Integration of mass spectrometry to characterize the gas evolution of batteries in thermal runaways using adiabatic calorimetry.

Abstract

Lithium-ion batteries are an essential energy storage technology, but their increasing energy density raises significant safety concerns. Reports of thermal runaway incidents highlight the urgent need for improved methods to study and mitigate these hazardous events. A key challenge in battery safety research is understanding the gas evolution during thermal runaway, as conventional techniques such as gas chromatography operate under conditions that do not fully replicate high-pressure, high-temperature environments. Here, we present a novel integration of adiabatic calorimetry (BTC-500) with high-pressure mass spectrometry to characterize gas evolution during lithium-ion battery thermal runaway. This approach enables real-time, high-frequency gas composition analysis under extreme conditions, overcoming limitations of conventional gas analysis techniques. Compared to standard gas chromatography, which requires sample transfer and offline analysis, in-situ mass spectrometry provides a direct and dynamic measurement of evolving gases. This allows for a more comprehensive understanding of reaction pathways, including the detection of transient species that may otherwise be missed. The study identified key differences in gas compositions between two battery types, highlighting the variability in decomposition reactions and gas evolution mechanisms. By providing real-time insights into the chemical processes occurring during thermal runaway, this method advances battery safety research. A better understanding of gas formation dynamics can inform the design of safer battery materials and improve predictive models for failure scenarios. These findings demonstrate how high-pressure mass spectrometry, when coupled with adiabatic calorimetry, can enhance safety assessments and accelerate the development of next-generation lithium-ion batteries.

Introduction

The increasing global demand for more powerful and energy-dense lithium-ion batteries has brought battery safety to the forefront of research. Reports of fire and explosions have become commonplace in the news, emphasizing the need for improved safety measures.

These fires are a result of thermal runaways, a process in which exothermic reactions within the battery enter a feedback loop. The accumulation of heat within the battery triggers a series of decomposition reactions that release heat and gases. The gases produced from the decomposition can be flammable, depending on the nature of the electrolyte. Oxygen can be released when the metal oxides that form the cathode, combined with the flammable gases and heat, can create ideal conditions for catastrophic fires and explosions.

As the temperature of a lithium-ion battery increases, a series of progressively complex reactions occur. At temperatures above 70°C, lithium salts decompose and react with solvents, forming a new Solid Electrolyte Interphase (SEI). Between 90-130°C, the SEI layer ($(CH_2OCO_2Li)_2$) decomposes, releasing heat and gases like C_2H_4, CO_2, and O_2, while the anode surface loses SEI protection at around 120°C, allowing embedded lithium to react with electrolyte solvents (e.g., ethylene carbonate, propylene carbonate), producing CxHy gases. Electrolyte decomposition begins around 110°C and continues up to 230°C, releasing fluoride compounds. Simultaneously, the separator shrinks and melts between 130-190°C, weakening structural integrity. At 200-300°C, cathode materials decompose, releasing O_2, with onset temperatures varying by material—e.g., ~150°C for $LiCoO_2$, ~220°C for NCM811, and ~310°C for $LiFePO_4$. Beyond 230°C, the binder polyvinylidene fluoride (PVDF) reacts with lithium and decomposes. By 235°C, thermal runaway occurs, producing gases such as CO_2, CO, H_2, CxHy, CxHyOz, CxHyF, POF_3, and HF, while the vaporized electrolyte adds further volatile components, intensifying the hazard.

These reactions do not occur strictly within the specified temperature ranges; as the temperature increases, the reactions become progressively more complex and intertwined.

H.E.L Group's BTC-500 is an adiabatic calorimeter designed to enable a comprehensive analysis of batteries' thermal behavior. It evaluates thermal, electrical, and mechanical stress responses, providing information on the battery's safe operating limits.

The aim of this Application Note is to study the gas evolution profile of two batteries using a novel combination of adiabatic calorimetry (BTC-500) and gas analysis using mass spectroscopy.

Material and Methods

Lithium ion batteries

Two batteries were used in this experiment: one with a capacity of 151 Ah and one with a capacity of 177 Ah. Both were at 100% SOC prior to the experiment.

Adiabatic Calorimetry (BTC-500) equipped with High-Pressure Mass Spectrometry

A Mass Spectrometer was attached to a BTC-500 (H.E.L Group, Hemel Hempstead, UK) in a way the gases produced during the LIB thermal runaway could be sampled. This allowed for the analysis of gas with very high-frequency data acquisition (50 ms per mass number) at high pressure (8 bar) and high temperature.

Figure 1. H.E.L's BTC-130 attached to a mass spectrometer.

Batteries were subjected to thermal runaway using Heat-Wait-Search plan. When the battery entered the thermal event, an in-situ online analysis was performed, providing real-time monitoring of the chemical reactions that were occurring. Periodic online sampling was conducted, taking samples at predefined intervals during the reaction. Additionally, gas samples were collected after the thermal runaway was completed, allowing the retrospective analysis of transient reactions that might have been missed.

Results and Discussion

Figure 2 shows the gas produced by two different types of battery. After the thermal runaway of a **151 Ah cell**, a large amount of **CO_2, H_2, CH_4, C_2H_4, CO**, and small amounts of **SO_2** and **mercaptamines** were detected. After the thermal runaway of a **177Ah cell**, a large amount of **CO, CO_2, H_2**, and small amounts of **toluene, trimethylamine N-oxide**, and **long-chain hydrocarbons** were identified.

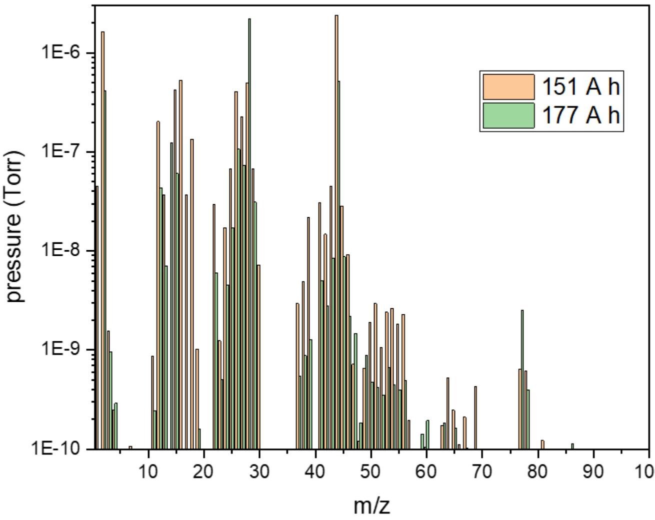

Figure 2. The composition of the gas produced two batteries (151 A h and 177 A h) that have undergone thermal runaway in a BTC-500.

Limitations of Conventional Methods: Currently, **gas chromatography (GC)** is the most commonly used method for gas analysis. However, GC requires analysis at relatively low pressures and temperatures, making it unsuitable for evaluating gas compositions under **high-temperature and high-pressure conditions**.

Advantages of In-Situ Online Analysis: The in-situ method allows gas analysis simultaneously with thermal runaway, reflecting the chemical states and reaction processes in real-time. This approach provides a more comprehensive understanding of the various chemical reactions occurring during each stage of thermal runaway.

H.E.L, in collaboration with third-party partners, has introduced a combined solution of the **BTC series** with high-pressure mass spectrometry (MS). This system enable s high-frequency data analysis at **50 ms per mass unit** and allows gas analysis to be conducted under **high-pressure and high-temperature conditions**.

Conclusion

H.E.L BTC-500 Adiabatic Accelerating Calorimeter equipped with a mass spectrometer (MS) enabled real -time, high-frequency gas composition analysis under extreme conditions of **high pressure** and **high temperature**, This set up enhanced the capability to monitor and study gas evolution during lithium-ion battery thermal runaway events.

Thermal runaway is a key focus in lithium-ion battery safety research. Understanding the gas generation mechanisms during thermal runaway can improve the safety of critical lithium-ion battery components, thereby enhancing the overall safety of the battery. The combination of BTC products with high-pressure mass spectrometry allows for faster monitoring of gas generation processes, providing more detailed gas composition data to aid in understanding gas generation mechanisms.