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THERMAL ANALYSIS OF SULFURIZATION OF POLYACRYLONITRILE WITH ELEMENTAL SULFUR

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Thermal analysis of sulfurization of polyacrylonitrile (PAN) with elemental sulfur was investigated by thermogravimetry and differential thermal analysis of the mixture of polyacrylonitrile and elemental sulfur up to 600°C. Due to the volatilization of sulfur, the different heating rate (10 and 20 K min^{-1}) and different mixture proportion of polyacrylonitrile and elemental sulfur were adopted to run the analysis. The different heating rates make the DSC curves of sulfur different, but make the DSC curves of PAN similar. In the DSC curve of sulfur for the heating rate of 20 K min^{-1} around 400°C, a small exothermic peak occurs at 400°C in the wide endothermic peak around 380~420°C, indicative of that there is an exothermic reaction around 400°C. In the DSC curves of the mixture, the peaks around 320°C are exothermic as the content of sulfur is below 3.5:1 and endothermic as the content of sulfur is over 4:1, indicating that one of the reactions between PAN and sulfur takes place around 320°C. In the TG curves of the mixture, the mass losses begin at 220°C, and sharply drop down from 280°C. The curves for the low sulfur content obviously show two steps of mass loss, and curves for the high sulfur content show only one step of mass loss, indicative of more sulfur is benefit for the complete sulfurization of PAN. This study demonstrates that the TG/DSC analysis can give the parameter for the sulfurization, even if the starting mixture contains the volatile sulfur.

Keywords: *DSC, elemental sulfur, polyacrylonitrile, pyrolysis, sulfur composite cathode materials, thermogravimetry*

Introduction

Recently, an interesting sulfur-containing composite cathode material for rechargeable batteries has been synthesized by heating a mixture of polyacrylonitrile (PAN) and sulfur at 280–500°C [1, 2]. Its electrochemical performance and mechanistic insight are investigated [1–14]. Its reversible capacity is 450~800 mAh g^{-1} and the cyclability is close to the practical use for rechargeable batteries. The pyrolysis was assumed previously to be similar to active carbon fibers or disordered carbon obtained by pyrolysing pure PAN [15, 16]. However, when heating the mixture of PAN and S, sulfur as the reducer may facilitate the dehydrogenation and cyclization of PAN [1, 2]. Meanwhile, as the cleavage of the S_8 ring and the formation of sulfur free radicals occur at relatively high temperatures, other reactions possibly also take place between the carbon-matrix of PAN and S [6]. The reproducibility of the electrochemical performance is low. The different electrochemical performances are obtained and the different mechanistic insights are assumed in the publications. Therefore, the further investigations need to be done to understand more about this material. Normally, the thermogravimetry and differential scanning calorimetric analysis (TG/DSC) is adopted to find out the parameters of the preparation, and to understand the mechanism insight of reaction during heating.

The pyrolysis of PAN has been investigated intensively. When heating PAN, a strong exothermic reaction begins at about 200°C and reaches a maximum peak at about 280°C [15–17]. When mixing with elemental sulfur, the pyrolysis of PAN should differ much from that of the pure PAN. Elemental sulfur shows unique pyrolytic performance [18–23]. The sulfur exists as a number of different allotropes. Below 95.6°C, the stable crystal form is rhombic, while above this temperature the element changes to a monoclinic form. Both these forms contain cyclic S_8 molecules. Sulfur is melted at 115.21°C. At temperatures just above its melting point, sulfur is a yellow liquid also containing S_8 molecules. At about 160°C, the sulfur atoms link together in chains and the liquid becomes more viscous. Above 200°C the viscosity decreases rapidly because the sulfur chain is broken into smaller molecules. The polymerization and decomposition of sulfur chains always take place during heating over temperature range of 160–500°C [20, 21]. Thermal analysis of sulfur related materials were studied [24–28], however, the thermal analysis of the material containing sulfur and polymer was not reported so far.

For further understanding of the pyrolysis of the mixture of PAN and elemental sulfur, in this study, the thermogravimetry and differential thermal analysis are applied to reveal what happens in the pyrolytic process.

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Experimental

Sulfur and polyacrylonitrile (PAN) were purchased from Aldrich and used as received. The mixture of sulfur and PAN was carried out by the ball-milling in an agate tank with agate balls at 500 rpm for 6 h by Planetary Ball Mill (QM, Nanjing University Instrument Plant, China) in alcohol medium. Before further processing, the mixture was dried at 120°C in vacuum for 24 h.

The measurements were carried out with a STA 409 PC/4/H Luxx® manufactured by Netzsch, Germany. The measuring parameters used are represented in Table 1.

Table 1 Measuring parameters of STA 409 PC/4/H Luxx®

Heating rate	10 or 20 K min^{-1}
Temperature range	50–550°C
Inert gas	Argon, flow rate: 75 mL min^{-1}
Sample crucible	Al_2O_3
Calibration test	Al_2O_3 – standard, temperature, sensitivity

Results and discussion

The volatilization of sulfur is considered to have a profound effect on the TG/DSC analysis. It leads to the mass loss and endothermic heat flow. The polymerization and decomposition of sulfur chains produce the heat flow. The vapor pressure of sulfur is from the sublimation below the melting point. It is about 0.01 mm Hg at 100°C, and goes up rapidly then. It is 2.0 mm Hg at 200°C, 13 mm Hg at 250°C, 50 mm Hg at 300°C, and 200 mm Hg at 360°C. The vapor pressure of elemental sulfur between 100~450°C is given in Fig. 1 [19]. This figure is helpful to understand the TG/DSC analysis of the sulfur-related materials.

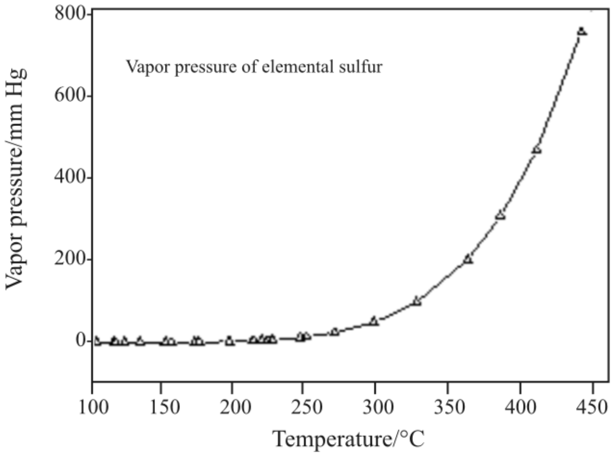

Fig. 1 The vapor pressure of elemental sulfur [19]

To verify the effect of sulfur volatilization, the TG/DSC analysis of elemental sulfur is carried out at different heating rate. Figure 2 shows the TG/DSC curves of elemental sulfur at heating rates of 10 and 20 K min^{-1}. In the DSC curve, the endothermic peaks around 100 and 120°C are respectively attributed to the transition of rhombic to monoclinic forms and solid–liquid transition of sulfur. The endothermic peak around 180°C is attributed to the decomposition of polymeric sulfur. The endothermic peaks around 380~420°C are attributed to the strong sulfur volatilization. The differences of the endothermic peaks around 100, 120 and 180°C between the DSC curves at heating rates of 10 and 20 K min^{-1} are much smaller than that around 380~420°C. The sulfur volatilization rate depends on the temperature in the certain crucible. It volatilizes much more around 380~420°C than at lower temperature. Therefore, the different heating rate makes the DSC curves different. Interestingly, in the DSC curve for the heating rate of 20 K min^{-1} around 400°C, a small exothermic peak occurs at 400°C in the wide endothermic peak around 380~420°C, indicative of that there is an exothermic reaction around 400°C. This exothermic peak is enshrouded by the endothermic peak from the volatilization at the heating rate of 10 K min^{-1}. In the following analysis, this exothermic peak is reproducible. It is probably the identification peak of sulfur.

In the TG curves of Fig. 2, the obvious mass losses begin at about 250°C, where the vapor pressure of sulfur is 13 mm Hg, much bigger that 2.0 mm Hg at 200°C, and show a sharp drop over 300°C. The mass losses end at 378°C for the curve of 10 K min^{-1} and 412°C for the curve of 20 K min^{-1}. Due to the volatilization of sulfur, 100% mass loss reaches before the melting point of sulfur.

The TG/DSC analysis of pure PAN is conducted at heating rates of 10 and 20 K min^{-1}, as shown in Fig. 3. In the TG curves, the mass losses begin at 308°C, where the decomposition of PAN takes place, for both heating rates. The mass losses are 39% for

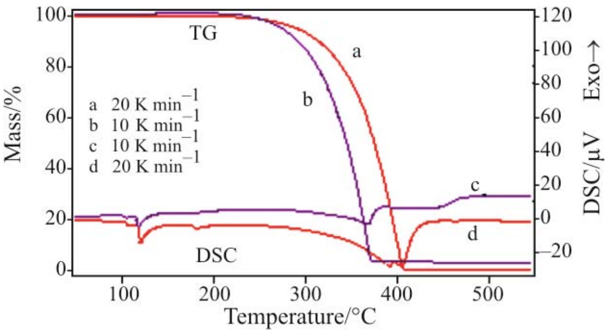

Fig. 2 TG/DSC curves of elemental sulfur at heating rates of 10 and 20 K min^{-1}

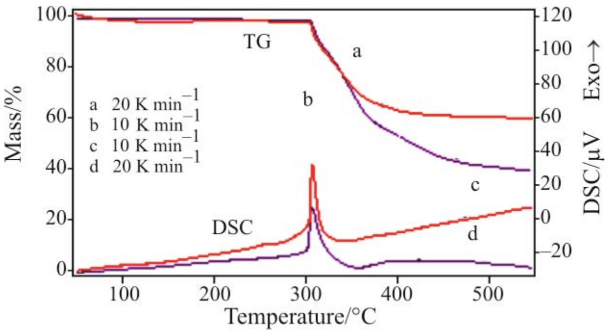

Fig. 3 TG/DSC curves of pure PAN at heating rates of 10 and 20 K min^{-1}

the heating rate of 20 K min^{-1} and 58% for the heating rate of 10 K min^{-1} at 500°C. In the DSC curves, the exothermic peaks occur at the same temperature (308°C) for both heating rate runs. This indicates that the heating rate has more different effect on the analysis of PAN than that of sulfur.

The TG/DSC analysis of the mixture with different proportion of sulfur and PAN at heating rates of 10 K min^{-1} is shown in Figs 4 and 5. In the DSC curve, the endothermic peaks around 100, 120 and 180°C are attributed to the form transition of sulfur. Due to the existence of PAN, the form of the endothermic peak changes as the content of sulfur is lower than 3.5:1 (molar ratio of S:–CN in PAN). The peaks around 100, 120 and 180°C are similar to that of sulfur as the content of sulfur is over 3.5:1. The peaks between 320 and 360°C present interesting result, they are exothermic as the content of sulfur is below 3.5:1 and endothermic as the content of sulfur is over 4:1. This indicates that the interaction between PAN and sulfur takes place around 320°C. As the content of sulfur is low, the heat flow from sulfur volatilization is low; the total heat flow mainly comes from the interaction between PAN and sulfur, showing exothermic. As the content of sulfur is high, the heat flow from the sulfur volatilization is high; the total heat flow mainly comes from the sulfur volatilization, showing endothermic. In DSC curve, the interaction between PAN and sulfur is enshrouded by the heat flow from the sulfur volatilization as the content of sulfur is high. So, as the content of sulfur decreases gradually, the interaction between PAN and sulfur is disinterred. It happens around 320°C.

In the TG curves of Fig. 5, the mass losses for the mixtures begin at 220°C, and sharply drop down from 280°C. The curves B, C and D obviously show two steps of mass loss, its second step between 330 and 370°C is similar to that of pure PAN, indicative of that this step of mass loss is related with the decomposition of PAN. The curves E, F and G show only one step of mass loss, no seconds step as curves B, C and D show.

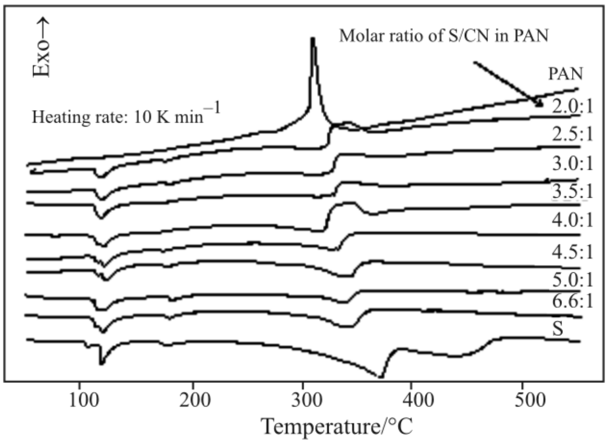

Fig. 4 DSC curves of the mixture with different proportion of sulfur and PAN at heating rates of 10 K min^{-1}

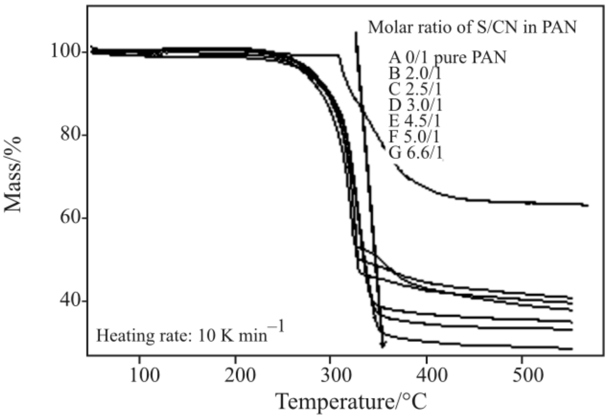

Fig. 5 TG curves of the mixture with different proportion of sulfur and PAN at heating rates of 10 K min^{-1}

The reason probably is as follows. As the content of sulfur is low, the reaction between PAN and sulfur is not complete, some chemically pure PAN remains, leading to the second step of mass loss. As the content of sulfur is high enough, the reaction between PAN and sulfur is complete, no chemically pure PAN remains. This demonstrates that the content of sulfur should be high enough to make the reaction complete when preparing the sulfur composite cathode.

To view the difference of analysis of the mixture at the different heating rate, the TG/DSC analysis of the mixture with different proportion of sulfur and PAN at heating rates of 10 K min^{-1} is shown in Figs 6 and 7. Unlike pure sulfur, the peaks for mixture around 320 and 360°C are at the same temperature range for the 10 and 20 K min^{-1} heating rate runs, however, the form of peak differs. It indicates that the heating rate has a big effect on the form of the peak, and small effect on the position of the peak. This is similar to the pure PAN, indicating that the existence of PAN has an effect on the volatilization of sulfur.

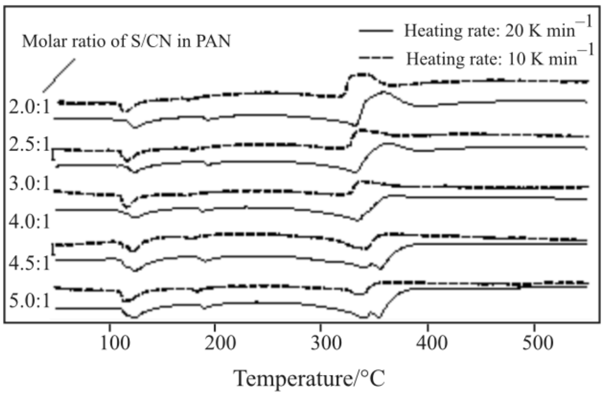

Fig. 6 DSC curves of the mixture with different proportion of sulfur and PAN at heating rates of 10 and 20 K min^{-1}

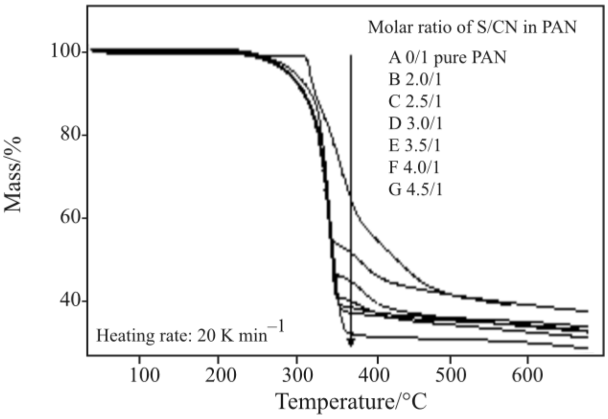

Fig. 7 TG curves of the mixture with different proportion of sulfur and PAN at heating rates of 20 K min^{-1}

There is an interaction between them. As shown in Fig. 7, the TG curves of 20 K min^{-1} heating rate run are similar to those of 10 K min^{-1} heating rate run, indicative of that the heating rate has little effect on the TG analysis of the mixture.

To pave the way of above analysis, the sulfur composite cathode materials with good electrochemical performance have been prepared [10], indicative of that the TG/DSC analysis can give the parameter for pyrolysis preparation, even the mixture contains the volatile component.

Conclusions

This study demonstrates that the different heating rate makes the DSC curves of volatile sulfur different, but makes the DSC curves of non-volatile PAN similar. In the DSC curve of sulfur for the heating rate of 20 K min^{-1} around 400°C, a small exothermic peak is observed at 400°C in the wide endothermic peak around 380~420°C, indicative of that there is an exothermic reaction around 400°C. This exothermic peak is enshrouded by the endothermic peak from the volatilization at the heating rate of 10 K min^{-1}. It is probably the identification peak of sulfur.

The analysis of the mixture with different proportion can reveal hided peak which is enshrouded by the volatilization of sulfur. In the DSC curves of the mixture of PAN and sulfur, the peaks around 320°C are exothermic as the content of sulfur is below 3.5:1 and endothermic as the content of sulfur is over 4:1, showing that one of the reactions between PAN and sulfur takes place around 320°C. In the TG curves of the mixture, the curves for the low sulfur content obviously show two steps of mass loss, and curves for the high sulfur content show only one step of mass loss, indicative of that more sulfur is benefit for the complete sulfurization of PAN. This study demonstrates that the TG/DSC analysis can give the parameter for the sulfurization, although the starting mixture contains the volatile sulfur.

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