

Application News

No. T151

Thermal Analysis

Investigation of Thermal Properties of Lithium-Ion Battery Components

■ Introduction

Lithium-ion batteries are used widely in household electrical appliances such as cell phones and laptop computers. A considerable increase in demand for lithium-ion batteries is predicted in the transportation sector, where they will be used in aeroplanes, hybrid vehicles, and electric vehicles. These applications will require an increase in the power density, efficiency, lifespan, and stability of these batteries. Lithium-ion batteries are composed of a number of parts, including a cathode, anode, electrolyte, and separator. Increasing the performance of lithium-ion batteries will require detailed investigation and analysis of the properties of each of these components, and of the battery as a whole, by instrument analysis. We describe an example investigation of the thermal properties of a lithium-ion battery by thermal analysis.

■ Investigation of Thermal Stability of Electrode Materials

Lithium-ion batteries have a risk of abnormal heat generation or fire from overcharge or from other causes. An investigation of the stability of the battery requires that the behavior of each component be evaluated during heating. The top line in Fig. 1 shows measurements obtained from the cathode active material (LiCoO₄) and electrolyte of a battery after charging using a differential scanning calorimeter. Charging causes the active material to become unstable, and from around 200 °C large exothermic peaks caused by degradation can be seen. This information is important for the selection and preparation of electrode materials since reducing these peaks shows components are more thermally stable and safer at higher temperatures.

The bottom line shows measurements obtained from the cathode active material and electrolyte of a battery before charging. The results show no major heat generation since the active material is stable before charging.

■ Measurement of Moisture Content in Electrode Materials

Lithium-ion batteries are sensitive to moisture and the moisture content of components must be controlled during manufacture. We describe using thermogravimetric analysis (TGA) to calculate the moisture content of LiFePO₄ and graphite electrode active materials.

The graph in Fig. 2 shows temperature on the horizontal axis and percentage weight loss on the vertical axis. Heating the samples and calculating weight loss up to 200 °C showed a small weight change of 0.033 % in the graphite. TGA is normally performed with several tens of milligrams of sample at most, but even smaller changes in weight can be detected by using macro-type thermogravimetric analyzers able to accommodate sample masses in the order of grams.

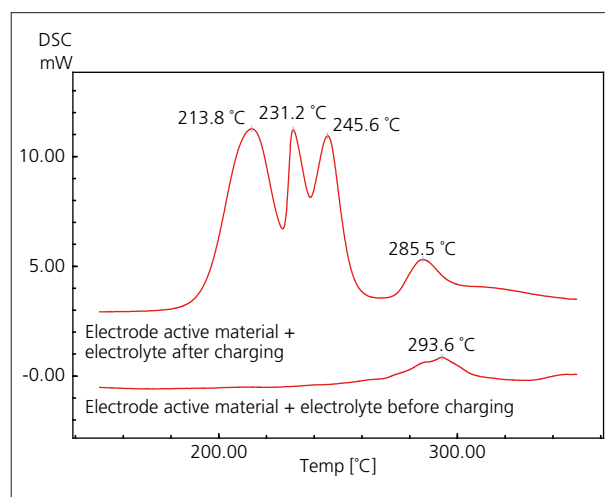


Fig. 1 Differential Scanning Calorimetry (DSC) Measurements of Electrode Active Material and Electrolyte

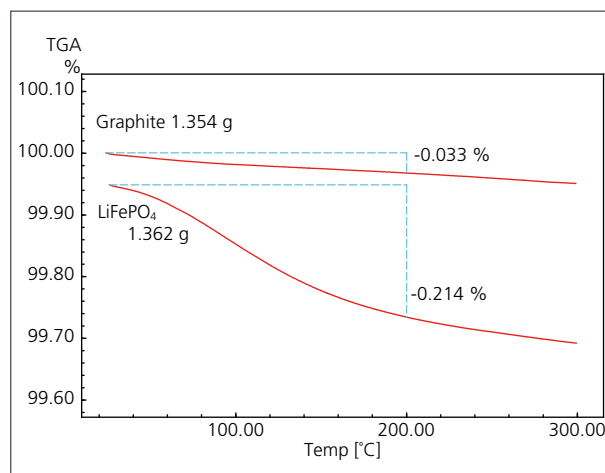


Fig. 2 TGA of Electrode Active Materials

Thermal Properties of Separator

The separator not only prevents short circuit of the cathode and anode but also allows passage of lithium ions and is an important component in terms of battery performance and safety. DSC measurements performed on three different separators are shown in Fig. 3.

Endothermic peaks were recorded for each separator that were probably caused by fusion (melting) of polyethylene in the region of 100 to 150 °C. Melting peak temperatures arose in the order of sample 1, 2, and 3 from lowest to highest temperature.

The separator probably shrinks when it is close to its melting temperature, and we predict that during abnormal heat generation it is safer that shrinking occurs at higher temperatures. A very minor endothermic peak can also be seen around 160 °C for sample 2, which is presumed to be caused by a very small amount of polypropylene in the separator.

Changes in separator dimensions caused by heat and measured by thermo-mechanical analysis (TMA) are shown in Fig. 4. TMA was used to measure extension and shrinking of the separator film while applying a negligible load in a tensile direction. The samples used were the same samples 1 and 2 measured previously with a differential scanning calorimeter, and measurements were taken from each sample in a machine direction (MD) and transverse direction (TD). Comparing the results from each sample, shrinking in both the MD and TD was observed at a higher temperature in sample 2, which corresponds to the results obtained by DSC. There was also less shrinking in the TD compared to the MD in both samples, and TD shrinking was smaller in sample 1 compared to sample 2. Considering safety from the perspective of short circuit prevention during abnormal heat generation, sample 1 is predicted to be less useful because it shrinks at a lower temperature, but also advantageous since it exhibits less TD shrinking.

The results of TMA of stress during shrinking are shown in Fig. 5. Shrink stress increases with increasing temperature, reaches a maximum at around 130 °C, after which it reduces.

These results also show the shrink stress is greater in the MD than TD. Although Fig. 4 shows almost no difference in dimensional changes during shrinking in the MD between samples 1 and 2, a noticeable difference between the samples is apparent in the MD in terms of shrink stress.

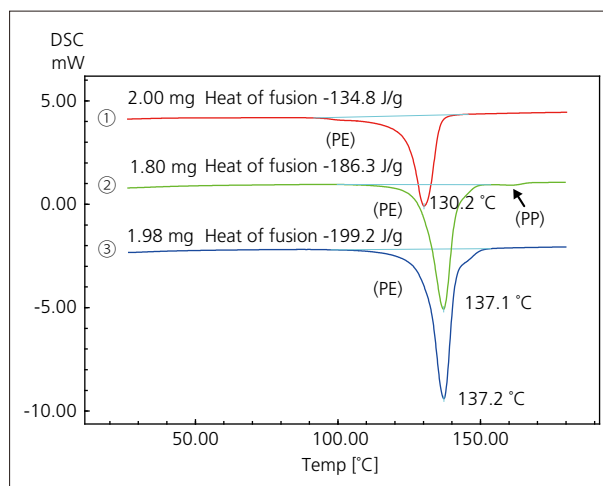


Fig. 3 DSC Measurement of Separators

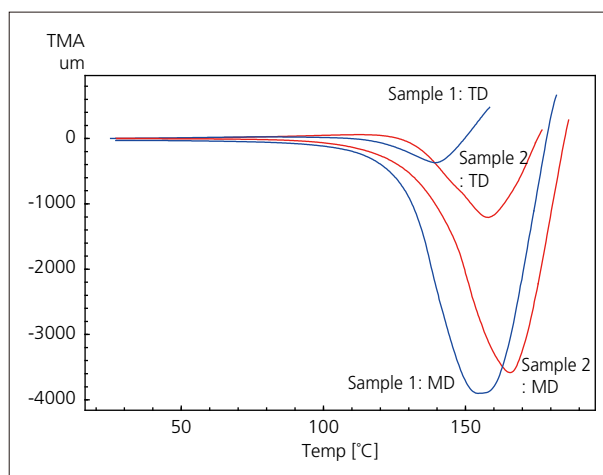


Fig. 4 TMA of Separators

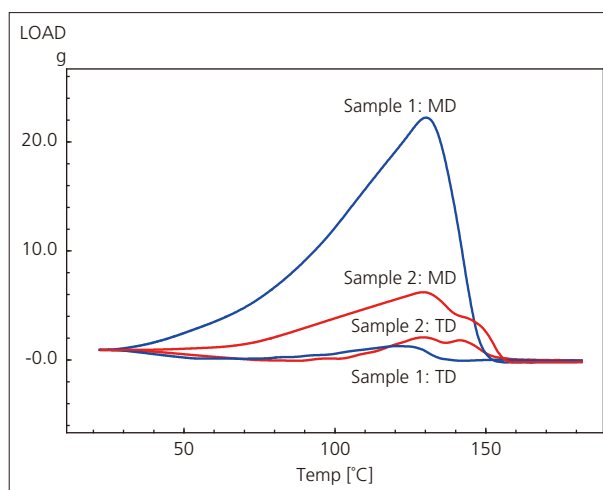


Fig. 5 TMA of Separators (Shrink Stress)