Waters™ | TA Instruments

ANALYTICAL SOLUTIONS FOR LITHIUM-ION BATTERY MATERIAL CHARACTERIZATION

SUPERCHARGING BATTERY MATERIAL CHARACTERIZATION FOR BETTER PERFORMING AND SAFER BATTERIES

Unlocking the full potential of lithium-ion batteries through material characterization

Greenhouse gas emissions such as carbon dioxide (CO_2) are the primary mitigation targets of the 2015 Paris Agreement. There are several mitigation strategies for achieving net-zero carbon emissions including more efficient transportation, adoption of renewable energy, and greater energy efficiency in homes and offices. One way to improve the efficiency of transportation, industrial equipment, and consumer electronics is by deploying lithium-ion battery technology.

Since Sony's early introduction of lithium-ion batteries in 1991 for consumer electronics, lithium-ion batteries have experienced tremendous advancements in energy efficiency, power output, and safety leading to the adoption of the battery technology in transportation and energy storage. Today, lithium-ion batteries offer many advantages over other high-quality rechargeable battery technologies such as nickel-cadmium (Ni-Cd) or nickel-metal-hydride (Ni-MH) including one of the highest energy densities of any battery technology; the ability to deliver large amounts of current to high-power applications; and the fact that lithium-ion batteries do not require routine maintenance to maintain their battery life. As a result of these performance advantages, lithium-ion battery technology dominates the battery market.

Due to the significant importance of lithium-ion battery technology, the 2019 Nobel Prize in Chemistry was awarded to John B. Goodenough, M. Stanley Whittingham, and Akira Yoshino for their contribution to the development of lithium-ion batteries. In Yoshino-san's Nobel acceptance speech, he stated that the: "Lithium-ion battery is expected to create the sustainable society […]." Indeed, the rapid adoption of lithium-ion battery technology in the automotive and consumer electronics markets in recent years seems to support Yoshino-san's vision. At the same time, the Nobel Laurates were very clear in their acceptance speeches that lithium-ion battery technology still requires more research in the areas of – cost, energy, power output, cycle-life, safety, and environmental impact – if the technology is to achieve its full potential. This document seeks to illustrate how Waters | TA Instruments can support R&D in new battery material and technology development by providing solutions for analytical characterization and testing.

Waters | TA Instruments understands the material characterization needs of lithium-ion battery developers and offers thermal analysis, microcalorimetry, rheology, liquid chromatography and mass spectrometry solutions to help battery researchers, formulators, and production specialists develop better performing and safer batteries.

AN OVERVIEW OF LITHIUM-ION BATTERY TECHNOLOGY AND MATERIAL CHARACTERIZATION

A lithium-ion battery is comprised of four main components – cathode, anode, separator, and electrolyte. In a working battery, lithium ions flow from the anode to the cathode during discharge. The lithium-ions flow in the reverse direction during recharging. Each individual battery cell outputs only a limited amount of energy and is often combined with other cells to form battery packs. Battery packs can in turn be combined to form battery modules for energy storage applications that require higher amounts of energy output such as electric vehicles and grid storage. The materials comprising the cathode, anode, separator, and electrolyte together help define a battery's run time, safety, cycle life, power, energy density, and costs. Hence, an analytical characterization of the materials comprising the main battery components for thermal, rheological, and molecular properties can lead to better performing and safer batteries. Tables 1 and 2 illustrate some of the areas where Waters | TA Instruments analytical solutions can provide insight into the battery components and materials.

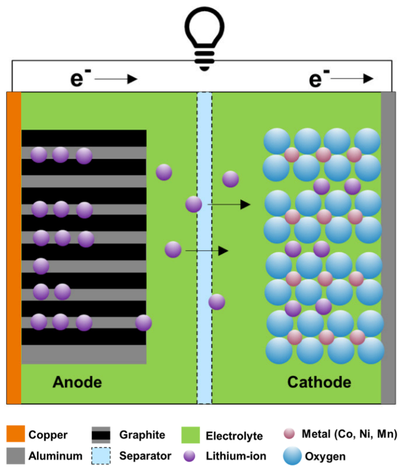


Figure 1. Schematic of a lithium-ion battery. The four main parts of a lithium-ion battery are the cathode, anode, electrolyte, and separator.

Application Areas						
	Battery Components					
Technique	Anode/ Cathode	Separator	Electrolyte	Performance & Safety	Raw Materials	Battery Cell
TGA	•	•	•	•	•	
DSC	•	•	•	•	•	
SDT	•	•	•	•	•	
TGA-EGA	•	•	•	•	•	
TMA		•		•		
DMA		•		•		•
IMC				•		•
Rheology	•		•	•	•	
HRMS		•	•	•	•	
FLASH	•			•		•

Table 1. A mapping of where materials characterization techniques can provide insights to the four main components, battery cell, and application areas of a lithium-ion battery.

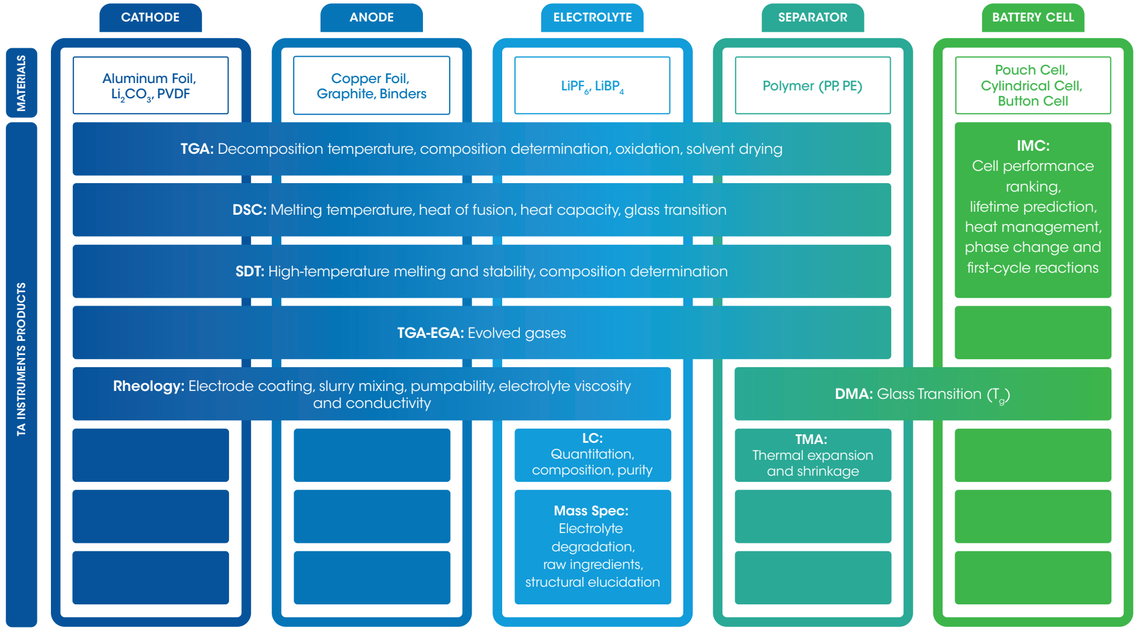


Table 2. Parameter insights provided by material characterization techniques of the four main components of a lithium-ion battery and the whole cell.

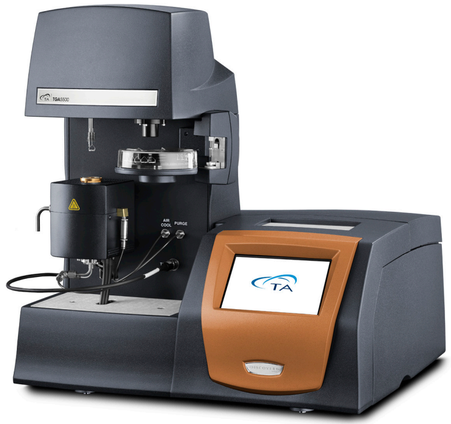
AN OVERVIEW OF OUR BATTERY MATERIAL CHARACTERIZATION SOLUTIONS

Battery thermal analysis improves lifetime, performance, and safety

A lithium-ion battery operates in an environment that constantly changes with regards to temperature. Some temperature changes are inherent to the electrochemical reactions occurring inside the battery while others arise from the battery's ambient working environment. Hence, temperature influences many factors important to the performance of a lithium-ion battery such as battery lifetime, energy density, power output, and safety. Due to the critical nature of understanding how battery materials respond to heat, the analytical suite of thermal analysis techniques play an important role in battery development. The following thermal analysis techniques provide key insights into lithium-ion battery material development:

Thermogravimetric Analysis (TGA):

Programmatically heats a sample material while measuring the material's mass change with a highly sensitive analytical balance. As a material is heated, cooled, or held constant, the mass of the sample may change. Loss of mass indicates possible decomposition or vaporization, while a gain in mass indicates possible oxidation, sorption or that the material is reacting with its gaseous surroundings. Thermal and oxidative stability of materials are critical properties examined by TGA. In battery research, TGA can provide insights into the temperatures at which battery materials start to degrade so that proper material selection can be achieved resulting in high performing and long-lasting batteries.



Thermogravimetric Analysis and Evolved Gas Analysis (TGA-EGA):

The connection, or hyphenation, of spectrometers to TGA units is common. They allow for the chemical analysis of gases that evolve from samples during TGA experiments. The most popular hyphenated spectrometers are mass spectrometers (MS), Fourier-transform infrared spectrometers (FTIR) and gas chromatograph-mass spectrometers (GC-MS). In battery research, understanding what, if any, chemical components are released during production or use can aid in better material selection, design, or additive modification. Impurity detections and failure analyses (e.g. thermal runaway) also benefit from off-gas analysis. As an example, detection of oxygen is quite common in battery research and a mass spectrometer is required for this.

AN OVERVIEW OF OUR BATTERY MATERIAL CHARACTERIZATION SOLUTIONS

Differential Scanning Calorimetry (DSC):

DSC measures the heat absorbed or released when a sample material is heated, cooled, or held isothermal. The heat flow is determined by comparing the heat flow difference between a sample material and a reference. DSC provides insights into the battery material's heat capacity, melting point and phase transitions such as crystallization behavior or glass transition. This can aid in quality control such as confirming whether a polyethylene batch is similar to the previous batch and detecting critical phase transitions that may influence battery operation.

Simultaneous DSC-TGA (SDT):

Combines the techniques of DSC-TGA together so that battery researchers can measure heat flow and weight change data with a single instrument. This combination allows battery researchers to understand battery phase transitions, such as melting points, crystallization and glass transitions, and material thermal stability. Simultaneous instruments can also be hyphenated with off-gas spectrometers.

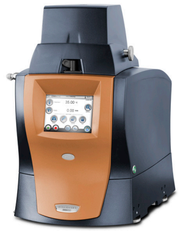
AN OVERVIEW OF OUR BATTERY MATERIAL CHARACTERIZATION SOLUTIONS

Thermomechanical Analyzer (TMA):

A TMA measures expansion or contraction of a material under temperature ramping or isothermal conditions using a variety of sample probes. It is associated with the measurement of softening points, glass transitions, and coefficient of thermal expansion (CTE). One of the applications of TMA within battery research is to study the barrier material's dimensional stability.

Dynamic Mechanical Analyzer (DMA):

A Dynamic Mechanical Analyzer (DMA) measures the mechanical properties of solids as a function of temperature, time, and/or humidity. These measurements are routinely used to characterize thermal events such as the glass transition, crystallization, curing, and aging, especially in polymeric materials. The measurements can then be used by engineers and scientists to develop materials with the right balance of strength, flexibility and durability when designing lightweight batteries with improved safety and longer cycle life over a wide range of operating conditions.



Laser/Light Flash Analysis:

The transient measurement technique of Laser/Light Flash provides the material properties of thermal diffusivity and thermal conductivity or characteristics of the heat transport within a material. Heat within a battery cell is generated while in use, during charging, and potentially during storage. The proper management of that heat will allow all battery components to remain within an appropriate operating temperature range that reduces the risk of thermal runaway and optimizes cell efficiency and product lifetime.

Rheometer:

Rheology is the study of the flow and deformation of materials. A rheometer is a precision instrument that applies deformations in a pre-programmed manner and measures the material's resistance in terms of its viscosity and modulus. The slurries used in the production of electrodes are a mix of solid particles, binder and solvent undergoing a range of deformations at different stages of the manufacturing process such as storage, mixing, coating and drying. These slurries therefore need to have a specific rheological profile to form uniform, defect-free coatings required for production of consistent, high-quality electrodes with high batch-to-batch repeatability and low scrap rates.

Isothermal Microcalorimetry (IMC):

Isothermal Microcalorimetry (IMC) is a non-specific and non-destructive technique for measuring the smallest reactions in a material during a physicochemical process. This is done by measuring the heat flow from the sample at a constant temperature. In battery research, isothermal calorimetry of li-ion cells covers three main areas of interest. The first is the thermal output of a cell from the point of view of heat management. The second is the understanding of structural evolutions in active materials as evidenced by entropy changes. The third is the isolation of heat from parasitic reaction to rank the performance of cells. Evaluations of pouch, coin, pacemaker, cell phone, and cylindrical batteries can be conducted under passive storage conditions or in tandem with a battery cycler.

AN OVERVIEW OF OUR BATTERY MATERIAL CHARACTERIZATION SOLUTIONS

High-resolution mass spectrometry (HRMS) and liquid chromatography (LC):

The intrinsic performance and safety of lithium-ion batteries depend on an analytical understanding of the electrolyte, additive raw materials and their chemical degradation. While additives make up approximately only 5% by volume or weight of the electrolyte solution, they play a key role in facilitating the formation of a solid-electrolyte interface, reducing gas generation, improving long-term cycling, enhancing thermal stability, and improving battery safety. Liquid and gas chromatography (LC and GC) combined with mass spectrometry provide key insights by characterizing electrolyte raw materials and chemical degradation. Analyzing these chemical components can be challenging with only a GC or LC technique since some molecules are volatile while others are non-volatile as well as polar and non-polar. Often GC and LC are used as complementary separation technologies to capture a wide range of compound classes with various volatilities and polarities. High-resolution mass spectrometry (HRMS) hyphenated to Ultra Performance Liquid Chromatography (UPLC) and GC separation technologies deliver molecular insight over a broad volatile and non-volatile chemical space to minimize loss of critical information.

High-Resolution Mass Spectrometry (HRMS):

A mass spectrometry technique that facilitates structural elucidation of molecular species by delivering high resolution accurate mass measurements of both the molecular and fragment ions (i.e., a molecular fingerprint). In HRMS, the accurate mass measurements are used to determine the elemental composition of an unknown chemical which can then be used to search structural databases (such as ChemSpider, PubChem etc.) to aid structural elucidation and ultimately the chemical annotation of a compound. For example, an elemental composition of $C_3H_3FO_3$ along with molecular fragmentation would return fluoroethyl carbonate (FEC) in a database search. In battery applications, the fine chemicals can be either volatile or non-volatile, so HRMS is hyphenated to a LC separation system for non-volatile chemical components and GC separation system for volatile organic components. Understanding electrolytes, additives, and their degradation products can lead to better performing, longer lasting, and safer batteries.

Ultra-Performance Liquid Chromatography (UPLC):

A liquid chromatographic technique for separating mixtures of non-volatile chemical components of a sample so that they are easier to detect by mass spectrometry and UV-detection. The UPLC mode of liquid chromatography exhibits increased resolution, speed, and sensitivity over traditional high-performance liquid chromatography (HPLC). Separating battery mixtures with chromatography aids battery researchers by simplifying the complex mixture of electrolytes, additives, and degradation products so that chemical identification and quantitation are easier to achieve.

Atmospheric Pressure Gas Chromatography (APGC):

A gas chromatographic technique for separating mixtures of gas-phase chemical components so that they are easier to detect by mass spectrometry. Traditional GC-MS utilizes electron ionization (EI) in a vacuum environment to ionize the chemical components prior to the analysis by mass spectrometry, but this technique leads to excessive fragmentation of the molecular ion of chemicals analyzed, making the identification difficult. Instead, the APGC is a soft chemical ionization performed at atmospheric pressure that utilizes a gentler ionization regime and enables almost intact molecular ion detection allowing for both structural elucidation and chemical quantitation of compounds separated by GC capillary column. Finally, the gas chromatography aids battery researchers by simplifying the complex mixture of electrolytes, additives, and degradation products so that chemical identification and quantitation are easier to achieve.

BATTERY MATERIAL CHARACTERIZATION APPLICATION EXAMPLES

TGA thermal stability and compositional amount of anode materials

Electrodes require binders and additives to ensure proper adhesion to the metal collector. For the anode electrode, carboxymethyl cellulose (CMC) is a common binder and styrene-butadiene rubber (SBR) is a common additive that provides flexibility. TGA measures the thermal degradation temperatures and composition of CMC, SBR and graphite active anode materials. The high sensitivity Tru-Mass Balance of the Discovery TGA ensures accurate measurement of each component in the electrode. For this test, the sample was loaded directly on a TGA platinum pan without any sample preparation.

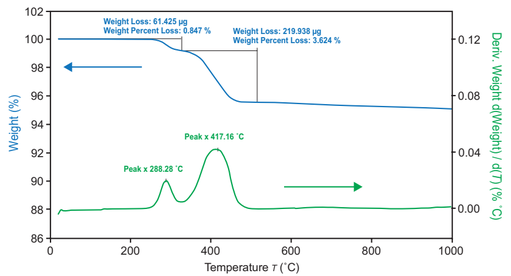


Figure 2. TGA curve of graphite anode in a TA Instruments Discovery TGA. The sample was heated to 1000 °C at 10 °C/min under inert conditions. The graphite anode materials contained CMC and SBR as binder and additive respectively. Thermogravimetric analysis shows that the graphite anode material was stable until approximately 288 and 417 °C resulting in small weight percent losses of 0.8% and 3.6%, respectively related to the CMC and SBR content.

Conclusion:

TGA measured the thermal stability and quantified the amount of binder and additive in the anode electrode. TGA can also provide quality control of the materials to ensure the same amount of active material, binder and additive are in each batch of the electrode. Insufficient amounts of binder will affect the active anode material's adhesion to the metal collector; too much binder will reduce the active material's content and affect the electrochemical reaction. Optimization of binder/additive ratios is essential for optimal battery performance and improvement of battery life.

SDT of Lithium Carbonate (Li_2CO_3) cathode precursor material

Lithium Carbonate (Li_2CO_3) is often used as a precursor for cathode materials in lithium-ion batteries. High temperature sintering processes are required, and the sintering temperature will impact the lithium salt residue, thus affecting the battery efficiency and cycle performance. The high-temperature thermal stability and phase transitions can be measured by the Discovery SDT 650. Evolved gas analysis can be used to identify off-gases with direct measurement during heating of the SDT. The sample was loaded directly on SDT alumina pan without any additional sample preparation.

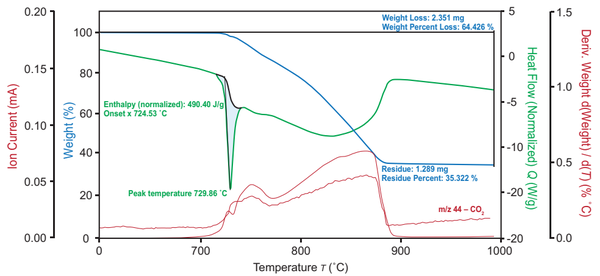


Figure 3. SDT measurement of both weight and heat flow signals of Li_2CO_3 from 25 °C to 1000 °C at 10 °C/min heating ramp. The measured onset of melting is detected at 724 °C with a heat of fusion of 490 J/g. The weight signal indicates a small amount of weight loss during melting which has been seen by other researchers as well. Mass spectrometer data is also overlayed in the graph and indicates that CO_2 (m/z 44) is released during the melting and decomposition.

Conclusion:

The SDT measured the thermal stability and melt phase transition of Li_2CO_3. Mass spectrometry detected CO_2 as an evolved gas during the heating process. A residue of approximately 35% was recorded. Knowing that some Li_2CO_3 remains unreacted during cathode production can influence battery performance.

DSC thermal stability and heat of reaction of electrolyte during thermal runaway

The thermal stability of lithium-ion batteries is a major concern in battery usage. Heating of the battery components due to either thermal or mechanical failure can cause thermal runaway reactions and lead to catastrophic failure of the lithium-ion battery. DSC can be used to measure small-scale thermal runaway reactions. In this example, reactions occurring in the electrolyte were measured using high-pressure capsules. The sample was loaded and sealed into the high-pressure capsule in a glove box. The DSC run was performed with nitrogen purge.

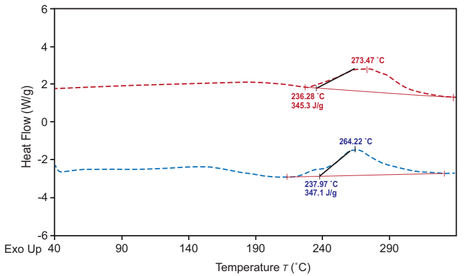


Figure 4. DSC curve of electrolyte measuring the onset, peak temperature, and heat of reaction during exothermic decomposition, or equivalently thermal runaway reaction. The onset temperature indicated the temperature runaway start, and the heat of reaction indicated the total heat release during the runaway reaction, which are two important parameters for battery safety evaluation.

Conclusion:

The onset temperature and heat of reaction from DSC measurements can be used to ensure that the battery thermal management system maintains the battery's temperature well below the onset temperature to prevent degradation and ensure battery safety.

TMA thermal expansion of battery separator to identify the orientation effect

In a lithium-ion battery, the separator, a permeable microporous membrane, is an essential component that prevents physical contact between the two electrodes, thereby preventing short circuits, but still allowing lithium ion transfer, which is essential to the function of the battery. The Discovery TMA 450 can measure the dimension change and the potential failure temperature of the separator. The high sensitivity of the dimension change measurement can detect both thermal expansion and shrinkage in different separator orientations. The sample was cut into 24 mm length and 2 mm uniform width and loaded on film and fiber probe. The temperature was ramped at 3 °C/min from -70 °C to 200 °C under nitrogen purge.

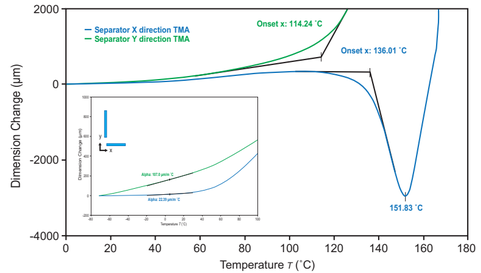


Figure 5. TMA measurements of the dimension change and thermal expansion coefficient of the separator in two different directions with TMA 450 film/fiber probe were recorded. The separator in the X-direction showed thermal shrinkage onset at 136 °C while no thermal shrinkage was observed in the Y-direction. The CTE value in X-direction is 22.39 µm/m °C while CTE value in Y-direction is 107 µm/m °C. The significant difference measured in the thermal expansion coefficient in the two directions indicates an orientation effect in the separator.

Conclusion:

The TMA 450 measured the thermal expansion of the separator and identified an orientation effect in both the X and Y directions. It is important to understand the orientation effect to prevent undesired expansion or shrinkage that can lead to mechanical failure in batteries.

BATTERY MATERIAL CHARACTERIZATION APPLICATION EXAMPLES

DMA mechanical properties of separator

The mechanical properties of any polymer are closely related to its structure and morphology. These properties can be easily measured using TA Instruments' line of DMA solutions as a function of temperature, time, and/or humidity to provide valuable information about the polymer structure and gain critical information of material behavior under a wide range of conditions. The key material properties obtained from a DMA experiment are shown in the table below:

Measurement	Definition	Significance	
Complex modulus (E*)	Total resistance to deformation	Higher E* indicates higher overall rigidity.	Characterize thermal events such as glass transition, crystallization, curing, aging.
Elastic or storage modulus (E')	Elasticity of the material	Higher E' indicates better mechanical integrity under load and deformation.	
Viscous or loss modulus (E")	Energy dissipated due to damping	Higher E" is desirable for higher toughness but frictional heat can reduce the material's dimensional stability over time	
Tan delta (tan δ)	Overall damping given by E"/E'	Higher damping is desirable for decreasing unwanted vibrations and increasing toughness.	

Table 3. Material properties obtained from DMA experiments

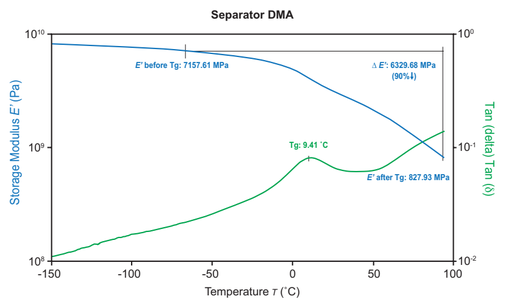


Figure 6. DMA of separator film in x-direction. Note the glass transition, Tg, at 9.41 °C (green curve) and a 90% drop in E' (blue curve) as the material undergoes a glass transition.

In a lithium-ion battery, the separator is a polymeric material that prevents physical contact between the two electrodes thereby preventing short circuits. It is critical that the mechanical properties and thermal events of the separator are thoroughly characterized using a DMA to ensure reliable isolation of the electrodes. Figure 6 shows a representative DMA thermogram of a battery separator film obtained using a Discovery DMA 850. The separator was cut into 15 mm length and 5.3 mm width and loaded a tension clamp. The oscillation temperature method utilized a ramp of 5 °C/min from -150 to 100 °C during mechanical oscillations of 20 µm amplitude at a frequency of 1 Hz.

Most separator films are polymeric and will exhibit a glass transition. The glass transition temperature (Tg) can be measured with various techniques, but DMA is by far the most sensitive. As shown in Figure 6, one of the ways to measure Tg using the DMA is using the peak of the tan δ curve (green). This measurement can serve as an important characterization metric for the separator, both in R&D labs for accelerating material development and in QC labs to ensure batch-to-batch repeatability.

The data in Figure 6 also shows that E' (blue curve) is reduced by almost 90% as the material undergoes a glass transition. Interestingly, the separator exhibits significant anisotropy in E' and E" when measured along two mutually perpendicular directions. This is useful information in determining the most appropriate orientation of the separator as it gets assembled into the battery.

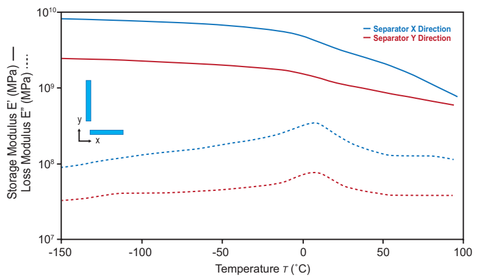


Figure 7. DMA of separator film in x- (blue) and y- (red) direction. The storage (E') and loss (E") moduli of the material are significantly different when measured along different directions.

Conclusion:

TA Instruments' DMAs allow users to accurately determine the modulus and Tg of the various solid components in a battery. These measurements can be used as a critical QC metric to ensure batch-to-batch repeatability as well as to define suitable operating temperature limits for the battery. The DMA can also be used to quantify the mechanical anisotropy of solid materials such as those observed in separator films. Collectively, these measurements provide critical information for design of lightweight batteries with the right balance of performance and safety.

Rheology to determine battery slurry viscosity

Electrode slurries are complex, non-Newtonian fluids that are a mixture of solid particles and polymeric binder in a solvent. They are subjected to a wide range of changing shear deformation rates at different stages of the electrode manufacturing process. The ideal slurry has a low viscosity for optimum mixing and coating (high shear rates), but a high enough viscosity for good levelling during drying and to minimize particle settling and agglomeration during storage (low shear rates).

Figure 8 shows the viscosity of an anode slurry under different shear rates on a TA Instruments Discovery Hybrid Rheometer (DHR). The sample was mixed before loading on the rheometer. The measurements were performed from 0.01 to 1000 s^{-1} at 25 °C using a 40mm parallel plate with solvent trap.

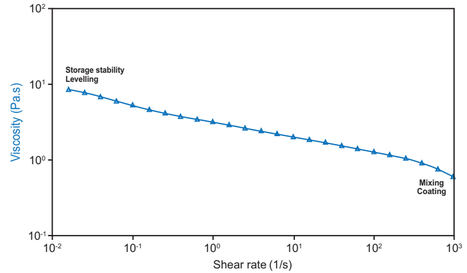


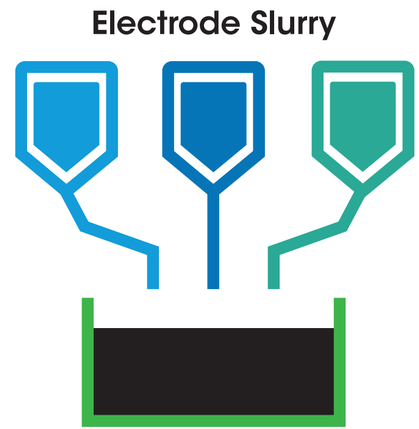
Figure 8. Viscosity vs shear rate of an LIB electrode slurry over 5 decades of shear rates. The slurry exhibits shear-thinning behavior with the viscosity decreasing with increasing shear rate.

The data in Figure 8 shows the viscosity of the slurry as measured over 5 decades of shear rates. The Advanced Drag Cup Motor technology of the DHR allows for the measurement to be performed in less than 20 minutes with a direct readout of the viscosity.

Initially, under low shear rates which simulate storage conditions, the viscosity is high to prevent settling and reduce the energy of mixing prior to coating. The low torque sensitivity of the DHR ensures accurate, repeatable measurements in this low shear rate region, providing greater confidence in the data.

As the shear rate increases, the slurry exhibits a typical shear-thinning behavior where the viscosity of the slurry decreases by almost a decade. This is important to ensure that the slurries can be mixed efficiently and have the right amount of flowability when applied onto the substrate.

The slurry rheology continues to play a critical role in the film-formation stage (a low shear rate process) where the rate of viscosity increase (known as thixotropy) ensures the levelling of the coatings. This is especially critical when electrodes with high coat weight for higher energy density are desired.



Conclusion:

Rheological measurements provide researchers with a reliable analytical tool for developing new formulations with improved performance and manufacturability. Understanding and controlling the slurry rheology helps in not only choosing an appropriate manufacturing process (roll-to-roll coating, slot-die coating, etc.) but also maximizes the production output to produce consistent, defect-free films of uniform coat weight and good contact with the electrode. These measurements can be used both in R&D and manufacturing settings owing to the DHR's highly intuitive user-interface that reduces operator training times and increases productivity.

BATTERY MATERIAL CHARACTERIZATION APPLICATION EXAMPLES

Thermal conductivity to determine in-plane thermal diffusivity of copper thin-films

Thermal conductivity is a very important parameter needed for designing a reliable battery thermal management system (TMS). The flash method measures thermal diffusivity that is related to thermal conductivity by specific heat and density. Flash diffusivity provides the most versatile, effective, accurate thermal diffusivity and conductivity measurements. Copper thin-film is used as anode collector and its in-plane thermal diffusivity is measured with DXF 200+. A copper thin-film sample with 25 µm thickness was loaded on in-plane fixture and measured at 25˚C.

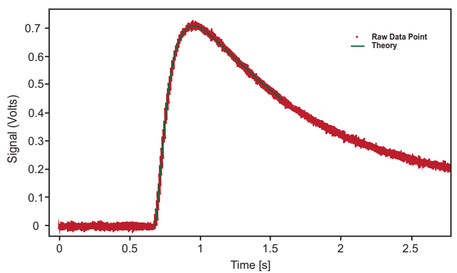


Figure 9. Thermogram of the copper thin film (red) fitted with Fin theoretical model (green) in excellent agreement. The thermal diffusivity was determined as 1.17 cm^2/s.

The DXF200+ can accurately measure the in-plane thermal diffusivity of micron-level thin film samples. The measurement and analysis are simple, direct, and reliable.

Conclusion:

The thermal diffusivity and thermal conductivity results collected using light flash techniques help researchers understand the effectiveness of certain battery components (electrodes, coatings, and separators) to dissipate heat away from the cell thus helping to improve battery performance and lifetime.

Isothermal microcalorimetric determination of parasitic power of an 18650 Li-cell.

The determination of the heat from parasitic reactions is useful for ranking cell chemistries and electrolyte chemistries. This approach has been successful in ranking electrolyte chemistries for various cathode active materials (LCO, NMC, NCA, LFP) and anode active materials (natural and artificial graphite, silicon).

Sample: 18650 Li-Cell

Measurement: Parasitic heat determination

Instrument: TAM IV Micro XL

Method: IMC-Cycler testing (Constant temperature (20 ˚C and 30 ˚C) with charge cycling the cell's full range (e.g. 3V to 4.2V) at C/10 for 10 cycles.

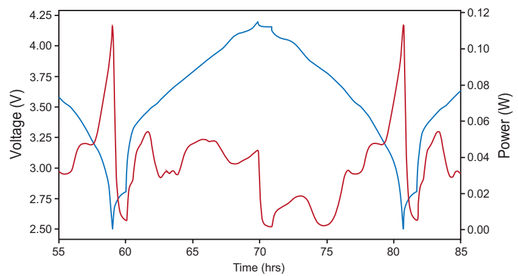


Figure 10. Raw data of voltage (blue) and power (red), versus time for an 18650-battery cell, cycled at C/10 in the TAM IV isothermal microcalorimeter.

Conclusion:

Determination of parasitic reactions for a battery cell can be calculated from the extracted voltage and heat flow data. This approach has been successfully used to allow comparison of different cell chemistries and sizes. The TAM IV microcalorimeter is used to rapidly rank the electrolyte chemistries for various cathode and anode active materials (natural and artificial graphite, silicon).

HRMS analysis of electrolyte and additive to understand degradation during charge cycles

HRMS hyphenated with APGC and LC can provide structural elucidation information for electrolytes and electrolyte additives as they undergo degradation during lithium-ion battery charge and discharge cycles. Advanced statistical methods such as principal component analysis (PCA) can quickly identify significant differences between battery charge/discharge cycles and isolate chemical components responsible for these differences. Subsequent structural elucidation by HRMS can indicate the types of structural degradation that occurs in the electrolytes and electrolyte additives. By understanding molecular degradation of the electrolyte and additives, battery researchers can develop better performing and safer batteries.

Sample	Electrolyte				
Instrument	Waters Xevo G2-XS QTof				
Inlet	ACQUITY I-Class UPLC				
Sample preparation	Electrolyte solution samples were extracted with dimethyl carbonate from batteries that had undergone charge/discharge.				
LC parameters	Column: HSS T3 2.1 x 100, 1.7 µm				
	Injection volume: 1.0 µL				
	Mobile phase A: 5 mM ammonium formate in water				
	Mobile phase B: MeOH				
Gradient		Flow rate (mL/min)	A	B	Curve
	initial	0.4	95	5	6
	10	0.4	5	95	6
	15	0.4	5	95	6
	15.5	0.4	95	5	6

Table 4. UPLC-HRMS experimental conditions

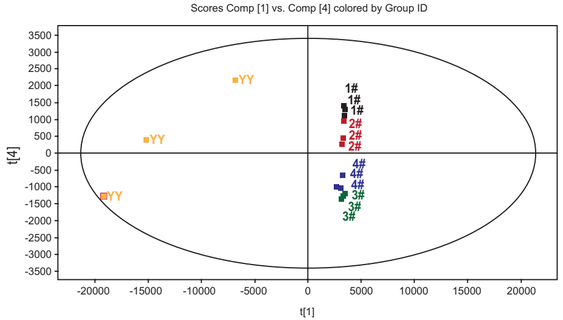


Figure 11. Principal component analysis (PCA) results comparing an electrolyte solution prior to the discharge-cycle (YY) to triplicate analyses of the samples that underwent 1, 40, 180 and 200 charge cycles (1#, 2#, 3#, 4#).

Conclusion:

The PCA results shown in the figure graphically illustrate statistical similarities and differences in the electrolyte samples as they underwent various charge / discharge cycles. The analysis was performed by HRMS combined with LC to study the non-volatile chemical components. The PCA groupings enable battery researchers to leverage the structural elucidation capabilities of mass spectrometry and quantitative capabilities of liquid chromatography to understand how electrolytes and additives chemically degrade from a molecular perspective. An understanding of molecular degradation pathways enables battery researchers to formulate electrolyte solvents that yield safer and better performing batteries.

A COMPREHENSIVE THERMAL ANALYSIS AND RHEOLOGY SOFTWARE SOLUTION

Our instruments' robust software package uses innovative technology for instrument control, data collection, data analysis, and reporting for thermal analysis and rheology. The intuitive user interface allows you to seemlessly program experiments and move easily between processing experiments, viewing and analyzing data.

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Reports: Easily prepare your data for presentation using the TRIOS Report feature. Drag and drop elements, corresponding to various data file components, can be inserted into a familiar word processing workspace, allowing for clear and concise formatting of all experimental parameters. Once created, simply apply the complete format to any data file, automating analysis and relevant details to communicate your findings.

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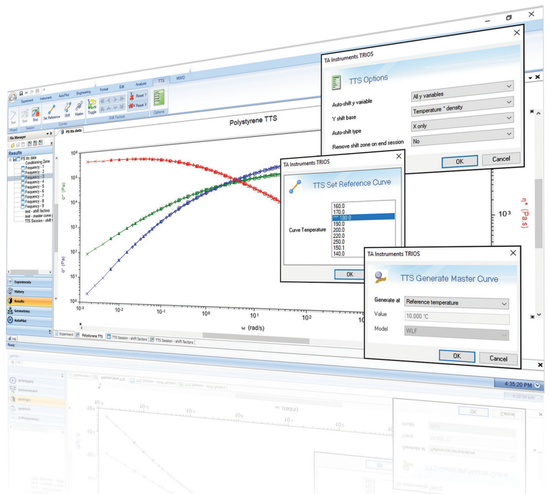

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