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ABSTRACT

Thermal runaway in lithium-ion batteries poses a serious safety hazard. Battery component material characterization can offer key insights early in development that correlate to battery performance and thermal stability. In this work, the thermal degradation of a cathode material was measured as a function of state-of-charge (SOC) using thermogravimetric analysis (TGA). Degradation byproducts were further analyzed in the same experiment with an in-line benchtop mass spectrometer coupled to the instrument (TGA-MS). The evolution and relative abundance of gases, such as oxygen, hydrogen, and carbon monoxide were observed as a function of temperature and mass loss as the cathode degrades. TA Instruments™ TGA Smart-Seal™ Pans were used to keep the samples under inert conditions while testing in a standard ambient environment, eliminating the requirement of placing the TGA in a glovebox when testing atmospherically-sensitive samples. TGA-MS can be utilized to guide formulation choices of new battery material, ultimately contributing to safer and higher-performance lithium-ion batteries.

INTRODUCTION

Lithium-ion batteries (LIBs) are the preferred power source for many portable devices due to their high energy density and long lifespan. Ongoing research aims to improve battery performance through material innovations in all battery components, with a strong focus on cathodes and anodes. The development of new cathode-active materials is primarily aimed at improving energy density, power, and cycle life. Cathodes made with lithium nickel manganese cobalt oxides (NMC) have emerged as a lower-cobalt alternative to lithium cobalt oxide, easing ethical concerns and cutting costs tied to cobalt sourcing. NMC cathodes follow the general formula $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, and their performance is tuned by adjusting the x:y:z ratios. Common variants include NMC 523 (50% Ni, 20% Mn, 30% Co), NMC 622 (60% Ni, 20% Mn, 20% Co), and NMC 811 (80% Ni, 10% Mn, 10% Co). Increasing the nickel content raises energy density while minimizing cobalt usage.

As these new materials are developed, emphasis on enhancing the understanding of key safety considerations remains a critical priority. Overcharging, excessive heat, or internal short circuits are among the conditions that can trigger thermal runaway in LIBs. Material decompositions are predominantly exothermic, and the heat these reactions add to the system will further accelerate the decomposition kinetics. This leads to self-heating behavior observed at the early onset of thermal runaway. The thermal runaway event is highly energetic, releasing particulates, toxic gases, and heat. Evaluating the safety and thermal stability of new materials for LIBs is often delayed until scaling to larger format cells. However, if the formulation is found to be unstable, development must restart at the material level. Conducting earlier phase investigations of LIB component material properties can shorten development time, reduce risk, and build a more comprehensive understanding of cell stability & safety.

One of the characteristic signs of NMC decomposition is the release of oxygen gas. Oxygen is shed from the lattice as NMC transitions from a layered metal oxide to a spinel or cubic rock-salt phase at higher temperatures [1] [2]. Identifying when and if oxygen and other gases evolve from LIB components is key to understanding thermal stability and battery safety. A decomposition pathway which generates oxygen can lead to combustion in an otherwise inert atmosphere. How we respond to, and ultimately contain, a battery fire will be fundamentally affected by the onset temperature and amount of oxygen released during thermal degradation.

The different variants of NMC will also differ in their thermal stability. The thermal stability tends to decrease as the nickel content increases, limiting the practical utility of NMC 811, despite its higher energy density [1]. Another factor influencing the safety profile of NMC 811 is its SOC, which influences the temperature at which thermal runaway begins. Previous work using differential scanning calorimetry (DSC) evaluated electrodes with 0%, 50%, and 100% SOC [3]. The 100% SOC NMC cathode had the earliest onset of thermal runaway and the most energy released through the full thermal ramp during cathode material degradation. Lower SOC cells store less potential energy and pose a reduced thermal hazard, displaying higher temperature onsets of exothermic runaway reactions.

To understand how both SOC and NMC decomposition mechanisms influence thermal stability of the cathode, thermogravimetric analysis (TGA) can be coupled with mass spectrometry (MS). TGA is a key tool in analyzing thermal stability of materials as a function of time, temperature, and atmosphere. TGA traditionally measures weight loss during a heating ramp, capturing the onset of degradation, quantifying total loss of degradation byproducts, and characterizing relative thermal stability between samples.

Degradation byproducts from a TGA experiment can be further studied when a TGA is combined with evolved gas analysis (EGA). Coupling a TGA instrument with a gas-phase spectrographic technique such as MS allows for off-gassed degradation byproducts to be analyzed [4]. Combustion byproducts such as oxygen, water, and carbon dioxide can be directly measured in real-time as they come off the sample during the TGA experiment. The appearance and abundance of those gases can be directly compared and correlated to the weight loss observed during thermal degradation.

Despite its value, this technique is somewhat uncommon with battery materials due to their sensitivity to ambient atmosphere and the requirement of a TGA sample to be run in an open pan within the instrument. Historically, this limitation necessitated placing the entire TGA in a glovebox to maintain sample integrity. One drawback to this workflow is that changes in glovebox pressure can affect the apparent weight signal, meaning a user cannot work in the glovebox for the duration of the measurement. When coupled with the size of the instrument, TGA testing of battery materials usually requires a dedicated glovebox for the instrument.

In this work, the TA Instruments TGA Smart-Seal Pan is used to maintain inert conditions on the benchtop for NMC 811 at various states of charge. A benchtop quadrupole MS was connected to the gas outlet of a Discovery TGA (Figure 1) and evolved mass fragments directly monitored continuously throughout a TGA-MS experiment. The resulting insights into decomposition behavior can enhance understanding of material breakdown and inform safer battery design.

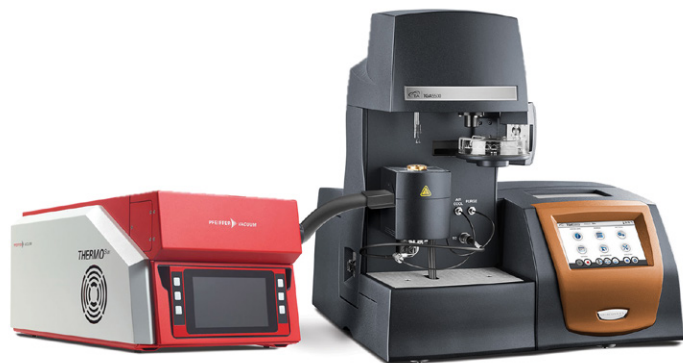


Figure 1. Discovery TGA™ 5500 connected to the ThermoStar™ Mass Spectrometer

EXPERIMENTAL

Powdered NMC 811 cathode samples were prepared by NEI Corporation. Batteries with different SOC were torn down and the electrode was washed with dimethyl carbonate (DMC) to remove electrolyte. The cathode material was then removed from the current collector. Dry cathode powder harvested from batteries at 0%, 50%, and 100% state-of-charge were used in this work. Those samples are identified as 0-SOC, 50-SOC, and 100-SOC, respectively.

The dried NMC 811 was sealed in glass vials under dry, inert atmosphere and stored in a nitrogen-purged glovebox until TGA pan preparation. All TGA sample preparation was done in a glovebox under nitrogen purge. Experiments were performed using TA Instruments TGA Smart-Seal Pans, shown in Figure 2.

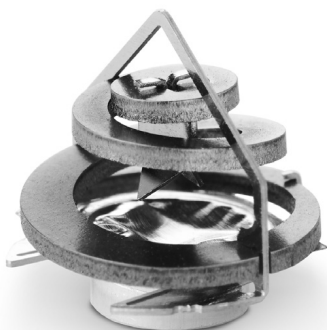


Figure 2. TGA Smart-Seal Pan

These pans allow for an atmospheric-sensitive sample to be run in a TGA while under inert atmosphere without the need to run the entire TGA experiment within a glovebox [5]. The hermetically sealed pans of the TGA Smart-Seal Pan System keep reactive atmosphere and moisture out, leaving the sample under inert conditions until the foil is pierced. The bail of the TGA Smart-Seal

Pan System is designed with a cutter on a spring composed of shape memory alloy. At approximately 55 °C the spring will actuate and bring the cutter down to pierce the foil and open the pan. This allows for samples within the TGA Smart-Seal Pan to maintain an inert atmosphere, as the pan will stay sealed until after the TGA furnace has been closed and purged with inert gas.

Samples were weighed out into TZero™ DSC pans and hermetically sealed with aluminum foil seals using the pan crimping die designed for the TGA Smart-Seal Pan System. More details on hermetically sealing the TZero pans for use in the TGA Smart-Seal Pan System can be found in TB104 [6]. After samples were added to the pans, the sealed pans were removed from the glove box and loaded into their corresponding bails of the TGA Smart-Seal Pan System and placed on the TGA Autosampler to await testing.

Thermogravimetric experiments were performed using a Discovery TGA 5500. Off-gas analysis was performed with a ThermoStar Mass Spectrometer from Pfeiffer Vacuum GmbH, which was directly connected to the TGA at the gas outlet, as shown in Figure 1. TGA Smart-Seal Pans were used to keep the samples under inert conditions while testing in a standard ambient environment, eliminating the requirement of placing the TGA in a glovebox when testing atmospherically sensitive samples. The MS has control software and data output that can be integrated with the TA Instruments TRIOS™ Software. This allows for evolved gas from thermal degradation or volatilization events to be collected, analyzed, and directly compared to temperature and weight loss data from the corresponding TGA experiments.

All pans were loaded with 11 ± 0.5 mg of dry NMC 811 powder. The same mass spectrometer bargraph recipe (1 – 50 AMU) was used to analyze the evolved gas from each TGA-MS experiment. A dwell time of 64 ms was used, resulting in a total scan time of 3.3 seconds for the whole range. Mass fragments were measured with the Secondary Electron Multiplier (SEM) enabled for added sensitivity. The MS data collection was triggered at the beginning of each thermal ramp by a signal sent from TRIOS Software. The TGA experiment was run under argon atmosphere. The balance and furnace purge rates were both maintained at 25 mL/min for the duration of the experiment. Immediately after beginning MS data collection, each sample was thermally ramped from room temperature to 600 °C at a rate of 20 °C/min.

RESULTS AND DISCUSSION

The TGA plots for the NMC samples of different SOC are shown in Figure 3. The total weight loss after the thermal ramp of the cathode material increases with the increasing state of charge. 100-SOC ended with 17.3 wt% loss, while 50-SOC and 0-SOC lost 10.6 wt% and 5.9 wt%, respectively. In addition, 100-SOC showed an early weight loss step above 100 °C that was not observed in the other samples. The first onset of weight loss for 100-SOC is at 120 °C. 50-SOC begins to show degradation at 236 °C. 0-SOC exhibited the highest thermal stability with an initial weight loss temperature of 252 °C.

The weight loss derivative can give insight into the nature of the thermal degradation. For example, a monomodal weight loss derivative peak may suggest a single degradation pathway. Less symmetrical derivative peaks or peaks with shoulders suggest multiple weight loss events and a more complex degradation pathway. Complex degradations can benefit from EGA analysis to help identify reaction pathways.

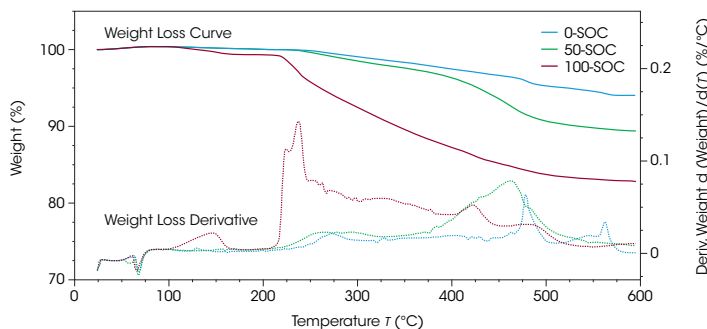


Figure 3. Weight loss curve (solid lines) and weight loss derivative (dotted lines) for NMC 811 at 0-SOC, 50-SOC, and 100-SOC, under an argon atmosphere

Figure 4 overlays ion-current signals of mass fragments corresponding to gases identified by MS during the TGA run. These evolved gas signals are plotted against temperature, alongside the concurrently recorded TGA data. 100-SOC is shown as a demonstration of the bulk of data, which can be observed in a single graph. The weight loss profile and weight loss derivative (shown in the black solid and dotted line, respectively) can be directly compared to the gas evolution temperature in the same experiment throughout thermal degradation.

The significant mass fragment signals which displayed changes during the TGA run are plotted. This includes the signals which correspond to hydrogen (H_2 , 2 AMU), water (H_2O , 18 AMU), fluoride (F, 19 AMU), nitrogen and carbon monoxide (N_2/CO , 28 AMU), oxygen (O_2 , 32 AMU), and carbon dioxide (CO_2 , 44).

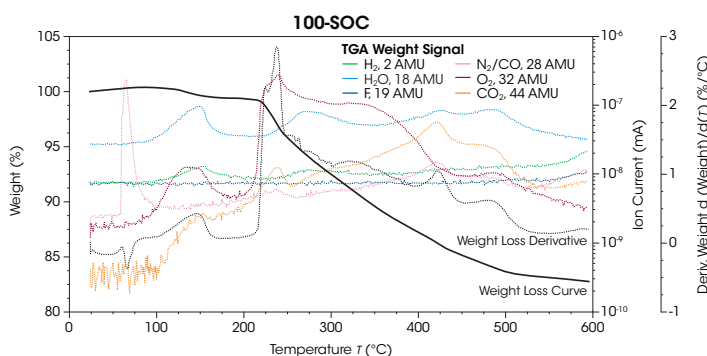


Figure 4. Weight loss and weight loss derivative for 100-SOC plotted against the signals for the observed mass fragments that evolved during the heating ramp

A large peak is observed early in the experiment for the signal for mass-to-charge (m/z) 28 AMU, which can correspond to nitrogen (N_2) or carbon monoxide (CO). The TGA experiment was run under a constant argon purge, but the samples were prepared in the Smart-Seal pans and sealed in a nitrogen purged glove box. It is possible that both nitrogen and carbon monoxide were detected at different points over the course of the experiment and observed in the 28 AMU signal.

To investigate this further, the ion current signals for 28 AMU were plotted along with 14 AMU in Figure 5. Mass-to-charge 14 AMU is another, typically weaker, signal of nitrogen in MS. For all samples, both 28 AMU and 14 AMU show large initial peaks indicating the release of nitrogen from within the sealed

TGA Smart-Seal Pans at the moment the pan was opened by the actuating coil. This serves to demonstrate the integrity of the hermetic seal on the TGA Smart-Seal Pans, ensuring that atmospherically sensitive samples remain under inert conditions. The pans were only opened by the bail of the TGA Smart-Seal Pan System once inside the closed TGA furnace under inert atmosphere. Following that initial peak of released nitrogen, there is no signal observed for 14 AMU while 28 AMU continues to evolve through the thermal ramp. Above 100 °C the m/z 28 AMU can be attributed to carbon monoxide.

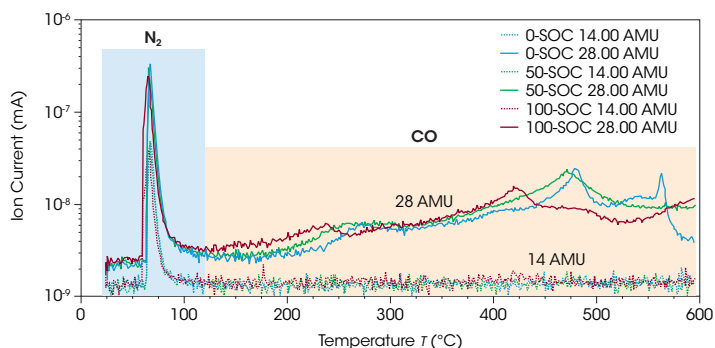


Figure 5. Ion current signals of m/z 14 AMU (nitrogen) and 28 AMU (nitrogen or carbon monoxide) for 0-SOC, 50-SOC, and 100-SOC during the entire TGA experiment

The TGA-MS data in Figure 6 can be used to compare degradation pathways of NMC 811 as a function of SOC. The production of a significant amount of any gas in a sealed container, like a battery cell, is a major concern for safety. However, the most pertinent gas to track from a safety and flammability perspective is oxygen, at 32 AMU. The ion current signals for oxygen (Figure 6E) most closely match the trends observed in the weight loss derivative signal of any of the observed gases, indicating that the loss of oxygen from the NMC sample is a large factor in the observed weight loss over the whole thermal degradation. In 100-SOC, the ion current signals for oxygen are stronger with an earlier temperature onset compared to the lower state of charge samples. This suggests a greater abundance of oxygen generated at lower temperatures, putting the fully charged NMC 811 at the highest risk of catastrophic failure. The general trend for thermal stability correlates well with SOC, with 100-SOC being the least stable, and 0-SOC being the most stable, in terms of the onset temperature for oxygen release. However, 50-SOC exhibits a later derivative peak (~460 °C) than is observed in 100-SOC and 0-SOC. That peak also corresponds to the strongest generation of oxygen for the entire temperature ramp of 50-SOC, which is at a much higher temperature than the other two samples. This may indicate a higher stability of the oxygen within the NMC lattice for 50-SOC relative to the fully charged or discharged samples.

A significant H_2O peak appears just above 100 °C in 100-SOC (Figure 6B), matching the initial weight loss event, which is absent in the samples with lower SOC. The powders were dried and kept under a dry inert purge throughout sample preparation, experimental setup, and testing. Water is typically generated as a combustion product during thermal degradation, but the strong appearance of water at the relatively low temperature of 100 °C in 100-SOC is a crucial safety consideration given the reactivity of water with battery components.

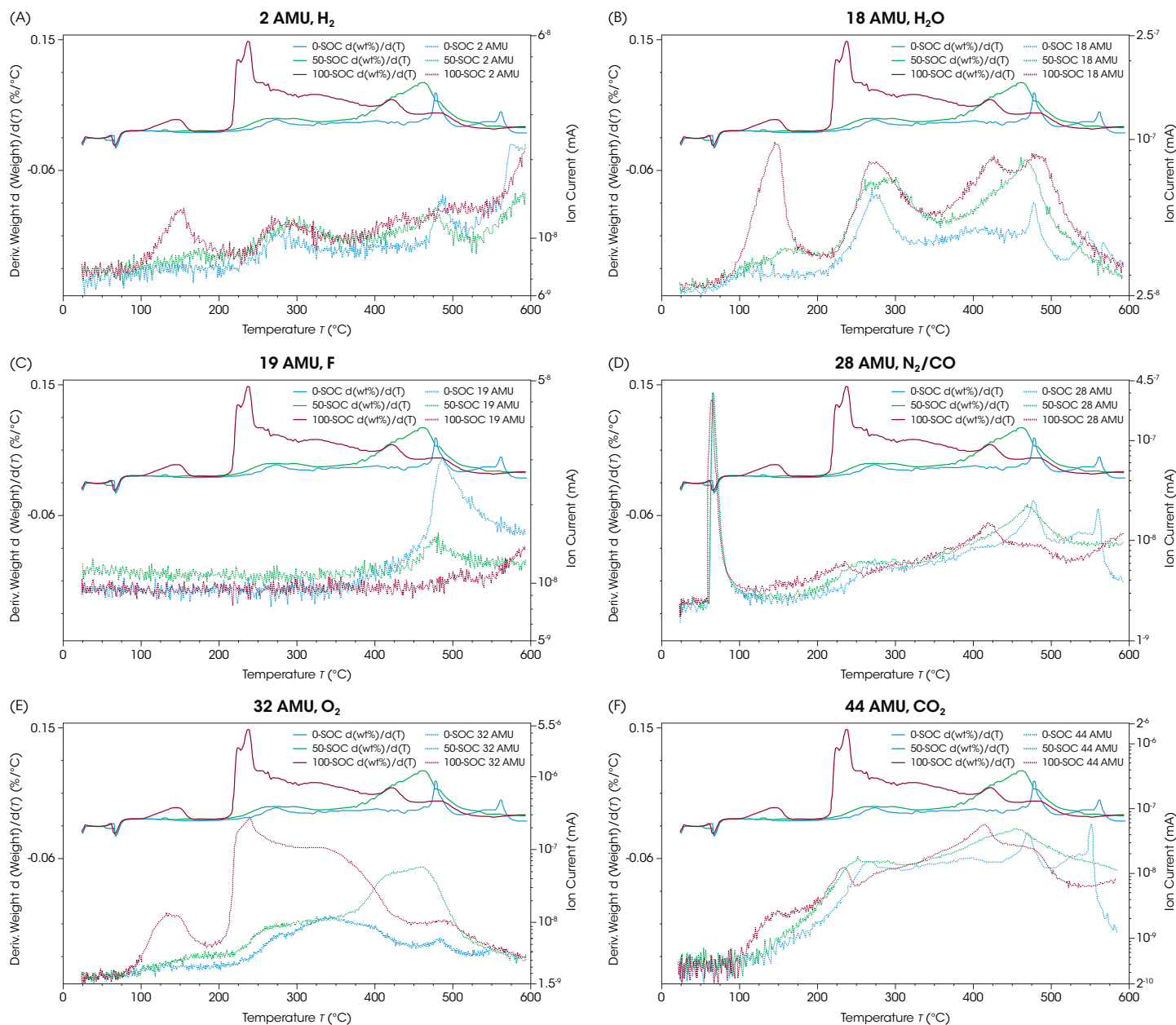


Figure 6. Weight loss derivative (top, shifted for clarity) and mass fragment signal (bottom, shifted for clarity) for 0-SOC, 50-SOC, and 100-SOC for (A) 2 AMU H₂, (B) 18 AMU H₂O, (C) 19 AMU F, (D) 28 AMU CO/N₂, (E) 32 AMU O₂, and (F) 44 AMU CO₂

Hydrogen evolution occurs throughout each sample's thermal decomposition, with a pronounced early appearance of H₂ in 100-SOC that coincides with a major water-related weight loss. Across all three SOC levels, the trend of the H₂ signal closely follows those of H₂O for most of the temperature range of the experiment, suggesting generation in the same degradation reactions that create the observed water. However, a sharp rise in H₂ is observed above 550 °C, which does not mirror the trend in water, potentially indicating the independent generation of hydrogen byproduct.

After the initial release of nitrogen at 55 °C the signals for m/z 28 AMU trend exactly with those observed of 44 AMU. For all samples the generation of CO₂ and CO are occurring together and in line with each other during cathode degradation. This

likely corresponds to the decomposition of the carbon-based conductive additives, and any trace organic residue. Despite the argon atmosphere, these components can undergo combustion due to the generation of O₂ by the sample.

Finally, the ion current signal m/z 19 AMU is observed in all samples beginning above 425 °C and exhibiting a peak at 500 °C for 0-SOC and 50-SOC. Mass-to-charge 19 AMU is typically recognized as fluoride ion. The signal trends inversely with SOC, with 0-SOC being the largest and 100-SOC being the smallest. Further investigation is required but the appearance of fluoride during thermal runaway may be due to residual polyvinylidene fluoride (PVDF) binder within the samples.

CONCLUSIONS

TGA-MS can provide early, materials-level insights into the thermal decomposition of LIB components. This proof-of-concept study using NMC 811 at different states-of-charge revealed trends in the relative thermal stability and monitored degradation byproducts relevant for safety. As SOC increases, the cathode's thermal stability decreases: 100-SOC powder lost more weight at lower temperatures and evolved comparatively larger amounts of hydrogen and oxygen than partially discharged samples. The production of these gases is a major reason why battery fires are difficult to extinguish. This work also demonstrated the utility of the new TGA Smart-Seal Pan by hermetically isolating air-sensitive cathode powders prior to testing, enabling accurate TGA-MS analysis on an instrument outside of a glove box. This significantly decreases the barrier to using TGA-MS on samples sensitive to atmosphere, allowing more researchers to study degradation pathways that guide future thermal management and improve safety at the materials-level.

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