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Synthesis of $Li_4Ti_5O_{12}$/carbon nanocomposites in supercritical methanol for anode in Li-ion batteries: Effect of surface modifiers

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ABSTRACT

$Li_4Ti_5O_{12}$/carbon (LTO/C) nanocomposites are synthesized by preparing surface-modified LTO nanoparticles in supercritical methanol and subsequently calcinating the modified LTO under an Ar/H_2 condition. The effects of surface modifiers with different functional groups and chain lengths (oleylamine, oleic acid, hexylamine) on the particle morphology, particle size, crystallinity, carbon structure, and electrochemical properties are examined. During heat treatment at 750 °C, the carbonization of the modifiers attached to the surface of LTO effectively inhibit the particle growth and reduce some of the Ti^{4+} in LTO to Ti^{3+}. A higher degree of surface modification, in the order of oleylamine > hexylamine > oleic acid, results in a higher carbon content, smaller particle size, and higher Ti^{3+} content; these factors may result in better battery performance of the LTO/C synthesized using oleylamine. At a low rate of 0.1 C, the LTO/C samples synthesized using the different surface modifiers exhibit similar discharge capacities of 175 mA h/g (which approaches the theoretical capacity of LTO), while at a high rate of 10 C, the discharge capacities are in the order of oleylamine (147.1 mA h/g) > hexylamine (124.2 mA h/g) > oleic acid (101.5 mA h/g). The LTO/C nanocomposites prepared using the three different surface modifiers exhibit excellent cyclability up to 200 cycles at 1.0 C.

1. Introduction

The increasing demand for high-energy and high-power lithium ion batteries for the development of hybrid electric vehicles (HEVs), electric vehicles (EVs), and energy storage systems (ESS) has stimulated considerable interest in new electrode materials for large-scale lithium ion batteries (LIBs) [1,2]. Recently, spinel-structured $Li_4Ti_5O_{12}$ (LTO) has attracted considerable attention as one of the most promising electrode materials for such large-scale applications, because of its low-cost starting materials, an extremely flat voltage range at around 1.5 V (vs. Li/Li^+), negligible formation of solid-electrolyte interface (SEI), relatively high reversible capacity of 175 mA h/g, and especially the long cycling performance due to no structural change (zero-strain insertion material) during charge–discharge process [3–6]. However, because of its low electrical conductivity and low lithium ion diffusion kinetics [7,8], coarse LTO particles suffer from poor rate performance that limits its wide adaptability for large-scale LIB applications. Two typical strategies have been developed to overcome the limitations associated with LTO. The first strategy involves designing a nanostructured LTO [4,9–12]. The nano-sized particle could shorten both the ionic and electronic transporting path, thus the kinetics of lithium ion intercalation can be enhanced and the battery performance can be improved. The second strategy employs a conductive layer coating on the LTO surface (such as a carbon layer, surface nitridation, phosphates, metals, etc.), in order to enhance the electronic conductivity between the particles and the electrode [3,13–21]. In addition, the uniform coverage of the carbon layer means it can act as a barrier layer in suppressing gas formation caused by the interfacial reaction between the LTO surface and the carbonate-based electrolyte [22].

Numerous methods have been developed for the synthesis of nanostructured and/or conductive layer-coated LTO with high rate capacity and excellent cycling stability. These include solid-state [3,21,23], sol–gel [20], solution combustion [4], hydrothermal [24,25], solvothermal [26], and supercritical

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hydrothermal/solvothermal synthesis [17,27–30]. Not only did the above strategies used to cover the LTO surface with a carbon layer provide a conductive layer on the surface of LTO, they were also successful in suppressing the particle growth during the heat-treatment. For example, used as carbon precursors, the polyaniline [20], cetyltrimethylammonium bromide [31], and block copolymer [15] uniformly covered the LTO surface, which also inhibited the particle growth during the carbonization at high temperatures. The uniform carbon coating on the nano-sized LTO particle effectively improved the charge–discharge properties of LTO, especially at a high rate. Although these methods have been shown to enhance the rate performance of LTO, the high material cost, multiple synthetic steps, and sophisticated synthetic procedures can be obstacles for commercial implementation. Thus, considerable efforts are still underway to develop simpler, more reliable, and less-expensive techniques that can produce nano-sized LTO with a uniform conductive layer coating on the surface.

Recently, a simple supercritical methanol (scMeOH, $T_c = 239\,^\circ\mathrm{C}$; $P_c = 8.1\,\mathrm{MPa}$) approach has been developed to form a uniform carbon layer on a nano-sized LTO surface [17]. Oleylamine ($CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2NH_2$) was used as a surface modifier to cover LTO surface at the early nucleation stage. After the calcinations in Ar/H_2 atmosphere, the oleylamine was converted to a carbon layer that completely and uniformly covered the individual LTO nanoparticle, thus forming a core–shell $Li_4Ti_5O_{12}$/carbon (LTO/C) nanocomposite structure. The resulting LTO/C showed a remarkable rate capability of 103 mA h/g at the high rate of 50 C, which outperformed other conductive layer-coated LTO samples [3,13–15,18–21,32–34]. However, the previous work relied on the use of an expensive surface modifier (oleylamine), so that commercial-scale production of the core–shell LTO/C nanocomposite using oleylamine would be highly limited. Herein, we report the effect of different surface modifiers on the physicochemical and electrochemical properties of LTO/C nanocomposites. We used oleic acid ($CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$) as a much less expensive surface modifier with different end-group functionalities and hexylamine ($CH_3(CH_2)_5NH_2$) with different carbon chain lengths compared with oleylamine. This allowed an excellent opportunity to compare the characteristics of LTO/C nanocomposites prepared using different surface modifiers and to understand the effect of carbon coating on battery performance. The sections that follow describe the crystallinity, crystallite size, surface area, carbon content, and carbon structure of the LTO/C nanocomposites prepared using the three different surface-modifiers. The charge–discharge capacities of the LTO/C nanocomposites at a constant rate of 1 C (that correspond to a current density of 175 mA/g) and high rate performance of up to 50 C (8750 mA/g) are discussed.

2. Experimental

2.1. Materials

Titanium tetraisopropoxide (TTIP, purity of 97%), lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$, purity of 98%), oleylamine ($NH_2CH_2(CH_2)_7CH{=}CH(CH_2)_7CH_3$, purity of 70%), and hexylamine ($CH_3(CH_2)_4CH_2NH_2$, purity of 99%) were purchased from Sigma-Aldrich, Co. (St. Louis, MO, USA). Oleic acid ($CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$, purity of 95%) was obtained from Daejung Chemicals and Metals, Co. (Gyonggido, Korea). Methanol (HPLC grade) was obtained from J.T. Baker (Phillipsburg, NJ, USA). Distilled and deionized (DDI) water was prepared using a Milli-Q® ultrapure water purification system equipped with a 0.22 μm filter (Billerica, MA, USA). Poly(vinylidenedifluoride) (PVDF, Kureha Chemical Industry Co., Tokyo, Japan), acetylene black (DENKA Co. Ltd., Tokyo, Japan), and 1-methyl-2-pyrrolidinone (NMP, purity of 98%, Alfa-Caesar, MA, USA) were used as received.

2.2. Apparatus and procedures

LTO/C nanocomposite was synthesized by first forming surface-modified LTO in supercritical methanol and subsequently calcining the modified sample in an Ar/H_2 condition. In a typical synthesis, 0.28 mmol of $LiOH{\cdot}H_2O$, the experimentally desired number of modifiers, and 0.35 mmol of TTIP were charged into 3.5 mL of methanol and the suspension was transferred to a SUS316 tube reactor with an inner volume of 11 mL. The modifier: TTIP ratio was fixed at 10: 8. The reactor was then soaked in a molten salt bath of which the temperature was maintained at 400 °C. The LTO particles produced in the reactor were collected and purified using three cycles of decantation and centrifugation using methanol. The purified surface-modified LTO particles were then dried in a vacuum oven for 6 h and then calcined at 750 °C under an Ar/5% H_2 condition with a flow rate of 100 mL/min for 5 h. The synthesized samples were designated according to the modifier and calcination temperature. For example, the samples synthesized using hexylamine before and after calcination were referred to as LTO-Hexyl and LTO-Hexyl-750C, respectively.

2.3. Characterization

The phase structure of the LTO particles was characterized using a Rigaku RINT2000 X-ray diffractometer (XRD, Tokyo, Japan) with Cu $K\alpha$ radiation at 40 kV and 50 mA. The morphology of the samples was analyzed using a Hitachi S-4100 scanning electron microscope (SEM, Tokyo, Japan) and a Tecnai-G^2 high-resolution transmission electron microscope (HR-TEM, FEI Co. Ltd., OR, USA). The organic functional groups on the surface of LTO were characterized using a NICOLET 380 Fourier transform infrared (FT-IR) spectrometer (Thermo Electron Co. NJ, USA). The Brunauer–Emmett–Teller (BET) surface area analysis was performed using a Belsorp-mini II apparatus (BEL Inc., Osaka, Japan). The thermal properties of the samples were measured using a DuPont Instruments TGA 2950 thermal gravimetric analyzer (TGA) under an air flow condition at a rate of 5 °C/min. The carbon structure of the LTO/C nanocomposites was characterized using a Nicolet Almega XR dispersive Raman spectrometer (Thermo Fisher Scientific Inc. MA, USA) equipped with an Nd:YAG laser. All the electrochemical studies were conducted using a CR 2032-type coin cell configuration. The composite electrodes were prepared by dispersing 87 wt% active material, 7 wt% acetylene black, and 6 wt% PVDF in NMP. The slurry was then cast uniformly on a Cu foil to prepare the electrode film, which was dried at a heating board at 80 °C for 24 h to remove the solvent. The electrode film was punched into 15 mm-diameter discs (area of 1.77 cm^2) and weighed. The electrolyte used was 1 M $LiPF_6$ dissolved in ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate solvent (volume ratio of EC: DMC: EMC = 1:1:1). A microporous polypropylene membrane with a thickness of 25 μm (Celgard 2500, Celgard LLC., NC, USA) was used as the separator and lithium metal was used as the cathode. The cell assembly was conducted in a glove box filled with ultra-high purity argon gas. The cells were galvanostatically charged and discharged in a voltage range of 1.0 to 2.5 V (vs. Li/Li^+) using a model WBCS 3000 battery test system (WonATech Corp., Korea) at room temperature. The cyclability was recorded at a rate of 1 C (1 C = 175 mA/g) for up to 200 cycles. The charge–discharge rate was varied from 0.1 C to 50 C for rate performance measurements.