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Degradation Analysis of a Solid-State Electrolyte using TG-IR-GC/MS

Introduction

Solid-state batteries (SSBs) are quickly becoming more popular as the industry looks to improve upon rechargeable battery performance and safety.[1] These are batteries which use a solid-state electrolyte in place of the more conventional liquid electrolyte. This provides a number of benefits including higher performance, cyclability and safety, all of which are currently acting as barriers to further development of lithium-ion batteries.

This work sets out to demonstrate the use of evolved gas analysis to understand the degradation products of a solid polymer electrolyte. This allows the user to not only understand the thermal degradation behaviour of the electrolyte but also gain a better understanding of the components present in the electrolyte.

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Experimental

Approximately 10 mg of a solid polymer electrolyte was analyzed using a PerkinElmer TG-IR-GC/MS evolved gas analysis system (Figure 1). Experimental conditions for each part of the analysis are shown in Table 1.

Figure 1. PerkinElmer TG-IR-GC/MS Evolved Gas System.

Results & Discussion

The degradation profile for the solid electrolyte is shown by the TGA curve in Figure 2.

Table 1. Experimental conditions used for measuring the degradation of a polymer electrolyte.

| TGA Parameters	
Temperature Range (°C)	30 - 1000
Heating Rate (°C/min)	20
Purge Gas	N_2 (30 – 850 °C, 100 mL/min), Air (850 – 1000 °C)
Transfer Line Parameters	
Transfer Line Temperature	280 °C
Flow Rate	80 mL/min
FT-IR Parameters	
Spectral Range (cm⁻¹)	4500 - 600
Resolution (cm⁻¹)	8
Scan Accumulations	2
GC Parameters	
Column	Elite-5ms 30 m x 0.25 mm x 0.25 µm (N9316282)
Inlet Temperature (°C)	280
Carrier Gas (Pressure)	Helium (12 psi)
GC Oven Parameters	50 °C for 1 min, 50 – 250 °C at 20 °C/min, hold for 10 minutes
MS Parameters	
Ion Energy	70 eV
Source Temperature	250 °C
Inlet Line Temperature	250 °C
MS Scan Range	50 – 350 u
Scan Time	0.2 s (Interscan delay of 0.05 s)
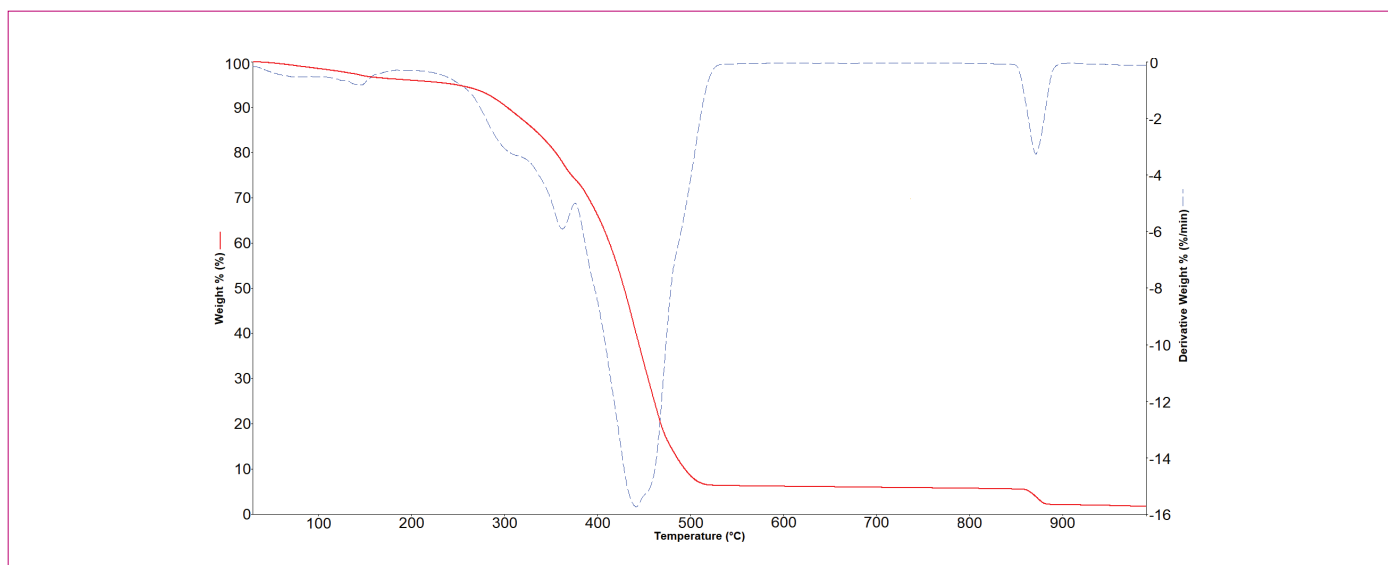
Figure 2. Weight loss (red) and derivative weight loss (blue) curves for the polymer electrolyte.

The material shows a relatively complex degradation profile with multiple weight losses, shown in Table 2.

Table 2. Weight loss values of a polymer electrolyte.

Temperature Range (°C)	Weight Loss (%)
30 - 200	4.08
200 - 315	7.89
315 - 375	13.67
375 - 550	68.07

Evolved gas analysis is used to better understand the degradation products. This allows the user to understand both the composition of the electrolyte as well as its gaseous degradation products.

The first step of the evolved gas measurement was FT-IR spectroscopy. FT-IR spectroscopy has a notable advantage here as it is a 'real-time' technique meaning that it is able to collect spectra of gases as they are evolved. However, unlike gas chromatography, FT-IR spectroscopy is measuring the gases without separation and so identification of mixtures can be more difficult using this technique alone. Nevertheless, during the initial TGA measurement of a polymer electrolyte, FT-IR spectroscopy can provide incredibly useful information such as confirmation of the main polymer and identification of functional groups present which can provide more confidence in results seen from GC/MS analysis. The FT-IR spectrum of the main weight loss (measured at approximately 440 °C) is shown in Figure 3 overlaid with a reference spectrum from the thermal degradation of poly(ethylene oxide) (PEO), a common polymer backbone used in solid state electrolytes. PerkinElmer's COMPARE™ algorithm was used to confirm the match between the gas evolved from pure PEO and that evolved from the polymer electrolyte. The correlation coefficient between the two spectra was calculated as 0.92, indicating a good match.

TG-IR also provides some information on the functional groups present in other, less prominent degradation products. FT-IR spectra of polymer electrolyte degradation products from three other temperatures of interest (300, 360 and 490 °C) are shown in Figure 4.
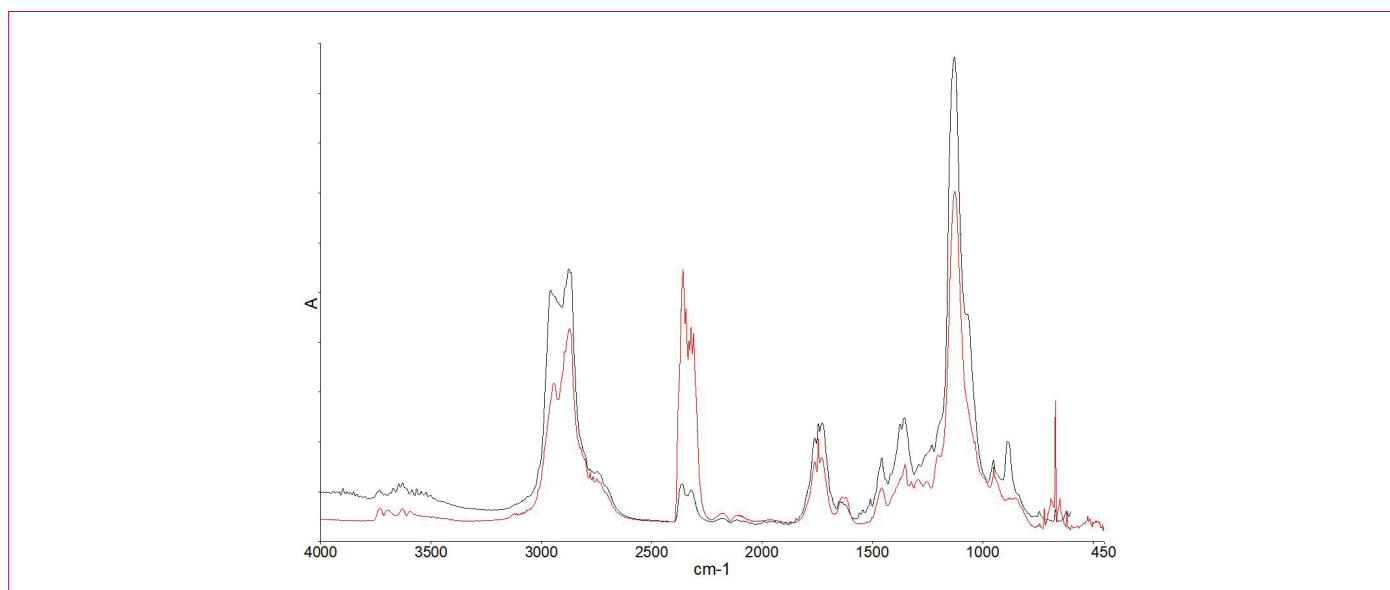

Figure 3. Spectrum collected during the main weight loss of the polymer electrolyte (440 °C, black) and reference spectrum from the degradation of poly(ethylene oxide) (red).
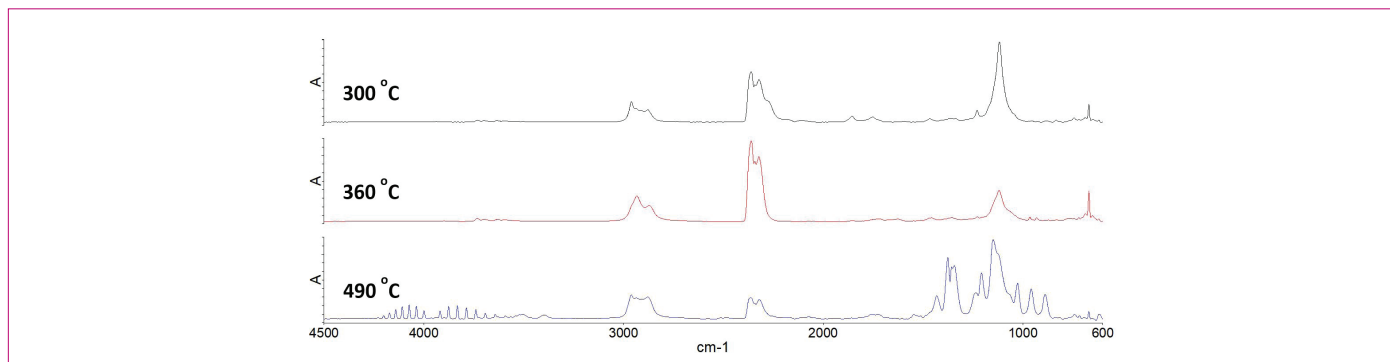

Figure 4. IR spectra of polymer electrolyte degradation products collected at 300 °C (black), 360 °C (red) and 490 °C (blue).

The spectra shown above are of components which are present at concentrations (360 °C, 0.6 mg/min), gaseous mixtures (490 °C) or a combination of the two (300 °C). The spectrum at 360 °C can be identified as the decomposition of poly(ethylene oxide) despite the rate of weight loss at this point being only 0.6 mg/min. This spectrum also aids in analysis of the data found at 300 °C. At 300 °C there is a shoulder on the CO_2 peak at 2257 cm^{-1} and a small peak 1230 cm^{-1} which are no longer present at 360 °C. Both these peaks correspond with an isocyanate functional group however a more comprehensive identification requires the use of GC/MS. The TIC chromatogram of the evolved gas at 300 °C with the compounds identified by searching the mass spectrum against the NIST™ database is shown in Figure 5.
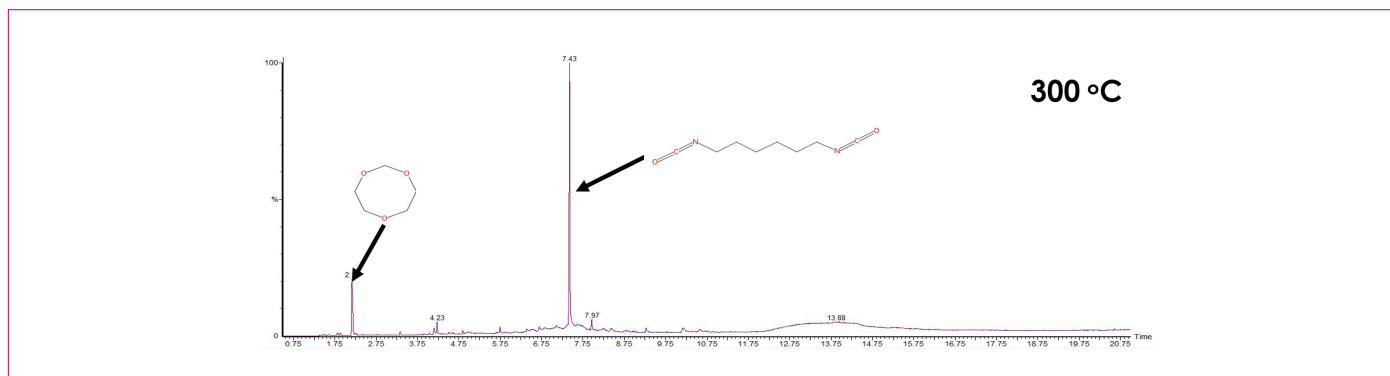

Figure 5. Chromatogram of gases evolved at 300 °C.

This chromatogram confirms two key points. First, the degradation of PEO has begun by 300 °C, as indicated by the cyclic trioxane. Secondly, that an isocyanate, specifically hexamethylene diisocyanate, a monomer in the synthesis of some solid-state electrolytes, is also evolved.[2]

The spectrum collected at 490 °C is more complex and searching it against commercially available FT-IR spectral libraries does not yield a score higher than 0.6. As such, this method alone cannot conclusively identify the evolved gas. However, the spectra do provide some information on the mixture of evolved gases. For example, the fine band structure from 4300 − 3600 cm^{-1} indicates the presence of HF. Furthermore, the doublet peak at around 1350 cm^{-1} may indicate the presence of an SO_2 group and the strong band at 1147 cm^{-1} may correspond to a C-F stretch. However, bands in this region of the IR spectrum could correspond to different functional groups so GC/MS is needed to provide more clarity. The chromatogram of the gases evolved at 490 °C is shown in Figure 6.
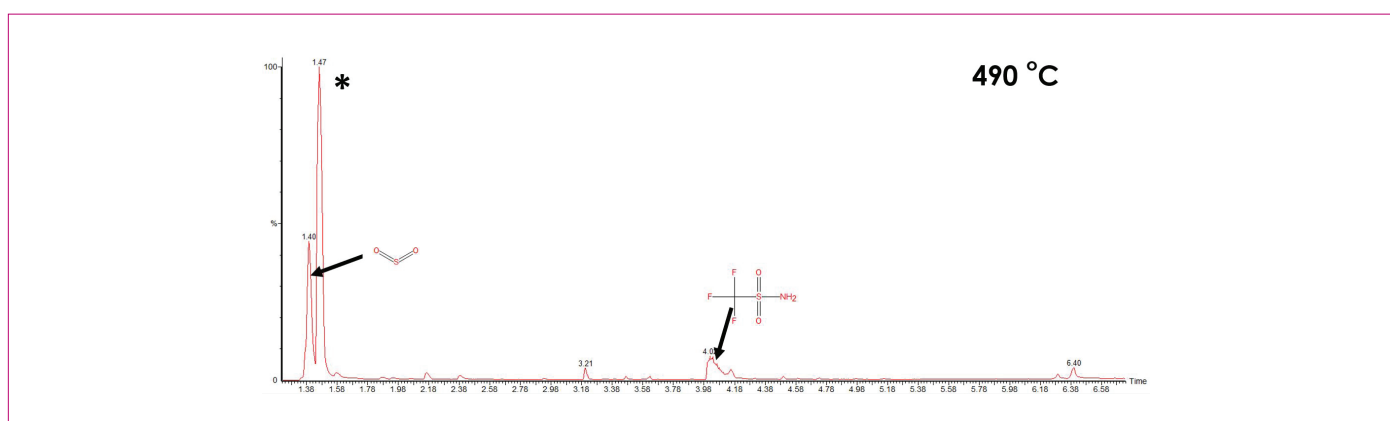

Figure 6. Chromatogram of gases evolved at 490 °C.

The two degradation products that are shown on the chromatogram could both be attributed to cleaving of the TFSI side chain from the PEO polymer backbone, a common configuration in solid-state electrolytes.[3] The peak marked by * did not give a good match in the NIST database. However, the best hit was an alkyl fluorophosphate which may have been the product of the degradation of one of the many phosphate-based additives present in polymer electrolytes.

Summary

TG-IR-GC/MS is a powerful tool for understanding the degradation of polymer electrolytes used in solid-state batteries. Thermogravimetric analysis provides users with an understanding of degradation patterns and temperatures while FT-IR spectroscopy provides real time data on evolved gases. Search and COMPARE™ algorithms can be used to identify some evolved gases but for low concentration components and more complex mixtures, GC/MS analysis is required making this the complete solution for degradation analysis of polymer electrolytes.

References

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2. Y. Kitazawa, K. Iwata, R. Kido, S. Imaizumi, S. Tsuzuki, W. Shinoda, K. Ueno, T. Mandai, H. Kokubo, K. Dokko and M. Watanabe, Chemistry of Materials, 2018, **30**, 252−261

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