Microfabricated Thin-Film Batteries: Technology and Potential Applications

by

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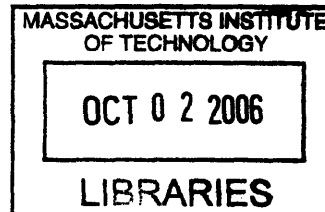Massachusetts Institute of Technology

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ABSTRACT

High-energy-density lithium ion batteries have enabled a myriad of small consumer-electronics applications. Batteries for these applications most often employ a liquid electrolyte system. However, liquid electrolytes do not allow for small scale and thin-film production as they require hermetic sealing. The aim for batteries in any size or shape, without the restrictions liquid components pose, has led to the development of solid electrolyte systems. All-solid-state thin-film batteries add a new dimension to the space of battery applications.

The purpose of this thesis is to assess the application potential for solid-state thin-film batteries, particularly with regard to CMOS integration. Such batteries were developed with the aim of creating a power unit on a silicon microchip. The various degrees of integration of thin-film batteries on a silicon wafer are examined. All of them show limitations that make fabrication of batteries on a wafer not viable at present from a business standpoint.

A search for other commercializable applications for thin-film batteries leads to solid-state bulk batteries made from thin-film batteries. The underlying technology here as well as the market situation and a potential business model are discussed.

Thesis Supervisor: Eugene A. Fitzgerald
Title: Merton C. Flemings-SMA Professor of Materials Science and Engineering

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Julia Greiner
Cambridge, July 2006

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Chapter 1

Introduction

1.1 Technology

Rechargeable batteries are used in a wide range of applications. In recent years, especially lithium-ion batteries experienced a large increase, taking over 50% [Linden and Reddy, 2002] of the market share for small consumer electronics applications. The performance reached by small portable consumer electronics, such as laptop computers or cell phones, today would not be possible without the development of Li-ion batteries and the high energy density, cycle life, and rate capacity they offer in a safe and low-cost product.

A specialized type of Li-ion batteries are thin-film, solid-state devices. These batteries were originally developed for semiconductor and printed circuit board applications. They are fabricated by thin-film deposition of all components, including a solid electrolyte.

Prof. Fitzgerald's group in the Department of Materials Science and Engineering at MIT took up this topic with the aim of creating a power unit on a microchip and integrating the energy supply unit on a silicon integrated circuit. This work required the development of a thin-film solid-state battery that is compatible with silicon integrated circuit fabrication methods. Thin-film *integrated* lithium-ion batteries were successfully produced in the course of this research.

1.2 Application Potential

Complementary metal oxide semiconductor (CMOS) technology is the most common dynamic random access memory (DRAM) element today. CMOS technology combines both n-channel and p-channel metal oxide semiconductor field effect transistors (MOSFETs) on a single substrate. These devices consume insignificant current except when switching from one logic state to the other. The low power consumption of CMOS technology makes thin-film batteries an appropriate power source for CMOS memories.

The feasibility of fabricating ultra-thin solid-state batteries in a way compatible with microelectronics processing technology allows integration on a wafer. Cells can be fabricated on the back of a wafer using integrated circuit processes. They can also be deposited on the back of a wafer that has CMOS circuits built on the front, and they could even be produced as an additional circuit element to provide local power within an integrated circuit.

Also the use of thin-film batteries in a rolled or stacked manner for bulk batteries as well as applications for non-volatile RAM may be useful and are assessed in this thesis.

1.3 Objectives

The objective of this thesis is to find a suitable application for CMOS-integrated or non-integrated thin-film batteries and develop a business model for it. To do so, several issues have to be addressed. After summarizing the necessary battery background, this thesis will assess various application possibilities of thin-film and in particular integrated thin-film batteries and address the optimal amount of integration with CMOS technology. The intellectual property situation one faces when commercializing thin-film batteries as well as competing technologies will also be discussed. Finally, in the course of proposing a business model the market situation for Li-ion batteries is analyzed.

Chapter 2

Technology

2.1 General Battery Background

A battery is an electrochemical cell that converts the chemical energy contained in its active materials into electric energy. This conversion happens by means of an electrochemical oxidation-reduction reaction.

2.1.1 Components of a Battery

The major components of a cell are two electrodes, referred to as the anode and cathode, and an electrolyte.

Anode The anode is the negative or reducing electrode which gives up electrons to the external circuit and is oxidized during the reaction. It can also be seen as a source of ions that move through the electrolyte. The anode should have low electronegativity and high electronic conductivity and is typically a light metal or metal-containing compound. Other desired properties of the anode are high coulombic output (quantified in units of Ah/g), ease of fabrication, and low cost.

Cathode The cathode is the positive or oxidizing electrode. It accepts electrons from the external circuit and is reduced during the electrochemical reaction. To enable fast electron

exchange, the cathode should have high electronic conductivity as well as high diffusivity and high insertion capability for the ion species of interest. These ions are inserted into and extracted from the cathode during charge and discharge, respectively.

Electrolyte The electrolyte provides the medium for charge transfer between the anode and the cathode. It should be ionically conductive and electrically insulating, which in practice is fulfilled by a high ionic conductivity compared to the electronic conductivity. The electrolyte is also required to build good contact with the electrode surfaces and to be chemically stable to avoid direct chemical reaction with the electrode materials. Typically, the electrolyte is a liquid, such as water or other solvents with dissolved salts, acids, or alkalis to grant ionic conductivity. Some batteries, including thin-film batteries, use ionically conductive solids as electrolytes.

The most advantageous combinations of anode, cathode, and electrolyte materials are those that will be lightest and give the highest cell voltage and capacity.

2.1.2 Operation of a Battery

When the cell is connected to an external load it is discharged, i.e. electrons flow from the anode, which is oxidized, through the load to the cathode, which is reduced. Once a neutral atom in the anode releases an electron to the outside circuit, the remaining ion travels through the electrolyte to the cathode where it receives an electron in a reduction reaction. Generally both positive and negative ions travel through the electrolyte to the cathode and anode respectively.

The driving force that enables the battery to deliver electrical energy to an external circuit is the change in the standard free energy ΔG^0 of a cell reaction. This can also be seen as the difference in the chemical potential of the transferred element between the anode and cathode. For two metal electrodes it is the difference in chemical potential between the two metals.

The standard free energy ΔG^0 of a cell reaction can be expressed as

$$\Delta G^0 = -nFE^0 \qquad (2.1)$$

n number of exchanged electrons per reaction (equal to the valence of the positive ion)

F Faraday's constant (96,487 C)

E^0 standard electromotive force or open-circuit voltage of a cell

Although the available energy of a battery depends on the electrochemical reactions at the electrodes, there are many factors that affect the magnitude of charge transfer. Losses occur primarily through activation polarization, which drives the electrochemical reaction at the electrode surface, and concentration polarization, which arises from the concentration differences of the reactants and products at the electrode surface and in the bulk. These effects consume part of the theoretically available energy and give it off as waste heat, thus not all the energy can be converted into electrical energy.

2.1.3 Classification of Batteries

The broadest classification is the battery's capability of being electrically recharged. Primary cells are non-rechargeable and secondary cells are rechargeable.

Primary Batteries   These batteries are discharged once and then discarded. They usually have a good shelf life, high energy density at moderate discharge rates, and little or no maintenance requirements.

Secondary Batteries   These batteries can be recharged to their original condition by passing current through them in the opposite direction to the discharge current. They have relatively high power density and high discharge rates. The energy density of secondary batteries is generally lower than that of primary batteries.

The specific energy of bulk lithium primary batteries reaches about 250Wh/kg whereas the bulk lithium-ion secondary batteries can reach around 150Wh/kg [Linden and Reddy, 2002]. Thin-film solid-state batteries can have higher energy densities as will be discussed in Section 2.2.

2.1.4   Theoretical Voltage, Capacity, and Energy

Theoretical Voltage   The standard potential of a cell can be calculated from free energy data of the active materials contained in the cell. The anode oxidation potential and the cathode reduction potential add up to the standard cell potential E^0 or open-circuit voltage (OCV). Standard reduction potentials for many materials are listed in tables, for instance in [Linden and Reddy, 2002].

Theoretical Capacity   While the theoretical voltage of a cell is determined by the type of active materials in the cell, the theoretical capacity is determined by the amount of active materials in the cell. It is the total quantity of electricity involved in the electrochemical reaction and is given in C or Ah or Ah/g. The electrochemical equivalents (atomic weight of the active materials in grams divided by the number of electrons involved in the reaction, given in g/Ah) for many materials can be found in tables [Linden and Reddy, 2002]. Usually the theoretical capacity is based on the active materials only. The electrolyte and other materials in the cell are not included in the weight for the capacity calculation.

Theoretical Energy   The capacity of a cell can also be expressed in terms of the energy that can be delivered. The theoretical energy (in Wh) is the standard potential (in V) times the theoretical capacity (in Ah). The specific energy is given in Wh/g and can be calculated taking only the active materials into account. However, it is more useful and more common to express it in terms of the weight of the whole battery. In this thesis the latter definition of specific energy will be used.

2.2   Thin-Film Solid-State Li-Ion Battery

2.2.1   Thin-Film Battery History

According to [Osaka and Datta, 2000], the first thin-film lithium batteries were reported in 1983 by a Japanese group [Kanehori et al., 1983]. They employed TiS_2 cathodes, amorphous lithium phosphosilicate electrolytes, and lithium anodes. This device turned out to be impractical as the electrolyte composition did not exhibit long-term stability in contact with lithium.

In another study a ternary sulfide glass electrolyte was used, which was observed to react with lithium forming a resistive film which caused a large increase in cell resistance [Creus et al., 1989]. The electrolyte instability problem was solved by coating the electrolyte with a layer of lithium iodide. LiI is stable in contact with lithium metal at the required potential but cannot be used alone as an electrolyte because of too-high electrical conductivity.

The development of lithium phosphorous oxynitride (LIPON) electrolytes advanced the thin-film battery technology. LIPON electrolytes are stable up to 5.5V versus lithium electrodes and do not need a protective layer. Goldner et al. first reported the fabrication of thin-film Li-ion batteries using a LIPON electrolyte, a $LiCoO_2$ cathode and a carbon anode [Goldner et al., 1996].

From there on, Oak Ridge National Laboratory (ORNL) set the benchmark for thin-film solid-state batteries. Most publications on thin-film batteries reference ORNL's work on batteries, and many are published by ORNL.

2.2.2 General Background

2.2.2.1 Li-Ion Rechargeable Batteries

Lithium is one of the most common active elements in solid-state batteries. It has low molecular weight (6.94g/mole), small ionic size (12.5nm radius) and low electronegativity (0.98Pauling) [Ariel, 2005]. Li-ion cells employ lithium intercalation compounds as positive and negative electrodes. Li ions travel back and forth between the electrode materials as the cell is charged and discharged, which is why Li-ion batteries are also referred to as rocking-chair batteries. The electrodes are typically materials with a layered or tunneled structure, and Li ions are intercalated or extracted from the interstitial space between the atomic layers of the active materials when the battery is charged or discharged. This mechanism is illustrated in Figure 2.1.

2.2.2.2 Solid-State Electrolyte

Most commercially available batteries use a liquid electrolyte. A liquid electrolyte has several advantages, including perfect contact with the electrodes and high ionic conductivity.
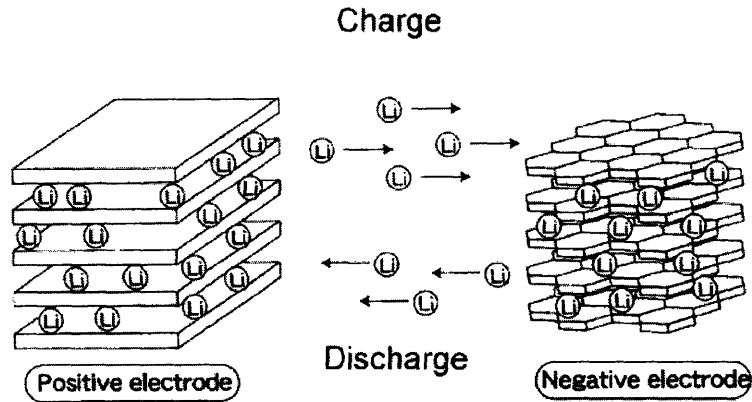
Figure 2.1: Charge/discharge mechanism of a Li-ion battery. Adopted from [Takamura, 2002].

Cells that contain a liquid electrolyte, however, may suffer from corrosion of the electrodes and also need hermetic and heavy packaging due to safety reasons.

An all-solid-state battery can achieve higher energy densities than liquid electrolyte batteries. It is the quality of the interface between electrodes and electrolyte and the lower ionic conductivity of the solid electrolyte that comprise the drawbacks. Solid electrolytes are much less temperature sensitive than liquid electrolytes. One reason that led to the development of solid-state batteries was the need for power sources for microelectronics applications. In such applications the batteries must survive solder re-flow conditions, nominally 250°C in air or nitrogen for 10 minutes. Batteries with liquid or polymer electrolytes and also cells that employ Li metal cannot sustain these conditions [Linden and Reddy, 2002].

The most common electrolyte used for solid-state batteries is the glassy lithium phosphorus oxynitride (LIPON). It is stable in contact with metallic (elemental) lithium up to potentials of 5.5V and has acceptable conductance in thin-film form [Yu et al., 1997], [Schultze et al., 2002].

2.2.3   Design of a Thin-Film Battery

A schematic drawing of a thin-film battery developed in ORNL is shown in Figure 2.2. The cells are fabricated by sequential deposition of the components. Most parts are deposited by radio frequency (RF) magnetron sputtering, except for the metallic current collector components, which are deposited by DC magnetron sputtering [Osaka and Datta, 2000]. ORNL developed Li, Li-free, and Li-ion batteries. Only the last ones will be discussed here. Lithium batteries (lithium anode) cannot survive the high temperatures required for the solder re-flow process as the melting point of lithium is 180.5°C. Li-free batteries with *in situ* plated lithium anodes [Neudecker et al., 2000] can only survive solder re-flow conditions prior to the initial plating which happens during initial charging.

Thin-film Li-ion batteries can be as thin as 1.4μm [Lee et al., 1999]. Typically such batteries are up to 25μm thick and have areas from a few square millimeters to tens of square centimeters.
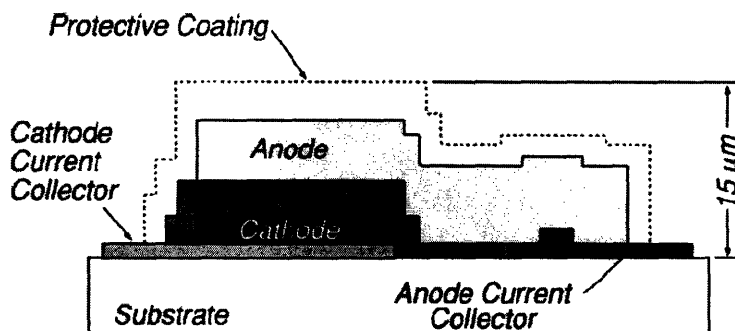
Figure 2.2: Schematic cross section of a thin-film lithium battery. Adopted from [Dudney, 2005].

2.2.4   Electrical Performance

The electrical properties of a thin-film battery depend very much on the cathode material. A very common cathode material is $LiCoO_2$. It has an OCV of 3.6-4.7V versus Li [Ariel, 2005] depending on the deposition conditions. Its obtainable theoretical energy density,

assuming full intercalation of one Li ion per CoO_2 unit cell and an average voltage of 4V, is approximately 1000Wh/kg. However, the CoO_2 structure becomes unstable when less than half of the Li is intercalated. Thus a more realistic theoretical energy density value is about 500Wh/kg [Ariel, 2005].

$LiCoO_2$ capacities from $59\mu Ah/cm^2\mu m$ [Jeon et al., 2005] to $69\mu Ah/cm^2\mu m$ [Dudney and Jang, 2003] were achieved with crystalline $LiCoO_2$ cathodes. The capacity of the active material is measured in units of $\mu Ah/cm^2\mu m$, which means μAh per cm^2 per μm layer thickness. Discharge is limited by the diffusive transport in the cathode and maximum power can only be achieved with very thin anodes. The trade-off here is that the cathode in this battery contains the lithium and thus its thickness determines the capacity of the battery. The thicker the cathode, the smaller the percentage of the maximum capacity that can actually be supplied from the battery.

Common anode materials amongst others are SiTON and V_2O_5, which typically offer OCVs in the 1.5 to 4.2V range. The specific energy density of the whole battery depends on all layers and their weight and is reported to reach up to 300Wh/kg [Cymbet, 2006].

2.3 Thin-Film Solid-State Integrated Battery

Nava Ariel in the Fitzgerald group at MIT applied microelectronics thin-film and processing expertise to fabricate ultra-thin batteries with overall thicknesses starting from $0.55\mu m$. Chemical mechanical polishing (CMP) was used to reduce the surface roughness of the layers considerably, allowing for a very thin electrolyte and very good interfacial quality between electrolyte and electrodes. This results in a lower battery series resistance and enables charging at faster rates.

2.3.1 Cell Design and Fabrication

Ariel's battery uses vanadium oxide (V_2O_5) as the anode, LIPON as electrolyte, and $LiCoO_2$ as a cathode. The cells are fabricated on silicon using microelectronics compatible processes that can also be used to deposit the cells on the back of microchips after the front-side circuitry is fabricated. First a metalization layer is deposited by e-beam evaporation. The $LiCoO_2$ layer is deposited by RF sputtering from a $LiCoO_2$ target in an argon environment. The LIPON layer is sputtered from a Li_3PO_4 target in a nitrogen environment

and the V_2O_5 layer is sputtered in an argon environment with oxygen background. The last layer is the upper metal contact of aluminum, which is deposited by DC sputtering. The wafer is then patterned using photolithography to produce cells of $2x2mm^2$, $1x1mm^2$, and $0.5x0.5mm^2$ size. Figure 2.3 shows a schematic illustration of the cell.
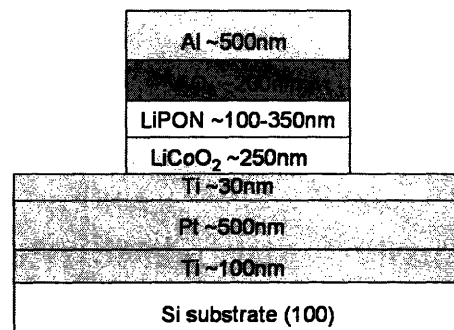
Figure 2.3: Schematic cross section of a V_2O_5/LIPON/LiCoO$_2$ battery. Modified from [Ariel, 2005].

2.3.2 Electrical Performance

V_2O_5 has an OCV of 3-3.7V versus lithium and $LiCoO_2$ has an OCV of 3.6-4.7V versus lithium [Ariel, 2005]. Based on these values the OCV for the V_2O_5/LIPON/LiCoO$_2$ system is about 1.5V. As the cell layers are so thin, the amount of charge that can be extracted from the cell is small. The capacity of $LiCoO_2$ is $69\mu Ah/cm^2\mu m$ (see Section 2.2.4). For a very thin cell like the one shown in Figure 2.3 with a cathode thickness of 250nm the capacity turns out to be $17.3\mu Ah/cm^2$. With an OCV of 1.5V this translates to an energy density of the $LiCoO_2$ of 206Wh/kg. This value is lower than that given in Section 2.2.4 as it takes the OCV of the V_2O_5/LIPON/LiCoO$_2$ into account which is lower that the OCV of $LiCoO_2$ versus lithium. Taking the weight of all battery components into account (electrolyte, electrodes, and metal contacts) with thicknesses as in Figure 2.3 and a 100nm thick electrolyte, the energy density of the hole battery is 17.8Wh/kg. This calculation shows that reduction of thickness in this extreme does not result in high energy density.

The main performance benefit of making a battery as thin as possible is the lower series resistance which results from the ultra-thin electrolyte and the possibility to charge at faster rates. Higher capacity values can be achieved by fabricating the cell in larger areas or by connecting the cells in parallel using multilevel fabrication technology used in microchip processing. The only possibility to increase energy density is to increase the thickness of the $LiCoO_2$ layer relative to the other layers.

2.4 Liquid Electrolyte Lithium-Ion Batteries

This section contains a short introduction in the performance and fabrication methods for Li-ion bulk batteries. Later in this thesis the application of thin-film batteries for the production of bulk batteries will be discussed and compared to the liquid electrolyte battery.

2.4.1 Electrical Performance

Existing Li-ion systems achieve an OCV of 2.5-4.2V and a specific energy of about 150Wh/kg. A comparison of Li-ion systems to other battery chemistries in terms of energy densities of conventional small, sealed battery systems is shown in Figure 2.4. The capacity ranges from 0.1Ah in small cells to 160Ah in large cells. A discharge rate of 5C continuous or 25C pulse has been demonstrated [Linden and Reddy, 2002]. (The current necessary to charge a battery from zero to full charge in 1 hour is referred to as the battery's 1C rate. The 5C rate is the current to charge or discharge the battery in 1/5 hours. For example for a 10Ah battery this would be 50A.)

Li-ion batteries have no memory effect, low self discharge, and long cycle life and are mainly used for mobile consumer electronics.

One disadvantage of Li-ion batteries is that they degrade when discharged below 2V and may vent when overcharged. Management circuitry that prevents over-charge or over-discharge has to be employed.
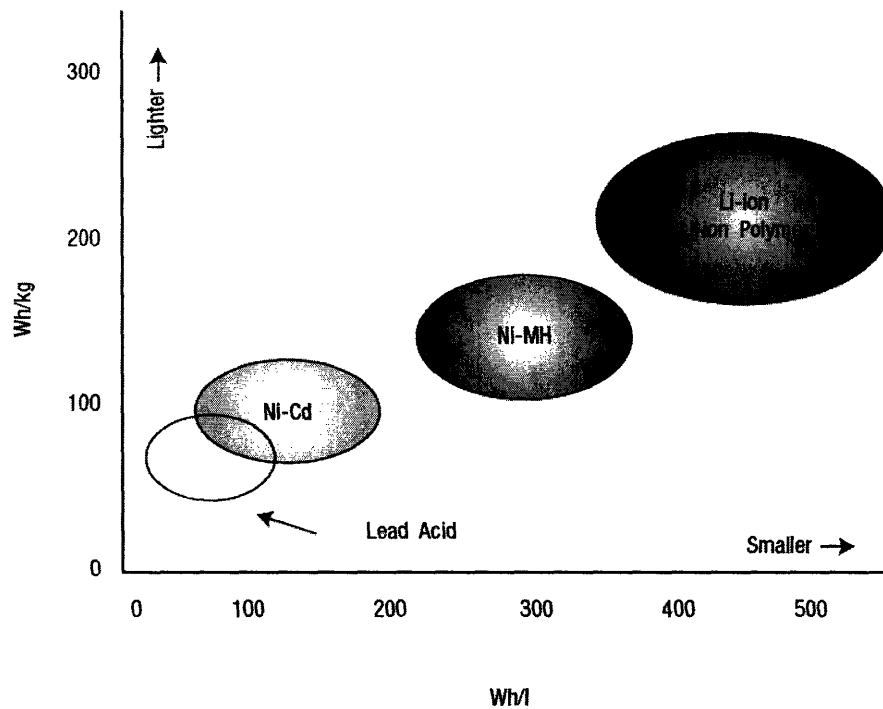
Figure 2.4: Comparison of energy densities of small, sealed battery systems. Adopted from [Brodd, 2005].

2.4.2 Structure

Li-ion batteries use a lithium metal oxide, often $LiCoO_2$, on a current collector of aluminum foil as a cathode. Typically graphitic carbon on a copper current collector is used as the anode. In the charge and discharge process the Li ions are extracted from or inserted into interstitial space between atomic layers of the anode and cathode materials. Most Li-ion batteries use liquid electrolytes, consisting of solutions of a lithium salt (e.g., $LiPF_6$) in an organic solvent. The electrolyte is usually almost completely absorbed into the electrode and separator materials. To meet the market demand, different designs of Li-ion batteries were developed, the most common being wound cylindrical or wound prismatic cells. Figure 2.5 shows a cross section of a wound cylindrical cell and Figure 2.6 shows a wound prismatic cell.
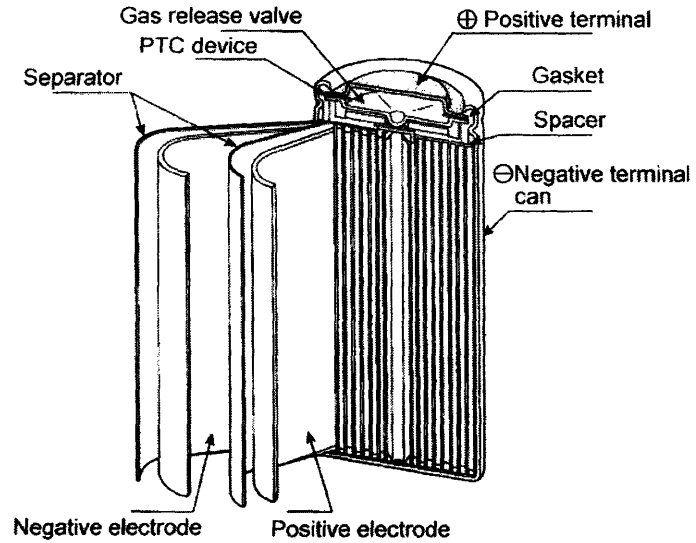
Figure 2.5: Cross-sectional view of a cylindrical Li-ion cell. Adopted from [Takamura, 2002].
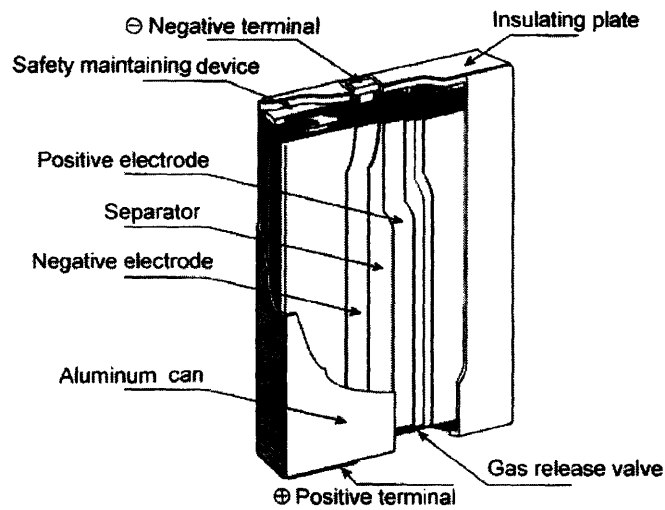
Figure 2.6: Construction of a prismatic Li-ion cell. Adopted from [Takamura, 2002].

2.4.3 Fabrication

A cathode mix is made from $LiCoO_2$, a binder, and a solvent material. This mix is coated on the aluminum foil (20μm thick). The anode mix is made from carbon, binder, and solvent and coated on a copper foil (10μm thick) current collector. The coating is done on both sides of the foil and is for both electrodes approximately 100μm thick. Dried rolls of electrodes are sliced into the required width and rolled up together with a separator. After the cell is inserted into a can, the anode lead is welded to the bottom of the can, electrolyte solution is added, the cathode lead is welded to the safety vent, and the can is closed with a crimped top cover.

One of the crucial points in this design is the adhesion of the electrode material to the current collectors. The binder is a polymer and plays an important role in adhesion. A trade-off decision has to be made on the amount of binder used. More binder improves adhesion, but it also influences energy capacity and drain capability.

Chapter 3

Applications

In this chapter different degrees of integration of a battery on a wafer are assessed. Applications that comprise just producing batteries on a wafer, batteries on the back of a microchip, and batteries on the front of a microchip within the electronic circuit will be explored. Furthermore multilayer thin-film batteries, Li-ion bulk batteries made from rolled-up thin-film batteries, and non-volatile memory applications will be discussed.

3.1 Considerations in Selecting a Battery

Before starting to think about possible applications one should recall a number of factors that must be considered when selecting a battery for a particular application.

An extensive list of selection considerations can be found in [Linden and Reddy, 2002]. Selected items of this list include:

- Type of battery: Primary or secondary.

- Electrochemical system: Matching the battery characteristics with the application requirements.

- Voltage: Operating voltage, maximum and minimum permissible voltages, profile of discharge curve.

- Load current and profile: Constant current, constant resistance or constant power; single-valued, variable, or pulsed load.

- Temperature requirements: Required operation temperature range.

- Service life: Time operation is required.

- Physical requirements: Size, shape, weight, and terminals.

- Charge-discharge cycle: Cycle requirement, characteristics of charging source.

- Environmental conditions: Vibration, shock, acceleration, pressure, humidity.

- Safety and reliability: Outgassing, leaking; failure rates.

- Maintenance: Ease of battery acquisition, replacement, and disposal or recovery.

- Cost: Initial cost, operating cost.

Not all of these items will be addressed in this paper as the technology under inspection is not very mature yet. There is, for example, no data existing on the possible service life and cycle life of the ultra-thin integrated batteries. But all of these points will become important once the basic potential of integrated batteries is known. However, when looking for thin-film battery applications in general (not only for ultra-thin integrated batteries) all points of the above list can already be addressed, as thin-film batteries have become a quite mature technology by now and are already being produced and sold.

One generalization can also already be made about solid electrolyte batteries. They are low-charge-rate batteries, operating in the microampere range with very long operational and shelf life. Therefore solid electrolyte thick-film batteries have been used in memory backup, cardiac pacemakers, and other applications that require high reliability and safety and long active life.

3.2   Competing Technologies

Batteries for Micropower Applications   The most common batteries for micropower applications today are thick-film cells (4-8mm thick) and miniature button cells. They are not directly comparable to thin-film cells because of their much bigger size and higher capacity. However, indirectly they are a competitive technology as thin-film batteries could reduce the need for button cells by providing power to a microchip directly in an integrated manner.

Ultracapacitors Another device that can be a competitor in some applications is the ultracapacitor or double layer capacitor (DLC). The peak specific power of DLCs is up to 100 times higher than that of batteries whereas the energy density is generally 20 to 50 times lower than that of batteries. Compared to regular capacitors, the capacity of ultracapacitors is 100 times higher than that of regular dielectric capacitors.

An ultracapacitor does, like a battery, have two electrodes and an electrolyte. Each electrode/electrolyte interface represents one capacitor and the complete cell can be considered as two capacitors in series. An advanced double layer capacitor uses high specific area carbon ($>1000 m^2/g$) as an electrode. Energy storage is achieved by ion accumulation at the electrode/electrolyte interface by the double layer effect [Osaka and Datta, 2000]. The specific capacitance is proportional to the carbon surface area and with $2000 m^2/g$ carbon a specific capacitance of $100F/g$ [Osaka and Datta, 2000] can be reached. Depending on the technology, voltages from $<1V$ to $3V$ are achieved. Due to the completely electrostatic operation, DLCs have very long cycle life.

Ultracapacitors are slowly approaching battery performance in terms of energy density. A carbon nanotube (CNT) enhanced ultracapacitor that has a very high surface area due to vertically aligned CNTs is being developed and is expected to achieve an energy density higher than 60Wh/kg [Signorelli et al., 2006].

The main ultracapacitor applications are in large current supply or as a secondary power source for undesired voltage drops. In lower power applications (less than $500\mu A$ backup current) ultracapacitors can be used as power backup for primary power outages for CMOS microcomputers and RAMs [Osaka and Datta, 2000].

Comparison of Energy Densities The energy densities of ultracapacitors, Li ion bulk batteries and Li ion thin-film batteries are compared in Table 3.1. Clearly ultracapacitors are favorable in applications where high power densities are needed, but cannot compete with the thin-film battery's energy densities.

A comparison of the energy densities for different battery chemistries is shown in Section 2.4.1 in Figure 2.4. Only Li-ion batteries are considered in this thesis, as they offer the best performance today.

Table 3.1: Comparison of energy densities for ultracapacitors and Li-ion batteries

Technology	Energy density [Wh/kg]	
Double layer capacitors	6	[Signorelli et al., 2006]
CNT enhanced capacitors	60	[Signorelli et al., 2006]
Li ion batteries (bulk)	100-158	[Linden and Reddy, 2002]
Li ion thin-film batteries	up to 300	[Cymbet, 2006]

3.3 Batteries on a Wafer

An ultra-thin integrated battery alone, like the one shown in Figure 2.3 on a silicon wafer, does not seem to have a lot of application potential. This battery would have to be mounted on the device it should power. If, however, the application has a size that allows a battery to be mounted on it, there is usually not much more utility for a very thin battery of $0.55\mu m$ compared to say a $15\mu m$ thin-film battery. On the contrary, the $15\mu m$ battery has a greater utility for most applications because of its much higher capacity.

Thus the fabrication of ultra-thin integrated batteries alone does not bear much application potential.

3.4 Batteries on the Back of a Microchip

3.4.1 Powering Ability of an Integrated Thin-Film Battery

The powering ability of a Li-ion thin-film integrated battery was compared to the requirements of existing technologies by Nava Ariel [Ariel, 2005]. Her calculation is reproduced here. A dynamic random access memory (DRAM) microchip with a size of $1.27cm^2$, consisting of $9.7 \cdot 10^7$ transistors (that is $7.6 \cdot 10^7$ transistors per cm^2) and operating at a clock speed of 1.684GHz, was considered. This chip consumes 2.4W, which is 2.182A at 1.1V. The calculation showed that $1.21 \cdot 10^5$ layers of $1.27cm^2$ area of the $0.55\mu m$ battery (with a 250nm thick $LiCoO_2$ layer) are needed to power the whole chip for an hour. This result means it is not possible to power such a chip with this multilayer technology as this would involve an unrealistic number of fabrication steps.

The calculation also shows that one layer could power 801 transistors at 1.684GHz or ten layers could power $1.35 \cdot 10^5$ transistors at 10MHz. These numbers indicate that the thin-film integrated battery could be practical on the back of a microchip for certain low power applications, for instance simple processors for microrobots.

3.4.2 Issues with Integration on a Chip

The idea of producing batteries on the back of a microchip is not only constrained by power requirements. It is also not favorable in terms of fabrication yield. In the semiconductor industry, converging production processes are always preferable to sequential processes as this results in additive yield losses instead of multiplicative yield losses. Building the battery on the back of a chip puts at risk all of the value that has been built into the chip.

These considerations suggest that the reasonable way to go is to produce the chip and battery separately and then stick them together but not produce them in an integrated manner. Also thicker cells and different material systems customized for the requirements of the microchip can be used this way.

Thin-film batteries that can be attached to the chip during assembling or packaging after the fabrication process offer a number of promising application possibilities, many of which are already pursued today by thin-film battery start-up companies. The batteries can add functionality and improve performance of integrated circuits, for example as a rechargeable power source for non-volatile SRAM, real-time clocks and microcontrollers.

Another very promising field is radio frequency identification (RFID). RFID tags are widely used in tracking, monitoring, identification, and security applications. Thin-film batteries could make RFID tags active leading to a large increase in reading and writing range without adding noticeable weight or volume to the tag.

Medical electronics also constitute a field of application for thin-film batteries, not only because of their size but also because of their safety due to solid electrolytes. Thin-film batteries can be used for implants, monitoring, diagnostic medication, micro-electro-mechanical systems (MEMS), and hearing aids.

3.5 Batteries as an Additional Circuit Element

Microelectronics-compatible fabrication methods make it possible to use thin-film integrated batteries as an additional circuit element to provide local power within the circuit. Interviews with Prof. Sodini from the Department of Electrical Engineering and Computer Science at MIT and people from R&D at Infineon Technologies showed that there is no apparent use for batteries within the circuit. The fact that circuit designers do not see a use for local power within the circuit at present might also be due to the fact that they are not used to having power sources available for integration.

There are, however, people in the field of microelectronics who expect microbatteries to play a significant role in microelectronic architectures. Minko Balkanski [Balkanski, 2000] believes that power generated on the spot rather than having it distributed from a remote power source will avoid major drawbacks in present architectures, electrical conduction leaks, and power losses. Once circuit designers see batteries as an additional tool, non-obvious applications within a circuit my become apparent and the use of distributed power sources could lead to a new type of three-dimensional integration in microelectronics.

3.6 Multilayer Thin-Film Batteries

A bulk battery can be produced by stacking many battery layers and connecting them in parallel or in series to achieve higher capacity or voltage, respectively.

Nava Ariel compared multi-layer thin-film V_2O_5/LIPON/$LiCoO_2$ cells to laptop and cell phone batteries [Ariel, 2005]. She assumed the layered cells to be connected in parallel with a bimetal contact layer consisting of 30nm of titanium and 500nm of aluminum for both electrodes and a silicon oxide layer between the cells as an insulating layer. A schematic illustration of this structure can be seen in Figure 3.1. The cells are connected by metal vias with insulated sidewalls.

A typical laptop battery with a capacity of 6600mAh is 2cm thick with an area of 184cm^2 and a weight of 500g. To estimate the number of battery layers needed, Nava Ariel uses the theoretical capacity available from a 500nm thick $LiCoO_2$ layer on an area of 184cm^2, assuming that 50% of the Li is free to leave the material. This active layer thickness results in 2526 layers connected in parallel needed to achieve the 6600mAh for
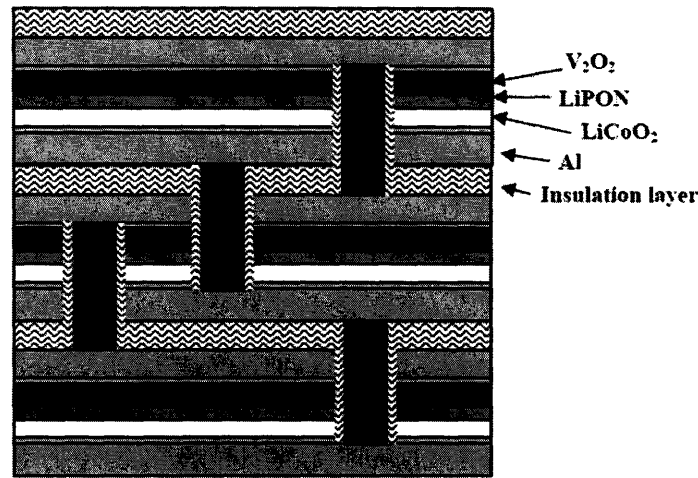
Figure 3.1: Schematic illustration of a multi-layer thin-film V_2O_5/LIPON/LiCoO$_2$ battery. The figure shows a stack of three cells connected in parallel. Adopted from [Ariel, 2005].

the laptop battery. The weight of this multi-layer battery turned out to be 295.18g, which is a 41% weight reduction compared to the 500g of a typical laptop battery.

The calculation outlined above, however, does not take the voltage requirements for a laptop battery into account. Typically laptop batteries have a voltage of 10.8V, some batteries have 9.4V, some even 14.8V (http://www.laptopbattery.net/). Assuming a voltage of 10.8V, the battery mentioned above with 6600mAh and 500g has a specific energy of 142.6Wh/kg. This value agrees with energy densities for Li ion bulk batteries with liquid electrolytes of 100-158Wh/kg given in literature [Linden and Reddy, 2002]. The energy density of the 2526 layer thin-film V_2O_5/LIPON/LiCoO$_2$ battery, which has an OCV of 1.5V (see Section 2.3.2), with 6600mAh and 295.18g, is 33.5Wh/kg.

Thus no weight reduction can be achieved with stacked ultra-thin integrated batteries as the energy density is too low to compare with Li-ion bulk batteries. For thicker thin-film batteries with a thickness of up to 30μm, energy densities of up to 300Wh/kg were demonstrated (see comparison of energy densities on page 31). These cells, if produced in many layers, can offer higher energy density than Li-ion batteries with liquid electrolytes. It would be most efficient to fabricate these batteries on large-area flexible substrates, which could be rolled up. Li-ion batteries with liquid electrolytes are produced in such a way.

3.7 Bulk Batteries from Rolled-up Thin-Film Batteries

As investigated in the previous section, ultra-thin-film batteries are not useful for the fabrication of bulk batteries, but thicker thin-film batteries could be very useful for that purpose. Thin-film batteries achieve reported energy densities of up to 300Wh/kg [Cymbet, 2006]. A bulk battery rolled-up from a thin-film battery can achieve higher energy densities than current Li ion systems with liquid electrolytes (around 150Wh/kg for liquid electrolyte systems, see page 31 and Figure 2.4) while also being inherently safer. For making a bulk battery from thin films an economic production method is necessary. The battery layers have to be produced in large areas, large enough to to roll up the thin-film batteries to bulk batteries.

In order to produce a high energy density battery, the parameters that can improve current performance of thin-film batteries have to be understood. Energy densities can be increased by:

- Decreasing the passive device volume relative to the active volume

- Increasing the practical density of the active material

- Finding new material systems with a chemistry of higher theoretical energy density

While the last point is fairly self-explaining as new materials with increased performance could of course always change the battery landscape, the first and second point are discussed in more detail below.

Decreasing the passive device volume relative to the active volume The optimum amount of active material (cathode or anode) has to be determined. More active material means higher battery capacity but diffusion issues in the cathode or anode can cause capacity loss which tends to be larger for thicker layers (see discussion in Section 2.2.4). For $LiCoO_2$-films thicker than about 8μm it takes too long to get the energy out of the film. A greater practical thickness could be achieved with a more electron- and Li-ion-conducting material.

The electrolyte has to be fabricated as thin as possible without risking leakage and shorts. Very good quality thin-films with small surface roughness have to be produced to insure fast charge rates, light weight, and reliability. This requirement does not pose a problem for small area thin-film batteries, but is a challenge for large-area and roll-to-roll fabrication.

The substrate should consist of a very light weight material that can withstand annealing. For a roll-to-roll process the substrate is required to be at least 25-$50\mu m$ thick and thus comprises a significant fraction of the battery's weight.

Increasing the practical density of the active material $LiCoO_2$ is deposited as a partially crystallized material. It can not be crystallized perfectly while maintaining contact with the substrate; either crystallization-related contraction rips the layer off, or the crystallization is constrained by the substrate. Both effects interact. Which one dominates and how dense the final layer turns out depends on deposition parameters as well as time and temperature of annealing. The typical $LiCoO_2$ density achieved for thin-film batteries fabricated at ORNL is 57% of the theoretical $LiCoO_2$ density.

For comparison, a composite electrode for liquid electrolyte systems consists of 85% weight of active materials, the rest being binder material (see also Section 2.4.3 for the design of liquid electrolyte batteries). In addition to that, cathodes are typically 30% porous to let in the liquid electrolyte. These two values result in an effective cathode density of about 60% ($0.85 \cdot 0.70$). As the electrolyte is almost completely absorbed in the porous electrode and separator materials, there is no thickness limitation for the electrodes.

3.7.1 Performance

The energy densities of a sample battery system is calculated here. The system has $LiCoO_2$ and Li metal electrodes, a LIPON electrolyte, and Al current collectors. The structure has dimensions as follows:

Material:	Thickness:
Al	50nm
LiCoO$_2$	8μm
LIPON	1μm
Li	2.5μm
Al	50nm

As discussed above, the capacity of LiCoO$_2$ is taken to be 57% of 69μAh/cm$^2\mu$m [Dudney and Jang, 2003], which is 39μAh/cm$^2\mu$m, and the density of LiCoO$_2$ is also taken to be 57% of the theoretical value of 5.02g/cm^2. The cell voltage is 4.2V. Results of this calculation are given in Table 3.2. This table does also include the results for a calculation with 100% of the theoretical LiCoO$_2$ density to show what can be achieved with increasing the density of the active material. The results in Table 3.2 do not include the weight of the

Table 3.2: Energy densities for a sample thin-film LiCoO$_2$/LIPON/Li battery system. The weight of current collectors, electrodes, and electrolytes, but not of the substrate are included in the calculation. The values for 57% LiCoO$_2$ density are realistic. The 100% density calculation is to show the improvement potential in increasing the LiCoO$_2$ density.

% of theoretical LiCoO$_2$ density	capacity per area [μAh/cm^2 μm]	specific energy density [Wh/kg]	volumetric energy density [Wh/l]
57	315	399	1139
100	552	460	1998

substrate. Thickness limitations for the substrate depend on the fabrication method for the batteries. To produce the batteries in large enough stripes to roll them up, roll-to-roll thin-film deposition processes have to be employed. For a roll-to-roll process, the substrate has to be at least 25-50μm thick, which reduces the energy density significantly. Other issues raised by the roll-to-roll requirement address the fabrication of the battery layers directly. Sputter roll-to-roll processes are available now, but materials choice determines the range of fabrication and manufacturing issues.

Concluding, bulk batteries from thin films can in theory achieve superior performance to liquid electrolyte systems. However, in practice several production issues have to be

overcome to produce batteries of high quality and at acceptable cost. Also, the development of Li ion batteries with liquid electrolytes has to be closely observed, as Li ion batteries are constantly being improved. Liquid electrolyte systems are easier and cheaper to fabricate (see Section 2.4.3) as fabrication does not employ expensive thin-film processing technology. It has to be carefully examined whether the superiority in performance of a new solid electrolyte technology is big enough to outweigh higher production cost. Current liquid electrolyte systems have energy densities of around 150Wh/kg (see page 31), but Sony announced recently that their next generation liquid electrolyte Li-ion battery will achieve an energy density of 210Wh/kg, making the performance advantage of bulk batteries from thin films considerably smaller.

3.8 Thin-Film Batteries as Non-Volatile Memory Cells

The size of ultra-thin solid state batteries suggests an unconventional battery application as non-volatile memory made from an array of tiny batteries. Each battery could comprise a memory cell with charged cells representing a "1" and discharged ones representing a "0". In order to evaluate this application, conventional and emerging non-volatile memory technologies are discussed below, before a possible design of battery memory is assessed.

3.8.1 Competing Memory Technologies

3.8.1.1 Conventional Memory Technologies

The three well established memory technologies today are static random access memory (SRAM), dynamic random access memory (DRAM), and Flash memory. Each of them has certain shortcomings. SRAM can be very fast but has large cell size and is volatile, which means it requires standby power. DRAM has small cell size, but it is also volatile. Flash memories are non-volatile, however they exhibit limited write endurance and low writing speed.

According to their respective properties, SRAM, DRAM, and Flash are used in different applications. A new memory technology that combines non-volatility with small size, high speed, and high write endurance could be used as universal memory and pursue the huge

market of the three memory technologies mentioned above, which comprised combined revenues of $26 billion in 2002 [Müller et al., 2003].

Flash is the only well established non-volatile memory technology today and is discussed further below. Emerging memory technologies are addressed in the following section.

Flash Memory   Flash devices store and sense charge on a floating gate. Charge storage and removal require current flow through the dielectric materials surrounding the floating gate, which implies high electric field stress and is one of the reasons for limited write endurance of Flash. Another shortcoming of Flash, the slow writing speed, is caused by the Flash erase and program operations not being done per memory cell but per memory block. Limited write endurance and slow writing speed have prohibited the use of Flash in computing applications. Its non-volatility, however, makes Flash a widely used technology in handheld and mobile appliances. The success of Flash in the non-volatile memory market is based on its cell size but not on its performance, as the cell size determines the cost per bit. All emerging technologies discussed below offer superior performance to Flash.

3.8.1.2   Emerging Memory Technologies

Ferro Electric Memory (FeRAM)   FeRAM devices achieve non-volatility by switching and sensing the polarization state of a ferroelectric capacitor that uses a ferroelectric film for a dielectric. The data is not stored as free charge, but as position of atoms within the crystal. When an electric field is applied to the capacitor, the crystals begin to polarize in the direction of the field, i.e. mobile atoms move within the crystal corresponding to the applied field. A common ferroelectric material is PZT (Pb (Zr, Ti)O_3). Figure 3.2 indicates the motion of atoms in the direction of the applied field in PZT. Ferroelectric materials are new to CMOS processing facilities and can be degraded by conventional CMOS processing conditions. Furthermore, the ferroelectrics must be physically and chemically isolated from the underlying CMOS structures.

FeRAMs have superior write access time and lower power consumption than Flash. The density, cycle times, and processing technology to use FeRAM as an embedded memory for system on chip (SoC) applications still need to be improved to make FeRAM an alternative for Flash, SRAM and DRAM.

O TI/Zr   ⊜ Oxygen   ● Pb
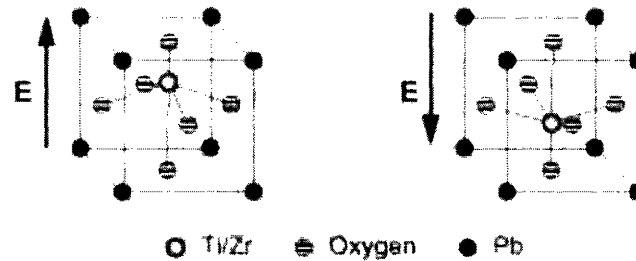
Figure 3.2: Crystal orientation in ferroelectric materials: PZT (Pb (Zr, Ti) O_3). Adopted from [Natarajan, 2004].

FeRAM products have been commercially available since 1992. They are offered today in densities of up to 512kb with stand alone cell sizes of around $6\mu m^2$. The products on the market are mostly used as embedded memory in microcontrollers for smart cards. The current development is targeting cell sizes down to $0.94\mu m^2$ for stand alone FeRAM and cell sizes of down to $0.54\mu m^2$ for embedded FeRAM. The read and write times of FeRAM cells are about 50ns with a write endurance of more than 10^{15} cycles [Müller et al., 2003].

Magneto-Resistive Memory (MRAM) In MRAM devices a magnetic tunnel junction (MTJ) is employed as the memory element. MRAM uses an effect called magneto-resistance, which is a change in electrical resistivity caused by the presence of a magnetic field. A MTJ cell consists of two ferroelectric materials separated by a thin insulating barrier. A small bias allows current to tunnel through the barrier. The tunneling current depends on the magnetic orientation of both magnetic layers with one of them being fixed and the second one being switchable via on-chip currents. The conductance of the barrier layer is highest or lowest when the magnetic moments in the ferromagnetic layers are parallel or antiparallel respectively.

No commercial MTJ based MRAM products are on the market today, but several companies are working on MRAM test chips. Test chip cell sizes are in the area of $1.6\mu m^2$ and can achieve write operations with read and write times of 10ns and write endurance of more than 10^{15} cycles [Müller et al., 2003].

Phase Change Memory (PCRAM) PCRAM devices use the resistivity difference between the crystalline and amorphous phase in chalcogenic glasses. The memory switching is a thermal process that involves a phase transformation from an amorphous to a crystalline state. To make the programmable volume amorphous, it is heated above its melting point by a resistive heater and cools rapidly when the heater is turned off. To make it crystalline, it is heated to just below its melting point allowing the atoms to line up in a crystalline manner.

PCRAM cell sizes are smaller than $0.5 \mu m^2$ today and offer write endurance of more than 10^{12} cycles with read and write times between 30 and 50ns [Müller et al., 2003]. Challenges in PCRAM development are the lowering of the high reset current (to make the programmable material amorphous) and reliability issues.

Programmable Metalization Cell (PMC) Memory One rarely mentioned technology in the field of non-volatile memories is the Programmable Metalization Cell (PMC) memory. It uses the electrochemical build-up of ions inside a solid electrolyte. The device includes an electrolyte layer in contact with an inert cathode and an anode that contains an oxidizable form of the metal in solution in the electrolyte. A forward bias causes an ionic current as long as there is oxidizable metal at the positive electrode. The electron current flow from the cathode causes reduction of the metal ions and hence a metal-rich electrodeposit builds up in the electrolyte, forming a nano wire that creates a conductive bridge between the electrodes. The process is reversible, as applying a reverse bias makes the electrodeposited material the oxidizable electrode. The ability to increase and decrease the metal content in the solid electrolyte allows for a controlled change of resistivity of the electrolyte and therefore for switching between high and low resistivity states.

PMCs offer physical scalability to tens of nanometers and a read and write speed of less than 30ns. A writing endurance of more than 10^{10} cycles was shown, and the device is expected to operate after as many as 10^{16} cycles [Kozicki et al., 2004].

There are many other memory technologies being developed, but the FeRAM, MRAM and PCRAM are most promising and are farthest in the development. All of them are also assessed in the International Roadmap for Semiconductors [ITRS, 2005]. PCM memory is not well known, but semiconductor manufacturing companies such as Infineon Technologies and Micron Technology seem to consider it interesting as they already licensed the

technology. The PMC technology is being commercialized by Axon Technologies Corporation [Axon, 2006]. All discussed emerging technologies show superior performance compared to Flash and are likely to be able to be embedded on the chip, a requirement for today's system on chip (SoC) applications.

3.8.2 Design and Performance of Battery Memory Cells

Memory from batteries could have a very simple structure. A memory chip could consist of an array of batteries, each battery representing a memory cell and transistors to address the cells.

No such small batteries have been produced yet. The following is a theoretical assessment of the microfabricated batteries' qualification for memory applications.

Materials Selection   Besides the desired properties for battery components discussed in Section 2.1.1, there are two main issues that determine materials selection for battery memory. First, the battery materials should be compatible with microelectronics processing technology, as the ability to embed memory on microchips is basically required for new memory technologies. Second, cell voltage is a strong constraint. Low cell voltage is desired to save energy, but higher cell voltage can increase the discharging speed as it enhances the ion transport through the electrolyte and thus decreases the time to switch between two states.

Design of a Memory Cell   In terms of storage density the battery memory can compete with other emerging technologies, as batteries should be able to work down to sizes of a few nanometers. This suggests that a memory cell including the battery and controlling transistors can be produced at least in the same size as memory cells of other emerging technologies, which is about $0.5\mu m^2$. Most likely battery memory cells can even be significantly smaller than $0.5\mu m^2$ and thus offer higher storage density than the other emerging technologies.

To choose the thickness of battery layers, the effects of thickness on battery performance have to be considered. The electrolyte layer is desirably made as thin as possible without the risk of shorts, to enable fast charging and discharging. The amount of active material, usually the volume of the cathode, determines the amount of charge that has to

be moved to switch the cell from the charged to the discharged state and vice versa. Here only the thickness of the cathode layer matters. The area does not change the charge and discharge times because larger cathode areas also imply larger electrolyte areas and thus more current flow. Thus the use of thin cathodes ensures fast switching. For read only memory (ROM) applications, however, one might consider using thicker cathode layers as the battery can be read out many times before it changes its state. Charging time does not matter for ROMs.

Sample Calculation   A discharge time was estimated for V_2O_5/LIPON/$LiCoO_2$ cells. Starting from the ionic conductivity of the LIPON electrolyte, the time it takes to move the charge in the form of Li ions that are intercalated in the cathode through the electrolyte was estimated. The number of Li ions that have to be moved was calculated from the volume of $LiCoO_2$ and its theoretical capacity of around $60\mu Ah/cm^2\mu m$ (see Section 2.2.4). Assuming a LIPON ionic conductivity σ of $3 \cdot 10^{-6} S/cm$ [Ariel, 2005], the current I that can flow through the electrolyte of thickness d and area A with an applied voltage V was calculated. Conductivity can in general be defined as

$$\sigma = \frac{d}{R \cdot A} \tag{3.1}$$

where R is the resistance of the conductor in question. In this case R is the ionic resistance of the electrolyte layer, equivalent to the electronic resistance in electronic conductors. Note that this is just an approximation of how much current can flow through the electrolyte layer. R does not represent the cell resistance that is usually described in equivalent circuits as an impedance resulting from a network of resistors and capacitors. It also does not take into account kinetic and reaction energetic barriers in the cathode or at the interface. The obtained current will be a high estimation of how much current can flow through the electrolyte layer and thus how long it takes to charge or discharge the cell. As the results will show, this estimation is sufficient to show that the charging and discharging times are too long to compete with other emerging memory technologies described in Section 3.8.1.2. Substituting R with V/I in Equation 3.1 and rearranging gives an equation for the current through the electrolyte depending on the electrolyte's conductivity, area, thickness, and the voltage across it.

$$I = \frac{\sigma \cdot V \cdot A}{d} \tag{3.2}$$

For discharging, the voltage across the electrolyte, V, is the cell's open circuit voltage (OCV). Equation 3.2 shows that a material system with higher OCV might be able to discharge faster. For this calculation the voltage across the electrolyte layer was assumed to be constant although it drops during discharge, which also slows down the discharging process and makes the discharging time even longer. The obtained times t required to transfer the charge contained in Li ions in a $LiCoO_2$ cathode across a LIPON electrolyte, based on the current through the electrolyte calculated from Equation 3.2, are shown in Table 3.3.

Table 3.3: Transfer time t across the electrolyte for the charge contained in Li ions intercalated in $LiCoO_2$ cathodes for several cathode and electrolyte thicknesses. The calculation was done for an OCV of 1.5V (as in the V_2O_5/LIPON/$LiCoO_2$system) and for an OCV of 3V, which could be achieved with a different anode material. The calculation with an OCV of 3V is to show that higher OCV can lead to faster transport through the electrolyte. Cell areas are not important in this calculation as the current density through the electrolyte is independent of cell area.

$LiCoO_2$ thickness $d_{LiCoO_2}[nm]$	LIPON thickness $d[nm]$	current density $J[A/cm^2]$		charge transfer time $t[s]$	
		OCV = 1.5V	OCV = 3V	OCV = 1.5V	OCV = 3V
250	100	0.5	0.9	$1.2 \cdot 10^{-1}$	$6.0 \cdot 10^{-2}$
100	60	0.8	1.5	$2.9 \cdot 10^{-2}$	$1.4 \cdot 10^{-2}$
80	60	0.8	1.5	$2.3 \cdot 10^{-2}$	$1.2 \cdot 10^{-2}$
60	20	2.3	4.5	$5.8 \cdot 10^{-3}$	$2.8 \cdot 10^{-3}$
20	10	4.5	9.0	$9.6 \cdot 10^{-4}$	$4.8 \cdot 10^{-4}$
10	10	4.5	9.0	$4.8 \cdot 10^{-4}$	$2.4 \cdot 10^{-4}$

Due to several simplifications mentioned above, the transfer time t is definitely shorter than the charge or discharge times for a cell will finally be. This simplified calculation, however, is sufficient to show that the charge and discharge time is much higher than the switching time required to compete with other emerging memory technologies. Read and write speeds for other emerging technologies are in the order of nanoseconds (see Section 3.8.1.2) whereas the lowest electrolyte transfer time for the thinnest calculated parameters (cathode and electrolyte thicknesses of 10nm) in Table 3.3 is in the order of hundreds of microseconds.

The long transfer times result in very long write times. However, reading the state of

the cell can be done very quickly without the requirement of a full charging or discharging process. For example in a cell with a 100nm thick cathode and 60nm thick electrolyte a reading process of 20ns could be done over 10^5 times. Thicker cathodes increase this number.

The calculations above clearly show that batteries are not likely to be used in RAM applications and the only possibility to use batteries as memory is in ROM applications. But even for ROM applications many issues, like self discharge of the batteries, would have to be addressed and tested. The only advantage that remains over other memory technologies might be higher storage density of the battery memory.

Summarizing, memory made from batteries will not have the performance to compete with other technologies' writing speeds. Only the development of new solid electrolyte materials with much higher ionic conductivity could make battery memory a viable option in future.

3.9 Applications: Conclusion and Outlook

All different degrees of integration of an ultra-thin-film battery on a wafer have substantial drawbacks. First, such a thin battery has very little capacity and most microchips need a lot more power than a reasonable number of battery layers can deliver. Second, in terms of fabrication yield it is favorable to produce the battery and microchip separately and then stick them together. This allows also for use of battery material systems that are not compatible with microelectronics processing technology and hence for better adjustment of battery performance to the required power.

The priorities here might still change in the future. If very-large-scale integration (VLSI) microelectronic circuits are to operate at very low temperatures, superconducting interconnects might become feasible resulting in higher speeds and lower power requirements.

Integrated batteries have no obvious application as an additional circuit element on the front of a microchip at present. This might change once circuit designers start to think about their design with the availability of local power on the chip in mind.

Although it is not beneficial to produce batteries on a microchip, the list of potential applications for attaching batteries to microchips is very long. They can add functionality and improve performance of integrated circuits, for example as a rechargeable power source

for non-volatile SRAM, real-time clocks, and microcontrollers. Other possibilities include increasing the range of RFID tags, and use in medical electronics.

Ultra-thin batteries offer a very low energy density and are thus not suitable for bulk battery applications. This might however be a promising application for thicker thin-film batteries that can reach a specific energy above 300Wh/kg.

Non-volatile random access memory (NVRAM) represents an unconventional battery application. The RAM could be made of an array of tiny batteries, charged ones representing a one and discharged ones a zero. Unfortunately, the low ionic conductivities of solid electrolytes do not allow for competitive writing speeds of battery memories.

Finally, looking into large-area fabrication possibilities and implementations for thin-film batteries might also reveal new potential applications.

Chapter 4

Intellectual Property

4.1 Basic Technology

Oak Ridge National Laboratory (ORNL) researchers dominate thin film publications as well as the patent landscape. Along with developing the cell, they basically patented each successful step in the development. Not only do they have patents on crucial battery components like the LIPON electrolyte, they also have patents on packaging thin-film batteries to create a barrier against penetration of air and water vapor as well as on methods for making the battery. Their early patents concentrate on batteries with Li anodes, but later ones do also deal with Li-ion and Li-free batteries. Very recent patents cover several improvement methods for thin-film batteries. The following list gives an overview of selected patents from ORNL. The list is meant to show that production of thin-film batteries is simply impossible without licensing ORNL patents.

Selected ORNL-related patents:

- Protective lithium ion conducting ceramic coating for lithium metal anodes and associate method, J. B. Bates, U.S. Patent No. 5,314,765 (May 24, 1994)

- Thin-film battery and method for making same, J. B. Bates, N. J. Dudney, G. R. Gruzalski, and C. F. Luck, U.S. Patent No. 5,338,625 (Aug. 16, 1994)

- Method for Making an Electrolyte for an Electrochemical Cell, J. B. Bates and N. J. Dudney, U.S. Patent No. 5,512,147 (Apr. 30, 1996)

- Packaging material for thin-film lithium batteries, J. B. Bates, N. J. Dudney, and K. A. Weatherspoon, U.S. Patent No. 5,561,004 (Oct. 1, 1996)

- Method for Making an Electrochemical Cell, J. B. Bates and N. J. Dudney, U. S. Patent No. 5,567,210 (Oct. 22, 1996)

- Rechargeable lithium battery for use in applications requiring a low to high power output, J. B. Bates, U. S. Patent No. 5,569,520 (Oct. 29, 1996)

- An electrolyte for an electrochemical cell, J. B. Bates and N. J. Dudney, U.S. Patent No. 5,597,660 (Jan. 28, 1997)

- Rechargeable lithium battery for use in applications requiring a low to high power output, J. B. Bates U. S. Patent No. 5,612,152 (Mar. 18, 1997)

- Battery with an in-situ activation plated lithium anode, B. J. Neudecker, N. J. Dudney, J. B. Bates, U.S. Patent No. 6,168,884 (Jan. 2, 2001)

- Thin film battery and electrolyte therefor, J. B. Bates, U.S. Patent No. 6,818,356 (Nov. 16, 2004)

- Long life thin film battery and method therefor, J. B. Bates, U.S. Patent No. 6,994,933 (Feb. 7, 2006)

4.2 IP from Companies

About six companies in the U.S. are based upon some of the above ORNL patents, but only two of them are really operating companies, *Cymbet Corporation* and *Infinite Power Solutions*. *Infinite Power Solutions* has only one patent so far, dealing with methods for encapsulation of electronic devices. *Cymbet Corporation* has received five patents so far. These patents set the stage for the commercialization of thin-film batteries. First they developed a low temperature fabrication method for thin-film batteries. By supplying energy in the form of energized ions of a second material to the material that is being deposited they control the growth of the crystalline structure of the film and avoid annealing. This procedure is the basis of another patent that integrates the battery into devices by fabricating it on the shell of the device. The low temperature fabrication method allows the battery to be produced on a very wide range of materials.

Cymbet patents pick up non-battery related ideas as well, so they do also mention capacitors formed on the shell of devices in their "device enclosures" patent. The company also worked on continuous processing of thin-film batteries, including processing with the substrate being supplied from a roll and moving in continuous motion. They do address many kinds of applications in their patents. One of them is the deposition of layers to form a battery and a photovoltaic (PV) cell and attachment of an integrated circuit (IC) to couple the PV cell to the battery for charging. Another application is a system comprising a thin-film battery and an activity-activated switch. The activity-activated switch places the battery in electrical communication with an electrical circuit that is also formed on the substrate. To conclude, Cymbet patents are very broad and cover many kinds of applications, such as electrical circuits attached to the battery which is attached to a substrate that has a PV cell beside the battery, supercapacitors on batteries, ICs on batteries, batteries on ICs, and many more.

Cymbet Corporation patents:

- Method and apparatus for integrated-battery devices, M. L. Jenson, J.J. Klaassen, U.S. Patent No. 6,805,998 (Oct. 19, 2004)

- Solid state activity-activated battery device and method, M. L. Jenson, J. J. Klaassen, J. Sullivan, C. A. Lemaire, R. E. Billion, U.S. Patent No. 6,906,436 (Jun. 14, 2005)

- Method of continuous processing of thin-film batteries and like devices, M. L. Jenson, U.S. Patent No. 6,924,164 (Aug. 2, 2005)

- Low-temperature fabrication of thin-film energy-storage devices, M. L. Jenson, U.S. Patent No. 6,962,613 (Nov. 8, 2005)

- Device enclosures and devices with integrated battery, M. L. Jenson, J. J. Klaassen, V. H. Weiss, J.-F. Yan, U.S. Patent No. 6,986,965 (Jan. 17, 2006)

4.3 Patent Applications

Some applications for patents will most likely also be relevant for the thin-film battery business. The list below shows patent applications from M.L. Jenson, inventor of all of Cymbet's patents mentioned above. One patent application deals with batteries with an

ultra-thin electrolyte. Supplying energy in the form of energized ions to the material being deposited assists in controlling growth and stoichiometry of the film. Electrolyte films processed with this method with thicknesses between 1 and 5000Å are claimed. Some embodiments include vanadium oxide as an electrode, LIPON as electrolyte, and a lithium intercalation material or metal as the other electrode. The described battery is very similar to the integrated batteries fabricated at MIT. However, no literature except in patents can be found about it as Cymbet most likely tried to keep their results confidential. The patent applications also deal with solid-state energy storage and energy conversion devices produced with the low-temperature method without the annealing step and employing a PV cell. Deposition of batteries on ICs and on thin-film capacitors as well as mounting thin-film batteries together with an antenna and an electric communications circuit on a support are also discussed.

Selected patent applications:

- Thin-film battery having ultra-thin electrolyte
  Appl. No. 20060063074

- Integrated capacitor-like battery and associated method
  Appl. No. 20050045223

- Method and apparatus for integrated battery-capacitor devices
  Appl. No. 20040185310

- Battery-operated wireless-communication apparatus and method
  Appl. No. 20020037756

Recapitulating, the thin-film battery patent landscape is dominated by only few people and organizations, but they put a lot of effort in protecting every somewhat obvious application.

Chapter 5

Business Model: Bulk Batteries from Thin Films

None of the apparent thin-film applications appears to be a viable option for a business model. Circuit designers do not know at present what to do with a local power source within the circuit, and fabrication on the back of a microchip is also not advantageous because of yield issues and the very limited power of an integrated thin-film battery. Applications that involve thicker thin-film batteries seem to be well addressed and protected with patents by Cymbet Corporation and Infinite Power Solutions. The markets they are addressing are very promising and are based on technologies in consumer electronics that are also expected to continue growing.

Considering this expected growing demand for thin-film batteries, there might still be space for another company provided that the technology and the two thin-film battery companies really take off. However, getting into a market in which the competitors are already ahead is a difficult task. One would have to find a niche product they did not consider yet and try to start gaining market share with this product.

Given the facts mentioned above, it seems more appealing to pursue completely new thin-film battery applications that are not related to the apparent thin-film battery usage. Such a new application would be rolling up thin-film batteries to fabricate bulk batteries as discussed in Section 3.7. I will estimate the business opportunities for the production of bulk batteries from thin films and propose a potential business model in the following sections.

5.1   Li-Ion Bulk Batteries: The Market Situation

Secondary or rechargeable batteries are widely used in two major categories of applications:

- The battery is used as an energy storage device that is charged by a prime energy source and delivers its energy on demand when the prime energy source is not available or cannot handle the load requirement.

- The battery is discharged and recharged after use (e.g., in consumer electronics and electric vehicles).

Lithium-ion batteries fall in the second category and have been growing during the last decade to capture a market share of 50% [Linden and Reddy, 2002] for small non-automotive consumer applications. The safety of this technology as well as its performance and cost-effectiveness have made it the standard power source for a broad array of markets, including cell phones, laptop computers, and personal data assistants.

The worldwide secondary battery market was approximately $20 billion per year in 2002 [Linden and Reddy, 2002]. About 12.5% of this was Li-ion market, which is about $2.5 billion. In 2003 the Li-ion battery market reached a size of $3 billion [Brodd, 2005] and for 2005 it was estimated to be $4 billion [Linden and Reddy, 2002].

The development of the production volume for Li-ion batteries from 1995 to 2002 can be seen in Figure 5.1.

5.1.1   Lithium-Ion Battery Production Today

There are no high-volume rechargeable Li-ion battery manufacturers in the U.S. despite the fact that U.S. companies are global leaders in primary battery production and technology. Most U.S. rechargeable cell manufacturers exited the business because of low return on investment compared to their existing businesses. The reasons for this situation were assessed thoroughly by the National Institute of Standards and Technology in their Advanced Technology Program [Brodd, 2005]. Customers for rechargeable batteries are large electronics companies. The development of a rechargeable battery requires knowledge of
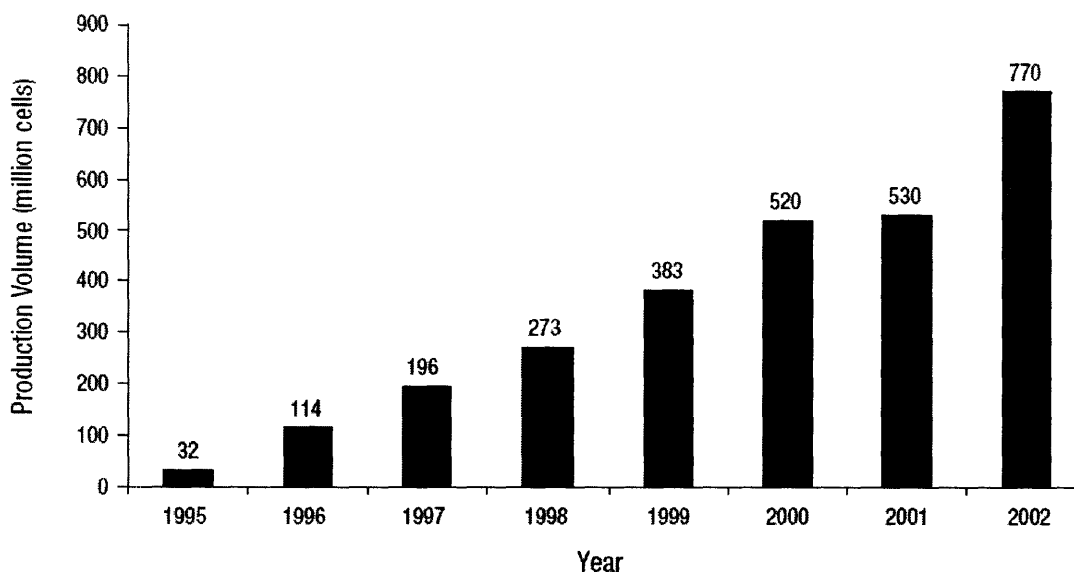
Figure 5.1: Worldwide production of Li-ion cells, 1995 - 2002. Adopted from [Brodd, 2005].

electrical requirements for emerging products as well as close contact with portable electronic device designers. Many Japanese electronics companies have Li-ion cell production within the same company. In the U.S., the battery manufacturers usually have little access to electronic device designers. When Li-ion batteries started to rise in the 1990s, U.S. companies prepared to establish sales and marketing groups in Japan to have access to portable electronics designers and thus to the market. However, it took too long to get accepted in the Japanese market as this market is not readily accessible for non-Japanese companies. This is the reason why Asian companies have established a dominant position in the production of Li-ion batteries. In fact, Japan manufactures 80% of Li-ion batteries today [Brodd, 2005].

5.2 Business Model Proposition

There are still opportunities for U.S. companies to enter niche markets such as medical, military, and space applications and small start-ups continue to do innovative research in

the Li-ion battery field.

A start-up company for the all-solid-state Li-ion batteries made from rolled-up thin-film batteries is in a similar position as a start-up company for Li-ion batteries with liquid electrolytes. The missing connection with the designers for portable electronics and the difficulty to establish those contacts would make the manufacturing of this technology undergo a similar development than the manufacturing of Li-ion liquid electrolyte batteries did, even if the battery turns out to be able to compete against the existing technology.

In order to enter the market in the U.S., niche markets have to be found in which the all-solid state composition, the safety, and the higher energy density make rolled-up thin films the battery of choice. Considering this complex environment in the Li-ion bulk battery industry, a product company that works closely with the designers of its costumer's products is the most reasonable choice for this technology.

5.3 Timeline from Conception to Production

The introduction of a new battery technology is a time-consuming process. The production innovation process consists of basically five stages [Brodd, 2005]:

1. Concept generation and validation: Idea, exploratory laboratory experiments, show repeatability of performance, find market.

2. Research: Scale-up experiments, characterize properties of the technology, evaluate commercial opportunity.

3. Applied Research: Build prototype cells, map performance.

4. Development: Establish initial product format, develop assembly processes, test and characterize a significant number of cells, construct business plan.

5. Advanced Development: Design product, design fabrication processes, scale-up prototype fabrication, run pilot factory trials.

Historically, the maximum time from conception to product introduction for a battery, in this case the alkaline primary cell, was 19 years [Brodd, 2005]. For Li-ion technology this process was completed within 10 years. An introduction of a new battery technology

is likely to take a time between these 10 and 19 years, with the applied research and the development phases being expected to take longest. The process starts to become very expensive in the development phase, and financing has to be secured at this point.

5.4 Cost and Financing

The time required for the development of rechargeable batteries is usually not acceptable for venture capitalists. They do also not want to fund expensive manufacturing facilities. The cost of existing automated Li-ion facilities that make three million cells per month is between $108 and $144 million annually [Brodd, 2005], this translates to an annualized cost of $3 to $4 per cell. This high cost results from high precision requirements and environmental controls. The numbers do include the cost of land but not the cost of research and development that was needed to design the technology and production equipment.

Expensive analytical equipment is required for Li-ion battery research and development. One possible solution to get around this expenditure is to collaborate with universities and use their facilities. In fact, this is probably the only viable possibility for start-ups. The total cost of developing a new battery from conception to production is estimated to be $100 million [Brodd, 2005]. This estimation does not include the cost of the production facility but it does include a small pilot operation. All these numbers refer to liquid electrolyte batteries but are expected to be in the right order of magnitude to estimate expenses for solid electrolyte batteries.

Due to their little attraction for venture capitalists, financing options for secondary battery companies are

- raise funds for manufacturing equipment by stock offerings

- license or sell themselves to an existing company

- go abroad and manufacture as cheaply as possible.

Labor costs do not play a significant role in an highly automated Li-ion battery factory, but they do in the battery pack assembly.

5.4.1 Expense Factors for the Cost of a Battery

There are several factors that have to be considered when determining the cost of a secondary battery. One is of course the initial cost, but the number of available charge-discharge cycles as well as the total charge delivered in a battery's lifetime are equally important. Secondary factors that have to be taken into consideration are maintenance, cost of charging, and associated equipment that may be necessary.

Li-ion manufacturers do not sell individual cells, they sell battery packs with safety devices (electronic control circuitry) included. The cost of cylindrical Li-ion batteries has been stated to $1.22/Wh in 2002 [Linden and Reddy, 2002].

The cost of bulk batteries from thin-film batteries will highly depend on the processing method. The fabrication process for liquid electrolyte batteries is described in section 2.4.3. The fact that the all-solid-state technology needs thin-film processing technology will most likely make the fabrication more expensive. However, costs can be saved as no hermetic sealing is required for solid electrolyte batteries. In any case, the performance will determine whether it pays to produce Li-ion bulk batteries from thin-films or not.

Chapter 6

Conclusion

6.1 Applications

This paper assessed various application possibilities for thin-film batteries. Different degrees of integration of the battery on a silicon wafer as well as non-integrated applications such as bulk batteries from thin films were examined.

The integration of batteries on the back of a microchip does not turn out to be favorable. First, production yield considerations suggest the separate production of batteries and chips to be more reasonable, as producing the battery on the back of a wafer full of microchips puts all the value that has been built into it before at risk. For battery-on-the-chip applications, the battery and chip can be stuck together after the actual fabrication. Secondly, a very thin integrated battery that is produced right on the back of the chip does not offer high enough capacity to power the existing density of CMOS transistors on a chip. The combination of chip and battery after fabrication is favorable here also, as a wider range of battery thicknesses and performances can be produced. With the integrated option, many thousands of battery layers would be needed to satisfy the power requirements of a typical chip. Only very few special microchips require low enough power to qualify for this option. So the benefit of having the battery directly on the chip is expected to be too low to justify the yield losses that would occur through fabrication.

Although it is not beneficial to produce batteries on a microchip there are many promising applications for combination of thin-film batteries with microchips. Thin-film batteries

can add functionality and improve performance of integrated circuits, for example as a rechargeable power source for non-volatile SRAM, real-time clocks, and microcontrollers. They can also be used to make radio frequency identification (RFID) tags active and increase their range or provide a safe power source for medical electronics. Thin-film batteries of this size scale are not an embryonic technology anymore and are already being commercialized.

My research for applications concluded in the realization that two options remain in order to develop a new commercialization strategy for thin-film batteries. One is to find applications for thin-film batteries that are not obvious and not yet being commercialized and the other is to concentrate on applications that rely on the size and special properties of the ultra-thin integrated batteries.

An application restricted to the smallest possible integrated batteries would be the use of batteries for non-volatile random access memory (NVRAM). The RAM could be made of an array of tiny batteries, charged ones representing a one and discharged ones a zero. However, with current electrolytes the charge and discharge rates are too low to compete with the writing speeds of other memory technologies.

Another option that is not being commercialized yet is a bulk battery produced by rolling up a thin-film battery. Ultra-thin batteries offer very low energy density and are thus not suitable for such bulk battery applications but thicker thin-film batteries can reach a specific energy above 300Wh/kg and might well be able to compete with existing Li-ion bulk batteries that have a specific energy of about 150Wh/kg.

6.2 Business Model

The only thin-film application examined in this thesis that is not commercialized yet and seems to have commercialization potential is the bulk battery made from thin films. Market opportunities for this application were assessed.

Many analogies can be drawn from the market situation of existing Li-ion batteries. The main costumers for Li-ion bulk batteries are consumer electronics producers. For this reason, battery companies have to work closely with designers for consumer electronics. Many consumer electronics companies are located in Japan and many of them do produce

their own batteries. Therefore it is difficult for foreign battery companies to get into the Li-ion market, a situation that resulted in 80% of the world's Li-ion batteries being produced in Japan. There is no high-volume Li-ion battery manufacturing in the U.S.; the only Li-ion companies in the U.S. are fairly small and address niche markets. A start-up company for Li-ion batteries from thin films would likely face a similar situation.

In order to enter the market in the U.S., niche markets have to be found that have a very high utility for the properties a solid-state Li-ion bulk battery can offer. A study of the liquid electrolyte Li-ion battery market shows that close contact between the battery designers and the designers of the battery's target products is crucial. In fact, the design of the battery and of the target products preferably occurs under the same roof. The most reasonable business model for this technology therefore couples the battery company with a consumer electronics company that will incorporate Li-ion batteries into its products.

Bibliography

Ariel, N. (2005). *Integrated Thin Film Batteries on Silicon*. PhD thesis, Massachusetts Institute of Technology. 19, 21, 22, 23, 32, 34, 35, 44

Axon (2006). *Axon Technologies Corporation Official Homepage*. http://www.axontc.com/. 43

Balkanski, M. (2000). *Solid-State Microbatteries for Electronics in the 21st Century*. Solar Energy Materials & Solar Cells, 62:21–35. 34

Bard, A. and Faulkner, L. (2001). *Electrochemical Methods: Fundamentals and Applications*. John Wiley & Sons, Inc., second edition.

Brodd, R. (2005). *Factors Affecting U.S. Production Decisions: Why are There No Volume Lithium-Ion Battery Manufacturers in the United States?*, Advanced Technology Program, National Institute of Standards and Technology: Working Paper 05-01. http://www.atp.nist.gov/eao/wp05-01/wp05-01.pdf. 25, 54, 55, 56, 57

Creus, R., Sarradin, J., Astier, R., Pradel, A. and Ribes, M. (1989). *The Use of Ionic and Mixed Conductive Glasses in Microbatteries*. Mater. Sci. Eng., B3:109. 19

Cymbet (2006). *Cymbet Corporation Official Homepage*. http://www.cymbet.com/. 22, 32, 36

Dudney, N. (2001). *Thin-Film Rechargeable Lithium, Lithium-Ion, and Li-free Batteries*. http://www.ornl.gov/sci/cmsd/main/Programs/BatteryWeb/index.htm.

Dudney, N. (2005). *Solid-State Thin-Film Rechargeable Batteries*. Materials Science and Engineering B, 116:245–249. 21

Dudney, N. and Jang, Y.-I. (2003). *Analysis of Thin-Film Lithium Batteries with Cathodes of 50nm to 4μm Thick LiCoO₂*. Journal of Power Sources, 119-121:300–304. 22, 38

63

Goldner, R., Liu, T., Slaven, S., Gerouki, A., P., Z., Haas, T., Arntz, F. and Jones, S. (1996). *Development of a Thin Film $Li_{1-y}CoO_2/Li_xC_6$ Rocking-Chair Battery*. Proceedings of the Symposium on Thin Film Solid Ionic Devices and Materials, pages 173–182. 19

ITRS (2005). *Process Integration, Devices, and Structures*, International Technology Roadmap for Semiconductors, 2005 Edition. http://www.itrs.net/Links/ 2005ITRS/PIDS2005.pdf. 42

Jeon, S.-W., Lim, J.-K., Lim, S.-H. and Lee, S.-M. (2005). *As-deposited $LiCoO_2$ Thin Film Cathodes Prepared by RF Magnetron Sputtering*. Electrochimica Acta, 51:268–273. 22

Kanehori, K., Matsumoto, K., Miyauchi, K. and Kudo, T. (1983). *Thin Film Solid Electrolyte and Its Application to Secondary Lithium Cell*. Solid State Ionics, 9&10:1445. 18

Kozicki, M., Gopalan, C., Balakrishnan, M., Park, M. and Mitkova, M. (2004). *Non-Volatile Memory Based on Solid Electrolytes*. Proceedings. 2004 Non-Volatile Memory Technology Symposium, pages 10–17. 42

Lee, S.-H., Liu, P., Tracy, C. and Benson, D. (1999). *All-Solid-State Rocking Chair Lithium Battery on a Flexible Al Substrate*. Electrochemical and Solid-State Letters, 2(9):425–427. 21

Linden, D. and Reddy, T. (2002). *Handbook of Batteries*. McGraw-Hill, second edition. 13, 17, 18, 20, 24, 29, 32, 35, 54, 58

Müller, G., Nagel, N., Pinnow, C.-U. and Röhr, T. (2003). *Emerging Non-Volatile Memory Technologies*. ESSCIRC 2004 - 29th European Solid-State Circuits Conference (IEEE Conference Proceedings), pages 37–44. 40, 41, 42

Natarajan, S. (2004). *Emerging Memory Technologies*. Proceedings of SPIE, 5274:7–13. 41

Neudecker, B., Dudney, N. and Bates, J. (2000). *"Lithium-Free" Thin-Film Battery with In Situ Plated Li Anode*. Journal of the Electrochemical Society, 147(2):517–523. 21

Osaka, T. and Datta, M. (2000). *Energy Storage Systems for Electronics*, volume 1 of *New Trends in Electrochemical Technology*. Gordon and Breach Science Publishers. 18, 21, 31

Prince, B. (2002). *Emerging Memories - Technologies and Trends*. Kluwer Academic Publishers.

Schultze, J., Osaka, T. and Datta, M., editors (2002). *Electrochemical Microsystem Technologies*, volume 2 of *New Trends in Electrochemical Technology*. Gordon and Breach Science Publishers. 20

Signorelli, R., Schindall, J. and Kassakian, J. (2006). *Carbon Nanotube Enhanced Ultracapacitor*. `http://lees.mit.edu/lees/posters/RU13_signorelli.pdf`. 31, 32

Takamura, T. (2002). *Trends in Advanced Batteries and Key Materials in the New Century*. Solid State Ionics, 152-153:19–34. 20, 26

Yu, X., Bates, J., Jellison, G. and Hart, F. (1997). *A Stable Thin-Film Electrolyte: Lithium Phosphorus Oxynitride*. J. Electrochem. Soc., 144(2):524–532. 20