymmetry in the line width, $W$, between the right and the left peak of the Fe(2) doublet, such that $W/W_+ > 1$ (left peak wider than right peak), while the Fe(1) doublet was far more symmetric. By ruling out causes such as preferred orientation and impurities, as discussed in greater detail in paper II, the peak asymmetry was proposed to result from the inherent structural properties of the LiFeSO$_4$F tavorite-phase. As shown in Figure 13b, which illustrates the structure based on reported neutron diffraction data [125], the Li-ions sit closer to the Fe(2)-site than to the Fe(1)-site, causing the former to be more prone to variations of the chemical environment. This is experimentally indicated by the systematically higher line widths observed throughout the literature for the corresponding inner doublet [99,102,105]. The asymmetry observed in this study was thus proposed to result from a possible scenario where the Li$^+$ is affecting the Fe(2)-atom in a way (described in more detail in paper II) that results in a negative correlation between the values of the center shift, CS, and the quadrupole splitting, QS. Such correlation is required to obtain the specific type of asymmetry described above. The reason for why this feature was significantly more pronounced in this work compared to previously reported studies can possibly be explained by the far more ordered samples obtained by the previously mentioned optimized synthesis, as indicated by the exceptionally narrow peak widths seen for both doublets compared to that presented in the literature [99,102,105].
The *triplite*-type polymorph

**Structural characterization using *ex situ* techniques**

While the majority of the work presented in this thesis was focused on the *tavorite* LiFeSO₄F, some effort has been made to study the high-voltage *triplite* polymorph. As mentioned earlier, the *triplite*-type LiFeSO₄F is thermodynamically more stable, and structurally more disordered, compared to the *tavorite*-type polymorph [89,106]. Hence, the *triplite*-type polymorph can be produced using more robust approaches which promote disorder.

The *triplite* LiFeSO₄F samples presented in this thesis were produced by solid-state high-energy ball-milling (a detailed description is given in the *Methodology* section). A 2 h ball-milling session was sufficient to induce crystallization of the LiFeSO₄F, but the XRD pattern, presented in Figure 1 in *paper V*, revealed a considerably disordered and possibly partly amorphous material as indicated by a significant peak broadening and low signal-to-noise ratio (low intensity). Additional annealing at 270 °C under primary vacuum resulted in considerably sharper reflections, as seen in the diffraction pattern in Figure 14. The *triplite*-type structure was refined within a monoclinic crystal system, space group *C*₂/c, resulting in unit cell parameters of \(a = 13.0355(9) \text{ Å}, b = 6.3891(4) \text{ Å}, c = 9.8471(8) \text{ Å}, \beta = 119.751(2)^\circ\), giving a cell volume of \(V = 712.023(86) \text{ Å}^3\), in good agreement with reported data [104]. No major reflections from crystalline impurities were observed, indicating overall high sample purity.

The Mössbauer spectrum of the *triplite*-type LiFeSO₄F, shown in Figure 15, displays a broad and non-resolved signal which required the use of three doublets to get a good spectral peak fit. All fitted peaks possess hyperfine parameters (presented in the Supporting Information of *paper V*) characteristic of Fe²⁺ in high-spin state, and no traces of Fe³⁺ impurities were detected. The necessity for using three Fe²⁺-doublets is in line with the statistic distribution between Li and Fe among the two metal-sites in the *triplite*-structure, Me(1) and Me(2), as such disorder is expected to result in a wide distribution of chemical environments.
Figure 14. Diffraction pattern and Rietveld refinement of triplite-type LiFeSO₄F. The red circles represent the experimental data, the black line is the calculated fit, and the green bars show the Bragg positions of the specified compounds. The blue line shows the difference between the experimental and calculated data.

Figure 15. Mössbauer spectrum of pristine triplite-type LiFeSO₄F.
Understanding the electrochemical performance limitations of LiFeSO₄F

The tavorite-type polymorph

Even though the optimized solvothermal synthesis of the tavorite-type LiFeSO₄F consistently rendered samples of high purity and atomic order, the electrochemical functionality obtained was significantly limited. This was usually manifested by large polarization in the galvanostatic cycling curves, subsequently resulting in low practical capacities. Similar results were obtained for a wide range of cathode formulations, examined both as binder free powders in Swagelok-type cells, and as cast electrodes in pouch cells. Interestingly, significant performance inconsistencies can also be noted in literature reports for materials produced by different groups and/or synthesis routes, despite similar grades of purity, crystallinity, and morphology of the samples [86,87,96–98,110].

PEDOT coating

Preliminary results from calendering of cast electrodes indicated that the physical, and hence electronic, contact between the electrode components have a big impact on the electrochemistry. Thus, in an attempt to improve the cycling performance, a strategy of coating the LiFeSO₄F material with an electronically conducting layer was targeted. Typically, cathode materials are coated with carbon layers, produced by pyrolysis of organic materials at high temperatures [67]. However, such method is not feasible for LiFeSO₄F due to its low decomposition temperature, around 350 °C [86,91,96]. Thus, the conductive polymer poly-3,4-ethylenedioxythiophene (abbreviated PEDOT) was chosen as the coating material, as it can be synthesized using low-temperature methods. In short, the coating method involved two main steps; i) a chemical delithiation step of the LiFeSO₄F to obtain a certain concentration of Fe³⁺ in the material, and ii) a polymerization step where a PEDOT layer was formed on the cathode particles using the Fe²⁺/Fe³⁺ redox couple in LiFeSO₄F as the oxidizing agent (the coating procedure is described in more detail in the Methodology section and in paper III). To investigate the effects from the conductive polymer on the electrochemical performance of the active material, samples from three different stages of the coating process (pristine, partially delithiated, and polymer coated) were characterized using a number of different techniques to track the chemical and electrochemical changes of the material, as presented below.

Since the coating method involves utilization of the Fe²⁺/Fe³⁺ redox couple within the LiFeSO₄F structure, the process could be monitored by following the oxidation state of the Fe using MS, as shown in Figure 16. The spectrum of the pristine LiFeSO₄F (Figure 16a) shows the characteristic set
Figure 16. Mössbauer spectra of pristine (a), partially delithiated (b), and polymer coated (c) LiFeSO₄F, highlighting the Fe²⁺/Fe³⁺ ratio at different stages of the PE-DOT coating process. Reprinted with permission from paper III. Copyright 2013 American Chemical Society.

of two sharp and well resolved doublets, with no sign of Fe³⁺ impurities. The spectrum of the chemically delithiated material (Figure 16b) indicates a successful oxidation to the composition Li₀.₇₄FeSO₄F, close to the targeted composition Li₀.₇₀FeSO₄F in this specific case. Finally, the spectrum of the polymer coated sample (Figure 16c) indicates a successful reduction process and relithiation of the LiFeSO₄F host structure, as suggested by the decrease in the Fe³⁺ concentration. Thus, the MS results provide indirect evidence of an overall successful polymer coating process, as the two-step procedure progressed as expected. The coating procedure was additionally monitored
using XRD by following the expected phase transitions of the LiFeSO$_4$F material due to the (de)lithiation steps, as presented in paper III. To obtain direct evidence of the PEDOT coating, different spectroscopic methods were utilized. Here, results obtained from a fourier transform infrared spectroscopy (FTIR) analysis are shown as an example (Figure 17). Interestingly, the pristine LiFeSO$_4$F sample was found to contain traces of the TEG reaction medium used during the synthesis despite thorough washing steps, as identified by the characteristic absorption bands at 3400 and 2875 cm$^{-1}$ [129,130] seen in Figure 17a. The amount of TEG residues varied between different batches and was in some cases below the detection limit. Nevertheless, the presence of the TEG was found to play a profound role on the electrochemical performance, as further discussed below. After the delithiation step of the coating procedure these residues were, however, absent in the spectrum (Figure 17b), probably washed away due to the thorough stirring in acetonitrile for 12 h. The remaining absorption bands could be attributed to the active material [131], the major one centered around 1100 cm$^{-1}$ originating from the sulfate anion [132]. Finally, from the spectrum of the polymer coated sample (Figure 17c), the presence of PEDOT in a p-doped state could be confirmed from the characteristic absorption bands at 1513, 1345, and 849 cm$^{-1}$ [133], not seen in the other spectra. Further chemical characterization of the PEDOT coating was conducted by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy (RS), as presented in paper III and IV.

![Figure 17. ATR-FTIR spectra of (a) pristine, (b) partially delithiated, and (c) PE-DOT coated LiFeSO$_4$F. The features positioned between 1800 and 2300 cm$^{-1}$ stem from absorption of the ATR crystal. Reprinted with permission from paper III. Copyright 2013 American Chemical Society.](image-url)
Figure 18. SEM (a-c), low magnification TEM (d-f), and high magnification TEM (g-i) images of pristine (left column), partially delithiated (middle column), and PEDOT coated (right column) LiFeSO₄F, respectively. Reprinted with permission from paper III. Copyright 2013 American Chemical Society.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to obtain information about the morphological aspects of the different samples, presented in Figure 18a-c and Figure 18d-i, respectively. Both the pristine and partially delithiated sample, presented in the left and middle column, respectively, showed very similar features of sharp edged, polyhedral-shaped, crystallites in the micrometer range. It should be noted that the TEG residues identified by FTIR could not be spotted visually in the images of the pristine sample, suggesting that they were present in very small amounts, or that they were unevenly distributed throughout the powder. The SEM analysis of the polymer coated sample (Figure 18c) revealed significant differences in the appearance of the powder. The particle surface had an apparent roughness, indicating a successful PEDOT coverage, and a significant agglomeration of the particles was observed. The charging of the sample during the image collection was also significantly reduced, providing a qualitative indication of improved electronic conductivity in the coated sample. The SEM interpretations were further strengthened by low magnification TEM imaging (Figure 18f), which provided clear evidence of polymer lumps on the surface of the particles, in some instances bridging the particles together. Moreover, a continuous and
conformal polymer layer could also be observed by high magnification TEM (Figure 18i). It seems reasonable to assume that the observed morphology of the LiFeSO₄F-PEDOT composite material could contribute to an improved percolating network, resulting in enhanced electronic conductivity within the final electrode.

Finally, after chemical and morphological analyses, the samples were subjected to electrochemical characterization under identical testing conditions; galvanostatic cycling in Swagelok-type cells at a rate of C/10, between cut-off potentials of 2.5 and 4.2 V, as presented in Figure 19. The performance of the pristine LiFeSO₄F shown in Figure 19a is highly representative for all the solvothermally produced samples within the work of this thesis. The material displayed a notably high polarization, resulting in a low practical capacity. After a few cycles, the reversible capacity stabilized around 10 mAh/g (Figure 19d). The partially delithiated sample, however, showed much improved electrochemical performance in comparison to the pristine material (Figure 19b), as seen by the considerably reduced polarization and increased capacity of 80 mAh/g for the initial cycles. Nevertheless, the material still displayed significant capacity fading, as seen in Figure 19d. The best performance was achieved with the PEDOT coated sample which displayed the lowest polarization (Figure 19c) and a very stable capacity of 110 mAh/g over the initial cycles (Figure 19d). Except for the first cycle where a significant overpotential was observed at the end of charge, possibly due to oxidation of left-over monomer residues, the material displayed a behavior close to that expected for an ideal biphasic insertion reaction with a very flat plateau region and sharp charge and discharge end-points. This is further emphasized in Figure 20, showing three consecutive cycles at the rate C/20 (after initial conditioning cycling). At this rate, a capacity of 122 mAh/g was obtained, with promising capacity retention for several different rates, as shown in the inset in Figure 20 (even more stable long-term cycling is presented in Figure 7 in paper IV). The near ideal performance of the PEDOT coated material is in contrast to many of the published results on the tavorite-type LiFeSO₄F [86,87,96,97] where the galvanostatic cycling curves are far more sloped in nature with significantly muted end-points, indicative of resistance limitations.
Figure 19. Galvanostatic cycling curves for pristine (a), partially delithiated (b), and PEDOT coated (c) LiFeSO$_4$F, with corresponding capacity retention over the first 20 cycles (d). Adapted with permission from paper III. Copyright 2013 American Chemical Society.

Figure 20. Galvanostatic cycling of PEDOT coated LiFeSO$_4$F at the rate of C/20, showing three consecutive cycles. The inset shows the capacity retention at three different rates, C/20, C/10, and C/2. Reprinted with permission from paper III. Copyright 2013 American Chemical Society.
By coupling the electrochemical results to the chemical and morphological analyses, the following mechanisms were proposed to be responsible for the differences in cycling performance.

**The pristine material:** The poor performance of the pristine material was attributed to the TEG residues, as identified by FTIR, presumably located on the particle surfaces. Considering its insulating nature, the adsorbed TEG was believed to inhibit efficient electron transport between the active material particles and the percolating carbon black powder, as schematically illustrated in Figure 21a. However, ionic blocking by the TEG layer could also be a possible mechanism.

**The delithiated material:** The significantly improved cycling performance observed for the delithiated material was attributed to the absence of the TEG residues. The clean particle surface allowed for a significant improvement in the electron transport between the electrode components, as illustrated in Figure 21b. However, the fairly low capacity was believed to result from a significant part of the active material being isolated from the current collector due to poor particle connectivity. Moreover, the constantly fading capacity indicates that an increasing portion of the active material kept detaching from the electrode during cycling, which was attributed to the volume changes associated with the Li\(^+\)-insertion/extraction in the active material.

**The PEDOT coated material:** The considerably improved performance of the PEDOT-coated material was explained in terms of improved electronic wiring between the electrode components. The high capacity was resulting from a larger degree of active material being in excellent electronic contact to the rest of the electrode components. The continuous polymer layer enabled electrons to efficiently enter the active material particles from all angles, as illustrated in Figure 21c. The stable long-term capacity retention indicates that the PEDOT maintained excellent mechanical and electrochemical stability during cycling, keeping good contact between the electrode components despite the periodical volume changes.
Figure 21. Schematic illustration of the proposed mechanisms responsible for the difference in electrochemical performance between the pristine (a), partially delithiated (b), and PEDOT coated (c) LiFeSO₄F. Reprinted with permission from paper III. Copyright 2013 American Chemical Society.
Optimization of the LiFeSO₄F-PEDOT composite

The study presented in paper IV provided a deeper understanding regarding the functionality of the LiFeSO₄F-PEDOT composite material. This involved an investigation of how the amount of PEDOT applied onto the LiFeSO₄F material influenced the electrochemical performance. The results from samples coated to degrees of 6.3, 12.5, and 24.3 wt% (as determined by TGA) and a thoroughly washed, non-coated, reference sample, are presented in Figure 22. In such comparison, it is necessary to take the redox activity of the PEDOT coating itself into account. Based on a typical reversible p-doping level of +1/3 per monomer unit [113], the polymer was assumed to contribute by a capacity of 38 mAh/g in the applied voltage window (2.7-4.1 V) when including the weight of the TFSI⁻ counter ion. Since the specific capacity of the coating is much lower than that of the LiFeSO₄F, a larger amount of coating reduces the theoretical capacity for the total composite, as illustrated by the full columns in Figure 22a. However, as a result of the enhanced electronic wiring established by the PEDOT, a trend of higher practical capacities as a function of polymer quantity was observed up to the point of approximately 12.5 wt%, as shown by the dashed lines in Figure 22a and the corresponding cycling curves in Figure 22b. The amount of 12.5 wt% seems sufficient to establish a connection between the majority of the electrode components, while the application of even more PEDOT, using 24.3 wt%, appeared to add extra weight penalty to the electrode as seen by the lowered practical capacity in Figure 22. Interestingly, while the use of 6.3 wt% of PEDOT resulted in a low practical capacity, the amount was still sufficient to vastly reduce the polarization of the cell to similar levels as for the samples of higher polymer amounts (Figure 22b). Once again, this highlights the important role of the surface chemistry to the electrochemical performance of LiFeSO₄F.

Figure 22. Comparison between the theoretical and practical discharge capacities obtained at a rate of C/10 for LiFeSO₄F-PEDOT composite materials of different polymer amounts (a), and the corresponding galvanostatic cycling curves showing the 10th cycle for each sample (b). Adapted from paper IV.
Optimization of cast electrodes

The electrochemical results presented up to this point were obtained by using binder-free electrodes loaded as powders into Swagelok-type cells. However, for commercial viability, a good electrochemical performance of cast electrodes is necessary. To test the LiFeSO$_4$F-PEDOT composite in such conditions, electrodes of the composition LiFeSO$_4$F/PEDOT/PVdF-HFP/carbon black (80/7/8/5 wt%) were cast onto Al-foil and densified to different degrees by calendering at different mechanical pressures, as described in *paper IV*. The electrochemical performance in pouch cells of electrodes with four different degrees of porosity is presented in Figure 23a, and the corresponding electrode morphology, as obtained by SEM, is presented in Figure 23b. The electrode porosity was estimated by comparing the geometrical volume of the electrode to the theoretical volume of a dense electrode [128]. The electrode of 55% porosity (non-calendered) showed very limited electrochemical performance, with the highest polarization and lowest capacity, despite the use of a PEDOT coating. These limitations were significantly decreased for the electrode of 42% porosity. The best cycling performance was, however, obtained for the electrodes with 35 and 22% porosity, which showed very similar low levels of polarization and high capacities during the initial cycles when cycled at low rates. Nevertheless, the densest electrode of 22% porosity possessed the most stable capacity retention during prolonged cycling, as shown in Figure 10 in *paper IV*. The observed trend in electrochemical performance as function of electrode density was attributed to the quality of the electronic connection between the electrode components. This is supported by the observed electrode morphologies as presented in Figure 23b. The least dense electrode showed large voids between the active material particles, seemingly unfavorable for a good

![Figure 23. Comparison of the electrochemical performance at a galvanostatic cycling rate of C/20 between cast LiFeSO$_4$F-PEDOT (6.3 wt% polymer) electrodes densified to different degrees (a), and the corresponding morphologies as obtained by SEM (b). The electrochemical performance obtained for the same batch in a Swagelok-type cell is included in (a) as a reference. Adapted from paper IV.](image-url)
electronic wiring. Moreover, the use of insulating PVdF-HFP binder might also have contributed to limitations of the electron transport. The densest electrode, on the other hand, possessed a smooth and compact surface with significant particle agglomeration. Such morphology seems favorable for the establishment of an intimate percolating network. The encouraging performance obtained for the densified cast electrodes is equivalent to that obtained in a Swagelok-type cell, as shown in Figure 23a. This gives a strong indication that the LiFeSO4F-PEDOT composite could work in a scaled-up commercial battery.

Performance improvement through heat treatments

In a separate unpublished project, improvement of the electrochemical performance of LiFeSO4F was found possible via heat treatment in a tube furnace, performed under flowing N2. However, the furnace was suspected to have a leak, allowing ingress of air, as the resulting powders (initially ivory white) tended to become red in color, characteristic of Fe3+ in oxides. Moreover, the color intensity was found to increase with higher temperatures and longer treatment times. Interestingly, with the trend of increasing color intensity followed an improvement in the electrochemical performance, as shown in Figure 24a. The most deeply red sample, heated at 270 °C for 42 h, displayed the least polarized cycling curve with a well defined plateau (Figure 24b), similar to the PEDOT coated samples. The initial discharge capacity at a cycling rate of C/10 was ca. 105 mAh/g, as shown in the inset of Figure 24b. XRD and MS analyses of this sample (not presented here), did not detect any significant impurities, indicating that the red color (the decomposition product) was restricted to the surface of the particles. In contrast to the PEDOT coated material, however, the thermally treated samples displayed a

Figure 24. Comparison of the electrochemical performance during the first cycle between pristine and thermally treated LiFeSO4F samples (a), and the long term performance of the sample treated at 270 °C for 42 h (b). The applied cycling rate was C/10.
significant increase in overpotential during the initial cycles, most clearly seen towards the end of charge and discharge as indicated by arrows in Figure 24b. The discharge capacity faded accordingly. This is probably due to loss of electronic contact between the electrode components as a result of the intrinsic volume changes of the LiFeSO$_4$F during the (de)lithiation processes.

While the underlying mechanism behind the thermally initiated performance improvement is not fully understood, the air leakage seems to have played a profound role in the result. To verify this, a reference samples was prepared by sealing pristine LiFeSO$_4$F into an evacuated silica glass ampoule to significantly reduce the risk of O$_2$ contamination. The sample was then subjected to the same heat treatment program as the best performing sample discussed above. The sealed sample did not display any color changes, and no improvement of the electrochemical performance was obtained. A plausible explanation to the observed phenomena is that the oxygen is involved in a cleaning process of the particle surfaces through combustion of the previously discussed TEG residues that were found to be present on the pristine LiFeSO$_4$F materials. Additionally, the TEG could possibly act as a reducing agent to generate compounds of high electronic conductivity on the surface of LiFeSO$_4$F, in a similar manner to what have been observed for LiFePO$_4$, where highly conducting Fe$_x$P residues significantly enhanced the electrochemical performance [134]. The findings strongly encourage further studies, preferably including surface sensitive techniques such as XPS, to better understand the nature of the thermally induced changes of the surface chemistry.

The triplete-type polymorph

PEDOT coating

The triplete-type LiFeSO$_4$F has generally shown worse electrochemical performance in literature reports compared to that of the Favorite-type polymorph [92,104,109]. This is usually manifested by a higher polarization, leading to lower practical capacities. Due to the promising results presented by the PEDOT coated Favorite-type LiFeSO$_4$F, it was intriguing to investigate the effects of a polymer coating on the triplete-type polymorph, as presented in paper V. Similar approaches were used as for the Favorite polymorph regarding the coating procedure and material characterizations.

Among the more striking differences between the polymorphs was the observed morphology of the pristine materials, as determined by SEM (Figure 25 and 26). The as-prepared triplete-type LiFeSO$_4$F (Figure 25a) displayed a very wide range of particle sizes, from a few nanometers up to over 5 μm. Moreover, the large particles possessed significant cracks and irregularities, and seemed to a certain extent to be agglomerates of smaller
Figure 25. SEM images of pristine (a and c) and PEDOT coated (b and d) triplite-type LiFeSO₄F. *Adapted from paper V.*

Figure 26. SEM images of pristine triplite-type LiFeSO₄F, highlighting the surface irregularities, cracks, and agglomerate nature observed for some of the large particles. *Adapted from paper V.*

particles, as indicated by Figure 26. After PEDOT treatment, the majority of the active material particles appeared even more agglomerated, indicating successful polymer coverage (Figure 25b). Additionally, the smooth parts of the surface of the pristine particles (Figure 25c) displayed a significant roughness after the PEDOT coating step (Figure 25d).
A comparison of the electrochemical performance between the pristine and the PEDOT coated material during galvanostatic cycling at the rate of C/20 is presented in Figure 27. Both samples display an average cycling potential of 3.9 V vs. Li/Li⁺, as expected for the triplite-type LiFeSO₄F [102–104]. Just as the tavorite LiFeSO₄F, the triplite polymorph displayed improved cycling performance upon PEDOT coating, as seen by the lowered polarization and increased practical capacity (Figure 27a). Moreover, the capacity retention was also better for the LiFeSO₄F-PEDOT composite (Figure 27b). Nevertheless, comparing the two polymorphs, the electrochemical functionality (polarization, practical capacity, and cyclability) obtained for the coated triplite LiFeSO₄F was never of as high quality as for the tavorite counterpart. The observed slow kinetics, manifested by the high polarization and low capacity, are in good agreement with many previously reported studies [89,104,109] and can be attributed to the limited Li⁺-conduction within the disordered triplite-type structure in combination with the long transportation distances through the evidently large particles. The distinct capacity fading during prolonged cycling could possibly be explained by fragmentation of the particle agglomerates present in the as-prepared material, as discussed above. This would create new, uncoated, surfaces with poor adhesion, resulting in loss of electric contact. Hence, the morphology of the pristine triplite LiFeSO₄F should ideally be optimized through particle size reduction and deagglomeration before proceeding with the PEDOT coating.

Figure 27. (a) Comparison of the galvanostatic cycling performance between pristine and PEDOT coated triplite-type LiFeSO₄F, and (b) the corresponding capacity retention over the initial 50 cycles. Adapted from paper V.
Structural changes in the *tavorite*-type LiFeSO₄F upon cycling

Since the discovery of the *tavorite*-type LiFeSO₄F, its Li⁺-insertion/extraction mechanism has been considered to be of a biphasic nature between the end-members LiFeSO₄F and FeSO₄F [86,87,92]. However, two other materials adopting the *tavorite*-type structure, namely LiVPO₄F and LiFeSO₄OH, have been shown to undergo two subsequent biphasic processes during extraction of one Li-ion per formula unit, as a result of the stabilization of distinct intermediate phases [84,85,88]. In connection to these findings, the possibility of stabilizing an intermediate phase within LiFeSO₄F was pinpointed in literature through density functional theory (DFT) calculations, but the authors stressed that its stabilization is negligible, and that there is no clear experimental evidence of its existence [88]. Nevertheless, during the course of the polymer coating project on the *tavorite*-type LiFeSO₄F presented above (particularly in paper III), some peculiarities were observed in the results of the chemically delithiated samples, including unidentifiable peaks in the diffraction patterns, and preferentially oxidized Fe-sites in the Mössbauer spectra. These findings indicated the stabilization of a new phase, differing from the well-known end-members, LiFeSO₄F and FeSO₄F. Hence, to obtain a deeper understanding of the structural transitions in the LiFeSO₄F-system caused by Li⁺-extraction/insertion, a thorough study was carried out (paper VI) based on *ex situ* characterizations of both chemically and electrochemically prepared LiₓFeSO₄F-samples (0 ≤ x ≤ 1).

**Chemically prepared LiₓFeSO₄F**

To screen the structural changes in the LiFeSO₄F-system for a wide range of Li⁺-compositions, several chemically delithiated samples were prepared from a batch of pristine material and analyzed by XRD, as shown in Figure 28. The compositions were indirectly determined by analyzing the Fe²⁺/Fe³⁺-ratio with MS, presented in the Supporting Information of paper VI. The diffraction patterns of the fully lithiated and fully delithiated samples (Figure 28a and 28f, respectively) show the expected characteristic peaks from these extensively studied phases [86,87,125], with no signs of crystalline impurities. However, the diffraction patterns of the partially delithiated samples (Figure 28b-e) show the presence of new reflections that cannot be attributed to the end-member phases, indicating the occurrence of a third phase. Some of the visually most resolved peaks of this new phase are marked by red triangles in Figure 28. The relative intensity of these peaks seems to be highest in the samples of composition Li₀.₄₄FeSO₄F and Li₀.₅₆FeSO₄F, suggesting phase stabilization close to the composition Li₀.₅FeSO₄F.
Electrochemically prepared Li$_x$FeSO$_4$F

To investigate the implications of the new phase on the electrochemical redox behavior, and to stabilize it under more well-defined conditions closer to equilibrium, PEDOT coated LiFeSO$_4$F was galvanostatically cycled in a Swagelok-type cell at a rate of C/100. In a full scale graph (Figure 29a), the cycling curve displays the characteristic well-defined plateau with sharp charge and discharge end points, indicative of a seemingly single biphasic reaction, similar to that of LiFePO$_4$ [52]. However, if the $y$-axis is rescaled for a better view of the nuances of the electrochemical trace (Figure 29b), two distinct plateaus centered around 3.585 and 3.600 V are clearly present during the charging process, separated by an inflection point. These features suggest the presence of two subsequent biphasic processes, and the position of the inflection point on the $x$-axis further indicates that the new phase has a distinct composition of Li$_{0.5}$FeSO$_4$F.

To get further structural information about this unidentified phase, a cell was cycled at C/100 and stopped as close as possible to the inflection point (Figure 30, inset), whereupon it was disassembled to retrieve the cathode powder for XRD and MS measurements. The collected Mössbauer spectrum, shown in Figure 30b, confirms an overall sample composition of Li$_{0.5}$FeSO$_4$F within the uncertainty of the measurement (the hyperfine parameters are presented in the Supporting Information of paper VI). The corresponding diffraction pattern, presented in Figure 30a, was found to be dominated by reflections (~90% contribution) that could not be ascribed to the
Figure 29. Representative voltage-composition plots of galvanostatically cycled LiFeSO₄F at the rate C/100, presented with a conventionally scaled $y$-axis (a), and a rescaled $y$-axis for a more detailed view of the nuances of the electrochemical trace (b). Adapted with permission from paper VI. Copyright 2014 American Chemical Society.

Figure 30. Rietveld refined ex situ XRD pattern (a) of a sample cycled galvanostatically at C/100 and stopped as close as possible to the global composition Li₀.⁵FeSO₄F (inset). The red circles represent the experimental data, the black line is the calculated fit, the blue line shows the difference curve between the experimental and calculated data. The green bars show the Bragg positions for the involved phases. In (b), the corresponding Mössbauer spectrum is shown. Adapted with permission from paper VI. Copyright 2014 American Chemical Society.

LiFeSO₄F or FeSO₄F end-member phases, which confirmed the formation of a completely new phase. The reflections could be refined within a triclinic system, space group $P\overline{1}$, resulting in unit cell parameters of $a = 5.1427(3)$ Å, $b = 5.2972(4)$ Å, $c = 7.3234(3)$ Å, $\alpha = 108.830(6)^\circ$, $\beta = 109.394(6)^\circ$, $\gamma = 94.274(5)^\circ$, giving a cell volume of $V = 174.382(18)$ Å³ (full refinement output is presented in the Supporting Information of paper VI). Based on the collected data, the discovered intermediate phase was denoted Li₁₁₂FeSO₄F.

The proposed structural model for the intermediate phase presents realistic features and strong structural similarities to the end-member phases, discussed in greater detail in paper VI. Moreover, the evolution of the unit cell...
parameters seem sensible as the removal of Li-ions from the fully lithiated end-member results in a gradual decrease of the unit cell volume, refined to 91.2, 87.2, and 81.8 Å³ for LiFeSO₄F, Li₁/2FeSO₄F, and FeSO₄F, respectively (presented as volume per formula unit, V/Z).

While the proposed structure for Li₁/₂FeSO₄F presented an overall conceivable alternative, the MS analysis unveiled information indicting the possible need of a superstructure for an even more accurate representation. This is based on the preferential oxidation observed between the Fe-sites, such that Fe(1) and Fe(2) contributed with ~2/3 and ~1/3, respectively, to the overall oxidation degree of 50% (Figure 30b). To describe such a charge ordering between these crystallographic sites with restricted oxidation states of the Fe to integer numbers, a unit cell of at least three times larger volume is needed compared to that used in this work. These contradicting features between the structural model and the Mössbauer spectra strongly encourage further studies to fully understand the structural nature of the intermediate phase.

Judging by the cycling curve in Figure 29b, the intermediate phase seems to stabilize only on charge as no inflection point is observed during discharge. Thus, to investigate the structural behavior during the lithiation process, a cell was stopped at a 50% discharged state, whereupon the cathode powder was analyzed in a similar manner as the samples discussed above. Interestingly, Li₁/₂FeSO₄F was found to be formed also during the discharge process. This somewhat contradicting behavior is not yet fully understood, and is encouraged to be investigated in further studies.

Finally, to verify the existence of two biphasic processes in the LiFeSO₄F-system, another two cells were cycled at C/100 and stopped as close as possible to the middle of the two observed plateaus (Figure 31b), whereupon they were disassembled for ex situ characterizations. The compositions were determined by MS to Li₀.2₂FeSO₄F and Li₀.₇₄FeSO₄F, as presented in paper VI. The powders were also examined by XRD and compared to the results of the Li₀.₅FeSO₄F-sample (Figure 31a). The diffraction pattern of the Li₀.₇₄FeSO₄F sample consisted of reflections only from LiFeSO₄F and Li₁/₂FeSO₄F, with no contribution from FeSO₄F. The diffraction pattern of the Li₀.₂₂FeSO₄F sample, on the other hand, revealed contributions from Li₁/₂FeSO₄F and FeSO₄F, with no traces of LiFeSO₄F. Hence, these findings confirmed that the Li⁺-extraction proceeds via two subsequent biphasic processes, which can be summarized by the following equations.

\[
LiFeSO₄F \rightleftharpoons Li_{1/2}FeSO₄F + 0.5Li^+ + 0.5e^- \quad (16)
\]

\[
Li_{1/2}FeSO₄F \rightleftharpoons FeSO₄F + 0.5Li^+ + 0.5e^- \quad (17)
\]
This is in contrast to the previously suggested Li\(^+\)-insertion mechanism, which was claimed to proceed through a single biphasic reaction, directly between LiFeSO\(_4\)F and FeSO\(_4\)F [86,101].

Figure 31. Ex situ XRD patterns (a) of electrochemically prepared Li\(x\)FeSO\(_4\)F samples of compositions \(x = 0.22, 0.49, \) and \(0.74,\) and the corresponding electrochemical traces (b). The positions at which the cells were stopped and disassembled are highlighted with a red dot. Adapted with permission from paper VI. Copyright 2014 American Chemical Society.
Conclusions and outlook

This work has provided new insights into the chemistry and electrochemistry of the tavorite and triplite-type polymorphs of LiFeSO₄F in the context of their use as positive electrode materials for Li-ion batteries. This has involved enriching the fundamental understanding regarding the synthetic preparations of these materials, e.g. conceiving how different synthesis conditions influence the properties of the final products. Another major contribution was the identification of material parameters which limit the electrochemical performance. In particular, both polymorphs showed significant susceptibility towards changes of the surface chemistry of the particles, which was shown to be possible to control for an optimized electrochemical operation. Moreover, the implications of Li⁺-insertion and extraction on the structural properties of LiFeSO₄F have also been studied.

A summary of the main conclusions ascertained through the presented work is given below, followed by thoughts regarding future research outlook for LiFeSO₄F.

Synthesis and structural characterization of pristine materials

By using in situ XRD, the solvothermal formation of the tavorite-type LiFeSO₄F was established to proceed via a direct phase transition from the structurally related FeSO₄·H₂O precursor when reacted together with LiF, in line with the recognized topotactic reaction mechanism. Additionally, an alternative reaction route was studied which had been claimed to proceed via a direct recrystallization from Li₂SO₄ and FeF₂. This reaction was, however, shown to be misinterpreted, as the starting precursors were found to quickly recrystallize into FeSO₄·H₂O and LiF as intermediate phases, which subsequently formed LiFeSO₄F in a similar manner as described above. The obtained knowledge is important as it pinpoints the existence of electrochemically interesting metastable phases that might only be synthesizable via exotic reaction mechanisms. This should encourage scientists to widen their perspectives regarding the choice of synthetic routes in the search for new battery materials. Moreover, this study also highlights the importance of using in situ techniques to “grasp the whole picture” when investigating dynamic processes.

By understanding the formation process of the tavorite-type LiFeSO₄F, the combined use of ex situ XRD and MS characterizations enabled optimization of an in-house solvothermal synthesis to reproducibly render pure and
highly ordered samples. The Mössbauer spectrum of the pristine LiFeSO\text{\textsubscript{4}}F was analyzed in great detail which allowed for correlations between the spectral features and the structural properties of the compound to be established. This resulted in a proposed assignment of the outer and inner Mössbauer doublets to the crystallographic Fe(1) and Fe(2) sites, respectively. The findings provide important information for experimentalists working on the tavorite-type LiFeSO\text{\textsubscript{4}}F, as it enriches the current knowledge of how to prepare the material using cost efficient methods, and how to better probe the quality of pristine samples.

Additionally, the triplite-type polymorph was synthesized using a facile, solid-state, high energy ball-milling technique.

**Understanding the electrochemical performance limitations**

Despite obtaining phase pure LiFeSO\text{\textsubscript{4}}F samples, the pristine materials showed significantly restricted battery performance. Further studies identified that the surface chemistry of the particles plays a profound role on the electrochemical characteristics.

Pristine tavorite-type samples were found to carry residues of the TEG reaction medium on the particle surface which severely restricted the redox reactions. This behavior was attributed to suppressed electron transport at the particle surface due to the insulating nature of the solvent. However, an ionic blocking mechanism by the TEG layer is also possible. The electrochemical functionality of the material was significantly improved by removing the TEG residues and applying a surface confined PEDOT coating. This was performed using a targeted low-temperature method that utilizes the Fe\textsuperscript{2+}/Fe\textsuperscript{3+} redox couple within LiFeSO\text{\textsubscript{4}}F as an intrinsic oxidizing agent. The coated materials displayed very well-defined and flat galvanostatic potential curves with sharp charge and discharge end points, in contrast to many of the previously published reports where indications of resistance limitations can be observed. The amount of PEDOT applied to the LiFeSO\text{\textsubscript{4}}F was shown to influence the total practical capacity obtained for the composite material, and indications were acquired of an optimal PEDOT amount of 10-15 wt\%. For cast composite electrodes, the porosity was shown to play an important role for the electrochemical performance, where low porosities generally resulted in lower polarizations, higher capacities, and longer cycling life times due to improved electronic contact between the particles.

The triplite-type LiFeSO\text{\textsubscript{4}}F showed similar improvements upon PEDOT coating, but due to the inherently more sluggish kinetics of solid-state Li\textsuperscript{+}-transport, in combination with a large particle size, the cell polarization was higher and capacities lower than for the tavorite-polymorph. Moreover, the coated triplite polymorph displayed less stable capacity retention which was speculated to partly result from an unfavorable agglomeration of the as-synthesized material, which led to fragmentation during cycling.
The findings show the importance of identifying and controlling the key parameters responsible for facile electrochemistry in the development of high performing cathode materials. As highlighted by the observed performance differences between the polymer coated tavorite and the triplite polymorphs, the required optimization measures can vary significantly between different compounds and must be tailored for each specific case. The acquired knowledge and the developed optimization techniques presented in this thesis extend beyond the scope of LiFeSO₄F, as they are equally valid and applicable for many other battery materials.

**Structural changes upon cycling**

The structural evolution of the tavorite-type LiFeSO₄F was investigated upon chemical and electrochemical extraction (and reinsertion) of Li-ions from the host framework. It was found that the (de)lithiation process occurs through two subsequent biphasic reactions due to the stabilization of a distinct intermediate phase, Li₁/₂FeSO₄F, never before experimentally identified. The intermediate was identified to form both on charge and discharge, even though the cycling curve suggested stabilization only during the former process. The findings helped to shed new light on the previously proposed Li⁺-insertion mechanism for the tavorite-type LiFeSO₄F.

**Research outlook**

During the course of the presented work many additional questions have arisen, and ideas for future projects have been generated. A few of those are communicated below.

**Particle size reduction:** The electrochemical performance of both LiFeSO₄F polymorphs has been shown to improve through application of electronically conducting surface layers. To circumvent the remaining kinetic limitations, the particle size would be the logical parameter to optimize next. Given the topotactic formation of the tavorite LiFeSO₄F, a particle size reduction should be targeted towards the FeSO₄·H₂O precursor. While similar approaches could be used regarding the triplite LiFeSO₄F, its greater phase stability also enables post-synthesis ball-milling techniques as viable alternatives.

**Further investigations of the intermediate phase, Li₁/₂FeSO₄F:** An overall reasonable structural model was proposed for the intermediate phase appearing during cycling of the tavorite LiFeSO₄F. However, uncertainties remain regarding the accuracy of this model due to indications of a possible superstructure. Moreover, the appearance of Li₁/₂FeSO₄F both on charge and discharge is contradictory to the electrochemical trace. In situ XRD (and neutron diffraction) should be pursued to obtain more detailed information about these phenomena.
Acknowledgements

First and foremost, I would like to thank my main supervisor Fredrik Björefors. Thank you for your support and encouragement throughout this project, your great balance between guidance and independence, and your tolerance towards my sometimes slightly twisted humor. I have really enjoyed working with you during these years.

I would also like to thank my co-supervisors for invaluable feedback and support. Kristina Edström, thank you for giving me the opportunity to work in this fantastic group, and for leading me into this specific project on LiFeSO₄F which I have very much enjoyed. Also to my industrial supervisor Anna M. Andersson, thank you for your guidance.

Torbjörn Gustafsson, thank you for your involvement and enthusiasm in this project, and for the numerous scientific (and non-scientific) discussions which I have learned a great deal from. You have been like a fourth supervisor to me. Thank you Tore Ericsson and Lennart Häggström for introducing me to the exciting world of Mössbauer spectroscopy, and for all the exciting studies we have conducted. It has been great working with you. Thank you Matthew Roberts for all your invaluable help, the friendship, and the amazing annual golf weeks. Thank you Rickard “the true irony man” Eriksson for the fun trips to Liiund and for the help with the in situ XRD projects, and Andreas “the iron boy” Blidberg for the collaborations and for sharing everything that is worth knowing about the center of the universe, Ludvika. I would also like to acknowledge the rest of my co-authors in the appended papers for their essential contributions; Reza Younesi, Jonas Ångström, Martin Sahlberg, Mario Valvo, Carl Tengstedt, and Cheuk-Wai Tai.

Thanks to all participants in the HVV project which this work was financed through, with special thanks to the organizers at Samarkand in Ludvika, Lars, Janna, Kathrine, and the others.

To all current and former friends and colleagues at the department, thank you for making my time here so pleasant. I have really enjoyed working together with you, as well as hanging out with you on the several non-work related occasions; the ski trips, the house parties, the Palermo Friday evenings (especially by the downstairs tables), and all the other after-work activities. Fredrik L., we have been through a long journey together, starting from the undergraduate studies, through master projects, and up until the PhD studies. Thanks for all the enjoyable moments and your positive and supporting attitude during the most stressful periods. Thank you Sara and Julia for
being the best spontaneous-birthday-party organizers (ever!), Mario for the many discussions about everything and nothing, and for the fun dart nights at Norrland’s, Stéven and Bertrand for all the football discussions including the frequent updates on Zlatan’s performance in the French league, Solveig for cheering me up with music during the thesis writing, and Reza “hej potatis” for feeding me with the most delicious cakes. Matt L., me old mucker, thanks for teaching me advanced British slang, and for approving the Oxford comma in my thesis subtitle. Thanks to the Sturegatan-crew, Daniel B., Ali-na and Gabi, for being the best neighbors. Chao, thanks for providing the best image in this thesis, and David for the great fun at Jeju (Neeehhh!).

Thank you Henrik for all the assistance in the lab, and Josh for the interesting discussions after my group seminars. Thanks Jonas Å., Mats T., and Mikael for enhancing my beer knowledge. Equally big thanks to all the remaining people in the battery group; Anti, Burak, Cesar, Charlotte, Chenjuan, Erik B., Fabian, Girma, Habtom, Jeff, Jia, Jonas H., Jonas M., Karima, Kasia, Leif, Mars, Maria, Mohammed, Nina, Ruijun, Sara Ma., Shruti, Sigtta, Taha, Tim, Viktor R., Wei, Wendy, Will, and Zhaohui. Special thanks to Bing for being the best possible office-mate.

I would also like to thank all the remaining people from the other parts of the department (the inorganic group, administration staff, technicians, etc.) for contributing to such a pleasant working environment during my time here; Anders E., Anders L., Andreas Be., Andreas L, Anna C., Anna P., Annika P., Christoffer S., Daniel S., Diana, Dou, Erik Le., Erik Li., Erika, Eva, Fang, Gunnar, Håkan, Jennie, Jesper, Jill, Johan C., Johan G., Jolla, Karin, Kersti, Kristina J., Kristina W., Linus, Matilda, Mats B., Matti, Mattis, Mir, Nils, Ocean, Paulius, Pavlin, Pedro, Perti, Peter B., Peter L., Rolf, Sarmad, Shuainan, Slavica, Song, Susen, Tatti, Tomas, Ulf, Viktor H., Yiming, and Yuan (I hope that I haven’t forgot too many names so far). Special thanks go to Yvonne Andersson who, together with Martin Sahlberg, gave me the opportunity to do my master project at the department, which later led to the PhD studies.

I also have to thank several friends from neighboring departments. Thank you Christoffer K. and Henrik O. for great fun at the ISE conference in Prague, Johanna and Erik for the golf rounds at Kåbo, Petter T. for fun chats in the lab, and Sara F. Å. for occasionally letting me steal sweets from your department.

I wouldn’t survive the PhD studies without complete breaks from the lab. For that I have to thank all the friends outside work. Special thanks go to the golf crew Martin, Alfred, Elias and Ludvig. Sofia, thanks for the enjoyable time we have spent together during the past few months.

Last but not least, I would like to thank all of my family, especially my mother and father, for the constant support and belief in me.

/Adam
References


Acta Universitatis Upsaliensis

Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology 1291

Editor: The Dean of the Faculty of Science and Technology

A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology. (Prior to January, 2005, the series was published under the title “Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology”.)

Distribution: publications.uu.se
urn:nbn:se:uu:diva-262715