Mechanochemical and Interfacial Engineering of Orthosilicates as Li-ion Battery Cathodes

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To my parents

Abstract

Lithium-ion batteries (LIBs) are in ever-growing demand for portable electronics and all electrical vehicles (EVs). This necessitates the development of new electrode materials especially cathodes with improved charge capacity & rate to meet the full application potential for large scale commercialization of EVs. The development of new cathode materials for LIBs is an active field of research. In this thesis, the relatively less explored low-temperature orthorhombic $(Pmn2_1)$ phase of lithium iron orthosilicate (Li₂FeSiO₄, LFS) is studied as a potential candidate for highenergy density cathode. In particular, LFS is synthesized, mechanochemically tuned, interfacially modified, and electrochemically characterized aiming to the design of stable and high-density performing cathodes. In this context, the first part of this research focused on mechanochemical processing of hydrothermally synthesised single phase low-temperature orthorhombic Pmn21 LFS (ortho-LFS) particles. Further, the structural and electrochemical behavior of mechanochemically treated LFS was probed via synchrotron-based X-ray diffraction (XRD), electron backscatter diffraction (EBSD), high-resolution transmission electron microscopy (HR-TEM) and galvanostatic charging/discharging, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) & differential capacity, respectively. The mechanochemical study led to the discovery that within a certain milling window, annealing-like structural changes occur opening up the pathway to higher accessible Li-ion storage capacity. More specifically controlled highenergy mechanical nanosizing was found to induce structural changes including lattice expansion, reduction of antisite defects and crystallinity improvement.

Next, to improve the electronic conductivity of ortho-LFS, high-energy milling in the presence of carbon black was employed at room temperature producing an LFS@C nanocomposite. During follow up electrochemical cycling of this material, it was discovered that such LFS@C nanocomposite exhibits electrochemically induced structural activation leading to doubling its reversible capacity from ~90 mAh g⁻¹ to ~180 mAh g⁻¹. Interestingly, this impressive increase in charge capacity was associated with simultaneous transitioning from solid solution to two-phase Li-ion storage mechanism clearly indicating in-operando structural transformation unlike previous studies, which attributed such capacity increase to mere electrolyte penetration. To probe further this behaviour, *ex-situ* post-mortem analysis of the electrode bulk & surface

chemistry was conducted using scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) techniques revealing the formation of a lithium fluoride (LiF) layer at the solid electrolyte interphase (SEI). Meanwhile, characterization performed with synchrotron-based XRD, X-ray absorption near edge structure (XANES) & extended X-ray absorption fine structure (EXAFS) as well as electron energy-loss spectroscopy (EELS) revealed progressive phase transition towards the inverse $Pmn2_1$ phase, which corresponded very well to an S-type kinetic model.

Finally, further improvement in electrochemical performance was sought via conductive polymer coating of the LFS crystals. Firstly, the LFS ($Pmn2_1$) nanocrystals were prepared by hydrothermal synthesis (200 °C) and mechanochemical annealing; then *in-situ* poly (3,4-ethylene dioxythiophene) (PEDOT) polymer coating was employed via a modified chemical delithiation/re-lithiation process. Electrochemical evaluation of such LFS@PEDOT (PLFS) nanocrystals revealed minimal polarization (ΔV) with excellent Li-storage performance despite their cycling at room temperature. PLFS nanocrystals delivered a high initial capacity of 220 mAh g⁻¹ with a record 1.33 Li extraction for the $Pmn2_1$ phase. Interestingly, galvanostatic charge/discharge, EIS and CV revealed accelerated phase transition in these core-shell nanocrystals along improved rate capability and enhanced cycling stability. Notably, PEDOT coating also acted as a passivating layer. *Ex-situ* post-mortem cathode material characterization by XANES, EXAFS, X-ray photoemission electron microscopy (X-PEEM), and scanning transmission X-ray microscopy (STXM) corroborated the excellent electrochemical performance of the newly designed PLFS nanocrystals.

Résumé

Les batteries au lithium-ion (BLI) sont de plus en plus en demande pour les appareils électroniques portables et tous les véhicules électriques (VE). Cela nécessite le développement de nouveaux matériaux d'électrodes, en particulier des cathodes avec une capacité et une vitesse de charge améliorées, afin d'atteindre le plein potentiel d'application pour la commercialisation à grande échelle des VE. Le développement de nouveaux matériaux cathodiques pour les BLI est un domaine de recherche actif. Dans cette thèse, la phase orthorhombique à basse température (Pmn2₁) relativement moins explorée de l'orthosilicate de lithium et de fer (Li₂FeSiO₄, LFS) est étudiée comme un candidat potentiel pour une cathode à haute densité énergétique. En particulier, le LFS est synthétisé, accordé mécanochimiquement, modifié par voie interfaciale et caractérisé par voie électrochimique dans le but de concevoir des cathodes stables et performantes à haute densité. Dans ce contexte, la première partie de cette recherche fut consacrée au traitement mécanochimique de particules de Pmn21 LFS (ortho-LFS) orthorhombiques monophasées synthétisées par voie hydrothermale. De plus, le comportement structural du LFS traitée mécanochimiquement fut d'abord étudiés par diffraction des rayons X (DRX), diffraction des électrons par rétrodiffusion (DERD) et par microscopie électronique à transmission à haute résolution (MET-FR). En deuxième lieu, son comportement électrochimique a été étudié à l'aide de tests cycliques chrono-galvanostatiques (charge/ décharge), puis par voltamétrie cyclique (VC), parspectrométrie d'impédance électrochimique (SIE) et enfin par capacité différentielle. L'étude mécanochimique permit de découvrir qu'à l'intérieur d'une certaine fenêtre de broyage, des changements structuraux de type recuit se produisent, ouvrant la voie à une capacité de stockage Li-ion plus élevée et accessible. On constata que la nanotechnologie mécanique à haute énergie contrôlée de façon plus spécifique induit des changements structuraux, y compris l'expansion des réseaux, la réduction des défauts antisites et l'amélioration de la cristallinité.

Ensuite, pour améliorer la conductivité électronique de l'ortho-LFS, un broyage à haute énergie en présence de noir de carbone fut utilisé à température ambiante pour produire un nanocomposite LFS@C. Les tests électrochimiques ont démontrés que ce matériau nanocomposite présente une activation structurale induite par voie électrochimique, permettant de doubler sa capacité réversible de ~90 mAh g⁻¹ à ~180 mAh g⁻¹. Il est intéressant de noter que l'augmentation

impressionnante de la capacité de charge fut associée au passage simultané d'un état monophasé en solution solide à un mécanisme de stockage Li-ion biphasé indiquant clairement une transformation structurale lors de l'opération, contrairement aux études précédentes qui attribuaient cette augmentation de capacité à une simple pénétration d'électrolyte. Pour approfondir notre compréhension de ce comportement, une analyse ex situ post-mortem de la masse de l'électrode et de la chimie de surface fut réalisée en utilisant la microscopie électronique à balayage (MEB), la microscopie électronique à transmission (MET), la spectroscopie à rayons X à dispersion d'énergie (SDE) et la spectroscopie photoélectrique à rayons X (SPX) pour révéler la formation d'une couche de fluorure de lithium (FLi) à l'interface électrolyte solide (IES). Pendant ce temps, la caractérisation effectuée à l'aide de la spectroscopie synchrotron DRX, de la spectroscopie de structure près du front d'absorption de rayons X (XANES) et l'absorption étendue des rayons X pour les structures fines (AEXFS) ainsi que spectroscopie de perte d'énergie électronique (SPEE) révélèrent une transition progressive de phase vers la phase inverse $Pmn2_1$, qui correspond très bien à un modèle cinétique du type S.

Enfin, une nouvelle amélioration des performances électrochimiques fut recherchée par l'application d'un revêtement polymère conducteur sur les cristaux LFS. Tout d'abord, les nanocristaux LFS (Pmn2₁) furent préparés par synthèse hydrothermale (200 °C) et par recuit mécanochimique; ensuite, un revêtement de polymère poly (3,4-éthylène dioxythiophène) (PEDOT) in situ fut utilisé par un procédé modifié de dé-lithiation/re-lithiation chimique. L'évaluation électrochimique de ces nanocristaux LFS@PEDOT (PLFS) révéla une polarisation minimale (ΔV) avec d'excellentes performances de stockage Li malgré leur cycle à température ambiante. Les nanocristaux PLFS fournirent une capacité initiale élevée de 220 mAh g⁻¹ avec une extraction record de 1,33 Li pour la phase Pmn21. Fait intéressant, la charge/décharge galvanostatique, la SIE et la VC révélèrent une transition de phase accélérée dans ces nanocristaux de type noyau-enveloppe ainsi qu'une capacité galvanique et une stabilité cyclique améliorées. Notamment, le revêtement PEDOT servit également de couche de passivation. La caractérisation ex situ post-mortem des matériaux cathodiques par XANES, AEXFS, la microscopie électronique à photo-émission de rayons X (MEPE-X) et la microscopie à rayons X à transmission par balayage (MXTB) confirmèrent l'excellente performance électrochimique des nanocristaux PLFS nouvellement conçus.

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Majid Rasool

April 2020

Foreword

This thesis is based on a manuscript-based format that is offered by McGill University as an alternative to the traditional thesis format. Chapter 3, 4 and 5 of this thesis has been published in peer-reviewed journals.

- <u>Rasool</u>, M.; Chiu, H. C.; Lu, X.; Voisard, F.; Gauvin, R.; Jiang, D.; Paolella, A.; Zaghib, K.; Demopoulos, G. P., Mechanochemically-tuned structural annealing: a new pathway to enhancing Li-ion intercalation activity in nanosized β_{II} Li₂FeSiO₄, *J. Mater. Chem. A* 2019, 7, 13705-13713.
- <u>Rasool</u>, M.; Chiu, H. C.; Gauvin, R.; Jiang, D.; Zhuo, J.; Ryan, D.; Zaghib, K.; Demopoulos, G. P., Unusual Li-ion intercalation activation with progressive capacity increase in orthosilicate nanocomposite cathode, *J. Phys. Chem. C* 2020, 124, 11, 5966-5977.
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Author contributions

- The <u>author of this thesis</u> has designed the experiments, carried out material synthesis, material characterizations, electrochemical measurements and *ex-situ* post-mortem characterizations presented in Chapters 3, 4 and 5 and prepared manuscripts for publications.
- <u>Professor Demopoulos</u> supervised the whole research, provided research direction and guidance, and extensively revised the manuscript drafts in their published form, as well as the other chapters of this thesis.

- <u>Dr. Chiu & Dr. Paolella</u> offered guidance on data interpretation and edited the manuscript for Chapter 3. Dr. Chiu aided in data interpretation for Chapters 4 and 5 as well.
- <u>Mr. Fred Voisard & Mr. Nicolas Brodush</u> carried out in-depth electron microscopy characterizations for Chapter 3. Mr. Nicolas helped with scanning electron microscopy characterizations for Chapter 4 and 5 as well.
- <u>Mrs. Zeng</u> assisted with hydrothermal synthesis for Chapter 5.
- <u>Mr. Zank assisted</u> with the preliminary polymer (PEDOT) tests for Chapter 5.
- <u>Professor Ryan</u> performed Mössbauer spectroscopy for Chapter 4.
- <u>Professor Jiang and Dr. Zhuo</u> have helped data collection of synchrotron based XRD, XANES, EXAFS, SXTM and PEEM at Canadian Light Source for Chapters 3, 4 and 5.
- <u>Professor Perepichka, Professor Gauvin and Dr. Zaghib</u> provided expert advice on conductive polymers (Chapter 5), microscopy and silicate cathode materials (Chapters 3, 4 and 5) respectively.

I hereby give copyright clearance for the inclusion of the above papers, of which I am corresponding author, into the Ph.D. dissertation of Mr. Majid Rasool.

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List of Abbreviations

Acetylene black
Brunauer–Emmett–Teller
Battery-powered electric vehicles
Carbon
Coulombic efficiency
Carbon-coated lithium iron silicate
Cyclic voltammetry
Diethyl carbonate
Dimethyl carbonate
Density functional theory
Electron backscatter diffraction
Ethylene carbonate
Energy-dispersive X-ray spectroscopy
Electron energy-loss spectroscopy
Electrochemical impedance spectroscopy
Electric vehicles
Extended X-ray absorption fine structure
Fourier transform infrared spectroscopy
Galvanostatic intermittent titration technique
Hybrid electric vehicles
High-resolution transmission electron microscopy
Highest occupied molecular orbital
LiCoO ₂
LiFePO ₄
Li ₂ FeSiO ₄
Lithium-ion batteries
Lithium fluoride

LMO	LiMn ₂ O ₄
LUMO	Lowest unoccupied molecular orbital
MLFS	Mechanochemically-tuned lithium iron silicate
NCA	LiNi _{0.8} Co _{0.15} Al _{0.05} O ₂
NMC	LiNi _{0.33} Mn _{0.33} Co _{0.33} O ₂
NMP	N-methyl pyrrolidinone
OCV	Open circuit voltage
Ortho-LFS	Low-temperature orthorhombic <i>Pmn2</i> ¹ LFS
PEDOT	Poly(3,4-ethylenedioxythiophene)
PITT	Potentiostatic intermittent titration technique
PLFS	Polymer (PEDOT) coated lithium iron silicate
PVDF	Polyvinylidene fluoride
SAED	Selected area electron diffraction
SEI	Solid electrolyte interphase
SEM	Scanning electron microscopy
STXM	Scanning transmission X-ray microscopy
TEM	Transmission electron microscopy
XANES	X-ray absorption near edge structure
X-PEEM	X-ray Photoemission electron microscopy
XRD	X-ray diffraction

1. Introduction

1.1. Growing Demand for LIBs

Climate change is the reality of current age, which is mainly caused by burning/combustion of fossil fuels.¹⁻² Now, there is a strong consciousness to develop low-cost and environmentfriendly energy conversion and storage systems.³ Neary quarter of total greenhouse gas emissions per capita in the major American cities are caused by ground transportation, which is heavily depended on fossil fuels.³⁻⁴ One way to reduce these emissions is the electrification of vehicles and the development of efficient and economical electrochemical energy storage systems.³ Electrochemical energy storage systems, such as batteries and supercapacitors are playing a crucial role in the area of renewable energy storage systems and electrification of transportation. Among all the technologically mature electrochemical energy storage systems, Li-ion batteries come closer to the internal combustion engines in terms of energy and power densities as shown in Figure 1.1(a), when compared with other conventional rechargeable batteries including Ni-Cd and leadacid batteries etc.⁵ LIBs possess outstanding features relatively to the other battery types, such as high operating voltage, high gravimetric and volumetric energy densities, no memory effect, low self-discharge rate and operation in a wide range of temperatures, etc.⁵⁻⁷ Research on the LIBs started in the early 1970s, and Sony commercialized the first LIB in 1991.⁸ Since then, LIBs have grown to become the dominant power storage solution for portable IT devices and now penetrated the market of transportation to replace conventional fuels and reduce CO₂ emissions.⁹ It is now generally accepted that lithium-ion batteries are particularly seen as the power source of choice for battery-powered electric vehicles (BEVs) and hybrid electric vehicles (HEVs).¹⁰ So far HEVs, has already provided proven benefits for the economy by combining an electrochemical battery along with gasoline combustion. But for complete hydrocarbon fuel-free transportation, BEVs are increasing in demand and commercialization of such vehicles is on the rise.^{7, 9} Development of BEVs has very rapidly passed from demonstration prototypes to very successful commercial products such as Tesla Model X, S & 3, Nissan LEAF, and others.^{5, 7, 11} However, the rapid commercialization of battery-powered electric vehicles (BEV) makes necessary a shift towards higher energy density LIBs. As shown in Figure 1.1(b), the global demand for LIBs is expected to

increase to around 210 GW h in 2025.¹² Several countries and car manufacturers have claimed that they would eliminate diesel cars as early as 2025,¹³ which reflects the continuously increasing demand for LIBs. Likewise, the US Department of Energy (DOE) targets an energy density of 300–400 Wh kg⁻¹ and a cost of US\$ 125 per kWh by 2022 for the large-scale commercialization of BEVs using Li-ion battery packs.¹⁴ According to reports the car market will be at a tipping point in 2022 when a battery-electric vehicle will have almost the same cost as a fuel vehicle.¹⁴ However, at present the energy density of state-of-the-art commercial LIBs is only 200–280 Wh kg⁻¹.^{6-7, 15} Thus, it is very crucial to develop next-generation LIBs with higher electrochemical performance. The development of novel anode and cathode materials provides a clear direction to meet these goals.⁸ Therefore, developing sustainable high-energy cathode materials are in need than ever before.¹¹ In this context, lithium iron silicate is a promising candidate for commercial LIBs with low cost, high-energy density and safety as discussed in section 1.2.



Figure 1.1. (a) Ragone plot for various energy storage devices and conversion devices; ¹⁶ and (b) global Li-ion batteries projection demand for the year 2025.¹²

1.2. LFS – A Sustainable Emerging Cathode

The energy density of a battery depends on specific capacity and output voltage, which is dependent on both the anode and cathode materials.⁵⁻⁶ Both anode and cathode need to be further improved. However, it is the cathode that is the bottleneck for the development of LIBs.^{5, 11} In fact, cathode materials affect energy density, rate capability and working voltage that leads to the cathode currently costing more than any other component in a typical Li-ion battery as shown in Figure 1.2.¹² Therefore, intense effort has been devoted to developing high specific capacity and high voltage cathodes. In light of the above requirements discussed in section 1.1, several materials have been studied as cathodes for Li-ion batteries. Conventional intercalation oxides are the most successful commercially cathode materials for Li-ion batteries.¹¹ However, they have several drawbacks regarding capacity, safety, and cost.¹¹ After the discovery of olivine structured LiFePO₄ (LFP) cathode material by J. Goodenough's group,¹⁷ this material has become very attractive both in terms of research and commercial development primarily due to its excellent cyclability and safety.¹⁸ However, the material suffers from low intrinsic electronic conductivity, a shortcoming that has been overcome via its carbon coating.¹⁸ Over the years nano-structuring of LFP has led to further improvement of LFP's performance in terms of rate capability. LiFePO₄ has a polyanion framework that allows long cycle life and structural stability.⁵ Typically, it can deliver a maximum specific capacity of about 170 mAh g⁻¹ at 3.4V versus Li/Li⁺ corresponding to one Li⁺ formula unit.⁶ As such LiFePO₄ cannot fulfill the demand for high energy density cathode materials. Therefore, there is a strong need for the development of new cathode materials with high energy density, safety and low-cost.

Among the different emerging cathode materials, lithium iron silicate (Li₂FeSiO₄) (LFS) has attracted a lot of attention because like LFP it belongs to the family of polyoxyanion compounds but theoretically has higher capacity.¹⁹ This is so because of its 2 Li⁺ per formula unit that could provide a specific capacity as high as 331 mAh g⁻¹, which is twice compared to that of LiFePO₄ and results in theoretical energy density of approximately 1120 W h kg⁻¹.¹⁹ At the same time, the polyoxoanion framework provides safety against thermal runaway.²⁰ Iron and silicon are two of the most abundant and low-cost elements in the earth's crust. However, there are some key factors hindering their practical application. For example, extensive research on the structural
properties of the orthosilicate materials (LFS) showed that they exhibit rich polymorphism, which includes low and high temperature orthorhombic and monoclinic crystal phases that complicate the synthesis of pure phases and their specific electrochemistry.^{19, 21} Moreover, there are reports that LFS materials suffer from low intrinsic electronic and ionic conductivity, hampering efforts to attain the desired second lithium-ion extraction.²² Additionally, LFS undergoes phase transformation during cycling, an issue that continues to attract research interest as it leads to capacity loss upon further cycling.²³⁻²⁴ Therefore, at present, there are several unresolved issues that require further studies to understand and ultimately control and optimize the electrochemical Li-ion storage performance of orthosilicates for high energy density cathodes.





Figure 1.2. Cost distribution of different components in LIBs, including cathode, anode, electrolyte, separator, and other materials.¹²

1.3. Objectives of this Research

The overall goal of this thesis is to focus on synthesis, in-depth material characterization and electrochemical evaluation of the low-temperature orthorhombic ($Pmn2_1$) phase of Li₂FeSiO₄ as high energy density Li-ion battery cathode. Following are the main objectives of this thesis:

1. Prepare low-temperature (200 °C) Li₂FeSiO₄ crystals via hydrothermal synthesis. Utilize mechanochemistry for nanoengineering and follow it by in-depth electrochemical evaluation.

2. Prepare mechanochemically tuned carbon-coated Li₂FeSiO₄ nanocomposite and evaluate its electrochemical properties. Follow it by in-depth *ex-situ* post-mortem analysis.

3. Develop *in-situ* formed conductive polymer-coated nanoparticles to enhance their Liion storage capacity and conductivity. Follow it by in-depth *ex-situ* post-mortem analysis.

1.4. Thesis Organization

This thesis has been organized into six chapters, with this Introduction constituting Chapter 1. In Chapter 2, a comprehensive literature review is presented, starting with a brief introduction to Li-ion batteries and their working principle. After that, it reviews the different types of cathode materials before attention is turned to the previous literature on Li₂FeSiO₄. In connection to the latter, it discusses the challenges facing silicates, i.e. polymorphism, phase transition and structural stability. This chapter concludes with comments on the possible direction to development of high-density silicate cathodes.

Chapter 3 discusses in-depth the effect of high-energy milling on the material properties and electrochemistry of the low-temperature orthorhombic LFS nanoparticles prepared via hydrothermal synthesis. Emphasis is given in revealing the newly observed mechanochemical annealing phenomenon. Surface changes before and after high-milling are discussed. Bulk characterization is presented, where reduction of anti-site defects and preferred crystal orientation induced by high-energy milling are discussed. Lastly, it provides electrochemical evaluation of such mechanochemically annealed LFS nanocrystals.

Chapter 4 discusses the electrochemistry and *ex-situ* post-mortem analysis of mechanochemically annealed LFS@C nanocomposite. In particular, it reports on the unexpected Li-ion intercalation activation during initial-dozen cycles that resulted in doubling the capacity of LFS. The LFS@C nanocomposite has formed passivating SEI layer that was characterized via EDS, *f-ratio* maps and XPS techniques. Synchrotron-based XRD revealed continuous *in-operando* phase transition governed by an *S-type* nucleation-growth model.

Chapter 5 describes the development of core-shell architectured LFS nanocrystals prepared by mechanochemical annealing and *in-situ* conductive polymer-coating. The excellent electrochemical response of these LFS@P nanocrystals is discussed in connection to in-depth *exsitu* post-mortem analysis involving synchrotron-based PEEM and SXTEM analysis.

Chapter 6 summarizes the global conclusions, it outlines the claims to originality and presents suggestions for future investigations.

1.5. References

1. Dessler, A. E.; Parson, E. A., *The science and politics of global climate change: A guide to the debate.* Cambridge University Press: 2019.

2. Kellogg, W. W., *Climate change and society: consequences of increasing atmospheric carbon dioxide*. Routledge: 2019.

3. Teixeira, A. C. R.; Sodré, J. R., Impacts of replacement of engine powered vehicles by electric vehicles on energy consumption and CO₂ emissions. *Transportation Research Part D: Transport and Environment* **2018**, *59*, 375-384.

4. Kennedy, C.; Steinberger, J.; Gasson, B.; Hansen, Y.; Hillman, T.; Havranek, M.; Pataki, D.; Phdungsilp, A.; Ramaswami, A.; Mendez, G. V., Greenhouse gas emissions from global cities. *Environ. Sci. Technol.* **2009**, *43* (19), 7297-7302.

5. Zubi, G.; Dufo-López, R.; Carvalho, M.; Pasaoglu, G., The lithium-ion battery: State of the art and future perspectives. *Renew. Sustain. Energy Rev* **2018**, *89*, 292-308.

6. Li, M.; Lu, J.; Chen, Z.; Amine, K., 30 years of lithium-ion batteries. *Adv. Mater.* **2018**, *30* (33), 1800561.

7. Schmuch, R.; Wagner, R.; Hörpel, G.; Placke, T.; Winter, M., Performance and cost of materials for lithium-based rechargeable automotive batteries. *Nat. Energy* **2018**, *3* (4), 267-278.

8. Nitta, N.; Wu, F.; Lee, J. T.; Yushin, G., Li-ion battery materials: present and future. *Mater*. *Today* **2015**, *18* (5), 252-264.

9. Ehsani, M.; Gao, Y.; Longo, S.; Ebrahimi, K., Modern electric, hybrid electric, and fuel cell vehicles. CRC press: 2018; pp 1 - 15.

10. Orecchini, F.; Santiangeli, A.; Dell'Era, A., EVs and HEVs using lithium-ion batteries. In *Lithium-Ion Batteries*, Elsevier: 2014; pp 205-248.

11. Andre, D.; Kim, S.-J.; Lamp, P.; Lux, S. F.; Maglia, F.; Paschos, O.; Stiaszny, B., Future generations of cathode materials: an automotive industry perspective. *J. Mater. Chem. A* **2015**, *3* (13), 6709-6732.

12. Pillot, C. In *Lithium ion battery raw material supply & demand 2016–2025*, Proceedings of the Advanced Automotive Battery Conference, Mainz, Germany, 2017.

13. McFadden, C. These 9 Countries Want to Ban Diesel Cars Very Soon. https://interestingengineering.com/these-9-countries-want-to-ban-diesel-cars-very-soon.

14. Howell, D.; Cunningham, B.; Duong, T.; Faguy, P., Overview of the DOE VTO advanced battery R&D program. *Annual Merit Review June* **2016**, *6*.

15. Reinhardt, R.; García, B. A.; Casals, L. C.; Domingo, S. G., A critical evaluation of cathode materials for lithium-ion electric vehicle batteries. In *Project Management and Engineering Research*, Springer: 2019; pp 99-110.

16. Muneer, T.; Kolhe, M.; Doyle, A., Electric vehicles: prospects and challenges. Elsevier: 2017.

17. Padhi, A. K.; Nanjundaswamy, K.; Goodenough, J., Phospho-olivines as positive-electrode materials for rechargeable lithium batteries. *J. Electrochem. Soc.* **1997**, *144* (4), 1188-1194.

18. Zaghib, K.; Guerfi, A.; Hovington, P.; Vijh, A.; Trudeau, M.; Mauger, A.; Goodenough, J.; Julien, C., Review and analysis of nanostructured olivine-based lithium recheargeable batteries: Status and trends. *J. Power Sources* **2013**, *232*, 357-369.

19. Ni, J. F.; Jiang, Y.; Bi, X. X.; Li, L.; Lu, J., Lithium Iron Orthosilicate Cathode: Progress and Perspectives. *ACS Energy Lett.* **2017**, *2* (8), 1771-1781.

20. Wang, J.; Sun, X., Olivine LiFePO₄: the remaining challenges for future energy storage. *Energy Environ. Sci.* **2015**, *8* (4), 1110-1138.

21. Lu, X.; Chiu, H.-C.; Bevan, K. H.; Jiang, D.-T.; Zaghib, K.; Demopoulos, G. P., Density functional theory insights into the structural stability and Li diffusion properties of monoclinic and orthorhombic Li₂FeSiO₄ cathodes. *J. Power Sources* **2016**, *318*, 136-145.

22. Girish, H. N.; Shao, G. Q., Advances in high-capacity Li_2MSiO_4 (M = Mn, Fe, Co, Ni, ...) cathode materials for lithium-ion batteries. *RSC Adv.* **2015**, *5* (119), 98666-98686.

23. Lv, X.; Zhao, X.; Wu, S.; Nguyen, M. C.; Zhu, Z.; Lin, Z.; Wang, C.-Z.; Ho, K.-M., Fe–Si networks and charge/discharge-induced phase transitions in Li₂FeSiO₄ cathode materials. *Phys. Chem. Chem. Phys.* **2018**, *20* (21), 14557-14563.

24. Singh, S.; Panda, M. R.; Sen, R.; Johari, P.; Sinha, A.; Meena, S. S.; Mitra, S., Study of Higher Discharge Capacity, Phase Transition, and Relative Structural Stability in Li₂FeSiO₄ Cathode upon Lithium Extraction Using an Experimental and Theoretical Approach and Full Cell Prototype Study. *ACS Appl. Energy Mater.* **2019**, *2* (9), 6584-6598.

2. Literature Review

In this chapter, the fundamentals of Li-ion batteries and most commonly used cathode materials are introduced first. This is followed by a review of Li₂FeSiO₄ (LFS) as an emerging cathode material and challenges faced by LFS to unleash its full potential. The final part of this chapter is dedicated to different crystal modification techniques such as mechanochemical nanosizing and surface coating methods of interest to the present work as means to improve the performance of lithium iron silicate cathodes.

2.1. Rechargeable Lithium-ion Batteries

The concept and development of a lithium-ion (Li-ion) battery dates back to 70 - 80s.¹⁻⁴ In the early 1970s, M. Stanley Whittingham developed a rechargeable non-aqueous Li metal battery while working at Exxon.⁵ It used a layered TiS₂ intercalation host as the positive electrode, Li metal as a negative electrode and LiClO₄ dissolved in dimethoxyethane (DME) and tetrahydrofuran (THF) as an electrolyte.⁶ However, due to the explosion hazard (dendrite growth of Li) during cycling, this battery was not successful.⁷ Nevertheless, it laid the foundation of commercial Li-ion batteries. Later in 1979, Lazzari and Scrosati reported a ~1.8 V rechargeable Li-ion battery system based on two intercalation electrodes, Li_xWO₂ anode and Li_xTiS₂ cathode.⁸ Earlier Michel Armand introduced the rocking chair concept for LIBs, according to which Li-ions diffuse from the anode to the cathode during charge and from the cathode to the anode during discharge.⁹⁻¹⁰ In 1980, John Goodenough and co-workers proposed layered lithium cobalt oxide (LiCoO₂) as cathode material.¹¹ LiCoO₂ doubled the cathode voltage compared to TiS₂ cathode.¹² With Goodenough's cathode as a basis, Akira Yoshino in Japan created the first commercially viable lithium-ion battery in 1985 using petroleum coke as an anode.¹³ This was followed with the introduction of graphite as anode that proved instrumental in Sony's 1991 first commercial LIB. ¹⁴ For their pioneering work in the development of lithium-ion batteries, John Goodenough, M. Stanley Whittingham and Akira Yoshino were presented with The Nobel Prize in Chemistry in 2019.¹⁵ Nowadays LIBs are used in everything from mobile phones to laptops, electric vehicles,

and stationary storage due to their lightweight, rechargeability and output power. The next section describes the working principle and basic features of LIBs.

2.2. Working Principle of LIBs

Lithium-ion batteries generally consist of three electrochemical components. (1) the negative electrode (anode), (2) the positive electrode (cathode) and (3) the electrolyte as shown in Figure 2.1. Typically, graphite is most commonly used as the anode material, and lithium cobalt oxide (LiCoO₂) is commonly used as cathode material in mobile electronics.⁴ The liquid electrolyte consists of a lithium salt, such as LiPF₆ dissolved in an organic solvent, e.g. ethylene carbonate/diethyl carbonate (EC/DEC).³ Here, both anode and cathode are intercalation type electrodes. Upon assembling, the cell is in fully discharged state, i.e., Li is stored in the cathode (e.g., in the form LiCoO₂).¹ Upon galvanostatic charging, i.e. when an external current is applied, it causes the Li ions to move from the cathode to anode, where they intercalate into the space between graphite layers. During this process, the cathode material is oxidized, and the anode material is reduced. When the anode is saturated with Li-ions, the battery is fully charged. When a fully charged battery is connected through a wire or load, electrical current flows from anode to cathode, releasing the energy stored during the original reaction. Meanwhile, the electrolyte conducts positive current in the form of Li⁺ cations. During this process, anode material is oxidized, and cathode material is reduced. This charging-discharging is repeated for hundreds or even thousand times before the battery is discarded.⁴

The reactions at the anode and cathode as well as the overall reaction are as follows:

Cathode:
$$LiCoO_2 \rightarrow Li_{1-x}CoO_2 + xLi^+ + xe^-$$
 (2.1)

Anode:
$$xLi^+ + xe^- + 6C \rightarrow LiC_6$$
 (2.2)

Full reaction:
$$LiCoO_2 + 6C \rightarrow Li_{1-x}CoO_2 + LiC_6$$
 (2.3)



Figure 2.1. Schematic describing the working principle of rechargeable lithium-ion batteries featuring graphite as anode, LiCoO₂ as cathode plus electrolyte, separator and current collectors.¹⁶

2.3. Important Characteristics of LIBs

The performance LIBs are evaluated in terms of a number of parameters including: (i) specific energy, (ii) specific capacity, (iii) specific power, (iv) coulombic efficiency and (v) electrolyte stability window. These parameters are discussed below:

Specific Energy (Wh Kg⁻¹) of LIBs can be obtained by the following equations:¹⁷

$$E = V_{ocv} \, x \, Q_{th} \tag{2.4}$$

$$V_{ocv} = -\Delta G / (nF) = |(\mu_{cathode} - \mu_{anode})/(nF)|$$
(2.5)

$$Q_{th} = nF / (M_w) \tag{2.6}$$

In equation 2.4, E is the specific (or gravimetric) energy (W h kg⁻¹) or volumetric energy density (W L⁻¹), V_{ocv} is the output voltage (V) and Q_{th} is the specific capacity (mA h g⁻¹), while in

equation 2.5, $\mu_{cathode}$ and μ_{anode} are the chemical potentials of cathode and anode materials, respectively. From this, the open circuit cell potential (V_{ocv}) of a LIB is determined. In equation 2.6, ΔG is the change of Gibbs free energy (J mol⁻¹), n is the exchanged number of electrons, F is the Faraday constant (96,485 C mol⁻¹), and M_w is the molar mass (g mol⁻¹).

The theoretical **specific capacity** (Q_{th}) of electrode materials is derived from the number of exchanged electrons per molecular weight. For example, in case of LFS: Li₂FeSiO₄ \rightarrow FeSiO₄ + 2Li⁺ + 2e⁻. In this case, M_w = 161.81 g mol⁻¹, n = 2, giving a theoretical capacity of 331 mAh g⁻¹. According to equations (2.4 – 2.6), high output voltage and specific capacity would result in high energy density. The real output voltage of batteries depends not only on the reversible potentials of both cathode and anode materials but also on the relative overpotentials of the two electrodes. Similarly, the practical specific capacity of an electrode in a real LIB is usually different from the theoretical one, especially at high current, due to resistances in the diffusion of ions inside the host material (intercalation or de-intercalation) and across the interface between electrode and electrolyte. Further if Li ions become "locked" (i.e. not exchangeable) inside the electrode, this will result in a loss of capacity. Therefore, the practical capacity of the active material when the constant current mode is commonly used, in this case, the practical capacity can be simply obtained as follows, where *Q_{real}* is the practical capacity, *I*(A) is the current and *t*(s) is time, respectively.¹⁷

$$Q_{real} = It \tag{2.7}$$

Specific Power (W kg⁻¹) is also a very important parameter in addition to specific energy of a battery. Power is the product of the current and the voltage, it can be expressed as specific or gravimetric (W kg⁻¹) and volumetric power density (W L⁻¹). It reflects the fast-charging/discharging capability of LIBs and how much power a battery can deliver on demand. The difference between specific energy and specific power can be appreciated with the image given in Figure 2.2. Generally, for EVs, achieving 80% state-of-charge within 20 min is crucial for consumer acceptance.¹⁸⁻¹⁹



Figure 2.2. Relationship between specific energy and specific power, reproduced from ref.²⁰

Coulombic Efficiency of a LIB is defined as the ratio between the charge and discharge capacity of the electrode:

$$C.E = Q_{dis}/Q_{ch} \times 100\% \tag{2.8}$$

The Coulombic efficiency is usually not 100%.⁴ The irreversible loss of capacity is primarily due to the chemical reactions between electrode and electrolyte, electrode volume change, or electrode decomposition (dissolution), etc.^{1, 4, 21}

Electrolyte Requirement: The use of proper electrolytes is very crucial for long term cycling of LIBs. As improper electrolyte may deteriorate LIB performance since the electrolyte will experience unwanted reactions at the electrode surface during operation. In thermodynamics, the stability of electrolyte requires the potentials of the electrolyte redox reactions to be outside the LIB operating voltage window, as shown in Figure 2.3. In equation 2.9, μ_{anode} and $\mu_{cathode}$ are the electrochemical potentials of anode and cathode, respectively, while *e* is the magnitude of electron charge. The stability window of the electrolyte E_g is the energy gap between its lowest unoccupied (LUMO) and highest occupied (HOMO) molecular orbitals as illustrated in Figure 2.3.

An anode whose electrochemical potential is higher than the LUMO will reduce the electrolyte until a passivating SEI (solid-electrolyte interphase) layer forms to block electron

transportation from the anode to the electrolyte. A cathode whose electrochemical potential is lower than the HOMO will oxidize the electrolyte until a passivating SEI layer builds a barrier to electron transportation from the electrolyte HOMO to the cathode. Thus, electrolyte stability requires the theoretical electrochemical potentials of anode (μ_{anode}) and cathode ($\mu_{cathode}$) locating within the thermodynamics stability window (E_g) of the electrolyte. The theoretical expression for electrolyte stability window is as follows:



 $eE_{cell} = \mu_{anode} - \mu_{cathode} \le E_g \tag{2.9}$

Figure 2.3. Interfacial electrode/electrolyte reaction diagram, E_g is the thermodynamic stability window of the electrolyte. E_{cell} is the thermodynamic cell potential (or V_{ocv}), which increases upon charging (as represented by the arrows) and decreases during discharging. μ_{anode} and $\mu_{cathode}$ are the theoretical electrochemical potentials of the anode and cathode, respectively. SEI is the solid-electrolyte interphase.¹⁷

2.4. Commercial Cathodes for LIBs

The energy density and power density of LIBs have been enhanced remarkably over the past 30 years with the development of new electrode materials.³ The commercialized cathode materials are summarized in Table 2.1 for LIBs. The main cathode materials that power portable devices, electronics and EVs are layered oxides (LCO: LiCoO₂, NMC111: LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂, NCA: LiNi_{0.80}Co_{0.15}Al_{0.05}O₂), olivine-based LiFePO₄ and spinel LiMn₂O₄.⁴ Alternatively, high-capacity Li-Mn-rich oxides (LMROs), high-voltage L_iMn_{1.5}Ni_{0.5}O₄, and high-capacity orthosilicates Li₂*M*SiO₄ (where M = Fe, Mn, Co, etc.) are the subject of extensive research efforts.²² Due to high demand for high energy & power dense packs of LIBs, there are still several challenges that need to be circumvented. For example, the practical discharge capacities of almost all the commercialized cathodes are only about half of the theoretical values (see Table 2.1).^{4, 14, 22} Therefore, alternative electrode materials and new strategies should be developed toward improving their performance as discussed in detail in section 2.5 & 2.7. The next section is dedicated to properties and issues related to commercial cathode material.

Cathode	Structure	Potential (V)	Theoretical/practical capacity (mAh g ⁻¹)
LiCoO ₂	Layered	3.8	274 / 148
LiFePO ₄	Olivine	3.4	170 / 165
LiMn ₂ O ₄	Spinel	4.1	148 / 120
LiNi _{0.33} Mn _{0.33} Co _{0.33} O ₂	Layered	3.7	280 / 160
LiNi _{0.80} Co _{0.15} Al _{0.05} O ₂	Layered	3.7	279 / 199

Table 2.1. Summary on structure, working potentials and capacity of different commercialized cathode materials

2.4.1. Layered Cathode - LiCoO₂ (Lithium Cobalt Oxide)

LiCoO₂ (LCO) was the first of the layered transition metal oxides to be commercialized and is still used today in batteries for consumer devices. In 1980, Goodenough *et al.*¹¹ reported layered LiCoO₂ (LCO) as a cathode material for LIBs. It has been the most successful cathode material for portable electronics such as smartphones.²³ Its crystal structure is shown in Figure 2.4a. It possesses *R-3m* space group with overall hexagonal symmetry, where Co and Li, located in octahedral sites, occupy alternating layers along the 111 planes in a cubic close-packed (ccp) oxygen array. Li-ions have 2-D diffusion pathways in LCO crystal lattice as shown in Figure 2.4b. The theoretical capacity of LCO is relatively high at 274 mAh g^{-1} (please refer to Table 2.1). Nevertheless, only about half of the theoretical capacity (~148 mAh g^{-1}) can be achieved when the cut-off charging voltage is 3.8 V.³ If the battery is charged at higher cut-off voltage, it will induce phase transitions, coupled with decreased Li⁺ diffusivity, leading to serious capacity decay during cycling.²⁴ Another issue with LCO is oxygen evolution during cycling, which ultimately leads to capacity fading and safety issues.^{3, 25} Similarly, high cost of cobalt is another major drawback of LCO.^{23, 26} Researchers attempted many approaches to circumvent the issues of LCO. To reduce high cost, achieve high practical capacity along improved thermal stability, doping and surface coating was adopted for LCO.^{3, 26-27} This gave birth to other commercial cathodes such as LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ (NMC) and LiNi_{0.80}Co_{0.15}Al_{0.05}O₂ (NCA) as discussed in next section.



Figure 2.4. (a) Crystal structure of LiCoO₂, where lithium ions (pink) reside between the closed packed octahedral cobalt oxide slabs (magenta), (b) along with its lithium diffusion pathway.²⁸

2.4.2. NMC (LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂) and NCA(LiNi_{0.80}Co_{0.15}Al_{0.05}O₂)

To solve the aforementioned issues of LCO motivated researchers to investigate other layered transition metal oxides. Out of this research, two new electrodes emerged: NMC (LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂) and (LiNi_{0.80}Co_{0.15}Al_{0.05}O₂) (or NCA). They are isostructural to LiCoO₂ but have higher specific capacities. The structural, chemical and thermal stabilities are also improved compared to LiCoO₂.²⁷ NMC contains two thirds lower Co content than LCO, which reduced cost and improved the structural stability in comparison with the parent material (LCO). The commercial NMC111 has a reversible capacity of about 160 mAh g⁻¹ with an average voltage of 3.7 V.²³ When the content of Ni increases to 0.6–0.9, the Ni-rich NMC can deliver higher capacity of 180–210 mAh g⁻¹.²⁹ But Ni-rich NMC has inferior cycling performance and poor thermal stability. Dixit *et al.*³⁰ attributed the poor thermal stability of Ni-rich NMC to the side reactions between Ni⁴⁺ ions and electrolyte, leading to O₂ release and electrolyte decomposition.

In addition to NMC, other representative Ni-rich layered oxides are the NCA family. The most popular composition of NCA is LiNi_{0.85}Co_{0.10}Al_{0.05}O₂, which has been successfully commercialized for electric vehicles such as Tesla vehicles.¹⁸ In the case of NCA, the incorporation of Al improved the thermal stability, although there are still safety concerns. The content of Al in NCA is generally low because high content of Al would lead to serious capacity decay and inferior Li⁺ ion diffusion kinetics.³¹ Similar to NMC, the common NCA shows high practical capacity but suffers from cation mixing, surface side reactions, and instability of highly charged state.³¹ Researchers adopted surface coating and concentration-gradient buffer strategies to improve the electrochemical performance of NCA.³²⁻³³

2.4.3. Spinel Cathode - LiMn₂O₄ (Lithium Manganese Oxide)

In search for the cheaper alternative to replace LiCoO₂, researchers developed the spinel LiMn₂O₄ (LMO), which has been successfully commercialized.^{4, 14, 23} As shown in Figure 2.5, LMO possesses 3-D Li⁺ ion transport pathway (*Fd–3m* space group). However, the practical capacity of LMO is low at ~120 mAh g⁻¹ at cut-off voltage of 4V, much lower than other counterparts as discussed earlier in section 2.4.1 & 2.4.2. Nevertheless, LMO suffers from poor

cycling stability particularly at elevated temperatures (due to the dissolution of Mn-ions into the electrolyte) and irreversible structural transformation resulted from Jahn-Teller distortion.^{27, 34} Surface coating and elemental doping are helpful in enhancing the cycling stability of LMO.³⁻⁴ Nowadays, the commercialization of LMO has been realized mainly due to its low cost, high thermal safety, and good rate performance.^{18, 22} However, restricted by its low energy density, LMO cannot be used as cathode for LIBs in electric vehicles. In general, LMO is often blended with NMC and NCA as cathode for LIBs in electric vehicles (such as the BMW i3 and Nissan Leaf) to reduce the overall cost and enhance safety.¹⁸ Moreover, the blend of LMO and NMC usually exhibits enhanced thermal stability, high capacity, and good cycling stability. Among various derivatives of LMO, the 5 V spinels such as LiMn_{1.5}Ni_{0.5}O4 (LMNO) are considered as promising alternative cathode materials for LIBs due to their high energy density arising from the high voltage (above 400 Wh kg⁻¹).²² The problems of LMNO though are similar to its parental archetype, LMO. Additional problem is the limited electrochemical stability window of common electrolytes, which restrict the application of LMNO.²⁷ Thus, developing more stable electrolyte is very meaningful for the commercialization of 5 V spinels in the future.



Figure 2.5. (a) Crystal structure of LiMn₂O₄, showing Mn-centered oxygen octahedra (green) and Licentered oxygen tetrahedra (magenta), (b) along with its corresponding lithium diffusion pathway.²⁸

2.4.4. Olivine Cathode – LiFePO₄ (Lithium Iron Phosphate)

Similar to LiCoO₂, in 1997, Goodenough and co-workers reported on the electrochemical properties of a new class of cathode material known as the phospho-olivine lithium iron phosphate (LFP).³⁵ It possesses orthorhombic structure with *Pnma* space group as shown in Figure 2.6, where $Li^+ \& Fe^{2+}$ occupy octahedral sites and P is located in tetrahedral sites in a somewhat distorted hexagonal close-packed (hcp) oxygen array.³⁶ The main advantages of LFP are the extremely stable voltage plateau with bi-phase lithiation process (~3.45 V vs. Li⁺/Li), high cycling and thermal stability, low cost, high abundance, and good environmental compatibility.³⁶ Additionally, LFP is inherently safer than the layered metal oxides due to strong bond between P-O in the phosphate framework. However, the theoretical capacity of LFP is only 170 mAh g⁻¹. In the meantime, LFP suffers from low intrinsic electronic and ionic conductivity, which has been ingeniously rectified via *in-situ* carbon coating during synthesis of the LiFePO₄- technology developed by Michel Armand and Hydro-Quebec researchers.³⁷



Figure 2.6. Crystal structure of olive LiFePO₄, showing PO₄ tetrahedra and FeO₆ octahedra along [001] plane.³⁶

In summary, the cathode material is the most critical component building LIBs with high specific energy density. Presently, almost half (~ 40%) of the overall cost is dedicated to cathode material in a typical Li-ion battery pack.²³ Therefore, to build sustainable batteries a cathode material should be made out of abundant elements and preferably can carry more than one lithium per transition metal and have high voltage. The material should be an excellent electronic/ionic conductor, be stable during cycling, i.e. no suffering irreversible structural changes; and finally be safe and environmentally friendly (non-toxic when disposed of).^{22, 38-39} It is in this context that lithium transition metal orthosilicates have gained great interest – the subject of this thesis.

2.5. Lithium Iron Silicates, Li₂FeSiO₄

All commercial the cathodes such as $LiCoO_2$, $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$, LiNi_{0.80}Co_{0.15}Al_{0.05}O₂, and LiFePO₄ have intrinsic limitations in terms of capacity (120-170 mAh g^{-1}), structural stability or safety. Therefore, it is imperative to exploit high-energy cathode materials⁴. Thus, the search for and development of high-capacity cathode materials have become an important activity for battery material researchers. In an effort to find cathode materials that are inexpensive, safe, sustainable in terms of abundant element composition and of high energy density, lithium metal orthosilicates, Li_2MSiO_4 (M = Fe, Mn, Co, or Ni), were proposed as promising cathodes for LIBs.⁴⁰ Li₂MSiO₄ has two Li per formula unit, which gives a high theoretical capacity of 331 mAh g⁻¹. The rigid framework constructed by silicate polyanions ensures good structural and thermal stability. Among different transition metal ion (Fe, Mn, Co or Ni) silicates, Li₂FeSiO₄ (LFS) has gained the most attraction as a possible candidate for commercial cathode application.⁴¹ Fe and Si are two of the most abundant elements in the earth's crust. First redox reaction (Fe²⁺/Fe³⁺) occurs at 2.8 V, while second redox reaction (Fe³⁺/Fe⁴⁺) occurs theoretically at around 4.5-4.8 V (vs. Li⁺/Li), providing a theoretical specific energy of approximately 1120 Wh kg^{-1,41} However, there are still major material chemistry challenges in transforming LFS into a high-performance cathode material. For example, it possesses different crystal phases due to very small differences in formation energies - which complicates the optimization of their properties for commercial cathode applications.⁴²⁻⁴⁵ Moreover, it suffers from low conductivity (electronic & ionic), phase transition during cycling and inability for two Liextraction during cycling, etc. As such there is a need for additional work to address and hopefully overcome these limitations. The following sections will be focusing on current challenges faced by LFS, such as polymorphism, electrochemical properties and phase transition during cycling etc.

2.6. Challenges Faced by Li₂FeSiO₄

2.6.1. Polymorphism

Extensive research shows that LFS crystallizes in various polymorphs. These polymorphs have been classified into two main classes as β and γ , low temperature and high temperature polymorphs respectively, as shown in Figure 2.7.46 Generally, three polymorphs of Li₂FeSiO₄ have been studied extensively: low-temperature orthorhombic (β_{II} , $Pmn2_i$), and the high-temperature monoclinic (γ_s , $P2_1/n$) and orthorhombic (γ_{II} , Pmnb) ones.⁴¹ They can be distinguished from each in the linking manner of the LiO₄, FeO₄, and SiO₄ tetrahedra, as shown in Figure 2.7. Particularly, Li site in low-temperature $(Pmn2_1)$ and high-temperature orthorhombic (Pmnb) is surrounded by four and three Fe²⁺ ions, respectively.⁴⁶ Meanwhile, in high-temperature monoclinic ($P2_1/n$) both Li sites are present. Notably, the local bonding environment of FeO4 among the three polymorphs is also different. For both $P2_1/n$ and $Pmn2_1$ phases, FeO₄ tetrahedra share one or no edges with LiO₄ tetrahedra. On the other hand, FeO₄ tetrahedra share two edges with LiO₄ tetrahedra in the *Pmnb* phase as shown in Figure 2.7b. These structures can be obtained via different synthesis techniques such as hydrothermal, sol-gel and solid-state synthesis, by varying reaction temperatures.⁴¹ Conventionally, the low-temperature orthorhombic LFS (β_{II} , *Pmn2*₁) is obtained at 200 °C,⁴⁷ while the high-temperature monoclinic (γ_s , $P2_1/n$) and orthorhombic (γ_{II} , *Pmnb*) is prepared by annealing in the temperature range of 600-900 °C.⁴⁸ Detailed information about the structural rearrangement, phase transitions and the change in the local environment of the lithium nuclei during the charge/discharge process is discussed in section 2.6.3 below.



Figure 2.7. Li₂FeSiO₄ polymorphs: high-temperature (a) monoclinic (γ_s , $P2_1/n$) & (b) orthorhombic (γ_{II} , *Pmnb*); and (c) low-temperature orthorhombic (β_{II} , *Pmn2*₁).⁴⁹

2.6.2. Electrochemical Behaviour of LFS

2.6.2.1. First Redox Reaction (Fe²⁺/ Fe³⁺): Li₂FeSiO₄ → LiFeSiO₄

Cathode materials rely on efficient transport of electrons and ions during intercalation/deintercalation. The distance between two adjacent Fe atoms in Li₂FeSiO₄ is 0.434 nm, which is much larger than in LiFePO₄ (0.387 nm). This leads to a large band gap of 2–3.3 eV and an extremely low electronic conductivity of 6×10^{-14} S cm⁻¹ at room temperature. The Li extraction potential for the Fe²⁺/ Fe³⁺ redox in LFS is ~3.1 V as first observed by Nyten *et al.*⁵⁰ in 2005, when they prepared and reported the first experimental characterization of Li₂FeSiO₄. The

electrochemical behavior was investigated via cyclic voltammetry and galvanostatic chargedischarge cycling tests. LFS crystals exhibited initial capacity of about 165 mAh g⁻¹ (1 lithium extraction/insertion) at relatively high temperature of 60 °C at C/16. Notably, after the first cycle, the potential was found to decrease from 3.10 to 2.8 V vs. Li⁺/Li, which is related to structural rearrangement or irreversible phase transition during cycling as discussed in detail in section 2.6.3.

Among the three LFS polymorphs (low-T orthorhombic $Pmn2_1$, monoclinic $P2_1/n$, and high-T orthorhombic Pnmb), it is mostly the monoclinic phase that has been studied because of its better electrochemical performance vis-à-vis the other polymorphs. For example, in 2008 Dominko *et al.*⁵² prepared several samples of LFS at different temperatures, namely low-T orthorhombic ($Pmn2_1$) at 150 °C, monoclinic ($P2_1/n$) at 700 °C and high-T orthorhombic (Pmnb) at 900°C, respectively. The electrochemical testing was carried out at relatively high temperature (60 °C) at a rate of C/20. The different samples showed different electrochemical behavior. High-T orthorhombic was shown to have the lowest reversible capacity, while the monoclinic exhibited best electrochemical performance. However, the charge capacity for all samples was less than 165 mAh g⁻¹ (1 lithium extraction/insertion) even if cycled at relatively high temperature of 60 °C. The authors attributed the poor reversible Li capacity performance to the large particle size and lack of carbon content, which can be improved via particle size reduction and surface coating etc. (please refer to section 2.7). Later research reported a similar electrochemical behavior of 1 or less Li extraction, but also significant electrochemically-induced structural changes after the initial cycles.^{41, 48, 53-55}

Returning to the first oxidation potential, Dominko *et al.*⁵⁶ observed that the redox reaction (Fe^{2+}/Fe^{3+}) for Li₂FeSiO₄ varied with different synthesis conditions. It was Sirisopanaporn *et al.*⁵⁷ who in 2011 solved this puzzle by linking the variable first oxidation potential to the Fe-O bonding environment of each polymorph structure as summarized in Table 2.2 and Figure 2.8. In Figure 2.8, the crystal structures of the three polymorphs obtained at different temperatures, are shown along their derivative plots obtained from (Potentiostatic Intermittent Titration Technique) PITT measurements at the first cycle. As it can be seen the initial first redox potential varies from one polymorph to the other (see Table 2.2). The redox potential of Fe^{2+}/Fe^{3+} is seen to shift with



Figure 2.8. Dependence of electrochemical potential among different polymorphs of LFS (LFS@200 is β_{II} , LFS@700 is γ_s , and LFS@900 is γ_{II}): (a) crystal structures and (b) derivative plots obtained from PITT measurements in the first, second, and fifth cycles for all three polymorphs.⁵¹

cycling converging to 2.8 V after the 5th cycle for all polymorphs. This lowering in potential is related to irreversible phase transition during cycling (see section 2.6.3). This potential dependence on polymorph structure can be explained in terms of the arrangement, orientation, size and distortion of the FeO₄ tetrahedra among different polymorphs.⁵⁸⁻⁵⁹ Thus, according to these previous studies, the shorter the Fe-O bond distance (see Table 2.2) and higher the distortion degree of FeO₄ tetrahedra, leads to higher Fe^{2+}/Fe^{3+} redox ability.

LFS	Space group	Fe-O bond distance (Å)	First oxidation potential $(Ee^{2+}/Ee^{3+}vs Li^{+}/Li^{+})$
LFS@200	$Pmn2_1$	2.0763	3.1 V
LFS@700	$P2_l/n$	2.0322	3.0 V
LFS@900	Pmnb	2.0261	2.9 V

Table 2.2. Variation of first oxidation potential with LFS structure.

2.6.2.2. Second Redox Reaction (Fe³⁺/ Fe⁴⁺): LiFeSiO₄ → FeSiO₄

The theoretical capacity of Li₂FeSiO₄ (331 mAh g⁻¹ corresponding to extraction of two Li⁺ ions per formula unit) is only possible if the second oxidation step of Fe^{3+} to Fe^{4+} is achieved. According to theoretical calculations, the redox potential for the second oxidation step of LFS (Fe^{3+}/Fe^{4+}) lies at about 4.8 V,⁴⁹ which is above the safe upper stability level of 4.5 V of typical electrolytes.⁶⁰ Muraliganth *et al.*⁵³ synthesized a nanostructured LFS sample (monoclinic $P2_1/n$) by a microwave-solvothermal process and based on the two first charge-discharge cycles estimated the second oxidation potential to be about 4.7 V vs. Li⁺/Li. Other researchers reported a much lower potential at about $\sim 4.3 V_{.}^{61}$ which created a debate among researchers about participation of Fe^{4+} . Till today, Li-ion extraction beyond one Li is a matter of controversy if it is linked to Fe^{3+} Fe^{4+} redox couple or if it involves redox activity by lattice O^{2-} especially at a higher voltage near 4.8 V.^{41, 62-64} X-ray oxygen K-edge XANES spectra ⁶² and DFT calculations ⁴⁵ as well as the work of Masese et al.⁶³ support the anion redox activity rather than the involvement of tetravalent iron for more than 1 lithium extraction. Meanwhile others like Lv et al.⁶⁴ or recently Sing et al.⁶⁵ do not rule out the involvement of both redox sources. Conclusively, the oxidation to Fe⁴⁺ remains unconfirmed. Therefore, in-depth understanding of the redox behavior and phase evolution of Li₂FeSiO₄ is still urgently needed. Intensive research should be undertaken to overcome this issue by optimizing the structural characteristics and properties of LFS electrodes, such as reducing the LFS particle size, carbon coating the nanoparticles, using carbon nanotubes, carbon coating, ion doping and porosity control, etc. (see section 2.7).⁴¹ For example, recently Ding et al.⁶⁶ prepared mesocrystals with a single crystal-like structure via solvothermal method with mixed structure of the $Pmn2_1$ (96.35%) and $P2_1/n$ (3.65%) phases. The mesocrystals Li₂FeSiO₄@C (M-LFS@C)

exhibited near reversible theoretical capacity for the first five cycles (~310 mAh g⁻¹). Moreover, the material showed good rate-capability and cycling stability when compared with Li₂FeSiO₄@C composite synthesized by sol–gel methods (SG-LFS@C) cycled at 1C as shown in Figure 2.9. They attributed this high capacity to Fe⁴⁺, based on CV analysis as shown in Figure 2.9b. In other words, they assumed the peak at 4.64 V to be due to Fe³⁺/ Fe⁴⁺ redox couple. However, considering the gradual disappearance of the peak with progressive scanning cycles, it might be alternatively thought this to have been due to electrolyte reaction that gradually stopped upon formation of a passivating (SEI-type) layer. Thus, the issue of second Li extraction and the associated redox mechanism remains unresolved.



Figure 2.9. (a) Galvanostatic charge-discharge curves for mesocrystal Li₂FeSiO₄ (M-LFS@C) cathode ranging from 1.5 to 4.7 V at 0.2 C. (b) Cyclic voltammogram curves for M-LFS@C at a scan rate of 0.1 mV s⁻¹. (c) Rate cycling performance for the carbon coated sol–gel prepared Li₂FeSiO₄ (SG-LFS@C) and M-LFS@C cathodes. (c) Charge/discharge cycling performance of the SG-LFS@C and M-LFS@C cathodes at 1 C.⁶⁶

2.6.3. Irreversible Phase Transition During Cycling

As mentioned earlier Li_2FeSiO_4 exhibits complex polymorphism. Their extensive polymorphs and crystal structures have been described previously in section 2.6.1 Among the polymorphs, orthorhombic-low & high temperature and monoclinic-high temperature, it's the latter that has been most often used in electrochemical studies. Several reports found that the monoclinic LFS material undergoes irreversible structural changes during the initial charge and discharge reaction as discussed earlier in section 2.6.2. Specifically, all the recent theoretical and experimental studies indicate a phase transition from monoclinic $P2_l/n$ to the thermodynamically stable "inverse" (or "cycled") *Pmn2*, phase during charging/discharging ⁴¹. Probing of the lithium pathways in the different polymorphs is done via Density Functional Theory (DFT) simulations. For example, Liivat *et al.*⁶⁷ and Armstrong *et al.*⁶⁸ have identified that Li-ions can migrate along only two directions in as-synthesized (prior to electrochemical cycling) $P2_1/n$, $Pmn2_1$ and Pmnbphases. Notably, all the aforementioned polymorphs have the tendency to transform into a thermodynamically stable orthorhombic phase (inverse $Pmn2_1$) during electrochemical cycling.⁶⁹ The inverse $Pmn2_1$ crystal structure has all the Fe-ions exchanging site with half of the Li-sites, moreover Li-ions can migrate along three different directions as shown in Figure 2.10.67 In other words, due to significant cation mixing induced during cycling, a new pathway opens up creating effectively three Li migration paths in the cycled or "inverse $Pmn2_1$ " phase as shown in Figure 2.10. So, it has been proposed, during electrochemical lithiation/de-lithiation, Li migrates in either a-direction (into the paper as denoted by arrows in Figure 2.10) or hopping in either b or c-direction (denoted by arrows). Further these atomic simulations have determined the lowest Li migration energy to be 0.9 eV, which is still greater than the 0.6 eV energy reported for LiFePO₄, therefore a rather poor rate capability is predicted for Li₂FeSiO₄.⁷⁰ However, it is known that via various crystal modification strategies such as cation doping or substitution combined with nanosizing can tune the size of Li migration path and the activation barrier, leading to enhanced Li diffusivity for improved electrochemical activity.^{3, 26, 41}



Figure 2.10. Three-dimensional Li diffusion pathways for inverse $Pmn2_1$ Li₂FeSiO₄. (a) The first pathway is an effective transport in the a-direction (A). (b) The second path (B) involves hoping in the b direction as indicated by arrows. (c) The third path (C) involves hoping in the c direction as indicated by arrows.⁶⁷

The subject of phase transitions in LFS though is not fully resolved. Thus Chen *et al.*⁴⁹ and Armstrong *et al.*⁶⁸ proposed that the monoclinic ($P2_1/n$) phase of Li₂FeSiO₄ transforms into a stable inverse orthorhombic ($Pmn2_1$) phase upon cycling. In contrast, Kojima *et al.*⁷¹ suggested that no phase transition occurs during cycling and contributed the structural difference to be only due to cation disordering of Li⁺, Fe²⁺, and Fe³⁺. To solve this dispute, Masese *et al.*⁷² designed an elaborate experiment to track the structural evolution of Li₂FeSiO₄ upon Li extraction. They studied the phase transformation mechanism (see Figure 2.11) by examining crystal structural changes induced by cycling at different C-rates and found that at very low C/50 rate, the crystal structure transformed to a stable orthorhombic (*Pnma*) phase but at high rate, C/10, the monoclinic phase converted to orthorhombic only after relaxation (i.e. after the cycled material was stored for some time). This rate-dependent phase transition was confirmed by Lu *et al.* at McGill, where monoclinic LFS transformed to orthorhombic during cycling at a very low C-rate (C/50) but not at high rate (C/10).⁴⁸ As mentioned earlier, almost all the previous studies have focused on the monoclinic phase of LFS and did not consider the stability (resistance to phase changes) when the

low or high-T orthorhombic phase is cycled. Therefore, further detailed studies are required to understand the phase transformation mechanism of each crystal structure. In summary, LFS material has many attractive features for commercialization as LIBs cathodes. However, their current structural idiosyncrasies require attention and new strategies to overcome them. Some of the possible strategies to prepare high-energy density silicate cathodes are discussed in the following section.



Figure 2.11. Rate-dependent phase transition of LFS crystal during cycling.⁷²

2.7. Strategies to Prepare High Capacity LFS

As it was shown in the previous sections, attainment of the full capacity of Li₂FeSiO₄ for reversible multi-cycle performance remains yet to be achieved. This has motivated research into alternative material design strategies to "unblock" or "activate" the full intercalation potential of these materials. Most of the strategies pursued leverage the knowledge advances made with the development of the polyanionic phosphates, such as nanosizing, defect elimination by annealing, conductive layer (carbon or polymer) coating, doping, porosity control etc. In the following sections a description of key aspects of some of these proven strategies is presented as they are used in the present work to enhance the storage capabilities of LFS.

2.7.1. Nanostructuring via Mechanochemistry

Particle size reduction to nanometer scale is a popular way to decrease diffusion length of lithium-ions and increase the active surface area of the electrode material. Notably, the lithiumion diffusion coefficient is a constant for a particular material and the time required for the intercalation of lithium-ions is a function of the square of the diffusion distance within an electrode material (see Figure 2.12).73 Thus, a decreased diffusion distance for lithium-ions through nanosizing is an effective way to improve the electrochemical performance of an electrode material. A comprehensive discussion of the role of nanosizing in improving the electrochemical performance of electrodes is provided elsewhere.⁷³⁻⁷⁷ Thus in the case of LiFePO₄ (LFP), whose ionic conductivity is even lower than its electronic conductivity, nanosizing has been deemed to be even more important than carbon coating to achieve good electrochemical performance.⁷⁸ Likewise, LFS suffers from low intrinsic conductivity properties (electronic and ionic) which hamper the lithium-ion extraction and insertion processes. The Li⁺ ion diffusion coefficient is very low, ranging between 10^{-12} and 10^{-20} cm² s⁻¹ at room temperature, which is obviously lower than that for the low conducting LiFePO₄ ($\sim 10^{-7}$ cm² s⁻¹).^{67, 79-80} Therefore, active surface engineering achieved by nanosizing the Li₂FeSiO₄ particles can shorten the diffusion distance for charge carriers while simultaneously increasing the surface area accessible to Li⁺ ions.⁷⁵ There are different strategies to prepare nanoscale Li₂FeSiO₄ crystals. One of them is to employ for example complexing agents during synthesis to control nucleation and growth/aggregation.⁸¹⁻⁸³ Another method is to use high-energy milling (mechanochemistry).⁸⁴

Mechanochemistry is a powerful tool that has been intensively used for several applications ranging from particle size reduction to synthesis.⁸⁴⁻⁸⁸ The term mechanochemistry is commonly used in a broad sense, covering physicochemical alteration (fragmentation, reaction, coating etc.) of materials induced mechanically via high-energy grinding.⁸⁹ Grinding is a general term describing material fragmentation by mechanical means.⁸⁵ It may refer to manual methods (mortar and pestle) or to non-manual methods such as conventional steel ball milling used extensively in industrial mineral processing operations. In recent years, an even more powerful method has become available that of high-energy milling that gave birth to mechanochemistry.⁸⁴ There are



Figure 2.12. A schematic representation of diffusion length of Li-ions in electrode-active materials.⁷³

different types of high-energy mills, some of which are shown in Figure 2.13. Mechanochemistry goes beyond simple particle reduction. In many instances it is used for low temperature "solid-state" reactive synthesis. In the latter case milling in the presence of a small amount of a solvent (water or organic) can dramatically facilitate the mechanochemical reactions between solid precursors (solvent-assisted mechanochemistry).⁸⁶ In the following section 2.7.1.1, a review of the effect of different milling parameters in mechanochemical processing of materials is presented including references to its application to LIB electrode preparation.

2.7.1.1. Parameters affecting high-energy milling

The purpose of an ideal device for mechanochemical milling is to exert the maximum amount of energy to break down the particle. High-energy planetary mills (e.g. those manufactured by Fritsch) are especially suitable for nanosizing due to their high energy density, simple set-up, handling and ease of cleaning.^{84, 90} Nonetheless, nanosizing can also be realized in a disc-vibration mills or shaker mills. There are several variables that influence the milling process, e.g. type of the mill, material of milling media, ball-to-powder ratio, filling extent of the milling chamber, amount and type of solvent, milling atmosphere, milling speed, milling time, etc.^{88, 91}



Figure 2.13. Several types of mills for high-energy milling: (a) ball mill, (b) planetary mill, (c) vibration mill, (d) stirring ball mill, (e) pin mill and (f) rolling mill.⁸⁴

Materials of milling media: The type of material used for the milling chamber, vial, or the balls is important due to impact of the balls on the inner walls of the milling chamber. Most common materials used as milling media include: steel (stainless, hardened chromium, tempered, tungsten carbide lined), tungsten carbide, zirconia, agate, alumina, silicon nitride, etc. (see Table 2.3).^{84, 88, 91} Generally, high-density and large balls give better results because of high impact forces on the powders.⁹¹ The balls should be denser than the material to be milled. Notably, one of the major problems with high-energy milling is contamination of the milled product from the erosion of the milling media. This contamination is directly connected to the hardness ratio of balls to powder samples.^{88, 92} Therefore, careful selection of the right milling media is required for optimum milling results.

Milling speed can have an important influence, but this varies with the type of mill. Above a certain critical speed, the balls will be pinned to the walls of the milling chamber and will not exert any impactful force on the powder, whereas, below a critical speed, there will not be enough force to break down the particles. Therefore, the appropriate milling speed should be sought according to the material in hand to break. Another important consideration is that at very high speeds, the milling chamber may overheat due to very high local pressure.⁸⁴

Material	Main Composition	Density (g cm ⁻³)	Abrasion
Agate	SiO ₂	2.65	Good
Corundum	Al ₂ O ₃	3.8	Fairly Good
Zirconium Oxide	ZrO ₂	5.7	Very Good
Stainless steel	Fe, Cr, Ni	7.8	Fairly good
Tempered Steel	Fe, Cr	7.9	Good
Tungsten carbide	WC	14.7 – 14. 9	Very good

Table 2.3. Properties of different milling media.⁸⁸

Milling time is the most important milling parameter for nanosizing according to many researchers.^{84, 86-87} Substantial reduction in particle size usually occurs with milling time, the relationship between milling time and generated specific surface area is shown in Figure 2.14 for the case of hexagonal boron nitride nanosizing.⁹¹ As it can be seen there are two stages, with surface area increasing initially-this stage corresponding to nanocrystal formation, thereafter decreasing with prolonged milling due to amorphization. Another complication from prolonged milling is that the level of contamination tends to increase with milling time or even leading to undesirable by-product phase formation.^{84, 86-87} Hence, again this parameter requires careful investigation for optimum results.

Ball to powder ratio is another milling parameter and represents the weight ratio of the milling balls to the powder charge. A wide range of ball to powder is usually used in a variety of investigations from values as low 1:1 to as high as 220:1. In Table 2.4, it is shown that 20:1 ratio is used commonly for nanosizing and synthesis of various materials.^{84, 87}

Choice of solvent for wet-milling is crucial as well. Generally, a solvent enables milling without powder agglomeration hence providing a more effective nanosizing and reaction environment. Moreover, the solvent should be inert vis-à-vis the milling media and powder subjected to high-energy milling.⁸⁸ Several solvents used for high-energy milling are summarized in Table 2.4.

Milling Atmosphere: The presence of air in the milling chamber can result in contamination via the formation of oxides etc.⁸⁸ As a result, milling is frequently carried out in inert atmosphere by either evacuating or filling with argon or helium the milling chambers.⁸⁸

In summary, several parameters need to be properly evaluated to define appropriate conditions for desired results in terms of particle size reduction and nanostructuring. In Table 2.4, several examples of LIB electrode materials or other relevant materials that were subjected to nanosizing by high-energy milling are provided along the applied range of parameter values.



Figure 2.14. Relationship between milling time and generated surface area (S, m² g⁻¹) during highenergy milling (vibration mill) of boron nitride (BN).⁹³

Table 2.4. Mechanochemical milling parameters applied to nanosizing and/or synthesis of various materials.

Material (Mill Type)	Solvent	RPM	Time (h)	Ball-to-Powder Ratio
			(11)	(mount & jur)
LiNi _{0.5} Co _{0.2} Mn _{0.3} O ₂ (Pulverisette 5, Fritsch) ⁹⁴	Acetone	350	3	20:1 (not specified)
Cr-doped LiFePO ₄ /C (Pulverisette 5, Fritsch) ⁹⁵	not specified	250	3	20:1 (Zirconia jars and media)
Vanadium Tetraphosphide (SPEX-8000 vibratory mill) ⁹⁶	not specified	not specified	48	20:1 (Hardened steel jars and media)
Ti–P Composites (Not specified) 97	not specified	not specified	54	20:1 (Hardened steel jars and media)
LiNi _{0.5} Mn _{1.5} O ₂ (planetary- type ball mill) ⁹⁸	not specified	400	0.5	5:1 (Zirconia jars and media)
Li ₂ MnO ₃ (Pulverisette 5, Fritsch) ⁹⁹	Acetone	150	1	20:1 (not specified)
$xLi_2MnO_3 \cdot (1-x)LiMO_2(M = Mn, Ni, Co)$ (planetary-type ball mill) ¹⁰⁰	Acetone	350	3	20:1 (not specified)
0.5Li ₂ MnO ₃ ·0.5LiCoO ₂ (FRITSCH Pulverisette 5) ¹⁰¹	Acetone	350	3	20:1 (not specified)
Fe ₅₀ Ni ₅₀ (FRITSCH Pulverisette 7) ¹⁰²	Not specified	1100	1-322	20:1 (steel jar and media)
Li ₇ La ₃ Zr ₂ O ₁₂ (FRITSCH Pulverisette 7) ¹⁰³	Isopropanol	Not specified	8-10	Not specified (Zirconia jars and media)
Zn/Se mixture (FRITSCH Pulverisette 7) ¹⁰⁴	Not specified	Not specified	200-800	Not specified (steel jar and media)
Magnetite nanoparticles (Fritsch Pulverisette 7) ¹⁰⁵	Not specified	200	10-96	20:1 (steel jar and media)
LiCoPO ₄ (vibratory ball mill Spex CertiPrep) ¹⁰⁶	Not specified	1425	Variable	22:1 (steel jar and media)
Al–Al ₂ O ₃ nanocomposite (SPEX 8000 mixer) ¹⁰⁷	Not specified	variable	variable	10: 1 (not specified)
LaMnO ₃ (FRITSCH Pulverisette 7) ¹⁰⁸	Not specified	700	variable	Not specified (Zirconia jars and media)

2.7.2. Carbon Coating

Carbon coating is a simple but extremely effective technique in enhancing the electronic conductivity of electrode materials especially in the case of LFP.^{37, 109} It helps to establish a conductive network for electron transport, thereby leading to a high capacity delivery and rate capability. A popular way toward this target is forming *in-situ* a carbon coating layer by hightemperature (600 - 800 °C) pyrolysis of organic precursor substances.^{27, 37, 73, 109-111} Carbon coating has been instrumental for improved cycling performance of several cathodes such as NMC, 112-113 LiMn₂O₄,¹¹⁴ and mainly LFP.¹¹⁵⁻¹¹⁶ The coating method, and the amount and the source of carbon used can significantly influence the effectiveness of the carbon film. Controlling the carbon coating thickness is challenging and different carbon sources & coating methods have been explored.^{110, 117-120} Such methods have been widely reported for phosphate-based materials,¹²¹⁻¹²² e.g. Wang et al.¹²³ prepared nanosized LiFePO₄ completely coated with carbon from a low-cost Fe³⁺ salt as shown in Figure 2.15. As graphically illustrated in Figure 2.15a, if surface coverage by carbon coating is only partial, then during electrochemical cycling, the electrons cannot reach all the positions where Li⁺ ion intercalation takes place resulting in polarization of the electrode. However, with full surface carbon coating (Figure 2.15b) electron transport is unhindered and the performance is maximized. Figure 2.15c shows a typical example of a particle made up of several primary crystallites with sizes ranging from 20-40 nm. The high-resolution TEM images clearly reveal that each primary crystallite is completely coated by a carbon layer to form a LiFePO₄/carbon core-shell structure (thickness of about 1-2 nm). As a result of such nanoscale carbon coating architecture the LFP@C cathode yielded excellent rate capability (Figure 2.15d) and cycling performance with less than 5% discharge capacity loss over 1100 cycles (Figure 2.15e) and the coulombic efficiency steady at nearly 100 %.

An alternate approach to *in-situ* carbon coating is to add acetylene black during highenergy milling. This is a convenient and inexpensive mechanical carbon coating method, and thus easy to scale up in commercial view. However, it is not necessarily as effective in terms of coverage and film thickness as the previous method. To improve the effectiveness of mechanical



Figure 2.15. (a) Illustration of electron-transfer pathway for LiFePO₄ particles partially coated with carbon and b) fully carbon-coated LiFePO₄ nanoparticles. (c) TEM/HRTEM images of LiFePO₄/carbon composite. (d) Rate capability tests at different current densities and e) capacity vs. cycle number along with coulombic efficiency.¹²³

coating researchers have replaced carbon with graphene. Thus, in one work NMC/graphene composites obtained via high-energy milling delivered high discharge capacity at different C-rates.¹²⁴ The enhanced cycling performance and rate capability of the NMC/graphene composite was attributed to an increase in grain connectivity and enhanced electronic conductivity. In summary, carbon coating is a proven technique for improving electronic conductivity for intrinsic low conducting cathode materials such as LFP. Same approach can be utilized to coat LFS nanoparticles.

2.7.3. Polymer Coating

An alternative approach to carbon coating to enhance the electronic conductivity of an electrode is to apply conductive polymer surface coating. Conductive polymer surface coating has proven to be an easy and effective way for improving the capacity retention, rate capability, and even thermal stability for a wide variety of cathode materials.¹²⁵ Surface coating can induce several positive effects such as (I) enhancing the electronic conductivity of the cathode material to facilitate charge transfer; (II) providing physical protection layer that reduces possible side reactions between cathode and electrolyte; and (III) improving structural stability.^{73, 125-127} In this context, conductive polymers are attractive coating can be achieved in a simple process under mild conditions or even at room temperature in contrast to the conventional carbon-coating process (>700 °C).¹²⁸⁻¹³¹ Several polymers have been studied for different battery electrode materials such as poly(3,4-ethylenedioxythiophene) (PEDOT),¹³¹ polypyrrole (PPy),¹³⁰ and PPy-doped PEG,¹³² which were shown to improve the electrochemical performance. Polymer coating increased their practical specific capacities, improved cycle life, rate capabilities and prevented side reactions on the surface.^{73, 125-127}

Among these conductive polymers, PEDOT appears to be the most effective surface modifier due to its structural stability and high electronic conductivity.¹²⁵⁻¹²⁷ An important attribute of these conductive polymers is that they can be engineered to provide highly continuous surface coverage with controllable nanoscale thickness.^{126-127, 133} For example, Lepage *et al.*¹³¹ applied PEDOT coating on LiFePO₄ (LFP) by inducing polymerization of 3,4-ethylenedioxythiophene



Figure 2.16. (a) Schematic illustration of the fabrication process of $Li_3V_2(PO_4)_3/PEDOT$ composite. (b) Specific discharge capacities and (c) cycle stability of PEDOT and carbon-coated $Li_3V_2(PO_4)_3$.¹³⁴

(EDOT) on the surface of partially de-lithiated LFP, which exhibited excellent cycling stability. Likewise, Kim *et al.*¹³⁴ adapted Lepage *et al.*'s method to produce polymer-coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ electrodes as shown in Figure 2.16a. As it is shown in Figure 2.16 b & c, the electrochemical properties of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ were significantly improved by coating it with the conducting polymer PEDOT.

Coating battery electrodes with PEDOT has been extended to different materials and techniques. Thus Li *et al.*¹³⁵ synthesized sulfur-impregnated carbon clusters for Li–S batteries using polymer coating (PEDOT), with the resulting cathode delivering much better performance than the uncoated cathode. In the meantime, Sobkowiak *et al.*¹³³ demonstrated the use of PEDOT coating for LiFeSO₄F materials using the *in-situ* coating approach of EDOT polymerization. Recently Xu *et al.*¹²⁷ used an oxidative chemical vapour deposition (oCVP) technique to build a protective conductive polymer (PEDOT) skin on layered oxide cathode materials. This technique
helped them coat the polymer on both primary and secondary nanoparticles as shown in Figure 2.17. The ultraconformal polymer coating was found to facilitate the transport of lithium ions and electrons, significantly suppressing the undesired layered to spinel/rock-salt phase transformation and the associated oxygen loss. In summary, nanosizing, carbon and polymer surface coating are very important material modification strategies for battery materials to enhance their electrochemical performances.



Figure 2.17. An illustration of the structural stability of both secondary/primary particle coating and secondary particle coating after long-term cycling with no cracks, whereas only secondary particle coating after long-term cycling shown significant amount of cracks.¹²⁷

2.8. Summary

Presently, all commercial cathodes have intrinsic limitations in terms of capacity, structural stability, cost, and safety. As an alternative, lithium iron silicate (Li₂FeSiO₄) is a promising cathode for LIBs due to its high theoretical specific energy (1120 Wh kg⁻¹), good structural & thermal stability, recourse abundance (Fe & Si) and low cost. However, their commercial development is hampered by several issues such as irreversible phase transition during cycling, rate-dependency, low intrinsic conductivity, Fe³⁺/Fe⁴⁺ redox participation during cycling and complex polymorphism. These issues are still not fully understood even after extensive research for more than a decade. Therefore, there are still several knowledge gaps that need to be overcome in order to achieve the full high-energy density potential of LFS cathodes.

To date, among the different crystal phases of LFS, it is the high-temperature monoclinic phase that has been mostly studied due to the relatively high initial capacity (≥ 1 Li). However, phase-pure monoclinic material is difficult to produce due to close energetics with the orthorhombic phase on one hand while on the other during cycling it transforms to the thermodynamically stable "inverse" low-temperature orthorhombic phase (*Pmn2*₁). Consequently, this phase might hold the key to unleash the full potential of LFS for LIBs. However, the singlephase low-temperature orthorhombic LFS (*Pmn2*₁) phase has not been studied extensively due to relatively poor initial Li-storage capacity (< 1 Li). There are very few systematic reports on mechanochemical crystal modification and interfacial engineering linked to the electrochemistry of LFS. While nanosizing has proven to play a key role in improving lithium diffusivity into several electrode materials including LFS the structural modification induced by high-energy milling remains largely unexplored as means of "activating" the intercalation kinetics of LFS. Effective high-energy milling for particle size reduction and nanostructuring needs extensive study of several parameters as discussed in detail in section (2.7.1). In response to this need, in chapter 3, the mechanochemistry of low-T orthorhombic LFS is investigated.

Carbon coating has been proven to be an effective technique to improve the electronic conductivity for several cathode materials. Typical carbon coating requires high-temperature (600 - 800 °C) for pyrolysis of organic compounds. In the case of low-T phase of LFS, this technique is not useful as it will lead to phase transition at this high-temperature due to very close formation

energy among different polymorphs. Alternatively, carbon coating may be applied by mechanical means during high-energy milling or replaced altogether by conductive polymer coating strategies. The first approach is investigated in chapter 4 in connection to phase transitions happening during cycling that lead to unusual progressive capacity increase. Meanwhile conductive polymer coatings offer the possibility not only to enhance the electronic conductivity but also to prevent parasitic reaction with the electrolyte. Currently, there are no reports in the literature where LFS is coated with such conductive polymer coating. This approach is explored in Chapter 5.

2.9. References

1. Nitta, N.; Wu, F.; Lee, J. T.; Yushin, G., Li-ion battery materials: present and future. *Mater. Today* **2015**, *18* (5), 252-264.

2. Tarascon, J.-M.; Armand, M., Issues and challenges facing rechargeable lithium batteries. In *Materials for Sustainable Energy: A Collection of Peer-Reviewed Research and Review Articles from Nature Publishing Group*, World Scientific: 2011; pp 171-179.

3. Li, M.; Lu, J.; Chen, Z.; Amine, K., 30 years of lithium-ion batteries. *Adv. Mater.* **2018**, *30* (33), 1800561.

4. Zubi, G.; Dufo-López, R.; Carvalho, M.; Pasaoglu, G., The lithium-ion battery: State of the art and future perspectives. *Renew. Sustain. Energy Rev.* **2018**, *89*, 292-308.

5. Whittingham, M. S.; Gamble Jr, F. R., The lithium intercalates of the transition metal dichalcogenides. *Mater. Res. Bull.* **1975**, *10* (5), 363-371.

6. Whittingham, M. S., Chalcogenide battery. Google Patents: 1977.

7. Whittingham, M. S., The role of ternary phases in cathode reactions. *J. Electrochem. Soc.* **1976**, *123* (3), 315-320.

8. Lazzari, M.; Scrosati, B., A cyclable lithium organic electrolyte cell based on two intercalation electrodes. *J. Electrochem. Soc.* **1980**, *127* (3), 773-774.

9. Armand, M., Intercalation electrodes. In *Materials for advanced batteries*, Springer: 1980; pp 145-161.

10. Scrosati, B., Lithium rocking chair batteries: an old concept? *J. Electrochem. Soc.* **1992**, *139* (10), 2776-2781.

11. Mizushima, K.; Jones, P.; Wiseman, P.; Goodenough, J. B., Li_xCoO_2 (0< x<-1): A new cathode material for batteries of high energy density. *Mater. Res. Bull.* **1980**, *15* (6), 783-789.

12. Thackeray, M.; David, W.; Bruce, P.; Goodenough, J. B., Lithium insertion into manganese spinels. *Mater. Res. Bull.* **1983**, *18* (4), 461-472.

13. Yoshino, A., The birth of the lithium-ion battery. Angew. Chem. 2012, 51 (24), 5798-5800.

14. Blomgren, G. E., The development and future of lithium ion batteries. *J. Electrochem. Soc.* **2017**, *164* (1), A5019-A5025.

15. The Nobel Prize in Chemistry 2019. https://www.nobelprize.org/prizes/chemistry/2019/summary/.

16. Liang, S.; Yan, W.; Wu, X.; Zhang, Y.; Zhu, Y.; Wang, H.; Wu, Y., Gel polymer electrolytes for lithium ion batteries: Fabrication, characterization and performance. *Solid State Ion.* **2018**, *318*, 2-18.

17. Lu, L., *Recent advances in energy storage materials and devices*. Materials Research Forum: 2017.

18. Schmuch, R.; Wagner, R.; Hörpel, G.; Placke, T.; Winter, M., Performance and cost of materials for lithium-based rechargeable automotive batteries. *Nat. Energy* **2018**, *3* (4), 267-278.

19. Electric cars could charge in 10 minutes with a new kind of battery

https://www.newscientist.com/article/2221740-electric-cars-could-charge-in-10-minutes-with-anew-kind-of-battery/

20. BU-105: Battery Definitions and what they mean. https://batteryuniversity.com/learn/article/battery_definitions.

21. Balasubramanian, M.; Lee, H. S.; Sun, X.; Yang, X.-Q.; Moodenbaugh, A.; McBreen, J.; Fischer, D. A.; Fu, Z., Formation of SEI on cycled lithium-ion battery cathodes: Soft X-ray absorption study. *Electrochem. Solid-State Lett.* **2002**, *5* (1), A22-A25.

22. Andre, D.; Kim, S.-J.; Lamp, P.; Lux, S. F.; Maglia, F.; Paschos, O.; Stiaszny, B., Future generations of cathode materials: an automotive industry perspective. *J. Mater. Chem. A* **2015**, *3* (13), 6709-6732.

23. Pillot, C. In *Lithium ion battery raw material supply & demand 2016–2025*, Proceedings of the Advanced Automotive Battery Conference, Mainz, Germany, 2017.

24. Aurbach, D.; Markovsky, B.; Rodkin, A.; Levi, E.; Cohen, Y.; Kim, H.-J.; Schmidt, M., On the capacity fading of LiCoO₂ intercalation electrodes:: the effect of cycling, storage, temperature, and surface film forming additives. *Electrochim. Acta* **2002**, *47* (27), 4291-4306.

25. Lu, Z.; Chen, G.; Li, Y.; Wang, H.; Xie, J.; Liao, L.; Liu, C.; Liu, Y.; Wu, T.; Li, Y., Identifying the active surfaces of electrochemically tuned LiCoO₂ for oxygen evolution reaction. *J. Am. Chem. Soc.* **2017**, *139* (17), 6270-6276.

26. Reinhardt, R.; García, B. A.; Casals, L. C.; Domingo, S. G., A critical evaluation of cathode materials for lithium-ion electric vehicle batteries. In *Project Management and Engineering Research*, Springer: 2019; pp 99-110.

27. Zhang, H.; Zhao, H.; Khan, M. A.; Zou, W.; Xu, J.; Zhang, L.; Zhang, J., Recent progress in advanced electrode materials, separators and electrolytes for lithium batteries. *J. Mater. Chem. A* **2018**, *6* (42), 20564-20620.

28. Zhang, T.; Li, D.; Tao, Z.; Chen, J., Understanding electrode materials of rechargeable lithium batteries via DFT calculations. *Progress in Natural Science: Materials International* **2013**, *23* (3), 256-272.

29. Noh, H.-J.; Youn, S.; Yoon, C. S.; Sun, Y.-K., Comparison of the structural and electrochemical properties of layered $Li[Ni_xCo_yMn_z]O_2$ (x=1/3, 0.5, 0.6, 0.7, 0.8 and 0.85) cathode material for lithium-ion batteries. *J. Power Sources* **2013**, *233*, 121-130.

30. Dixit, M.; Markovsky, B.; Schipper, F.; Aurbach, D.; Major, D. T., Origin of structural degradation during cycling and low thermal stability of Ni-rich layered transition metal-based electrode materials. *J. Phys. Chem. C* **2017**, *121* (41), 22628-22636.

31. Xu, J.; Lin, F.; Doeff, M. M.; Tong, W., A review of Ni-based layered oxides for rechargeable Li-ion batteries. *J. Mater. Chem. A* **2017**, *5* (3), 874-901.

32. Zhou, P.; Meng, H.; Zhang, Z.; Chen, C.; Lu, Y.; Cao, J.; Cheng, F.; Chen, J., Stable layered Ni-rich LiNi_{0.9}Co_{0.07}Al_{0.03}O₂ microspheres assembled with nanoparticles as high-performance cathode materials for lithium-ion batteries. *J. Mater. Chem. A* **2017**, *5* (6), 2724-2731.

33. Shi, J.-L.; Qi, R.; Zhang, X.-D.; Wang, P.-F.; Fu, W.-G.; Yin, Y.-X.; Xu, J.; Wan, L.-J.; Guo, Y.-G., High-thermal-and air-stability cathode material with concentration-gradient buffer for Liion batteries. *ACS Appl. Mater. Interfaces* **2017**, *9* (49), 42829-42835.

34. Ouyang, C.; Shi, S.; Lei, M., Jahn–Teller distortion and electronic structure of LiMn₂O₄. *J. Alloys Compd.* **2009**, *474* (1-2), 370-374.

35. Padhi, A. K.; Nanjundaswamy, K.; Goodenough, J., Phospho-olivines as positive-electrode materials for rechargeable lithium batteries. *J. Electrochem. Soc.* **1997**, *144* (4), 1188-1194.

Yuan, L.-X.; Wang, Z.-H.; Zhang, W.-X.; Hu, X.-L.; Chen, J.-T.; Huang, Y.-H.; Goodenough,
J. B., Development and challenges of LiFePO₄ cathode material for lithium-ion batteries. *Energy Environ. Sci.* 2011, *4* (2), 269-284.

37. Julien, C. M.; Zaghib, K.; Mauger, A.; Massot, M.; Ait-Salah, A.; Selmane, M.; Gendron, F., Characterization of the carbon coating onto LiFePO₄ particles used in lithium batteries. *J. Appl. Phys.* **2006**, *100* (6), 063511.

38. Whittingham, M. S., Lithium Batteries and Cathode Materials. *Chem. Rev.* 2004, *104* (10), 4271-4302.

39. Whittingham, M. S.; Zawodzinski, T., Introduction: Batteries and Fuel Cells. *Chem. Rev.* 2004, *104* (10), 4243-4244.

40. Simoneau, M.; Hovington, P.; Armand, M.; Michot, C.; Ravet, N.; Christopher, M. New lithium insertion-type electrode material with an orthosilicate structure for use in redox reactions. US6085015-A, 04 Jul 2000.

41. Ni, J. F.; Jiang, Y.; Bi, X. X.; Li, L.; Lu, J., Lithium Iron Orthosilicate Cathode: Progress and Perspectives. *ACS Energy Lett.* **2017**, *2* (8), 1771-1781.

42. Sirisopanaporn, C.; Dominko, R.; Masquelier, C.; Armstrong, A. R.; Mali, G.; Bruce, P. G., Polymorphism in Li₂(Fe,Mn)SiO₄: A combined diffraction and NMR study. *J. Mater. Chem.* **2011**, *21* (44), 17823-17831.

43. Eames, C.; Armstrong, A. R.; Bruce, P. G.; Islam, M. S., Insights into Changes in Voltage and Structure of Li₂FeSiO₄ Polymorphs for Lithium-Ion Batteries. *Chem. Mater.* **2012**, *24* (11), 2155-2161.

44. Nishimura, S.-i.; Hayase, S.; Kanno, R.; Yashima, M.; Nakayama, N.; Yamada, A., Structure of Li₂FeSiO₄. *J. Am. Chem. Soc.* **2008**, *130* (40), 13212-13213.

45. Lu, X.; Chiu, H.-C.; Bevan, K. H.; Jiang, D.-T.; Zaghib, K.; Demopoulos, G. P., Density functional theory insights into the structural stability and Li diffusion properties of monoclinic and orthorhombic Li₂FeSiO₄ cathodes. *J. Power Sources* **2016**, *318*, 136-145.

46. Sirisopanaporn, C.; Dominko, R.; Masquelier, C.; Armstrong, A. R.; Mali, G.; Bruce, P. G., Polymorphism in Li₂(Fe, Mn)SiO₄: A combined diffraction and NMR study. *J. Mater. Chem.*2011, 21 (44), 17823-17831.

47. Zeng, Y.; Chiu, H.-C.; Rasool, M.; Brodusch, N.; Gauvin, R.; Jiang, D.-T.; Ryan, D. H.; Zaghib, K.; Demopoulos, G. P., Hydrothermal crystallization of Pmn2₁ Li₂FeSiO₄ hollow mesocrystals for Li-ion cathode application. *Chem. Eng. J.* **2019**, *359*, 1592-1602.

48. Lu, X.; Wei, H.; Chiu, H.-C.; Gauvin, R.; Hovington, P.; Guerfi, A.; Zaghib, K.; Demopoulos, G. P., Rate-dependent phase transitions in Li₂FeSiO₄ cathode nanocrystals. *Sci. Rep.* **2015**, *5*, 8599.

49. Chen, R.; Heinzmann, R.; Mangold, S.; Chakravadhanula, V. S. K.; Hahn, H.; Indris, S., Structural Evolution of $Li_2Fe_{1-y}MnySiO_4$ (y = 0, 0.2, 0.5, 1) Cathode Materials for Li-Ion Batteries upon Electrochemical Cycling. *J. Phys. Chem. C* **2013**, *117* (2), 884-893.

50. Nytén, A.; Abouimrane, A.; Armand, M.; Gustafsson, T.; Thomas, J. O., Electrochemical performance of Li₂FeSiO₄ as a new Li-battery cathode material. *Electrochem. Commun.* 2005, 7 (2), 156-160.

51. Sirisopanaporn, C.; Masquelier, C.; Bruce, P. G.; Armstrong, A. R.; Dominko, R., Dependence of Li₂FeSiO₄ Electrochemistry on Structure. *J. Am. Chem. Soc.* **2011**, *133* (5), 1263-1265.

52. Dominko, R.; Conte, D.; Hanzel, D.; Gaberscek, M.; Jamnik, J., Impact of synthesis conditions on the structure and performance of Li₂FeSiO₄. *J. Power Sources* **2008**, *178* (2), 842-847.

53. Muraliganth, T.; Stroukoff, K. R.; Manthiram, A., Microwave-Solvothermal Synthesis of Nanostructured Li_2MSiO_4/C (M = Mn and Fe) Cathodes for Lithium-Ion Batteries. *Chem. Mater.* **2010**, *22* (20), 5754-5761.

54. Yabuuchi, N.; Yamakawa, Y.; Yoshii, K.; Komaba, S., Low-temperature phase of Li₂FeSiO₄: crystal structure and a preliminary study of electrochemical behavior. *Dalton Trans.* **2011**, *40* (9), 1846-1848.

55. Zaghib, K.; Ait Salah, A.; Ravet, N.; Mauger, A.; Gendron, F.; Julien, C. M., Structural, magnetic and electrochemical properties of lithium iron orthosilicate. *J. Power Sources* 2006, *160* (2), 1381-1386.

56. Dominko, R.; Conte, D. E.; Hanzel, D.; Gaberscek, M.; Jamnik, J., Impact of synthesis conditions on the structure and performance of Li₂FeSiO₄. *J. Power Sources* **2008**, *178* (2), 842-847.

57. Sirisopanaporn, C.; Masquelier, C.; Bruce, P. G.; Armstrong, A. R.; Dominko, R., Dependence of Li₂FeSiO₄ Electrochemistry on Structure. *J. Am. Chem. Soc.* **2011**, *133* (5), 1263-1265.

58. Islam, M. S.; Dominko, R.; Masquelier, C.; Sirisopanaporn, C.; Armstrong, A. R.; Bruce, P. G., Silicate cathodes for lithium batteries: alternatives to phosphates? *J. Mater. Chem.* 2011, *21* (27), 9811-9818.

59. Zhou, H.; Einarsrud, M.-A.; Vullum-Bruer, F., In situ X-ray diffraction and electrochemical impedance spectroscopy of a nanoporous Li₂FeSiO₄/C cathode during the initial charge/discharge cycle of a Li-ion battery. *J. Power Sources* **2013**, *238*, 478-484.

60. Xu, K., Electrolytes and Interphases in Li-Ion Batteries and Beyond. *Chem. Rev.* 2014, *114* (23), 11503-11618.

61. Zhao, Y.; Li, J.; Wang, N.; Wu, C.; Ding, Y.; Guan, L., In situ generation of Li₂FeSiO₄ coating on MWNT as a high rate cathode material for lithium ion batteries. *J. Mater. Chem.* **2012**, *22* (36), 18797-18800.

62. Lu, X.; Chiu, H.-C.; Arthur, Z.; Zhou, J.; Wang, J.; Chen, N.; Jiang, D.-T.; Zaghib, K.; Demopoulos, G. P., Li-ion storage dynamics in metastable nanostructured Li₂FeSiO₄ cathode:

Antisite-induced phase transition and lattice oxygen participation. J. Power Sources 2016, 329, 355-363.

63. Masese, T.; Tassel, C. d.; Orikasa, Y.; Koyama, Y.; Arai, H.; Hayashi, N.; Kim, J.; Mori, T.; Yamamoto, K.; Kobayashi, Y., Crystal structural changes and charge compensation mechanism during two lithium extraction/insertion between Li₂FeSiO4 and FeSiO4. *J. Phys. Chem. C* **2015**, *119* (19), 10206-10211.

64. Lv, D.; Bai, J.; Zhang, P.; Wu, S.; Li, Y.; Wen, W.; Jiang, Z.; Mi, J.; Zhu, Z.; Yang, Y., Understanding the high capacity of Li₂FeSiO₄: in situ XRD/XANES study combined with first-principles calculations. *Chem. Mater.* **2013**, *25* (10), 2014-2020.

65. Singh, S.; Panda, M. R.; Sen, R.; Johari, P.; Sinha, A.; Meena, S. S.; Mitra, S., Study of Higher Discharge Capacity, Phase Transition, and Relative Structural Stability in Li₂FeSiO₄ Cathode upon Lithium Extraction Using an Experimental and Theoretical Approach and Full Cell Prototype Study. *ACS Appl. Energy Mater.* **2019**, *2* (9), 6584-6598.

66. Ding, Z.; Zhang, D.; Feng, Y.; Zhang, F.; Chen, L.; Du, Y.; Ivey, D. G.; Wei, W., Tuning anisotropic ion transport in mesocrystalline lithium orthosilicate nanostructures with preferentially exposed facets. *NPG Asia Mater.* **2018**, *10* (7), 606.

67. Liivat, A.; Thomas, J. O., Li-ion migration in Li₂FeSiO₄-related cathode materials: A DFT study. *Solid State Ion.* **2011**, *192* (1), 58-64.

68. Armstrong, A. R.; Kuganathan, N.; Islam, M. S.; Bruce, P. G., Structure and Lithium Transport Pathways in Li₂FeSiO₄ Cathodes for Lithium Batteries. *J. Am. Chem. Soc.* **2011**, *133* (33), 13031-13035.

69. Lv, X.; Zhao, X.; Wu, S.; Nguyen, M. C.; Zhu, Z.; Lin, Z.; Wang, C.-Z.; Ho, K.-M., Fe–Si networks and charge/discharge-induced phase transitions in Li₂FeSiO₄ cathode materials. *Phys. Chem. Chem. Phys.* **2018**, *20* (21), 14557-14563.

70. Yang, J. L.; Zheng, J. X.; Kang, X. C.; Teng, G. F.; Hu, L.; Tan, R.; Wang, K.; Song, X. H.; Xu, M.; Mu, S. C.; Pan, F., Tuning structural stability and lithium-storage properties by d-orbital hybridization substitution in full tetrahedron Li₂FeSiO₄ nanocrystal. *Nano Energy* **2016**, *20*, 117-125.

71. Kojima, A.; Kojima, T.; Sakai, T., Structural analysis during charge-discharge process of Li₂FeSiO₄ synthesized by molten carbonate flux method. *J. Electrochem. Soc.* **2012**, *159* (5), A525-A531.

72. Masese, T.; Orikasa, Y.; Tassel, C.; Kim, J.; Minato, T.; Arai, H.; Mori, T.; Yamamoto, K.; Kobayashi, Y.; Kageyama, H.; Ogumi, Z.; Uchimoto, Y., Relationship between Phase Transition Involving Cationic Exchange and Charge-Discharge Rate in Li₂FeSiO₄. *Chem. Mater.* **2014**, *26* (3), 1380-1384.

73. Wang, K. X.; Li, X. H.; Chen, J. S., Surface and interface engineering of electrode materials for lithium-ion batteries. *Adv. Mater.* **2015**, *27* (3), 527-545.

74. Chen, Z.; Qin, Y.; Amine, K.; Sun, Y.-K., Role of surface coating on cathode materials for lithium-ion batteries. *J. Mater. Chem.* **2010**, *20* (36), 7606-7612.

75. Lee, K. T.; Cho, J., Roles of nanosize in lithium reactive nanomaterials for lithium ion batteries. *Nano Today* **2011**, *6* (1), 28-41.

76. Wang, Y.; Li, H.; He, P.; Hosono, E.; Zhou, H., Nano active materials for lithium-ion batteries. *Nanoscale* **2010**, *2* (8), 1294-1305.

77. Centi, G.; Perathoner, S., The role of nanostructure in improving the performance of electrodes for energy storage and conversion. *Eur. J. Inorg. Chem.* **2009**, *2009* (26), 3851-3878.

78. Gaberscek, M.; Dominko, R.; Jamnik, J., Is small particle size more important than carbon coating? An example study on LiFePO₄ cathodes. *Electrochem. Commun.* **2007**, *9* (12), 2778-2783.

79. Araujo, R. B.; Scheicher, R. H.; de Almeida, J.; da Silva, A. F.; Ahuja, R., First-principles investigation of Li ion diffusion in Li₂FeSiO₄. *Solid State Ion*. **2013**, *247*, 8-14.

80. Araujo, R. B.; Scheicher, R. H.; De Almeida, J.; da Silva, A. F.; Ahuja, R., Lithium transport investigation in Li_xFeSiO₄: A promising cathode material. *Solid State Commun.* **2013**, *173*, 9-13.

81. Pei, B.; Yao, H.; Zhang, W.; Yang, Z., Hydrothermal synthesis of morphology-controlled LiFePO₄ cathode material for lithium-ion batteries. *J. Power Sources* **2012**, *220*, 317-323.

82. Meligrana, G.; Gerbaldi, C.; Tuel, A.; Bodoardo, S.; Penazzi, N., Hydrothermal synthesis of high surface LiFePO₄ powders as cathode for Li-ion cells. *J. Power Sources* **2006**, *160* (1), 516-522.

83. Brochu, F.; Guerfi, A.; Trottier, J.; Kopeć, M.; Mauger, A.; Groult, H.; Julien, C.; Zaghib, K., Structure and electrochemistry of scaling nano C–LiFePO₄ synthesized by hydrothermal route: complexing agent effect. *J. Power Sources* **2012**, *214*, 1-6.

84. Baláž, P.; Achimovičová, M.; Baláž, M.; Billik, P.; Cherkezova-Zheleva, Z.; Criado, J. M.; Delogu, F.; Dutková, E.; Gaffet, E.; Gotor, F. J., Hallmarks of mechanochemistry: from nanoparticles to technology. *Chem. Soc. Rev.* **2013**, *42* (18), 7571-7637.

85. Gilman, J. J., Mechanochemistry. Science 1996, 274 (5284), 65-65.

86. Bowmaker, G. A., Solvent-assisted mechanochemistry. ChemComm 2013, 49 (4), 334-348.

87. Muralidharan, N.; Brock, C. N.; Cohn, A. P.; Schauben, D.; Carter, R. E.; Oakes, L.; Walker, D. G.; Pint, C. L., Tunable mechanochemistry of lithium battery electrodes. *ACS nano* 2017, *11* (6), 6243-6251.

88. Baláž, P., Mechanochemistry in Minerals Engineering. In *Mechanochemistry in Nanoscience* and *Minerals Engineering*, Springer: 2008; pp 110 - 125.

89. James, S. L.; Adams, C. J.; Bolm, C.; Braga, D.; Collier, P.; Friščić, T.; Grepioni, F.; Harris, K. D.; Hyett, G.; Jones, W., Mechanochemistry: opportunities for new and cleaner synthesis. *Chem. Soc. Rev.* 2012, *41* (1), 413-447.

90. James, S. L.; Friščić, T., Mechanochemistry. Chem. Soc. Rev. 2013, 42 (18), 7494-7496.

91. Janot, R.; Guérard, D., Ball-milling in liquid media: Applications to the preparation of anodic materials for lithium-ion batteries. *Prog. Mater. Sci.* **2005**, *50* (1), 1-92.

92. Balogh, J.; Bujdoso, L.; Kaptas, D.; Kemeny, T.; Vincze, I. In *The role of impurities in the crystallization of ball-milled amorphous alloys*, Materials science forum, Trans Tech Publ: 1998; pp 63-68.

93. Streletskii, A.; Permenov, D.; Bokhonov, B.; Kolbanev, I.; Leonov, A.; Berestetskaya, I.; Streletzky, K. A., Destruction, amorphization and reactivity of nano-BN under ball milling. *J. Alloys Compd.* **2009**, *483* (1-2), 313-316.

94. Noh, J.-K.; Kim, S.; Kim, H.; Choi, W.; Chang, W.; Byun, D.; Cho, B.-W.; Chung, K. Y., Mechanochemical synthesis of Li₂MnO₃ shell/LiMO₂ (M= Ni, Co, Mn) core-structured nanocomposites for lithium-ion batteries. *Sci. Rep.* **2014**, *4*, 4847.

95. Shin, H. C.; Park, S. B.; Jang, H.; Chung, K. Y.; Cho, W. I.; Kim, C. S.; Cho, B. W., Rate performance and structural change of Cr-doped LiFePO₄/C during cycling. *Electrochim. Acta* **2008**, *53* (27), 7946-7951.

96. Kim, Y.-U.; Cho, B. W.; Sohn, H.-J., The Reaction Mechanism of Lithium Insertion in Vanadium Tetraphosphide A Possible Anode Material in Lithium-Ion Batteries. *J. Electrochem. Soc.* **2005**, *152* (8), A1475-A1478.

97. Woo, S.-g.; Jung, J.-H.; Kim, H.; Kim, M. G.; Lee, C. K.; Sohn, H.-J.; Cho, B. W., Electrochemical characteristics of Ti–P composites prepared by mechanochemical synthesis. *J. Electrochem. Soc.* **2006**, *153* (10), A1979-A1983.

98. Oh, S. H.; Jeon, S. H.; Cho, W. I.; Kim, C. S.; Cho, B. W., Synthesis and characterization of the metal-doped high-voltage spinel LiNi_{0. 5}Mn_{1. 5}O₄ by mechanochemical process. *J. Alloys Compd.* **2008**, *452* (2), 389-396.

99. Kim, S.; Noh, J.-K.; Yu, S.; Chang, W.; Chung, K. Y.; Cho, B.-W., Effects of transition metal doping and surface treatment to improve the electrochemical performance of Li₂MnO₃. *J. Electroceramics* **2013**, *30* (3), 159-165.

100. Kim, S.; Kim, C.; Noh, J.-K.; Yu, S.; Kim, S.-J.; Chang, W.; Choi, W. C.; Chung, K. Y.; Cho, B.-W., Synthesis of layered–layered $xLi_2MnO_3 \cdot (1-x)LiMO_2$ (M= Mn, Ni, Co) nanocomposite electrodes materials by mechanochemical process. *J. Power Sources* **2012**, *220*, 422-429.

101. Kim, S.; Kim, C.; Jhon, Y.-I.; Noh, J.-K.; Vemuri, S. H.; Smith, R.; Chung, K. Y.; Jhon, M. S.; Cho, B.-W., Synthesis of layered–layered _{0.5}Li₂MnO₃. _{0.5}LiCoO₂ nanocomposite electrode materials by the mechanochemical process and first principles study. *J. Mater. Chem.* **2012**, *22* (48), 25418-25426.

102. Djekoun, A.; Otmani, A.; Bouzabata, B.; Bechiri, L.; Randrianantoandro, N.; Greneche, J., Synthesis and characterization of high-energy ball milled nanostructured Fe₅₀Ni₅₀. *Catal. Today* **2006**, *113* (3-4), 235-239.

103. Buschmann, H.; Dölle, J.; Berendts, S.; Kuhn, A.; Bottke, P.; Wilkening, M.; Heitjans, P.; Senyshyn, A.; Ehrenberg, H.; Lotnyk, A., Structure and dynamics of the fast lithium ion conductor "Li₇La₃Zr₂O₁₂". *Phys. Chem. Chem. Phys.* **2011**, *13* (43), 19378-19392.

104. Gotor, F.; Achimovicova, M.; Real, C.; Balaz, P., Influence of the milling parameters on the mechanical work intensity in planetary mills. *Powder Technology* **2013**, *233*, 1-7.

105. De Carvalho, J.; De Medeiros, S.; Morales, M.; Dantas, A.; Carriço, A., Synthesis of magnetite nanoparticles by high energy ball milling. *Appl. Surf. Sci.* **2013**, *275*, 84-87.

106. Rabanal, M.; Gutierrez, M.; Garcia-Alvarado, F.; Gonzalo, E.; Arroyo-de Dompablo, M., Improved electrode characteristics of olivine–LiCoPO₄ processed by high energy milling. *J. Power Sources* **2006**, *160* (1), 523-528.

107. Prabhu, B.; Suryanarayana, C.; An, L.; Vaidyanathan, R., Synthesis and characterization of high volume fraction Al–Al₂O₃ nanocomposite powders by high-energy milling. *Mater. Sci. Eng. A* **2006**, *425* (1-2), 192-200.

108. Zhang, Q.; Saito, F., Mechanochemical synthesis of LaMnO₃ from La₂O₃ and Mn₂O₃ powders. *J. Alloys Compd.* **2000**, *297* (1-2), 99-103.

109. Wang, J.; Sun, X., Understanding and recent development of carbon coating on LiFePO₄ cathode materials for lithium-ion batteries. *Energy Environ. Sci.* **2012**, *5* (1), 5163-5185.

110. Li, H.; Zhou, H., Enhancing the performances of Li-ion batteries by carbon-coating: present and future. *ChemComm* **2012**, *48* (9), 1201-1217.

111. Gong, Z. L.; Yang, Y., Recent advances in the research of polyanion-type cathode materials for Li-ion batteries. *Energy Environ. Sci.* **2011**, *4* (9), 3223-3242.

112. Marcinek, M. L.; Wilcox, J. W.; Doeff, M. M.; Kostecki, R. M., Microwave plasma chemical vapor deposition of carbon coatings on LiNi_{V3}Co_{V3}Mn_{V3}O₂ for Li-ion battery composite cathodes. *J. Electrochem. Soc.* **2009**, *156* (1), A48-A51.

113. Lin, B.; Wen, Z.; Han, J.; Wu, X., Electrochemical properties of carbon-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ cathode material for lithium-ion batteries. *Solid State Ion.* **2008**, *179* (27-32), 1750-1753.

114. Patey, T. J.; Büchel, R.; Ng, S.; Krumeich, F.; Pratsinis, S. E.; Novák, P., Flame co-synthesis of LiMn₂O₄ and carbon nanocomposites for high power batteries. *J. Power Sources* **2009**, *189* (1), 149-154.

115. Lu, C.-Z.; Fey, G. T.-K.; Kao, H.-M., Study of LiFePO₄ cathode materials coated with high surface area carbon. *J. Power Sources* **2009**, *189* (1), 155-162.

116. Joachin, H.; Kaun, T. D.; Zaghib, K.; Prakash, J., Electrochemical and thermal studies of carbon-coated LiFePO₄ cathode. *J. Electrochem. Soc.* **2009**, *156* (6), A401-A406.

117. Chen, Z.-y.; Zhu, H.-l.; Ji, S.; Fakir, R.; Linkov, V., Influence of carbon sources on electrochemical performances of LiFePO₄/C composites. *Solid State Ion.* **2008**, *179* (27), 1810-1815.

118. Yan, X.; Yang, G.; Liu, J.; Ge, Y.; Xie, H.; Pan, X.; Wang, R., An effective and simple way to synthesize LiFePO₄/C composite. *Electrochim. Acta* **2009**, *54* (24), 5770-5774.

119. Ong, C.-W.; Lin, Y.-K.; Chen, J.-S., Effect of Various Organic Precursors on the Performance of LiFePO₄/C Composite Cathode by Coprecipitation Method. *J. Electrochem. Soc.* 2007, *154* (6), A527-A533.

120. Shin, H. C.; Cho, W. I.; Jang, H., Electrochemical properties of carbon-coated LiFePO₄ cathode using graphite, carbon black, and acetylene black. *Electrochim. Acta* **2006**, *52* (4), 1472-1476.

121. Chen, Z.; Dahn, J., Reducing carbon in LiFePO₄/C composite electrodes to maximize specific energy, volumetric energy, and tap density. *J. Electrochem. Soc.* **2002**, *149* (9), A1184-A1189.

122. Rui, X. H.; Li, C.; Chen, C. H., Synthesis and characterization of carbon-coated $Li_3V_2(PO_4)_3$ cathode materials with different carbon sources. *Electrochim. Acta* **2009**, *54* (12), 3374-3380.

123. Wang, Y.; Wang, Y.; Hosono, E.; Wang, K.; Zhou, H., The design of a LiFePO₄/carbon nanocomposite with a core–shell structure and its synthesis by an in situ polymerization restriction method. *Angew. Chem.* **2008**, *47* (39), 7461-7465.

124. Venkateswara Rao, C.; Leela Mohana Reddy, A.; Ishikawa, Y.; Ajayan, P. M., LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂–graphene composite as a promising cathode for Lithium-ion batteries. *ACS Appl. Mater. Interfaces* **2011**, *3* (8), 2966-2972.

125. Ouyang, J., Recent Advances of Intrinsically Conductive Polymers. *Acta Phys. Chim. Sin* **2018**, *34* (11), 1211-1220.

126. Kirchmeyer, S.; Reuter, K., Scientific importance, properties and growing applications of poly (3, 4-ethylenedioxythiophene). *J. Mater. Chem.* **2005**, *15* (21), 2077-2088.

127. Xu, G.-L.; Liu, Q.; Lau, K. K.; Liu, Y.; Liu, X.; Gao, H.; Zhou, X.; Zhuang, M.; Ren, Y.; Li, J., Building ultraconformal protective layers on both secondary and primary particles of layered lithium transition metal oxide cathodes. *Nat. Energy* **2019**, *4*, 484–494.

128. Yano, H.; Kudo, K.; Marumo, K.; Okuzaki, H., Fully soluble self-doped poly (3, 4ethylenedioxythiophene) with an electrical conductivity greater than 1000 S cm⁻¹. *Sci. Adv.* **2019**, *5* (4), eaav9492.

129. Zeng, W.; Wang, L.; Peng, X.; Liu, T.; Jiang, Y.; Qin, F.; Hu, L.; Chu, P. K.; Huo, K.; Zhou, Y., Enhanced Ion Conductivity in Conducting Polymer Binder for High-Performance Silicon Anodes in Advanced Lithium-Ion Batteries. *Adv. Energy Mater.* **2018**, *8* (11), 1702314.

130. Park, K. S.; Schougaard, S. B.; Goodenough, J. B., Conducting-polymer/iron-redox-couple composite cathodes for lithium secondary batteries. *Adv. Mater.* **2007**, *19* (6), 848-851.

131. Lepage, D.; Michot, C.; Liang, G.; Gauthier, M.; Schougaard, S. B., A soft chemistry approach to coating of LiFePO₄ with a conducting polymer. *Angew. Chem.* **2011**, *50* (30), 6884-6887.

132. Fedorková, A.; Oriňáková, R.; Oriňák, A.; Talian, I.; Heile, A.; Wiemhöfer, H.-D.; Kaniansky, D.; Arlinghaus, H. F., PPy doped PEG conducting polymer films synthesized on LiFePO₄ particles. *J. Power Sources* **2010**, *195* (12), 3907-3912.

133. Sobkowiak, A.; Roberts, M. R.; Younesi, R.; Ericsson, T.; Häggström, L.; Tai, C.-W.; Andersson, A. M.; Edström, K.; Gustafsson, T. r.; Björefors, F., Understanding and controlling the surface chemistry of LiFeSO₄F for an enhanced cathode functionality. *Chem. Mater.* **2013**, *25* (15), 3020-3029.

134. Kim, J.; Yoo, J. K.; Jung, Y. S.; Kang, K., Li₃V₂(PO₄)₃/Conducting Polymer as a High Power 4 V-Class Lithium Battery Electrode. *Adv. Energy Mater.* **2013**, *3* (8), 1004-1007.

135. Li, W.; Liang, Z.; Lu, Z.; Yao, H.; Seh, Z. W.; Yan, K.; Zheng, G.; Cui, Y., A sulfur cathode with pomegranate-like cluster structure. *Adv. Energy Mater.* **2015**, *5* (16), 1500211.

3. Mechanochemically-Tuned Structural Annealing

As reviewed in Chapter 2, LFS is a promising cathode material because of its theoretical energy density and sustainable features in terms of abundant element sourcing. However, its complex crystal structure in terms of polymorphs and evolution during cycling have hampered its development. Thus, in this chapter that reports the results from the first part of the thesis work, the focus is on studying the low-temperature orthorhombic phase of LFS in terms of hydrothermal synthesis & high-energy milling to control its size, morphology and crystal structure. Bulk material characterization is presented along with its in-depth analysis, performed via XRD, EBSD, SEM & TEM. High-energy milling (or otherwise known as mechanochemical processing) was employed for the purpose of nanosizing, aiming to improve the Li-ion diffusion kinetics-a well known strategy for Li-ion battery materials. Via systematic variation of milling conditions though the LFS nanocrystals (~50nm), nanosized within a certain window, were found to undergo structural annealing (a phenomenon not reported previously) manifested by lattice expansion, reduced defects and preferred crystal orientation. Electrochemical evaluation of the mechanochemically prepared LFS nanocrystals revealed enhanced Li-ion storage functionality-a discovery that is further explored in Chapters 4 and 5.

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3.1. Abstract

In this work, a relatively inactive cathode material, β_{II} orthorhombic Li₂FeSiO₄ with *Pmn2*₁ space group, is shown to undergo crystal structural changes when subjected to nanosizing by highenergy milling that have a pronounced activation impact on Li-ion intercalation electrochemistry. In particular, we present evidence of mechanically-induced structural annealing including lattice expansion, reduction of anti-site defects and preferred crystal orientation, opposite of what expected typically from nanosizing. As result of this type of unreported structural activation for orthosilicates, a threefold increase of the accessible discharge (=intercalation) capacity of the highenergy milled $Pmn2_1$ material is attained much higher than what would be expected solely from surface area increase due to nanosizing and surface area increase. Such mechanochemicallyinduced structural annealing activates Li-ion diffusion (one order of magnitude enhancement in D_{Li}) into less accessible sites via the combined effects of anti-site defect removal and modulation of the Fe-O coordination adjustment. Structural activation of intercalation materials via controlled mechanochemistry opens new possibilities in nanoengineering high energy density Li-ion storage electrodes.

3.2. Introduction

Lithium transition metal orthosilicates (LMS or Li_2MSiO_4 , where M = Fe, Mn or Co) have attracted much attention as they possess two lithium ions per formula unit hence double theoretical capacity (331 mAh g⁻¹) compared to currently commercialized intercalation cathode materials in Li-ion batteries (LIB).¹⁻⁴ Another attractive feature is their strong Si-O bonds in the polyoxyanionic framework that drastically enhance their thermal stability.⁴⁻⁵ LMS materials therefore are considered to have significant potential to develop into high energy density and safe cathodes for Li-ion battery technology. Among the orthosilicate cathode materials, Li_2FeSiO_4 (LFS) is of particular interest because of its inherent sustainability advantage made of abundant and benign silicon and iron elements. However, there are still major material chemistry challenges to render Li₂FeSiO₄ into high-performance cathode material.

Extensive research has shown that LFS crystallizes in various polymorphs belonging in two main structure types: one is the low-temperature orthorhombic (β_{II} , $Pmn2_1$) and the other is high-temperature monoclinic (γ_s , $P2_1/n$) form, respectively.^{2, 4, 6} Conventionally, the hightemperature monoclinic (γ_s , $P2_1/n$) is prepared by annealing in the temperature range of 600-800 °C,^{2, 6-9} while the low temperature orthorhombic LFS (β_{II} , $Pmn2_1$) is obtained at 200 °C by hydrothermal synthesis.^{6, 10-13} Of the two polymorphs it is the high-temperature monoclinic phase that has been studied as cathode with very little attention paid to the electrochemical performance of $Pmn2_1$ phase due to its reported low reversible capacity.^{1, 3, 10} Interestingly, all the recent theoretical and experimental studies indicate a phase transition from monoclinic $P2_1/n$ to thermodynamically stable inverse $Pmn2_1$ phase during charging/discharging.^{1, 8, 14-17} Notably, the inverse $Pmn2_1$ is isostructural with normal $Pmn2_1$. However, all the Fe have exchanged sites with half of Li. Therefore, from both practical and theoretical standpoints, the transition pathway of LFS going from monoclinic ($P2_1/n$) to orthorhombic phase ($Pmn2_1$), then eventually into the inverse $Pmn2_1$ seems rather energy inefficient and strain-causing, leading to cathode performance deterioration.¹⁷⁻¹⁹

In this context, it is of interest to evaluate if the $Pmn2_1$ LFS phase may provide strain-free Li intercalation/de-intercalation for potentially longer stable cycling performance in light also of recent computational results that predict to be more mechanically stable than the monoclinic counterpart.²⁰ As first reported by Dominko et al.,¹⁰ however, the low-temperature Pmn2₁ LFS is characterized by poor Li-ion intercalation storage and conductivity that have prompted researchers to resort to nanosizing and carbon coating to enhance its electrochemical performance.²¹⁻²² Nanosizing is a well-established strategy for improving the performance of Li-ion cathode materials via shortening the Li-ion diffusion length.²³ As such we decided to probe the structural and electrochemical behavior of the low-temperature orthorhombic Pmn21 LFS (ortho-LFS) that we obtained by hydrothermal synthesis ⁶ after first subjecting it to high-energy milling. It is then that we discovered that mechanochemical treatment within certain milling window leads to annealing-like structural changes that open up the pathway to higher accessible Li-ion storage capacity well beyond what would be expected solely on the basis of the nanosizing effect.²³ More specifically controlled high-energy mechanical nanosizing was found to induce structural changes including lattice expansion, reduction of anti-site defects and crystallinity improvement. This discovery was unexpected as typically particle size reduction is known to be accompanied with reduced crystallinity 23 and creation of defects 24 after high-energy milling. For example, as reported recently by Kim et al.²⁵ and Xiong et al.,²⁶ the relatively inactive NaFePO₄ maricite phase upon nanosizing by high-energy milling for at least 12 hours transformed to highly disordered/amorphous material with high electrochemical storage capacity. By contrast we report here mechanochemical activation of a relatively inactive cathode material - the orthorhombic β_{II} $/Pmn2_1$ LFS – via mechanically-induced structural annealing. This unreported structural activation phenomenon is of broad significance bringing a new perspective in the rich emerging research area of tunable mechanochemistry of battery materials.²⁷

3.3. Experimental Section

3.3.1. Material Synthesis

Ortho-LFS was synthesized using hydrothermal method adapted from Sirisopanaporn et al.⁶ In a typical experiment 200 mL precursor solution is prepared using 0.01 moles of fumed silica (SiO₂), 0.01 moles of iron chloride (FeCl₂.4H₂O) and 0.04 moles of lithium hydroxide monohydrate (LiOH.H₂O). First, 0.04 moles of LiOH.H₂O is dissolved in deoxygenated water under stirring until a clear solution is obtained. Next, 0.01 moles of SiO₂ were added to the solution while keeping the volume of the mixture constant at 160 mL. This was followed by an ultrasonication step at 37 Hz for 1.5 h to achieve a clear mixture. The mixture was then transferred to a Nitrogen-filled glovebox along with 0.01 moles of FeCl₂.4H₂O. Then 0.01 mol of FeCl₂.4H₂O was dissolved in 40 mL of deoxygenated water (stored inside glove box) and stirred for 5 minutes. The ferrous chloride and Li/Si solutions were then mixed slowly using a peristaltic pump. Finally, the mixed solution was poured into the stainless-steel autoclave (450 mL capacity from PARR), equipped with Teflon liner and closed inside the glove box. The temperature was raised to 200 °C and the mixture was stirred for 6 h at 300 rpm under argon gas atmosphere. After autoclaving, the cooldown precipitates were recovered by filtration and washed with saturated LiOH solution inside N₂-filled glove box. The product was further washed with acetone and dried under vacuum for 12 hours at 100 °C.

3.3.2. High-Energy Milling

To reduce the particle size of ortho-LFS powder, Planetary Micro Mill PULVERISETTE 7 premium line (Fritsch) was used. Solvent-assisted milling was employed to grind 0.8 g of ortho-LFS in 15 mL of isopropanol with grinding media (1 mm balls) of 50 g of zirconium oxide (ZrO₂) in each milling jar (80 mL). All preparation steps were carried out inside the N₂-filled glove box to avoid oxidation of LFS. High-energy milling jars were filled with LFS powder, solvent along with grinding media and sealed inside glovebox. The sealed jars were transferred to planetary mill and milled for 1, 3, 5, 8, and 10 cycles at 250 rpm, of one-hour each cycle with 30-min break between cycles. For more details refer to Appendix A. After milling, the jars were transferred back to glovebox for filtration and drying under vacuum at 80 °C overnight.

3.3.3. Electrochemistry

A typical electrode was prepared as following: a paste is prepared by mixing the active material (ortho-LFS), carbon black and binder polyvinylidene fluoride (PVDF) at a ratio 8:1:1 in N-Methyl-2-pyrrolidone (NMP) solvent. All components were mixed thoroughly with manual grinding for about 30 min. The homogeneous paste is then cast on ethanol-washed aluminum foil and dried for 2 hours at 50 °C. After drying, the electrode sheet was transferred to vacuum oven and kept overnight at 80 °C, to remove any traces of solvent. After drying, the electrode sheet was punched out into circles with 1 cm in diameter for half-cell assembly. A typical cell consists of the above fabricated LFS-C-PVDF¹ electrode as the cathode, lithium metal as the anode, and organic electrolyte comprising of 1 M LiPF₆ dissolved in mixed EC/DMC (1:1 by volume) solvent. A polypropylene-polyethylene-polypropylene (PP/PE/PP) film (Celgard 2300) is used as a separator. The cells prior to electrochemical testing are stored in glovebox for 24 hours to allow for complete wetting of electrodes by electrolyte. Galvanostatic charge-discharge cycling tests were performed with the cycler from Arbin (BT2000) or the battery analyzer from MTI Corporation, in the voltage range from 1.5 V to 4.5 V vs. Li⁺/Li. Electrochemical Impedance Spectroscopy (EIS) and Cyclic Voltammetry (CV) was done using a Bio-Logic VSP potentiostat and EC-Lab software for data analysis.

3.4. Material Characterization

Microstructure analysis and electron diffraction techniques were performed with a Hitachi SU–8000 cold-field emission scanning electron microscope and a Philips CM200 transmission electron microscope (TEM) at 200 kV, respectively. Kikuchi patterns collected from assynthesized LFS were indexed as *Pmn2*₁ using Channel 5 software.²⁸ The indexing reliability was estimated by Mean Absolute Deviation (MAD) values. A Micromeritics TriStar 3000 apparatus was used for N₂ adsorption/desorption, in order to determine the Brunaer-Emmett-Teller (BET) surface area (refer to Appendix A). Advanced synchrotron X-ray characterization was conducted at the Canadian Light Source (CLS). The samples for PXRD analysis were loaded in 0.5 mm inner

¹ Each final electrode contains approximately 2.1 mg cm⁻² of active material.

diameter Kapton capillaries which were sealed at both ends with a Loctite adhesive. Diffraction signals were collected using the Canadian Macromolecular Crystallography Facility beamline (CMCF-BM or 08B1-1) at CLS. 08B1-1 is a bending magnet beamline with a Si (111) double crystal monochromator. 2-dimensional (2D) data was obtained using a Rayonix MX300HE detector with an active area of 300 mm × 300 mm. The patterns were collected at an energy of 18 keV ($\lambda = 0.68880$ Å) and capillary-detector distance of 250 mm. The sample-detector distance, detector centering and tilt were calibrated using a lanthanum hexaboride (LaB₆) standard reference material from the National Institute for Standards and Technology (NIST SRM 660a LaB₆) and the calibration parameters were applied to all patterns. After calibration, the 2D patterns were integrated to obtain standard 1D powder diffraction patterns. A pattern from an empty Kapton capillary was subtracted from the sample data during integration. TOPAS (Version 4.2, Bruker AXS, Karlsruhe, Germany) was employed for Rietveld refinement. The degree of crystallinity (DOC) was determined by EVA software (refer to Appendix A).

3.5. Results & Discussion

3.5.1. Structure of Nanosized ortho-LFS

Figure 3.1 shows morphological comparison of pristine ortho-LFS vs. nanosized samples via SEM and HR-TEM characterizations. The SEM images (Figure 3.1a & Figure A1 in the Appendix A) show that the hydrothermally synthesized secondary aggregated particles of pristine ortho-LFS with average size of \sim 1 µm have a complex multi-faceted exterior morphology and a pomegranate-like interior comprised of primary nanocrystallites. Despite claims that such multi-faceted crystal morphology could be beneficial from a cathode performance standpoint as it should facilitate infiltration of electrolyte according to Kageyama *et al.*,¹¹ no such outcome was observed-see later electrochemical section- prompting us to nanosize the material by subjecting it to high-energy milling.

For nanosizing, variable milling times from 1-h to 10-h were tested to systematically elucidate the impact of high-energy milling process on the ortho-LFS crystals and their electrochemical response. The SEM images in Figure 3.1b, c show the LFS nanoparticles obtained after 1-h and 5-h of high-energy milling, respectively. SEM and HRTEM of sample 8-h and 10-h



Figure 3.1. Morphological comparison of pristine ortho-LFS vs. high-energy milled LFS via SEM and HR-TEM images. (a), (b) and (c) SEM images of pristine ortho-LFS and the ones after high-energy milling of 1-h and 5-h samples, respectively. Similarly, (d), (e) and (f) are HRTEM images of pristine ortho-LFS and the ones after high-energy milling of 1-h and 5-h samples, respectively with inset of SAED.

are presented in Figure A2 in the Appendix A. It can be observed that the size of secondary particles has significantly decreased after 1 and 5-h of high-energy milling. Nanocrystal size was calculated using ImageJ software ²⁹ and found to be mostly in the range of 50 nm after 5-h milling. Moreover, the reduction in secondary particle was quantitatively evaluated via surface area evolution, from 17.54 m² g⁻¹ of the as-synthesized pristine LFS to 41.06 m² g⁻¹, 51.02 m² g⁻¹ and 57.01 m² g⁻¹ respectively after 1-h, 3-h and 5-h milling (BET data are presented in Figure A3) as described in the Appendix A. Thus, the primary crystallite size (calculated from BET surface area as described in Appendix A) was reduced from 107.4 nm of the as-synthesized pristine LFS to 45.2 nm, 36.7 nm and 32.8 nm respectively after 1-h, 3-h and 5-h high-energy milling, results that are largely consistent with the SEM image observations. But high-energy milling in addition to nanosizing, morphology changes and surface area effect we found to effect in an unexpected way the crystal structure of LFS as evident by HRTEM and selective area electron diffraction (SAED) analysis (Figure 3.1d, e, f). Thus, as per Figure 3.1d the pristine ortho-LFS crystal spacing is 0.363 nm, which corresponds to (011) plane of *Pmn2*₁ phase as confirmed with the SAED inset. The 1-

h milled product has d-spacing of 0.313 nm which corresponds to (200) crystal plane of $Pmn2_1$ phase of LFS. The 5-h sample (Figure 3.1f) has d-spacing of 0.534 nm which corresponds to (010) plane. In Figure 3.1d, the SAED pattern of pristine LFS sample indicates poly-nanocrystalline structure.³⁰ The elongated and distorted diffraction spots with streaks make the SAED pattern in Figure 3.1e of 1-h milled LFS standing out from others. This distinction pattern may be attributed to creation of dislocations or strain accumulation upon high-energy milling.³⁰⁻³¹ However, interestingly these temporarily induced defects seem to have been largely removed with further milling; thus, the HRTEM (Figure 3.1f) of 5-h sample shows highly bright planes with diffraction features indicative of strong orientation (inset SAED) in Figure 3.1f. After these unexpected findings, we further examined by TEM the 5-h sample (see results in Figure A7, Appendix A) and found its 10-15 nm sized nanocrystals to undergo oriented-attachment along certain preferred crystalline orientation. It is deduced therefore that the long-range order of *Pmn2*₁ LFS crystals to improve after 5-h of milling (compare Figure 3.1d and 3.1f). These findings are further supported below by XRD characterization.

The XRD patterns of nanosized ortho-LFS samples prepared at different milling times were collected using synchrotron source ($\lambda = 0.7523$ Å) and are shown in Figure 3.2. The crystal structure for all samples can be assigned to the (JCPDs 01-080-7251) Pmn2₁ orthorhombic phase as confirmed using Rietveld refinement and EBSD analysis below (see Figure 3.3). Notably, there exists an amorphous hump at 20 about 9-10° in the pristine LFS, which becomes less significant as milling proceeds until it reaches its minimum at 5 hours. This was an unexpected finding implying that the short-range ordered LFS crystallized into Pmn21 orthorhombic during highenergy milling, indicating therefore an enhancement in LFS crystallinity as previously suggested by the HRTEM images (see Figure 3.1). However, when the milling time exceeds 5 hours, the crystal structure starts to lose its long-range order becoming progressively amorphous as evident by peak broadening and the relative increase of the hump at 9-10° of 20 in the case of 8-h and 10h milled ortho-LFS samples (see Figure 3.2). In addition to bulk structure probing, the surface chemistry of LFS, before and after milling, was characterized via XPS and EDS. These characterizations, shown in Figure A4, A5 & A6, did not reveal any discernable surface features for the samples obtained after optimum milling time (up to 5-h) but the 8-h milled sample did show some changes. Thus, XPS analysis showed the presence of oxidized iron species (Fe³⁺) while EDS



Figure 3.2. XRD characterization using synchrotron source ($\lambda = 0.7523$ Å) of ortho-LFS collected after high-energy milling for 1, 3, 5, 8 and 10-h.

analysis yielded evidence of heterogeneous distribution of Fe and Si on the surface of the 8-h milled sample that was not electrochemically activated-see results below. The presence of Fe³⁺ is not surprising as nanosized LFS is highly sensitive to surface oxidation as previously documented,³² while the heterogeneous distribution of Fe and Si most likely is due to observed amorphization that is known to be more pronounced near the particle surface.³³ Returning to structural analysis, the relative fraction of amorphous LFS was determined using EVA software and reported in Figure A8 of Appendix A, clearly showing the crystallinity to increase with increasing milling time up to 5-h before the material becomes progressively more amorphous. Therefore, there exists an optimized working window of high-energy milling duration from 3 to 5 hours leading to crystal structure improvement. It is postulated that the observed recrystallization (see Figure 3.1 and 3.2) and preferred crystal orientation (see Figure A7, Appendix A) is the result of mechanical energy-induced crystal annealing (due to high local pressure and temperature).³¹

The amorphization of battery materials upon prolonged high-energy milling is well documented as is for example the case of crystalline maricite (NaFePO₄) that was rendered amorphous after >12 hours of milling by Kim *et al.*²⁵ and Xiong *et al.*,²⁶ but it is the first time as far we know that high-energy mechanochemical processing using optimized milling protocols is reported to improve the crystallographic properties (preferred orientation and reduced defects) of battery materials.^{31, 34}

3.5.2. Crystal Refinement

Figure 3.3a shows the synchrotron XRD pattern of pristine LFS collected using synchrotron X-ray with wavelength = 0.7523 Å and fitted using TOPAS software.³⁵ All peaks can be correctly assigned to Bragg position of low-temperature orthorhombic $(Pmn2_1, \beta_{II})$ phase. The refined lattice constants are, a (Å) = 6.2691, b (Å) = 5.3429, c (Å) = 4.9563 which are consistent with the published crystal models.^{7, 21} Therefore, pristine ortho-LFS was phase-pure, which is certainly advantageous over mixed phase LFS materials obtained by high-temperature processing as result of favorable energetic phase coexistence.¹⁵⁻¹⁶ After milling for 5 hours, just like the SAED results (see Figure 3.1f), it can be seen LFS still be indexed as *Pmn2*, orthorhombic phase (refer to Figure A9, Appendix A for 1-h and 3-h sample). Moreover, the primary crystallite size of pristine ortho-LFS obtained from refinement is about 45 nm reduced to 39 nm after high-energy milling for 5 hours, which is consistent with our SEM results (see Figure 3.1) and BET results. Further to confirm phase identification EBSD data was collected as shown in Figure 3.3b. Kikuchi patterns collected from as-synthesized LFS were indexed as *Pmn2*, using Channel 5 software.²⁸ The indexing reliability was estimated using MAD values (expressed as angle in degrees), which indicate the misfit between the measured and the calculated angles between bands, where large MAD values indicate high misfit degree and low indexing reliability.^{28, 36} Pristine LFS sample was indexed as $Pmn2_1$ with MAD value of 1.453°, while the 5-h milling sample indexed as $Pmn2_1$ with MAD value of 1.432°. For EBSD of 1-h and 3-h sample, refer to Figure A10 in the Appendix A. Therefore, EBSD analysis is again consistent with our XRD refinement and HRTEM results.

Based on the structural refinement outcomes from EBSD and XRD, it is reasonable to consider that the long-range order of LFS crystals remains *Pmn2*₁ symmetry after controlled high-



Figure 3.3. (a) Top to bottom: XRD pattern of pristine LFS sample obtained with synchrotron source $(\lambda \sim 0.7523 \text{ Å})$ and refined with $Pmn2_1$ space group ($R_{wp} = 4.60$, $R_p = 3.51$ and GOF = 2.95) using TOPAS software. The 5-h sample was also refined with $Pmn2_1$ space group. (b) Electron back scattering (EBSD) images of pristine LFS indexed as $Pmn2_1$ with MAD value of 1.453°, 5-h sample indexed as $Pmn2_1$ with MAD value of 1.432°.

energy milling as discussed earlier. However, some subtle structural changes induced by highenergy milling could be detected upon in depth analysis on the pristine and 5-h milled samples.

Close comparative examination of the refined XRD features of pristine ortho-LFS and the 5-h LFS sample over the 8 to 14-degree range (Figure A11, Appendix A) reveals peak shift towards the lower angle direction meaning lattice expansion. As given in Figure 3.4a, the crystal structure of ortho-LFS exhibits isotropic expansion where all three lattice constants increase due to high-energy milling. Such lattice expansion has been observed in previous mechanochemical studies ³¹ to occur prior to onset of amorphization as compensation against the generation of larger surface energy (ΔG_{surf}) than volume energy (ΔG_{vol}) below a critical nanograin size as predicted by crystallization thermodynamics.³⁷ Within the regime of "optimized milling" (i.e., within 3-5 hours), there is about 1.5 % enlargement of each axis of ortho-LFS unit cell. Ortho-LFS can be considered as a quasi-2D framework where Li ions diffuse along (010) plane in the interlayer space



Figure 3.4. (a) Lattice constants estimated from Rietveld refinements. (b) Intermixing between Li and Fe, acquired from Rietveld refinement results. Herein, Li/Fe (i.e., Li ions occupy yellow Fe sites) and Fe/Li (Fe ions occupy grey Li sites) are presented for pristine and milled samples after 1, 3 and 5-h milling. (c) Illustration of unit cell ortho-LFS possessing a quasi-2D framework for Li-ion diffusion along (010) (the shadow plane in blue), which is in the interlayer space between the slabs made of FeO₄ and SiO₄ tetrahedra, readily facilitating Li-ion diffusion in the ortho-LFS crystals.

between the slabs made of FeO₄ and SiO₄ tetrahedra as illustrated by the shadow plane in Figure 3.4c.^{3, 14, 38} Lattice expansion means the diffusion pathway of Li ions getting broadened and less obstructed. Hence, such lattice expansion should readily facilitate Li-ion diffusion in the ortho-LFS crystals, therefore as result the electrochemical activity of LFS is expected to improve as well.

Another change induced by 5-h high-energy milling is in the occurrence of Li-Fe anti-site defects. Thus, as extracted from Rietveld refinement results, there exists high concentration of Li-Fe anti-site defects in the pristine ortho-LFS crystals as shown in Figure 3.4b. Thus, Fe ions substitute Li ions at grey tetrahedral sites (Fe_{Li} with almost 20 % occupancy) and 40 % of Fe lattice sites (yellow) are occupied by Li ions (Li_{Fe}). Cation anti-site defects are commonly observed in hydrothermally synthesized polyanion Li-ion intercalation compounds such as the olivine phase of LiFePO₄, which result in reduction of their accessible capacity and Li-ion transport properties.³⁹ Interestingly, both Li_{Fe} or Fe_{Li} anti-sites were substantially removed after optimum high-energy milling (see data in Figure 3.4b), and as such Li-ion intercalation activity is enhanced as indeed demonstrated in the next section. The favorable effect the elimination of anti-sites has on Li-ion intercalation can be understood by making reference to Figure A12 in the APPENDIX A. Thus in anti-site-free *Pmn2*₁ Li₂FeSiO₄, Li and Fe atoms occupy different crystallographic sites (Li1 (4b site) and Fe1 (2a site)).^{14, 40} Cation anti-sites tend to block the lithium diffusion pathway in either a or c direction (refer to Figure A12b, Appendix A) hence their reduction leads to enhanced Li-ion intercalation activity in analogy to the olivine LFP system.³⁹

3.5.3. Activated Li-ion Intercalation

The electrochemical activity improvement of $Pmn2_1$ obtained after mechanical annealing by high-energy milling can be readily appreciated by comparing the voltage profiles at C/50 (1C = 166 mAh g⁻¹) before and after milling for different times as shown in Figure 3.5 (also see Figure A13 in the Appendix A). At room temperature (RT, 25 °C) (Figure 3.5a), the first discharge capacity of the pristine LFS is about 30 mAh g⁻¹, which subsequently fades to about 25 mAh g⁻¹ after 5-6 cycles (see Figure A14, Appendix A) and further down to ~15 mAh g⁻¹ after 40 cycles (see Figure A17c, Appendix A). Such a low attained capacity is mainly attributed –other than the poor intrinsic electronic/ionic conductivity of orthosilicate compounds,⁴¹⁻⁴² to the structural "inactivity" of the ortho-LFS that seems to have dissuaded researchers from studying this phase.



Figure 3.5. (a) Galvanostatic charge-discharge curves of pristine ortho-LFS and 3-h and 5-h milled samples at C/50 from 1.5 to 4.5 V vs. Li^+/Li at room temperature; (b) Energy density vs. milling time; and (c) surface-normalized energy density per m².

Our present study, however, reveals the mechanically-induced annealing of ortho-LFS via optimized high-energy milling leads to activation, i.e. enhancement of Li-ion intercalation. Thus, after 1-h milling the ortho-LFS delivers a higher initial discharge capacity, namely ~55 mAh g⁻¹ (@ RT) and better capacity retention compared to pristine LFS sample (see Figure A13 & A14, Appendix A). For the 3-h milled sample, the reversible capacity increased even more and stabilized at 63 mAh g⁻¹ (see Figure 3.5a and A13 & A14, Appendix A). Meanwhile, the initial discharge capacity for the 5-h milled sample was 90 mAh g⁻¹ as shown in Figure 3.5a subsequently stabilizing at ~70 mAh g⁻¹ discharge capacity after 6 cycles (see Figure A14, Appendix A). In other words, the discharge capacity improved nearly 300% via high-energy milling for 5 hours. Moreover, the Coulombic efficiency improved and stabilized to ~99% from pristine to 5-h sample (see Figure A15 and A17c, Appendix A for 20 and 50 cycles respectively). Such significant increase in capacity of the mechanochemically-annealed ortho-LFS conducted at room temperature (without any addition of carbon) has not been reported before. However, longer milling duration i.e., 8-h and 10-h milled samples (see Figure A13 & A14, Appendix A) exhibit very poor capacity of only 26 and \sim 22.5 mAh g⁻¹ (lower than that of the pristine material) for the initial cycle respectively and suffer capacity fade in the subsequent cycles (see Figure A14). Similarly, the Coulombic efficiency of 8-h and 10-h samples significantly deteriorates with cycling (see Figure A15). For comparison, galvanostatic tests at C/50 were also conducted at elevated temperature (55 °C) as presented in A16, Appendix A. Pristine LFS sample delivers about 50 mAh g⁻¹at 55 °C, while discharge capacity significantly increases up to 140 mAh g⁻¹ after milling for 5 hours, which is 85 % of 1 lithium extraction comparable to previously reported data for high-energy milled ortho-LFS in the presence of carbon.²¹⁻²² However, in those previous studies no structural analysis was attempted to elucidate the origin of the observed capacity enhancement, the latter merely attributed to nanosizing and carbon coating. Recently though researchers studying Na-ion intercalation in another relatively inactive cathode material, NaFePO₄ by Kim et al.²⁵ and Xiong et al.,²⁶ have reported significant enhancement of storage capacity upon high-energy milling not simply due to nanosizing but because of induced structural disorder leading to open diffusion pathways.

As a first step in demonstrating that the observed enhanced intercalation activity is not merely due to nanosizing (i.e. shortening of diffusion path), we evaluated the effect of nanosizing itself by normalizing the obtained capacities and corresponding energy densities on the basis of specific surface area (mWh $g^{-1} m^{-2}$). Thus, upon integration of initial discharge capacities with voltage for the different milled samples the energy density was determined and plotted as shown in Figure 3.5b. These values were then normalized by dividing with the corresponding surface area (mWh $g^{-1} m^{-2}$) and plotted in Figure 3.5c with respect to the high-energy milling time. As it can be seen in Figure 3.5b, the specific energy (mWh g^{-1}) follows a quasi-linear relation to high-energy milling time, increasing from 50 mWh g^{-1} for pristine sample to 199 mWh g^{-1} for 5-h milled material. If this increase were simply due to nanosize effect, then the surface area-normalized energy densities (mWh $g^{-1} m^{-2}$) in Figure 3.5c should have shown no increase with milling time. Instead as it can be seen we have progressive increase with milling time implying that the increased capacity is not strictly due to nanosizing but also due to structural changes induced by mechanochemical annealing as determined in the previous section.

To obtain further electrochemical insight as to the origin of the observed enhancement on the Li-ion storage upon mechanochemically-induced structural annealing, we acquired differential capacity plots from galvanostatic charging/discharging data for milled and pristine samples as shown in Figure 3.6 (2nd cycle data). In the case of pristine sample, a very broad redox couple can be seen at 3V and 2.4V respectively (Figure 3.6a). After 1 hour of milling, the 2nd cycle differential capacity curves show a shift from 3V to 2.54V for the oxidation peak and from 2.41V to 2.47 V for the reduction peak corresponding to Fe^{2+}/Fe^{3+} couple of $Pmn2_1$ LFS after 1st cycle.^{7, 43} This redox potential shift from pristine to 1-h milled sample is attributed to a change in the bonding environment (Fe-O) after milling as in analogy has been discussed for different LFS phases by Sirisopanaporn *et al.*⁷ Further milling for 3-h and 5-h resulted in only modest shift for the oxidation peak and no change for reduction peak. Most impressively, after optimized high-energy milling, polarization (ΔV) is reduced from 0.63V for pristine sample to 0.08V for 5-h sample, as shown in Figure 3.6 & Figure A17a, b. At the same time the peaks increase in size clearly indicating that lithium-ion intercalation storage has significantly improved after optimum high-energy milling (3 to 5 h). Interestingly, the disordered samples obtained after 8-10 h milling exhibit similar broad redox peaks and large polarization as the pristine material exhibits (refer to Figure A18 in Appendix A), clearly demonstrating the importance of proper tuning the mechanochemical processing conditions to optimize the nanosized cathode structure for enhanced reversible intercalation. The enhanced intercalation kinetics for the 5-h milled sample is further probed by

Cyclic Voltammetry (CV) as shown in Figure A19. The lithium diffusion coefficient (D_{Li}) derived from the CV data (refer to Figure A19 and Table A3 in the Appendix A) is found to be one order of magnitude higher for the optimized 5-h mechanically annealed sample than that of the pristine. Similarly, EIS spectra collected for pristine and 5-hours milled materials confirmed the enhanced intercalation kinetics acquired from dQ/dV and CV (refer to Figure A20 and Table A4 in the Appendix A). With these additional electrochemical measurements, we have demonstrated that by tuning the mechanochemical processing conditions it is possible to promote structural annealing in terms of lattice expansion, preferred crystal orientation and anti-site defect reduction and thereby cause multi-fold enhancement of the Li-ion intercalation kinetics.



Figure 3.6. Differential capacity curves calculated from the 2^{nd} galvanostatic charge/discharge cycle of (a) pristine and after high-energy milling of (b) 1-h, (c) 3-h and (d) 5-h ortho-LFS samples.

3.6. Conclusion

In this work new insightful evidence is presented of the electrochemical activity of a nanosized cathode material, the low-temperature orthorhombic phase ($Pmn2_1$, β_{II}) of Li₂FeSiO₄, being unexpectedly enhanced via structural annealing induced upon controlled high-energy milling. Such mechanochemically-tuned structural annealing leads to isotropic crystal lattice expansion, preferred crystal orientation and defect reduction within the regime of "optimized milling" having pronounced impact on intercalation electrochemistry, a three-fold increase in storage capacity associated with one order enhancement of Li-ion diffusion coefficient. Lattice expansion means the interlayer space between the slabs made of FeO₄ and SiO₄ tetrahedra getting broadened rendering the diffusion pathway of Li ions less obstructed with the simultaneous reduction of Li-Fe anti-site defects. Mechanochemical activation via controlled high-energy milling offers new powerful possibilities in our efforts to unlock the high energy density potential of orthosilicate and other emerging intercalation cathode materials.

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3.8. References

1. Ni, J. F.; Jiang, Y.; Bi, X. X.; Li, L.; Lu, J., Lithium Iron Orthosilicate Cathode: Progress and Perspectives. *ACS Energy Lett.* **2017**, *2* (8), 1771-1781.

Billaud, J.; Eames, C.; Tapia-Ruiz, N.; Roberts, M. R.; Naylor, A. J.; Armstrong, A. R.; Islam,
M. S.; Bruce, P. G., Evidence of Enhanced Ion Transport in Li-Rich Silicate Intercalation
Materials. *Adv. Energy Mater.* 2017, 7 (11), 1601043.

3. Ferrari, S.; Capsoni, D.; Casino, S.; Destro, M.; Gerbaldi, C.; Bini, M., Electrochemistry of orthosilicate-based lithium battery cathodes: a perspective. *Phys. Chem. Chem. Phys.* **2014**, *16* (22), 10353-10366.
4. Islam, M. S.; Dominko, R.; Masquelier, C.; Sirisopanaporn, C.; Armstrong, A. R.; Bruce, P. G., Silicate cathodes for lithium batteries: alternatives to phosphates? *J. Mater. Chem.* **2011**, *21* (27), 9811-9818.

5. Gong, Z. L.; Yang, Y., Recent advances in the research of polyanion-type cathode materials for Li-ion batteries. *Energy Environ. Sci.* **2011**, *4* (9), 3223-3242.

 6. Sirisopanaporn, C.; Dominko, R.; Masquelier, C.; Armstrong, A. R.; Mali, G.; Bruce, P. G., Polymorphism in Li₂(Fe, Mn)SiO₄: A combined diffraction and NMR study. *J. Mater. Chem.* 2011, 21 (44), 17823-17831.

7. Sirisopanaporn, C.; Masquelier, C.; Bruce, P. G.; Armstrong, A. R.; Dominko, R., Dependence of Li₂FeSiO₄ Electrochemistry on Structure. *J. Am. Chem. Soc.* **2011**, *133* (5), 1263-1265.

Masese, T.; Orikasa, Y.; Tassel, C.; Kim, J.; Minato, T.; Arai, H.; Mori, T.; Yamamoto, K.; Kobayashi, Y.; Kageyama, H.; Ogumi, Z.; Uchimoto, Y., Relationship between Phase Transition Involving Cationic Exchange and Charge-Discharge Rate in Li₂FeSiO₄. *Chem. Mater.* 2014, *26* (3), 1380-1384.

9. Wei, H.; Lu, X.; Chiu, H.-C.; Wei, B.; Gauvin, R.; Arthur, Z.; Emond, V.; Jiang, D.-T.; Zaghib, K.; Demopoulos, G. P., Ethylenediamine-Enabled Sustainable Synthesis of Mesoporous Nanostructured Li₂Fe^{II}SiO₄ Particles from Fe (III) Aqueous Solution for Li-Ion Battery Application. *ACS Sustainable Chem. Eng.* **2018**, *6* (6), 7458-7467.

10. Dominko, R.; Conte, D. E.; Hanzel, D.; Gaberscek, M.; Jamnik, J., Impact of synthesis conditions on the structure and performance of Li₂FeSiO₄. *J. Power Sources* **2008**, *178* (2), 842-847.

11. Kageyama, H.; Hashimoto, Y.; Oaki, Y.; Imai, H., Six-armed twin crystals composed of lithium iron silicate nanoplates and their electrochemical properties. *Crystengcomm* **2015**, *17* (44), 8486-8491.

12. Ding, Z.; Zhang, D.; Feng, Y.; Zhang, F.; Chen, L.; Du, Y.; Ivey, D. G.; Wei, W., Tuning anisotropic ion transport in mesocrystalline lithium orthosilicate nanostructures with preferentially exposed facets. *NPG Asia Mater.* **2018**, *10* (7), 606.

13. Zeng, Y.; Chiu, H.-C.; Rasool, M.; Brodusch, N.; Gauvin, R.; Jiang, D.-T.; Ryan, D. H.; Zaghib, K.; Demopoulos, G. P., Hydrothermal crystallization of Pmn2₁ Li₂FeSiO₄ hollow mesocrystals for Li-ion cathode application. *Chem. Eng. J.* **2019**, *359*, 1592-1602.

14. Armstrong, A. R.; Kuganathan, N.; Islam, M. S.; Bruce, P. G., Structure and Lithium Transport Pathways in Li₂FeSiO₄ Cathodes for Lithium Batteries. *J. Am. Chem. Soc.* **2011**, *133* (33), 13031-13035.

15. Lu, X.; Wei, H.; Chiu, H. C.; Gauvin, R.; Hovington, P.; Guerfi, A.; Zaghib, K.; Demopoulos, G. P., Rate-dependent phase transitions in Li₂FeSiO₄ cathode nanocrystals. *Sci. Rep.* **2015**, *5*, 8599.

16. Lu, X.; Chiu, H.-C.; Bevan, K. H.; Jiang, D.-T.; Zaghib, K.; Demopoulos, G. P., Density functional theory insights into the structural stability and Li diffusion properties of monoclinic and orthorhombic Li₂FeSiO₄ cathodes. *J. Power Sources* **2016**, *318*, 136-145.

17. Lu, X.; Chiu, H.-C.; Arthur, Z.; Zhou, J.; Wang, J.; Chen, N.; Jiang, D.-T.; Zaghib, K.; Demopoulos, G. P., Li-ion storage dynamics in metastable nanostructured Li₂FeSiO₄ cathode: Antisite-induced phase transition and lattice oxygen participation. *J. Power Sources* **2016**, *329*, 355-363.

18. Li, L.; Zhu, L.; Xu, L.-H.; Cheng, T.-M.; Wang, W.; Li, X.; Sui, Q.-T., Site-exchange of Li and M ions in silicate cathode materials Li₂MSiO₄ (M= Mn, Fe, Co and Ni): DFT calculations. *J. Mater. Chem. A* **2014**, *2* (12), 4251-4255.

19. Yang, J. L.; Zheng, J. X.; Kang, X. C.; Teng, G. F.; Hu, L.; Tan, R.; Wang, K.; Song, X. H.; Xu, M.; Mu, S. C.; Pan, F., Tuning structural stability and lithium-storage properties by d-orbital hybridization substitution in full tetrahedron Li₂FeSiO₄ nanocrystal. *Nano Energy* **2016**, *20*, 117-125.

20. Vajeeston, P.; Fjellvåg, H., First-principles study of structural stability, dynamical and mechanical properties of Li₂FeSiO₄ polymorphs. *RSC Adv.* **2017**, *7* (27), 16843-16853.

21. Yabuuchi, N.; Yamakawa, Y.; Yoshii, K.; Komaba, S., Low-temperature phase of Li₂FeSiO₄: crystal structure and a preliminary study of electrochemical behavior. *Dalton Trans.* **2011**, *40* (9), 1846-1848.

22. Devaraju, M. K.; Tomai, T.; Honma, I., Supercritical hydrothermal synthesis of rod like Li₂FeSiO₄ particles for cathode application in lithium ion batteries. *Electrochim. Acta* **2013**, *109*, 75-81.

23. Lee, K. T.; Cho, J., Roles of nanosize in lithium reactive nanomaterials for lithium ion batteries. *Nano Today* **2011**, *6* (1), 28-41.

24. Gibot, P.; Casas-Cabanas, M.; Laffont, L.; Levasseur, S.; Carlach, P.; Hamelet, S.; Tarascon, J. M.; Masquelier, C., Room-temperature single-phase Li insertion/extraction in nanoscale Li_(x)FePO₍₄₎. *Nat. Mater.* **2008**, *7* (9), 741-747.

25. Kim, J.; Seo, D.-H.; Kim, H.; Park, I.; Yoo, J.-K.; Jung, S.-K.; Park, Y.-U.; Goddard III, W. A.; Kang, K., Unexpected discovery of low-cost maricite NaFePO₄ as a high-performance electrode for Na-ion batteries. *Energy Environ. Sci.* **2015**, *8* (2), 540-545.

26. Xiong, F.; An, Q.; Xia, L.; Zhao, Y.; Mai, L.; Tao, H.; Yue, Y., Revealing the atomistic origin of the disorder-enhanced Na-storage performance in NaFePO₄ battery cathode. *Nano Energy* **2019**, *57*, 608-615.

27. Muralidharan, N.; Brock, C. N.; Cohn, A. P.; Schauben, D.; Carter, R. E.; Oakes, L.; Walker, D. G.; Pint, C. L., Tunable mechanochemistry of lithium battery electrodes. *ACS nano* 2017, *11* (6), 6243-6251.

28. Brodusch, N.; Demers, H.; Gauvin, R., Nanometres-resolution Kikuchi patterns from materials science specimens with transmission electron forward scatter diffraction in the scanning electron microscope. *J. Microsc.* **2013**, *250* (1), 1-14.

29. Schneider, C. A.; Rasband, W. S.; Eliceiri, K. W., NIH Image to ImageJ: 25 years of image analysis. *Nat. Methods* **2012**, *9* (7), 671-675.

30. Asadabad, M. A.; Eskandari, M. J., Electron Diffraction. In *Modern Electron Microscopy in Physical and Life Sciences*, Janecek, M.; Kral, R., Eds. InTech: Rijeka, 2016; pp 10 - 20.

31. Baláž, P.; Achimovičová, M.; Baláž, M.; Billik, P.; Cherkezova-Zheleva, Z.; Criado, J. M.; Delogu, F.; Dutková, E.; Gaffet, E.; Gotor, F. J., Hallmarks of mechanochemistry: from nanoparticles to technology. *Chem. Soc. Rev.* **2013**, *42* (18), 7571-7637.

32. Deng, C.; Zhang, S.; Gao, Y.; Wu, B.; Ma, L.; Sun, Y.; Fu, B.; Wu, Q.; Liu, F., Regeneration and characterization of air-exposed Li₂FeSiO₄. *Electrochim. Acta* **2011**, *56* (21), 7327-7333.

33. Da Silva, K. L.; Menzel, D.; Feldhoff, A.; Kübel, C.; Bruns, M.; Paesano Jr, A.; Düvel, A.; Wilkening, M.; Ghafari, M.; Hahn, H., Mechanosynthesized BiFeO₃ nanoparticles with highly reactive surface and enhanced magnetization. *J. Phys. Chem. C* **2011**, *115* (15), 7209-7217.

34. Zhang, Q.; Liu, S.-J.; Yu, S.-H., Recent advances in oriented attachment growth and synthesis of functional materials: concept, evidence, mechanism, and future. *J. Mater. Chem.* **2009**, *19* (2), 191-207.

35. Coelho, A., Whole-profile structure solution from powder diffraction data using simulated annealing. *J. Appl. Crystallogr.* **2000**, *33* (3 Part 2), 899-908.

36. Schwartz, A. J.; Kumar, M.; Adams, B. L.; Field, D. P., Electron Backscatter Diffraction in Materials Science. Springer US: 2009; pp 65-80.

37. Mullin, J. W., Crystallization. 3rd ed.; Butterworth Heinemann, Oxford: 1993; pp 172–263.

 Saracibar, A.; Van der Ven, A.; Arroyo-de Dompablo, M. E., Crystal Structure, Energetics, And Electrochemistry of Li₂FeSiO₄ Polymorphs from First Principles Calculations. *Chem. Mater.* 2012, 24 (3), 495-503. 39. Paolella, A.; Turner, S.; Bertoni, G.; Hovington, P.; Flacau, R.; Boyer, C.; Feng, Z. M.; Colombo, M.; Marras, S.; Prato, M.; Manna, L.; Guerfi, A.; Demopoulos, G. P.; Armand, M.; Zaghib, K., Accelerated Removal of Fe-Antisite Defects while Nanosizing Hydrothermal LiFePO₄ with Ca²⁺. *Nano Lett.* **2016**, *16* (4), 2692-2697.

40. Liivat, A.; Thomas, J. O., Li-ion migration in Li₂FeSiO₄-related cathode materials: A DFT study. *Solid State Ion.* **2011**, *192* (1), 58-64.

41. Nytén, A.; Abouimrane, A.; Armand, M.; Gustafsson, T.; Thomas, J. O., Electrochemical performance of Li₂FeSiO₄ as a new Li-battery cathode material. *Electrochem. Commun.* 2005, 7 (2), 156-160.

42. Girish, H. N.; Shao, G. Q., Advances in high-capacity Li_2MSiO_4 (M = Mn, Fe, Co, Ni, ...) cathode materials for lithium-ion batteries. *RSC Adv.* **2015**, *5* (119), 98666-98686.

43. Singh, S.; Raj, A. K.; Sen, R.; Johari, P.; Mitra, S., Impact of Cl Doping on Electrochemical Performance in Orthosilicate (Li₂FeSiO₄): A Density Functional Theory Supported Experimental Approach. *ACS Appl. Mater. Interfaces* **2017**, *9* (32), 26885-26896.

4. Cycling-Induced Li-ion Intercalation Activation

Following up on optimized parameters of mechanochemical treatment to produce structurally-annealed LFS nanocrystals as described in Chapter 3, this chapter focuses on the electrochemistry and associated material changes during cycling. In this part of the work mechanochemical treatment of LFS is done in the presence of carbon with the purpose of boosting conductivity yielding a LFS@C nanocomposite. Mechanochemical carbon coating was employed as conventional carbon-coating at high temperature (~600 °C) using pyrolysis of organics is not suitable for low-temperature orthorhombic ($Pmn2_1$) phase. Electrochemical evaluation and detail analysis (dQ/dV, CV & EIS) revealed the unusual progressive increase of charge capacity over the first twelve cycles. Although, this gradual capacity increase during cycling had been observed by few researchers previous, it had been underestimated in significance attributing it to mere delayed electrolyte wetting/infiltration. Post-mortem analysis via EELS, HRTEM, SEM, XPS, EBDS & synchrotron-based XANES provides evidence of an underlying phase transition and surface alteration to occur during cycling that are advanced as the cause for the observed activation of Lion intercalation storage.

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4.1. Abstract

Lithium iron silicate Li₂FeSiO₄ (LFS) has received significant attention as Li-ion intercalation cathode material. However, it exhibits relatively poor Li-ion intercalation kinetics. In this work, mechanochemically annealed low-temperature orthorhombic (β_{II} , *Pmn2*₁) LFS@C nanocomposite is shown to exhibit unusual Li-ion intercalation activation during cycling. In particular, we present evidence of impressive two-fold capacity increase over the initial dozen cycles from 90 mAh g⁻¹ to 180 mAh g⁻¹. Interestingly a clear shift in Li-storage mechanism was triggered by the *in-situ* activation of the orthosilicate structure from a solid solution to bi-phasic

type. This unusual electrochemical behavior was further analysed by a systematic study on surface chemistry and crystal structure. Surface chemistry evaluation revealed a thick LiF-rich layer formation during cycling, which enabled stable cycling. More strikingly, a progressive irreversible *in-situ* phase transition during the initial dozen cycles was revealed, which activated ion transport by two orders of magnitude. Such unreported electrochemically-induced structural activation provides unexplored opportunities for unlocking the full potential of high capacity nanostructured orthosilicate and other types of Li-ion battery cathodes.

4.2. Introduction

Lithium ion batteries (LIBs) use intercalation compounds for both the anode and the cathode.¹⁻² Since the initial commercialization of the LiCoO₂-Graphite LIB in the early 90s,³ we have seen in recent years significant progress in developing improved intercalation materials with some of them reaching the commercial level such as LiNi_xMn_yCo_zO₂, LiFePO₄ and Li₄Ti₅O₁₂ etc.¹⁻^{2,4-5} This was mainly achieved by evaluating and controlling their complex intercalation chemistry. Notably, all these materials have intrinsic limitations in terms of capacity, structural stability and safety.^{2, 6}

In this context, polyanionic lithium iron orthosilicate (Li₂FeSiO₄) is of special interest due to its high theoretical capacity (331 mAh g⁻¹). This results from the 2e⁻ reaction mechanism which leads to double capacity compared to its commercial counterpart LiFePO₄.⁷⁻⁸ The cathode material has also excellent safety against thermal runaway, low cost and resource abundance for large-scale electric vehicle (EV) LIBs.^{7, 9-13} However, there are still major material chemistry challenges in transforming Li₂FeSiO₄ (LFS) into a high-performance cathode material. For example, it possesses different crystal phases due to very small differences in formation energies – which complicates the optimization of their properties for commercial cathode applications.^{7, 14-18} Almost all the recent theoretical and experimental studies indicate a phase transition from monoclinic *P21/n* to the thermodynamically stable inverse *Pmn2*₁ phase during charging/discharging.¹⁹⁻²¹ This type of irreversible phase transitions are typically associated with capacity fade during cycling as they prevent the fully reversible insertion of Li ions into these intercalation electrodes.²²⁻²⁴ Thus, it raises the issue of structural stability and long-term cyclability of LIBs.

Similarly in the case of LFS, like other intercalation cathodes, several studies report capacity fade during cycling.²⁵⁻²⁹ However contrary to typical capacity fade behaviour, there are reports showing LFS to exhibit gradual capacity increase during electrochemical cycling, although the authors failed to capture the significance of this phenomenon or studying it further. For example, Xu *et al.*,³⁰ Fan *et al.*³¹ and Zhao *et al.*³² have reported gradual capacity increase that stabilized after several cycles that the authors merely attributed to electrolyte taking time to completely wet/infiltrate the cathode material; no surface or structural characterization was undertaken or further hypothesis was given. Such phenomenon has been observed nevertheless in the case of Li-rich layered oxide cathode materials.³³⁻³⁵ Thus Ye *et al.*³⁶⁻³⁸ reported this gradual capacity increase for Li-rich layered oxides to relate to *in-situ* electrochemical activation of Li₂MnO₃ phase prompted by metal doping. No other systems have been reported exhibiting such intriguing behaviour. Therefore, it is of great interest in understanding the origin of such electrochemically-induced activation process as it may lead to nanoengineering high-energy density cathodes with improved charging/discharging performance as potentially is the case of LFS.

To this end, we have synthesized the low-temperature orthorhombic phase $(Pmn2_1)$ of Li₂FeSiO₄ using hydrothermal synthesis at 200 °C for 6 hours. Due to poor Li-ion intercalation storage and conductivity of the low-temperature $Pmn2_1$ LFS phase, we subjected it to high-energy mechanochemical milling in the presence of carbon black at room temperature to render it as LFS@C nanocomposite. As we have reported elsewhere, this mechanochemical treatment under controlled (time and rpm) conditions leads to crystal structure annealing in addition to nanosizing.³⁹ During follow up electrochemical cycling of this material, it is when we discovered that such LFS@C nanocomposite exhibits electrochemical-induced structural activation leading to doubling its reversible capacity from 90 mAh g⁻¹ to ~180 mAh g⁻¹. Interestingly, this impressive increase in charge capacity was associated with simultaneous transitioning from solid solution to two-phase Li-ion storage mechanism clearly indicating *in-operando* structural transformation unlike previous studies, which attributed such capacity increase to mere electrolyte penetration. To probe further this behaviour, we conducted *ex-situ* post-mortem analysis of the electrode surface chemistry using SEM, TEM, EDS and XPS techniques revealing the formation of a lithium fluoride (LiF) layer at the solid electrolyte interphase (SEI). On the other hand, bulk

characterization performed by XRD, XANES and EELS revealed progressive phase transition towards the inverse $Pmn2_1$ phase. This newly described cycling-induced electrochemical activation phenomenon of mechanochemically prepared LFS@C nanocomposite opens a new avenue for developing high energy density nanosilicate cathodes for LIB applications.

4.3. Experimental Section

4.3.1. Material Synthesis

Li₂FeSiO₄ (LFS) was synthesized using hydrothermal method adapted from Sirisopanaporn et al.¹² In a typical experiment 200 mL precursor solution was prepared using 0.01 moles of fumed silica (SiO₂), 0.01 moles of iron chloride (FeCl₂.4H₂O) and 0.04 moles of lithium hydroxide monohydrate (LiOH.H2O). First, 0.04 moles of LiOH.H2O was dissolved in deoxygenated water under stirring until a clear solution was obtained. Next, 0.01 moles of SiO₂ were added to the solution while keeping the volume of the mixture constant at 160 mL. This was followed by an ultra-sonication step at 37 Hz for 1.5 h to achieve a clear mixture. The mixture was then transferred to a Nitrogen-filled glovebox along with 0.01 moles of FeCl₂.4H₂O. Then 0.01 mol of FeCl₂.4H₂O was dissolved in 40 mL of deoxygenated water (stored inside glove box) and stirred for 5 minutes. The ferrous chloride and Li/Si solutions were then mixed slowly using a peristaltic pump. Finally, the mixed solution was poured into the stainless-steel autoclave (450 mL capacity from PARR), equipped with Teflon liner and closed inside the glove box. The temperature was raised to 200 °C and the mixture was stirred for 6 hours at 300 rpm under argon gas atmosphere. After autoclaving, the cooldown precipitates were recovered by centrifuge separator and washed with saturated LiOH solution inside N₂-filled glove box. The product was further washed with acetone and dried under vacuum for 12 hours at 100 °C.

4.3.2. High-Energy Milling

To reduce the particle size of ortho-LFS powder, Planetary Micro Mill PULVERISETTE 7 premium line (Fritsch) was used. Solvent-assisted high-energy milling was employed to grind 0.8 g of ortho-LFS in 15 mL of isopropanol with grinding media (1 mm balls) of 50 g of zirconium oxide (ZrO₂) in each milling jar (80 mL). To increase the electronic conductivity of LFS, 10 % carbon black (vis-à-vis the amount of LFS) was also added by keeping the same weight ratio.

Milling cylinders were filled with LFS powder, solvent, carbon black along with grinding media and sealed inside glovebox under N₂ atmosphere. All preparation steps were carried out inside the N₂-filled glove box to avoid oxidation of LFS. The sealed cylinders were transferred to milling machine and typically milled for 5 cycles at 250 RPM, where each cycle lasted for one hour as per protocol established in our previous work.³⁹ The break between each cycle was 30 min. After milling cylinders were then transferred back to the glove-box for centrifuge separator and drying under vacuum at 80 °C overnight.

4.3.3. Material Characterization

Microstructure analysis and electron diffraction techniques were performed with a Hitachi SU-8000 cold-field emission scanning electron microscope (SEM) and a Philips CM200 transmission electron microscope (TEM) at 200 kV, respectively. Electron energy loss spectroscopy (EELS) was performed with a Jeol JEM-2100F with a field effect gun operating at an acceleration voltage of 200 KV. For TEM/EELS samples preparation, active material electrodes (LFS@C nanocomposite) were carefully cleaned with DMC and dried (3-4 hours) inside the glove box. Subsequently, active material was scrapped from the Aluminium current collector and transferred to a carbon grid. All samples were sealed inside the glovebox and degassed again for 30 min at the TEM/EELS workstation prior to data collection. A Micromeritics TriStar 3000 apparatus was used for N2 adsorption/desorption, in order to determine the Brunaer-Emmett-Teller (BET) surface area. Advanced synchrotron X-ray characterization was conducted at Canadian Light Source (CLS). The samples for powder X-ray diffraction (PXRD) analysis were loaded in 0.5 mm inner diameter Kapton capillaries which were sealed at both ends with a Loctite adhesive. Diffraction signals were collected using the Canadian Macromolecular Crystallography Facility beamline (CMCF-BM or 08B1-1) at CLS. 08B1-1 is a bending magnet beamline with a Si (111) double crystal monochromator. 2-dimensional (2D) data was obtained using a Rayonix MX300HE detector with an active area of 300 mm × 300 mm. The patterns were collected at an energy of 18 keV ($\lambda = 0.7523$ Å) and capillary-detector distance of 250 mm. The sample-detector distance, detector centering and tilt were calibrated using a lanthanum hexaboride (LaB₆) standard reference material from the National Institute for Standards and Technology (NIST SRM 660a LaB₆) and the calibration parameters were applied to all patterns. After calibration, the 2D patterns were

integrated to obtain standard 1D powder diffraction patterns. A pattern from an empty Kapton capillary was subtracted from the sample data during integration. TOPAS (Version 4.2, Bruker AXS, Karlsruhe, Germany) was employed for Rietveld refinement. X-ray absorption near edge structure (XANES) was performed at the Fe K-edge at 17 keV photon energy; energy calibration was performed by determining the first inflection point of standard Fe and Yt XANES, for the respective energies. XANES samples were prepared by cleaning the active material electrodes with DMC and dried inside the glovebox for 3-4 hours. Active material was scrapped and pasted onto Kapton film and sealed inside the glovebox for data collection at CLS. X-ray photoelectron spectroscopy (K-Alpha XPS, Thermal Fisher Scientific Inc.) was performed for surface characterization. Raman spectroscopy (Bruker Senterra dispersive Raman microscope) and ⁵⁷Fe Mössbauer spectroscopy were performed for bulk characterization.

4.3.4. Electrochemical Tests

A typical electrode was prepared as follows: a paste was prepared by mixing the highenergy milled active material LFS@C nanocomposite, carbon black and binder polyvinylidene fluoride (PVDF) at a ratio 8:1:1 in N-Methyl-2-pyrrolidone (NMP) solvent. All components were mixed thoroughly with manual grinding for about 30 min. The homogeneous paste was then cast on ethanol-washed aluminum foil and dried for 2 hours at 50 °C. After drying, the electrode sheet was transferred to vacuum oven and kept overnight at 80 °C, to remove any traces of solvent. After drying, the electrode sheet was punched out into circles with 1 cm in diameter for half-cell assembly. Each final electrode contains approximately 2.1 mg cm⁻² of active material. A typical cell consisted of the above fabricated LFS-C-PVDF electrode as the cathode, lithium metal as the anode, and a standard battery grade electrolyte comprising of 1 M LiPF₆ dissolved in mixed EC/DMC (1:1 by volume) solvent purchased from BASF and directly used after opening inside the glovebox. A polypropylene-polyethylene-polypropylene (PP/PE/PP) film (Celgard 2300) is used as a separator. The cells were stored in glovebox for 24 hours prior to electrochemical testing to allow for complete wetting of electrodes by electrolyte. Galvanostatic charge-discharge cycling tests were performed at RT with the cycler from Arbin (BT2000) or the battery analyzer (Model # BST8MA) from MTI Corporation, in the voltage range from 1.5 V to 4.5 V vs. Li⁺/Li.

Electrochemical Impedance Spectroscopy (EIS) and Cyclic Voltammetry (CV) was done using a Bio-Logic VSP potentiostat and EC-Lab software for data analysis.

4.4. Results and Discussion

4.4.1. Mechanochemically Annealed LFS Nanocomposite

The XRD pattern of as-prepared by hydrothermal synthesis Li₂FeSiO₄ (LFS) can be found in Appendix Figure B1. All peaks were correctly assigned with the aid of TOPAS software to Bragg positions of low-temperature orthorhombic phase (β_{II} , $Pmn2_1$) consistent with the results presented elsewhere.⁴⁰ Therefore, the as-prepared LFS by hydrothermal synthesis was phase pure (except minor iron oxide impurities estimated at $\sim 5\%$ - refer to Figure B1 in the Appendix B), which is certainly advantageous over high-temperature phases of LFS suffering from significant monoclinic and orthorhombic phase coexistence.7, 21 The SEM images in Figure B2 show that the hydrothermally synthesized secondary aggregated particles of as-prepared LFS have an average size of ~1 µm. Notably, it is known that LFS suffers from low intrinsic conductivity properties (electronic and ionic) which hamper the lithium ion extraction and insertion processes. The Li⁺ ion diffusion coefficient is very low, ranging between 10⁻¹² and 10⁻²⁰ cm² s⁻¹ at room temperature, which is obviously lower than that for the low conducting LiFePO₄ ($\sim 10^{-7}$ cm² s⁻¹).⁴¹⁻⁴³ It is well accepted that a nanoscale particle size provides short Li⁺ ion diffusion path, which facilitates the Li intercalation kinetics in LFS electrode. As suggested by previous simulation and experimental studies nanosizing on one hand and carbon coating on the other are good means to promote Li-ion diffusion and electronic conductivity respectively.^{14, 44-47} However, standard carbon coating process involves heating the active material with a carbon source like lactose at a temperature near 700 °C.48 Since that temperature is likely to induce phase transition of the as-prepared low-temperature orthorhombic LFS ($Pmn2_1$) phase to the monoclinic ($P2_1/n$) phase,^{19, 21} the LFS particles were instead subjected to high-energy milling in the presence of carbon black under ambient conditions building on our recent carbon-free mechanochemical-induced annealing work.³⁹ To this end, pristine LFS sample was milled together with carbon black for 5h at 250 rpm as per protocol established previously.39



Figure 4.1. Synchrotron-based XRD pattern of LFS@C nanocomposite sample obtained after hydrothermal synthesis and mechanochemical annealing (synchrotron source, $\lambda = 0.7523$ Å) and refined with *Pmn2*₁ space group (R_{wp} = 4.20, R_p = 3.43 and GOF = 2.38) using TOPAS software. Lattice parameter values obtained from fitting are a = 6.29231 (Å), b = 5.35212 (Å) and c = 4.96224 (Å). (b) SEM and (c) TEM morphology of LFS@C nanocomposite showing nanoparticles covered with thin carbon layer as indicated with arrows.

The resulting powder of LFS@C nanocomposite was analyzed using XRD as shown in Figure 4.1a. All peaks can still be correctly assigned to Bragg position of low temperature orthorhombic phase (β_{II} , $Pmn2_1$) after mechanochemical annealing. It should be added also that as per in-depth analysis we presented in our recent work,³⁹ this type of mechanochemical annealing leads to reduction of anti-site defects and simultaneous development of preferred crystal orientation. The LFS@C nanocomposite possessed a high BET surface area of 64.3 m² g⁻¹, extracted from N₂ adsorption-desorption isotherm plots shown in Figure B3. Further, SEM and TEM images are shown in Figure 4.1b & 4.1c. The SEM image shows the high-energy milled LFS particles with reduced size of about 50 nm. This was further examined with TEM imaging as shown in Figure 4.1c, where a clearly distinguishable carbon layer is observed enveloping LFS nanoparticles in the carbon matrix; see also HRTEM in Figure B4.

To further characterize the carbon layer in the LFS@C nanocomposite material, XPS, FTIR and Raman were performed. In Figure 4.2a, XPS spectra confirm the carbon layer on the surface



Figure 4.2. Characterization of carbon and iron species ($Fe^{2+} \& Fe^{3+}$) on the surface and in the bulk of LFS@C nanocomposite using XPS, FTIR and Mössbauer spectroscopy, respectively. (a) XPS spectra of carbon, (b) XPS spectra of iron species ($Fe^{2+} \& Fe^{3+}$) on the surface, (c) FTIR spectra and (d) Mössbauer spectra.

of LFS@C sample. In Figure B5, the Raman peaks at 1332 cm⁻¹ and 1595 cm⁻¹, typically corresponding to the D and G bands of graphite, provide further evidence on the existence of graphitized carbon ⁴⁹. Similarly, FTIR spectra shown in Figure 4.2c indicate presence of carbon bonds at 1501 cm⁻¹ and 1434 cm⁻¹, respectively along with SiO₄ stretching and bending as indicated by illustration in Figure 4.2c. Moreover, we checked the LFS@C nanocomposite for Fe signal using XPS and Mössbauer spectra as shown in Figure 4.2b & d. In Figure 4.2b, the peak appearing at $2P_{3/2}$ with binding energy of 710.70 eV corresponds according to fitting made with Advantage software to ferrous signal and a small ferric satellite signal. The minor presence of ferric was further confirmed by Mössbauer spectroscopy as per results in Figure 4.2d. The two peaks at ~ -0.2 and ~ 2.2 mm/s correspond to Fe²⁺ contribution from the LFS sample. The minor peak appearing at ~0.6 mm/s arises from Fe³⁺ contribution apparently reflecting some superficial ferric iron formation from air exposure during handling. This was determined to be ~ 8% similar to our previous work ⁵⁰ and lower than that of other works reporting anywhere between 10% and 30% ferric iron.^{7, 51} The predominance of Fe²⁺ in the mechanochemically annealed orthorhombic

phase (*Pmn2*₁) LFS nanocrystals prior to cycling was also confirmed by EELS & XANES as per additional data presented later in Figure 4.8.

4.4.2. Unusual Li-ion Intercalation Activation

Figure 4.3 shows different electrochemical measurements of LFS@C nanocomposite material. In Figure 4.3a & c, galvanostatic charging & discharging curves at a very low C-rate (C/50) and room temperature, almost near equilibrium, are shown separately for clarity for the first 11 cycles. Cycle number vs. specific capacity (mAh g⁻¹) including Coulombic efficiency up to 50 cycles are shown in Figure 4.3e. As shown in Figure 4.3a & c (only some cycles are plotted for clarity), during the initial cycle, LFS@C delivers charge/discharge capacity of about 90 mAh g⁻¹. It must be noted here that the first discharge capacity of the pristine *Pmn2*₁ LFS is only about 30 mAh g⁻¹, which fades significantly upon cycling.³⁹ Such a low attained capacity is due to the structural "inactivity" of low T ortho-LFS that is overcome after mechanochemical annealing that has been shown to enhance ion transport via defect elimination.³⁹ But what is really interesting is that the mechanochemically prepared LFS@C nanocomposite after the 1st cycle not only did not exhibit capacity fade but showed instead an unusual electrochemically-induced capacity increase response. Interestingly, the discharge capacity started to increase after each cycle namely from 90 mAh g⁻¹ to 180 mAh g⁻¹, *i.e.* a two-fold increase from 1st to 11th cycle. The slight over one Li (180 mAh g⁻¹ vs. 166 mAh g⁻¹) excess capacity may be attributed to redox activity by lattice oxygen as reported previously by Masese et al.52 as well as our group based on O K-edge XANES analysis 21 and DFT calculations ¹⁵ and less likely - due to relatively low potential (4.5V) - to tetravalent iron.⁵³

Another notable observation is that after the 5th cycle, not only there is a significant capacity increase but also it started to change its electrochemical charge storage behavior from solid solution to two-phase mechanism ⁵⁴ as indicated by a shift from slanted to plateau-like curves (marked by dashed lines in Figure 4.3c). This intriguing electrochemical behavior is further elucidated by generating differential capacity plots from charge/discharge curves as shown in Figure 4.3b & d. Thus, as the capacity increased, both charge and discharge voltage increase from 2.66 V to 2.93V and 2.56 V to 2.61 V, respectively, which reflects complex phase evolution in silicates as noted in a previous study ²¹ (see section 4.4.4 for detail discussion). At the same time, the peaks intensity became sharper and increased in size, e.g. for charging profiles area under the



Figure 4.3. Electrochemical response of LFS@C nanocomposite samples. (a) Galvanostatic charging cycles at C/50 at room temperature and (b) their respective differential capacity curves (dQ/dV) along with cycle numbers. (c) Galvanostatic discharging cycles and (d) their respective differential capacity curves. (e) Cycle number vs. specific capacity of LFS@C nanocomposite cycled at C/50 and room temperature (indicated in blue open circles) along with Coulombic efficiency as indicated in red color using open circles.

peak for 5th cycle increased from 0.12795 to 0.66618 after 11th cycle. Similarly, for discharging profiles, there is an increase for area under peak from 1st cycle (0.0828) to 11th cycle (0.1262). This clearly indicates that lithium-ion intercalation storage has significantly improved after cycling-induced electrochemical activation, which also evident from stabilized Coulombic efficiency (see Figure 4.3e) when compared to initial cycles. Following this electrochemical activation, the capacity self-adjusted (due to apparent structure relaxation) at around 140 mAh g⁻¹ after 40th cycle as shown in Figure 4.3e and Appendix Figure B6. Interestingly, both Xu *et al.*30 and Zhao *et al.*³² separately observed this gradual capacity increase and subsequent stabilization, however, they did not observe any significant change in Li-storage mechanism possibly due to cycling at relatively high C-rate (0.2C and 1C, respectively). Meanwhile, Fan *et al.*³¹, did observe a significant change in Li-storage mechanism after 20th cycle along with gradual capacity increase. However, all these authors did not highlight in any way the significance of this behaviour, merely attributing it to electrolyte taking time to completely wet/infiltrate the cathode material, nor they performed any *ex-situ* surface or crystal structural change characterization of the cycled cathode as reported subsequently in sections 4.4.3 and 4.4.4, where a clear phase transition is observed.

To evaluate and understand further this intriguing behaviour, cyclic voltammetry (CV) was performed at a scanning rate of 0.05 mV/s in the voltage range from 1.5 V to 4.5 V as shown in Figure 4.4a. From the CV profiles, the $Fe^{2+/}Fe^{3+}$ redox couple for initial cycles can be seen located at about 2.49 V (along with tiny peak at 3.6V as indicated with arrows in Figure 4.4a) and 2.12 V versus Li⁺/Li for the charge and discharge, respectively. After the 10th cycle, we observed a significant shift of the redox couple peaks to 2.93/2.48 V, similar to voltage shifts obtained from differential capacity as shown in Figure 4.3b & 4.3d. In the meantime, the area under the peaks increased significantly compared to initial cycle. At the same time, the peaks increased in size clearly indicating that lithium-ion intercalation storage has significantly improved, which confirms our previous results obtained from the galvanostatic charging/ discharging as shown in Figure 4.3. After the 45th cycle, the voltage reduced again and stabilized around redox couple of 2.87/2.38V. This redox potential shift of LFS@C during cycling is attributed to a change in the bonding environment (Fe-O) due to structural changes as in analogy has been discussed for different LFS phases by Sirisopanaporn *et al.* and others.^{16, 55-57} This clearly aligns well with the presented galvanostatic cycling results suggesting the observed gradual increase of capacity during cycling



Figure 4.4. Electrochemical evaluation of LFS@C nanocomposite via (a) cyclic voltammetry at the scan rate of 0.05 mV/s and (b) impedance spectroscopy performed at room temperature (RT) between 1MHz to 1Hz.

of LFS@C to be associated with an underlying phase transition. Strikingly, the tail ends of CV profiles decrease in size as well, indicating possible passivating SEI layer formation during cycling, as confirmed via SEM, TEM and XPS in section 4.4.3 below.

Further, we collected electrochemical impedance spectroscopy (EIS) measurements as shown in Figure 4.4b along the equivalent circuit. The intercept at the Re(Z) axis represents the ohmic resistance (R_s) of total resistances of electrolyte, separator and electrical contacts. The R_s value as it can be seen in Table B1 remains the same at $8.2\pm0.1\Omega$ from 1st to 50th cycle indicating that the electrodes were well infiltrated with electrolyte not responsible for the observed capacity increase that previous works had suggested.³⁰⁻³² The semicircle at high frequency is related to the

SEI layer, denoted as R_{SEI} . The semicircle at medium frequency range relates to the charge transfer resistance (R_{ct}). The inclined line is the Warburg impedance (Z_W), which is associated with Li⁺ ion diffusion in the active particles.⁵⁸ The equivalent circuit is presented in Figure 4.4b inset. It can be seen that as the LFS@C nanocomposite was cycled, the R_{ct} decreased significantly compared to initial cycles, please refer to Table B1 for fitting results. Meanwhile, R_{SEI} has increased significantly after initial cycles due to apparent growth of the passivating film as it was further confirmed by SEM, TEM and XPS results that we discuss in detail in section 4.4.3. Moreover, the EIS spectra of "pristine electrode" of LFS@C and after cycling are shown in Figure B7 and Table B2 (at a very low frequency of 0.5 mHz); from these it can be clearly deduced that the diffusion kinetics has considerably improved upon cycling. This electrochemical performance improvement is linked to cycling-induced phase transition as elaborated in detail in section 4.4.4 that leads to *in situ* activation of the intercalation process.

4.4.3. In-situ LiF-Containing SEI Formation

The intriguing behavior of LFS@C nanocomposite prompted us to look further into what happened during electrochemical cycling. As an initial guess, we debated whether this apparent phase transition during cycling is due to either *in situ* surface alteration or bulk structure change. Therefore, initially LFS@C was investigated using SEM and TEM. In Figure 4.4a, SEM morphology of pristine electrode is shown, where the LFS@C electrodes are dispersed in carbon black and PVDF. Interestingly, after 5th cycle, the electrode morphology started to change, and it appeared to be covered by a thin layer (SEI), this continued as the material was cycled further. After 30 cycles, a very thick SEI layer was formed as shown in Figure 4.5d. Upon handling the electrodes, some cracks were formed with visible layer beneath, which again confirms the thick SEI layer formation on the surface, as shown in Appendix Figure B8. This was further probed with TEM imaging technique as shown in Figure 4.5e - h. For pristine electrode sample, we can see that LFS@C nanoparticles are dispersed in carbon and binder, as distinguished by Z-contrast. However, after cycling for 30 cycles, the Z-contrast has increased significantly. Further evidence can be seen in Appendix Figure B9, where the EDS maps, which were collected along with TEM are shown. For pristine electrode, the elements O, C, Fe & Si are present. However, after the 30th cycle, a new peak corresponding to fluorine (F) is observed, which indicates possible formation of



Figure 4.5. Post-mortem analysis of LFS@C nanocomposite samples by comparing the morphology of pristine electrode with cycled electrodes. (a) SEM morphology of pristine electrode of LFS@C nanocomposite sample and after (b) 5th, (c) 11th and (d) 30th cycle, collected at fully discharge state, respectively. Similarly, (e) TEM morphology of pristine electrode sample LFS@C nanocomposite sample and after (f) 5th, (g) 11th and (h) 30th cycle. (i) EDS maps were collected to probe the chemical changes induced on the surface after cycling. Here *f*-ratio maps for fluoride, iron, oxygen and silicon are shown for pristine electrode and after 30th discharge cycle, respectively. *f*-Ratio is defined as $f = \frac{I_A}{I_A + I_B}$, where I_A and I_B are the net characteristic X-ray intensities in one spectrum.⁵⁹

a LiF-containing SEI layer.⁶⁰ This was also confirmed by collecting *f*-ratio maps as shown in Figure 4.5i & Figure B10, where the F signal is seen to have significantly suppressed the signal of other elements after cycling (30th cycle). To further confirm this finding, XPS measurements were also made as shown in Figure 4.6, comparing the pristine electrode to the cycled LFS@C electrode. Only fluorine signal is plotted here for discussion. F signal coming from the binder (PVDF in our case) was obtained for the pristine electrode before cycling. After 5 cycles, a new peak started to



Figure 4.6. XPS conducted before and after cycling for identification of species on the surface. (a) Pristine LFS@C nanocomposite electrode before cycling and discharge-state electrodes after (b) 5^{th} , (c) 11^{th} and (d) 30^{th} cycle.

emerge at 610 eV. This indicates the presence of metal fluoride F signal, which confirms the TEM results (see Figure 4.5) of SEI formation with LiF. After 11th cycle, this peak increased further in size, which confirms our previous results of SEM/TEM and EDS results. After 30th cycle, the electrode surface showed a very strong signal from the metal fluoride F, which must be coming from LiF as suggested before. The formation of such LiF layer has been reported previously to take place on LFS exposed to LiPF₆ electrolyte.⁶¹⁻⁶² Similarly, in our case, LiF has formed on the interface of exposed LFS@C nanocomposite cycled electrodes. Moreover, the formation of LiF during cycling has been shown to act as a passive layer allowing the intercalation electrode to have long-term stability.⁶³ However, in our case, more in-depth analysis is required to understand the origin of the increased capacity observed during cycling.

4.4.4. In-situ Crystal Phase Transition

We further examined this phenomenon with XRD, EELS and XANES spectroscopy techniques. We analyzed cells at discharge state after 5th, 11th and 30th cycles to probe the crystal changes the LFS is undergoing during electrochemical galvanostatic cycling. These cycles were selected in particular based on the results reported in Figure 4.3a & 4.3c, as during those discharge cycles the electrochemical response of LFS@C nanocomposite has changed from sloped curves indicative of solid solution to plateau-like two-phase mechanism. The investigation of the samples with synchrotron-based XRD is shown in Figure 4.7a. As we can see from the pristine LFS@C nanocomposite electrode, all the peaks correspond to Pmn21 phase. However, after few cycles, namely at 5th cycle, we can clearly distinguish the 5th cycle pattern from that of the pristine LFS@C nanocomposite electrode, as now there are two new tiny peaks emerging (marked with shaded bars) attributed to the (112) and (212) planes of inverse $Pmn2_1$ phase (simulated patterns of both phases are shown in Figure B11). These two new peaks kept growing from 5th to 11th cycle. This indicated a clear in situ electrochemically-induced irreversible phase transition corresponding to the unusual electrochemical response of LFS@C nanocomposite. After the 30th cycle, no apparent significant increase or growth of the two peaks was observed. These two new peaks can be assigned to a known phase of inverse β_{II} , *Pmn2*₁ (fitting results are shown in Figure B12). It is also possible that we have a new polymorph of LFS depending on the degree of cation mixing and amount of distortion in the structure upon cycling,^{7, 17} which would require additional in-depth crystal analysis. However, here we would like to emphasize that the structural changes during galvanostatic cycling are clearly evident from the XRD results, revealing new irreversible phase transition. In Figure 4.7b, the phase transition percentage of β (new) phase against the original mother matrix was calculated and its formation is described by a S-type nucleation-growth crystallization kinetic model,^{23, 64} namely as lag phase, nucleation phase and plateau phase. The electrochemical phenomena occurred previously (see Figure 4.3 & B6) can be explained with the aid of Figure 4.7b, where after the first cycles, no apparent crystal changes occurred (lag phase), however after the 5th cycle, the β phase starts emerging (~25%) (nucleation stage), thereafter entering the growth stage (~90% after the 11th cycle corresponding to almost 1 lithium extraction, see Figure 4.3 & B6), eventually reaching the point of no-further transition after 30th cycle,



Figure 4.7. (a) Post-mortem analysis of LFS@C nanocomposite electrodes using Synchrotron-based XRD. Data was collected for pristine electrode and cycled electrodes (at fully discharged state) after 5th, 11th and 30th discharge cycle. (b) New phase (β) percentage was calculated using XRD data and plotted vs. number of cycles along with schematics of phase transition-activation.

signalling attainment of the stabilized discharge capacity range. These phase changes have important ramifications in terms of intercalation kinetics, as it is known that $Pmn2_1$ phase has only 2-dimensional Li⁺ ion diffusivity, whereas the inverse $Pmn2_1$ phase (cation mixing) obtained after cycling has 3-dimensional diffusivity pathways (crystal structure model illustrations are shown in Figure B13) ¹⁶⁻¹⁷ hence activating the electrochemical performance of LFS@C nanocomposite material as shown in Figure 4.3.

We further probed the discharge cycled material using EELS and XANES spectroscopy. Figure 4.8a & b show the EELS O-K edge and Fe-L_{2.3} spectra of the pristine LFS@C nanocomposite electrode, 5th, 11th and 30th cycle discharged cathode materials. Oxygen K-edge showed characteristic peaks at 538 eV for all selected discharge cells, while no significant changes occurred during cycling. Although the feature assignment of the O K-edge spectrum is not clear yet, we can be certain that the pre-edge at about 531 eV is directly related to the orbital hybridization of FeO4 tetrahedra. According to our previous research, Lu et al.²¹ reported that the monoclinic LFS exhibits similar pre-edge features attributed to the hybridization of oxygen and Fe^{2+} with the ideal spin of 4. In other words, this feature can be used as an indication of the degree of Fe-O covalency. In the meantime, Fe³⁺ with higher spin would lead to a new feature at lower energy because of its higher effective nuclear charge transfer.^{21, 65-66} For all selected discharge cycles, only subtle changes are evident. Thus, after the 11th cycle, a subtle pre-edge feature emerged that disappeared after the 30th cycle, which means the stable cycled LFS phase exhibited lower covalency. Other than this peak variation upon cycling, there was no new feature formed indicating that the crystal was completely re-lithiated at discharged state of Li₂FeSiO₄. In Figure 4.8b, the Fe-L_{2.3} spectra of the pristine after 5th, 11th and 30th cycled materials are shown, according to which only Fe²⁺ species are present. In this case, the peak observed at 710 eV corresponds to Fe²⁺ feature. There was no significant intensity and peak shift, indicating no ferric present at the discharge state. This confirms our previous results of O K-edge. Finally, we probed the pristine electrode and the electrode after 30th cycle with Fe K-edge XANES, the respective spectra shown in Figure 4.8c. Here, by comparing the pristine sample (black line) with cycle sample (red line), a slight shift in energy from pristine to 30th cycle sample can be observed along with some transformation of the post-edge features. These spectral features thus provide further evidence that LFS has undergone irreversible phase transition, clearly confirming the phenomena discussed earlier in Figure 4.7. Similarly, in Appendix Figure B14, where the pre-edge was plotted by extracting the background, we see that there was no significant change occurring after 30th cycle, indicating that LFS was fully lithiated and transformed into a new phase as mentioned previously. The observed change in peak symmetry is therefore attributed to the continuous evolution of structure during cycling. Figure 4.8d shows the Fe K-edge Fourier transform EXAFS spectra of pristine electrode and after 30 cycles. The first main peak (indicated with dashed vertical lines)

corresponds to the Fe–O shell mode. Before and after cycling, there is a slight increase in the Fe–O bond length, which is directly related to its different crystal phases – which in our case is transitioning from $Pmn2_1$ to inverse $Pmn2_1$.^{7, 39, 55} This observation confirms our previous results of phase transformation as Fe–O bond length remains largely uniform for all different crystal phases of Li₂FeSiO₄.⁵⁵ These results shed new light on the complex intercalation chemistry of silicate cathodes paving the way towards attainment of their full capacity potential.



Figure 4.8. Electron energy loss spectroscopy (EELS) of (a) Oxygen K-edge and (b) Fe $L_{2,3}$ – edge for LFS@C nanocomposite electrodes before (pristine) and after charging/discharging for 5, 11 and 30 cycles. Electrodes were characterized at fully discharged state. (c) Similarly, the normalized Fe K-edge XANES spectra before (pristine) and after 30 cycles. (d) Fe K-edge Fourier transformed EXAFS spectra before (pristine) and after 30 cycles.

4.5. Conclusion

Understanding the evolution of complex phase transition mechanism and its control in Li₂FeSiO₄ plays a key role in unlocking its full capacity potential. Strikingly, in this study mechanochemically annealed LFS@C nanocomposite manifested an unexpected in-situ electrochemical activation behavior. Cycling at near equilibrium conditions (C/50) showed impressive capacity increase during the initial dozen cycles. Notably, during cycling its Li-storage mechanism transitioned as well from solid solution to bi-phasic type, which gave birth to progressive capacity increase. Unlike suggestions in previous studies, electrolyte infiltration is not the reason behind this impressive capacity increase. Upon surface chemistry characterization, the formation of a passivating LiF layer was revealed contributing to long-term cyclability by preventing side reactions. In the meantime, post-mortem analysis of the cathode after different number of cycles revealed LFS to undergo transformation to the inverse *Pmn2*₁ phase via a S-type nucleation-growth kinetic model in striking correspondence with the observed gradual increase of capacity and the bi-phasic storage mechanism. This type of largely previously unnoticed electrochemically-induced structural activation of the Li-ion storage process not only provides new insight of the dynamics of intercalation materials but also offers new means of optimizing the performance of high-density Li-ion battery electrodes.

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4.7. References

1. Nitta, N.; Wu, F.; Lee, J. T.; Yushin, G., Li-ion battery materials: present and future. *Mater. Today* **2015**, *18* (5), 252-264.

2. Goodenough, J. B.; Park, K.-S., The Li-ion rechargeable battery: a perspective. J. Am. Chem. Soc. 2013, 135 (4), 1167-1176.

Van Schalkwijk, W.; Scrosati, B., In *Advances in Lithium-Ion Batteries*, Springer: 2002; pp 1 5.

4. Etacheri, V.; Marom, R.; Elazari, R.; Salitra, G.; Aurbach, D., Challenges in the development of advanced Li-ion batteries: a review. *Energy Environ. Sci.* **2011**, *4* (9), 3243-3262.

5. Scrosati, B.; Hassoun, J.; Sun, Y.-K., Lithium-ion batteries. A look into the future. *Energy Environ. Sci.* **2011**, *4* (9), 3287-3295.

6. Whittingham, M. S., Ultimate limits to intercalation reactions for lithium batteries. *Chem. Rev.* 2014, *114* (23), 11414-11443.

7. Ni, J. F.; Jiang, Y.; Bi, X. X.; Li, L.; Lu, J., Lithium Iron Orthosilicate Cathode: Progress and Perspectives. *ACS Energy Lett.* **2017**, *2* (8), 1771-1781.

8. Ferrari, S.; Capsoni, D.; Casino, S.; Destro, M.; Gerbaldi, C.; Bini, M., Electrochemistry of orthosilicate-based lithium battery cathodes: a perspective. *Phys. Chem. Chem. Phys.* **2014**, *16* (22), 10353-10366.

9. Islam, M. S.; Dominko, R.; Masquelier, C.; Sirisopanaporn, C.; Armstrong, A. R.; Bruce, P. G., Silicate cathodes for lithium batteries: alternatives to phosphates? *J. Mater. Chem.* **2011**, *21* (27), 9811-9818.

10. Girish, H. N.; Shao, G. Q., Advances in high-capacity Li_2MSiO_4 (M = Mn, Fe, Co, Ni, ...) cathode materials for lithium-ion batteries. *RSC Adv.* **2015**, *5* (119), 98666-98686.

11. Tan, R.; Yang, J.; Zheng, J.; Wang, K.; Lin, L.; Ji, S.; Liu, J.; Pan, F., Fast rechargeable allsolid-state lithium ion batteries with high capacity based on nano-sized Li₂FeSiO₄ cathode by tuning temperature. *Nano Energy* **2015**, *16*, 112-121.

12. Sirisopanaporn, C.; Dominko, R.; Masquelier, C.; Armstrong, A. R.; Mali, G.; Bruce, P. G., Polymorphism in Li₂(Fe,Mn)SiO₄: A combined diffraction and NMR study. *J. Mater. Chem.* **2011**, *21* (44), 17823-17831.

Ellingsen, L. A.-W.; Hung, C. R.; Majeau-Bettez, G.; Singh, B.; Chen, Z.; Whittingham, M. S.; Strømman, A. H., Nanotechnology for environmentally sustainable electromobility. *Nat. Nanotechnol.* 2016, *11* (12), 1039 - 1051.

14. Yang, J. L.; Zheng, J. X.; Kang, X. C.; Teng, G. F.; Hu, L.; Tan, R.; Wang, K.; Song, X. H.; Xu, M.; Mu, S. C.; Pan, F., Tuning structural stability and lithium-storage properties by d-orbital hybridization substitution in full tetrahedron Li₂FeSiO₄ nanocrystal. *Nano Energy* **2016**, *20*, 117-125.

15. Lu, X.; Chiu, H.-C.; Bevan, K. H.; Jiang, D.-T.; Zaghib, K.; Demopoulos, G. P., Density functional theory insights into the structural stability and Li diffusion properties of monoclinic and orthorhombic Li₂FeSiO₄ cathodes. *J. Power Sources* **2016**, *318*, 136-145.

 Saracibar, A.; Van der Ven, A.; Arroyo-de Dompablo, M. E., Crystal Structure, Energetics, And Electrochemistry of Li₂FeSiO₄ Polymorphs from First Principles Calculations. *Chem. Mater.* 2012, 24 (3), 495-503.

17. Lv, X.; Zhao, X.; Wu, S.; Nguyen, M. C.; Zhu, Z.; Lin, Z.; Wang, C.-Z.; Ho, K.-M., Fe–Si networks and charge/discharge-induced phase transitions in Li₂FeSiO₄ cathode materials. *Phys. Chem. Chem. Phys.* **2018**, *20* (21), 14557-14563.

18. Vajeeston, P.; Fjellvag, H., First-principles study of structural stability, dynamical and mechanical properties of Li₂FeSiO₄ polymorphs. *RSC Adv.* **2017**, *7* (27), 16843-16853.

19. Lu, X.; Wei, H.; Chiu, H.-C.; Gauvin, R.; Hovington, P.; Guerfi, A.; Zaghib, K.; Demopoulos, G. P., Rate-dependent phase transitions in Li₂FeSiO₄ cathode nanocrystals. *Sci. Rep.* **2015**, *5*, 8599.

20. Masese, T.; Orikasa, Y.; Tassel, C.; Kim, J.; Minato, T.; Arai, H.; Mori, T.; Yamamoto, K.; Kobayashi, Y.; Kageyama, H.; Ogumi, Z.; Uchimoto, Y., Relationship between Phase Transition Involving Cationic Exchange and Charge-Discharge Rate in Li₂FeSiO₄. *Chem. Mater.* **2014**, *26* (3), 1380-1384.

21. Lu, X.; Chiu, H.-C.; Arthur, Z.; Zhou, J.; Wang, J.; Chen, N.; Jiang, D.-T.; Zaghib, K.; Demopoulos, G. P., Li-ion storage dynamics in metastable nanostructured Li₂FeSiO₄ cathode: Antisite-induced phase transition and lattice oxygen participation. *J. Power Sources* **2016**, *329*, 355-363.

22. Vetter, J.; Novák, P.; Wagner, M. R.; Veit, C.; Möller, K.-C.; Besenhard, J.; Winter, M.; Wohlfahrt-Mehrens, M.; Vogler, C.; Hammouche, A., Ageing mechanisms in lithium-ion batteries. *J. Power Sources* **2005**, *147* (1-2), 269-281.

23. Chiu, H. C.; Lu, X.; Zhou, J.; Gu, L.; Reid, J.; Gauvin, R.; Zaghib, K.; Demopoulos, G. P., Capacity fade mechanism of Li₄Ti5O₁₂ nanosheet anode. *Adv. Energy Mater.* **2017**, *7* (5), 1601825.

24. Nazri, G.-A.; Pistoia, G., In *Lithium batteries: science and technology*, Springer Science & Business Media: 2008; pp 478-503.

25. Qiu, H.; Yue, H.; Zhang, T.; Ju, Y.; Zhang, Y.; Guo, Z.; Wang, C.; Chen, G.; Wei, Y.; Zhang, D., Enhanced electrochemical performance of Li₂FeSiO₄/C positive electrodes for lithium-ion batteries via yttrium doping. *Electrochim. Acta* **2016**, *188*, 636-644.

26. Kam, K. C.; Gustafsson, T.; Thomas, J. O., Synthesis and electrochemical properties of nanostructured Li₂FeSiO₄/C cathode material for Li-ion batteries. *Solid State Ion.* **2011**, *192* (1), 356-359.

27. Zhang, L.-L.; Duan, S.; Yang, X.-L.; Peng, G.; Liang, G.; Huang, Y.-H.; Jiang, Y.; Ni, S.-B.; Li, M., Reduced graphene oxide modified Li₂FeSiO₄/C composite with enhanced electrochemical performance as cathode material for lithium ion batteries. *ACS Appl. Mater. Interfaces* **2013**, *5* (23), 12304-12309.

28. Yan, Z.; Cai, S.; Zhou, X.; Zhao, Y.; Miao, L., Sol-gel synthesis of nanostructured Li₂FeSiO₄/C as cathode material for lithium ion battery. *J. Electrochem. Soc.* **2012**, *159* (6), A894-A898.

29. Shen, S.; Zhang, Y.; Wei, G.; Zhang, W.; Yan, X.; Xia, G.; Wu, A.; Ke, C.; Zhang, J., Li₂FeSiO₄/C hollow nanospheres as cathode materials for lithium-ion batteries. *Nano Res.* **2019**, *12* (2), 357-363.

30. Xu, Y. M.; Shen, W.; Zhang, A. L.; Liu, H. M.; Ma, Z. F., Template-free hydrothermal synthesis of Li₂FeSiO₄ hollow spheres as cathode materials for lithium-ion batteries. *J. Mater. Chem. A* **2014**, *2* (32), 12982-12990.

31. Fan, X.-Y.; Li, Y.; Wang, J.-J.; Gou, L.; Zhao, P.; Li, D.-L.; Huang, L.; Sun, S.-G., Synthesis and electrochemical performance of porous Li₂FeSiO₄/C cathode material for long-life lithiumion batteries. *J. Alloys Compd.* **2010**, *493* (1-2), 77-80.

32. Zhao, Y.; Li, J.; Wang, N.; Wu, C.; Ding, Y.; Guan, L., In situ generation of Li₂FeSiO₄ coating on MWNT as a high rate cathode material for lithium ion batteries. *J. Mater. Chem.* **2012**, *22* (36), 18797-18800.

33. Zheng, J.; Myeong, S.; Cho, W.; Yan, P.; Xiao, J.; Wang, C.; Cho, J.; Zhang, J. G., Li-and Mn-Rich Cathode Materials: Challenges to Commercialization. *Adv. Energy Mater.* **2017**, *7* (6), 1601284.

34. Jang, Y. I.; Huang, B.; Wang, H.; Sadoway, D. R.; Chiang, Y. M., Electrochemical cyclinginduced spinel formation in high-charge-capacity orthorhombic LiMnO₂. *J. Electrochem. Soc.* **1999**, *146* (9), 3217-3223.

35. Yu, S.-H.; Yoon, T.; Mun, J.; Park, S.; Kang, Y.-S.; Park, J.-H.; Oh, S. M.; Sung, Y.-E., Continuous activation of Li₂MnO₃ component upon cycling in Li_{1.167}Ni_{0.233}Co_{0.100}Mn_{0.467}Mo_{0.033}O₂ cathode material for lithium ion batteries. *J. Mater. Chem. A* **2013**, *1* (8), 2833-2839.

36. Ye, D.; Sun, C.; Chen, Y.; Ozawa, K.; Hulicova-Jurcakova, D.; Zou, J.; Wang, L., Ni-induced stepwise capacity increase in Ni-poor Li-rich cathode materials for high performance lithium ion batteries. *Nano Res.* **2015**, *8* (3), 808-820.

37. Ye, D.; Zeng, G.; Nogita, K.; Ozawa, K.; Hankel, M.; Searles, D. J.; Wang, L., Understanding the Origin of Li₂MnO₃ Activation in Li-Rich Cathode Materials for Lithium-Ion Batteries. *Adv. Funct. Mater.* **2015**, *25* (48), 7488-7496.

38. Ye, D.; Wang, B.; Chen, Y.; Han, G.; Zhang, Z.; Hulicova-Jurcakova, D.; Zou, J.; Wang, L., Understanding the stepwise capacity increase of high energy low-Co Li-rich cathode materials for lithium ion batteries. *J. Mater. Chem. A* **2014**, *2* (44), 18767-18774.

39. Rasool, M.; Chiu, H.-C.; Lu, X.; Voisard, F.; Gauvin, R.; Jiang, D.; Paolella, A.; Zaghib, K.; Demopoulos, G. P., Mechanochemically-tuned structural annealing: a new pathway to enhancing Li-ion intercalation activity in nanosized β_{II} Li₂FeSiO₄. *J. Mater. Chem. A* **2019**, *7*, 13705-13713

40. Yabuuchi, N.; Yamakawa, Y.; Yoshii, K.; Komaba, S., Low-temperature phase of Li₂FeSiO₄: crystal structure and a preliminary study of electrochemical behavior. *Dalton Trans.* **2011**, *40* (9), 1846-1848.

41. Araujo, R. B.; Scheicher, R. H.; de Almeida, J.; da Silva, A. F.; Ahuja, R., First-principles investigation of Li ion diffusion in Li₂FeSiO₄. *Solid State Ion.* **2013**, *247*, 8-14.

42. Liivat, A.; Thomas, J. O., Li-ion migration in Li₂FeSiO₄-related cathode materials: A DFT study. *Solid State Ion.* **2011**, *192* (1), 58-64.

43. Araujo, R. B.; Scheicher, R. H.; De Almeida, J.; da Silva, A. F.; Ahuja, R., Lithium transport investigation in Li_xFeSiO₄: A promising cathode material. *Solid State Commun.* **2013**, *173*, 9-13.

44. Chen, Z. X.; Qiu, S.; Cao, Y. L.; Qian, J. F.; Ai, X. P.; Xie, K.; Hong, X. B.; Yang, H. X., Hierarchical porous Li₂FeSiO₄/C composite with 2 Li storage capacity and long cycle stability for advanced Li-ion batteries. *J. Mater. Chem. A* **2013**, *1* (16), 4988-4992.

45. Lee, K. T.; Cho, J., Roles of nanosize in lithium reactive nanomaterials for lithium ion batteries. *Nano Today* **2011**, *6* (1), 28-41.

46. Vajeeston, P., Ionic conductivity enhancement by particle size reduction in Li₂FeSiO₄. *Mater*. *Lett.* **2018**, *218*, 313-316.

47. Armstrong, M. J.; O'Dwyer, C.; Macklin, W. J.; Holmes, J. D., Evaluating the performance of nanostructured materials as lithium-ion battery electrodes. *Nano Res.* **2014**, *7* (1), 1-62.

48. Wang, J.; Yang, J.; Tang, Y.; Liu, J.; Zhang, Y.; Liang, G.; Gauthier, M.; Karen Chen-Wiegart, Y.-c.; Norouzi Banis, M.; Li, X.; Li, R.; Wang, J.; Sham, T. K.; Sun, X., Size-dependent surface phase change of lithium iron phosphate during carbon coating. *Nat. Commun.* **2014**, *5*.

49. Ferrari, A. C.; Robertson, J., Interpretation of Raman spectra of disordered and amorphous carbon. *Phys. Rev. B* **2000**, *61* (20), 14095-14107.

50. Zeng, Y.; Chiu, H.-C.; Rasool, M.; Brodusch, N.; Gauvin, R.; Jiang, D.-T.; Ryan, D. H.; Zaghib, K.; Demopoulos, G. P., Hydrothermal crystallization of Pmn2₁ Li₂FeSiO₄ hollow mesocrystals for Li-ion cathode application. *Chem. Eng. J.* **2019**, *359*, 1592-1602.

51. Armstrong, A. R.; Kuganathan, N.; Islam, M. S.; Bruce, P. G., Structure and Lithium Transport Pathways in Li₂FeSiO₄ Cathodes for Lithium Batteries. *J. Am. Chem. Soc.* **2011**, *133* (33), 13031-13035.

52. Masese, T.; Tassel, C. d.; Orikasa, Y.; Koyama, Y.; Arai, H.; Hayashi, N.; Kim, J.; Mori, T.; Yamamoto, K.; Kobayashi, Y., Crystal structural changes and charge compensation mechanism during two lithium extraction/insertion between Li₂FeSiO4 and FeSiO₄. *J. Phys. Chem. C* **2015**, *119* (19), 10206-10211.

53. Singh, S.; Panda, M. R.; Sen, R.; Johari, P.; Sinha, A.; Meena, S. S.; Mitra, S., Study of Higher Discharge Capacity, Phase Transition, and Relative Structural Stability in Li₂FeSiO₄ Cathode upon Lithium Extraction Using an Experimental and Theoretical Approach and Full Cell Prototype Study. *ACS Appl. Energy Mater.* **2019**, *2* (9), 6584-6598.

54. Billaud, J.; Eames, C.; Tapia-Ruiz, N.; Roberts, M. R.; Naylor, A. J.; Armstrong, A. R.; Islam,
M. S.; Bruce, P. G., Evidence of Enhanced Ion Transport in Li-Rich Silicate Intercalation
Materials. *Adv. Energy Mater.* 2017, 7 (11), 1601043.

55. Eames, C.; Armstrong, A. R.; Bruce, P. G.; Islam, M. S., Insights into Changes in Voltage and Structure of Li₂FeSiO₄ Polymorphs for Lithium-Ion Batteries. *Chem. Mater.* **2012**, *24* (11), 2155-2161.

56. Sirisopanaporn, C.; Masquelier, C.; Bruce, P. G.; Armstrong, A. R.; Dominko, R., Dependence of Li₂FeSiO₄ electrochemistry on structure. *J. Am. Chem. Soc.* **2010**, *133* (5), 1263-1265.

57. Seo, D.-H.; Kim, H.; Park, I.; Hong, J.; Kang, K., Polymorphism and phase transformations of $Li_{2-x}FeSiO_4$ ($0 \le x \le 2$) from first principles. *Phys. Rev. B* **2011**, *84* (22), 220106.

58. Levi, M.; Salitra, G.; Markovsky, B.; Teller, H.; Aurbach, D.; Heider, U.; Heider, L., Solid-State Electrochemical Kinetics of Li-Ion Intercalation into Li_{1-x}CoO₂: Simultaneous Application of Electroanalytical Techniques SSCV, PITT, and EIS. *J. Electrochem. Soc.* **1999**, *146* (4), 1279-1289.

59. Brodusch, N.; Demers, H.; Gauvin, R., The f-Ratio Method for X-Ray Microanalysis in the SEM. In *Field Emission Scanning Electron Microscopy*, Springer: 2018; pp 55-65.

60. Fan, L.; Zhuang, H. L.; Gao, L.; Lu, Y.; Archer, L. A., Regulating Li deposition at artificial solid electrolyte interphases. *J. Mater. Chem. A* **2017**, *5* (7), 3483-3492.

61. Dippel, C.; Krueger, S.; Kraft, V.; Nowak, S.; Winter, M.; Li, J., Aging stability of Li₂FeSiO₄ polymorphs in LiPF₆ containing organic electrolyte for lithium-ion batteries. *Electrochim. Acta* **2013**, *105*, 542-546.

62. Dippel, C.; Krueger, S.; Kloepsch, R.; Niehoff, P.; Hoffmann, B.; Nowak, S.; Passerini, S.; Winter, M.; Li, J., Aging of Li₂FeSiO₄ cathode material in fluorine containing organic electrolytes for lithium-ion batteries. *Electrochim. Acta* **2012**, *85*, 66-71.

63. Choudhury, S.; Archer, L. A., Lithium fluoride additives for stable cycling of lithium batteries at high current densities. *Adv. Electron. Mat.* **2016**, *2* (2), 1500246.

64. Chiu, H.-C.; Lu, X.; Zhou, J.; Gu, L.; Reid, J.; Gauvin, R.; Zaghib, K.; Demopoulos, G. P., Annealing-regulated elimination of residual strain-induced structural relaxation for stable highpower Li₄Ti5O₁₂ nanosheet anodes. *Nano Energy* **2017**, *32*, 533-541.

65. Laffont, L.; Delacourt, C.; Gibot, P.; Wu, M. Y.; Kooyman, P.; Masquelier, C.; Tarascon, J. M., Study of the LiFePO₄/FePO₄ Two-Phase System by High-Resolution Electron Energy Loss Spectroscopy. *Chem. Mater.* **2006**, *18* (23), 5520-5529.

66. Castro, F. C.; Dravid, V. P., Characterization of Lithium Ion Battery Materials with Valence Electron Energy-Loss Spectroscopy. *Microsc. Microanal.* **2018**, *24* (3), 214-220.

5. Conductive Polymer Coating

In this chapter, the final part of the present research is reported. In particular the work described here aims at improving further the electrochemical performance of the mechanochemically-engineered LFS nanocrystals by coating them with the conductive polymer, PEDOT. Polymerization of PEDOT (poly (3,4-ethylene dioxythiophene) on the surface of the LFS nanocrystals is done *in-situ* by a modified 2-step chemical process. First, bare mechanochemically-prepared LFS nanocrystals are partially de-lithiated with the help of a chemical oxidant and then PEDOT-coated and re-lithiated in the presence of a lithium salt. The core-shell structured LFS@PEDOT nanocrystals exhibit more than one-Li capacity and relatively stable cycling performance. To explain the improved electrochemical performance, detailed post-mortem structural and surface characterization by a suite of advanced methods is presented.

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5.1. Abstract

Lithium iron silicate (LFS) attracts a lot of attention due to its 330 mAh g⁻¹ theoretical capacity (2 Li⁺ per formula unit). However, inherently it exhibits poor Li-ion intercalation kinetics, interfacial reactivity and complex phase transitions resulting in lower than one Li⁺ capacity and poor retention. In this work, a core-shell architecture was devised largely overcoming these obstacles. At first, the nanostructure of $Pmn2_1$ LFS is annealed via mechanochemical processing enabling the activation of Li-ion diffusion. Subsequently, the LFS nanocrystals are coated via *insitu* PEDOT polymerization involving partial chemical de-lithiation/re-lithiation, the latter catalyzed with FeCl₃. As a result of the devised mechanochemical/interphasial engineering of the LFS@PEDOT nanocrystals their Li-ion storage capacity was augmented to >1 Li, namely 200 mAh g⁻¹ after 50 cycles or 1.2Li⁺ units-the highest capacity reported for the *Pmn2*₁LFS cathode. A key attribute of the new PEDOT coating technique is the generation of a Fe³⁺-rich sub-surface

layer that contributes to structure stabilization via accelerated phase transition to inverse $Pmn2_1$ phase, in addition to rendering the nanocrystals electronically conductive and protected against reaction with electrolyte. Such core-shell engineered nanocrystals provide a powerful paradigm in developing viable high-energy density cathodes for next generation Li-ion batteries.

5.2. Introduction

Today the hunt for sustainable intercalation cathode materials having higher power/energy density intensifies due to explosive demand for affordable high-performance electric vehicles (EVs).¹⁻⁴ Energy density, rate capability and working voltage of lithium ion batteries (LIBs) depend largely on the type of cathode.¹ Current commercial cathode materials have reached their intrinsic limits in terms of specific capacity and structural stability as most of them can only transfer 0.5–1.0 electrons per formula unit during charge/discharge.⁵ In this context, lithium iron silicate compound is a promising sustainable cathode material, as it is made of abundant elements and has the theoretical potential of delivering 2 times higher specific capacity than conventional intercalation cathodes due to their two Li⁺ ions per formula unit.⁶

Despite their great potential, the development of lithium iron silicate (Li₂FeSiO₄) cathodes has been hampered as result of their inherent low intrinsic conductivity and structural instability.⁷ To address these limitations researchers resort to nanosizing and carbon coating to enhance their electrochemical performance.⁸⁻⁹ Nanosizing is a well-established strategy for improving the performance of Li-ion cathode materials via shortening the Li-ion diffusion length.¹⁰ For poor electronic conducting materials, carbon coating has been shown to be quite effective as in the case of LiFePO4.¹¹⁻¹² Typically, this involves high-temperature (600 - 800 °C) pyrolysis of organic substances.¹² However, such methods are unsuitable for the low-temperature orthorhombic (*Pmn2*₁) phase of Li₂FeSiO₄ (LFS) due to phase transition at high-temperature, as silicates exhibit rich polymorphism and close formation energies.⁶, ¹³⁻¹⁴ As noted recently though, much more research should be devoted to *Pmn2*₁ phase as due to its thermodynamic and mechanical stability may prove ultimately very rewarding as opposed to the most commonly investigated high temperature monoclinic phase.¹⁴⁻¹⁵ To preserve the low-temperature LFS phase while modifying its surface for electronic conductivity enhancement, an alternative surface coating strategy is to use electronically conducting polymers.¹⁶⁻¹⁷ Conductive polymers are attractive coating agents for
electrode surfaces in terms of improving electrical conductivity and can be coated in a simple process under mild conditions or even at RT in contrast to the conventional carbon-coating process.¹⁸⁻²¹ Electrochemically stable polymers including poly(3,4-ethylenedioxythiophene) (PEDOT),²¹ polypyrrole (PPy),²⁰ and PPy doped with the polyethyleneglycole (PEG) ²² have shown to improve the electrochemical performance of several different materials increasing their practical specific capacities, improving their cycle life, rate capabilities and preventing side reactions on the surface.^{16-17, 23-24} Among these conductive polymers, PEDOT is known to be the most effective conductive polymer due to its structural stability and high electronic conductivity.^{16,} ²⁴ An important attribute of conductive polymers is that they can be engineered to provide highly continuous surface coverage with controllable nanoscale thickness.^{16, 24-25} In the case of LiFePO₄ (LFP), polymerization of 3,4-ethylenedioxythiophene (EDOT) was conducted on the surface of partially de-lithiated LFS to form thin PEDOT coating, which exhibited excellent cycling stability.²¹ Likewise, Kim et al.,²⁶ Li et al.,²⁷ and Sobkowiak et al.²⁵ demonstrated the use of PEDOT coating for completely different materials using the *in-situ* EDOT polymerization approach. Inspired by this, we thought mechanochemically activated $Pmn2_1$ LFS nanocrystals²⁸ to be ideal candidate for polymer (PEDOT) coating as strategy to push towards higher than one Li⁺ storage capacity cathodes.

In this work, we designed robust core-shell LFS@PEDOT nanocrystals, where the core was engineered via mechanochemical annealing and shell was *in-situ* chemically polymer coated. Firstly, the low-temperature orthorhombic ($Pmn2_1$) phase of LFS was prepared via hydrothermal synthesis at 200 °C.²⁹ Subsequently, the LFS product was mechanochemically annealed via high-energy milling under optimal conditions that improves Li-ion intercalation in $Pmn2_1$ phase as per our recent work.²⁸ Then, for the first time as far it concerns silicate cathode materials, we applied a poly(3,4-ethylenedioxythiophene) (PEDOT) coating on the nanocrystals via the modification of an earlier *in-situ* polymerization method described by Lepage *et al.*²¹ Electrochemical evaluation of such LFS@PEDOT (PLFS) nanocrystals revealed quasi bi-phasic Li-storage mode, where polarization (ΔV) is minimal compared to previous reports.⁶ PLFS nanocrystals delivered a high initial capacity of 220 mAh g⁻¹ and this impressively at room temperature (RT)-a record 1.33 Li⁺ units for the $Pmn2_1$ phase. Interestingly, galvanostatic

charge/discharge, EIS and CV revealed improved rate capability and enhanced cycling stability, both thanks to the PEDOT coating process. Thus, pristine and post-mortem LFS@PEDOT cathode characterization by XPS, XANES, EXAFS, X-PEEM, STXM, and HRTEM revealed accelerated phase transition towards the stable inverse $Pmn2_1$ phase triggered by the presence of a Fe³⁺-rich sub-surface layer, an unexpected by-product of the interphasial engineering process. This discovery proves that other than providing a conductive coating that serves also as passivating layer against electrolyte degradation, the PEDOT coating process may alter the near surface zone of the host intercalation particle with important consequences. As such the present work provides a powerful paradigm of creative integration of mechanochemical and interphasial nanocrystal engineering in our pursuit of high-energy density cathodes not only for silicate but also other > 1Li/formula unit materials.

5.3. Experimental Section

5.3.1. Material Synthesis

5.3.1.1. Hydrothermal Synthesis of Li₂FeSiO₄ (LFS)

Li₂FeSiO₄ (LFS) was synthesized using a hydrothermal method adapted from Sirisopanaporn *et al.*^{29, 59} In a typical experiment, 200 mL precursor solution was prepared using 0.01 moles of fumed silica (SiO₂), 0.01 moles of iron (II) chloride or iron (II) sulphate (FeCl₂.4H₂O or FeSO₄. 7H₂O) and 0.04 moles of lithium hydroxide monohydrate (LiOH.H₂O). First, 0.04 moles of LiOH.H₂O was dissolved in deoxygenated water under stirring until a clear solution was obtained. Next, 0.01 moles of SiO₂ were added to the solution while keeping the volume of the mixture constant at 160 mL. This was followed by an ultra-sonication step at 37 Hz for 1.5 h to achieve a clear mixture. The mixture was then transferred to a Nitrogen-filled glovebox. Then 0.01 mol of FeCl₂ or FeSO₄ was dissolved in 40 mL of deoxygenated water (stored inside glove box) and stirred for 5 minutes. The ferrous solution and Li/Si solutions were then mixed slowly using a peristaltic pump. Finally, the mixed solution was poured into the stainless-steel autoclave (450 mL capacity from PARR Instruments, 4520 Bench Top Reactor), equipped with Teflon liner and closed inside the glove box. The temperature was raised to 200 °C and the mixture was stirred for 6 hours at 300 rpm under argon gas atmosphere. After autoclaving, the cooldown precipitates were recovered by centrifuge separator and washed with saturated LiOH solution inside N₂-filled glove box. The product was further washed with acetone and dried under vacuum for 12 hours at 100 °C.

5.3.1.2. High-Energy Milling

For mechanochemical treatment of LFS, a Planetary Micro Mill PULVERISETTE 7 premium line (Fritsch) was used. Solvent-assisted high-energy milling involved grinding 0.8 g of ortho-LFS in 15 mL of isopropanol with grinding media (1 mm balls) of 50 g of zirconium oxide (ZrO₂) in milling jars of 80 mL capacity. Milling cylinders were filled with LFS powder, solvent, and the grinding media and sealed inside glovebox under N₂ atmosphere. In some tests carbon black (~10%) was also added to produce mechanically carbon coated LFS. All preparation steps were carried out inside the N₂-filled glove box to avoid oxidation of LFS. The sealed cylinders were transferred to the planetary mill and typically milled for 5 cycles at 250 RPM, where each cycle lasted for one hour as per protocol established in our previous work.²⁸ The break between each cycle was 30 min. At the end of milling the jars were transferred back into the glove-box for centrifuge separation and drying under vacuum at 80 °C. Mechanochemically prepared LFS is labeled as MLFS. The mechanically carbon-coated LFS sample is labeled as CLFS.

5.3.1.3. PEDOT Coating

PEDOT coating was applied by modifying the *in-situ* chemical polymerization method reported elsewhere.^{21, 25-26} The method consists of two de-lithiation/re-lithiation steps. In step one LFS is partially de-lithiated by limited oxidation of Fe^{II} to Fe^{III} using a chemical oxidant, e.g. hydrogen peroxide. In step two, *in-situ* polymerization of EDOT is triggered in the presence of a Li salt (LiTFSI) by taking advantage of the intrinsic oxidation power of the partially oxidized (Fe^{III})/de-lithiated material. However, as described in the SI in more detail no polymerization would take place on the surface of the partially de-lithiated LFS. This obstacle was overcome by using a small amount of FeCl₃ as catalyst-promoter. Briefly here is the modified coating procedure. MLFS (1.04 g) was added to water (20 mL). The mixture was stirred vigorously while acetic acid (0.2 mL) and then hydrogen peroxide (0.5mL) were added. The mixture continued to be stirred for 15 min before being washed with water and dried overnight at 60 °C under vacuum. This oxidative treatment induces partial de-lithiation necessary to prepare Li_{2-x}Fe_{1-x}^{II}Fe_x^{III}SiO₄ for polymer

coating. This oxidative treatment induces partial de-lithiation necessary to prepare $Li_{2-x}Fe_1$. $x^{II}Fe_x^{III}SiO_4$ for polymer coating. This material is labeled DLFS. To induce PEDOT coating on DLFS nanoparticles, a solution of anhydrous FeCl₃ (0.0811g) in methanol (5 mL) was first prepared in which LiTFSI (0.13 g) was dissolved by stirring for 15 min or so. Subsequently, DLFS (0.20 g) and EDOT (0.1 mL) were added to the LiTFSI/FeCl₃/methanol solution and left overnight under constant magnetic stirring. The solvent was then evaporated in a petri dish at 60° for 2 hours (see Figure C6). The coated material was finally washed with methanol & acetonitrile and dried at 60°C overnight under vacuum. Further details on the FeCl₃-catalyzed procedure of PEDOT coating are provided in Appendix under section C3. The PEDOT-coated LFS sample is labeled as PLFS.

5.3.2. Material Characterization

Microstructure analysis and electron diffraction techniques were performed with a Hitachi SU-8000 cold-field emission scanning electron microscope (SEM) and a Philips CM200 transmission electron microscope (TEM) at 200 kV, respectively along with Energy-dispersive Xray spectroscopy (EDS). Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8-Advantage powder diffractometer with Co-K α radiation ($\lambda = 1.78892$ Å, 35 kV; 15 mA) in a 20 range between 10° and 80° with increment of 0.01° and a dwell time of 2.5 s per step. Advanced synchrotron X-ray characterization was conducted at Canadian Light Source (CLS), where samples were loaded in 0.5 mm inner diameter Kapton capillaries which were sealed at both ends with a Loctite adhesive. Diffraction signals were collected using the Canadian Macromolecular Crystallography Facility beamline (CMCF-BM or 08B1-1) at CLS. 08B1-1 is a bending magnet beamline with a Si (111) double crystal monochromator. 2-dimensional (2D) data was obtained using a Rayonix MX300HE detector with an active area of 300 mm × 300 mm. The patterns were collected at an energy of 18 keV ($\lambda = 0.7523$ Å) and capillary-detector distance of 250 mm. The sample-detector distance, detector centering and tilt were calibrated using a lanthanum hexaboride (LaB₆) standard reference material from the National Institute for Standards and Technology (NIST SRM 660a LaB₆) and the calibration parameters were applied to all patterns. After calibration, the 2D patterns were integrated to obtain standard 1D powder diffraction patterns. A pattern from an empty Kapton capillary was subtracted from the sample data during integration. TOPAS (Version 4.2, Bruker AXS, Karlsruhe, Germany) was employed for Rietveld refinement.

X-ray absorption near edge structure (XANES) & Extended X-Ray Absorption Fine Structure (EXAFS) was performed at the CLS. XANES spectra were collected at the beamline BL02B2, SPring-8, equipped with a large Debye – Scherrer camera. The wavelength of the incident X-ray beam was 0.50005 Å. X-ray photoemission electron microscopy (X-PEEM) measurements were performed at the spectromicroscopy beamline of CLS. The monochromatic X-ray beam was focused using an ellipsoidal mirror to a ~20 μ m spot on the sample in X-PEEM and incident at a grazing angle of 16°. The sample was biased at –20 kV with respect to the X-PEEM objective lens, and the base pressure of the X-PEEM chamber was maintained at ~10⁻⁹ Torr. Image stacks (sequences) for a specific field of view at the O and Fe K-edges were measured. The acquired X-PEEM data were analyzed using aXis2000. Raman spectroscopy (FTIR) was used to probe chemical differences between the samples. Thermal gravimetric analysis (TGA) was used to estimate the amount of polymer in the PLFS sample. The analysis was carried out between 25 and 600 °C under a constant flow of Argon with a heating rate of 10 °C/min.

5.3.3. Electrochemical Tests

A typical electrode was prepared as follows: a paste was prepared by mixing the highenergy milled active material LFS@C nanocomposite with or without PEDOT coating, carbon black and binder polyvinylidene fluoride (PVDF) at a ratio 8:1:1 in N-Methyl-2-pyrrolidone (NMP) solvent. All components were mixed thoroughly with manual grinding for about 30 min. The homogeneous paste was then cast on ethanol-washed aluminum foil and dried for 2 hours at 50 °C. After drying, the electrode sheet was transferred to a vacuum oven and kept overnight at 80 °C, to remove any traces of solvent. After drying, the electrode sheet was punched out into circles with 1 cm in diameter for half-cell assembly. Each final electrode contains approximately 2.1 mg cm⁻² of active material. A typical cell consisted of the above fabricated electrode as the cathode, lithium metal as the anode, and an organic electrolyte comprising of 1 M LiPF₆ dissolved in mixed EC/DMC (1:1 by volume) solvent. A polypropylene-polyethylene-polypropylene (PP/PE/PP) film (Celgard 2300) was used as a separator. The cells were stored in glovebox for 24 hours prior to electrochemical testing to allow for complete wetting of electrodes by electrolyte. Galvanostatic charge-discharge cycling tests were performed at RT with the cycler from Arbin (BT2000) or the battery analyzer (Model # BST8MA) from MTI Corporation, in the voltage range from 1.5 V to 4.5 V vs. Li⁺/Li. Electrochemical Impedance Spectroscopy (EIS) and Cyclic Voltammetry (CV) was done using a Bio-Logic VSP potentiostat and EC-Lab software for data analysis.

5.4. Results and Discussion

5.4.1. PEDOT Encapsulated LFS Nanocrystals

Figure 5.1a provides a graphical description of the three-step process of engineering the PEDOT-encapsulated LFS nanocrystals. As a first step, the hydrothermally produced low-temperature orthorhombic *Pmn2*₁ material is subjected to mechanochemical annealing as per our previous work.²⁸ In step two the mechanochemically prepared nanocrystals are subjected to partial de-lithiation by oxidation; and in step three PEDOT is induced to polymerize on the particle surface yielding the LFS@PEDOT core-shell nano-architecture.

Synchrotron XRD characterization of as-prepared LFS confirmed to be the lowtemperature orthorhombic Pmn21 phase as shown in Figure C1 in agreement with published results.³⁰ The as-prepared LFS was in the form of secondary aggregated particles with an average size of ~1 μ m (SEM images in Figure C2). Given the Li⁺ ion diffusion coefficient is very low in LFS, ranging between 10⁻¹² and 10⁻²⁰ cm² s⁻¹ at room temperature,³¹⁻³³ the as-prepared material was subjected to nanosizing to provide a short Li⁺ ion diffusion path.^{10, 34} To this end the asprepared LFS was mechanochemically treated in a high-energy mill that as shown in our recent work not only reduces the particle size but also leads - within a certain set of conditions, 250 rpm and 5 hours – to crystal structure annealing.²⁸ This can be verified with the synchrotron-based XRD pattern in Figure C3, where all diffractions peaks are correctly assigned to Bragg position of low-temperature orthorhombic phase (β_{II} , $Pmn2_I$). As per additional characterization data presented at the SI, the ball milled material has 57 m² g⁻¹ (BET isotherm plots in Figure C4) and primary crystal size of about 50 nm (SEM and TEM images in Figure C5). Such mechanochemically-induced structural annealing we have demonstrated that activates Li-ion diffusion via the combined effects of anti-site defect removal and modulation of the Fe-O coordination environment.²⁸ This nanostructured sample is labeled MLFS from here on.



Figure 5.1. (a) Graphical representation of the three-step process for engineering the PEDOT encapsulated LFS nanocrystals. (b) Graphical illustration of two-step process of *in-situ* chemical polymerization of EDOT on MLFS nanoparticles.

For rendering the particles conductive, typically this is done by carbon coating involving heating the active material with a carbon source at a temperature around 600 - 800 °C.^{12, 34} However, that temperature is prohibitive in the case of the low-temperature orthorhombic LFS (*Pmn2*₁) phase as it will convert to the monoclinic (*P2*₁/*n*) phase.³⁵⁻³⁶ Therefore, we employed poly(3,4-ethylenedioxythiophene) (PEDOT) polymer coating under ambient conditions via chemical de-lithiation/re-lithiation process as schematically illustrated in Figure 5.1b and described in detail in Experimental Section 5.3 and the Appendix, section C3. PEDOT coating was achieved via polymerization of EDOT monomer ^{21, 26} in a two-step procedure described in Figure 5.1b. Firstly, MLFS nanocrystals were partially de-lithiated via oxidation with H₂O₂ as shown in Figure 5.1b. This material is labeled DLFS. Interestingly, direct chemical de-lithiation of asprepared LFS material was not possible (see Figure C7), thus again confirming the need for

nanosizing the micro-sized LFS particles for rendering the surface reactive. Subsequently, the DLFS nanocrystals were coated via *in-situ* chemical polymerization in the presence of LiTFSI salt and EDOT monomer along a small amount of FeCl₃ that acted as a promoter (see Figure 5.1b). While other Fe-containing cathode materials like LiFePO₄ (Lepage *et al.*²¹) and LiFeSO₄F (Sobkowiak *et al.*²⁵) were successfully PEDOT-coated thanks to the oxidation power of their intrinsic Fe^{III}/Fe^{II} couple this did not work in the case of LFS-this most likely reflecting its lower redox potential, 2.8 V vs. 3.4/3.5 V for LFP/ LiFeSO₄F. This led us to try anhydrous FeCl₃ in catalytic amount as is known to promote the polymerization of EDOT.³⁷ For details on the FeCl₃-modified polymerization process refer to Appendix, section C3. For the rest of the discussion, the LFS@PEDOT coated material is labeled as PLFS.

To confirm the formation of PEDOT coating, we characterized the PLFS material, after the de-lithiation step and also after the re-lithiation/polymerization step, by both bulk and surface analysis as shown in Figure 5.2 & 5.3. XRD analysis revealed that partial de-lithiation (DLFS, Li₂. $_{x}Fe^{II}_{1-x}Fe^{III}_{x}SiO_{4}$) of MLFS, induced by the surface chemical reaction with H₂O₂, has happened as evident by the new peaks (denoted with symbol ^) starting emerging in Figure 2a. Possible trace levels of side-reaction impurities, such as iron oxides (Fe₂O₃, Fe₃O₄) are denoted with an asterisk (*). Upon chemical re-lithiation/polymerization, the PLFS material showed no significant difference compared to MLFS material except a bit lower intensity peaks but no more signs of iron oxide impurities. This could be due to partial re-lithiation (see confirmation results in section 5.4.2 & 5.4.3). There were no detectable peaks emanating from PEDOT coating as it is apparently in the amorphous state, consistent with previous polymerization studies of EDOT.^{26, 38} The amount of polymer coating was determined by TGA analysis to be about ~15% as shown in Figure C8.

Interestingly, surface or near-surface chemistry changes were induced by the coating process as evidenced by XPS, FTIR and Raman analysis. Thus, XPS confirmed that the sulphur and carbon peaks coming from the PEDOT coating can be clearly seen in the case of the PLFS material (refer to Figure 5.2b & Figure C9). Notably, un-coated (PEDOT) samples i.e. LFS, MLFS, and DLFS, also show C1s signals (but of reduced size), which is likely due to surface contamination during sample handling under air exposure.³⁹⁻⁴⁰ The FTIR spectrum for as-prepared LFS (seen in Figure 5.2c) shows only the fingerprint features of silicate group, namely the SiO₄



Figure 5.2. Evaluation of bulk and surface chemistry of LFS (as-prepared), MLFS (mechanochemically-annealed), DLFS (partially de-lithiated), and PLFS (PEDOT-coated) materials. (a) Bulk analysis via PXRD. (b) Surface chemistry evaluation via XPS where S signal can be seen after PEDOT coating (PLFS sample). (c) FTIR and (d) Raman spectra of LFS and PLFS.

stretching (526 cm⁻¹) and bending (890 cm⁻¹) vibrations. For PLFS sample though several new FTIR peaks emerged indicative of the formation of PEDOT, namely the C=C ring vibration at ~1185 cm⁻¹ and the C–S vibration at 929 cm⁻¹. These vibration features are in line with the polymerized PEDOT material,^{21,41} confirming the formation of PEDOT on the surface of the LFS nanocrystals. The Raman spectra of as-prepared LFS and PLFS are shown in Figure 5.2d. The LFS sample shows no visible peaks in the PEDOT vibration region, while the PLFS sample shows several bands attributable to PEDOT.⁴² The strong band at 1443 cm⁻¹ is assigned to the stretching vibration of C=C ring. The upward shift for this peak compared with the standard peak of PEDOT ⁴² enhances the electronic conductivity of the polymer.



Figure 5.3. (a) EDS maps of PLFS material, where Fe, Si, O, S maps along with secondary & backscattered electron images are shown. (b) TEM image of PLFS nanocrystals along (c) a HRTEM image revealing a 12 nm layer, and (d) the corresponding SAED pattern.

The core-shell nanostructure of the PLFS material is further elucidated with the TEM, HRTEM & SEM images shown in Figure 5.3b & c and Figure C10, C11 & C12. There, a notable contrast between the LFS nanocrystal cores and PEDOT shells is clear. PEDOT forms sheath-like outer layers (~12 nm), which completely encapsulates the MLFS nanocrystals as shown in Figure 5.3c & C11. In Figure 5.3d, SAED pattern is shown with different planes corresponding to $Pmn2_1$ phase, where the highly bright planes are indicative of strong crystal plane orientation, a feature resulted from the mechanochemical annealing step that we reported elsewhere.²⁸ To verify that the surface layer on the MLFS is PEDOT, we conducted elemental mapping by means of energydispersive X-ray spectroscopy (EDS), as shown in Figure 5.3a & Figure C13. Uniform carbon (C) and sulphur (S) distribution in the material proves that all the LFS nanocrystals are covered by the sulfur-rich PEDOT layers. A schematic of the core-shell architecture of PLFS nanocrystals is provided in Figure C14.

5.4.2. Robust Li-Storage Mechanics of PLFS

The robust electrochemical performance of PLFS (*Pmn2*₁) nanocrystals obtained after PEDOT-encapsulation of the mechanochemically annealed LFS material can be readily appreciated by comparing the voltage profiles at C/40 (1C = 166 mAh g⁻¹) shown in Figure 5.4a. The PLFS electrode delivered exceptional discharge capacity of ~220 mAh g⁻¹ after 2nd cycle at room temperature (RT) or 1.3 Li units. This is almost 2.5 times improvement over the non-PEDOT coated MLFS or CLFS nanocrystals as it can be seen in Figure C17. Another prominent feature of the electrochemical performance of PLFS is its Li-ion storage mechanism, which corresponds to a quasi bi-phasic mode with minimal polarization (Δ V), highly desirable attributes for a high performance cathode.⁴³⁻⁴⁵ By contrast the PEDOT-free LFS nanomaterials, LFS, MLFS, and CLFS exhibit solid-solution storage and high polarization-refer to Figure C17.

The Li-ion storage mechanism in PLFS was evaluated further with the differential capacity plot (dQ/dV) obtained from 2^{nd} cycle and shown in Figure 5.4b. The 1^{st} cycle of PLFS is given in Figure C15 along with its dQ/dV. Notably, the 1^{st} discharge cycle delivered ~210 mAh g⁻¹, which increased subsequently in the 2^{nd} cycle. Likewise, the anodic/cathodic peaks for Fe²⁺/Fe³⁺ couple shifted from 2.93 V/ 2.65 V to 2.84/ 2.68 V from 1^{st} to 2^{nd} cycle, respectively. This potential shift during the initial cycles is commonly observed in silicates and attributed to phase transition towards "inverse" or "cycled" *Pmn2*₁ phase.^{6, 46} The first cycle potential usually reported to be at ~3.1 V,⁴⁷ in our case though we observed it at ~2.9 V. This lower voltage is directly related to the Fe-O bond length (see section 5.4.3 for confirmation).⁴⁷ We further analysed this behaviour by cycling voltammetry (CV) of PLFS cathode at high-temperature (45 °C) as shown in Figure C16. As it can be seen, the 1^{st} and 2^{nd} cycle transition is minimal and peak size & area under peaks also increase after 1^{st} cycle, which confirms discharge capacity increase after 1^{st} cycle.

To investigate further the enhanced Li-ion storage functionality of PLFS we decided to evaluate electrochemically the chemically de-lithiated material, DLFS. Intriguingly, we discovered that the chemical de-lithiation step not only prepared the oxidized surface of DLFS



Figure 5.4. Electrochemical performance of PLFS evaluated via galvanostatic charge/discharge. (a) 2^{nd} cycle at C/40 and room temperature and its (b) corresponding differential capacity curves. Rate performance: galvanostatic charge/discharge curves at different rates (c) and vs. cycle number (d). (e) Long-term cycling of PLFS at different C-rates.

required for the subsequent in-situ polymerization step (refer to Figure 5.1b) but played a key role in facilitating the phase transition during the first two cycles as shown in Figure C18. Thus the CV scans of DLFS sample showed the redox couple peaks at 2.85 V/2.52 V to be essentially identical with those of the "inverse" or "cycled" $Pmn2_1$ phase.⁴⁸ Moreover, we cycled DLFS sample as well and we found to exhibit lower polarization in the 1st cycle compared to LFS, MLFS and CLFS samples (see Figure C19). We must remark here that according to both experimental and theoretical signs, the transition pathway, during the cycling of LFS, towards the stable "inverse" $Pmn2_1$ phase is rather energy-inefficient and strain-causing leading to cathode performance deterioration.^{35, 49} The discovery that this phase transition can be effectively by-passed upon application of the FeCl₃-modified PEDOT coating process on mechanochemically annealed LFS nanocrystals as observed in this work it provides a powerful strategy to reach more than one lithium extraction in a stable reversible manner. But this discovery has even broader significance as it implies that the PEDOT coating process other than endowing the active host core crystals with a conducting layer can have additional material altering effects that till now were gone unnoticed.

The question however that needs to be answered is how exactly the PEDOT coating process induced the observed accelerated phase transition. This may relate to creation of a sub-surface Fe^{III}-rich layer. As an initial guess, we postulate that after chemical re-lithiation associated with the in-situ EDOT polymerization step, part of the near-the-surface oxidized Fe^{III} has remained as sub-surface layer as illustrated in Figure 5.1b. In other words, we suggest that the PLFS nanocrystals prior to cycling were modestly de-lithiated with a possible bilayer ferrous/ferric zoning near the surface. This was indeed confirmed via ex-situ post-mortem synchrotron-based analysis discussed in the next section (see Figure 5.6 & Figure C24). Recently, Okita et al.⁵⁰ demonstrated Fe³⁺- rich LiCoPO₄ (LCFP) crystals to show enhanced stability during cycling. Likewise, in the case of PLFS, the ferric layer beneath the near surface ferrous (Fe^{II}) layer (as depicted in Figure 5.1b) that results from the chemical de-lithiation & re-lithiation of the near surface zone occurring as part of the PEDOT coating process is facilitating phase transition towards the stable cycled phase. Meanwhile, participation of PEDOT proper in the redox process is excluded as when a pure PEDOT sample was cycled between 1.5 - 4.5 V, it showed no redox activity in the potential range of LFS (refer to Figure C20). The PLFS electrode was cycled at different C-rates at RT demonstrating excellent rate performance as shown in Figure 5.4c & d.

Similarly, in Figure 4e, the cycle life & capacity retention at different C-rates is demonstrated for up to 100 cycles. Notably, the PEDOT coating, other than contributing to cycling stability as result of the accelerated phase transition triggered by the Fe^{III}-rich layer, has additional stabilizing role by preventing side-reactions of LFS with the electrolyte as it is deduced by comparing the tail ends (that signals electrolyte reaction) at ~4.5V of CV curves of CLFS and PLFS electrodes (see Figure C21). Strikingly, the PLFS CV tail end is totally suppressed, indicating that PEDOT is acting as passivating layer against degradation of electrolyte.²⁴

Further electrochemical analysis on PLFS nanocrystals is shown in Figure 5.5. Cyclic Voltammetry scans up to ten cycles obtained at 0.16 mV/s shown in Figure 5.5a indicate the redox couple is located at ~2.9 V/2.45 V for 1st cycle remaining essentially unchanged even after 10 cycles confirming our previous results in Figure 5.4a, b & Figure C16. The enhanced intercalation kinetics for the PLFS sample is further probed by Cyclic Voltammetry (CV) at different scan rates as shown in Figure C22. The Li-ion diffusion coefficient (D_{Li}) derived from the CV data (refer to Figure C22 and Table C1) for the PLFS and MLFS electrodes is found to be one order of magnitude higher than that of LFS suggesting the increased intercalation kinetics to relate to the mechanochemical annealing step as per previous results.²⁸ Further, we collected electrochemical impedance spectroscopy (EIS) results as shown in Figure 5.5c along with the equivalent circuit (Figure 5.5b). The intercept at the Re(Z) axis represents the ohmic resistance (R_s) of total resistances of electrolyte, separator and electrical contacts. The semicircle at high frequency is related to the SEI layer, denoted as R_{SEI}. The semicircle at medium frequency range relates to the charge transfer resistance (R_{ct}). The inclined line is the Warburg impedance (Z_W), which is associated with Li⁺ ion diffusion in the active particles.⁵¹ It can be seen that, as the PLFS sample was cycled, the R_{ct} decreased significantly compared to initial cycles-refer to Table C2 for fitting results. Meanwhile, RS_{EI} is seen to increase with cycling, apparently due to SEI film thickening during cycling-as confirmed by XPS and X-PEEM analysis presented in section 5.4.3, and observed in other LIB electrodes.52-54

Further to elucidate the enhanced intercalation in PLFS nanocrystals via EIS (1 MHz to 0.02 Hz), we compared the pristine electrode samples of PLFS and CLFS before and after cycling as shown in Figure 5.5d, e & f. The equivalent circuit and fitting results are given in Figure C23 & Table C3, respectively. Note that in this case the equivalent circuit was expanded to consider



Figure 5.5. Electrochemical evaluation of PLFS nanocrystals via (a) Cyclic Voltammetry performed at 0.16 mV/s and (b & c) Impedance Spectroscopy (1 MHz to 1 Hz) and the corresponding circuit; (d, e & f) comparison of PLFS electrode diffusion kinetics with that of CLFS electrode via EIS (1 MHz to 0.02 Hz) resistances.

also R_{pt} , the resistance associated with the phase transition process. For CLFS sample, the R_{pt} after cycling is seen to have reduced significantly and the tail end to shift towards Re(Z) values. Contrarily, the R_{pt} for PLFS sample was already very low compared to CLFS and decreased even further after cycling. A direct comparison between the two electrodes can be seen in Figure 5.5d, where the EIS results from the two electrodes are plotted together. The superiority of the polymer-coated (PLFS) electrode is truly remarkable, even for freshly assembled or pristine electrodes prior

to cycling. This impressive electrochemical performance improvement is attributed to the two-step engineered core-shell nano-architecture that indeed provides a new paradigm in materializing the high-energy density potential of silicate cathodes with enhanced stability and reasonable rate capability.

5.4.3. *Ex-situ* Postmortem Analysis

Samples of cycled discharge electrodes were further investigated via synchrotron-based characterization. X-ray absorption near-edge (XANES) iron K-edge spectra are shown in Figure 5.6a, where pristine LFS vs. PLFS and cycled PLFS electrode (discharge-state) samples are compared. As it can be seen, there is a slight shift in energy between pristine LFS and PLFS samples. Similarly, this was confirmed by Fe K-edge Fourier transform (EXAFS) spectra of pristine LFS vs. PLFS electrodes as shown in Figure 5.6b. The first main peak (indicated with dashed vertical lines) corresponds to the Fe-O shell mode. EXAFS results for LFS vs. PLFS showed different Fe-O bond length, this confirms our previous results of mechanochemical induced structural annealing during high-energy milling reported elsewhere.²⁸ The PLFS material, before and after cycling did not exhibit any significant change, in agreement with the CV data of Figure 5.5a and C16, owed to accelerated phase transition of $Pmn2_1$ to cycled (or inverse) $Pmn2_1$ phase as they have similar Fe-O length.⁴⁸ We further subjected the PLFS electrodes to X-ray photoemission electron microscopy (X-PEEM) analysis combined with XANES collected at Fe Ledge and the data is shown in Figure 5.6c. X-PEEM is a powerful tool capable of imaging surface structures with tens of nanometer spatial resolution. Used in combination with XANES provides simultaneously morphology and composition information. As it can be seen the pristine electrode of PLFS has a mixture of Fe^{2+} and Fe^{3+} species, which was also confirmed by examining pristine PLFS electrodes with a bulk synchrotron characterization technique, scanning transmission X-ray microscopy (STXM) (see Figure C24). This characterization data clearly confirms our earlier hypothesis in connection to presented electrochemical evaluation that a Fe³⁺ rich sub-layer induced by the de-lithiation and re-lithiation steps occurring during PEDOT coating catalyzes the phase transition towards the stable inverse $Pmn2_1$ phase. Moreover, iron L-edge spectra almost completely shifted to Fe²⁺ after cycling, indicating that the crystal was essentially fully re-lithiated at discharged state as shown in Figure 5.6c.

Oxygen K-edge and its corresponding X-PEEM mapping results are shown in Figure 5.6d. The peak at ~ 530 eV is directly related to the orbital hybridization of FeO₄ tetrahedra,⁵⁵ similar patterns were acquired from STXM as shown in Figure C25. After cycling, the pre-edge oxygen feature is found to be quite low and most of features present in PLFS pristine electrode to have disappeared (Figure 5.6d). We interpret this drastic change to arise from the formation of a rather thick SEI layer, which was confirmed with XPS and X-PEEM combined with XANES F K-edge results shown in Figure C26 & C27. As it can be seen, the F signal coming from the binder (PVDF in our case) was obtained for the pristine electrode before cycling. After cycling, the electrode surface showed a very strong signal from metal fluoride F, which must be LiF. The formation of such passivated LiF layer has been reported previously to take place on LFS electrodes.⁵⁶⁻⁵⁷ Interestingly, the formation of LiF during cycling has been shown to act as a passive layer allowing the intercalation electrode to have long-term stability.⁵⁸



Figure 5.6. (a) XANES iron K-edge and (b) EXAFS of as-prepared LFS electrode vs. pristine PLFS and cycled PLFS electrodes collected at discharged state. X-PEEM (inset) combined with XANES spectra of (c) L-edge iron and (d) K-edge oxygen for pristine PLFS and cycled PLFS electrodes collected at discharged state.

5.5. Conclusion

In this work, the electrochemical activity of the low-temperature orthorhombic phase $(Pmn2_1, \beta_{II})$ of Li₂FeSiO₄ is shown to be remarkably enhanced via the combined effects of mechanochemical annealing and PEDOT coating by *in-situ* polymerization of EDOT involving chemical de-lithiation and re-lithiation steps. The newly engineered core-shell LFS@PEDOT nanocrystals exhibited >1 Li-ion storage capacity, good rate-capability, and cycling stability. Another prominent feature of the electrochemical performance of the LFS@PEDOT cathode is its Li-ion storage mechanism, which corresponds to a quasi bi-phasic mode with minimal polarization (ΔV) , highly desirable attributes for a high-performance cathode. PEDOT coating itself acted as passivating layer preventing undesirable side reactions with the electrolyte. Moreover, a LiF-thick SEI contributed further to cycling stability. Finally of great significance is the discovery that the FeCl₃-modified PEDOT coating process other than its benefits of enhanced conductivity and passivation induces near surface compositional changes that could have a remarkable impact on the functionality of the cathode. Thus, evidence was found of the formation of Fe^{III}-rich subsurface layer in the PEDOT-coated LFS that induced fast structural phase-transition from Pmn21 to inverse *Pmn2*₁ phase leading to enhanced cycling stability. This new dimension of the PEDOT coating process opens new interphasial engineering strategies that in tandem with mechanochemical activation offer new powerful possibilities in our efforts to unlock the high energy density potential of orthosilicate and other emerging intercalation cathode materials.

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J. Zhou assisted with synchrotron data collection and processing at CLS. G. P. Demopoulos directed the research and assisted in manuscript writing.

5.7. References

1. Reinhardt, R.; García, B. A.; Casals, L. C.; Domingo, S. G. A Critical Evaluation of Cathode Materials for Lithium-Ion Electric Vehicle Batteries. In *Project Management and Engineering Research*, Springer: 2019; pp 99-110.

2. Nitta, N.; Wu, F.; Lee, J. T.; Yushin, G. Li-Ion Battery Materials: Present and Future. *Mater. Today* **2015**, *18* (5), 252-264.

3. Zubi, G.; Dufo-López, R.; Carvalho, M.; Pasaoglu, G. The Lithium-Ion Battery: State of the Art and Future Perspectives. *Renew. Sustain. Energy Rev.* **2018**, *89*, 292-308.

4. Li, M.; Lu, J.; Chen, Z.; Amine, K. 30 Years of Lithium-Ion Batteries. *Adv. Mater.* 2018, *30* (33), 1800561.

5. Whittingham, M. S. Ultimate Limits to Intercalation Reactions for Lithium Batteries. *Chem. Rev.* **2014**, *114* (23), 11414-11443.

6. Ni, J. F.; Jiang, Y.; Bi, X. X.; Li, L.; Lu, J. Lithium Iron Orthosilicate Cathode: Progress and Perspectives. *ACS Energy Lett.* **2017**, *2* (8), 1771-1781.

7. Girish, H. N.; Shao, G. Q. Advances in High-Capacity Li_2MSiO_4 (M = Mn, Fe, Co, Ni, ...) Cathode Materials for Lithium-Ion Batteries. *RSC Adv.* **2015**, *5* (119), 98666-98686.

8. Tan, R.; Yang, J.; Zheng, J.; Wang, K.; Lin, L.; Ji, S.; Liu, J.; Pan, F. Fast Rechargeable All-Solid-State Lithium Ion Batteries with High Capacity Based on Nano-Sized Li₂FeSiO₄ Cathode by Tuning Temperature. *Nano Energy* **2015**, *16*, 112-121.

9. Kam, K. C.; Gustafsson, T.; Thomas, J. O. Synthesis and Electrochemical Properties of Nanostructured Li₂FeSiO₄/C Cathode Material for Li-Ion Batteries. *Solid State Ion.* **2011**, *192* (1), 356-359.

10. Lee, K. T.; Cho, J. Roles of Nanosize in Lithium Reactive Nanomaterials for Lithium Ion Batteries. *Nano Today* **2011**, *6* (1), 28-41.

11. Julien, C. M.; Zaghib, K.; Mauger, A.; Massot, M.; Ait-Salah, A.; Selmane, M.; Gendron, F. Characterization of the Carbon Coating onto LiFePO₄ Particles Used in Lithium Batteries. *J. Appl. Phys.* **2006**, *100* (6), 063511.

12. Wang, J.; Sun, X. Understanding and Recent Development of Carbon Coating on LiFePO₄ Cathode Materials for Lithium-Ion Batteries. *Energy Environ. Sci.* **2012**, *5* (1), 5163-5185.

13. Lu, X.; Chiu, H.-C.; Bevan, K. H.; Jiang, D.-T.; Zaghib, K.; Demopoulos, G. P. Density Functional Theory Insights into the Structural Stability and Li Diffusion Properties of Monoclinic and Orthorhombic Li₂FeSiO₄ Cathodes. *J. Power Sources* **2016**, *318*, 136-145.

14. Lv, X.; Zhao, X.; Wu, S.; Nguyen, M. C.; Zhu, Z.; Lin, Z.; Wang, C.-Z.; Ho, K.-M. Fe–Si Networks and Charge/Discharge-Induced Phase Transitions in Li₂FeSiO₄ Cathode Materials. *Phys. Chem. Chem. Phys.* **2018**, *20* (21), 14557-14563.

15. Vajeeston, P.; Fjellvåg, H. First-Principles Study of Structural Stability, Dynamical and Mechanical Properties of Li₂FeSiO₄ Polymorphs. *RSC Adv.* **2017**, *7* (27), 16843-16853.

Kirchmeyer, S.; Reuter, K. Scientific Importance, Properties and Growing Applications of Poly
 (3, 4-Ethylenedioxythiophene). J. Mater. Chem. 2005, 15 (21), 2077-2088.

17. Wang, K. X.; Li, X. H.; Chen, J. S. Surface and Interface Engineering of Electrode Materials for Lithium-Ion Batteries. *Adv. Mater.* **2015**, *27* (3), 527-545.

 Yano, H.; Kudo, K.; Marumo, K.; Okuzaki, H. Fully Soluble Self-Doped Poly (3, 4-Ethylenedioxythiophene) with an Electrical Conductivity Greater Than 1000 S Cm⁻¹. *Sci. Adv.* 2019, 5 (4), eaav9492. Zeng, W.; Wang, L.; Peng, X.; Liu, T.; Jiang, Y.; Qin, F.; Hu, L.; Chu, P. K.; Huo, K.; Zhou,
 Y. Enhanced Ion Conductivity in Conducting Polymer Binder for High-Performance Silicon
 Anodes in Advanced Lithium-Ion Batteries. *Adv. Energy Mater.* 2018, 8 (11), 1702314.

20. Park, K. S.; Schougaard, S. B.; Goodenough, J. B. Conducting-Polymer/Iron-Redox-Couple Composite Cathodes for Lithium Secondary Batteries. *Adv. Mater.* **2007**, *19* (6), 848-851.

21. Lepage, D.; Michot, C.; Liang, G.; Gauthier, M.; Schougaard, S. B. A Soft Chemistry Approach to Coating of LiFePO₄ with a Conducting Polymer. *Angew. Chem.* **2011**, *50* (30), 6884-6887.

22. Fedorková, A.; Oriňáková, R.; Oriňák, A.; Talian, I.; Heile, A.; Wiemhöfer, H.-D.; Kaniansky,
D.; Arlinghaus, H. F. PPy Doped PEG Conducting Polymer Films Synthesized on LiFePO₄
Particles. *J. Power Sources* 2010, *195* (12), 3907-3912.

23. Ouyang, J. Recent Advances of Intrinsically Conductive Polymers. *Acta Phys. Chim. Sin* **2018**, *34* (11), 1211-1220.

24. Xu, G. L.; Liu, Q.; Lau, K. K.; Liu, Y.; Liu, X.; Gao, H.; Zhou, X.; Zhuang, M.; Ren, Y.; Li,
J. Building Ultraconformal Protective Layers on Both Secondary and Primary Particles of Layered
Lithium Transition Metal Oxide Cathodes. *Nat. Energy* 2019, *4*, 484–494.

25. Sobkowiak, A.; Roberts, M. R.; Younesi, R.; Ericsson, T.; Häggström, L.; Tai, C.-W.; Andersson, A. M.; Edström, K.; Gustafsson, T. r.; Björefors, F. Understanding and Controlling the Surface Chemistry of LiFeSO₄F for an Enhanced Cathode Functionality. *Chem. Mater.* **2013**, *25* (15), 3020-3029.

26. Kim, J.; Yoo, J. K.; Jung, Y. S.; Kang, K. Li₃V₂(PO₄)₃/Conducting Polymer as a High Power
4 V-Class Lithium Battery Electrode. *Adv. Energy Mater.* 2013, *3* (8), 1004-1007.

27. Li, W.; Liang, Z.; Lu, Z.; Yao, H.; Seh, Z. W.; Yan, K.; Zheng, G.; Cui, Y. A Sulfur Cathode with Pomegranate-Like Cluster Structure. *Adv. Energy Mater.* **2015**, *5* (16), 1500211.

28. Rasool, M.; Chiu, H.-C.; Lu, X.; Voisard, F.; Gauvin, R.; Jiang, D.; Paolella, A.; Zaghib, K.; Demopoulos, G. P. Mechanochemically-Tuned Structural Annealing: A New Pathway to Enhancing Li-Ion Intercalation Activity in Nanosized β_{II} Li₂FeSiO₄. *J. Mater. Chem. A* **2019**, *7*, 13705-13713

29. Zeng, Y.; Chiu, H.-C.; Rasool, M.; Brodusch, N.; Gauvin, R.; Jiang, D.-T.; Ryan, D. H.; Zaghib, K.; Demopoulos, G. P. Hydrothermal Crystallization of *Pmn2*₁ Li₂FeSiO₄ Hollow Mesocrystals for Li-Ion Cathode Application. *Chem. Eng. J.* **2019**, *359*, 1592-1602.

30. Yabuuchi, N.; Yamakawa, Y.; Yoshii, K.; Komaba, S. Low-Temperature Phase of Li₂FeSiO₄:
Crystal Structure and a Preliminary Study of Electrochemical Behavior. *Dalton Trans.* 2011, 40 (9), 1846-1848.

31. Araujo, R. B.; Scheicher, R. H.; de Almeida, J.; da Silva, A. F.; Ahuja, R. First-Principles Investigation of Li Ion Diffusion in Li₂FeSiO₄. *Solid State Ion.* **2013**, *247*, 8-14.

32. Liivat, A.; Thomas, J. O. Li-Ion Migration in Li₂FeSiO₄-Related Cathode Materials: A DFT Study. *Solid State Ion.* **2011**, *192* (1), 58-64.

33. Araujo, R. B.; Scheicher, R. H.; De Almeida, J.; da Silva, A. F.; Ahuja, R. Lithium Transport Investigation in Li_xFeSiO₄: A Promising Cathode Material. *Solid State Commun.* **2013**, *173*, 9-13.

34. Wang, J.; Yang, J.; Tang, Y.; Liu, J.; Zhang, Y.; Liang, G.; Gauthier, M.; Karen Chen-Wiegart, Y.-c.; Norouzi Banis, M.; Li, X.; Li, R.; Wang, J.; Sham, T. K.; Sun, X. Size-Dependent Surface Phase Change of Lithium Iron Phosphate During Carbon Coating. *Nat. Commun.* **2014**, *5*, 1-8.

35. Lu, X.; Wei, H.; Chiu, H.-C.; Gauvin, R.; Hovington, P.; Guerfi, A.; Zaghib, K.; Demopoulos,
G. P. Rate-Dependent Phase Transitions in Li₂FeSiO₄ Cathode Nanocrystals. *Sci. Rep.* 2015, *5*, 8599.

36. Lu, X.; Chiu, H.-C.; Arthur, Z.; Zhou, J.; Wang, J.; Chen, N.; Jiang, D.-T.; Zaghib, K.; Demopoulos, G. P. Li-Ion Storage Dynamics in Metastable Nanostructured Li₂FeSiO₄ Cathode:

Antisite-Induced Phase Transition and Lattice Oxygen Participation. *J. Power Sources* **2016**, *329*, 355-363.

37. Gueye, M. N.; Carella, A.; Faure-Vincent, J.; Demadrille, R.; Simonato, J.-P. Progress in Understanding Structure and Transport Properties of PEDOT-Based Materials: A Critical Review. *Progress in Materials Science* **2019**, 100616.

38. Zeng, Y.; Han, Y.; Zhao, Y.; Zeng, Y.; Yu, M.; Liu, Y.; Tang, H.; Tong, Y.; Lu, X. Advanced Ti-Doped Fe₂O₃@ PEDOT Core/Shell Anode for High-Energy Asymmetric Supercapacitors. *Adv. Energy Mater.* **2015**, *5* (12), 1402176.

39. Swift, P. Adventitious Carbon—the Panacea for Energy Referencing? *Surf. Interface Anal* **1982**, *4* (2), 47-51.

40. Miller, D.; Biesinger, M.; McIntyre, N. Interactions of CO₂ and CO at Fractional Atmosphere Pressures with Iron and Iron Oxide Surfaces: One Possible Mechanism for Surface Contamination? *Surf. Interface Anal* **2002**, *33* (4), 299-305.

41. Ma, D. L.; Cao, Z. Y.; Wang, H. G.; Huang, X. L.; Wang, L. M.; Zhang, X. B. Three-Dimensionally Ordered Macroporous FeF₃ and Its in-situ Homogenous Polymerization Coating for High Energy and Power Density Lithium Ion Batteries. *Energy Environ. Sci.* **2012**, *5* (9), 8538-8542.

42. Sakamoto, S.; Okumura, M.; Zhao, Z.; Furukawa, Y. Raman Spectral Changes of PEDOT– PSS in Polymer Light-Emitting Diodes Upon Operation. *Chem. Phys. Lett.* **2005**, *412* (4-6), 395-398.

43. Zhang, W.-J. Structure and Performance of LiFePO₄ Cathode Materials: A Review. *J. Power Sources* **2011**, *196* (6), 2962-2970.

44. Yao, B.; Ding, Z.; Zhang, J.; Feng, X.; Yin, L. Encapsulation of LiFePO₄ by in-Situ Graphitized Carbon Cage Towards Enhanced Low Temperature Performance as Cathode Materials for Lithium Ion Batteries. *J. Solid State Chem.* **2014**, *216*, 9-12.

45. Saikia, D.; Deka, J. R.; Chou, C.-J.; Lin, C.-H.; Yang, Y.-C.; Kao, H.-M. Encapsulation of LiFePO₄ Nanoparticles into 3D Interpenetrating Ordered Mesoporous Carbon as a High-Performance Cathode for Lithium-Ion Batteries Exceeding Theoretical Capacity. *ACS Appl. Energy Mater.* **2019**, *2* (2), 1121-1133.

46. Islam, M. S.; Dominko, R.; Masquelier, C.; Sirisopanaporn, C.; Armstrong, A. R.; Bruce, P. G. Silicate Cathodes for Lithium Batteries: Alternatives to Phosphates? *J. Mater. Chem.* 2011, *21* (27), 9811-9818.

47. Sirisopanaporn, C.; Masquelier, C.; Bruce, P. G.; Armstrong, A. R.; Dominko, R. Dependence of Li₂FeSiO₄ Electrochemistry on Structure. *J. Am. Chem. Soc.* **2011**, *133* (5), 1263-1265.

48. Eames, C.; Armstrong, A. R.; Bruce, P. G.; Islam, M. S. Insights into Changes in Voltage and Structure of Li₂FeSiO₄ Polymorphs for Lithium-Ion Batteries. *Chem. Mater.* **2012**, *24* (11), 2155-2161.

49. Masese, T.; Orikasa, Y.; Tassel, C.; Kim, J.; Minato, T.; Arai, H.; Mori, T.; Yamamoto, K.; Kobayashi, Y.; Kageyama, H.; Ogumi, Z.; Uchimoto, Y. Relationship between Phase Transition Involving Cationic Exchange and Charge–Discharge Rate in Li₂FeSiO₄. *Chem. Mater.* **2014**, *26* (3), 1380-1384.

50. Okita, N.; Kisu, K.; Iwama, E.; Sakai, Y.; Lim, Y.; Takami, Y.; Sougrati, M. T.; Brousse, T.; Rozier, P.; Simon, P. Stabilizing the Structure of LiCoPO₄ Nanocrystals Via Addition of Fe³⁺: Formation of Fe³⁺ Surface Layer, Creation of Diffusion-Enhancing Vacancies, and Enabling High-Voltage Battery Operation. *Chem. Mater.* **2018**, *30* (19), 6675-6683.

51. Levi, M.; Salitra, G.; Markovsky, B.; Teller, H.; Aurbach, D.; Heider, U.; Heider, L. Solid-State Electrochemical Kinetics of Li-Ion Intercalation into Li_{1-x}CoO₂: Simultaneous Application of Electroanalytical Techniques SSCV, PITT, and EIS. J. Electrochem. Soc. 1999, 146 (4), 1279-1289.

52. Luo, F.; Chu, G.; Xia, X.; Liu, B.; Zheng, J.; Li, J.; Li, H.; Gu, C.; Chen, L. Thick Solid Electrolyte Interphases Grown on Silicon Nanocone Anodes During Slow Cycling and Their Negative Effects on the Performance of Li-Ion Batteries. *Nanoscale* **2015**, *7* (17), 7651-7658.

53. Zheng, Y.; He, Y.-B.; Qian, K.; Li, B.; Wang, X.; Li, J.; Chiang, S. W.; Miao, C.; Kang, F.; Zhang, J. Deterioration of Lithium Iron Phosphate/Graphite Power Batteries under High-Rate Discharge Cycling. *Electrochim. Acta* **2015**, *176*, 270-279.

54. Dedryvère, R.; Laruelle, S.; Grugeon, S.; Gireaud, L.; Tarascon, J.-M.; Gonbeau, D. XPS Identification of the Organic and Inorganic Components of the Electrode/Electrolyte Interface Formed on a Metallic Cathode. *J. Electrochem. Soc.* **2005**, *152* (4), A689-A696.

55. Laffont, L.; Delacourt, C.; Gibot, P.; Wu, M. Y.; Kooyman, P.; Masquelier, C.; Tarascon, J.
M. Study of the LiFePO₄/FePO₄ Two-Phase System by High-Resolution Electron Energy Loss
Spectroscopy. *Chem. Mater.* 2006, *18* (23), 5520-5529.

56. Dippel, C.; Krueger, S.; Kraft, V.; Nowak, S.; Winter, M.; Li, J. Aging Stability of Li₂FeSiO₄ Polymorphs in LiPF₆ Containing Organic Electrolyte for Lithium-Ion Batteries. *Electrochim. Acta* **2013**, *105*, 542-546.

57. Dippel, C.; Krueger, S.; Kloepsch, R.; Niehoff, P.; Hoffmann, B.; Nowak, S.; Passerini, S.; Winter, M.; Li, J. Aging of Li₂FeSiO₄ Cathode Material in Fluorine Containing Organic Electrolytes for Lithium-Ion Batteries. *Electrochim. Acta* **2012**, *85*, 66-71.

58. Choudhury, S.; Archer, L. A. Lithium Fluoride Additives for Stable Cycling of Lithium Batteries at High Current Densities. *Adv. Electron. Mat.* **2016**, *2* (2), 1500246.

59. Sirisopanaporn, C.; Dominko, R.; Masquelier, C.; Armstrong, A. R.; Mali, G.; Bruce, P. G. Polymorphism in Li₂(Fe,Mn)SiO₄: A Combined Diffraction and Nmr Study. *J. Mater. Chem.* **2011**, *21* (44), 17823-17831.

6. Synopsis

In this final chapter, global conclusions are drawn in order to put in perspective the work undertaken, followed by claims to originality and suggestions for future work.

6.1. Conclusions

In this thesis, the low-temperature β_{II} orthorhombic phase (*Pmn2*₁ space group) of Li₂FeSiO₄ (LFS) was studied as Li-ion battery cathode. While most of the previous studies have focused on the high-temperature γ_s monoclinic phase (*P2*₁/*n* space group) few studies are available on the β_{II} orthorhombic phase. This appears to be to large extent due to the earlier observation the latter phase to be less electroactive than the former one. Thus, in this work focus was placed on studying different means to enhance the intercalation activity of β_{II} LFS phase. This was done via an extensive investigation of material structural modifications prior to cycling and after cycling and relating to electrochemical response. The key findings are summarized below:

Phase-pure β_{II} orthorhombic Li₂FeSiO₄ was hydrothermally synthesized, which following galvanostatic charging-discharging at very low rate yielded very poor capacity (ca. 30 mAh g⁻¹) confirming previous observations of poor intercalation activity. In order to enhance its Li-ion diffusion kinetics hence obtain higher capacity, the material was subjected to nanosizing by highenergy milling. High-energy milling was done in the presence of isopropanol hence its description as mechanochemical process. By careful characterization of the high-energy milled samples generated under variable milling time & planetary speed (rpm) conditions, it was discovered the material not only to undergo nanosizing but also structural changes. This was an unexpected result largely unreported in the battery material literature. Thus, within a window of optimized mechanochemical conditions it was shown structural annealing to occur resembling the most familiar thermal annealing phenomenon. Such mechanochemically-induced annealing was found to lead to isotropic crystal lattice expansion, preferred crystal orientation and defect reduction, which had pronounced impact on intercalation electrochemistry. Effectively the mechanochemically-prepared nanocrystals were endowed with newly opened pathways for Li-ion diffusion (one order of magnitude enhancement in D_{Li}) into less accessible sites hence achieving

three-fold increase in storage capacity (ca. 90 mAh g⁻¹) much higher than simple nanosizing. It was concluded on the basis of XRD, differential capacity, cyclic voltammetry and EIS measurements that such structural "activation" was due to the combined effects of anti-site defect removal and modulation of the Fe–O coordination environment.

Building on the observed activation of β_{II} LFS nanocrystals via mechanochemical annealing, next carbon was added during high-energy milling in order to render the particles conductive by mechanical (as opposed to thermal) C coating. This treatment led to formation of an LFS@C nanocomposite cathode. Upon galvanostatic evaluation, the nanocomposite was found to exhibit a two-fold progressive capacity increase (reaching ~180 mAh g⁻¹) during the initial twelve cycles-a phenomenon that had escaped the attention in previous studies involving LFS cathodes. Intriguingly, the Li-storage mechanism completely shifted as well to bi-phasic type from solid solution mode. It was hypothesized the observed additional Li-ion storage to relate to cycling-induced structural changes that was confirmed upon detailed post-mortem bulk and surface characterization. Thus, upon surface analysis, it was discovered that a thick SEI layer (LiF) was formed, which enabled stable cycling. Further bulk analysis revealed a continuous *in-situ* phase transition to have occurred obeying an S-type nucleation-growth kinetic model, which corresponded very well to the observed gradual increase of storage capacity.

Finally, to further improve the performance of the mechanochemically-activated β_{II} LFS nanocrystals, the latter were coated with the conductive polymer, PEDOT (poly(3,4-ethylenedioxythiophene)) by a modified *in-situ* polymerization technique. The technique involved partial de-lithiation near the surface of the nanocrystals using a chemical oxidant followed by the *in-situ* polymerization step. Thus, very robust core-shell LFS@PEDOT nanocrystals were prepared with very high electrochemical functionality surpassing in performance previous studies involving the low-temperature β_{II} orthorhombic phase of LFS. The core-shell structured LFS@PEDOT nanocrystals registered minimal polarization (ΔV) and an impressive 220 mAh g⁻¹ initial capacity at C/40 and room temperature (RT), with relatively reasonable retention of 200 mAh g⁻¹ after 50 cycles. After careful characterization, it was concluded that PEDOT coating brings added benefits to the performance of the LFS nanocrystals other than the originally targeted enhanced electronic conductivity. Firstly, PEDOT coating leads to the formation of a passivating

layer protecting the nanocrystals from side reactions with the electrolyte; and secondly the subsurface Fe^{3+} -rich layer generated by the chemical de-lithiation seems to play a "catalytic" role in accelerating phase transition towards the inverse *Pmn2*₁ phase resulting in enhanced cycling stability.

6.2. Claims of Originality

- 1. For the first time, crystal structure annealing is achieved for an intercalation cathode material via controlled high-energy milling/mechanochemical treatment.
- 2. Such mechanochemically-induced crystal structure annealing in the case of β_{II} orthorhombic Li₂FeSiO₄ is shown to improve Li-ion intercalation kinetics via crystal reorientation and reduction of defects.
- Origin of cycling-induced progressive capacity increase of high-energy milled carbon-coated LFS is unveiled to relate to an irreversible *in-situ* phase transition governed by an S-type nucleation-growth kinetic model.
- 4. In-situ polymerization of PEDOT has been controlled and applied for the first time as conductive coating layer ("core-shell" structure) on mechanochemically-annealed β_{II} Li₂FeSiO₄ nanocrystals. Such core-shell nanocrystal engineering provides a new direction towards achieving higher than one-Li storage functional silicate cathodes.

6.3. Future Work

No doubt orthosilicates, and LFS in particular the subject of this thesis, remain promising materials as high-energy density cathodes for next-generation LIBs considering their > 1 Li storage capacity potential and their inherent sustainability value. Nevertheless, there are still significant gaps in our material chemistry and engineering knowledge of this type of intercalation compounds before their full potential is realized. Toward this goal, the following considerations with regard to future research directions are made:

1. Having established in the present work that the intercalation storage kinetics of the β_{II} LFS can be activated to reach ≥ 1 Li storage capacity via mechanochemical annealing and PEDOT coating next the cycling stability should be enhanced. This can be done for example by doping. The latest results from a parallel study in our laboratory¹ that found Co substitution to enhance the cycling stability of β_{II} LFS are encouraging in this regard. However, additional systematic cation but also anion substitution studies deserve further investigation.

- 2. On another front, to improve the sluggish kinetics and structural stability of β_{II} LFS (with space group $Pmn2_1$), a thorough study should be conducted on how to directly synthesize the inverse $Pmn2_1$ phase or "cycled" phase thus avoiding capacity fade problems due to phase transition phenomena. The inverse $Pmn2_1$ phase possesses 3D Li-ion intercalation channels, low energy barrier and stable framework hence the desire to target this phase.
- 3. The role of the Fe³⁺-rich sub-surface layer observed to form during the PEDOT coating process deserves further probing as part of the studies in enhancing the cycling stability of LFS.
- 4. Of interest also is to probe the charge compensation mechanism for the LFS@PEDOT cathode that showed > 1 Li storage capacity. Is the extra Li (beyond 1) accommodated via the Fe³⁺/Fe⁴⁺ redox couple, via O redox activity or via electrolyte side reaction? This is a controversial issue in literature,² the elucidation of which can be critical to achieving the full potential of these cathodes.
- 5. In connection to point no 4, a detailed study on finding a suitable electrolyte for high voltage charging (4.5-5.0 V) to fully approach the two-electron reaction capacity and thus establish the inherent stability of LFS is an important prerequisite.

6.3.1. References

1. Zeng, Y.; Chiu, H.-C.; Ouyang, B.; Song, J.; Zaghib, K.; Demopoulos, G. P., Unveiling the mechanism of improved capacity retention in *Pmn2*₁ Li₂FeSiO₄ cathode by cobalt substitution. J. Mater. Chem. A 2019, 7 (44), 25399-25414.

2. Singh, S.; Panda, M. R.; Sen, R.; Johari, P.; Sinha, A.; Meena, S. S.; Mitra, S., Study of Higher Discharge Capacity, Phase Transition, and Relative Structural Stability in Li₂FeSiO₄ Cathode upon Lithium Extraction Using an Experimental and Theoretical Approach and Full Cell Prototype Study. ACS Appl. Energy Mater. 2019, 2 (9), 6584-6598.

Appendix A

Supporting information for Chapter 3 – Mechanochemically-Tuned Structural Annealing



Figure A1. SEM images of pristine Li_2FeSiO_4 (ortho-LFS) prepared using hydrothermal synthesis at 200°C at different resolutions.



Figure A2. (a) and (b) SEM images of 8 and 10-h high-energy milled samples, respectively. (c) and (d) HRTEM images of 8 and 10-h high energy milled samples with inset of SAED. Notably, after 10-h of high-energy milling, the material has undergone significant disordering/amorphization as confirmed by XRD analysis (see Figure 3.2), degree of crystallinity (see Figure A8) and SAED pattern that shows polycrystalline features (see Figure A2d), very similar to pristine sample as discussed in the manuscript.

A1. High-Energy Milling (optimized milling)

To reduce the particle size of Li₂FeSiO₄ (LFS) powder, a Planetary Micro Mill PULVERISETTE 7 premium line (Fritsch) was used. Several parameters were checked prior to select the optimized milling conditions mentioned in manuscript. For wet milling, ethanol, methanol and isopropanol were tested as liquid media. However, isopropanol was selected due to its relatively high boiling point (80.37 °C). For milling parameters, several (rotation per minute) RPMs and time durations were tested as shown in the Table below:

RPM	1-hour	3-hour	5-hour	8-hour	10-hour
50	Х	Х	Х	Х	X
150	Х	Х	Х	х	Х
250	X	X	X	X	X
350	Х	х	Х	Х	Х
450	X	X	X	X	X

Table A1. Different milling parameters tested prior to find the "optimized milling" conditions.

For low rpm (50 and 150), the LFS samples had shown agglomerates even after 5-hour milling and no crystal refinement was observed. For 250 rpm, please refer to the manuscript. For high rpm (both 350 and 450 rpm), even after 1-3 hour of milling, the sample began to lose its crystal order and become amorphous, similarly no observation was made for crystal refinement. Therefore, only 250 rpm with different milling time was further analysed and several samples were tested at Canadian Light Source (CLS) for Synchrotron based- XRD analysis as discussed in the manuscript.

A2. BET Analysis

Figure A2 shows the Brunauer Emmett-Teller (BET) adsorption curves for different samples. The specific surface area can be determined by physical adsorption of a gas on the surface of the solid (powder sample). The amount of adsorbate gas is calculated which corresponds to a monomolecular layer on the surface. This physical adsorption of gas is due to Van der Waals forces between the adsorbate gas molecules and the adsorbent surface area of the powder sample. The determination is usually carried out at the temperature of liquid nitrogen. As with any theory, there are several assumptions made prior to the adsorption calculation i.e. homogeneous surface, local equilibrium, limited molecular interaction etc.¹ The specific surface area can be calculated from the amount of gas adsorbed by the following equation.

$$S = \frac{V_m NA}{22,400 \times m}$$

The constant N is Avogadro's number, V_m is the adsorbed monolayer volume, A is the crosssectional area of single adsorbed gas molecule, m is the mass of nanomaterials used in the measurement and 22,400 represents the Standard Temperature and Pressure (SSTP) volume of one mole of gas. The extracted specific surface from BET (as shown in Figure A3) can be used to determine the equivalent spherical particle diameter using the following equation:

$$D_{BET=\frac{6000}{\rho \cdot S_{\omega}}}$$

Where D_{BET} is the average diameter of a spherical particle, S_{ω} represents the measured surface area of the powder in m² g⁻¹, and ρ is the theoretical density in g cm⁻³.²



Figure A3. Nitrogen adsorption-desorption isotherm plots of ortho-LFS samples prepared at different milling times: (a) Pristine, (b) 1-h, (c) 3-h, and (d) 5-h samples.



Figure A4. XPS data collected for various samples before and after high-energy milling. XPS data collected for various samples before and after high-energy milling. All the spectra were collected for 50 scans and no additional smoothing was performed. Here in (a) the Fe spectra show all the samples to correspond to Fe^{2+} except 8-h sample that corresponds to Fe^{3+} . However minor satellite peaks of Fe^{3+} can be seen for the shorter time (1-h to 5-h) milled samples as more clearly revealed upon data fitting for deconvolution of the spectra in Figure A5. No trace of Fe^{3+} can be seen for the pristine LFS in Figure A5. (b) The Li spectra show no new peaks appearing after high-energy milling but only a slight shift after milling (optimized conditions); the 8h-sample is excluded from discussion here due to surface oxidation. (c) O and (d) Si spectra show no new peaks either, i.e. they remain the same even after milling for 8 hours.


Figure A5. Deconvolution fitting of XPS iron spectra corresponding to (a) pristine ortho-LFS and (b) 5h-milled LFS; the background was subtracted using *Advantage* software. For pristine sample the iron spectra could be fitted with Fe2p_{3/2}, Fe2p_{1/2} and their corresponding satellite peaks. Peaks of Fe2p_{3/2} at 710 eV and Fe2p_{1/2} at 723 eV correspond to Fe²⁺ along with their corresponding satellite peaks. For 5h-LFS sample, Fe²⁺ peak occurred at 710 eV dominates along its satellite peaks but a trace of Fe³⁺ at 718 eV appears to be present.



Figure A6. EDS maps collected to probe the chemical changes induced on the surface before and after high-energy milling. Here f-ratio maps of oxygen, silicon and iron are shown for pristine ortho-LFS, 5-h and 8-h samples, respectively. f-Ratio is defined as $f = \frac{I_A}{I_A + I_B}$, where I_A and I_B are the net characteristic X-ray intensities in one spectrum.³ Oxygen maps for pristine and 5-h sample show homogeneous distribution. By far the biggest surface changes are manifested by the 8-h sample. In this case in addition to the extensive surface oxidation revealed by the presence of Fe³⁺ in the XPS analysis (Figure A4), significant heterogeneous distribution of Fe and Si appears to have occurred possibly due to observed amorphization that is known to be more pronounced near the particle surface.⁴ Given that the 8-h milled sample was found to have become predominantly amorphous/disordered characterized by poor intercalation performance no further investigation of it was pursued.



Figure A7. A lacy carbon grid was dipped in the slurry of pre-vacuum dried 5-h milled sample for characterization of the primary nanoparticles. (a) TEM image of the initial dried suspension collected after resting for 30 mins showing primary nanoparticles ranging in size from 10 to 15 nm. In inset, SAED shows diffractions rings indicative of polynanocrystals. (b) Corresponding HRTEM image showing lattice planes in these primary nanoparticles with various lattice directions as indicated by arrows and circles along with grain boundaries. (c) TEM image of the 5-h milled material collected after prolonged resting (~24 h). It can be clearly seen the primary nanocrystallites to have developed a self-assembled nanoarchitecture –see rectangles and the corresponding diffraction pattern in SAED image (inset); such diffraction pattern with its spot-like appearance confirms the formation of single nanocrystal architecture.⁵⁻⁶ (d) Corresponding HRTEM image showing the crystal planes in the same lattice direction/orientation.

A3. Determination of Degree of Crystallinity

The degree of crystallinity (DOC) was determined by EVA software. Initially the background was manually selected. This background doesn't represent amorphous or crystalline part of the sample. After removing the background, scattering only from crystalline and amorphous part can be determined by creating two patterns for each part. A ghost background was created to evaluate the amorphous region (without diffusing or cutting any crystalline peaks). This ghost amorphous background can be appended, which can be used to compare with the crystalline region of the sample. Therefore, in the final step, the DOC can be calculated using integrated area between the amorphous and crystalline region by the following equation:

$$DOC = \frac{Crystalline Area}{Crystalline Area + Amorphous Area}$$

The weight fraction of amorphous area, W_{amorph} as shown in Figure A8, can be calculated from:

 $W_{amorph} = 1 - DOC$



Figure A8. The weight fraction of amorphous area W_{amorph} for different milled samples at 250 RPM.



Figure A9. Top to bottom: 1-h sample was refined with $Pmn2_1$ space group with corresponding refinement values of R_{wp} : 3.83, R_p : 2.76 and GOF: 2.37; 3-h milled sample: R_{wp} : 3.81, R_p : 2.90 and GOF: 2.59.

Table A2. Refined crystallographic parameters for (a) pristine Li_2FeSiO_4 , (b) 1-h sample, (c) 3-h sample and (d) 5-h sample

Site	Np	x	У	Z	Atom	Осс	Beq
Lil	4	0.94078	0.16415	0.77161	Li	0.8125	1
					Fe	0.1875	1
03	4	0.78850	0.67776	0.89258	0	1	1
Fel	2	0.00000	0.15270	0.44373	Fe	0.6251	1
					Li	0.3749	1
01	2	0.00000	0.86603	0.29966	0	1	1
02	4	0.32465	0.28832	0.79103	0	1	1
Si	2	0.00000	0.82524	0.88782	Si	1	1

(a) Pristine sample

Lattice parameters

a (Å)	6.2691995	
b (Å)	5.3429072	
c (Å)	4.9563822	

 $R_{wp}\!\!:$ 4.60, $R_p\!\!:$ 3.51 and GOF: 2.95

(b) 1-h sample

Site	Np	x	У	Z	Atom	Осс	Beq
Lil	4	1.00000	0.14475	0.76592	Li	0.834	1
					Fe	0.166	1
03	4	0.76792	0.64786	0.89780	0	1	1
Fel	2	0.00000	0.16376	0.40531	Fe	0.6679	1
					Li	0.3321	1
01	2	0.00000	0.83511	0.20163	0	1	1
02	4	0.29230	0.30180	0.78520	0	1	1
Si	2	0.00000	0.84917	0.83568	Si	1	1

Lattice parameters

a (Å)	6.2702395	
b (Å)	5.3425342	
c (Å)	4.9592315	

 $R_{wp}\!\!:$ 3.83, $R_p\!\!:$ 2.76 and GOF: 2.37

(c) 3-h Sample:

Site	Np	X	У	Ζ	Atom	Осс	Beq
Lil	4	1.00000	0.13709	0.77421	Li	0.8674	1
					Fe	0.1326	1
03	4	0.77448	0.64890	0.88844	0	2.231	1
Fel	2	0.00000	0.15870	0.41157	Fe	0.7348	1
					Li	0.2652	1
01	2	0.00000	0.82258	0.41157	0	1	1
02	4	0.27807	0.28859	0.76866	0	1	1
Si	2	0.00000	0.84284	0.84102	Si	1	1

Lattice parameters

a (Å)	6.2754813	
b (Å)	5.3519562	
c (Å)	4.9626168	

 $R_{\rm wp}\!\!:$ 3.81, $R_p\!\!:$ 2.90 and GOF: 2.59

(d) 5-h Sample:

Site	Np	X	У	Ζ	Atom	Осс	Beq
Lil	4	0.98778	0.12210	0.80765	Li	0.8953	1
					Fe	0.1047	1
03	4	0.77511	0.67023	0.89673	0	1	1
Fel	2	0.00000	0.16656	0.43305	Fe	0.7906	1
					Li	0.2094	1
01	2	0.00000	0.86883	0.29089	0	1	1
02	4	0.33543	0.28576	0.80246	0	1	1
Si	2	0.00000	0.80728	0.87672	Si	1	1

Lattice parameters

a (Å)	6.2829135
b (Å)	5.3525385
c (Å)	4.9670688

 $R_{wp}\!\!:$ 3.73, $R_p\!\!:$ 2.73 and GOF: 2.25



Figure A10. Electron back scattering (EBSD) images of 1-h milling sample indexed as $Pmn2_1$ with MAD value of 1.423° and 3-h milling sample indexed as $Pmn2_1$ with MAD value of 1.451°.



Figure A11. XRD comparison between pristine ortho-LFS and 5-h milled sample between 8 to 14 degree to determine subtle changes caused by high-energy milling.



Figure A12. Illustration of crystal structure of $Pmn2_1$ Li₂FeSiO₄: (a) free of anti-sites and (b) as prepared with Fe_{Li} defects; the lithium pathway (denoted by arrows) is blocked in the latter case. The illustration was created using VESTA software. Li and Fe atoms occupy different crystallographic sites in the ideal $Pmn2_1$ structure of Li₂FeSiO₄, denoted as Li1 (4b site) and Fe1 (2a site), respectively.⁷⁻⁸ During electrochemical lithiation/de-lithiation, Li migrates in either a-direction (into the paper as denoted by red cross) or a zig-zag c-direction (denoted by blue arrows). When there are significant Fe_{Li} anti-site defects, the lithium diffusion pathway in either a or c direction is blocked as depicted by black cross and arrows.



Figure A13. Galvanostatic charge/discharge of (a) pristine, (b) 1-h, (c) 3-h, (d) 5-h, (e) 8-h and (f) 10-h ortho-LFS samples at C/50 (room temperature) milled materials between 1.5 to 4.5 V vs. Li⁺/Li.



Figure A14. Specific charge/discharge capacity vs. cycle number of pristine, 1-h, 3-h, 5-h, 8-h and 10-h ortho-LFS samples at C/50 (room temperature) between 1.5 to 4.5V vs. Li⁺/Li. For clarity cycle numbers are plotted from 3 cycles onwards as initial cycles (1 and 2) are already plotted in Figure A13.



Figure A15. Coulombic efficiency vs. cycle number of pristine, 1-h, 3-h, 5-h, 8-h and 10-h ortho-LFS samples



Figure A16. Comparison of galvanostatic charge/discharge curves of pristine ortho-LFS and 5-h milled samples cycled at C/50 at room temperature and 55 °C from 4.5 to 1.5 V vs. Li⁺/Li. Dashed lines are used to denote the samples cycled at RT, while solid lines are used to denote samples cycled at 55 °C, respectively.



Figure A17. Galvanostatic charge/discharge curves over 50 cycles (1.5 to 4.5V): Polarization comparison, (a) pristine and (b) 5-h samples. (c) Capacity and Coulombic Efficiency vs. Number of cycles. Cycling at C/50 and RT between 1.5 to 4.5V.



Figure A18. Differential capacity curves calculated from galvanostatic charge/discharge curves of (a) pristine ortho-LFS and after high-energy milling of (a) 8-h and (b) 10-h.



Figure A19. Cyclic voltammetry scans at different rates for (a) pristine and (c) 5-h samples along corresponding $I_p vs. v^{0.5}$ plots in (b) and (d) respectively.

Note to Figure A19.

The apparent diffusion coefficient (D_{Li}) of lithium ions is estimated from the linear relationship between the peak current (I_p) and the square root of the scan rate ($v^{0.5}$) according to the following equations:

$$I_{p} = 2.69 \text{ x } 10^{5} \text{ n}^{3/2} \text{ A x } \text{D}^{1/2} \text{ v}^{1/2} \text{ C}_{\text{Li}}^{\frac{1}{2}}$$
(A.1)

$$D_{Li} = [k / (2.69 x 10^{5} n^{3/2} A x C_{Li})]^{2}$$
(A.2)

where I_P (Amps) is the peak current, A (cm²) is the contact area between electrode and electrolyte, n is the number of electrons involved in redox process, C_{Li}^* is the bulk concentration of lithium ions in the electrolyte (0.04 mol cm⁻³ for the Li₂FeSiO₄ cathode), and v is the scan rate in V/s. Cyclic voltammetry of the pristine and milled samples was performed with scan rates ranging from 0.1 to 0.5 mV/s as shown in Figure A19a,c. Figure A19b,d show the peak current has a linear relationship with square root of scan rate, which is a typical behavior for diffusion-controlled processes.⁹ The calculated apparent diffusion coefficient is given in Table A3.

Table A3. Calculated apparent diffusion coefficient for pristine and 5-h milled samples obtained by varying the CV scan rates from 0.1 mV/s to 0.5 mV/s.

Sample - D _{Li} (cm ² /s)	Anodic (oxidation)	Cathodic (reduction)
Pri - LFS	2.33 x 10 ⁻¹⁴	6.12 x 10 ⁻¹⁴
5h - LFS	2.89 x 10 ⁻¹³	5.23 x 10 ⁻¹³



Figure A20. EIS spectra of pristine and 5-h milled samples. The intercept at the Re(Z) axis represents the ohmic resistance (R_s) of total resistances of electrolyte, separator and electrical contacts. The semicircle relates to the charge transfer resistance (R_{ct}). The inclined line is the Warburg impedance (Z_W), which is associated with Li⁺ ion diffusion in the cathode active particles.¹⁰ The EIS curves were fitted by an equivalent circuit with the aid of EC-Lab software (see inset of Figure A20). The fitting results are presented in Table A4 below. R_{CT} is significantly less for the 5-h sample than the corresponding one for pristine sample exemplifying the enhanced intercalation kinetics induced as result of the mechanochemical annealing effect confirming our CV results reported in Figure A19.

Table A4. EIS fitting results for pristine and 5-h milled samples.

Sample	$\operatorname{Rs}(\Omega)$	$\mathbf{R}_{\mathrm{CT}}(\mathbf{\Omega})$
Pri - LFS	10.2	412.5
5h - LFS	8.3	78.6

A4. References

1. Brame, J.; Griggs, C. Surface Area Analysis Using the Brunauer-Emmett-Teller (BET) Method: Standard Operating Procedure Series: SOP-C; US Army Engineer Research and Development Center-Environmental Laboratory ...: 2016.

2. Zhou, M.; Wei, Z.; Qiao, H.; Zhu, L.; Yang, H.; Xia, T., Particle size and pore structure characterization of silver nanoparticles prepared by confined arc plasma. *J. Nanomater.* **2009**, *2009*, 3.

3. Brodusch, N.; Demers, H.; Gauvin, R., The f-Ratio Method for X-Ray Microanalysis in the SEM. In *Field Emission Scanning Electron Microscopy*, Springer: 2018; pp 55-65.

4. Da Silva, K. L.; Menzel, D.; Feldhoff, A.; Kübel, C.; Bruns, M.; Paesano Jr, A.; Düvel, A.; Wilkening, M.; Ghafari, M.; Hahn, H., Mechanosynthesized BiFeO₃ nanoparticles with highly reactive surface and enhanced magnetization. *J. Phys. Chem. C* **2011**, *115* (15), 7209-7217.

5. Zhang, Q.; Liu, S.-J.; Yu, S.-H., Recent advances in oriented attachment growth and synthesis of functional materials: concept, evidence, mechanism, and future. *J. Mater. Chem.* **2009**, *19* (2), 191-207.

6. Li, M.; Schnablegger, H.; Mann, S., Coupled synthesis and self-assembly of nanoparticles to give structures with controlled organization. *Nature* **1999**, *402* (6760), 393.

7. Liivat, A.; Thomas, J. O., Li-ion migration in Li₂FeSiO₄-related cathode materials: A DFT study. *Solid State Ionics* **2011**, *192* (1), 58-64.

8. Armstrong, A. R.; Kuganathan, N.; Islam, M. S.; Bruce, P. G., Structure and Lithium Transport Pathways in Li₂FeSiO₄ Cathodes for Lithium Batteries. *J. Am. Chem. Soc.* **2011**, *133* (33), 13031-13035.

9. Denis, Y.; Fietzek, C.; Weydanz, W.; Donoue, K.; Inoue, T.; Kurokawa, H.; Fujitani, S., Study of LiFePO₄ by cyclic voltammetry. *J. Electrochem. Soc.* **2007**, *154* (4), A253-A257.

10. Levi, M.; Salitra, G.; Markovsky, B.; Teller, H.; Aurbach, D.; Heider, U.; Heider, L., Solid-State Electrochemical Kinetics of Li-Ion Intercalation into Li_{1-x}CoO₂: Simultaneous Application of Electroanalytical Techniques SSCV, PITT, and EIS. *J. Electrochem. Soc.* **1999**, *146* (4), 1279-1289.

Appendix B

Supporting information for Chapter 4 – Cycling-Induced Li-ion

Intercalation Activation



Figure B1. XRD pattern of as-prepared Li₂FeSiO₄ sample obtained with synchrotron source ($\lambda = 0.7523$ Å) and refined with *Pmn2*₁ space group (R_{wp} = 4.60, R_p = 3.51 and GOF = 2.95) using TOPAS software. Lattice parameters obtained from fitting are a = 6.2691995 (Å), b = 5.3429072 (Å) and c = 4.956382 (Å). The '*' indicate the presence of minor iron oxide impurities (Fe₂O₃, Fe₃O₄ and Fe (OH)₃). By comparing the relative peak areas, the iron oxides were estimated to amount to about ~5% of the LFS material.



Figure B2. SEM images of as-prepared Li₂FeSiO₄ by hydrothermal synthesis at 200°C at different resolutions.



Figure B3. Nitrogen adsorption-desorption isotherm plot of LFS@C nanocomposite sample after mechanochemical treatment in the presence of carbon.



Figure B4. (a) HRTEM of LFS@C nanocomposite and its corresponding (b) *fast Fourier transform* (FFT) obtained using Image J software, respectively.



Figure B5. Raman spectroscopy indicating D and G bands for carbon presence in LFS@C nanocomposite sample.



Figure B6. (e) Charge/discharge plots after 20, 30 and 50th cycle of LFS@C nanocomposite at C/50.

Table B1.	EIS	fitting	results	for	LFS@C	nanocomi	oosite
Table D1.	LID	munig	results	101	LIDWC	nanocom	JUSITE.

Sample	$R_{S}(\Omega)$	Rsei(Ω)	R _{CT} (Ω)
LFS - c2	8.1	15.2	118.3
LFS – c11	8.3	29.5	92.3
LFS – c20	8.2	35.2	79.4
LFS - c50	8.3	39.3	48.3



Figure B7. EIS comparison at a very low frequency (0.5 mHz) between pristine LFS@C nanocomposite electrode and after 30^{th} cycle. (a) Equivalent circuit model used to obtain the results, notably, where $R_{PT}(\Omega)$ denotes the phase transition during cycling.¹⁻³ (b) White open circle symbol corresponds to EIS of freshly assembled LFS@C electrode. Black solid circles correspond to cycled LFS@C electrode after 20^{th} cycle. It can be clearly seen that the intercalation kinetics are changed completely after cycling. Obtained results are present in Table B2 below. $R_{PT}(\Omega)$ has reduced significantly after *in-situ* electrochemical phase transition. (c) An enlarged plot of red box shown in (b).

Sample	$R_{S}(\Omega)$	$R_{SEI}(\Omega)$	$R_{CT}(\Omega)$	$\mathrm{R}_{\mathrm{PT}}\left(\Omega ight)$
LFS – Pristine	8.3	4.3	127.9	87,010
LFS - c30	8.2	41.2	86.2	10,254

Table B2. EIS fitting results for pristine LFS@C nanocomposite electrode and after 30th discharge cycle.



Figure B8. SEM image of *ex-situ* electrode of LFS@C nanocomposite at different resolutions after 30^{th} cycle, where cracks were introduced during handling.



Figure B9. Energy-dispersive X-ray spectroscopy (EDS) maps of pristine LFS@C nanocomposite electrode vs. after 30 cycles of galvanostatic charging/discharging collected along with TEM.



Figure B10. *f*-ratio maps for Carbon are shown for pristine LFS@C nanocomposite electrode and after 30^{th} discharge cycle.


Figure B11. Simulation of normal $Pmn2_1$ phase and inverse $Pmn2_1$ (or "cycled") of Li₂FeSiO₄ obtained via PDF- 4+ 2019 software.



Figure B12. Le-Bail fitting results obtained for LFS@C nanocomposite after 30 cycles (collected at discharge state) via TOPAS software. Lattice parameters obtained from fitting are a = 6.2421(3) (Å), b = 5.3924(7) (Å) and c = 5.0119(5) (Å).



Figure B13. Illustrations of crystal structure models drawn by Vesta Software. (a) $Pmn2_1$ phase of LFS, where all tetrahedra point towards the same direction. Li-ions can migrate along only in two directions. (b) In the inverse $Pmn2_1$ (electrochemically cycled structure), where all the Fe-ions exchange site with half of the Li2-site, Li-ions can migrate along in three different directions.⁴ (c) For a visual aid, crystal structure was drawn without tetrahedra of Lithium, where Li and Fe atoms occupy different crystallographic sites in the ideal $Pmn2_1$ structure of Li₂FeSiO₄, denoted as Li1 (4b site) and Fe1 (2a site), respectively.⁴⁻⁵ During electrochemical lithiation/de-lithiation, Li migrates in either a-direction (into the paper as denoted by the red cross) or a zig-zag c-direction (denoted by blue arrows). After cycling, significant cation mixing occurred, a new pathway opens up and the lithium can diffuse into zig-zag b-direction (red-arrows) as well.



Figure B14. Zoomed-in pre-edge of XANES iron K-edge spectra of pristine LFS@C nanocomposite electrode and after 30 cycles, the background was subtracted using Origin software.

B1. References

1. Orazem, M. E.; Tribollet, B., *Electrochemical impedance spectroscopy*. John Wiley & Sons: 2017.

2. Sen, U. K.; Johari, P.; Basu, S.; Nayak, C.; Mitra, S., An experimental and computational study to understand the lithium storage mechanism in molybdenum disulfide. *Nanoscale* **2014**, *6* (17), 10243-10254.

3. Shaju, K.; Rao, G. S.; Chowdari, B., Li ion kinetic studies on spinel cathodes, Li(M_{1/6}Mn_{11/6})O₄ (M= Mn, Co, CoAl) by GITT and EIS. *Journal of Materials Chemistry* **2003**, *13* (1), 106-113.

4. Armstrong, A. R.; Kuganathan, N.; Islam, M. S.; Bruce, P. G., Structure and Lithium Transport Pathways in Li₂FeSiO₄ Cathodes for Lithium Batteries. *J. Am. Chem. Soc.* **2011**, *133* (33), 13031-13035.

5. Liivat, A.; Thomas, J. O., Li-ion migration in Li₂FeSiO₄-related cathode materials: A DFT study. *Solid State Ion.* **2011**, *192* (1), 58-64.

Appendix C

Supporting information for Chapter 5 – Conductive Polymer Coating

C1. Hydrothermally Synthesized Li₂FeSiO₄ (LFS)



Figure C1. XRD pattern of as-prepared Li₂FeSiO₄ (LFS) material obtained with synchrotron source ($\lambda = 0.7523$ Å) and refined with *Pmn2*₁ space group (R_{wp} = 4.60, R_p = 3.51 and GOF = 2.95) using TOPAS software. Lattice parameters obtained from fitting are a = 6.2691995 (Å), b = 5.3429072 (Å) and c = 4.956382 (Å).



Figure C2. SEM images at different resolutions of as-prepared Li₂FeSiO₄ (LFS) by hydrothermal synthesis at 200°C.

C2. Mechanochemically Prepared LFS (MLFS)



Figure C3. XRD pattern of mechanochemically treated MLFS material after 5h of high-energy milling obtained with synchrotron source ($\lambda = 0.7523$ Å) and refined with *Pmn2*₁ space group (R_{wp}: 3.73, R_p: 2.73 and GOF: 2.25) using TOPAS software. Lattice parameters obtained from fitting are a = 6.2829135 (Å), b = 5.3525385 (Å) and c = 4.9670688 (Å).



Figure C4. Nitrogen adsorption-desorption isotherm plots of mechanochemically treated MLFS sample.



Figure C5. Morphology of LFS after mechanochemical treatment via SEM and HR-TEM images. (a) SEM image, (b) TEM image and its corresponding (c) HRTEM image of MLFS sample with inset of SAED. Nanocrystal size was calculated using ImageJ software¹ and found to be mostly in the range of 50 nm. MLFS sample has d-spacing of 0.534 nm which corresponds to (010) plane, along with SAED pattern of highly bright planes with diffraction features indicative of a strong orientation of crystal planes.

C3. PEDOT Encapsulated LFS Nanocrystals (PLFS)



Figure C6. (a) Petri dish with MLFS, lithium salt (LiTFSi), and monomer (EDOT) in methanol solution ready for evaporation; and (b) after complete evaporation (color changed after evaporation). (c) Comparison of LFS and PLFS powder samples before and after PEDOT coating.



Figure C7. Chemical de-lithiation of as-prepared LFS, i.e. without prior mechanochemical activation via high-energy milling. As-prepared LFS crystals ($\sim 1 \mu m$) largely remained the same after chemical de-lithiation. Several oxidation agents (i.e. Br₂, NO₂BF₄, H₂O₂, etc.) were tried, however, the LFS did not oxidize and all attempts failed; this indicates the strong need for nanosizing the LFS crystals before coating.

Notes to Figure C6 & C7:

PEDOT stands for poly(3,4-ethylenedioxythiophene), is a type of thiophene based conjugated polymer. The PEDOT coating was performed in a two-step process.

First Step: The first step for chemical *in-situ* polymerization of PEDOT requires partial delithiation of the surface via oxidation. Lepage et al.² reported partial chemical de-lithiation of LiFePO₄ using hydrogen peroxide (H₂O₂) as an oxidizing agent. Similarly, in our case, numerous attempts were made for partial de-lithiation for as-prepared LFS using their procedure. However, all of them were unsuccessful even when the H₂O₂ concertation was increased ten times. Moreover, the temperature was also raised to 60° C while stirring to increase the reactivity, yet it was unsuccessful. Then the oxidizing agent was changed to bromine (Br₂) and nitronium tetrafluoroborate (NO₂BF₄), which has been reported to oxidize LiFePO₄ and LiFeSO₄F materials,^{3, 4} yet the crystals largely remained the same as indicated by the XRD peaks shown in Figure C7, where no significant changes were observed after vigorous oxidation. However, when LFS was subjected to high-energy milling for mechanochemical activation, the oxidation procedure worked with the initial concentration reported for H₂O₂ and CH₃COOH, respectively.⁴, ⁵ This confirms the need for nanosizing the micro-sized LFS crystals for enhancing the surface reactivity which promoted oxidation.⁶ The partial surface oxidation was confirmed via XRD (see Figure 5.2) and ferric (Fe^{3+}) layer was formed on the surface of MLFS nanoparticles as shown in the illustration in Figure 5.1b & C6. This partially de-lithiated (Li_(2-x)FeSiO₄) sample is labeled as DLFS. It is reported that the oxidized transition metal ions in the de-lithiated phase promote the polymerization of the 3,4-ethylenedioxythiophene (EDOT) monomer to the conductive PEDOT.², ⁵ However, in case of LFS, it was quite challenging to coat the MLFS nanoparticles without any initiator as discussed below. Moreover, chemical de-lithiation ensures that the surfaces of each particle are exposed to the solution, therefore polymerization is expected to occur predominantly on the de-lithiated surface of the particles. Thereof the exposed surface becomes coated with polymer coating (PEDOT) (see Figure 5.1b & C6).

Second Step: After partial chemical de-lithiation of the surface, polymer coating requires in-situ chemical polymerization of EDOT monomer on the surface of the partially de-lithiated surface. In case of LFP (~3.5 V). Lepage et al.² reported that polymerization of EDOT and the Li reinsertion occur simultaneously in the absence of other oxidants or initiators. Likewise, Kim et al.⁵ and Sobkowiak et al.⁴ reported chemical polymerization without any initiator in case of Li₃V₂(PO₄)₃ (~4.0 V) and LiFeSO₄F (~3.5 V), respectively. However, in case of LFS, due to relatively lowvoltage (~2.8 V) polymerization didn't occur simultaneously in the presence of DLFS, LiTFSI and EDOT, respectively. After several unsuccessful attempts under ambient conditions even when excessive amounts of LiTFSI and EDOT was used, we decided to use chemical oxidant but only in catalytic amounts to polymerize EDOT on DLFS nanoparticles. We used anhydrous FeCl₃ as a catalyst as it has been reported to polymerize EDOT under ambient conditions.⁷⁻⁹ Several tests were carried out to find a suitable FeCl₃ to EDOT ratio. We varied ratios from 1:20 to 1:120 (FeCl₃: EDOT), respectively. At 1:100 molar ratio, polymer coating was found to be successful under ambient conditions. Visible color change was observed upon solvent evaporation (at 60 °C) as shown in Figure C6a, b. After washing and drying the material overnight, it permanently turned into dark blueish color as shown in Figure C6c. Notably, during re-lithiation, some ferric (Fe³⁺) remained inside the bulk as indicated in illustration 1b, which was confirmed via XANES, X-PEEM and STXM (see Figure 5.6 & C24).



Figure C8. TGA analysis of as-prepared LFS and after PEDOT coating (PLFS sample). The estimated weight of PEDOT coating is \sim 15 %.



Figure C9. Sulphur (S) XPS spectra for LFS, DLFS and PLFS samples, where S signal is clearly identified after polymer coating.



Figure C10. SEM images of PEDOT encapsulated LFS nanocrystals at different resolutions.



Figure C11. TEM images at different resolutions of PEDOT-encapsulated MLFS nanoparticles; compare to non-encapsulated MLFS in Figure C5.



Figure C12. EDS maps collected simultaneously during TEM & HRTEM imaging of PLFS sample show the presence of the characteristic S & C signal of PEDOT, samples were collected on a Cu-grid.



Figure C13. (a) Carbon EDS map of PLFS sample on C-tape. (b) (a) EDS maps of PLFS sample, where Fe, Si, O, S maps were collected on Cu-tape.



Figure C14. Illustration of PLFS core-shell architecture, where the core is made of nanosized mechanochemically annealed LFS nanocrystals and the shell of conducting PEDOT layer.

C4. Electrochemistry of Robust LFS@PEDOT



Figure C15. First cycle of PLFS sample along with its differential capacity, where arrows indicate the peaks corresponding to the Fe^{2+}/Fe^{3+} redox couple; galvanostatic charging/discharging was performed at room-temperature (RT) and C/40.



Figure C16. Cyclic voltammetry of PLFS cathode at 45 °C to elucidate the voltage shift due to phase transition during the first two cycles.¹⁰



Figure C17. First cycle charge/discharge comparison for as prepared LFS, MLFS, CLFS (at C/50), and PLFS sample (at C/40); galvanostatic charging/discharging tests were performed at room-temperature (RT).



Figure C18. Electrochemical performance of de-lithiated LFS (DLFS) evaluated via (a) CV and (b) Galvanostatic charging/discharging for the first few consecutive cycles; tests were performed at room-temperature (RT) and C/40.



Figure C19. (a) & (b) Comparison of the 1^{st} cycle of de-lithiated LFS vs. PLFS. (c) 1^{st} cycle comparison of LFS, MLFS, CLFS, DLFS and PLFS samples; charging/discharging tests were performed at room-temperature (RT) and C/40.



Figure C20. Cyclic voltammetry of pure PEDOT cycled between 1.5 and 4.5 V, where it can be seen that there is no notable electrochemical activity in the LFS active redox potential range (2 - 4.0 V).



Figure C21. CV comparison of CLFS & PLFS samples for side reaction with electrolyte at ~4.5 V, where arrows indicate suppression of side oxidation/reduction reactions with electrolyte at the tail ends.





The apparent diffusion coefficient (D_{Li}) of lithium ions is estimated from the linear relationship between the peak current (I_p) and the square root of the scan rate $(v^{0.5})$ according to the following equations:

$$I_{p} = 2.69 \text{ x } 10^{5} \text{ n}^{3/2} \text{ A x } \text{D}^{1/2} \text{ v}^{1/2} \text{ C}_{\text{Li}}^{\frac{1}{2}}$$
(1)

$$D_{Li} = [k / (2.69 \text{ x } 10^{5} \text{ n}^{3/2} \text{ A x } \text{C}_{Li})]^{2}$$
(2)

where I_P (Amps) is the peak current, A (cm²) is the contact area between electrode and electrolyte, n is the number of electrons involved in redox process, C_{Li}^* is the bulk concentration of lithium ions in the electrolyte, and v is the scan rate in V/s. The peak current has a linear relationship with square root of scan rate, which is a typical behavior for diffusion-controlled processes.¹³ The calculated apparent diffusion coefficient is given in Table C1.

Table C1. Calculated apparent diffusion coefficient for LFS, MLFS and PLFS samples obtained by varying the CV scan rates.

Sample - D _{Li} (cm ² /s)	Anodic (oxidation)	Cathodic (reduction)
LFS	2.33 x 10 ⁻¹⁴	6.12 x 10 ⁻¹⁴
MLFS	2.89 x 10 ⁻¹³	5.23 x 10 ⁻¹³
PLFS	1.49 x 10 ⁻¹³	3.98 x 10 ⁻¹³

Table C2. EIS	fitting results for	PLFS electrode.	where $c(x)$ re	epresents the c	vele number.
	inting results for	I LI D CICCIOUC,		epresents the e	yele mumber.

Sample	$R_{S}(\Omega)$	$R_{SEI}(\Omega)$	$\mathbf{R}_{\mathrm{CT}}(\mathbf{\Omega})$
PLFS – c2	4.1	5.3	60.1
PLFS – c10	4.1	8.5	50.6
PLFS – c20	4.2	9.2	48.3
PLFS – c30	4.0	11.5	43.6
PLFS – c40	4.0	15.8	36.2
PLFS – c50	4.0	15.9	33.3



Figure C23. Equivalent circuit model used to obtain the results for EIS data presented in Figure 5.5d, notably, where new element $R_{PT}(\Omega)$ denotes the phase transition during cycling.¹¹⁻¹³

Table C3. EIS fitting results for pristine and cycled electrodes (after 30th discharge cycle).

Sample	$R_{S}(\Omega)$	Rsei(Ω)	$\mathbf{R}_{\mathrm{CT}}\left(\Omega ight)$	$\mathrm{R}_{\mathrm{PT}}\left(\Omega ight)$
CLFS – Pristine	4.3	3.2	128.4	5,256
CLFS – Cycled (30 th)	4.2	41.2	86.2	2,820
PLFS – Pristine	4.2	3.6	89.3	1,253
PLFS – Cycled (30 th)	4.3	48.3	50.3	1,152



Figure C24. Iron L-edge of PLFS electrode prior to cycling evaluated via STXM, where red and green spectra correspond to the chemical mapping obtained via STXM. Both areas show a mixture of iron species ($Fe^{2+} \& Fe^{3+}$) present prior to electrochemical cycling. STXM (Scanning transmission X-ray microscopy) is an element-sensitive spectroscopy method with spatial information in terms of chemical and electronic structures.



Figure C25. O K-edge of PLFS electrode prior to cycling evaluated via STXM, where red and green spectra correspond to the chemical mapping.



Figure C26. Comparison of PLFS electrode samples before and after cycling. (a) Pristine PLFS indicating Fluorine (F) signal from PVDF (binder in the electrode). (b) Cycled PLFS showing strong peak at 685 eV, which is attributed to LiF formation on the surface during cycling.^{14, 15}



Figure C27. X-PEEM (inset) combined with F K-edge XANES spectroscopy of the cycled PLFS sample (electrode collected at discharged state). Two peaks, one at ~690 eV and the other at ~692 eV can be assigned to the PVDF (binder in the composite electrode) and LiF, respectively.¹⁶ After cycling, binder contribution (~ 690 eV) is completely suppressed by the intense peak (~692 eV) of LiF.

C5. References

1. Schneider, C. A.; Rasband, W. S.; Eliceiri, K. W. Nih Image to Imagej: 25 Years of Image Analysis. *Nat. Methods* **2012**, *9* (7), 671-675.

2. Lepage, D.; Michot, C.; Liang, G.; Gauthier, M.; Schougaard, S. B. A Soft Chemistry Approach to Coating of LiFePO₄ with a Conducting Polymer. *Angew. Chem.* **2011**, *50* (30), 6884-6887.

3. Andersson, A. S.; Kalska, B.; Häggström, L.; Thomas, J. O. Lithium Extraction/Insertion in LiFePO₄: An X-Ray Diffraction and Mössbauer Spectroscopy Study. *Solid State Ionics* **2000**, *130* (1-2), 41-52.

4. Sobkowiak, A.; Roberts, M. R.; Younesi, R.; Ericsson, T.; Häggström, L.; Tai, C.-W.; Andersson, A. M.; Edström, K.; Gustafsson, T. r.; Björefors, F. Understanding and Controlling the Surface Chemistry of LiFeSO₄F for an Enhanced Cathode Functionality. *Chem. Mater.* **2013**, *25* (15), 3020-3029.

5. Kim, J.; Yoo, J. K.; Jung, Y. S.; Kang, K. Li₃V₂(PO₄)₃/Conducting Polymer as a High Power 4 V-Class Lithium Battery Electrode. *Adv. Energy Mater.* **2013**, *3* (8), 1004-1007.

6. Rasool, M.; Chiu, H.-C.; Lu, X.; Voisard, F.; Gauvin, R.; Jiang, D.; Paolella, A.; Zaghib, K.; Demopoulos, G. P. Mechanochemically-Tuned Structural Annealing: A New Pathway to Enhancing Li-Ion Intercalation Activity in Nanosized β_{II} Li₂FeSiO₄. *J. Mater. Chem. A* **2019**, *7*, 13705-13713

7. Zhang, X.; Lee, J.-S.; Lee, G. S.; Cha, D.-K.; Kim, M. J.; Yang, D. J.; Manohar, S. K. Chemical Synthesis of PEDOT Nanotubes. *Macromolecules* **2006**, *39* (2), 470-472.

8. Corradi, R.; Armes, S. Chemical Synthesis of Poly (3, 4-Ethylenedioxythiophene). *Synthetic metals* **1997**, *84* (1-3), 453-454.

9. Blidberg, A.; Valvo, M.; Alfredsson, M.; Tengstedt, C.; Gustafsson, T.; Björefors, F. Electronic Changes in Poly (3, 4-Ethylenedioxythiophene)-Coated LiFeSO₄F During Electrochemical Lithium Extraction. *J. Power Sources* **2019**, *418*, 84-89.

10. Lu, X.; Chiu, H.-C.; Arthur, Z.; Zhou, J.; Wang, J.; Chen, N.; Jiang, D.-T.; Zaghib, K.; Demopoulos, G. P. Li-Ion Storage Dynamics in Metastable Nanostructured Li₂FeSiO₄ Cathode: Antisite-Induced Phase Transition and Lattice Oxygen Participation. *J. Power Sources* **2016**, *329*, 355-363.

11. Orazem, M. E.; Tribollet, B. *Electrochemical Impedance Spectroscopy*. John Wiley & Sons: 2017.

12. Sen, U. K.; Johari, P.; Basu, S.; Nayak, C.; Mitra, S. An Experimental and Computational Study to Understand the Lithium Storage Mechanism in Molybdenum Disulfide. *Nanoscale* **2014**, *6* (17), 10243-10254.

13. Shaju, K.; Rao, G. S.; Chowdari, B. Li Ion Kinetic Studies on Spinel Cathodes, $Li(M_{1/6}Mn_{11/6})O_4$ (M= Mn, Co, CoAI) by GITT and EIS. *J. Mater. Chem.* **2003**, *13* (1), 106-113.

Dippel, C.; Krueger, S.; Kraft, V.; Nowak, S.; Winter, M.; Li, J. Aging Stability of Li₂FeSiO₄
 Polymorphs in LiPF₆ Containing Organic Electrolyte for Lithium-Ion Batteries. *Electrochim. Acta* 2013, *105*, 542-546.

15. Dippel, C.; Krueger, S.; Kloepsch, R.; Niehoff, P.; Hoffmann, B.; Nowak, S.; Passerini, S.; Winter, M.; Li, J. Aging of Li₂FeSiO₄ Cathode Material in Fluorine Containing Organic Electrolytes for Lithium-Ion Batteries. *Electrochim. Acta* **2012**, *85*, 66-71.

16. Balasubramanian, M.; Lee, H. S.; Sun, X.; Yang, X.-Q.; Moodenbaugh, A.; McBreen, J.; Fischer, D. A.; Fu, Z. Formation of SEI on Cycled Lithium-Ion Battery Cathodes: Soft X-Ray Absorption Study. *Electrochem. Solid-State Lett.* **2002**, *5* (1), A22-A25.