Cold sintering process for fabrication of a high volumetric capacity Li$_4$Ti$_5$O$_{12}$ anode

Joo-Hwan Seo$^a$, Kris Verlinde$^a$, Ramakrishnan Rajagopalan$^{b,c}$, Enrique D. Gomez$^{a,c,d}$, Thomas E. Mallouk$^e$, Clive A. Randall$^{a,c,*}$

$^a$ Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA
$^b$ Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802, USA
$^c$ Materials Research Institute, The Pennsylvania State University, University Park, PA 16802, USA
$^d$ Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802, USA
$^e$ Department of Chemistry, The Pennsylvania State University, University Park, PA, 16802, USA

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ABSTRACT

The cold sintering process (CSP) is useful for densifying lithium ion battery composite electrodes to achieve higher volumetric capacity density. Lithium titanate is one of the most promising anode materials to replace graphite in conventional anodes, as it enhances safety in large scale applications. A densified binder-free LTO-based anode was fabricated by the cold sintering process. The composite anode was first formed by tape casting with a binder and then was heat treated to remove the binder. The binder-free composite was humidified with water to provide a transient liquid phase and then moved onto a current collector. The wetted composite was cold sintered at 120 °C under a uniaxial pressure of 500 MPa and directly deposited on a current collector. The density of the LTO/CNF composite anode was 2.82 g/cm$^3$ (87% relative density). The volumetric capacity densities of the cold sintered anodes were found to be ~380 mAh/cm$^3$.

1. Introduction

Lithium ion batteries (LiBs) are attractive for large scale electric energy storage applications such as electric vehicles and grid storage with renewable energy power generation due to their high energy density, long cycle life and relative low cost [1–6]. One of the key issues for LiBs in large scale energy storage applications is safety, as the operating environments and total stored energy are more extreme than those found in portable electronic devices [7–9]. Conventional LiBs employing a graphite-based anode have safety issues due to the possibility of internal short circuiting originating from lithium dendrite growth [10–14]. Lithium titanate (Li$_4$Ti$_5$O$_{12}$, LTO) with a cubic spinel (AB$_2$O$_4$, A = Li, B = Li, Ti) structure is one of the most promising alternative anode materials for Li-ion batteries because of advantages in enhanced safety, high operating voltage, and relatively high capacity (175 mAh/g). Moreover, LTO is easy to fabricate and has good cycling performance [9,15–20].

Despite these advantages of LTO, the low volumetric capacity of LTO-based electrodes is a challenge for its use in mainstream applications [1,9]. In order for LTO to be useful in portable electronic devices, for EVs, smart grids, and even smaller multilayer ceramic batteries the volumetric capacity must be increased [21–23]. LTO (175 mAh/g, 613 mAh/cm$^3$) has a lower theoretical gravimetric and volumetric capacity than graphite (372 mAh/g, 837 mAh/cm$^3$), the anode material that is typically used in commercial LiBs [13,24]. The theoretical density of LTO (3.5 g/cm$^3$) is much lower than most oxides. For example, most oxide-type cathode materials have a density of ~5 g/cm$^3$. On a practical level, this means that we must increase the packing density of the LTO-based anode in order to increase the overall volumetric energy density of Li-ion cells with conventional cathodes. Some of the present research strategies are focused on developing fabrication processes for LTO-based materials with high tap density to improve their volumetric performance. This involves powder synthesis and powder packing strategies with size distributions such as hydrothermal methods, the sol–gel route, spray drying, and carbon coating of the powders to minimize the inactive binder content [3,8,25–28]. With cold sintering there is no need to use binders in the final assembly or to use spray dried particles, thereby eliminating several processing steps. Typically, inactive materials can take up to 50% of the total volume of composite electrodes fabricated by conventional tape-casting and/or calendaring processes [29,30]. These inactive components include materials such as conductive carbon, binders and pores [31]. Therefore,
a process that enables the removal of binders and reduces the porosity is needed to increase the volumetric energy density of LTO electrodes. Recently a low temperature sintering process, named cold sintering process, was developed for the densification of various families of ceramics and ceramic-based composites [32]. The cold sintering process utilizes a transient aqueous liquid phase that assists the dissolution and precipitation processes, enabling densification of particulate materials under uniaxial pressure at a relatively low sintering temperature (< 300 °C). The cold sintering process can achieve relative densities up to 90% and beyond [33,34]. A wide range of ceramics and ceramic-based composites with various functional materials, including semiconductors, ferroelectrics, thermoelectrics, two-dimensional and structural materials, have all been densified successfully by cold sintering [33,35–40]. This low temperature densification process is useful for densification of battery materials such as composite electrodes, solid electrolytes and even for fabrication of all-solid-state batteries. There have been several studies reporting the application of the cold sintering process for the densification of the battery materials, for example cathodic olivine structured LiFePO_4, solid electrolytes such as NASICON (sodium (Na) superionic conductor, NaM_2(PO_4)_3 (M = Ge, Ti, Zr))-type Li_1.5Al_0.5Ge_1.5(PO_4)_3, to increase the density and volumetric capacity of the electrodes as well as the ionic conductivity of solid electrolytes [41–46].

The objective of this study was to explore cold sintering to improve the volumetric capacity density of an anode material, specifically LTO-based materials. The structure-property-processing relations have been accessed with this system and are discussed in the context of electrochemical performance.

2. Experimental approach

A green tape LTO anode was fabricated by the tape-casting method previously reported by our group for cathodes [47,48]. LTO ceramic powders purchased from MTI Corporation were used as the active material. Carbon nanofiber (CNT) was provided by Mitsubishi Materials, Inc. and used to increase the electronic conductivity. A mixture of LTO and CNF (90/10 w/w) was added to a polypropylene container with milling media based on yttria-stabilized ZrO_2 beads and an ethanol solvent, where they were ball milled for over 24 h. After drying the slurry, the powder mixture was then ground with a mortar and pestle. A slurry was prepared by mixing these powders, binder (QPAC40, Empower Materials) and plasticizer (S-160, Tape Casting Warehouse). The mass ratio of the LTO/CNF powder mixture, binder, plasticizer, and solvent in the slurry was 17.8:7.3:0.3:74.2. After stirring overnight, a 70 μm-thick green tape was cast with a doctor blade onto a mylar substrate. The green tape was then dried at room temperature overnight and punched into disks with a diameter of 12 mm. The samples were heat treated at 250 °C for 1 h at a ramp rate of 3 °C/min in order to burn out all the organics. A binder-free anode tape was then composed of 90 wt% LTO and 10 wt% CNF. The LTO/CNF composite film was then humidified for 30 min over water heated at 80 °C on a hot plate. This step enables the uptake of the transient liquid phase through the vapor, and thereby avoids problematic capillary
forces induced by adding the transient phase directly as a liquid. The wetted tape was transferred onto aluminum foil, which was used both as a substrate and a current collector. The cold sintered process was done using a laboratory platen hot press at 120 °C for 30 min under 500 MPa.

The density of the cold sintered electrode was determined by a geometric method using the weight/volume ratio of the electrodes. The volume of the electrode was calculated by multiplying the area and thickness of the electrodes. The relative density was computed based on the mass fraction and intrinsic densities of 3.5 and 1.95 g/cm³ for the LTO and CNF phases, respectively. The crystalline phases present in the cold sintered tape were determined by X-ray diffraction using a PANalytical Empyrean diffractometer with a Cu-Kα radiation source at a scan rate of 0.02° between 10 and 80 degrees 2-theta. The microstructural and elemental distributions of the cold sintered anode were characterized using scanning electron microscopy (SEM), NanoSEM.

Fig. 3. SEM images of (a) ball milled powder mixture of LTO and CNF, (b–f) cross-sectional surface of a cold sintered anode at different magnifications with EDS maps.
630 and transmission electron microscopy (TEM), using a FEI Talos with energy dispersive spectroscopy (EDS) to assess grain structure and carbon distribution. Fractured cross-sectional SEM characterization was performed by using a polished electrode. The TEM specimen was prepared by a standard sample preparation process to obtain electron transparency including polishing and ion beam milling (Gatan, PIPS II).

The electrochemical performance was evaluated with a 2032 type coin cell assembled in a MBraun argon-filled glove box with a cold sintered LTO electrode as the working electrode. Lithium foil was used as the reference and counter electrode. A liquid electrolyte, 1 M lithium hexafluorophosphate solution in ethylene carbonate and dimethyl carbonate (1 M LiPF₆ with EC/DME (1:1 v/v), Sigma-Aldrich), was used with a porous polyvinylidene difluoride membrane (Amersham) as a separator. The electrochemical measurements were conducted with a galvanostatic charge/discharge system (Neware BTS4000) in the range of 1–2.5 V at charge/discharge rates of 0.1–1C at room temperature. Cyclic voltammetry was also performed in the range of 0.8–2.6 V vs Li⁺/Li at a scan rate of 0.1 mV/s. The specific capacity of the anodes was calculated based on the mass of active material. The volumetric capacity was computed using the total volume of the anode not including the aluminum current collector.

3. Results and discussion

Fig. 1 illustrates the basic fabrication process of binder-free LTO/CNF composite anodes using the cold sintering process. A phase analysis was conducted to confirm the phase purity of the LTO composite after the cold sintering process. X-ray diffraction patterns of pure LTO powder, the cold sintered LTO electrode and a reference pattern of LTO are shown in Fig. 2. All the peaks could be assigned to the LTO phase, and the relative intensities were similar suggesting there was no preferred orientation in the sintered sample. The only other peaks identified were those from the Al foil substrates.

Fig. 3 shows images of a powder mixture of LTO/CNF and cross-sectional images of a cold sintered LTO/CNF composites anode. As shown in Fig. 3a, it can be observed that the LTO and CNF powders were homogeneously dispersed through the wet ball milling process. The electrochemical measurements were conducted with a galvanostatic charge/discharge system (Neware BTS4000) in the range of 1–2.5 V at charge/discharge rates of 0.1–1C at room temperature. Cyclic voltammetry was also performed in the range of 0.8–2.6 V vs Li⁺/Li at a scan rate of 0.1 mV/s. The specific capacity of the anodes was calculated based on the mass of active material. The volumetric capacity was computed using the total volume of the anode not including the aluminum current collector.


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Fig. 4. TEM and EDS mapping images of a cold sintered LTO/CNF composite anode, (a) and (c) show the dense microstructure, and (b) has an inset with a graphitic turbostratic structure within the carbon fibers.
Fig. 3d–f, the LTO and CNF were uniformly distributed between the LTO grains, and throughout the thick films. The carbon nanofiber network between active materials in the highly densified electrode structure is distributed to provide a continuous pathway, with their high conductivity and high aspect ratio. Therefore, the nanofiber network interconnects the current collector and the electroactive LTO phase, thus enabling exchange of the Li-ion. 

A more detailed analysis of the microstructure of the cold sintered composite was performed using TEM. Fig. 4 shows LTO grains and the carbon phase distributed in the cold sintered composite. Dense microstructures in the entire region were observed, with very little porosity between the LTO phase and the carbon. The inset image in 4b shows some of the details of the carbon, where fringes can be observed corresponding to the graphitic layers in the carbon fibers. The inset shows the presence of carbon onions at the interface. This result is quite unprecedented as the transformation of allotropes with tubular morphology such as carbon nanotubes and nanofibers to spherical carbon onions usually requires a localized pressure as high as 10 GPa and temperatures greater than 2000 °C. Such transformations have been shown to be initiated in carbon nanotubes through laser irradiation, spark plasma sintering, hydrogen plasma post treated and direct high temperature high pressure treatment. In this study, we show that a similar transformation can occur under cold sintering conditions through rupture of carbon nanofibers to yield bent graphitic sheets which can then be transformed into onion-like rings characterized by layer spacings of ~0.36 nm.

CV measurement was performed to investigate the phase transformation associated with the lithium insertion/extraction in the LTO lattice. Well-defined reversible redox peaks at 1.72/1.44 V are observed as expected, corresponding to the redox reaction of Ti^{4+}/Ti^{3+}. The electrochemical performance of the cold sintered LTO/CNF composite anodes were evaluated by galvanostatic measurements in the voltage range of 1–2.5 V to fully utilize the capacity of the LTO. Charge/discharge rates between 0.1C and 1C were applied to evaluate the rate capabilities of the cold sintered anodes. The voltage profiles of first cycle of each C-rate measurement are shown in Fig. 5b. The cold sintered LTO/CNF composite anode exhibits flat plateaus around 1.55 V during charge/discharge, as typically observed in other reported LTO-based anodes. The discharge voltage dropped with increasing current density due to polarization. As expected, the capacity decreased at higher current density. At the low rate of 1C, the cold sintered LTO anode delivered a specific capacity and volumetric capacity of 153 mAh/g and 379 mAh/cm³, respectively. It should be noted that the volumetric capacity of cold sintered anodes is much higher than those of LTO-based electrodes, measured at the same current density of 0.1C, previously reported in the literature. The high volumetric capacity is attributed to the highly densified and binder-free structure of the cold sintered electrodes, which minimizes the volume of inactive components. At a high C-rate of 1C, the cold sintered LTO composite electrode exhibits a gravimetric and volumetric capacity of 115 mAh/g and 285 mAh/cm³, respectively. It may be possible to further improve the rate capability of the cold sintered LTO/CNF electrodes by introducing a conductive carbon layer on the LTO or by carbon coating to enhance electronic conductivity, and by employing finer or nano-sized primary LTO particles to reduce the lithium-diffusion distance.

When the cycling performance of the cold sintered composite electrode was evaluated at 0.2C over 150 cycles, the capacity faded to 69% of its initial value. However, the cold sintered composite electrode still exhibited a volumetric capacity of 225 mAh/cm³ after 150 cycles. The coulombic efficiency was ~99.8% over all measurements taken.

4. Conclusions and summary

In conclusion, high volumetric capacity anodes based on LTO for enhanced safety Li-ion batteries can be fabricated by the cold sintering process. A binder-free tape of LTO/CNF composite was prepared by tape-casting followed by binder burn-out. The thin composite anode
was densified at 120 °C by cold sintering. The density of the cold sintered electrodes was 87% of the theoretical density and a highly densified microstructure was observed. The cold sintered composite anode delivered a high volumetric capacity of ~380 mAh/cm³ at low current density and showed good cycling stability with a volumetric capacity of 225 mAh/g after 150 cycles at 0.2C. These results indicated that the cold sintering process is an effective method for improving the volumetric capacity of electrodes for Li-ion batteries. These results suggest it may be possible to use the cold sintering process to fabricate high density composite electrolytes and all-solid-state batteries as well.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could appear to influence the work reported in this paper.

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