Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

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

Spray-drying assisted synthesis of a $Li_4Ti_5O_{12}$/C composite for high rate performance lithium ion batteries

Ji-Hyun Park[a,b], Seok-Won Kang[a,c,*], Tae-Soon Kwon[a], Ho Seok Park[b,**]

[a] Korea Railroad Research Institute, 176 Cheoldo bangmulgwan-ro, Uiwang, Gyeonggi-do 16105, Republic of Korea
[b] School of Chemical Engineering, Sungkyunkwan University (SKKU), Suwon, Gyeonggi-do 16419, Republic of Korea
[c] Division of Energy and Environmental Technology, University of Science & Technology, Daejeon 34113, Republic of Korea

ARTICLE INFO

Keywords:
Carbon layer
Glucose
High rate performance
Lithium titanium oxide (LTO)
Spray-drying

ABSTRACT

Spinel crystalline lithium titanium oxide ($Li_4Ti_5O_{12}$ or LTO) has gained attention as a possible alternative material to graphite for use as anodes in lithium-ion rechargeable batteries due to its low volume expansion and dendrite-free long-term stability. However, the rate capability of LTO is limited by its low electronic conductivity, which results in a large polarization resistance between electrodes. In this study, we demonstrate a spray-drying-assisted carbon coating approach to synthesize LTO/C composites for enhanced lithium-insertion capacity and facilitated charge-discharge reaction kinetics. The thin carbon layer of LTO/C composite contributes to suppressing particle growth by forming passivating carbon layers. In addition to the decrease in particle size for short lithium-diffusion pathways, the highly conductive carbon layers reduce the interfacial resistance between the electrode and electrolyte by enhanced electrical conductivity. The electrochemical performances of the spray-drying-prepared LTO/C composite such as the specific capacity, cycle and rate capabilities, and impedance are compared with pristine LTO and carbon-coated LTO synthesized without spray-drying. The LTO/C prepared from glucose exhibits a 11.15% enhancement in rate characteristics of pristine LTO at 0.5 C after 100 cycles. These results indicate that the carbon coating layer promotes charge transfer and ion diffusion as well as provides a buffering effect for improved rate and cyclic capabilities.

1. Introduction

The widespread use of fossil fuels to drive internal combustion engines has resulted in increased concerns over air pollution from CO_2, heavy metals, and ultra-fine dust particles. Correspondingly, this has raised interest in the use of electrical sources of energy for household and industrial applications. In this regard, hybrid electric vehicles (HEV) and renewable energy systems (e.g. solar power plants) are of particular interest. Lithium-ion batteries (LIBs) are currently the main power source used to store and supply electrical energy for portable electronic devices and large-scale energy storage systems. The use of LIBs for large-scale applications is highly dependent on their cost, safety, and lifetime. Hence, the selection of appropriate battery materials is pivotal. Accordingly, a tremendous amount of research has focused on the development of energy storage materials with high energy and power densities. Graphite is currently the most widely used as an anode material due to its high capacity of 372 mA h/g, flat potential plateaus, and high-yield production. However, the volume changes of graphite during charge/discharge processes lower their long-term cycling stability. Additionally, Li dendrite formation occurs even at high rates (e.g., 1 and 2 C) and is a major impediment to their use for high-power applications [1]. To resolve these issues, composites with transition metal oxides [2,3], carbon-based materials [4,5], and graphene [6–8] have been explored as possible alternative materials to graphite.

Among the composites with transition metal oxides, cubic spinel lithium titanium oxide (LTO: $Li_4Ti_5O_{12}$) exhibits a particularly excellent structural stability (i.e., volume change below 1% during charge/discharge), a stable voltage plateau at approximately 1.5 V vs. Li^+/Li, and a theoretical capacity of 175 mA h/g [9]. Unfortunately, LTO is an electronic insulator resulting from the influence of empty Ti 3d-states, which leads to a large polarization resistance and poor performance when cycled at high rates [10–13]. Thus far, various processing routes like novel synthesis method [14–16], ion doping [17–20], surface modification [21], and carbon coating [22–27] have been proposed to improve the rate performance of LTO. Carbon coating on LTO increases the charge transfer rates and protects the LTO surface from undesirable side reactions caused by the acidic electrolyte. The carbon coating layer

* Corresponding author at: Korea Railroad Research Institute, 176 Cheoldo bangmulgwan-ro, Uiwang, Gyeonggi-do 16105, Republic of Korea.
** Corresponding author.
E-mail addresses: swkang@krri.re.kr (S.-W. Kang), phs0727@skku.edu (H.S. Park).

http://dx.doi.org/10.1016/j.ceramint.2017.10.217
Received 28 August 2017; Received in revised form 9 October 2017; Accepted 29 October 2017

is expected to provide electronic conducting pathways that will both enhance the electronic conductivity and prevent electrode polarization during high-rate operations.

In this study, we present a synthesis method to obtain carbon-coated LTO nanoparticles (denoted as LTO-CS) for stable high-rate performance LIBs. Our method is based on spray-drying method using colloidal suspensions composed of ternary precursor materials such as TiO_2, Li_2CO_3, and carbon sources (e.g., glucose). Specifically, LTO-CS was synthesized in-situ by a spray-drying method using the solution mixture of precursor materials. The nano-structured carbon layer is hypothesized to reduce the Li^+ ion diffusion path length and offer electrical conduction pathway. The structure and phase composition of LTO-CS were analyzed using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and powder X-ray diffraction (XRD) techniques. Additionally, the electrochemical performance was assessed with cyclic voltammetry, galvanostatic cycling, and impedance spectroscopy measurements.

2. Materials and methods

2.1. Synthesis of LTO-CS

Prior to the spray-drying process, a solution mixture of ternary precursor materials is prepared via a previously reported method [23]. Preparation of the aqueous solution mixture of ternary precursor materials consisted of mixing lithium carbonate (Li_2CO_3, Alfa Aesar, 99%), rutile-structured titanium oxide (TiO_2, Sigma-Aldrich, 99.5%), and glucose ($C_6H_{12}O_6$, Sigma-Aldrich), which is the carbon source. First, the rutile phase TiO_2 nanoparticles (~ 21 nm) of high purity were dissolved into distilled water with glucose before the obtained mixture is heated at 80 °C for 1 h under continuous magnetic stirring. The final mixture is prepared by adding Li_2CO_3 into the obtained solution, which was dispersed by continuous magnetic stirring for 12 h at 80 °C. The molar ratio between Li and Ti in the transition metal oxide and the carbon content in the $Li_4Ti_5O_{12}$/C composite was approximately 4.1:5 and 4 wt %, respectively.

The solution is then cooled down to room temperature and diluted by a factor of 2. A polymeric dispersant (e.g., Gum Arabic, Sigma-Aldrich) was mixed into the solution via an ultrasonic bath for 30 min to form a relatively homogenous mixture. The dispersed solution (~ 15 ml) was sprayed onto a titanium plate, which maintained a uniform surface temperature of 150 °C and evaporated the solvent instantaneously via a controllable hot plate (PC-420D-230, Corning) and a compressor (Monster comp001, China). The $Li_4Ti_5O_{12}$/C composite powders were obtained by a spray-drying process, collected, and calcined at 800 °C for 2 h in a furnace purged with Ar gas. In order to compare the performance advantages associated with LTO-CS to similar materials, pristine LTO and an $Li_4Ti_5O_{12}$/C composite (denoted as LTO-C) were prepared without using the spray-drying process. LTO-C is synthesized by the direct calcination of the solution mixture of TiO_2, Li_2CO_3, and glucose without the spray-drying process. Pristine LTO was prepared based on the same protocol as LTO-C, but without carbon sources.

2.2. Characterization

The structure and phase composition of the samples were analyzed via X-ray powder diffraction (XRD, D8 ADVANCE, Bruker Corporation) with Cu K radiation generator in the 2θ range of 10–90°. The microstructure and morphology of the samples were observed by a field emission scanning electron microscope (FE-SEM, JSM-7600F, JEOL) to estimate particle size. Additionally, high-resolution transmission electron microscopy (HR-TEM, JEM ARM 200F, JEOL) was used to observe the coated carbon layer on the surface of LTO-CS and LTO-C. Quantitative analysis of the carbon content in LTO-CS and LTO-C composites was performed using TG/DTA (Thermogravimetry Differential Thermal Analyzer, Seiko Exstar 6000, SEICO). Furthermore, the measurement of pore size and surface area was made by using a BET (Brunauer-Emmett-Teller, BELSORP-miniII) equipment to analyze the porous characteristics of the carbon coating layer. The Raman spectra of the samples were also measured using a high-resolution Raman microscope (inVia Raman microscopes, Renishaw) with a Ar-ion laser of 514 nm.

2.3. Electrochemical characterization

The electrochemical performances of LTO-CS, LTO-C, and pristine LTO samples were tested using the CR2032 coin-type half-cells. The prepared LTO-based sample (LTO-CS, LTO-C, or pristine LTO) was used as an anode material, Polyvinylidene fluoride (PvdF, MTI Korea) as a binder, and Super P as a conductor. The active material slurry was made by homogeneously mixing the three aforementioned components in a weight ratio of 80:10:10 via a Thinky electrode slurry mixer (ARE-310, MD BROS) and dissolving them in N-methyl-2-pyrrolidone (NMP, MTI Korea). The mixed slurry was uniformly coated on copper foil using a micrometer film applicator (MHA1-13, Mitutoyo Co.) and dried at 120 °C for 12 h in a vacuum drying oven (SH-VDO-08NG, SH Scientific). The electrode sheets fabricated for CR2032 coin-type cells were measured as 14 mm in diameter, 30–40 μm in thickness, and their average mass loadings were 1–2 mg/cm^2. The coin-type half-cells were assembled with Li metal as a counter electrode in an Ar-filled glove box (KK-011AS-EXTRA, Kiyon). The electrolyte used in the experiments consisted of a 1 M $LiPF_6$ solution (MTI Korea) in Ethylene carbonate (EC), Dimethyl carbonate (DMC), and Diethyl carbonate (DEC) with a volume ratio of 1:1:1. The electrochemical characterization of the samples were performed by CV (Cyclic Voltammetry) at a scan rate of 0.5 mV between 1.0 and 3.0 V using a potentiostat (VSP, Bio Logic Science Instrument). The rate and cycling tests of the assembled cells were carried out under different charge and discharge rates from 0.1C to 10 C between 1.0 and 3.0 V at room temperature using a battery tester (4300 K, MACCOR). The electrochemical impedance spectrum (EIS) was measured by using a potentiostat (Ivium-n-Stat, Ivium) in the frequency range from 100 kHz to 10 mHz with 10 mV amplitude.

3. Results and discussion

As illustrated in Fig. 1, LTO-CS particles are synthesized by spray-drying assisted method that can control the particle size and enable us to synthesize nanoparticles of uniform morphology. This method is suitable for a large-scale production and has several advantages over

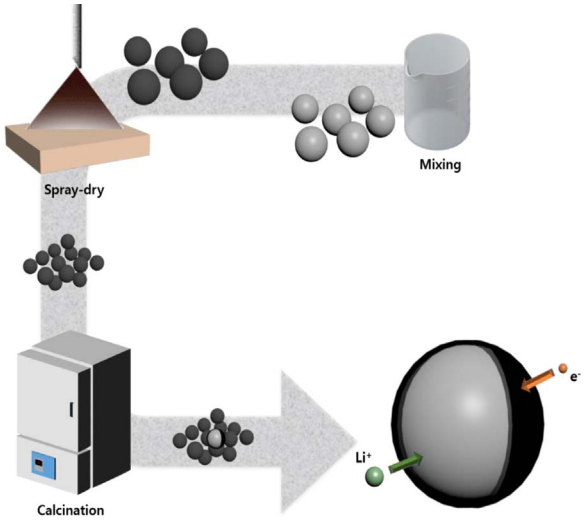

Fig. 1. Scheme showing the synthetic process for preparing LTO-CS nano-powders based on the spray-drying technique.