Short communication

Dynamic TGA–FTIR studies on the thermal stability of lithium/graphite with electrolyte in lithium-ion cell

Hui Yang [*], Xiao-Dong Shen

College of Materials Science and Engineering, Nanjing University of Technology, 5 Xinmofan Road, Nanjing, Jiangsu Province 210009, China

Abstract

Graphite anode could initialize the thermal runaway of lithium-ion cells due to its spontaneous exothermic reactions above the critical temperature. In order to explore the mechanisms of these reactions, a series of experiments were carried out with on-line coupled thermogravimetric analyser–Fourier transform infrared spectrometer (TGA–FTIR). The reactions under study essentially involved metallic lithium reacting with electrolyte and the thermal decomposition of natural graphite GDR at various states of charge (SOC). It is found that metallic lithium reacts with ethylene carbonate (EC) violently at around $180\,^\circ$C producing CO_2 and dilithio butylene dialkoxide which could further react with $LiPF_6$ and/or PF_5 to produce POF_3. At the relatively low temperature (about $60\,^\circ$C), CO_2 produced from both 0% SOC and 100% SOC GDR samples is attributed to the decomposition of organic compounds in solid electrolyte interface (SEI) film. In addition, the amount of POF_3 produced from 0% SOC GDR sample is more than that from 100% SOC GDR sample. Further, fully intercalated GDR sample shows a structural collapse, a solid-state exothermic reaction at $\sim 260\,^\circ$C. Based on the TGA–FTIR results obtained from these exothermic reactions, detailed thermal decomposition paths are proposed in this paper.

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1. Introduction

It is well known that the thermally unstable lithiated graphite can cause safety issues of Li-ion cells: primary SEI (P-SEI) film decomposition is an exothermic reaction which could initialize a series of exothermic reactions, such as the reaction between intercalated lithium and electrolyte to form a secondary SEI (S-SEI) film, and the structure collapse of lithiated graphite [1]. In this paper, the P-SEI film is the film electrochemically formed on the graphite surface during initial cycles, while the S-SEI film is the film chemically formed on the graphite surface during thermal runaway process [1,2]. Extensive studies have been carried out to investigate the thermal runaway mechanism, but most studies were only focused on the thermal behavior, e.g. onset temperature, peak temperature and enthalpy, via either DSC or ARC techniques [1–5]. Several possible reaction pathways [1,2] were proposed but without further verification. In addition, the extremely complex compositions of the P-SEI film (such as lithium ethylene dicarbonate [6], lithium oxalate [7], lithium methoxide [7], and more), with electrolyte precipitates and intercalated/trapped lithium, make the thermal runaway mechanism exploration more difficult. In order to clarify this mechanism, we performed the on-line coupled TGA–FTIR tests of various samples: metallic lithium with electrolyte and natural graphite GDR samples at various SOCs. TGA–FTIR makes it possible to study detailed thermal decomposition path by monitoring evolution of gas products as a function of temperature and weight change. Specifically, the reaction products and their relative abundance extracted from infrared spectra acquired during the TG analysis could be easily related to sample weight loss.

2. Experimental

The graphite anodes laminated on the $25\,\mu$m thick copper current collector were composed of 92% natural graphite GDR and 8 wt.% polyvinylidene fluoride (PVDF) binder with a loading of $4.37\,$mg cm^{-2} active material. Electrochemical cells were assembled in Argon filled glove box (water and oxygen contents

* Corresponding author. Tel.: +86 25 83587238; fax: +86 25 83587238.
  E-mail addresses: yh3799@yahoo.com, yang@iit.edu (H. Yang).

<10 ppm). The electrochemical cells were made from Swagelok fittings with graphite anodes (1.6 cm^2 area), Li reference and counter electrodes, and a Celgard (3501) as the separator. The electrolyte used was 1.2 M LiPF$_6$/ethylene carbonate (EC): ethyl methyl carbonate (EMC) (3:7 wt.%) (Quallion). The graphite anodes were galvanostatically charged/discharged at a low rate of C/25 (60 μA cm^{-2}) using a battery cycler (BT-2043 Arbin cycler, College Station, TX) between 1 V versus Li/Li$^+$ and 10 mV versus Li/Li$^+$ for two formation cycles to build up the solid electrolyte interface. The cells were finally charged to different states of charge (0% SOC or 100% SOC), for TGA measurements. After opening the cell in the Ar-filled glove box carefully, the extra electrolyte was removed from the surface of the electrode and the electrode materials were recovered from the current collector and used as TGA samples. Metallic Li and 1 M LiPF$_6$/ethylene carbonate (EC) were used as received. The water content of the electrolyte is less than 10 ppm. All the sample handlings were performed in an inert atmosphere with no air exposure even momentarily.

The on-line TGA–FTIR is consisted of a thermogravimetric analyzer (TGA model 2960, TA Instruments) and a Fourier Transform Infrared Spectrometer (Nexus 470, Nicolet) equipped with a temperature controlled transmission gas cell. The coupling between TGA and FTIR is via quartz capillary array. Both FTIR gas cell and the capillary array were heated to 200 °C while running the experiments to prevent deposits on the gas cell and capillary walls. To ensure inert atmosphere environment, TGA and FTIR gas cell and the coupling line were all housed in Argon atmosphere (glovebag), while FTIR spectrometer was completely isolated from the gas cell, capillary array and TGA. Special care was taken to ensure that FTIR optical path was properly purged in such a way that background infrared signal from residual moisture and carbon dioxide (CO$_2$) is negligible during the experimental run. The inert working condition of on-line TGA–FTIR was checked with copper oxalate by following Mullen et al.'s [8] work.

The on-line TGA–FTIR measures the change in sample weight as a function of temperature under non-isothermal condition, 10 °C min^{-1}, while simultaneously monitoring the volatile components evolved from samples as a result of thermal decomposition. The gas phase products were continuously transferred to FTIR gas cell through capillary array by using Ar as carrier gas, containing less than 10 ppm of moisture, at a flow rate of 220 ml min^{-1}. The FTIR spectra were continuously acquired at a resolution of 4 cm^{-1} and summed over 32 scans during the thermogravimetric (TG) measurements. The mass loss reported in this work has 1% error. In all the experiments, the heat rate of TGA is 10 °C min^{-1} and the flow rate of Ar carrier gas containing less than 10 ppm moisture is 220 ml min^{-1}.

3. Results and discussions

Thermogravimetry (TG) and derivate thermal analysis (DTA) profiles of metallic Lithium with electrolyte (1 M LiPF$_6$ in EC) obtained, at a heating rate of 10 °C min^{-1}, is presented in Fig. 1A. The mass of the remaining solid residue is about 16 wt.% of its original mass when temperature reaches 300 °C.
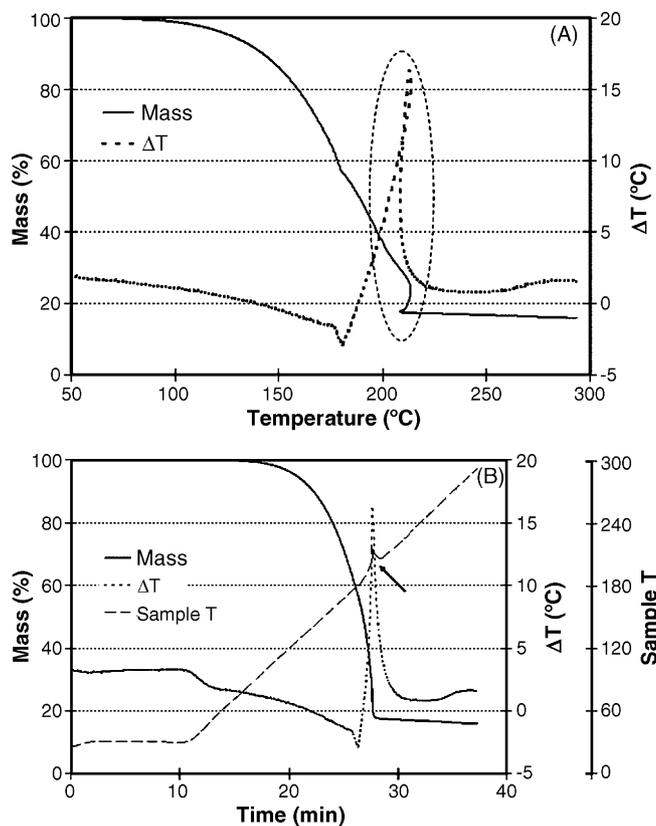

Fig. 1. (A) Mass loss (left) and derivative thermal analysis ΔT (right) vs. temperature during thermal decomposition of metallic with 1 M LiPF$_6$/EC electrolyte (1.452 mg Li + 19.834 mg electrolyte) at a heating rate of 10 °C min^{-1} in argon (flow rate: 220 ml min^{-1}) containing <10 ppm H$_2$O; (B) mass loss (left), ΔT (1st right) and sample temperature (2nd right) vs. experiment time in the same experiment.

The fluctuation observed between 200 °C and 220 °C in both TG and DTA curves (circled with the dashed line) can be attributed to a huge exothermic reaction happened at about 200 °C which causes a drastic increase in the sample temperature over the target temperature (over shoot). To clarify this, the TG, DTA and sample temperature are also plotted versus experiment time in Fig. 1B. The overshoot sample temperature is very clear in Fig. 1B as marked by the arrow. The overshoot sample temperature cools down to target temperature after the exothermic reaction which causes TG and DTA curves back and forth in Fig. 1A. The evolution of gas products as a result of sample thermal decomposition or volatilization was simultaneously monitored by FTIR during TGA experiment and is presented in Fig. 2A. The typical FTIR spectrum acquired at 208 °C, along with standard spectrum of gas-phase EC, PF$_5$, POF$_3$ and HF are shown in Fig. 2B. As seen clearly in Fig. 2B, only CO$_2$, POF$_3$ and EC are detected in the gas phase. No other species, such as PF$_5$ and HF are detected. The evolution of carbon dioxide starts from ∼60 °C, and constantly evolves at a rate of 0.00048 a.u. mg^{-1}, till ∼190 °C. Then the evolution rate of carbon dioxide dramatically increases and forms a sharp peak at 208 °C. There is a second small CO$_2$ evolution peak centered at 228 °C. The EC evaporation can be detected by FTIR in a broad temperature range, from 90 °C to 290 °C, with the peak temperature