

Short communication

Thermal gravimetry–mass spectrometry studies on the thermal stability of graphite anodes with electrolyte in lithium-ion battery

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Abstract

Thermal reactions of a lithiated graphite anode in 1 M LiPF₆-ethylene carbonate (EC)/dimethyl carbonate (DMC) (50:50 vol.%) in the temperature range 40–320 °C were investigated by TG–MS analysis. Studies by TG–MS during thermal reactions detected a small exothermic peak around 140 °C due to CO₂ ($m/z = 44$) evolution, which suggests partial destruction of the SEI formed on the graphite and/or decomposition of the electrolyte through the SEI. In addition, the main exothermic reaction above 280 °C, which is associated with simultaneous evolution of C₂H₄O ($m/z = 44$), is caused by direct reaction of the lithiated graphite with solvent.
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Keywords: Graphite anode; Thermogravimetry–mass spectrometry; Thermal stability

1. Introduction

It is well known that the fully lithiated graphite anode is unstable because the intercalated lithium reacts with the electrolyte [1,2]. Although the thermal stability of the graphite anode upon intercalation has been studied [3], the dynamic reaction mechanisms have not been clarified. In addition, the solid electrolyte interphase (SEI) formed on the lithiated carbon anode has attracted the attention of many researchers because of its contribution to the thermal stability [4–6]. Therefore, the analysis of thermal reactions associated with the lithiated graphite anode, SEI and electrolyte is required for the understanding of the reaction mechanisms relating to safety. In the present study, thermogravimetry–differential thermal analysis–gas chromatography/mass spectrometry (TG–DTA–GC/MS) was used to explore the thermal reaction of the lithiated graphite with the electrolyte.

2. Experimental

Electrodes containing 95 wt.% graphite (LF-18D), 5 wt.% PVdF were coupled with lithium in coin cells, with 1 M LiPF₆

in 1:1 (v/v) EC+DMC as the electrolyte. The cells were charged and discharged between 1.50 and 0.01 V at a current density of 0.6 mA cm⁻². After the cycling test, the fully charged carbon electrodes with electrolyte were subjected to TG–MS analysis. Each sample was packed into a stainless steel pan, which was crimp-sealed in a glove box filled with Ar. Analysis of the gaseous species emanating from the crimp-sealed pan during heating up to 320 °C at 5 °C min⁻¹ under helium flow was carried out by introducing the gas into the MS without using a column (TG–MS mode).

3. Results and discussion

The TG–DTA studies carried out during the thermal reaction with a fully lithiated graphite electrode in contact with the electrolyte (Fig. 1) detected a mild heat generation process starting from 130 °C, with a small peak at 140 °C and a sharp exothermic peak at 295 °C, with no accompanying leakage. On the other hand, in the case of a large amount of gas leakage (Fig. 2a), a small exothermic peak at 280 °C was observed after the large weight loss. The gas evolution during the thermal reaction was monitored by the MS signal (Fig. 2b). The mass signal of $m/z = 44$ at 140 °C was assigned to carbon dioxide (CO₂), while the mass peak at 280 °C was

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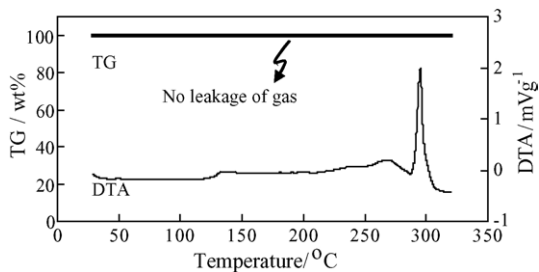


Fig. 1. TG–DTA profile of lithiated graphite electrode with 1M LiPF₆/EC+DMC (1:1) electrolyte in a case in which there was no leakage.

assigned to saturated cyclic ethers, such as 1,3,6-trioxocane ($m/z = 118$) and 1,4-dioxane ($m/z = 88$). In addition, a broad peak for the $m/z = 88$ mass signal due to the evolution of ethylene carbonate (EC) was detected. These results suggest that the main exothermic reaction above 280 °C does not occur in the absence of EC. Furthermore, a small exothermic peak at 140 °C related to CO₂ evolution may indicate destruction of the SEI component and/or decomposition of the electrolyte through the SEI. Fig. 3 shows the TG–DTA curve and MS profile obtained under conditions of small leakage. Even in this case, both typical exothermic peaks were observed at 105 and 260 °C (referring to Fig. 1). The former peak is assigned to the evolution of CO₂ in the temperature range from 100 to 250 °C. The latter sharp exothermic peak arose from the evolution of a C₂H₄O species, such as acetaldehyde or ethylene oxide, that produces fragments that are different from CO₂, as shown in Fig. 3b. Thus, these TG–MS studies reveal that the thermal instability above 260 °C leads to the consumption of EC.

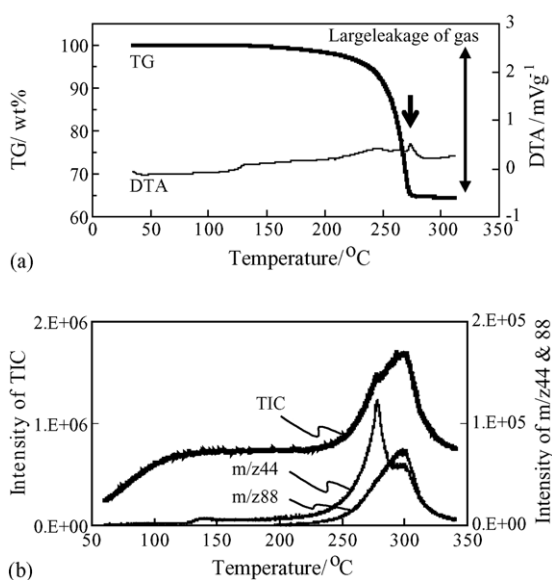


Fig. 2. TG–MS profile of lithiated graphite electrode with 1M LiPF₆/EC+DMC (1:1) electrolyte in a case in which there was large leakage.

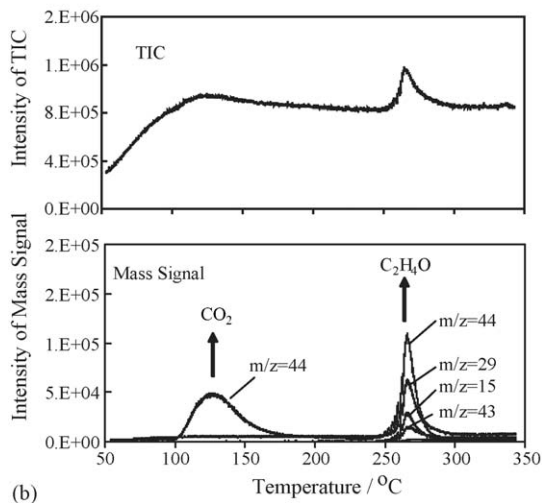
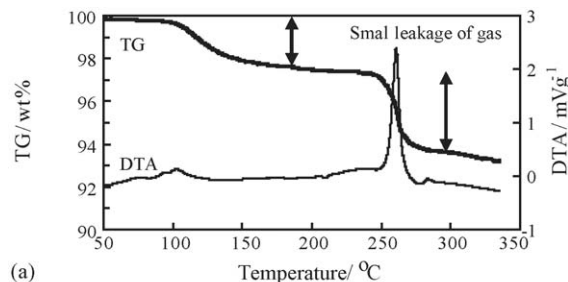


Fig. 3. TG–MS profile of lithiated graphite electrode with 1M LiPF₆/EC+DMC (1:1) electrolyte in a case in which there was slight leakage.

4. Conclusion

Studies by TG–MS during thermal reactions detected a small exothermic peak around 140 °C due to CO₂ evolution, which suggests partial destruction of the SEI formed on the graphite and/or decomposition of the electrolyte through the SEI. Moreover, the main exothermic reaction above 280 °C, which is associated with evolution of C₂H₄O, is caused by direct reaction of the lithiated graphite with solvent. As a result, the exothermic reaction of lithiated carbon and electrolyte must be considered in order to improve the thermal stability of the graphite anode.

Acknowledgement

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