Methods for Testing and Analyzing Lithium-Ion Battery Cells intended for Heavy-Duty Hybrid Electric Vehicles

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Abstract

Lithium-ion batteries designed for use in heavy-duty hybrid vehicles are continuously improved in terms of performance and longevity, but they still have limitations that need to be considered when developing new hybrid vehicles.

The aim of this thesis has been to study and evaluate potential test and analysis methods suitable for being used in the design process when maximizing lifetime and utilization of batteries in heavy-duty hybrid vehicles.

A concept for battery cell cycling on vehicles has been evaluated. The work included development of test equipment, verification of hardware and software as well as an extended period of validation on heavy-duty trucks. The work showed that the concept has great potential for evaluating strategies for battery usage in hybrid vehicles, but is less useful for accelerated aging of battery cells.

Battery cells encapsulated in flexible packaging material have been investigated with respect to the durability of the encapsulation in a demanding heavy-duty hybrid truck environment. No effect on water intrusion was detected after vibration and temperature cycling of the battery cells.

Aging of commercial battery cells of the type lithium manganese oxide - lithium cobalt oxide / lithium titanium oxide (LMO-LCO/LTO) was investigated with different electrochemical methods to gain a deeper understanding of the origin of performance deterioration, and to understand the consequences of aging from a vehicle manufacturer's perspective. The investigation revealed that both capacity loss and impedance rise were largely linked to the positive electrode for this type of battery chemistry.

Postmortem analysis of material from cycle-aged and calendar-aged battery cells of the type LMO-LCO/LTO and LiFePO4/graphite was performed to reveal details about aging mechanisms for those cell chemistries. Analysis of cycle-aged LMO-LCO/LTO cells revealed traces of manganese in the negative electrode and that the positive electrode exhibited the most severe aging. Analysis of cycle-aged LFP/graphite cells revealed traces of iron in the negative electrode and that the negative electrode exhibited the most severe aging.
Sammanfattning

Litiumjonbatterier anpassade för användning i tunga hybridfordon förbättras kontinuerligt med avseende på prestanda och livslängd men har fortfarande begränsningar som måste beaktas vid utveckling av nya hybridfordon.

Syftet med denna avhandling har varit att studera och utvärdera potentiella prov- och analysmetoder lämpliga för användning i arbetet med att maximera livslängd och utnyttjandegrad av batterier i tunga hybridfordon.

Ett koncept för battericykling på fordon har utvärderats. Arbetet innefattade utveckling av testutrustning, verifiering av hårdvara och mjukvara samt en längre periods validering på lastbilar. Arbetet har visat att konceptet har stor potential för utvärdering av strategier för användandet av batterier i hybridfordon, men är mindre användbar för åldring av batterier.

Batterier kapslade i flexibelt förpackningsmaterial har undersömts med avseende på kapslingens hållbarhet i en krävande hybridlastbilsmiljö. Ingen påverkan på fuktinträngning kunde påvisas efter vibration och temperaturcykling av de testade battericellerna.

Äldring av kommersiella battericeller av typen litiummanganoxid - litiumkoboltoxid/litiumtitanoxid (LMO-LCO/LTO) undersökes med olika elektrokemiska metoder för att få en djupare förståelse för prestandaförändringens ursprung och för att förstå konsekvenserna av åldrandet ur en fordonstillverkarens användarperspektiv. Undersökningen visade att både kapacitetsförlust och impedanshöjning till största delen var kopplat till den positiva elektroden för denna batterityp.

Post-mortem analys av material från cyklade och kalenderåldrade kommersiella battericeller av typen LMO-LCO/LTO och LiFePO4/grafit utfördes för att avslöja detaljer kring åldringsmekanismerna för dessa cellkemier. Vid analys av cyklade LMO-LCO/LTO celler påvisades mangan i den negativa elektroden samt uppvisade den positiva elektroden kraftigast åldring. Vid analys av cyklade LFP/grafit celler påvisades järn i den negativa elektroden samt uppvisade den negativa elektroden kraftigast åldring.
List of appended papers

I. Novel Field Test Equipment for Lithium-Ion Batteries in Hybrid Electrical Vehicle Applications  
Pontus Svens, Johan Lindström, Olle Gelin, Mårten Behm and Göran Lindbergh  
_Energies_ 2011;4: 741-57

II. Li-Ion Pouch Cells for Vehicle Applications—Studies of Water Transmission and Packing Materials  
Pontus Svens, Maria Hellqvist Kjell, Carl Tengstedt, Göran Flodberg, and Göran Lindbergh  
_Energies_ 2013;6: 400-410

III. Non-uniform aging of cycled commercial LiFePO4/graphite cylindrical cells revealed by post-mortem analysis  
Matilda Klett, Rickard Eriksson, Jens Groot, Pontus Svens, Katarzyna Ciosek Högström, Rakel Wreland Lindström, Helena Berg, Torbjörn Gustafsson, Göran Lindbergh, Kristina Edström  
_Journal of Power Sources_ 257 (2014) 126-137

IV. Analysis of ageing of commercial composite metal oxide – Li4Ti5O12 battery cells  
Pontus Svens, Rickard Eriksson, Jörgen Hansson, Mårten Behm, Torbjörn Gustafsson and Göran Lindbergh  
Manuscript submitted to _Journal of Power Sources_

V. Lithium-ion battery cell cycling and usage analysis in a heavy-duty truck field study  
Pontus Svens, Mårten Behm and Göran Lindbergh  
Manuscript

VI. Uneven film formation across depth of porous graphite electrodes from cycling in commercial Li-ion batteries  
Matilda Klett, Pontus Svens, Carl Tengstedt, Antoine Seyeux, Jolanta Swiatowska, Göran Lindbergh, and Rakel Wreland
Lindström

Manuscript

Not included in the Thesis:

**HEV lithium-ion battery testing and driving cycle analysis in a heavy-duty truck field study**
P. Svens, J. Lindström, M. Behm and G. Lindbergh
ECS Transactions, 41 (32) 13-26 (2012)

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My contribution to the different papers in the thesis

I. Planned the work and executed the experiments, main author of the text
II. Planned the main part of the work and executed the cell testing and the main part of the cell and test set-up preparation, main author of the text
III. Contributed to the planning of the work and the disassembly of cells, the main contributor to SEM and EDX measurements, participated in the writing
IV. Planned the work and executed all experiments except XRD, main author of the text
V. Planned the work and executed the experiments, main author of the text
VI. Contributed to the planning of the work and to SEM and EDX measurements, participated in the writing
**Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>HEV</td>
<td>Hybrid electric vehicle</td>
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<tr>
<td>EGR</td>
<td>Exhausts gas regulation</td>
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<tr>
<td>SCR</td>
<td>Selective catalytic reduction</td>
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<tr>
<td>NO\textsubscript{x}</td>
<td>Generic term for mono-nitrogen oxide gases</td>
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<td>ISO</td>
<td>International organization for standardization</td>
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<td>USABC</td>
<td>United states advanced battery consortium LLC</td>
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<td>EUCAR</td>
<td>European council for automotive R&amp;D</td>
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<tr>
<td>SOC</td>
<td>State of charge</td>
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<tr>
<td>OCV</td>
<td>Open circuit voltage</td>
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<tr>
<td>LMO</td>
<td>Lithium manganese spinel oxide</td>
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<tr>
<td>LCO</td>
<td>Lithium cobalt oxide</td>
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<tr>
<td>LTO</td>
<td>Lithium titanium oxide/Lithium titanate</td>
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<tr>
<td>LFP</td>
<td>Lithium iron phosphate</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid electrolyte interphase</td>
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<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>EC</td>
<td>Ethylene carbonate</td>
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<tr>
<td>DMC</td>
<td>Dimethyl carbonate</td>
</tr>
<tr>
<td>EMC</td>
<td>Ethyl methyl carbonate</td>
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<tr>
<td>ECU</td>
<td>Electronic control unit</td>
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<tr>
<td>BMU</td>
<td>Battery management unit</td>
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<tr>
<td>CAN</td>
<td>Controller area network</td>
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<tr>
<td>PWM</td>
<td>Pulse width modulation</td>
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<tr>
<td>PCB</td>
<td>Printed circuit board</td>
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<tr>
<td>DC/DC</td>
<td>Voltage converter (direct current)</td>
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<tr>
<td>I/O</td>
<td>Input and output</td>
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<tr>
<td>NTC</td>
<td>Negative temperature coefficient</td>
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<tr>
<td>DUT</td>
<td>Device under test</td>
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<tr>
<td>C-rate</td>
<td>1C-current discharges a battery in 1 h</td>
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<tr>
<td>WVTR</td>
<td>Water vapor transmission rate</td>
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<tr>
<td>ASTM</td>
<td>American Society for testing and materials</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
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<tr>
<td>EDX</td>
<td>(or EDS) Energy dispersive X-ray spectroscopy</td>
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<tr>
<td>FIB</td>
<td>Focused ion beam</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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<tr>
<td>CCC</td>
<td>Constant current cycle</td>
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<tr>
<td>HEVC</td>
<td>Hybrid electric vehicle cycle</td>
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<tr>
<td>CSC</td>
<td>City suburban cycle</td>
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<tr>
<td>UDDS</td>
<td>Urban dynamometer driving cycle</td>
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1 INTRODUCTION

1.1 HYBRID ELECTRIC VEHICLES
Increased demands on lowered tail-pipe emissions from new vehicles forces the automotive industry to include alternative fuels and electrification in the vehicle developing process. Tail-pipe emissions from individual vehicles have been reduced considerably during the last decades [1, 2], but worldwide total emissions from the transport sector have increased considerably with the growing number of vehicles [3, 4]. To address this problem, new vehicle technologies such as hybridization have started to emerge. Introduction of hybrid electric vehicles, HEVs, to the market has the potential of significantly reducing tail pipe emissions. Reduction of vehicle fuel consumption with subsequent reduction of tail-pipe emission has historically followed emission legislations. In Europe for example, vehicle emission regulations have been used since 1988, starting with directive 88/77/EEC for vehicles with diesel engines and directive 88/76/EEC for vehicles with petrol engines [5, 6]. The present European emission standard for passenger cars is called Euro 5 and was introduced in 2008. The Euro 5 emission standard introduced a lowered NO\textsubscript{x} limit compared to the former Euro 4 standard [7, 8]. The upcoming Euro 6 standard is meant to be introduced in September 2014. The corresponding emission standard for heavy-duty vehicles with an allowed total weight over 12000 kg (class N3 vehicles) is called Euro VI and was introduced in December 2013. It comprises lowered emission levels of both hydrocarbons and NO\textsubscript{x} as well as particulate matters. The goal for European heavy-duty vehicle manufacturers is to meet the Euro VI standard using existing and mature technology such as exhaust gas regulation (EGR), selective catalytic reduction (SCR) and particle filters. Even if hybridization is not needed to meet the Euro 6/VI standard, experts are convinced that hybridization will play an important role in future vehicle technology [9-12].

Another benefit with hybridization is the potential of reducing local emissions by, for example, introducing hybrid buses to decrease inner city
2 | Introduction

air pollution. London politicians have become aware of this potential and the regional public traffic company in London, Transport for London (TfL) are gradually replacing all inner city buses in London with hybrid buses. In January 2012, 200 hybrid buses were already in use and today around 600 hybrid buses are in operation [13]. The long-term plan is to have more than 1700 hybrid buses in London by 2016 and also introduce pure electric buses on some routes [14]. Other cities are following this trend of introducing hybrid city buses, for example the regional public transportation operator Keolis in Stockholm, Sweden. They will acquire more than 50 hybrid buses during 2014 [15].

The motivation for transportation companies to choose hybrid vehicles instead of conventional vehicles needs to be both economical and environmental. Fuel saving is a major driving force and hence the additional cost for the hybrid system needs to be low enough to achieve a reasonably short payback time for the HEV customer. Companies that have a policy to be “green” could also improve their public image by having hybrid vehicles in the fleet. Even if there is a potential for reducing tail-pipe emissions by for example using ethanol as fuel, a global study performed by the company Arthur D. Little regarding the usage of different fuel types and hybridization of heavy-duty vehicles predicts that diesel fuel still will be the dominating source of energy for the transport sector in 2020 [16]. However, the trend in this study is that the usage of alternative fuels will increase while diesel fuel usage will stagnate, or even decline. Furthermore, hybridization is predicted to be an increasing technology for heavy-duty vehicles with focus on hybridization of city buses and distribution trucks. The study also concludes that the major obstacle for hybrid vehicle development is the additional energy storage; the battery system.

1.2 Battery System

A battery system consists of a number of battery cells that are individually monitored and balanced, and a cooling system, all placed in a rigid container. Cell monitoring and balancing systems keep all cell voltages within operating limits and the cooling system guarantees operation within temperature limits. Today the most promising battery technology for both passenger car HEVs and heavy-duty HEVs is lithium-ion battery systems. This is due to higher energy and power capabilities compared to
other battery technologies, such as lead-acid and nickel-metal hydride (NiMH).

To ensure optimal HEV-battery lifetime, it is important to understand how the batteries are ageing by performing tests both in laboratory and in real applications. Battery ageing in laboratory can be done by running tests that continuously cycle batteries between a fully charged and fully discharged state, or by using specific test cycles that intend to emulate actual usage. There are several standardized test cycles available from different organizations, for example ISO, USABC and EUCAR [17-19]. Since ageing of batteries is time consuming, different ways of accelerating ageing can be used to shorten the test time, for example elevated temperature or increased allowed voltage span. Increasing the temperature to accelerate battery ageing is however problematic since, depending on battery chemistry, certain chemical reactions are more temperature dependent than others [20]. This could make battery ageing different in the laboratory than in a real application and would hence provide an incorrect estimation of the battery lifetime. Even if laboratory testing is performed at a similar temperature compared to real life applications, the test cycle is not completely reflecting how a HEV-battery is used in real applications. One problem with estimating battery lifetime from laboratory measurements is that the usage of the battery can have a large spread in the real application if the hybrid vehicle strategy is allowing for that. To handle this, testing can be performed on an estimated worst-case scenario to have a marginal for the spread of battery usage. Results from too harsh testing could however lead to a too intense battery service plan for the customer and this would add unnecessary cost. A method for estimating battery lifetime more accurately could result in extended time between battery services and consequently lowered cost for the customer. This is even more problematic for heavy-duty hybrid vehicles compared to hybrid passenger cars since the runtime is much higher in the previous case. A battery pack is most likely not predicted to last the whole lifetime of a heavy-duty HEV, and due to high battery cost, one or several battery pack replacements could jeopardize the business case for a heavy-duty HEV. It is hence of great importance that battery lifetime estimations are accurate and that battery usage is optimized for long life. The high cost [10, 21] of HEV battery systems is a major issue. Even with an estimated cost for a lithium-ion battery system
as low as $300/kWh, the growth of for example light-duty HEVs is predicted to be rather small during the next 30 years [9, 10].

Results published on battery ageing from real life tests have in the past mainly focused on NiMH-battery systems, since those batteries up to now have been the best choice for hybrid passenger car manufacturers such as for example Toyota and Honda. There are only a handful of publications available regarding real life studies on lithium-ion batteries for propulsion of vehicles, and hardly anything regarding heavy-duty HEVs. Liaw et al have published several articles regarding real life studies on plug-in hybrids, focusing on driving cycle analysis (DCA) [22-25]. Idaho National Lab (INL) performed a large study on HEV-battery ageing between 2001 and 2005. The HEVs in that test were equipped with NiMH-batteries and battery capacity loss was calculated from measurements at the beginning and at the end of the test [26, 27].

1.3 THE BATTERY CELL

Commercial lithium-ion battery cells are available in mainly three formats; cylindrical metal can, prismatic metal can and flexible packaging. The latter is normally called pouch cell packaging. Cylindrical cells are for example widely used in laptops and pouch cells are used in mobile phones. All three cell formats are possible candidates for the automotive industry when designing electrified vehicles. However, each cell format has both advantages and disadvantages. The cylindrical cell is a proven design with established high volume production, especially for certain cell dimensions, for example the 18650 cell. This cell is 18 mm in diameter and 65 mm long and is used in for example the electric car Tesla Model S [28]. The cylindrical geometry of the cell withstands internal pressure well without changing shape. Since the electrodes and separators inside this type of cell are rolled together in a jellyroll fashion, there is a risk for uneven temperature distribution during cycling, especially for larger cell formats. This temperature distribution could in turn generate uneven ageing. The prismatic cell design is more favourable regarding temperature distribution in large cells and requires less volume when assembled into modules compared to the cylindrical cell. This cell type is used by several vehicles manufacturers and is for example used in the electric car Mitsubishi i-Miev [29]. The metal can design is a better choice regarding mechanical integrity compared to the pouch cell but is more expensive. Since the automotive industry is very cost driven, and
since batteries for electrified vehicles in general are expensive, the flexible packaging is an attractive choice despite lower mechanical integrity. The shortcoming of mechanical strength can however be attended to by protection within the battery module. Another uncertainty regarding pouch cells, especially considering the complete lifetime of a battery pack, is the chemical integrity. Flexible packaging materials for lithium-ion batteries consists of multilayered laminates that are heat sealed during production. The multilayered laminates consist of several layers of polymer films and an aluminium foil. This aluminium foil is a good protection against diffusion of species out from the battery cell as well as into the cell. This type of packaging material are widely used in for example the food industry and the pharmaceutical industry where the demands are high regarding low diffusion rate of both oxygen and water through the packaging. One concern is however how the thermal polymer welds of this type of packaging withstands for example water intrusion during the lifetime of a battery in the harsh environment of a vehicle. Jansen et al. have earlier reported about water intrusion into pouch cells [30, 31]. The methods used in that work for detecting water intrusion was Karl Fisher titration combined with buret titration. The Karl Fisher method detects traces of water in the electrolyte while buret titration detects HF. Since water reacts with the commonly used LiPF$_6$ salt in lithium ion batteries to form HF, both analysis methods mentioned above are needed to measure the total amount of water that have penetrated the cell.

1.4 LITHIUM-ION CELL CHEMISTRY

The lithium-ion battery cell is also known as the “rocking-chair” battery since lithium-ions (Li$^+$) are moving between the electrodes during charge and discharge, without being reduced to metallic form. This incorporation of lithium-ions into the crystal structure of the electrode materials is called intercalation. Figure 1 shows the principle of the lithium-ion battery during discharge, displaying the negative and the positive electrode with the electrolyte-soaked separator in between.
During discharge, an oxidation process that releases electrons occurs at the negative electrode and a reduction process that consumes electrons occurs at the positive electrode. This generates an electric current that flows from the positive electrode to the negative electrode through an external load. Lithium ions simultaneously deintercalate from the negative electrode material, travel in the electrolyte through the separator and intercalates into the positive electrode material.

Research on lithium-ion batteries started already in the 1970’s and the “rocking-chair” concept was established in 1976 by Whittingham [32]. It took however until 1990 for the breakthrough that lead to commercialization and market introduction of the lithium-ion battery by Sony Corporation [33]. Some examples of technical issues with those early lithium-ion batteries intended for consumer electronics were short lifetime and poor safety. Although present lithium-ion batteries are safer and have improved lifetime, the operating environment and the usage of batteries in a HEV application, especially a heavy-duty HEV application, are quite different compared to consumer electronics applications. This requires new strategies regarding usage of the batteries to obtain optimal performance and long lifetime. For example, usage of the battery in a
heavy-duty HEV involves high charge currents as well as high discharge currents. In some cases, the charge currents can be similar or even higher than the discharge currents. Since lithium-ion batteries historically have been used in applications with higher demands on discharge currents, the cells have normally been designed with a higher discharge current capability. Today however, battery cells capable of handling both high discharge currents and high charge currents are commercially available.

1.4.1 POROUS ELECTRODES
The electrode material in rechargeable lithium-ion battery cells commonly consist of a mixture of electrochemically active material, electrically conductive material and a binder. During cell production, both sides of a thin metal foil sheet are covered with a suspension of this mixture. After further processing, including removing the solvent, the electrode is ready to be assembled into battery cells. Since the electrode material is porous, electrolyte will be present throughout the thickness of the electrode material after cell assembly. This type of electrode design leads to large active surface areas where electrochemical reactions can occur, and this makes it possible to apply high cell currents while keeping the current densities inside the cell low.

1.4.2 NEGATIVE ELECTRODE
The most common negative electrode active material used in lithium-ion batteries is graphite. When charging a battery cell with graphite electrode, lithium ions are inserted between graphite layers. The electrode reaction is presented below.

\[ C_6 + Li^+ + e^- \leftrightarrow LiC_6 \]

Lithiated graphite has an electrochemical potential close to Li/Li\(^+\) which, when combined with a suitable positive electrode active material, results in a cell with high voltage and high energy density. The electrolyte solvent is however not stable at this potential, hence formation of a surface film due to irreversible reactions between lithium ions and the solvent is occurring. This surface film is called solid electrolyte interphase (SEI) and contains LiF and several other components depending on electrolyte composition [34, 35]. The SEI grows during the initial charge and discharge cycles to stabilize at a certain thickness eventually, making the graphite surface passive to further reactions. However, several studies have shown that the SEI has a dynamic behaviour and is depending on
battery state of charge (SOC), the history of usage and the cell temperature [36, 37]. This dynamic behaviour of the SEI is unwanted since it consumes cyclable lithium and causes loss of negative electrode active material [38]. The low electrochemical potential of graphite can also result in lithium plating during charge, especially at low temperatures [39]. Since lithium plating can cause accelerated ageing, charging in low temperatures needs to be avoided to guarantee long battery life.

Lithium titanate, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ or LTO, is a negative electrode active material that meets the demands from the automotive industry regarding high power charging in HEVs. The electrode reaction is presented below.

$$\frac{1}{3}\text{Li}_4\text{Ti}_5\text{O}_{12} + \text{Li}^+ + e^- \leftrightarrow \frac{1}{3}\text{Li}_7\text{Ti}_5\text{O}_{12}$$

Lithium titanate has an electrochemical potential of 1.55 V vs. Li/Li$^+$ with a flat voltage vs. capacity behaviour. The flat voltage behaviour is due to coexistence of the two phases $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_7\text{Ti}_5\text{O}_{12}$ [40, 41]. There are several benefits using lithium titanate as negative electrode active material instead of the commonly used graphite. One advantage is the zero-strain nature of the material that allows intercalation and deintercalation of lithium ions with insignificant volume change. This vouches for low mechanical stress of the material even during high current cycling and is beneficial for long cycle life. Another advantage is the high electrochemical potential of 1.55 V which is within the electrochemical stable potential window for the electrolyte. This minimizes the driving force for lithium consuming surface film formation. The lack of surface film also has a benefit for safety since breakdown of the negative electrode surface film is considered to be the source of heat in a lithium-ion battery cell during thermal runaway [42]. However, although not in the same extension as for graphite, formation of SEI on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been reported to occur, foremost during cycling by consumption of solvent while gas, mainly consisting of $\text{CO}_2$, $\text{H}_2$ and $\text{CO}$ is formed [43]. In addition, the high electrochemical potential makes it possible to charge this type of cell with high currents even at low temperatures without risk for lithium plating. The drawback is lower cell voltage, ~2.4 V compared to ~3.7 V for a lithium-ion cell containing graphite, with following lower energy density. However, it is possible to
cycle cells containing LTO within in a wide SOC-window without sacrificing lifetime due to the zero-strain nature of the material.

This electrode chemistry is today used in lithium-ion batteries intended for optimizing idle stop-start functionality in mild hybrid passenger cars. One example is Suzuki that uses lithium titanate based cell chemistry in the 12V lithium-ion pack that is used in parallel with the normal lead-acid battery in the car model Wagon R [44, 45].

1.4.3 POSITIVE ELECTRODE

A widely used positive electrode active material for lithium-ion batteries is lithium cobaltite, LiCoO₂ or LCO. This layered transition metal oxide is delithiated during charging according to the following reaction:

\[ 2\text{LiCoO}_2 \leftrightarrow 2\text{Li}_{0.5}\text{CoO}_2 + \text{Li}^+ + \text{e}^- \]

\( \text{Li}_{0.5}\text{CoO}_2 \) is the lowest delithiation degree for a reversible electrochemical reaction for this material. If delithiated further, irreversible oxygen evolution will occur [46]. It is also reported in literature that heavily cycled lithium cobaltite electrode active material can transform into a more inert cubic spinel form, \( \text{Li}_2\text{Co}_2\text{O}_4 \), causing irreversible capacity loss [47-49]. Lithium cobaltite has a high electrochemical potential vs. \( \text{Li}/\text{Li}^+ \) and in combination with a suitable negative electrode active material the cell voltage, as well as the energy density will be high. Due to the high energy density, LiCoO₂/graphite cells have been frequently used in consumer electronic products during the last decades. The disadvantages of this cell chemistry is poor safety and high cost.

To address battery safety and cost issues, intense research was performed during the 1990th on the positive electrode active material manganese spinel oxide, \( \text{LiMn}_2\text{O}_4 \) or LMO [46, 50]. During lithiation a transformation from \( \text{Mn}_2\text{O}_4 \) to \( \text{LiMn}_2\text{O}_4 \) takes place in two steps, manifested as two distinctive voltage plateaus at \( \sim 4.0 \text{ V} \) and \( \sim 4.15 \text{ V} \) in the discharge curve [46]. The electrode reaction is presented below.

\[ \text{LiMn}_2\text{O}_4 \leftrightarrow \text{Mn}_2\text{O}_4 + \text{Li}^+ + \text{e}^- \]
Further lithiation is possible but intercalation of LiMn$_2$O$_4$ to Li$_2$Mn$_2$O$_4$ only provides a potential of ~3V vs. Li/Li$^+$. Delithiation back to the 4 V-region involves irreversible capacity loss.

There are several reports in the literature describing Mn$^{2+}$ dissolution for this material, especially during usage at elevated temperatures. The proposed ageing mechanism is formation of Mn$^{3+}$ due to acid dissolution of the spinel structure. The acidic environment is reported to relate to HF formed by decomposition of the lithium salt, LiPF$_6$. The Mn$^{3+}$ ions are reacting further forming Mn$^{4+}$ and Mn$^{2+}$, of which Mn$^{2+}$ is dissolved in the electrolyte. Formation of HF is in literature often related to reaction between the lithium salt and traces of water in the electrolyte, according to the reactions below.

\[
\text{LiPF}_6 \leftrightarrow \text{LiF} + \text{PF}_5
\]

\[
\text{PF}_5 + \text{H}_2\text{O} \leftrightarrow \text{PF}_3\text{O} + 2\text{HF}
\]

If the water content inside battery cells are kept low, and if electrode matching is done properly to prevent over-lithiation, the manganese spinel oxide is an attractive material for use in battery systems for hybrid vehicles [51]. In addition, for applications where high power is needed, the manganese spinel oxide could be coated or mixed with lithium cobaltite to enhance conductivity [52-54].

Another positive electrode material that has been studied intensively from late 1990s until today is the lithium iron phosphate, LiFePO$_4$ or LFP [55, 56]. This material has an olivine structure and deintercalates into FePO$_4$ during charging [41].

\[
\text{LiFePO}_4 \leftrightarrow \text{FePO}_4 + \text{Li}^+ + \text{e}^-
\]

Similar to lithium titanate, LiFePO$_4$ and FePO$_4$ coexists throughout almost the whole SOC-window [57, 58]. This results in a flat potential of 3.45 V vs. Li/Li$^+$. Despite a poor rate capability and a lower potential for this material compared to lithium cobaltite and lithium manganese spinel oxide, LFP based batteries are used in for example heavy-duty HEVs [59, 60]. High rate capability for battery cells with LFP is achievable by using small particles and mixing the material with conductive carbon during production [61, 62]. LFP is considered to be a safer material due to the
strong bonding of oxygen in the phosphate group. This results in better resistance to thermal runaway compared to other positive electrode materials [63] and this is favourable in a HEV application. The usage of low cost raw materials is also an advantage compared to nickel and cobalt containing positive electrodes. The relatively low electrode potential and hence lower energy content is a disadvantage of LFP.

1.4.4 SEPARATOR
To prevent internal short circuit in a lithium-ion cell, an electronically insulating polymer film separates the positive electrode from the negative electrode internally. The most common type of this polymer film used in commercial lithium-ion cells today is the PP/PE/PP separator. This type of separator consists of three polymer layers where the outer layers consist of polypropylene (PP) and the inner layer of polyethylene (PE). The separator has pores large enough to allow electrolyte to pass through while small enough to hinder contact between positive and negative electrode material. The inner PE-layer has a melting point of about 130 °C that is lower than the melting point of the PP-layers. The pores in the PE-layer will close above this temperature and this will provide a shutdown function for the cell during for example an external short circuit [64].

1.4.5 ELECTROLYTE
The electrolyte in a commercial lithium-ion cell normally consists of a lithium salt dissolved in a solvent mixture that also contains small amounts of additives. The additives can be of different types such as flame-retardants and red-ox shuttles. The lithium salt is commonly LiPF$_6$ that has adequate qualities regarding for example electrochemical stability and usable temperature range for a commercial lithium-ion battery. Examples of solvents used in commercial lithium-ion battery cells are ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC).
2 SCOPE OF THE THESIS

2.1 RESEARCH CONTEXT

Most of the work in this thesis was carried out within the framework of a co-operation between academy and Swedish heavy-duty vehicle industry. The partners in this group, called the Lithium-ion cluster, are Scania CV AB, VOLVO AB, KTH, Chalmers and Uppsala University. The main objective with this co-operation has been to seek answers regarding ageing of battery cells intended for heavy-duty hybrid electric vehicles. Four PhD students with different backgrounds and research focus have been working together in this constellation to obtain a broader knowledge of battery cell ageing from a material and modelling point of view, as well as from large cell cycling and a vehicle-testing point of view. Another goal has been to spread knowledge about the separate research projects within the group and publish joint research papers. All research projects within this co-operation were financed separately.

This project was divided into two parts, where Scania CV AB financed the first part together with the Swedish Energy Agency in the program PFF - program Road Vehicle research. This part of the work resulted in the licentiate thesis Development of a Novel Method for Lithium-Ion Battery Testing on Heavy-Duty Vehicles (ISBN 978-91-7501-192-9). Scania also financed the second part of the project together with the Swedish Energy Agency, in the program Energy Efficient Road Vehicles, FFI - program Energy and Environment.

The first part of this project focused on realizing an idea within Scania regarding a concept for testing battery cells on-board heavy-duty vehicles. This work resulted in one paper in the thesis. This battery-testing concept was also used to evaluate a hybrid vehicle strategy on vehicles, and resulted in one paper in the thesis. Early during the project, two lithium-ion battery chemistries were considered most interesting as candidates for HEVs at Scania, and were hence focused on in the following work. The two lithium-ion chemistries were LMO-LCO/LTO and LFP/graphite.
The work throughout this project has focused on ageing of commercial lithium-ion battery cells. In the beginning of the project, a question regarding the integrity of lithium-ion pouch cell encapsulations arose. This question was addressed and resulted in one paper in the thesis. One goal within this project was to identify non-destructive methods suitable for detecting battery ageing on-board HEVs. Two promising methods, incremental capacity analysis and differential voltage analysis were successfully evaluated on LMO-LCO/LTO battery cells and resulted in two papers in the thesis. Knowledge about opening commercial battery cells and collecting electrode material for analysis was present within the Lithium-ion cluster group. This knowledge was used in several papers in the thesis to obtain more detailed information about battery ageing in commercial cells.

2.2 AIM

The overall aim for this work was to evaluate methods for testing and analyzing commercial lithium-ion battery cells intended for use in heavy-duty HEVs. The evaluated methods should be useful in the development of HEV battery systems in terms of optimizing usage and minimizing long-term cost.

Real life battery testing onboard vehicles, scaled down to cell level has been evaluated. Performing battery cell testing onboard conventional vehicles can result in both cost and time benefits compared to full scale HEV testing due to better availability of vehicles and inexpensive test system. Another big advantage with single cell testing on conventional vehicles is the possibility to periodically perform onboard battery performance tests, something that usually is not possible when testing batteries on HEVs. This type of testing has a potential to be a useful complement to laboratory testing and HEV testing.

A method for testing the integrity regarding humidity for flexible battery cell encapsulations was evaluated. A shift from rigid battery cell encapsulations to flexible battery cell packaging in HEVs raises questions regarding mechanical and chemical integrity during the life of a vehicle. In this work, the aim was to study the influence of mechanical and thermal stress on flexible battery cell packaging, focusing on resistance against water intrusion.
Several methods for analyzing ageing of power optimized commercial battery cells were evaluated on two different cell chemistries; LMO-LCO/LTO and LFP/graphite. Cycle-aged and calendar-aged cells were compared regarding capacity reduction and impedance rise. Changes on electrode level were analyzed both with electrochemical methods such as incremental capacity analysis and differential voltage analysis, as well as with material analysis methods. The aim was to acquire a deeper understanding about the influence of individual electrode ageing on full cell performance.

The work on the concept for testing battery cells on-board heavy-duty vehicles was motivated by the lack of available field test equipment and published papers on field-testing of commercial lithium-ion batteries intended for heavy-duty HEVs.

The pouch-cell integrity work was motivated by the lack of reports in literature on tests of pouch cells exposed to vibrations and temperature cycling in a heavy-duty vehicle environment.

The evaluation of incremental capacity analysis and differential voltage analysis was motivated by lack of reported work using these methods on commercial LMO-LCO/LTO battery cells intended for usage in heavy-duty HEVs.

The detailed analysis of ageing mechanisms in commercial LFP/graphite cells was motivated by the lack of reported work on this cell type regarding ageing when using a current cycle representative to a HEV city bus driving cycle.
Scope of the thesis
3 **EXPERIMENTAL**

3.1 **ON-BOARD REAL TIME FIELD TEST EQUIPMENT**

3.1.1 **MATERIALS AND EQUIPMENT**

Test equipment intended for real time battery cell testing on conventional vehicles was specified, designed, manufactured, verified and validated within this project. The purpose of the test equipment was to evaluate the concept of performing real time cell level battery testing on-board conventional heavy-duty vehicles, to a low cost and with a relatively short test time.

The battery cells used in the verification phase of the test equipment were commercial LFP/graphite cells rated to 3.6Ah. The batteries used in the validation phase were commercial LMO-LCO/LTO cells rated to 3.1Ah.

3.1.2 **CONCEPT**

The developed test method, intended for usage on conventional heavy-duty vehicles, is based on the concept that the existing starter battery in a vehicle can be used for both charging and discharging the tested battery cell. Using electric power from the starter battery and sensor information from the vehicle internal communication network (Controller Area Network, CAN [65]), makes it possible to emulate a HEV-environment for the tested battery cell. The test equipment hardware consists of three parts;

1. the electronic control unit (ECU), which contains software for converting vehicle sensor data to corresponding battery cell currents.
2. the battery management unit (BMU), which contains hardware and software for performing battery cycling and measurements, including handling data storage.
3. the device under test (DUT) which includes one tested battery cell, one reference cell, two temperature sensors, eight power resistors and one aluminium holder. The concept is shown in Figure 2.
Vehicle sensor information on CAN is continuously monitored and this information makes it possible to cycle the tested battery in real time with a current depending on the driving pattern of the vehicle.

3.1.3 HARDWARE
The system was designed so that the communication with the vehicle is handled solely by the ECU and all battery cell interactions are handled by the BMU. This division enables hybrid vehicle specific software to be exclusively implemented in the ECU, making it possible to use the BMU together with other HEV software systems.

The main parts of the BMU hardware are the power electronics in form of a step-up, step-down DC/DC-converter, the microprocessor and the data storage unit, all placed on the same printed circuit board (PCB), as shown in Figure 3a.
Figure 3: (a) BMU schematic and (b) BMU hardware layout.

Figure 3b shows the BMU hardware layout with the main parts and essential inputs and outputs marked. The power electronics part of the BMU is essentially a two-quadrant, four-phase DC/DC converter with high efficiency. This two-quadrant design permits bidirectional power flow (positive and negative currents) that allows the battery cell to be both charged and discharged. The DC/DC converter is controlled and monitored by the microprocessor, which in turn is controlled by the ECU via the CAN-interface. The maximum available current is ± 160 A.

Power is taken from the 24 V-system during charging and power will be delivered back to the 24 V-system during discharging. This approach requires that the electrical system has the capacity to both deliver and receive the needed power without introducing disturbances in vehicle performance.

The DUT consists of two battery cells, two temperature sensors attached to opposite sides of one battery, and eight power resistors in a series connection, all placed in an aluminium casing (Figure 4). One cell is cycled while the other is used as reference. The power resistors are used for heating the battery cell when necessary, to be able to resemble a true HEV-battery temperature.
Figure 4: Example of a battery housing with place for cylindrical battery cells and temperature sensors (circular opening), and power resistors (square openings).

Before verification and validation, the BMU, DUT and cables (including fuses on power cables) were placed in an aluminium casing as seen in Figure 5.

Figure 5: Assembly of the BMU, DUT and connecting cables in an aluminium casing.

During field-testing, the cell voltage was measured and recorded with a sample rate of 10 Hz and an accuracy of ±0.01 V. The cell current was measured with a sample rate of 10 Hz and a measurement accuracy of ±0.1 A. Two temperature sensors were used for measuring battery surface temperatures and one sensor for measuring the ambient temperature inside the aluminium casing. The temperatures were measured with a sample rate of 0.1 Hz and an accuracy of ±0.5 °C.
3.1.4 SOFTWARE
The software in the ECU essentially converts real time sensor data received from the vehicle to a signal for controlling the current through the tested battery cell. This current should correspond to the current in an HEV-battery. The hybrid strategy software from a Scania hybrid truck was chosen to be the foundation of the software in the ECU. The hybrid strategy software makes decisions about how to apply the available electrical motor (EM) power in the HEV into the drive train, based on information about vehicle and battery status, for example vehicle speed and acceleration, and battery SOC and temperature. Since HEV-specific components are missing in conventional trucks, those components have to be emulated by software in the test equipment. The signals needed are generated using vehicle sensor information available in conventional trucks. The hybrid strategy used in both the verification and validation phase was developed for Scania hybrid trucks and buses. This hybrid strategy allows higher charging rates than discharging rates with the intention of using the abundance of charging power available when braking to maximize the usage, i.e. use a large SOC-window of the battery pack. Since mild hybridization has been found to be the most cost-effective approach for Scania vehicles as well as the use of a relatively small battery pack, the allowed cycle depth is high for this strategy, between ~20 % and ~80 % SOC, to obtain sufficiently high cyclable energy. The hybrid strategy is optimized for reducing fuel consumption and is designed to allow battery SOC and battery power to follow the driving pattern.

3.1.5 MOUNTING
During verification and validation, test equipment was mounted on the starter battery box on Scania trucks (Figure 6). The ECU was placed in the cabin, close to the connection point for the CAN-communication.
3.2 CELL PACKAGING INTEGRITY

Commercial lithium-ion battery pouch cells (130 mm x 200 mm, 12 Ah) were studied to investigate the integrity of the cell encapsulation. Three cells were exposed to vibration and temperature cycling at Scania CV AB according to standard ISO16750-3 [11], paragraph 4.1.2.7, “Test VII - Commercial vehicle, sprung masses”. The cells were vibrated for 144 hours while the temperature was ramped between -25 °C and +60 °C at a rate of ~4 °C/minute. A vibration equipment LDS V8 and temperature chamber Vötsch VCV 7120-5 were used. The battery cells were mounted on a holder according to Figure 7 and were not electrically connected during the test.
Capacity measurements (1C at 25 °C) were performed before and after the environmental testing of the cells. An Amrel PLA 800-60-300 electrical load was used together with a NI 9219 National Instruments data acquisition equipment and the test was performed in a B.I.A Climatic MTH 4-30 climate chamber.

All battery cells were completely discharged before opening the encapsulations. The cells were opened by making an incision with a scalpel on the side opposite to the current collector tabs and no thermal welds were affected by this procedure. Electrodes and separator were gently removed from the cells. Residual electrolyte was thereafter allowed to evaporate from the empty encapsulations for 12 hours in a fume hood. When drying was completed, the battery packages were prepared for integrity measurements; Swagelok connectors with welded washers were attached to the battery packages with epoxy glue as shown in Figure 8. The opening made earlier was sealed with epoxy glue together with a plastic bar to stabilize the set-up.

A commonly used method for testing resistance to water intrusion for flexible packaging material is water vapour transmission rate measurement, WVTR \[66\]. WVTR measurements were performed according to the standard method for water vapour transmission rate through plastic films and sheeting, ASTM F 1249-05 \[67\]. A schematic overview of the WVTR-measurement set-up is presented in Figure 9.
The Test object in Figure 9 consisted of two battery packages that were enclosed in plastic boxes, as shown in detail in Figure 10. Preconditioning of the packages was carried out in an environment where the humidity was close to 0 %. Temperature and humidity measurements inside the plastic boxes that were acting as a climate chambers for the battery packages were done with Rotronic HygroPalm HY-Palm 0 sensors (Figure 10).

Two different equipments were used for the WVTR measurements, a Mocon Permatran W 3/31 MG with a water vapor detection limit of 30 µg
per package and day, and a Mocon Aquatran Model 1 with a water vapor detection limit of 2.5 µg per package and day. Both test equipments handle two samples simultaneously. The Mocon Permatran uses an IR-detector while the Mocon Aquatran uses an electrochemical detector, a coulometric phosphorous pentoxide sensor. WVTR measurements performed on the Permatran equipment were preceded by preconditioning of the packages by purging with nitrogen at a flow rate of 150 ml/min for about 7 days at 23 °C. The flow rate of nitrogen during measurement was 10 ml/min and the examination time for each sample was 45 minutes. The water vapour transmission rate was studied at 100 % relative humidity (RH) and 23 °C. Before starting measurements on the Aquatran equipment, preconditioning was performed by first purging packages, tubing, the Agilent BMT moisture trap and valves with nitrogen at a flow rate of 170 ml/min during 45 days at 50 °C. In this set-up, the packages and valves were placed inside boxes filled with drying agent (Figure 10). The entire set-up was heated up in a Firlabo SP260BVEHF climate chamber during preconditioning. Additional purging with dry nitrogen was carried out for 7 days at 23 °C after connecting the set-up to the Aquatran equipment. Only the tubing, the Agilent moisture trap and the valves in the two lower boxes in Figure 10 were purged during this step. In addition, silicon grease (Dow) was applied to all valves to counteract contamination of water. The flow rate of nitrogen during measurement was 23 ml/min. The examination time for one test cycle was 5 hours. The water vapour transmission rate was studied at 80 % RH using a KCl solution to ensure a condition below the dew point at 23 °C, which was the temperature during testing. The WVTR measurements were performed on two cells, one vibrated and one un-stressed, using both the Permatran and the Aquatran equipment.

3.3 LMO-LCO/LTO CELL AGEING

Commercial power-optimized LMO-LCO/LTO cells with a rated initial capacity of 3.1 Ah and a nominal voltage of 2.4 V were acquired from a reputable supplier for this study. Cycling of cells was done both on vehicles and in laboratory using the in-house developed real time battery test equipment.

In the laboratory study one cell was continuously charged and discharged with a constant current (6.8 A) between lower and upper voltage limits specified by the supplier (1.8 V and 2.8 V respectively). Cycling was
performed at 55 °C and the total testing time was 9 months, corresponding to 9201 full cycles. The performance of the cycle-aged cell was measured periodically during the test. Capacity measurements were performed on the in-house developed battery cycling equipment and impedance measurements on a Solartron SI 1260 Impedance/Gain-phase analyzer. A reference cell was stored at room temperature (~ 25 °C) during the test period. Both cells originated from the same batch. At the end of test, the performance of the cells was investigated with electrochemical methods followed by disassembling the cells and harvesting of electrode materials. The harvested electrode samples were analysed using electrochemical and material characterisation methods.

In the field test, three cells were cycled onboard three heavy-duty trucks from Scania CV AB. Each vehicle was prepared with one test equipment containing two battery cells, one cell that was cycled and one that was used as reference. The reference cells were charged to a SOC-level close to 50 % before testing and after every measurement occasion. During the field test, the reference cells were not connected and were hence allowed to self-discharge. All cells in the field study originated from the same batch.

At the end of test, the performance of the cells was investigated with electrochemical methods and material analysis methods. Electrode samples were also harvested and analysed.

### 3.4 LFP/Graphite Cell Ageing

Commercial power-optimized LFP/Graphite cells with a rated initial capacity of 2.3 Ah and a nominal voltage of 3.3 V were acquired from a reputable supplier for this study. Cycling of cells was performed in laboratory using both a continuous charge/discharge cycle and a current cycle representative to a HEV city bus driving cycle. The continuously charged and discharged cell was cycled between 2.0 V and 3.6 V with a current of 8.63 A, and with an average cell temperature of ~34 °C. A cut-off current of 0.57 A was used in the charging step. The HEV-cycled cell was charged with currents up to 34 A, and discharged with currents up to 53 A. The cell was cycled between ~35 % and ~50 % SOC and SOC-calibration was performed after every 3rd 70 min cycling period. The average cell temperature during cycling was ~38 °C and the ambient temperature was ~22 °C. A reference cell was stored at room temperature
(~22 °C) and at ~45 % SOC during the test period. All cells originated from the same batch.

At the end of test, the performance of the cells was investigated with electrochemical methods and material analysis methods. Electrode samples were harvested from all cells and analysed.
4 RESULTS AND DISCUSSION

4.1 ON-BOARD REAL TIME FIELD TEST EQUIPMENT VERIFICATION

Verification of the developed test equipment was done on a prototype Scania HEV truck. This test made it possible to compare the current through a tested battery cell with an actual HEV-battery pack current. The result from the test is presented in Figure 11.

![Figure 11: Current through the tested battery cell (upper plots) and current through the HEV battery pack (lower plots). (a) Verification test of about 45 minutes. (b) Magnification of the test between 640 s and 710 s.](image)

Zooming in between 640 s and 710 s shows the similarity between the current through the tested battery cell and the HEV-battery current (Figure 11b). Comparing the accumulated charge passed through the tested battery cell with the value for the HEV-battery pack during the test run indicates similar cycling with a difference of only 3%. This is a satisfying result since the HEV-battery pack consisted of a different battery type than the tested cell. The results also confirm that the emulated hybrid vehicle functions are influencing the tested battery the way they are supposed. For example, current peaks due to gear changes
are clearly seen at 654 s, 662 s, 675 s and 702 s in Figure 11b, both for the tested battery cell and the HEV-battery. The conclusion from the verification results is that the test equipment has a most promising potential to be used as a HEV-emulator for battery cells placed on conventional vehicles.

4.2 Driving cycle analysis

Analysis of how the driving patterns for the three trucks in the field study correlated to battery usage was performed. Figure 12 shows distribution plots over vehicle speed, battery cell SOC and battery cell charge/discharge power. Figure 12a shows the vehicle speed distribution for all trucks and it is clear that truck 1 mostly has been driving at low speeds, typically around 20 km/h and very seldom above 60 km/h. Two broad peaks are seen around 20 km/h and 50 km/h and a very small peak around 89 km/h. This represents a typical inner city transportation type of drive pattern. Truck 2 has a relatively even speed distribution up to 60 km/h, and there are two distinctive peaks around 80 km/h and 89 km/h. Truck 2 spends a large time driving at speeds higher than 60 km/h which is reflected in the highest average speed of the three test vehicles. Truck 3 has a similar speed distribution as truck 2 but lacks a peak at around 80 km/h and spends a large part of the driving at speeds below 30 km/h. This type of driving pattern is typical for intercity transportation where the vehicles are driving both within cities and between cities. The driving pattern for truck 1 is similar to the City Suburban Cycle (CSC) presented in Figure 12b. The CSC is a chassis dynamometer test schedule for heavy-duty vehicles developed within the West Virginia University [69] and has an average speed of 22.8 km/h. Truck 2 and 3 have driving patterns similar to the Urban Dynamometer Driving Schedule (UDDS) in Figure 12b. The UDDS was developed for chassis dynamometer testing of heavy-duty vehicles by the US Environmental Protection Agency (EPA) [68]. The average speed for this driving schedule is 30.4 km/h. Figure 12c shows SOC distributions for all three trucks. The cycled cell on truck 1 shows a Gaussian-like SOC distribution centred around 50 % while the cells on truck 2 and 3 show distributions with peaks at SOC-levels lower than 50 %. The probable cause for this is the driving at higher speeds for truck 2 and 3 since the hybrid strategy tends to drive battery SOC towards the lower limit during acceleration. The cycled cell on truck 1 is seldom discharged to the lower
SOC-limit at 20 %, probably due to relatively short time between acceleration and braking in most cases. The cycled cell on truck 2 has a distinctively high peak at around 20 % SOC and a wide peak around 40 % SOC. Frequent highway driving is the probable cause for this. The cycled cell on truck 3 has a small peak around 20 % SOC but the main distribution is around 30 % SOC. The difference between SOC-distributions for the cells on truck 2 and 3 can be explained by looking at the corresponding vehicle speed distributions. Truck 2 appears have been driving frequently on roads where the speed limit changes between 80 km/h and 90 km/h. It is also seen that the peak around 80 km/h in the speed distribution plot for truck 2 actually consists of three peaks. This indicates extensive acceleration and braking even at highway speeds that should have caused cycling of the battery cell to some extent. This could explain the wide peak around 40 % SOC, even though truck 2 spends the least amount of time driving at low speeds of the three trucks. The sole distinctive peak around 89 km/h in the speed distribution plot for truck 3 indicates that there is only minor acceleration and braking at highway speeds with subsequent minor cell cycling, and this would correlate to the peak at 20 % SOC.
Figure 12: Distribution plots for the complete test period showing (a) vehicle speed (resolution 0.5 km/h), (b) vehicle speed for two reference driving schedules, (c) battery cell SOC (resolution 0.5 %) and (d) battery cell power (resolution 0.1 W). Charge power is positive.

Figure 12d shows cell power distributions for the trucks. Negative power values correspond to discharging and positive power values to charging. The cell power reflects how the hybrid strategy is using the battery and this parameter is scalable for comparison with HEV battery pack power. The evaluated hybrid strategy was developed with the assumption that there is an excess of available braking energy in most cases. Hence, the charging and discharging strategies are not the same. The charging power is proportional to the driver-demanded power according to equation 1.

\[
P_{ch} \propto \left\{ \frac{P_{dd}}{P_{lim}} \right\}
\]  

[1]

\(P_{ch}\) is the charge power and \(P_{dd}\) the driver-demanded power. \(P_{lim}\) is the limited hybrid system input power that depends on both battery limitations and electric motor limitations. A comparison between \(P_{dd}\) and
$P_{\text{lim}}$ is done continuously, and the lowest value is chosen. A proportionality sign in equation 1 is used since other braking methods such as retarder and exhaust braking are also involved when charging the battery. It is clearly seen that the cycled cell on truck 1, which has a typical inner city transportation driving pattern, has the largest charge power peak around 160W. This is most probably due to more frequent and harder braking connected to the inner city driving pattern. The cycled cell on truck 2 also has a distinctive peak at 160 W while the cycled cell on truck 3 lacks charge peaks above 35 W. The difference in charge power distribution for the cycled cell on truck 3 compared to truck 2 is most likely due to softer braking in the previous case. The weight of the vehicles would also affect the charge power since a heavier vehicle would have more kinetic energy requiring harder braking during deceleration, which would generate higher positive power peaks for the tested battery cell. Discharge power distributions for all cycled cells have a smooth appearance connected to the discharge strategy, which is presented below.

$$P_{\text{disch}} \propto \frac{SOC - SOC_L}{SOC_U - SOC_L} \frac{v}{v_{\text{max}}} \left\{ P_{\text{dd}/2}, \frac{P_{\text{lim}}}{P_{\text{lim}}} \right\}$$

[2]

$P_{\text{disch}}$ is the battery discharge power and $P_{\text{dd}}$ the driver-demanded power. $P_{\text{lim}}$ is the limited hybrid-system output power and depends on both battery limitations and electric motor limitations. A comparison between $P_{\text{dd}/2}$ and $P_{\text{lim}}$ is done continuously, and the lowest value is chosen. $SOC_U$ is the upper limit of the SOC-window (80 %) and $SOC_L$ is the lower limit (20 %). $v$ is the vehicle speed and $v_{\text{max}}$ is the maximum allowed vehicle speed (89 km/h). It is seen from equation 2 that the allowed discharge power in general is lower than the allowed charge power. In addition, the discharge power is also scaled by vehicle velocity and actual battery SOC. Hence, a high SOC and high vehicle velocity will generate a high discharge power. The vehicle speed scaling factor explains the discharge power peak close to zero that is seen for all cycled cells (truncated in Figure 12d for better visibility). This strategy results in smooth discharge curves as seen in Figure 12d.

Table 1 in Paper V presents the most important driving pattern and battery usage results from the field test. It is seen from the table that truck 2 has the highest average speed due to more frequent highway driving compared to truck 1 and 3. In spite of this, the cycled cell on
truck 2 was exposed to higher energy throughput per driving distance compared to the cell on truck 3. This is almost certainly connected to the different type of highway driving truck 2 has experienced in combination with an overall harder braking pattern, possibly connected to heavier goods transportation. The highest energy throughput per driving distance is found for the cycled cell on truck 1. This is expected due to the typical inner city transportation driving pattern this truck has experienced. It is also seen in Table 1 that the average cell charge power for all trucks are higher than the average cell discharge power. This is also expected since it is the main characteristic of the tested hybrid strategy. The total travelled distance for each truck during the test period is low but representative for this type of delivery trucks that are only operated during dayshifts and not on weekends. Hence, the equivalent number of full cycles (defined in section 4.4.1 from equation 3) is low even for the cell on truck 1 that has been cycled for almost two years, and the cycling time is only about 6 % of the total testing time. Thus, calendar ageing has a significant impact on battery pack lifetime for this type of driving and has to be addressed in the design phase. This test concept should have a great potential for comparing different hybrid strategies in a real application in order to validate simulations. For example, by using a large fleet of vehicles, a large spread of battery usage would give a good input to how different hybrid strategies combined with different battery cells would influence energy throughput. However, evaluation of hybrid strategies with this test concept also has some limitations. For example, a HEV could have a different gear-shifting pattern compared to a conventional vehicle, and this is difficult to emulate with the test concept. Validation of battery management strategies such as for example SOC-estimation and SOC-calibration is another possible field of application for this test concept. In this case, the test concept has an additional advantage compared to testing on real HEVs due to its capability to perform periodical SOC-calibrations and performance tests during vehicle operation.

4.3 **CELL PACKAGING INTEGRITY**

Three cells were vibrated for 144 hours while the temperature was ramped between -25 °C and +60 °C at a rate of ~4 °C/minute. Capacity measurements performed on the vibrated and temperature cycled battery cells showed no difference compared to fresh reference cells. The total
spread in capacity between all tested cells was less than 0.5%. This indicated that vibration and temperature cycling of the cells had no significant influence on electrochemical performance.

The first test of water intrusion into flexible cell encapsulations was performed on a Mocon Permatran equipment (Figure 13a). At time zero in Figure 13a, the humidity surrounding the packages was changed from 0 % RH to 100 % RH. However, no change in WVTR level could be correlated to the change of humidity level outside the packages in this test. The rapid reduction of detected humidity during the beginning of the test indicated presence of water in the polymer inside the encapsulation as well as on surfaces inside the test set-up. This implied that a more rigorous drying process should have been applied prior to the measurement.

In the second test a Mocon Aquatran equipment was used. This equipment has an order of magnitude lower detection limit compared to the Permatran. The comprehensive preconditioning enabled studies of very low water vapour concentrations (Figure 13b). Nevertheless, it was not possible to reach the detection limit of the instrument during this test either. The peaks seen in Figure 13b relate to changes in gas flow due to flow adjustments and changing of gas tube, and have no correlation to water vapour transportation through the encapsulation.

Figure 13: (a) WVTR results from both Mocon Permatran-W 3/31 MG and Mocon and Aquatran Model 1 equipments. (b) WVTR results from Mocon Aquatran Model 1 equipment. Cell A is the encapsulation from a fresh battery cell. Cell B is an encapsulation from a vibrated and temperature cycled cell.
The measured water vapour transmission rate approached values close to 40 µg/(package day), i.e. an order of magnitude higher than the detection limit of the equipment. It could not be confirmed if there was a leakage within the test set-up including all valves and connections, or an internal test equipment issue connected to the automatic calibration system causing this elevated signal. However, the transmission rate of water through the encapsulations remained below the background level throughout the complete test for both the vibrated cell and the reference cell, indicating that the encapsulation material and thermal welds are virtually defect free even after vibration and temperature cycling. Hence, the forces on the welds caused by the vibration and temperature cycling seem to be insufficient to induce defects in the cell packaging material. This test method shows potential for analysing water integrity of battery pouch cells. However, working in a dry environment as well as employing extensive precondition before testing is essential to be able to measure the extremely small water transmission rates into a pouch cell that, during the lifetime of a heavy-duty HEV, could cause premature ageing of the battery pack.
4.4 **Ageing of Commercial LMO-LCO/LTO Battery Cells**

In this study, cells were cycled both in laboratory and on vehicles.

### 4.4.1 Full Cell Capacity Measurements

The capacity of the cell cycled in laboratory was measured periodically during the test period. Figure 14a shows discharge curves for the cycled cell at different cycle numbers, when discharged with 3.6 A (~1C rate initially). Figure 14b shows discharge curves for both the cycled-aged and the calendar-aged cell prior to cell opening. It is seen that the cycle-aged cell capacity measured at 3.6 A prior to cell opening (Figure 14a) is significantly lower than the measured C/40 capacity (Figure 14b), indicating a high cell impedance. It is also seen from Figure 14a that there is a significant difference between the capacity at the end of testing (at cycle number 9201) and the capacity measured just before opening the cell. This difference could be a result of calendar ageing since the cell was stored at ~25 °C for several months between end of test and the last measurement before cell opening.

At end of test (9201 cycles or 71 kWh) the cycle-aged cell had lost 29 % of the starting capacity while the calendar-aged cell had retained its capacity during the test period, indicating negligible capacity loss due to calendar ageing at room temperature for this type of cell.
Initial discharge capacity for all cells in the field study was measured in laboratory prior to testing. Capacity measurements were also performed a number of times during the field test. Equivalent full cycles were calculated from the total cycled energy and the initial cell capacity according to equation 3:

\[ N_{eq} = \frac{W_{tot}}{2 \cdot U_{nom} \cdot Q_{init}} \]  

\[ [3] \]

\( N_{eq} \) is the equivalent number of full cycles, \( W_{tot} \) is the accumulated energy throughput for the cycled cell, \( U_{nom} \) is the specified nominal battery voltage and \( Q_{init} \) is the measured initial battery capacity. Figure 15 shows discharge curves from different measurement occasions for the cycle-aged cells, as well as discharge curves for the calendar-aged reference cells.
Figure 15: Discharge capacity (C/20) at different equivalent cycles ($N_{eq}$) for (a) cycle-aged cell on truck 1 (b) calendar-aged cell on truck 1, (c) cycle-aged cell on truck 2, (d) calendar-aged cell on truck 2, (e) cycle-aged cell on truck 3 and (f) calendar-aged cell on truck 3.

The cycled cell on truck 1 experienced a capacity loss of 3.0 % after 1072 equivalent cycles and 6.6 % after 1496 equivalent cycles (Figure 15a). The total energy cycled through the cell during the test was 25 kWh. The corresponding capacity loss for the reference cell was 1.2 % and 1.5 % respectively (Figure 15b). The cycled cell on truck 2 experienced no capacity loss after 79 cycles but 1.3 % after 859 cycles compared to 0.5 % for the corresponding reference cell at the end of test (Figure 15c and d).
The total energy cycled through the cell during the test was 14 kWh. The cycled cell on truck 3 experienced no capacity loss after either 177 or 419 cycles while the corresponding reference cell had experienced a capacity loss of 0.5% at the end of the field study (Figure 15e and f). The total energy cycled through the cell during the test was 7 kWh.

4.4.2 Half cell capacity measurements

When opening the cells from the laboratory study, it was observed that the can of the cycle-aged cell was noticeably more swollen compared to the calendar-aged cell. Moreover, there was no free electrolyte in the can of the cycle-aged cell as in the can of the calendar-aged cell. This implies that electrolyte had been consumed in gas producing reactions, possibly causing loss of cyclable lithium. Half cell capacities of harvested electrode material samples are presented in Figure 16.

Figure 16: (a) Calendar-aged and cycle-aged positive electrode discharge capacity (C/40 and C/100), (b) Calendar-aged and cycle-aged negative electrode discharge capacity (C/40 and C/100).

Figure 16a displays voltage profiles for positive electrode samples showing a 27% lower discharge capacity for the cycle-aged sample than for the calendar-aged sample. Voltage profiles of negative electrode samples are presented in Figure 16b, and are only showing about 5% difference in discharge capacity between cycle-aged and calendar-aged samples.

To be able to do analysis of ageing on the cells from the field study, half cell measurements were done on a fresh cell originating from the same cell generation as the tested cells. The results from those measurements are presented in section 4.4.6.
4.4.3 FULL CELL ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Figure 17 shows impedance (Nyquist) plots for the cells from the laboratory test. Figure 17a shows an overview of Nyquist plots for different cycle numbers. The Nyquist plots are separated and presented in Figure 17b, c and d for better visibility. The calendar-aged cell impedance is also presented in Figure 17b, showing only a minor change in impedance compared to a pristine cell. It is noticeable from Figure 17b that the semicircle in the frequency region ~500Hz – 1Hz is extremely small when the cells are fresh, indicating very fast charge transfer kinetics. During ageing, the most visible change is the significant growth of this semicircle.

Figure 17: Nyquist plots at SOC 50 % and 25 °C for both cycle-aged and calendar-aged cells. (a) All data. (b) From initial performance to cycle 1279, including calendar-aged cell. (c) From cycle 1633 to 3445. (d) From cycle 5671 to the measurement occasion prior to cell opening.

Impedance measurements were also performed on all cells in the field study and the results are presented in Figure 18. The most visible change in impedance is a growth of the semicircle and a shift to the right for all cycled cells. This trend is in line with the findings from the laboratory test.
4.4.4 HALF CELL ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Impedance measurements were performed on the half cells with harvested electrode material from the cells tested in laboratory. Figure 19 shows Nyquist plots for both cycle-aged and calendar-aged half cell samples of both electrodes and Figure 19b shows a zoomed-in picture.

Figure 18: Nyquist plots at SOC 50% and 23 °C for both cycled and calendar-aged cells. Blue square markings represents 1 Hz and red represents 0.01 Hz. (a) Cells from truck 1, (b) cells from truck 2 and (c) cells from truck 3.

Figure 19: (a) Impedance for positive and negative electrode half cell samples. (b) Zoomed in picture
The cycle-aged positive electrode sample has an extremely large semi circle (~500 kHz-0.1 Hz) compared to the calendar-aged electrode sample, signifying that the positive electrode is the main impedance contributor for the cycle-aged cell. It is also seen that the difference in negative electrode impedance between the calendar-aged half cell sample and the cycle-aged half cell sample is small, emphasising that the impedance rise of the cycle-aged cell mainly is related to the positive electrode. Studies on commercial battery cells containing LCO as well as LMO positive electrode material have earlier reported similar large growth of semicircles for aged positive electrode material, with increased interfacial impedance as one of several proposed root causes [70-72]. Presence of Li$_2$Co$_2$O$_4$ could be another possible explanation to the increased impedance seen for the cycle-aged cell since Li$_2$Co$_2$O$_4$ has lower conductivity than LiCoO$_2$.

### 4.4.5 Incremental Capacity Analysis

Incremental capacity analysis (dQ/dV) is a method that identifies areas in the voltage profile correlated to phase equilibrium of active electrode material, manifested as flat regions in the voltage profile. Several research groups have earlier reported results from full cell dQ/dV analysis. Smith et al. have performed dQ/dV analysis on aged cells containing LMO/graphite and LCO/graphite including analysis of corresponding half cells [73, 74]. Dubarry et al. have performed cycle ageing of cells containing LFP/graphite and used dQ/dV to identify ageing mechanisms [75, 76]. Changes in the dQ/dV curves can help to identify ageing mechanisms in a battery cell. This method has also been investigated for usage in electrified vehicles to estimate state of health (SOH) of a battery pack [77, 78]. Figure 20a shows full cell dQ/dV of both charge and discharge data from both the cycle-aged and the calendar-aged cell from the laboratory study. The plots reveal a distinctive peak at ~2.35 V and two diffuse peaks at ~2.45 V and ~2.6 V respectively. Since LMO only has two peaks according to literature [52, 79-83], the existence of a third peak should relate to the presence of LCO. The peaks in Figure 20a should only relate to the positive electrode material since the negative electrode consists of a two-phase material with only one very broad voltage plateau. Figure 20b shows dQ/dV-plots for the cycled cell at different currents and it is observed that even a C/40-current rate is too high to be able to clearly identify all peaks. Reducing the current rate to C/100 makes it
possible to identify three peaks corresponding to the peaks observed for the calendar-aged cell. In addition, it is clear that there are only small differences in voltage for charge and discharge peaks respectively indicating that the polarization is small at this current. A broadening of the LCO peak and the LMO peaks is seen when comparing the plot for the cycle-aged cell with the plot for the calendar-aged cell (Figure 20a), indicating slower electrode kinetics [84] for both LCO and LMO in the cycle-aged cell. Figure 20c shows dQ/dV-plots for half cells with positive electrode material. The plots show peaks at ~3.9 V vs. Li/Li⁺, verifying presence of LCO [52, 79]. The additional peaks at ~4.0 V and ~4.15 V confirms presence of LMO [80]. A broadening of the LCO peak and the LMO peaks is also seen here. The observed broadening of dQ/dV-peaks for both LCO and LMO could relate to metal ion transportation between LCO and LMO. For example, substitution of manganese for cobalt in the LMO structure has previously been reported in literature [53, 54]. A broadening of the LCO peak could also be due to transformation of LCO into the more inert cubic spinel form, Li₂Co₂O₄, causing irreversible capacity loss. Another possible mechanism that could cause loss of positive electrode active material is Mn²⁺ dissolution.
Figure 20: dQ/dV plots for (a) calendar aged cell (C/20) and cycle aged cell (C/100), (b) cycle-aged cell at different currents, (c) positive electrode vs. lithium (C/100) and (d) negative electrode vs. lithium (C/100).

Figure 20d shows dQ/dV vs. potential plots for half cells consisting of harvested negative electrode material. The distinct single peak at ~1.55 V vs. Li/Li+ clearly confirms the presence of LTO [85, 86]. This peak is broader and lower for the cycle-aged cell than for the calendar-aged cell indicating slower electrode kinetics [85]. This could be an indication that surface film formation has occurred during cycling by consumption of solvent, possibly together with gas formation.
4.4.6 Differential Voltage Analysis

Differential voltage analysis (dV/dQ) was used to identify ageing of the cells in the laboratory study and the field study. Data from both full cells and half cells were used to calculate electrode-balancing using a graphical user interface program developed in MatLab®. The fitting procedure used is presented in detail in Paper IV and includes half-cell measurements on both positive and negative electrode material samples. dV/dQ data from the positive electrode sample are fitted to full-cell dV/dQ data according to equation 4.

\[
\frac{dV_{celt}}{dQ_{celt}} = \frac{1}{s_{pos}} \frac{dV_{pos}(s_{pos}q_{pos} + \delta_{pos})}{dq_{pos}} \quad [4]
\]

It is in this case possible to fit dV/dQ data only from the positive electrode to full cell data since the two distinctive peaks in the full cell dV/dQ plot (Figure 21c) solely relate to the positive electrode for this cell type. This is due to a flat discharge curve for the negative electrode resulting in a dV/dQ plot without peaks (Figure 21d).

The calculated OCV-curve is in turn obtained by subtracting the negative electrode potential from the positive. However, to get the half cell OCV-curves to fit the full cell OCV-curve, the x-axis values have to be scaled. In addition, the OCV-curves need to be shifted along the x-axis for each electrode relative the full cell OCV, according to equation 5.

\[
V_{celt}(Q_{celt}) = V_{pos}(s_{pos}q_{pos} + \delta_{pos}) - V_{neg}(s_{neg}q_{neg} + \delta_{neg}) \quad [5]
\]

The results for the cells from the laboratory study are presented in Figure 21a and b, showing fitted and measured OCV curves for the calendar-aged and the cycle-aged cell respectively, including fitted positive and negative half cell data.
From this analysis it is discovered that this cell is limited by the positive electrode at completely discharged state and by the negative electrode at completely charged state for both the cycle-aged and the calendar-aged cell, even though the positive electrode has lower capacity than the negative electrode for the cycle-aged cell and vice versa for the calendar-aged cell. There is only a small difference between the slippage ($\delta_{\text{pos}}$) of the calendar-aged positive electrode and the cycle-aged positive electrode. The slippage for the cycle-aged negative electrode ($\delta_{\text{neg}}$) is however significantly larger than the calendar-aged negative electrode slippage and is due to loss of positive electrode active material. From Figure 21a it is possible to see that this cell is unbalanced already in its pristine condition. Although there is an excess of positive electrode active material in the calendar-aged cell, the full capacity of the negative electrode active material is not used, corresponding to a slippage of -177 mAh. For the cycle-aged cell it is seen that the positive electrode capacity has
diminished and that the negative electrode capacity, that is only slightly reduced, has slipped considerably to the left (Figure 21b). Due to this behaviour, the positive electrode capacity is not fully utilized and the cell capacity is hence smaller than the limiting electrode capacity in this case as well. This behaviour is opposite to what is seen for cells with LFP positive electrode and graphite negative electrode in a similar work presented in Paper III, where the negative electrode contributes to the largest part of the loss of cell capacity. In that work, electrode balancing using dV/dQ fitting was not performed, but an estimation of lithiation degree of both positive electrode samples and negative electrode samples from initial charge/discharge cycles of corresponding half cells was done. When comparing Figure 21a and b it is seen that the utilization of the positive electrode has increased while the utilization of the negative electrode has decreased after ageing. The increased utilization of the positive electrode indicates some loss of active lithium during cycling. There is however still an excess of cyclable lithium, as shown by the negative slip of the negative electrode in both cases. Figure 22 shows schematic plots that better visualizes the difference in electrode balancing when having an excess of cyclable lithium (Figure 22a) and when having a shortage of cyclable lithium (Figure 22b).

![Figure 22: Schematic plots showing example of electrode imbalance when there is a surplus of positive electrode active material, here represented by the LMO phase. (a) There is more cyclable lithium available in the positive electrode than is possible to use. (b) There is shortage of cyclable lithium to fully utilize the positive electrode capacity.](image-url)
The negative electrode is limiting the cell capacity in both cases and the individual electrode capacities is the same in both cases. It is seen that when the negative electrode is fully lithiated in Figure 22a, the positive electrode still has cyclable lithium available (x=0.15). In Figure 22b, the negative electrode is fully delithiated when the positive electrode still could be lithiated further (x=0.85). Both the cycle-aged cell in Figure 21b and the calendar-aged cell in Figure 21a shows a similar behaviour as seen in the schematic plot in Figure 22a. In addition, there is an excess of cyclable lithium in the negative electrode (y>0 when x=1) in both cases. It is seen in Figure 21a and b that the slip of the negative electrode for the cycle-aged cell is larger than the slip for the calendar-aged cell. It is also seen that the excess of cyclable lithium in the positive electrode has diminished. This means that the utilization of the positive electrode has increased while the utilization of the negative electrode has decreased. The increased utilization of the positive electrode is due to loss of cyclable lithium while the decreased utilization of the negative electrode is due to loss of positive electrode active material.
dV/dQ-analysis of the LMO-LCO/LTO cells from the field study was done and compared to the results obtained from the laboratory study. Figure 23 displays dV/dQ vs. discharge capacity plots for the cells in the field study.

Figure 23: dV/dQ plots corresponding to the discharge curves in Figure 15. (a) Cycle-aged cell on truck 1, (b) calendar-aged cell on truck 1 (c) cycle-aged cell on truck 2, (d) calendar-aged cell on truck 2, (e) cycle-aged cell on truck 3 and (f) calendar-aged cell on truck 3.
The ratio between the height of the two peaks in the dV/dQ plots in Figure 23 are different for all cycled cells at the end of test compared to the calendar aged reference cells. This is a clear indication that all cycled cells have experienced ageing of the positive electrode even though the discharge capacity for the cycled cell on truck 3 indicates the opposite (Figure 15e). The distance between the peaks correlates to the capacity of the positive electrode and a larger distance between peaks corresponds to a higher electrode capacity. It is seen in Figure 23a, c and e that the distance between peaks has become smaller between measurement occasions for all cycled cells while no difference is seen for the corresponding measurements on reference cells in Figure 23b, d and f. This suggests that all cycled cells have experienced loss of positive electrode active material to some extent. To understand if it is possible to obtain loss of positive electrode active material without observing an influence on the cell capacity, a graphical representation of the electrode balancing within the cell is used (Figure 24a). It is seen in Figure 24a that the cells used in the field study have similar behaviour as the cells used in the laboratory study, even though they were from a newer batch with a slightly changed cell chemistry. The cells have an initial excess of positive electrode active material and the negative electrode is limiting the cell capacity when fully charged. From the laboratory study, it was seen that the main part of the ageing was loss of positive electrode active material, resulting in a smaller positive electrode capacity curve. If only positive electrode active material is lost, the left end of the positive electrode capacity curve will move rightwards in Figure 24a while the right end of the curve stays in position. This would result in a simultaneous loss of cell capacity. However, since loss of positive active electrode material essentially creates a virtual excess of cyclable lithium for this cell type, loss of cyclable lithium in combination with loss of positive electrode active material would instead make the right end of the positive electrode capacity curve to move leftwards while the left end stays in position. In the latter case, the cell capacity will initially be unaffected since there is an excess of positive electrode active material. This could be the case for the cycled cell on truck 3 since there is an influence on dV/dQ from cycling but not on cell capacity. If both loss of positive electrode active material and loss of cyclable lithium are taking place simultaneously, the dV/dQ peaks should also move towards each other, which is the case for the cycled cells in truck 2 and 3 in Figure 23c and e. However, for the cell
on truck 1 the dV/dQ curve at 1496 cycles seems to have shifted to the left compared to the previous measurement, indicating that only positive electrode active material has been lost in this case. This suggests that this cell type experiences both loss of positive electrode active material and loss of cyclable lithium in the beginning of cycling. During further cycling, the rate of cyclable lithium loss seems to decrease gradually while loss of positive electrode active material seems to continue. Hence, the initial excess of positive electrode active material seen for this cell type is not possible to access completely due to this increasing surplus of cyclable lithium relative the positive electrode, causing an imbalance between the electrodes in the cell.

Figure 24: a) Internal cell matching for a fresh cell b) Fitted positive electrode dV/dQ data to full cell dV/dQ data

4.5 MATERIAL ANALYSIS

4.5.1 SEM AND EDX ON LMO-LCO/LTO MATERIAL

SEM-imaging was done to study the appearance and morphology of harvested electrode material from the LMO-LCO/LTO cells tested in laboratory. Micrographs for both positive and negative electrode materials are presented in Figure 25. Positive electrode samples are shown in Figure 25a and b, and negative electrode samples in Figure 25c and d. No obvious difference between cycle-aged and calendar-aged materials could be seen for either the positive or the negative electrode, indicating only minor SEI build-up on both electrodes. However, since SEM has a certain image depth profile depending on the penetration of the electron beam into the analyzed material, more surface specific analysis methods would be required to confirm this statement.
Presence of both Mn and Co in the positive electrode material was confirmed using energy dispersive X-ray spectroscopy, EDX. The EDX-mapping pictures in Figure 26a and b display Co-containing areas as green and Mn-containing areas as purple. The findings confirm presence of both LCO and LMO in the positive electrode material. Figure 26a shows a calendar-aged positive electrode sample and Figure 26b shows a cycle-aged positive electrode sample. The interfaces between particles for the cycle-aged material in Figure 26b seem to be more diffuse than the interfaces between particles for the calendar-aged material in Figure 26a. This could possibly indicate that transportation of material between LCO and LMO has occurred during cycling.
Figure 26: EDX-mapping pictures a) Calendar-aged positive material b) cycle-aged positive material. Green color represents the cobalt signal, magenta color represents the manganese signal, c) Point-EDX plot from position 1 and 2 in Figure 26a, d) Point-EDX plot from position 1 and 2 in Figure 26b.

Figure 26c and d present point-EDX plots from the specified positions 1 and 2 in Figure 26a and b. The point-EDX curves give information about the relationship between the manganese signal and the cobalt signal for the different coloured areas in Figure 26a and b. In addition, it is observed that the relationship between the manganese signal and the oxygen signal is significantly higher for the cycle-aged cell sample compared to the calendar-aged one. This behaviour is not seen for the relationship between the cobalt and the oxygen signal, indicating that the LMO phase is more affected by cycling than the LCO phase. EDX was also performed on both cycle-aged and calendar-aged negative electrode samples. Those results show that manganese is present throughout the porous negative electrode of the cycled-aged cell sample but not in the calendar-aged one. This supports the findings from the positive electrode samples and strengthens the theory that the LMO phase has been more affected by cycling than the LCO phase. This statement is supported by XRD-measurements presented in Paper IV.
4.5.2 SEM AND EDX ON LFP/GRAFITE MATERIAL
SEM was used to perform a morphological comparison of electrode material from LFP/graphite cells cycled in a laboratory test. Three cells were analyzed; one cell that had been continuously charged and discharged (CCC), one cell that had been cycled with a current cycle representative to a HEV city bus driving cycle (HEVC), and one calendar-aged reference cell (CAL). Samples were harvested from positions on the electrode jellyroll according to Figure 27. When comparing electrode samples from Midpoint and Edge locations of each cell, graphite showed the largest differences in morphology due to usage and location in the jellyroll.

Figure 27: Schematic representation of unrolled electrodes from tested cells, showing the positions from where the analyzed samples were harvested.
Micrographs of samples from the positive LFP electrode are presented in Figure 28.

The LFP composite electrodes consist of rather uniformly shaped particles, as seen in Figure 28. No obvious difference in appearance was found for the LFP electrode samples (the LFP Edge samples were omitted since no visible difference from the Midpoint samples was seen).
Micrographs of samples from the negative graphite electrode are presented in Figure 29.

For the graphite electrode, the CAL cell has similar appearance at Midpoint and Edge areas, showing the graphite flakes in the electrode samples in Figure 29a and b. In contrast, the CCC Midpoint sample, shown in Figure 29c, has a thick, deposited layer that, though cracked, covers the entire sample surface so that the underlying graphite flakes
cannot be seen. However, at the CCC Edge location (Figure 29d), the graphite flakes are clearly visible, but with a slightly granulated surface that is not observed for either of the CAL electrode samples in Figure 29a and b. A comparison between the two locations of the HEVC electrode in Figure 29e and f shows less variation than the same comparison for the CCC electrode. However, a more granulated surface can be distinguished on the Edge sample compared to the Midpoint, which is more similar to the morphology of the CAL graphite samples.

The apparently severe and spatially uneven degradation of the graphite electrode was investigated using EDX. Figure 30 shows the results from the EDX analysis of the graphite electrode samples. A Cu-signal from the current collector is present for all samples, indicating that this method should be considered a bulk analysis technique. Fluorine, phosphorous and oxygen are also detected in all samples, as expected for batteries using LiPF$_6$-based electrolytes in carbonate solvents [87].

![Figure 30: EDX spectra from the negative electrodes of the HEVC, CCC, and CAL aged cells.](image)

However, the intensity of these peaks in relation to the carbon peak varies, indicating that there are different amounts of these species in each case. The probing depth of carbon is limited by its low energy emission, and varying thickness of surface layers can explain the relative carbon
signal intensity. The spectrum of the CCC Midpoint sample shows the highest intensity of F, O and P compared to the intensity of C, thus indicating a thicker surface layer, and a significant peak assigned to Fe (at 6.4 keV) is also seen. The corresponding EDX measurement on the Edge sample shows lower intensities of the peaks for F, O, and P compared to the intensity of C and no obvious Fe peak. For the HEVC electrode, the Fe signal is present in the Midpoint spectrum but not in that of the Edge sample. This is similar to the CCC electrode and the relation between O and F at both locations is similar to the corresponding locations of the CCC graphite. However, the intensities of F, O, and P are not so high compared to the intensity of C. Finally, Midpoint and Edge samples from the CAL cell show no trace of Fe and only small peaks for F, O, and P compared to C. Note that the F peak is overlapping with the Fe peak at ~0.7 keV (Fe Lα=0.705 keV and F Kα=0.677 keV). This could result in an apparently larger F-peak for the samples containing Fe. The results support the SEM findings regarding the observed spatially uneven degradation of the negative electrode. The CCC Midpoint appears to be the worst degraded sample, and this was also confirmed by electrochemical measurements and by XPS presented in Paper III. To investigate if an uneven degradation also was present along the depth of the porous negative electrode for the CCC Midpoint sample, SEM and EDX analysis were performed on cross-sections of the sample. Figure 31 shows micrographs, including EDX-mapping on a cross-section of the CCC Midpoint sample. This cross-section related to a crack in the material obtained during sample preparation.
Figure 31: EDX-maps for the CCC Midpoint sample. (a) Carbon signal (red), (b) oxygen signal (cyan), (c) phosphorous signal (green) and (d) fluorine signal (yellow).

The cross-section of the cycle-aged electrode shows a high carbon signal in the interior of the porous electrode but lower intensity at the top (Figure 31a). This indicates presence of additional material at the surface, which in Figures 31b to d is shown to consist of oxygen, phosphorous and fluorine. Among these, phosphorous and oxygen appear more localized at the top part of the electrode sample. The cycled-aged sample also shows a weak Fe-signal in the surface of the porous electrode that is not seen for the calendar-aged sample (not presented here). This is an indication that Fe has been dissolved from the positive electrode and incorporated into the SEI on the negative side. EDX-analysis performed on the CAL sample (Figure 32) does not reveal uneven surface film formation. In this case, the carbon signal has a rather uniform intensity both for the surface and interior (Figure 32a). The oxygen and phosphorous signals are very small, indicating no or little surface film formation throughout the porous
electrode (Figure 32b and c). However, Figure 32d shows that a fluorine signal is detected, although at a very low intensity level.

![Figure 32: EDX-maps for the calendar aged electrode sample. (a) Carbon signal (red). (b) Oxygen signal (cyan). (c) Phosphorous signal (green). (d) Fluorine signal (yellow)](image)

According to Figure 31c and d, the intensity of the phosphorus signal seems to be more uneven throughout the cycle-aged porous electrode compared to the intensity of fluorine. For a more detailed examination of the film formed throughout the electrode depth of the cycle-aged graphite, a cross-section was obtained using focused ion-beam (FIB) milling. EDX-measurements were done at different points of surface film along the depth of the electrode to investigate any variation in film compositions. Figure 33 displays this cross-section.
Figure 33: Pictures of the FIB cross-section and EDX-plots of the cycle-aged material, with complete cross-section and overlaid EDX line-scan of P (top-left), magnification of particle from the upper part of the electrode (top-right), magnifications of Top (middle-right) and Bottom (lower-right) zones marked in the electrode cross-section, and averaged EDX spectra for marked SEI areas (bottom-left). The Top curve consists of data from all four marked areas in the Top picture while the Bottom curve consists of data from the two marked areas in the Bottom picture. Both curves are normalized to the same peak-height for the carbon signal (truncated in the picture).

The entire cross-section can be seen in the upper left plot in Figure 33, together with two positions along the depth marked as Top (approximately between 3 \( \mu \text{m} \) and 9 \( \mu \text{m} \) depth), and Bottom (approximately between 25 \( \mu \text{m} \) and 31 \( \mu \text{m} \) depth) and a magnified
Results and discussion

 particle from above the TOP region. From the Top and Bottom SEM images, it can be seen that, in addition to the thick film on the top of the electrode, large amounts of deposits are found around and in-between the graphite particles further down in the electrode, giving the electrode a rather dense appearance. It should be noted that the Top and Bottom micrographs were obtained with a 3 kV acceleration voltage which makes the appearance different than the full cross-section micrograph (left in Figure 33) that was obtained with a 20 kV acceleration voltage. The Particle micrograph was obtained with a 15 kV acceleration voltage. An EDX line scan (overlaid left in Figure 33) shows that phosphorous has a significant declining trend during the first 10 µm in agreement with the findings from EDX area scans (Figure 31). No clear trends could be seen for either oxygen or fluorine line scans (not presented here), where both had high signals throughout the electrode cross-section. Especially the oxygen line scan signal was seen to vary considerably depending on where the measurement was performed, together with a variation of the carbon signal from the graphite particles. EDX line scans should in this case hence be considered a tool for approximate trends. To avoid the noise from graphite seen in line scan spectra, EDX was performed on several specific points aiming between the particles. These points are marked in the Top and Bottom SEM images. The corresponding EDX spectra are shown at the bottom-left position in Figure 33. The spectra show accumulated signals from all marked positions in the Top and Bottom micrographs and are normalized with respect to the carbon signal. When measured in this way, it is seen that the elemental composition of the deposits close to the separator has a significantly higher phosphorus signal than the deposits further down into the graphite layer, and that oxygen also follows this trend. Again, the fluorine signal has no obvious declining trend and the SEI close to the top of the cross-section also shows an iron signal (Fe Kα=6.4 keV) that is not present for SEI further down into the graphite layer. The gallium signal seen in the EDX-plots comes from the FIB-process. The Particle micrograph of a carbon particle from the upper part of the electrode (top-right position in Figure 33) indicates some additional degradation of the active material itself. The particle seems to fall apart along the layers of the graphite, which could be a sign of exfoliation and cracking from solvent co-intercalation and gaseous reduction products forming within the particles. This could be one contributing mechanism to the large capacity loss seen for this
electrode according to Paper III. The findings are supported by electrochemical measurements and ToF-SIMS measurements presented in Paper VI.

Uneven current distributions are known to be present throughout the depth of porous electrodes during usage and this could, as shown in this work, result in uneven film formation around particles in graphite electrodes. In the case of the battery cells studied here, constant current cycling at 3.75 C within a ~100 % SOC-window caused significant uneven film formation at certain positions of the jellyroll. This extent of uneven surface film was not found in electrode samples from a cell aged under HEV conditions, even though that cell had been cycled at significantly higher currents. However, that cell had been cycled within a narrower SOC-window and approximately at a 5 °C higher skin temperature. The temperature difference between the cells could have influenced the surface film formation since a slightly higher cell temperature would lower the overall impedance of the cell, possible making the current distribution more even. Cycling of the HEVC-cell in a narrow SOC-window (~35 % to ~50 % SOC) avoided SOC-regions more favorable for SEI-growth and lithium plating on graphite (high SOC), and SOC-regions where volume changes in the graphite structure is highest (both low and high SOC). This should also have an impact on the differences in SEI-growth seen for the HEVC-cell compared to the CCC-cell, both over the length of the electrode tape as well as throughout the depth of the porous electrode. This study hence indicates that cycling in a wide SOC-window is more detrimental than high currents for this type of cells.
5 CONCLUSIONS

The aim of this thesis has been evaluation of methods for testing and analyzing commercial battery cells intended for heavy-duty HEVs.

The first part of this work focused on development and validation of a novel test method for battery cycling on-board vehicles. This test method uses the existing battery system on a heavy-duty truck to cycle a lithium-ion battery cell onboard the vehicle. Battery cell cycling is performed in real-time using vehicle driving data and hybrid strategy software to emulate a HEV environment. The concept was successfully validated for 24 months in a field test. The initial intention to observe significant battery cell ageing during the test period was not fulfilled, mainly due to low yearly mileage of the used test vehicles. However, even if this method is not preferable when accelerated ageing of battery cells is desirable, it has a large potential for fast and inexpensive comparison of hybrid strategies, as well as evaluation of battery algorithms for different cell chemistries, in a real-life application.

Driving cycle analysis of three trucks in a field study showed two types of driving patterns. Connection between battery usage and driving pattern was confirmed. An inner city driving pattern resulted in the highest cycled energy per driving distance as expected. A large difference in cycled energy per driving distance was found for the trucks with an intercity driving pattern. This difference was presumed to be related to variations in braking patterns. The analysis also reveal that the evaluated hybrid strategy can deliver relatively high cycled energy per driving distance even for intercity traffic driving, although the SOC-window is shifted towards the lower limit in that case.

A study on flexible battery packaging material regarding resistance to water intrusion was done on commercial lithium-ion battery cells with promising results. No elevated water intrusion level was detected even after vibration and temperature cycling of the battery cells. The evaluated
test method showed limitations due to the normally very low water diffusion rate into pouch battery cells. However, testing in dry room using a test set-up with carefully dried test objects should make the method suitable for this kind of studies.

The electrochemical analysis methods dQ/dV and dV/dQ were proven useful for identifying ageing mechanisms in commercial LMO-LCO/LTO battery cells. When used in combination with SEM, EDX and XRD an even more detailed understanding of the ageing mechanisms was obtained. Negative electrode material harvested from a cycle-aged cell showed, as expected, low capacity loss and minor impact on impedance while positive composite LMO-LCO electrode material showed both significant capacity loss and increased impedance. The analysis indicated that the LMO phase was most affected by cycling although both phases showed signs of deterioration. The stored reference cell showed a superior resistance to calendar ageing. Cells cycled in a field study showed minor changes in both capacity and resistance, but it was possible to connect the ageing to the positive electrode also in this case.

Harvested positive electrode material from cycled commercial LFP/graphite cells showed no obvious ageing when analysed with SEM and EDX. Negative graphite electrode samples from two differently cycled cells both showed signs of ageing. The negative graphite electrode sample from a cell exposed to a continuous charge/discharge cycle experienced the most severe ageing. Deterioration of the graphite electrode active material was identified to be an uneven growth of SEI both spatially and in depth, and connected to loss of cyclable lithium.
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