Showcasing collaborative research from Prof. Byungwoo Park’s group in the Department of Materials Science and Engineering at Seoul National University, and Dr. Chunjoong Kim in the Environmental Energy Technologies Division at Lawrence Berkeley National Laboratory.

Title: Effective wrapping of graphene on individual Li$_4$Ti$_5$O$_{12}$ grains for high-rate Li-ion batteries

An effective way of synthesizing graphene-wrapped Li$_4$Ti$_5$O$_{12}$ (LTO) was developed by solid-state reaction between graphene oxide-wrapped P25 (TiO$_2$) and Li$_2$CO$_3$. Graphene wrapping of TiO$_2$ followed by chemical lithiation led to effective confinement of LTO by graphene. As a result, our graphene-wrapped LTO showed high rate capability.
An effective way of synthesizing graphene-wrapped Li$_4$Ti$_5$O$_12$ particles was developed by solid-state reaction between graphene oxide-wrapped P25 (TiO$_2$) and Li$_2$CO$_3$. Compared to the previously reported graphene/Li$_4$Ti$_5$O$_12$ composites, prior wrapping of TiO$_2$ with subsequent chemical lithiation led to more effectively confined Li$_4$Ti$_5$O$_12$. The Li$_4$Ti$_5$O$_12$ tightly bound by graphene exhibited a remarkable specific capacity of 147 mA h g$^{-1}$ at a rate of 10 C (1 C = 175 mA g$^{-1}$) after 100 cycles. This rate capability is one of the highest values among reported Li$_4$Ti$_5$O$_12$ with 150 ± 50 nm grains. The improved rate capability was attributed to the enhanced electronic conductivity of each Li$_4$Ti$_5$O$_12$ grain via uniform graphene wrapping, with single-grain growth during annealing from the initial ~25 nm TiO$_2$ nanoparticles enclosed by outer graphene sheets. Graphene-eliminated Li$_4$Ti$_5$O$_12$ by thermal decomposition was also directly compared to the graphene-coated sample, to clarify the role of graphene with nearly equivalent particle size/morphology distributions.

Introduction

Historically, lithium-ion batteries have been one of the most important and highly attractive power sources for energy storage. Common applications for Li-ion batteries have been focused on portable devices. The importance of rechargeable batteries is more highlighted as an alternative power supply for various types of electric vehicles (EV/HEV/PHEV) or energy storage systems (ESS) since the demand for green energy sources emerges from the finite amount of fossil fuels. However, commercial Li-ion batteries still cannot satisfy the requirements of those large-scale power sources, and encounter the necessity of breakthroughs in terms of power/energy densities, safety, and long-term stability. Although graphite is most commonly used as an anode, it exhibits serious safety problems induced by dendritic growth of Li due to the low operating voltage (~0.2 V vs. Li$^+/Li$). Spinel Li$_4$Ti$_5$O$_12$ (LTO) is one of the most promising candidates for an alternative anode material, since it exhibits excellent Li-ion insertion/extraction reversibility with approximately zero volume change (Li$_4$Ti$_5$O$_12$ + 3Li$^+$ + 3e$^-$ $\leftrightarrow$ Li$_7$Ti$_5$O$_12$, $\Delta V = 0.2%$), and exceptional stability due to the high operating voltage (1.55 V vs. Li$^+/Li$) by suppressing parasitic reactions (e.g., electrolyte decomposition). Despite these advantages, the commercialization of LTO is still limited because of its intrinsic insulating property ($\sigma < 10^{-13}$ S cm$^{-1}$), not fully utilizing the theoretical capacity of 175 mA h g$^{-1}$ at a high current rate. 

Recently, graphene-based electrode materials exhibiting enhanced electrochemical properties have been intensively reported. With high electronic conductivity and superior mechanical properties, graphene can suppress the volume expansion during lithiation especially in the case of Si and SnO$_2$, yielding improved cycle-life performance. With widespread use of graphene as an enhancer for the electronic percolation of LTO electrodes, many groups have reported excellent electrochemical performances of LTO. Nonetheless, uniform coating on active materials with graphene is still challenging, even though the electrostatic interactions between the positively-charged metal oxide and negatively-charged graphene oxide (GO) are known to provide a facile route for coating.

To date, the synthesis of graphene-wrapped lithium-metal oxide from GO-wrapped metal oxide and Li precursors is not reported. The subsequent solid-state reaction allows more uniform and conformal coating of graphene on the LTO surface, due to the volume increase by $3\text{TiO}_2 \rightarrow \text{Li}_4\text{Ti}_5\text{O}_{12}$.
(ΔV = 32%), and controlled grain growth of entangled nanoparticles within the graphene sheets during the high-temperature sintering.

Here, we introduce an effective way of synthesizing graphene-wrapped LTO particles by using a simple solid-state reaction between GO-wrapped TiO$_2$ and Li$_2$CO$_3$, where the former is prepared by using electrostatic interactions with commercial P25 (TiO$_2$ nanoparticles with ~25 nm diameter: Degussa). Considering that the highest reported capacity of LTO with particle sizes of 10–50 nm is 110–140 mA h g$^{-1}$ at a rate of 10 C (1 C = 175 mA g$^{-1}$)$^{24,60-64}$, our graphene-wrapped Li$_4$Ti$_5$O$_12$ exhibits one of the highest capacities among the reported LTOs: 147 mA h g$^{-1}$ at a rate of 10 C after 100 cycles with larger grains of 150 ± 50 nm for higher packing density. These drastic improvements are possible from the uniform coating of graphene on the individual LTO grains which undergo single-grain growth during annealing from the initial ~25 nm TiO$_2$ nanoparticles, enclosed by outer graphene sheets. To further identify the role of graphene with nearly the same particle size and morphology, graphene-eliminated LTO by thermal decomposition is also directly compared with the graphene-coated sample.

Results and discussion

The strategy towards the effective graphene-wrapping on the LTO grains is illustrated in Fig. 1. With the GO-wrapped TiO$_2$ nanoparticles by electrostatic interactions, the formation of LTO involves simple mixing with Li$_2$CO$_3$ followed by reductive annealing to achieve ~150 nm LTO grains enclosed by graphene.

Transmission electron microscopy (TEM) images in Fig. 2 confirm the wrapping of TiO$_2$ nanoparticles by GO. After 850 °C annealing, most of the LTO particles are well wrapped by wrinkled-flexible graphene. While the low-magnification TEM [Fig. 2d] image is consistent with the SEM image [Fig. 2c], high-magnification TEM clearly exhibits that individual LTO grains are uniformly wrapped by graphene. Starting from the GO wrapping of initial ~25 nm TiO$_2$ nanoparticles, single-grain growth to 150 ± 50 nm (Figs. S1 and S2†) is induced after high-temperature sintering. Some of the single-grain LTOs assume thick coating layers since more than one group of graphene oxides, each of which consists of 2–3 layers of graphene oxide, randomly wrap the nearby TiO$_2$ nanoparticles during the synthesis of GO-wrapped TiO$_2$ nanoparticles (Fig. 2e). It should be noted that the images are selected from repeated microscopy measurements so that they are representative of the samples.

The electrochemical performance of bare and graphene-wrapped LTO exhibits both stable cycle life and rate capability (Fig. 3). Among the graphene-wrapped LTO with various amounts of graphene, the 2.1 wt% graphene-wrapped LTO exhibits 147 mA h g$^{-1}$ at 10 C after 100 cycles. While the 10 C retention for 1.0 wt% graphene-wrapped LTO (Fig. 3b) is worse due to the insufficient amount of graphene for complete wrapping, the 4.5 wt% graphene-wrapped LTO exhibits even lower rate retention compared to the 1.0 wt% graphene-wrapped LTO. Thick graphene wrapping may inhibit the Li$^+$ diffusion, because of the low Li-ion diffusivity ($\sim$10$^{-11}$ cm$^2$ s$^{-1}$) through the perpendicular direction to the graphene layers.$^{5,65,66}$
From the electrochemical impedance spectroscopy (EIS) shown in Fig. S3,† the charge-transfer resistance ($R_C$) of graphene-wrapped LTO is clearly optimum for the 2.1 wt% graphene–LTO electrode, consistent with the rate-retention results of Fig. 3b. Meanwhile, the optimum amount of graphene in this work cannot be the ultimate value, and the real optimum must be between 1.0 and 4.5 wt%. The amount of graphene oxide (5, 10, and 15 wt%) was initially chosen as evenly distributed numbers over a wide range, and the fraction numbers, such as 2.1 wt%, are the amounts of graphene after 850 °C annealing.

The high-rate delithiation capability is ~105 mA h g⁻¹ at 100 C with 2.1 wt% graphene wrapping, as shown in Fig. 3c. Such a high-rate capability is again rarely found in previous LTO publications. Furthermore, the capacity retention is approximately 83% of the initial value after 100 cycles at both 50 and 100 C (Fig. S4†). The capacity of the graphene-wrapped LTO electrode without carbon black exhibits 116 mA h g⁻¹ at 10 C (Fig. S5†), confirming that the significant electronic conductivity is obtained by the uniform coating nature of graphene on individual ~150 nm LTO grains.

The shortened Li⁺-diffusion length can contribute to the enhancement in rate capability, since the particle size of bare LTO is larger than the graphene-wrapped LTO. Therefore, we eliminated only graphene from the 2.1 wt% graphene-wrapped LTO, without changing the particle size/morphology distribution (by post thermal decomposition at 500 °C for 3 h in air: Fig. S6†). The graphene-eliminated LTO shows a capacity of ~100 mA h g⁻¹ at 10 C (Fig. 3d and e) which is higher than that of the bare LTO (~65 mA h g⁻¹). Since the increase in electronic conductivity is more noticeable than the decrease in Li⁺-diffusion path (consistent with Fig. S7† in terms of $R_C$), it can be concluded that the contribution from the enhanced electronic conductivity is more significant than that from the decreased Li⁺-diffusion path, in enhancing the rate capability of LTO with ~150 nm grains.

It is currently accepted that during the electrochemical lithiation into Li$_2$Ti$_5$O$_{12}$, the reaction extends from a particle to a nearby particle of LTO with the formation of mixed Ti⁴⁺/Ti³⁺ oxidation states.⁶⁵–⁶⁷ LTO with mixed oxidation states is electronically conductive, and the rate determining process exists at the boundary of LTO particles.⁶⁶ Therefore, the enhanced rate capability can be understood by the intimate surface contact between individual LTO grains by uniform wrapping of graphene. Consequently, the single-grain growth of LTO within the graphene sheets by a solid-state reaction with ~32% volume increase is the key factor of this high-level functionality. With the spinel framework of LTO providing a three-dimensional network of channels for facile interstitial Li diffusion, single-grain growth is more favorable for Li-ion diffusion than the formation of polycrystalline phase since grain boundaries inhibit the interstitial diffusion of Li⁺.⁶⁶–⁶⁸ Furthermore, the graphene-wrapped LTO with ~150 nm grains is more advantageous than nanosized LTO in terms of packing density for the volumetric energy density, and this simple strategy can boost the utilization of the graphene-wrapped LTO in certain applications, such as grid-type energy storage systems or electric vehicles.

**Conclusions**

The graphene-wrapped LTO grains were synthesized by simple solid-state reaction from GO-wrapped P25 (~25 nm TiO₂) and Li₂CO₃. The graphene-wrapped LTO manifested an excellent specific capacity of 147 mA h g⁻¹ at a lithiation/delithiation of 10 C after 100 cycles, which is one of the highest values among reported LTOs with 150 ± 50 nm grains. This improved rate capability was attributed to the enhanced electronic conductivity of individual LTO grains via uniform graphene wrapping. In addition, graphene-eliminated LTO was directly compared with the graphene-coated LTO, to clarify the role of graphene with nearly the same particle size/morphology distributions. We believe that the work described herein suggests a route towards an effective wrapping of metal oxides by electron-conducting materials, and thereby enhances their electrochemical performance. Better control of nanostructural architecturing can definitely raise the performance of LTO electrode materials, and our unique synthetic method is applicable to other lithium-metal oxide materials for the uniform graphene wrapping on the individual grains. The graphene-wrapped LTO is also expected to be beneficial for the tap density, taking advantage of the relatively large size of the particles (~150 nm). A larger scale synthesis of the graphene-wrapped LTO will help us identify its tap density, which may be one of our future works.
Acknowledgements

This research was supported by the National Research Foundation of Korea (MEST: NRF, 2010-0029065). JC and CK were supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the US Department of Energy (DOE) under the Batteries for Advanced Transportation Technologies (BATT) Program.

References

Supporting Information

Effective Wrapping of Graphene on Individual Li$_4$Ti$_5$O$_{12}$ Grains for High-Rate Li-Ion Batteries

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Experimental Methods

Preparation of Graphene Oxide: Graphene oxide was synthesized from natural graphite flakes (325 mesh, Sigma-Aldrich) by modified Hummers’ method. In an ice bath, 1 g of graphite, 1 g of NaNO$_3$, and 46 ml of concentrated H$_2$SO$_4$ were stirred for 30 min. Then, 5 g of KMnO$_4$ was slowly added into the mixture and stirred at 35°C. After 2 h, 100 ml of deionized (DI) water was slowly added to the mixture and stirred for 30 min at 98°C. In order to reduce the residual permanganate (MnO$_4^-$) and MnO$_2$ to soluble MnSO$_4$, 8 ml of H$_2$O$_2$ (30%) was slowly added to the solution. The solution was centrifuged and washed with HCl (10%) and DI water, and the final product was dried in vacuum overnight. The dried graphite oxide was added to DI water, and the mixture was sonicated for 2 h to exfoliate the graphite.
oxide to graphene oxide. In order to confirm the formation of graphite oxide, x-ray diffraction (XRD) was measured. The peak shift of the (002) plane from 3.39 Å to 8.16 Å by XRD was observed (Fig. S8), confirming graphite oxide. The atomic force microscopy (AFM) observation of graphene oxides clearly revealed that the synthesized graphene oxides by Hummers’ method had a width of ~3 μm and a thickness of ~1 nm (Fig. S9, Supporting Information). Since graphene, by definition, is a one-atom-thick layer of graphite, the graphene used in this study should be referred to as reduced graphene oxide. The terminology “graphene” is used throughout this article for convenience’s sake.

**Synthesis of Graphene-Wrapped LTO:** 0.5 g of P25 (TiO$_2$ nanoparticles with ~25 nm in diameter: Degussa) nanoparticles were dispersed in distilled water by ultrasonication for 1 h. Then, the P25 aqueous solution was added into the different amounts of 0.5 mg ml$^{-1}$ graphene-oxide aqueous solution under magnetic stirring at pH 2, and the relative amounts of graphene oxide with respect to P25 corresponded to 5, 10, or 15 wt. %. After 4 h, the product was collected by centrifugation, and was dried at room temperature in vacuum overnight. Then, the resultant graphene-oxide-wrapped P25 nanoparticles were mixed mechanically with Li$_2$CO$_3$ (as a lithium precursor) at a Li:Ti molar ratio of 4.1:5 using acetone to form a slurry. Finally, the resulting products were annealed at 850°C for 10 h under H$_2$/Ar (4 vol. % H$_2$ in argon) atmosphere. After the pyrolysis, the graphene oxide turned into graphene (reduced graphene oxide), and the resultant graphene contents were found to be 1.0, 2.1, or 4.5 wt. % in graphene-wrapped LTO. For comparison, bare Li$_4$Ti$_5$O$_{12}$ was also prepared in a similar manner without the use of graphene oxide. The XRD peaks (Fig. S10) of the bare and graphene-wrapped LTO particles with various amounts of the graphene (1.0, 2.1, or 4.5 wt. % of graphene) were ascribed to the pure phase of well-crystallized LTO$^2$ with negligible impurity phases such as Li$_2$TiO$_3$, TiO$_2$, and so on.

**Materials Characterization:** The crystal structure of the prepared samples was characterized by XRD (New D8 Advance: Bruker). The morphology of synthesized materials was analyzed using field-emission scanning electron microscopy (FE-SEM, SU70: Hitachi), and transmission electron microscopy (TEM) was carried out on a JEOL 2100 microscope operated at 200 kV. The relative compositions of graphene were measured using CHNS...
analyzer (Flash EA 1112: Thermo Electron Corp.), and the results are listed in Table S1 (Supporting Information). Raman spectra were collected with a “Labram” Raman microscope system from ISA Group Horiba. The samples were excited with a 488 nm Ar⁺ laser with the power adjusted to ≤ 2 mW. The system was setup in the backscattering configuration with an 80× objective, providing a beam diameter of ~2 μm. As shown in Fig. S11, broad peaks at ~1360 and ~1600 cm⁻¹ are assigned to the D and G bands of graphene, respectively, which indicate the reduction of graphene oxide to graphene. The nitrogen adsorption/desorption isotherms were obtained at 77 K using a Micromeritics ASAP 2010 instrument. The specific surface areas of the graphene (incorporated in the composite) and 2.1 wt.%-graphene-wrapped LTO were obtained by the Brunauer-Emmet-Teller (BET) methods (Fig. S12, Supporting Information). The obtained specific surface areas of graphene and the 2.1 wt. %-graphene-wrapped LTO are ~49 m² g⁻¹ and ~31 m² g⁻¹, respectively.

Electrochemical Measurement: Electrochemical performance of graphene-wrapped LTO was measured using coin-type half cells (2016 type) with a Li counter electrode. The working electrodes were prepared with active materials, carbon black, and PVDF binder at a weight ratio of 8:1:1. In the case of the working electrode without carbon black, the electrode consisted of a mixture of 90 wt. % of active materials and 10 wt. % of PVDF binder. The slurry was cast on Cu foil and dried at 110°C in vacuum for 10 h. The electrolyte contained 1 M LiPF₆ in ethylene carbonate and diethylene carbonate (1/1 vol. %) (Cheil Industries Inc.). The loading density of the electrodes was 1.40 – 1.65 mg cm⁻². The cells were charged and discharged between 2.5 and 0.9 V by applying various current densities. Electrochemical impedance spectra were measured using a potentiostat (CHI 608C: CH Instrumental Inc.) at 1.5 V after 100 cycles with AC amplitude of 5 mV in the frequency range from 10 mHz to 10⁵ Hz.

References
<table>
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<tr>
<th>Sample</th>
<th>Li$_2$Ti$<em>5$O$</em>{12}$ (wt. %)</th>
<th>C (wt. %)</th>
</tr>
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<tr>
<td>1.0 wt. %-Graphene-Wrapped LTO</td>
<td>98.9</td>
<td>1.04</td>
</tr>
<tr>
<td>2.1 wt. %-Graphene-Wrapped LTO</td>
<td>97.8</td>
<td>2.14</td>
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<tr>
<td>4.5 wt. %-Graphene-Wrapped LTO</td>
<td>95.5</td>
<td>4.46</td>
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</tbody>
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**Table S1.** The relative graphene compositions of graphene-wrapped LTO samples. The compositions were measured by a CHNS elemental analysis.

**Fig. S1.** Grain-size distribution of the 2.1-wt.-% graphene-wrapped LTO.
**Fig. S2.** SEM image of the bare LTO.

**Fig. S3.** Electrochemical impedance spectroscopy of the bare and graphene-wrapped LTO with various amounts of graphene measured at 1.5 V after 100 cycles.
Fig. S4. Capacity retention of the graphene-wrapped LTO with 2.1 wt. % graphene at 50 and 100 C delithiation (lithiation rate = 1 C).
Fig. S5. Coin cells without carbon black: (a) Rate capability (first cycle at the given rate) and (b) rate retention of the graphene-wrapped LTO (3.0 wt. % graphene) at different current rates.
**Fig. S6.** Comparison of the individual colors of the prepared samples.

**Fig. S7.** Electrochemical impedance spectroscopy of the bare, graphene-wrapped LTO, and graphene-eliminated LTO measured at 1.5 V after 100 cycles.
**Fig. S8.** XRD patterns of the natural graphite and graphite oxide.

**Fig. S9.** (a) An AFM image of graphene oxides dispersed in aqueous solution and (b) respective height profile.
**Fig. S10.** XRD patterns of the bare and graphene-wrapped LTO with various amounts of graphene.

**Fig. S11.** Raman spectrum of the 2.1-wt.-% graphene-wrapped LTO.
Fig. S12. $N_2$ adsorption/desorption isotherm of 2.1 wt. %-graphene-wrapped LTO. The inset displays that of graphene only.