Hierarchical Li$_4$Ti$_5$O$_{12}$-TiO$_2$ composite microsphere consisting of nanocrystals for high power Li-ion batteries

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**Abstract**

Highly mesoporous lithium titanate hierarchical microspheres (LTO-HS) consisting of nanosized octahedron-like crystals were innovatively designed as high performance and safe anode materials for lithium-ion battery applications. This unique structural control allows us to capitalize on the exemplary surface areas (electrolyte contact) and short Li-ion diffusion path lengths of nanosized particles, while overcoming the challenge of low power tapping density by integrating them into microsized spheres. A thin carbon coating was applied on the surface of LTO-HS (C-LTO-HS) in order to overcome the inherently limited electronic conductivity of these oxide materials. Moreover, this coating technique was found to induce the formation of some anatase TiO$_2$, resulting in uniquely structured anode materials with active multi-component duality. Notably, the C-LTO-HS composite electrode delivers a remarkable capacity of over 230 mA h g$^{-1}$ when discharged at 0.2 C, which is much higher than the theoretical capacity of pure Li$_4$Ti$_5$O$_{12}$ (175 mA h g$^{-1}$) and ascribed to the existence of anatase TiO$_2$ (330 mA h g$^{-1}$) in the C-LTO-HS structure. Furthermore, this electrode yielded excellent cycling and rate capabilities of about 120 mA h g$^{-1}$ (compared to 90 mA h g$^{-1}$ for LTO-HS) at a current density of 10 C for up to 100 cycles. These unique mesoporous spheres with deliberately controlled nanostructure arrangements show significant promise as anode materials for lithium-ion batteries, fabricated by a simplistic two step hydrothermal procedures, and capable of providing high volumetric energy density and long cycle life.

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1. Introduction

Over the past few decades, there have been significant advancements toward renewable and sustainable energy technologies in order to address the forthcoming depletion of fossil fuel reserves and rapidly increasing green-house gas emissions. With approximately 1 billion vehicles on the road and the transportation sector emitting over 5 billion tons of carbon dioxide per year [1], there are immense advantages and market opportunity available for the commercialization of electric vehicles (EVs) or hybrid electric vehicles (HEVs) [2–7]. These electric vehicles however require on the development of high performance, advanced rechargeable batteries in order to provide practical performance and extended range driving capabilities. Currently, lithium-ion batteries (LIB) providing both high power and energy densities are the most promising and extensively investigating technology for EV and HEV propulsion [8–14]. Commercial LIBs rely extensively on the use of graphite as anode materials [15–19], however graphite based anodes cannot satisfy the performance demands of many modern applications in terms of safety, rate and cycling capabilities, and it remains a pertinent technical challenge to develop unique, high performance anode chemistries [11,20–24].

Being inherently safe and chemically compatible with the electrolyte, titanium based materials are considered the most promising alternative to the anode materials used in commercial LIBs [1,13,25,26]. Specifically, spinel phase lithium titanate (Li$_4$Ti$_5$O$_{12}$), possessing the Ti$^{4+}$/Ti$^{3+}$ redox couple and showing extremely flat discharge and charge plateaus at approximately 1.55 V (vs. Li/Li$^+$), can ideally suppress electrolyte reduction and formation of the solid-electrolyte interphase (SEI) layer on the surface of the electrode, while furthermore possessing zero-strain Li ion insertion (no structural changes) characteristics that lead to excellent cycling stability [27–31]. On the other hand, anatase TiO$_2$ is also considered one of the best Li ion host candidates among Ti-based materials, due to the fact that TiO$_2$ exhibits very fast Li ion insertion/extraction, and low volumetric expansion (ca. 3–4%) during charge and discharge processes [25,32–34].

 Morphological and structural control is an important strategy that must be employed in order to capitalize on the inherent advantages of these Ti-based materials. Specifically, utilizing nanoscale
materials will provide improved rate performances due to: (i) their favorable size that ensures shorter diffusion paths for Li-ion transport from the core of the particles to the surface, and (ii) their large surface areas that enhance the electrode/electrolyte interfacial contact leading to higher charge/discharge rates [35–39]. More recently, dual-phase Li$_4$Ti$_5$O$_12$–TiO$_2$ nanocrystallines have been synthesized by various methodologies, displaying a high electrochemical performance in Li-ion batteries [34,40–42]. However, decreasing the particle sizes to this range may result in low power tap densities which will inevitably reduce the volumetric energy density of the LIB cells, along with poor active material interconnectivity throughout the bulk of the electrode [43]. Conversely, micronized particles with high power tap densities generally suffer from a poor capacity and low rate capabilities due to the long Li-ion diffusion pathways [44]. By innovative structural design, it should be possible to combine the inherent benefits of both nano- and micronized active materials. Up to now, to our best knowledge, no hierarchical dual-phase TiO$_2$–Li$_4$Ti$_5$O$_12$ microsphere consisting of nanocrystals has been reported in Li-ion battery application.

Herein, we report the design of micronized (3–4 μm) spherical particles with a high degree of mesoporosity and comprised of numerous interconnected nanoscale (ca. 60 nm) octahedron-like crystals. This unique structure allows for a high power packing density, while also providing fast ion transfer and sufficient interfacial contact between the active materials and the electrolyte, important considerations for high rate performance electrode materials. These Li$_4$Ti$_5$O$_12$–LiTiO$_2$ spheres (LTO-HS) were prepared by a simple and readily up-scalable hydrothermal technique using as-synthesized mesoporous TiO$_2$ microsphere substrates and lithium hydroxide precursors, followed by a thermal treatment in air [45]. While the interconnected nature of these mesoporous spheres will aid significantly in electron transport, in order to further overcome the inherent electronic conductivity limitations of these Ti-based materials, a carbon coating technique is applied hydrothermally using glucose as the carbon source [46]. This technique also induced the serendipitous formation of some anatase TiO$_2$, resulting in carbon coated multi-component active materials (C-LTO-HS) possessing a novel anode material nanostructure that is critical for high charge–discharge capacity, ultrahigh rate capabilities and excellent cycling properties.

2. Experimental

2.1. Material synthesis

To synthesize the microscale mesoporous spheres, we used highly mesoporous anatase phase hierarchical TiO$_2$ spheres (Fig. S1) prepared by a solvothermal method. In a typical synthesis, 0.65 mL titanium n-butoxide (TBT) was added to 40 mL acetic acid (HAc) with stirring. After a few minutes, the mixture of TBT and HAc was transferred into a 50 mL Teflon-lined stainless steel autoclave. Subsequently, the autoclave was sealed and placed in an electronic oven and maintained at 160 °C for 12 h [44]. The as-prepared
powder samples were washed extensively with ethanol and then dried in air at 60 °C. To obtain the anatase TiO₂ phase from Ti-complex [47], the as-prepared powder samples were annealed at 500 °C in air for 3 h. Carbon free lithium titanate hierarchical spheres were prepared by reacting the hierarchical TiO₂ spheres with LiOH via a hydrothermal process. Specifically, 50 mg of TiO₂ mesoporous spheres were dispersed in 30 mL of 0.15 M LiOH aqueous solution and reacted at 180 °C for 12 h, followed by a heat treatment at 800 °C for 4 h in air. For carbon coated TiO₂ and Li₄Ti₅O₁₂ hierarchical spheres, the as-prepared lithium titanate material was further hydrothermally reacted in 15 mL glucose (Li₄Ti₅O₁₂-LiTiO₂:glucose wt% = 7:3) aqueous solution at 180 °C for 18 h. After drying, the as-prepared product was annealed at 600 °C for 3 h in an argon-flowing furnace.

2.2. Material characterization

The crystal structure of the powders was studied using an X-ray diffraction (XRD, Bruker AXS D8 Advance) system with Cu Kα radiation from 10° to 70°. A field emission scanning electron microscope (FE-SEM, LEO FESEM 1530), transmission electron microscope (TEM, Philips CM300, equipped with energy dispersive X-ray spectroscopy (EDS)) and high-resolution transmission electron microscope (HRTEM) were used to examine the morphologies and crystalline structures of the samples. X-ray photoelectron spectroscopy (Thermal Scientific K-Alpha XPS spectrometer) was used to investigate the Ti valence in C-LTO-HS composite material.

2.3. Electrochemical characterization

The anode slurry was prepared by mixing the active materials and carbon black (Super P) with a polyvinylidene fluoride (PVDF) binder at a typical weight ratio of 80:10:10, and then coated onto the copper foil which pellets of 10 mm in diameter were cut as electrodes. 2032-type coin cells with two-electrodes (Ti-based materials/Cu & Li) were assembled in an Ar-filled dry glove box. 1 M LiPF₆ in ethyl carbonate (EC)/dimethyl carbonate (DMC) (3/7 by volume) was used as electrolyte and two pieces of porous 25 μm thick polypropylene were used as separators. Unless specified, the discharge-charge cycling was performed between 1.0 and 2.5 V (vs. Li/Li⁺) at different C-rates at room temperature on a battery tester (Neware). The electrochemical impedance spectroscopy (EIS) was carried out in the frequency range from 100 kHz to 100 mHz on an electrochemical workstation (VersaSTAT MC, Princeton Applied Research), and the amplitude of the alternating voltage was 10 mV. The impedance parameters were determined by fitting of the impedance spectra using Z-view software, and cyclic voltammetry (CV) testing was performed between 1 and 2.5 V with...
a scan rate of 0.1 mV s⁻¹. The diameter of the electrodes is 1 cm, and the material loading of each electrode varies from 0.8 to 1 mg.

3. Results and discussion

In this study, hierarchical TiO₂ spheres (Fig. S1) were used as the starting material for the synthesis of Li₄Ti₅O₁₂ based hierarchical spheres via a hydrothermal process with LiOH. The morphology of the resultant hierarchical spheres is clearly revealed by scanning electron microscopy (SEM) as shown in Fig. 1. The low- and high-magnification SEM images of the as-prepared sample show a spherical morphology with a uniform diameter of approximately 3–4 μm (Fig. 1b and c). They are densely packed with octahedron-like nanocrystals (ca. 60 nm) with high surface areas and good interconnectivity to neighboring particles.

The morphology and internal structure of the carbon free LTO-HS and carbon coated C-LTO-HS are further characterized by transmission electron microscopy (TEM). The TEM images in Fig. 2a and b show mesoporous structure with uniformly distributed pores throughout the bulk of the spheres, rather than only on the surface. This type of mesoporous network can provide a highly beneficial electrode arrangement as the open space increases active site exposure with the electrolyte and can effectively facilitate Li⁺ mass transport. The high-resolution TEM (HRTEM) shown in Fig. 2c clearly displays the lattice fringes of LTO-HS, indicating the highly crystalline nature of the as-prepared materials. The HRTEM image of C-LTO-HS in Fig. 2d reveals that the carbon forms a thin layer that covers the entirety of the nanosized particle surfaces as confirmed by energy dispersive X-ray (EDX) mapping (Fig. 3). The distribution of C element is wrapped up those of Ti and O, which indicates that C distributes uniformly on the surface of crystals. Furthermore, the coated carbon layer has a uniform thickness of ca. ~3 nm, creating a highly conductive network throughout the entirety of the mesoporous sphere structure.

![Image](image_url)

Fig. 3. TEM image of nanocrystal composed in C-LTO-HS sphere (a) and the corresponding EDX mapping images of Ti (b), O (c), and C (d) elements.

![Image](image_url)

Fig. 4. XRD patterns of (a) LTO-HS and (b) C-LTO-HS materials.
The powder X-ray diffraction (XRD) pattern of carbon free (LTO-HS) and carbon coated (C-LTO-HS) powders are shown in Fig. 3. In both samples, diffraction peaks are well indexed to the cubic spinel phase Li4Ti5O12 (JCPDS No. 49-0207); however the presence of some other diffraction peaks were also observed for both materials. For LTO-HS, the small diffraction peaks at 43.7° and 63.5° are ascribed to the (2 2 0) and (2 2 0) crystal faces of LiTiO2 (JCPDS No. 74-2257), respectively, indicating that LiTiO2 (Fig. 52) did not undergo complete conversion to form Li4Ti5O12 at 800 °C for 4 h. In addition, during the hydrothermal carbon coating process, the residual LiTiO2 reacts with O2 in order to produce TiO2 or the Li4Ti5O12 can be converted to TiO2. This is evidenced by the anatase TiO2 peaks (JCPDS No. 89-4921) observed in the C-LTO-HS diffraction pattern, which is not an undesirable occurrence due to the high theoretical capacity (330 mAHg⁻¹) of this phase. The calculated crystallite size of primary particles in LTO-HS and C-LTO-HS using the Scherrer equation is approximately 53 nm and 58 nm, respectively. X-ray photoelectron spectroscopy (XPS) results shown in Fig. S3 reveal de-convolution of the Ti 2p signal into two distinct peaks at 458.6 and 464.2 eV, corresponding to Ti2p3/2 and Ti2p1/2 core level binding energies of Ti4+, respectively. This confirms the complete conversion of formation of LiTiO2 (Ti3⁺) to TiO2 (Ti4⁺), along with the presence of Li4Ti5O12 (Ti4⁺) in C-LTO-HS.

To evaluate the electrochemical performance of the as-prepared and carbon coated Li4Ti5O12 based anode materials in lithium ion batteries, half-cells with metallic lithium film as the counter electrode and reference electrode were prepared. Shown in Fig. 5 are the corresponding LTO-HS and C-LTO-HS galvanostatic charge and discharge curves of first three cycles at a rate of 0.2 C within a potential window from 1.0 to 2.5 V (V vs. Li/Li⁺). The LTO-HS electrode (Fig. 5a) displayed a flat plateau in the voltage range between 1.5 and 1.6V, which is a typical characteristic of two-phase lithium insertion and extraction processes of main Li4Ti5O12. As shown in Fig. 5b, the C-LTO-HS based electrode has two voltage plateaus in the discharge and charge curves due to the presence of both spinel Li4Ti5O12 and anatase TiO2 phases.

Fig. 6 shows the cyclic voltamogram (CV) curves of LTO-HS and C-LTO-HS between 1.0 and 2.5 V with a voltage scan rate of 0.1 mV s⁻¹. The position of the oxidation and reduction peaks for LTO-HS at 1.64 and 1.51 V, respectively, are similar to those of C-LTO-HS and attributed to the redox reactions of Ti4⁺/Ti3⁺ in Li4Ti5O12 [6,10,39]. This further confirms that the spinel structure foundation of Li4Ti5O12 did not change during the carbon coating process. It should be noted that a second pair of redox peaks are observed for the C-LTO-HS electrode. The oxidation and reduction peaks at 2.09 and 1.67 V, respectively, correspond to the cathodic and anodic peak potentials of anatase TiO2 [5,11,30,34], which is consistent with the results of charge–discharge profile (Fig. 5b).

The potential differences between the Ti3⁺/Ti4⁺ redox peaks of LTO-HS and C-LTO-HS are 130 mV and 120 mV, respectively, indicating slightly reduced polarization of the electrode associated with Li⁺ insertion/extraction [34].

The practical LIB electrochemical performance of the anode electrodes are characterized using 2032 type coin cells. The discharge curves of LTO-HS and carbon coated C-LTO-HS electrodes at different current rates are presented in Fig. 7a and b, respectively. Flat discharge plateaus at about 1.55 V are observed in both electrodes due to Li ions being extracted from the spinel Li4Ti5O12 phase [1,10,29]. The plateaus at around 1.8 V for the C-LTO-HS electrode correspond to lithium intercalation/deintercalation in anatase TiO2 [1,30], which is in agreement with the results of the anodic peak potential observed in the cyclic voltamograms. Compared to the carbon free LTO-HS electrode, the C-LTO-HS electrode is able to deliver much higher discharge capacity at the same rates. For example, at a current rate of 0.2 C, the initial discharge capacity of LTO-HS is 174 mAHg⁻¹, while the C-LTO-HS electrode delivers an initial discharge capacity of 240 mAHg⁻¹. The rate performance of LTO-HS and C-LTO-HS electrodes at various charge–discharge rates from 0.2 C to 30 C are compared in Fig. 7c. The C-LTO-HS composite electrode shows a superior rate performance with discharge capacity of 120, 93, and 77 mAHg⁻¹ at 10 C, 20 C and 30 C, respectively, while LTO-HS electrode have only maintained the discharge capacities of 74, 56, and 45 mAHg⁻¹ at 10 C, 20 C and 30 C, respectively. Fig. 7d compares the cycling performance of these.

![Fig. 5. The first three charge–discharge curves at 0.2 C of (a) LTO-HS/Li and (b) C-LTO-HS/Li half cells.](image)

**Fig. 6.** CV curves of (a) LTO-HS and (b) C-LTO-HS composite electrodes at a scan rate of 0.1 mV s⁻¹ between 1.0 and 2.5 V.
two electrodes at 10 C after cycling 5 times at a rate of 0.2 C in the voltage range of 1.0–2.5 V. As shown in Fig. 7d, C-LTO-HS demonstrates a much higher capacity and better cycling performance compared to that of LTO-HS. After 100 cycles, the discharge capacity of C-LTO-HS is maintained at 118 mAh g\(^{-1}\), which is much higher than 78 mAh g\(^{-1}\) of LTO-HS. The greatly improved lithium storage properties (capacity, rate performance and stability) of C-LTO-HS composite microspheres in comparison to LTO-HS is attributed to its high electronic conductivity due to the thin layer of carbon encapsulating individual nanocrystals, along with the higher theoretical capacity of TiO\(_2\) (330 mAh g\(^{-1}\)). Upon comparison with similar work on dual phase Li\(_x\)Ti\(_5\)O\(_{12}\)-TiO\(_2\) materials, the benefit of our unique mesoporous spheres with deliberately tailored nanostructures becomes apparent. Rahman et al. [34] developed similar carbon coated dual phase materials consisting of agglomerates of Li\(_x\)Ti\(_5\)O\(_{12}\) and TiO\(_2\) nanoparticles. Specifically, the authors reported good electrochemical performance including a capacity of 165 mAh g\(^{-1}\) at a rate of 1 C. Conversely, our materials with highly interconnected mesoporous structures displayed a capacity of 193 mAh g\(^{-1}\) at the same rate, amounting to a 17% increase. Moreover, when measured at 10 C up to 100 cycles, the discharge capacity of C-LTO-HS electrode depicted a higher capacity and stability of 118 mAh g\(^{-1}\) (93% of initial discharge capacity) compared to the Rahman et al. reported composite material (110 mAh g\(^{-1}\) (82% of initial discharge capacity)) [34].

Fig. 7c shows a significant improvement in the capacity of C-LTO-HS at different current rates from 0.2 C to 30 C compared to LTO-HS. To further compare the electrical conductivity of carbon-free LTO-HS and carbon coated C-LTO-HS electrodes, electrochemical impedance spectroscopy (EIS) measurement are conducted, and the corresponding Nyquist plots of both electrodes are obtained as shown in Fig. 8. \(R_s\) and \(R_{ct}\) in the equivalent circuit (inset in Fig. 8) are the ohmic resistance and charge transfer resistance, respectively, and \(W\) represents the Warburg impedance of Li ion diffusion into the active materials. Each curve in Fig. 8 has a depressed semicircle in the high-middle frequency range (\(R_{ct}\) and CPE) and an oblique straight line in the low frequency region (\(W\)) [48]. The C-LTO-HS electrode exhibits higher charge transfer resistance (641.2 \(\Omega\)) than that of LTO-HS electrode (405.8 \(\Omega\)). It is well known that the carbon coating on C-LTO-HS could enhance the conductivity of the active materials, enabling much easier charge transfer at the electrode/electrolyte interface and consequently decreasing the overall cell internal resistance. Thus, the higher charge transfer resistance of C-LTO-HS can be ascribed to the higher
diffusion resistance of Li in TiO2, and the fast charge-transfer kinetics of LTO-LS (Li4Ti5O12−LiTiO2, Fig. 4) electrode could be attributed to Ti3+ groups which enhanced the conductivity of the electrode [40, 49−51], which can provide logical explanation for the reduced performance improvements observed for C-LTO-LS in comparison with LTO-LS as higher current rates (Fig. 7c and d).

For comparison, Li4Ti5O12−C and C-TiO2 composites also have been prepared using sol−gel [52] and hydrothermal methods [46], respectively. Compared to LTO-LS materials, Li4Ti5O12−C based Li-ion battery indicates a similar stability with slightly higher capacity than LTO-LS anode (Fig. S4). It is well known that facile lithium ion diffusion through the nano architecture mesoporous Li4Ti5O12 microspheres and fast electron transport through the carbon are thought to be responsible for the obtained high lithium storage capacity. Even when the current was increased to a rate of 10 C, the discharge capacity can also reach a higher capacity of 95 mA h g−1 (Fig. S5). This higher rate capability of Li4Ti5O12−C can be further verified by EIS measurements (Fig. S6). It can be seen clearly that the Rs of Li4Ti5O12−C (210 Ω) is much smaller than that for LTO-LS electrode, which indicates that the carbon coating could enable much easier charge transfer at the electrode/electrolyte interface. The cycling performance of the C-TiO2 composite microsphere with an unchanged structure (Fig. S7) at 0.2 C in the voltage range of 1.0−2.5 V was measured and shown in Fig. S8. After 100 cycles, the discharge capacity for the TiO2−C electrode was measured to be 195 mA h g−1, 67% of initial discharge capacity, which is much lower than that of C-Li4Ti5O12−TiO2−C (C-LTO-LS) electrode. Fig. S9 shows the comparison of the rate capabilities between TiO2−C microspheres and pure TiO2. As shown in Fig. S8, the C-TiO2 electrode indicates a higher rate performance due to the improvement of conductivity by carbon coating, however, the specific discharge capacity of C-TiO2 (86 mA h g−1) at 10 C is still lower than that of C-LTO-LS (121 mA h g−1) because of higher diffusion resistance of Li in TiO2.

4. Conclusion

In summary, a facile two-step hydrothermal method was developed to synthesize highly mesoporous carbon coated Li4Ti5O12−TiO2 composite microspheres consisting of numerous interconnected octahedron-like nanocrystals. Their application was investigated and reported as anode electrode materials for LIB technologies. These multi-component active materials employed unique nanostructure design techniques that allow us to capitalize on the distinct advantages of: (i) using nanoscale particles that can provide high solid−electrolyte interfacial surface areas, excellent Li-ion access and short diffusion pathways resulting in high active material utilization, and (ii) mesoporous microsized particles that can facilitate effective electrolyte access into the bulk of the materials, while furthermore ensuring high power tapping densities and good structural and electronic interconnectivity throughout the bulk of the electrode. The C-LTO-LS composite electrode showed excellent discharge capacities of 120, 93, and 77 mA h g−1 at 10 C, 20 C and 30 C, respectively, and furthermore no capacity fading over 100 cycles at a current rate of 10 C. The performance capabilities were superior to that of LTO-LS, as well as similar multi-component Li4Ti5O12−TiO2 materials reported in the literature. These superior performances were attributed to enhancements arising from the carbon coating technique employed (and partial TiO2 formation), and the uniquely designed nanostructure of C-LTO-LS, respectively. The utilized synthesis technique opens up a new, highly promising direction for the fabrication of novel, hierarchically structured composite anode materials. This approach provided demonstrated improvements to the anode capacity and cycle life while providing inherent advantages in terms of safety. Thus, these materials are considering highly promising replacements to conventional LIB anode materials that can be used for numerous applications including EVs and HEVs.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2013.06.073.

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