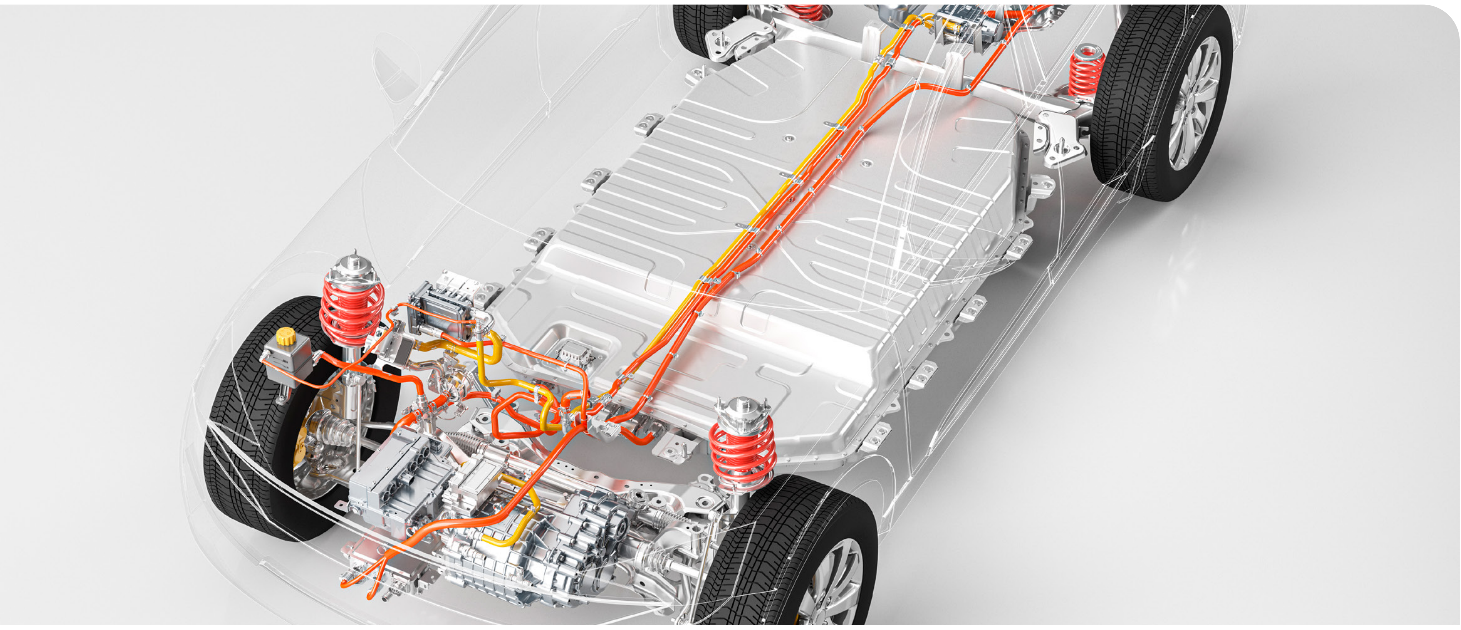
Karlsruhe Institute of Technology

Improving lithium-ion battery safety for electric vehicles

The Calorimeter Center - Advanced Materials and Batteries

INSTITUTE OF APPLIED MATERIALS – APPLIED MATERIALS PHYSICS



Institute for Applied Materials

KIT - The Research University in the Helmholtz Association

Karlsruhe Institute of Technology

Calorimeters to advance battery safety

Ensure your lithium-ion cells are safe

With six accelerating rate calorimeters of different sizes – from coin to large pouch, or prismatic automotive cell format – the IAM-AWP at KIT offers the evaluation of thermodynamic, thermal, and safety data for lithium-ion cells on material, cell, and pack level. This data can be used on all levels of the value chain – from the safe design on the materials level up to the thermal management and the adaptation of safety systems. Our fields of research and range of tests encompass both normal and abuse conditions:

Normal condition tests include:

- Isoperibolic cycling measurements which provide constant environmental temperatures; and
- Adiabatic cycling measurements which ensure that there is no heat exchange between the cell and its surroundings.

Each of these allows:

- Measurement of the temperature curve and distribution for full cycles, or application-specific load profiles;
- Determination of generated heat;
- Separation of heat in reversible and irreversible parts; and
- Ageing studies.

Abuse condition tests include:

- Thermal abuse – the heat-wait-seek, ramp heating and thermal propagation test;
- Electrical abuse – external short circuit, overcharge and overdischarge testing; as well as
- Mechanical abuse – nail penetration test.

Each of these allows:

- Temperature measurement;
- External or internal pressure measurement;
- Gas collection;
- Post-mortem analysis; and
- Ageing studies – identifying the change of risk potential with an increasing degree of ageing.

INSTITUTE FOR APPLIED MATERIALS – APPLIED MATERIALS PHYSICS (IAM AWP)

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Learn more about Battery Safety & Calorimetry here

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IN December 2020, the European Commission communicated its Sustainable and Smart Mobility Strategy, designed in part to outline how the EU's transport sector will significantly reduce its emissions. The strategy has determined that at least 30 million zero-emission vehicles will be in operation on European roads by 2030, and by 2050 nearly all cars, vans, buses, and new heavy-duty vehicles will be zero-emission. The enormous shift away from internal combustion engine (ICE) vehicles saw almost 1,365,000 electric vehicles (EVs) sold in Europe during 2020.

Therefore, the lithium-ion battery, essential for hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs), and EVs, is seeing massive demand. To highlight this, the global demand for lithium battery materials has doubled since 2020 from just over 300,000 tonnes of lithium carbonate equivalent (LCE) to at least 650,000 tonnes of LCE in 2022.

With the increased demand for lithium-ion batteries (LIBs), a desire to increase their energy density, and policies in place to encourage the uptake of EVs, consumers, battery manufacturers and OEMs all have an ongoing and invested interest in the safety of the batteries.

In this publication, not only can you view a feature from EASAC analysing the overarching need to reduce carbon emissions in the transport sector, EuRIC will also outline their report, which aims to minimise lithium battery fires and improve the environmental impact of electrical waste and its processing. CIC energiGUNE also appears discussing their SAFELiMOVE battery project, which leads the way to develop safer solid-state batteries for EVs, and I will explain the work of the IAM-AWP's Calorimeter Centre showcasing what battery failure tests can be performed for mechanical, electrical and thermal abuse to provide confidence to the EV sector.

I have also provided an update to the HELIOS (High-pErformance modular battery packs for sustainable urban electrOmobility Services) project, funded under the Horizon 2020 Framework Programme. Now, a year old, I lead the Work Package 4 – 'Cell and battery pack testing and modelling'. Our primary objective is to determine the coupled electrochemical, thermal, and safety data required as input parameters for the modelling or as validation data for the simulation results. The Karlsruhe Institute of Technology (KIT) operates Europe's largest battery calorimeter laboratory, providing seven robust adiabatic Accelerating Rate Calorimeters (ARCs). The ARCs can test various sizes of battery, from coin to large pouch or prismatic automotive format – in combination with cyclers, which enables the evaluation of thermodynamic, thermal and safety data for lithium-ion cells on material, cell, and pack level under adiabatic and isoperibolic environments for both normal and abuse conditions (thermal, electrical, mechanical). The data acquired from our tests provide unrivalled information to manufacturers to gain a better insight as to when any initial reaction begins, but also crucial for OEMs or a battery management system developer to know which parameters have to be observed to be sure the first reaction does not lead to thermal runaway.

Our centre is committed to ensuring that safe batteries, whether they are LIBs or emerging solid-state technology, provide the EV sector with the confidence to progress and meet our shared decarbonisation goals.

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Reducing carbon emissions in the transport sector

Dr William Gillett, Director of EASAC'S Energy Programme, discusses their recommendations for decarbonising transport

AT COP26 in November 2021, the European Academies Science Advisory Council (EASAC) hosted a side event where they presented their updated findings of the 2019 'Decarbonisation of Transport: options and challenges' report. The EASAC report was produced by 18 experts from 12 European countries and was endorsed by the national science academies of all EU Member States, Norway, Switzerland, and the UK.

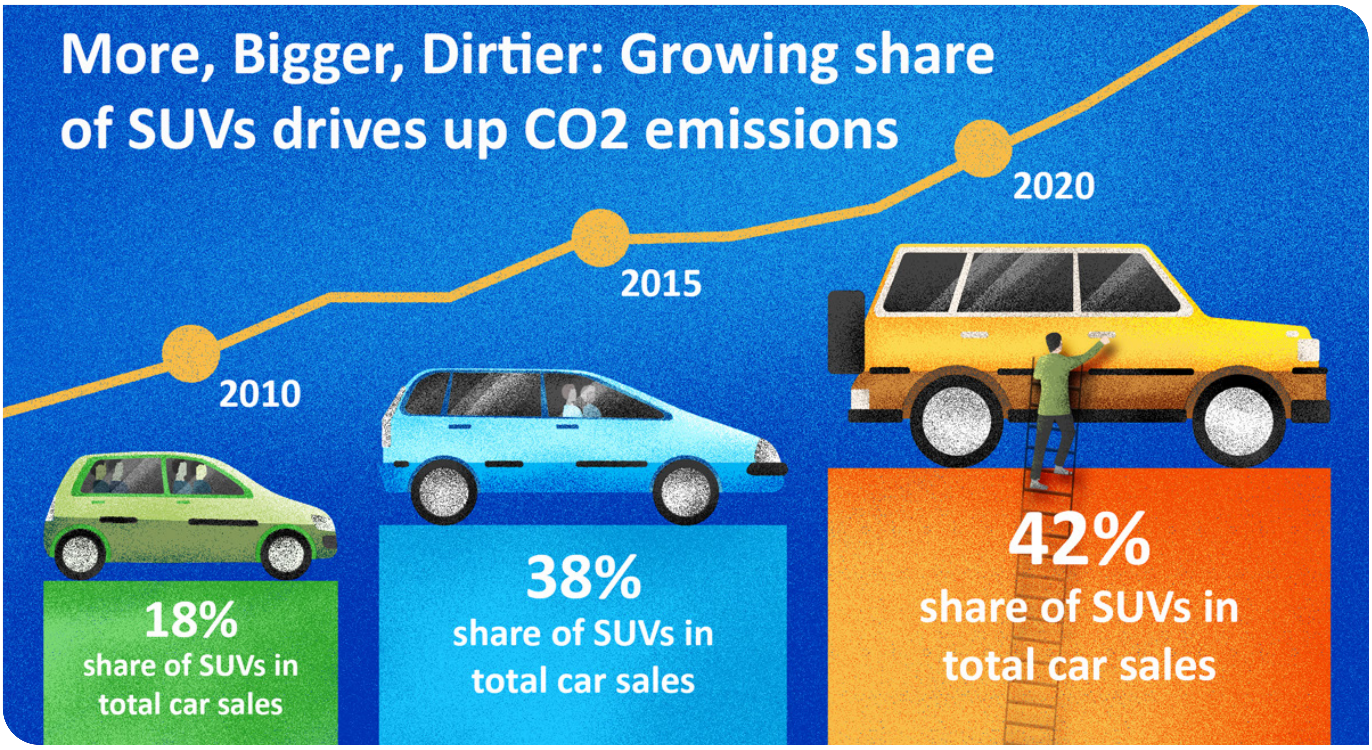
Emily Potts, Deputy Editor of The Innovation Platform, asked Dr William Gillett, Director of EASAC's Energy Programme, about their recommendations to policymakers for reducing carbon emissions from the transport sector.

Can you outline EASAC's policy recommendations for phasing out internal combustion engine (ICE) vehicles? What can be done to reverse the growth in motorised transport demand?

Stronger 'avoid, shift, and improve' policies are needed to reduce carbon emissions from motorised transport. In addition, we must reverse the EU policy that "curbing mobility is not an option". There is no silver bullet solution for reversing growth in motorised transport demand, but there are many complementary options that can be implemented together. Recently, we have seen how transport can be avoided by video conferencing and home working.

'Shifting' starts with increasing walking and cycling, especially in urban areas. This requires only modest infrastructure costs and brings valuable health benefits. Passenger and freight transport should be shifted to modes with lower carbon emissions (trains, buses, trams, inland waterways, and also electric vehicles).

Performance of motorised transport can be improved through vehicle design, replacing ICEs with more



SUVs rank among the top causes of energy-related carbon dioxide (CO2) emission increases over the last decade. Illustration by EASAC, based on IEA data 2021

efficient hybrid powertrains, and using sustainable energy carriers (including low-carbon electricity, hydrogen, biogas, liquid biofuels, synthetic fuels and, for marine applications, ammonia). However, with electrification, it is important to urgently decarbonise electricity supply by increasing low-carbon electricity generated on the grid. Otherwise, climate benefits remain limited.

Can you explain why the increasing sales of SUVs are counteracting emission reduction efforts and what can be done at a policy level to curb this?

The International Energy Agency (IEA) reported in December 2021 that SUV numbers increased globally by more than 35 million over the past 12 months, increasing annual CO_2 emissions by 120 million tonnes. Global SUV sales have proven remarkably resilient throughout the pandemic,

growing by over 10% between 2020 and 2021. In 2021, SUVs were on course to account for more than 45% of global car sales – a new record for both volume and market share.

Over 98% of SUVs on the world's roads today still rely on ICEs. However, in 2021 around 55% of the electric car models on the market were SUVs, up from 45% two years ago and, for the first time, the electrification ratio of new SUVs matches that of non-SUV cars. Nevertheless, SUVs rank among the top causes of energy-related carbon dioxide (CO_2) emission increases over the last decade. According to the IEA, if SUVs were a country, they would rank sixth in the world for absolute emissions in 2021, emitting over 900 million tonnes of CO_2.

EASAC recommends that policymakers should introduce measures and regulations to decrease consumer demand for oversized passenger vehicles and oversized ICEs, including taxation, awareness campaigns, and better labelling, as well as targets for phasing them out.

How does size present a challenge toward the electrification of SUVs?

SUVs are heavier and consume around 20% more energy per passenger kilometre than a medium-sized car. They require more energy in the manufacturing process and larger batteries that consume critical minerals. Being heavier than conventional cars, SUVs produce more particulate emissions from their tyres and brakes.

Regarding long-term solutions, what developments in charging infrastructure will be crucial to transport decarbonisation?

Above all, it is important to install public charging points in sufficient numbers and in all regions. Providing enough public charging points for people living in apartments and terraced housing, who cannot install their own chargers, is a challenge, especially in urban areas.

Most European car owners regularly travel less than about 30km per day, which can easily be achieved using electricity in a battery electric vehicle (BEV) or plug-in hybrid electric vehicle (PHEV). However, car owners periodically make long journeys, for example, for holidays. Therefore, charging infrastructure is needed on highways as most BEVs still have a range of less than 300km.

The battery capacities of BEVs are typically between 40 and 80kWh. They can be recharged slowly overnight using a cable from an average house. Alternatively, fast chargers such as those installed at motorway service stations can recharge typical BEVs within 20 to 60 minutes using power supplies rated at 50 or 120kW. A new generation of superchargers rated at 350kW or higher, together with advances in battery technology, is expected to reduce charging times

to 15 or perhaps ten minutes within the next seven to ten years, but this may be constrained by the power available from the local grid.

Fast charging stimulates degradation and causes overheating, so its frequent use reduces battery life. Battery research is ongoing, and more is needed to minimise degradation and lifetime reduction caused by charging and to optimise grid management for clusters of fast and superchargers.

What other innovations or policies are needed to ensure that EU decarbonisation targets are met?

There is no silver bullet to deliver decarbonisation targets. The range of policies and innovations needed is as wide as the gap between current emission levels and those that would limit global warming to less than 1.5°C.

One key EASAC recommendation is that EU policies must address the timely phase-out of fossil fuels by using integrated regulations and incentives across the transport, energy, buildings, and industry sectors that will increasingly compete for low carbon energy supplies. International collaboration and citizen engagement will also be needed as falling fossil fuel consumption makes oil and gas prices more volatile. Binding target dates for phasing out fossil fuels and subsidised scrapping schemes to accelerate the renewal of the road transport fleet should be implemented as soon as possible.

Generating electricity for transport via the large-scale use of forest biomass instead of coal risks exacerbating climate change in the short term because burning trees produces an increase in CO_2 emissions that may persist in the atmosphere for decades or even centuries. The rationale that this increase will eventually be reabsorbed by forest regrowth fails to recognise these timescales. Policymakers are still discussing changes to EU legislation to ensure that the use of forest bioenergy fully meets climate and biodiversity objectives.

Hybridisation and optimisation of ICE vehicle and powertrain design should continue through legislation, standards, and high visibility vehicle labelling campaigns. PHEVs offer a valuable ‘bridge’ to a fully electrified transport future, but only if they are largely used in electric mode. PHEV battery sizing must be regulated to ensure electric driving for at least 50-70kms, and public campaigns and incentives must be used to promote PHEV driving in electric mode. Policies are also needed to limit carbon leakage through overseas battery manufacturing for EVs and to support (clean) battery manufacturing in the EU.

Hydrogen can be relatively easily stored and is well suited for difficult-to-electrify applications such as trucks, ships, and steel production, but it is currently produced almost entirely from fossil fuels. In contrast, ‘renewable’ hydrogen can be produced by the electrolysis of water using renewable electricity, and ‘low-carbon’ hydrogen can be created using low-carbon electricity or by steam reforming of natural gas combined with carbon capture and storage. International trade in renewable hydrogen could open up opportunities for its production in very sunny or windy locations at competitive costs, for example, on offshore ‘energy islands’.

European Academies easac Science Advisory Council

Dr William Gillett
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Lithium battery fires in WEEE – An urgent problem

The European Recycling Industries' Confederation (EuRIC) is the umbrella organisation that encompasses a network of European Member States and National recycling associations. It is the link between the recycling industry and the European Union, acting as the platform for co-operation and the exchange of best practices across the industry.

EuRIC represents key companies included in the collection, processing, recycling, transport, and trade of various recyclables (metals, paper, plastics, tyres, construction & demolition waste from household or industrial waste, WEEE, ELV, Packaging, etc.) across Europe.

The confederation aims to promote recycling, an activity that is driven by the efforts of Small and Medium-size Enterprises (SMEs), working alongside a small selection of – equally important - larger corporations. All of them are local and global actors who provide non-outsourceable job opportunities and produce – locally – commodities that are traded and priced on a global scale.

The environmental benefits of EuRIC's initiatives are vast. Not only does the promotion of safe recycling save natural resources, but it massively reduces pollution and helps limit energy consumption.

EuRIC and its members support a value chain approach and strive to nurture constructive relationships at all levels with stakeholders benefiting from recycling activities, including public authorities, manufacturers, producer responsibility schemes, academia, and NGOs.

WEEE – collection and treatment

A key issue that is currently affecting the Waste Electrical and Electronic Equipment (WEEE) management chain is that of battery-caused fires, costing waste management facilities millions of euros every year and acting as a strong barrier to making Europe circular and carbon neutral. In response to this, EuRIC and the WEEE Forum, with the active contribution of experts from various organisations including EERA, EUCOBAT, Municipal Waste Europe, and the WEEELABEX Organisation (hereafter referred to as the Batteries Roundtable), have produced a comprehensive report outlining the issues around battery fires, their causes, and how the industry that manages the collection and treatment of spent batteries and electronic waste.

The Batteries Roundtable outline the key advice in their recent report aiming to reduce battery fires and improve the environmental impact of electrical waste and its processing

The European Green Deal and the new Circular Economy Action Plan identify 'electronics' as key products within the value chain in which recycling plays a major role in achieving sustainability goals.

WEEE can adjust every step of their processing chain in order to limit the instances of battery fires and safely contain and handle them when they do occur. The report outlines important information such as best practices in handling and processing WEEE and the processes that facilities managing WEEE should begin to adopt to limit the possibility of battery-caused fires.

Recommendations and good practices compiled in the report aim at reducing the occurrence of thermal events caused by events such as short circuits, in which the poles of the same battery become connected due to external material, and physical shock, in which the batteries can become damaged and overheat, and also the issue of heat exposure, with temperatures above 60°C and below -20°C able to severely damage batteries.

However, the expected contribution of the waste management industry to these EU strategies is at risk and the waste management and recycling sector is in need of a strategy that will support it in tackling fires caused by WEEE containing lithium batteries.

Lithium batteries and the risk they pose

The term 'lithium battery' refers to a family of batteries with varying chemistries, comprising several types of cathodes and electrocytes. Lithium batteries are generally divided into two categories, including primary (non-rechargeable) batteries which are lithium metal batteries that have lithium compounds and lithium metal as an anode, and secondary (rechargeable) batteries which are lithium-ion batteries where the lithium is only present in an ionic form in the electrolyte.

Lithium batteries, and in particular lithium-ion batteries, are key to the quality of life of the majority of people within modern society and they are the first choice of technology for a plethora of electronic and electrical equipment including laptops, mobile phones, tablets, and electric vehicles, whereas lithium metal batteries typically exist within watches, calculators, and car key fobs. The rise in usage and demand for portable electronics such as mobile phones and tablets, alongside environmental initiatives that champion electric vehicles, has driven the market growth of lithium batteries significantly.

However, with an increase in the use of lithium batteries also comes an increase in their disposal and an increase in the need to safely collect and recycle the materials within them. However, this can be difficult as the batteries become fragile and, if punctured or damaged, pose a high risk to the functionality of the collection but also of the recycling plan as they have an increased possibility of a thermal event.

Not only do thermal events present a significant risk of triggering further thermal events in surrounding stored batteries but they may also release combustible gasses, with the smoke from the fire containing carcinogenic, toxic, and corrosive substances.

Because of this, the appropriate storage and handling of lithium batteries, along with the necessary knowledge of how to respond if thermal events arise is something that should be widespread amongst personnel in WEEE management facilities personnel.

Thermal events can lead to what is known as a 'battery incident', in which a failing battery initiates a thermal event and acts as a point of ignition for the surrounding WEEE, which is typically a highly flammable mixture of metals and plastic, plus flammable contaminations (liquids, fats, dust, etc.).

A severe event can destroy large volumes of WEEE, emit toxic fumes, and damage buildings and treatment equipment, which are often equipped with expensive detection equipment and not built to withstand intense heat.

There are seven key types of thermal events including hot spot, sparks, smoke, slow-burning fire (no flame), slow-burning fire (flame), intense fire (rapid fire), and even escalating to explosions. These fires can have a serious affect on waste recycling facilities, endangering the lives of those who work there and even, in severe cases, causing the plant to be shut down for multiple days to contain and treat the fire and its aftermath. This has a huge knock-on effect financially and on the further recycling chain.

The extreme cost of these fires is often related to repairing or replacing the equipment and infrastructure damaged during a thermal event, temporary interruption or ending of operations, loss of waste burned – and hence of materials that would have been otherwise recycled and injected into the market - during the thermal event, maintenance, and replacement of extinguishing means. Other recently identified costs include the treatment of water used during the extinguishing of the fires, as it may contain persistent organic pollutants.

Other significant costs arising from the situation are associated with the transportation of WEEE containing batteries to another treatment facility in the event of a planned or unforeseen shutdown due to a severe thermal event, installation of additional detection and mitigation measures, changes in the infrastructure of the facilities, adaptation of operational protocols and training, insurance costs and additional requirements and/or limits imposed by licencing authorities. As of 2018, the average cost of all those incidents was estimated at €190,000, which can represent a significant burden for an individual company and especially for an SME.

Recommendations and best practices

The industry managing WEEE – containing batteries and single batteries is a key contributor to the EU's circular economy and battery fires can have a significant knock-on effect to this, causing loss of profits at every level. Furthermore, the steady increase of fires caused by WEEE – containing batteries is affecting the policies of insurance companies, and the waste industry has raised concerns about the difficulty to obtain proper insurance coverage amid an increase of insurance premiums, coverage exclusions, or through simply not being able to obtain insurance. This poses a serious problem for companies whose activity permit, that they must obtain to operate, is reliant on them obtaining insurance coverage.

As part of the collation of the batteries roundtable report, a questionnaire was disseminated amongst companies and facilities carrying out the collection, sorting, transporting, and recycling of WEEE – containing batteries and single batteries. This questionnaire found that there is no significant relationship between the type of activities carried out on-site, those facilities that declared a thermal event in 2018, and those with good practices and mitigation measures implemented.

Reducing risk

The removal of batteries in the first treatment steps is key to reducing risk. This can ensure that all batteries are then appropriately handled and stored and reduces the risk of items being processed for recycling with live batteries still present inside. Further to this, the report has also detailed advice for manufacturers; advising that they make batteries removable manually or with commonly available tools where possible, and that they also mark clearly on devices where batteries are present to avoid the most obvious batteries being removed and smaller batteries being left and inappropriately entering machinery.

WEEE needs to be appropriately labelled to indicate what sorts of batteries it contains; this would allow waste sorters and processors to ensure all batteries have been removed and appropriately stored according to their specific requirements.

Further to this, it is essential that battery manufacturers build a

strong educational relationship with recycling process plants to ensure that all waste operators know the specifics of battery chemistry, the types of batteries they may encounter, and where they can find more information on safely removing and processing these batteries.

As it has been established by the Circular Economy Action Plan that '80% of a products environmental impacts are determined in the design phase' this relationship and close co-operation between battery producers and recycling companies is crucial to reducing the environmental impact of the industry.

Not only do recycling operators need to know more about how the batteries they handle react to pressures such as heat or damage, but the battery manufacturers also need to actively work towards creating more resistant and less fragile battery products. Simple measures such as adding a flame retardant to the battery's electrolytes could cause a significant reduction in the causation of battery fires which are typically triggered by fragile battery products combusting.

The guidance within the report details that when batteries are removed from items they should then be placed in a separate barrel amidst layers of vermiculite, a natural mineral that is ostensibly fireproof, able to withstand great temperatures without transferring the heat. These barrels should then be stored outside, underneath a cover to protect from direct sunlight, and away from any walls that back onto the main recycling or storage facilities. This way, if a fire does occur, it is less likely to spread and risk a widescale battery incident.

If facilities must store batteries inside it is prudent that they ensure that waste is separated by high walls to reduce the risk of a fire spreading. Facilities must also forge strong relationships with local firefighting organisations/departments, outlining to staff and the fire department a set action plan in case a fire does break out. This would ensure staff are moved to safety and the fire department is contacted as quickly as possible and have the information they need to act immediately upon arriving at the scene.

Moving forward with WEEE

EuRIC together with the WEEE Forum and the aforementioned organisations recommend that the good practices detailed in the report are adapted to every facility individually and these practices are detailed individually depending on what part of the process the facility focuses on. They further advise that facilities closely examine the costs of implementing these best practices against the cost of handling battery fires, as in nearly all cases the cost of changing processes and providing training is less than that of the cost of fire caused damages.

The problem of battery fires is not solely linked to schemes, technologies, or skills related to collecting and recycling batteries, but also to the absolute need to better connect the dots between design and end-of-life treatment. More attention needs to be paid by policy-makers in order to tackle this problem. If manufacturers improve the design of batteries, the number of fires will decrease.

This problem cannot be completely tackled without help from the EU institutions, and policymakers have to quickly act should we wish to reach the target set by the new Circular Economy Action Plan and the EU Green Deal.

Through this joint report, it is EuRIC's objective to provide the battery value chain, from manufacturing to recycling, with the best guidance available to date on how to limit and reduce battery fires. This will help to protect the economy around battery recycling that provides so many crucial jobs across Europe and will also reduce the environmental impact of the recycling industry.

EuRIC
www.euric-aisbl.eu

The role of calorimetric methods in improving battery safety in the electric vehicles sector

The European Commission's recently announced 'Sustainable and Smart Mobility Strategy' lays the groundwork for the green and digital transformation of the EU's transport system to reduce emissions by 90% by 2050.

A key pillar of the strategy is the plan to introduce at least 30 million zero-emission electric cars (Fig. 1), powered by large lithium-ion batteries (Fig. 2), onto Europe's roads, replacing the use of petrol and diesel vehicles.

While lithium-ion battery technology has many advantages, including high specific energy, long cycle life, and low self-discharge rates, consumers are reluctant to switch to electric vehicles, amid concerns over their safety which has hindered the development of the market.

Transport is a key environmental issue for the European Commission, accounting for over a quarter of total greenhouse gas emissions in the EU

Fig.1 Typical electric car on a charging station

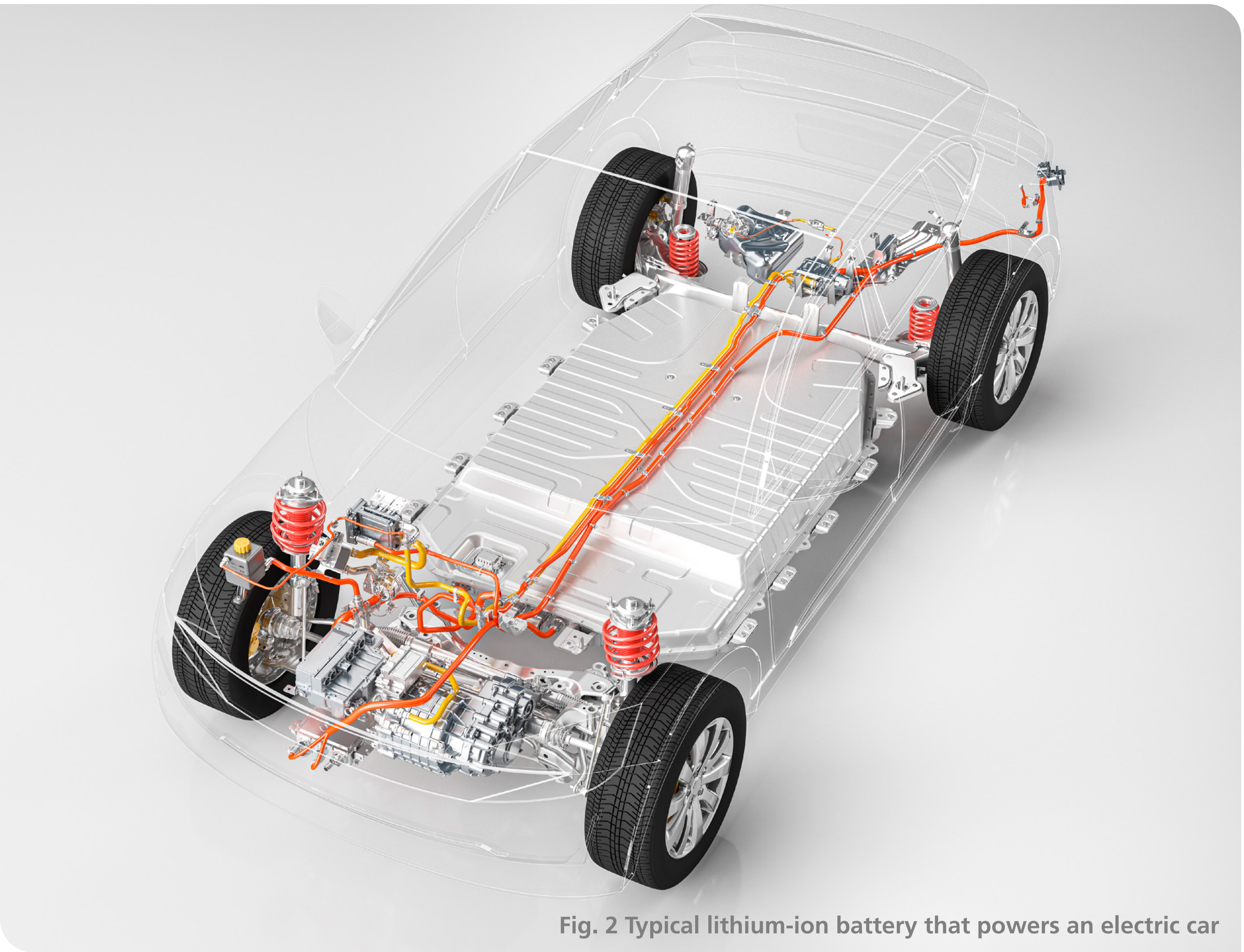


Fig. 2 Typical lithium-ion battery that powers an electric car

Safety issues

A thermal runaway (an uncontrollable temperature increase) in lithium-ion batteries can cause them to ignite or even explode. Although such instances are rare, they can affect public opinion around the safety of electric vehicles (EVs).

The upscaling and market acceptance of electric vehicles powered by lithium-ion batteries is therefore reliant on a holistic safety assessment.

The causes and effects of thermal runaway can be very diverse and complex (as highlighted in Fig. 3). Cell designs, component integrity, manufacturing, and ageing processes all critically influence Li-ion batteries' safety. Internal or external mechanical, operating or thermal stresses can lead to internal heating of the cell, which initiates different exothermal reactions, followed by a further temperature and pressure increase.

Benefits of Battery Calorimetry

Measuring heat data during chemical reactions, known as Calorimetry, allows the quantitative data collection required for optimum battery performance and safety. Sophisticated battery calorimetry enables new and quantitative correlations to be found between different critical safety and thermally related parameters, which is essential for identifying how many Watts a cell will

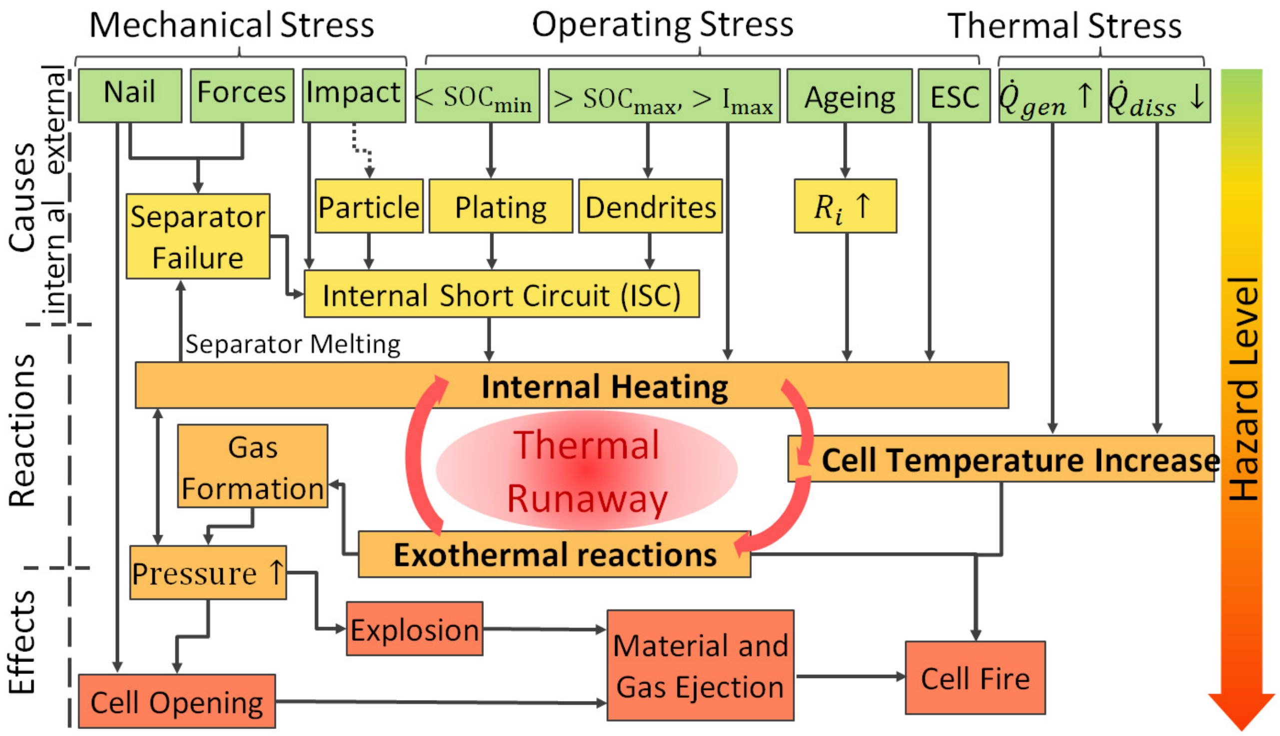


Fig. 3 Causes and effects of thermal runaway in lithium-ion cells during normal use, abuse or accidents

produce under every condition, so the battery and thermal management systems can be adapted. The temperature, heat and internal pressure evolution of batteries can be studied while operating cells under conditions of normal use, abuse or accidents.

Abuse tests without a calorimeter have two main disadvantages:

- The maximum safe temperature would be underestimated; and
- The consequences would be understated in terms of severity and speed.

Tests carried out in a calorimeter are much more sensitive than hotbox tests and reveal the entire thermal runaway process with the different stages of exothermic reactions, providing data that is essential for battery and thermal management as well as safety system design. Combined with multi-scale electrochemical-thermal modelling, these tests provide a powerful tool for predicting thermal runaway prevention and ageing.

Holistic safety assessment

a) Materials level

On a materials and components level, differential scanning calorimetry (DSC) and extremely sensible Tian-Calvet calorimeters can provide thermophysical parameters such as heat capacity or thermal conductivity and analyse in detail the possible phase transformations and the thermal stability of new battery materials.

b) Small-scale cell level

On a small-scale cell level, isothermal and larger-scale Tian-Calvet calorimeters from Setaram Instrumentation allow the determination of the heat generated during cycling with great accuracy. Using such calorimeters allows for 21700 format cylindrical cells with a maximum capacity of 5 Ah (currently used in the Tesla Model 3, for example) to be studied. However, such calorimeters are not designed to withstand the high temperatures and explosions that can occur during a thermal runaway.

c) Large-scale cell level

The next level is robust adiabatic Accelerating Rate Calorimeters (ARCs), which are available in a range of sizes, and enable the evaluation of thermodynamic, thermal and safety data for lithium-ion cells on material, cell and pack level for both normal and abuse conditions (thermal, electrical, mechanical).

The IAM-AWP Calorimeter Center, was established in 2011, operates Europe's largest Battery Calorimeter Laboratory, which provides seven ARCs from Thermal Hazard Technology ranging from the size of a coin to 40 cm x 30cm automotive pouch or prismatic format with capacities of up to 150 Ah (see Fig. 4). These robust battery calorimeters allow the evaluation of thermodynamic, thermal, and safety data for lithium-Ion batteries under quasiadiabatic and isoperibolic environments for normal, thermal, electrical, and mechanical abuse conditions. The cell is inserted into the calorimeter chamber, which has heaters and

Fig. 4 IAM-AWP Battery Calorimeter Laboratory with seven Accelerating Rate Calorimeters of different sizes

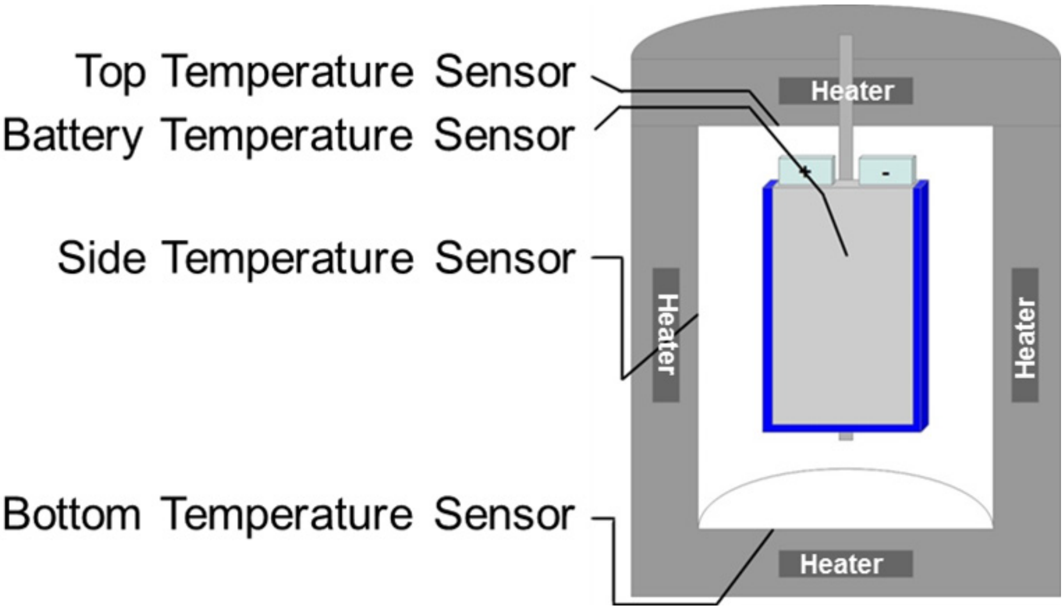
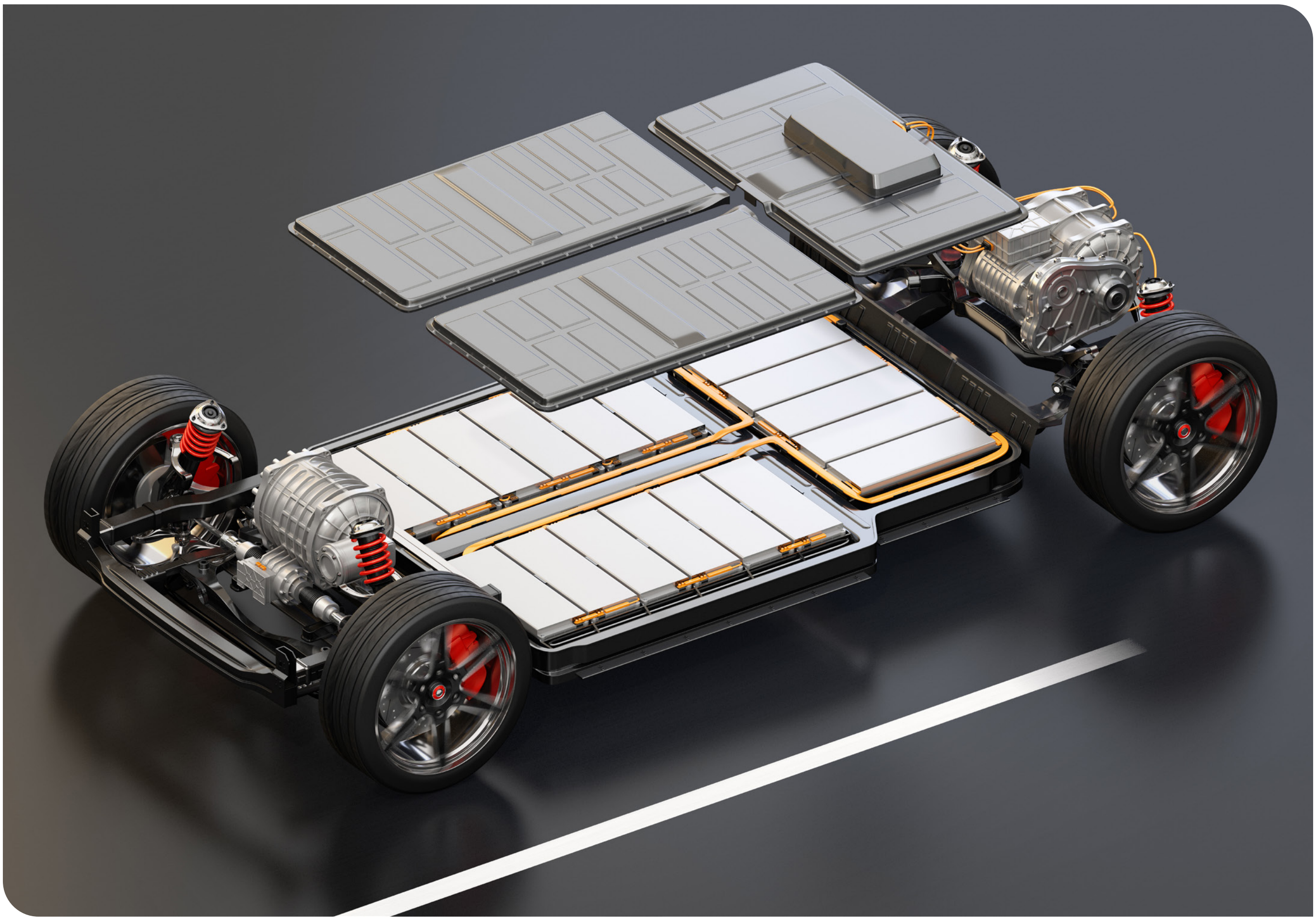


Fig. 5 Principle of an accelerating-rate calorimeter calorimeter

thermocouples located in the lid, bottom and sidewalls (see Fig. 5), which adjust the required ambient conditions that are characterised by the related thermocouples.

d) Small-scale pack level

The recent article in issue 4 of *The Innovation Platform* details how the largest available ARC allows us to study the thermal propagation in small-scale packs to develop and qualify suitable countermeasures, such as heat protection barriers[1]. Thermal propagation means that the thermal runaway propagates from one cell to the neighbouring cells, and this cascading effect can lead to the complete destruction of the module or pack.



Safety testing in battery calorimeters

It is well-known that the failure of lithium-Ion batteries can be caused by mechanical, electrical, or thermal abuse, as outlined in the relevant safety testing standards, such as UN 38.3, SAE-J2464, IEC-62133, GB/T 31485 and UN GTR100.2. The following three safety tests can be performed in the ARCs on cells for EV applications:

Mechanical abuse: Nail and crush test

When an applied force deforms the EV battery, mechanical abuse occurs. This could be caused by a car crash, for example, or puncturing the battery in the bottom of a chassis by a sharp object. This is simulated in the ARC by pushing a nail, or a blunt object into the cell, which provides a pass/fail type test to qualify cells and quantitative data by measuring the cell temperature, cell voltage, and evolved heat. The mechanical abuse often causes an internal short circuit because the battery's separator is damaged or punctured.

Electrical abuse: External/internal short circuit test, overcharge test, over-discharge test

Electrical abuse refers to the abnormal operation of electrical components, such as short-circuiting, overcharging, and over-discharging. Typically, electrical abuse is related to a failure of the battery management system. However, the trend for fast charging might also increase the risk of thermal runaway because it can lead to the deposition of highly reactive lithium on the carbon anode – the so-called lithium plating. The reason for that effect is that the

Fig. 6: Examples for cylindrical (top left), prismatic (bottom left) and pouch (right) cells after thermal runaway initiated by an HWS test in an ARC

lithium ions migrate faster than they can intercalate. The electrical abuse of automotive format cells can be replicated in the ARC by applying an external short circuit, overcharging or over-discharging, leading to different failure modes.

Thermal abuse: Heat-Wait-Seek test, ramp heating test, thermal propagation test

The most frequent abuse test performed in ARCs is for thermal abuse, using the Heat-Wait-Seek (HWS) test. As soon as self-heating is detected within the cell, the heaters in the calorimeter chamber immediately follow any change of the cell temperature preventing the heat transfer to the chamber. This causes the cell's temperature to rise until a thermal runaway occurs, or the chemicals for this exothermal reaction are consumed entirely. For the Ramp Heating test, which mimics a Hot Box test, the temperature of the cells is increased at a constant rate instead of using the stepwise heating method. For the thermal propagation test, a thermal runaway is initiated using one of the abuse conditions described above and the effect on the neighbouring cells is observed.

However, with manufacturers aiming to increase the energy density of cells further, new abuse conditions are emerging, as the limits of the electrochemical systems of Lithium-Ion batteries are reached. According to a recent article[2], research has indicated that a new type of abuse condition, electrochemical abuse, is the underlying mechanism for the emerging causes of battery failure.

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1 *The Innovation Platform* – Issue 4, page 102: Innovative calorimetric methods for safer batteries in the renewable energy sector.

2 Wensheng Huang, Xuning Feng, Xuebing Han, Weifeng Zhang, and Fachao Jiang, Cell Reports Physical Science 2, 100285, 20 January, 2021.

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Current activities in the WP 4 ´Cell and battery pack testing and modelling' of the HELIOS project

Electric cars and buses powered by a lithium-ion battery (see Fig. 1) are a strategic driver within the European Union's new mobility strategy that should lead the transition to a clean and digital economy by reducing the carbon footprint of the transport sector by 90% by 2050. Therefore, the European Commission is investing in ground-breaking electric vehicle (EVs) know-how to make Europe a global market leader in their sustainable production and use. This will reduce dependence on Asian cell producers and place at least 30 million electric cars on Europe's roads as substitutes for those with internal combustion engines.

HELIOS participants

The HELIOS (High-pErformance modular battery packs for sustainable urban electrOmobility Services) project was funded under the Horizon 2020 Framework Programme. This European project, launched on 1 January 2021, has received approximately €10m from the European Commission. HELIOS is co-ordinated by Aarhus University (AU), and the following 18 partners from eight countries are working together on improved modular battery packs:

Dr Carlos Ziebert, head of IAM-AWP's Calorimeter Center, KIT, explains how calorimeters can help to develop safer, more efficient battery packs in the Horizon 2020 project, HELIOS

Fig. 1: Electric car and electric bus on their charging stations

- Aarhus University (Denmark)
- Karlsruhe Institute of Technology (Germany)
- Izmir Institute of Technology (Turkey)
- Aalto University (Finland)
- IREC (Spain)
- RDIUP (France)
- NVISION (Spain)
- VESTEL EV Charging Solutions (Turkey)
- VITESCO (Germany)
- IDNEO (Spain)
- BOZANKAYA (Turkey)
- Universitat Politécnica de Catalunya (Spain)
- Center for Solar Energy and Hydrogen Research Baden-Württemberg (Germany)
- Danish Technological Institute (Denmark)
- TU Sofia (Bulgaria)
- TUBITAK MAM (Turkey)
- European Copper Institute (UK)
- KNEIA (Spain)

From KIT, the group 'Batteries – Calorimetry and Safety' at the Institute of Applied Materials – Applied Materials Physics (IAM-AWP), led by Dr Carlos Ziebert, participates and brings together their expertise in the field of battery calorimetry.

HELIOS objectives

By bringing together the expertise of industry and academia, the HELIOS project aims at developing and integrating innovative materials, designs, technologies, and processes to create a new concept of a lighter, smarter, and more eco-friendly hybrid battery pack. The hybridisation concept consists of high energy (HE) and high power cells (HP). While the HE cells ensure a long driving range, the HP cells should enable fast charging and additional power for a short period if needed. The final battery pack should be modular and scalable for a wide range of electric vehicles used in urban electromobility services. It should provide improved performance, energy density, safety, lifetime, and LCoS (Levelised Cost of Storage). The range encompasses mid-size electric vehicles to electric buses. A Mitsubishi iMiEV at the Aarhus University and a Sileo S12 e-bus from Bozankaya (see Fig. 2) will be used as demonstrators for the performance and improvements of the HELIOS modular battery packs.

For this purpose, novel developments that integrate hardware and software solutions for the smart control of electrical and thermal management systems that exploit advanced materials, power electronics, sensors, and cutting-edge ICT, such as cloud-based Big Data analysis, Artificial Intelligence, and IoT (Internet of Things) technologies running in the cloud are investigated and implemented.

These combined approaches allow us:

- To increase energy and power density;
- To enhance key characteristics like ultra-high power charging;
- To improve safety;
- To improve E-fleet control and health management strategies to extend lifetime;
- To create optimised EV charge and discharge procedures and predictive maintenance schedules;
- To monitor the SOC (State of Charge), SOH (State of Health), and carbon footprint for each battery pack throughout its entire life cycle, which allows an effective integrated supply chain for the manufacture, reuse, and recycling of Li-ion battery packs to be established;
- To show better LCA (life cycle assessment, new methodologies for recycling and metal recovery after EoL (end of life), and already a material selection with better overall LCA;
- To improve battery pack design and performance with reduced LCoS based on a circular economy approach where the modular battery packs can be easily reused in a range of second life applications before EoL recycling; and
- To assess the HELIOS solution effectiveness in different urban electromobility models such as car-fleets and e-bus fleets.

Fig. 2: Sileo S12 e-bus produced by Bozankaya

Activities in Work Package 4 – 'Cell and battery pack testing and modelling'

The HELIOS project work plan is organised into ten linked Work Packages (WPs), as shown in Fig. 3. In the first six months, the 'Batteries – Calorimetry and Safety' group at KIT was involved in cell selection and the definition of test matrices In WP 2 and WP 1, respectively. Ziebert leads Work Package 4 – 'Cell and battery pack testing and modelling', which started in April 2021.

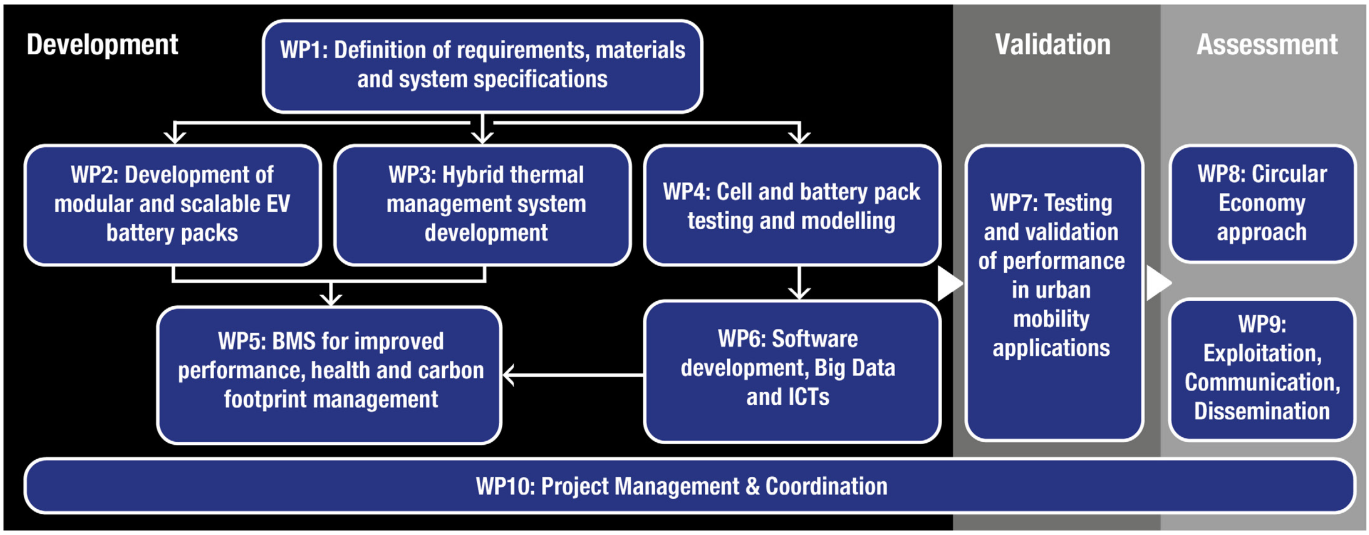

Fig. 3: Pert Chart of HELIOS work plan

The main objectives of WP4 are to expand and improve the state-of-the-art within cell and battery modelling, state estimation, fault detection, prognostics, and health management by utilising the available information from various sensing technologies and cell tests. It is also expected that the battery pack can be safer by detecting internal faults inside the battery before the faults propagate.

The main scientific objective of the work performed at KIT, DTI, and ZSW in Task 1, 'Cell and battery pack testing' is to determine the coupled electrochemical, thermal, and safety data of both the HE and HP cells that are required as input parameters for the modelling or as validation data for the simulation results. These data are acquired on the materials, cells, and pack level under normal use and abuse testing scenarios for fresh and aged cells and are stored and aggregated in a data warehouse platform that DTI has provided.

With the test matrices that have been defined in WP 1, all testing needs at cell level have been readily addressed, and in WP4, it has been decided which partner will perform which tests and how many. The related test matrices for the module and pack level will be set up later when the pack design is more mature and the requirements from the system level have been defined.

In parallel to the test matrix development, the different check-up procedures during the ageing test, also known as reference performance tests (RPTs) and the EOL criteria to know when to stop the ageing procedures, have been defined.

At the KIT, seven adiabatic accelerating rate calorimeters (ARCs) of different sizes (see Fig. 4) in combination with battery cyclers with various current and voltage ranges are used for quantitative studies on the heat generation and dissipation of single Li-ion cells, but also on small battery packs, during charging and discharging under defined thermal conditions. Such data make it possible to optimise charge and discharge management and analyse ageing processes in the cells.

By measuring the specific heat capacity and the heat transfer coefficient, which also serve as input parameters for the thermal modelling, the measured temperature data can be converted into generated and dissipated heat data, which are needed for the adjustment of the thermal management systems and the validation of the thermal models. Heat flux Sensors (HFS) are used to provide:

- Values for the specific heat capacity;
- Heat transfer coefficients for the different sides of a cell; and
- Values for the generated heat.

Special electrochemical and thermodynamic analyses are performed for a deeper scientific

Fig. 4: IAM-AWP Battery Calorimeter Laboratory with seven Accelerating Rate Calorimeters of different sizes

understanding of various reaction mechanisms. For the cell operation, these include:

- The identification of the reversible heat contributions associated with the entropy of the cell reaction;
- The quantification of the irreversible heat contributions from the internal resistance of the cell; and
- The analysis of the contributions from side reactions.

The abuse or safety testing aims to identify all possible risks conditions. These conditions are then analysed to clearly define mitigation measures to be used in the design, control, and usage of the cells and packs.

Using the seven ARCs, abuse testing at the cell level is carried out at KIT by applying electrical, mechanical, and thermal abuse test scenarios and studying the heat, gas, and pressure generation under these conditions. The self-heating and the thermal runaway are characterised to determine the critical parameters and thresholds for safe cell operation and thermal stability.

Moreover, comprehensive ageing tests have started at the cell level. At first, fresh cells are stored in temperature chambers at different temperatures and states of charge and then characterised at fixed time intervals to study the influence of this storage (calendar ageing) on cell performance. Secondly, cells of the same type are aged at different charge/discharge rates or with different load profiles (full cycles, partial cycles, driving cycles (cyclic ageing)).

The described extensive cell testing in WP 4 will generate a large amount of data that will help improve the different levels of modelling that will be developed in the second year to bring the HELIOS project to the road of success.

Acknowledgements

This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement No 963646. This document reflects the view of its author only. The funding agency is not responsible for any use that may be made of the information it contains.

HELIOS

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SAFELiMOVE, safer solid-state batteries for electric vehicles

The battery of the electric vehicle of the future is currently at a decisive stage. The different technologies competing to lead the electric mobility market are involved in a silent but definitive battle. In fact, the major vehicle manufacturers are taking part in this race, investing large amounts of resources (primarily financial) in the main technological players in the sector.

It is difficult to know the outcome, but it seems clear that the winner will have to provide an efficient response to four major issues: safety, range, charging time, and, of course, price.

CIC energiGUNE has been working for more than ten years - since it was launched in 2011 - taking steps in the identification of a technology that answers all the questions to the highest level of satisfaction. In this sense, the research centre's commitment to solid-state batteries has led them to be one of the top three institutions in Europe in the field of energy storage. This was led by researchers such as Michel Armand, the pioneer of today's lithium batteries and father of solid-state batteries with polymer electrolyte.

This experience and knowledge allow CIC energiGUNE to be one of the leading players in the research and development of the batteries of the future, being an active participant in some of the major international initiatives currently underway in this regard. One of the most outstanding, led by CIC energiGUNE itself, is the SAFELIMOVE battery project.

The SAFELiMOVE battery project is leading the way to develop safer solid-state batteries for electric vehicles. Led by CIC energiGUNE, here they explain their latest achievements

SAFELIMOVE battery: a project born from the European Union's commitment to electric vehicles

The European Union aims to be a benchmark in the battery sector for electric vehicles, aspiring to be responsible for 30% of battery production by 2030 and to have at least 30 million electric vehicles on its roads by the same year.

In this context, a project like SAFELiMOVE appears, promoted by Europe under the umbrella of the Horizon 2020 program, to position the European industry in a global battery market that will generate €250bn per year, at continental level, from 2025.

Through these types of initiatives, Europeans will be able to meet the challenges and needs of their automotive industry, which will need gigafactories close to its production plants with the capacity to meet a demand of 400Gwh, by developing and building the batteries of the future in Europe.

Furthermore, it should not be forgotten that transport is responsible for around a quarter of the European Union's greenhouse gas emissions, more than two-thirds of which come from road transport. The development of advanced batteries to power electric vehicles, such as the one proposed by SAFELiMOVE, is essential to reduce carbon emissions and achieve European ecological and economic sustainability while, at the same time, strengthening the electric transport supply chain in Europe.

SAFELiMOVE battery collaboration

Through this collaboration of some of the leading agents in the sector, SAFELiMOVE seeks to offer substantial competitive advantages, such as increasing driving range by an additional 300km on a single charge, reducing charging time, increasing safety by eliminating the potentially flammable liquid electrolyte, and lowering the cost of the battery by 50%, thanks to the use of highly efficient materials and processes.

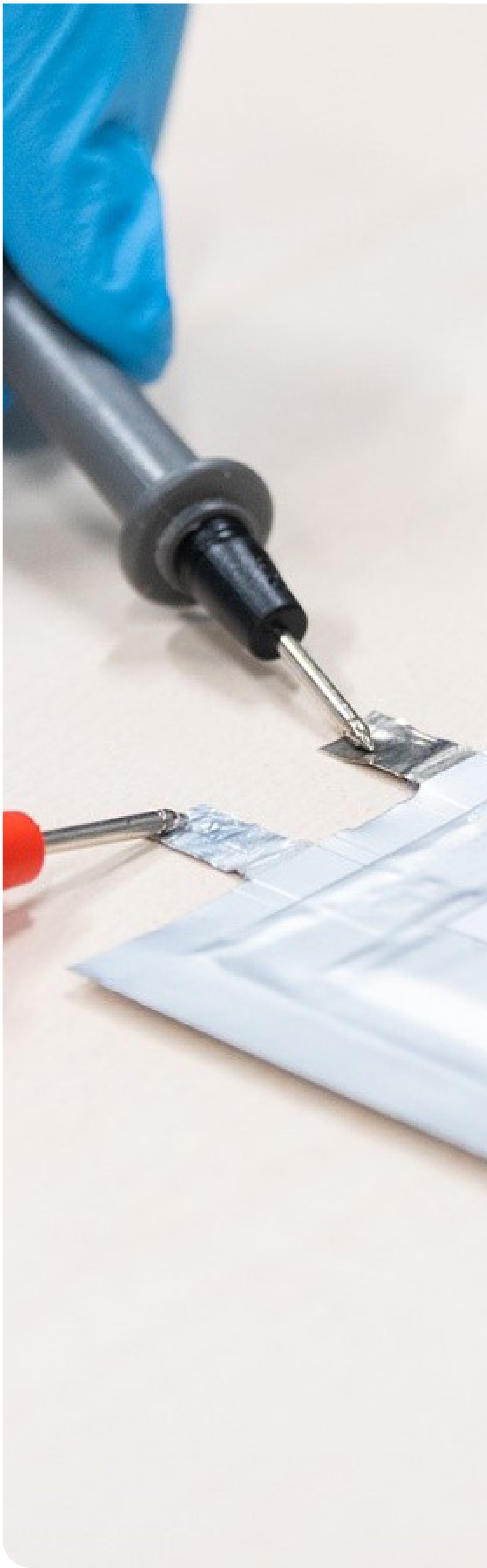
For this purpose, the SAFELiMOVE battery project counts on the participation of companies specialised in materials development, such as:

- Schott (Germany) with its innovative inorganic materials;
- Umicore (Belgium) with its advanced cathodes;
- Hydro-Québec (Canada) with its state-of-the-art lithium metal;
- The battery modelling experts Avesta Battery & Energy Engineering (Belgium);
- The battery manufacturer SAFT SAS (France);
- The OEMs Renault (France) and Toyota (Belgium); and finally,
- Life Cycle Engineering (Italy) in charge of Life Cycle Assessment.

These organisations are supported by five leading European research centers in the field; the Technische Universität Berlin (TUB), Commissariat à l'Energie Atomique et aux Energies Alternatives (CEA), RWTH Aachen University, Cidetec Energy Storage and Ikerlan, and are led by CIC energiGUNE.

In this way, the technology developed by SAFELiMOVE is expected to make achievements in the following aspects:

- Development of a battery with gravimetric and volumetric energy densities up to two times higher than the ones currently on the market (450 Wh/kg and 1200 Wh/L versus 240 Wh/kg and 600 Wh/L);



- Development of a battery easily adaptable to operate at room temperature (versus 80°C required for a commercial battery pack using lithium metal) by incorporating a hybrid electrolyte of ceramic and highly ionic conductive polymer, capable of meeting the typical operating conditions of electric vehicles;
- Identification of a safe technology based on a solid-state concept that allows working with lithium metal anodes of high specific capacity, which reduces the risk of secondary reactions, instabilities and fires derived from the use of conventional liquid electrolytes;
- Promotion of a sustainable technology based on reduced dependence on critical raw materials such as cobalt (reduced in the active material to only 5%) and free of graphite (lithium metal anode);
- Increased competitiveness compared to current technologies, which will result from the combination of innovative, high-performance materials with efficient and cost-effective cell design;
- Development of a new technology for industrial-scale processing of solid-state batteries; and
- Development of a battery that meets consumer needs which is fast charging, has sufficient autonomy and has long battery life.

SAFELiMOVE – tangible results through advanced battery materials

A battery cell is very much defined by the materials and the interaction of materials within the cell. For this reason, the development of a set of advanced battery materials is, therefore, one of the core activities within the SAFELiMOVE project.

The individual material properties already define the cell's potential in terms of energy density and cycling performance. However, what is even more important is the interaction of the materials with each other in the complex environment of a battery cell.

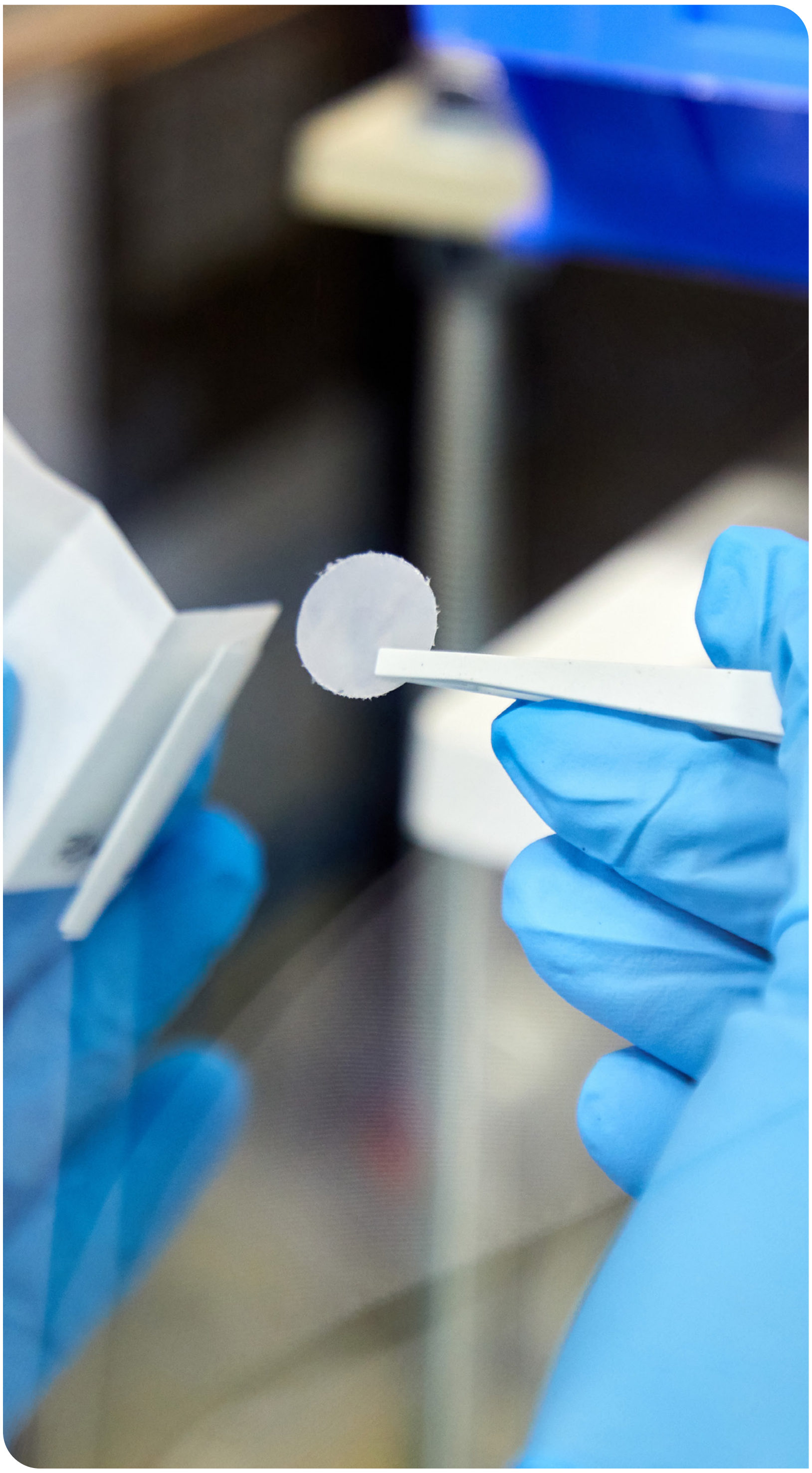
To meet this challenging task, Schott, Umicore, Hydro Quebec, Abee, and CIC energiGUNE cooperate in developing materials, which will be adopted to each other for effective lithium transport. The material development is done in three steps, and after each step, the new materials are evaluated by means of interphase phenomena and cell behaviour.

Despite all COVID-19 limitations, the first milestone was reached on time in July 2020. An initial set of materials comprising the new polymer and oxidic electrolytes, NMC cathode material and an ultrathin lithium metal foil was developed. The materials were characterised and checked for compatibility. Fabrication in lab-scale was established, and the materials were provided to other project partners for further characterisation and cell fabrication as they will be the basis to guide future improvements to next-generation materials.

The successful development of these materials enabled the consortium led by CIC energiGUNE to achieve the second milestone: the fabrication of the first batch of coin and mono-layer pouch cells.

These mono-layer pouch cells were assembled using the materials developed by the partners. The next step was to use these cells for interface characterisation and electrochemical testing, which is currently ongoing.

The feedback on comprehensive testing of delivered coin and mono-layer solid-state cells is guiding the development of improved next-generation solid electrolyte and active SAFELiMOVE materials, as well as the optimisation of the cell design and tailor the cell manufacturing procedure.



But this is only the beginning. If the project estimations are met, the batteries developed within the framework of SAFELiMOVE will offer a higher energy density of 450 Wh/kg (which translates into greater autonomy in the use of electric vehicles), faster charging (thus reducing waiting times) and a longer service life (thereby boosting savings and sustainability). As a reference to understand the expected qualitative leap thanks to the new generations of battery technologies such as the ones developed at SAFELiMOVE, a conventional battery currently offers densities of around 250 Wh/Kg, which is almost half of what is expected with these new developments.

Our research will mean that electric vehicles using SAFELiMOVE batteries will be more competitive thanks to their greater autonomy, faster charging and improved safety. These benefits will increase their market share and contribute to the objective of decarbonisation of transport in the European Union.

In this regard, the first results obtained after the first year and a half of SAFELiMOVE's work promise a largely satisfactory end result, thus having the foresight to achieve the objectives with which the project was born. Work is now continuing with a view to December 2023, the end date of the project, when it is expected to be able to offer a technological solution that will meet the expectations generated and enable the energy transition of the future; a great desire but also a challenge for the European Union.

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Karlsruhe Institute of Technology

View partner profile here

Calorimeters to advance thermal management and battery safety

The development of safe lithium-ion cells is of utmost importance for a breakthrough in the electrification of transport and for stationary storage, because an uncontrollable increase in temperature of the entire system (the so-called ‘thermal runaway’) can cause an ignition or even explosion of the battery with the simultaneous release of toxic gases.

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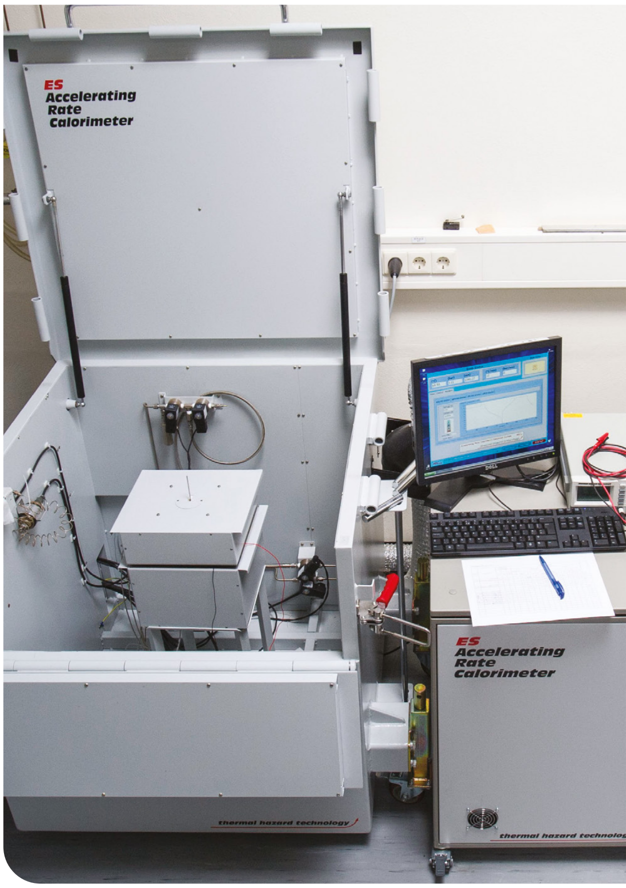

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