Journal of Power Sources 366 (2017) 185–192

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Rationalizing thermal reactions of C_6Li_x negative electrode with nonaqueous electrolyte

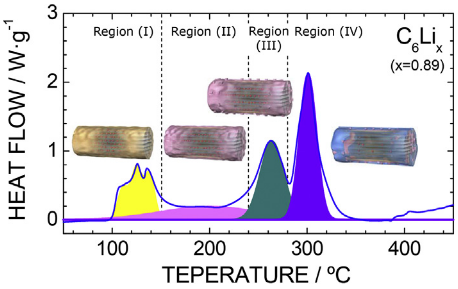
Kazuhiko Mukai*, Takao Inoue, Madoka Hasegawa

Toyota Central Research & Development Laboratories, Inc., 41–1 Yokomichi, Nagakute, Aichi 480–1192, Japan

HIGHLIGHTS

- The thermal stability of C_6Li_x with nonaqueous electrolyte was investigated.
- Reactions were divided into four different temperature regions.
- We have rationalized the change in enthalpy for each reaction.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 June 2017
Received in revised form
17 August 2017
Accepted 10 September 2017

Keywords:
Lithium-ion battery
Thermal runaway
Graphite
Differential calorimetry analysis
Exothermic reaction
Nonaqueous electrolyte

ABSTRACT

Exothermic reactions at elevated temperatures (T) between Li-intercalated C_6Li_x negative electrodes and nonaqueous electrolytes play a crucial role in the thermal runaway of lithium-ion batteries. However, despite intensive studies so far, the origin of the reactions has not been fully understood, particularly from the viewpoint of a material balance. In this paper, we performed differential scanning calorimetry (DSC) analyses up to 450 °C for samples with $x = 0.22$, 0.45, 0.67, and 0.89, which were prepared from a graphited mesophase-pitch-based carbon fiber. The DSC profiles for C_6Li_x with 1 M $LiPF_6$ dissolved in ethylene carbonate (EC)/diethylene carbonate (DEC) solution (EC/DEC = 3/7 by volume) were found to be divided into four different T regions regardless of x. That is, Region (I) below 150 °C, Region (II) for 150 °C < $T \leq$ 240 °C, Region (III) for 240 °C < $T \leq$ 270 °C, and Region (IV) above 270 °C. By combining with results for X-ray diffraction measurements and scanning electron microscopic analyses, we have rationalized the change in enthalpy (ΔH) of each Region taking into account the given material balance. Strategies for inhibiting the thermal runaway of LIBs are also discussed.

1. Introduction

Demand for lighter and more compact lithium-ion batteries (LIBs) knows no bounds. As the energy density of LIBs increases, thermal stability at elevated temperatures above ~80 °C becomes a big issue, because flammable organic electrolytes are used in conventional LIBs [1,2]. To examine the thermal stability of LIBs and/or electrode materials for LIBs, differential scanning calorimetry (DSC) analyses [3–6] and accelerating rate calorimetry (ARC) analyses [7–11] have been applied. DSC analyses are effective for investigating the initiation temperature and change in enthalpy (ΔH) of an exothermic/endothermic reaction [12], whereas ARC analyses are useful for studying the adiabatic self-heating rate and onset temperature of thermal runaway [13]. Recently, we developed an all-inclusive microcell (AIM) for DSC [6] and ARC [11] measurements, and clarified that the exothermic reaction in a graphite negative

---

* Corresponding author.
E-mail address: e1089@mosk.tytlabs.co.jp (K. Mukai).

http://dx.doi.org/10.1016/j.jpowsour.2017.09.027

electrode at ~260 °C plays an important role in the thermal runaway. Here the AIM comprises all battery components, such as electrode materials and a separator, so as to work as a battery by itself [6,11].

The thermal stability for Li-intercalated graphite (C_6Li_x) in the presence of electrolytes has been examined by several researchers since the late 1990s [4,7,8,10,14–23]. However, despite such intensive studies, the mechanism for the reaction between C_6Li_x and electrolytes is still controversial. For instance, Biensan et al. [14] reported that two exothermic peaks around 120 and 260 °C are found for the combination of C_6Li and 1 M $LiPF_6$ dissolved in propylene carbonate (PC)/ethylene carbonate (EC)/dimethyl carbonate (DMC) electrolyte. Although they assigned the two exothermic peaks as a reaction between C_6Li and the electrolyte ($\Delta H = 350$ J g^{-1}), and a reaction between C_6Li and a polyvinylidene fluoride (PVdF) binder, respectively, the latter exothermic peak almost disappeared in some cases without any explanation [14]. In contrast, Yamaki and coworkers [16,19] reported only a strong exothermic peak around 280 °C ($\Delta H > 1120$ J g^{-1}) for the combination of C_6Li and 1 M $LiPF_6$(EC/DMC) electrolyte. They first assigned the exothermic peak as a reaction between PVdF and Li metal in PVdF [16], then re-assigned it as a decomposition reaction of a solid electrolyte interphase (SEI) [19]. Recently, Cao et al. [22] showed a strong exothermic peak at around 120 °C for the combination of C_6Li and 1 M $LiPF_6$(EC/DMC) electrolyte, and reported that the associated ΔH is decreased from 987 to 297 J g^{-1} upon incorporating an N,N-diallyic-diethyoxyl phosphamide (DADEPA) additive into the electrolyte. However, their original reference ΔH value ($= 987$ J g^{-1}) is about three times larger than the ΔH value ($= 350$ J g^{-1}) reported by Biesan et al. [14].

To examine the reactions of C_6Li_x with electrolytes at elevated temperatures, we performed DSC analyses for C_6Li_x samples using a graphitized mesophase-pitch-based carbon fiber (MCF). This selection is due to its particle morphology with a radial-like texture [24], enabling us to clarify the contributions of SEI at edge planes to the thermal stability. Moreover, to establish equations for each thermal reaction, we conducted structural and morphological analyses using powder X-ray diffraction (XRD) measurements and scanning electron microscopic (SEM) analyses equipped with an energy dispersive X-ray (EDX) spectroscope. We also employed the kJ mol^{-1} dimension to describe ΔH values, although the J g^{-1} dimension was used in previous papers [4,8,14,17–19,21–23]. As a result, we have rationalized each exothermic reaction of C_6Li_x with a $LiPF_6$-based electrolyte, and clarified the critical reaction leading to the thermal runaway of LIBs.

2. Experimental

2.1. Electrochemical measurements

The powder sample of MCF was obtained from Petoka Co. Ltd. The Brunauer–Emmett–Teller (BET) surface area of this sample was 1.2 m^2 g^{-1}. We first examined the electrochemical reactivity of MCF in a nonaqueous lithium cell. A slurry, which comprises 95 wt% of the MCF powder and 5 wt% of a PVdF binder dissolved in an N-methyl-2-pyrrolidone (NMP) solution, was cast onto a Cu foil (15 mmϕ) by a doctor blade method. NMP was then evaporated under vacuum at 120 °C for 12 h. Li metal was pressed into a sheet onto a SUS plate with 19 mmϕ, and was used as the counter electrode. The electrolyte used was 1 M $LiPF_6$ dissolved in EC/diethyl carbonate (DEC) [EC/DEC = 3/7 by volume, denoted as $LiPF_6$(EC + DEC)] (Kishida Chemical Co. Ltd.). The separator used was a 25 μm-thick polyethylene membrane (TonenGeneral Sekiyu K. K.). The MCF/Li cell was operated in the voltage range between 0.01 and 3.0 V vs. Li^+/Li at a current of 0.17 mA and 20 °C. As seen in Fig. S1, the discharge and charge curves for the MCF/Li cell indicate typical electrochemical properties of graphite materials [24,25]. The ratio of discharge capacity to charge capacity for the initial cycle is about 94.5%.

2.2. DSC measurements

The electrochemical reaction was also used to prepare the DSC samples. About 10 mg of the MCF powder containing the PVdF binder was cast onto a glass plate, and then dried under vacuum at 120 °C for 12 h. The weight ratio of MCF/PVdF was 95/5. The resulting composite was pressed into a pellet of 10 mm in diameter and ~0.5 mm in thickness. The MCF/Li cells were fabricated in an Ar-filled glove-box; after achieving desired Li compositions, the cells were deconstructed in the Ar-filled glove-box again. The applied current was 0.17 mA, which corresponds to a current density of ~0.216 mA cm^{-2} (C/165). The Li-intercalated MCF powder, C_6Li_x, (4.75 mg) together with the $LiPF_6$(EC/DEC) electrolyte (2.6 μL) was installed into a SUS pan with 6 mm in diameter and 5 mm in height. We did not wash C_6Li_x samples with DEC before the DSC measurements, but, only for the $x = 0.89$ sample, we examined effects of the washing. Note that DSC profiles using an Al pan sometimes indicate several sharp endothermic peaks above ~250 °C [4,15], probably due to leakage of the Al pan during the measurements. DSC measurements were conducted up to 450 °C at a scan rate of 5 °C min^{-1} (Thermo plus EVO2, DSC8230L, Rigaku Co. Ltd.). The temperature and ΔH in the DSC system were calibrated using the fusion temperature (T_f) and its specific enthalpy (ΔH_f) of three different metals; $T_f = 156.6$ °C and $\Delta H_f = 28.5$ J g^{-1} for In, $T_f = 232.0$ °C and $\Delta H_f = 59.6$ J g^{-1} for Sn, and $T_f = 327.5$ °C and $\Delta H_f = 23.2$ J g^{-1} for Pb. In this paper, a positive ΔH value means that the reaction proceeds exothermically, whereas a negative ΔH value means that the reaction proceeds endothermically. The weight of the SUS was monitored before and after the measurements to ensure that there is no leakage during the measurements. The above procedure is essentially the same as those reported previously [6,11]. The amounts of the C_6Li_x samples and the $LiPF_6$(EC/DEC) electrolyte are summarized in Table S1.

Besides the DSC analyses for the C_6Li_x samples with the $LiPF_6$(EC + DEC) electrolyte, DSC analyses for elements of the $LiPF_6$ salt, EC solvent, and DEC solvent, were performed. Furthermore, DSC analyses for the $x = 0.89$ sample without the $LiPF_6$(EC + DEC) electrolyte, with the $LiPF_6$ salt, with the EC solvent, with the DEC solvent, and with the PVdF binder, were conducted. We also examined effects of a supporting salt on the DSC profile for the $x = 0.89$ sample; i.e., instead of $LiPF_6$(EC + DEC), 1 M $LiBC_4O_8$ (LiBOB) dissolved in EC/DEC [EC/DEC = 3/7 by volume, denoted as LiBOB(EC + DEC)] (Rockwood Lithium Japan K. K.) was used.

2.3. SEM-EDX analyses and XRD measurements

The particle morphologies and chemical compositions before and after heat treatments were investigated by the SEM-EDX analyses (S-4300, Hitachi High-Technologies Co. Ltd.). The crystal structure was also studied by XRD measurements with Cu-Kα radiation (RINT-2200, Rigaku Co. Ltd.). About 10 mg of the C_6Li_x sample with $x = 0.89$ was packed into a Swagelok plug (SS-1210-P) with a Swagelok cap (SS-1210-C) in the Ar-filled glove-box. The sample was then heated at 150, 200, 280, or 450 °C for 1 h, and rapidly cooled to room temperature.

3. Results

3.1. Electrochemical properties

We prepared four different C_6Li_x samples to investigate the x