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Application News

IRSpirit™, DSC-60 Plus, DTG-60

Characterization of Lithium-Ion Battery Binders

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User Benefits

- ◆IRSpirit can be used to evaluate the composition of electrode materials, and the combination of electrode materials can be expected to improve battery characteristics such as energy density.
- ◆DTG-60 and DSC-60 Plus can be used to evaluate the thermal characteristics of electrode materials in order to optimize and improve the thermal stability of batteries.

■ Introduction

In recent times, there have been discussions about the safety and environmental sustainability of lithium-ion batteries (LIBs). Intensive research is also carried out on inactive materials such as separators, conductive agents and binders, so that the battery cells can be manufactured by a completely water-based route without the use of organic solvents [1].

Binders are an important part of electrode formulation in LIBs because they maintain the physical structure and prevent the electrode from falling apart. Poly(vinylidene-fluoride) (PVDF) is usually used as cathode binder, due to its excellent chemical and electrochemical resistance, good thermal and mechanical stability, and suitable rheological properties with carbon materials. However, environmentally unfriendly solvents are used during the electrode manufacturing process [2]. In environmentally-friendly electrode fabrication processes, water-soluble polymeric binders such as sodium carboxymethylcellulose (NaCMC) and styrene–butadiene rubber (SBR) are used instead [3].

This application news describes the use of Fourier Transform Infrared Spectrometry (FTIR), Thermogravimetric Analyzer (TGA) and Differential Scanning Calorimeter (DSC) for characterization of 3 types of battery binders - NaCMC, PVDF and SBR.

■ Experimental

The battery binders were purchased from Beyond Battery Pte Ltd, Singapore. The SBR sample solution was coated on a glass slide and dried at room temperature (RT) overnight to remove water solvent before FTIR and DSC analysis. The PVDF and NaCMC samples were analyzed without any pre-treatment.

FTIR

The samples were measured using Shimadzu FTIR IRSpirit (Fig. 1) and QATR™-S single reflection ATR accessory with diamond prism. The measurement conditions are shown in Table 1.

Table 1 Instrument and Analytical Conditions for FTIR

Instruments	: IRSpirit QATR-S (Diamond)
Resolution	: 4 cm^{-1}
Accumulation	: 45
Apodization function	: Happ-Genzel
Detector	: DLATGS

Fig. 1 IRSpirit™ FTIR with QATR™-S

TGA

TGA was used to measure decomposition temperature to obtain thermal stability results. The sample was placed in an aluminium pan and placed in a Shimadzu simultaneous DTA-TGA model DTG-60 (Fig. 2) with an empty aluminium pan as reference. The measurement conditions are shown in Table 2. Each sample was analysed at least 2 times.

Table 2 Instrument and Analytical Conditions for DTG-60

Temperature Range	: RT → 580 °C
Heating/Cooling Rate	: 10 °C/min
Atmosphere	: Nitrogen (300 mL/min)

The samples were also measured in Air instead of Nitrogen.

DSC

The glass transition temperature and melting temperature were determined according to ISO 11357-2 [4] and 11357-3 [5] respectively. The sample was placed in an aluminium pan and transferred to the Shimadzu DSC-60 Plus (Fig. 2) furnace with an empty aluminium pan as reference. The measurement conditions are shown in Table 3. Each sample was analysed at least 2 times.

Table 3 Instrument and Analytical Conditions for DSC-60 Plus

Temperature Range (NaCMC)	: RT → 200 °C, 5 min → -100 °C, 5 min → 200 °C
Temperature Range (PVDF)	: RT → 210 °C, 5 min → -100 °C, 5 min → 210 °C
Temperature Range (SBR)	: RT → 100 °C, 5 min → -100 °C, 5 min → 100 °C
Heating/Cooling Rate	: 20 °C/min
Atmosphere	: Nitrogen (100 mL/min)

Fig. 2 DTG-60 (left) DSC-60 Plus (right)

■ Results and Discussion

FTIR Results

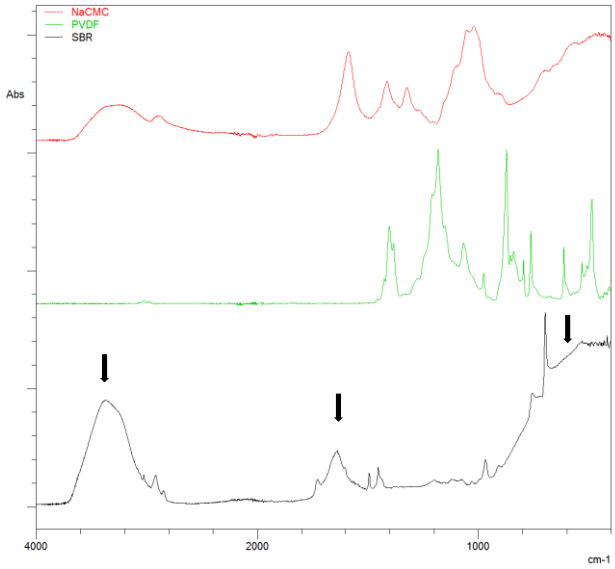

Fig. 3 IR Spectra of battery binder samples

Fig. 3 shows the IR spectra of the battery binder samples. For SBR, absorption peaks from water (3800 – 2800 cm^{-1} , 1800 – 1500 cm^{-1} , 1000 cm^{-1} and below) were observed as marked by arrows in Fig. 3. The strong absorption water peaks would mask the absorption peaks from SBR. Thus, the SBR sample was dried by coating on a glass slide and left overnight to remove the water before the sample was remeasured. Fig. 4 shows the IR spectra of SBR solution and dried SBR. With the absence of water absorption peaks, the absorption peaks of SBR are more prominent, especially in the wavenumber region of 1000 cm^{-1} and below.

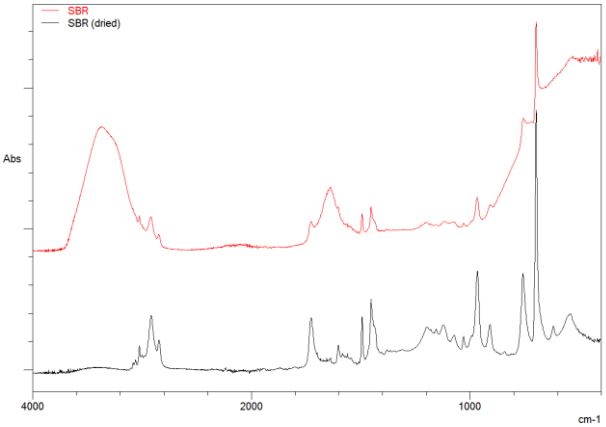

Fig. 4 IR Spectra of SBR and SBR (dried)

DTG-60 Results

The decomposition temperature of battery binders were investigated by TGA to obtain thermal stability results. The decomposition temperature is defined as the temperature where the TGA signal starts to decrease by 2 %. Each sample was measured 2 times - Fig. 5 and Fig. 6 show the TGA results of one of the 2 measurements when carried out in Nitrogen and Air respectively. The average results of 2 measurements are summarized in Table 5.

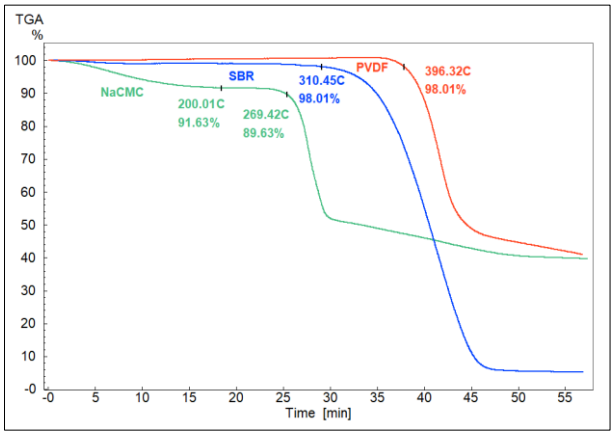

Fig. 5 TGA graphs for battery binders in Nitrogen

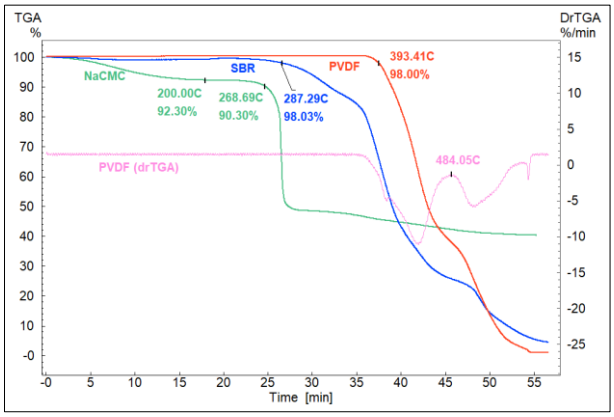

Fig. 6 TGA graphs for battery binders in Air

Table 4 Thermal stability of battery binders in Nitrogen and Air

	NaCMC	PVDF	SBR
Decomposition Temperature in Nitrogen (°C)	269.3 °C	398.6 °C	312.8 °C
Decomposition Temperature in Air (°C)	268.6 °C	396.4 °C	286.4 °C
Weight Change from 30-575 °C in Nitrogen	59.6 %	58.7 %	94.5 %
Weight Change from 30-575 °C in Air	59.6 %	99.2 %	95.2 %

Notes:
1) The data shows the average results from 2 measurements (RSD < 2 %).
2) For NaCMC, the weight loss up to 200°C is due to loss of water [7]. Thus, the 2 % weight loss is calculated from 200 °C .

The temperature range used for the preparation and drying of battery electrodes during manufacturing is 20 – 90 °C [6]. The decomposition temperatures for NaCMC, PVDF and SBR are more than 90 °C in Nitrogen and Air. Thus, NaCMC, PVDF and SBR can be used for manufacturing of battery electrodes at 20 – 90 °C .

Overall, PVDF with the highest decomposition temperature is the most stable, followed by SBR and then NaCMC. The thermal stability for NaCMC is similar in both Nitrogen and Air. PVDF also has similar thermal stability in both Nitrogen and Air. However, SBR has different thermal stability in Nitrogen and Air. SBR decomposed at a lower average temperature of 286.4 °C in Air than Nitrogen (312.8 °C). Thus, SBR has higher thermal stability in Nitrogen than Air.

TGA can also be used to study the degradation of battery binders by monitoring the weight loss. The weight loss from 30 – 575 °C for NaCMC in both Nitrogen and Air are almost similar where about 60 % has degraded at 575 °C. For PVDF, the weight loss from 30 – 575 °C is greater in Air than Nitrogen. PVDF shows 2 stages of weight loss in Air as shown in the drTGA signal (Fig. 6). The first weight loss from 30 – 484 °C could be associated with defluorination of PVDF whereas the second weight loss after 484 °C is likely the decomposition/degradation of the remaining carbon where carbon dioxide is produced [8]. As for SBR, about 95 % has degraded at 575 °C in both Air and Nitrogen.

DSC-60 Plus Results

The thermal properties of battery binders can be measured by DSC. Each sample was measured 2 times. Fig. 7 shows the DSC results of one of the 2 measurements and the average results of 2 measurements are summarized in Table 5.

NaCMC exhibits an average broad peak at 115.2 °C. As NaCMC is hygroscopic [9], this peak is attributed to the presence of adsorbed moisture and evaporation of physically bound water in the cellulosic structure upon heating [7]. This is also shown by weight loss TGA results when the NaCMC was heated to more than 115 °C (Fig. 5, Table 4). When NaCMC was heated the second time, there is no longer broad peak at 115.2 °C (Fig. 7) as water has been removed in the first heating.

The average glass transition and melting temperatures of PVDF are at -38 °C and 163.9 °C respectively. PVDF also display an average crystallization temperature of 121.7 °C (Table 6). As for SBR, it has an average glass transition temperature of 15.7 °C.

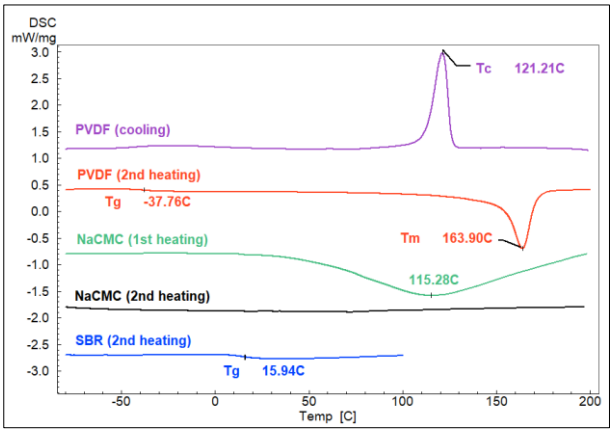

Fig. 7 DSC graphs for battery binders

Table 5 Thermal properties of battery binders

	NaCMC	PVDF	SBR
Glass Transition Temperature, Tg (2nd heating)	-	-38.0 °C	15.7 °C
Melting Temperature, Tm (2nd heating)	-	163.9 °C	-
Crystallization Temperature, Tc (cooling step)	-	121.7 °C	-
Evaporation Temperature (peak) (1st heating)	115.2 °C	-	-

Notes:
The data shows the average results from 2 measurements (RSD < 2 %).

■ Conclusion

Battery binders are important components in LIBs. Thus, it is vital to characterize the properties of battery binders, whether for use in R&D or manufacturing sector. Three battery binders, NaCMC, PVDF and SRB were analyzed with FTIR, DSC and TGA methods. FTIR can be used to evaluate the composition of electrode materials, and the combination of electrode materials can be expected to improve battery characteristics such as energy density. In addition, TGA and DSC can be used to evaluate the thermal characteristics of electrode materials in order to optimize and improve the thermal stability of batteries.

■ References

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