Insights into Electrochemical Energy Storage by use of Nanostructured Electrodes

DAVID REHNLUND
Abstract

Template-assisted electrodeposition is a powerful technique for fabricating complex nanostructured electrodes. Through the use of pulsed-electrodeposition nanostructured electrodes of Al, Cu and Sn have been realised and subsequently coated electrochemically with V$_2$O$_5$, MnO, Li, Cu$_2$O and a polymer electrolyte. Nanorods with a multi-layered Cu$_2$O/Cu structure have likewise been produced through electrodeposition. Nanostructured electrodes are ideal for studying electrochemical energy storage and have as such been used to investigate the electrochemistry of conversion and alloying reactions in detail.

Key properties of the Cu$_2$O conversion reaction were found to be dependent on the particle size. Prolonged cycling was seen to induce an electrochemical milling process which reduced the particle size. This process was found to improve the cell capacity retention due to improved accessibility of the material. The redox potential at which the particles react was found to be size dependent as smaller particles reacted at lower potentials.

The Li-alloying reaction was also investigated by analysing several different alloy-forming materials. All materials exhibited a decline in capacity during cell cycling. This decline was observed to be time dependent and could as such be explained by a diffusion limited process. Moreover, the capacity losses were found to occur during partial lithiation of the electrode material leading to Li trapping in the electrode material. Li trapping was also observed for commonly used anode current collectors as the metals have some solubility for Li. Conducting boron-doped diamond electrodes were however seen to be resistant to Li diffusion and are therefore recommended as viable current collectors for anodes handling metallic lithium (i.e. Li-alloys and Li metal).

David Rehnlund, Department of Chemistry - Ångström, Inorganic Chemistry, Box 538, Uppsala University, SE-751 21 Uppsala, Sweden.

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urn:nbn:se:uu:diva-263482 (http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-263482)
Till mami, papi o dea
“One must be sane to think clearly, but one can think deeply and be quite insane.”

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

I Electrodeposition of vanadium oxide/manganese oxide hybrid thin films on nanostructured aluminum substrates.  
**D. Rehnlund**, M. Valvo, K. Edström, L. Nyholm.  

II The impact of size effects on the electrochemical behavior of Cu$_2$O-coated Cu nanopillars for advanced Li-ion microbatteries.  

III Electrodeposition of thin poly(propylene glycol) acrylate electrolytes on 3D-nanopillar electrodes.  
B. Sun, **D. Rehnlund**, M.J. Lacey, D. Brandell.  

IV Electrochemical fabrication and characterization of Cu/Cu$_2$O multilayered micro and nanorods in Li-ion batteries.  
*Nanoscale*, 7(2015) 13591–13604

V Microbatteries based on 3D Li and Cu$_2$O coated Cu nanorods.  
*In manuscript*

VI Diffusion controlled trapping of elemental lithium in alloy forming materials and current collectors for lithium based batteries  
*In manuscript*

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The author also contributed to the following published works that are not included in this thesis:

i. Electrochemical elaboration of electrodes and electrolytes for 3D structured batteries. 
M. Valvo, M. Roberts, G. Oltean, B. Sun, **D. Rehnlund**, D. Brandell, L. Nyholm, T. Gustafsson, K. Edström. 
*Journal of Materials Chemistry A*, 1(2013) 9281-9293

ii. Substrate with doped diamond layer for lithium-based systems
**D. Rehnlund**, S. Böhme, L. Nyholm
Patent application
My contribution to the included papers

I. I planned and performed all the experiments and also participated in the results discussion. I wrote the final manuscript, with input from the co-authors.

II. I planned and performed the syntheses as well as part of the characterisation. I participated in the discussion and development of the manuscript.

III. I provided the 3D substrates and helped to develop the electropolymerisation process. I also approved the final proof of the paper.

IV. I planned and performed the synthesis and the SEM, EDS and electrochemical analyses. I participated in the interpretation of all results and wrote the final manuscript with input from the co-authors.

V. I planned and executed all experiments, except the ICP-AES analysis. I also wrote the manuscript, with assistance from the co-authors.

VI. I planned and executed most of the experiments. Co-authors contributed with ICP-AES, HAXPES, SIMS as well as the synthesis and characterisation of the nanostructured Sn electrodes. I contributed to the scientific discussion of all results and wrote the main part of the manuscript.
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<td>Three-dimensional</td>
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<td>Anodic Aluminium Oxide</td>
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<td>Boron-doped Diamond</td>
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Introduction

*Men love to wonder, and that is the seed of science.*
- Ralph Waldo Emerson

The technological revolution of the previous century has undoubtedly been powered by the combustion of fossil fuels. This finite power source has however also had some negative impacts. Most notably, the long-term use of fossil fuels as a power source has caused serious carbon dioxide emissions, leading to the current global climate change. This has led to an increasing call for more sustainable, renewable, and emission-free energy sources upon which the future energy market must be based. Significant progress has been made by the development of renewable power sources based on solar, wind and biofuels. Yet, suitable energy storage systems have been unable to match this rapid development and thus pose limits to the introduction of a new global energy market. The current leading power source is electrochemical energy storage with its champion, the lithium-ion battery. Lithium-ion batteries are efficient, lightweight, reliable and rechargeable power sources that enabled the consumer electronics revolution in the 1990’s. However, the ever-increasing demand for high energy and power density in current applications such as electric vehicles and microelectronics calls for the next generation of lithium-ion batteries. How then can current battery technologies be improved to meet these market demands?

Gaining a deeper understanding of the key electrochemical processes that take place inside lithium-ion batteries is required in order to develop new and improved electrochemical cells. Nanostructured materials lie at the heart of fundamental advances in efficient energy storage and conversion. Since material properties become different on the nanoscale, much effort is currently being dedicated to the synthesis, structure control and property improvement of nanomaterials. Particularly, the inexpensive formation of periodically ordered structures (e.g. nanopores, nanotubes and nanorod arrays) with a periodicity lower than 100 nm, has triggered extensive research in the field. Electrodeposition has proved useful in this development, as complex 3D nanostructures can be achieved with precise control of the morphology and composition.

The research presented in this thesis focuses on developing nanostructured electrodes that can be used to target and investigate key properties of electrochemical energy storage.
1. Small scale energy storage

*Science never solves a problem without creating ten more.*
- George Bernard Shaw

1.1 Nanostructured materials

Nanomaterials are defined as materials with units in the nanoscale (i.e. < 100 nm) for at least one dimension. Nanostructured materials (e.g. nanoparticles, nanowires and thin films) are of great scientific interest, as they effectively bridge the gap between the atomic and bulk scales. Bulk materials are expected to exhibit constant physical properties regardless of size, but at the nanoscale this is often not the case. Size dependent properties have been observed as quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles, and shifted standard potentials in electrochemical cells.

Development of nanostructured substrates is for example performed within the field of microelectronics, which primarily uses lithography as preparation technique. Due to the associated high costs of lithographic production, researchers are currently pursuing different avenues of fabrication. In this regard, electrochemical fabrication tools have emerged with the beneficial properties of low cost, low operating temperatures and high versatility. Electrochemical anodization of titanium is an excellent example of an advanced nanostructuring where nanoporous TiO$_2$ can be used to promote integration between the medical implant and tissue growth (i.e. osseointegration). Nanostructured aluminium oxide is another case of nanostructuring where the Al$_2$O$_3$ typically is used for wear protection. Anodization of metals like aluminium can also yield highly ordered nanoporous membranes by careful control of the electrochemical synthesis. These membranes are widely used as 3D templates in template assisted electrodeposition where nanosized nanorods can be grown in the pores. Like conventional electrodeposition, the material selection rests upon the possibility of producing an electrolyte containing the ionized element of choice dissolved in an aqueous, organic solvent or ionic liquid. For high aspect ratio nanorods, it is crucial to obtain good contact between the template and substrate. This can be achieved either by deposition (i.e. sputtering or evaporation) of a conductive substrate directly on the membrane or by simply applying pressure during the assem-
bly \(^3\). Through the use of nano- and microporous membranes (i.e. anodized aluminium oxide or track-etched polycarbonate) a vast variety of metallic nanowires have been electrochemically synthesized, including: Al \(^{13-16}\), Co \(^{17}\), Ni \(^{18-21}\), Fe \(^{22}\), Cu \(^{6, 18, 23, 24}\), NiFe \(^{25}\), FeCo \(^{26}\) nanowire arrays as well as Co/Cu \(^{27}\), Ni/Pt \(^{28}\), NiFe/Cu \(^{29}\), Ag/Co \(^{30}\) and Cu/CuO \(^{31}\) multi-layered nanowires.

Multi-layered nanostructures are composed of alternating layers of materials with thickness in the nanometer scale. By periodically depositing materials with different physical properties, unique nanostructuring can be achieved. The resulting nanostructures show enhanced mechanical \(^32\), tribological \(^33\), magnetic \(^{34-36}\) and photoelectrochemical \(^{37, 38}\) properties.

There are two techniques used for the electrochemical synthesis of multi-layers, namely dual-bath and single-bath deposition. Dual-bath deposition utilizes two separate electrolytes in which each layer is exclusively deposited. The electrode is moved between the electrolyte containers to grow a multi-layered structure, resulting in a simple yet time consuming synthesis. In a single-bath deposition, all precursors are confined in the same electrolyte, which requires delicate control of the concentrations of the electroactive species and the applied current density or potential to achieve well defined multi-layers \(^2\). This approach is naturally more demanding regarding the control of the process parameters. However rapid deposition of thin layers is possible making the technique ideal for nanostructuring. In spite of the difficulties encountered in order to acquire control of the fabrication process, 1D nanostructures (i.e. nanowires) are ideal systems for studying transport phenomena at the nanoscale \(^39\).

Nanostructured materials have led to major advances in electrochemical energy storage, particularly regarding lithium-ion batteries. The discovery of the conversion reaction mechanism \(^{40}\), which involves the formation of nanosized metal particles in a Li$_2$O matrix \(^{41, 42}\), is an excellent example of a breakthrough that has been achieved due to nanotechnology. Moreover, present use of nanomaterial technologies makes it possible to utilize materials previously considered unsuitable for battery applications. The best illustration of this is carbon-coated nano LiFePO$_4$, which today is one of the most widely studied materials for positive lithium-ion battery electrodes \(^1, 43\).

1.2 The lithium-ion battery principle

Batteries are composed of two electrodes separated by an ionically conductive material called an electrolyte. The two electrodes have different chemical potentials, dictated by the electrochemical reactions that occur at each electrode. Connecting the two electrodes to an external device causes an electrical current to flow through the cell. Meanwhile, lithium ions are shuttled from the more negative electrode to the more positive to maintain
charge balance and to convert chemical energy into electrical energy through faradaic reactions. A common misconception is that the transport of lithium ions is the main driving force in the battery. The lithium ions are actually merely acting as counter ions compensating for the change of oxidation state in the material upon oxidation and reduction. This process is illustrated in the schematic representation in Figure 1.

![Figure 1](image)

**Figure 1.** Schematic representation of a lithium-ion battery cell during discharge. Electrons move from the anode to the cathode, accompanied by Li⁺ ions, as the cathode is reduced. This current flowing in the external circuit can be used to power an electrical device.

After discharge, a voltage or a current can be applied to rechargeable, so called secondary batteries, to return the cell to its original charged state. The amount of electrical energy per mass or volume that a battery can deliver is a function of the cell’s voltage and capacity, which are dependent on the electrode chemistry of the system. Another important parameter is the power that the battery can deliver. This depends partly on the battery engineering but mainly on the inherent battery electrochemistry.
1.3 Microbatteries

A microbattery is defined as an electrochemical power source fabricated on the same scale (and sometimes substrate) as semiconductor devices using microfabrication techniques. The rapidly developing field of microelectronics has brought forth plenty of small devices such as medical implants, micro sensors, self powered integrated circuits and microelectromechanical systems (MEMS). Microbatteries suitable to power such devices are required to have volumes of 1-10 mm$^3$, including the associated packing. Since high-energy storage density is required, the lithium-ion microbattery systems should be preferential as these outperform similar energy storage systems in small-scale applications.

The rapid development of MEMS has thus created a demand for research on reliable and versatile lithium-ion microbatteries. Meeting the increased power demands of modern MEMS devices has become an increasing challenge due to the limited space available for the power supplies. In the last 15 years, thin film technologies have produced lithium-ion microbatteries in the form of surface mountable devices with thicknesses of up to about 10 µm. Increased capacity is obtained by increasing the electrode thickness, thereby providing more active material. However, in order to access the entire charge, decreasing discharge rates are typically required as the film thickness increases.

The conventional way of dealing with capacity per space limitations is to wind the film up, as to include a large surface area into a small volume. Unfortunately, this approach is undesired as the battery components tend to be brittle. Winding the battery might therefore lead to mechanical failure and ultimately short circuits. Planar cells are thus generally a must for reliable microbatteries. As such, large footprint areas are required to obtain large capacities. This has lead to the concept of capacity per footprint area (mAhcm$^{-2}$), which constitutes the main unit when comparing microbatteries. The growing housing need during modern urbanisation is analogously to the situation for current microbatteries. This issue was solved by extending constructions in the third dimension, thereby allowing a larger population in a fixed area (e.g. Manhattan, New York), as is illustrated in Figure 2. Similarly, 3D electrodes are used in lithium-ion microbatteries to enable increased charge storage capacities while maintaining rapid transport of lithium-ions through the electrode materials and minimising the footprint area.
Figure 2. Illustration of the improved storage capability associated with a 3D architecture in contrast to the conventional 2D.
1.4 3D microbattery design

The term 3D battery generally refers to “cells comprising anodes and cathodes which have active surface areas exposed in three dimensions” \(^{50}\). The 3D microbattery concept is designed to provide high energy densities as well as power densities. This is in contrast to planar batteries, where energy density is either traded for power density or vice versa. The 3D microbattery concept is achieved through 3D electrode architecture that provides increased mass loading of active material while simultaneously minimising the footprint area and thickness of active material on the electrode \(^{45, 51, 52}\).

Figure 3a illustrates the 3D principle where cylinders of at least one nano-sized dimension are stacked in rows of intermittent cathodes and anodes. Clearly, the sizes and relative placement of the electrodes determine the microbattery performance. Maximizing the number density (i.e. cylinders/cm\(^2\)) for the cathodes and anodes, while minimizing the separation between them, increases both the energy and power density. However, by decreasing the interpillar distance increased strain is put on the electrolyte’s electrical isolation properties as significant leakage currents can be expected due to the substantial electrical field imposed over the thin electrolyte layer. Electrolytes with extremely poor electrical conductivity are hence required. While such a 3D integrated design has yet to be realised, it is expected that the fabrication of 3D electrode configurations will be based on current lithographic technologies or template based deposition routes \(^3, 50\). Multiple architectures have been proposed by Long et al. \(^{45}\) based on electrode assemblies in periodic arrays or using aperiodic assemblies, as is shown in Figure 3. A common feature of the 3D microbattery designs is that the ion transport between the electrodes remains one-dimensional at the microscopic level.

![Figure 3. Proposed 3D architectures for microbatteries based on: (a) an array of interdigitated cathode and anode rods; (b) periodically aligned arrays of anode and cathode plates; (c) an array of anode rods coated with solid electrolyte and backfilled with cathode material; (d) an aperiodic ‘sponge’ structure of a cathode network, which is coated with solid electrolyte and where the remaining volume has been filled with an anode material. Reprinted with permission from \(^{45}\). Copyright (2004) American Chemical Society.](image-url)
1.5 3D current collectors

The starting point for any nanostructured electrode lies in fabricating a 3D architectured substrate, the latter of which often simultaneously serves as the current collector. As previously described, fabrication of 3D substrates can be performed by either template-assisted deposition (i.e. bottom-up fabrication) or lithography (top-down fabrication). A schematic illustration of the processes is presented in Figure 4.

The morphology and dimensions of the resulting nanostructures are dictated and tuned by the choice of template or mask. Porous templates have been used to grow nanorods of Cu, Ni, and Al, all of which are suitable 3D current collectors for lithium-ion microbatteries. Pikul et al. have shown an alternative route where porous Ni current collectors were grown through the use of self-assembled plastic beads, see Figure 4b. Owen et al. have utilised a similar interlocked electrode design with commercially available reticulated vitreous carbon substrates while Peled et al. have designed a different interdigitated structure based on microperforated Si substrates coated with Ni. Microrods can also be constructed through top-

![Figure 4. Schematic representation of bottom-up fabrication via template-assisted electrodeposition of metallic nanostructures employing (a) a porous membrane and (b) self-assembled plastic beads or via (c) top-down lithographic fabrication.](image-url)
down fabrication via photolithography and etching. The method, developed by Dunn et al. \textsuperscript{56}, uses UV-mask patterning and subsequent pyrolysis to selectively fabricate columnar carbon microstructures (see Figure 4c).

1.6 3D electrodes

The final 3D electrode is fabricated by incorporating an active material on the nanostructured current collector. The materials all have unique electrochemical storage properties however a distinction is typically made between materials operating at a low voltage (i.e. anodes) and those operating at a high voltage (i.e. cathodes). Anode materials are further divided into three subgroups depending on their mechanism of Li storage, namely intercalation, conversion and alloying. TiO\textsubscript{2} is a typical intercalation anode material that has been realised for lithium-ion microbatteries in the form of thin films \textsuperscript{13} as well as nanotubes \textsuperscript{57}. As the main anode material for conventional lithium-ion batteries, carbon has similarly been investigated for microbatteries in the form of nanotubes \textsuperscript{58}. Electrochemical energy storage through the conversion reaction, see the reaction below, requires the use of metal oxides (i.e M\textsubscript{x}O\textsubscript{y}), which are transformed into metal nanoparticles in a Li\textsubscript{2}O matrix upon lithiation.

\[ M\textsubscript{x}O\textsubscript{y} + 2yLi^+ + 2ye^- \leftrightarrow yLi\textsubscript{2}O + xM \] (1)

Irrespective of the significant volume expansion accompanied by this conversion reaction, high reversibility is often observed for 3D conversion materials. This behaviour can be explained by the highly reactive metallic nanoparticles embedded in a Li\textsubscript{2}O matrix, which are formed during the initial reduction of the metal oxide \textsuperscript{42}. Reversible electrochemical energy storage is more easily obtainable with nanostructured electrodes, making these ideal for studying conversion reactions. Cuprous oxide \textsuperscript{6, 31}, iron oxide \textsuperscript{24} and tin oxide \textsuperscript{59} are examples of such conversion materials that have been realised as 3D electrodes. Current research investigates avenues of incorporating alloying anode materials in future 3D anodes based on the large storage capability of this reaction. Si being the foremost candidate is capable of alloying up to 3.75 lithium atoms per silicon atom \textsuperscript{60}. Unfortunately such large storage capacities are coupled with significant volume expansion (280% for Si \textsuperscript{61}), which can lead to severe stability issues \textsuperscript{62}. However innovative nanoengineering can accomodate repetitive volume fluctuations, as demonstrated by the use of Si honeycomb structures \textsuperscript{63}.

Electrochemical energy storage in cathode materials is almost exclusively achieved through intercalation of Li\textsuperscript{+} in highly crystalline metal oxides,
phosphates and silicates. Manufacturing crystalline thin films with current deposition techniques (i.e. PVD, electrodeposition and sol-gel) is typically very challenging. Although especially problematic for intercalation based cathode materials, research has shown that the lithium-ion transport can be improved through the use of thin films. Advances in microbattery research has facilitated the production of conformal coatings of LiCoO$_2$, MoOS$_2$, FeS$_2$, CuS$_x$, V$_2$O$_5$, MnO$_2$ and LiFePO$_4$ on 3D nanostructured supports. Polymers present an interesting alternative to these inorganic compounds where the polymer chain is oxidised and reduced leading to anion storage and extraction due to electrostatic attraction and repulsion, respectively. The most commonly used polymers are polyaniline and polypyrrole, which have both been deposited on 3D substrates.

$$A^- + PP y \rightarrow PP y^+ A^- + e^-$$ (2)
2. Aims

This thesis aims at developing nanostructured electrodes to be used in electrochemical cells where they can provide valuable insight into key mechanisms with minimised influence from unwanted side reactions (e.g. via binders and additives). Throughout the thesis, electrodeposition has been used as the prime synthesis technique followed by characterisation of the materials using chemical analyses.

Vanadium oxide/manganese oxide coated aluminium nanorods
Vanadium oxide is a powerful cathode material suitable for microbattery applications. This study focused on developing a synthetic route to coat aluminium nanorods with vanadium oxide while protecting the surface from corrosion due to the harsh environment employed during the vanadium oxide electrodeposition. The aim was thus to create a powerful 3D cathode for microbattery use.

Cu$_2$O coated Cu nanorods
Cu$_2$O coatings on Cu nanorods through spontaneous oxidation give rise to 3D electrodes with excellent adhesion between the materials. This presents a unique opportunity to study the conversion reaction mechanism involving Cu$_2$O and Li$^+$ in a lithium-ion battery. The study was carried out to investigate if Cu nanostructured electrodes with a thin native Cu$_2$O coating could be fabricated through template-assisted electrodeposition. The electrochemical behaviour of the Cu$_2$O coating associated with the conversion reaction in a lithium-ion battery was also of interest to the study.

Polymer electrolyte coating on 3D Cu substrates
Polymer electrolytes are suitable for solid-state lithium-ion microbatteries, which have the crucial benefit of improved safety and volume efficiency compared to liquid electrolyte based batteries. In this study, the aim was to investigate if it was possible to coat complex 3D nanostructured electrodes with a thin polymer electrolyte using electrochemical deposition. Codeposition of a lithium containing salt was another important side goal.

Multi-layered Cu$_2$O/Cu nanostructured electrodes
The ability to electrochemically form multi-layers in a one-step synthesis is an interesting feature of the copper system. The study was aimed at investi-
gating if it was possible to electrochemically deposit metal/metal oxide multi-layers in the form of nanostructures, a feature so far only realised by PVD techniques. Using an all-electrochemical synthesis route, this study aimed to fabricate Cu$_2$O/Cu multi-layered nanorods with control over the layer growth. The study also addressed the issue of whether the cell capacity can be increased by increasing the Cu$_2$O layer thickness.

3D microbattery based on Li and Cu$_2$O coated Cu nanorods
This study was focused at developing an electrochemical synthetic route to coat Cu nanostructured electrodes with a Li thin film. The resulting electrodes would then be used to produce a lithium-ion microbattery whole cell solely utilising 3D electrodes produced electrochemically.

Li trapping in metallic current collectors
The degradation of Li-alloy electrodes is a topic of great interest to the battery community as if solved could result in improved possibilities to manufacture batteries with extended life-times. This study aimed at investigations of the mechanism responsible for the loss of capacity during the use of alloy forming anode materials and to examine an alternative failure mechanism previously not discussed in literature. The focus was to investigate several Li-alloys commonly used in lithium-ion batteries as to see if there was a general trend for the Li-losses in the Li-alloys.
3. Methods

*I suppose it is tempting, if the only tool you have is a hammer, to treat everything as if it were a nail.*

-Abraham Maslow

3.1 Electrodeposition of 3D electrodes

Electrodeposition has emerged as a particularly promising technique for easy and cost-effective preparation of nanostructures, allowing the realization of 3D current collectors coated with functional layers\(^3,47\). The technique offers low temperature fabrication and coating of 3D nanostructures with high versatility when it comes to controlling the growth parameters. Electrochemical fabrication of nanostructured current collectors is generally achieved through template-assisted electrodeposition, as illustrated in Figure 4a. Previous research within the group has been based on the use of porous polycarbonate and AAO templates to synthesize free-standing metal nanopillars\(^14,71\). Similar strategies involve the electrodeposition of metal onto self-assembled polymer microbeads to generate a porous 3D current collector\(^53\). An alternative, top-down approach involves electrochemical etching to yield metal oxide nanotubes\(^38,72\). Well-defined nanostructured electrodes are typically achieved by pulsed potentiostatic or galvanostatic electrodeposition, designed to improve the mass transport in the template\(^3\).

In this thesis, nanostructured electrodes have been fabricated via template-assisted electrodeposition. 3D current collectors with Al and Cu nanorods have been produced and served as the nanostructured foundation for all studies. Subsequent electrode material coatings on these 3D substrates have been deposited electrochemically in the form of MnO\(_x\), VO\(_x\), Cu\(_2\)O, Li and poly(propylene glycol) acrylate polymer electrolyte. Multi-layered Cu\(_2\)O/Cu nanorods have likewise been synthesized via a single-bath electrodeposition procedure in which different current densities were used to selectively deposit Cu and Cu\(_2\)O.
3.2 Structural and elemental characterisation

A wide arsenal of techniques is available in the search for structural information concerning materials. Common techniques include X-ray diffraction in addition to Raman and photoelectron spectroscopy, where the materials are excited by a high energetic source (i.e. X-rays or laser). Microscopic techniques like scanning electron microscopy and transmission electron microscopy further strengthen the characterisation by offering detailed analyses of the microstructure. In addition, elemental analysis can be obtained on a microscopic level by incorporating an energy-dispersive spectrometer or electron energy loss spectroscopy.

3.2.1 Powder X-ray diffraction

Powder X-ray diffraction is a technique that localises atomic positions in a crystal through diffractive scattering of the incident X-ray beam. The detection of diffraction patterns is based on the diffraction phenomenon that occurs when X-rays with a wavelength in the order of the interatomic distances interacts with ordered material. In the present work, the structural phase compositions have been determined with this technique using a Siemens D5000 and a Brucker D8 diffractometer equipped with a CuKα radiation source.

3.2.2 X-ray photoelectron spectroscopy

In X-ray photoelectron spectroscopy (XPS), the chemical environment of the outermost sample layer is characterized. The technique uses X-rays to excite the atoms leading to the release of photoelectrons. The energy difference of incoming X-rays and outgoing photoelectrons is connected to the binding energy of the excited photoelectron, which depends on the chemical environment of the atom it originates from. The excess energy is transferred to the photoelectron as kinetic energy. Measurements of the photoelectron kinetic energy thus provide elemental identification and information about chemical shifts. XPS has for example been used to detect changes in the oxidation state of vanadium oxide nanotubes during electrochemical cycling. The chemical shift for a vanadium oxide thin film was also investigated in Paper I employing XPS using a spectrometer Physical Systems Quantum 2000 with a monochromatised Al Kα radiation source. Hard X-ray photoelectron spectroscopy (HAXPES) utilises high energy synchrotron-generated X-rays to increase the probing depth. Therefore, it is possible to probe beyond the surface into the bulk of a material in a significantly less destructive manor than when using sputtering profiles. The method proved highly beneficial for studying Li in B-doped diamond electrodes in Paper VI.
3.2.3 Raman spectroscopy

Detection of specific Raman signatures is achieved by exciting the sample with a monochromatic laser beam which causes vibration and rotation of the molecules in solutions or vibrations in solid matter \(^75\). A small fraction of the scattered light portrays a frequency change denoted as the Raman shift, which is detectable by a CCD camera \(^75\). The technique was recently used to examine silver nanowires which were found to induce an enhanced Raman scattering known as surface enhanced Raman scattering (SERS) \(^76\). The technique proved particularly useful in Paper I where it characterised MnO\(_x\) thin films on 3D Al substrates. Experimental data were in this case gathered utilizing a Renishaw 2000 Raman spectrometer equipped with a 50 mW air-cooled laser (Spectra Physics), an excitation source (514 nm) coupled to an optical microscope (Leica) and a Peltier-cooled CCD detector for spectral detection.

3.2.4 Scanning electron microscopy

The scanning electron microscopy (SEM) technique involves the detection of excited electrons emitted from the sample during exposure to an electron beam of high intensity. High-vacuum is required to allow an undisturbed pathway for the electron beam and the emitted electrons. A topographic image of the sample surface is formed by measuring variations in electron intensity emitted from different parts of the surface. SEM is a particularly important tool for investigating nanostructures and has recently been used to detect individual layers in copper based superlattice structures \(^77\). In this thesis, a Zeiss Leo 1550 SEM and a MERLIN HR-SEM instrument were used to investigate the morphology of the fabricated nanostructures.

3.2.5 Transmission electron microscopy

Over the last few decades, transmission electron microscopy (TEM) has become a key characterisation technique in material analysis. The technique operates in two modes providing both image and diffraction information from a single analysis. A highly coherent beam of monoenergetic electrons is used to probe the thin film sample, thereby promoting few scattering events as each electron traverses the sample \(^78\). A characteristic electron beam with short wavelength and high energy is focused on a small area, typically 1 \(\mu m^2\) or less \(^78\). Combined, these qualities provide high lateral spatial resolution, a feature charismatic of TEM. Successful analysis relies heavily on the sample preparation where mechanical and ion beam milling is used to thin the sample preferably to a thickness of 100 nm or less \(^78\).

One important drawback with TEM stems from its limited depth resolution. Although the electron scattering information originates from a 3D sam-
ple, the image is projected onto a 2D detector. As such, the resulting image is composed of a convolution of microstructural features present on the lateral scale. The micrograph can contain contrast brought forth by several contributions: mass contrast, thickness contributions, diffraction contrast and phase contrast. TEM is a prime tool for studying nanostructures and has for example been used to identify phase boundaries on TiO$_2$ covered aluminium nanopillars. In this thesis, the technique has been employed to investigate the effect of electrochemical milling on the particle size in copper nanostructures in Paper II as well as probing the Cu$_2$O/Cu multi-layered interface in Paper IV.

### 3.2.6 Energy-dispersive spectroscopy

Energy-dispersive spectrometry (EDS) is an elemental characterisation technique usually coupled to a microscopical method such as SEM or TEM. The incoming high-energetic electrons interact with the surface atoms leading to excitation. This excess energy, which is unique for every atomic transition, will then be either emitted as X-rays, an auger electron or undergoes self-absorption. The EDS instrument detects the emitted X-rays thus producing a spectrum depending on the kinetic energy of the incoming radiation. Elemental identification is possible as each core shell excitation carries a specific kinetic fingerprint for the atom. A spectrum can be obtained for almost any sample as long as it can be analysed by the microscope. The resulting spectrum may vary depending on the applied accelerating voltage as it affects the excitation volume in the material. For studies of thin films it is desirable to minimize the electron range and use an accelerating voltage just greater than the critical ionization voltage for the X-ray line of interest.

Modern EDS detectors are capable of detecting elements with atomic numbers larger than three.

The energy dispersive technique is commonly used during microscopical studies of nanomaterials including superlattice nanostructures where compositional mapping of layer boundaries is employed to identify individual layers. Likewise, elemental oscillations in Cu$_2$O/Cu multi-layered microrods were identified by EDS in Paper IV.

### 3.2.7 Electron energy loss spectroscopy

Electron energy loss spectroscopy (EELS) is a powerful elemental analysis technique capable of detecting all elements in the periodic table. EELS is used with TEM and STEM where the interactions between the electron beam and the sample are analysed. As the material is exposed to an electron beam, some electrons will undergo inelastic scattering causing them to loose kinetic energy. This energy loss can be measured, as the incoming kinetic energy is known. With this information it is possible to identify the elemental com-
position of the material and even the oxidation state of the detected elements. EELS has recently been used to track lithium transport in FeF$_2$ nanoparticles in-situ during conversion reaction $^{80}$. The technique allowed elemental mapping of the Cu$_2$O/Cu multi-layer interphase in Paper IV.

3.2.8 Inductively coupled plasma-atomic emission spectrometry

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) is a powerful elemental analysis tool capable of detecting a wide range of elements from lithium to uranium. The technique offers multi-element analyses of minute amounts of trace elements $^{81}$. The sample is usually introduced into the plasma as a liquid, thereby requiring a suitable preparation method for solid samples. In the plasma, the sample is ionized and transported to the coupled mass spectrometer for elemental detection $^{81}$. ICP-AES has for example recently been implemented for in-situ measurements of metals dissolving due to electroerosion $^{82}$. In this thesis the technique has been used to characterise Li deposits in Paper V and Li diffusion in different substrates in Paper VI.

3.2.9 Secondary Ion Mass Spectrometry

Secondary ion mass spectrometry (SIMS) uses a focused ion beam to sputter the target thereby displacing and ionizing atoms on the surface which are then captured and characterised by a mass spectrometer. SIMS is typically used for depth profiling of elemental dopants and contaminants in materials with a detection limit in the ppm – ppt range. This powerful lateral detection technique is thus well suited for diffusion studies of individual elements through one or several material interfaces. SIMS has recently been used to probe Li diffusion through TaN thin films for microelectronics applications $^{83}$. SIMS was used in Paper VI to investigate the Li barrier properties of boron-doped diamond electrodes.
3.3 Electrochemical characterisation

3.3.1 Cyclic voltammetry

In cyclic voltammetry (CV), the current is recorded as the potential is swept between two end points causing reduction and oxidation of electroactive species. The shape of the voltammogram gives information about the oxidation and reduction potentials and the current controlling process. By varying the potential scan rate and hence, the experimental time-scale, insights into the reversibility of the electrochemical reaction can be obtained. Careful evaluation of the resulting voltammogram can also provide information on the kinetic properties and distribution of particle sizes as was shown in Paper II. The technique is thereby suitable for initial electrochemical analyses of battery cells where information regarding the redox reactions is particularly beneficial for a better understanding of results obtained with controlled current, i.e. chronopotentiometric, techniques.

3.3.2 Chronopotentiometry

When a constant current is forced through an electrochemical cell, the potential of the working electrode takes on the potential necessary to enable an electrochemical reaction capable of sustaining the selected current. Controlled current techniques are useful for studying multicomponent systems and multistep reactions where the measured potential changes as the surface concentrations of the electroactive species vary. When one reaction is unable to sustain the current density the potential shifts to a value where another reaction capable of delivering the desired current density can occur. The thickness of an electroactive coating can be determined from the required oxidation or reduction charge by measuring the transition-time for the redox reactions during a constant current experiment.

This thesis studies the characteristics of potential-time curves obtained during constant current electrolysis and the shapes of voltammograms. Electrochemical methods have been used to investigate the electrochemical properties of vanadium oxide [I], cuprous oxide [I, II and IV], lithium [V] and tin [VI].

3.3.3 Battery cell assembly

To study the electrochemical properties of the present nanostructured electrodes in lithium-ion batteries, electrochemical evaluation was performed using a thin film (i.e. coffee-bag) electrochemical cell. The cells were constructed by stacking the 3D electrode (working electrode), an electrolyte soaked polymer separator (Solupor) and a lithium foil (counter and reference
electrode), as is illustrated in Figure 5. In the presented studies, 1 M LiPF$_6$ salt was dissolved in ethyl carbonate/diethyl carbonate (2:1) and used as the electrolyte. Prior to the assembly, all electrodes were dried in an argon atmosphere to remove moisture, which can give rise to side-reactions when exposed to the other cell components. The cells were assembled and sealed in an Ar-filled glove box (M-Braun) having moisture and oxygen levels below 1 ppm.

*Figure 5.* ‘Coffe bag’ cell assembly where the anode (e.g. Cu$_2$O) is stacked together with an electrolyte soaked separator and the cathode (e.g. V$_2$O$_5$).
4. Results and discussion

*The most exciting phrase to hear in science, the one that heralds new discoveries, is not ‘Eureka!’ but ‘That’s funny…’*

- Isaac Asimov

4.1 Nanostructured current collectors

This thesis rests upon the backbone of nanostructured metallic substrates that can amplify delicate electrochemical signals, thereby giving a unique opportunity to investigate the key features of electrochemical energy storage. Aluminium and copper nanorods have been grown to serve as current collectors for 3D cathodes and anodes, respectively.

4.1.1 Copper nanorods

Copper is widely used as a current collector for anodes in lithium-ion batteries because it is considered not to alloy with lithium at low potentials. This is not entirely true as will be described in Section 4.6.

Copper nano- and microrods were grown by electrodeposition involving the reduction of $\text{Cu}^{2+}$ to Cu into the pores of a membrane with the nominal pore size of the desired rods dimensions. Rods with diameters ranging from 80 nm to 2 µm were produced to meet the requirements of the subsequent coating depositions. Ligands like diethylenetriamine (DETA) were used to stabilize the $\text{Cu}^{2+}$ ions with the aim of providing a more controllable deposition. Electrodeposition was performed using an initial short potential pulse, designed to initiate nucleation and seed the substrate, followed by a pulsed constant current scheme where alternating cathodic current pulses were applied including low (i.e. 2-6 mA/cm$^2$) and high (i.e. 30-90 mA/cm$^2$) current densities. Pulsed-electrodeposition has previously been used for the fabrication of copper rods\textsuperscript{24,71} and has been designed to improve the mass transfer, which is especially important for template-assisted electrodeposition where the mass transfer rate is limited within the narrow template pores. The deposition process is visualised in Figure 6 where nanorods are grown on top of a substrate (e.g. Cu).
Nanorods are grown by first attaching a porous template to the flat substrate. The initial nucleation introduces the growth of small islands on the substrate with nanorods peaking up. During the continued deposition the islands expand eventually merging with neighbouring islands as can be seen in the centre image of Figure 6b. When all islands have merged and the entire surface is covered continued deposition is carried out in the template pores leading to the growth of nanorods. The final 3D electrode can be visualised as a forest of nanorods covering the surface. The morphology of the rods can be observed in the inset of Figure 6c.

The fabrication of advanced 3D current collectors based on high aspect ratio Cu nanostructures can greatly increase the surface area. By analysing the rod dimensions and density on the substrate it is possible to estimate the surface area gain factor. This unit of measure is a practical tool for 3D electrochemists to evaluate the surface increase due to nanoarchitecturing. The surface area gain factor is exclusively dependant on the membrane properties (i.e. pore density and dimensions), which ultimately determine the 3D architecture.

Figure 7. SEM micrographs of Cu nanorods grown using PC (a) and AAO (b) membranes. The highlighted area shows the rod density used to calculate the overall surface area gain factor.
Polycarbonate (PC) and anodic aluminium oxide (AAO) constitute the most common templates for nanorod fabrication. In Figure 7 a template of each type with inherent pore sizes of 200 nm are compared. As seen the rod dimensions differ somewhat as the AAO template generates highly cylindrical rods as opposed to the slightly distorted nanorods formed employing PC templates. Most importantly the rod density differs greatly between the two templates as AAO yields about two times as many rods per µm² compared to PC. This feature is mirrored in the surface area gain factor with PC and AAO factors of about 45 and 80, respectively. The dense packing of the nanorods obtained with AAO does however leave little room between the rods making subsequent coating of the rods somewhat complicated. PC membranes are as such superior when it comes to studying coating deposition routes for 3D electrodes. If, however, the goal is to obtain high energy and power densities then AAO templates are the better choice.

4.1.2 Aluminium nanorods

Aluminium often serves as a current collector for cathodes that operate at high potentials. Aluminium has a low standard potential (i.e. -1.66 V vs. SHE) making the material prone to oxidation. However the Al₂O₃ is rapidly formed in contact with oxygen which stabilises the current collector even at high potentials. Aluminium is thereby often used as current collector for cathodes in lithium-ion batteries.

3D aluminium current collectors can be fabricated by growing Al nanorods through template-assisted electrodeposition. The synthesis differs from the growth of Cu nanorods as it requires an inert atmosphere due to the high reactivity of aluminium towards water and oxygen. Instead of a conventional aqueous electrolyte, ionic liquids are typically used for Al electrodeposition. Apart from the environmental conditions required for Al electrodeposition, the fabrication is essentially performed in a similar manor to that of Cu nanorods. Aluminium nano- and microrods have been fabricated based on previous knowledge present within the group [14, 16].
4.2 Active material coating on 3D electrodes

4.2.1 $V_2O_5/MnO_x$ coated Al microrods

3D aluminium substrates offer several important advantages for possible applications such as current collectors for electrochemical devices. The poor corrosion resistance of aluminium however limits the number of possible coating techniques when depositing active layers, e.g. metal oxides. Electrodeposition of vanadyl sulphate takes place under highly oxidising conditions in a low pH electrolyte. This synthesis is thereby an excellent model system for investigating thin film deposition on Al substrates in corrosion promoting environments.

4.2.1.1 Electrodeposition on uncoated aluminium

Vanadium oxide is typically formed by electrochemical oxidation forming $V^{V}$ species. The reaction is pH dependant and above pH 1.8 the reaction occurs through an initial oxidation yielding $V^{V}$ followed by precipitation of $V_2O_5$, as is seen below.

\[ 10VO^{2+} + 18H_2O \rightarrow H_2V_{10}O_{28}^4- + 34H^+ + 10e^- \]  (3)

\[ H_2V_{10}O_{28}^4- + 4H^+ \rightarrow 5V_2O_5 + 3H_2O \]  (4)

In addition to producing $V_2O_5$, the reaction is associated with significant proton production making the local environment highly corrosive. This feature proved challenging when coating aluminium substrates as can be seen in Figure 8.

*Figure 8.* Electrodeposition of vanadium oxide on uncoated planar (red line) and coated 3D (blue line) aluminium substrates (a). SEM micrograph showcasing pitting corrosion on an uncoated aluminium substrate after an attempted vanadium oxide electrodeposition (b).
The vanadium oxide synthesis was first investigated on planar aluminium substrates to establish a working deposition process. The potentiostatic deposition (red line) gave rise to a steady increase in the current density, uncharacteristic of the expected diffusion controlled current response. A continuous current density increase is typically observed when the electrode surface area is increased, e.g. due to corrosion. Aluminium corrosion was indeed possible as the applied potential and the acidic electrolyte facilitated aluminium oxidation without the formation of a passivating Al₂O₃ layer. Production of Al³⁺ ions thus followed in accordance with the Pourbaix diagram for aluminium.⁸⁷ Evidence of corrosion was found by analysing the substrate after the deposition, where indications of pitting corrosion were observed by SEM, see Figure 8b, and aluminium was also found in the electrolyte using ICP-AES. The instability of the aluminium substrate thereby inhibited the vanadium oxide coating procedure, as any deposited material would detach upon the corrosion of the underlying aluminium substrate.

4.2.1.2 Electrodeposition on MnOₓ coated aluminium

To circumvent the aluminium corrosion problem during vanadium oxide electrodeposition, a new synthesis route was developed. In this approach, an intermediate metal oxide layer was implemented to act as a protective coating for the Al substrate thus facilitating the vanadium oxide deposition. Manganese oxide was selected based on the fact that MnO₂ is stable in the pH/voltage window required for V₂O₅ deposition and as the material can be readily grown by electrodeposition,⁸⁸ thereby maintaining an all-electrochemical synthesis.

In the pulsed galvanostatic deposition approach used, manganese hydroxide was formed due to a local pH increase caused by the reduction of water, as is shown below. Aluminium microrods were as such first coated with Mn(OH)₂ which then may undergo oxidation to MnO₂ during the vanadium oxide synthesis and accordingly protect the Al surface.

\[
\begin{align*}
2H_2O + 2e^- & \rightarrow 2OH^- + H_2(g) \quad (5) \\
2OH^- + Mn^{2+} & \rightarrow Mn(OH)_2 \quad (6)
\end{align*}
\]

As the manganese oxide interlayer may undergo several phase transformations due to aging and oxidation during the subsequent vanadium oxide electrodeposition, it was more generally referred to as MnOₓ. The MnOₓ coated 3D Al substrates were used in the subsequent potentiostatic deposition of V₂O₅, as can be seen in the chronopotentiogram of Figure 8a (blue line). In this case, a stable current density of 1.3 mA/cm² was observed throughout the experiment, suggesting that the MnOₓ layer inhibited the aluminium corrosion sufficiently to enable deposition of vanadium oxide. Oxidation of VO²⁺ cannot solely explain the current response detected, as it would give rise to a diffusion
controlled current response. Instead the current response was found to originate from combined oxidation of Mn\textsuperscript{2+}, VO\textsuperscript{2+} and water. As the operating potential was +1 V (vs Ag/AgCl) while that required for the oxidation of water at pH 2.7 is +0.87 V (vs Ag/AgCl), the oxidation process was proposed to involve a catalytic step in which V\textsuperscript{V} oxidizes water as is indicated below.

\[
\begin{align*}
4V^{IV} & \rightarrow 4V^{V} + 4e^- \\
4V^{V} + 2H_2O & \rightarrow 4V^{IV} + O_2 (g) + 4H^+
\end{align*}
\] (7) (8)

4.2.1.3 Structural characterisation

SEM/EDS analyses after the deposition, see Figure 9, revealed intact Al microrods indicating that the MnO\textsubscript{x} coating provided sufficient corrosion protection to facilitate the vanadium oxide deposition. Further studies of the microrods revealed the presence of a homogenous V\textsubscript{2}O\textsubscript{5}/MnO\textsubscript{x} hybrid thin film with trace electrolyte agglomeration between some microrods.

![Figure 9. Vanadium oxide/manganese oxide coated aluminium microrods as seen by SEM side-view (a) SEM coupled to EDS (b).](image)

Further analysis of the electrochemically coated Al microrods using XPS confirmed the presence of vanadium oxide as seen in the V\textsubscript{2p\textsubscript{3/2}} spectra depicted in Figure 10a. The analysis showed the presence of both V\textsuperscript{V} and V\textsuperscript{IV} species (i.e. 45% V\textsuperscript{V} and 55% V\textsuperscript{IV}) indicating that the deposition gave rise to a vanadium oxide with mixed oxidation states, in good agreement with previous findings \textsuperscript{89},\textsuperscript{90}. The presence of V\textsuperscript{IV} can be explained by the reduction of vanadium (V) oxide while H\textsuperscript{+} is intercalated into the structure. No traces of manganese oxide were found on the surface and sputter profiles could not be recorded due to the complex morphology of the 3D substrate. Instead, the underlying coating was probed by SERS relying on localised surface plasmon resonance originating from the Al nanostructured substrate. Several features were detected in the Raman spectra utilising a 785 nm laser source (blue line), with the most prominent peak at 647 cm\textsuperscript{-1}, see Figure 10b. The positions of the peaks are in good agreement with previous findings for manganese oxide and the peaks were found to be due to MnO\textsubscript{2}. Furthermore, the short amplification distance of SERS (i.e. a few nanometers) did not
allow detection of vanadium oxide indicating that the manganese oxide film covered the entire 3D aluminium substrate. The structural characterisations thus indicated that mixed valent vanadium oxide had been deposited on MnO$_x$ thin film coated aluminium microrods.

Figure 10. XPS analysis of the V$_2$O$_5$/MnO$_x$ coated Al microrods featuring the V$_{2p}$ spectra (a) as well as a SERS analysis revealing a MnO$_2$ characteristic signature.

4.2.2 Li coated Cu nanorods

Lithium is the ideal anode material with its low standard potential (i.e. -3 V vs. SHE) as well as the highest theoretical capacity of all elements (i.e. 3860 mAhg$^{-1}$). 3D lithium electrodes should thus be very interesting for microbatteries which aim at high capacities per footprint area. Electrodeposition of lithium on Cu nanorods was therefore pursued. The Li electrodeposition was performed in two steps: first the potential was scanned from 3.1 V to -0.25 V as to carefully reduce the native Cu$_2$O oxide and initiate the Li nucleation. Additional Li deposition was then performed by applying a constant potential of -0.25 V for 365 seconds to reach a deposition charge of 1 C.

Figure 11. Electrodeposition of Li on Cu nanorods using initial linear sweep voltammetry (a) followed by chronoamperometry at -0.25 V vs. Li$^+/Li$. 
The initially recorded linear sweep voltammogram displayed characteristic features of Cu$_2$O reduction at about 0.8 V vs. Li$^+$/Li followed by the onset of Li plating below 0 V. The shape of the subsequent chronoamperogram indicated continued nucleation during the Li plating.

Li electroplating on Cu nanorods was seen to generate a smooth deposit with the thin Li film following the nanostructured architecture. The coating was observed more as of a swelling of the Cu nanorods as the diameter was increased by about 50 nm. The deposited Li amount was found to be 0.1 mg by ICP-AES elemental analyses. This translates to an average Li layer thickness of 38 nm, which agrees well with the SEM results. The swelling of the 3D Cu substrate upon Li electroplating results from the significant solubility of Li in Cu, a feature that is further investigated in Section 4.6.

*Figure 12.* SEM micrographs of Cu nanorods before (a) and after (b) Li thin film deposition.
4.2.3 Cu$_2$O coated Cu nanorods

Cu nanostructured electrodes are advantageous, as the native cuprous oxide can be used as anode material. By utilising spontaneous oxidation of copper, it is possible to obtain a Cu$_2$O thin film coating with excellent adhesion to the Cu nanorod substrate. Cu$_2$O growth can also occur through the comproportionation reaction between Cu and Cu$^{2+}$. Apart from the top and side-view SEM analyses in Figure 6, TEM was also used to probe the surface. The oxide coating on the Cu nanorod can be seen in Figure 13. The thickness of the latter layer was about 10-15 nm, with some extensions as observed in Figure 13b.

![Figure 13](image-url)

Figure 13. TEM analyses of a 200 nm Cu nanorod showing the Cu$_2$O coating on the Cu nanorod core (a) and a magnification of the phase boundary between Cu$_2$O and Cu (b).

The chemical composition of the outermost surface layer was further investigated by XPS. The Cu2p and O1s spectra in Figure 14a-b confirmed the presence of Cu$_2$O and additional peaks could be assigned to Cu and Cu(OH)$_2$. Copper hydroxide can be a residue from the template removal process which utilises 1 M NaOH, or simply hydration, as the Cu$_2$O surface was exposed to the atmosphere. Phase analyses of the Cu nanostructures revealed a crystalline Cu substrate with some evidence of crystalline Cu$_2$O. However, the Cu$_2$O appeared to be essentially amorphous or nanocrystalline, a feature that proved beneficial to the conversion reaction discussed in Section 4.3.3.
Figure 14. XPS analysis of Cu nanorods featuring the Cu2p (a) and O1s (b) spectra. Phase analysis of as-deposited Cu nanorods was also performed by XRD (c).

4.2.4 Cu2O/Cu multi-layered nanorods

Electrochemical synthesis of cuprous oxide and copper multi-layers using a one-bath procedure rests upon the possibility of depositing the materials at different current densities. At low current densities the single electron reduction reaction of Cu2+ to Cu+ is sufficient to maintain the current and Cu2O is produced. When the current density is increased the latter process can no longer maintain the current and a two-electron reduction reaction instead takes place thereby producing Cu. The electrochemical reactions generating Cu2O and Cu are presented below, where Cu2+ ions are presented in the form of a copper citrate complex (i.e. Cu2H2Cit2+).

\[
\begin{align*}
[Cu_2H_2Cit_2]^{4-} + 2e^- + H_2O &\rightarrow Cu_2O + 2Cit^{3-} \\
[Cu_2H_2Cit_2]^{4-} + 2Cu + 2OH^- &\rightarrow 2Cu_2O + 2Cit^{3-} \\
[Cu_2H_2Cit_2]^{4-} + 4e^- + 2H_2O &\rightarrow 2Cu + 2Cit^{3-} + 2OH^- 
\end{align*}
\] (9) (10) (11)

Unfortunately, there are several obstacles that can limit the electrochemical synthesis. As indicated in reaction (11), the copper deposition gives rise
to a local pH increase, which has been shown\(^\text{92}\) to produce spontaneous potential oscillations which in turn generates mixed Cu\(_2\)O/Cu deposits under galvanostatic conditions. In order to obtain multi-layers with control over the layer thicknesses these potential oscillations should be avoided. The multi-layered deposition is further complicated by the fact that the Cu\(_2\)O layer should be reduced to Cu during copper deposition. Luckily the formation of an initial copper layer was found to protect the underlying cuprous oxide layer. This cathodic passivation effect was crucial for the successful growth of Cu\(_2\)O/Cu multi-layered nanostructures. It was found that the problems described above could be circumvented with a pulsed galvanostatic deposition process, aided by the cathodic passivation effect. Electrodeposition of Cu\(_2\)O/Cu multi-layers using three different templates is presented in Figure 15.

![Figure 15. Electrodeposition of Cu\(_2\)O/Cu multi-layers in templates with nominal pore diameters of 50 nm (black curve), 200 nm (red curve) and 1 \(\mu\)m (blue curve), respectively. The Cu\(_2\)O layers were grown with a set of short cathodic current pulses by applying 0.1 mAcm\(^{-2}\) and 1 mAcm\(^{-2}\). Longer pulses with a current density of 10 mAcm\(^{-2}\) were used to deposit the copper layers.]

The Cu\(_2\)O layer deposition process comprised a large number (i.e. 700) of short (i.e. 0.1 and 1 s long) galvanostatic pulses with low current densities (i.e. 0.1 and 1 mAcm\(^{-2}\)), whereas each copper layer was grown using a single 55 s long pulse with a higher current density (i.e. 10 mAcm\(^{-2}\)). The sequence
was then repeated to produce multi-layers. This procedure was designed to hinder spontaneous potential oscillations and to produce Cu$_2$O/Cu multi-layers with controllable layer thicknesses.

*Figure 16. SEM micrograph of 1 μm wide Cu$_2$O/Cu multi-layered rods.*

The strategy proved successful as is evident from the multi-layered microrod in Figure 16. Multi-layered structures were effectively grown in all three templates yielding rods with diameters of 80 nm, 200 nm and 1 μm, respectively. The 50 nm template was seen to generate rods with a diameter closer to 80 nm and these rods will henceforth be referred to as 80 nm rods. Even though the electrodeposition scheme applied in each synthesis was identical, the nature of the templates influenced the resulting multi-layered rods as different thicknesses of the Cu and Cu$_2$O layers were obtained. SEM analyses of all three-rod dimensions revealed a trend of growing Cu$_2$O layer thicknesses when decreasing the template pore size. For the 80 nm rods the average Cu$_2$O layer was 3.2 times thicker than the average Cu layer thickness, in contrast to the Cu$_2$O/Cu thickness ratio of 1.4 found for the 1 μm rods. This feature is believed to originate from the synthesis conditions as the largest pore density was present for the 50 nm template. This translates into a lower current density in each pore, which in turn shifts the deposition towards the Cu$_2$O low current regime. The rods also portrayed a ‘bamboo-like’ morphology indicating that the diameters of the Cu$_2$O and Cu layers differed somewhat. It is reasonable to expect oxidation of the Cu layers, which would give rise to an extended Cu rod diameter and this could hence explain the observed feature.

Experiments with EDS line scanning and SEM with a backscattered electron detector confirmed the presence of multi-layers with different Cu and O
contents. To gain further knowledge regarding the interphase between the layers TEM was used to study a single 80 nm rod, as is shown in Figure 17.

**Figure 17.** HAADF-STEM analysis (a) of the interphase between a Cu$_2$O and a Cu layer coupled to EELS mapping of the Cu and O signal in the highlighted area (b).

HAADF-STEM mode analysis revealed distinct layer boundaries throughout the multi-layered nanorods. EELS mapping over the interphase indicated the presence of a higher Cu concentration in the lighter (i.e. denser) region seen in the HAADF-STEM mode. Analogous O mapping showed a similar clear phase boundary. An overlay of both maps clearly shows the presence of two separate phases one being cuprous oxide (i.e. red region) and the other corresponding to copper (i.e. turquoise region). The cuprous oxide layer was, however, seen to also contain some copper nanoparticles. Furthermore, the ‘bamboo’ morphology observed in SEM could also be detected in the TEM analysis. EELS oxygen mapping over the copper layer did however fail to identify any surface oxide. Oxidation of the copper surface is still believed to be the reason for the observed morphology since spontaneous oxide growth was observed for the Cu nanorods as is described in Section 4.2.3.
4.3 Electrochemical insights into Cu\textsubscript{2}O conversion

The electrochemical properties and performance of cuprous oxide have been investigated in several studies, which have discussed several key features related to the conversion reaction of Cu\textsubscript{2}O in a lithium-ion battery. The conversion reaction is carried out by reducing cuprous oxide which yields copper nanoparticles embedded in a lithium oxide matrix. The reverse reaction is then performed by oxidation of the copper nanoparticle to cuprous oxide thus releasing lithium-ions back into the electrolyte.

\begin{equation}
\text{Cu}_2\text{O} + 2\text{Li}^+ + 2e^- \leftrightarrow 2\text{Cu} + \text{Li}_2\text{O}
\end{equation}

Hard wiring Cu\textsubscript{2}O to a nanostructured substrate, as has been performed throughout this thesis, offers many advantages for studies of the conversion reaction. Direct electrical contact between Cu\textsubscript{2}O and the Cu nanorod core offers a low contact resistance. In fact, in the present case no electronic conduction limitations were expected as the total resistance for each nanorod was found to be about 2 $\Omega$, with the thin Cu\textsubscript{2}O coating contributing with a mere 0.07 $\Omega$. Mass transport limitations along the complicated nanostructures should not greatly affect the system as the total diffusion time for Li$^+$ ions moving along the entire length of a nanorod was estimated to be 0.6 s. Even though cuprous oxide suffers from a modest volume expansion of 22% during reversible conversion reaction, this volume expansion effect should also be alleviated by wiring the oxide to a nanostructured substrate. The 3D copper electrode was found to be an excellent model system to study the fundamental mechanisms of the conversion reaction. No binder or additives were present, which enabled conclusions to be drawn solely based on the behaviour of the cuprous oxide.

Cuprous oxide has been intensively studied throughout this thesis in the form of thin film coatings and multi-layered nanostructures. All this electrochemical probing has provided three important insights into how cuprous oxide behaves during the electrochemical conversion reaction in a lithium-ion battery.

4.3.1 Particle size vs. redox potential

The basic electrochemical behaviour of the cuprous oxide conversion reaction is best illustrated by cyclic voltammetry as presented in Figure 18.
Figure 18. Cyclic voltammogram for Cu₂O thin film coated Cu nanorods detailing the first three cycles obtained at a scan rate of 0.1 mV/s. The dependence of the redox potential on the particle size is schematically shown by the grey spheres with different diameters.

Several distinct peaks are seen during the first cathodic scan, which normally are explained by the reduction of Cu₂O followed by formation of a solid electrolyte interphase (SEI) layer due to electrolyte decomposition. This could explain most of the cathodic scan if it were not for the significant charge present at potentials lower than 1 V. Moreover, the presence of two reduction peaks during the second cathodic scan is peculiar, as the SEI formation process is known to be irreversible and passivating. The multiple redox peaks and the broad potential window was instead ascribed to the presence of Cu₂O nanoparticles with a distribution of sizes. It is known that the potential at which a particle is oxidised or reduced depends on its size. Normally the effect is minimal and difficult to observe, however, by downscaling to the nanoscale it is possible to observe a significant shift in redox potential. The effect was also notable for the Cu₂O multi-layered nanorods in Paper IV. Cyclic voltammograms of multi-layered rods with different dimensions, see Figure 19, all appeared similar with two distinct peaks for the reduction as well as for the oxidation. The important difference is the proportion of charge located in the different potential windows (i.e. the sizes of the peaks). There seems to be a general trend of decreasing reduc-
tion potentials when decreasing the rod dimensions (i.e. from 1 µm to 80 nm). This effect is best illustrated by comparing as-synthesised and heat treated 200 nm rods. The shapes of the voltammograms on the oxidation scans clearly differed as the heat treated exhibited a significantly larger proportion of its charge at higher potentials while the as-synthesised sample featured a more even distribution. This can be explained by assuming the presence of larger particles in the heat treated 200 nm multi-layered rods. Particle growth during annealing is a logical assumption and thus supports the theory regarding particle size dependant redox potentials.

Figure 19. Cyclic voltammograms for 80 nm, 200 nm (as-synthesised and heat treated) and 1 µm multi-layered rods recorded at a scan rate of 0.1 mV/s.

The hypothesis that the nanoparticle size distribution was responsible for the observed wide potential window is further supported by TEM analysis performed on the Cu nanorods after the cycling, see Figure 20.
Electrochemical conversion of Cu$_2$O is here seen to generate Cu nanoparticles of diverse sizes. The average particle size was approximately 14 nm but significantly smaller particles were clearly also present. Based on the CV and TEM results it was thus concluded that the wide electroactive potential window for Cu$_2$O/Cu electrodes was caused by the presence of a distribution of nanoparticles with different sizes.

4.3.2 Electrochemical milling

Long term cycling analyses coupled to rate performance evaluation of the Cu$_2$O thin film coating demonstrated an interesting capacity evolution. After 270 cycles of extensive rate performance analyses the applied current density was lowered to the initial value. From then on the capacity was seen to increase above its initial value ending at 0.265 mAh/cm$^2$ after 390 cycles. In Paper II this value was reported to be 130 % of the theoretical capacity. New findings regarding the electrochemical performance of Cu$_2$O thin films on planar electrodes shows that a reversible capacity of about 5 µAh/cm$^2$ can be
reached, which offers a better understanding of the theoretical capacity of 3D Cu$_2$O/Cu electrodes. With this new information the capacities would correspond to an efficiency of about 50 % for the first three cycles. Significant capacity retention was however observed during extensive cycling as about 94 % of the theoretical capacity was recovered after 390 cycles. The main reduction peak (i.e. II) in Figure 18 should in fact mainly be ascribed to Cu$_2$O reduction with a minimal contribution from SEI formation.

In the initial conversion reaction the Cu$_2$O coating seems to be almost fully reduced while only half of the reduced material could be re-oxidised initially. The subsequent reduction charge is then limited by the previous oxidation charge as it controls the amount of Cu$_2$O available for reduction. In order to understand the described capacity behaviour one has to look at the mechanism of the conversion reaction. The main limitation in the system is believed to originate from the oxidation reaction. Since the oxidation starts at the electrode/electrolyte interface and continues inwards, the reaction rate becomes limited by the diffusion rate of Li$^+$ ions through the growing Cu$_2$O layer. The oxidation current should thus decrease with time as the Cu$_2$O layer grows thicker.

The oxidation charge was however seen to increase during prolonged cycling, a feature that is believed to be connected to an electrochemical milling process taking place during the conversion reaction. As the coating is repeatedly reduced and oxidised, particles break down to yield smaller and smaller particles. As such new grain boundaries between the particles are formed thus introducing new pathways for the lithium-ions to be transported deeper within the coating. The amount of accessible cuprous oxide is thereby increased which in turn increases the capacity. The process should also decrease the general particle size meaning that a larger portion of the material will be operating at lower potentials. This conclusion is in good agreement with the post-mortem TEM analysis illustrated in Figure 20.

4.3.3 Electroactive layer

After extensive analyses of the Cu$_2$O coated rods one important question remains. Can the capacity of a Cu$_2$O rod based electrode be increased by increasing the Cu$_2$O layer thickness? This question can be addressed by analysing the electrochemical performance of the different multi-layered Cu$_2$O/Cu rods fabricated in Paper IV.

The electroactive layer thickness was estimated based on the assumption that the entire Cu$_2$O layer was electroactive for the 80 nm rods at a scan rate of 0.1 mV/s. This assumption is supported by the fact that a capacity of 21 µAh/cm$^2$ was obtained at sufficiently low scan rates, since this value is close to the theoretical value of 19 µAh/cm$^2$. Based on this assumption and the normalised capacity data found in Figure 21, the thicknesses of the electro-
active Cu$_2$O layer were found to be about 40, 30, 23 and 25 nm for the 80 nm, 200 nm, 200 nm heat treated and 1 µm rod electrodes, respectively. Accordingly, the general thickness of the electroactive Cu$_2$O layer was about 20-40 nm. Moreover, the thickness was found to decrease with increasing rod diameter and heat treatment. The latter conclusion is interesting as it suggests that crystal growth decreases the yield of the electrochemical conversion reaction. One possible explanation could be that as the grains grow the amount grain boundaries decreases which limits the transport pathways for the Li$^+$ ions. During the conversion reaction Li$^+$ ions are able to migrate either through the Cu$_2$O/Cu particles (i.e. grains) or through the surrounding Li$_2$O (i.e. grain boundaries). It is logical to assume that a more rapid transport is achieved through the Li$_2$O. It would thus seem that the conversion reaction benefits from an amorphous or nanocrystalline structure, where the Cu$_2$O particles are more easily accessible. This feature should be enhanced during cycling as the electrochemical milling process takes place, thereby reducing the particle size and introducing new grain boundaries. This is in contrast to intercalation materials which generally require high crystallinities to provide high efficiencies and reversibility.

*Figure 21.* Capacity plots obtained from multirate CVs recorded for scan rates ranging from 0.1 to 100 mV/s. The capacity is presented as the footprint areal capacity (left y-axis) and as the effective areal capacity (right y-axis) which takes the 3D electrode area into account.
The electroactive layer thickness was seen to decrease when increasing the scan rate to stabilise at about 5 nm for scan rates equal to or larger than 5 mV/s. The main limitation for the system is likely the passivating Cu$_2$O layer on top of the remaining Cu/Li$_2$O matrix during oxidation, causing the incomplete oxidation seen in Figure 21.

The diffusion coefficient of Li$^+$ ions in Cu$_2$O was estimated from the linear relationship between the thickness of electroactive layer and time, according to the equation below.

$$\Delta = \sqrt{2Dt}$$  \hspace{1cm} (13)

For scan rates of 0.1, 0.2, 0.8 and 5 mV/s electroactive thicknesses of 40, 28, 18 and 5 nm were obtained, respectively. With an estimated diffusion coefficient of $2\times10^{-16}\text{cm}^2\text{s}^{-1}$, it would seem that the Li$^+$ ions interact significantly with the O$^{2-}$ ions upon their transport through the Cu$_2$O layer.

These present results show that it is challenging to increase the capacity by increasing the Cu$_2$O layer thickness since the thickness of the electroactive layer is limited by slow Li$^+$ ion transport through the Cu$_2$O layer.
4.4 Polymer electrolyte coating

In order to fabricate a lithium-ion microbattery cell an electrolyte soaked separator is required to electrically separate the 3D anode and cathode. Solid-state polymer electrolytes can offer ionic transport while physically separating both electrodes. This offers a major improvement for microbatteries, as the cell volume can be greatly reduced. As such, polymer coating techniques have been investigated for 3D electrodes to evaluate their applicability for microbattery fabrication.

Polymer coating of 3D Cu electrodes with a native oxide was performed by two kinds of electropolymerisation routes. Attempts at constant current deposition and pulsed current deposition were compared so as to identify the most viable route for coating these complex nanostructured surfaces. The pulsed current scheme was designed to improve mass transport by adding a relaxation period between deposition pulses. This allowed for minimization of local depletion or accumulation of reactants, thus rendering a more uniform surface area coverage. SEM images of the resulting polymer coatings are displayed in Figure 22. The constant current deposition resulted in a general coverage apart from the fact that most of the microrod tips were left uncoated, see Figure 22c. In comparison, the pulsed current deposition yielded a conformal and uniform coating neatly following the 3D architecture as seen in Figure 22d. The latter polymer coating thickness was found to be 200-300 nm. The reason for this superior coating is likely connected to the improved mass transport facilitated by the relaxation pulse. By allowing the reactants to diffuse during the relaxation pulse it is more likely that a uniform coverage of the complex 3D architecture can be obtained.
Figure 22. SEM micrographs of uncoated Cu microrods (a,b) and electropolymerised polymer coatings obtained by constant current deposition (c) and pulsed current deposition (d).

Complete coverage of the 3D electrode surface is of paramount importance since the polymer electrolyte is designed to function as an electrical separator for the 3D anode and cathode. Uncoated microrod tips would naturally be a major issue as these could easily come in contact with the opposite electrode and short-circuit the cell. The pulsed electropolymerisation route is not limited in this fashion. The polymer coverage can be analysed electrochemically by employing a redox probe and monitoring the redox activity before and after depositing the polymer film. This technique is a simple tool for investigating the result of the polymer film deposition as a compliment to the SEM analysis. As seen in Figure 23, a dramatic reduction in the current density occurred when applying the polymer coating as compared to for uncoated substrates. Given the residual detection of a small oxidation current, this indicates that the polymer film had a large resistance that limited but did not eliminate the redox reaction. The background current can be explained by poor crosslinking in the polymer film causing some of the redox probe (i.e. hydroquinone) to dissolve into the polymer. This was confirmed by FTIR as the as-synthesised polymer electrolyte was found to contain a significant amount of unreacted acrylate monomers. This problem could however be greatly reduced by annealing the polymer at 50 °C which increased the degree of crosslinking.
Figure 23. Cyclic voltammograms of an uncoated 3D substrate (black), and a polymer coated 3D electrode before (red) and after annealing at 50 °C for 15 hours (blue).

During the electropolymerisation a lithium-ion salt (i.e. LiTFSI) was introduced and co-deposited into the polymer film. By doing so the entire synthesis was simplified, as no salt post-doping was required. The surface chemical composition was characterised by XPS, which showed F1s, N1s and S2p3/2 peaks all characteristic of LiTFSI. The chemical composition seemed uniform as analyses at five different sampling spots all showed the same LiTFSI characteristic peaks. The results thus indicate that codeposition of the LiTFSI salt is possible during the electropolymerisation.
4.5 3D microbattery assembly

Although several nanostructured electrodes have been realised assembling them into a final 3D microbattery becomes challenging due to their dense nanorod population. 3D microbattery designs are mainly focused on positioning the 3D anode and cathode very close (i.e. in the nanometer regime) to each other. However, this is difficult to realise as short circuits can occur if nanorods from each electrode come in contact. A simpler solution would be to separate the 3D electrodes by a thin separator as is commonly used in a half-cell assembly where the electrodes are cycled versus lithium foil. This approach has proven successful when assembling two 3D electrodes based on nanorod and aperiodic architecture. A similar concept was used in Paper V with both the cathode and anode based on the 3D nanorod design. In this setup Cu nanorod current collectors were used for both electrodes with the native Cu$_2$O coating on the cathode (i.e. positive electrode) and a Li coating on the anode (i.e. negative electrode). A Li foil was also used as a reference electrode to allow individual monitoring of the potentials of both the working (i.e. Cu$_2$O/Cu) and counter (Li/Cu) electrodes, as is seen in Figure 24.

The cell was dimensioned to be limited by the Cu$_2$O (i.e. WE) electrode as the Li coating on the CE corresponded to a deposition charge of 1 C. Initial oxidation of the Li (i.e. CE) electrode was seen at around 0 V indicating Li stripping. This process was however unable to supply a sufficient charge to fully reduce the Cu$_2$O as evidenced by its rapid potential increase after about 10 hours cycling. The Li electrode was instead seen to shift over to oxidation of the underlying copper nanoparticles formed during reduction of the native Cu$_2$O on the Cu current collector. Continued cycling was then obtained by reversibly cycling Cu$_2$O and Li$_2$O on both electrodes thereby transforming the 3D microbattery into a symmetrical cell with identical electrode materials. The

Figure 24. Galvanostatic microbattery cycling showing the individually monitored working (WE) and counter (CE) potentials as well as the cell potential (a) in addition to the footprint areal capacity and $Q_{ox}/Q_{red}$ evolution over 40 cycles (b).
fact that an insufficient Li oxidation capacity was present after the lithium deposition was a somewhat surprising finding since the deposition charge should have been about three times larger than the available charge of the Cu$_2$O electrode. This result can however be rationalised by considering that the solubility of lithium in copper is about 18 % at room temperature. It is then logical to assume that Li could diffuse into the 3D Cu current collector. The Li is assumed to start moving into the Cu nanorods during the deposition, which means that when the electrode is finally assembled in the 3D microbattery a significant part of the Li would be located within the Cu nanorods. Retrieving this charge during microbattery cycling will then be difficult as the process is controlled by the diffusion rate of Li in Cu after depleting the surface layer. This process is further investigated in Section 4.6.

After exhausting the Li capacity, the cell continued to cycle reversibly as a symmetrical cell comprising of two Cu$_2$O/Cu electrodes undergoing alternative oxidation and reduction. The cell capacity dropped from 0.27 to 0.15 mAhcm$^{-2}$ during this transformation. Steady capacity decline followed with a $Q_{\text{ox}}/Q_{\text{red}}$ efficiency of 98 %. Incomplete oxidation is believed to be the reason for the latter slight capacity decline which likely is connected to the low diffusion rate of the lithium-ions through the formed Cu$_2$O layer as discussed in Section 4.3.3.

### 4.5.1 Coulombic efficiency

The term coulombic efficiency as commonly used in battery electrochemistry is a measure of the reversibility of a redox reaction. In the world of batteries, it is defined as the ratio between discharge and charge, and depicts the portion (i.e. percentage) of the inserted coulombic charge which is possible to extract during the discharge. Modern lithium-ion batteries are constantly being evaluated based on this parameter, and coulombic efficiency is widely used to determine the usefulness of certain battery chemistries. The goal is to have a minimum coulombic efficiency of 99 % for a battery to be considered applicable. This might seem sufficient for a reversible system like the lithium-ion battery, however even with 99 % coulombic efficiency, a capacity of only 37 % should remain after 100 cycles. Several times throughout this thesis, coulombic efficiencies below 99 % have been reported. Yet, no dramatic capacity decrease has been observed. In fact, for the Cu$_2$O system capacity increase has been the general trend when exposing the electrode material to prolonged cycling. The problem lies in how the coulombic efficiency is obtained. Coulombic efficiency is typically determined for each redox cycle and then presented over the course of hundreds of cycles. Since the calculation of the coulombic efficiency only contains one charge and discharge capacity any kind of statistical uncertainty is impossible to establish. This means that the error bars for each point is unknown and can vary greatly.
Dahn and co-workers are currently trying to address this issue by refining the technique of measuring coulombic efficiency as to give a better image of the true electrochemical performance of most batteries. The group has focused on developing new electrochemical techniques that more accurately measure the potential enabling a more precise calculation of the coulombic efficiency. Although certainly important for the understanding of the battery performance, the calculation of coulombic efficiencies do not address some fundamental statistical issues. An alternative route would be to determine the capacity loss over a period of cycles and define a coulombic efficiency based on this. Although the issue of statistical accuracy remains, this new approach better illustrates the behaviour of the cell and could possibly provide a more accurate prediction of the capacity evolution during continued cycling. Figure 25 illustrates the difference between the conventional term and this new approach. The traditional way of determining coulombic efficiency resulted in values ranging from 100.2 to 104.5 %, making any kind of prediction of the capacity evolution difficult. By calculating the charge ratio between the first and last cycle (i.e. 100th cycle) an average coulombic efficiency of 100.8 % was obtained, see the dotted line in Figure 25. This value clearly better represents the behaviour of the system and should also enable a better prediction of the continued capacity evolution. The fact that the coulombic efficiencies exceeded 100 % can be explained by the fact that only 50 % of the initially reduced Cu$_2$O could be oxidised during the first cycle. This excess of reduced charge was gradually oxidised during prolonged cycling resulting in $Q_{\text{ox}}/Q_{\text{red}}$ ratios larger than unity. The comparison highlights the importance of correctly evaluating the performance of the electrodes, especially for conversion materials that typically underperform during the first charging (i.e. oxidation) cycle.
Figure 25. Reinterpretation of the prolonged cycling of the 200 nm multi-layered rods used in Paper IV. Conventional coulombic efficiency (red triangles) is compared to the efficiency determined by monitoring the capacity evolution over 100 cycles (dotted line).
4.6 The origin of Li losses in Li-alloys

One of the most promising avenues for future electrochemical energy storage lies in the prospect of storing charge in elements that readily alloys with lithium. Alloying materials (e.g. Si, Sn and Al) can store large quantities of charge which yield high gravimetric capacities. The alloying reaction is however accompanied by a considerable volume expansion that can cause particles to break up exposing them to the electrolyte. Irreversible decomposition of the electrolyte follows as it comes in contact with the freshly exposed electrode material. This process has so far been the prime explanation for the capacity fading observed when using alloying electrodes in lithium-ion batteries.

4.6.1 Time domain dependant capacity

The negative effects caused by the volume expansion could possibly be alleviated through the use of nanostructured electrodes such as nanorods that are hard wired to the substrate. Sn nanorods were therefore electrodeposited in a similar manor to the Cu nanorods and studied in a lithium-ion battery. Cyclic voltammetry indicated initial reduction of the native oxide and SEI formation followed by Li deposition and oxidation through the alloying reaction.

\[ xLi^+ + xe^- + Sn \leftrightarrow Li_xSn \]  

(14)

The process was however not fully reversible as is evident from Figure 26b where the capacity for scans to 2.5 V was seen to degenerate over time. Irreversible SEI formation due to volume expansion could possibly explain the capacity fading. Another possibility could however be Li trapping in the material due to diffusion as the inserted lithium should diffuse into the Sn nanorods. This process is time dependant whereas the SEI formation reaction should depend on the potential. In order to evaluate which process was responsible for the capacity fading the initial experiment was repeated with two modifications. First, the potential limit for the oxidation was set to 1 V. The second experiment used the same new potential limitation with an added time delay between the oxidation and reduction scans. Restricting the potential did improve the performance, and a significant initial capacity increase was followed by a steady decline. Introducing a time delay equal to the time needed to cycle to 2.5 V and back was seen to drastically affect the capacity decline, and after 70 cycles the trend was identical to that seen for cycling to 2.5 V. It thus seems as if the capacity decline was mostly time dependant and could as such be explained by Li trapping due to diffusion.
Figure 26. Cyclic voltammetry analyses of Sn nanorods during Li alloy formation and oxidation (a). The oxidation capacity as a function of the potential window and the time domain of the experiment is also presented (b).

The cycled Sn nanorods were analysed by ICP-AES to detect the presence of any residual Li in the rods. The rods were analysed after a full oxidation scan after which there should be no residual Li. As seen in Figure 27 residual Li was however present in the rods even in their oxidised state. Moreover, the Li amount increased during cycling indicating a build up of Li in the nanorods, as would be expected for a diffusion controlled process. These data thereby illustrates the problem of reversibly extracting lithium from alloying materials, a process that is hindered by two-way diffusion as is further described below.

Figure 27. Residual Li trapped in Sn nanorods after an oxidative scan.

4.6.2 Li trapping model

This section is dedicated to the description of the cause of the Li trapping within lithium alloy forming materials. Based on previous evidence for Li trapping in Al\textsuperscript{96-98} and Si\textsuperscript{99} electrodes, a model is presented which should be applicable to Li-alloy forming materials in general.
The principle of Li insertion and extraction in an alloy forming material is illustrated for a nanoparticle in Figure 28. Starting with the host material (1) the alloying reaction takes place at the surface and moves into the nanoparticle core (2). A diffusion gradient is thus formed allowing the inserted Li atoms in the alloy to diffuse towards the host core, thereby leaving “vacancies” at the surface which can be filled by newly formed Li. This continuous surface alloying causes a one-way diffusion into the nanoparticle core. Continued alloying of the host takes place (3) until the reduction process is terminated either manually or by an increasing overpotential. After the reduction step the nanoparticle can either be fully alloyed or partially alloyed (4). In this model the nanoparticle is only partially alloyed as to present the effects that this can cause.

Extracting the inserted Li takes place during the dealloying step starting with the partially alloyed nanoparticle having a host core covered with the Li-alloy (5). Li extraction takes place at the surface (6) thereby freeing up “vacant” positions in the outermost surface layer. Since the alloy is covered in host material two-way diffusion of Li occurs via diffusion both towards the surface and the core. This process continues as long as the concentration of Li in the core is lower than in the alloy layer. Continued Li extraction (7) is thus limited by the Li diffusion rate through the surface host layer. Since this process is limited by the diffusion rate (i.e. diffusion coefficient) the distance to which extraction is possible can be determined by equation 13. If the conditions (i.e. time domain) for Li insertion and extraction are the equal then equal penetration depths should be obtained. The two-way diffusion causing Li to diffuse into the bulk during dealloying can thereby be seen as a Li trapping mechanism as these atoms cannot be extracted during the time domain of the experiment. Accordingly residual Li will be left in the nanoparticle core at the end of the dealloying process (8). During extensive cycling this process will accumulate causing a capacity decrease. With that being said, the remaining Li can readily be extracted if the time domain of the experiment is changed as to allow the remaining Li to diffuse to the surface and be oxidised.

Since the mechanism of Li trapping is a diffusion-limited process, the thickness of the active material will greatly affect how severe the Li trapping effect will be. For large particles and thick films this issue will severely affect the cycle life, as a significant portion of the initial charge will be trapped within the material. Downsizing the material through the use of e.g. nanoparticles will decrease the available diffusion distance for Li when the material is not fully alloyed. Another viable strategy could be to fully alloy the material causing one-way diffusion to take place during dealloying.

A recent study 99 on the rate performance of Si anodes revealed that the alloying step was limiting during rapid cycling. This can be explained by considering the process of inserting Li atoms into a nanoparticle. As the nanoparticle alloy layer increases into the core the number of “vacant” Li
positions decreases. This increasingly difficult process builds up an overpotential which can cause the reduction to terminate due to the set potential window. This is a problem for alloy forming materials which react close to the standard potential of Li (i.e. -3.0 V vs. SHE) where Li plating can occur.

Figure 28. Schematic model of Li trapping in a particle during the alloying-dealloying reaction.

4.6.3 Li trapping in current collectors

The Li trapping process has so far been seen to affect the reversibility of cycling alloying materials. Li diffusion into the current collector is however also an issue for copper current collectors as was seen in Section 4.5. A similar effect can also be expected for other metallic current collectors, which is why the most common current collector metals used for anodes were investigated. Ni, Ti and Cu sheets were exposed to metallic Li in an inert atmosphere (i.e. glovebox with [H₂O] and [O₂] < 1ppm). After a one-week annealing at 50 °C, the metals were separated from the lithium foil and ICP-AES analyses of the residual Li contents in the current collectors were performed. The results, presented in Figure 29, show similar Li content in all current collectors. The fact that residual Li was found in Ni and Ti is surprising considering that no solubility for lithium can be found in their phase diagrams 100, 101, unlike for Cu. This experiment indicates that metals that according to their phase diagrams should be unreactive towards lithium might have some solubility for lithium. In fact, since both Ti and Ni contradict the common knowledge of inert current collectors one could expect similar behaviour for most metals.
4.6.4 Li barrier layer

In order to minimise Li trapping in the current collector, a candidate must be found that does not readily alloy with Li while maintaining the chief task of supplying the current to the electrode material. Since the small lithium atoms seem to readily diffuse into metals, the focus was on finding a suitable material with a very dense and rigid structure. Diamond was therefore selected based on the short and extremely strong bonding associated with its sp³ hybridisation. By introducing boron doping, the material can be transformed into a conductor while preserving the mechanical properties of diamond \(^{102}\).

To analyse the material as a possible Li diffusion barrier an analogous experiment to the one performed on Ti, Ni and Cu was carried out (see Section 4.6.3). Over the course of one week several samples were treated with lithium and analysed for their residual Li content. Li was indeed detected even for the boron-doped diamond samples but the levels were significantly lower than those observed for the metals, as is seen in Figure 29. The fact that Li levels at least 80 times lower were observed for the BDD suggests that the material is more resistant to Li diffusion. The hypothesis is further supported by the fact that the Li content remained stable over the course of one week. If Li can indeed penetrate into the BDD then an increasing Li content is to be expected over time. BDD electrodes exposed to Li were also analysed by SIMS. Through sputtering profiles it was established that essentially no Li could be detected inside the BDD film. BDD electrodes thus appear to be suitable current collectors for batteries based on metallic lithium (i.e. Li-alloy or Li metal) electrodes. Electrochemical analyses were therefore performed with extensive Li plating and stripping on a BDD electrode and a Cu reference sample.

Figure 29. Residual Li in boron-doped diamond after exposure to a lithium foil as measured by ICP-AES (a) as well as a comparison with the amounts found when exposing common current collector metals (i.e. Ni, Cu and Ti) to a Li foil for 7 days.

The electrochemical analyses were designed to deposit and remove 0.5 mAh charge of Li by using coulombic limitations during the cycling. Secondary
potential limitations were also used to insure that only the Li deposition/stripping reaction took place. The reaction reversibility was analysed by studying the ratio between the oxidation (i.e. $Q_{\text{ox}}$) and reduction (i.e. $Q_{\text{red}}$) charges. During the first two cycles the BDD electrode obtained 100 % $Q_{\text{ox}}/Q_{\text{red}}$ after which the efficiency dropped to 85 %. A gradual increase in efficiency followed up to 91 % to finally settle at 100 % efficiency after 95 cycles. The Cu electrode behaved slightly different with an initial decrease in efficiency followed by an increase culminating at 100 % efficiency after 28 cycles. Insight into the failing mechanism was obtained by studying the voltage profiles seen in Figure 30 b-c. Gradually increasing reductive potentials were required for the Cu electrode while no such behaviour was observed for the BDD electrode. In the latter case a steady lithium deposition potential of around -0.05 V was observed. The fact that both electrodes eventually regained full reversibility was found to be caused by short-circuiting of the cells due to Li dendrite growth.

![Figure 30. Li deposition and stripping on Cu (orange) and BDD (black) current collectors showing the ratio between the oxidation (i.e. Li stripping) and reduction (i.e. Li deposition) charges (a). Cell voltage profiles for Cu (b) and BDD (c).](image)

In order to investigate the effects causing the capacity loss, a cycled BDD electrode was probed by HAXPES. The electrode was removed from the lithium-ion battery cell in its oxidised state (i.e. the potential was 1 V vs. Li$^+/\text{Li}$) and analysed by synchrotron sourced HAXPES. A single peak at 284.5 eV was detected in the C1s spectra for both the sample and the reference sample. It is interesting to compare the binding energy for the cycled sample with that for the uncycled diamond reference sample. Li introduced into the BDD bulk by diffusion is expected to shift the C-C binding energy as has previously been observed for Li in graphite $^{103}$. Essentially no shift in binding energy could be observed, which however does not necessarily prove that the BDD film was impermeable to lithium. Nevertheless the results suggest that the extent of Li penetration is minor if present at all. It
would thereby seem that Li penetration into the BDD was not the reason for the poor efficiency seen during cycling in Figure 30. BDD electrodes are therefore believed to be suitable current collectors for anodes based on lithium deposition and stripping (i.e. Li-alloys or Li metal).

*Figure 31.* C1s HAXPES spectra for cycled boron-doped diamond (orange) and uncycled BDD (black) electrodes, respectively.
5. Conclusions

*Get your facts first, then you can distort them as you please.*
- Mark Twain

Nanostructured electrodes can be effectively produced via template-assisted electrodeposition. The key aspect of electrodeposition enabling fabrication of complex nanostructures has been the use of pulsed-electrodeposition. This strategy resulted in the successful growth of Cu, Sn and Al nanostructured substrates as well as advanced multi-layered Cu$_2$O/Cu nanostructured electrodes. Various coatings on 3D substrates have also been realised exclusively through electrodeposition. These include V$_2$O$_5$, Mn$_x$O, Li, Cu$_2$O and a polymer electrolyte. Nanostructured electrodes are ideal for studying electrochemical reactions taking place during energy storage as no binders or additives are required. Nanostructured electrodes have therefore been used to probe key aspects of electrochemical energy storage in lithium-ion batteries, mainly surrounding the conversion and alloying reaction.

Studies into the conversion reaction of Cu$_2$O revealed the presence of a distribution of particles with different sizes present in the material during cycling. The potential at which each particle was reduced/oxidised was found to be dependent on the particle size giving rise to a broad electrochemical potential window for the Cu$_2$O material. Essentially the entire Cu$_2$O could be converted to Cu and Li$_2$O during the initial reduction however only 50% of the charge could be extracted during subsequent oxidation. The initially lost capacity could however be retained during extensive cycling due to the electrochemical milling process which reduces the particle size and introduces new grain boundaries. The improved electrochemical performance is believed to originate from improved Li access due to the newly formed grain boundaries. Multi-layered rods with varied Cu$_2$O layer thicknesses were fabricated for which the electroactive layer for Cu$_2$O was found to be about 20-40 nm thick during low rate cycling and 5 nm thick during rapid cycling. The Li diffusion coefficient in Cu$_2$O is believed to be the limiting factor determining the electroactive layer thickness. Similar conclusions have been drawn for Ti$_2$O and could as such point towards a general feature for metal oxides.

The Li-alloying reaction was investigated for several different alloy-forming materials all of which showed signs of Li trapping during cycling. This limiting factor was found to occur when the material was partially lithi-
ated causing Li diffusion into the core due to a two-way diffusion process. The main limitation for these alloying materials has previously been believed to be the volume expansion occurring during Li insertion. The presented data suggests that Li trapping is the main limitation for nanostructured materials as the volume expansion was found to actually increase the capacity. The increased surface area created during volume expansion results in better access to the host material ultimately increasing the cell capacity.

Li atoms were furthermore seen to penetrate into the anode current collector causing a loss of capacity. The most common materials (i.e. Cu, Ti and Ni) were all found to host similar amounts of Li leading to the conclusion that most metals are permeable to Li. Li losses in the current collector constitutes a general problem for reversible energy storage and needs to be addressed if anodes handling metallic lithium (i.e. Li-alloy or Li metal) are to be introduced in future batteries. Conducting boron-doped diamond electrodes were investigated for this purpose. Several experiments where the BDD was exposed to Li metal indicated that little to no Li diffusion into the BDD electrode was present. BDD is therefore proposed as a viable current collector for anodes handling metallic lithium.
6. Svensk sammanfattning

1990 kommersialiserade Sony det första litiumjonbatteriet vilket startade den elektroniska revolutionen med utveckling av portabla elektriska enheter. Nu några årtionden senare är portabel elektronik en del av vardagen. För trådlösa enheter krävs strömkällor av lämpliga storlekar och energimängder, vilket har gjort att litiumjonbatteriet har erövrat elektronikmarknaden. Lithiumjonbatterier har förmågan att levera stora strömmar och kan sedan återuppladdas genom att man med en motriktad ström driver litiumjonerna tillbaka till deras ursprungsspositioner. Detta energitäta batteri används i nuläget i allt från mobiltelefoner till elektriska fordon.

Parallellt med den snabba utvecklingen av batterier inom portabel elektronik har också ett växande intresse uppkommit för batterianvändning i småskaliga tillämpningar. Små sensorer och robotar med dimensioner av en miljondel meter har utvecklats för diverse olika användningsområden så som medicinska implantat och så kallade labb-åt-ett-chip. Lithiumjonbatterier är även här den främsta kandidaten till att driva dessa system. Miniaturiseringen av lithiumjonbatterier introducerar dock nya utmaningar eftersom tillräcklig effekt och energitäthet ej uppnås med konventionell batteridesign. På samma sätt som höghus utvecklats för att få plats med en ökande population på en begränsad yta kan denna 3D princip också appliceras på lithiumjonmikrobatterier.

*Figure 32. Illustration av hur en större mängd laddning kan lagras i en 3D arkitektur till skillnad mot den konventionella 2D arkitekturen.*
3-dimensionella elektroder används i mikrobatterier för att kunna lagra en större laddningsmängd på en begränsad area. Genom att belägga dessa 3D strukturer med en tunn film av aktivt material kan även hög effekt erhållas då litiumjonerna snabbt transporterar genom materialet. 3D strömtiledare utgör stommen av elektroden där den utökade arean erhålls av den 3-dimensionella arkitekturen som kan åstadkommas på olika sätt. Genom att elektrokemiskt klä 3D strukturer med ett aktivt material (t ex. kopparoxid) behövs inga bindemedel eller additiv för elektroden. 3D elektroder kan därmed användas för att effektivt studera viktiga mekanismer kring energilagring i litiumjonbatterier.

I denna avhandling har 3D strömtiledare tillverkats genom elektrodeponering för att därefter beläggas med en tunn film av elektrodmateriale. Elektrodeponering använder ström för att deponera strukturer och för att belägga dessa med olika elektriskt ledande material. Med hjälp av denna metod har cylinderformade nanometer stora pelare av aluminium och koppar deponrats på ett substrat. 3D aluminium nanopinnar har sedan täckts med ett tunt lager vanadinoxid genom att först deponera manganoxid vilket möjliggör deponering under de oxidande förhållanden som krävs för vanadinoxid. 3D koppar nanopinnar har en naturlig oxid som kan lagra laddning i ett litiumjonbatteri. Multilagrade 3D koppar elektroder har även framställts där omväxlande skikt av koppar och kopparoxid utgör nanopinnarnas struktur. Energilagring i kopparoxid uppstår genom en konverteringsreaktion där kopparoxid omvandlas till kopparnanopartiklar i en litiumoxidmatris. Ett flertal studier kring denna reaktion har visat att partiklar med olika storlekar finns i material samt att deras storlek bestämmer vid vilken potential de reagerar. Kopparoxidens reaktion med litiumjoner leder även till elektrokemisk målning av materialet vilket ger succesivt mindre partiklar och på så sätt skapas nya transportvägar för litiumjonerna in i materialet.

Energilagring kan även åstadkommas genom att lagra litium i legeringsmaterial (t ex. Si och Sn). Denna process medför en stor volumexpansion då en ansenlig mängd litium införs i materialet vilket gör att hela elektroden sväller. Legeringsmaterial är kända för hög kapacitet men dålig stabilitet under flertal battericykler. Denna bristande prestanda har tidigare förklarats genom volumexpansionen som uppstår när legeringen bildas. I denna avhandling presenteras en annan modell vilken bygger på att litium diffunderar in i material vilket försvårar processen att extrahera allt litium och på så sätt fastnar en del litium i elektroden.
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Don’t worry, everybody gets paid.
-Leif Hammarström

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