

Thermal Characterization of the Battery Electrolyte LiAsF_6 – Safe Handling in the Glovebox

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Introduction

Battery electrolytes play a crucial role in energy storage and are an essential component of modern battery technologies. These substances enable the flow of ions between the electrodes, which is essential for charging and discharging the battery. In recent years, research into battery electrolytes has made significant progress toward improving the efficiency, safety and lifespan of batteries. With the increasing importance of electric vehicles and renewable energy, understanding and advancing electrolytes is central to a sustainable energy future.

However, hazards such as overheating or thermal runaway need to be considered and investigated. Thermal analysis provides insight into the thermal properties, such as phase transition or decomposition, of these materials.

Representing the numerous battery electrolytes, the widely used lithium hexafluoroarsenate (LiAsF_6) was examined for caloric effects and mass changes using simultaneous thermal analysis.

Measurement Conditions

Due to the hygroscopic properties of LiAsF_6 , the sample was prepared in the glovebox under argon to prevent the material from absorbing water. The STA measurement was also carried out in an argon-purged glovebox. Detailed measurement parameters can be found in table 1.

Table 1 Measurement parameter used for the investigation with the STA 449 Jupiter®

| Parameter | Sample LiAsF_6 |
|---------------------|---------------------------|
| Sample weight | 12.1 mg |
| Crucible | Concavus® Al, pierced lid |
| Sensor | TGA-DSC c_p , type S |
| Furnace | SiC |
| Temperature program | RT to 600°C |
| Heating rate | 10 K/min |
| Gas atmosphere | Argon |
| Gas flow | 70 ml/min |

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Measurement Results

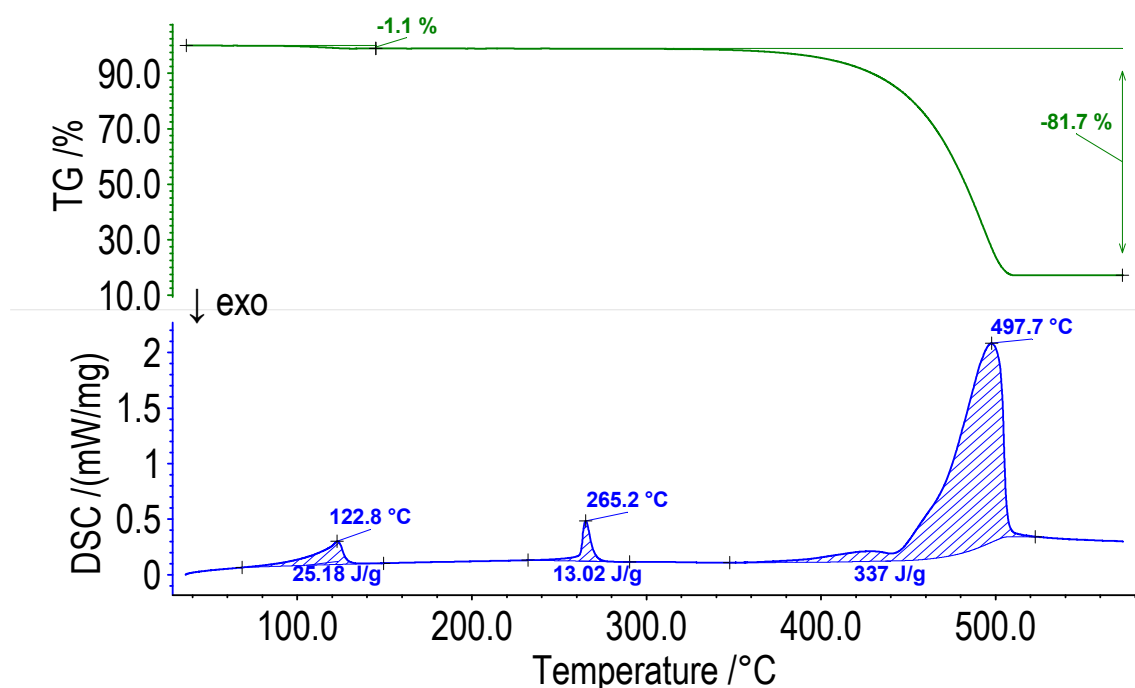
The TGA-DSC results are depicted in figure 1. The mass-loss curve shows two steps of 1.1% and 81.7%. The first mass-loss step can presumably be attributed to the release of moisture. The second mass-loss step is due to the decomposition of the LiAsF_6 . Two endothermic effects with peak temperatures of 122.8°C and 497.7°C and enthalpies of 25.18 J/g and 337 J/g can be detected from the DSC curve; these correlate to the mass-loss steps. Besides that, at a temperature of 265°C, a reversible solid-solid phase transition of LiAsF_6 changing from rhombohedral phase to cubic can be identified¹.

Summary

The characterization of energetic effects and the decomposition of the battery electrolyte LiAsF_6 was successfully carried out using simultaneous thermal analysis. Thanks to the ability to carry out the sample preparation and

STA measurement inside a glovebox, even materials that would otherwise react with the surrounding atmosphere – such as the LiAsF_6 material investigated – can be successfully measured. Based on the data obtained, it can be seen that LiAsF_6 remains stable until the solid-solid phase transformation at around 265°C. At temperatures above 300°C, the material decomposes under inert conditions. This information provides additional knowledge with regard to potential hazards such as overheating and thermal runaway.

All NETZSCH instruments can be operated in a glovebox, allowing the analysis of materials that are sensitive to environmental conditions or have toxic properties. By using a glovebox, such materials can be processed and analysed under controlled conditions, isolated from the surrounding environment. This allows experimental results to be obtained that would not be possible without these protective measures, as the material retains its properties while human safety is ensured.



1 Temperature-dependent mass-loss curve (TGA, green) and heat-flow curve (DSC, blue) of LiAsF_6 .

¹Gavrichev, K.S., Sharpataya, G.A., Gorbunov, V.E. et al. Thermodynamic Properties and Decomposition of Lithium Hexafluoroarsenate, LiAsF_6 . Inorganic Materials 39, 175–182 (2003). <https://doi.org/10.1023/A:1022102914631>