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

Greenhouse gas emissions such as carbon dioxide (CO2) 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 contributions 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 Laureates 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 characterisation 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.

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

<table>
<thead>
<tr>
<th>Technique</th>
<th>Anode/ Cathode</th>
<th>Separator</th>
<th>Electrolyte</th>
<th>Performance &amp; Safety</th>
<th>Raw Materials</th>
<th>Battery Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGA</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>DSC</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>SDT</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>TGA-EGA</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>TMA</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>DMA</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>IMC</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>Rheology</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>HRMS</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>FLASH</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
</tbody>
</table>

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

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

<table>
<thead>
<tr>
<th>Technique</th>
<th>Anode/ Cathode</th>
<th>Separator</th>
<th>Electrolyte</th>
<th>Performance &amp; Safety</th>
<th>Raw Materials</th>
<th>Battery Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGA</td>
<td>Decomposition temperature, composition determination, oxidation, solvent drying</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>DSC</td>
<td>Melting temperature, heat of fusion, heat capacity, glass transition</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>SDT</td>
<td>High-temperature melting and stability, composition determination</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>TGA-EGA</td>
<td>Evolved gases</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>TMA</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>DMA</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>IMC</td>
<td>Cell performance ranking, lifetime prediction, heat management, phase change and first-cycle reactions</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>Rheology</td>
<td>Electrode coating, slurry mixing, pumpability, electrolyte viscosity and conductivity</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>HRMS</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>FLASH</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
</tbody>
</table>

[Diagram showing the schematic of a lithium-ion battery and the mapping of where characterisation techniques can provide insights to the four main components, battery cell, and application areas of a lithium-ion battery.]

Table 3. Parameters inferred from material characterisation techniques of the four main components of an lithium-ion battery and the whole cell.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Anode/ Cathode</th>
<th>Separator</th>
<th>Electrolyte</th>
<th>Performance &amp; Safety</th>
<th>Raw Materials</th>
<th>Battery Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGA</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>DSC</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>SDT</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>TGA-EGA</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>TMA</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>DMA</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>IMC</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>Rheology</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>HRMS</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
<tr>
<td>FLASH</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
</tr>
</tbody>
</table>
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.
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 this 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 to these applied deformations. The parameters 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. It is done by measuring the heat flow from the sample at a constant temperature. In battery research, isothermal calorimetry of lithium-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, in 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
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 polarities 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 C₃H₅FO₃ 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 liquid separation for non-volatile chemical components and GC separation system for volatile organic components.

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 MS/MS. 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 gentle 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.
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, carboxylated polyvinylidene chloride (CMC) is a common binder and styrene-butadiene rubber (SBR) is a common additive that provides flexibility. TGA measures the thermal degradation temperature and composition of CMC and SBR and graphite active anode materials. The high sensitivity of 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 additional sample preparation.

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 in each batch of the electrode. Insignificant amounts of binder will affect this active anode material’s adhesion to the metal collector; too much binder will reduce the active material’s content and affect the electrochemical performance. Optimal mixing ratios are essential for optimal battery performance and improvement of battery life.

SDT of Lithium Carbonate (Li₂CO₃) cathode precursor material

Lithium Carbonate (Li₂CO₃) 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 Li₂CO₃ 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. Eclipsed gas analysis can be used to identify off-gases with direct measurement during heating of the SDT. The sample was loaded directly on an SDT alumina pan without any additional sample preparation.

Conclusion:

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. One DSC run was performed with nitrogen purge.

Conclusion:

TMA thermal expansion of battery separator to identify the orientation effect

TMA measured the thermal stability and identified the orientation effect in the separator. The TMA 450 measured the thermal expansion of the separator and identified an orientation effect in the separator. X-direction showed thermal shrinkage onset at 136°C while no thermal shrinkage was observed in the Y-direction. The sample was cut into 24 mm length and 2 mm uniform width and loaded on the TMA 450. The temperature was ramped at 3°C/minute from -70°C to 200°C under nitrogen purge.

Conclusion:

### BATTERY MATERIAL CHARACTERIZATION APPLICATION EXAMPLES

- **SDT of Lithium Carbonate (Li₂CO₃) cathode precursor material**
  - Lithium Carbonate (Li₂CO₃) 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 Li₂CO₃ 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. Eclipsed gas analysis can be used to identify off-gases with direct measurement during heating of the SDT. The sample was loaded directly on an SDT alumina pan without any additional sample preparation.

- **TMA thermal expansion of battery separator to identify the orientation effect**
  - TMA measured the thermal stability and identified the orientation effect in the separator. The TMA 450 measured the thermal expansion of the separator and identified an orientation effect in the separator. X-direction showed thermal shrinkage onset at 136°C while no thermal shrinkage was observed in the Y-direction. The sample was cut into 24 mm length and 2 mm uniform width and loaded on the TMA 450. The temperature was ramped at 3°C/minute from -70°C to 200°C under nitrogen purge.

- **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. One DSC run was performed with nitrogen purge.

- **Conclusion:**
  - The thermal stability and heat of reaction from DSC measurements can be used to ensure that the battery thermal management system maintains the battery temperature well below the onset temperature to prevent degradation and ensure battery safety.
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 DMA in terms 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:

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Definition</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complex modulus $E'$</td>
<td>Elastic or storage modulus</td>
<td>Overall rigidity, higher $E'$ indicates better mechanical behavior</td>
</tr>
<tr>
<td>Loss modulus $E''$</td>
<td>Elastic or storage modulus</td>
<td>Overall damping given by $E''/E'$</td>
</tr>
<tr>
<td>$E^*$</td>
<td>Viscous or energy dissipated due to deformation</td>
<td>Higher damping is desirable for decreasing unwanted vibrations and increasing toughness.</td>
</tr>
<tr>
<td>Temperature $T$ (°C)</td>
<td></td>
<td>Characterize thermal events such as glass transition, crystallization, curing, aging.</td>
</tr>
</tbody>
</table>

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:

Table: Material properties obtained from DMA experiments

<table>
<thead>
<tr>
<th>Separator X Direction</th>
<th>Storage Modulus $E'$ (MPa)</th>
<th>Loss Modulus $E''$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-150°C</td>
<td>7157.61 MPa</td>
<td>5329.68 MPa</td>
</tr>
<tr>
<td>0°C</td>
<td>827.93 MPa</td>
<td>6329.68 MPa</td>
</tr>
</tbody>
</table>

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 separator is a polymeric material that prevents physical contact between the two electrodes thereby preventing short circuits. It is critical that the separator is highly durable and optically characterized under a wide range of conditions.

Most separator films are polymeric and will exhibit a glass transition. The glass transition temperature $T_g$ can be measured with various techniques, but DMA is a tool for the most sensitive. As shown in Figure 6, one of the ways to measure $T_g$ 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.

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

Conclusion: TA Instruments’ DMAs allow users to accurately determine the modulus and $T_g$ 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 designing lightweight batteries with the tightest possible 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. Collectively, these components are subjected to a wide range of changing shear deformation rates at different stages of the electrode manufacturing process. The ideal slurry has low viscosity for good coating, sufficient viscosity to carry the coating by gravity and high enough viscosity for good levelling during drying and to minimize particle settling and agglomeration during storage (low shear rate).

Figure 7 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 0.1 to 1000 s⁻¹ at 25°C using a 40mm parallel plate with solvent trap.

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 shear sensitivity of the DHR ensures accurate, repeatable measurements in this low shear rate region, providing greater confidence in the data.

The slurry rheology continues to play a critical role in the film-formation stage (a low shear rate process) where the rate of viscosity decrease (known as the slope) ensures the levelling of the coatings. This is especially critical when electrodes with high coating weight are desired. The DHR can be used to quantify the viscosity of the slurry as measured over 5 decades of shear rates.

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 shear sensitivity of the DHR ensures accurate, repeatable measurements in this low shear rate region, providing greater confidence in the data.

As the shear 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 fluidity 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 decrease (known as the slope) ensures the levelling of the coatings. This is especially critical when electrodes with high coating weight are desired. The DHR can be used to quantify 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 shear sensitivity of the DHR ensures accurate, repeatable measurements in this low shear rate region, providing greater confidence in the data.

As the shear 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 fluidity when applied onto the substrate. The ideal coating characteristics are dependent on the slurry rheology, which can be measured using a rheometer. This information is critical for choosing an appropriate manufacturing process (roll-to-roll coating, slot-die coating, etc.) and maximizing the production output while controlling the slurry rheology to produce consistent, defect-free films of uniform coat weight and good contact with the electrode. These measurements can be used in R&D and manufacturing settings using the DHR’s highly intuitive user interface that reduces operator training times and increases productivity.

Conclusions: Rheological measurements provide a reliable and accurate 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 while controlling the slurry rheology to produce consistent, defect-free films of uniform coat weight and good contact with the electrode. These measurements can be used in R&D and manufacturing settings using the DHR’s highly intuitive user interface that reduces operator training times and increases productivity.
Thermal conductivity is a very important parameter needed for designing reliable battery thermal management systems (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 in situ at 25°C. The DXF200+ can accurately measure the in-plane thermal diffusivity of micron-level thin film samples.

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 in situ at 25°C. The DXF200+ can accurately measure the in-plane thermal diffusivity of micron-level thin film samples.

BATTERY MATERIAL CHARACTERIZATION APPLICATION EXAMPLES

ISOThermal Microcalorimetric Determination of Parasitic Power of an 18650 Li-ion 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, LIB) and anode active materials (natural and artificial graphite, silicon).

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 different cell chemistries and sizes. The approach has been successfully used to allow comparison of different cell chemistries and sizes. The TAM IV microcalorimeter is used to rapidly rank different cell chemistries and sizes.

HRMS analysis of Electrolyte and Additive to understand degradation during charge cycles

HRMS hyperpolarized with ARSc and LC can provide structural elucidation information for electrolytes and electrolyte additives as they undergo structural 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 identify 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.

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 grouping enables 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

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.

Analysis:
- Save routine analyses to the Analysis library, then apply them with a single click, streamlining your workflow and increasing productivity. Share these analyses by saving an Analysis Template to ensure the exact parameters are used in collaborative environments.

Control Charts:
- Conveniently store and track analysis results from your data archive in a single file. Detect trends in your data and flag unacceptable results so you can keep your process moving without interruption.

User Models and Variables:
- Define your own analysis models to precisely fit your experimental data within TRIOS. The intuitive interface gives you full control over mathematical functions and adjustable fitting parameters, while TRIOS solves the equation. Save your custom models to quickly apply them to future experiments. Every TRIOS data file contains a standard set of variables based on instrument type. If the required variable isn’t available, quickly create your own using the User Variable feature to obtain the results you require.

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 seamlessly program experiments and move easily between processing experiments, viewing and analyzing data.

Thoughtful features such as automated calibration routines, multiple calibration sets, real-time test method editing, and inter-laboratory data and test method sharing provide unmatched flexibility, while one-click analysis and custom reporting save productivity to new heights.

Our experience with over 10,000 installations has shown that when users are well trained, systems receive routine preventive maintenance, and problems and concerns are addressed promptly, the result is improved instrument performance, increased uptime, and reduced cost of ownership.

The Lifetime Support Plan (LSP) has been designed to make this comprehensive support available for a modest, easily budgeted annual subscription fee, that is predicated on the benefits of uninterrupted coverage initiated at installation and continued for the life of the instrument. Benefits of this plan include:
- Optimized instrument performance
- Well trained users
- Maximized uptime
- Protection from unexpected repair costs
- Easily budgeted operating expenses
- Reduced cost of ownership

This support product is available only for new instruments at the time of purchase, or prior to the end of the warranty period. Once initiated, the LSP is renewable annually to provide uninterrupted coverage for the life of the instrument.

BE ASSURED: CHOOSE TA INSTRUMENTS GLOBAL SERVICES
MORE INFORMATION

www.tainstruments.com/applications/battery-material-testing