Thermal Analysis

Applications Booklet

Thermal Analysis of Lithium Ion Batteries

Application Examples

METTLER TOLEDO

Thermal Analysis of Lithium Ion Batteries Applications Guide

Preface

The increasing market of consumer electronics, smartphones and Electric Vehicles (EVs) is driving advances in battery research to provide safe, low-cost and lightweight/high-capacity power sources. For this, METTLER TOLEDO delivers complete solutions for battery testing laboratories and manufacturing, which support the development of new types of batteries as well as stringent QA/QC procedures that require multiple methods and analyses to assure the quality and safety of battery materials.

Innovative analytical solutions for thermal analysis can be used to test individual battery components, like anode/cathode electrode materials, separator, electrolytes, and more. Risks associated with thermal runaway situations such as overheating and possible explosion, are especially important for the use of lithium ion batteries (LIBs) in EV applications; critical tools for the investigation of batteries' thermal stabilities, exothermic reactions and enthalpies include differential scanning calorimetry (DSC), thermogravimetry (TGA) and thermomechanical analysis (TMA). To acquire more information about degradation components from a single experiment, a METTLER TOLEDO TGA or TGA/DSC can be hyphenated to a suitable gas analysis system to perform, for example, Fourier transform infrared spectroscopy, mass spectroscopy, gas chromatography-mass spectroscopy or micro gas chromatography-mass spectroscopy (respectively FTIR spectroscopy, MS, GC/MS; Micro GC(/MS).

This application booklet provides an overview of LIB technology and demonstrates how various thermal analysis techniques can be employed for a host of R&D and QC applications.

Disclaimer
The selected application examples presented in this guide were conducted with the utmost care and in accordance with our present knowledge. METTLER TOLEDO does not assume responsibility for the safety or accuracy of experiments carried out using the methods or instruments described in this handbook.

When chemicals, solvents and gases are used, general safety rules and the instructions given by the manufacturer or supplier must be observed.

Content

Content

1. Introduction to Lithium Ion Battery Technology

In 2019, John B. Goodenough, M. Stanley Whittingham and Akira Yoshino received the Nobel Prize in Chemistry for their shared contribution to the development of lithium ion rechargeable batteries (LIBs) that power the majority of portable electronic devices. More recently, LIBs have also become the focus of interest for electric vehicle (EV) applications (Figure 1) due to their numerous benefits such as lightweight, rapid charging, high energy density and long lifespan.

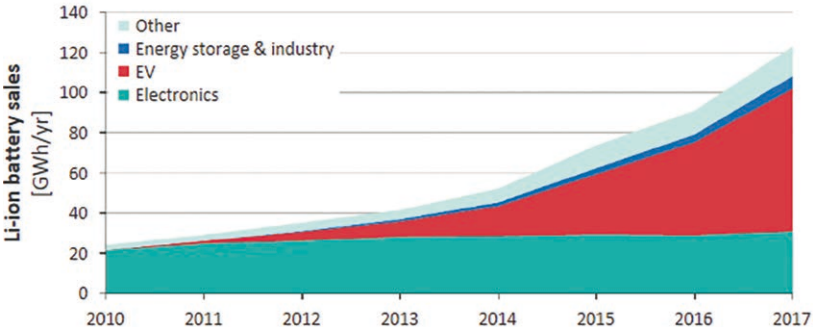

Figure 1. Annual growth in LIBs in main market segments.

Tsiropoulosetal. JRC EUR 29440 EN (2018)

Basic working principle of a Li-ion battery

The schematic in Figure 2 shows the LIB intercalation mechanism (i.e. the reversible inclusion of ions into the positive and negative electrodes). LIBs consist of a positive electrode (cathode), negative electrode (anode), and electrolytic solution. When the cell is charging, the cathode (usually lithium cobalt oxide) is oxidized and the anode (usually graphite) is reduced. When the cell is discharging, the reverse occurs. The Li^+ ions do not partake in the overall electrochemical reaction and remain in their oxidized state (see equations in Figure 2). They travel between the anode and cathode by diffusion through a liquid electrolyte consisting of organic solvents, lithium salts and various additives. The separator ensures the anode and cathode are kept electrically isolated but is porous enough to allow the electrolyte and Li^+ ions to pass easily through it.

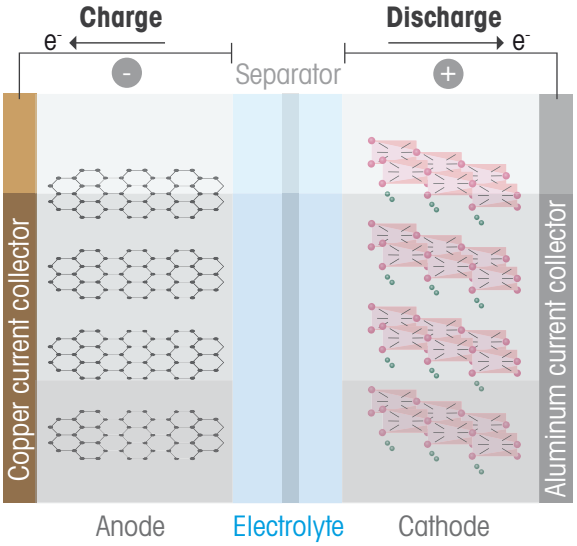

Figure 2. Schematic showing the LIB intercalation mechanism through the charging and discharging process. Cathode material: Lithium cobalt oxide ($LiCoO_2$); Anode material: Graphite ($LixC_6$).

Charge

Anode: $C_6 + x\ Li^+ \rightarrow Li_xC_6$

Cathode: $LiCoO_2 \rightarrow Li_{1-x}CoO_2 + x\ Li^+$

Discharge

Anode: $Li_xC_6 \rightarrow C_6 + x\ Li^+$

Cathode: $Li_{1-x}CoO_2 + x\ Li^+ \rightarrow LiCoO_2$

2. An Overview of the Various Thermal Analysis Techniques

Thermal Analysis (TA) is the term used to describe the analytical techniques that measure the physical and chemical properties of a sample as a function of temperature or time. The sample is subjected to a temperature program, which consists of a series of preselected segments, in which the sample is heated or cooled at a constant rate or held isothermally. Effects can also be investigated in different atmospheres, for example, air (oxidizing) or nitrogen (inert).

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) measures the heat flow produced in a sample when it is heated, cooled, or held isothermally at constant temperature. The measurement signal is the energy absorbed or released by the sample in milliwatts. Melting points, crystallization behavior, specific heat capacity and chemical reactions are just some of the many properties and processes that can be measured by DSC.

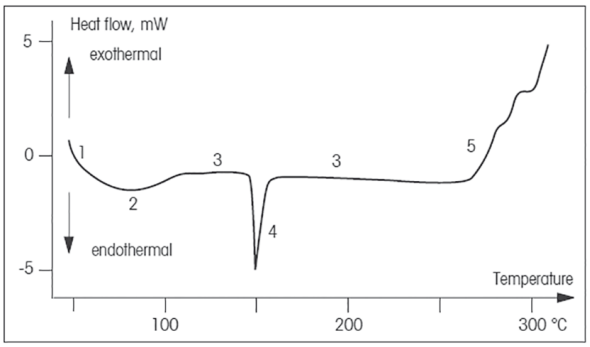

Figure 2.1. Typical DSC curve of a crystalline substance:
1 initial deflection proportional to the heat capacity of the sample
2 evaporation of moisture
3 part of the DSC curve with no thermal effects, i.e. baseline
4 melting peak
5 onset of oxidation in air

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Thermogravimetric Analysis

Thermogravimetric analysis (TGA) measures the mass of a sample as it is heated, cooled or held at a constant temperature in a defined atmosphere – usually nitrogen (inert) or air/oxygen (oxidative). The mass is measured using a highly sensitive electronic balance. Interfering buoyancy or gas flow effects are blank curve corrected. Volatile components evolved from the sample can also be analyzed (EGA, Evolved Gas Analysis) by coupling a mass spectrometer to TGA module.

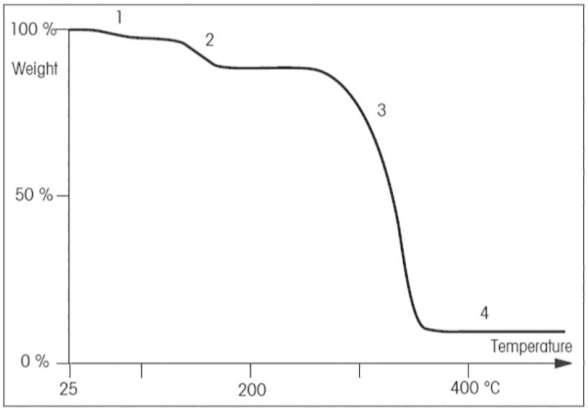

Figure 2.2. Typical TGA curve of a pharmaceutical preparation:
1 volatile components (moisture, solvents)
2 loss of water of crystallization
3 decomposition
4 residue (ash, fillers, carbon black or soot formed during decomposition in an inert atmosphere)

www.mt.com/ta-tga

Thermomechanical Analysis

Thermomechanical analysis (TMA) is used to study the dimensional changes of a material as a function of temperature or time. In TMA, the sample is subjected to a constant force, an increasing force, or a modulated force, whereas in dilatometry, dimensional changes are measured using the smallest possible load. Depending on the measurement mode used, TMA allows you to measure:

- thermal expansion and shrinkage behavior,
- softening, and
- changes in mechanical properties of materials induced by physical or chemical transitions such as the glass transition, crystallization, melting and curing.

www.mt.com/ta-tma

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) is used to study the viscoelastic properties and behavior of a wide range of materials. Samples are subjected to a sinusoidal mechanical stress as a function of temperature or frequency. Depending on the measurement mode used, DMA determines either the shear modulus, or the Young's modulus. The most important results obtained from DMA are the temperatures that characterize a thermal effect, the loss angle (the phase shift), the mechanical loss factor (the tangent of the phase shift), and the tensile or shear storage and loss moduli.

www.mt.com/ta-dma

Evolved Gas Analysis

In the broader definition, evolved gas analysis (EGA) investigates the nature of volatile products released by a substance as it is heated. This can be done using many different types of techniques and equipment. Coupling a METTLER TOLEDO TGA or TGA/DSC to an FTIR, MS, GC/MS or Micro GC(/MS), creates a TGA-EGA system. The thermogravimetric analyzer records the loss-of-mass of the sample while the evolved gas analyzer simultaneously provides information about the gaseous products evolved (e.g. moisture, solvents or additives) from processes such as evaporation, desorption, decomposition, and chemical reactions (add ref to EGA handbook).

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3. How to Leverage State-of-the-art Thermal Analyzers For Improved Battery Performance and Safety

METTLER TOLEDO contributes to the development and quality control of batteries with comprehensive and robust measurement solutions. Whether the aim is to verify the state of battery components (QC) or to gain knowledge about new materials (R&D), our suite of thermal analyzers provide critical information about battery materials and the test conditions under which the data is obtained to determine the suitability of the battery technology for the intended application. Common applications and their corresponding TA techniques are summarized in Table 1.

	Application areas				
	Battery components				
TA technique	Electrodes/ binder	Separator	Electrolyte	Performance & safety	Raw materials
Differential scanning calorimetry (DSC)	•	•	•	•	•
Thermogravimetric analysis (TGA)	•	•	•	•	•
Thermomechanical analysis (TMA)		•		•	
Dynamic mechanical analysis (DMA)		•		•	
Evolved gas analysis (TGA-EGA)	•	•	•	•	•

Table 1. The main thermal analysis techniques and their corresponding applications for the characterization of battery components/raw materials and assessment of battery performance and safety.

3.1. Electrode (anode and cathode) characterization

The performance and safety of electrodes is largely influenced by charge/discharge induced ageing and degradation of cathode active material.

Providing precise measurements for heat capacity, decomposition temperatures and enthalpy determination, thermal analysis techniques are fundamental aids in thermal stability studies. To acquire more information about degradation components from a single experiment, a METTLER TOLEDO TGA or TGA/DSC can be hyphenated to a suitable gas analysis system to perform, for example, Fourier transform infrared spectroscopy, mass spectroscopy, gas chromatography-mass spectroscopy or micro gas chromatography-mass spectroscopy (respectively FTIR spectroscopy, MS, GC/MS; Micro GC(/MS).

3.2 Separator analysis

Separators for Li-ion batteries have a crucial impact on battery performance, life, as well as reliability and safety. They must be thin to allow Li+ ions to move quickly between the anode and cathode but the structural integrity of the separator is important, because its degradation could lead to an internal short circuit.

Thermal analysis is used to characterize the thermal properties of separators, typically made from polyolefins (e.g. PP or PE). Technological limitations of such membranes include penetration resistance, shrinkage and meltdown. These properties can be investigated by means of Thermogravimetry (TGA), differential scanning calorimetry (DSC) and thermomechanical analysis (TMA).

3.3 Characterization and testing of electrolytes

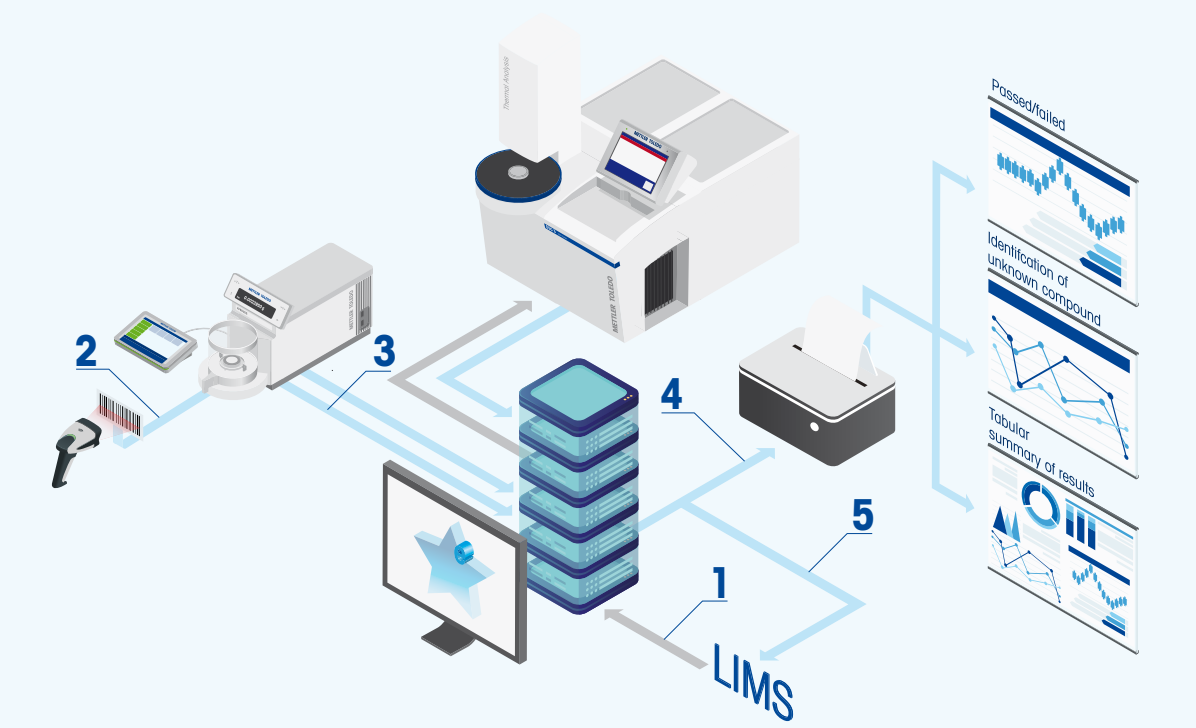
Differential scanning calorimetry (DSC) can be used in QC to study the composition and content of carbonates in electrolytic solutions, which have important implications for the cycling stability, energy density and safety of lithium ion batteries. DSC also provides information about electrolyte melting and crystallization for determining the minimum temperatures for charging/discharging processes.

4. Power Your Battery Analysis with the Most Comprehensive and Flexible TA Software on the Market

Today's analytical laboratories face growing demand for increased production capacity – often with limited resources. This poses a huge challenge for QC laboratories who must still achieve reliable results and compliant documentation. More and more labs are therefore turning to automated QC systems that carry out many labor-intensive and error-prone tasks formerly performed by humans.

METTLER TOLEDO provides a unique combination of technical capabilities and Laboratory Information Management Systems, or LIMS, connectivity to support this trend in thermal analysis. Central to this is the innovative STARe thermal analysis software, through which complete investigation of materials is managed and controlled – from sample management and measurement to interpretation and validation of results. Within the software all measurement methods, measurement data and calibration data and evaluations of results are stored in a secure database with date and time stamp. Therefore, they are traceable at all times. It is impossible to delete or change data by accident.

The ideal TA workflow, detailed in the schematic below, seamlessly integrates automation with DSC technology. The workflow, from the perspective of automation, can be structured into five steps.



Step 1: LIMS order
The LIMS system sends a request to the STARe software to run an experiment, evaluate results and generate a report.

Step 2: Sample identification
Sample containers can be labeled with barcodes for quick, error-free sample identification and transfer to STARe. The barcode reader may be connected to either the PC or a METTLER TOLEDO balance.

Step 3: Sample weigh-in via STAReX
Weighing results can be transferred electronically from a METTLER TOLEDO balance to STARe by interfacing the TA software directly with LabX® – METTLER TOLEDO's balance software. The STAReX™ link reduces transcription errors, speeds up the analytical process and facilitates the second person review required by regulated industries.

Step 4: Automatic result evaluation
Following a measurement, the resulting curve must be evaluated. Particularly where repeated analyses must be performed, automated evaluations – e.g. via the STARe EvalMacro option – can speed up repetitive tasks and eliminate operator bias. EvalMacro performs evaluations of the same type fully automatically and enables graphical comparison and statistical evaluation of results to ensure they lie within predefined limits.

Step 5: LIMS result transfer
In the final step, results are transferred to the LIMS database, which supports most file formats, including graphics (e.g. tiff), text files and List & Label reports.

4.1 Some practical software options

Fully integrated automated workflows are supported by adding relevant software options such as:

EvalMacro – with the reliable sample changer and the automatic evaluation of results, experiments can be fully automated from the measurement to the display and storage of the results.

Quality Control – sample measurements can be compared to known reference curves and results transferred to a statistics table for quick and easy statistical evaluations and trend analysis.
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Reference Library – facilitates the interpretation of results and helps with materials' identification, e.g. for failure analysis.
www.mt.com/ta-libraries

Data Integrity – provides password access-control to the application, assigns user-rights for each user-level, classifies data based on levels of sensitivity, and assigns users to groups or projects.
www.mt.com/ta-dataintegrity

LIMS Connectivity – automate workflows, integrate laboratory operations, and manage samples and associated information.

For more software information:
www.mt.com/ta-swupdates

Robust endurance-tested sample robot functions reliably and efficiently throughout the day.

www.mt.com/ta-automation

5. Applications and Their Thermal Analysis Techniques

The overview summarizes the effects and properties that can be investigated by thermal analysis techniques.

DSC	Differential Scanning Calorimetry	**TMA**	Thermomechanical Analysis	**EGA**	Evolved Gas Analysis
TGA	Thermal Gravimetric Analysis	**DMA**	Dynamic Mechanical Analysis	**HS**	Hot Stage Microscopy

	DSC	TGA	TMA	DMA	EGA	HS
Compositional analysis	•	•			•	
Chemical reactions	•	•			•	
Comparative analysis (lots, batches, etc.)	•	•	•	•	•	•
Content determination		•				
Crystallization/Crystallinity	•					•
Decomposition/ Degradation/Pyrolysis	•				•	
Enthalpy changes	•					
Evaporation/Drying		•				•
Expansion coefficients			•			
Gelatinization	•					
Gelation			•			
Glass transition	•		•	•		
Heat of transition	•					
Identification	•	•			•	
Interactions/Compatibility	•					
Kinetic analysis	•	•				
Loss factor/Damping				•		
Melting point/melting range	•					•
Oxidative stability	•	•			•	
Phase diagrams	•					
Phase transitions	•					•
Polymorphism/Pseudo-Polymorphism	•					•
Purity determination	•					•
Safety investigations	•					
Shear Modulus				•		
Shrinking/Swelling			•			
Sorption/Desorption		•				
Specific heat capacity	•					
Thermal stability	•	•			•	•
Viscoelastic behavior			•	•		
Young's Modulus			•	•		

Table 2. Overview of techniques and applications.

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6. Application Examples

6.1 Thermal stability of $LiFePO_4$ cathode material in electrolyte

Understanding a battery's thermal stability is a critical safety parameter. In this example, simultaneous thermal analysis (TGA/DSC) was used to show how the thermal stability of a popular cathode material, $LiFePO_4$, changes with temperature.

Sample	Lithium iron phosphate ($LiFePO_4$), black powder, mixed phosphate of Lithium (Li^{+}) and Iron (Fe^{2+})	
Measurement	Measuring cells:	TGA/DSC
	Crucible:	TGA: alumina 70 µL, no lid
	Sample preparation:	As received, no preparation, about 23 mg
	TGA/DSC measurement:	Heating from 30 °C to 1000 °C at 10 K/min, air 50 mL/min Blank curve corrected

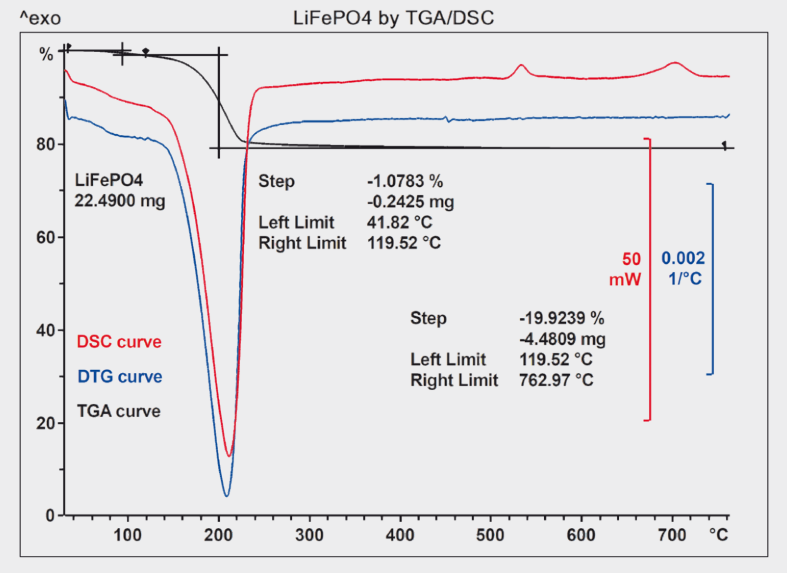

Figure 1. TGA, DSC and DTG curves of $LiFePO_4$ in the presence of electrolyte.

Figure 1 shows the TGA analysis of $LiFePO_4$ cathode material; the sample exhibits several decomposition steps. The first mass loss of 1.1% (up to 120 °C) is probably due to moisture. This is immediately followed by the decomposition of the electrolyte material (19.9%), which finishes at about 300 °C. The numerical values are listed in Table 1.

For comparison, pure $LiFePO_4$ was measured under identical conditions. The results showed that the material is stable up to high temperatures (well above 500 °C).

	$LiFePO_4$
1st weight loss (30–120 °C)	1.1%
2nd weight loss (120–800 °C)	19.9%
Residue at 800 °C	79.0%

Table 1. TGA results of $LiFePO_4$.

Conclusion

TGA/DSC can be used to investigate processes such as vaporization and decomposition of battery cell materials. The results indicate that the $LiFePO_4$ cathode material is stable up to about 150 °C. The thermal stability is largely dependent on the electrolytic solution used. More information about decomposition products can be achieved using hyphenated techniques such as TGA-MS, TGA-FTIR and TGA-GC/MS.

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6.2 Characterization of an electrolyte mixture

The electrolytic solutions commonly used in commercial lithium batteries consist of organic solvents, lithium salts and some additives. The organic solvents are mainly cyclic carbonates, such as propylene carbonate and ethylene carbonate, or chain carbonates, for example, ethyl methyl carbonate and diethyl carbonate. Composition and ratio of these carbonates have important implications for the cycling stability, the energy density, and the safety of lithium ion batteries.

Sample	Ethyl methyl carbonate and propylene carbonate mixture	
Conditions	Measuring cell:	DSC
	Crucible:	Aluminum 40 µL with lid
	Sample preparation:	None, used as received
	DSC measurement:	Heating from –130 °C to 40 °C at 10 K/min
	Atmosphere:	Nitrogen, 50 mL/min

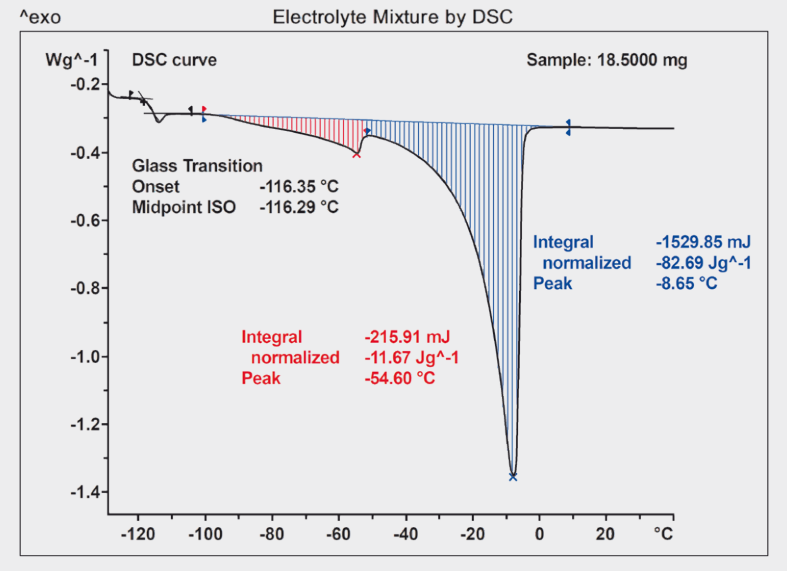

Figure 1. First heating run of a mixture of ethyl methyl carbonate and propylene carbonate.

The DSC curve of the first heating run displayed in Figure 1 shows a glass transition near –116 °C followed by a broad endothermic melting peak. The melting of the binary mixture leads to partially overlapping endothermic peaks on the DSC curve. Propylene carbonate melts at a lower temperature with a peak at –54.6 °C. The melting enthalpy of the major solvent component amounts to –82.69 Jg-1. The content of this component in the solvent mixture is 76.6% based on the literature value of 107.97 J/g for the heat of fusion of ethyl methyl carbonate [1].

A battery working with this type of electrolyte can only be charged above about 0 °C, i.e. when the electrolyte is liquid. Discharging the battery is possible down to slightly lower temperatures. However, the determination of a respective minimum temperature is more complex as it requires isothermal crystallization measurements at a number of different temperatures.

Conclusion

DSC measurements allow the study of the composition and content of carbonates in electrolytic solutions, which play an important role in the development and quality control of lithium ion batteries. In addition, based on the melting/crystallization behavior of the electrolyte, low temperature specification for charging/discharging processes can be established.

References

[1] Michael S. Ding, Liquid-Solid Phase Equilibria and Thermodynamic Modeling for Binary Organic Carbonates, J. Chem. Eng. Data, 2004, 49, 2, 276-282, https://doi.org/10.1021/je034134e

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6.3 Analysis of microporous separators by TGA and TMA

Separators in LIBs are microporous polyolefin membranes with a pore size of less than 10 nm. In this example, TGA and TMA were used for the quality control of a separator material made of polypropylene (PP) film.

Sample	PP film	
Conditions	Measuring cells:	TGA and TMA
	Crucible:	TGA: alumina 70 µL, no lid
	Sample preparation:	TMA: Fiber attachment As received, no preparation, about 10 mg for TGA and a 15 mm long film for TMA. The effective sample length in between the clamps is 10 mm
	TGA measurement:	[1] heating from 50 °C to 600 °C at 20 K/min, nitrogen 50 mL/min [2] heating from 600 °C to 800 °C at 20 K/min
	Atmosphere:	Oxygen 50 mL/min, Blank curve corrected
	TMA measurement:	[1] heating from 35 °C to 200 °C at 5 K/min
	Atmosphere:	Nitrogen, 50 mL/min

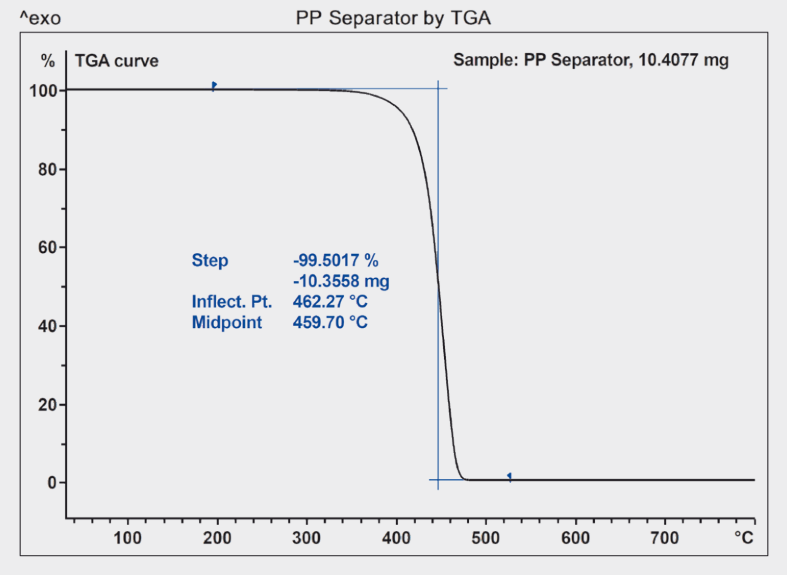

Figure 1. TGA curve of a PP film used as separator material in LIBs.

Figure 1 shows the TGA curve of the PP film. Decomposition starts at about 380 °C and the inflection temperature of the mass loss step is 462 °C. After switching from a nitrogen to oxygen atmosphere, no further mass loss is observed. Therefore, decomposition occurs in a single step, which is typical for pure PP.

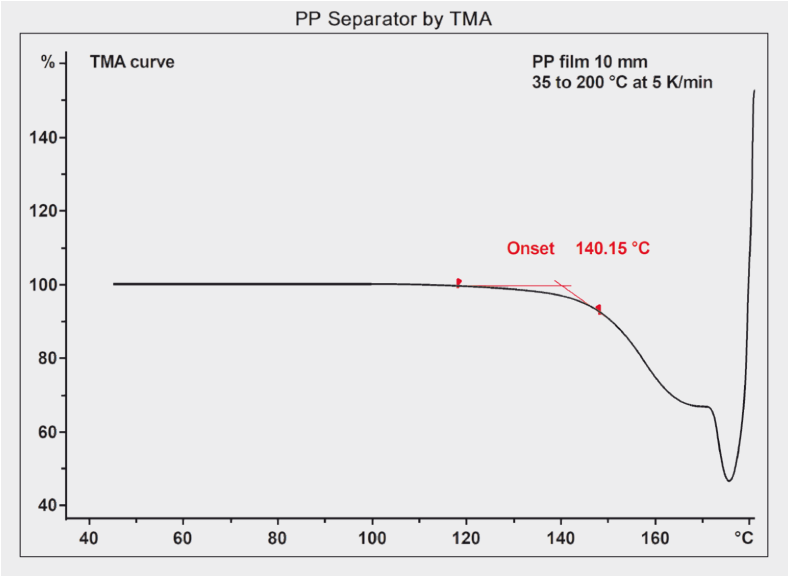

Figure 2. TMA curve of a PP film used as separator material in LIBs.

PP films undergo catastrophic shrinkage at higher temperatures. Therefore, separator shutdown is a useful safety feature for preventing thermal runaway reactions in LIBs. TMA was used to characterize the shrinkage and melting behavior of the separator membrane. The shrinkage of PP takes place in two steps, in which different types of crystals are formed. Closure of the pores occurs during the first shrinkage between 140 °C and 170 °C. The second shrinkage process takes place up to about 175 °C. At higher temperatures, the sample elongates due to melting. The onset temperature of the first shrinkage at 140 °C corresponds to maximum application temperature of the separator.

Conclusion

In the above examples, TGA was used to confirm the absence of impurities, which could compromise battery performance. For safety purposes, it is important that the separator shuts down (i.e. pore closure) before the onset of melting. This could be confirmed by TMA.

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www.mt.com/ta-tma

6.4 Quality control of PVDF by TGA and DSC

In recent decades, polyvinylidene fluoride (PVDF) has been a popular choice of binder material for LIBs, especially in cathodes. The fluoropolymer, produced by the polymerization of vinylidene difluoride, exhibits excellent electrochemical and thermal stability and good adhesion between the current collectors and electrode films.

PVDF of high purity is important for providing enhanced battery safety and performance. In this example, DSC was used to measure caloric effects, e.g., the glass transition and melting, while the decomposition and combustion of PVDF was studied by means of TGA.

Sample	PVDF pellet raw material	
Conditions	Measuring cells:	TGA and DSC
	Crucible:	TGA: alumina 70 µL, no lid
		DSC: aluminum 40 µL, pierced lid
	Sample preparation:	As received, no preparation, about 15 mg
	TGA measurement:	[1] heating from 35 °C to 900 °C at 20 K/min, nitrogen 50 mL/min
		[2] cooling from 900 °C to 300 °C at 20 K/min,nitrogen 50 mL/min
		[3] heating from 300 °C to 900 °C at 20 K/min, oxygen 50 mL/min
	Atmosphere:	Oxygen 50 mL/min, Blank curve corrected
	DSC measurement:	[1] first heating* from –80 °C to 225 °C at 20 K/min
		[2] cooling from 225 °C to –80 °C at 20 K/min
		[3] second heating* from heating from –80 °C to 225 °C at 20 K/min
		*The first heating provides information on the thermal history of the sample; the cooling curve and second heating curve provide information on the sample material.
	Atmosphere:	Nitrogen, 50 mL/min

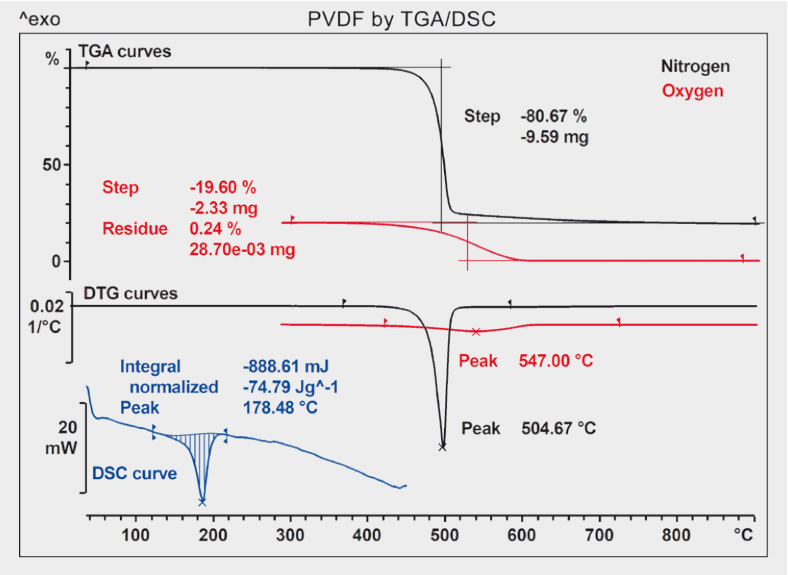

Figure 1. TGA/DSC results of PVDF pellet and insulation.

Figure 1 displays the TGA, DTG and DSC curves of PVDF measured in a METTLER TOLEDO TGA/DSC. The sample was first heated to 900 °C under inert conditions (black curves). The material decomposes in one mass loss step of 80.7%, reaching a maximum rate at 504 °C. After cooling to 300 °C, the atmosphere was switched from nitrogen to oxygen, which results in combustion of the carbon additives at about 550 °C (red curves) of about 19.6%. The lower part of Figure 1 displays the simultaneous DSC curve under nitrogen up to 450 °C. The melting of PVDF is observed at 178 °C.

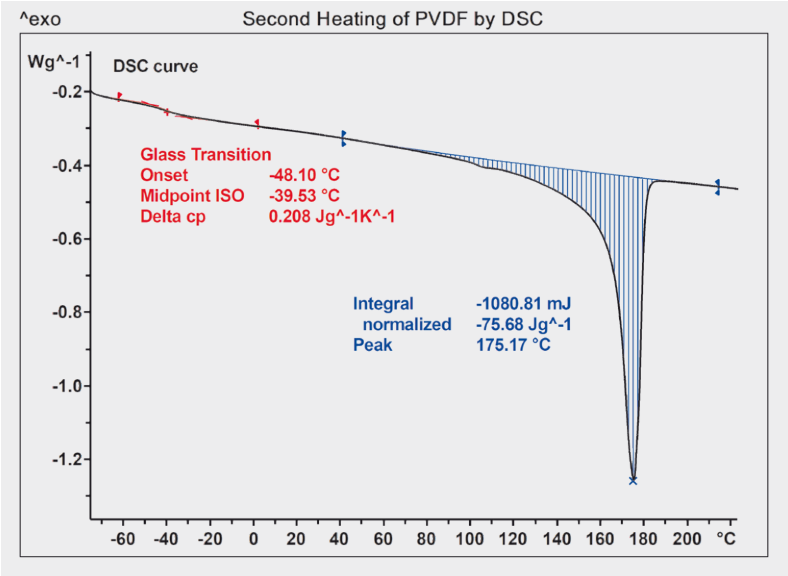

Figure 2. Second heating of PVDF by DSC.

Figure 2 shows the second DSC heating curve of the PVDF sample. PVDF exhibits a glass transition at about –40 °C and a melting at about 175 °C. The enthalpy change at the glass transition is 0.21 J/g/K and the melting enthalpy is 76 J/g.

TGA		DSC	
Depolymerization		Glass transition	
Step	DTG peak	Temperature	ΔC_p
80.7%	505 °C	–39.5 °C	0.21 J/g/K
Burning of carbon		Melting	
Step	DTG peak	Peak	Enthalpy
19.6%	547 °C	175.2 °C	76 J/g
Residue 0.24%			
Melting*			
Peak	Enthalpy		
178.5 °C	76 J/g		
* (Only with TGA/DSC instrument)			

Conclusion

Thermogravimetric analysis shows that the PVDF sample was stable at high temperatures: no thermal degradation occurs below about 450 °C. In addition, DSC allows for a detailed characterization of key QC parameters such as glass transition, melting and crystallinity.

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6.5 Conversion of graphene oxide into graphene (anode material)

Graphene is characterized by a number of outstanding properties (high electrical conductivity, huge specific surface area, mechanical strength and a two dimensional structure) that makes it a frequently used anode material in LIBs. A simple and inexpensive route to obtain graphene is to reduce graphene oxide, which can be easily obtained from graphite. Graphene oxide is an oxidized form of graphene, laced with oxygen-containing groups. If reduced, its layered structure remains, and graphene is obtained. The reduction of graphene oxide can be readily investigated by TGA/DSC.

Sample	Graphene oxide (GO)	
Conditions	Measuring cell:	TGA/DSC
	Crucible:	Alumina 70 µL, no lid
	Sample preparation:	As received, no preparation, about 5.07 mg
	TGA/DSC measurement:	30 min isothermal at RT (to eliminate residual oxygen in the furnace); heating from RT to 800 °C at 10 K/min.
	Atmosphere:	Nitrogen, 50 mL/min
		Blank curve corrected; the isothermal at RT is not shown

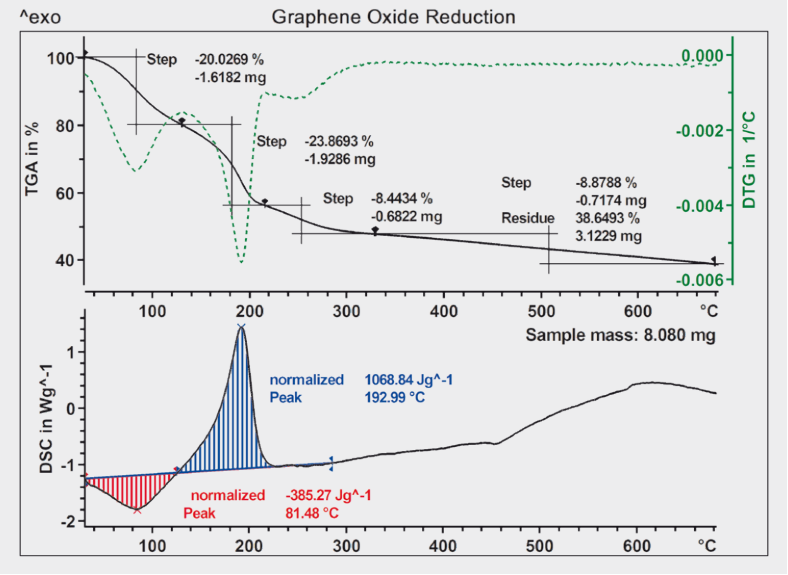


Figure 1. Graphene oxide measured by TGA/DSC; upper part: TGA and DTG curves; lower part: DSC curve.

Evaluation

The upper part of Figure 1 shows the TGA curve of graphene oxide and the lower part, the simultaneously measured DSC curve. In contrast to graphene, graphene oxide is hygroscopic. Therefore, the first step (in blue) indicates a mass loss due to water (endothermic DSC signal). This is overlapped by the thermal elimination of the oxygen-containing functional groups. This elimination step is not clearly not completed at 800 °C, i.e. the residue consists of both graphene as well of some (unknown) amount of graphene oxide. To completely reduce graphene oxide, one could increase the final temperature, add an isothermal at e.g. 800 °C, or use a reducing agent such as inert hydrogen as reactive gas.

Conclusion

Thermal reduction of graphene oxide is an important processing step in the fabrication of many graphene-based anodes. The stepwise reduction of graphene oxide can be easily followed by TGA/DSC.

7. Testing of Electrolytes and Electrodes Using (Karl-Fischer) Titration

Besides comprehensive TA solutions, METTLER TOLEDO also offers titration applications to test battery components. The electrolytic solutions commonly used in commercial lithium batteries consist of organic solvents (mostly cyclic and linear carbonates), lithium salts and various additives. Electrolytes and other Li-ion battery materials must be free of water because even trace amounts react with the electrolyte to produce aggressive by-products including hydrofluoric acid (HF) that compromise battery performance and safety. Coulometric Karl Fischer Titration can accurately determine the electrolyte's water content. In addition, acid-base titration has proven to be a reliable method to test the HF content of the battery's electrolyte.

As the density of a liquid depends on its molecular composition, a quick density check with a METTLER TOLEDO density meter can help to reveal electrolyte contaminations with water or other impurities.

Besides the electrolyte, electrodes can be tested for water prior to using them in the battery. The METTLER TOLEDO InMotion KF oven heats the solid material to elevated temperatures, extracts its water and guides it to a coulometric Karl-Fischer titrator, where it is detected. The analytical method is fully automated and the operator only needs to fill the vials and start the method by OneClick™.

Furthermore, titration can be used to determine the metal content (eg. cobalt, managenese, iron, nickel) of cathode material as well as to test the material for impurities such as chlorides, hydroxides and carbonates.

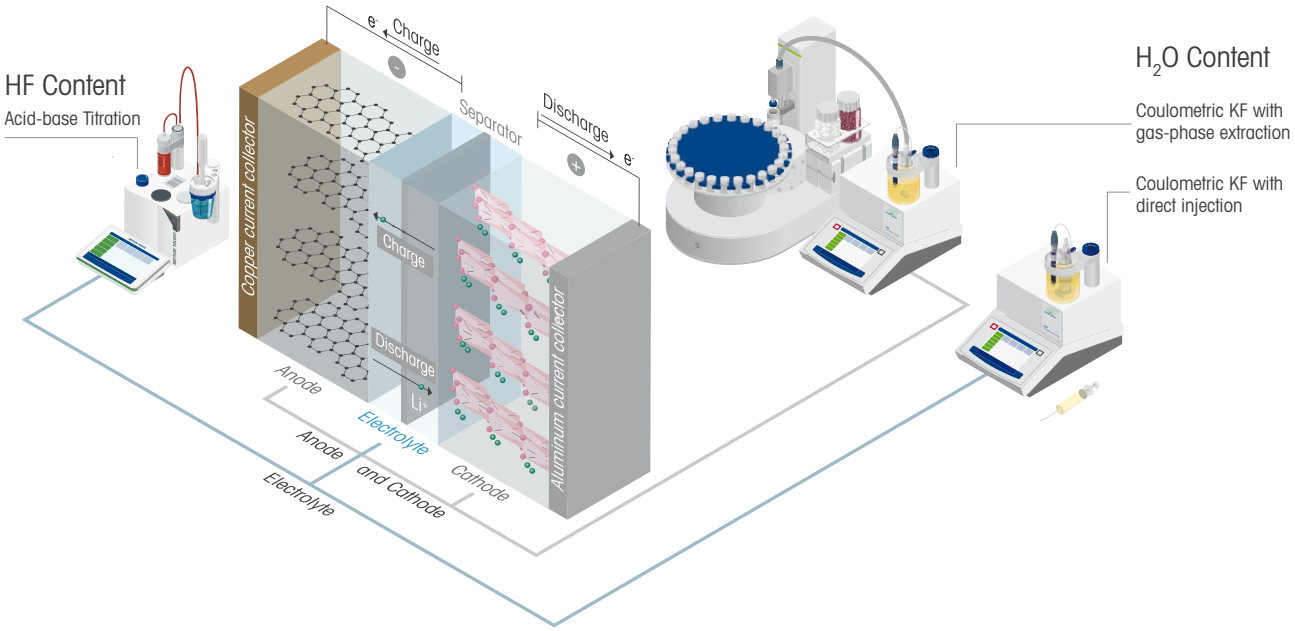


Figure 1. Left: Excellence T5 Titrator; middle right: C30S coulometric KF titrator and InMotion KF oven; right: C30S coulometric KF titrator.

Find out more about METTLER TOLEDO titration:

- **www.mt.com/titration**
- **www.mt.com/density**
- **www.mt.com/li-ion-battery**

8. Instrument Calibration and Adjustment

We want to be able to rely on the data that the measuring instrument has delivered. But how can we achieve this goal? We must invest a little bit of time and effort to calibrate and perhaps adjust the instrument as part of a regularly scheduled maintenance plan (Figure 5.1).

Calibration is the act of checking the accuracy of a measuring instrument by comparing measurement results using a reference substance for which the "true" value of the measured property is known.

Adjustment is defined as modifying the specific instrument parameters so that the measurement results of the calibration performed afterward are within the tolerance limit.

In thermal analysis, the ordinate (X-axis) and the abscissa (Y-axis) need to be calibrated:

Ordinate
- Heat flow, peak area (DSC)
- Mass (TGA, automatically performed in the electronic microbalance)
- Length (displacement) and force (TMA and DMA)

Abscissa
- Temperatures
- τ_{lag}, which makes the temperature independent of the heating rate (at the sample crucible position)
- Time (e.g. for isothermal measurements) derived from the quartz clock of a microprocessor (extremely accurate)

We recommend an initial calibration interval of one month, which can be doubled if results repeatedly lie within acceptable error limits. Conversely, the calibration interval should be further reduced to half in the case of several unacceptable measurements.

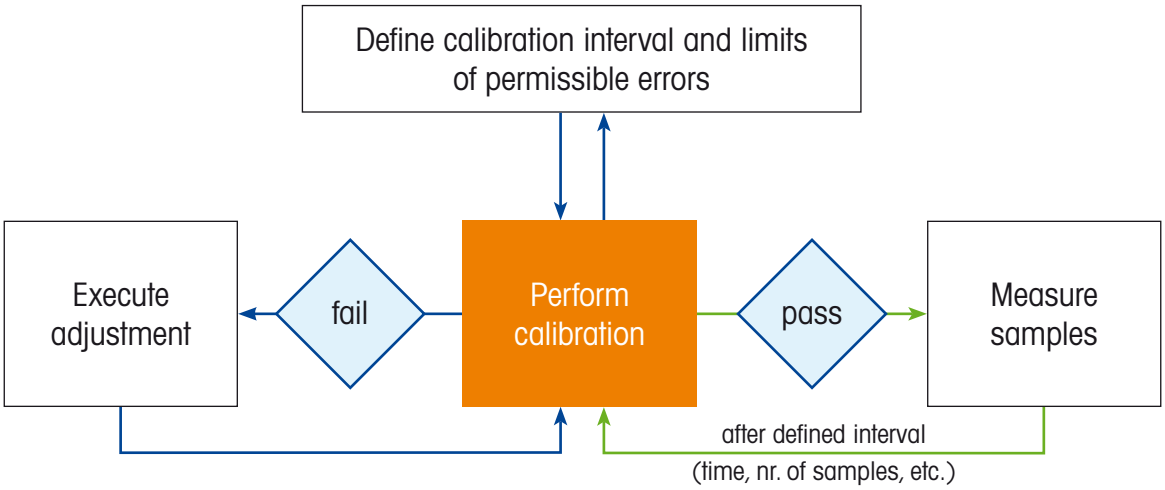


Figure 1. Flow chart for calibration, adjustment and measurements.

FlexCal™ – fully traceable and time-saving calibration and adjustment

Conventional thermal analysis instruments must be readjusted each time experimental conditions such as atmosphere, heating rate or crucible type are changed. METTLER TOLEDO's FlexCal functionality implemented in STARe software includes the methods and database to store and handle the necessary adjustment parameters.

FlexCal provides four important functionalities

1. Using a clever algorithm, FlexCal calculates missing adjustment parameters such as crucible type, atmosphere and heating rate.
2. FlexCal sends the correct adjustment parameters to the instrument whenever the gas is switched during a measurement.
3. STARe software can enforce the use of adjusted and calibrated parameter sets, as required for regulated industries.
4. STARe software also checks the calibration due date. If exceeded, the unit cannot be used until properly calibrated.

In summary, with the database-supported calibration model, FlexCal, thermo-analytical results, such as the onset of melting or heat of fusion, no longer depend on the heating rate, the type of crucibles and gas atmosphere selected.

www.mt.com/ta-calibration
www.mt.com/ta-acc

9. Excellent Crucibles, Accessories and Reference Materials

Crucibles for thermal analysis

Crucibles serve as containers for samples during thermoanalytical measurements. They guarantee that the sensor is not contaminated by the measurement. The type of crucible used for a measurement can have a large effect on the quality of the results obtained, and in addition, also influences important characteristics of the DSC measuring cell. Considering the relevant factors before the measurement can often help to save time later on when interpreting the curve.

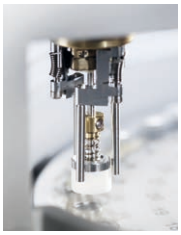
METTLER TOLEDO offers an extremely wide range of crucibles.

- Aluminum crucibles – various types and sizes
- Crucibles made from copper, platinum or gold
- Medium pressure crucible – stainless steel
- High pressure crucibles – stainless steel, gold plated, nimonic
- Alumina crucibles (aluminum oxide)
- Polycrystalline aluminum oxide – a sapphire-like material
- Glass crucibles

Select the right crucible type – and improve your measurement quality.

Crucible sealing press

The press allows the pan to be sealed very easily. Under the pressure of the plunger the pan is cold welded hermetically with the lid. With 3 exchangeable assemblies you adjust the sealing press to the various crucibles. Sealing tools for high pressure crucibles are also available.



Sample robot

All DSC and TGA models from METTLER TOLEDO can be automated. The sample robot can process up to 34 samples even if every sample requires a different method and a different crucible. The sample robot is very robust and operates reliably 24 hours a day and throughout the whole year.

Reference materials

METTLER TOLEDO markets the reference substances needed for calibration and adjustment of thermal analysis instruments. The following reference substances are traceable to the manufacturer.

Substance	Indium	Tin	Lead	Zinc	Aluminum	Gold	Palladium
Symbol	In	Sn	Pb	Zn	Al	Au	Pd
T_f in °C	156.6	231.9	327.5	419.6	660.3	1064.2	1554.0
ΔH_f in J/g	28.5	60.1	23.0	107.5	397.0	63.7	162.0
Order no	00 119 442	51 140 621	00 650 013	00 119 441	51 119 701	51 140 816	51 140 817

www.mt.com/ta-crucibles

10. For More Information

Outstanding Services
METTLER TOLEDO offers you valuable support and services to keep you informed about new developments and help you expand your knowledge and expertise, including:

News on Thermal Analysis
Informs you about new products, applications and events.
- **www.mt.com/ta-news**
- **www.mt.com/ta-app**
- **www.mt.com/ta-knowledge**

Handbooks
Written for thermal analysis users with background information, theory and practice, useful tables of material properties and many interesting applications.
- **www.mt.com/ta-handbooks**

Tutorial
The Tutorial Kit handbook with twenty-two well-chosen application examples and the corresponding test substances provides an excellent introduction to thermal analysis techniques and is ideal for self-study.

Title	Order number
Tutorial Kit (handbook only)	30281946
Tutorial Kit (handbook and samples)	30249170

- **www.mt.com/ta-handbooks**

Videos
Our technical videos explain complex issues concerning thermal analysis instrumentation and the STARe software – whether it's sample preparation, installation, creating experiments or evaluating measurement results.
- **www.mt.com/ta-videos**

UserCom
Our popular, biannual technical customer magazine, where users and specialists publish applications from different fields.
- **www.mt.com/ta-usercoms**

Applications
If you have a specific application question, you may find the answer in the application database.
- **www.mt.com/ta-applications**

Webinars
We offer web-based seminars (webinars) on different topics. After the presentation, you will have the opportunity to discuss any points of interest with specialists or with other participants.
- **www.mt.com/ta-webinars** (Live Webinars)
- **www.mt.com/ta-ondemand** (On Demand Webinars)

Training
Classroom training is still one of the most effective ways to learn. Our User Training Courses will help you get the most out of your equipment. We offer a variety of one-day theory and hands-on courses aimed at familiarizing you with our thermal analysis systems and their applications.
- **www.mt.com/ta-training** (Classroom)
- **www.mt.com/ta-etraining** (Web-based)

Overview of METTLER TOLEDO
Thermal Analysis Application Handbooks

The following application handbooks are available and can be purchased:
www.mt.com/ta-handbooks

Introductory Handbooks	Language	Order number	Details
Thermal Analysis in Practice Volume 1 Fundamental Aspects (350 pages)	English	51725244	
Thermal Analysis in Practice Volume 2 Tips and Hints (48 pages)	English	30306885	
Thermal Analysis in Practice Volume 3 Tutorial Examples (92 pages)	English	30281946	Handbook and Tutorial samples 30249170
Thermal Analysis in Practice Volume 4 Validation (280 pages)	English	51725141	
Thermal Analysis in Practice Volume 5 Evolved Gas Analysis (40 pages)	English	30748024	

Applications Handbooks	Language	Order number	Details
Thermal Analysis of Elastomers Volumes 1 and 2 Collected Applications (290 pages)	English	51725061 51725057 51725058	Volumes 1 and 2 Volume 1 Volume 2
Thermal Analysis of Thermoplastics Collected Applications (154 pages)	English	51725002	
Thermal Analysis of Thermosets Volumes 1 and 2 Collected Applications (320 pages)	English	51725069 51725067 51725068	Volumes 1 and 2 Volume 1 Volume 2
Thermal Analysis of Pharmaceuticals Collected Applications (104 pages)	English	51725006	
Thermal Analysis of Food Collected Applications (68 pages)	English	51725004	
Evolved Gas Analysis Collected Applications (216 pages)	English	51725056	
Thermal Analysis of Polymers Selected Applications (40 pages)	English	30076210	

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