Measurement of Carbon Amount in Carbon-coated Graphite by Thermal Analysis

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Carbon-coated natural graphite is a promising candidate for lithium-ion battery anode material. The amount of carbon-coating plays a very significant role in the electrochemical performance of this type of anode material. A simple and believable method based on the thermal analysis of air oxidation for carbon-coated natural graphite has been introduced to measure carbon-coating weight portions in the composite material.

The great demand for high-energy-density rechargeable lithium-ion batteries has spurred extensive research on electrode materials. Graphite is an important anode material for lithium-ion batteries. In recent years, carbon-coated graphite has become more attractive than graphite mainly because most of the merits of graphite can be preserved while most of the demerits of graphite can be avoided by carbon-coating modification.[1–7]

We have applied thermal vapor decomposition (TVD) technique in preparing carbon-coated natural graphite.[5–7] Electrochemical performance of carbon-coated natural graphite has been related with relative amounts of the graphite "core" and the carbon-coating "shell". It was found that the weight portion of carbon-coating in the composite material is a key factor in controlling the electrochemical characteristics. Therefore it becomes urgent to detect carbon-coating amount correctly. The "crude" method for measuring carbon amount is to compare the weights of the graphite powders before and after TVD process. This method might cause some errors unless the resulted TVD-carbon coated graphite could be completely collected. Recently, a more believable way based on thermal analysis of air oxidation for carbon-coated natural graphite have been investigated.

From the previous thermal analysis on air-oxidation of pitch cokes preheated at different temperatures (Figure 4 in Reference 7),[7] we noticed that for the as-received coke and the graphitized coke (preheated at 2800 °C), the temperatures at which rapid oxidation begins to occur are quite different. This fact reminded us of the resolution of carbon-coated natural graphite into two separated "components" during the course of air oxidation. We related the carbon-coating to the raw pitch coke and the core-part natural graphite to graphitized coke respectively. It was expected that with the rise of temperature in TG-DTA, the air oxidation propagated from the carbon-coating to the natural graphite core layer by layer. If the oxidation processes for both parts (carbon-coating and natural graphite core) can be clearly deconvoluted in the whole temperature range of TG-DTA, the carbon-coating amount can be deduced from the TG curve by counting the decrease of the sample's weight after the first oxidation (carbon-coating's burning).

Carbon-coated natural graphite was prepared as described in the previous report.[5] The air oxidation of graphite samples was investigated by thermal analysis TG-DTA (thermal gravimetry and differential thermal analysis) using a TG-8100 thermal analyser system (TAS100 system, Rigaku Ltd., Japan) at a heating rate of 10 °C/min with a 30 ml/min flow of air.

Figure 1 shows the typical TG-DTA curves of air oxidation for the original pure natural graphite. It can be observed from the TG curve that the weight loss of natural graphite in the air flow takes places from ca. 600 °C, which corresponds to the left foot of the peak in DTA curve, and almost finished at ca. 860 °C, which corresponds to the right foot of the peak in DTA curve. The TG curve in this temperature region drops down smoothly, whereas the DTA curve reaches a maximum value at the temperature of about 839 °C.

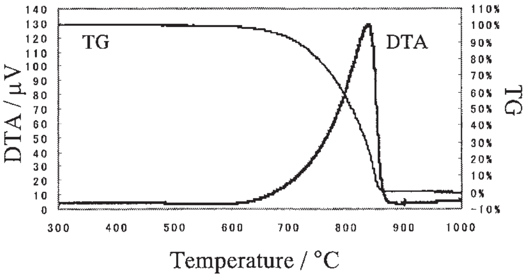

Figure 1. Typical TG-DTA traces of the air oxidation for original pure natural graphite.

In contrast, Figure 2 shows the typical TG-DTA curves of air oxidation for a carbon-coated natural graphite sample. The TG curves in Figure 2 are roughly similar to that in Figure 1. The most noticeable difference between Figure 2 and 1 lies in the appearance of the "parasite" small peak at ca. 703 °C besides the big peak at ca. 809 °C in the DTA curve. As compared with the peak at 839 °C in the DTA curve in Figure 1, the large peak at ca. 809 °C in the DTA curve in Figure 2 can be attributed to the air oxidation of the natural graphite core. Then the small peak at 703 °C can be ascribed to the air oxidation of carbon-coating.

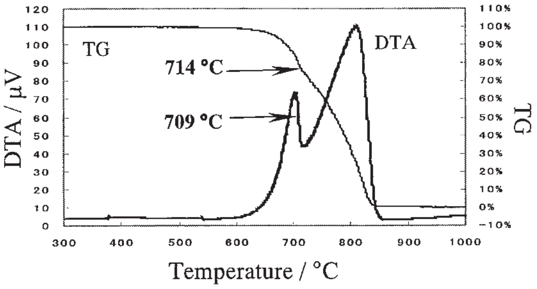

Figure 2. Typical TG-DTA traces of the air oxidation for carbon-coated natural graphite.

Since the two processes of air oxidation corresponding to carbon-coating and natural graphite core, respectively, can be clearly resolved in TG-DTA curves as shown in Figure 2, it is possible to detect the carbon-coating amount from thermal analysis. Then the most important task is to decide the temperature at which the first air oxidation process (burning of carbon-coating) terminates. By close observation of the TG curve of Figure 2, we can find a ''knick'' point at ca. 714 °C which locates in the drop-down part. The temperature corresponding to this point may be taken as the key temperature dividing the two air oxidation processes. Thus the weight loss ratio at this point can be tentatively regarded as the carbon-coating weight portion in the whole carbon-coated natural graphite sample.

Alternatively, a more delicate way can be developed to find the termination temperature of the air oxidation for carbon-coating by the analysis of DTA curves. This method is basically referred from the textbook.[8] In the DTA curve of Figure 2, there is one valley between the two peaks. The termination temperature point locates between the first peak and the valley. So we take all the points in this temperature region for consideration. The DTA values of these points are subtracted by DTA_b (DTA value of the base line in the curve). Then natural logarithms of the $DTA-DTA_b$ values are plotted against temperature as shown in Figure 3. It demonstrates an inverse ''S'' shape roughly. In the meddle of this curve, a linear part can be found, which corresponds to the temperature region where almost no reaction occurs. So it seems that the initiation of the second air oxidation (burning of the graphite core) and the termination of the first air oxidation (burning of carbon-coating) don't occur at the same time. The two separate curved parts connected to the linear part in the left and right sides correspond to the air oxidation processes of the carbon-coating and the natural graphite core, respectively. The joint point of the left-side curved part and the linear part just stands for the termination point of the carbon-coating air oxidation. The temperature corresponding to this point is 709 °C. Then the carbon-coating amount can be deduced from the weight loss at this temperature in the TG curve of Figure 2. To prove the validity of this method, we have carried out the additional thermal analysis on the oxidation of the mixtures composed of known amounts of natural graphite and cokes. The results thus obtained agreed with the weight portions of the cokes very well. The studies about correlations of the carbon-coating amount obtained in the above way with both the electrochemical and physical properties of carbon-coated natural graphite are in progress.

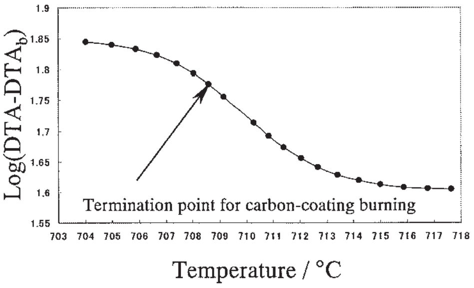

Figure 3. Natural logarithmic plot of $DTA-DTA_b$ ($Log(DTA-DTA_b)$) vs temperature for the DTA trace in Fig. 2.

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