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Continuous synthesis of $Li_4Ti_5O_{12}$ nanoparticles in supercritical fluids and their electrochemical performance for anode in Li-ion batteries

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HIGHLIGHTS

- Continuous synthesis of $Li_4Ti_5O_{12}$ (LTO) using supercritical fluids.
- Addition of Li source prior to calcination is required to obtain phase-pure LTO.
- Supercritical water/air-calcined LTO exhibits excellent capacity at below 4 C.
- Supercritical methanol/H_2-calcined LTO exhibits better rate performance at above 8 C.

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ABSTRACT

A continuous supercritical fluid process is adopted for the synthesis of lithium titanium oxide ($Li_4Ti_5O_{12}$, LTO) nanoparticles for applications in lithium ion batteries. The effect of various synthetic conditions, including concentration, residence time, precursor ratios, and supercritical fluids on the phase purity and particle properties are examined. The as-synthesized samples in supercritical water (scH_2O) or in supercritical methanol (scMeOH) exhibit nanoparticles with sizes of 4–10 nm, but retain an amount of Li of 6.8–8.6 mol.% less than that of the stoichiometric Li content in LTO. The deficient amount of Li is added and calcined in an air or H_2/Ar flow at 600 °C. The calcined LTO exhibits phase-pure LTO with high crystallinity. The air-calcined LTO synthesized in scH_2O exhibits an initial discharge capacity of 174.2 mAh g^{-1} at 0.1 C, good rate performance of up to 4 C (133.4 mAh g^{-1}), and excellent long-term cyclability for up to 200 cycles. The H_2/Ar-calcined LTO synthesized in scMeOH exhibits an ultrathin and uniform carbon layer on the nanosized LTO with a thickness of 0.5–1 nm. It thus shows much better high-rate performance for charge–discharge rates of above 8 C compared to the air-calcined LTO synthesized in scH_2O.

1. Introduction

Current development in electronic devices, electric vehicles, and energy storage systems urgently demands new types of power sources with high energy capacity, high power density, durability, and good safety with a restricted volume and weight. Lithium-ion batteries (LIBs) are excellent candidates for such applications because of their high energy density, light weight, no memory effects, low self discharge, and long lifespan [1,2]. At present, carbon-based materials (generally graphite) are the most commonly-used anode materials in small-scale commercial LIBs. However, safety issues caused by solid-electrolyte formation (SEI) and volume change during the charge–discharge process, low energy density, and low rate performance associated with graphite-based composite electrode hinder the wide utilization of carbon-based materials in large-scale LIBs [3]. Therefore, numerous studies on potential anode materials to replace the graphite-based electrode are currently being carried out worldwide. Among these potential anode materials, spinel-structured $Li_4Ti_5O_{12}$ (LTO) is considered one of the most promising [4]. The advantages of LTO include good safety due to no structural change (zero-strain insertion material) during the charge–discharge process, an extremely flat voltage range at around 1.5 V (vs. Li/Li^+), relatively high

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reversible capacity (175 mAh g^{-1}), negligible solid-electrolyte interface (SEI) formation, long cycling performance, and low cost of starting materials [5]. However, coarse LTO particles exhibit low electrical conductivity and low lithium ion diffusion kinetics, resulting in low capacity at high charge–discharge rates, thus limiting its wide application in large-scale LIBs [6]. Recently, various approaches have been developed to overcome the low rate performance of LTO, including nanostructured LTO [7,8] and conductive material coating (e.g., carbon layer, surface nitridation, surface phosphidation, etc.) [9–12].

As expected, the electrochemical performance of LTO is highly dependent on its synthetic conditions. Conventionally, LTO particles are synthesized using a solid-state method with TiO_2 and Li_2CO_3 or LiOH as the precursors. In the typical solid-state method, the precursors are mixed using techniques such as ball-milling for an extended period of time, and the mixture is then calcined at temperatures as high as 800–1000 °C for a long period of 12–24 h to obtain highly-crystalline and phase-pure LTO [5,6,13]. The high synthetic temperature and long processing time induce a high energy consumption, low product throughput, and coarse LTO particles due to interparticle agglomeration. To overcome the limitations of the solid-state reaction method for producing LTO, various methods such as sol–gel [14], spray-pyrolysis [7], hydrothermal [15], solvothermal [16], and combustion process [8] have been developed. For large-scale production, however, synthetic methods are expected to have low production and material costs, require less complicated procedures, use less toxic chemicals, and be easy to scale-up. In this regard, the development of a more reliable, simpler, faster, and more eco-friendly process of producing high-performance LTO remains a considerable challenge.

The synthesis of nanomaterials in supercritical water (scH_2O, scH_2O, $T_c = 374.1$ °C, $P_c = 22.1$ MPa) or in supercritical alcohols (e.g., supercritical methanol, scMeOH, $T_c = 239$ °C, $P_c = 8.1$ MPa) offers unique synthetic conditions and material properties due to the beneficial properties of supercritical fluids, including extremely low viscosity, zero surface tension, tunable density by controlling process parameters, and high supersaturation ratio [17,18]. In addition, the extremely high particle formation rate (few seconds to few minutes) in supercritical fluids allows a continuous flow reactor configuration to develop, and thus large-scale production of active materials can be easily implemented. In fact, a commercial-scale, scH_2O-based continuous flow reactor system with a production capability of 1000 tons per year has been constructed in Korea for producing a lithium phosphate active material. Various types of active materials for use in LIBs have been synthesized in supercritical fluids either in a continuous or in a batch mode: TiO_2 [19], $LiFePO_4$ [20], $LiCoO_2$ [21], $LiMn_2O_4$ [22], Li_2FeSiO_4 [23], Li_2MSiO_4 (M = Fe, Mn, Co) [23–25], $LiMnPO_4$ [20], and $Li_4Ti_5O_{12}$ [11,26–30]. Recently, it has been demonstrated that highly crystalline, phase-pure LTO particles can be synthesized using titanium (IV) isopropoxide (TTIP) and lithium hydroxide (LiOH) as the precursors and using scH_2O as the solvent in a batch reactor [28,29]. When scMeOH was used as the solvent in the batch reactor, hierarchically porous LTO microspheres with enhanced electrochemical performance were obtained [26,27].

Herein, the first study of continuous synthesis of LTO in scH_2O or in scMeOH using a flow reactor system is described to examine the feasibility of the mass production of LTO particles. The batch-type synthesis of LTO in scH_2O or in scMeOH has been explored previously [26–29]. The significant difference in the setup between the batch and continuous reactors, however, led to the formation of LTO with significantly different properties, even though similar process parameters and supercritical fluids were examined. The exploration of the continuous synthesis in supercritical fluids is extremely important for developing economically-viable, high-pressure and high-temperature process and thus for successful commercialization [31]. The following section discusses the effect of residence time, concentration, precursor ratio, and supercritical fluid on the crystallinity, crystallite size, surface area, and morphology of LTO particles. The effect of various calcination conditions on the physicochemical properties and electrochemical performance are discussed. High-rate performance of up to 50 C and long-term cyclability of up to 200 cycles of the calcined LTO are presented. Lastly, the electrochemical properties of the LTO synthesized in scMeOH or in scH_2O were compared with LTO synthesized using the solid-state method.

2. Experimental

2.1. Materials

Titanium tetraisopropoxide (TTIP, purity of 97 wt.%) and lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$, purity of 98 wt.%) were purchased from Sigma–Aldrich (St. Louis, MO, USA) and used as received. 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). Methanol, ethanol and isopropyl alcohol (IPA) (HPLC grade) was obtained from J.T. Baker (Phillipsburg, NJ, USA). Acetylene black (DENKA Co., Ltd., Tokyo, Japan), poly(vinylidenedifluoride) (PVDF, Kureha Chemical Industry Co., Tokyo, Japan), and 1-methyl-2-pyrrolidinone (NMP, purity $\geqslant$ 98 wt.%, Alfa-Caesar, MA, USA) were used as received.

2.2. Apparatus and procedures

All the LTO nanoparticles were synthesized continuously using in scH_2O or in scMeOH. The details of the reactor system and synthetic procedure have been described in previous papers [32]. To synthesize LTO, the DDI water or methanol was first introduced to the reactor system using two high-pressure pumps at an experimentally desired pressure of 30 MPa. The temperatures of the reactor and the preheater were then increased to an experimentally desired reactor temperature of 400 °C using the furnace. After the experimentally desired temperature and pressure were reached, the precursor solution was introduced to the reactor system. The concentration of the precursor solution in the feed tank was varied from 0.05 to 0.2 M. Typically, the temperature of the reactor and the mixing tee can be maintained at 400 ± 3 °C over the length of the reactor and the pressure can be maintained at 30 ± 0.1 MPa over the entire reaction time. The synthetic conditions and the code of the samples obtained under the different conditions are summarized in Table 1. After the reaction, the particles in the metal filters were collected, washed, filtered, and dried at 60 °C in a vacuum oven for 24 h. The as-synthesized particles were then calcinated at a temperature of 600 °C with air or Ar/5% H_2, with a flow rate of 100 mL/min for 5 h.

2.3. Characterization

X-ray diffraction patterns (XRD) were recorded using Rint 2000, Rigaku, Japan with Cu K_α radiation at 40 kV and 50 mA. The surface morphology of the powders was analyzed using scanning electron microscopy (SEM) (Hitachi S-4100, Tokyo, Japan). The Brunauer–Emmett–Teller (BET) surface area analysis was performed through a Belsorp-mini II apparatus (BEL Inc., Osaka, Japan). Elemental analysis of the Li contents in the samples was carried out using atomic absorption spectroscopy (AAS) (iCE3500 AA system, Thermo Scientific, MA, USA). Elemental analysis of the Ti contents in the samples was carried out using inductively coupled plasma-optical emission spectrometry (ICP-EOS) (iCAP6500, Thermo Scien-