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Gas Sampling and Analysis of 18650 Lithium-Ion Batteries by GC-TOF-MS

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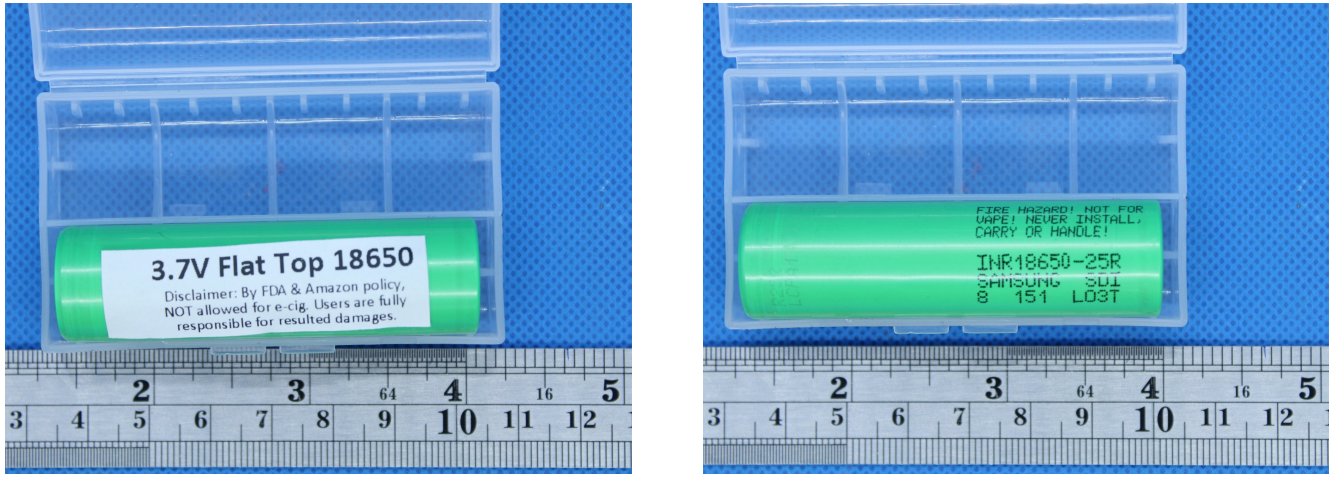
Published Date 05/09/2024

Method Overview

- Gas was extracted from a commercial 18650 lithium-ion battery by carefully puncturing the cell casing and resealing with an adhesive gas-sampling septum. The cell atmosphere was then sampled with a gas-tight syringe and analyzed by GC-MS.
- Volatile and semi-volatile compounds were identified by library matching with JEOL's msFineAnalysis software.
- Permanent gasses were not separated chromatographically but were identified by exact mass analysis.



Samsung SDI INR 18650-25R Lithium-ion Battery

Discussion

- N_2, Ar, CO_2, and CH_4 were the primary gas species detected. Ar may reflect intrusion of glovebox atmosphere during sampling.
- Electrolyte components dimethyl- and ethyl methyl- carbonate were detected.
- Presence of light hydrocarbons (CH_4 → C_3H_8) and CO_2 in a pristine/uncycled cell is indicative of electrolyte breakdown during cell assembly and initial SEI formation.
- No H_2O or HF are identified in the cell gas.
- Trace C12 hydrocarbon was also detected but may be residue from the septum adhesive.

Gas Sampling

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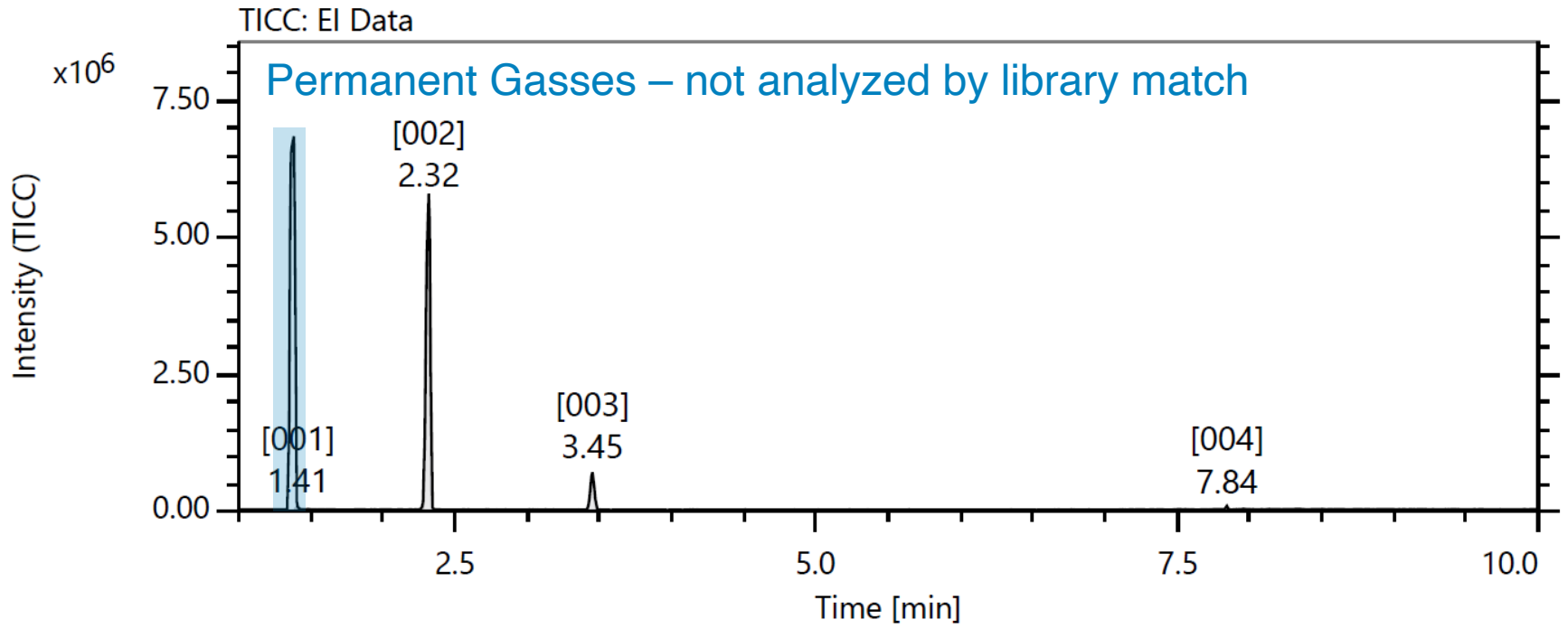
- Cell transferred to Ar-filled glovebox.
- Small puncture made in negative terminal and sealed immediately gas sampling septum.
- Cell atmosphere was sampled with a gastight syringe.

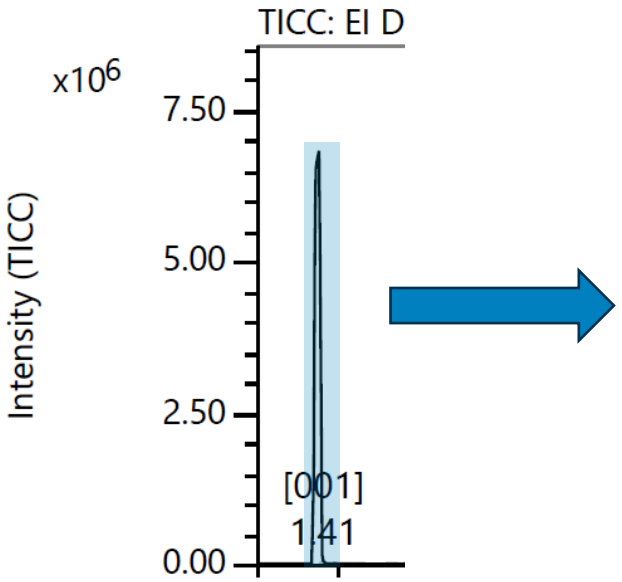
Results, GC-MS

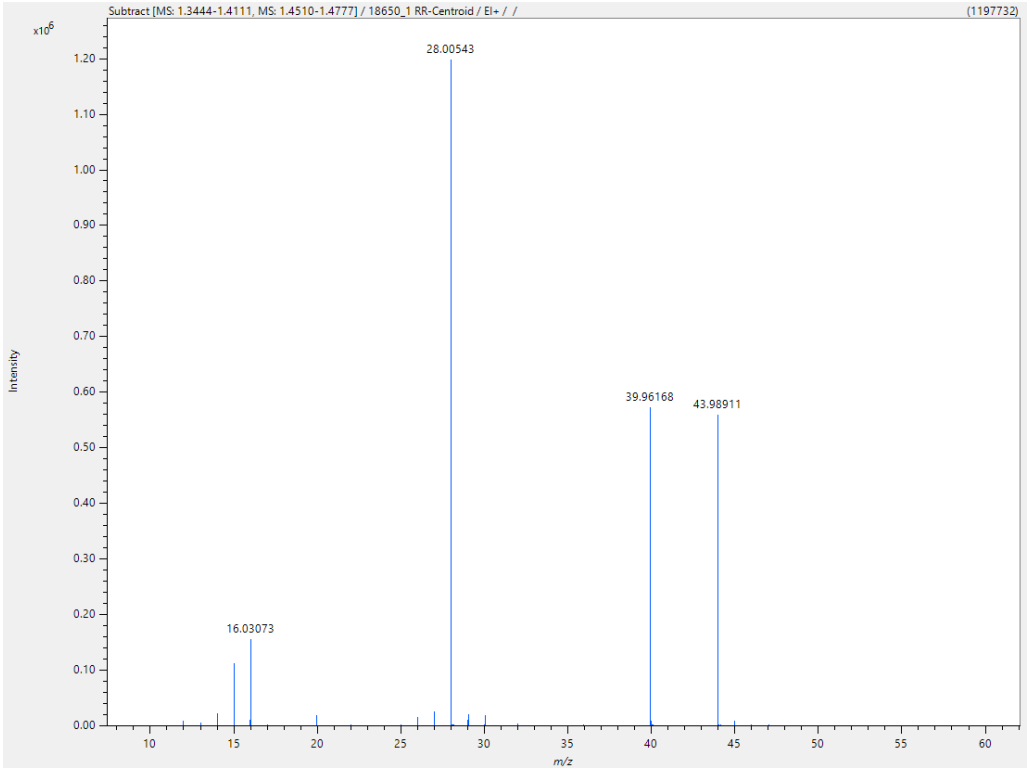


ID	RT [min]	Width [s]	Area	Area [%]	Height	Library Name	Similarity	Formula
001	1.41	19.60	434263	4.0%	74831	Ethane	745	C2 H6
002	2.32	4.80	10905273	100.0%	5665001	Dimethyl Carbonate	920	C3 H6 O3
003	3.45	5.60	1375424	12.6%	701109	Ethyl methyl carbonate	905	C4 H8 O3
004	7.84	2.40	59965	0.5%	72585	2,2,4,6,6-pentamethyl heptane	924	C12 H26

Results, GC-MS

Permanent Gasses – analyzed by exact mass





Formula	Mass [Da]	Intensity	Relative Intensity [%]	Mass Error [mDa]
C H4	**16.03073**	**170938.6**	**5.93%**	**-0.02**
N2	**28.00543**	**1317477.93**	**45.67%**	**-0.17**
C2 H4	28.03045	108550.03	3.76%	-0.3
C H O	29.0024	11583.77	0.40%	0.21
C2 H6	30.04624	20531.5	0.71%	-0.17
O2	31.98905	2893.5	0.10%	-0.23
Ar	**39.96168**	**629950.5**	**21.84%**	**-0.16**
C O2	**43.98911**	**615119.7**	**21.32%**	**-0.17**
N2 O	43.99964	6823.7	0.24%	-0.87
C3 H8	44.0614	183.4	0.01%	-0.66
C2 H4 F	47.02857	829.7	0.03%	-0.58

Formulas assigned to each m/z peak based on exact mass.

Appendix: Method Details, Gas Extraction

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- 100 uL of gas sample was collected in a triple-purged gastight syringe and immediately transferred to the GC injector. 50 uL was purged just before injection. Column oven ramp conditions are shown below.
- Mass spectra were collected in electron ionization mode (70 eV) from m/z = 6 to 800 with perfluorotributylamine used for in-line m/z calibration.
- Compound identification was determined by comparison to the NIST 2020 main library comprising >300,000 unique compounds. Compounds with match scores below 700/1000 are not included in the analysis – mass spectra for unidentified compounds can be provided if requested.
- Gas composition was determined from exact masses of distinct peaks in the mass spectrum. Identities are assigned to the best-match formula (lowest mass difference) from the element set below with a cutoff of 1 mDa.

Step	Rate [°C/min]	Temperature [°C]	Hold Time [min]
Initial	0	35	6
Step 1	10	85	0
Step 2	30	250	2

Symbol	Min	Max
C	0	20
H	0	40
O	0	5
N	0	3
P	0	1
S	0	1
F	0	8
Ar	0	1
Si	0	2

Appendix: Instrument

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JEOL JMS-T2000GC AccuTOF™ GC-Alpha

- Exceptional mass accuracy (~0.05 mDa)
- Instrument detection limit = 18.7 fg
- m/z range 4 - 6,000 Da
- Comparison of mass spectra to >300,000 library compounds

Capabilities and Accessories

- Electron, Chemical, and Field Ionization
- Liquid, headspace, and solid-phase microextraction injection modes
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CM000023631 1 samples, 2 techniques	2022-06-24	1	Sample Received	Repeat
CM000021056 1 samples, 2 techniques	2022-01-25	1	Executing	Repeat
CM000020337 0 samples, 4 techniques	NA	0	Waiting for samples	Repeat
CM000020336 1 samples, 4 techniques	2022-01-03	1	Waiting for samples	Repeat

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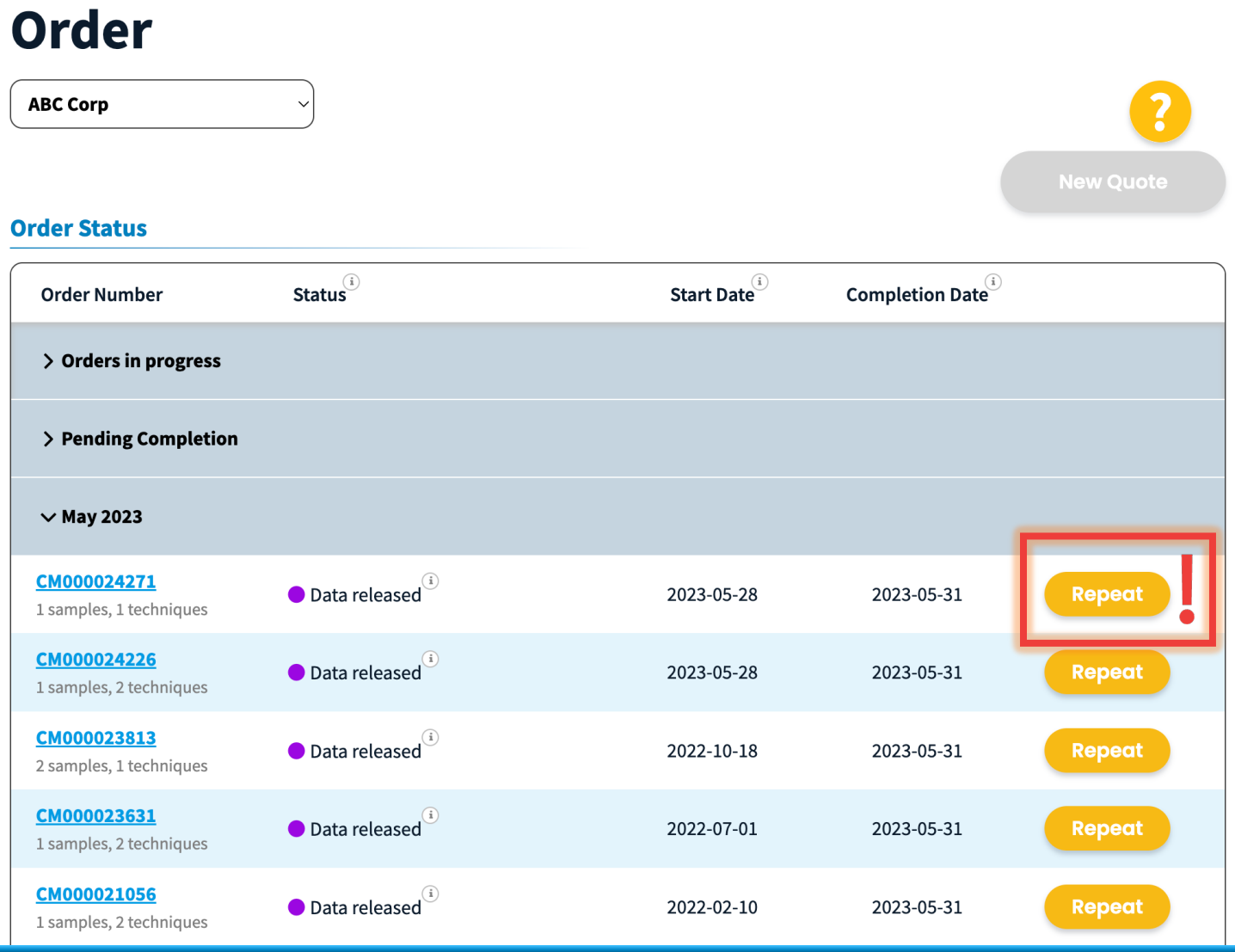

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Thank You.

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