



Short communication

Thermal reactivity study of spinel lithium titanium oxide material for lithium ion battery by thermal and spectral analysis

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HIGHLIGHTS

- The thermal stability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ material with different state of charge is investigated.
- It can be supposed that the lithium-rich $\text{Li}_7\text{Ti}_5\text{O}_{12}$ phase has higher reactivity with electrolytes.
- FT-IR spectrum is used to analyze thermal reaction of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_7\text{Ti}_5\text{O}_{12}$ electrode with increasing temperature.

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ABSTRACT

This paper reports the study on thermal reactivity of spinel lithium titanium oxide ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) material. Thermalgravimetry and Differential scanning calorimetry (TG/DSC) is used to investigate the relevant profiles of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_7\text{Ti}_5\text{O}_{12}$ electrodes. TG results show $\text{Li}_7\text{Ti}_5\text{O}_{12}$ electrode material has higher thermal weight loss, which is 26.7% below 600 °C, significantly larger than that of 20.4% for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode. Moreover, the onset exothermal temperature for $\text{Li}_7\text{Ti}_5\text{O}_{12}$ electrode material is lower and total exothermal energy is higher. Fourier transform infrared (FT-IR) spectroscopy confirms that more C=O group containing compound are generated on $\text{Li}_7\text{Ti}_5\text{O}_{12}$ electrode. One species can be decomposed below 460 °C, and the other one can be decomposed below 600 °C. It is conclude that the aforementioned two species leads to higher thermal reaction of $\text{Li}_7\text{Ti}_5\text{O}_{12}$ electrode.

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1. Introduction

Safety concern is one of the most important issues for the development of lithium ion batteries, especially for large-size applications in hybrid electric vehicles (HEVs) and electric vehicles (EVs). Safety of lithium-ion cells is mainly related to thermal behavior of the materials in the cell. Several exothermic reactions occur inside a cell as its temperature increases. The important exothermic reactions that take place during thermal runaway of lithium-ion batteries are summarized as follows: (a) Solid electrolyte interface (SEI) layer decomposition; (b) Reaction of intercalated lithium with electrolyte; (c) Reaction of intercalated lithium with fluorinated binder; (d) Electrolyte decomposition; (e) Positive active material decomposition or perhaps the positive material reacts directly with electrolyte.

By far as we know, most of relevant research focused on the thermal stability of cathode materials and carbon anodes [1–12], which involve the relative thermal stabilities of LiCoO_2 , LiNiO_2 , LiMn_2O_4 , LiFePO_4 and various doped derivatives of these materials [4–7,13,14].

For anode materials studies, Zhang et al. [4] reported DSC results for mixtures of lithiated carbon (MCMB-28) and electrolyte (1 M LiPF_6 in 1:1 EC: DMC). They found a peak beginning at 130 °C that was small and independent of the degree of lithium intercalation. Du Pasquier et al. [10] have also studied thermal reactions of negative electrodes. They reported a breakdown of the SEI layer (120–140 °C) followed by reaction of Li_xC_6 with electrolyte (210–230 °C). This study also noted the presence of rapid reactions between PVDF based binders and metallic lithium or Li_xC_6 above 300 °C. This exothermic reaction was attributed to dehydrofluorination of PVDF and formation of LiF and hydrogen. Biensan et al. [6] reported their thermal studies. For LiPF_6 in 1:1:3 PC: EC:

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DMC electrolyte, they found a peak at 120 °C (350 J g⁻¹) attributed to reaction of Li_xC₆ with electrolyte. They also report a value of 1500 J g⁻¹ for the reaction of Li_xC₆ with PVDF, which begins near 240 °C, peaks at about 290 °C, and ends at about 350 °C.

In contrast to conventional graphite anodes, negligible volume change occurs during the insertion of lithium ions in the spinel structure of Li₄Ti₅O₁₂, leading to the formation of a rock-salt type Li₇Ti₅O₁₂ material [15]. Although Li₄Ti₅O₁₂ has an extreme flat operation potential plateau at about 1.55 V vs. Li⁺/Li, which results in lowered energy density for cells, it could be well used in most of electrolyte systems and does not form solid electrolyte interface (SEI). The possible loss in energy density can be compensated by intrinsic ultra-long cycle-life and promising safety behavior [16,17]. When coupled with a 4 V cathode material, the cell provides a nearly 2.5 V operating voltage, twice the voltage of a nickel-metal hydride cell [18]. In addition, spinel Li₄Ti₅O₁₂ is considered to be promising for high-power lithium-ion secondary batteries [15,19–23], and the Li₄Ti₅O₁₂/LiMn₂O₄ chemistry may be attractive for this applications.

Recently, there is an interesting result that Li₄Ti₅O₁₂ is considered as a passivation electrode material. Dedryvere et al. [24] demonstrate that organic species resulting from solvents degradation are present at the surface of the Li₄Ti₅O₁₂ electrode in a LiMn_{1.6}Ni_{0.4}O₄/Li₄Ti₅O₁₂ cell. The analysis of C 1s spectra show that the organic species include C=O and O–C=O environments of carbon by XPS. This result also shows an accumulation process of the organic species at the surface of the electrode, and it seems that the accumulation of organic species (evidenced by XPS) occurs with the global cycling time but especially with the time spent at high potential for the LiMn_{1.6}Ni_{0.4}O₄/Li₄Ti₅O₁₂ cell.

Before lithium-ion batteries can be used in large-scale applications, their performance still needs to be improved with regard to battery cycle life, rate capability and safety. Safety issues must be addressed to make lithium-ion batteries suitable as reliable power sources. However, the overall amount of information available on the thermal reactivity of Li₄Ti₅O₁₂ materials is insufficient, although some prior studies are available in the literature [25,26]. In this paper, we report on the thermal reactivity of Li₄Ti₅O₁₂ material by TG/DSC in the range from room temperature to 1000 °C that contain its weight loss, onset temperature of exothermic reaction, exothermic energy, and the in-depth relationship between its thermal reactivity and state of charge is also established. In addition, exothermic behavior of materials is first interpreted by FT-IR spectroscopy.

2. Experimental

2.1. Preparation of Li₄Ti₅O₁₂

Li₄Ti₅O₁₂ is synthesized by solid-state method using TiO₂-anatase, Li₂CO₃ as starting materials. Stoichiometric amounts of TiO₂, Li₂CO₃ are mixed in alcohol for 0.5 h at room temperature. The mixture is evaporated in vacuum condition at 110 °C for 0.5 h to get a precursor. Then the precursor is preheated at 450 °C for 0.5 h, and at last sintered at 800 °C for 12 h under air atmosphere to obtain a final Li₄Ti₅O₁₂.

2.2. Characterization

Powder X-ray diffraction measurement is carried out to identify the crystal structure of the obtained material on a Rigaku MutiFlex Diffractometer (D/max-2500, Japan) using Cu K α -radiation at 20 kV and 4 mA. The scanning range of 2 θ is from 10° to 90°. The surface micro-image of the obtained Li₄Ti₅O₁₂ powder is observed using a Scanning Electron Microscope (JEOL, JSM-5600LV, Japan) with an accelerating voltage of 20 kV. Thermal analysis of materials is performed with a TG/DSC (TA, Q600 SDT, USA) instrument and

measuring atmosphere for TG/DSC is in air. The powders are heated at 10 °C min⁻¹. Fourier transform infrared spectroscopy (FTIR-8400, SHIMADZU, Japan) is performed on KBr-supported samples.

CR2032 coin-type cells are utilized for electrochemical tests. The cells are fabricated of positive electrode, which consists of 80 wt% Li₄Ti₅O₁₂ powder, 10 wt% carbon black and 10 wt% PVDF, Li metal sheet as negative electrode, polymer separator and liquid electrolyte. The separator is a micro-porous polypropylene membrane Celguard 2400, and the electrolyte solution is 1 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) with a weight ratio of 1:1:1. The cells are assembled in an argon-protected glove box.

A LAND CT2001A 8-channel automatic battery test system (Wuhan Jinnuo Electronics Co., Ltd) is used to carry out constant current charging/discharging in a voltage range of 1.0–2.5 V. Cyclic voltammetry is performed on a CHI660D Electrochemical Workstation (Shanghai Chenhua Instruments Co., Ltd) over a sweep voltage range of 1.0–2.5 V at 0.01 mV s⁻¹ to characterize the redox reaction of Li₄Ti₅O₁₂ electrode during the electrochemical process.

To prepare the sample for thermal stability study, a cell is discharged to a desired capacity corresponding to an active material of Li_{4+x}Ti₅O₁₂ (0 < x < 3). The discharged cell is disassembled in an argon protected glove box. Then the positive electrode is washed in DMC to remove original electrolyte. After drying, the positive material (containing PVDF and carbon black) is scraped from Al current

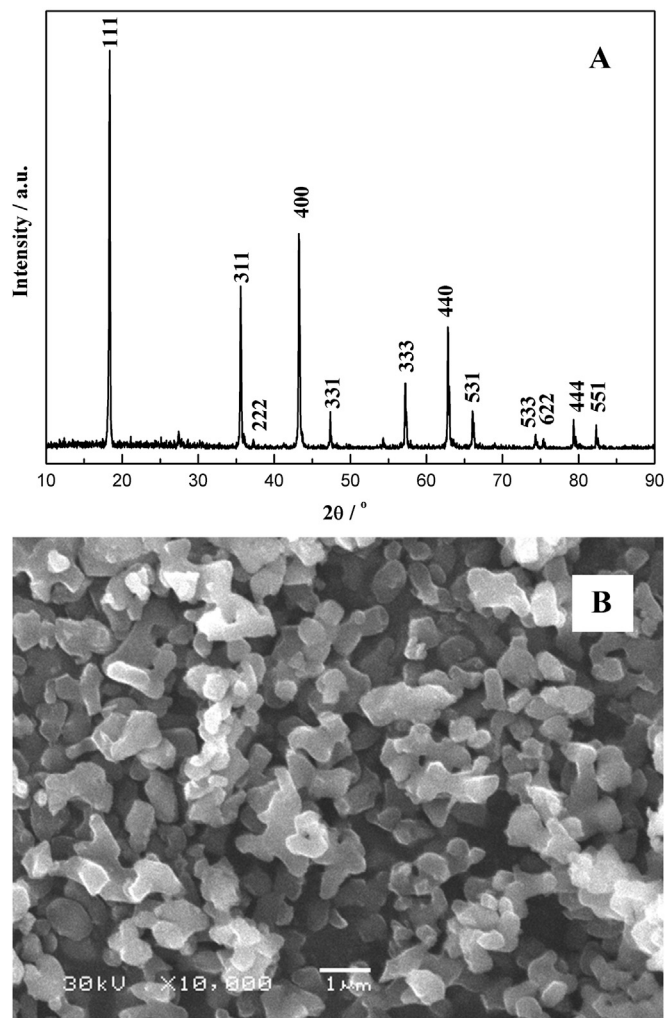


Fig. 1. XRD pattern (A) and SEM image (B) of the prepared-Li₄Ti₅O₁₂.

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