APPLICATION NOTE

Batteries – Thermogravimetry-FT-IR

Characterization of PVDF Binder for Li-Ion Batteries by Means of TGA-FT-IR

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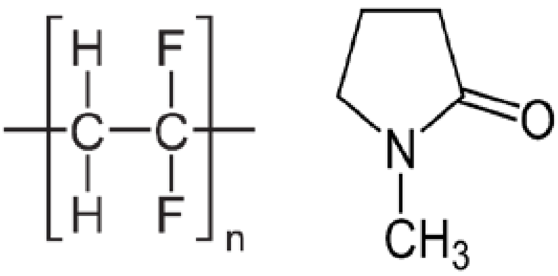
Introduction

A battery binder is a polymer material used to affix active materials, such as electrodes, onto the collector foil. It ensures that the electrode particles stay in place during charge and discharge cycles while allowing ions to move freely. One of the most common binders used for lithium-ion batteries is PVDF (polyvinylidene fluoride). It combines several advantages like mechanical strength, adhesive potential, chemical and electrochemical stability, solubility in organic solvents and swelling property with respect to the electrolyte.

The structural formulas of PVDF and NMP are depicted in figure 1. PVDF is always applied together with a solvent to create a homogeneous slurry. NMP (N-Methyl-2-pyrrolidon) is primarily used as the solvent for PVDF. Due to its high chemical resistance, NMP is often recycled and can be reused after a drying process. NMP plays a critical role, since it enables homogeneous layers on the electrode material, thereby improving the quality of the electrodes in terms of power, energy density and battery life.

Measurement Conditions

The measurement conditions are detailled in table 1.



1 a) Structural formula of PVDF b) Structural formula of NMP.

Table 1 Measurement conditions

Instrument	PERSEUS® TG *Libra*®
Temperature range	Room temperature to 1000°C
Heating rate	10 K/min
Purge gas	Nitrogen and air (40 ml/min)
Crucible	Al_2O_3, open (85 µl)

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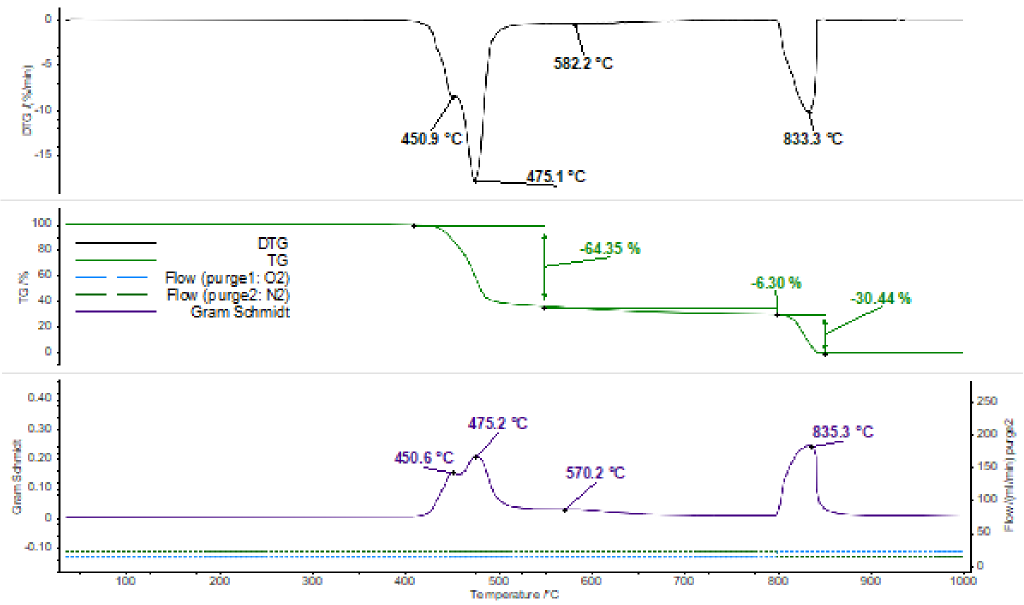
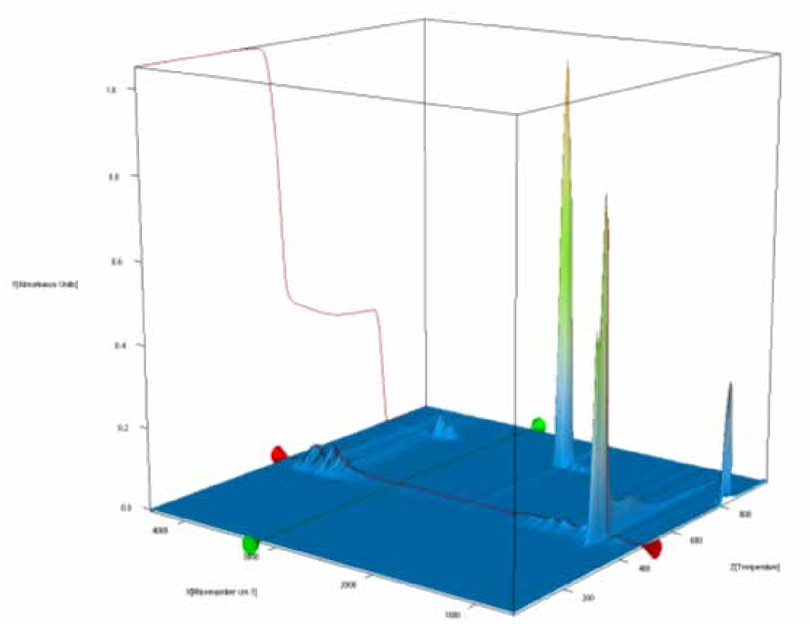
Measurement Results and Discussion

At the beginning, pure PVDF was investigated to determine the thermal stability, the decomposition behavior and the evolved gases. In the second step, PVDF dissolved in NMP was analyzed. Both samples were heated to 800°C in an inert atmosphere. Between 800°C and 1000°C, an oxidizing atmosphere was applied. The decomposition of pure PVDF starts above 400°C. In total, three steps of pyrolysis were detected. After switching the gas atmosphere to air, the combustion of the pyrolytic carbon takes place. The curve indicates that for all mass-loss steps, IR active substances are released (see figure 2)

The 3-dimensional plot displays all measured IR spectra in correlation with the temperature and the TGA curve; see figure 3.



2 Temperature-dependent mass change (TGA, green), rate of mass change (DTG, black) and Gram-Schmidt curve (purple) of pure PVDF.



3 3D plot of all detected IR spectra of pure PVDF, TGA curve plotted in red at the back of the cube

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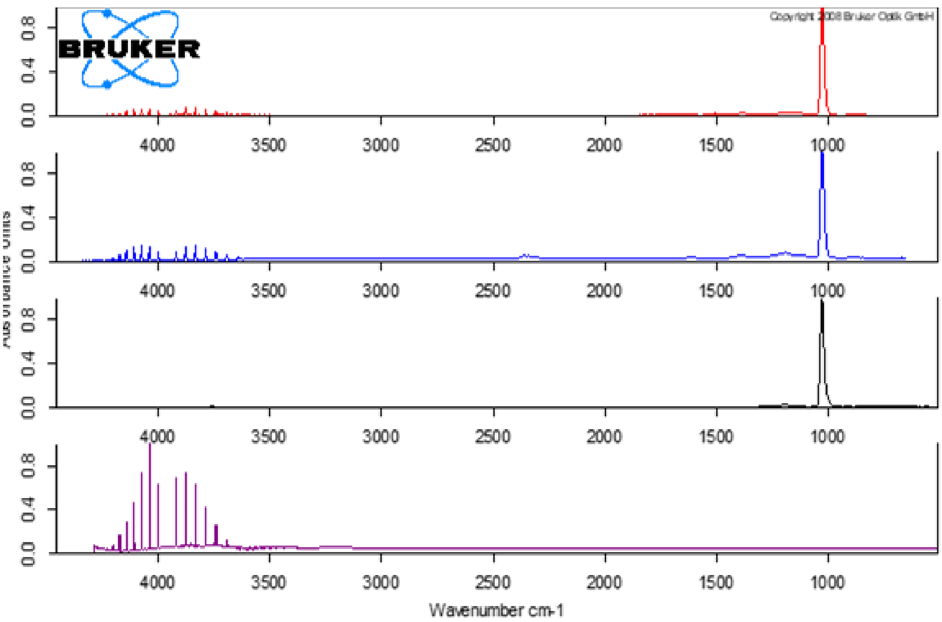
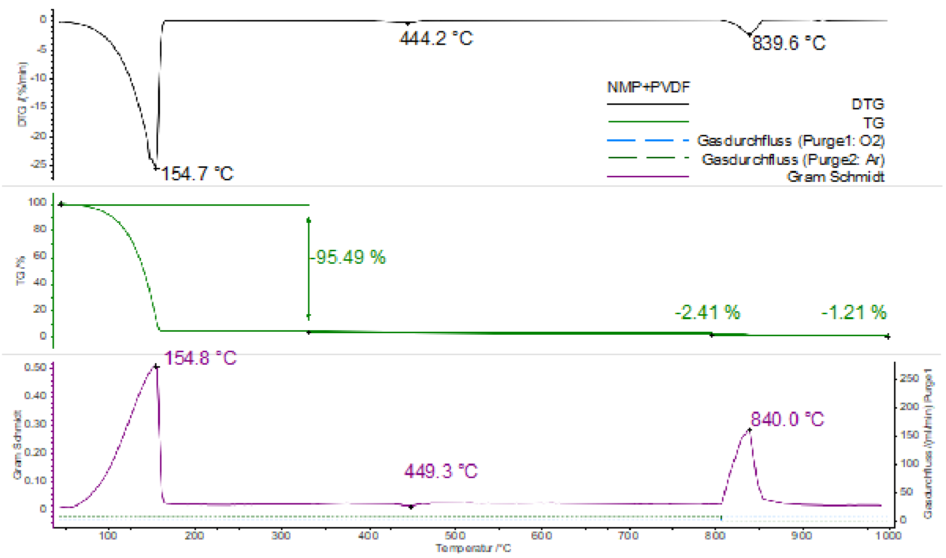
The gas spectra occurring during pyrolysis at 460°C and 570°C are extracted and compared to the gas phase libraries. In this way, silicon fluoride and hydrogen fluoride were identified. This is in good accordance with literature data[1). It is to be assumed that the SiO_2, which is used as a coating in the heated interface between TGA and FT-IR, reacts with HF to become the silicon fluoride detected.

The TGA-FT-IR measurement on NMP in combination with PVDF (figure 5) was performed under the same measurement conditions. Under inert conditions to 800°C, two mass-loss steps of 95% and 2% were detected. The combustion under oxidizing conditions above 800°C led to the burn up of pyrolytic carbon and the release of carbon dioxide. A mass loss of 1.2% was detected. Using the FT-IR technique, it was possible to identify the released products.



4 Extracted spectra at 460°C (red) and 570°C (blue) compared to the library spectra of SiF_4 (black) and HF (purple).



5 Temperature-dependent mass change (TGA, green), rate of mass change (DTG, black) and Gram-Schmidt curve (purple) of PVDF in NMP.

[1)] Pyrolysis GC/MS Data book of Synthetic Polymers, Tsuge Shin, Ohtani Hajime, Watanabe Chuichi, Elsevier, 2011

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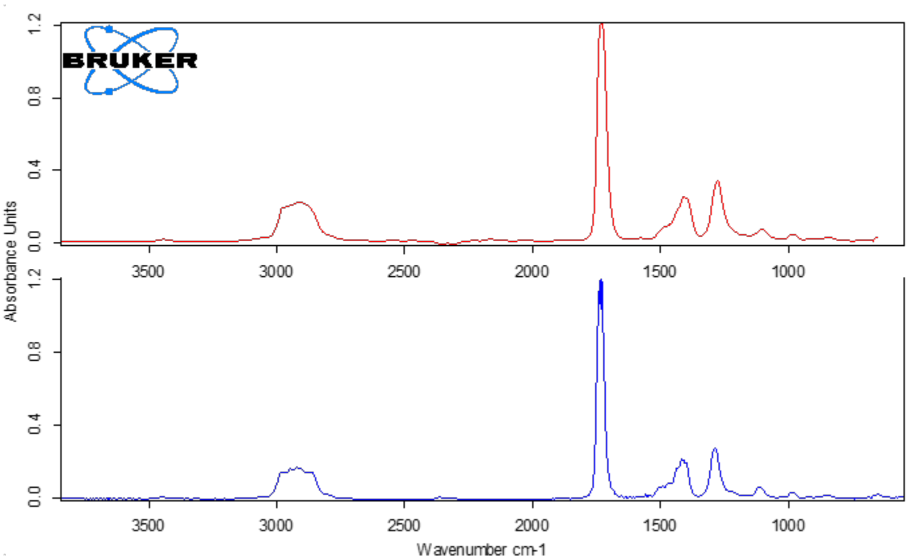
The measured spectrum at 155°C was extracted and compared with the NIST library of gas phase spectra (figure 6). Very high similarity with the library spectrum of NMP was found, so it was possible to prove that NMP evaporates and does not decompose during heating. In principle, it is therefore possible to recycle NMP after the drying process in battery production.

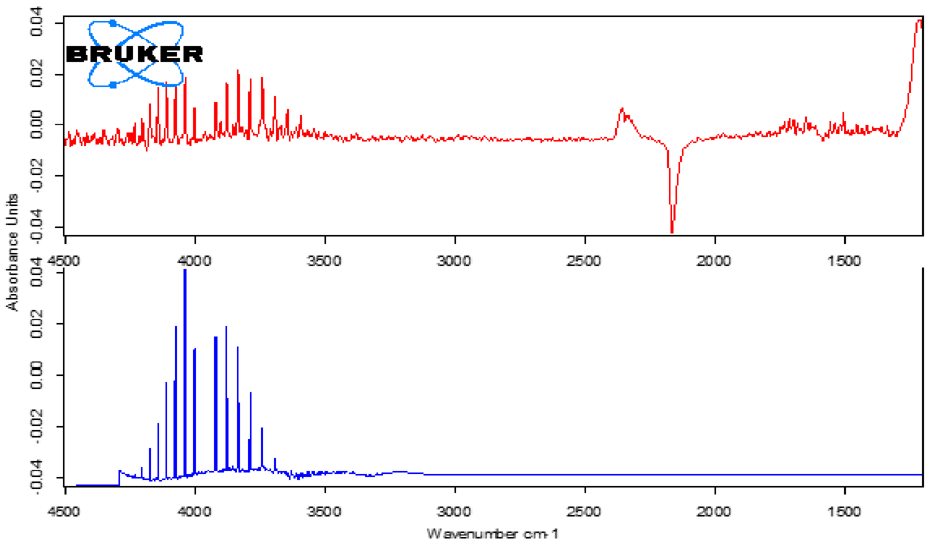
The measured spectrum at 432°C, which was related to the second mass-loss step, was identified as the release of hydrogen fluoride. Thus, the decomposition of PVDF during this mass-loss step is demonstrated (figure 7).

Summary

With the help of TGA-FT-IR analysis, it is possible to characterize a typical solution of PVDF in NMP for battery production. Along with the evaporation of NMP, also the decomposition of PVDF was easily identified by evolved gas analysis. TGA-FT-IR coupling is thus also well suited for analyzing corrosive gases like HF.



6 Extracted spectra of PVDF in NMP (red) at 155°C compared to the library spectra of NMP (blue).



7 Extracted spectra at 432°C (red) of PVDF in NMP compared to the library spectrum of HF (blue).

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