Final report

STALLION Project: “Safety testing approaches for large Lithium-ion battery systems”(1st of October 2012 to 31st of March 2015)

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° ENER/FP7/308800/STALLION.

SEVENTH FRAMEWORK PROGRAMME

CONTENTS

1 SUMMARY

1.1 Project description

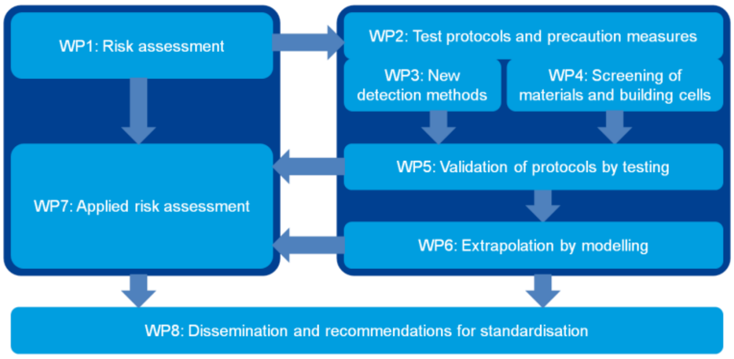
The STALLION project aims to set up a complete framework of methodologies and protocols for safety testing of stationary Li-ion batteries for large-scale grid applications. STALLION will incorporate the state of the art in the relevant technological areas like materials, cell architecture and detection methods.

Results will lead to a handbook on comprehensive and generic safety measures for large grid connected batteries. STALLION will contribute to the standardization framework for large-scale Li-ion battery testing and to a faster and safer deployment of Li-ion Batteries for grid application.

The STALLION project is funded by the European Commission (EC) under the 7th Framework Programme, topic Energy.2012.7.3.2 (Facilitating the deployment of safe stationary batteries) and collaborates with the STABALID (STAtionary Batteries LI-ion safe Deployment) project.

The methodology of this project aims at systematically identifying risks, addressing and validating the mitigation strategies along the two axes (system level and life cycle stage). A typical PDCA (plan-do-check-act) cycle (or safety cycle) is followed.

In the ‘plan’ phase (WP1) of this cycle the safety risks at all stages of the life cycle are assessed, based on real experiences and cases. This will result in an exhaustive list of possible safety-related failure modes and their relative priority . Based on this priority and each of its constituents the project will also develop a guideline about the maximal tolerable values for a safe system.



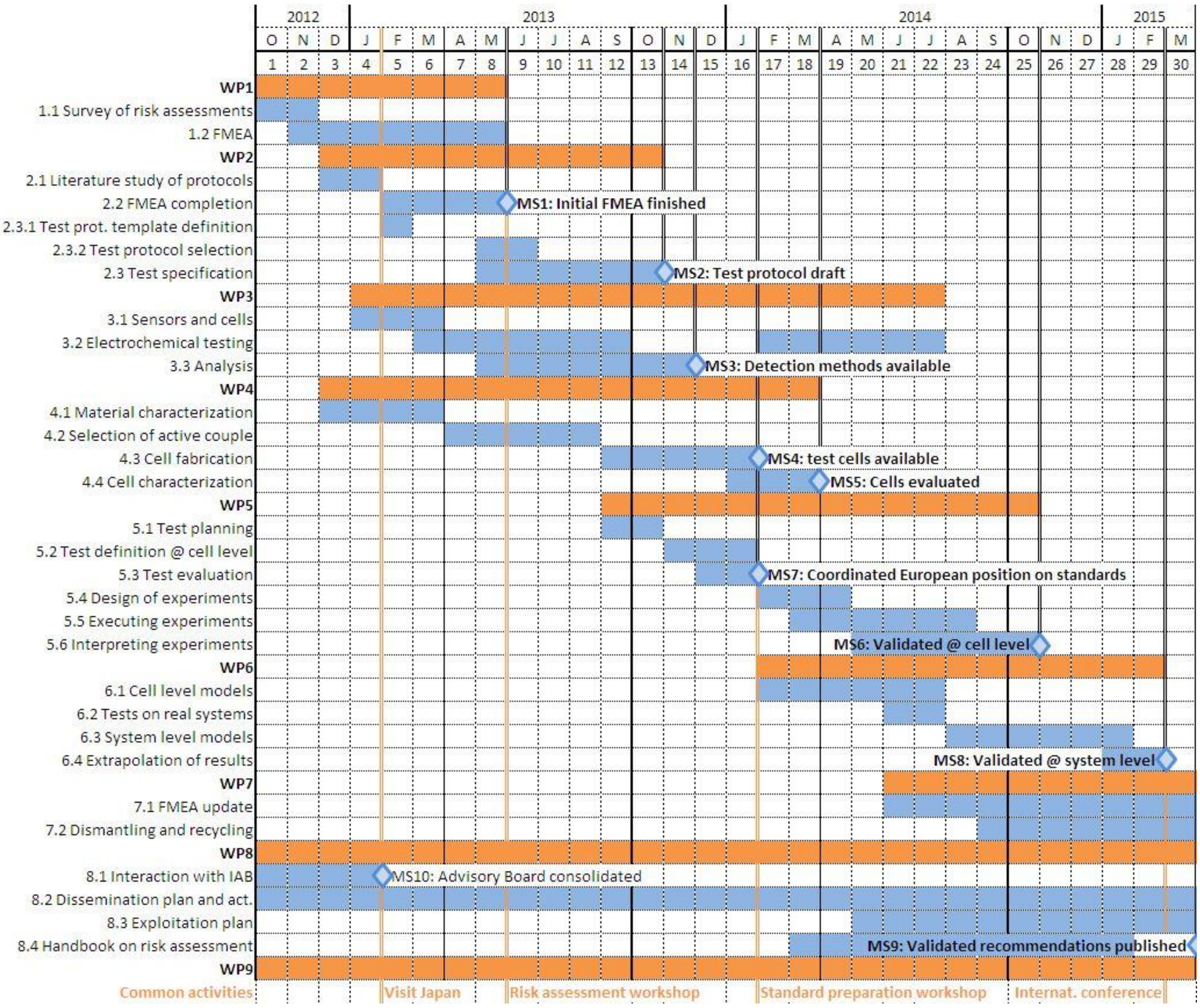
In the ‘do’ phase the necessary test protocols and precaution measures are developed to address each of the identified risks. These precaution measures can be the following:

- Design options that either reduce the probability of the failure mode or reduce its effect (WP4).
- Detection methods that increase the probability of detection of a failure mode (WP3).
- Test protocols that can be used to predict a certain failure (WP2). These test protocols will be elaborated further.

The ‘check’ phase of the project will consist of putting the developed protocols to the test. At cell and module level we will do this by executing the defined suitability, reliability and abuse tests on commercially available and prototype cells (WP5). This should lead to a conclusion on whether the defined tests actually suit their purpose at cell level. The results of these cell-level tests will be statistically validated and extrapolated to the system level (WP6) using modelling based on validated cell and system level models. Modelling results obtained at system level will be also validated experimentally through a Flexible Validation Platform. Five validation platforms have already been identified.

In the ‘act’ phase of the project (WP7), the suitability of the defined test protocols at system level will be evaluated and the remaining risk level can be quantified.
The final part of the project consist of the dissemination of the framework to the interested stakeholders (national and local authorities, integrators and end users of batteries…) in the form of a handbook and accompanying training materials. This framework should enable these stakeholders to make informed decisions.

1.2 Project plan



1.3 Project objectives

The main objectives of the STALLION project were the following:

1. Perform a thorough **risk assessment** for a large stationary Li-Ion battery at all system levels and during all its lifecycle stages, based on an overview of existing risk assessments in this area and on the knowledge and expertise of all partners and Advisory Board members.
2. Establish the **state of the art** for large stationary Li-Ion batteries in the fields of advanced sensors and materials. Since we believe both battery materials and sensors have a significant impact on the probability, severity and detectability of safety risks, we need a thorough assessment of current developments in this area to be able to recommend the necessary mitigation measures for (future) large battery systems.
3. Select the most prominent risks, based on the risk priority and existing mitigation measures, and **define new and improved test procedures** for these risks.
4. **Validate the test procedures**, defined during the first reporting period, by executing them in a state-of-the-art test lab.
5. **Validate the measures** (test procedures, new materials and innovative sensors), identified during the risk assessment (first reporting period), by modelling at cell, module and system level.
6. **Improve the defined test procedures** based on the validation results.
7. **Propose the improved test procedures for standardization** to the appropriate standardization committee.
8. **Update the risk analysis**, based on the assessment of the state of the art (first reporting period) and the validation results. This should result in a significantly decreased risk level for the large stationary Li-ion battery system.
9. Assess the risks during recycling and **develop a guideline for a safe handling of used batteries before and during recycling.**
10. **Develop a handbook and training materials** to disseminate the learnings and the risk assessment method from STALLION to interested audiences.
11. **Dissemination of results** via scientific conferences and publications and in Advisory Board meetings.

2 MAIN RESULTS

2.1 Risk assessment

The STALLION project made a literature study containing a survey of risk assessments and standards for energy storage systems. The report was titled ‘*STALLION document template*’. On the one hand it dealt with risks in alternative applications for Lithium ion batteries such as electric vehicles, community energy storage systems, wind turbine connected storage buffers for smooth integration of wind power and autonomous UPS systems. On the other hand it dealt with alternative battery technologies specifically used for large-scale stationary application such as sodium sulfur, lead acid, zinc air and redox flow systems. In addition it considered existing standards for energy storage systems in all types of applications.

Although risk assessments are in most cases considered to be confidential the general conclusions and lessons learnt in this literature search provided valuable input for the risk assessment performed in the second task of this WP.

Using the experience on all levels of the system, available at the partners and based on the information gathered in the aforementioned literature study, the STALLION consortium has performed a thorough risk assessment analysis. This analysis identifies and quantifies safety risks related to the application of large-scale, grid-connected, stationary Li-ion energy storage systems. A well-known method to chart risks in a qualitative way is a Failure Modes, Effect & Criticality Analysis (FMECA).This method starts from a system diagram. Therefore, the consortium partners have proposed a generic system design to apply the risk assessment. The energy storage system was subdivided into components on five levels: system, pack, module, block and cell level.

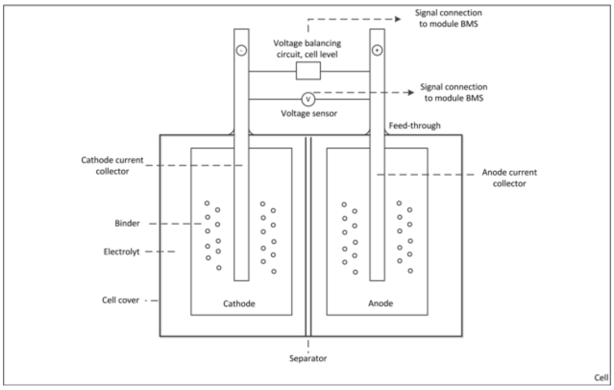


Figure 1: cell level system diagram

In a next step, the risks at each of these level were inventarized. During the preparation of this phase, two issues with the FMECA methodology were identified. The first issue has to do with the use of Risk Priority Numbers (RPN) as a measure of risk criticality. Typically RPNs are the multiplication of a severity and an occurrence number (and detectability if available). Since in this project, we focus on safety risks (and not the whole scale from cosmetic to safety risks) and since we deal with a generic system (for which no experience data exists), both the severity and occurrence ranges were adapted to range between 1 and 4. Therefore there is only a limited variation for the RPN numbers. Nevertheless it is questionable whether all risks with an equal RPN score are equally critical. E.g. a risk can receive an RPN score of 4 in several ways (e.g. severity of 4 and occurrence of 1 or severity of 2 and occurrence of 2) which are very different. Therefore a dedicated methodology was applied within the STALLION project to derive the major risks per level and for the whole system, based on the aforementioned risk matrix, in which three areas or Risk Classes were identified. Risk Class 1 was considered as acceptable. Risk Class 2 was considered as noticeable and Risk Class 3 was considered as critical.

A second issue with the FMECA methodology is the fact that it relies on the experience and inspiration of the people around the table to come up with an exhaustive list of all risks. In the STALLION project a more systematic process was followed (based on system functions and guide words) to make sure all possible risks were identified.

During a two-day workshop the participants reviewed the schematic drawings for all levels and the spreadsheet containing a breakdown structure of all components per level. Based on the component functions and the guide words, an exhaustive risk analysis was performed, in which the broad range of experience in the STALLION consortium proved invaluable. In a next step the risks were quantified and Risk Priority Numbers (RPN) were calculated within the FMECA methodology for all 'unwanted events' considering their 'effect on system level'. Then unwanted events and their potential failure causes were assigned to Risk Classes, based on their position in the risk matrix. This led to the identification of 5 critical risks together with 17 potential causes summarized in the table below.

	Fire ignition at cell level	
a	Cell on fire due to overcharge or undercharge	Malfunction of voltage balancing system
b		Malfunction of control action of System BMS, Pack BMS or Module BMS
c		Malfunction of voltage sensor
d		Malfunction of temperature sensor
e		Decomposition of electrolyte (overcharge, high temperature)
f	Cell on fire due to damaged cell cover	Punctures in pouch cell can facilitate moisture intrusion and thus corrosion
g	Cell on fire due to internal short circuit over separator	Punctures in separator (dendrite formation)
h		Malfunction of separator (material faults)
	Fire propagation	
i	System on fire	Malfunction of fire extinguisher system (failure or under dimensioning)
	Failure of battery intelligence	
j	Wrong control	Malfunction of control action of System BMS, Pack BMS or Module BMS
k		Malfunction of communication between various levels of intelligence (sensors, voltage balancing system, BMS)
	Short circuit	
l	Short circuit in module or pack, leading to local damage and:or fire	Failure of fuse
m	Short circuit in pack, leading to local damage and/or fire	Failure of Insulation Resistance Monitor

	External exposure to high voltages	
n	High voltage on module cover	Human error
o	High voltage on pack cover	Failure of pack cover earthing
p		Failure of insulation resistance monitor
q		Failure of electrical contactor

Table 1: Major risks and potential causes for large-scale (≥1 MW), stationary, grid-connected Lithium ion storage systems during operation

The most critical risk is a battery system on fire. The fire can originate at cell level and propagate further to system level. Although there are already several safety measures incorporated to prevent fire ignition at cell level or to protect the system against fire propagation, failures of these safety measures are considered critical.

The next risk identified is failure of the intelligence of the battery system and of the communication between the various levels of intelligence. In case of control issues the safety is undermined.

Another potential risk is that of short circuit on module or pack level leading to local damage and/or fire.

Finally, it is recognized that the high voltages in the battery system contain a significant risk. Failure of internal protection measures to prevent external access to these high voltages is considered as a major risk, especially during maintenance.

Subsequently, the STALLION consortium proposed a Top-10 of risks for large-scale (≥1 MW), stationary, grid-connected Lithium ion storage systems during operation. This Top-10 was used as input for the Risk Assessment workshop together with STABALID, which was meant to discuss the results and conclusions of the risk analysis with both Advisory Boards.

	Top-10 of risks for large-scale (≥1 MW), stationary, grid-connected Lithium ion storage systems during operation	**Relation with row numbers [Table 1]**
1	Failure of power supply to System Demand Controller, SBMS and pack BMS : undermines safety measures in case of wrong control	[j, k]
2	Fire extinguisher not able to extinguish the fire (failure or underdimensioned): no adequate fire suppression in case of fire	[i] initial fire could be caused by [a-h]
3	Failure of Insulation Resistance Monitor: no adequate detection of wire faults, leading to possible short circuits in case of two faults. This may be due to moisture.	[m]
4	Short circuit over separator in cell due to puncture or material fault: internal short circuit that may lead to fire	[g, h]
5	Wrong behaviour of cell voltage sensor, may be due to disconnection: wrong control actions that may lead to over- or undercharge that can lead to fire	[a, c]
6	Wrong behaviour of block/cell temperature sensor, may be due to disconnection: wrong control actions that may lead to charging when it should not that can lead to fire	[d]
7	Cell on fire due to overcharge (malfunction in balancing, undetected sensor failure…)	[a – e]

8	Cell on fire due to previous undercharge (malfunction in balancing, undetected sensor failure…)	[a – e]
9	Cell on fire due to damaged pouch and moisture intrusion	[f]
10	Fuse failure (resulting in short circuit causing system damage (Fire))	[l]

Table 2: top-10 risks for large-scale (≥1 MW), stationary, grid-connected Lithium ion storage systems during operation.

The FMECA exercise was performed elaborately for the operational life stage and subsequently for other stages of battery life. During transport & storage exposure to shocks and vibrations, extreme temperatures and lack of inspection are additional risk events. During the other life cycles (installation & commissioning, maintenance & repair, decommissioning and recycling) the most important additional risk events are: danger to personnel due to malfunction of control and safety functions and due to human failure.

The system description and FMECA analysis was published in the report: '*Failure Mode, Effect and Criticality Analysis for stationary, grid-connected, large-scale, Li-ion storage systems'*.

2.2 Establishing the state of the art

2.2.1 Sensors

To be able to evaluate innovative sensors and in several other phases of the project, we needed battery cells and modules for experimenting. An overview of the lithium-ion cell and module offering for grid connected energy storage systems was realized and analysed with four selection criteria:

- easy to supply
- interest regarding the application and the STALLION goals
- energy or power oriented
- possibility to purchase module

It was also intended to select cells with various geometries (prismatic, cylindrical, pouch cells) to evaluate the influence of the geometry on safety.This approach resulted in the selection of four relevant cells:

- Pouch cell NCO-LTO 16.5Ah
- Cylindrical cell (aluminium casing) LFP-graphite 15Ah
- Prismatic plastic cell LFP-graphite 40Ah
- Pouch cell LFP-LTO 20Ah

The objective of this task was to identify sensors able to give state of safety (SoS) indication. As shown in the risk assessment, the main dangerous phenomenon in battery failure is thermal runaway, which could be due to overheating, overcharging, or internal short-circuit. Overheating could be managed using temperature sensors. Overcharging can be managed using an SoC measurement. The most difficult to detect in advance is internal short-circuit. SoC measurement methods are however not easily available for all types of lithium-ion batteries, as some chemistries have a very small voltage variation with SoC. Moreover, SoC-voltage relation is modified by temperature and cell ageing.

Three types of sensors were then identified and supplied:

- Strain gauges for the measurement of the cell bending
- Thermal sensors to follow the temperature evolution
- Acoustic sensors considering the noise generated by the electrochemical activity (insertion of lithium inside graphite foil, crack of the electrode material, gas bubble blow up, …)

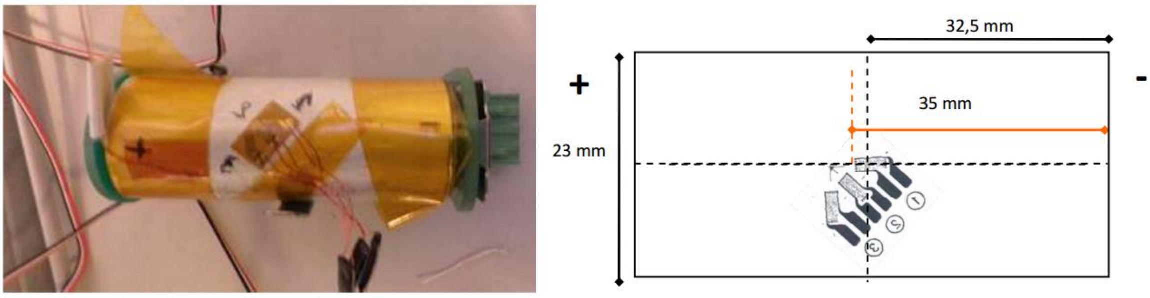


Figure 2: 26650 cell, monitored by a strain gauge

Prior to advanced testing, each cell was tested “as received”. Reception tests protocol includes mechanical verifications and standard electrical performances measurements:

- Open Circuit Voltage (OCV) at reception
- Shipping State-of-Charge (SoC) and nominal C/2 capacity and energy determination (last cycle of a series of 3)
- Internal impedance at 1kHz at SoC=100%.
- Mechanical measurements (length, diameter or width and thickness)
- Weight

After that, a long study was necessary to improve the attachment and positioning of the sensors on the different cells. Indeed, the position of the sensors on the Li-ion cell is one crucial point that must be optimized in order to obtain the most sensitive answer of the signal recorded.

Regarding e.g. the strain behavior of the cell, the internal conception of the cell itself (type of the envelope, nature of the metal, presence of a mandrel, nature of the active materials and electrolyte) will obviously impact the amplitude of the signal and the strain signature during normal and abuse conditions.

This study has shown that a thermal sensor remains the more indicative sensor for in operando recording. However this sensor does not give indication about SoH (State-of-Health). Temperature is well homogeneous on the architecture of cell that we have studied in STALLION.

The strain gauge could be a good solution for SoH and SoS, but the method and protocol to attach it to a cell need to be improved. This remark is more specific to soft packaging cells.

The acoustic sensor has shown the ability to identify SoS before thermal runaway. However, utilisation and miniaturisation of this sensor need to be adapted for all types of cell architecture.

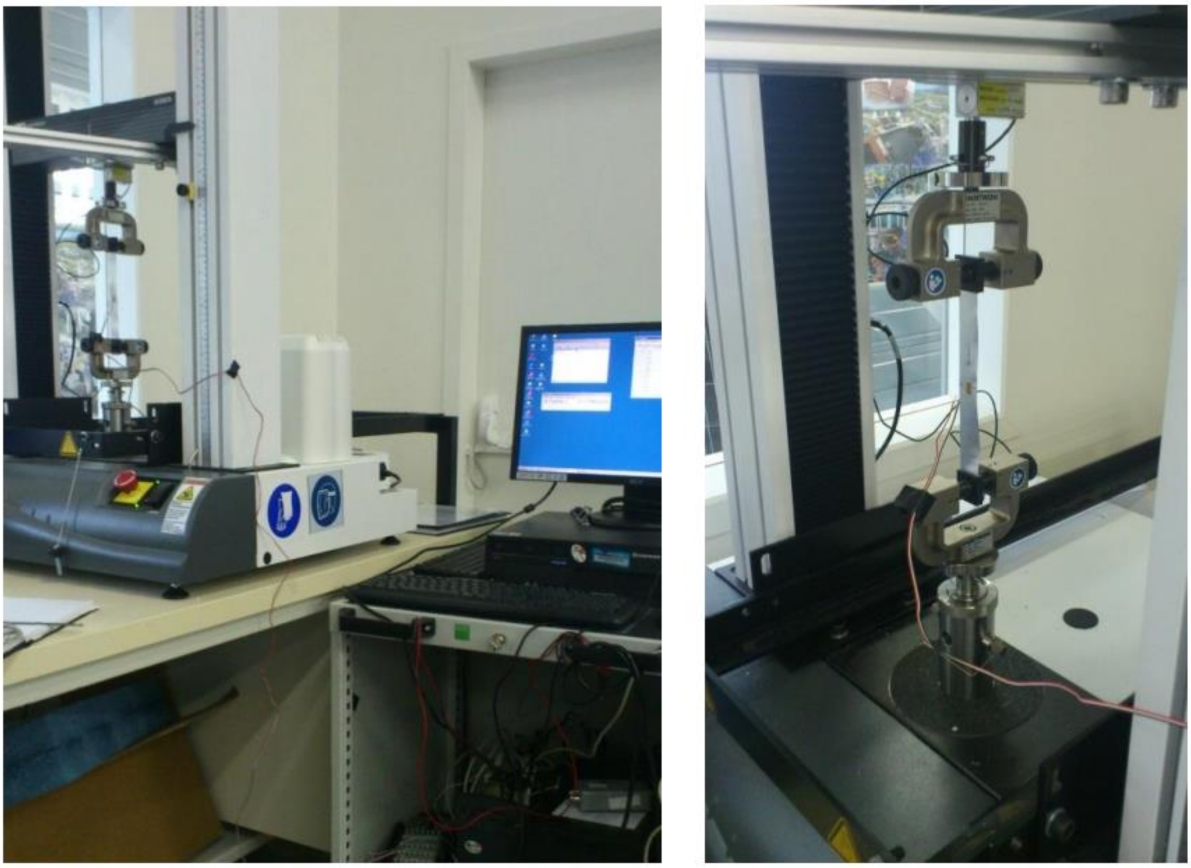


Figure 3: Validation of gauge-cell assembly on tensile-testing machine

Each of the selected sensing strategies (stress gauges, acoustic sensors, and thermal sensors) was tested on the different commercial cells in normal operation and abuse conditions. This allowed optimizing the sensing strategies in order to generate suitable, reliable and sensitive information enabling the accurate detection of specified and relevant failure modes of the tested cells. The results were documented in a report.

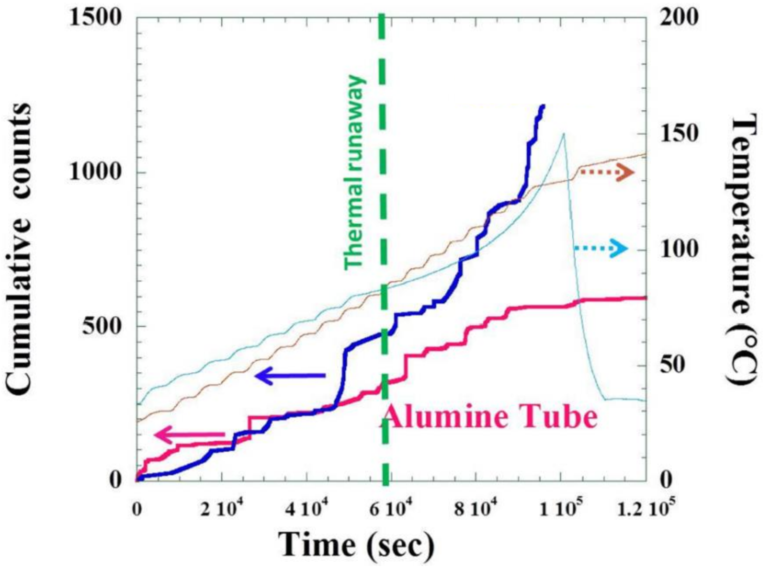


Figure 4: Temperature and acoustic signal for cell (blue) and aluminum tube (pink)

The main conclusions show that thermal sensors remain the most indicative sensors for in operando recording. However this sensor does not give indication about SOH. Temperature is homogeneous on the architecture of the cells that we have studied in the STALLION project. The deformation gauge could be a good solution for SOH and SOS, but methods and protocols for instrumenting the different types of cells need to be improved, mainly for soft-packaging cells. Acoustic sensors have shown the ability to identify SOS before thermal runaway. However, utilization and miniaturization of this sensor needs to be adapted for all types of cell architecture. An interesting perspective is also the coupling of different kinds of sensors to improve the sensitivity of SOS indication, and to enable the use of lower cost sensors, by mitigating the influence of lower quality signals of the individual sensors.

2.2.2 **Materials**

2.2.2.1 Material selection

Analysis was done to consider the most suitable active couples for large ESS applications depending on the type of usage. From this analysis, we developed a methodology for selection of best suited materials for any large ESS application.

The proposed methodology to determine best suited active materials for a specific large application should be based on the following three pillars:

- **Safety** or reliability test to identify safest materials
- **Price** analysis of less expensive active materials
- Convert end-users needs and complete systems characteristics to battery and materials **characteristics**.

Then safety, price and characteristics of the active redox couples should be correlated in order to select the best suited materials. As an example, for some high power applications price of material should not be as important as in large energy oriented systems with much more volumes. The characteristic approach can be less important when a system is aiming at different applications (energy back up + frequency regulation) as it is often the case when we get closer to the end user. Also, the safety of the material can be moderated by a specific battery design. Very reactive redox couples could be used in a safe cell if design is appropriate.

However, considering the importance of cathode and anode couples in any case, a reflection on active redox couples should be done by the end user in regard of expected system characteristics.

A methodology has been detailed and mapped.

The methodology has been used on the following list of the Umicore’s commercially available **active materials**:

- NMC 111 / Graphite
- NMC 111 /LTO
- Low Cobalt NMC PSD + / Graphite
- Low Cobalt NMC PSD ++ / Graphite
- High Nickel NMC PSD - / Graphite
- High Nickel NMC PSD ++ / Graphite
- LFP Power / Graphite
- NCA PSD - / Graphite
- NCA PSD + / Graphite

The following **tests** have been performed by Umicore on small (0.6 Ah) pouch cells:

- Charge and Discharge rate capacity vs 0.2 C @ C, 5C, 25C

- HPPC power in W/kg at 50% SoC during charge and discharge
- Temperature properties vs 25°C at -20°C and +60°C
- Cycle life at Room Temperature (RT) (1C in charge / 1C in discharge) after 200, 400 and 1000 cycles
- At RT, number of cycles after which 80% of initial output is reached
- Cycle life at RT (2C in charge / 3C in discharge) after 200, 400 and 1000 cycles
- Cycle life at RT (3C in charge / 10 C in discharge after 200 and 400 cycles
- Cycle like life at 45°C (1C in charge / 1C in discharge) after 200 cycles
- Recovered Capacity after 1 month at 60°C
- Recovered Capacity after 3 months at 60°C

The graph below represents four possible segments of energy storage systems and the key required characteristics and specific tests for each of the segments.

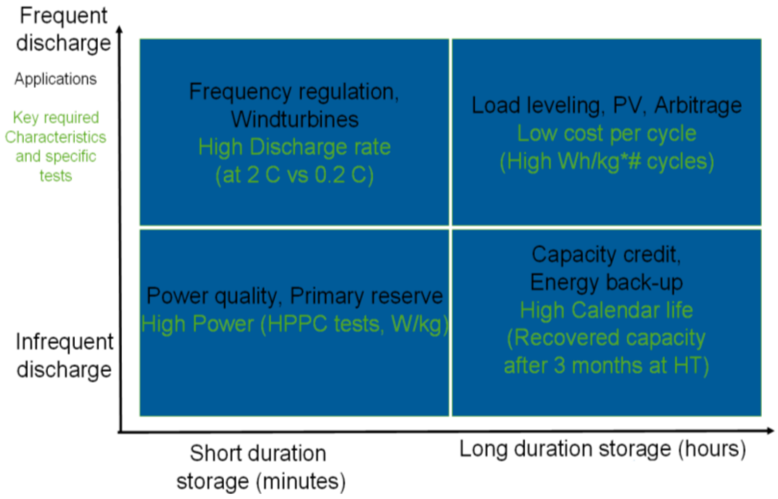


Figure 5: Key characteristics and specific tests for each applications

At the end of the process, the following materials were sent to CEA for further analysis in the next task:

- Cathode materials: LFP, High Nickel NMC PSD ++, Low Cobalt NMC PSD ++
- Anode Materials: LTO

CEA did a second selection of active materials. The goal was to validate their chemical stability in electrolyte media, evaluate the impact on the micro-structure of abusive condition such as overcharge intrusion and finally, measure specific parameters requested for thermal modeling (WP6). Chemical stability was controlled by measuring material dissolution in electrolyte using the ICP (Inductively Coupled Plasma) technique. Structural stability upon overcharge was evaluated by microscopy and XRD (X-ray Diffraction) and thermal behavior was characterized by DSC (Differential Scanning Calorimetry) tests. These analyses showed that $LiFePO_4$ (LFP) and $Li_4Ti_5O_{12}$ (LTO) were the most stable materials with negligible dissolution, low thermal reactivity even at fully charged state and no structural issue upon overcharge. On the contrary, NMCs materials (High Nickel NiMnCo-KHX12, Low Cobalt NiMnCo-BX9) suffer from irreversible structural transformation and high thermal reactivity.

LFP, LTO an NMC Low Cobalt were selected and material samples were sent to LIACON for cell fabrication

2.2.2.2 Cell manufacturing

Based on the materials selected, LIACON produced prototype cells for safety testing. It was decided to build four types of prototype cells, based on two anode materials and two cathode materials:

- LFP – LTO
- LFP – graphite
- NMC – LTO
- NMC – graphite

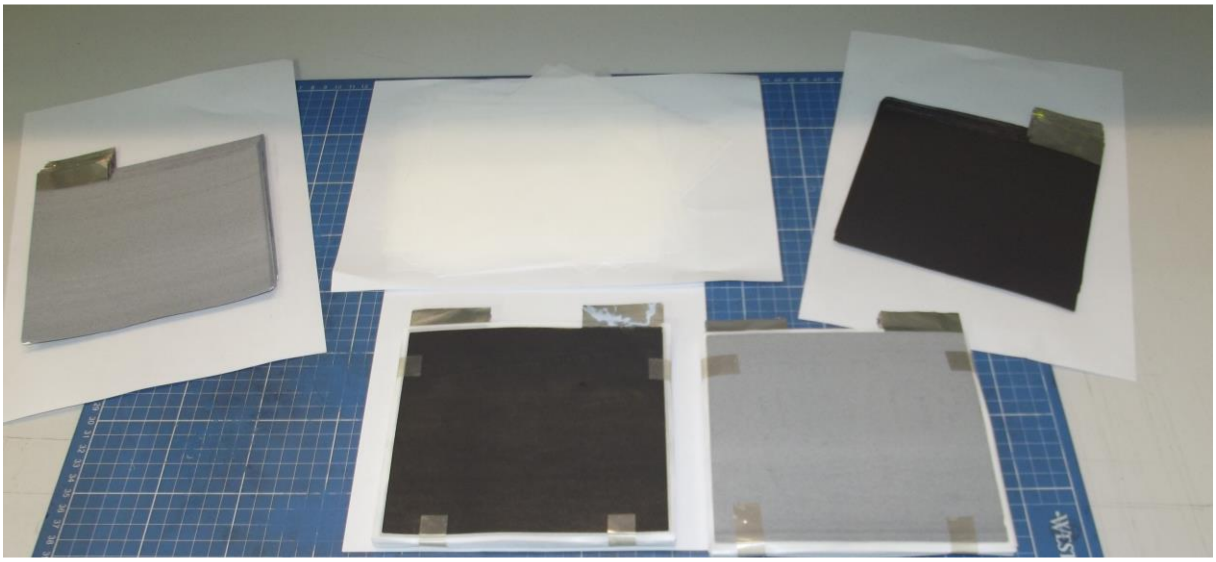


Figure 6: LTO cells in production process

2.2.2.3 Cell characterization

A characterization test was defined, consisting of both long charges and discharges and short and long pulses at various temperatures. The purpose of this test is to get information on the capacity, OCV curve and internal resistance at various temperatures and SoC levels. Both the commercial cells and the prototypes, produced in STALLION were characterized, aged and tested for safety.

The cell characterization tests were defined with the intention to get an in-depth understanding of the characteristics of each of the cells. For that purpose, extensive initial testing was performed on the 8 cell types (4 commercial + 4 prototypes) in order to acquire data for several objectives.

First, cycles were performed at 4 discharge rates with nominal charge C/2, at 4 different temperatures, to study the cells rate capability. For each temperature, this was followed by two C/25 charge/discharge cycles for estimation of OCV, and current pulses at different C-rates and 12 SOC values to determine R, RC parameters of the electrical equivalent circuit for the subsequent modeling.

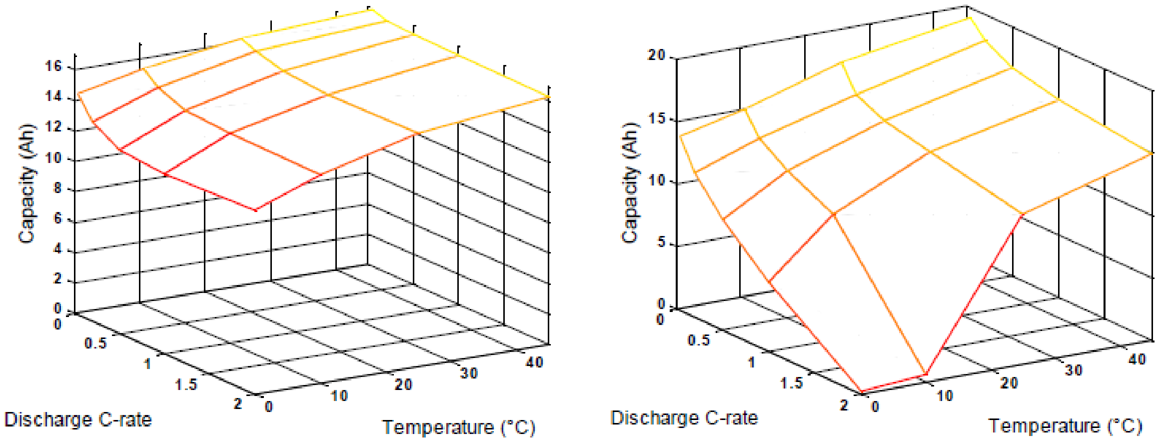
Then, the cells were equipped with several thermocouples, thermally insulated and subjected to charge/discharge cycles at 3 different charge and discharge rates and temperatures, and to user profiles at 25°C. Two profiles were selected:

- DST – Dynamic Stress Test profile from IEC 62660-1
- Grid-connected application profile, simulating smoothing of PV production with additional discharge in the evening and SOC adjustment at night.

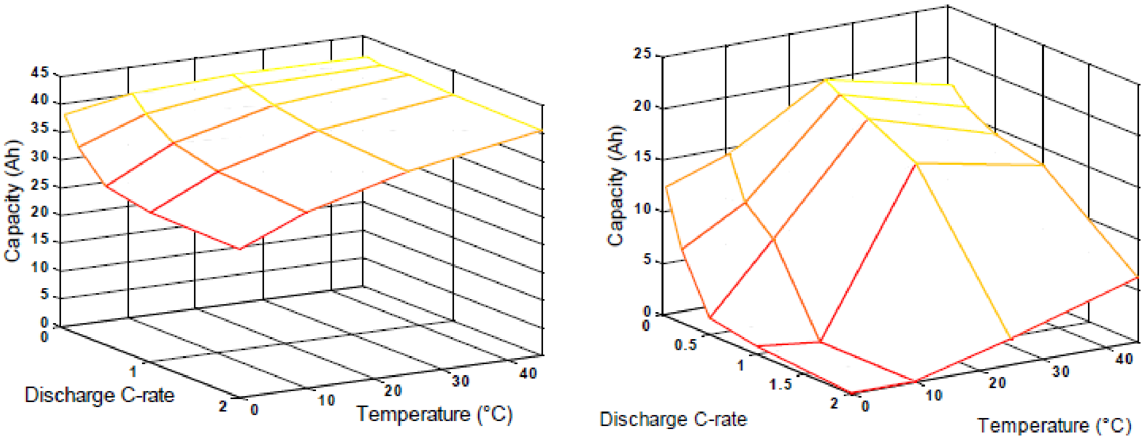
The results of the characterization tests to determine the parameters of the electrical equivalent circuit and to validate the thermal model were used in the modelling addressed later in this report.

For commercial cells, the two LFP/C cells have a similar behaviour, with moderate capacity loss at high discharge rate and at low temperature as opposed to the two cells with LTO negative electrode. As expected, the capacity increases with temperature and decreases with discharge rate. The LCO/LTO cells show poor performance at high rate, which was already observed in other cases and clearly confirms that these are “energy-type” cells and not “power-type”. However, the datasheet allows a maximum discharge rate of 4C.

Unsurprisingly, the energy density of prototype cells is lower than for commercial cells. However this is not a problem since the main target of this task is to compare the different electrode materials with the same cell design. In particular here, the comparison of the measured energy densities is coherent with the materials used, with LFP lower than NMC and LTO lower than C. Values are clearly related to cell voltage, but not only since the specific capacity is also in this order. Concerning the rate capability, the same tendencies can be noted as for the commercial cells.



Cylindrical LFP/C Pouch NCO/LTO



Prismatic LFP/C Pouch LFP/LTO

Figure 7: Capacity of the commercial cells vs temperature and discharge rate

2.2.2.4 Safety testing

The internal short circuit test of IEC 62660-2 was used as a measure of cell safety. So this test procedure was performed on three samples of each cell type. This allows for an objective comparison of safety characteristics between all the cells that were used in the STALLION project. This served a triple purpose:

- It provides a benchmark of cell safety. This benchmark can then be used to check whether the test procedures that were developed in the project, are able to distinguish between safer and less safe cells. However to be able to do this, we need an objective measure for the safety of each of the cells, which is in this case provided by the safety tests.
- It allows us to gauge whether the materials that were used to build the prototype cells, lead to an improved safety at cell level. Obviously you have to take into account that these cells are prototypes and hence have a lower maturity level (when it comes to performance and safety) than the commercial cells.
- It is needed to verify whether aged cells are less safe than new cells. This is an important aspect to take into account when building large stationary battery systems since these need to be safe not only during their first day of operation, but also during their entire lifetime.

Thermal stability and overcharge tests in ARC were also performed on fresh commercial cells.

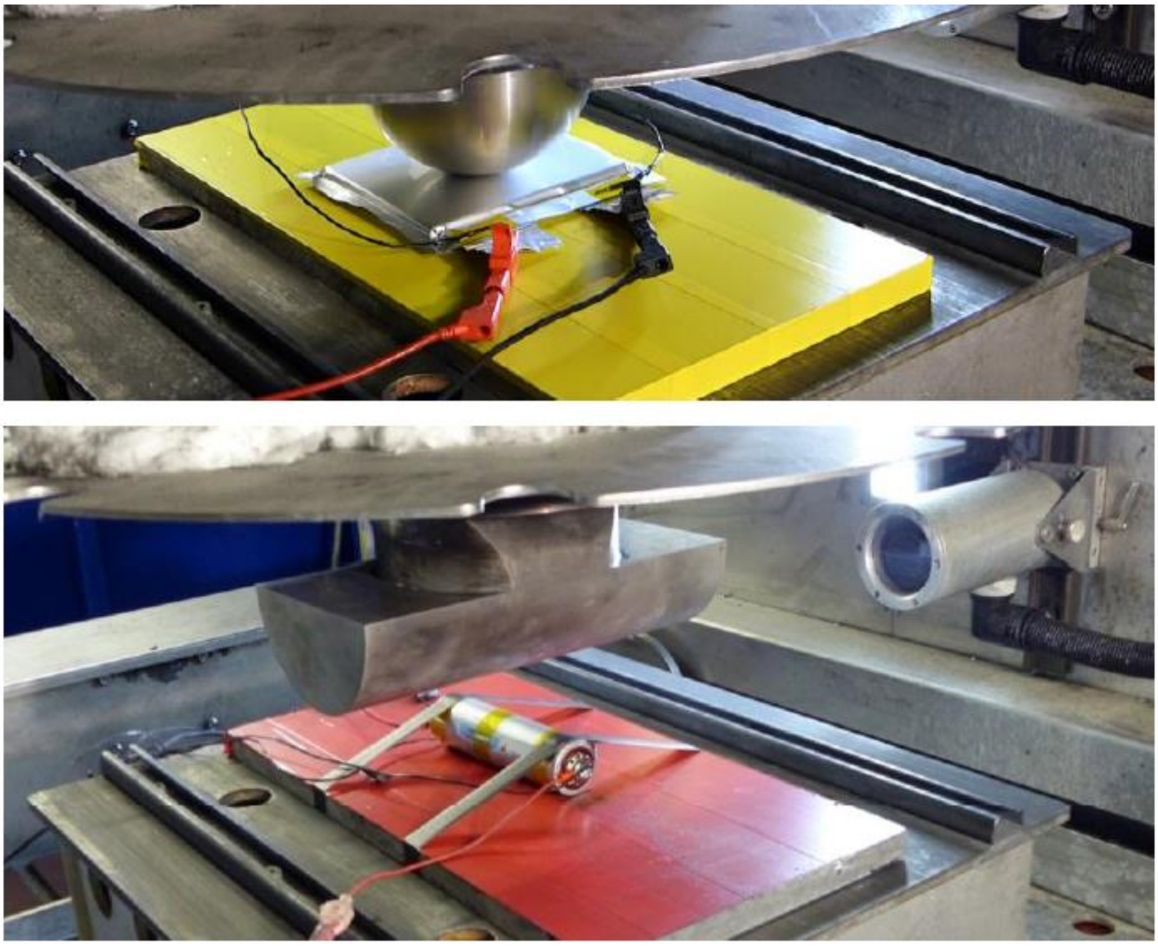


Figure 8: Internal short circuit test setup for prismatic and cylindrical cells

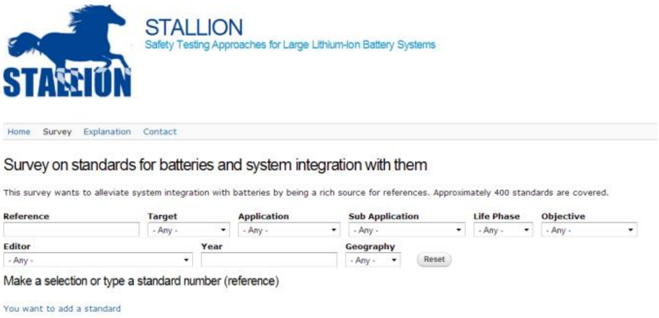
2.2.2.5 Cell aging

Although the cell aging behaviour is an important characteristic when developing a large stationary battery system, studying the aging behaviour in itself was not the main reason for aging cells. The purpose of aging cells was the fact that aged cells are suspected to be less safe than new cells. This hypothesis was verified by the safety testing of aged cells. However the result was inconclusive due to the lack of severity of the standard internal short circuit test.

2.3 New test procedures

2.3.1 Literature study

To inventarize the state of the art, a thorough overview and analysis of existing test procedures was performed. This overview was not limited to large stationary Li-Ion batteries but rather extended to all battery applications (portable, vehicle…) and all grid-connected appliances (converters, transformers…) since both can



Survey on standards for batteries and system integration with them

This survey wants to alleviate system integration with batteries by being a rich source for references. Approximately 400 standards are covered.

Reference:
Target: - Any -
Application: - Any -
Sub Application: - Any -
Life Phase: - Any -
Objective: - Any -
Editor: - Any -
Year:
Geography: - Any -

Make a selection or type a standard number (reference)

You want to add a standard

Figure 9: battery standards web tool

deliver inputs when it comes to either battery technology related risks or risks that are mainly related to the application area. This overview can be consulted via the STALLION web site (STALLION battery standards). This web tool can be used to search in a database of about 400 test standards, by filtering on several keywords. The tool also allows for cross-searches. For each standard, a short explanation is given together with a link to the actual standard or where it can be purchased.

2.3.2 **Test definition**

Based on the list of prominent risks and the overview of relevant test standards a selection of 10 risks was made for which we decided to develop detailed test protocols:

- Propagation of thermal runaway between cells or modules
- Internal short circuit in a cell
- Overcharge of a module
- Undercharge because of extended storage
- Rough handling of the battery container during transport or installation
- Module cycling without cooling
- Deformation of module due to an accident
- Flooding of the battery container
- External short circuit of a module
- Malfunctioning of the BMS

The remaining prominent risks were also identified to be important, but for the mitigation of these risks design requirements were found to be a better option than the definition of a test procedure:

- Touchable external voltage
- Insulation failure due to moisture

The defined test procedures either cover risks for which no test procedure exists or describe present tests more stringently with a focus on the specific application of large stationary battery systems. These test procedures follow a rigorous template to ensure that as little as possible is left for interpretation. The following aspects are specified:

- Purpose: this describes the failure mode the procedure is intended for
- Approach: this describes in general terms how the procedure test for the intended failure mode
- Items to be tested: this describes the items to be tested in the procedure
- Test equipment: this describes the mandatory and optional test equipment that is needed to execute the test procedure and gather the necessary data
- Precondition: this describes the condition the device under test and its environment are in before the start of the test
- Test procedure: this describes the detailed steps and the pass/fail criteria of the test procedure
- Post condition: this describes the condition the device under test is in after the test

These test protocols were initially developed separately by STALLION and STABALID. This led to test procedures with varying degrees of overlap between both consortia. However since the EC understandably insisted that both projects would come forward with a coordinated European position on the related standards, we felt that it would be worthwhile to co-develop these test procedures further and come up with a common proposal to the relevant standard committees. This has obviously increased the effort that has been invested in discussing the proposals and trying to reach a proposal that both consortia can support. Nevertheless, this increased effort has certainly led to a higher quality. These common test procedures were then presented to the Advisory Boards of both projects in the Standard Preparation workshop. This again led to some review remarks that were incorporated in the final proposal, which was published in a report, containing detailed descriptions of the tests defined in the FMECA.

2.4 Validation of test procedures

The defined test procedures are so-called binary classification tests. They are meant to classify the devices under test into two classes: safe and unsafe (with respect to the failure mode the test procedure was designed for). Such a test procedure is often used in medical diagnostic testing (i.e. testing for the presence of a disease). Two important measures of such a test are the sensitivity (the ability to identify unsafe devices as unsafe) and the specificity (the ability to identify safe devices as safe). Ideally both measures are 100% since a low sensitivity means that unsafe devices would pass the test (i.e. be evaluated as being safe). A low specificity means that safe devices would fail the test. When performing a large number of tests (the practice in evaluating medical diagnostic tests) on a known sample of the population, these qualities are easily calculated. However in our case this is a very difficult and expensive way of working since it would be extremely expensive to use thousands of devices for testing, especially since the tests are destructive. Therefore, a compromise was made between statistical relevance and cost when calculating the need for test devices (cells, modules…). Based on an extensive test plan and an experimental design, a total of 208 cell tests and 7 module tests were performed.

2.4.1 Feasibility tests

Both in the STALLION and STABALID consortia, partners are involved with a large experience in running a commercial test lab (VDE and TÜV Süd). Therefore, already in the definition and especially during the review of the tests, it was made sure that the test procedures can actually be executed in a state-of-the art test lab. This can involve the availability of specific infrastructure (e.g. several ways of starting a thermal runaway in a cell) but also aspects like personnel safety (e.g. not storing an overcharged module). Feasibility tests’ were performed for all the defined test procedures. The purpose of these feasibility tests was to validate the feasibility of performing the defined test procedures in a test lab. Various aspects were evaluated:

- Completeness of the test procedure
- Correctness of the test procedure
- Clarity of the test procedure
- Feasibility of the test procedure (e.g. availability of test devices, applicability to DUT’s…)

Some minor remarks were made on the correctness test procedures based on these feasibility test. Furthermore some changes were proposed to limit the costs of performing the tests. These recommendations have been taken along to improve the test procedures.

2.4.2 Validation tests

The purpose of executing the experiments defined in D5.2 is twofold.

- The first goal is to find out whether the test procedure is able to distinguish between safe and unsafe devices. Therefore test outcomes of the feasibility and validation tests, executed in WP5 should be correlated to the outcomes of the safety tests, performed in WP4.
- A second goal is to gauge the dependency of the test results on the specific circumstances of the test. Therefore the validation tests are performed using an experimental design structure while varying the important circumstances of the respective tests (temperature, current, pressure…)

Based upon the test protocol definitions, detailed test cases are defined. A first test case describes each test procedure as defined. This experiment will be executed on several cells or modules to gauge the ability of the procedure to distinguish between safe and unsafe cells or modules. Then several other experiments are defined where certain parameters are varied in a structured way (so-called design of experiments). The intention is to quantify the sensitivity of the defined test procedure with respect to its parameters and maybe even to improve the test procedure in case its quality (sensitivity and/or specificity) would increase under different circumstances.

Case	Cell type	Temperature	Current
T4.6.1	Sinopoly	40°C ± 5°C	It
T4.6.2	Sinopoly	40°C ± 5°C	It/5
T4.6.3	Sinopoly	10°C ± 5°C	It
T4.6.4	Sinopoly	10°C ± 5°C	It/5
T4.6.5	Leclanché	40°C ± 5°C	It
T4.6.6	Leclanché	40°C ± 5°C	It/5
T4.6.7	Leclanché	10°C ± 5°C	It
T4.6.8	Leclanché	10°C ± 5°C	It/5
T4.6.9	LifeBatt	40°C ± 5°C	It
T4.6.10	LifeBatt	40°C ± 5°C	It/5
T4.6.11	LifeBatt	10°C ± 5°C	It
T4.6.12	LifeBatt	10°C ± 5°C	It/5
T4.6.13	Dispatch Energy	40°C ± 5°C	It
T4.6.14	Dispatch Energy	40°C ± 5°C	It/5
T4.6.15	Dispatch Energy	10°C ± 5°C	It
T4.6.16	Dispatch Energy	10°C ± 5°C	It/5

Figure 10: experiments for polarity reversal test case

Figure 11: The effect of performing an overcharge on one of the selected cells

Based on the test results of the validation tests, both the quality of the defined test procedure and its dependency on the various test circumstances are evaluated.

The quality of the test procedure is evaluated by comparing the outcome of the test on the various cells with the outcome of the safety tests on the cells in WP4. Based on this comparison, it can be gauged whether the developed test procedures do a good job in distinguishing between safe and unsafe cells.

On the other hand, the test outcomes under the various circumstances can be compared. The outcomes are compared in two ways. First the typical test outcomes under the different circumstances are compared. This could indicate that the test is more severe under certain circumstances (e.g. higher temperature). Depending on the overall severity of the test, this can lead to a recommendation to perform the test under different circumstances than what was initially defined to make it more or less severe. A second aspect that is taken into account is the 'noise' that is generated by each of the circumstances. If the test outcomes are more variable under certain circumstances, than this is obviously a disadvantage since it is clearly preferable that test are repeatable and reproducible.

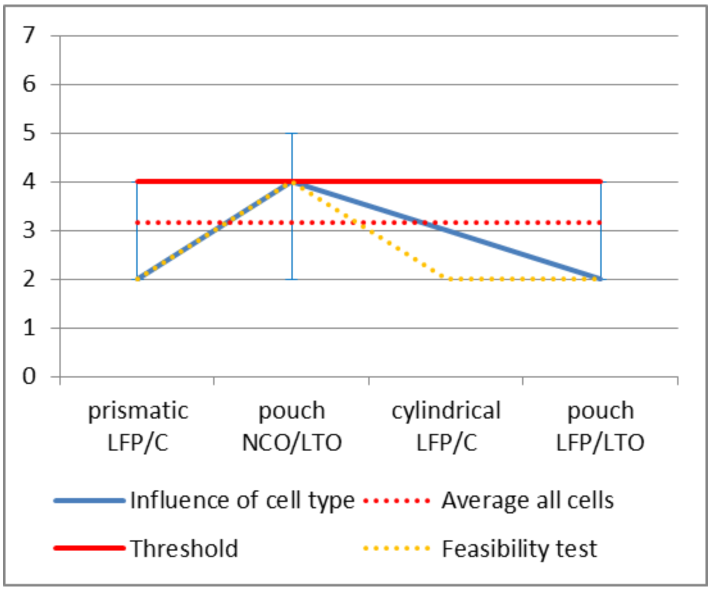


Figure 12: Validation of the overcharge test (EUCAR hazard level)

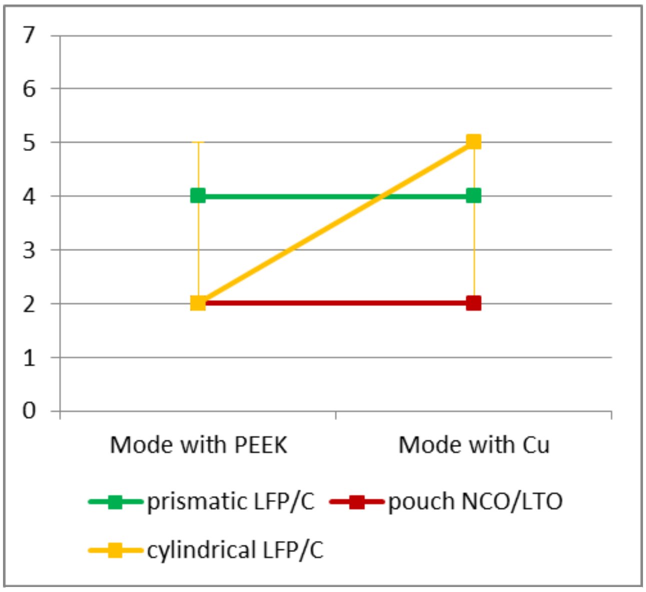


Figure 13: Effect of impactor material on the outcome of the internal short-circuit test

The results of the evaluation of existing test procedures are documented in D5.4 and the recommendations have been taken along in the draft standard document for stationary batteries (D5.5). This draft standard document has been agreed upon between the STABALID and STALLION consortia.

2.5 Measures validated by modelling

As explained in the previous chapter, it is not realistic to achieve full statistical relevance only by performing tests. Tests are also performed either at cell or at module level. To be able to extrapolate the results of the validation testing to system level, modelling was performed at cell, module and system level.

2.5.1 Cell and module level modelling

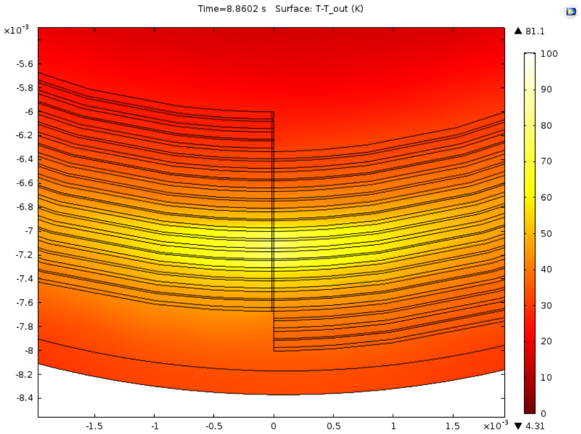


Figure 14: Thermal effect of an internal short circuit

A literature study was made on the modelling of cell and module behaviour under several abuse conditions (overcharge, short-circuit…). Based on this study, both white-box and black-box cell-level models were developed and used to study the behaviour of the cells under abusive conditions. The white-box cell-level models were used to study the effect of internal short-circuit since this is essentially a process internal to the cell.

The thermal behaviour of a cell was studied using an R-RC model and CFD code. The use of a CFD tool, as FLUENT, allows understanding the effect of natural convection. Since a hot cylinder is hung in ambient air, it tends to generate natural air movement around it. The CFD images clearly show the chimney effect which occurs around the cylinder. The bottom side is submitted to cold ambient air whereas the top is located in dead area where air is hotter and consequently the cell is not cooled in the same way. Physical phenomenon and level of temperature are quite well described.

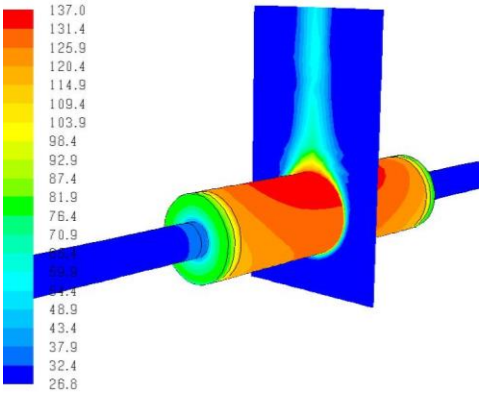


Figure 15: Natural convection around a cylindrical cell

A cell, instrumented with 13 thermocouples on the external wall, was submitted to an external short circuit. Measured local temperatures at the top and the bottom are strongly different: around 40°C. The module-level model, developed by CEA in T6.3 was validated using both experimental tests and data from literature. Both models show an excellent correlation with the real behavior of the cell and the module.

Figure 16: Cell, equipped with 13 temperature sensors

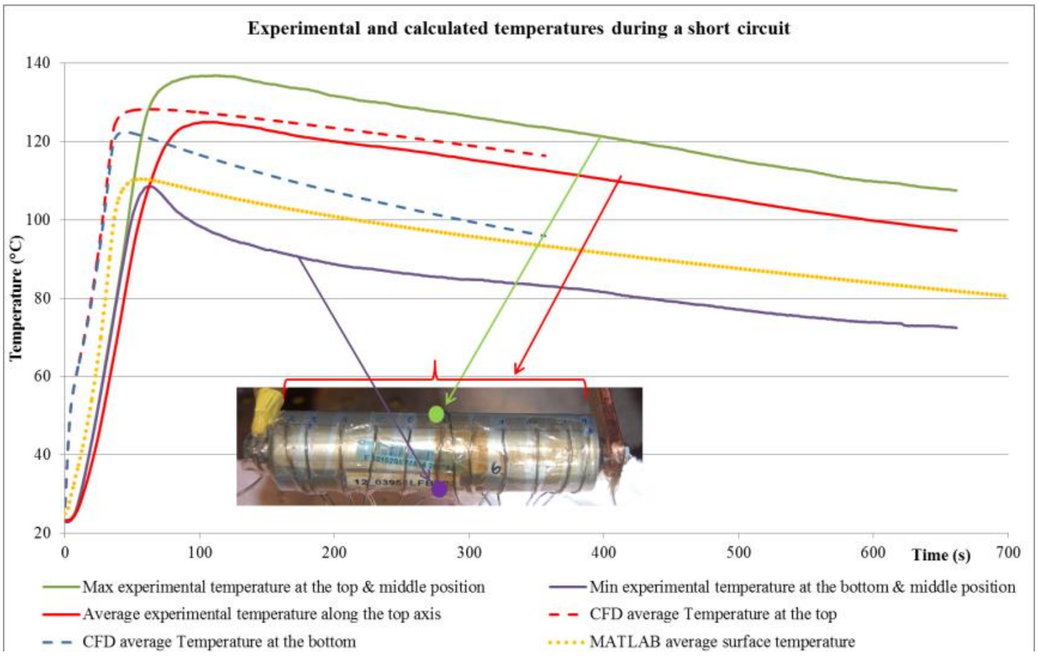


Figure 17: Correspondence between modeling and experimental results

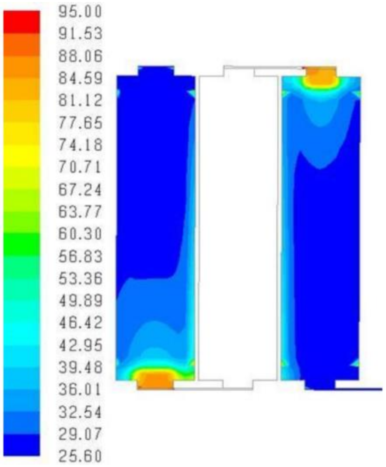


Figure 18: The propagation of thermal runaway between cylindrical cells

Using the cell-level models and the characterization data on the module level, module-level models were built by CEA using Matlab and FLUENT CFD. Based on this model, it can be concluded that forced air flow in a longitudinal direction leads to a homogeneous temperature distribution in the module. Based on this thermal model, several abnormal working conditions were simulated and validated, mainly related to the module-level tests, defined in WP2. Air flow was shown to be an adequate means of limiting the heat propagation between cells. But regarding the propagation of thermal runaway, it was shown that the major means of propagation is the electrical connection between neighbouring cells.

2.5.2 System level modelling

Fault tree analysis was used to study the propagation of the most prominent failures across the system levels and to get a deeper insight into the most critical risks. An FMECA only provides limited insight into the cause-and-effect relations. To be able to assess the effect of certain measures (materials, sensors and test procedures) that were developed previously, we needed the more detailed fault-tree analysis. This also allowed us to identify potential remaining weak links and to come up with ideas for additional measures to improve the overall system safety.

Fault-tree analysis uses a top-down approach, starting from an undesired effect as the root (most often shown at the top). It then resolves the event into its immediate causes and this resolution of events continues until basic causes are identified. This fault-tree can then be used to understand how different basic events contribute to the chosen undesired effect.

Using this fault tree, but progressing in the opposite direction, so-called event-trees can be built. These event trees use a single basic event as the root and describe the potential (undesired) effects that can be the result of the chosen basic effect. Both fault-trees and event-trees are interesting when evaluating the risks in a particular system. Fault-trees can help to answer the question what needs to be improved to decrease the criticality of a certain undesired effect. Using the tree and the associated probabilities, the ‘weakest links’ can be identified by determining the sub-trees with the highest probability. Based on this analysis, additional measures can be introduced and their effect on the overall risk level can be evaluated. Event-trees on the other hand, help to see the complete picture when investigating a certain basic event. Based on the success of measures at each level, a single basic event can have a multitude of possible effects.

These effects are not immediately clear from e.g. an FMECA. Using the fault tree analysis, we came up with a methodology to model the multi-level architecture in a better way using the FMECA methodology.

2.6 Improved test procedures

The proposals for improvements to the test procedures, both from the modelling and from the testing were then discussed with the STABALID consortium to arrive at a common proposal for standardized test procedures for large stationary Li-ion battery systems . This proposal is unique in the sense that it is validated by thorough testing and not solely based on expert opinion.

2.7 Input to standardization

STALLION partners were actively involved with the IEC SC21A in order to get the improved test procedures integrated in an existing or new standard with respect to the safety of stationary Li-ion batteries. A number of these procedures are currently under discussion in the IEC 62897 standard proposal.

2.8 Updated risk analysis

At the beginning of the project, a thorough risk assessment was performed, using the FMECA methodology. Already at this time, some changes to the standard FMECA methodology were proposed. During the modelling phase, for the most critical failures, a system-level model was developed, using fault-tree analysis, an alternative methodology to FMECA. From this fault-tree analysis, we found that the initial FMECA was not taking the multi-level system architecture with prevention, detection and mitigation measures at several levels. Therefore we came up with a slightly different approach to the FMECA that focused on the failure rate of the functional components and incorporated the safety measures into the probability of detection. Moreover the effects of a failure only propagated one level at a time and system level-effects were dealt with only at the system level of the FMECA. Since this methodology lead to a more realistic assessment of the risks, the initial FMECA was redone, using this new approach.

In a second step, the measures that were developed previously were introduced into the FMECA as additional measures. This allowed us to assess the increased safety level, due to these additional measures. Where needed to increase system safety to an acceptable level, additional measures were added, inspired by the modelling (e.g. compartimentation to prevent propagation, increased SIL level of BMS…).

2.9 Guideline for recycling

We published a guideline for recycling that covers in-depth the entire end-of-life stage of a battery. It deals in-depth with all the possible means of transportation for used and damaged batteries. Furthermore it describes a state-of-the-art battery recycling process and the rules and regulations that apply. Last but not least it contains and in-depth risk analysis for the recycling stage.

Since at the end-of-life we are dealing with aged and possibly damaged batteries, the risks in this phase are quite specific and are therefore treated in a separate document. This guideline covers three separate topics. Firstly an in-depth guideline was developed with respect to the transportation of aged and damaged batteries by different means of transportation. In a second step, a general description of a typical recycling process was developed. Last but not least, the most prominent risks during this recycling phase were assessed.

2.10 Handbook and training materials

The "STALLION Handbook on safety assessments for large-scale, stationary, grid-connected Li-ion energy storage systems" is meant to guide interested parties through the relevant safety aspects of large-scale, stationary, grid-connected, Li-ion battery, energy storage systems. The Handbook is one of the main final results of the STALLION project. The handbook describes:

- safety aspects of Li-ion batteries and the importance of safety assessments for Li-ion systems
- examples of projects with stationary, large-scale, grid-connected Li-ion storage systems
- the STALLION method for the FMECA, including: system description, identification of all failures, risk mitigating measures, quantification of the failures by ascribing a severity and probability levels
- additional risk mitigating measures proposed by STALLION
- outcomes of the STALLION safety assessment

The STALLION Handbook will be used for raising awareness on Li-ion battery safety and explaining STALLION's risk assessment methodology. Intended audiences are DNOs, utilities, local authorities, municipalities and policy makers, insurance companies and BESS system integrators.

2.11 Dissemination and exploitation of results

2.11.1 Dissemination

The International Advisory Board for the STALLION consortium consists of the following participants:

	Last name	First name	Organization	Country
1	Furukawa	Akio	Battery Association of Japan (IEC SC21A)	JP
2	Wakke	Paul	VDE	DE
3	Pierson	Etienne	Laborelec	BE
4	Ikeda	Hisatoshi	University of Tokyo (IEC SC21A)	JP
5	Bozelie	Jan	Alliander	NL
6	Mosley	Kimberley	IEEE	USA
7	Steele	Alistair	Scottish & Southern Energy	UK
8	Stevens	Renaud	Soitec	FR
9	Poggi	Philippe	Université de Corse	FR
10	Belmans	Ronny	ETP Smart Grids	BE
11	Inoue	Takefumi	GS-Yuasa (IEC SC21A)	JP

The role of the advisory board was multifold:

- Involvement in risk assessment workshops
- Connection with standardization working groups (IEC TC21/SC21A, IEC TC120, VDE)
- Feedback on other initiatives and research projects
- Support in dissemination activities
- Support for internationally accepted pre-standards (IEC TC21/SC21A, IEC TC120)

A summary of dissemination activities during the project are given below:

- Project deliverables including STALLION's FMECA, the Handbook on safety assessment and training materials
- Common deliverables with STABALID project
- Website (http://www.stallion-project.eu/)
- Public seminars
- STALLION-STABALID IAB meetings (24 April 2013 @ Paris; 28 January 2014 @ Arnhem; 10 March 2015 @ Dusseldorf)
- Conference papers and presentations
- Standardization activities
- Meetings with other parties
- Other dissemination activities

2.11.2 Exploitation

Table 3 lists results obtained and corresponding exploitation opportunities.

Table 3 Overview of obtained results and exploitation opportunities within STALLION

Obtained results	Exploitation opportunities

Thermal model for cell	Advisory services on thermal cell modelling
Thermal model for module	Advisory services on thermal module modelling
Fault Tree Analysis (FTA) on system level	Advisory services on FTA on system level
Failure Mode Effect and Criticality Analysis methodology (FMECA)	-Advisory services on FMECA on large-scale, stationary, Li-ion, grid-connected battery systems -Both **VITO** and **DNV GL** performed risk assessments commercial projects on battery safety in 2013-2014
BMS safety test procedures	-Advisory services: recommendations on safety functions of BMS -**VDE** implemented STALLION recommendations in their safety testing procedures in preparation of the IEC standards 62619 (final version for voting) and 62897 (new working group)
Safety test protocols	-Advisory services: knowledge on safety test protocols -Commercial testing and certification services -Input for standardization
Prototype cells	-Knowledge which enables improvements in cell making -IP • -**LIACON** used lessons learned from STALLION to improve their Li-ion cells and their manufacturing processes (e.g. like improved sealing of the pouch envelop and enhanced quality testing).
Selection method for a safe cathode-anode material combination	-dissemination of selection method -IP -Umicore has improved internal cell manufacturing process based upon lessons learned
Safety procedures for battery dismantling	-dissemination of safety procedures for battery dismantling -IP -Umicore has improved dismantling process based upon lessons learned
Handbook on risk analysis for large-scale, stationary, Li-ion, grid-connected battery systems	-dissemination of handbook
Training materials on risk analysis for large-scale, stationary, Li-ion, grid-connected battery systems	Training to target groups (DNOs, utilities, authorities, users, etc. -public awareness -public acceptance of large-scale, stationary, Li-ion, grid-connected battery systems
Draft standard (D2.3)	Stallion-Stabalid tests: input for IEC SC21A and IEC TC120

3 OVERALL PROJECT RESULTS

3.1 Validated safety framework for large stationary battery systems

One of the main results of the STALLION project is a safety framework that can be used by stakeholders (local authorities, network operators, building contractors, industrial parties…) to understand and evaluate the safety issues related to the installation of large stationary Li-Ion batteries. This framework consists of a proven systematic risk assessment methodology to gauge the safety and risks involved in a particular installation, published as a handbook and training materials.
Additionally an overview was made of existing applicable standards and regulations in the broad field of electrical energy storage.

3.2 Solid overview on the state of the art in battery safety

Battery materials have the largest influence on battery safety. Therefore the STALLION project has studied several performant battery materials and their influence on system safety. Also the recyclability of these materials and the related safety issues have been studied.

A second important aspect of system safety is the ability to predict or detect safety issues and prevent or mitigate their effects. Therefore the STALLION project has evaluated several new sensor types and their ability to detect safety issues at an early stage.

The impact of these new developments, together with existing and new measures in stationary batteries have been taken into account in the applied risk assessment and in the fault-tree analysis of the most prominent risks. This leads to a quantified impact on the system-level safety of stationary battery systems.

3.3 Contribution to standards related to safety testing for stationary Li-Ion batteries

The STALLION and STABALID consortia have cooperated to develop a number of safety testing procedures specifically aimed at large stationary Li-Ion battery systems. These procedures were proposed to the IEC SC21A Working Group 5 that is responsible for the IEC 62619 standard with respect to safety requirements for large format secondary lithium cells and batteries for use in industrial applications and the IEC 62620 standard with respect to large format secondary lithium cells and batteries for use in industrial applications. Following the initiative of several STALLION partners, they have also approved a new working item IEC 62897 on the more specific topic of safety for stationary energy storage systems with Lithium batteries. Some of the STALLION test procedures are included in this standard proposal. These proposed test procedures have been thoroughly validated during the project and hence are not only the result of expert opinion.

4 POTENTIAL IMPACT AND USE

4.1 Faster and safer introduction of Li-Ion stationary batteries in electricity grids to support renewable energy

In our path towards a carbon-neutral society, renewable energy plays an important role. Electric grid operators are facing challenges to balance supply and demand in more efficient and effective means and improve abilities to deal with the intermittent, distributed generation, variable line losses and the constraints of each local transmission and distribution grid. Moreover, significant investments are required in order to maintain system reliability and power reserve margins. Instead of using conventional solutions like steam-powered plants (either using fossil, nuclear or bio-fuel), grid-connected storage is a very viable option for this. Therefore, one of the objectives defined in the road map of the ETP Smart Grids is to increase the role of storage in distribution grids for improved power quality, reliability and reduction of kWh price. Feasibility studies have shown that energy storage technologies can also provide enhanced system efficiencies and even can increase environmental benefits. However the main issue for the introduction of new technologies like stationary storage in low and medium voltage grids is the fact that people are often very reluctant to allow these technologies to be applied (relatively) close to their homes. Based on the validated safety framework, we support the faster and safer introduction of Li-Ion stationary batteries because this framework provides guidance to stakeholders (e.g. local authorities) to realistically evaluate the risks involved and to inform the people correctly about the risks and benefits involved. Additionally we compiled an extensive list of standards and regulations in the field of electrical energy storage. This overview can be used in development and installation projects to select the most applicable standards in the given situation.

By also taking into account and specifically focusing on the recycling stage, STALLION contributes to the rational use of resources.

4.2 Contribution to the international standardization framework

Based on a thorough risk assessment in WP1, STALLION has developed a number of safety test procedures in WP2. Subsequently these test procedures were validated using both testing and modelling approaches. This led to a number of changes to the test procedures, published in D5.5. The developed test procedures form the basis of the new standard proposal IEC 62897 that was initiated by Germany, more specifically in the person of Heiko Sattler of VDE, one of the STALLION partners. During the subsequent meetings of the IEC SC21, the STALLION representatives have made sure that the clear system-focus of this standard proposal was maintained and is now further developed within this SC21A.

4.3 Increased competitiveness of the European battery industry

Standardization brings important benefits to business by providing a solid foundation upon which to develop new technologies. The existence of standards contributes to facilitate a new market growth by providing a common ground for different organizations to work in a new environment.

4.4 Improvements to the FMECA methodology, when applied at design stage

In the risk assessment of the STALLION project, we used the FMECA methodology because it is an established method and it doesn't rely on the availability of historic data, which is not available in our case. However during this process, some weaknesses of this methodology were identified, when applying it to a multi-level 'virtual' system. For each of these weaknesses, improvements were proposed and these improvements were validated during the applied risk assessment of WP7. These improvements have been presented at scientific conferences and will be submitted for publication in a peer-reviewed journal. These improvements can then be used by projects in comparable situations to enhance the quality of the risk assessment.

4.5 Advancing the state of the art in the application of sensors

In the STALLION project, existing sensors were applied in the field of safety monitoring of lithium ion batteries. Initial validation results have shown promising potential for both strain gauge and acoustic sensors to detect thermal runaway at an early stage. These findings will be published in a peer-reviewed scientific journal. Based on these results, some of the STALLION partners are currently engaging in a project proposal to bring these technologies to market introduction. Since thermal runaway is identified as one of the main risks for lithium-ion batteries, this kind of development could help to promote the usage of lithium-ion batteries, where they are now sometimes rejected for safety reasons.