APPLICATION NOTE

Batteries – Thermogravimetry

Determination of the Amount of Active Material in Innovative Battery Materials by Means of Thermogravimetry (TG)

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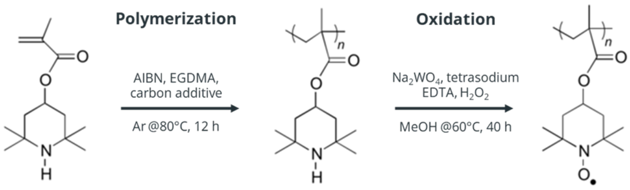
Introduction

As the demand for lithium-ion batteries continues to rise, driven by the growing adoption of electric vehicles and the integration of renewable energy sources, concerns have arisen regarding the availability and affordability of crucial raw materials. The escalating trend in raw material prices observed in recent years further underscores the pressing need to explore alternatives that capitalize on readily available and more uniformly distributed resources while maintaining comparable performance. In response to these challenges, researchers have actively explored diverse materials as potential alternatives to lithium-ion batteries [1]. We previously reported how thermoanalytical techniques can be valuable in supporting electrochemical energy storage research with regard to lithium-ion batteries [2, 3, 4] and here, we will show how they are capable of contributing to the investigation of emerging materials for batteries.

Particularly organic materials for batteries show promise due to their utilization of abundant and (potentially) renewable carbon-based compounds [5]. However, they are usually characterized by very low electronic conductivity that hinders their application as anodes and cathodes, since the supply of electrons is fundamental to the progression of electrochemical reactions. To overcome this issue, a substantial amount of conductive carbon is added to these compounds to enhance their conductivity. However, this carbon is an inactive compound (i.e., it does not store or release energy when charging or discharging the battery) and it decreases the achievable energy density by reducing the weight fraction of active material available in the electrode. Hence, finding the optimal quantity of conductive carbon in organic electrodes is a fundamental challenge to improvement of their performance in batteries. In the specific case of this application note, a redox-active polymer (poly(2,2,6,6-tetramethyl-1-piperidinyloxy methacrylate, or PTMA) was synthesized with several carbon additives in varying weight ratios between the polymer and carbon (see **figure 1** for a scheme of the synthesis) [6]. We then describe how thermogravimetric analysis was applied to quantify the actual amount of polymer and conductive carbon present in the sample, in order to check whether the planned ratio between these two components was conserved during the two-step synthesis process.



1 Scheme of the synthesis process of the PTMA polymer mixed with the conductive carbon additive.

Measurement Conditions

The thermogravimetric analysis was performed with a TG 209 ***F1*** *Libra*®. All the tests were performed at a heating rate of 5 K/min with a total gas flow of 40 ml/min. Alumina open crucibles (85 µl) were used, filled with 10 ± 0.010 mg of sample material. The samples were designated as follows (theoretical weight ratios):

PTMA-GN15:	85% PTMA, 15% graphene nanoplates
PTMA-SP15:	85% PTMA, 15% carbon black
PTMA-MW15:	85% PTMA, 15% multi-walled carbon nanotubes
PTMA-MW10:	90% PTMA, 10% multi-walled carbon nanotubes
PTMA-MW5:	95% PTMA, 5% multi-walled carbon nanotubes
PTMA-MW2.5:	97.5% PTMA, 2.5% multi-walled carbon nanotubes

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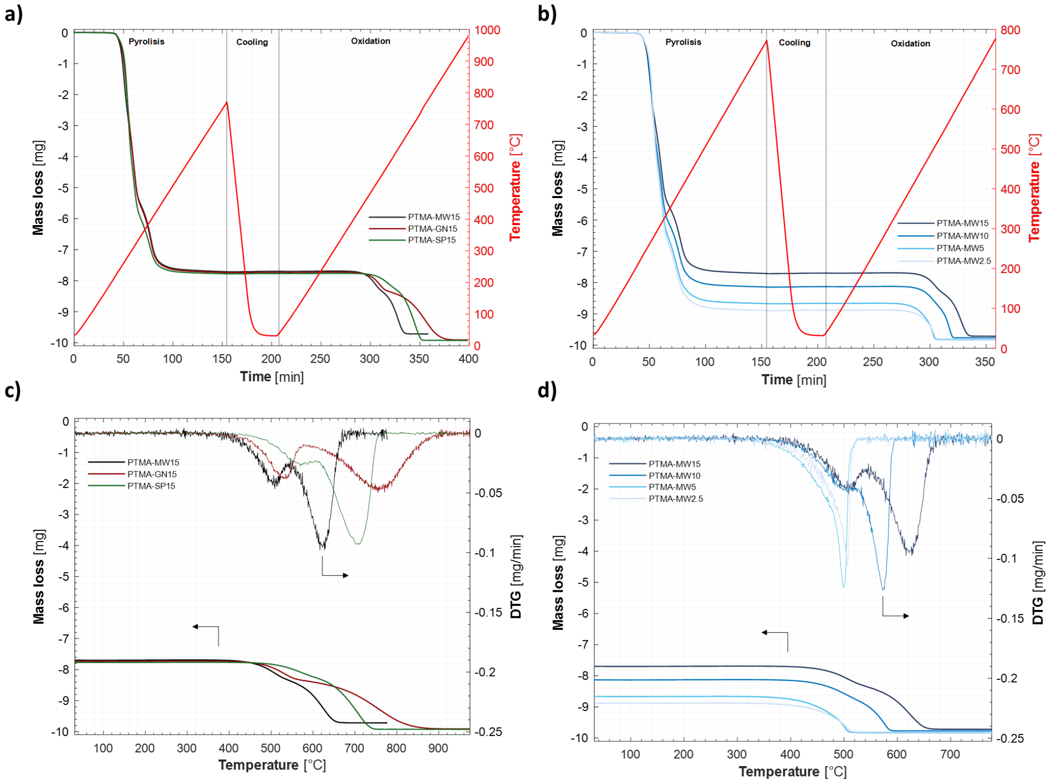
Measurement Results

The synthesized batches underwent analysis via TG, employing a two-step protocol. Initially, pyrolysis was conducted in an inert gas (N_2) environment, reaching 800°C, succeeded by a cooling period. Subsequently, oxidation took place in a mixture of 5% O_2 and 95% N_2, again reaching 800°C for samples containing multi-walled carbon nanotubes and 1000°C for the samples containing the other types of conductive additives. This was done to ensure complete combustion of the carbon, which was successfully achieved for each sample (see **figures 2a** and **2b** for the trend of the temperature during the experiment and the related TG and DTG for each sample).

The pyrolysis stage induces decomposition of the polymeric component with most decomposition by-products being gaseous and leaving the crucible. However, a minor portion of the polymer decomposes into pyrolysis soot, characterized as carbon particles [7]. Consequently, the mass loss during pyrolysis does not precisely reflect the polymer weight fraction, as a significant yet minor portion persists as a solid product. The subsequent oxidation step is essential for elimination of the remaining carbon species, constituting a mixture of pyrolysis soot and conductive carbon additive.

DTG during oxidation revealed two peaks in certain samples (**figures 2c** and **2d**). The lower-temperature peak is linked to the oxidation of pyrolytic soot resulting from polymer pyrolysis in the temperature range between ca. 400°C and 550°C, while the (eventual) second peak corresponds to the combustion of the conductive additive [7]. Measurement of the mass loss to the point where the absolute value of the DTG reached a minimum between the two peaks enabled estimation of the polymer quantity in the mixture by combining the mass loss from pyrolysis and the oxidation of pyrolytic soot.

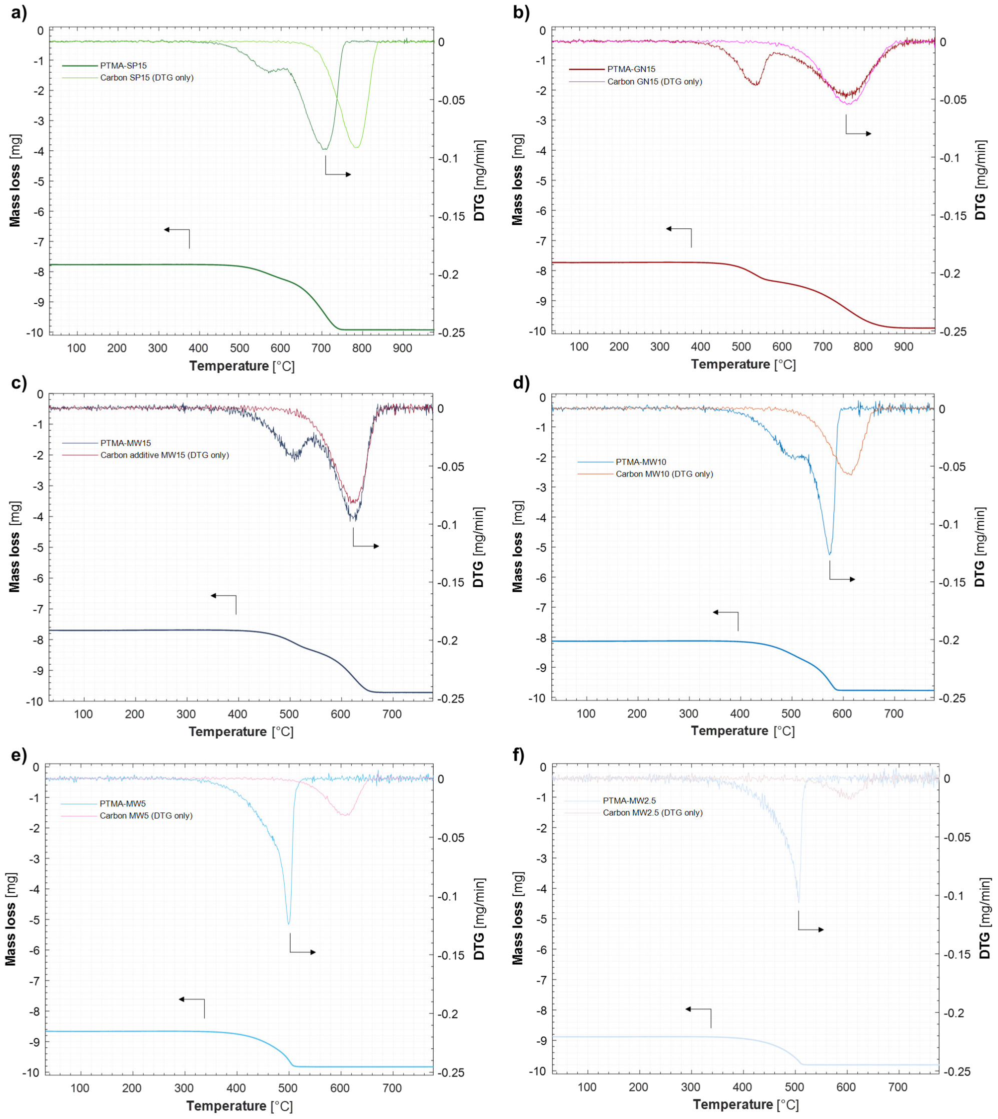
Along with the experiment on the PTMA-carbon samples, the conductive carbon additives themselves were the subject of TG experiments. Crucibles were loaded with the quantity of carbon additive expected in 10 mg of the respective polymer-carbon blend. For instance, for the PTMA-MW15 sample, 1.5 mg of additives were used in this experiment, which corresponds to a 15-% weight fraction in 10 mg of the polymer-carbon mixture.



2 **a)** TG results for the PTMA-MW15, PTMA-GN15, and PTMA-SP15 samples; **b)** TG results for the PTMA-MW15, PTMA-MW10, PTMA-MW5, and PTMA-MW2.5 samples; **c)** details on the oxidation part of the TA results on the three samples from Figure 2a, with the respective DTG curves; and **d)** detail on the oxidation part of the TG results on the four samples from Figure 2b, with the respective DTG curves. Reproduced from [6] under the terms of the CC-BY-NC-ND 4.0 license. Copyright 2023, American Chemical Society

Figure 3 illustrates a comparison between the mass loss derivative during sample oxidation and that of the corresponding carbon additive alone. Presentation of the mass loss on the y-axis as an absolute value instead of as a percentage is useful for checking whether the DTG peak at higher temperature observed in the PTMA-carbon samples aligns with the oxidation peak of the respective carbon additives.

Notably, for PTMA-GN15 and PTMA-MW15, the second peak in sample oxidation corresponded well to the carbon additive oxidation peak (see **figures 3b and 3d**). In the case of samples PTMA-SP15 and PTMA-MW10, the second oxidation peak occurred at a lower temperature than that of the carbon additive (**figures 3a and 3d**). This discrepancy may arise from the heat released during the preceding oxidation of the pyrolysis soot, potentially lowering the activation energy for carbon additive oxidation, and suggesting an intimate contact between the polymer and the additive. Lastly, samples PTMA-MW5 and MW-2.5 lacked the second peak (figure 2d and **figures 3e and 3f**), making it impossible to differentiate between the two contributions. This may be due to the very low amount of conductive additive present in those samples (5% and 2.5%, respectively, in weight), the oxidation of which was drastically enhanced by the energy released by the combustion of the pyrolysis soot formed by the polymer.



3 **a)** TG results for the PTMA-MW15, PTMA-GN15, and PTMA-SP15 samples; **b)** TG results for the PTMA-MW15, PTMA-MW10, PTMA-MW5, and PTMA-MW2.5 samples; **c)** details on the oxidation part of the TG results on the three samples from Figure 2a, with the respective DTG curves; and **d)** detail on the oxidation part of the TG results on the four samples from Figure 2b, with the respective DTG curves. Reproduced from [6] under the terms of the CC-BY-NC-ND 4.0 license. Copyright 2023, American Chemical Society

Table 1 Results of the actual samples' compositions

Sample	Additive	Mass loss during pyrolysis [mg]	Mass loss during oxidation related to polymer [mg]	Temperature @ DTG minium [°C]	Planned sample composition[a]	Actual sample composition[b]
PTMA-GN15	Graphene nanoplates	7.72	0.64	607	85/15	83.6/15.4/1.0
PTMA-SP15	Carbon black	7.76	0.51	580	85/15	82.7/16.6/0.7
PTMA-MW15	Multi-walled carbon nanotubes	7.69	0.67	543	85/15	83.5/13.5/3-0
PTMA-MW10	Multi-walled carbon nanotubes	8.13	0.63	520	90/10	87.6/10.1/2.3
PTMA-MW5	Multi-walled carbon nanotubes	8.67	-	-	95/5	-
PTMA-MW2.5	Multi-walled carbon nanotubes	8.89	-	-	97.5/2.5	-

[a] Polymer/conductive additive weight ratio
[b] Polymer/conductive additive/impurities weight ratio

The results of the actual samples' compositions are detailed in **table 1**. The actual sample composition is obtained by dividing the mass losses associated with the polymer and the carbon, as well as the residual mass in the crucible (residuals), by the initial amount of sample mass in the crucible (10 mg) and multiplying by 100 to obtain a percentage.

Conclusion

The thermogravimetric analysis confirmed the presence of a polymer part and a carbon part in the sample, and the residual mass at the end of oxidation indicated the quantity of non-volatile residuals present in the samples due to remainders of the synthesis process. These measurements allowed for calculation of an accurate composition of the powder samples. The weight fraction of PTMA resulting from the TG curves was about 1.5 to 2.5% lower than the theoretical one, probably due to a small fraction of non-polymerized monomer after the first synthesis step which was washed away during the product processing. Nevertheless, the planned composition was successfully obtained within a reasonable degree of accuracy, confirming the efficacy of the synthesis process chosen. Moreover, determination of the redox-active polymer weight fraction in the sample enabled accurate calculation of the capacity of the batteries built with the PTMA-carbon mixtures as cathodes.

References

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