Characterization and Analysis of PVDF Used as a Lithium-Ion Battery Binder

Introduction

PVDF (Polyvinylidene fluoride), along with other polymers such as SBR and PTFE, is commonly used as a binder in the anode of lithium-ion batteries. It is the most common material used as a binder due to its electrochemical and chemical stability, and high adhesion to the current collector. The binder serves several purposes, including aiding film formation and improving dispersion of the active material in the solvent. Like many battery components, understanding both the chemical composition and thermal behaviour of PVDF is incredibly important for predicting performance, especially under the harsh conditions of a lithium-ion battery.
FT-IR Experimental

PVDF binder was measured using the PerkinElmer Spectrum Two™ Infrared Spectrometer (Figure 1) with a diamond crystal universal attenuated total reflectance (UATR) accessory.

The PVDF powder was measured, as received, with no further sample preparation. The data collection parameters employed are shown in Table 1.

Table 1: Data collection parameters used for infrared analysis of PVDF.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range</td>
<td>4000 – 650 cm⁻¹</td>
</tr>
<tr>
<td>Resolution</td>
<td>4 cm⁻¹</td>
</tr>
<tr>
<td>Number of Scans</td>
<td>4</td>
</tr>
<tr>
<td>Corrections</td>
<td>Atmospheric Vapour Compensation (AVC)</td>
</tr>
</tbody>
</table>

In order to verify the identity of the polymer, it was searched against the PerkinElmer Polymer Library.

Results and Discussion

The infrared spectrum of PVDF, overlaid with the best hit result from the library search, is shown in Figure 2.

The library search score for this hit was 0.98, indicating a very good match.

DSC Experimental

Differential scanning calorimetry (DSC) was used to study the effect of cooling rate on the thermal properties of PVDF. A sample of PVDF was cooled from 200 °C to -80 °C at 5, 10, 20, 50, 100, 200, 300 and 500 °C/min using a PerkinElmer DSC 8500 (Figure 3) with a He purge (40 mL/min). After each cooling step the material was held at -80 °C for 2 minutes before being heated at 300 °C/min to 200 °C. Using a fast-heating approach ensures the sample does not recrystallize during heating and therefore gives more accurate data for ΔH, of the material formed during cooling.

The DSC curves for different cooling rates are shown in Figure 4.

Results and Discussion

The DSC curves for different cooling rates are shown in Figure 4.

Figure 1: PerkinElmer Spectrum Two FT-IR Spectrometer with UATR Accessory.

Figure 2: ATR-IR spectrum of PVDF (Black) overlaid with library best hit (Green).

Figure 3: PerkinElmer DSC 8500

Figure 4: PVDF scans at 300 °C/min after cooling at different rates.
Pyris™ software may be used to calculate the enthalpy of fusion ($\Delta H_f$) as well as melting point ($T_m$). Interestingly, both enthalpy of fusion and melting point decreased in a logarithmic fashion with increasing cooling rate, as can be seen in the graphs depicted in Figure 5.

By dividing the experimental value for $\Delta H_f$ by the theoretical value for $\Delta H_f$ for 100% crystalline PVDF (105 J/g), the crystallinity of the samples cooled at different rates can be approximated. The estimations of the crystallinity of these materials ranged from 50.6% for PVDF cooled at 5 °C/min down to 46.1% for PVDF cooled at 500 °C/min.

**Results and Discussion**

The TGA weight loss curve for PVDF is shown in Figure 7.

The first weight loss could be associated with defluorination of the polymer, analogous to the decomposition of poly(vinyl chloride).\(^2\) The second weight loss, occurring after the introduction of air, is likely the decomposition of the remaining carbon, producing $\text{CO}_2$.

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**TGA Experimental**

The PerkinElmer TGA 8000 (Figure 6) was used to examine the pyrolysis behaviour of PVDF. This information can be incredibly useful to know for scenarios wherein the battery enters thermal runaway. TGA analysis was carried out in a platinum crucible. The sample was heated from 50 to 725 °C at 20 °C/min under nitrogen. The gas was switched to air at 725 °C then heated to 900 °C at 20 °C/min.
Summary

FT-IR spectroscopy provides a fast and easy method for the identification of PVDF by using commercial spectral libraries and the Search function in Spectrum 10™ software. DSC and TGA allows users to obtain information on the thermal behaviour of battery components, providing valuable insight into how a material might react to changing conditions within a cell.

2. S. Ma, J. Lu, and J. Gao, Energy & Fuels, 2002, 16 (2), 338-342