Characterizing a Lithium-Ion Battery Recycling Stream using Evolved Gas Analysis and Multi-Step Pyrolysis

Application Note
Battery

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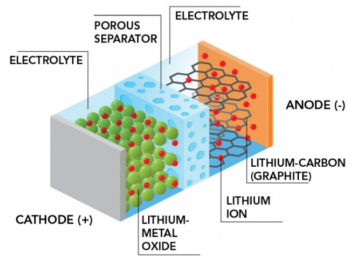
Abstract
This application note investigates the lithium-ion battery recycling stream using Evolved Gas Analysis coupled with Multi-Step Pyrolysis GC-MS to identify the quality of the recycled materials.

Introduction

A typical rechargeable lithium-ion battery consists of four main parts, cathode, separator, anode, and electrolyte. Polymer binder material is located within the anode and cathode electrodes to hold the graphite on the anode, as well as lithium metal-oxide on the cathode, to keep the electrodes from degradation during charge-discharge cycles. Used lithium-Ion batteries can be recycled to recover valuable metals to manufacture fresh batteries. Organic binders present in batteries shredded for recycling can reduce the efficiency of metal extraction. Two common binder materials are poly(vinylidene fluoride) (PVDF), and poly(vinyl pyrrolidinone) (PVP). A simple way to test any part of the battery recycling stream for contamination of these polymers can be done using Evolved Gas Analysis (EGA) and Multi-step Pyrolysis (MSP) GC-MS. This technique can also be used for identifying any type of organic materials in the battery recycling stream, whether they are from the binder, the separator, or if there is residual solvent from the recycling process. In this application note, a sample from a battery recycling stream was analyzed by EGA+ MSP to investigate the organic content as well as determine the presence of two common polymer fillers in car batteries: PVP and PVDF.



Experiment Setup

A sample of the Lithium-Ion Battery Recycling Stream, 100 μg, was loaded into a DISC tube for analysis. A fused silica transfer line was used to connect the GC inlet to the MS detector in a preliminary EGA run. After which, a 30 meter long 5% phenyl capillary column was used for multi-step pyrolysis. A vent-free adapter was installed to enable a fast switch between the fused silica and the column without losing vacuum in the mass spectrometer.

EGA

Pyroprobe 6150
Initial: 50°C
Final: 800°C
Ramp Rate: 100°C per min
Interface: 300°C
Transfer Line: 320°C
Valve Oven: 300°C

GC-MS
Column: Fused silica (1m x 0.10mm)
Carrier: He 1.00mL/min 50:1 spl
Injector: 320°C
Oven: 300°C
Ion Source: 250°C
Mass Range: 35-700amu

Multi-Step Pyrolysis

Pyroprobe 6150
DISC:
300°C 30 sec
600°C 30 sec

Interface: 300°C
Transfer Line: 320°C
Valve Oven: 300°C

GC-MS
Column:
5% phenyl (30m x 0.25mm x 0.25μm)
Carrier:
He 1.00 mL/min, 80:1 spl
Injector: 320°C
Oven: 40°C for 2 minutes
20°C/min to 300°C (5min)
Ion Source: 250°C
Mass Range: 35-700amu

Results and Discussion

As a fast-screening technique, evolved gas analysis was performed on the sample; the DISC temperature was ramped up at 100 °C/min from 50°C to 800°C and the GC oven was kept at 300°C, and a short piece of fused silica connected the injection port to the detector. The results in Figure 1 show EGAs of the sample, PVP, and PVDF. The sample had 3 main regions of outgassing, the first region occurred between 200°C and 400°C, the second region occurred between 400°C and 600°C, and the third region, which had a large presence of m/z 44, representing carbon dioxide gas, occurred between 700°C and 900°C.

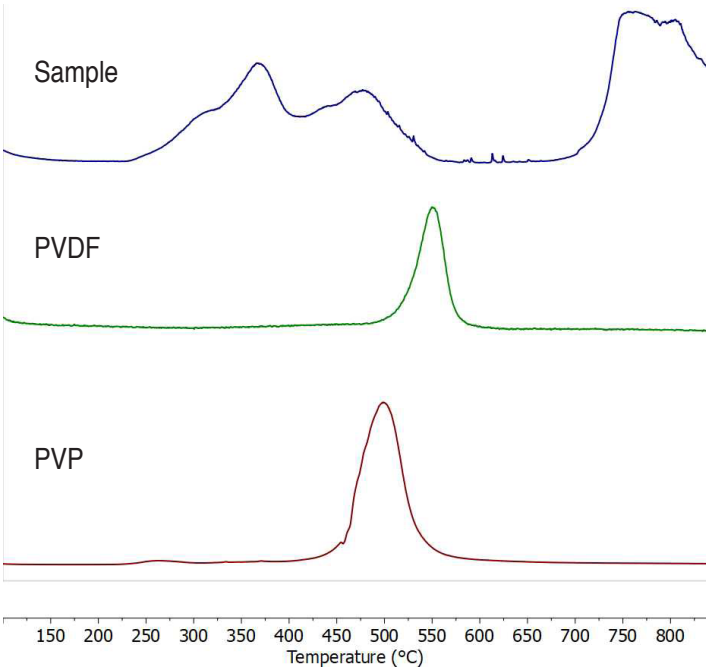


Figure 1. EGAs at 100°C per minute from top to bottom: Sample, PVP, and PVDF.

Both PVP and PVDF started their degradation at over 450°C, at which the sample had nearly finished degrading. This preliminarily indicates that neither PVP nor PVDF were present. The first region of the sample had a large presence of m/z 99 (Figure 2), and when the composite mass spectrum is compared against the NIST library, its top match was for 1-methyl-2-pyrrolidinone. To learn details on chemical composition of the first two degradation regions, multi-step pyrolysis was performed at 300°C and 600°C (Figure 3).

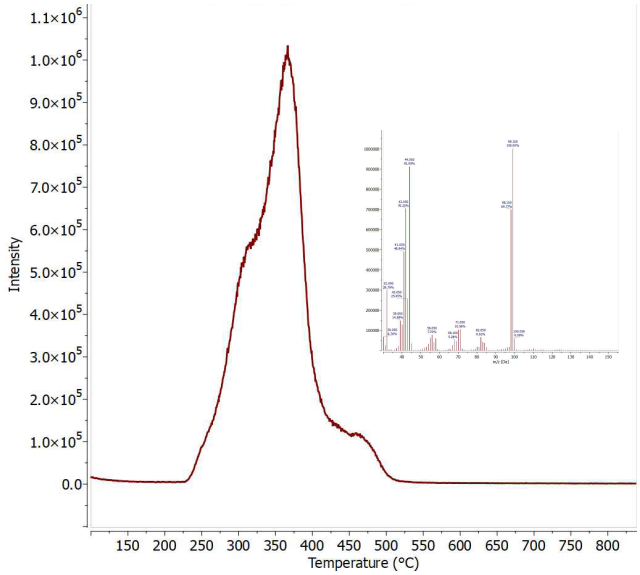


Figure 2. m/z 99 EIC and mass spectrum of sample EGA.

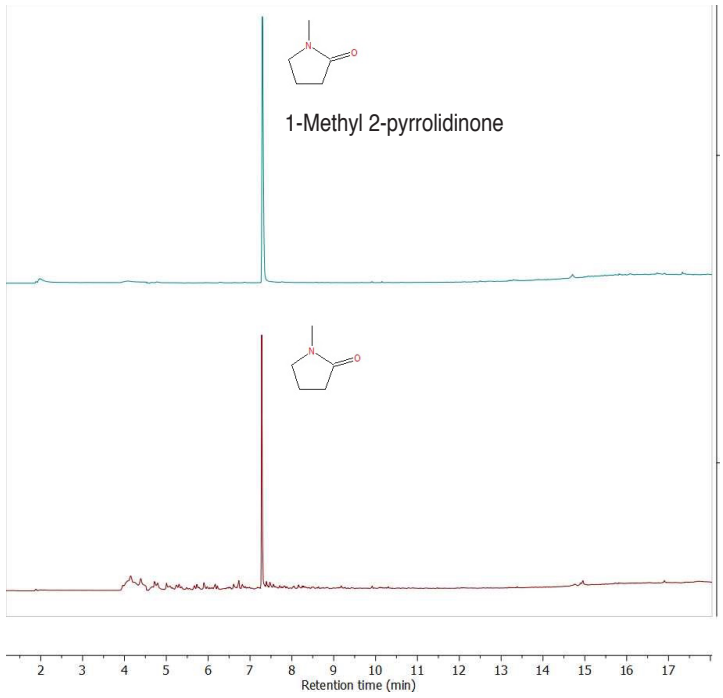


Figure 3. MSP stack of sample at 300°C (top) and 600°C (bottom).

As indicated in the EGA, 1-Methyl 2-pyrrolidinone (NMP) dominated both chromatograms. NMP is a dipolar aprotic solvent used in rechargeable battery recycling by dissolving any binders and allowing for the effective recovery of critical metals[1].

NMP is also the side group structure and pyrolysis product of PVP but a further examination shows other PVP pyrolysates are not present. For example, when PVP is pyrolyzed, one of the largest peaks is for the monomer 1-ethenyl, 2-pyrrolidinone (Figure 3).

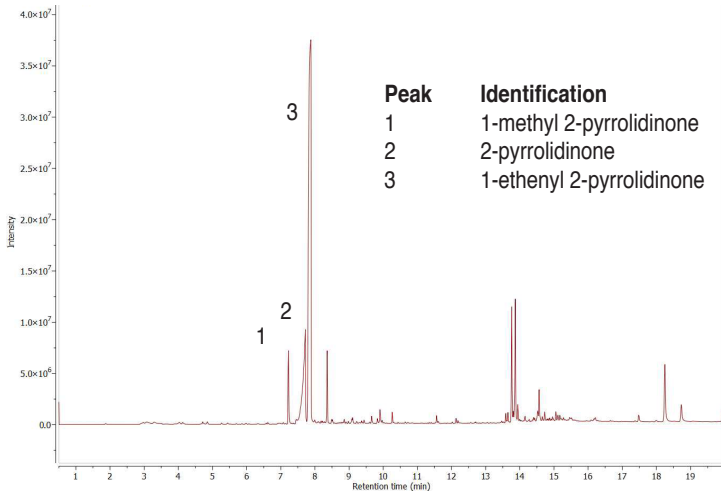


Figure 3. PVP at 600°C.

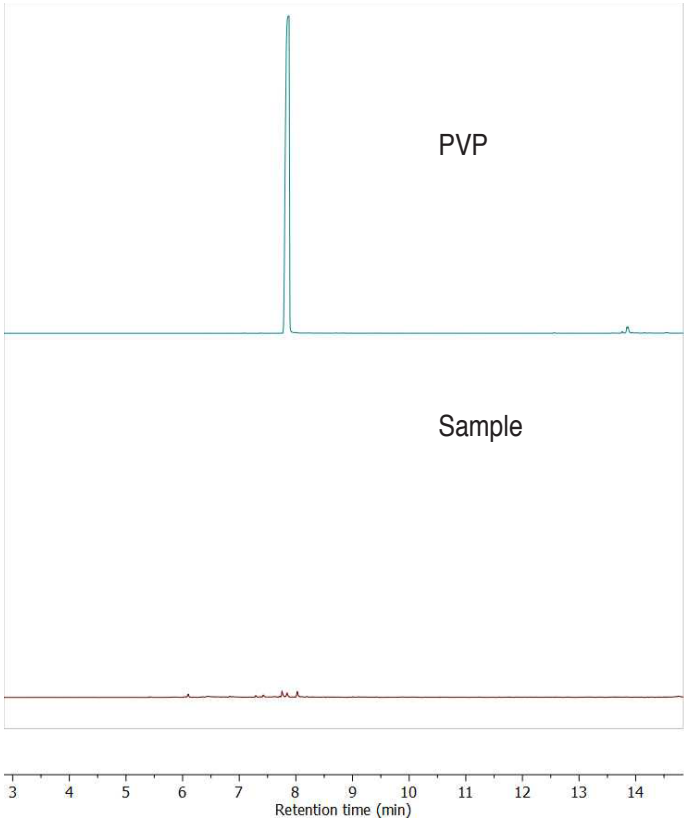


Figure 4. m/z 111 of PVP (top) and sample (bottom) at 600°C.

This monomer had a large presence of m/z 111 in its mass spectrum, which was not present in the sample pyrogram (Figure 4).

When the polymer binder PVDF were pyrolyzed, it produced fluoroalkenes with various chain lengths, each with a common m/z of 113 to represent C_3HF_4+ (Figure 5). Figure 6 shows m/z 113 of both PVDF and the sample pyrolyzed at 600°C; while peaks were present in the sample, the retention times did not correspond with the fluoroalkene series in PVDF, indicating that PVDF was absent.

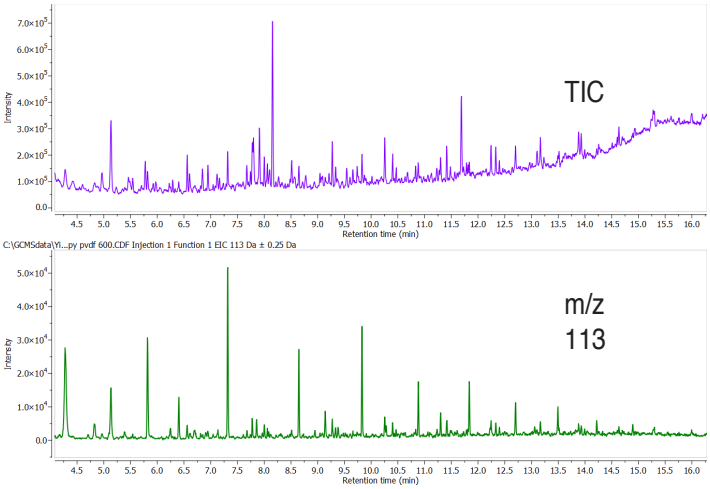


Figure 5. TIC (top) and m/z 113(bottom) of PVDF at 600°C.

If the peak spectra, not including the NMP peak, of the 600°C run are co-added together in Mnova's MSChrom with CDSPlugin, and compared against the CDS Pyrolysis Database (Figure 7), a top match was for poly(vinyl alcohol-co-ethylene) (Figure 8), which is a polymer that can be can be used in the separator[2].

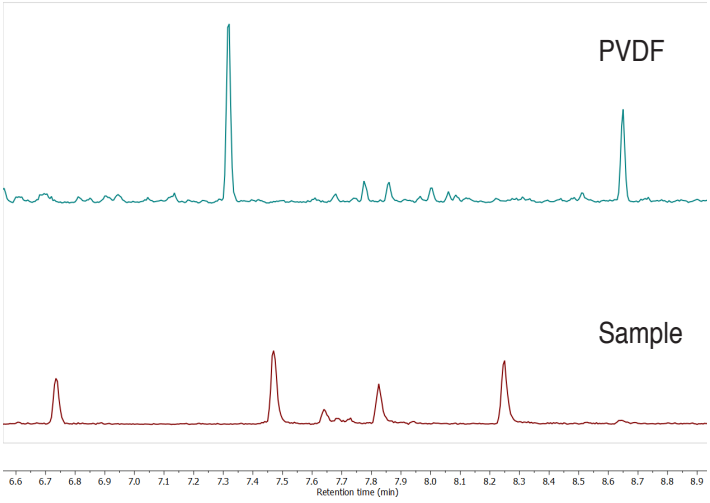


Figure 6. m/z 113 of PVDF (top) and sample (bottom)at 600°C.

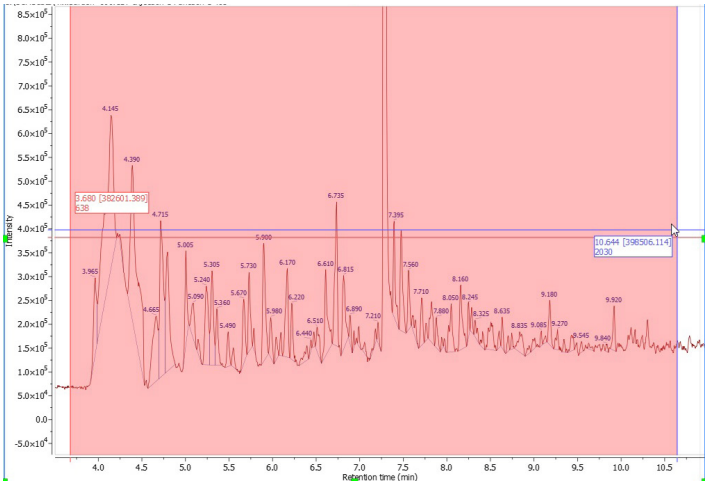


Figure 7. Co-adding mass spectra to search against the CDS Pyrolysis database.

Score	Polymer Name
909	Poly(vinyl alcohol-co-ethylene) ethylene 32 mol %

Figure 8. CDS Pyrolysis Database Search Results.

Conclusion

A sample from a rechargeable battery recycling stream was studied using EGA and MSP to investigate the presence of organic material including common binders, PVP and PVDF. While the sample was negative for PVP and PVDF, a solvent commonly used during the chemical recycling of rechargeable batteries, NMP was discovered, and a different polymer, most likely used in the separator, was tentatively identified using the CDS Pyrolysis Database coupled with Mnova's MSChrom.

References

1.Harreus, Albrecht Ludwig et al. "2-Pyrrolidone",(2011). Ullmann's Encyclopedia of Industrial Chemistry. Weinheim: Wiley-VCH.

2. Wang, Dong et al.," High performance hybrid Al2O3/poly(vinyl alcohol-co-ethylene) nanofibrous membrane for lithium-ion battery separator", Electrochimica Acta V176, 10 September 2015, pp 949-955.