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INSTRUMENTAL-ANALYTICAL INVESTIGATION OF VENTING GASES FROM LITHIUM-ION TRACTION BATTERIES WITH LITHIUM IRON PHOSPHAT CATHODE

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MOTIVATION

Lithium-ion high-voltage batteries are key to modern electromobility and energy storage due to their high energy density, durability, and efficiency. They are widely used in electric vehicles and stationary storage.[1] The choice of cathode material greatly affects battery performance and safety. Common cathodes include lithium nickel manganese cobalt oxide (NMC), lithium iron phosphate (LFP), and lithium nickel cobalt aluminum oxide (NCA).[2] NMC and NCA offer high energy density, ideal for long-range, high-power applications.[3] LFP, though lower in energy density, provides better thermal and chemical stability and longer cycle life, making it suitable for safety-critical uses. Lower production costs have also driven a growing industry shift toward LFP technology.[2,4] However, lithium-ion batteries still pose safety risks. Thermal overload, damage, or faults can cause thermal runaway, leading to intense heat, fire, or explosions.[5] These events release flammable and toxic gases, raising concerns for health, safety, and the environment—especially in enclosed spaces—prompting ongoing research.[6]

METHOD

To analyse vent gases from lithium-ion batteries, thermal runaway must be safely induced. Tests are carried out in a sealed carbon steel pressure vessel (40 bar, 170 L, AVN GmbH), shown in Figure 1 (left). Two 50 Ah LFP cells (double testing, one cell per test) are then overcharged at 2 C (100 A) using a lab power supply (EA PSI 9080-12) to trigger thermal runaway. After cooling, gases are collected into a multi-foil bag and analysed. Then the gas is split via a PTFE filter and T-piece into two streams, each regulated by mass flow controllers (Bronkhorst EL-FLOW). One stream passes through two wash bottles with 20 m**M** $Na_2CO_3/NaHCO_3$, then a cooled dichloromethane impinger. The other flows into an impinger containing 2 m**M** of 2,4-dinitrophenylhydrazine (DNPH) dissolved in acetonitrile. These solvents absorb specific analytes. Figure 1 (right) shows the described setup.

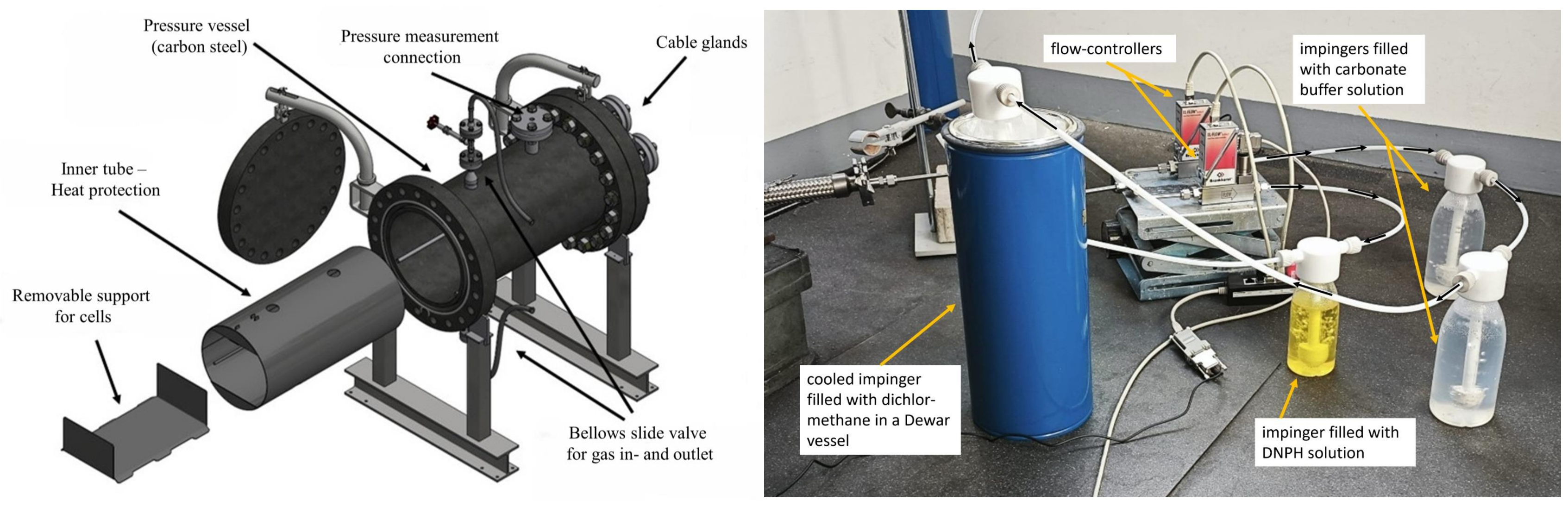

Figure 1: Experimental setup. Schematic three-dimensional representation of the pressure vessel (left) and test setup with mass flow controllers and impingers (right)

RESULTS AND DISCUSSION

Gas chromatography analysis

Gas samples from the multi-foil collection bags are analysed using gas chromatography (GC, 990 Micro GC, Agilent) with a thermal conductivity detector (TCD). This setup enables detection of hydrogen — a major explosion risk during thermal runaway — and quantifies other vent gases, including CO, CO_2, methane, ethane, ethene, ethyne, and total propane/propene. The resulting gas composition, normalised to 100 %, and the corresponding chromatogram are shown in Figure 2.

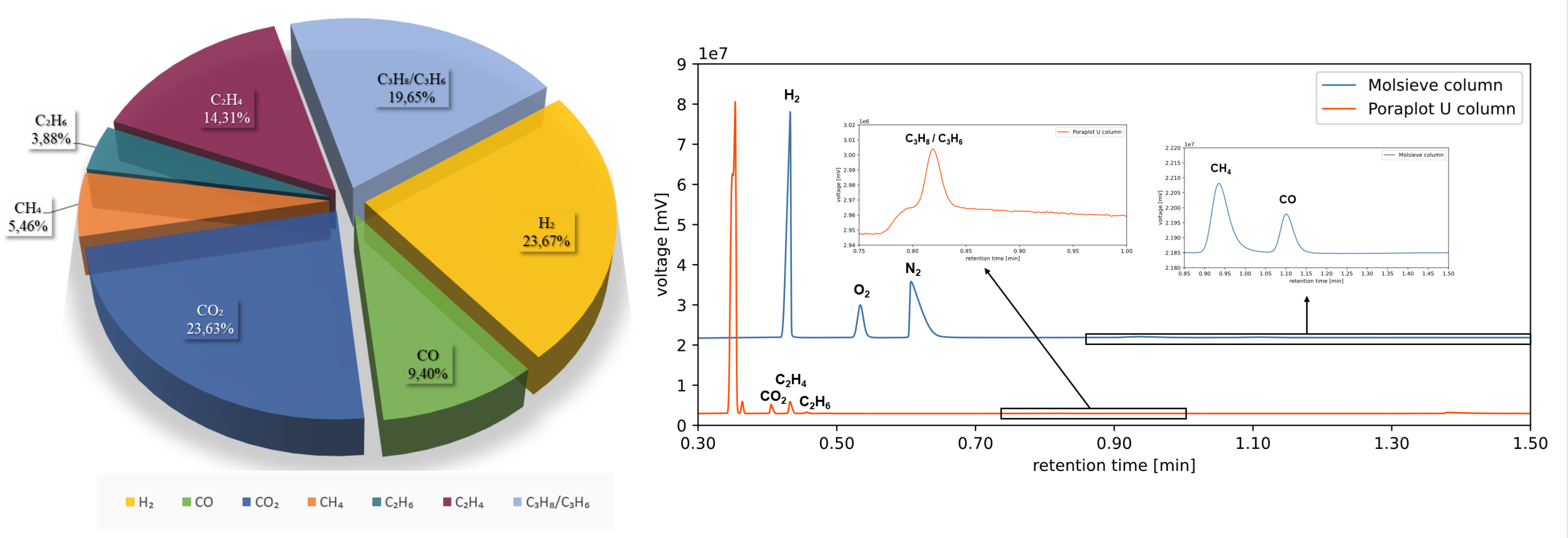

Figure 2: Percentage Composition of Venting Gas in LFP cells (Standardized to 100%) (left) and GC-chromatograms from one tested LFP cell with two channels (baseline correction offset + 2.0 mV for molsieve column) with zoom for smaller peaks (right)

The measured hydrogen content of 24% aligns with the results from other studies[7,8] and exceeds the lower explosive limit, posing a significant safety risk. Furthermore, high levels of flammable gases, such as propane, propene and ethene, were detected, which increases the hazard even further.

Gas chromatography with coupled mass spectrometry analysis

The vent gases were introduced into dichloromethane and analysed qualitatively using GC-MS (GC-2010 Plus, Shimadzu) to identify organic components. Many of these compounds are highly flammable or toxic and pose significant safety risk. The results are presented in Figure 3.

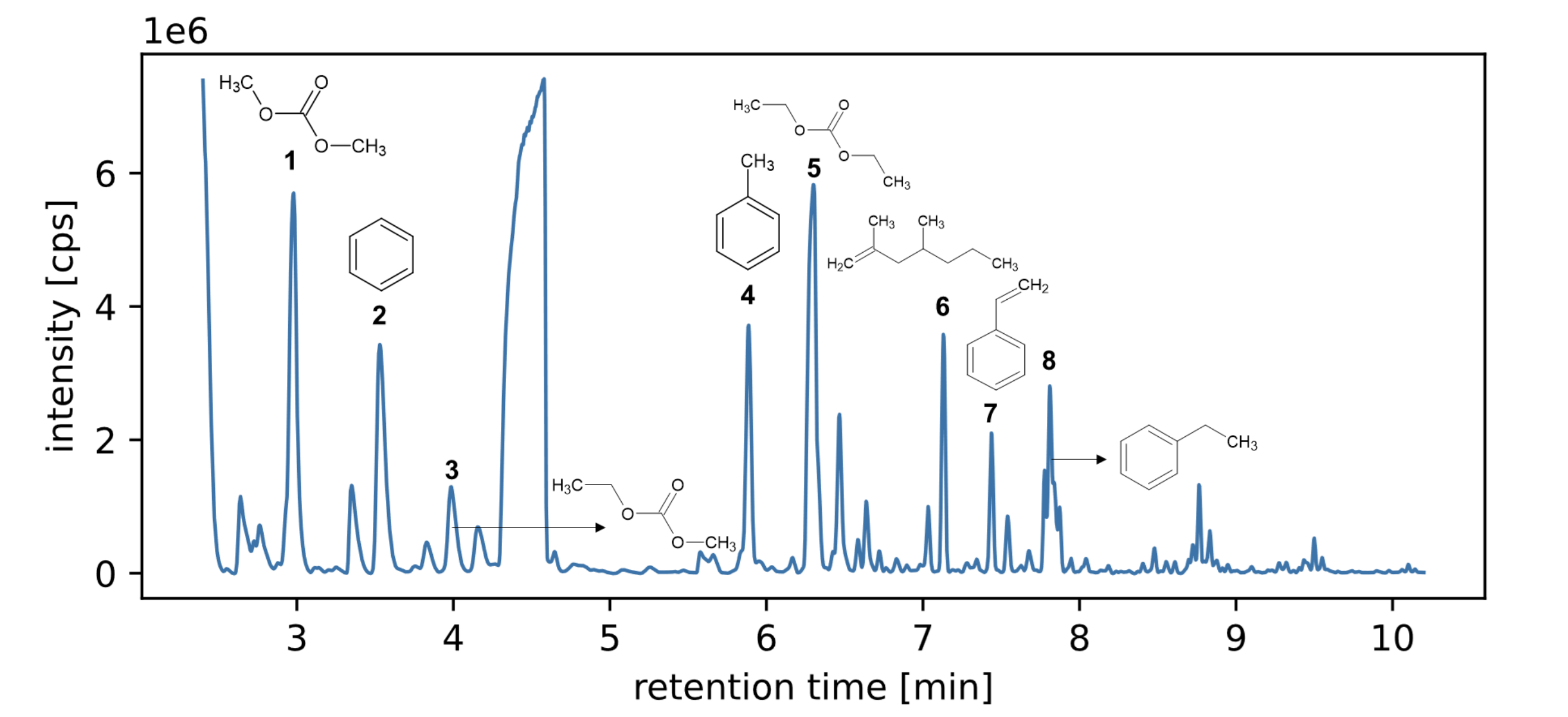

Figure 3: GC-MS-chromatogram of the dichloromethane solution from one tested LFP cell

The organic carbonates (1, 3, 5) are components of the electrolyte solvent in the LFP cell, which are classified as highly flammable under thermal runaway conditions. The presence of additional components was also detected, which are indicative of fire decomposition products. These are not only a consequence of fires in lithium-ion batteries, but also occur in other contexts.

In addition, a headspace GC-MS was used for the carbonate buffer to detect dissolved organics that may not have entered the dichloromethane solution. The results are shown in Figure 4. This measurement also revealed organic carbonates.

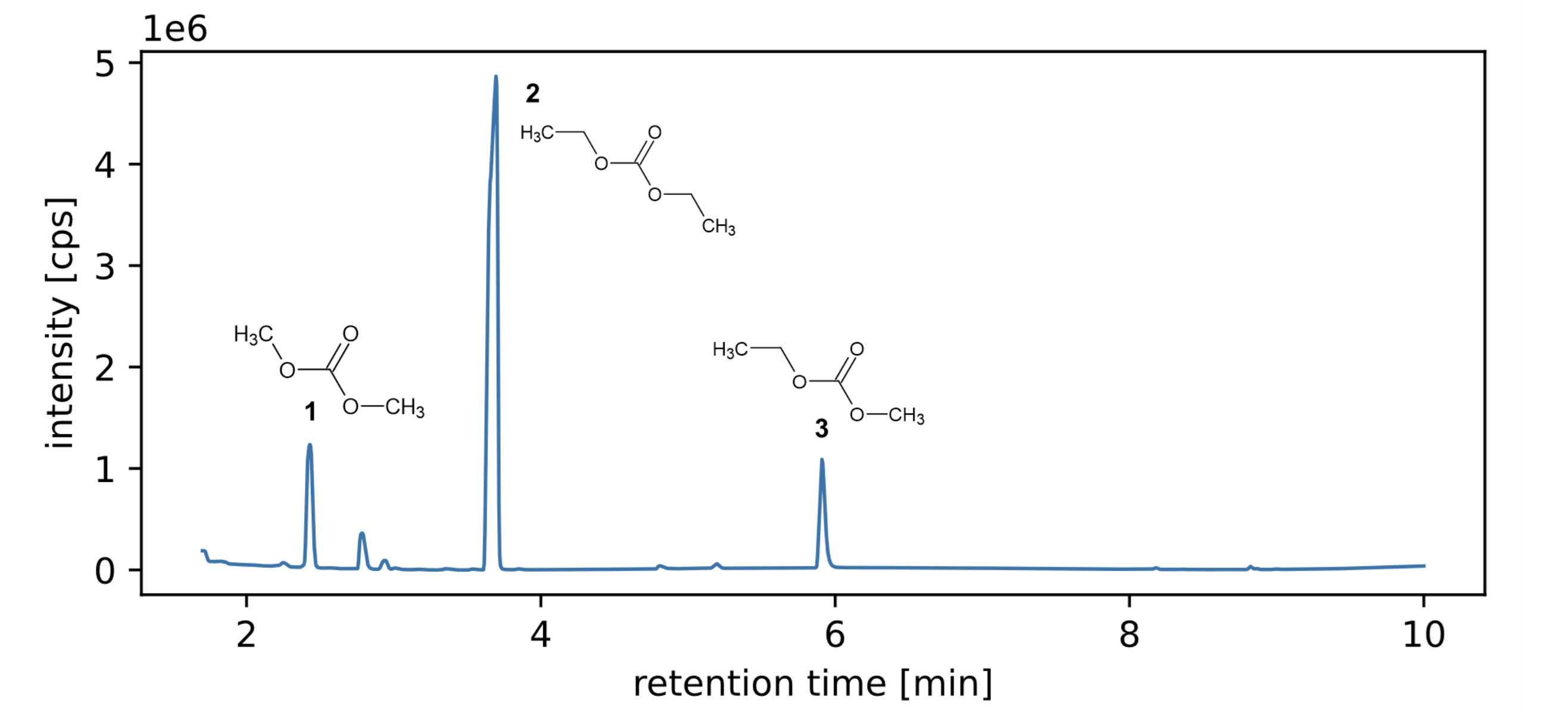

Figure 4: Headspace GC-MS-chromatogram of the carbonate buffer from one tested LFP cell

Hydrogen fluoride analysis

Another gas released during lithium-ion battery thermal runaway is hydrogen fluoride (HF). Due to its corrosiveness, direct chromatographic analysis is not feasible. Instead, the exhaust gas is passed through two impingers containing carbonate buffer in series, as a single impinger cannot fully absorb HF.[9] The buffer solutions are then analysed using ion chromatography (Dionex ICS 200, Thermo Fisher Scientific) with a conductivity detector to measure the fluoride content. As demonstrated in Figure 5, the chromatogram of a carbonate solution extracted from one of the analysed LFP cells is presented.

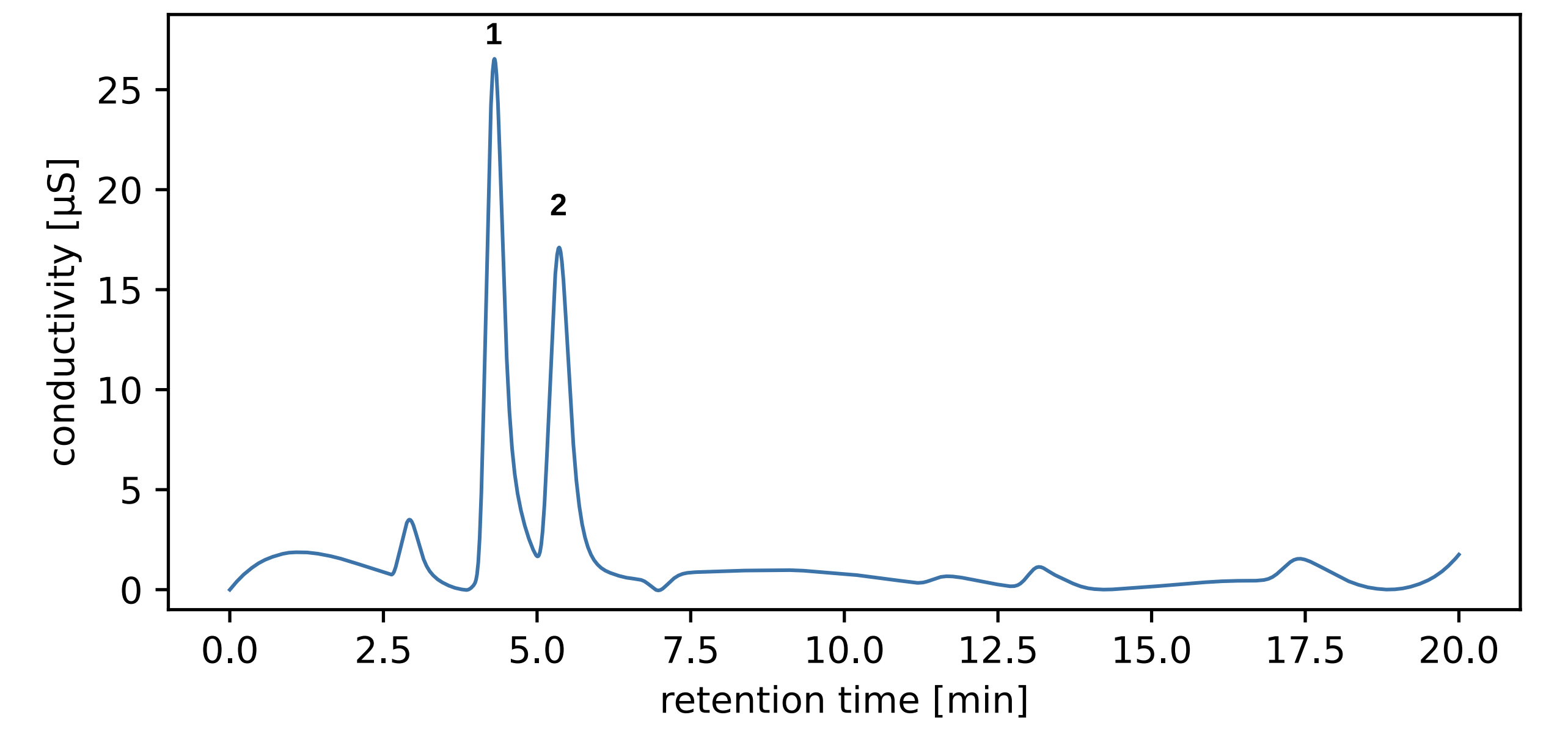

Figure 5: Ion chromatogram of the carbonate buffer from one tested LFP cell

The chromatogram shows two key peaks: Peak 1 for fluoride and Peak 2, which indicates the presence of organophosphates. The theoretical HF concentration was estimated using the geometric series method by Günther et al.[9] In the tested cells, the HF content was 1099.86 ppmv (0.27 mg/Wh).

SUMMARY

In this study, thermal runaway was triggered by controlled overcharging of two prismatic 50 Ah LFP cells. Gas sampling and analysis were conducted via gas chromatography (GC-TCD, GC-MS, HS-GC-MS) and ion chromatography (IC). The venting gases contained high concentrations of hydrogen (23.67 vol%), exceeding the lower explosive limit. Along with substantial levels of propane, propylene and ethylene. There is therefore a considerable risk of fire and explosion. Hydrogen fluoride (HF) was detected indirectly via IC after absorption in carbonate buffer, with a concentration of 1099.86 ppmv (0.27 mg/Wh), lower than values reported from other scientists but still toxicologically relevant. Organic carbonate solvents (dimethyl-, ethylmethyl-, and diethyl carbonate) were detected, along with combustion by-products such as benzene, toluene, xylene, and styrene, all of which are hazardous due to their flammability. Additionally, ion chromatograms revealed a secondary peak near the fluoride signal, suggesting the presence of organophosphate compounds. Given their potential neurotoxicity and environmental impact, further characterization and toxicological evaluation of these species are recommended. These findings highlight that, while LFP cells offer enhanced thermal stability, their vent gas emissions during failure events remain a critical safety concern, warranting further investigation into gas composition, mitigation strategies, and regulatory implications.

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