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Article in Small · August 2014
DOI: 10.1002/smll.201303894

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Donut-Shaped \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) Structures as a High Performance Anode Material for Lithium Ion Batteries

**Anulekha K. Haridas, Chandra S. Sharma,** * and **Tata N. Rao***

Battery electrode materials, when used in nanocrystalline form, exhibit high performance with regard to charge/discharge rates and specific capacities near to their theoretical values due to their lower diffusion length at smaller dimensions.\(^1\) These triumphs at the nanoscale became promising for application in electric vehicles, where high acceleration speeds correspond to high charging rates (C rates), and full charging in shorter times allows long driving ranges.\(^2\) While graphite is commercially used as an anode due to its high capacity and low cost, it encounters capacity deterioration with increasing numbers of cycles, particularly during fast charge/discharge rates.\(^3\) The formation and thickening of a solid electrolyte interphase (SEI) layer on the graphite anode has been found to be the reason for this, which eventually leads to low Coulombic efficiency. Moreover, Li dendrite formation, due to a low Li-intercalation potential (0.1 V vs Li/Li\(^+\)), and decomposition of the SEI layer at higher temperatures, can cause short circuiting as well as ignition of the battery.\(^[1,4]\) Even though it offers a lower theoretical specific capacity of 175 mAh/g, lithium titanate (LTO) gains importance due to its long and stable voltage plateau of 1.5 V, which does not allow the deposition of Li dendrite on the electrode surface, unlike in the case of carbon electrode.\(^[3]\) Another interesting property of LTO is its zero crystal strain due to its low volume change of less than 0.2% during charge/discharge-induced phase transformations between \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) and \( \text{Li}_7\text{Ti}_5\text{O}_{12} \).\(^[6]\) which facilitates excellent capacity retention. Moreover, it provides environmental safety and can work even at slightly elevated temperatures.\(^[7]\) While there are several merits with LTO to be qualified for high-power batteries, its only disadvantage compared to other materials is its low conductivity, which is about \(10^{-12}\) S/cm, imparting practical difficulties in terms of having a low capacity under high charge/discharge conditions. Several attempts to improve its conductivity have been explored by various researchers by providing carbon coatings \(^[8a,b]\) and synthesizing LTO–graphene\(^[8c]\) and LTO–CNFs\(^[8d,e]\) composites. Alternatively, approaches like nanostructuring, three-dimensional (3D) architecturing, and also fabricating porous structures have been attempted in order to enhance the contact surface area of the material with the electrolyte as well as to reduce the Li ion diffusion length to a greater extent.\(^[9a,b]\) Various types of LTO nanostructures such as particles,\(^[9c]\) nanofibers,\(^[9d]\) nanotubes,\(^[9e]\) nanosheets,\(^[9f]\) and porous structures such as aerogels\(^[9g]\) and microspheres\(^[9h,i]\) have been studied for many years for getting a better LTO rate cycling performance.

Although nanocrystalline LTO offers the excellent advantages discussed above, there are many practical limitations associated with this material. Firstly, if nano-LTO is used as a particulate film, the loosely bound particles can cross over the microporous separator in the cell, thereby leading to short circuiting of the electrodes. Secondly, Li ion transport in the electrolyte phase becomes difficult when electrode thickness increases (>100 µm),\(^[10a]\) causing voltage drop, thus reducing the cell capacity. Under these conditions, if nanomaterials are used for electrodes, the material’s utility will be lowered for a given thickness, resulting in a low volumetric energy density. As the tap density of the nanomaterials is very low,\(^[10b]\) it is difficult to get good film density in the electrode even after calendering (smoothing and pressing a material at high pressures). Hence, there is a need to optimize the density, structural characteristics of the nanocrystalline active material and thickness of the electrode to achieve the best performance in terms of good volumetric energy density at a high rate with excellent capacity retention over a large number of cycles. For this purpose, an ideal system would be a porous 3D nanostructured sub-micrometer sized donut shape (as shown in the Figure 1), which is composed of well sintered and highly interconnected nanograins that offer shorter diffusion lengths for Li ions with enhanced electrolyte transport through the mesoporous donut structure. This novel structure can thus provide increased tap density as compared to nanomaterials, due to agglomerated nanoparticles in the donut structure together with shorter diffusion lengths for lithium ions. To the best of our knowledge, we present for the first time the fabrication of an inorganic 3D donut-shaped LTO sub-micrometer structure composed of nano-sized grains via a combination of sol–gel and electrospinning techniques. In this article, the fabrication and electrochemical performance...
of LTO sub-micrometer porous donuts in half cell mode are highlighted, and their superior performance is demonstrated in comparison with that of commercial dense LTO particles.

The sol–gel method of preparing particles, aerogels, xerogels, etc. has been explored for some time and is well known for obtaining materials in a very pure form. Fabrication of nano/sub-micrometer particles by electrospraying using high voltage is also well known. In electrospraying, the atomization process takes place with a solution of comparatively low viscosity when applied with high voltage, overcoming its surface tension and forming spraying jets. As the spraying jets reach the collecting electrode (negative), the solvent evaporates and particles get deposited on the collector. In order to prepare LTO sub-micrometer donuts, lithium titanate sols of particular viscosities were prepared and electrosprayed at high voltage. The obtained sub-micrometer donuts were then calcined at the required temperature for the spinel phase formation, followed by their structural and electrochemical characterization.

LTO sols with varying molar ratios of Li:Ti prepared in ethanol were electrosprayed using a needleless electrospinning setup. The viscosity of the LTO sol prior to electrospraying was measured as 36 ± 8 mPa s at a constant shear rate of 1000 s. Drops of LTO sol were put on to the pike spinning electrode and the voltage was slowly increased from zero to 31.8 kV with a constant distance of 5 cm between the pike electrode and collector. The formation of donut-shaped nanostructures is possibly due to the low viscosity of the LTO sol. It can also be ascribed to an initial stage of fiber formation, where spraying jets do not stretch to yield fibrous structures. Normally for the formation of fibers by the electrostatic method, the spinning solution viscosity ranges from 100 to 1000 mPa s, while we intentionally made it as low as 36 mPa s to create a donut-shaped structure. Figure 2 A1,A2 shows field-emission scanning electron microscope (FESEM) images of as-obtained sub-micrometer donuts. Further, sub-micrometer donuts were calcined at a temperature of 750 °C in air for about 4 h to induce crystallinity as well as to obtain strongly interconnected, well-retained grains to facilitate good electron transport during operation. As there is extensive loss of lithium at high temperatures, in order to obtain the required spinel LTO phase, lithium acetate concentration in the LTO sol was increased considerably from Li:Ti = 4:5 and above. A rutile titania impurity present in

Figure 1. Schematic to compare the lithium ion diffusion kinetics in lithium titanate submicrometer particles and donut shapes with nanograins.

Figure 2. A,B) FESEM images of lithium titanate sub-micrometer donuts before (A1,A2) and after (B1,B2) calcination. C) XRD patterns of donuts calcined at 750 °C with various Li:Ti mole ratios in the spraying sol.
the stoichiometric ratio of Li:Ti was removed by increasing the molar ratio of Li:Ti to 5:5 (1:1), which resulted in phase-pure LTO after calcination. The X-ray diffraction (XRD) patterns in Figure 2C illustrate the pure LTO phase formation by gradually varying lithium acetate concentration. Post-calcination of sub-micrometer donuts as revealed by FESEM (Figure 2B1,B2) were observed as 3D porous structures of 500 nm in size with 200–250 nm wall thickness comprising 60–100 nm sized primary grains. Furthermore, unlike as-deposited donuts (Figure 2A1,A2), calcined donuts show well interconnected and sintered grains formed during the grain growth upon calcination, as expected. The morphology and crystalline structure of commercial LTO is shown in Figure S1.

As a further insight into the structure of the 3D nano-structured LTO donut, specific surface area and porosity were measured and compared with the commercial LTO using the BET method. The 3D nanostructured LTO donut exhibited a BET surface area of 12.04 m²/g, which was more than three times the commercial LTO (3.76 m²/g). Similarly, an increase in average pore width and total pore volume was observed with the donut LTO in comparison with the commercial LTO. The summary of the BET analysis is given in the Table 1.

The electrochemical performance of LTO sub-micrometer donuts was studied and compared with a commercial LTO powder with an average particle size of 300 nm. In order to understand the electrode kinetics, cyclic voltammetry was performed at varying scan rates from 0.05 to 0.5 mV/s (Figure 3A1,B1). At 0.05 mV/s, a pair of cathodic and anodic peaks were observed for both commercial LTO and LTO sub-micrometer donuts at 1.5 and 1.6 V, which can be

<table>
<thead>
<tr>
<th>Material type</th>
<th>BET surface area [m²/g]</th>
<th>Average pore size [nm]</th>
<th>Pore volume [cm³/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial LTO</td>
<td>3.76</td>
<td>7.69</td>
<td>0.011</td>
</tr>
<tr>
<td>3D nanostructured LTO sub-micrometer donut</td>
<td>12.04</td>
<td>8.92</td>
<td>0.034</td>
</tr>
</tbody>
</table>

Table 1. Summary of BET analysis of Commercial LTO and LTO sub-micrometer donut.

Figure 3. Comparison of electrochemical performance of commercial LTO (A) and LTO sub-micrometer donuts (B). A1 and B1 correspond to cyclic voltammograms whereas A2 and B2 show the charge/discharge capacity at various charging rates. A3, B3 show the galvanostatic charge/discharge cycling performance (200 cycles) at 0.1C for commercial and donut shape LTO nanostructures.
attributed to lithium insertion/extraction processes in spinel LTO electrodes. The well-resolved redox peaks in the LTO sub-micrometer donuts appeared to be sharper than for the commercial LTO, indicating fast insertion/extraction of Li ions in the crystalline donut structure, whereas broad peaks were observed for commercial LTO, indicating sluggish behavior. Furthermore, with increasing scan rates, peak separation increased in both cases. However, while retaining the sharp shapes, the potential difference of redox peaks for LTO sub-micrometer donuts was found to be smaller when compared to that of the commercial material, indicating faster electrode kinetics. The improved charge transfer kinetics in LTO donuts is also supported by the observation of lower charge transfer resistance in the electrochemical impedance spectra. The charged transfer resistance for LTO donuts observed in the Nyquist plot (Figure S2) is 485 Ω, which is about one third of the value (1560 Ω) observed for the commercial LTO. This is further in line with the BET surface area measurements as summarized in Table 1. Higher surface area and increased average pore width and total volume for the 3D nanostructured LTO donut enable the electrolyte to occupy the nanograins and pores in the donut much more effectively than in the commercial LTO, confirming the improved charge transfer kinetics in the LTO donuts due to its unique structural advantage.

Galvanostatic charge/discharge curves of LTO sub-micrometer donuts and commercial LTO at varying current rates are depicted in Figure 3A2, B2. The cells were charged and discharged initially at 0.1C rates for 8 cycles, and then charging rates were increased simultaneously to 20C. At a lower charge/discharge current rate of 0.1C, LTO sub-micrometer donuts and commercial LTO show reversible capacities of 159 mAh/g and 170 mAh/g, respectively. Although commercial LTO shows a slightly increased initial capacity, this started fading from the second cycle onwards and stabilised at 165 mAh/g. On increasing the current density, both commercial LTO and LTO sub-micrometer donuts show almost straight voltage plateaux with a small overpotential. When cycled at a charging rate of 1C, specific capacities of 144 mAh/g and 123 mAh/g were observed, respectively, for LTO sub-micrometer donuts and commercial LTO. Interestingly, at higher charging rates (3C, 5C, and 10C) higher specific capacities (131, 120, 100 mAh/g, respectively) were obtained for LTO sub-micrometer donuts than for commercial LTO. Further, when put back to the 1C rate, LTO sub-micrometer donuts showed a 99% retention in capacity as compared to 94% shown by the commercial material (Figure 3A2, B2). The cycling performances of the cells for 200 cycles at 1C rate are shown in Figure 3A3, B3. A specific capacity of 140.6 mAh/g (Figure 3B3) and 90 mAh/g are obtained for LTO sub-micrometer donuts and commercial LTO, respectively. In the case of commercial LTO (Figure 3A3), a rapid falling of capacity was observed from 0 to 200 cycles of charge and discharge with a capacity retention of 93%, whereas a capacity retention of 97% was observed for LTO sub-micrometer donuts even after 200 cycles of charging/discharging. This exceptional cycling performance of LTO sub-micrometer donuts can be ascribed to their high crystallinity and structural veracity with small grain size. Also, the porous nature of donut-shaped LTO sub-micrometer structures as per the BET studies has effectively reduced the lithium ion diffusion pathway (Figure 1, Table 1) providing fast charge/discharge and good rate capabilities. The lower charge transfer resistance observed for the porous LTO sub-micrometer donuts (three times smaller than commercial LTO) also supports the high rate capacity due to the faster charge and Li ion transfer in the sub-micrometer donut structure.

To conclude, we have successfully fabricated donut-shaped 3D sub-micrometer structures of Li4Ti5O12 comprising small grains by means of combining sol–gel and electrospinning techniques. This novel porous donut structure consisting of well-interconnected nanocrystalline grains exhibits excellent electrochemical kinetics in comparison with commercial materials with respect to rate cycling and rate capability. The mesoporous 3D donut-shaped LTO sub-micrometer structure has enabled fast insertion and removal of lithium ions by reducing the diffusion length, demonstrating its potential practical application in Li ion batteries for electric vehicles.

**Experimental Section**

**Fabrication of LTO Sub-micrometer Donuts by Sol-gel/Electrospinning Route:** Lithium titanate sol was prepared by mixing titanium (IV) isopropoxide (TIP) and lithium acetate dihydrate at Li:Ti molar ratio of 4:5. Initially, solutions of lithium acetate and TIP were prepared separately by adding specific amounts of lithium acetate in ethanol, and mixing TIP in acetyl acetone/ethanol mixture (1:10) where, acetylacetone was used as a chelating agent. Later lithium acetate solution was added drop-wise to TIP sol under constant stirring and the solution was agitated continuously for about 30 min. Concentrated hydrochloric acid was added dropwise (1 mL) to the above solution until a clear golden yellow solution was formed. The so obtained yellow colored Lithium titanate sol was then aged for 6 h and was electrospayed on to aluminum foil using needle-less electrospinning. A schematic, illustrating synthesis of sub-micrometer donuts using needleless electrospinning set up is given in the Figure S3. Electrospinning equipment consists of an upper positive electrode and a lower negative electrode. An aluminum foil was pasted beneath the upper electrode in order to collect the formed sub-micrometer donuts. The LTO sol was put drop wise on to the pike electrode and voltage was increased gradually from 0 kV to 32 kV. At a particular voltage range of 30–32 kV and the electrode distance of 5 cm, spraying jets started emerging from the tip of pike electrode. The collected electrospayed powders were then examined for morphology and size using FESEM. The obtained donut-shaped powders were calcined in air at a temperature of 750 °C for 4 h and were characterized by XRD for the required spinel phase formation.

**Characterization of LTO Sub-micrometer Donuts:** The viscosity of Lithium titanate sol was measured at a constant shear rate of 1000 s⁻¹ using Anton Par viscometer Physica MCR 51 at a temperature of 26 °C. FESEM (Hitachi model S4300SE(N)) was used to analyze the size and surface morphology of electrospayed LTO sub-micrometer donuts at an accelerating voltage of 20 kV. X-ray diffraction analysis was conducted by using Bruker D8 advanced with Cu Kα radiation at a scanning rate of 7°/min from diffraction peaks.
angle 10° to 90°. Later the diffraction patterns were analyzed using Match software for the required phase formation. Surface area, total pore volume and average pore size of LTO sub-micrometer donuts were measured using surface area analyzer of Micrometrics ASAP 2020 using BET method.

Electrode Preparation and Electrochemical Testing of LTO Sub-micrometer Donuts: For preparing electrode, the obtained LTO sub-micrometer donuts were mixed with conducting carbon and PVDF binder in the mass ratio of 75:15:10. The mixture was then made into a paste by adding N-methyl 2-pyrrolidone (NMP) and was transferred into a copper foil of battery grade as a dense thin film. The copper foil with electrode material was then dried in oven for about 12 h. After calendaring the film, 12 mm circular discs were cut from the same using a disc cutter. 2032 coin cells were assembled inside a glove box in argon atmosphere using CMC/DMC (1:1) and LiPF₆ mixture as electrolyte and Li foil as counter electrode. A whatman glass micro fiber filter of battery grade was used as separator. Later followed by 6 h stabilization of prepared coin cells, galvanostatic charge-discharge measurements were performed from 0.1 to 10C rates at voltage range of 1 to 2.5 V. Cyclic voltammograms were recorded at varying scan rates from 0.05 to 0.5 mV/s at the same voltage range using Arbin instruments. Further, electrochemical impedance spectroscopy (EIS) was conducted using potentiotstat (Solartron) from frequency range of 0.01 to 1 MHz. For comparison, the electrochemical performance of commercial LTO was also studied.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

TNR and AKH acknowledge Nanomission grant provided by Department of Science and Technology (DST), India, to carry out this work. We are also thankful to Mrs. A. Jyothirmayi at ARCI Hyderabad for electrochemical impedance measurements.

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Received: December 22, 2013
Revised: July 1, 2014
Published online: 5