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Thermal Annealing and Graphene Modification of Exfoliated Hydrogen Titanate Nanosheets for Enhanced Lithium-ion Intercalation Properties

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Hydrogen titanate has been considered as a promising lithium intercalation material due to its unique layered structure. In the present work, we fabricate 2D graphene/hydrogen titanate hybrid nanosheets for application as anode materials in lithium-ion batteries. $H_2Ti_3O_7$ nanosheets are synthesized by exfoliation of a layered precursor via interacting bulky tetrabutylammonium (TBA^+) cations, followed by ion exchange with Na^+ ions and washing with water. The as-prepared hydrogen titanate nanosheets are well-dispersed exhibiting ultra-thin thickness with a lateral size up to a few micrometers. The sample is then annealed at 450, 650 and 850 °C, to optimize its Li^+-intercalation property. Heating at 450 °C leads to well-crystallized hydrogen titanate with a trace amount of TiO_2. Heating at 650 and 850 °C results in mixed sodium titanates, since some sodium ions in the interlayer structure cannot be washed away and become chemically bonded to [TiO_6] octahedra at high temperatures. Electrochemical properties of all the four samples are then evaluated by charged/discharged for 100 electrochemical cycles at 0.01–2.5 V *vs.* Li^+/Li at a specific current of 170 mA g^{-1}. The unannealed hydrogen titanate delivers the highest initial discharge capacity of 130.5 mA h g^{-1}, higher than 124.6 mA h g^{-1} from hydrogen titanate annealed at 450 °C, as well as 101.3 and 63.8 mA h g^{-1} from hydrogen titanate annealed at 650 and 850 °C, respectively, due to the high surface area from well-dispersed unannealed nanosheets. However, after 100 electrochemical cycles, well-crystallized hydrogen titanate annealed at 450 °C retain the highest charge capacity of 115.2 mA h g^{-1}, corresponding to a capacity retention of 92.5%, while unannealed hydrogen titanate exhibits a final capacity of 72.1 mA h g^{-1} and a capacity retention of only 55.2%. To further improve energy density of lithium-ion battery, graphene/hydrogen titanate hybrid nanosheets are fabricated by adding graphene nanosheets into hydrogen titanates. The initial charge capacities of unannealed and annealed hydrogen titanate at 450 °C are significantly increased to 170.7 and 233.9 mA h g^{-1}, respectively. A charge capacity of 101.0 mA h g^{-1} is retained for unannealed hydrogen titanate with graphene-modification after 100 electrochemical cycles since well-dispersed hydrogen titanate nanosheets can be mixed with 2D graphene more uniformly and thus facilitates diffusion of Li^+ ions and retard aggregation of active materials.

KEY WORDS: Hydrogen titanate; Sodium titanate; Graphene nanosheets; Exfoliation process; Lithium-ion battery

1. Introduction

In the past decade, TiO_2 and its derived nanomaterials have been intensively investigated owing to their multifunctional properties and wide applications in lithium-ion batteries[1–4], dye-sensitized solar cells[5–10], photocatalysis[11,12], and biosensors[13]. More recently, much attention has been paid to fabricating electrodes composed of alkali metal titanate family which is related to hydrogen titanate as well as their Li, Na, and K salts. Electrochemical behaviors of lithium intercalation into these titanate electrodes have been well addressed[14–21]. Titanates with layered structure are composed of corrugated chains of edge and corner sharing [TiO_6] octahedra in which alkali ions occupy the interlayer spaces. This layered structure facilitates intercalation of Li^+ ions by providing short and direct path for Li^+ ions transport through interlayer spaces, and better accommodation of volume change caused by Li insertion/extraction.

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Therefore, titanates are considered as very promising active materials for applications in Li-ion batteries with high charge/discharge capacity, high-energy density, and long cycle life.

A common method to synthesize titanates is hydrothermal approach. Tsai and Teng obtained titanate nanotubes by using bulk TiO_2 powder and NaOH as precursors in a hydrothermal process[22]. Titanate nanorods, nanowires, nanofibers, and nanobelts have also been prepared from TiO_2 by using a simple hydrothermal treatment with alkaline followed by acid washing[23,24]. Among alkali metal titanates, hydrogen titanate with unique electrochemical performance is considered as a very promising lithium intercalation material for high-energy rechargeable Li-ion batteries and electrochemical super-capacitors[14−16,25,26]. Li et al. reported a hydrothermal synthesis of layered hydrogen titanate nanowires with the composition of $H_2Ti_3O_7$ and investigated their lithium intercalation properties for applications as electrodes in lithium-ion batteries[17]. The initial discharge capacity of the as-prepared micron-long $H_2Ti_3O_7$ nanowires could reach 296.6 mA h g^{-1} at a specific current of 300 mA g^{-1}, and could keep a very high capacity of 132.2 mA h g^{-1} even at a very high specific current of 2500 mA g^{-1}. Such excellent electrochemical properties of hydrogen titanate are attributed to the open layered structure with a much larger interlayer spacing than common intercalation compounds. Wei et al. successfully synthesized layer-structured $H_2Ti_3O_7$ nanowires with lengths up to several micrometers via hydrothermal process, which delivered a discharge capacity of 100 mA h g^{-1} at 40 A g^{-1} demonstrating excellent rate performance due to shorter Li-ion diffusion distance for their insertion/extraction into/from layered $H_2Ti_3O_7$ nanowires[27]. Sodium titanates with a basic formula of $Na_2Ti_nO_{2n+1}$ have also been tested as anode materials for Li-ion batteries due to their good electrochemical lithium insertion properties. This material has a stable structure during Li-ion insertion/extraction processes with the presence of sodium in the pristine material[14]. Lithium can be reversibly inserted into rod-like $Na_2Ti_6O_{13}$ with a capacity of 150 mA h g^{-1} at the *C*/3 rate[14]. For $Na_2Ti_3O_7$, the initial Li-ion interaction capacity was only 44 mA h g^{-1} at a specific current of 10 mA g^{-1}; this value was equivalent to 0.5 electron transfer per formula unit[15]. Rudola et al. recently evaluated electrochemical performance of $Na_2Ti_3O_7$ for application as anode material in Na-ion batteries. $Na_2Ti_3O_7$ electrode exhibited a first discharge capacity of 177 mA h g^{-1} and a relative low cycling stability with capacity retentions of 55.3% after 90 cycles at the 0.1 *C* rate over a voltage window of 0.01−2.5 V *vs*. Na/Na^+[28]. However, all the work summarized above either presented very low cycling stability of batteries based on alkali metal titanates or did not report any cycling performance. Moreover, among these reports, alkali metal titanates were obtained in the form of one-dimensional (1D) structure such as nanotube, nanowire, nanorod, and nanobelt. Even though 1D structure provides a direct pathway for Li-ion transport, these 1D nanostructures exhibited either defects or random alignments causing poor electronic transport during Li-ion insertion/extraction leading to low capacity and impeding its practical application.

Graphene, a single layer of two-dimensional carbon lattice, has recently emerged as a novel nanomaterial for applications in energy storage technology owing to its very light weight, large surface area, and extremely high electron mobility ($\sim$15,000 cm^2 V^{-1} s^{-1}) at room temperature[29−31]. Such merits suggest that graphene nanosheets can be an ideal conductor to be mixed with metal oxides to improve their electrochemical performances. Graphene based nanocomposite electrode materials such as TiO_2[32−34], SnO_2[35−37], WO_3[38], Co_3O_4[39,40], MnO_2[41] etc. have been explored showing enhanced storage capacity and cycling stability. It has been demonstrated that incorporation of graphene into these composites greatly facilitates electrical conductivity by decreasing the charge transfer resistance of active material and prevents the aggregation of active material during cycling. However, there are few reports about nanocomposites based on graphene/alkali metal titanate nanosheets, due to the challenge of combining 1D nanostructure of alkali metal titanate with two-dimensional (2D) graphene nanosheets. One solution is to develop 2D titanate nanosheets which have similar morphology with graphene sheets and can thus hybridize with graphene more uniformly.

To the best of our knowledge, electrochemical property of hydrogen titanate with 2D nanosheet structure has never been studied. Herein, we fabricate 2D hydrogen titanate nanosheets via chemical exfoliation of a layered precursor through acid treatment and ion-exchange with bulky organic ions and Na^+ ions, followed by washing with water. Thermal annealing of the as-prepared hydrogen titanate nanosheets at different temperatures is carried out to optimize their electrochemical properties for applications as anode materials in lithium-ion batteries. Moreover, graphene nanosheets are added to titanate nanosheets to further enhance their Li-ion intercalation properties owing to significantly increased electronic conductivity from graphene. Both titanate nanosheets and hybridization with graphene nanosheets are achieved for the first time. Electrochemical cycling performances of these materials are also explored, showing significantly enhanced Li-ion intercalation properties.

2. Experimental

Lamellar solids of lepidocrocite-type cesium titanate $Cs_xTi_{2-x/4}\square_{x/4}O_4$ ($\square$: vacancy, $x = 0.7$) was synthesized via a conventional solid-state calcination[42,43]. A stoichiometric mixture of Cs_2CO_3 (Alfa Aser, 99.99%) and TiO_2 (anatase, 99%, Sigma Aldrich) was calcinated at 1073 K for 20 h with a molar ratio of 1:5.3. After cooling, the calcinated products were ground and calcinated repeatedly. Subsequent acid leaching converted them into protonated forms of $H_xTi_{2-x/4}\square_{x/4}O_4\cdot H_2O$[44,45]. The protonated titanate was derived through repeated ion exchange of Cs with proton. The resulted powder ($\sim$2 g) was stirred in 200 ml hydrochloric acid solution with a concentration of 1 mol l^{-1} for 24 h. After Cs extraction was completed via four cycles of ion exchange, the acid-treated product was thoroughly washed with water to remove acid residue and dried under ambient condition.

The as-prepared $H_xTi_{2-x/4}\square_{x/4}O_4\cdot H_2O$ was treated with tetrabutylammonium hydroxide (TBAOH, $(C_4H_9)_4NOH$, $\sim$40% solution, Fluka) to delaminate into nanosheets. A weighed amount (2 g) of $H_xTi_{2-x/4}\square_{x/4}O_4\cdot H_2O$ was shaken vigorously in an aqueous solution (500 ml) of TBA hydroxide, for two weeks at room temperature. The amount of TBA hydroxide was 5-fold excess to the exchangeable capacity of 4.12 meq g^{-1} for $H_xTi_{2-x/4}\square_{x/4}O_4\cdot H_2O$.

Typically, 100 ml colloidal suspension of TBA-intercalated titanate was poured into 100 ml of NaOH aqueous solution (1 mol l^{-1}). Wool-like precipitates were yielded and the mixture was stirred overnight. After filtration and washing with distilled water, a post-calcination process is also necessary to remove organic residues and to form a high-crystalline phase. The