From Current Collectors to Electrodes

Aluminium Rod Structures for Three-dimensional Li-ion Micro-battery Applications

GABRIEL OLTEAN
Abstract

The potential use of 3D aluminium nanorod structures as current collectors and negative electrodes for 3D Li-ion micro-batteries was studied based on the use of relatively simple and cost-effective electrochemical and sol-gel deposition techniques. Aluminium rod structures were synthesised by galvanostatic electrodeposition using commercial porous membranes as templates. It was shown that the use of a short (i.e., 50 ms long) potential pulse (i.e., -0.9 V vs. Al^{3+}/Al) applied prior to a pulsed current electrochemical deposition gave rise to homogeneous deposits with more even rod heights. Electrophoretic and sol-gel deposition of TiO_2 on the same substrates were also studied. The use of the sol-gel technique successfully resulted in a thin coating of amorphous TiO_2 on the Al nanorod current collector, but with relatively small discharge capacities due to the amorphous character of the deposits. Electrophoretic deposition was, however, successful only on 2D substrates. Anodisation of titanium was used to prepare 3D TiO_2 nanotube electrodes, with a nanotube length of 9 um and wall thickness of 50 nm. The electrodes displayed high and stable discharge capacities of 460 µAh/cm^2 at a 0.1 C rate upon prolonged cycling with good rate capability.

The 3D aluminium nanorod structures were tested as negative electrodes for Li-ion cells and the observed capacity fading was assigned to trapping of LiAl alloy inside the aluminium electrode caused by the diffusion of lithium into the electrode, rather than to pulverisation of the aluminium rods. The capacity fading effect could, however, be eliminated by decreasing the oxidation potential limit from 3.0 to 1.0 V vs. Li^{+}/Li. A model for the alloying and dealloying of lithium with aluminium was also proposed. Finally, a proof-of-concept for a full 3D Li-ion micro-battery with electrodes of different geometries was demonstrated. The cell comprised a positive electrode, based on LiFePO_4 deposited on a carbon foam current collector, with an area gain factor an order of magnitude larger than that for the Al nanorod negative electrode. This concept facilitates the balancing of 3D Li-ion cells as the positive electrode materials generally have significant lower specific energy densities than the negative electrodes.

Keywords: 3D micro-batteries, aluminium, titanium oxide, current collectors, negative electrodes, electrodeposition, electrophoretic deposition, sol-gel synthesis

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List of Papers

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


IV Oltean, G., Tai, C.-W., Edström, K., Nyholm, L. (2014) On the origin of the capacity fading for aluminium negative electrodes in Li-ion batteries. Submitted.


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My contribution to the papers

Paper I. I planned and executed all the experimental work. I wrote the manuscript and was involved in all discussions.

Paper II. I planned most of the experiments and executed all the experiments. I was involved in all discussions and wrote the manuscript.

Paper III. I planned most of the experiments and built the pouch cells and characterised them electrochemically. I was involved in all discussions.

Paper IV. I planned and executed all the experiments (except the TEM characterisation). I wrote the manuscript and was involved in all discussions.

Paper V. I planned all the experiments and synthesised the aluminium rod electrodes, built the pouch cells and carried out the electrochemical characterisation. I wrote the manuscript and was involved in all discussions.

Published papers not included in this thesis:

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1. Introduction

1.1 Scope of the thesis
This thesis deals with the investigation of the potential use of aluminium in three-dimensional Li-ion micro-batteries. Three-dimensional aluminium rod structures are synthesised by galvanostatic electrodeposition. The use of 3D aluminium rods as a current collector for 3D electrodes is demonstrated by coating these structures with a TiO$_2$ model active material. For comparative reasons, 3D TiO$_2$ nanorod electrodes are also characterised in Li-ion cells. The use of aluminium as a negative electrode is studied by investigating the lithiation and delithiation of the 3D Al nanorod electrode. Finally, a three-dimensional Li-ion battery with a negative electrode composed of aluminium rods and a positive electrode composed of LiFePO$_4$ coated on a piece of carbon foam is demonstrated.

1.2 Li-ion batteries
Li-ion batteries are today the key energy storage devices for a wide range of portable electronics. Already ten years after the commercialisation of the first Li-ion battery, the battery market was dominated by these cells. Li-ion batteries offer the highest gravimetric and volumetric energy densities out of all the available commercial rechargeable battery systems [1]. The schematic operating principle of a Li-ion battery is presented in Figure 1.
A Li-ion battery consists of two electrodes (one negative and one positive) separated by a lithium-ion conducting and electron insulating electrolyte. During discharge of the battery, the active material of the negative electrode is oxidised, releasing lithium ions into the electrolyte and electrons through the outer circuit. When the electrons reach the positive electrode, the active material in the positive electrode undergoes reduction and lithium ions are inserted into its structure. The flow of electrons in the outer circuit will create an electrical current, thus providing the energy to power different devices. When charging the battery, the opposite reactions occur accompanied by a flow of lithium ions from the positive electrode towards and into the structure of the negative electrode.

More than two decades after the introduction of the first cell on the market, Li-ion batteries are still among the state-of-the-art reversible energy storage devices available on the market. Therefore, a lot of research is dedicated to these electrochemical systems. The development of nanostructured materials boosted battery research, as materials were reconsidered for their use in Li-ion batteries due to their novel nanoscale properties [2]. There is a wide choice of chemistries available for Li-ion systems which have enabled a wide range of application for these devices. Li-ion batteries can be designed for energy storage coupled to renewable energy production [3], energy storage for grid support [4] and power devices for hybrid and electrical vehicles [5].

Figure 1. Schematic representation of the discharge of a Li-ion battery.
Even though the first commercialised Li-ion battery consisted of a polypyrrole electrode, which subsequently was replaced with a carbon negative electrode, and a LiCoO$_2$ positive electrode, today’s Li-ion batteries which are used for powering portable electronics still contain similar materials [6,7]: graphite and LiCoO$_2$. Because of the multitude of projected uses for this battery technology, involving up-scaling and thus the need for tons of materials, graphite and LiCoO$_2$ do not satisfy the safety, cost and environmental demands associated with the use in large scale energy storage devices.

The graphite negative electrode offers a theoretical specific capacity of 372 mA/h/g at a potential close to 0 V vs. Li$^+$/Li. During cycling, by reduction of electrolyte on the surface of the electrode, a passivating film (named solid electrolyte interphase or SEI) is formed. The successful use of this negative electrode relies on the stabilisation of the SEI layer. Furthermore, co-intercalation of electrolyte solvent molecules can occur between the graphene sheets, leading to exfoliation of the material [6] which is prevented by a stable SEI. The low operating voltage is, however, also a concern, as lithium plating can occur on the surface of the electrode which can lead to internal short circuits. Three classes of materials for use as negative electrodes, and thus substitutes for graphite, have been studied so far [7]: insertion, conversion and alloying compounds. Besides graphite, TiO$_2$ and Li$_4$Ti$_5$O$_{12}$ are also well studied insertion materials which show stable capacities upon cycling and good rate capabilities, especially in the case of Li$_4$Ti$_5$O$_{12}$. They cycle, however, at relatively high potentials vs. Li$^+$/Li ($\approx$ 1.5 V) and are feasible only if high voltage cathodes are used. A second class of negative electrodes is constituted of metal oxides that undergo a conversion reaction upon lithiation. The metal ions are reduced to metal atoms which are embedded in a matrix of Li$_2$O. Although the specific energy density obtained with these compounds is up to three times higher than that for graphite, they cycle at high potentials vs. Li$^+$/Li and show quite a high polarisation upon lithium extraction. Finally, a third category is composed of compounds which can alloy with lithium (e.g., Al, Sb, Si, Sn, Pb and In). The most studied is Si, which alloys with 4.4 Li$^+$ per Si with a specific energy density of approximately 3600 mA/h/g. The alloying and dealloying reactions occur, however, with large volume changes during the cycling leading to particle cracking and loss of electrical contact and hence battery capacity fading.

The use of LiCoO$_2$ as positive material for hybrid and electric vehicle applications raises an environmental concern because of the use of cobalt. Similar layered oxide materials based on Ni (i.e. LiNiO$_2$) have been studied, but with limited success [6]. LiMn$_2$O$_4$ spinel has also been studied as a potential positive active material and, even if the transport of Li$^+$ ions takes place in three dimensions, dissolution of manganese and subsequent reduction on the negative electrode have been reported. Substituting part of the manganese with nickel and cobalt can circumvent the dissolution problem
and make spinel electrodes commercially feasible [7]. One of the most used positive electrode material nowadays is the olivine structure LiFePO\textsubscript{4} [7]. Although the Li\textsuperscript{+} ions are transported only in one dimension and the electronic conductivity is rather low, LiFePO\textsubscript{4} positive electrodes present a stable cycling life, good rate capabilities and are inexpensive. Batteries operating with LiFePO\textsubscript{4} positive electrodes are inherently safe due to the higher stability of phosphates as compared to oxides.

1.3 Li-ion three-dimensional micro-batteries

The development of Li-ion batteries cannot keep up the pace of the microelectronics industry. Traditional thin film Li-ion cells do not offer high enough capacity per footprint area to be able to confer on-board power for small devices such as sensors and actuators. The use of thick film electrodes would provide the needed energy density, but will in turn decrease the power density of the cell, as the lithium ions would have to travel on too long diffusion paths. Three-dimensional (3D) Li-ion batteries were proposed as a possible solution to this problem [8]. Designing the electrodes in 3D increases the total area of the electrode and thus the active mass per footprint area. This leads to an increase in energy density without compromising the power density, as the electrodes still would be based on thin films. Four different architectures for building full 3D batteries were proposed, and these are schematically represented in Figure 2 [9]: 1) the interdigitated geometry which consists of electrode arrays of rods separated by a solid electrolyte; 2) the trench geometry, which is similar to the interdigitated one but consists of electrode arrays of plates; 3) the concentric architecture with one electrode as an array of rods which is covered by a layer of solid electrolyte and the rest of the space being filled by the other electrode material; and 4) the aperiodic geometry which consists of a porous electrode on which the electrolyte is deposited conformally while the rest of the space is filled with the counter electrode material.
The major part of the research conducted on 3D Li-ion batteries is focused on different techniques for synthesising 3D electrodes and on the deposition of solid polymer electrolytes coating these electrodes. The most common method for the synthesis of 3D electrodes starts from three-dimensional current collectors made through a template synthesis approach followed by deposition of an electroactive material on these structures.

Taberna et al. [10] described the synthesis of pillars of copper current collector followed by subsequent electrodeposition of Fe$_2$O$_4$ as an active material. Successful depositions of nickel-tin alloy [11], bismuth [12], tin [13] and Cu$_2$Sb [14] on copper 3D current collectors were also reported. The synthesis of the corresponding aluminium three-dimensional current collector was reported by Perre and co-workers [15]. The latter type of structure was covered with TiO$_2$ by atomic layer deposition [16] or with LiCoO$_2$ by spray-coating [17]. Using the aperiodic approach, different porous foams can be used as current collectors. Manganese dioxide has been deposited on reticulated vitreous carbon foam [18] and polyaniline has been deposited on reticulated vitreous carbon foam and carbon felt strands [19]. Asfaw et al.
synthesised high surface area carbon foams and used them as negative electrode materials and as current collectors for polyaniline in Li-ion cells. Mazor and co-workers [21] deposited LiFePO₄ onto Au coated perforated silicon substrates.

The deposition of the solid electrolyte is a crucial step, as the electrolyte layer has to be thin, conformal and pinhole-free. El-Enany et al. [22] described the deposition of polyacrylonitrile films on vitreous carbon, nickel foams and MnO₂ substrates. Sun and co-workers coated LiFePO₄ particles with polyetheramine substituted with a metachrylic group separator [23], electropolymerised polypropylene glycol diacrylate on polyaniline covered reticulated vitreous carbon foams [19] and coated copper pillars with high molecular weight poly(trimethilene carbonate) [24]. Hadar et al. [25] proposed the electrophoretic deposition of composite yttria-stabilized zirconia onto gold plated silicon perforated substrates.

Even though different 3D micro-batteries have been conceptually envisaged [26,27], only a few examples of complete 3D Li-ion batteries have been reported so far [28-33]. Nathan et al. [28] reported the fabrication of a micro-battery on 3D perforated silicon microchannel plates. They first deposited a nickel current collector, then a MoO₃S₅ cathode, a PVDF-SiO₂ membrane separator and a combined graphite anode and current collector. The capacity per footprint area of the cell was around 2 mAh/cm², but the large dimensions of the microchannels (i.e., 40 µm in diameter and 500 µm in length) decreased the energy density per volume unit of the cell. Ergang and co-workers [29] deposited a polymer electrolyte on a three-dimensionally ordered macroporous carbon electrode and filled the rest of the space with a V₂O₅ ambigel cathode. The cell rapidly lost capacity during the first 10 cycles, most probably due to the low conductivity of the gel cathode. Min et al. [30] fabricated interpenetrating arrays of carbon as an anode and dodecylbenzenesulfonate doped polypyrrole as a cathode and cycled this battery in liquid electrolyte. This cell, however, suffered from short circuiting, most probably due to the small distance between the anode and cathode arrays. Kotobuki and co-workers [31,32] reported the fabrication of 3D batteries consisting of a Li₀.₃₅La₀.₅₅TiO₃ separator with a honeycomb structure, with Li₄Mn₅O₁₂ as the anode and LiCoO₂ or LiMn₂O₄ as the cathodes. These cells presented low discharge capacities, with values of 7.3 µAh/cm² and 32 µAh/cm², respectively. Finally, Pikul et al. [33] reported a cell comprised of interdigitated porous nickel scaffolds with NiSn and MnO₂ deposited active materials. Although the cell presented an areal capacity of 4 mAh/cm², only 15 cycles were reported.
1.4 Aluminium in Li-ion batteries

Aluminium is extensively used as a current collector for the positive electrode in commercial Li-ion batteries as it is stable up to 4.5 V vs. Li⁺/Li in most organic electrolytes. It is relatively inexpensive, has a high electronic conductivity and it is readily available as high purity thin foils and plates [34]. Besides being the perfect current collector candidate for positive electrodes, aluminium was already in 1971 shown to alloy with lithium at low potentials vs. Li⁺/Li [35]. Despite the early discovery of the alloying reaction, the practical use of aluminium as negative electrode in Li-ion batteries has been hindered by severe capacity fading upon cycling and low coulombic efficiencies.

There is no consensus regarding the origin of the capacity fading for Al negative electrodes. Recent research on aluminium electrodes for Li-ion batteries assign the poor cycling to pulverisation of the electrode due to volume changes associated with the alloying and dealloying processes, and several different means have been used to try to tackle this problem. The effect of the thickness of the aluminium film [36,37] and size of the aluminium particles [38] on the cycling behaviour against metallic lithium have been studied, but the results are contradictory. Different types of aluminium substrates [39] and different morphologies of aluminium [40] were shown to improve the cycling of the electrode. The use of certain amounts of inactive elements (for example metals that do not react with lithium) in the composition of the electrode [41,42] or coating of the aluminium particles [43] were reported to buffer the volume expansion and hence contribute to higher cycling stability. Finally, the use of aluminium nanowires and nanorods was proposed for buffering the volume expansion during cycling against lithium [44-47].

Although the common conception is that the volume expansion during lithium alloying is detrimental to the integrity of the aluminium electrode, the volume expansion for lithiated aluminium is only 95% as compared to more than 300% in the cases of tin and silicon. The initial studies on lithium and aluminium alloying also indicated that the cyclability of the aluminium electrode mainly was limited by the diffusion of lithium in the aluminium phase. The formation of lithium rich alloys (i.e., Li₃Al₂ and Li₉Al₄), leading to more than 100% of volume expansion upon cycling, was suggested [48,49], but only the LiAl alloy has been identified by X-ray diffraction [50]. Upon alloy formation, lithium was shown to nucleate on the surface of aluminium and the alloy was shown to grow in a three-dimensional manner [51]. Besenhard [52] suggested that the reason for the big capacity loss during the first cycle is the retention of lithium within the aluminium electrodes, but that during cycling this retention capacity is filled up and the coulombic efficiency becomes almost 100%. Several papers report that the capacity retention of the aluminium electrode is improved when alloying with a given
amount of lithium and when only cycling about 2% of the alloy [53-55], or after heat treatment of the aluminium electrode [56]. Several research groups have determined the diffusion coefficient of lithium in aluminium [57-60], with reported values between $10^{-8}$ and $10^{-11}$ cm$^2$/s depending on the evaluation method. Finally, Owen and co-workers [61,62] proposed two models for the alloying and dealloying of lithium and aluminium which will be discussed in more detail later in this thesis.

1.5 Titanium oxide in Li-ion batteries

Titanium oxide (TiO$_2$) has been studied in detail as an insertion host for lithium ions. The most commonly used polymorph of TiO$_2$ for Li-ion battery applications is anatase, as its open structure favours lithium ion insertion. Anatase was shown to reversibly intercalate up to 0.5 lithium ions per titanium atom (Li$_{0.5}$TiO$_2$) with a theoretical capacity of 168 mAh/g [63-68]. Nanoparticles have, however, proven to host up to 0.8 lithium ions per formula unit [69-71]. Although the rutile polymorph of TiO$_2$ is not as good host for lithium ions as anatase, it was shown to reversibly intercalate 0.5 lithium ions per formula unit when cycled at elevated temperatures [72] or if the particles are nanometre-sized [73]. TiO$_2$-B, a synthetic polymorph of titanium oxide, has also shown a promising lithium ion intercalation capacity when the particles are in within the nanometre domain [74-76].

Mesoporous titania nanotubes [77] and vertically aligned TiO$_2$ nanotubes [78] were shown to have both higher gravimetric capacities and higher power capabilities as compared to anatase particles. The template free synthesis of self-supported, ordered titanium oxide nanotubes has recently attracted a lot of attention due to their high surface area for a given foot-print area. Ordered arrays of TiO$_2$ hollow nanotubes [79-83], or nanotubes filled with oxide nanoparticle [84,85], have been proposed as potential anodes for 3D Li-ion micro-batteries. Despite their high surface area, these electrodes show rather modest discharge capacities per unit area, with stable cycling capacities as high as 0.3 mAh/cm$^2$ at rather low discharge currents and without prolonged cycling reported.
2. Methods

This chapter contains a brief description of the methods used in this thesis and their application for 3D Li-ion micro-batteries. Electrodeposition was used for the synthesis of three-dimensional aluminium nanorod structures. TiO$_2$ was deposited onto 3D Al current collectors by electrophoretic and sol-gel deposition. Anodisation was employed for the synthesis of titanium oxide nanotubes and thick alumina layers on 3D aluminium rods. The electrochemical characterisation of the batteries presented in the thesis was done by cyclic voltammetry and galvanostatic cycling. Materials characterisation was carried out with standard techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD) and transmission electron microscopy (TEM).

2.1 Electrodeposition

Electrodeposition is an electrochemical technique that is widely used in industry. The electrodeposition of metals and alloys has found application in electrometallurgical processes like electrowinning, electrorefining, electroplating and electroforming [86]. A schematic representation of an electrodeposition cell is given in Figure 3. The reduction of the metal ions from the electrolyte solution constitutes the electrochemical reaction taking place at the working electrode. The counter electrode closes the electrical circuit. The electrochemical reaction taking place at the counter electrode is the oxidation of the metal which the electrode is made of. If the working and counter electrode are made of the same metal, the concentration of metal ions in the electrolyte solution remains constant. The third electrode is the reference electrode, which measures the absolute potential of the working electrode.
Electrodeposition can be conducted either by controlling the potential or by controlling the current. As different electrode reactions take place at different potentials, controlled potential electrodeposition will allow only some reactions to take place. Current controlled electrodeposition, on the other hand, has the advantage that the deposited mass is proportional to the time of deposition. Given that the faradaic efficiency of the current is known, a precise amount and thickness of the deposit can hence be achieved.

Electrodeposition is often applied for the manufacturing of 3D Li-ion battery components as it is an inexpensive and straightforward method [9]. Electrodeposition has been used for the synthesis of copper [10], aluminium [15], nickel on perforated substrates [28] and porous nickel scaffold [33] three-dimensional current collectors. It has likewise been employed for the deposition of thin layers of Fe₃O₄ [10], NiSn alloy [11], Bi [12], Sn [13] and Cu₂Sb [14] on copper pillar current collectors, MnO₂ on reticulated carbon foam [18], polyaniline on carbon foams [19], molybdenum oxy-sulfide on nickel-coated perforated substrates [28], polypyrrole on carbon posts [30] and NiSn and MnO₂ on Ni scaffolds [33]. Finally, electrodeposition has been used for the deposition of solid electrolyte materials. Polyacrylonitrile films were deposited on vitreous carbon, nickel foams and on MnO₂ electrode material [22], while polypropylene glycol diacrylate was electropolymerised on polyaniline covered reticulated vitreous carbon foams [19]. Poly(phenylene oxide) has also been electrodeposited on the surface of a three-dimensional macroporous carbon electrode [29].
2.2 Electrophoretic deposition

Electrophoretic deposition is an electrochemical technique which is complementary to electrodeposition as this technique can be used for the deposition of non-conductive particles. Any charged particle can be deposited by this method, provided that it is present in a suspension. Upon application of an external electric field, charged particles that are present in the electrolyte suspension migrate to the electrode that has the opposite charge. Electrophoretic deposition can be viewed as a special case of electrodeposition, as the current generated by the voltage difference is supported by faradaic reactions taking place at the electrodes.

The electrophoretic deposition is a complex process which depends on a variety of parameters which can be divided into two categories: those related to the suspension and those related to the process [87]. The most important parameters related to the suspension are particle size, zeta potential and the stability of the suspension. Smaller particle sizes can prevent settling due to gravitational effects and minimize cracking of the deposited film. The zeta potential of the particles plays a crucial role in electrophoretic deposition. It will determine the direction in which the particles will migrate (i.e., to the cathode if the particles are positively charged or to the anode if they are negatively charged) and the interaction between the charged particles. The stability of the suspension is important as well. If the suspension is not stable enough, the particles will tend to settle rather than migrate to the targeted electrode. On the other hand, if the suspension is too stable, the repulsion forces between the particles will be too large and the deposition will not occur. The most important parameters related to the deposition process are the deposition time, which will determine the thickness of the deposit, and the applied voltage, which determines the speed of the process. Although the most commonly used form of electrophoretic deposition is the controlled voltage electrophoretic deposition mode, alternating current and pulsed direct current deposition methods have also been developed [88].

The only examples of using electrophoretic deposition for 3D Li-ion micro-battery applications are those from Peled’s group [21,25]. They demonstrated the electrophoretic deposition of pristine and modified LiFePO₄ onto gold coated perforated silicon substrates [21]. By adding conductive carbon, PVDF binder and a non-ionic surfactant, the electrochemical properties of the modified LiFePO₄ electrode were found to be substantially improved. Electrodepositing a conductive layer of copper sulfide further improved the cycling of the electrode, which displayed an areal capacity greater than 2 mAh/cm². The electrophoretic deposition of a composite yttria-stabilized zirconia polyethyleneimine membrane onto gold plated silicon perforated substrates was likewise described [25]. The latter authors were successful in depositing this membrane on a 2D substrate of LiFePO₄/Au/Si and in cycling this electrode against lithium by impregnating the membrane with LiPF₆.
EC:DEC electrolyte. When they attempted to electrophoretically deposit first LiFePO₄ and then the composite membrane, the two layers were, however, too thick and partially blocked the microchannels of the substrate.

2.3 Sol-gel synthesis

Sol-gel synthesis has been intensively used for the synthesis of porous materials. The process starts from a colloidal solution of a precursor, also known as a sol, which undergoes hydrolysis and condensation reactions [89]. Depending on the number of functional groups that undergo hydrolysis, the condensation step can lead to the formation of linear or three-dimensional polymeric units. The condensation will proceed until the polymeric units occupy the entire volume of the sol and the gel forms. The polymeric units of the gel can entrap a liquid phase and, when drying in the supercritical state, pores are formed and thus a porous material, called an aerogel, is obtained. If the drying is made by evaporation, the pores of the gel will collapse, the gel will shrink upon drying and a xerogel is obtained. One very important application of sol-gel synthesis is the deposition of thin films [89]. In this case, the sol is directly deposited on a substrate by means of dip-coating, spin-coating or spraying, and the gelation occurs directly on the targeted substrate. Evaporation of the solvent results in the formation of a film on the targeted substrate. A schematic description of the possibilities associated with sol-gel syntheses is shown in Figure 4.

Sol-gel synthesis has been extensively used in the deposition of electrode materials, or even electrolytes, for 3D Li-ion micro-batteries. Shaijumon et al. [17] deposited LiCoO₂ onto a 3D aluminium current collector by spray-coating a sol-gel precursor solution followed by drying. Long and Rolison [27] proposed a possible architecture for an aperiodic 3D Li-ion battery which starts from an aerogel of the negative electrode, which is coated by electrolyte, while the rest of the space within the pores is filled with the positive electrode. A three-dimensionally ordered macroporous carbon aerogel was synthesized by sol-gel method to be used as a negative electrode [29]. After electrodeposition of a solid polymer electrolyte, the rest of the space of the porous structure was filled with a V₂O₅ xerogel. Finally, Kotobuki et al. [31,32] infiltrated sol-gel precursors into the pores of a honeycomb membrane to synthesize Li₄Mn₅O₁₂, LiCoO₂ and LiMn₂O₄ electrodes, respectively.
2.4 Anodisation

Anodisation is an electrochemical process in which an oxide is grown on the surface of a metal electrode as a result of the oxidation of the electrode. Anodisation has been used for a long time in corrosion science, as a simple and efficient way to grow thick oxide films on the surface of metals for corrosion protection [90]. The electrochemical cell is often relatively simple consisting of a working electrode (i.e., the metal to be anodised), a counter electrode, a power source and a conductive electrolyte solution. When an electric field is applied between the two electrodes, the surface of the working electrode undergoes oxidation to metal ions which can react with oxygen ions from the solution to form the metal hydroxide or oxide. The growth of the oxide will continue by migration of either oxygen ions to the metal/metal oxide interface or metal ions to the metal oxide/electrolyte interface. Nevertheless, it is worth to mention that not all metals can undergo anodisation. In order to be able to electrochemically grow an oxide layer on the surface of a metal, the following criteria have to be satisfied [90]: i) the metal must be able to oxidize in an oxygen containing solution, ii) the formed metal oxide must be chemically stable or at least hard to dissolve in the electrolyte solution, and iii) the formed metal oxide must not be too conductive as to prevent unwanted oxidation reactions on its surface.

Figure 4. Schematic representation of sol-gel processing.
Although not directly used in the fabrication of components for 3D Li-ion micro-batteries, anodised alumina has been used as a template for electrode-position of copper [10] and aluminium [15] 3D current collectors. Anodisation has thus been used for the manufacturing of hexagonally ordered porous alumina membranes [91-94] and it was shown that the choice of electrolyte (sulphuric, oxalic or phosphoric acid) influenced the pore diameters and inter-pore distances, while the choice of anodisation potential affected the ordering and homogeneity of the pores. The anodisation of titanium, on the other hand, has been used to synthesize parallel aligned TiO$_2$ nanotubes which have been proposed as electrodes in three-dimensional Li-ion micro-batteries [79-83].

2.5 Electrochemical testing

Cyclic voltammetry and galvanostatic cycling are the two methods mainly used for electrochemical testing in this thesis.

Cyclic voltammetry is an electrochemical technique in which the potential of the working electrode is scanned between two potential limits at a certain scan rate [95]. The current is recorded and the voltammogram is the representation of the current vs. the applied potential. This technique is very useful for studying electrochemical processes (i.e. reduction and oxidation reactions) which take place in a battery and it provides information about the potentials at which the reactions take place and about the degree of completion of the reactions within a given electrochemical window.

Galvanostatic cycling is a controlled current technique [95] in which a known current is applied and the potential response is followed as a function of time within a selected potential range. The shape of the E-t curve can give valuable information regarding the potential at which the electrochemical reactions take place. The magnitude of the current determines the rate of the charge or discharge of the battery and, as the current is constant, the capacity is proportional to the time required for the charge or discharge.
3. Results and discussion

Aluminium is a relatively inexpensive material readily available in high purity and a variety of shapes and sizes. For the above mentioned reasons, it would be desirable to use aluminium in 3D Li-ion micro-batteries, as it would decrease the cost of these devices. Simple and cost effective methods are also desired for the 3D structuring of aluminium and for the subsequent deposition of materials onto aluminium. The deposition of aluminium in the pores of commercial membranes was reported using potentiostatic electrodeposition [15]. Would galvanostatic electrodeposition offer some advantages in the quality of the obtained 3D structure? For a successful implementation of these 3D aluminium rods as current collectors active electrode materials also need to be deposited. Are there any relatively simple and cost effective methods for the deposition of active materials onto 3D aluminium rod current collectors? Could aluminium in fact be used as a negative electrode? This chapter will answer the above mentioned scientific questions in the light of the obtained results during my PhD studies.

3.1 3D aluminium rod synthesis

The three-dimensional aluminium rod structures were synthesised by galvanostatic electrodeposition of aluminium within the pores of a commercial alumina membrane. Template electrodeposition of aluminium nanowires and nanorods has been reported previously [96-98], but Perre and co-workers [15] were the first to describe the direct electrodeposition of aluminium rods on aluminium substrates. They conducted the electrodeposition in a potentiostatic mode, utilizing a pulsed potential programme. The first potential pulse, -0.4 V vs. Al³⁺/Al, was applied for a short time and deposition of aluminium occurred at this stage, since the obtained current was cathodic. The second potential step was applied for 200 ms and involved a potential of -0.1 V vs. Al³⁺/Al. The recorded current in this step was anodic, yielding a re-oxidation of a part of the deposited aluminium. Even if the obtained nanorods were vertical and parallel on the aluminium substrate, the height of the rods was not as homogenous as for the copper nanorods obtained by Taberna et al. [10]. Nevertheless, as there was no previous report on the galvanostatic deposition of aluminium nanorods, constant and pulsed current electrode-
position was used with the aim to increase the homogeneity of the deposited rods (see paper I).

It is worth mentioning that the electrodeposition of aluminium is significantly more difficult than that of copper, as aluminium is electrodeposited from AlCl$_3$ at a potential that does not permit the use of aqueous electrolytes (i.e., -1.67 V vs. SHE). Furthermore, aluminium chloride is very reactive towards water which means that it must be handled in the inert atmosphere of a glove box. The setup used for the galvanostatic deposition of aluminium nanorods is presented in Figure 5.

![Figure 5. The electrochemical cell used for the deposition of aluminium nanorods.](image)

Dialkylimidazolium chloroaluminate ionic liquids have been shown to be the most suitable electrolytes for the electrodeposition of aluminium [99,100]. The equilibrium in these ionic liquids can be represented by Equation 1 [101]:

$$2\text{AlCl}_4^- = \text{Al}_2\text{Cl}_7^- + \text{Cl}^- \quad (1)$$

If the ionic liquid is acidic, the equilibrium in reaction 1 is shifted towards the right. The electrodeposition of aluminium can only be realised from acidic ionic liquids, as the reduction of the AlCl$_4^-$ ion takes place at lower potentials than the reduction of the EMI cation [99]. For this reason, an excess of AlCl$_3$ was added to the EMICl to give a molar ratio of 2:1. The reduction of the Al$_2$Cl$_7^-$ anion is described by Equation 2 [101]:

$$4\text{Al}_2\text{Cl}_7^- + 3\text{e}^- = \text{Al} + 7\text{AlCl}_4^- \quad (2)$$
Table 1. The influence of different parameters on the galvanostatic deposition of Al.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Current programme</th>
<th>Nucleation potential (V vs. Al(^{3+}/\text{Al}))</th>
<th>Number of cycles/time</th>
<th>Homogeneous deposit</th>
<th>Even height of pillars</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Pulsed</td>
<td>None</td>
<td>5000</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>A2</td>
<td>Pulsed</td>
<td>None</td>
<td>6000</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>A3</td>
<td>Pulsed</td>
<td>None</td>
<td>7000</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>A4</td>
<td>Pulsed</td>
<td>-0.7</td>
<td>7000</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>A5</td>
<td>Pulsed</td>
<td>-0.8</td>
<td>7000</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>A6</td>
<td>Pulsed</td>
<td>-0.9</td>
<td>7000</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>A7</td>
<td>Pulsed</td>
<td>-0.9</td>
<td>5000</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>A8</td>
<td>Constant</td>
<td>None</td>
<td>9600 s</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>

Table 1 summarises the different samples that were galvanostatically electrodeposited. The constant current deposition was conducted with a current of -1 mA, while the pulsed current programme consisted of a current of -5 mA for 0.2 s followed by a 2 s long rest period (i.e., zero current). Before the galvanostatic experiments were started, the aluminium working and counter electrode plates were polarised at -0.5 V vs. Al\(^{3+}/\text{Al}\) for 60 seconds to reduce the native oxide layer on the aluminium surface.

Figure 6 presents scanning electron microscope (SEM) images for the eight samples described in Table 1. As it can be seen from the micrograph for sample A3, the pulsed current deposition resulted in an inhomogeneous deposit. The deposit had a “cauliflower” morphology, even after long deposition times (i.e., 7000 cycles). The reason for this inhomogeneity was studied by decreasing the deposition time. Samples A1 and A2 were thus deposited for 5000 and 6000 cycles, respectively. Sample A1 presented some isolated islands of rods on the surface of the aluminium plate, with a very poor coverage of the substrate. With more time allowed for the deposition, these island of rods grew larger and larger and the coverage of the deposit increased substantially (see the micrograph for sample A2). Nevertheless, 7000 cycles were still not sufficient for all the islands to collapse into one another and render homogeneity to the deposit. From the micrographs for samples A1-A3 it is clear that the reason behind the inability to obtain a homogeneous deposit was the small number of nuclei formed at the beginning of the deposition experiment. Aluminium nucleates mainly at the defects present on the surface of the aluminium plate at the beginning of the galvanostatic electrodeposition. These nuclei then start to grow in the pores of the membrane in an island-like manner. The rods that are taller will, however, grow at a slower rate than the shorter ones due to the iR drop in the pores of the membrane. Despite this, these islands will not collapse into a homogeneous deposit even after long deposition times.
It is known that the rate of formation of nuclei can be increased by increasing the overpotential [102]. For this reason, short potential pulses (i.e., 50 ms long) were applied to facilitate the formation of the initial nuclei on the surface of aluminium. From the SEM images for the above mentioned samples (i.e., A6 and A7) it is clear that the number of the initial nuclei on
the surface of the aluminium plate was higher and that the homogeneity of the deposits increased substantially when increasing the nucleation overpotential. The highest value for the potential pulse employed was -0.9 V vs. Al\(^{3+}/Al\) as the reduction of the EMI\(^+\) cation has been reported to take place at around -1 V vs. Al\(^{3+}/Al\) [99]. A nucleation potential of -0.9 V vs. Al\(^{3+}/Al\) gave rise to a homogeneous deposition after 7000 cycles, with a narrow distribution of the rod heights. Even after 5000 cycles of pulsed current deposition (see sample A7), the deposit was homogeneous, although the rods had uneven heights. This confirms that there was a levelling-out effect in the growth of the aluminium rods, with higher rods growing at a slower pace than the shorter ones.

Finally, constant current galvanostatic electrodeposition of the aluminium rods was also attempted. The deposition resulted in a homogeneous deposit, but the distribution of the height of the rods was not as narrow as for the optimized pulsed current deposition for 7000 cycles, as seen in Figure 7. The levelling-out of the height distribution of the rods was more effective for the pulsed current deposition, most probably due to the diffusion of Al\(_2\)Cl\(_7\)^- ions in the pores of the alumina membrane during periods of zero current. The chronopotentiogram recorded during the constant current electrodeposition experiment (see Paper I, Figure 2) clearly shows that the potential was constant at around -0.5 V vs. Al\(^{3+}/Al\) (a potential where the deposition of aluminium takes place) for 3000 s. After 3000 s, the potential drifted away to more negative values. As the current was applied continuously, the Al\(_2\)Cl\(_7\)^- ions were depleted in the pores of the membrane and the diffusion of new ions was not that efficient as during the pulsed current deposition. This resulted in an excess of AlCl\(_4^-\) ions, rendering the ionic liquid basic rather than acidic. As the current no longer could not be sustained by the reduction of the Al\(_2\)Cl\(_7\)^- ions, the potential drifted to more negative values, where the reduction of AlCl\(_4^-\) ions was possible. The reduction of AlCl\(_4^-\) ions takes place at more negative potentials than that for the reduction of the EMI\(^+\) cation, meaning that the deposition of aluminium rods was accompanied by the reduction of the electrolyte, as it has been previously shown [99].

![Figure 7. High magnification SEM micrographs of samples A6 (a) and A8 (b). See Table 1 for the description of the samples.](image)
The use of a short nucleation potential pulse before the deposition contributes to the formation of many initial nuclei on the surface of the aluminium plate which lead to a more homogeneous deposit, covering the entire surface of the substrate. Pulsed current deposition clearly provides narrower rod height distributions than constant current electrodeposition.

From now on, the 3D aluminium structures that will be referred to in the text were synthesized by pulsed current deposition (-5 mA for 0.2 s followed by rest period for 2 s, 7000 cycles) with a nucleation potential of -0.9 V vs. Al\textsuperscript{3+}/Al applied for 50 ms prior to the galvanostatic deposition experiment.

3.2 3D aluminium as a current collector

The most common use of aluminium in Li-ion batteries is as a current collector for the positive electrode [34]. Nevertheless, as aluminium is stable above 1 V vs. Li\textsuperscript+/Li, it can also be used as a current collector for high potential anodes. This section is dedicated to the use of three-dimensional aluminium rod structures as current collectors for Li-ion micro-batteries electrodes. The deposition of an active material onto the aluminium current collector is investigated by using inexpensive and relatively straightforward techniques. The electrode material chosen for electrophoretic deposition (section 3.2.1) and sol-gel synthesis (section 3.2.2) was titanium oxide (Paper II). TiO\textsubscript{2} has been intensively studied as an active material for Li-ion batteries, which makes it a perfect model material for deposition on 3D aluminium current collectors. In section 3.2.3, the study of lithium ion intercalation in three-dimensional titanium oxide nanotubes, fabricated by anodisation, is presented for comparative purposes (Paper III).

3.2.1 Electrophoretic deposition of TiO\textsubscript{2} on 3D aluminium

To use aluminium as a substrate for electrodeposition is not straightforward, even though Edström et al. [9] showed that electrodeposition constitutes a simple and cost-effective technique for the synthesis of 3D electrodes for Li-ion micro-batteries. The majority of electrodeposition baths are either acidic or basic, which causes significant corrosion of aluminium substrates. For this reason, electrophoretic deposition was instead attempted for the coating of the aluminium current collectors with a TiO\textsubscript{2} active material (Paper II). Even if the electrophoretic deposition is based on the migration of charged particles to the opposite charged electrode under an electric field, this process is in fact merely a special case of electrolysis. The current between the working and the counter electrodes is thus supported by electrochemical reactions at the two electrodes.

The electrophoretic deposition of TiO\textsubscript{2} particles has previously been studied for structural and functional applications of composite materials [103-
and for applications in dye-sensitized solar cells [106-108]. The use of electrophoretic deposition of TiO$_2$ for applications in Li-ion batteries has, however, not been reported previously. As an initial study, P 25 (containing around 80% anatase and 20% rutile) and pure anatase particles were deposited by electrophoresis on flat aluminium substrates. P 25 was chosen as it is composed of small particles (with diameters between 25 and 40 nm), which are commercially available since they are frequently used for solar cells. Pure anatase particles, with a mean diameter of 25 nm, were also employed for electrophoretic deposition, as the rutile phase was shown to have inferior lithium ion insertion properties as compared to anatase.

Figure 8 presents SEM images of P 25 particles electrophoretically deposited on a planar aluminium substrate for 90 seconds. The experiment was also carried out for 60 seconds, but the P 25 particles did then not homogeneously cover the substrate, and for 120 s, which resulted into a too thick deposited layer. The latter aspect is of concern for the deposition on 3D substrates, as the available space between the rods of the current collector is limited. Despite this, the electrophoresis of P 25 particles for 90 seconds resulted in a homogenous coverage of the substrate, as can be seen in Figure 8a. The deposit contained cracks, indicating that a deposit which cracked upon drying was formed. From the higher magnification micrograph in Figure 8b, it is clear that the obtained deposit was dense and porous. No particle agglomeration could be observed in the SEM images and the deposited particles had a mean diameter of around 35 to 40 nm, in good agreement with the specifications for the P 25 powder.

Electrophoretic deposition of pure anatase on the planar aluminium substrates was also attempted. Figure 9 presents the SEM images of electrophoretically deposited (90 s) anatase particles on an aluminium plate. From the lower magnification micrograph (Figure 9a) it can be seen that the deposition was not as homogeneous as in the case of the P 25 particles, with only about 80% coverage of the aluminium substrate. The deposit was also not that dense and no cracks could be found in the SEM analysis. Even though
the particle size was around 25 nm (corresponding to the particle size of the anatase powder), the particles agglomerated into bigger aggregates, with sizes in the micrometre range. It should, however, be pointed out that this agglomeration could have taken place already in the starting material.

![Image of SEM images of pure anatase particles electrophoretically deposited on a planar aluminium substrate for 90 s obtained using low (a) and high (b) magnification.](image)

**Figure 9.** SEM images of pure anatase particles electrophoretically deposited on a planar aluminium substrate for 90 s obtained using low (a) and high (b) magnification.

As the electrophoretic deposition of pure anatase particles resulted in the formation of large agglomerates, only the electrophoresis of P 25 titania particles was attempted on 3D aluminium rod substrates. The three-dimensional aluminium structure described in section 3.1 could, however, not be used for this purpose, as the distance between the aluminium rods would not be sufficient for the deposition of an active material layer by electrophoresis. Instead 3D aluminium rods were deposited on aluminium substrates through the pores of polycarbonate membranes with 1 and 2 µm pore sizes, respectively, using the optimised pulsed current protocol described in Paper I. The corresponding SEM images are shown in Figures 10a and 10b. It is seen that the coverage of the rods was not that homogeneous and the rods were not aligned in parallel as in the case of the deposits presented in Chapter 3.1. This can be explained by the fact that the pores of the polycarbonate membranes were not as homogeneous as those in the alumina membranes. The distance between the rods was hence in the order of one to a few micrometres, depending on the membrane used, which provided sufficient space for the deposition of an electrode layer. The results of the electrophoretic deposition of P 25 TiO₂ onto the two different 3D aluminium substrates are presented in Figures 10c and 10d, respectively. Even though titania particles were deposited on the substrates in both cases, the deposits were unfortunately two-dimensional. The particles deposited on the 2 µm aluminium current collectors reached the bottom of the rods, but the deposit was unfortunately not conformal and did thus not follow the shape of the rods. On the other hand, for the 1 µm diameter rods the P 25 particles were deposited only on the upper parts of the rods. This is a clear indication of agglomerat-
tion of the P 25 particles during 3D deposition which was not present for the deposition on the 2D planar aluminium substrate.

Electrophoretic deposition is a simple and straightforward deposition technique for the deposition of TiO$_2$ onto planar aluminium substrates. The resulting P 25 particles deposits were dense and porous and homogeneously covered the surfaces of the 2D aluminium substrates. The 3D aluminium substrates, however, complicated the electrophoresis process and the resulting deposits were clearly not conformal. For this reason it is concluded that electrophoretic deposition is not a suitable method for the deposition of electrode materials onto 3D aluminium rod current collectors.

3.2.2 Sol-gel deposition of TiO$_2$ on 3D aluminium

Sol-gel deposition is another simple and cost effective method for the deposition of thin films. Sol-gel deposition from a titanium iso-propoxide precursor has been reported for the manufacturing of electroluminescent devices [109], photocatalytic devices [110], solar cells [111,112] and Li-ion batteries [113-115]. Lafont et al. [113] synthesised mesoporous nanosized TiO$_2$ materials by a modified sol-gel route and prepared a slurry (80% TiO$_2$, 10% carbon black and 10% PVDF) which was cast on an aluminium foil. They showed that almost one lithium ion per Ti atom could be inserted in a two-
phase structural transition. Issac and co-workers [114] described a sol-gel route to obtain a nanocrystalline Ti$_{2/3}$Sn$_{1/3}$O$_2$ anode material starting form titanium iso-propoxide and SnCl$_4$·5 H$_2$O. They could cycle this material for at least 100 cycles, with the discharge capacity fading from 500 mAh/g in the second cycle to about 300 mAh/g in the 100$^{th}$ cycle. TiO$_2$ and carbon nanofibers were synthesised by Yang et al. [115] as composite electrodes from a mixture of polyacrylonitrile and titanium iso-propoxide. These electrodes could be cycled for 100 cycles with capacities around 200 mAh/g.

The sol-gel synthesis used for the coating of the 3D aluminium current collectors was straightforward (Paper II), as titanium iso-propoxide was merely mixed with NMP to a concentration of 0.1 M in an argon filled glove box. Different volumes (i.e., 10 and 15 µL) of this precursor solution were then applied onto aluminium current collectors composed of rods with a diameter of 1 µm. The high surface area of the electrode was expected to act as a sponge, as capillary forces should cause absorption of the precursor and a distribution of it over the rods. After a 15-minute long rest period, the samples were taken out of the glove box and the titanium iso-propoxide was allowed to react with moisture from air to give titanium oxide. The samples were subsequently heat-treated at 350 °C to ensure a complete evaporation of the electrolyte and formation of a TiO$_2$ film. SEM images of the TiO$_2$ on 3D aluminium current collectors are presented in Figures 11a and 11b, respectively. There is a certain degree of roughness of the deposited rods that could indicate the deposition of a thin TiO$_2$ layer when comparing with those for the bare rods (see Figure 3 in Paper II). If the entire amount of titanium precursor would have been deposited as a thin and even layer, the thickness of the deposited TiO$_2$ layer should have been 40 nm for the 10 µL impregnated 3D aluminium current collector and 60 nm for the 15 µL impregnated substrate. In this calculation the area gain factor for the current collectors was also included. Such very thin layers are, unfortunately, impossible to detect using SEM. The corresponding EDS analysis presented in Figures 11 c and 11 d, however, confirmed the presence of both titanium and oxygen on the aluminium pillars. X-ray diffraction experiments were also carried out, but the only observed reflections were those of the aluminium substrate. It was hence concluded that thin, amorphous layers of TiO$_2$ were indeed obtained by the impregnation of titanium iso-propoxide on 3D aluminium current collectors.
Figure 11. SEM images (a and b) and elemental analysis (c and d) for 3D Al current collectors obtained after impregnation with a) 10 µL and b) 15 µL of Ti isoproxide solution, respectively, and after subsequent heat treatment in air at 350 °C. The corresponding EDS analysis results are displayed in c) and d).

The two above mentioned electrodes were also cycled against metallic lithium in Li-ion pouch cells. The results of the first three cycles together with the capacity retention during the cycling are presented in Figure 12. Both electrodes displayed big capacity losses upon the first cycle. The formation of a SEI layer could not explain the difference between the discharge and the charge capacities, as the electrolyte is not expected to decompose at potentials above 1 V vs. Li⁺/Li. The discharge capacities were larger than the charge capacities for all cycles, even if the capacities stabilized upon the cycling. This result indicates that lithium ions were trapped in the electrode on each cycle. This is not surprising, considering that titanium oxide is amorphous and that there are no defined structural channels for the insertion and extraction of lithium ions. Nevertheless, upon cycling the discharge capacities were stabilised at approximately 1 µAh/cm² for the 10 µL impregnated current collector and at 1.5 µAh/cm² for the 15 µL impregnated sample, respectively. Cyclic voltammograms for the 15 µL impregnated electrode, recorded vs. metallic lithium (see Figure 6 in Paper II), indicated the presence of a pseudo-capacitive behaviour, with no clear reduction peaks
and broad oxidation peaks. It is worth mentioning that the heat treatment (which facilitates crystallisation of the active material layer) was not conducted at a temperature higher than 350 °C as the transition from anatase to rutile was reported to take place already at 390 °C [116].

Figure 12. Potential vs. capacity plots for the first three cycles for electrodes impregnated with 10 µL (a) and 15 µL (b) Ti iso-propoxide, respectively, and their corresponding cycling stabilities (c and d).

It is concluded that sol-gel is a suitable technique for the deposition of layers of electrode materials onto three-dimensional aluminium current collectors. Optimization of the quantity and crystallinity of the deposited materials are, however, required for the successful implementation of this method with respect to TiO2 as a 3D Li-ion battery material.

3.2.3 Highly ordered 3D TiO2 nanotube electrodes
The synthesis of TiO2 nanotubes was studied as an alternative synthesis method for 3D titania electrodes since the TiO2 amorphous electrodes on the 3D aluminium current collectors did not reach their full capacity (see Paper III).

TiO2 nanotubes have previously been studied for application in Li-ion micro-batteries [79-83], but the homogeneity and the aspect ratio of the electrodes were rather low. The wall thickness of the electrodes ranged between
10 and 20 nm and the height of the tubes was around 1 µm (except for the 8.2 µm long nanotubes reported in ref. [83]). Schmuki’s group [117] showed that by a careful selection of the organic electrolyte and optimized concentration of fluoride ions long, hexagonally ordered titania nanotubes could be formed. They also showed that the hexagonal arrangement of the TiO2 nanotubes could be improved by using a two-step anodisation approach [118].

Anodisation of titanium (paper III) was conducted in a fluoride containing ethylene glycol electrolyte by applying one-step or two-step anodisation protocols. Irrespective of the number of steps applied, the obtained TiO2 nanotubes were hexagonally arranged and the tubes had a diameter of around 150 nm and a wall thickness of 50 nm. The length of the nanotubes could easily be controlled by changing the anodisation time. The difference between the one-step and two-step anodised titania nanotubes was that the one-step anodised samples presented merely short-range ordering with a non-homogeneous surface containing a lot of defects, as is seen in Figure 13a. The surface of the two-step anodised nanotubes was, on the other hand, smooth, homogeneous and hexagonally arranged (see Figure 13b).

As-prepared, 9 µm long TiO2 nanotubes were used as electrodes against metallic lithium in Li-ion pouch cells. The cells were cycled for 100 cycles at a rate of 0.1 C (i.e., 10-hour discharge and 10-hour charge) and the cycling stability results are presented in Figure 14a. Although the initial discharge capacities were close to 500 µAh/cm², the capacities dropped to half of their initial values in the second cycle and then faded rapidly with increasing cycle number. This behaviour was more accentuated for the electrode obtained after one-step anodisation. Considering the big differences in the surface structure and homogeneity of the nanotubes for the two different electrodes this was not surprising. The large amount of lithium ions that is trapped in the electrodes and which thus cannot be extracted upon charging of the cells is in good agreement with the results obtained for the 3D thin and amorphous TiO2 electrodes described in Section 3.2. The amorphous nature

![Figure 13. SEM images of the as-prepared TiO2 nanotubes obtained with the one-step (a) and two-step (b) anodisation process.](image)
of the electrodes facilitates lithium ion trapping as it does not offer prede-
finned structural channels for the insertion and extraction of lithium ions.

By annealing the one- and two-step anodised titania nanotube electrodes
at 350°C for 10 hours, well crystallised anatase electrodes were obtained.
These electrodes were also cycled against metallic lithium at a rate of 0.1 C
in Li-ion pouch cells, and the results are presented in Figure 14b. The one-
step anodised electrode exhibited a quite rapid capacity fading during the
first 50 cycles, after which the capacity began to reach a steady state above
200 µAh/cm². The anatase electrode obtained by two-step anodisation was,
on the other hand, stable upon cycling. After an initial 15% loss of capacity
between the first and the second cycle, the cycling was quite stable and a
capacity of about 460 µAh/cm² was retained after 100 cycles with coulombic
efficiencies close to 100%.

Figure 14. Capacity vs. cycle number for the as-prepared TiO₂ electrodes produced
by one- or two-step anodisation process (a) and annealed anatase TiO₂ nanotube
electrodes produced by one- or two-step anodisation process (b). Full symbols repre-
sent the discharge capacities while empty symbols represent the charge capacities.

The first two charge and discharge cycles and a cyclic voltammogram for the
anatase TiO₂ nanotube electrode synthesised by two-step anodisation are
presented in Figure 15. Lithium ion insertion in the titanium oxide structure
takes place at around 1.8 V vs. Li⁺/Li, while lithium ion extraction is ob-
served at around 1.9 V vs. Li⁺/Li, respectively. The cyclic voltammogram
shows the corresponding titanium reduction and oxidation peaks. The capac-
ity difference between the discharge and the charge on the first cycle is due
to the entrapping of a small amount of lithium ions in the electrode. The
second cycle, however, does not present a significant difference between the
charge and discharge capacities, exhibiting a coulombic efficiency higher
than 98%.
Figure 15. Potential vs. capacity plot (a) and cyclic voltammogram recorded at a 0.01 mV/s scan rate (b) for a two-step anodised TiO$_2$ anatase nanotube electrode vs. metallic lithium.

The rate capability of this electrode was likewise tested based on the good capacity and cycling stability of the 9 µm long anatase TiO$_2$ nanotubes electrode synthesised by two-step anodisation. The results are shown in Figure 16a. It is clear that the electrode had good capacity retention even when rate tested, as the value of the capacity at low cycling rates (i.e., 0.1 C) was fully recovered after extensive cycling at higher rates. The capacity decreased with increasing cycling rates, as expected from the polarization effects induced by higher rates. Nevertheless, when cycling at a rate of 5 C (i.e., 12-minute discharge and 12-minute charge), a sharp capacity decrease was observed. However, the subsequent cycling was not influenced, as the capacities were recovered when cycling at lower rates again. To further investigate this effect, cyclic voltammograms were recorded at a scan rate of 1 mV/s as is depicted in Figure 16b. This scan rate was chosen so that the peak current would be of the same magnitude as the current used in the galvanostatic cycling at 5 C rate (i.e., 3 mA). It is clearly seen that when the lower cut-off potential was 1.5 V vs. Li$^+$/Li, the reduction reached its maximum just before the reverse of the scan. This is an indication that the reduction of Ti$^{4+}$ to Ti$^{3+}$ did not reach its full capacity. If the lower cut-off potential was changed to 1.2 V vs. Li$^+$/Li, the reduction peak became clearly visible and the reduction reaction reached its full capacity. If the lower cut-off voltage of the pouch cell was changed from 1.5 V to 1.2 V vs. Li$^+$/Li when cycled at a 5 C rate, the discharge capacity increased by a factor of 1.5. The capacity at 5 C rate was, however, two times lower than the one at 0.1 C rate. This effect was ascribed to kinetic limitations associated with the structural changes taking place upon the insertion and the extraction of lithium ions.
Figure 16. a) Rate capability test for a 9µm anatase TiO$_2$ nanotube electrode. Full symbols represent the discharge capacities while empty symbols represent the charge capacities. b) Cyclic voltammograms for a 9 µm anatase TiO$_2$ nanotube electrode recorded using a scan rate of 1 mV/s and different cathodic potential limits.

Due to the length of the TiO$_2$ nanotubes (i.e., 9 µm), iR drop effects could be a reason for not utilising all the material for lithium ion insertion and extraction. From the geometry of the electrode, the total area, volume and mass of the TiO$_2$ could be calculated. The 9 µm long anatase nanotube electrode synthesized by two-step anodisation had a stable discharge capacity of 184 mAh/g at a 0.1C rate. This was close to the theoretical capacity of 168 mAh/g for the insertion and extraction of 0.5 lithium ions per titanium.

TiO$_2$ anatase nanotube electrodes with 4.5 and 14.5 µm long nanotubes (synthesised by two-step anodisation) were also tested vs. metallic lithium. A comparison of the capacities attained with the three electrodes with different nanotube lengths is shown in Figure 17. Although the initial capacity for the electrode composed of 14.5 µm long nanotubes was 1.5 times larger than that for the 9 µm nanotube electrode, the capacity was not stable during cycling. This could have been caused either by an increasing iR drop along the length of the tubes or by detachment of the tubes from the titanium substrate during cycling. The electrode with 4.5 µm long tubes, on the other hand, displayed stable cycling at capacity values of 250 µAh/cm$^2$. The capacity was about half of that for the electrode with 9 µm long nanotubes, indicating that all the available TiO$_2$ was electrochemically active at least up to a nanotube length of 9 µm.
Figure 17. Cycling stability plots for anatase TiO$_2$ nanotube electrodes with different tube lengths synthesised by two-step anodisation. Full symbols represent the discharge capacities while empty symbols represent the charge capacities.

The previous research articles describing the use of TiO$_2$ nanotubes as potential electrodes for Li-ion batteries [79-83] used electrodes which were made of tubes with wall thicknesses of 10 to 20 nm. Thin tube walls offer the advantage of short diffusion paths for lithium ions, which in turn is beneficial for the rate capability of the electrode. For this reason, TiO$_2$ nanotube electrodes with 30 nm wall thickness were also synthesised. The latter were obtained by chemical etching of the nanotubes with a wall thickness of 50 nm after the two-step anodisation. The electrode with 30 nm thick tube walls displayed stable capacities during cycling and the value of the discharge capacity was around 70% of that obtained for the electrode with 50 nm thick nanotube walls, as is seen in Figure 18a. This result was expected based on the difference between the amounts of titanium oxide in the two electrodes. The rate capability of the two electrodes was also compared and the result is plotted in Figure 18b. There was no significant difference between the rate capability for the electrodes with wall thicknesses of 50 and 30 nm, respectively. The ratio between the capacity obtained at a 5 C rate and that obtained at a rate of 0.1 C was 0.52 in the case of the electrode with 50 nm thick tube walls and 0.48 in the case of the electrode with 30 nm tube walls. This result shows that the decrease of the wall thicknesses does not affect the rate capability significantly and that 50 nm represents a short enough lithium ion diffusion length for the two-step anodised electrodes.
Finally, the synthesis parameters of the TiO₂ nanotube electrodes and their cycling performances are listed in Table 2. The performance parameters include the discharge capacity of the first cycle at 0.1 C (Q₁@0.1C), the 100th cycle at 0.1 C (Q₁₀₀@0.1C) and the discharge capacity at 5 C (Q@5C). There is a strong correlation between the electrode performance and the synthesis conditions employed. First, the crystalline structure plays a crucial role as the amorphous electrodes display great (i.e., 50%) capacity losses in the first cycle and capacity fading during cycling. The surface arrangement of the nanotubes also plays an important role as the electrodes obtained after two-step anodisation displayed stable capacities upon cycling since the nanotubes were homogeneous and hexagonally arranged. The thickness of the walls of the tubes did not have a significant influence on the rate capability and electrodes with tube lengths of up to 9 µm did not suffer from any significant capacity fading during extended cycling.

Table 2. Correlation between experimental parameters and cycling performance of the TiO₂ nanotube electrodes.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Anodisation steps</th>
<th>Crystallinity</th>
<th>Length of tubes (µm)</th>
<th>Tube wall thickness (nm)</th>
<th>Q₁@0.1C µAh/cm²</th>
<th>Q₁₀₀@0.1C µAh/cm²</th>
<th>Q@5C µAh/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>1 Amorphous</td>
<td>9</td>
<td>50</td>
<td>475</td>
<td>105</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T2</td>
<td>2 Amorphous</td>
<td>9</td>
<td>50</td>
<td>485</td>
<td>185</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T3</td>
<td>1 Anatase</td>
<td>9</td>
<td>50</td>
<td>430</td>
<td>200</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T4</td>
<td>2 Anatase</td>
<td>9</td>
<td>50</td>
<td>605</td>
<td>460</td>
<td>235</td>
<td></td>
</tr>
<tr>
<td>T5</td>
<td>2 Anatase</td>
<td>4.5</td>
<td>50</td>
<td>200</td>
<td>235</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>T6</td>
<td>2 Anatase</td>
<td>14.5</td>
<td>50</td>
<td>835</td>
<td>600</td>
<td>265</td>
<td></td>
</tr>
<tr>
<td>T7</td>
<td>2 Anatase</td>
<td>9</td>
<td>30</td>
<td>380</td>
<td>355</td>
<td>170</td>
<td></td>
</tr>
</tbody>
</table>
3.3 3D aluminium as a negative electrode

Besides its use as a current collector for the positive electrodes in Li-ion batteries, aluminium could also be used as a negative electrode since it alloys with lithium. The gravimetric capacity that can be achieved with aluminium is about 1000 mAh/g, and the alloying potential is close to that of lithium deposition (i.e., approximately 0.15 V vs. Li⁺/Li). Aluminium thus has higher gravimetric and volumetric energy densities than graphite, while the penalty in terms of a higher potential is not very large. Upon alloying and dealloying there are, however, electrode volume changes of about 95%. This chapter will present a detailed study of the deposition and extraction of lithium into/from aluminium electrodes (Paper IV), followed by a proof-of-concept of a three-dimensional Li-ion cell with a 3D aluminium rod negative electrode and a positive electrode composed of LiFePO₄ coated on a carbon foam current collector (Paper V).

3.3.1 Lithium and aluminium electrochemical alloying

The use of aluminium as a negative electrode for Li-ion batteries has not yet been implemented as there are severe problems with capacity fading associated with the cycling of aluminium electrodes against lithium. The common belief in the Li-ion battery research community is that the volume expansion of the electrode during lithiation and delithiation is the origin of the rapid capacity fading for the aluminium electrode upon cycling. Recent research in this field has therefore been focused on different formulations and morphologies of aluminium electrodes designed to better accommodate these volume changes. Some of the reported results are, however, contradictory. Aluminium electrodes in forms of nanorods [44], nanowires [45] or columnar thin films [46] and their electrochemical behaviour against lithium have been reported. These 3D structures are believed to better accommodate the volume expansions and to reduce the pulverisation of electrochemically active mass. Au et al. [44] showed that the electrochemical performance of aluminium nanorods was dependent on the substrate chosen for the deposition of the rods. Zein el Abedin and co-workers [45] showed by cyclic voltammetry that they could reversibly deposit and strip lithium on their aluminium nanowire electrode and, when galvanostatically cycled against metallic lithium, the capacity in fact increased during the first four cycles. Sharma et al. [46] studied the effect of the inclination angle of the substrate in an electron-beam evaporator on the porosity for the obtained aluminium thin films. They found that an inclination of 75° led to porous thin films, which resembled nanorods and were considered to be best suited for electrochemical testing. We have also tested 3D aluminium rod structures vs. lithium by cyclic voltammetry using Li-ion pouch cells (Paper IV) and some of the obtained voltammograms are depicted in Figure 19.
Figure 19. Cyclic voltammograms for a 3D aluminium rod electrode vs. metallic lithium recorded between 0.1 and 3.0 V vs. Li⁺/Li at a scan rate of 1 mV/s.

The shapes of the voltammograms indicate that the capacity was fading rapidly upon cycling and already after ten cycles it had dropped to values around 3 µAh/cm². Three reduction peaks are seen on the first cycle. Two of these, at 1.5 and 0.5 V vs. Li⁺/Li, respectively, were seen only on the first cycle. As the former was positioned at a potential which was too high for the decomposition of electrolyte (i.e. about 0.8 V vs. Li⁺/Li), it was most likely due to the reduction of residual water in the pouch cell. The latter peak could, however, have been due to electrolyte reduction and formation of a SEI. Besides this, a reduction peak at around 0.15 V vs. Li⁺/Li and an oxidation peak at 0.5 V vs. Li⁺/Li can be observed. These peaks correspond to the reduction of lithium ions and the oxidation of the deposited lithium (i.e., to alloying and dealloying). The reduction reaction, however, only starts after the reversal of the potential scan indicating that a nucleation barrier needed to be overcome in order to start the alloying reaction between aluminium and lithium. The oxidation charge was smaller than the reduction charge for each cycle, suggesting either pulverisation of the aluminium rods after each alloying cycle or that lithium is trapped in the aluminium electrode after each lithiation step.

Recently, Liu et al. [47] published a transmission electron microscope study of the lithiation of aluminium wires. They showed that the native oxide layer coating the aluminium wires was transformed into a glass-like structure upon reduction. This surface structure prevented the nanowire from breaking and thus preserved the shape of the wire upon cycling. To further study the effect of the alumina layer on aluminium rod electrodes on their cycling performance, aluminium rod electrodes with 30 and 60 nm thick Al₂O₃ layers, respectively, were synthesised by anodisation of the aluminium rod electrodes (Paper IV). Figure 20 shows a TEM image of an aluminium rod with a 60 nm thick alumina layer.
The result of the anodisation was a thick, amorphous shell of aluminium oxide, homogeneously covering the crystalline aluminium core. The diameter of this core-shell structure was found to be 200 nm, which is in good agreement with the initial diameter of the aluminium rod. Cyclic voltammetry experiments were carried out for pouch cells containing aluminium rod electrodes with 30 and 60 nm thick oxide layers, respectively. The voltammograms are shown in Figure 21. The shape of the voltammograms is similar to that for the aluminium rod electrode with a native alumina layer. The peak currents on the first cycle were four times larger for the electrodes with the thicker oxide layer as compared to for the native oxide coated electrode. This was most probably due to an increase in the surface area for the anodised electrodes. It can be seen in the TEM image that the surface of the alumina shell was quite smooth, while the interface between the alumina shell and the aluminium core was rough. The roughening of the aluminium surface could have increased the surface and hence the peak currents for the electrodes with the thicker alumina layers. The capacity was, however, fading rapidly during the first ten cycles, just as for the aluminium rod electrode coated with the native oxide layer. For all the electrodes, the oxidation charges were smaller than the corresponding reduction charges, suggesting that some lithium was trapped in the aluminium electrode after each alloying step. Since a nucleation overpotential was observed on each reduction cycle it was concluded that some of the deposited lithium was indeed trapped in the aluminium electrode.

Figure 20. TEM image of an aluminium rod with a 60 nm thick Al₂O₃ layer.
Figure 21. Cyclic voltammograms for 3D aluminium rod electrodes coated with 30 nm (a) and 60 nm (b) oxide layers, respectively. The electrodes were cycled vs. metallic lithium between 0.1 and 3.0 V vs. Li⁺/Li at a scan rate of 1 mV/s.

The capacity retention was hence not improved significantly in the presence of the thicker aluminium oxide layers on the aluminium rods. Furthermore, the decrease in the reduction charges was seen to follow the same overall trend for all the studied aluminium rod electrodes (see Figure 2d in Paper IV). This led to the conclusion that the reason behind the capacity fading was not active material pulverisation or detachment. To demonstrate this the anodic scan limit was changed from 3.0 to 1.0 V vs. Li⁺/Li as initial studies on the electrochemical alloying of lithium with aluminium suggested that the rapid capacity fading of the aluminium electrodes was due to diffusion of lithium into the aluminium phase [48-62]. The cyclic voltammograms for the three different aluminium rod electrodes with the lower oxidation potential limit are presented in Figure 22. In this case the capacity did not decrease, but increased with increasing cycle number. For the electrode with the native oxide layer, the capacity increased during the first five cycles after which the capacity remained practically constant. For the electrodes with the thicker oxide layers, the capacity increased continuously during the 100-cycle experiment. This gradual increase in capacity was explained by an electromilling effect [119]. As the thicker oxide layers on top of the aluminium rods should impede the electrochemical milling of the aluminium rods, the capacity of the thicker alumina coated electrodes should increase more slowly than for the native oxide coated electrode. All the electrodes, however, reached similar reduction charges after 100 cycles. Despite the observed increase in capacity during cycling, the coulombic efficiency was still lower than 100%, indicating that some lithium was continuously trapped within the electrode.
Figure 22. Cyclic voltammograms for 3D aluminium rod electrodes coated with a native (a), 30 nm (b) and 60 nm (c) thick oxide layers, respectively. The electrodes were cycled vs. metallic lithium between 0.1 and 1 V vs. Li⁺/Li at a scan rate of 1 mV/s.
The voltammetric behaviour seen for the three different aluminium rod electrodes led to the formulation of a model for the alloying and dealloying between lithium and aluminium. The different stages of the model are schematically depicted in Figure 23. Initially, the electrode consists of aluminium and a surface layer of aluminium oxide. When the reduction is initiated, lithium ions diffuse through the alumina layer and undergo reduction on the aluminium surface to nucleate the alloy. Once the nucleation has begun, the thickness of the LiAl alloy phase grows from the Al/Al$_2$O$_3$ interface towards the bulk of the aluminium electrode. When the potential scan is reversed, the oxidation of the alloy starts and lithium is thus oxidised to lithium ions which then diffuse back into the electrolyte. The dealloying reaction starts at the LiAl/Al$_2$O$_3$ interface and proceeds towards the bulk of the electrode. However, as the lithium can diffuse both towards the electrolyte interface and towards the bulk of the electrode, a layer of LiAl will become trapped within the electrode giving rise to a continuous diffusion controlled capacity loss upon cycling.

If the oxidation potential limit is set high (i.e., at 3 V vs. Li$^+/\text{Li}$), there is plenty of time for lithium to diffuse from the trapped alloy layer into the surrounding aluminium between the oxidation and the subsequent reduction. The net result of this will be the formation of a thicker alloy layer with a lower concentration of lithium, as is schematically shown in Figure 23d. The increase of the thickness of the alloy layer will hence decrease the thickness of the electrochemically active layer of aluminium. On the following reduction less lithium will thus alloy with aluminium and the capacity will continue to decrease during cycling until a steady-state situation is reached. If the oxidation potential limit is reduced to 1 V vs. Li$^+/\text{Li}$, the diffusion time between the oxidation and the subsequent reduction is made smaller and the influence of the diffusion of the lithium trapped within the electrode will be smaller. The thickness of the electrochemical active aluminium layer will therefore not decrease as much and the capacity should more quickly become stable during cycling. The diffusion effect will, however, not be entirely suppressed, as coulombic efficiencies lower than 100% still should be obtained.
3.3.2 An Al/LiFePO₄ full 3D Li-ion cell

A characteristic feature of all reports concerning full 3D Li-ion micro-batteries [28-33] is that both the negative and positive electrodes have had similar geometries. Generally, the specific energy densities of the negative electrodes are larger than those of the positive electrodes and larger quantities of the positive active material are therefore needed to obtain a properly balanced cell. As deposition of the active material in the form of a thicker layer would result in a decrease in the rate capability of the positive electrode, a higher area gain factor for the latter as compared to that for the negative electrode is desired.

A full 3D Li-ion cell, composed of electrodes with different geometries, is proposed for the first time in Paper V. The cell comprises an aluminium rod negative electrode and a positive electrode composed of LiFePO₄ coated on a piece of carbon foam, separated by a glass fibre separator soaked in liquid electrolyte, as is schematically shown in Figure 24. The SEM images of the two electrodes are presented in Figure 1 in Paper V. The area gain factor of the negative electrode was around 10 (as shown in Paper IV), while that for the carbon foam (on which the LiFePO₄ was deposited) was approximately 90 [120]. The large difference (i.e., almost an order of magnitude) between the area gain factors for the two electrodes facilitates the deposition of large enough quantities of LiFePO₄ in the form of a thin film in close contact with the carbon foam current collector.
The electrochemical performance and capacity retention during cycling for the Al/LiFePO₄ 3D cell are presented in Figure 25. The aluminium electrode was pre-cycled vs. lithium between 1.0 and 0.1 V vs. Li⁺/Li, as it was shown in Paper IV that pre-cycling is necessary to obtain the full capacity of the aluminium rod electrode. The open circuit voltage (OCV) of the discharged cell was 0.9 V and, during the first charge of the cell, the potential increased to 3.25 V, after which it settled at a plateau of approximately 3.15 V. This initial overpotential, which was observed only on the first charge, is in good agreement with the overpotential observed for the nucleation of lithium on the aluminium surface in Paper IV. Upon discharge, a potential plateau was observed at around 2.95 V.
Figure 25. Electrochemical performance (a) and capacity retention (b) for the 3D Al/LiFePO$_4$ Li-ion battery.

As is seen from Figure 25, the capacity of the cell decreased during cycling. Since the discharge capacity was smaller than the charge capacity, this decrease was ascribed to a loss of lithium inventory. This is not surprising, since it was shown in Paper IV that the coulombic efficiency was lower than 100% for the aluminium electrode due to the diffusion of lithium in the electrode.

Morales et al. [121] built 2D Li-ion batteries consisting of either an Al or LiAl negative electrode combined with a LiFePO$_4$ positive electrode. They showed that the cycling performance for the LiAl/LiFePO$_4$ cell was better than that for the Al/LiFePO$_4$ battery as it displayed a slightly higher specific capacity and better capacity retention. For this reason, the pre-cycling of the aluminium electrode was also stopped in the lithiated state and a Li$_x$Al/LiFePO$_4$ 3D Li-ion cell was built and tested (Paper V). The electrochemical and cycling performance of the latter cell are presented in Figure 26.

Figure 26. Electrochemical performance (a) and capacity retention (b) for the 3D Li$_x$Al/LiFePO$_4$ Li-ion battery.
The cycling stability of the cell was, however, not improved when a partially lithiated aluminium negative electrode was used (Paper V). Nevertheless, the results were still somewhat different from those obtained with the 3D cell containing the Al negative electrode. The OCV of the cell was around 2.8 V, indicating a partially charged micro-battery and there was no nucleation overpotential on the first charge, as the alloy was already present on the surface of the negative electrode. Finally, the polarization between the charge and discharge plateaus was slightly smaller in the case of the LiAl/LiFePO₄ 3D cell, at least for the first cycles.

It can be concluded that the use of electrodes with different geometries can be beneficial in 3D Li-ion micro-batteries from the perspective of the cell balancing. The 3D cells reported here should, however, merely be regarded as model systems with limited cycle stabilities due to the inherent properties of the aluminium electrode. By using electrodes with different architectures, new possibilities to employ electrode materials which would not work in a 2D configuration appear.
4. Conclusions and outlook

The use of aluminium as current a collector and a negative electrode in 3D Li-ion micro-batteries has been studied in the present thesis. The work was divided into three main parts: the synthesis of 3D aluminium rod structures and the use of the obtained structures as current collectors and negative electrodes, respectively.

The galvanostatic deposition of aluminium into the pores of a commercial alumina membranes was studied (Paper I). It was shown that pulsed current electrodeposition gave better results than the constant current technique, as the height of the rods was more even in the former case. Applying a 50 ms short nucleation pulse (-0.9 V vs. Al\textsuperscript{3+}/Al) prior to the electrodeposition resulted in a homogeneous deposit of nanorods, covering the entire surface of the aluminium substrate.

The deposition of a model electrode material (i.e., TiO\textsubscript{2}) onto 3D aluminium rod current collectors was studied employing electrophoretic and sol-gel deposition (Paper II). Electrophoretic deposition of P 25 particles (80 % anatase and 20 % rutile) on 2D planar substrates gave rise to a homogenous and dense deposit of particles, while the deposits obtained with electrophoresis of pure anatase particles were less homogeneous and also contained aggregated particles. Electrophoretic deposition of P 25 on 3D aluminium rod substrates was not successful as the deposits were not conformal with respect to the substrate. The use of a sol-gel impregnation deposition method, on the other hand, facilitated the deposition of a thin, conformal and amorphous layer of TiO\textsubscript{2} onto the 3D aluminium substrate. The electrochemical performance of these electrodes was, however, limited by the amorphous structure of the TiO\textsubscript{2} layer. It is concluded that sol-gel is a promising technique for deposition of electrode materials on 3D aluminium rod current collectors.

Anodised TiO\textsubscript{2} nanotubes with large surface areas were studied as 3D electrodes (Paper III). It was shown that the best electrochemical performance was obtained with 9 µm long anatase tubes with 50 nm wall thickness synthesised by two-step anodisation. The TiO\textsubscript{2} nanotube electrode displayed a long cycle life with excellent capacity retention and good rate performance. At high rates it was shown that higher discharge capacities could be obtained by changing the electrochemical cycling window.

The electrochemical alloying between aluminium and lithium was studied for the possible use of aluminium rods as negative electrodes in 3D Li-ion cells (paper IV). In contrast to the common belief that volume changes upon
cycling are the cause of capacity fading for aluminium electrodes, no evidence for electrode pulverisation or detachment of the rods was found. Decreasing the oxidation potential limit from 3.0 to 1.0 V vs. Li⁺/Li increased the cycling life of the aluminium electrodes substantially and the electrodes could be cycled for at least 100 cycles with no capacity fading. The cycling efficiency was, however, still lower than 100 %, indicating that lithium diffused into the bulk of the electrode upon cycling. Thick oxide layers obtained by anodisation of the aluminium rods did not provide any improvement regarding the electrochemical performance of the aluminium rod electrode.

Finally, 3D Li-ion cells with Al or Li₄Al nanorod negative electrodes and a positive electrode composed of LiFePO₄ coated on a carbon aperiodic substrate were constructed and characterised electrochemically (Paper V). The cells were, however, not cycling successfully due to loss of lithium inventory in the aluminium rod electrode. Despite this, a proof-of-concept for a full 3D Li-ion cell with electrodes of different geometries was reported for the first time. LiFePO₄ was deposited on a carbon foam substrate which had nine times higher area gain factor than the aluminium rod electrode since the specific energy density for LiFePO₄ is lower than that for Al. The advantage of having different geometries for the two electrodes is that this can be used to obtain better balancing of the cells.

Future work should be focused on 3D Li-ion micro-batteries composed of electrodes with different geometries. A development of this concept could provide new possibilities for the combination of electrode materials which would not work in a 2D cell configuration due to capacity mismatches. Aluminium rods could be used as negative electrode in 3D Li-ion micro-batteries provided that the thickness of the active material is maintained sufficiently small to inhibit the lithium diffusion effects.
Sammanfattning på svenska

Litiumjonbatterier används idag i praktiskt taget i alla mobil telefoner och bärbara datorer samt i en stor del av vår bärbara elektronik eftersom denna typ av batterier har den bästa energi lagringskapacitet av alla uppladdningsbara batterier som finns på marknaden.


Tredimensionella litiumjonbatterier kan sägas vara inspirerade av våra omgivande byggnader. Precis som det finns mer plats i ett tiovåningar högt hus än i en villa med samma bottenyta, får 3D-elektroder plats med mer aktivt material på samma bottenyta som tvådimensionella elektroder och kan därför lagra mer energi. Att 3D-elektroder har stora tillgängliga areor betyder också att de aktiva materialen kan deponeras som väldigt tunna skikt på de stora ytorna. 3D-batterier kan därför innehålla stora mängder energi samtidigt som de möjliggör snabba urladdningar/laddningar av batteriet (dvs.
hög effekt). Det finns olika geometrier som kan användas för att bygga 3D-batterier och några vanliga typer visas i Figur 1.

Figur 1. Fyra olika typer av geometrier för 3D-mikrobatterier.

Det är vanligt att man börjar bygga upp ett tredimensionellt batteri genom att syntetisera en 3D-strömtillledare för att sedan deponera alla andra lager ovanpå denna. I avhandlingen har den elektrokemiska syntesen av 3D-strukturer av aluminium studerats. Aluminium har tillverkats i form av nanometerjocka pinnar stående på ett aluminiumsubstrat. För att få dessa pinnar, har aluminium deponerats elektrokemisk i porerna av ett poröst membran som sedan har tagits bort genom att man löser upp membranet i en vätska innehållande kromjoner.


TiO$_2$ syntetiserades också direkt genom oxidation av en titanplatta (s.k. andodisering). Med hjälp av rätt anodiseringslösning kunde hexagonalt arrangerade nanotuber tillverkas på titansubstratet. Tuberna var 9 µm (dvs. 9·10$^{-6}$ m) långa och hade 50 nm (dvs. 50·10$^{-9}$ m) tjocka väggar. Dessa 3D-elektroder bestående av nanotuber hade en hög urladdningskapacitet och kunde cyklas flera hundra gånger utan tappa kapacitet. Detta är väldigt lovande för användningen som elektroder i 3D-litiumjonmikrobatterier.

Aluminium reagerar elektrokemisk med litium och bildar en legering (LiAl), vilket gör att man i princip skulle kunna använda aluminium också som den negativa elektroden i ett litiumjonbatteri. Problemet är bara att aluminium inte cyklar så bra mot litium under långvarig användning. Kapaciteten minskar med antalet cykler vilket inte är acceptabelt för ett praktiskt

Slutligen, byggdes en prototyp för ett 3D-litiumjonmikrobatteri med hjälp av två elektroder med olika geometrier. Den negativa elektroden bestod av en 3D-elektrod av aluminiumpinnar medan den positiva elektroden bestod av LiFePO₄ deponerat på ett poröst aperiodiskt kolsubstrat. Den effektiva arean för kolsubstratet var nio gånger större än den för aluminiumelektroden. Eftersom energidensiteten för LiFePO₄ är 170 mAh/g, medan den är 1000 mAh/g för aluminium, är det en stor fördel att kunna använda en positivelektrod med en store area. Man kan deponera LiFePO₄ som ett tunt skikt och fortfarande använda den mängd material som behövs för att balansera cellen så att ett funktionellt mikrobatteri kan erhållas.
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