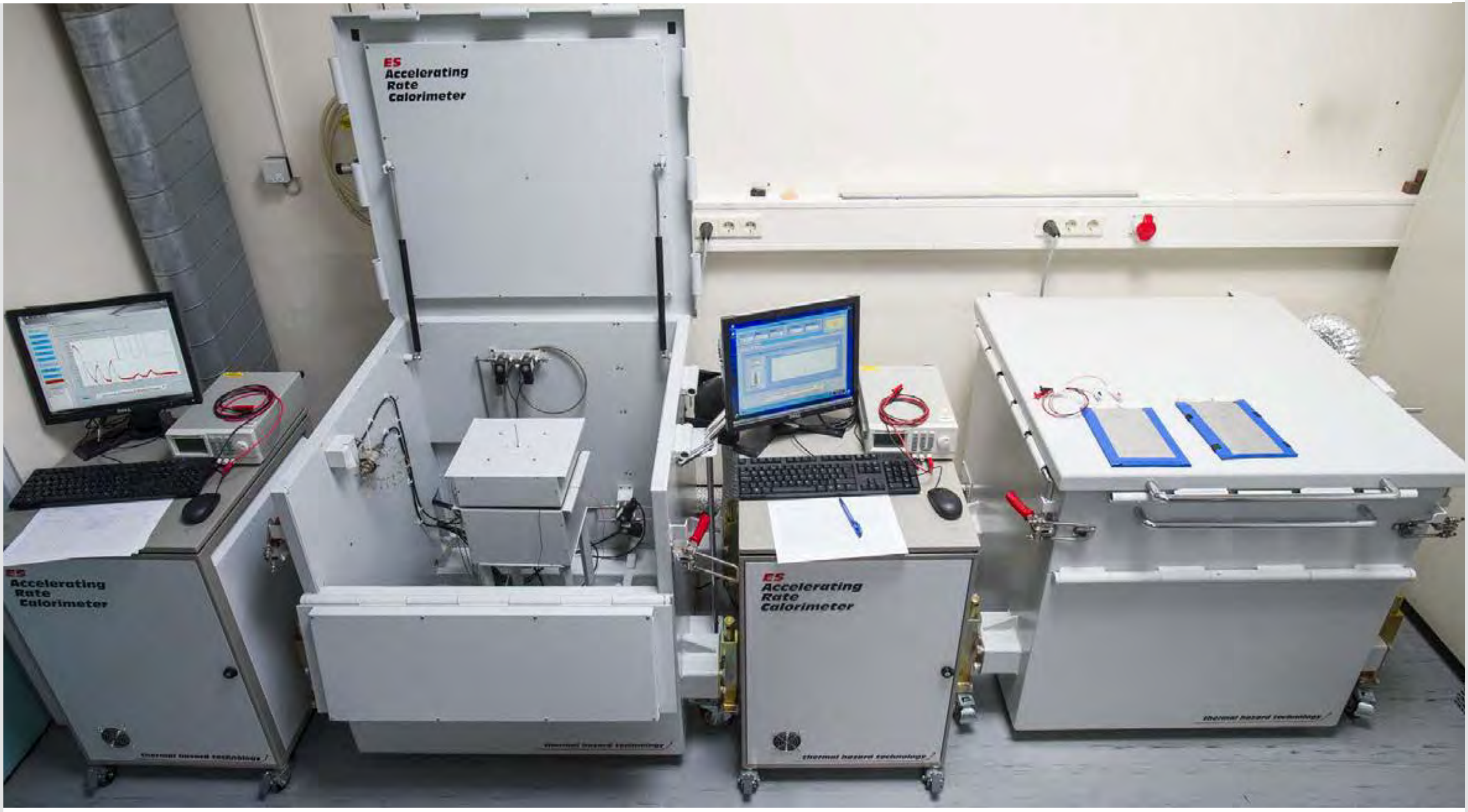
How calorimetry can help in battery research

The Calorimeter Center – Advanced Materials and Batteries

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



Contents

Introduction to the Calorimeter Center

Fig.1 Insertion of a 40 Ah pouch cell into a large-size Accelerating Rate Calorimeter (ARC)

Established in 2011 the Calorimeter Center at the Karlsruhe Institute of Technology's (KIT) Institute for Applied Materials – Applied Materials Physics, operates Europe's largest battery calorimeter laboratory. It provides six Accelerating Rate Calorimeters (ARCs) of different sizes (s. Fig. 1) – from coin to large pouch or prismatic automotive format – which allow the evaluation of thermodynamic, thermal and safety data for Lithium-ion cells on material, cell and pack level under quasiadiabatic and isoperibolic environments for both normal and abuse conditions (thermal, electrical, mechanical).

The center and the expertise are well established and get recognized and requested more and more by the automotive and storage industry. This unique laboratory is part of the Calorimeter Center, which encompasses further important infrastructures for research, development and testing of Lithium-ion batteries, such as gloveboxes for cell assembly and disassembly, temperature chambers for different temperature ranges, a thermocamera and cyclers. In addition it contains differential scanning calorimeters (DSC), thermo-gravimetric analyzers (TGA), laser flash analyzers (LFA) and extremely sensible Tian-Calvet calorimeters which provide thermodynamic parameters such as heat capacity, thermal conductivity or formation enthalpy on the materials level.

With these facilities, and the established technical and methodological expertise, the IAM-AWP is now - seen worldwide - one of the few institutions that investigate both the thermodynamics and the safety of batteries and their materials. The IAM-AWP has done in recent years pioneering work in this area.

How can Calorimetry help in Battery Research?

1) Research for improving performance parameters

- **Higher energy or power density**
- **Smaller heat release during operation**
- **Faster charging**
- **Increased cycle life and thermal life**

Isothermal coin cell calorimeter

Tian-Calvet calorimeters

Small-size ARC

Medium -size ARC

2) Research for improving safety parameters

- **Higher safe operating temperature**
- **Better resistance to thermal/mechanical/ electrical abuse**
- **Reduced hazards from cell venting and opening**
- **Less energy release during decomposition**

Large-size ARC

Pressure measurement in ARC

Nail penetration test in ARC

Benefits of Battery Calorimetry

Fig.2 Two accelerating rate calorimeters in the Battery Calorimeter Laboratory

Calorimetry – or the process of measuring heat data during chemical reactions – allows the collection of quantitative data required for optimum battery performance and safety. This data is important, because you need to know how many Watts a cell will produce under certain conditions. This information can then be used to adapt the battery and thermal management systems. Sophisticated battery calorimetry combined with thermography allows finding new and quantitative correlations between different critical safety and thermally related parameters. Fig.2 shows two of the Accelerating Rate Calorimeters (ARC) at the IAM-AWP Calorimeter Center. In these ARC's the temperature, heat and internal pressure evolution can be studied, while operating cells under conditions of normal use, abuse or accidents. Thus they provide a powerful tool for thermal runaway prevention and ageing prediction. Such abuse tests without calorimeter have two main disadvantages:

- The maximum safe temperature would be underestimated (i.e. the battery would be perceived to be less hazardous).
- The thermal runaway consequences would be understated in terms of severity and speed of incident.

Moreover the Heat-Wait-Seek (HWS) in the calorimeter is much more sensitive than a hotbox test and reveals the entire process of the thermal runaway with the different stages of exothermic reactions.

Quantitative Measurement of Thermal Data

The ARC's can be used for studies on heat generation and dissipation of single Li-ion cells and are coupled to battery cyclers in order to perform the tests during charging and discharging of the cells or batteries under defined thermal conditions which are a) quasiadiabatic or b) isoperibolic. The cell is inserted into the calorimeter chamber, which has heaters and thermocouples located in lid, bottom and side walls, that adjust the required ambient conditions [1].

a) Quasiadiabatic Cycling

In the quasiadiabatic mode the heaters in the calorimeter chamber follow immediately any change of the cell temperature preventing the heat transfer to the chamber. This simulates ambient conditions for a cell in a pack, where the densely packed neighboring cells, prevent, or at least greatly reduce, the heat release to the environment. This leads to a continuous increase of the cell temperature with every cycle, as can be seen in Fig.3a.

b) Isoperibolic Cycling

Isoperibolic means that the calorimeter walls are maintained by the heaters at a constant temperature, while measuring the variation of the surface temperature of the cells, which is shown in Fig.3b. In this case the cell temperature reaches its initial temperature again after each cycle. Such data make it possible to optimize charge and discharge management and to analyse ageing processes in the cells. By measuring the specific heat capacity and the heat transfer coefficient the measured temperature data can be converted into generated and dissipated heat data, which are needed for the adjustment of the thermal management systems [2]. E.g. in Fig. 3b the heat dissipation rate is shown for a low C/8 discharge rate reaching a maximum of 0.75 W. Integration over one discharge half cycle gives a dissipated heat of 6.4 kJ and a total generated heat of 7.9 kJ. Moreover the spatial temperature variation can be recorded via thermography methods.

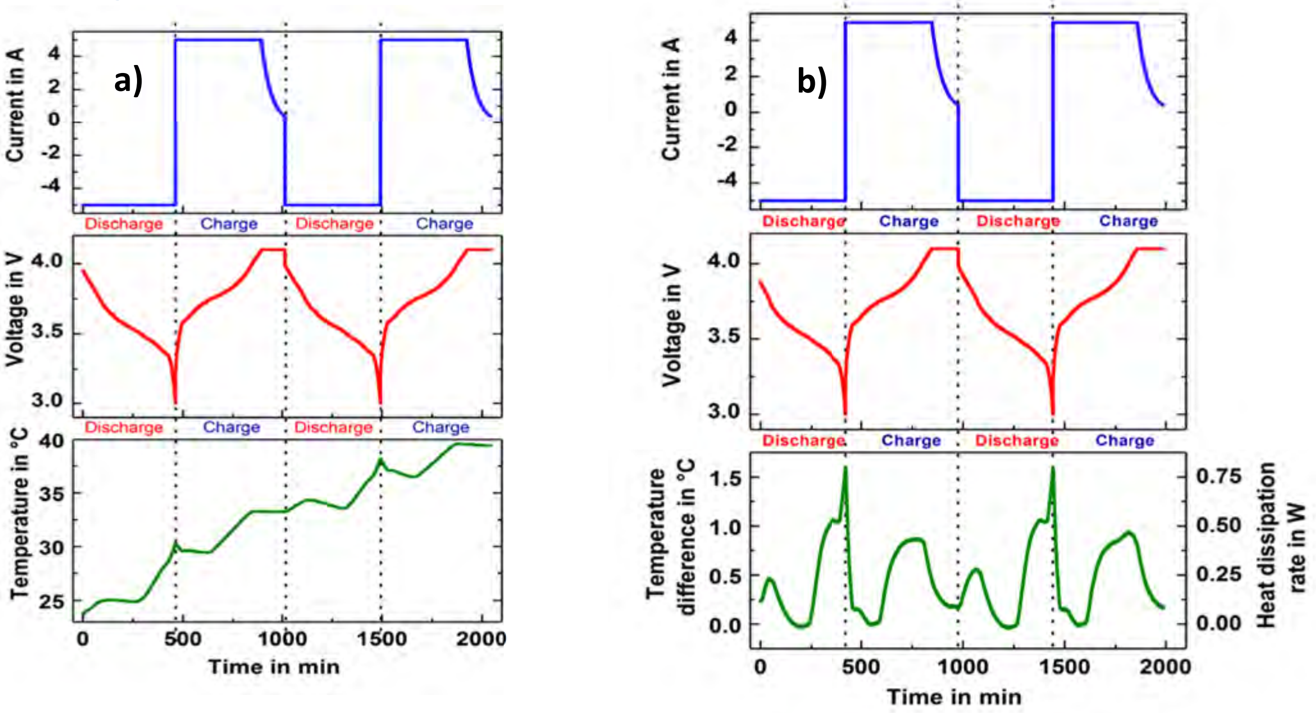


Fig.3 Temperature variation of a 40 Ah cell in an ARC at C/8 rate and 25 °C during: a) quasiadiabatic cycling   b) isoperibolic cycling

Abuse Tests in Battery Calorimeters

Both Tian-Calvet calorimeter C80 and the ARC's can provide thermal stability data on materials level, e.g. of anodes, cathodes or electrolytes or there combinations [3]. In the ARC's safety tests on cell and in the large-scale ones also on pack level can be performed under conditions of:

a) Electrical abuse: External/internal short circuit test, overcharge test, overdischarge test

In the ARC the temperature increase by applying an external short circuit or during an internal short circuit, which might be caused e.g. by a production fault in the cell, can be measured. In addition the cell failure modes can be studied during overcharging or deep discharging [4].

b) Mechanical abuse: Nail penetration test

In the large-scale ARC a nail can be pushed into the cell in a controlled way to simulate an accident where an object penetrates the cell. The ARC allows to measure the heat of reaction during this test.

c) Thermal abuse: Ramp heating test, Heat-Wait-Seek test, thermal propagation test

While the Ramp heating tests heats the cell up at a constant rate the Heat-Wait-Seek (HWS) test starts in the *Heat mode* by heating up the cell in 5 K temperature steps. At the end of each step the *Wait Mode* is activated to reach thermal equilibrium. Then the system enters *Seek Mode*, which seeks the temperature rate and ends with two possible modes - *Exotherm Mode* (quasiadiabatic conditions) or *Heat Mode*. If the measured temperature rate is larger than the onset sensitivity (typically 0.02 K/min), the system goes into *Exotherm Mode*. On the other hand, if the temperature rate is smaller, the system goes back into *Heat Mode*. [5]. The HWS test can be combined with the measurement of internal cell pressure as shown in Fig. 4. This plot clearly shows at first that a pressure increase occurs much earlier than a self-heating and at second that the cell goes into thermal runaway even if the safety vent opens and releases gases leading to pressure drop. Thus the measurement of the internal pressure could be used for the early prediction of processes leading to thermal runaway. This method has been adapted from cylindrical cells to pouch cells and prismatic automotive cells. Moreover the large-scale ARC's allow studying the thermal runaway propagation in order to develop and qualify suitable countermeasures, such as heat protection barriers (s. Fig.5). If a thermal runaway is initiated on cell 1-3, the protection material in this example is able to delay the thermal runaway propagation to cell 4 by 9 minutes.

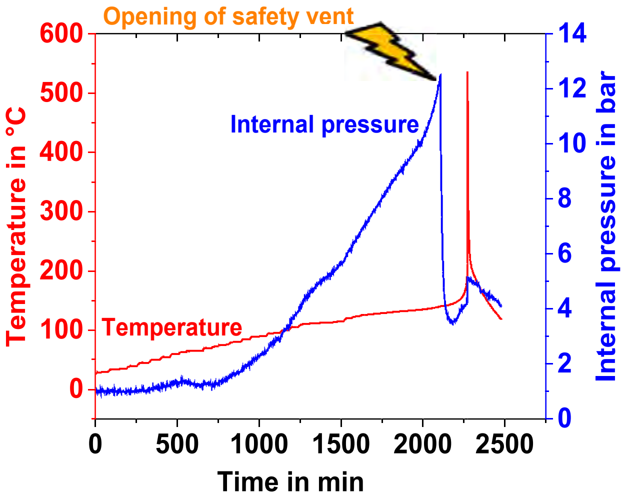


Fig.4 Temperature and internal pressure variation during thermal abuse of 18650 cell

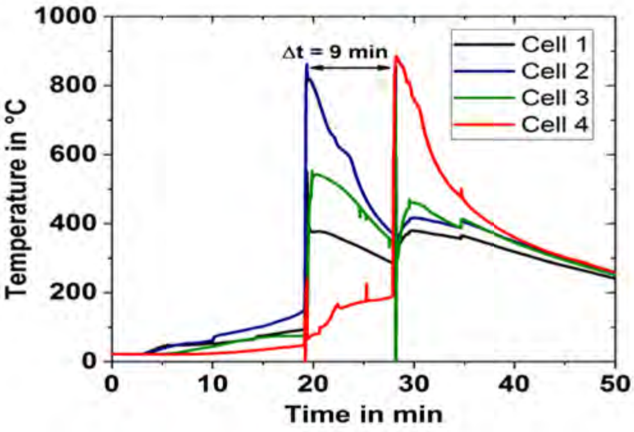


Fig.5 Material qualification for extension of thermal propagation time

Conclusions

As a result of the different tests quantitative and system relevant data for temperature, heat and pressure development of materials and cells are provided. These data can be used on all levels of the value chain, from safe design on materials level up to thermal management and adaptation of safety systems or implementation into modelling and simulation tools. In near future, battery calorimetry will be also needed to assess the thermal and safety properties of advanced materials such as solid state batteries or other systems, which could replace Lithium such as Sodium or Magnesium. This has to be started already now on the smaller scale level and has to be continued to ensure that the cells can be up-scaled and remain safe. Thus, there are still enough challenges that have to be overcome and we hope that our Calorimeter Center in close cooperation with our partners in the EERA (European Energy Research Alliance) Joint Programme on Energy Storage and our partners from academia will help the European Industry to make further progress in the battery field, which is urgently needed to reach a low-carbon future, to foster European leadership and to create new jobs as it should be achieved by the European Battery Alliance.

References

[1] C. Ziebert, A. Melcher, B. Lei, W.J. Zhao, M. Rohde, H.J. Seifert, *Electrochemical-thermal characterization and thermal modeling for batteries*, in: L.M. Rodriguez, N. Omar, eds., EMERGING NANOTECHNOLOGIES IN RECHARGABLE ENERGY STORAGE SYSTEMS, Elsevier Inc., ISBN 978032342977 (2017).

[2] E. Schuster, C. Ziebert, A. Melcher, P. Franke, M. Rohde, H.J. Seifert, *Thermal behavior and electrochemical heat generation in a commercial 40 Ah lithium ion pouch cell*, Journal of Power Sources **268** (2015) 580-589.

[3] A. Hofmann, M. Migeot, E. Thißen, M. Schulz, R. Heinzmann, S. Indris, Th. Bergfeldt, B. Lei, C. Ziebert, Th. Hanemann, *Novel Ethylene Carbonate Based Electrolyte Mixtures for Li-Ion Batteries with Improved Safety Characteristics*, ChemSusChem **8** (2015) 1892-1900.

[4] A. Hofmann, N. Uhlmann, C. Ziebert, O. Wiegand, A. Schmidt, Th. Hanemann, *Preventing Li-ion cell explosion during thermal runaway with reduced pressure*, Appl. Thermal Eng. **124** (2017) 539-544.

[5] B. Lei, W. Zhao, C. Ziebert, A. Melcher, M. Rohde, H.J. Seifert, Experimental analysis of thermal runaway in 18650 cylindrical cells using an accelerating rate calorimeter, Batteries 3 (2017) 14, doi:10.3390/batteries3020014.

CV

Dr. Carlos Ziebert earned his PhD in Physics from the Saarland University, Germany in 2002. In the same year, he joined the KIT. He has more than 15 years of international R&D experience in thin film technology, modelling and thermal characterization of materials for energy systems and more than 60 peer-reviewed articles. Since 2011, his research is focused on electrochemical and thermal characterization of Li-ion cells. He has been leader in five projects related to electrochemical energy storage and from 2011-2013 he was the manager of the EERA Joint Programme on Energy Storage (JPES). Currently Dr. Ziebert is the head of the Calorimeter Center at IAM-AWP.

Karlsruhe Institute of Technology

The Calorimeter Center – Advanced Materials and Batteries

Ensure your Lithium-ion cells perform well and are safe

With six Accelerating Rate Calorimeters of different sizes – from coin cell to large pouch or prismatic automotive format – and extremely sensible Tian-Calvet calorimeters the Calorimeter Center at the IAM-AWP of KIT offers the evaluation of thermodynamic, thermal and safety data for Lithium-ion and post-Lithium cells on material, cell and pack level. These data can be used on all levels of the value chain – from the safe materials design up to the optimization of the thermal management and the safety systems. Our fields of research and range of tests encompass both normal conditions and abuse conditions:

Normal condition tests include:

- Isoperibolic cycling, which provide constant environmental temperatures;
- Quasiadiabatic cycling, which ensure that there is almost no heat exchange between the cell and the surroundings

Each of these allows:

- Measurement of 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 – heat-wait-seek, ramp heating and thermal propagation test;
- Electrical abuse – external short circuit, overcharge and overdischarge test; 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 – change of risk potential with increasing ageing degree.

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