Negative Electrode Materials for Lithium Ion Batteries

Elina Pohjalainen
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Elina Pohjalainen

A doctoral dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the Aalto University School of Chemical Technology for public examination and debate at lecture hall V1 at the Aalto University School of Chemical Technology (Espoo, Finland) on the 10th of June, 2016, at 12 noon.

Aalto University
School of Chemical Technology
Department of Chemistry
Research Group of Electrochemical Energy Conversion and Storage
Abstract

Lithium ion batteries have become the primary energy source for portable electronics, and their utilization in larger scale applications is increasing as well. Numerous electrode materials have been investigated for lithium ion batteries and several different materials are also found in commercial cells. The properties, cost and safety of the battery strongly depends on the selected electrode materials and cell design. The focus of this thesis is on negative electrode materials and electrode manufacturing methods that are environmentally friendly and safe for large scale and high power applications.

First part of this thesis studies Li$_4$Ti$_5$O$_{12}$ (LTO) as a negative electrode material. Especially the effect of the particle morphology on the electrochemical performance is evaluated in detail. It is shown by comparing two LTO materials with same crystalline structure but different morphology that small particle size and large surface area has a beneficial effect on the battery performance. In addition, different behavior in terms of (de)lithiation voltages and lithium storage is observed in the LTO surface than in the bulk. Thus it is shown that the performance of LTO can be tailored by affecting the particle morphology. Moreover, the role of carbon additives in the LTO electrodes is studied. The effect of carbon additives on the performance of LTO electrodes is minimal when moderate conditions (low currents at room temperature) are used. However, in more demanding conditions (high currents and/or low temperatures) the beneficial effect of carbon additives is observed. The effect of carbon additives is more obvious with LTO with smaller particle size, and it is concluded that the effect of carbon additives depends both on the particle and electrode morphology.

In the second part of the thesis, a water soluble acrylate binder Acryl S020 is studied for aqueous preparation of LTO and graphite negative electrodes. Commonly used PVDF (polyvinylidene fluoride) binder is costly and requires harmful NMP (N-methyl pyrrolidone) as a solvent and thus alternative methods are searched for. It is shown that similar capacities are achieved with LTO electrodes using an Acryl S020 binder manufactured with an aqueous process when compared to the LTO electrodes using a PVDF binder. Moreover, pilot scale slot die coating and gravure printing methods are tested in the electrode manufacturing and cycle lives of over 500 are obtained with both methods. Also water absorption/desorption of LTO is shown to be nearly reversible, and thus the aqueous process seems applicable for the preparation of LTO electrodes. Promising results are also obtained with the graphite electrodes using the Acryl S020 binder as better capacities at high C-rates and low temperature are achieved when compared to the graphite electrodes using a CMC (carboxymethyl cellulose) + SBR (styrenebutadiene rubber) binder combination.

Keywords  lithium ion batteries, negative electrodes, electrode fabrication

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Preface

The work presented in this thesis was carried out at the Department of Chemistry at Aalto University between June 2009 and February 2016 (excluding maternity leave between August 2014 and July 2015). Funding from Tekes in Nomali and Nofali projects is gratefully acknowledged.

First of all I want to thank my supervisor and advisor Dr. Tanja Kallio who offered me the opportunity to do this doctoral thesis in the interesting field of lithium ion batteries. Especially the beginning of my research work was challenging and I couldn’t have made it without the constant support from her.

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Elina Pohjalainen
Espoo, April 2016
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List of Publications

This doctoral dissertation consists of a summary and of the following publications which are referred to in the text by their Roman numerals

I Elina Pohjalainen, Taina Rauhala, Markus Valkeapää, Jani Kallioinen, Tanja Kallio, Effect of Li$_4$Ti$_5$O$_{12}$ particle size on the performance of lithium ion battery electrodes at high C-rates and low temperatures, *The Journal of Physical Chemistry C*, 119 (2015) 2277-2283.


Author’s Contribution

Publication I  Effect of Li$_4$Ti$_5$O$_{12}$ particle size on the performance of lithium ion battery electrodes at high C-rates and low temperatures

The author defined the research plan together with the co-authors and did all the experimental work excluding full cell testing at low temperature, XRD and HR-TEM. She actively developed experimental methods for electrode and cell fabrication. She interpreted the results and wrote the manuscript.

Publication II  Comparative study of carbon free and carbon containing Li$_4$Ti$_5$O$_{12}$ electrodes

The author defined the research plan together with the co-authors and did all the experimental work. She interpreted the results and wrote the manuscript.

Publication III  Water soluble acrylate binder for graphite electrodes in lithium-ion batteries

The author defined the research plan together with the co-authors. She planned and instructed the electrochemical measurements conducted by Olli Sorsa, and participated in them actively. She did SEM characterization, interpreted the results and wrote the manuscript.

Publication IV  Water soluble binder for fabrication of Li$_4$Ti$_5$O$_{12}$ electrodes

The author defined the research plan together with the co-authors. She performed majority of the electrochemical characterization. She interpreted the results and wrote the manuscript together with the co-authors.

Espoo, April 26th, 2016

____________________________________

Assoc. Prof. Tanja Kallio
**List of Abbreviations and Symbols**

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<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
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<tr>
<td>AMAC</td>
<td>poly(acrylamide-co-diallyldimethylammonium chloride)</td>
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<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller theory of adsorption</td>
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<td>BETI</td>
<td>lithium bisperfluorothanesulfonimide</td>
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<tr>
<td>CC</td>
<td>constant current</td>
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<td>CCCV</td>
<td>constant current, constant voltage</td>
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<td>CMC</td>
<td>carboxymethylcellulose</td>
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<td>CNT</td>
<td>carbon nanotube</td>
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<td>CV</td>
<td>cyclic voltammetry</td>
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<td>DEC</td>
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<td>DMC</td>
<td>dimethyl carbonate</td>
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<td>EC</td>
<td>ethylene carbonate</td>
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<td>EIS</td>
<td>electrochemical impedance spectroscopy</td>
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<td>EMC</td>
<td>ethyl methyl carbonate</td>
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<td>EV</td>
<td>electric vehicle</td>
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<td>HEV</td>
<td>hybrid electric vehicle</td>
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<td>HRTEM</td>
<td>high resolution transmission electron microscopy</td>
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<td>LCO</td>
<td>lithium cobalt oxide</td>
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<td>LFP</td>
<td>lithium iron phosphate, LiFePO$_4$</td>
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<td>LIBOB</td>
<td>lithium bis(oxalato) borate</td>
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<td>LMO</td>
<td>lithium manganese oxide, LiMn$_2$O$_4$</td>
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<td>LTO</td>
<td>lithium titanate, Li$_4$Ti$<em>5$O$</em>{12}$</td>
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<td>NCA</td>
<td>LiNi$<em>{0.8}$Co$</em>{0.15}$Al$_{0.05}$O$_2$</td>
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<td>Abbreviation</td>
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<tr>
<td>NMC</td>
<td>LiNi_{1/3}Mn_{1/3}Co_{1/3}O_{2}</td>
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<td>NMP</td>
<td>N-methylpyrrolidone</td>
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<td>OCP</td>
<td>open circuit potential</td>
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<td>PAA</td>
<td>polyacrylic acid</td>
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<td>PAN</td>
<td>polyacrylonitrile</td>
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<td>PVDF</td>
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<td>SBR</td>
<td>styrenebutadiene rubber</td>
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<td>SEI</td>
<td>solid electrolyte interface</td>
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<td>SEM</td>
<td>scanning electron microscopy</td>
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<td>SOC</td>
<td>state of charge</td>
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1. Introduction

Lithium ion batteries were first commercialised in the early 1990’s by Sony [1]. Since then lithium ion batteries have become the primary energy source for portable electronics due to their high energy density, light weight, long cycle life and low self-discharge rates [2]. Recently, concerns about climate change and dependence on fossil fuels have accelerated the development of electric vehicles (EV) and hybrid electric vehicles (HEV) and increased the demand for renewable energy sources. Furthermore, large scale energy storage options are needed to even out the supply and demand of electricity produced from renewables and to ensure the reliability of the grid. These three main applications for lithium ion batteries (portable electronics, transport and stationary storage) set very different requirements for the energy storage system. For example, high power capability is essential in EV and HEV applications as well as enhanced safety. High energy density on the other hand is important in both portable applications and EVs/HEVs, whereas it is not necessarily a priority in all stationary storage applications.

The properties and performance of the lithium ion battery are largely dictated by the choice of electrode materials, and thus the optimal electrode combination also depends on the intended application. For example, energy density (Wh l\(^{-1}\)) or specific energy (Wh kg\(^{-1}\)) are determined by the potential (V) and capacity (Ah kg\(^{-1}\)) of the cell, and those in turn depend on the properties of the electrode materials. Ragone plot comparing specific energy and specific power (W kg\(^{-1}\)) of different types of energy storage and conversion technologies is presented in Figure 1, and typical battery characteristics of some commercial rechargeable battery types are presented in Table 1. The energy and power density (or specific energy/power) of lithium ion batteries are generally higher than those of other rechargeable batteries such as lead acid, nickel-cadmium (NiCd) or nickel metal hydride (Ni-MH) batteries [3]. Also self-discharge rates of lithium ion batteries are significantly lower than those of Ni-MH batteries (2% vs. 15-25%/month) [2]. Cycle life of a lithium ion battery depends on the chemistry of the system. It is usually defined as full charge and discharge cycles while retaining more than 80% of the original capacity [4]. Typically \(\geq 1000\) cycles are achieved with lithium ion batteries, and with some configurations more than 10000 cycles have been reported [5].
Lithium cobalt oxide (LiCoO$_2$, LCO) and graphite were the choices for positive and negative electrode materials in the first commercial lithium ion batteries [1]. Since then a broad range of new materials for electrodes have been under development. Layered oxides (LiCoO$_2$, LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (NMC), LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ (NCA)), lithium iron phosphate (LiFePO$_4$, LFP) and spinel LiMn$_2$O$_4$ (LMO) are probably the most investigated materials for positive electrodes and all found in commercial lithium ion batteries [7,8]. For negative electrode materials graphite is still most widely used, but also lithium titanate (Li$_4$Ti$_5$O$_{12}$, LTO) based batteries have been commercially available for some years now, and batteries using silicon incorporated into carbon based negative electrodes have recently come on the market too. Although graphite has been successfully used in the negative electrodes of lithium ion batteries for more than 20 years already, it has some disadvantages related to the low lithium insertion potential: lithium plating on the surface of graphite may occur during high current charging and at low temperatures which has a detrimental effect on the performance and safety of the battery [9,10]. Thus safer material options are needed for graphite, and LTO is a promising candidate especially for applications requiring high power densities or wide temperature range. Although a few commercial lithium ion batteries already utilize LTO as a negative electrode material, all the properties of LTO are not yet fully understood. In this thesis the performance of LTO is optimized by altering both the particle and electrode...
morphology. In the second part of the thesis electrode manufacturing using environmentally friendly water soluble binder is studied for LTO and graphite. Furthermore, the most important electrode materials for both positive and negative electrodes are reviewed in Chapter 2 as well as other components of the lithium ion cell.

LTO is a negative electrode material with the very unique characteristics of almost zero volume change during charging/discharging and very flat charging/discharging voltage profiles [11,12]. In the first part of this thesis, the performance and electrochemistry of LTO is discussed. By comparing two similar LTO materials with different particle morphology, the effect of properties such as particle size and surface area on the electrochemical performance is evaluated in Publication I. It is shown that the morphology of LTO particles greatly affects the charging/discharging behaviour as reduced particle size and large secondary particle structures have a favourable effect on the performance. In addition to the enhanced capacity, also different surface potentials and excess Li storage are observed for smaller LTO particles. The results in Publication I show that the properties of LTO can be tailored by modifying the morphology of the LTO particles by simple end treatment in the synthesis procedure.

Moreover, the effect of carbon in LTO electrodes is studied in Publication II. Although carbon additives are generally used for the electrode manufacturing of lithium ion batteries, carbon free LTO electrodes have gained attention recently as very promising results with completely carbon free LTO electrodes have been published [13,14]. In publication II it is shown that carbon additives have some effect on the performance of LTO electrodes at more demanding conditions (high C-rates and low temperatures) even though the performance of the carbon free and carbon containing LTO electrodes at low C-rates and room temperature is indeed similar. The magnitude of the effect caused by carbon additives depends on the LTO particle morphology and is also shown in cycle life behaviour. The use of carbon additives is an important aspect for the industrial manufacturing of LTO electrodes as preparation of electrode slurries containing carbon black has its own challenges.

In the last part of the thesis, electrode manufacturing and the use of a water soluble binder is discussed. Traditionally lithium ion batteries are manufactured using polyvinylidene fluoride (PVDF) as a binder and N-methylpyrrolidone (NMP) as a solvent [2]. Also a carboxymethyl cellulose (CMC) and styrenebutadiene rubber (SBR) combination in aqueous media is commonly used for manufacturing of graphite electrodes. As PVDF is rather expensive and NMP environmentally unfriendly, and CMC+SBR combination prone to bacteria growth, other aqueous electrode fabrication methods have been widely studied. Therefore, water soluble acrylate binder Acryl S020 is studied and the concept is applied for preparation of LTO (Publication IV) and graphite (Publication III) electrodes. LTO and graphite as electrode materials possess different challenges as graphite has considerable volume change during intercalation of lithium and formation of solid electrolyte interface (SEI) layer whereas LTO has negligible volume change and no considerable SEI formation, but tends to ab-
sorb significant amounts of humidity which is known to be detrimental for lithium ion batteries using LiPF₆ as an electrolyte salt. In Publication IV it is shown that the water absorption and desorption process is reversible and excess water can be removed by careful drying. Similar performance of LTO electrodes with Acryl Sozo and PVDF were obtained and also promising results with pilot scale gravure printing and slot die coating methods were achieved as very stable capacities of more than 500 cycles were obtained. In addition to this, also graphite electrodes manufactured using Acryl Sozo showed similar or better performance than those using CMC+SBR as a binder combination in Publication III.
2. Materials for lithium ion batteries

Lithium ion batteries are rechargeable batteries in which lithium ions move between positive and negative electrodes through the electrolyte and electrons flow through the external circuit. The structure of a lithium ion battery is presented in Figure 1 and shows the most important cell components: positive and negative electrodes and electrolyte. When the battery is charged, lithium ions and electrons move from the positive electrode that is oxidized to the negative electrode that is reduced, and during discharge vice versa [2]. In lithium ion batteries, numerous different (electrode) materials are utilized in contrast to other battery technologies, however they are all based on lithium ion transport and storage between the negative and positive electrodes. The performance, cost and safety of the lithium ion battery depends strongly on the selected battery chemistry and design.

Figure 2. Structure of a lithium ion cell using graphite negative electrode and layered metal oxide positive electrode.

In this chapter the most important electrode materials are reviewed. In general, active electrode materials for lithium ion batteries are structures that can host lithium ions repeatedly. Based on the reaction mechanism, electrode materials can be categorized into three types: insertion, alloying and conversion type of materials [15]. Insertion compounds such as LiCoO₂ and graphite are the conventional materials for lithium ion batteries where lithium ions are inserted into unoccupied interstitial sites of the host lattice. This induces shrinking and expansion of the host lattice as lithium ions are inserted/removed. However due to relatively small changes and stability of the host lattice, stable capacities are
usually obtained over a relatively long time, however the capacity is limited by the number of available insertion sites [16]. Alloying materials include several options such as Si and Sn that react electrochemically with lithium forming Li-X-alloys (where X is for example Si, Sn). This involves breaking of the bonds between the host atoms and formation of a new LiX phase [17]. Conversion reactions on the other hand involve electrochemical reaction of a transition metal compound MX with lithium ions yielding metallic nanoparticles in a LiX matrix [18]. Alloying and conversion reactions both have the advantage of much higher capacity when compared to intercalation compounds. However, insertion/de-insertion of lithium into/from the allying and conversion types of materials involves breaking of the bonds of the host lattice and severe volume change of the material. This causes significant problems in mechanical stability leading to poor cycle life. Here the focus is on the most extensively researched electrode materials that are at a commercial stage already. These are mostly insertion compounds, as allying and conversion type of electrode materials are still far from commercialization (maybe with the exception of Si based negative electrodes).

2.1 Positive electrode materials

Several potential materials exist for the positive electrodes of lithium ion batteries of which transition metal oxides and polyanion compounds are possibly the most intensively researched. Layered transition metal oxide LiCoO₂ (LCO) was the first to be commercialized and is still used in many commercial lithium ion batteries especially in portable electronics [7,19]. LCO consists of alternating layers of Co₂ and Li (Figure 2A) where both Co and Li are octahedrally coordinated [20]. This layered structure enables facile lithium diffusion pathways and thus results in high electronic and ionic conductivity [8]. Other advantages of LCO include high insertion/extraction voltage (average 3.8 V vs. Li/Li⁺), good cyclability, and low self-discharge rates. The theoretical capacity of LCO is as high as 274 mAh g⁻¹, however the practical capacity is limited to only 150 mAh g⁻¹ due to instability of the structure and capacity fade when more than 50-70 % of lithium ions are extracted [21,22]. Moreover, LCO based Li ion batteries are rather costly due to the high price of Co and low thermal stability is a major issue as exothermal release of oxygen from LCO can lead to a phenomenon called thermal runaway and which can cause the battery to burst into flames [7,23,24].

Due to the high cost and safety problems of LCO, alternative positive electrode materials are needed for lithium ion batteries intended for large scale applications. A successful approach has been a (partial) substitution of Co in LiCoO₂ with Mn, Ni, and Al and leading to a development of a variety of LiMxCo1−xO₂ and LiMₓM₂yCo₁−ₓ−yO₂ compounds [25]. Of the ternary layered oxides, the most widespread in commercial use so far have been LiNi₀.₅Mn₀.₅Co₀.₅O₂ (NMC) and LiNi₀.₈Co₀.₁₅Al₀.₀₅O₂ (NCA) compounds, although there are also other options available [7]. NMC can be described as a solid solution of LiCoO₂, LiMnO₂ and LiNiO₂ with valences 2+, 3+ and 4+ for Ni, Co and Mn, respectively. Capacities of 150-200 mAh g⁻¹ can be obtained with NMC depending on the applied
voltage window with an average voltage of 3.7 V vs. Li/Li', where Ni and Co are both oxidized while Mn remains 4+ [26,27]. With NCA also capacities of 200 mAh g⁻¹ can be achieved with mainly Ni oxidizing at an average voltage of 3.7 V vs. Li/Li' [28,29]. Of these two layered transition metal oxides, NCA has higher energy density, whereas NMC has higher thermal stability and is thus the safer option [25,30,31].

Figure 3. Structures of positive electrode materials: A) layered LiCoO₂, B) spinel LiMn₂O₄, C) olivine LiFePO₄ [32] and D) discharge curves of several positive electrode materials, adapted from [7]. Reproduced with permission from Elsevier.

Spinel LiMn₂O₄ (LMO) is an alternative positive electrode material to layered transition metal oxides, as Mn is cheap, abundant and environmentally friendly when compared to Co and Ni based oxides. The structure of LMO is a cubic three dimensional framework with Mn occupying octahedral 16d and Li tetrahedral 8a sites (as in spinel LTO) presented in Figure 2B. The structure allows facile Li transport in 3D structure and relatively high electronic conductivity [33]. (De)lithiation occurs at a relatively high potential of 4.1 V vs. Li/Li' and two plateaus can be observed in the charging/discharging curves as shown in discharge curve in Figure 2D. However, the practical capacity is rather low 120 mAh g⁻¹. In addition LMO based cells suffer from problems in long-term stability, especially at elevated temperatures, both during cycling and storage. The main reason for the capacity fading is Mn²⁺ dissolution in LiPF₆ containing electrolytes after the disproportionation reaction

\[ 2\text{Mn}^{3+}_{\text{solid}} \rightarrow \text{Mn}^{4+}_{\text{solid}} + \text{Mn}^{2+}_{\text{Solution}} \]

[2]. Also other mechanisms for capacity fading have been proposed such as Jahn Teller distortion of Mn³⁺ at deep discharge [34], oxygen loss during cycling [35] etc. Several approaches have been proposed to stabilize LMO electrodes such as partial substitution of Mn [36,37] and surface coating/modification of LMO [38,39], however more work is still needed in order to extend the materials lifespan.
LiFePO₄ (LFP) is another alternative to layered positive electrode materials that has gathered huge interest since its introduction in 1997 [40] and has also been commercialized already. LFP has an olivine structure that consists of PO₄³⁻ tetrahedral units with Fe(II) in corner-shared octahedral positions and Li in chains of edge sharing octahedral positions (Figure 2C). When charged, Fe(II) is oxidized to Fe(III) in a heterogeneous two phase reaction at very constant potential (similar to LTO) at a potential of 3.4 V vs. Li/Li⁺ [40]. The practical capacity obtained with LFP is close to the theoretical capacity which is 170 mAh g⁻¹. LFP has several advantages over LiCoO₂ and its derivatives such as lower cost and nontoxicity. Also high thermal stability of LFP [41,42] together with the operation voltage being well inside the electrolyte stability window allows manufacturing of high power cells with good safety and very long cycle life [5,43]. A disadvantage of the low potential is the low energy density of the cell. Also poor ionic and electronic conductivity [44,45] has been a major issue in utilisation of LFP. Diffusion of lithium in LFP is highly anisotropic as diffusion of Li ions occurs one dimensionally in channels along the [010] channel indicating the importance of the quality of LFP as impurities and defects can easily block these channels [46]. Improvements to ionic/electronic conductivity of LFP have been achieved by reduction of particle size [47], carbon coating [48,49] and doping [50]. Electrochemistry and phase behaviour of LFP is a complicated issue and depends for example on the particle size and charging/discharging conditions [51-53]. The effect of nanosize on two phase behaviour of LFP in contrast to LTO is discussed shortly in Chapter 4.1. Other olivine structures LiMPO₄ (M=Mn, Co, Ni) have also been actively researched as they have a higher voltage than LFP and thus higher energy density. However, LiMnPO₄ shows rather poor kinetics [54,55] whereas LiCoPO₄ and LiNiPO₄ have voltages close to or beyond the electrolyte stability window [56-58] limiting their practical applications.

2.2 Negative electrode materials

Carbonaceous structures are the most commonly used materials in negative electrodes of lithium ion batteries and numerous different types of carbon materials have been tested and are commercially available for use in lithium ion battery electrodes. The first commercial lithium ion batteries were constructed with petroleum coke as negative electrode, but nowadays graphitic negative electrodes are most common [2]. Graphite electrodes have the advantage of low cost, abundance, high electrical conductivity and relatively high energy density due to a low lithium insertion potential of 0.1-1 V vs. Li/Li⁺ and relatively good capacity of 372 mAh g⁻¹ when fully reacted to LiC₆ [7]. The properties of carbonaceous negative electrodes depend strongly on the structure of carbon. Available carbon materials range from natural graphite to synthetic materials formed by pyrolysis with different precursors. They are often divided into two general categories that are soft carbons i.e. graphite or graphitizing carbon, and hard carbons i.e. non-graphitizing carbons. Hard carbons are highly disordered structures that show higher capacities than graphite electrodes even exceeding
the theoretical capacity. However, also larger irreversible capacities are related to the first few cycles of hard carbon electrodes. Also impurities affect the performance of carbon electrodes and for example hydrogen-containing carbons have been investigated widely. [16,59,60]

In graphitic carbon, atoms are arranged in a hexagonal array forming planar sheets i.e. graphene layers stacked on top of each other. Intercalated lithium is located between graphene layers on top of hexagonal C ring in a way to avoid near neighbour occupation. Stacking of graphene layers changes from A-B-A-B-A to A-A-A-A-A (Figure 3C) as lithium is inserted between them and the distance between graphene layers increases by approximately 10% [61]. Intercalation of lithium into graphite occurs through a mechanism called staging. This means that lithium in not uniformly intercalated between graphene layers but is distributed in certain distant layers rather than occupying neighbouring layers. Staging mechanisms are illustrated in Figure 3B where stage 1 corresponds to the fully lithiated structure LiC₆, stage 2 has lithium intercalated between every other graphene layer, stage 3 has lithium intercalated between every third graphene layer etc. Existence of different stages is also manifested in charging/discharging curves as several distinctive plateaus are observed corresponding to transitions between different stages (Figure 3A) [62,63]. It should be noted that transition between stages 4 and 2 involves several stages, namely stage 3, stage 2L and stage 2, all of which are not marked in the Figure 3A. A perfect graphitic structure is certainly a simplified picture of real electrodes as in real materials varying amounts of disorder exist. Thus all the stages are not always observed in charging/discharging curves but rather sloping curves are observed instead of distinct plateaus for some type of carbon electrodes.
Figure 4. A) Typical charge discharge curve of graphite electrode (adapted from Publication III), B) staging of the lithiated graphite structure and C) A-B-A-B-A and A-A-A-A-A stacking of graphite layers.

As the insertion of lithium in graphite occurs at a very low potential, near the reduction potential of lithium, the safety at high C-rates and low temperatures is compromised. Also the Li insertion potential is well below the stability window of commonly used electrolyte components leading to a reduction of electrolyte molecules and formation of a solid electrolyte interface (SEI) during the first cycle. This causes the irreversible capacity loss observed with graphite electrodes during the formatting cycle. However, the formation of a SEI layer is essential in functioning of graphite electrodes as it prevents further decomposition of electrolyte in subsequent cycles. The composition of the SEI depends on the properties of graphite, electrolyte composition and cycling parameters. In any case it is a complicated layer with a thickness from few Å to even hundreds of Å which contains inorganic compounds from the reduction of salt anions such as LiF, LiCl and Li₂O and organic compounds from the reduction of electrolyte solvents such as Li₂CO₃ and different Li-alkyl-carbonates [64,65].

Li₄Ti₅O₁₂ is an alternative negative electrode material to carbonaceous electrodes. It has a theoretical capacity of 175 mAh g⁻¹ and a lithium insertion potential of 1.55 V vs. Li/Li⁺ [11]. Due to the relatively low capacity and high lithium insertion potential leading to a low cell voltage, the energy density of the
cells with this negative electrode material is rather low. However, the high insertion potential is also well above the reduction potential of commonly used organic electrolytes and thus no SEI is expected to form to the same extent as with graphite. In addition to this no lithium plating is likely to occur even at high currents or low temperature and the ability to endure high currents makes LTO an ideal material for high power applications as well as for large scale applications.

LTO has a cubic spinel structure with a space group of $Fd\overline{3}m$ [11]. The unit cell contains eight formula units of $(\text{Li}_3)_8[\text{Li}_1\text{Ti}_5]_{16d}(\text{O}_{12})_{32a}$, in which $\frac{3}{4}$ of lithium occupy tetrahedral 8a site, $\frac{1}{4}$ of lithium and all titanium share octahedral 16d site, and oxygen occupy 32e sites (Figure 4). Three lithium ions can be reversibly inserted into the LTO structure while three Ti$^{4+}$ are reduced to Ti$^{3+}$. The inserted lithium ions occupy site 16c and simultaneously lithium at site 8a also migrate to 16c leading to a rock salt type structure $(\text{Li}_6)_{16c}[\text{Li}_1\text{Ti}_5]_{16d}(\text{O}_{12})_{32a}$. During lithiation the lattice axes change from 8.3595 Å to 8.3538 leading to a decrease in the unit cell volume of only $0.1-0.2\%$ [66-68]. Extremely small change in the cell volume and structural stability of the $[\text{Li}_1\text{Ti}_5]_{16d}(\text{O}_{12})_{32a}$ framework during the lithium insertion/extraction process defines LTO as a zero strain material [12]. This predicts high mechanical stability and long cycle life for the material, and indeed very long cycle lives have been reported with LTO/LFP cells [5,6].

![Figure 5. Left: Structure of Li$_4$Ti$_5$O$_{12}$. Red dots represent oxygen, green tetrahedras lithium and blue octahedras lithium/titanium. Right: structure of lithiated Li$_7$Ti$_5$O$_{12}$. Lithium originally at green tetrahedral sites (8a) has migrated to green octahedral sites (16c) with inserted lithium also at octahedral sites.](image)

Another peculiar feature of LTO is the flat voltage profile over a wide range of states of charge (SOC) as presented in Figure 5. This is generally considered to indicate a two phase reaction mechanism between lithium rich and lithium poor LTO phases involving a sharp interface between the phases [66,69,70]. It has also been suggested that two phase segregation is a kinetically induced non-equilibrium state that relaxes at room temperature to a solid solution material containing lithium rich and lithium poor domains with size less than 9 nm [71,72]. Lithium insertion beyond Li$_4+x$Ti$_5$O$_{12}$ ($3 \leq x \leq 4.5$) is also possible and it involves simultaneous lithium occupancy at 8a and 16c sites and leads to a theoretical capacity of 260 mAh g$^{-1}$. However, as the simultaneous Li occupation of
8a and 16c sites is energetically unfavourable due to the short distance between these sites, this requires a voltage below 0.5 V vs. Li/Li\(^+\) and is associated with a slightly larger volume expansion of 0.4% and increased stress [73,74].

![Charge/Discharge Curve](image)

**Figure 6.** Example of a charge/discharge curve of LTO in a Li/1M LiPF\(_6\) in EC:DMC/LTO half cell.

### 2.3 Electrolytes and other components of the cell

In addition to the active electrode materials that store lithium ions, a lithium ion battery also contains several other components. Electrodes themselves consist of active electrode materials coated on current collectors together with a conductive additive to enhance electrical conductivity and a binder to add mechanical strength. Current collectors are usually aluminium foils for positive electrodes and copper foils for negative electrodes, however in the case of high voltage negative electrodes such as LTO aluminium foils are also an option. Binders are typically polymeric compounds, such as PVDF, but several other possibilities exist. Different binder materials for lithium ion battery electrodes are reviewed in Chapter 5.1. Conductive additives are typically different types of carbon materials such as carbon black. Carbon additives in the case of LTO electrodes are discussed in more detail in Chapter 4.2. The amounts of carbon additives and binder are typically less than 2% each in commercial lithium ion battery electrodes [75].

The function of an electrolyte in a lithium ion cell is to transport the electroactive ions (lithium) between the electrodes and block the transport of electrons. The electrolyte has to be compatible with both electrodes, i.e. be stable towards both a reductive negative electrode and an oxidative positive electrode, and this rules out utilisation of aqueous electrolytes for most electrode combinations. Electrolytes used in lithium ion batteries include both liquid and solid electrolytes. Liquid electrolytes have been the most common choices in commercial batteries and typically include LiPF\(_6\) in a mixture of ethylene carbonate (EC) and other linear carbonates. EC has a high dielectric constant, i.e. it is able to dissolve salts in high concentrations but it also has a high melting point and is thus
mixed with other compounds such as dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethyl methyl carbonate (EMC) that have lower melting point and viscosity but also a lower dielectric constant. The combination of EC and linear carbonates show high stability towards oxidation on positive electrode surface and although they react at carbon negative electrode potentials, they form a stable and passivating SEI on carbonaceous electrodes. LiPF$_6$ has high conductivity and is sufficiently safe, however it is also expensive, hygroscopic and forms HF in contact with water. Therefore several other options for electrolyte salt have been investigated such as LiBF$_4$, lithium bis(oxalato) borate (LIBOB), lithium bisperfluoroethanesulfonimide (BETI, LiN(SO$_2$C$_2$F$_5$)$_2$) but so far LiPF$_6$ has remained dominant as it best combines necessary characteristics.

In addition to lithium salt and solvents, the liquid electrolyte also contains additives that are used for example to improve formation of the SEI, stabilize LiPF$_6$ and protect from overcharging, to list a few. The most commonly used electrolyte additive appears to be vinylene carbonate (VC), while numerous other option are also available, for example vinyl ethylene carbonate (VEC), fluoroethylene carbonate (FEC) and LIBOB [77-79]. Liquid electrolyte in the cell is impregnated in a microporous film that separates the positive and negative electrodes, i.e. a separator [2]. Typically separators are made of polyolefin materials such as polyethylene, polypropylene or a combination of the above as they fulfil the strict requirements of mechanical properties and chemical stability at acceptable cost. Solid electrolytes are an alternative to liquid electrolytes and the options include organic polymer and gel electrolytes and inorganic ceramic electrolytes [80]. They have the advantage of improved safety but the ionic conductivities of the solid electrolytes are typically lower than those of liquid electrolytes. Also liquid electrolytes have the advantage of better accommodation to volume changes of the electrodes.
3. Experimental methods

3.1 Electrode fabrication

Electrode preparation involved mixing of the electrode materials and subsequent coating of the obtained electrode slurry on a metal foil. Carbon black (Timcal) was used as a conductive additive. PVDF was used as a binder in NMP based slurries (Publications I, II, and IV). Acryl S020 (Publications III and IV) or CMC with SBR (Publication III) were used as binders in aqueous electrode processing. Coating was performed using a laboratory scale doctor blade on an aluminium (LTO electrodes in Publication I, II and IV) or copper foil (graphite electrodes in Publication III). Coating thicknesses and calendering forces were optimized to obtain the desired electrode loading and porosity. Electrodes were dried under vacuum at ≥110 ° overnight to get rid of all humidity before assembling the cells in an argon filled glove box. Electrode loadings were kept constant when comparing the performances of different electrodes, with typical variation of 0.2 mg (LTO) cm⁻², and no more than 0.5 mg (LTO) cm⁻².

In publication IV also pilot scale slot die coating and gravure printing methods were tested. In the gravure printing method, electrode slurry is transferred on a metal printing cylinder (gravure cylinder) by rotating the cylinder in electrode slurry while the excess slurry is wiped from the cylinder surface by a doctorblade. Then the aluminium foil substrate is pressed onto the printing cylinder by an impression roller resulting in a direct transfer of the slurry on the aluminium substrate. In the slot die coating method, electrode slurry is supplied to the die at a constant speed and applied through a slot onto the moving aluminium foil substrate. The principles of the coating methods described above are shown in Figure 6.

![Figure 7. Electrode coating methods: A) laboratory scale doctorblade coating, B) pilot scale gravure printing and C) pilot scale slot die coating.](image)

3.2 Electrochemical characterization

Most of the electrochemical measurements were conducted using a two electrode set up in coin cells (Figure 7a and c). In the two electrode set up lithium
metal foil acts as both counter and reference electrode. The advantage of the two electrode set up is its simplicity, however the disadvantage is the possible polarization of the lithium electrode at high current densities which affects the measured voltage values [81]. Lithium electrodes are also not stable in the standard liquid organic electrolytes resulting in a constant growth of the SEI layer and increase in the electrode resistance over time [82]. Cells using lithium counter electrode are referred to as half cells. As they contain excess capacity in the Li counter electrode side this enables the study of the test electrode without the effect of Li loss at the counter electrode. However, the Li loss at the test electrodes is also hidden by the excess amount of Li available, and thus full cell measurements are needed in order to determine the cycle life characteristics of the studied electrode material in more detail. Thus full cells were utilized in cycle life testing using LiFePO4 (Publication I) and NMC (Publication III) positive electrodes with LTO and graphite negative electrodes. The electrolyte was standard 1M LiPF6 in 1:1 EC:DMC, except in the case of graphite electrode cycle life testing where 1M LiPF6 in 1:1 EC:DMC with 2 w-% vinylene chloride (VC) electrolyte additive was used (Publication III).

In the case of impedance measurements, a three electrode set up was used to study the test electrode in more detail and to minimize the effect of the counter electrode resistance. Lithium metal foil was used as both counter and reference electrode in a Hohsen three electrode test cell (Figure 7 b and d). In this set up the Li reference electrode is in the shape of a ring placed between two separators. The reference electrode and cell geometry significantly affect the obtained impedance response of the electrode and uniaxial placement of the reference electrode has been shown to produce more reliable impedance data [83,84].

Figure 8. A and C) two electrode 2016 coin cells, and B and D) Hohsen three electrode test cell using ring shaped reference electrode.
Probably the most common electrochemical characterization method for lithium ion battery materials is galvanostatic measurements i.e. charging and discharging measurements as presented for LTO in Figure 5. In this method constant current (CC) is applied on the system and the voltage response is measured as a function of time until a cutoff voltage or cutoff time is reached. Sometimes CCCV (constant current-constant voltage) method is used for charging especially in the case of graphite cells where a constant voltage step is added at the end of the constant current charging step. Charging and discharging measurements give information for example on the capacity of the material i.e. the ability of the material to store energy, and cycle life behaviour, i.e. stability of the material. By using different charging/discharging conditions such as different current rates and temperatures, information on the reaction kinetics and transportation phenomena can also be obtained.

Another widely used electrochemical characterization method is cyclic voltammetry (CV) in which voltage is linearly swept at different scan rates between specified vertex values while the current response is measured. This method gives information on both the stability and kinetics of the electrode material (Publication I). Based on measured peak maxima, peak widths and peak separation qualitative information of the kinetics of the material can be deduced, and different approaches have also been suggested to quantitatively gather kinetic parameters from CV data in the case of porous electrodes with a two phase reaction [85].

Electrochemical impedance spectroscopy (EIS) is another somewhat different characterization method. In this technique an alternating sinusoidal potential signal is applied and the current response is recorded as a function of the frequency, or vice versa an alternating sinusoidal current signal is applied and the potential response is recorded. Different processes such as mass transfer, electronic/ionic conduction, capacitive effects and charge transfer dominate in an electrochemical cell depending on the applied frequency. Thus by applying a frequency range in an EIS scan, information is gathered on the limiting factors and resistances of the measured cell. The advantage of the EIS technique is its non-destructiveness and fast and easy implementation, however the interpretation of the results by using equivalent circuits is not always straightforward. As EIS is a very sensitive technique, two electrode measurements with lithium counter electrode do not provide sufficient information on the material of interest and thus a three electrode set up (Publication I and II) or symmetric cell approach have been applied [86,87] (Publication III) for EIS measurements. In the symmetric cell approach, two graphite negative electrodes at 50% SOC were harvested from the preliminary treated Li/graphite half cells and combined in symmetric cells for EIS measurements to omit the contributions from the Li counter electrode (Publication III).

### 3.3 Material characterization

Several methods complementary to electrochemical characterization can be used to study lithium ion battery materials either prior to or following cycling.
Also in-situ characterization methods have become more and more common \cite{88,89} and for example in-situ X-ray diffraction (XRD), neutron diffraction and high resolution transmission electron microscopy (HRTEM) have been used to study phase transformations in LTO and LFP electrodes \cite{90-92}. In this thesis, X-ray diffraction (XRD) is utilized to study the phase purity and crystalline structure of the pristine LTO electrode materials (Publication I and II), and in addition evidence of the crystal size can be obtained from the peak widths. Particle size and morphology has a significant effect on the performance of lithium ion battery materials. Thus, scanning electron microscopy (SEM) (Publications I, II, III), HRTEM (Publication I) and atomic force microscopy (AFM) (Publication IV) are applied to study the morphology and size of the electrode materials as well as the structure of the electrodes. Indirect evidence of the morphology can also be obtained by surface area measurements using BET (Brunauer-Emmett-Teller) adsorption technique (Publication I and II). Water content even in trace amounts is an important issue in manufacturing of Li ion batteries. Therefore thermogravimetry (TG) was used to study the water absorption and desorption characteristics of lithium titanate material (Publication IV) where the water content of the sample is measured at different temperatures and relative humidity conditions \cite{93}. 
4. LTO as a negative electrode material

4.1 Particle morphology vs. electrochemical properties

Charge transport through the electrode materials is generally considered to be the limiting step in lithium ion batteries [94]. Therefore the performance of the battery can be enhanced by reducing the particle size of the active materials which in turn reduces the lengths of diffusion paths and increases the surface area and available sites for lithium insertion [47]. In the case of LTO, micron-sized material usually shows poor rate capability whereas with nano-sized materials very high capacities even at high rates have been achieved [95]. Kavan et al. have studied lithium insertion using LTO thin film electrodes and materials with a surface area of 1.3-196 m² g⁻¹ corresponding to the particle size range of 9 nm - 1 µm [96]. Their systematic study of charge capability as a function of particle size revealed optimum performance with 100 m² g⁻¹ and 20 nm particles. There have been numerous attempts to enhance the high rate capability of LTO by designing different types of nanostructures. For example LTO nanoparticles [97-99], LTO hollow structures [100-102], and LTO nanotubes [103-105] have been reported as an effective means of reducing the rate limiting diffusion pathway leading to enhanced performance.

However, with nanosized materials some disadvantages also emerge when compared to similar materials that are micronsized. First nanosized materials might promote parasitic reactions when the contact area between electrode materials and electrolyte is increased. This is an important issue as the stability of the LTO surface towards the electrolyte has been under debate lately [106]. Another disadvantage of nanosize electrode material is lower tap density leading to lower electrode loadings and overall energy density [107]. Disadvantages of nanosized LTO particles have been attempted to be tackled by creating hybrid materials with small primary particles forming large secondary structures that possess the advantages of nanosizing without compromising the demand for high energy density (Publication I) [95,108-111]. In publication I this type of LTO structures consisting of primary particles with less than 100 nm mean size forming spherical aggregates of 10-50 µm were investigated (Figure 8). With this approach 30% higher LTO tap densities were achieved when compared to LTO material with larger primary particles and minimal aggregation forming secondary particles. Very promising results have been achieved also using LTO nanocrystallites forming compact LTO spheres that have a very high tap density of 1.2 g cm⁻³ [111]. The high rate capability of such dense LTO structure was explained by fast Li and electron transport along grain boundaries inside the secondary LTO particles.
In Publication I the electrochemical performance of LTO particles with small primary size forming large aggregates (LTO-SP as smaller primary particle) was compared to that of LTO particles with larger primary particle size and less aggregates (LTO-LP as larger primary particle). As both LTO-SP and LTO-LP samples were synthesized using the same high temperature solid state synthesis resulting in the same crystalline structure in bulk, we are able to study the effect of particle morphology alone. Electrochemical performance in terms of obtained capacities is similar for LTO-SP and LTO-LP when low C-rates are used at room temperature. However when high currents (>1C) and low temperatures are used better capacities are obtained with LTO-SP and the difference was over 10% at 10C at room temperature. This was attributed as a beneficial effect of smaller particle size and larger surface area as a higher amount of surface sites and shorter diffusion paths facilitate lithium transport in LTO-SP when compared to LTO-LP.

Another difference between LTO-SP and LTO-LP was also observed when the shapes of the charge discharge curves and cyclic voltammograms of LTO-SP and LTO-LP were compared, as presented in Figure 9. Although typical flat charge/discharge curves with similar average charging/discharging potentials were obtained for both LTO-SP and LTO-LP, the shapes of the curves are different. For LTO-LP with the larger particle size the flat area is extended over almost the entire capacity range, whereas for LTO-SP with the smaller particle size sloping charging/discharging curves near the end members Li$_4$Ti$_5$O$_{12}$ and Li$_7$Ti$_5$O$_{12}$ are obtained resulting in a reduced voltage plateau. Also in CVs narrower peaks are observed with LTO-LP whereas for LTO-SP sloping of both cathodic and anodic peaks are observed in the high voltage end where x in Li$_{4+x}$Ti$_5$O$_{12}$ is close to zero.

Similar reduction of the voltage plateau and two phase domain is also observed in other two-phase transition materials, for example in nanosized LFP. However, in the case of LFP the reduction of the voltage plateau is attributed to strain and interface energy between the end members Li$_8$FePO$_4$ and Li$_{1-\beta}$FePO$_4$. There is a difference of 6.5% in the molar volume between the lithium rich and lithium poor LFP phases which in the case of nanosized LFP results in the re-
duction of the miscibility gap [40,52,112]. By contrast to LFP, LTO has a negligible change in lattice parameters during charging/discharging (0.1-0.2% [66,67]) and thus the origin of the curved voltage plateaus is also different. Similar reduction of the voltage plateau has been found in very small LTO particles (12 and 31 nm) by Borghols et al. [113]. This can be explained by different redox potentials at the near surface region vs. bulk as has been shown theoretically by DFT calculations by Ganapathy and Wagemaker [114]. The calculated insertion voltage of the LTO surfaces were significantly higher than the bulk voltage [114] as is experimentally observed in Publication I and [113]. Moreover, calculations show a strong dependence of storage properties on surface orientation [114] and indeed LTO-SP and LTO-LP have different surface planes based on observations on HRTEM as (400) and (111) surface planes are observed for LTO-SP and LTO-LP.

![Figure 10](image-url)

**Figure 10.** A) Charge–discharge curve of LTO-SP and LTO-LP electrodes and B) CV of LTO-SP and LTO-LP electrodes (Publication I). Active material loadings on the electrodes are 4.6-4.7 mg (LTO) cm^{-2}.

In addition to differences observed in dynamic conditions i.e. when current is applied, also different behaviour in open circuit potentials (OCP) were observed for LTO-SP and LTO-LP as presented in Figure 10. Although both samples stabilize to the same voltage value of 1.56 V vs Li/Li^+ after lithiation, the process is much faster for LTO-LP. This is suggested to result from overlithiation of the surface region. Although simultaneous occupancy of 8a and 16c sites is usually energetically unfavourable it is more feasible at the surface sites than in the bulk which results in an overlithiated phase \( \text{Li}_{7+x}\text{Ti}_5\text{O}_{12} \) in the LTO-SP particles with the high surface area (Publication I). Recently it has been observed by comparing LTO with different particle sizes using in-situ neutron powder diffraction that in smaller LTO particles 8a sites at the surface region are refilled with Li faster than Li transfer from 8a sites to 16c sites which results in simultaneous Li occupancy of 8a and 16c sites [115]. Also Borghols et al. observed simultaneous occupation of 8a and 16c sites that explained the larger capacities observed with a smaller particle size and capacities exceeding the theoretical capacity [113]. In publication I simultaneous occupancy of 8a and 16c sites in LTO-SP results in slower relaxation between the overlithiated phase \( \text{Li}_{7+x}\text{Ti}_5\text{O}_{12} \) present in the surface and \( \text{Li}_4\text{Ti}_5\text{O}_{12}/ \text{Li}_7\text{Ti}_5\text{O}_{12} \) phases present in bulk.
To summarize, the distinctive properties observed with nanosized LTO materials are not only the effect of more available surface sites and shorter diffusion paths, but also excess storage and different thermodynamics at the surface sites. Hence the properties of the LTO electrode could be altered by controlling the size and shape and thus surface orientation of the LTO particles. Here it is shown that by a simple end treatment in the synthesis process, particle morphology and surface properties of LTO can be affected that further affects the electrochemical performance of the LTO material.

4.2 Conductivity and the use of conductive additives in LTO electrodes

LTO is an electronic insulator with a conductivity as low as $10^{-8}...10^{-13}$ S cm$^{-1}$ due to the large band gap between the occupied O 2p and empty Ti 3d states [68,116,117]. Therefore several attempts have been made to enhance the conductivity of LTO and hence the performance of the material in a lithium ion battery. These include for example doping with Mg [116,118], Nb [119], Zn [120], as well as with numerous other elements. By doping of Li$^+$, Ti$^{4+}$ or O$^{2-}$ sites by different ions, a mixed Ti$^{3+}$/Ti$^{4+}$ state can be created to increase the concentration of charge carriers and an increase in conductivity of several orders of magnitude to $10^{-2}$ S cm$^{-1}$ have been reported with Mg doping [116]. Also carbon coating of LTO [121-124], LTO-carbon nanotube (CNT) [125,126] and LTO-graphene [127,128] composites have been widely studied as potential methods to improve the performance of LTO. However, recently views on the necessity of carbon additives and on how detrimental the low conductivity of pristine LTO really is have been challenged as results of LTO electrodes without carbon coating or conductive additives have been published [13,14]. These recent results suggest that the conductivity of pristine LTO is not as problematic as has been considered until now.

Functioning of the LTO electrodes without carbon additives or carbon coating is enabled on the one hand by the zero strain nature of LTO and on the other hand by an increase in conductivity at the early stage of lithiation [14,129]. The
conductivity of LTO has been reported to increase very fast after only a few percent lithiation and reach a value of 2.46 S cm\(^{-1}\) at room temperature as Ti\(^{4+}\) is partially reduced to Ti\(^{3+}\) and Ti 3d orbitals occupied [129]. The conductive phase Li\(_{7-\beta}\)Ti\(_5\)O\(_{12}\) is formed on LTO particle surfaces in the vicinity of the current collector where it very quickly propagates across particle surfaces towards the electrode surface facing the separator creating a conductive network throughout the electrode [14]. During the following delithiation the conductivity of LTO is again decreased, however not to the original levels of pristine LTO indicating a presence of Ti\(^{3+}\) charge carriers remaining in the material even after delithiation.

Several other electrode materials such as TiO\(_2\), LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) and LiCoO\(_2\) without carbon additives show poor cycling performance due to either low conductivity of the carbon free electrode or notable volume change during lithiation/delithiation causing mechanical degradation [14].

As some other studies indicate poor performance of LTO electrodes without carbon additives [130], the effect of particle morphology on the performance of carbon free LTO electrodes was studied using LTO-SP and LTO-LP particles with different surface areas and particle sizes (Publication II). The performance of LTO-SP and LTO-LP is similar in both carbon free (0% C) and carbon containing (3%) samples at low C-rates and at room temperature. However, at higher C-rates (>1C) and low temperature (-20 °C) difference is observed between 0% and 3% carbon containing electrodes such that 3% C electrodes show larger capacities and the difference is more pronounced with LTO-SP with larger surface area as shown in Figure 11 (Publication II). The effect of carbon additives thus depends on the LTO particle size and morphology as shown by different behaviour of LTO-SP (large surface area and high packing density) and LTO-LP (larger particle size and smaller surface area) with and without carbon additives. As the smaller particle size and larger surface area of LTO-SP provide shorter solid state diffusion pathways and more surface sites for lithium intercalation and yet carbon additives have more impact in the case of LTO-SP electrodes, these results suggest that the different morphology of LTO-SP and LTO-LP electrodes plays an important role on the performance of the electrode. Carbon addition alters the porosity and morphology of the electrode and thus can have more pronounced effect in the case of more densely packed LTO-SP electrodes. The importance of interparticle contacts is emphasized in carbon free electrodes in order to create a conductive network that enables fast charge transport throughout the electrode.
In addition to the influence on rate capability, carbon additives also affect the cycle life behaviour of LTO electrodes. It has been reported that carbon additives increase reactivity towards the electrolyte especially at high temperatures [131]. However, carbon as a thin coating layer on the surface of LTO particles seems to suppress electrolyte reduction and gas formation [124,132,133]. In the case of LTO with a high surface area and without a protecting carbon coating (as in LTO-SP) it seems that although beneficial for rate capability, the high surface area also increases reactivity towards the electrolyte promoting parasitic reactions and thus has a negative effect on cycle life as presented in Figure 12 (Publication II). LTO-SP with 0% carbon showed poorer stability when compared to LTO-SP with 3% carbon or LTO-LP at room temperature. At higher temperature (60 °C) the stability of both LTO-LP and LTO-SP is deteriorated substantially as the capacity drops fast after 50 to 60 cycles.

In conclusion, the effect of carbon additives in LTO electrodes depends both on the particle and electrode morphology. Several factors affect the performance of the battery electrode including both active material properties (such as parti-
Particle size and morphology, crystalline structure/purity etc.) and electrode properties (thickness, porosity, material ratios etc.) and as many of such properties are interdependent, it is often complicated to discriminate the effects of different factors. However, in Publication II it was concluded that the effect of carbon additives on the performance of LTO electrode is observed in more demanding cycling conditions and the effect is more pronounced in LTO electrodes with smaller particle size and larger surface area (LTO-SP). The effect on cycle life is a combination of the presence of carbon additives and LTO particle morphology [134] and surface properties [135].
5. Electrode fabrication method using water soluble acrylate binder

5.1 Binder materials for lithium ion batteries and electrode manufacturing

Traditionally lithium ion battery electrodes are prepared using a PVDF binder in an N-methylpyrrolidone (NMP) solution. Requirements for the binder are rather demanding as it should have high mechanical stability at a low content and good electrochemical stability over a wide potential and temperature range. PVDF as an electrode binder has the advantage of high electrochemical stability and strong binding strength, as well as the ability to absorb electrolyte for facile Li ion transport [136]. It functions well with several cathode materials such as LiCoO₂, LiNi₀.₅Mn₀.₅O₂ (NMC), LiNi₀.₈Co₀.₁₅Al₀.₀₅O₂ (NCA) and LiFePO₄ (LFP) and is widely adopted in commercial use. However, it also has some drawbacks such as relatively high cost, and low flexibility that causes a problem in mechanical stability in the case of large volume changes of the material during cycling [137]. Also stability and safety aspects with graphite have been brought up as PVDF has been reported to react exothermally with graphite in a lithiated state under extreme conditions [138].

Another disadvantage related to the use of PVDF is that it requires NMP as a solvent. NMP is expensive, hazardous to health, and environmentally unfriendly, and therefore different alternatives are searched for. Especially water soluble binders have gathered much interest as water being cheap and harmless would be an ideal solvent for electrode processing. Moreover, aqueous electrode processing would mean less strict control of the processing humidity and faster drying in electrode manufacturing, thus simplifying the fabrication of electrodes [136]. Combination of carboxymethylcellulose (CMC) and styrenebutadiene-rubber (SBR) has been successfully used for graphite electrode manufacturing in commercial lithium ion batteries where SBR works as a primary binder and CMC as a thickening agent. Also several other water soluble binders have been successfully studied for graphite electrode manufacturing including Acryl S020 (Publication III), poly(acrylamide-co-diallyldimethylammonium chloride) (AMAC) [139], polyacrylic acid (PAA) [140,141] and poly(acrylonitrilebutylacrylate) [142] to mention a few.

Although the majority of research on water soluble binders is focused on graphite negative electrodes or alloying/conversion electrodes due to their challenges and obvious need for improvements in mechanical stability, several different binders have also been tested in preparation of LTO electrodes. For example water soluble Acryl S020 (Publication IV), CMC [143-146], CMC and SBR [147], PAA [148], guar gum and tara gum [149] and PEG-based copolymer (poly(PEGMA-co-MMA-co-IBVE)) [150] have been reported for LTO electrodes as well as polyacrylonitrile (PAN) [151], polymerized ionic liquid nanoparticle
[152] and rosin as additive to PVDF binder [153] in NMP based LTO electrode manufacturing.

The selected binder greatly affects the morphology of manufactured electrodes. For example it has been reported that electrodes with lower binder content [154] and higher compactness [155] have been obtained with water soluble CMC when compared to electrodes with PVDF. Thus the binder also affects the performance of the electrodes in a battery as electronic and ionic conduction is highly dependent on the morphology. Porosity of the structure has the opposite effect in electronic and ionic conduction as electronic conduction limits the performance in low packing densities due to poor contacts while ionic conduction dominates in dense electrodes. Thus the optimum porosity is a compromise between electronic and ionic conduction and for example in LFP electrodes the optimum porosity has been determined as 30-35 % [156]. The same applies to the amounts of binder and conductive additive. The conductivity can be increased by adding more carbon to the electrode structure, however the addition of nanosized carbon also requires more binder. The addition of binder on the other hand lowers the electrode density and PVDF binder has a negative effect on electronic and ionic conduction, but then enhances the mechanical strength of the composite electrode. Thus the amount and ratios of conductive additive and binder must be optimized for the selected active material and intended application [157]. Due to the insulating nature of PVDF binder, different types of conductive polymers have also been investigated for lithium ion battery electrodes [158,159].

The nature of the binder affects not just the final electrode structure but also electrode manufacturing process as the suspension properties and particle dispersion depend on the binder [160,161]. Particle interactions are naturally very different in organic solvents with low polarity when compared to polar solvents and aqueous solutions. Also different drying kinetics of NMP and aqueous solutions affect the particle distribution in the electrode sheets as the evaporation of the solvent causes migration of the binder towards the electrode surface [162]. Due to the numerous variables in electrode processing, electrode slurries must be optimized for the specific system in terms of binder/solvent nature, slurry mixing technique and solvent concentration.

### 5.2 Graphite electrodes with acrylate binder

Graphite electrodes for commercial lithium ion batteries are typically manufactured using CMC and SBR binder combination. Although CMC is widely used for the preparation of lithium ion battery electrodes, CMC based electrode slurries suffer from bacterial growth. In publication III, acrylate based binder Acryl S020 was applied for preparation of graphite electrodes and the results were compared to electrodes prepared with a combination of CMC and SBR. Similar capacities were obtained with Acryl S020 and CMC+SBR graphite electrodes at low C-rates and room temperature. However, better performance was achieved at high C-rates and low temperature (0 °C) with Acryl S020 when compared to CMC+SBR as shown in Figure 13. Stability of the Acryl S020 electrodes was
similar as those of CMC+SBR indicating a similar tolerance for volume change of the graphite structure. The results obtained in Publication IV showed the potential of Acryl S020 binder for fabrication of graphite electrodes.

![Graph showing specific capacities of the graphite electrodes with the Acryl S020 and CMC+SBR binder in Li/graphite half cells at C-rates 0.1C, 0.2C, 0.5C and 1C and temperatures 0 °C, 20 °C, and 40 °C.](image)

Figure 14. Specific capacities of the graphite electrodes with the Acryl S020 and CMC+SBR binder in Li/graphite half cells at C-rates 0.1C, 0.2C, 0.5C and 1C and temperatures 0 °C, 20 °C, and 40 °C.

The differences in performance between electrodes with different binders can be attributed to the effect of the binder on the electrode structure. For example graphite electrodes with PAA binder have been reported to be more resistant to pressing of electrodes which yields a more porous structure at higher density when compared to electrodes manufactured with CMC+SBR or PVDF [141]. Similarly the Acryl S020 based electrodes were found to tolerate higher calendering forces than electrodes manufactured with CMC+SBR and also result in a slightly different electrode structure based on observations with SEM (Publication IV). This difference in structure affects the performance of graphite electrodes at high C-rates and low temperature (Publication IV). Earlier it has been found that the low temperature performance of graphite electrodes is different for electrodes manufactured also with CMC+SBR and PVDF and this was attributed to structural effects [163]. The favourable effect of the Acryl S020 binder on the electrode structure and on the measured performance can be explained by enhancement of both electron transfer through the conductive network and lithium transport in the porous electrode structure.

### 5.3 Lithium titanate electrodes with acrylate binder

In addition to graphite, Acryl S020 was also introduced for the manufacturing of LTO electrodes (Publication IV). Aqueous electrode processing and the use of the Acryl S020 binder in the case of LTO electrodes has entirely different challenges than in the case of graphite electrodes. Extremely small changes in lattice dimensions of LTO during cycling brings less challenges in mechanical stability
during cycling than in the case of graphite. However, LTO tends to absorb substantial amounts of water which brings challenges for the drying step of manufacturing as the currently used electrolyte is highly sensitive to moisture. Water absorbance of LTO powder has been measured to be up to 20 times larger than for LFP [93]. However, TG studies as shown in Figure 14 show that the water absorption/desorption process in LTO is nearly reversible [Publication IV]. Thus with careful drying conditions waterless LTO electrodes can be prepared using aqueous electrode processing. Also it has been reported that the Acryl S020 binder in the case of LiFePO4 electrodes reduces the water absorbance of active material whereas a CMC binder was reported to increase the absorbance as CMC is known to absorb water readily [164].

![Figure 15. Water absorption/desorption TG measurement for LTO powder (solid line), temperature (upper dashed line) and humidity (lower dashed line). (Publication IV)](image_url)

In Publication IV, Acryl S020 was used as a binder in LTO negative electrodes and the results were compared to PVDF based LTO electrodes. Charging and discharging experiments using Li/LTO half cells indicated similar capacities and resistance for the LTO electrodes manufactured with either Acryl S020 or PVDF. Obtained capacities at low C-rate were close to the theoretical capacity (175 mAh g⁻¹) and the capacity loss at 10C was 39% when compared to the capacity measured at 0.1C. These results indicate that the Acryl S020 electrodes have potential to be used in high power applications. Also cycle life tests indicate similar stability for the Acryl S020 and PVDF electrodes as stable capacities were measured for over 200 cycles with high current and energy efficiencies. Furthermore, pilot scale manufacturing of electrodes with the Acryl S020 binder was tested using gravure printing and slot die coating methods. These methods produced electrodes with very different loadings, 0.7 mg cm⁻² active material on aluminium foil with gravure printing and 3.8 mg cm⁻² with slot die coating. Stable cycle life of over 500 cycles were achieved with both the methods as presented in Figure 15. Of these methods, material loadings achieved with slot die coating technique are on the same scale as electrode loadings in commercial lithium ion batteries whereas loadings achieved with gravure printing technique might be too low for practical applications.
Despite the promising results achieved with the water soluble Acryl S020 binder in preparation of LTO electrodes, the applicability of water based processing depends on the stability of LTO in contact with moisture. Severe swelling has been observed in lithium ion pouch cells using LTO as negative electrode in combination with different positive electrode materials [165-168]. Gas generation in LTO cells has been observed both during cycling or storage, especially at elevated temperatures and the main gaseous products have been analyzed as H₂, CO, CO₂, and C₂H₄ as well as other hydrocarbons [106,169,170]. Debate on the origins of gassing in LTO cells is still going on as some studies claim that the potential of LTO [166] or reactivity of LTO surface towards electrolyte [106,171] causes gas generation while other studies argue that gassing mainly originates from the reduction of trace water in LTO cells [168,170,172]. The latter view highlights the need for strict control of humidity in the production of LTO cells in order to avoid the swelling issue. Quite surprisingly, Burns et al. reported results on the impact of water in the electrolyte of LTO/LCO cells. Although swelling of the LTO/LCO cells during the formation cycle increased as a function of water content in the electrolyte, this had no detrimental effect in the cell performance up to 1000 ppm water addition [173].

Quite a few studies exist on cation exchange of Li₄Ti₅O₁₂ material. Li⁺ in LTO structure can be exchanged with H⁺ from aqueous solution and it has been found that LTO in acidic solutions is not stable against proton exchange [174]. Lithium ions mainly at 8a sites were replaced by H⁺ from the acidic solution and the exchange was greater with ball milled LTO samples due to increased surface area. Aqueous LTO solutions are basic in nature which might hinder proton exchange to some extent and negligible Li dissolution has been measured in aqueous LTO electrode slurries using typical LTO concentration and exposure times [147]. However, Li dissolution is increased in acidic solutions, or if the immersion time is increased, or LTO concentration decreased. As our preliminary studies show some amount of Li dissolution in aqueous LTO slurries stored for long time (> several months), further work is needed to study the stability of
aqueous LTO electrode slurries in conditions similar to industrial electrode processing.
6. Conclusions and suggestions for future research

In this thesis, various aspects of the negative electrodes of lithium ion batteries are studied. The emphasis is on lithium titanate materials and electrodes as both the effect of particle morphology (Publication I) and carbon additives (Publication II) are studied in detail using different cycling conditions. Lastly electrode preparation using water soluble acrylate binder is applied on the preparation of both LTO and graphite electrodes (Publications III and IV).

The effect of particle size and morphology of LTO on the performance of lithium ion batteries was studied in Publication I. Two different LTO materials were selected possessing the same crystalline structure but different particle morphology. Different behaviour was observed depending on the particle morphology such that smaller size and large surface area was beneficial for lithium transport at high currents and low temperature as better capacitites were obtained. Sloping charge discharge curves were observed for LTO with smaller particle size and larger surface area indicating different electrochemical environments in bulk and surface. Also simultaneous occupation of 8a and 16c sites near the surface region were observed with LTO of larger surface area. Thus the observed differences between LTO particles of different size are not only a result of shorter diffusion paths and a larger number of available surface sites but also different thermodynamics and excess Li storage at the surface region. This opens up possibilities to influence the electrode properties by morphology and surface modification of the LTO electrode material.

In addition to this, the effect of carbon additives on the performance of LTO electrodes was evaluated using two different LTO materials in Publication II. It was concluded that carbon additives have minimal effect on the performance of the LTO electrodes in moderate conditions (low C-rates and room temperature) but when more demanding conditions are applied (either high C-rates or low temperatures) the carbon containing LTO electrodes produced larger capacities than the carbon free LTO electrodes. The effect of carbon additives was more evident for LTO with smaller particle size and larger surface area and thus the effect of carbon additives depends on both LTO particle and electrode morphology. The presence of carbon additives is an important aspect for industrial electrode manufacturing. Thus, the need for carbon additives in LTO electrodes in a specific battery configuration and application must be carefully evaluated and the effect of carbon additives on cycle life studied in more detail.

Substitution of an organic solvent based electrode manufacturing process by a more environmentally friendly aqueous method is an effective means to reduce the costs and environmental burden of lithium ion battery manufacturing. Application of a water soluble acrylate binder Acryl S020 was tested in the manufacturing of LTO and graphite negative electrodes. By using Acryl S020 binder the use of harmful and expensive NMP solvent can be omitted and thus cheaper
and environmentally friendly aqueous electrode processing can be used instead. This approach was tested in LTO and graphite negative electrodes that possess different type of challenges. With LTO and Acryl S020 stable capacities were obtained for over 500 cycles as presented in Publication IV. Also pilot scale electrode fabrication methods, gravure printing and slot die coating, produced promising results. Although LTO absorbs water readily, it was shown by TG that the water absorption desorption process is reversible and therefore aqueous processing seems applicable for LTO electrodes. However the possible proton exchange and its extent in aqueous electrode slurries should be further evaluated, and the effect on cycle life should be tested using pouch cells in full cell configuration instead of half cells to detect potential gassing issues.

Acryl S020 was also tested with graphite negative electrodes. Graphite electrodes are routinely manufactured using water soluble CMC and SBR binders. However, considerable volume changes in the case of graphite when compared to LTO electrodes brings additional challenges in obtaining mechanical stability. In Publication III it was demonstrated that in addition to LTO with negligible volume change, Acryl S020 is also applicable to manufacturing of graphite electrodes. Results were compared to the usual CMC+SBR combination, and similar cycle lives were obtained with Acryl S020 and CMC+SBR combination whereas better results were obtained with Acryl S020 when high C-rates and low temperature (0 °C) were used. These results of Acryl S020 binder in Publications III and IV show promise as a potential new binder for different types of lithium ion battery electrodes.
References


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Negative Electrode Materials for Lithium Ion Batteries

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